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A
SYSTEM OF INSTRUCTION
IN
QUALITATIVE CHEMICAL ANALYSIS.

BY

DR. C. REMIGIUS FRESENIUS,

PROFESSOR OF CHEMISTRY AND NATURAL PHILOSOPHY, WIESBADEN.

Fourth Edition.

EDITED BY

J. LLOYD BULLOCK, F.C.S.

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EDITOR'S PREFACE

TO THE

FOURTH EDITION.

THE demand for a Fourth Edition of this work, at once proves, incontestably, that it must possess great intrinsic merits, and that its value is recognized by British chemists.

To what has already been said in the former prefaces, there is nothing to add, except that the usefulness of the present edition is greatly enhanced by the addition of methods for the Qualitative Analysis of mineral waters, common waters, soils, ashes of plants, animals and manures, and the detection of poisons for forensic purposes.

This fourth English version corresponds with the eighth German edition.

J. LLOYD BULLOCK.

22, *Conduit Street*, *March*, 1855.

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 of Giessen, have 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 anything of Giessen, will bear testimony to the rigid economy of time, and the resolute adoption of every improvement in method which characterize 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; 2nd, The absence of explanations of the causes of phenomena, *i. e.* the *theory* of the operations and reactions; and 3rd, 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 intrusted 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, October* 1, 1843.

EDITOR'S PREFACE

TO THE

SECOND EDITION.

THE rapid sale of the first English Edition of this Work has justified the anticipation of the illustrious Chemist, at whose suggestion I undertook to place it at the service of the English student of chemistry. The numerous commendations it received from the press, I may be allowed to say, in my capacity of Editor, it fully deserves. The present edition is almost a new work, so numerous and important are the additions and alterations, which are so incorporated into its structure that they could not be produced separately. It represents the FOURTH GERMAN edition. Several new works on the same subject, of various pretensions, have made their appearance in this country since this was published—they have not retarded, on the contrary, they seem rather to have facilitated its sale.

The increasing taste for practical chemistry, indicated by this efflux of books, calls especially for works detailing methods which may be safely followed and implicitly relied on. I venture to affirm, that in this respect, the work of Dr. Fresenius is pre-eminent. Moreover, those works intended particularly for the use of students who enjoy the advantage of tuition in a laboratory, omit many things which it is absolutely necessary for him to know from some sources. Indeed this is the only work in the English language adapted for self-instruction. With a previous general acquaintance with chemistry, derived from attendance on a course of lectures, or from the perusal of some introduction to the science of which many excellent ones exist, any person may take up this work, and make himself an expert analyst. And after all the assistance given by a teacher, the chemist, when left to his own resources, still requires a guide to whom he may safely have recourse for facts which have escaped his memory. Both as a systematic course of study, and as a book of reference, Dr. Fresenius' work is unrivalled. It has been duly appreciated, since it is now translated into most European languages, and reprinted in America.

J. LLOYD BULLOCK.

22, *Conduit Street, May,* 1846.

EDITOR'S PREFACE

TO THE

THIRD EDITION.

EVERY successive addition of this work must necessarily be in advance of all former editions. The science itself is in a state of continual progress. The author, occupying a distinguished position in the foremost rank of chemists, whose original labours perpetually extend its boundaries, of course includes the latest discoveries in his scientific instructions. He supervises every sheet of my translation, incorporating as we proceed, every fact ascertained, and every improvement devised in the processes. The work, therefore, represents the state of the science at the moment we go to press; and in this respect, as well as in its other transcendent merits, it stands unrivalled.

If anything were needed in the former editions, it was a simple method of arranging the numerous references in the systematic course; this defect is now supplied. A marginal number is printed to each paragraph, which will greatly facilitate the student in turning from one point to another, and tracing his path through the various processes.

J. LLOYD BULLOCK.

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, "Elementary Instruction in Qualitative Chemical Analysis." This method I can confidently recommend from my own personal experience to all who are desirous of obtaining instructions 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.

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PART I.

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PRELIMINARY REMARKS.

DEFINITION, DESIGN, OBJECTS, AND IMPORTANCE OF QUALITATIVE CHEMICAL ANALYSIS, AND CONDITIONS WHEREON A SUCCESSFUL STUDY OF THE SCIENCE DEPENDS.

Chemistry is that science which treats of the various substances constituting our earth, of their composition and decomposition, and of their mutual relations and deportment in general. 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 examination of their constituents. If this examination is confined to the *nature* and *properties* of the latter, the analysis is called *qualitative ;* but if the *quantity* of every individual element is to be ascertained, the analysis is termed *quantitative.* The object of qualitative analysis, therefore, is to exhibit the constituent parts of an unknown substance in forms *already known,* and which consequently admit of safe inferences as to the nature of every individual element. The value of its method depends on two conditions, viz., it must attain the object in view with unerring certainty, and in the most expeditious manner. The object of quantitative analysis, on the other hand, is to exhibit the elements revealed by the qualitative investigation, in forms which permit the most accurate determination of the weight of each constituent.

These different ends are, of course, attained respectively by very different ways and means. It is obvious, therefore, that the study of qualitative analysis must be separately pursued from that of quantitative analysis, and that the former must precede the latter.

Having thus generally defined the design and objects of qualitative analysis, we will now proceed to discuss briefly, in the first place, the preliminary information which qualifies students successfully to cultivate this branch of chemical science, the relative rank which it occupies, the objects to which it applies, and the advantages derived from it; and, in the second place, the main points whereon its study is based, and the principal parts into which it is divided.

It is, above all, absolutely indispensable for a successful pursuit of qualitative investigations, that the student should possess some knowledge of the chemical *elements*, and of their most important combinations, as well as of the principles of chemistry in general; and that he should combine with this knowledge some readiness in the apprehension of chemical processes. The practical part of this science demands, moreover, strict order, great neatness, and a certain skill in manipulation. If the student joins to these qualifications the habit of invariably ascribing the failures with which he may happen to meet, to some error or defect in his operations, or, in other words, 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.

But, although chemical analysis is based on general chemistry, and cannot be cultivated without some previous knowledge of the latter, yet, on the other hand, we have to look upon it as one of the main pillars upon which the entire structure of the science rests; since it is of almost equal importance for all branches of theoretical as well as of practical chemistry; and I need not expatiate here on the advantages which the physician, the apothecary, the mineralogist, the rational farmer, the manufacturer, the artisan, and many others, derive from analytical chemistry.

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

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

In the present work, however, we purpose to confine ourselves to those elements and compounds which are more generally employed in pharmacy and in the arts and manufactures.

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

1. THE ANALYTICAL OPERATIONS.
2. THE REAGENTS AND THE MODE OF THEIR APPLICATION.
3. THE DEPORTMENT OF THE VARIOUS BODIES WITH REAGENTS.
4. THE SYSTEMATIC COURSE AND METHOD OF QUALITATIVE ANALYSIS.

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

SECTION I.

OPERATIONS.

§ 1.

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

The following are the principal operations in qualitative analysis.

§ 2.

1. SOLUTION.

The term "*solution*," in its widest sense, is applied to the perfect union of a fluid with another substance, no matter whether gaseous, liquid, or solid. But we call solution more properly *absorption* if the dissolved substance is *gaseous;* if *liquid*, the term *mixture* is more frequently made use of. The application 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 solution is effected, is called the *solvent*. We term the solution *chemical*, if the solvent enters into chemical combination with the substance dissolved; *simple*, if no definite combination takes place.

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

A *chemical* solution contains the dissolved substance not in the same state nor possessed of the same properties as before; the dissolved body is no longer free, but intimately combined with the solvent, which latter also has lost its original properties; a new substance has thus been produced, and the solution manifests therefore now the properties of this new substance. A chemical solution also may be *accelerated* by elevation of temperature, and this is indeed usually the case, since 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—the combining proportions of substances being invariable, and altogether independent of the gradations of temperature.

The reason of this is, that in chemical solution, the solvent and the body upon which it acts have invariably opposite properties, which they strive mutually to neutralize. Further solution ceases as soon as this tendency of mutual neutralization is satisfied. The solution is in this case said to be saturated, or more properly *neutralized*, and the point which denotes it to be so is termed the point of saturation or neutralization. The most familiar illustration of this is found in the acids and alkalies or bases. Such substances require, in the first place, to be converted to the fluid state by means of a simple solvent. When the opposite properties of acid and base are mutually neutralized, and the new compound is formed, the actual transition to the fluid state will ensue only if the new compound possesses the property of forming a simple solution with the liquid present; *e. g.* if 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 acetate of lead produced in the water of the menstruum.

Crystallization and precipitation are the reverse of solution, since they have for their object the conversion of a fluid or dissolved substance to 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; in many cases they merge into one another. We must, however, consider them separately here, since they differ essentially in their extreme forms; and, moreover, since the special objects which we purpose to attain by their application are, in most cases, very different.

§ 3.

2. CRYSTALLIZATION.

We understand by the term crystallization, in a more general sense, every operation, or process, whereby bodies are induced to pass from the fluid to the solid state, and to assume certain regular, determinate, geometrical forms. But, as these forms, 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 accessory idea of a *slow* separation—of a *gradual* conversion to the solid state. The formation of crystals depends on the regular arrangement of the ultimate constituent particles of bodies (*molecules* or *atoms*); it can only take place, therefore, if these atoms possess perfect freedom of motion, and thus in general only when a substance passes from the fluid or gaseous to the solid state. Those cases in which the mere ignition, or the softening or moistening of a solid body suffices to make the tendency of the molecules to a regular arrangement (crystallization) prevail over the diminished force of cohesion—(such as, for instance, the turning white and opaque of moistened barley-sugar)—are to be regarded as exceptions to the rule.

To induce crystallization, the causes of the fluid or gaseous form of a substance must be removed. These causes are either *heat alone, e. g.* in the case of fused metals; or *solvents alone,* as in the case of an aqueous solution of common salt; or *both combined,* as in the case of a hot and saturated aqueous solution of nitrate of potassa. In the first case we obtain crystals by cooling the fused mass; in the second, by evaporating the menstruum; and in the third by either of these means. The most frequently occurring case is that of crystallization by cooling hot saturated solutions. The liquors which remain after the separation of the crystals are called *mother-waters,* or *mother-liquors.* The term *amorphous* is applied to such solid bodies as have no crystalline form.

We have recourse to crystallization generally either to obtain the crystallized substance in a solid form, or to separate it from other substances dissolved in the same menstruum. The form of the crystals also affords in some cases an excellent means of distinguishing between otherwise analogous bodies; for instance, between nitrate of soda and nitrate of potassa.

The process of crystallization is usually performed in dishes, or, in the case of very small quantities, in watch glasses.

§ 4.

3. PRECIPITATION.

This operation differs from crystallization in this much, that the dissolved substance 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 sinks to the bottom of the vessel, or ascends, or remains suspended in the liquid. Precipitation is either caused by a modification of the solvent; thus sulphate of lime (gypsum) separates immediately from its solution in water upon the addition of alcohol; or it ensues in consequence of the separation of an educt insoluble in the menstruum; thus, when ammonia is added to a solution of sulphate of alumina, the latter salt is decomposed, and the alumina, not being soluble in water, precipitates. Precipitation takes place also, when by the action of simple or double chemical affinity new compounds are formed which are insoluble in the menstruum; thus, oxalate of lime precipitates upon adding oxalic acid to a solution of acetate of lime; chromate of lead upon mixing chromate of potassa with nitrate of lead. In decompositions of this kind, induced by simple or double affinity, one of the new compounds remains generally in solution, and the same is sometimes the case also with the educt; thus in the instances just mentioned, the sulphate of ammonia, the acetic acid, and the nitrate of potassa, remain in solution. It may, however, happen also that both the product and the educt, or two products, precipitate, and that nothing remains in solution; this is the case, for instance, when a solution of sulphate of magnesia is mixed with water of baryta; or a solution of sulphate of silver with chloride of barium.

Precipitation is applied for the same purposes as crystallization, viz., either to obtain a substance in the solid form, or to separate it from other substances dissolved in the same menstruum. But in qualitative analysis we resort to this operation more particularly for the purpose of detecting and distinguishing substances by the color, properties, and general deportment which they exhibit when precipitated either in an isolated state or in combination with other substances. The solid body separated by this process, is called the *precipitate*, and the substance which acts as the immediate cause of its 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.

The terms *turbid, turbidity,* are made use of to designate the state of a fluid which contains a precipitate so finely divided and so inconsiderable in amount, that the suspended particles, although impairing the transparency of the fluid, yet cannot be clearly distinguished. The separation of flocculent precipitates may generally be promoted by a vigorous shake of the vessel; that of crystalline precipitates, by stirring the fluid and rubbing the sides of the vessel with a glass rod; elevation of temperature is also an effective means of promoting the separation of most precipitates. The process is therefore conducted, according to circumstances, either in test-tubes, flasks, or beakers.

The two operations described respectively in §§ 5 and 6, viz., *filtration* and *decantation*, serve to effect the mechanical separation of fluids from matter suspended therein.

§ 5.

4. Filtration.

This operation consists simply in passing the fluid from which we wish to remove the mechanically suspended solid particles, through a filtering apparatus, formed usually by a properly arranged piece of unsized paper placed in a funnel; an apparatus of this description allows the fluid to trickle through with ease, whilst it completely retains the solid particles. We employ smooth filters and plaited filters: the former, in cases where the separated solid substance is to be made use of; the latter in cases where it is simply intended to clear the solution. Smooth filters are prepared by double folding a circular piece of paper, so that the folds form right angles. The preparation of plaited filters is more properly a matter for ocular demonstration than for description. In cases where the contents of the filter require washing, the latter must not project over the edge of the funnel. It is in most cases advisable to moisten the filter previously to passing the fluid through it; since this not only tends to accelerate the process, but also renders the solid particles less liable to pass through the pores of the filter. The paper selected for filters must be as free as possible from inorganic substances, especially from such as are dissolved by acids, sesquioxide of iron, lime, &c. Swedish filtering paper answers the purpose best; the common filtering paper of commerce requires careful washing with dilute hydrochloric acid to fit it for use in accurate analyses. To this end the paper is cut into quarter sheets and a layer of ten or twelve of them placed in a shallow porcelain dish, and digested for several hours at a moderate heat with a mixture of one part of hydrochloric acid and nine parts of water. The dilute acid is then poured off, and the paper repeatedly washed with water (finally distilled water), until litmus paper is no longer reddened by the washings; the water is then drained off, and the sheets are carefully placed, in a heap, upon some

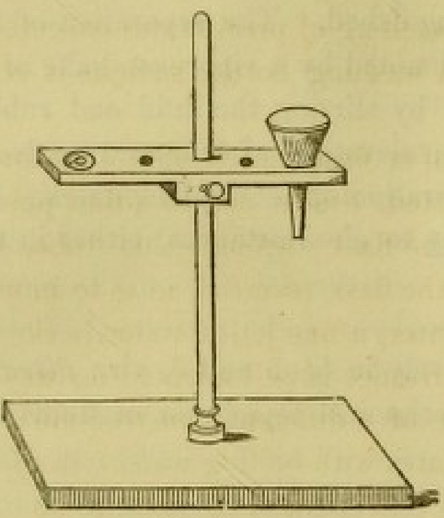

Fig. 1.

blotting paper, and left there until they can be taken off singly without injury; they are then hung up to dry on lines in a place free from dust. Good filtering paper must allow fluid to pass readily through; but, on the other hand, it must also completely retain even finely-pulverulent precipitates, such, as *e. g.* sulphate of baryta, oxalate of lime, &c. If a paper of this kind cannot be readily procured, it is advisable to keep two sorts, one of greater density for the separation of very finely divided precipitates, and one of greater porosity for the speedy separation of grosser particles. The funnels must be either of glass or of porcelain (§ 14, 11); they are usually placed on an appropriate stand, to keep them in a fixed position. The stand illustrated by Fig. 1, is particularly well adapted for the reception of the small-sized funnels used in qualitative analyses.

§ 6.

5. DECANTATION.

This operation is frequently resorted to instead of filtration, in cases where the solid particles to be removed are of considerably greater specific gravity than the liquid in which they are suspended; since, in that case, they will speedily subside to the bottom, rendering it easy, either to decant the supernatant fluid by simply inclining the vessel, or to remove it by means of a syphon or pipette.

Fig. 2.

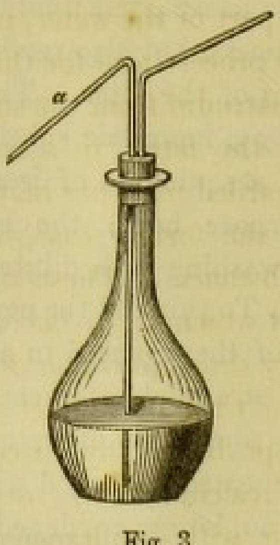

Fig. 3.

In cases where filtration or decantation are resorted to for the purpose of obtaining the solid substance, the latter must be freed afterwards by repeated washing from the liquid still adhering to it. This operation is termed *washing* or *edulcoration*. The washing of precipitates collected on a filter is usually effected by means of a washing bottle, such as is represented by Fig. 2.

The washing bottle, Fig. 2, consists of a flask closed with a perforated cork, into which a small glass tube is fitted, drawn out to a fine point at the top (*a*). If air be blown into the flask through this tube, and, when the air is sufficiently compressed, the flask reversed, so as to immerse the inner aperture of the tube in the water, a fine jet of water is expelled with a certain degree of force; this contrivance is well adapted for washing precipitates. Fig. 3 represents a bottle of a different construction; this is used more especially to wash precipitates with boiling water: it affords, moreover, the advantage that it enables the operator to produce an uninterrupted stream of water. The engraving needs no explanation; the tube *a* is drawn out to a fine point at its anterior aperture.

There are four operations which serve to separate volatile substances from less volatile, or from fixed bodies, viz., *evaporation*, *distillation*, *ignition*, and *sublimation*. The two former of these operations are applied exclusively to fluids, the two latter exclusively to solids.

§ 7.

6. EVAPORATION.

This operation is of very frequent occurrence. It serves to separate volatile fluids from less volatile, or from fixed bodies (no matter whether solid or fluid), in cases where the residuary substance alone is of importance, whilst the evaporating matter is entirely disregarded;—thus, for instance, we have recourse to evaporation for the purpose of removing from a saline solution part of the water, in order to induce the salt to crystallize; we resort to this process also for the purpose of removing the whole of the water of the menstruum from the solution of a non-crystallizable substance, so as to obtain the latter in a solid form, &c. The evaporated 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 invariably attained by converting the fluid which is to be removed to the gaseous state. This is generally done by the application of heat; sometimes, also, by leaving the fluid for a certain time in contact with the atmosphere, or with confined air constantly kept dry by hygroscopic substances (hydrate of sulphuric acid, chloride of calcium, &c.); or, finally, in many cases, by placing the fluid in rarified air, with simultaneous application of hygroscopic substances. As the great object in evaporating processes in qualitative analysis is to guard against the least contamination, and as the evaporating fluid is the more liable to this the longer the operation lasts, the process is usually conducted with proper expedition, over the flame of a spirit or gas-lamp in a private room, free from dust and not exposed to draughts of air. If the operator has no room of the kind, he must have recourse to the much less suitable proceeding of covering the dish; this may be effected advantageously by placing over the latter a large glass funnel secured by a retort holder, leaving sufficient space between the edges of the funnel and those of the dish; the funnel is placed in a somewhat oblique position, so that the drops running down its sides may be received in a glass. Or the dish may be covered with a sheet of filter paper previously freed from inorganic substances by washing with dilute hydrochloric acid (see § 5); were common and unwashed filter paper used for the purpose, the sesquioxide of iron, lime, &c., contained in it, would dissolve in the vapors evolved (more especially if acid), and the solution, dripping down into the evaporating fluid, would speedily contaminate it. These precautions are necessary of course only in accurate analyses. Larger quantities of fluid are evaporated best in an obliquely placed glass flask covered with a cap of pure filtering paper, over a charcoal fire or gas; or also in a retort. Evaporating processes at 212° are conducted in an appropriate steam apparatus, or in the water-bath illustrated by Fig. 4.

Fig. 4.

§ 8.

7. Distillation.

This operation serves to separate a volatile liquid from a less volatile or fixed substance (no matter whether solid or fluid), and subsequently to recover the evaporated fluid. In order to attain this object, it is necessary to reconvert the liquid from the gaseous form in which it evaporates, into the fluid state. A distilling apparatus consists consequently of three parts, no matter whether admitting of separation or not. These three parts are—1st, a vessel in which the liquid to be distilled is heated, and thus converted into vapor; 2nd, an apparatus in which this vapor is cooled again or *condensed*, and thus reconverted to the fluid state; and 3rd, a vessel which

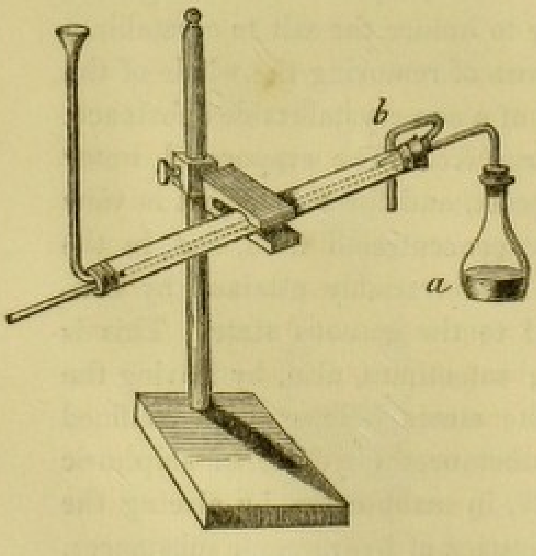

Fig. 5.

receives the thus reproduced fluid (the distillate). For the distillation of large quantities, we use either a metallic apparatus (a copper still with helmet, and condensing-tube of tin or pewter), or large glass retorts; in analytical investigations we generally employ the apparatus illustrated by Fig. 5.

§ 9.

8. Ignition.

Ignition is, in a certain measure, for solid bodies what evaporation is with regard to fluids; since it serves (at least generally) to separate volatile substances from less volatile, or from fixed bodies, in cases where the residuary substance alone is of importance. Ignition always requires the application of a high temperature, and in this it differs from exsiccation. The form or state which the eliminated substance assumes on cooling —whether it remains gaseous, as in the ignition of carbonate of lime; or assumes the liquid state as in the ignition of hydrate of lime; or solidifies, as in the ignition of a mixture containing chloride of ammonium —is a matter of perfect indifference as to the term applied to the operation.

The process of ignition is mostly employed to effect the elimination of a volatile body. In some instances, however, substances are ignited simply for the purpose of modifying their state, without any volatilization taking place; thus the sesquioxide of chromium is converted by ignition into its insoluble modification, &c.

Crucibles are the vessels made use of in ignition. In operations on a large scale, hessian or black-lead crucibles are used, heated by charcoal or coke; in analytical experiments small-sized crucibles or dishes are selected, either of porcelain, platinum, or silver, according to the nature of the substance to be ignited; these crucibles or dishes are heated over a *Berzelius* spirit-lamp or a similarly constructed gas-lamp.

§ 10.

9. Sublimation.

The term *sublimation* designates the process which serves to expand solid bodies into vapor by the application of heat, and subsequently to recondense the vapor to the solid state by refrigeration;—the substance volatilized and recondensed is called a *sublimate*. Sublimation is consequently a *distillation of solid bodies*. We have recourse to this process mostly to effect the separation of substances possessed of different degrees of volatility. Its application is of the highest importance in analysis for the detection of several substances, *e. g.* of arsenic. The vessels used in sublimation are of various shapes, according to the different degrees of volatility of the substances operated upon. In sublimations for analytical purposes we generally employ sealed glass tubes.

§ 11.

10. FUSION AND FLUXING.

We designate by the term "fusion" the conversion of a solid substance into a fluid form by the application of heat; fusion is most frequently resorted to for the purpose of effecting the combination or the decomposition of bodies. The term "fluxing" is applied to this process in cases where substances, either altogether insoluble or very difficult of solution in water and acids, are, by fusion in conjunction with some other body, modified or decomposed in such a manner, that they, or the new-formed compounds, subsequently admit of solution in water or acids. Fusion and fluxing are conducted either in porcelain, silver, or platinum crucibles, according to the nature of the compound. The crucible is supported on a triangle of moderately stout platinum wire, resting on, or attached to, the ring of the spirit* or gas-lamp.

The application of fluxing is especially required for the analysis of the sulphates of the alkaline earths, and also for that of many silicates. The flux most commonly used is carbonate of soda or carbonate of potassa, or, better still, a mixture of both, in equal atomic proportions (see § 74). In certain cases, hydrate of baryta is used instead of the alkaline carbonates (see § 75). But in either case the operation is conducted in platinum crucibles.

I have to add here 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 potassa, caustic potassa, metals, sulphides, or alkaline cyanides, should be fused in such vessels; nor ought readily deoxidizable metallic oxides, organic metallic salts, or phosphates to be ignited in them in the presence of organic compounds. It is also detrimental to platinum crucibles, and especially to their covers, to expose them directly to an intense charcoal fire, since the action of the ashes, under such circumstances, gives readily rise to the formation of silicide of platinum, which renders the vessel brittle. It is always advisable to support the platinum crucible in which a process of ignition or fusion is to be conducted, on a triangle of platinum wire. Soiled platinum crucibles are cleaned by fusing in them bisulphate of potassa, and boiling afterwards with water.

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

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* Triangles of thick iron wire, especially where they are to be laid upon the still stouter brass ring of the lamp, carry off too much heat to allow of the production of very high temperatures.

§ 12.

11. Deflagration.

We understand by the term "*deflagration*," in a more extended sense, every process of decomposition attended with noise or detonation—(the *cause* of the decomposition is a matter of perfect indifference as regards the application of the term in this sense).

We use the same term, however, in a more restricted sense, to designate the oxidation of a substance in the dry way, at the expense of the oxygen of another admixed substance (usually a nitrate or chlorate), and connect with it the idea of a sudden and violent combustion attended with vivid incandescence and noise or detonation. Deflagration is resorted to either to produce the desired oxide—thus tersulphide of arsenic is deflagrated with nitrate of potassa to obtain arseniate of potassa;—or it is applied to prove the presence or absence of a certain substance—thus salts are tested for nitric or chloric acid, by fusing them in conjunction with cyanide of potassium, and observing whether this process will cause deflagration or not, &c.

To attain the former object, the perfectly dry mixture of the substance under examination and of the deflagrating agent, is projected in small portions into a red hot crucible. Experiments of the latter description are invariably made with very minute quantities; the process is, in such cases, best conducted on a piece of thin platinum foil, or in a small spoon.

§ 13.

12. The use of the blowpipe.

This operation belongs exclusively to the province of analytical chemistry, and is of paramount importance in many analytical processes. We have to examine here, 1, the apparatus; 2, the mode of its application; and, 3, the results of the operation.

The blowpipe 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" (*Löthrohr*), by which the Germans designate it. It consists of three distinct parts; viz. 1st, a tube through which air is blown from the mouth; 2nd, a small vessel into which this tube is screwed air-tight, and which serves to collect and retain the moisture of the air blown into the tube; and, 3rd, a smaller tube, which is likewise fitted into this vessel, and forms a right angle with the larger tube; this small tube has a very fine aperture at its anterior extremity (§ 14, 4). The blowpipe serves to conduct a fine and continuous stream of air into the flame of a candle or lamp. Such a flame presents, under ordinary circumstances, three distinct parts to the eye; viz. 1st, a dark nucleus in the centre (Fig. 6, *a*); 2nd, a luminous part surrounding this nucleus (*b*); and, 3rd, a feebly luminous mantle encircling the whole flame (*c*). The dark nucleus is formed by the gases which the heat evolves from the oil or fat, and which cannot burn here from want of oxygen. In the luminous sphere these gases come into contact with a certain amount of oxygen, although insufficient for their complete combustion. The hydrogen of the carbide of hydrogen evolved burns therefore principally here, whilst the carbon separates in a state of intense white heat, causing thus the luminousness of this part. In the outer coat, the access of air is no longer limited, and all the gases not yet burned are consumed here. This part of the flame is the hottest; oxidizable bodies oxidize therefore with the greatest possible rapidity when placed in it, since all the conditions of oxidation are here united, viz. high temperature and an unlimited supply of oxygen. This part of the flame is accordingly called the *oxidizing flame*.

Fig. 6.

On the other hand, oxides having a tendency to yield up their oxygen, suffer *reduction* when placed within the *luminous* part of the flame, the oxygen being withdrawn from them by the carbon and the still unconsumed carbide of hydrogen present in this sphere. The luminous part of the flame is therefore called the *reducing flame*.

Now, if we conduct a fine stream of air from the side into a flame we have oxygen, not merely around the outer, but also in the inner part. Combustion takes place, therefore, in both parts. But this stream of air rushing with a certain force into the flame, carries forward the gases evolved, mixes intimately with them, and effects their combustion at a certain distance from the aperture of the blowpipe. This point, which is marked by a bluish light, is the hottest part of the whole flame, since the intimate intermixture of the air with the gases favors here the most complete combustion. The luminous part of the flame being thus surrounded on both sides by very hot flames, acquires likewise an extraordinary increase of heat; this elevation of temperature forms the principal object which we intend to attain by the application of the blowpipe. The hottest part of the flame lies now, of course, somewhat beyond the apex of the inner nucleus. In a reducing flame of this description many bodies will fuse readily which a common flame would leave unaltered. The heat of the oxidizing flame also is considerably increased by the blowpipe being more strongly concentrated upon one point.

A common spirit-lamp suffices in most cases to produce the requisite flame; in processes of solution, however, and in cases where a very high degree of heat is required, an oil-lamp or a strong wax candle must be used.

The *current* is produced by the cheek muscles alone, and not by the lungs. The way of effecting this may be readily acquired by practising for some time to breathe calmly with puffed-up cheeks, and whilst holding the blowpipe between the lips; a little practice and patience will soon enable the student to produce a continuous, even, and steady current.

The *supports* on which the substances to be examined are exposed to the blowpipe flame, are generally either charcoal, or platinum wire or foil. In the choice of charcoal intended for blowpipe experiments, we have to look more particularly to its being thoroughly burned, otherwise it will split and throw off the substances placed on it (see § 78). The substances to be examined are put into small conical cavities scooped out with a penknife or with a little tin tube. We generally employ charcoal as a support, when we want to reduce a metallic oxide, or to ascertain the degree of fusibility of a substance.

Metals which are volatile at the heat of the ordinary flame evaporate wholly or in part upon the reduction of their oxides. But these metallic vapors are re-oxidized in passing through the outer flame, and the oxide thus produced forms a slight incrustation around the substance upon the charcoal. Many of these incrustations exhibit characteristic colors which serve to assist in the detection of the metals.

The platinum wire as well as the foil are selected rather thin, but not too much so (see § 14, 6 and 7). We make use of platinum wire generally when fusing bodies in conjunction with fluxes (see §§ 81 and 82), for the purpose of inferring their nature from the color and other properties of the bead produced.

What renders the application of the blowpipe particularly useful in chemical experiments is the great expedition with which the intended results are attained. These results are of a twofold kind, viz. either they afford us simply an insight into the general properties of the examined body, and enable us accordingly only to determine the *class* to which it belongs, *i. e.* whether it is fixed, volatile, fusible, &c.; or the phenomena which we observe enable us at once to recognize the particular body which we have before us. We shall have occasion to describe these phenomena when treating of the deportment of the different substances with reagents.

APPENDIX TO THE FIRST SECTION.

§ 14.

APPARATUS AND UTENSILS.

As the student cannot well be supposed to be acquainted with the apparatus, &c., necessary for the processes of chemical analysis, I deem it advisable to furnish him here with a list of those articles which are required for the performance of simple experiments and investigations. I shall at the same time point out the principal qualities which these articles should possess.

1. A **Berzelius spirit-lamp.**[*] The vessel containing the spirit of wine should be connected with the wick-holder by means of a narrow tube, to avoid explosions; the chimney should not be too narrrow. The stopper on the aperture through which the spirit of wine is poured must not close air tight.

2. A **lamp-stand** with moveable rings and brackets.[†]

3. A **glass spirit-lamp** with ground glass cap and brass wick-tube.

4. A **brass or german silver blowpipe**, with a mouth-piece made of horn or bone (compare § 13). The principal tube should be about seven inches in length, 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 or screwed air-tight into the small vessel which is intended to collect and retain the moisture of the air blown through the pipe. It is advisable to have two small tubes, one with a wider, and the other with a narrower opening. Most of the small tubes usually sold at the chemical instrument makers are fitted simply with a small perforated platinum plate at their aperture. Those, however, which are provided with a finely perforated patinum cap are more durable; whenever the jet of these caps happens to be stopped up, the obstruction may be at once removed by igniting the cap before the blowpipe.

5. A **platinum crucible**, holding about a quarter of an ounce of water, and not too deep in proportion to its breadth, with a cover of the form of a shallow dish.

6. A **piece of platinum foil**, about two inches long and one inch in breadth, of sufficient thickness, and as clean and smooth as possible.

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[*] The application of gas in analytical chemistry in this country usually supersedes the Berzelius spirit-lamp.

[†] A brass ring to support dishes and flasks in the process of ebullition, and a ring of moderately stout iron wire to support the wire triangle in which the crucibles are placed in the process of ignition or fusion. Glass vessels, more particularly beakers, which it is intended to heat over the lamp, are usually placed upon a circular piece of net made of fine iron wire such as used in the making of sieves of medium fineness.

7. **Several 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 bottle filled with water, since most of the beads produced by fusion or fluxing dissolve in water; by this means the wires may always be kept clean.

8. **A stand with from twelve to twenty test tubes.** The latter may vary from six to eight inches in length, and must be of different width. They should be made of thin white glass, and so well annealed that they no not crack even though boiling water be poured into them. The brim must be quite round, and slightly turned over; it ought not to have a lip, since the latter is of no 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 unexceptionable, both in shape and durability.

11. **Several glass funnels** of various sizes. They must be inclined at an angle of 60°, and merge into their tube at a definite angle.

12. A **washing bottle** holding from twelve to sixteen ounces of water (see § 6).

13. **Several glass rods and tubes.** The latter are bent, drawn out, &c., over a Berzelius spirit-lamp, the former rounded at the ends before the blowpipe.

14. A selection of **watch-glasses.**

15. A small **agate mortar.**

16. Several small **iron spoons.** The bowl and the handle are made of one piece; the bottom of the bowl is about the size of a sixpence.

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

18. A **wooden filtering stand** (see § 5).

19. A **tripod** of thin iron, on which the dishes, &c., are placed which it is intended to heat over the small spirit-lamp.

SECTION II.

REAGENTS.

§ 15.

Various phenomena may manifest themselves upon the decomposition or combination of bodies. In some cases liquids change their color, in others precipitates are formed; sometimes effervescence takes place, and sometimes deflagration, &c. Now, if these phenomena are very striking, and attendant only upon the combination or decomposition of two definite bodies, it is obvious that the presence of one of these bodies may be detected by means of the other: *e. g.* if we know that a white precipitate of certain definite properties is formed upon mixing baryta with sulphuric acid, it is clear that, if upon adding baryta to any liquid, we obtain a precipitate exhibiting these properties, we may conclude that this liquid contains sulphuric acid.

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

These are divided into *general* and *special* reagents, according to the different objects attained by their application. By *general* reagents we understand those which serve to determine the *class* or *group* to which the substance under examination belongs; and by *special* reagents those which serve to detect *individual* substances. That the limits between these two divisions cannot be drawn with any degree of precision, ought not to be considered a valid objection to this classification, which is simply intended to accustom the student to keep invariably in mind whether he purposes to ascertain the *group* to which the substance under examination belongs, or to determine the latter *individually*.

The terms *characteristic* and *sensitive* or *delicate* are made use of to designate the two principal properties upon which the greater or less utility of a reagent depends. We call a reagent *characteristic*, if the alteration attendant upon the detection of the substance tested for, is so distinctly marked as to admit of no mistake. Thus, iron is a characteristic reagent for copper, protochloride of tin for mercury, because the phenomena produced by these reagents, viz. the separation of metallic copper and of globules of mercury, admit of no mistake. We call a reagent *sensitive* or *delicate* if its action is clearly perceptible, although a very minute quantity only of the substance tested for be present; such is, for instance, the action of starch upon iodine. A great many reagents are *both* characteristic and delicate; thus, for instance, terchloride of gold for protoxide of tin; ferrocyanide of potassium for sesquioxide of iron, and oxide of copper, &c.

I need scarcely mention that reagents must in general be chemically pure, *i. e.*, they must contain no extraneous substance in admixture, since, if this be not the case, the indications which they give cannot be relied upon. We must therefore make it an invariable rule to *test the purity of reagents before we use them*, no matter whether they be articles of our own production or of purchase.* The instructions which I shall give in

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* Although the *necessity* of this is fully admitted on all hands, we find that the *practice* is but too often neglected; thus it is by no means uncommon to see alumina entered among the substances detected in an analysis, simply because the solution of potassa used as one o

this respect when treating of the various reagents individually, refer, of course, only to such contaminations as are likely to arise from the mode of their respective preparation, but not to accidental admixtures.

One of the most common sources of error in qualitative analysis proceeds from missing the proper measure—the right quantity—in the application of reagents. Such terms as "*addition in excess*," "*supersaturation*," &c., often induce novices to suppose that they cannot add *too* much of the reagent, and thus some will *fill* a test tube with acid, simply to supersaturate a few drops of an alkaline fluid, whereas every drop of acid added, after the neutralization point has once been reached, is to be looked upon as an *excess* of acid. On the other hand, the addition of an insufficient amount is to be equally avoided, since a reagent, when added in insufficient quantity, often produces phenomena quite different from those which will appear if the same reagent be added in excess: *e. g.* a solution of chloride of mercury yields a *white* precipitate, if tested with a *small* quantity of hydrosulphuric acid; but if treated with the same reagent *in excess*, the precipitate is *black*. Experience has, however, proved that the most common mistake beginners make, is to add the reagents too copiously. The reason why this over-addition must impair the accuracy of the results, is obvious; we need simply bear in mind that the changes effected by reagents are perceptible within certain limits only, and that accordingly they may be the more readily overlooked the nearer we approach these limits by diluting the fluid.

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

We divide reagents into two classes, according as the state of fluidity which is indispensable for the manifestation of the action of reagents upon the various bodies, is induced by the application of heat, or by means of liquid solvents; we have accordingly, 1, *Reagents in the humid way*; and 2, *Reagents in the dry way*. For greater clearness and simplicity, we subdivide these two principal 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.

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the reagents happened to contain that earth; or iron, because the chloride of ammonia used contained a minute quantity of that metal, &c.

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

II. SPECIAL REAGENTS.

a. Reagents which serve principally for the detection of the BASES.

b. Reagents which serve principally for the detection of the ACIDS.

B. REAGENTS IN THE DRY WAY.

I. FLUXES.

II. BLOWPIPE REAGENTS.

A. REAGENTS IN THE HUMID WAY.

I. GENERAL REAGENTS.

a. Reagents principally used as simple solvents.

§ 16.

1. WATER ($H O$).

Preparation.—Pure water is obtained by distilling spring-water from a copper-still, with helmet and condensing tube of pure tin, or (but less advantageous) from a glass retort. The distillation is carried to about three-fourths of the quantity operated upon. Rain water collected in the open air may in many cases be substituted for distilled water.

Tests.—Pure distilled water must leave no residue upon evaporation. Nitrate of silver, chloride of barium, oxalate of ammonia, and lime-water, must not impair its transparency, nor impart the least tint to it.

Uses.—We use water * principally as a simple solvent for a great variety of substances. It serves moreover to effect the transformation of several neutral metallic salts into soluble acid, and insoluble basic compounds ; this is the case more particularly with terchloride of antimony and with the salts of bismuth.

§ 17.

2. ALCOHOL ($C_4 H_6 O_2 = Ae O, H O$).

Preparation.—Two sorts of alcohol are used in chemical analyses : viz. 1st, spirit of wine of 0·83 or 0·84 spec. gr. (*spiritus vini rectificatissimus* of the shops) ; and 2nd, absolute alcohol. The latter may be prepared by distilling the former from fused chloride of calcium, or by adding to it anhydrous sulphate of copper, shaking the mixture, decanting the fluid, and redistilling it.

Tests.—Pure alcohol must completely volatize, and ought not to cause the slightest smell of fusel oil, when rubbed between the hands ; nor should it redden litmus paper.

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* In analytical experiments we use only distilled water ; whenever therefore the term "water" occurs in the present work, distilled water is meant.

Uses.—Many substances are soluble in alcohol, whilst others are insoluble in this menstruum. Alcohol is therefore frequently employed to effect the separation of the former from the latter; for instance, to separate chloride of strontium from chloride of barium. Alcohol serves likewise to precipitate from aqueous solutions such substances as are insoluble in it, *e. g.* malate of lime. We use alcohol moreover for the production of various kinds of ether (especially of acetic ether, which is particularly characterized by its agreeable odor); and likewise to cooperate with acids in the reduction of certain substances, for instance, of binoxide of lead, chromic acid, &c. Alcohol serves also for the detection of various substances which impart a characteristic tint to its flame; such are especially boracic acid, strontia, soda, and potassa.

§ 18.

3. ETHER ($C_4\ H_5\ O = Ae\ O$).

Ether finds but very limited application in the analysis of inorganic bodies. It serves indeed almost exclusisely to detect and isolate bromine (§ 44); and for this purpose the officinal ether of commerce is sufficiently pure and strong.

b. Reagents which are principally used as chemical solvents.

§ 19.

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

Preparation.—Pour a cooled mixture of seven parts of concentrated sulphuric acid and two parts of water, over four parts of chloride of sodium in a retort; expose the retort, with slightly raised neck, to the heat of a sand-bath, until the evolution of gas ceases; conduct the evolved gas, by means of a double-limbed tube, into a flask containing 6 parts of water, and take care to keep this receiver constantly cool. To prevent the gas from receding, the tube ought only to dip about one line into the water of the receiver. Should the sulphuric acid employed in the process contain nitric acid, the gas which passes over first (and which in that case contains chlorine), must be received separately. The hydrochloric acid produced is diluted with water until its specific gravity is from 1·11 to 1·12.

Tests.—Hydrochloric acid intended for the purposes of chemical analysis must be perfectly colorless, and leave no residue upon evaporation; it should not discolor indigo-solution upon ebullition. Chloride of barium ought not to produce any precipitate, either in the highly diluted acid (sulphuric acid), nor even after ebullition with nitric acid (sulphurous acid). Hydrosulphuric acid must leave it unaltered. Sulphocyanide of potassium must not impart the least red tint to the diluted acid.

Uses.—Hydrochloric acid serves as a solvent for a great many substances. It dissolves lower and higher oxides in the form of chlorides, the solution being, in the case of the higher oxides, mostly attended with liberation of chlorine.—Salts with insoluble or volatile acids are also converted by hydrochloric acid into chlorides, with separation of the original acid; thus carbonate of lime is converted into chloride of calcium, with liberation of carbonic acid. Hydrochloric acid dissolves salts with non-volatile and soluble acids, *apparently* without decomposing them (*e. g.* phosphate of lime); but we must suppose that solutions of this description arise from the formation of a metallic chloride and of a soluble acid salt of the acid of the dissolved compound; thus, for instance, in the case of phosphate of lime, we must assume that chloride of calcium and acid phosphate of lime are formed. This explanation, however, will not serve for salts with acids forming no soluble acid compound with the base present; in such cases we must assume that the acid of the dissolved salt is present in the solution in a free state (borate of lime). Hydrochloric acid is also applied as a *special* reagent for the detection and separation of oxide of silver, suboxide of mercury, and lead (see below); and likewise for the detection of free ammonia (with which it produces in the air dense white fumes of chloride of ammonium).

§ 20.

2. NITRIC ACID (NO_5).

Preparation.—Add to nitric acid of commerce, which almost invariably contains sulphuric acid and hydrochloric acid, a solution of nitrate of silver, as long as a precipitate of chloride of silver continues to form; let the precipitate subside, decant the perfectly clear supernatant fluid into a retort, and distil to within a small quantity of the whole amount; dilute the distillate, if necessary, with water until the specific gravity of the diluted acid is equal to 1·2.

Tests.—Pure nitric acid must be colorless, and leave no residue upon evaporation on a platinum knife. The addition of solution of nitrate of baryta, or of nitrate of silver, must not cause the slightest turbidity. It is advisable to dilute the acid with water before adding these reagents, otherwise nitrates will precipitate.

Uses.—Nitric acid serves, in the first place, as a chemical solvent for metals, oxides, sulphides, oxygen salts, &c. The way in which the nitric acid effects the solution of metals and sulphides, is this: it oxidizes these bodies first, at the expense of part of its own oxygen, and converts the produced oxides subsequently into nitrates. Most oxides dissolve in nitric acid directly as nitrates, and the same is the case with most of the insoluble salts with weaker acids, the latter being expelled by the nitric acid in the process of solution. Salts with soluble and non-volatile acids are dissolved by nitric acid in the same manner as by hydrochloric acid. (See

§ 19.) Nitric acid serves moreover very frequently as an oxidizing agent; thus it is used, for instance, to convert the protoxide of iron into the sesquioxide; to decompose hydriodic acid and the iodides, &c.

§ 21.

3. Nitro-hydrochloric acid. *Aqua Regia.*

Preparation.—Mix one part of pure nitric acid with from three to four parts of pure hydrochloric acid.

Nitric and hydrochloric acids decompose each other, forming mostly as shown by *Gay-Lussac,* two compounds which are gaseous at the ordinary temperature, $NO_2\ Cl_2$ and $NO_2\ Cl$, at the same time water and free chlorine are liberated. If we use one equivalent of NO_5 to three equivalents of HCl, we may assume that only chloro-hyponitric acid ($NO_2\ Cl_2$) chlorine and water are formed ($NO_5 + 3\ HCl = NO_2\ Cl_2 + Cl + 3\ HO$.)

This decomposition ceases when the fluid is saturated with the gas; but it recomences the instant that this state of saturation is disturbed by the application of heat, or by the decomposition of the acid. The presence of the free chlorine, and also, but in a very subordinate degree, that of the acids named, renders aqua regia the most powerful solvent for metals (with the exception of those which form insoluble compounds with chlorine. Nitro-hydrochloric acid serves principally to effect the solution of gold and platinum, which metals are insoluble both in hydrochloric and in nitric acid, and also for the decomposition of various metallic sulphides, *e. g.* cinnabar, &c.

§ 22.

4. Acetic acid ($C_4H_3O_3 = \bar{A}$).

Preparation.—A highly concentrated acetic acid is not required in qualitative analytical processes; the common acetic acid of commerce, which contains 30 per cent of anhydrous acid, and has a specific gravity of 1·048, answers the purpose.

Tests.—Pure acetic acid must leave no residue upon evaporation, and—after saturation with carbonate of soda — emit no empyreumatic odor. Hydrosulphuric acid, solution of nitrate of silver, and solution of nitrate of baryta must not impair the transparency of the dilute acid, not even after addition of ammonia. Solution of indigo must not lose its color, when heated with it.

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

Uses.—Acetic acid possesses a greater solvent power for some substances than for others;—it is used, therefore, to distinguish the former from the latter; thus it serves, for instance, to distinguish oxalate of lime from phosphate of lime. We apply acetic acid also for the acidulation of fluids, in cases where we wish to avoid the use of mineral acids.

§ 23.

5. Chloride of ammonium ($N H_4$, Cl).

Hydrochlorate of Ammonia.—Muriate of Ammonia.—Sal Ammoniac.

Preparation.—Select sublimed white sal ammoniac of commerce. If it contains iron, you must purify it. For that purpose, add to the solution some sulphide of ammonium, let the precipitate which forms subside, and filter; add hydrochloric acid to the filtrate, until the latter manifests a feebly acid reaction; boil the mixture some time, saturate with ammonia, filter, if necessary, and crystallize. For use, dissolve one part of the salt in eight parts of water.

Tests.—Solution of chloride of ammonium, when evaporated on a platinum knife, should leave a residue which must subsequently upon continued application of heat, completely volatilize. Sulphide of ammonium must leave it unaltered. Its reaction must be perfectly neutral.

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

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

§ 24.

1. Reagent papers.

a. Blue litmus paper.

Preparation.—Digest one part of litmus of commerce with six parts of water, and filter the solution; divide the intensely blue filtrate into two equal parts; saturate the free alkali in the one part, by stirring with a glass rod, dipped in very dilute sulphuric acid, and repeating this process, until the color of the fluid just appears red; add now the other part of the filtrate, pour the fluid into a dish, and draw slips of fine unsized paper through it; suspend these slips over threads, and leave them to dry. The color of litmus paper must be perfectly uniform, and neither too light nor too dark.

Uses.—Litmus paper serves to detect the presence of free acid in fluids, since acids change its blue color to red. It is to be borne in mind, however, that the soluble neutral salts of most of the heavy metallic oxides produce the same effect.

β. REDDENED LITMUS PAPER.

Preparation.—Stir blue tincture of litmus with a glass rod dipped in dilute sulphuric acid, and repeat this process until the fluid begins to look distinctly red. Steep slips of paper in the tincture, and dry them as in *a*. The dried slips must look distinctly red.

Uses.—Pure alkalies and alkaline earths, and the sulphides of their metals, restore the blue color of reddened litmus paper; alkaline carbonates and the soluble salts of several other weak acids, especially of boracic acid, possess the same property. This reagent serves therefore for the detection of these substances in general.*

γ. GEORGINA PAPER (*Dahlia paper*).

Preparation.—Boil the violet-colored petals of *Georgina purpurea* (purple dahlia) in water, or digest them with spirit of wine, and steep slips of paper in the tincture obtained. The latter should be neither more nor less concentrated than is necessary to make the paper, after drying, appear of a fine and light violet blue color. Should the color too much incline to red, this may be remedied by adding a very little ammonia to the tincture.

Uses.—Georgina paper is reddened by acids, whilst alkalies impart a beautiful green tint to it. It is therefore an extremely convenient substitute both for the blue and the reddened litmus paper. This reagent, if properly prepared, is a most delicate test both for acids and alkalies. Concentrated solutions of caustic alkalies turn Georgina paper yellow, by destroying the coloring matter.

δ. TURMERIC PAPER.

Preparation.—Digest and heat one part of bruised turmeric root with six parts of spirit of wine; filter the tincture obtained, and steep slips of fine paper in the filtrate. The dried slips must exhibit a fine yellow tint.

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* Mr. A. S. Taylor has suggested that a very delicate test paper for detecting alkalies may be prepared by steeping slips of paper in an acid infusion of rose petals.

Uses.—Turmeric paper serves, like reddened litmus paper and Georgina paper, for the detection of free alkalies, &c.; as they change its yellow color to brown. It is not quite so delicate a test as the other reagent papers; but the change of color which it produces is highly characteristic, and very distinctly perceptible in many *colored* liquids; we cannot well dispense, therefore, with this paper. When testing with turmeric paper, it is to be borne in mind that, besides the substances enumerated in *β.*, several other bodies (boracic acid, for instance) possess the property of darkening its yellow color.

All reagent papers are cut into slips, which are kept in small well-closed boxes or stoppered bottles of dark glass.

§ 25.

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

Sulphuric acid of commerce (freed, if necessary, from nitric acid, by boiling) is sufficiently pure for the purposes of qualitative analysis. Should it, however, contain arsenic, this must be removed before the acid can be applied for the detection of arsenic by Marsh's method. The following process serves to effect this purpose: dilute the acid with six parts by weight of water, and saturate the fluid with hydrosulphuric acid; let the mixture stand in a moderately warm place until it is quite clear; then filter it from the precipitate, and boil the filtrate until it is perfectly inodorous.

Test.—Sulphuric acid, when boiled with a very minute quantity of indigo solution, must not destroy its blue color. When mixed with pure zinc and water, it must yield hydrogen gas, which, on being passed through a red-hot tube, does not deposit the slightest trace of arsenic (compare § 127). If the sulphuric acid is intended to serve for the detection and separation of very small quantities of lead, it must be perfectly free also from that metal. In cases of the kind, which, however, occur only rarely, an acid is used which has been purified by distillation (*acidum sulphuricum rectificatum.* This purified acid must leave no residue upon evaporation on platinum, and must remain perfectly clear upon dilution with four or five parts of spirit of wine.

Uses.—Sulphuric acid has for most bases a greater affinity than almost any other acid; and it is therefore used principally for the liberation and expulsion of other acids, especially of phosphoric, boracic, hydrochloric, nitric, and acetic acids. It serves also for the liberation of iodine from metallic iodides. In this latter process, it oxidizes the metals at the expense of its own oxygen, and is accordingly reduced to the state of 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 owing to the great affinity which sulphuric acid possesses 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 certain gases, more particularly of hydrogen and hydrosulphuric acid. It serves also as a *special* reagent for the detection and precipitation of baryta, strontia, and lead; for this purpose it is diluted with five parts of water.

§ 26.

3. Hydrosulphuric acid (*sulphuretted hydrogen*) (H S).

Preparation.—Hydrosulphuric acid gas is evolved best from sulphide of iron, which is broken into small lumps, and then treated with dilute sulphuric acid. Fused sulphide of iron may be procured so cheaply in commerce that it is hardly worth while to take the trouble of preparing it expressly. However, if you wish to prepare it yourself, this may be done by heating iron turnings in a hessian crucible with a hole in the bottom, and projecting small lumps of sulphur upon the ignited mass, until the whole is converted into sulphide of iron; the sulphide formed runs through the hole in the bottom of the crucible, and is received in a coal-shovel placed in the ash-pit. Or, introduce an intimate mixture of thirty parts of iron filings and twenty-one parts of flowers of sulphur, gradually, and in small portions at a time, into a red-hot crucible, awaiting always the incandescence of the portion last introduced, before proceeding to the addition of a fresh one. When you have thus put the whole mixture into the crucible, cover the latter closely, and expose it to a more intense heat, sufficient to make the sulphide of iron fuse more or less.

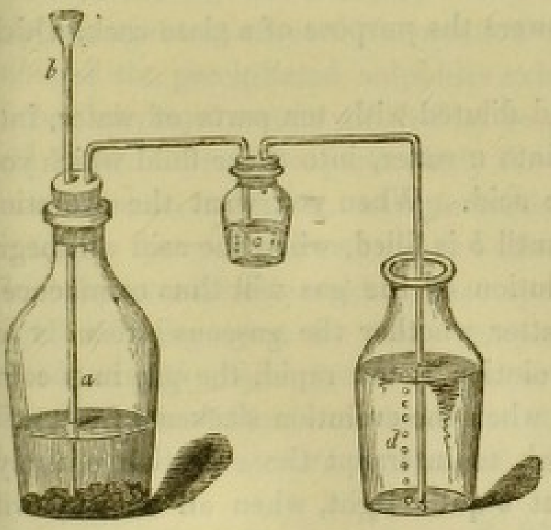

Fig. 7.

The evolution of the gas is effected in the apparatus illustrated by Fig. 7.

Pour water over the sulphide of iron in *a*, add strong sulphuric acid, and shake the mixture; the evolved gas is washed in *c*. When you have evolved a sufficient quantity of gas, pour the fluid off from the still undecomposed sulphide of iron, wash the bottle repeatedly with water, fill it with water, and keep it in that state. If you neglect this, the apparatus becomes speedily incrusted with crystals of sulphate of iron, which tends to interfere with subsequent processes of evolution of gas.

If you have often occasion to use hydrosulphuric acid, the repeated emptying and cleansing of the evolution flask becomes troublesome. I have therefore devised a new apparatus, which enables the operator to dispense with the cleansing of the evolution flask. Fig. 8 shows the construction of this apparatus. *d c* is a small tube of vulcanized India rubber in which is inserted a short piece of glass-rod fitting loosely in it; at *o*, a silk cord is passed twice round the tube; by drawing this cord tight, the passage of the gas may be completely interrupted; by drawing it a little less tight, the gaseous current may be more or less decreased.

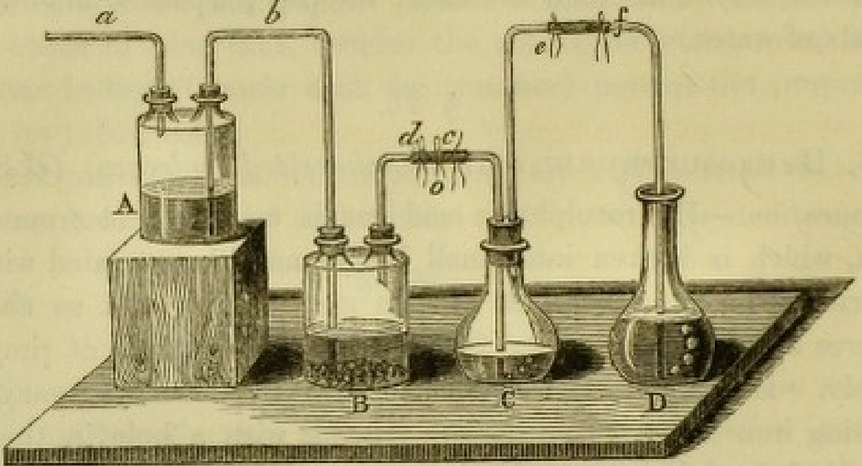

Fig. 8.

This simple contrivance fully answers the purpose of a glass cock, which it is not always easy to procure.

Put into A strong sulphuric acid diluted with ten parts of water, into B fused sulphide of iron in lumps, into C water, into D the fluid which you intend to treat with hydrosulphuric acid. When you want the evolution to commence, blow air through *a* until *b* is filled, when the acid will begin to flow from A into B, and the evolution of the gas will thus commence; the evolution regulates itself, no matter whether the gaseous stream is restricted or not at *o*, since, if the evolution is too rapid, the gas in B compels the acid to recede to A, whilst, when the evolution slackens, fresh acid flows over from A to B. If you wish to interrupt the evolution entirely, you need simply to draw the cord at *o* quite tight, when all the acid will flow back into A, and the evolution of gas entirely cease. As the sulphide of iron in B is secluded from the air, no oxidation of it can take place, and the apparatus remains therefore always in working order, provided the acid be from time to time withdrawn from A, which is effected most conveniently by means of a syphon.

Sulphuretted hydrogen water (*solution of hydrosulphuric acid*) is prepared by conducting the gas into very cold water, which has been previously freed from air by boiling. The operation is continued until the water is completely saturated with sulphuretted hydrogen gas, which may be readily ascertained by closing the mouth of the flask with the thumb, and shaking it a little: if, upon this, a pressure is felt from within, tending to push the thumb off the aperture of the flask, the operation may be considered at an end; but if, on the contrary, the thumb feels sucked into the mouth of the flask, this is a sure sign that the water is still capable of absorbing more gas.

Sulphuretted hydrogen water must be kept in well-closed vessels, otherwise it will soon suffer complete decomposition. The best way of preserving it unaltered for a very long time is to pour the fresh prepared solution immediately into small phials, and to place the latter, carefully corked, in an inverted position, into small vessels filled with water.

Tests.—Pure sulphuretted hydrogen water must be perfectly clear, and strongly emit the peculiar odor of the gas; when treated with sesquichloride of iron, it must yield a copious precipitate of sulphur. Addition of ammonia must not impart a blackish appearance to it.

Uses.—Hydrosulphuric acid has a strong tendency to undergo decomposition with metallic oxides, forming water and metallic sulphides; and the latter being mostly insoluble in water, are usually precipitated in the process. The conditions under which the precipitation of certain sulphides ensues differ materially;—by altering or modifying these conditions, we may therefore divide the whole of the precipitable metals into groups, as will be found explained in § 27. Hydrosulphuric acid is therefore an invaluable agent to effect the separation of metals into the principal groups. Some of the precipitated sulphides exhibit a characteristic color indicative of the individual metals which they respectively contain. Hydrosulphuric acid serves thus more particularly for the special detection of tin, antimony, arsenic, cadmium, manganese, and zinc. For more ample information upon this point, I refer to the third section. The great facility with which hydrosulphuric acid is decomposed, renders this substance also a useful reducing agent for many compounds; thus it serves, for instance, to reduce salts of sesquioxide of iron to salts of protoxide, chromic acid to the state of sesquioxide of chromium, &c. In these processes of reduction, the sulphur separates in the form of a fine white powder.

§ 27.

4. HYDROSULPHATE OF SULPHIDE OF AMMONIUM (*Sulphide of ammonium*) (NH_4S, HS).

Preparation.—Transmit hydrosulphuric acid gas through solution of ammonia to complete saturation, *i. e.* until the mixture ceases to precipitate a solution of sulphate of magnesia.

The fluid obtained must be kept in well-stoppered bottles, since contact with the atmosphere would cause its decomposition.

Tests.—Hydrosulphate of sulphide of ammonium is colorless at first, and deposits no sulphur on being mixed with acids; when exposed to the contact of the air, it acquires a yellow tint, owing to the formation of pentasulphide of ammonium. (NH_4, S_5). This yellow coloration does not render the reagent unfit for use; but it is to be borne in mind that it will *now* deposit sulphur when mixed with acids. Hydrosulphate of sulphide of ammonium must be transparent; upon the application of heat, it must volatilize without leaving a residue; it must not precipitate, nor even render turbid solution of magnesia or solution of lime.

Uses.—It has been mentioned already in the preceding paragraph that the separation of the metallic oxides precipitable by hydrosulphuric acid, and their consequent arrangement into groups, depends upon certain conditions respectively necessary for their precipitation. The *presence* of an alkali forms one of these conditions—its *absence* forms another—which means that certain sulphides precipitate only when the menstruum is alkaline, as they are soluble in acids; whilst others precipitate only when the menstruum is acid, as they are soluble in alkaline sulphides. Now the hydrosulphate of sulphide of ammonium—(which we will call in future, for briefness' sake, simply *sulphide of ammonium*)—may be looked upon as a reagent in which hydrosulphuric acid acts in conjunction with ammonia; we have here accordingly the conditions necessary to effect the precipitation of the above mentioned first group of sulphides, combined with those required to *prevent* the precipitation of the sulphides of the other group, or to effect their re-solution, when precipitated from acid solutions; to attain the latter object, the precipitate must be digested with the reagent. Sulphide of ammonium intended for the latter purpose must, in certain cases, contain an excess of sulphur, which may be readily given by digestion with that substance. If the fluid has already acquired a yellow tint from contact with the air, there is no necessity to add sulphur to it.

Besides the metallic sulphides, the precipitation of which is effected by the joint action of hydrosulphuric acid and ammonium, sulphide of ammonium precipitates, by the sole action of its ammonium, alumina and sesquioxide of chromium as hydrated oxides; and also substances contained in a state of simple solution in a free acid; for instance, phosphate of lime from its solution in hydrochloric acid; this property of sulphide of ammonium must not be lost sight of in experiments. In this process a salt of ammonia is formed, and hydrosulphuric acid escapes.

§ 28.

5. HYDROSULPHATE OF SULPHIDE OF SODIUM (NaS, HS).

Preparation.—Transmit hydrosulphuric acid gas through solution of soda to complete saturation. Keep the fluid in well-stoppered bottles. If you wish the mixture to contain some higher sulphide of sodium, digest it with some pulverized sulphur.

Uses.—Sulphide of sodium is substituted for sulphide of ammonium, to effect the separation of sulphide of copper from compounds of sulphur soluble in alkaline sulphides, *e. g.* from protosulphide of tin;—as sulphide of copper is not quite insoluble in sulphide of ammonium.

§ 29.

6. Potassa (KO) and soda (NaO).

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

a. Common solution of soda.

Preparation.—Put into a clean cast-iron pan provided with a lid, 5½ parts of crystallized carbonate of soda of commerce, and 20 parts of water, heat to boiling, and add, in small portions at a time, milk of lime prepared by treating 1½ part of burnt lime with 4 parts of warm water, and allowing the mixture to stand in a covered vessel until the mass is uniform. After the addition of the lime boil the mixture a quarter of an hour longer, and then filter a small portion of the fluid, and see whether the filtrate still causes effervescence in hydrochloric acid. If this is the case, the boiling must be continued, and, if necessary, some more milk of lime added to the fluid. When the solution is perfectly free from carbonic acid, cover the pan, allow the fluid to cool a little, and then draw off the clear solution from the residuary sediment, by means of a syphon filled with water, and transfer it to a glass flask. Boil the residue twice more with water, and draw off the fluid in the same way. Cover the flask closely with a glass plate, and allow the lime, still suspended in the fluid, to subside completely. Scour the iron kettle perfectly clean, pour the clear solution back into it, and evaporate it to 11 or 12 parts. The solution so prepared contains from 9 to 10 per cent of soda. It must be clear, colorless, and as free as possible from carbonic acid; sulphide of ammonium must not impart a black color to it. Traces of silicic acid, alumina, and phosphoric acid, are usually found in a solution of soda prepared in this manner; on which account it is unfit for use in accurate experiments.

Solution of soda is kept best in bottles closed with ground glass caps. In default of capped bottles, common ones with ground stoppers may be used; but in that case, the neck must be wiped perfectly dry and clean inside, and a slip of writing paper rolled round the stopper; since, if these precautions are neglected, it will be found impossible, after a time, to remove the stopper.

b. Hydrate of potassa purified with alcohol.

Preparation.—Dissolve some sticks of caustic potassa of commerce in rectified spirit of wine in a stoppered bottle, by digestion and shaking; let the solution deposit, and decant the clear liquid, or filter it, if necessary; evaporate the clear fluid in a covered silver dish over the spirit-lamp, until no more fumes escape; adding from time to time, during the evaporation, some water, to prevent blackening of the mass. Place the silver dish in cold water, until it has sufficiently cooled; remove the cake of caustic potassa from the dish, and break it in a hot mortar into coarse lumps; keep them in a well closed glass bottle. When required for use, dissolve one of the pieces in water.

The hydrate of potassa so prepared is sufficiently pure for most purposes, it contains a minute trace of alumina, but is usually free from phosphoric acid, sulphuric acid, and silicic acid. The solution must remain clear upon addition of sulphide of ammonium; hydrochloric acid must scarcely cause effervescence. The solution acidified with hydrochloric acid must upon evaporation to dryness leave a residue which dissolves in water to a clear fluid; when boiled with molybdate of ammonia, it must exhibit no yellow color; and, when treated with ammonia, it ought not to deposit slight flakes of alumina immediately; but only after standing several hours in a warm place.

c. *Hydrate of potassa prepared with baryta.*

Preparation.—Dissolve pure crystals of baryta (§ 48) by heating with water, and add to the solution pure sulphate of potassa, until a portion of the filtered fluid diluted, and acidified with hydrochloric acid no longer gives a precipitate on addition of a further quantity of the sulphate (16 parts of crystals of baryta require 9 parts of sulphate of potassa). Let the turbid fluid deposit, decant the clear solution, and evaporate it in a silver dish as in *b*. The hydrate of potassa so prepared is perfectly pure, except that it contains a trifling admixture of sulphate of potassa, which is left behind upon dissolving the hydrate in a little water. This hydrate is only rarely required, as for instance, to detect minute traces of alumina.

Uses.—The great affinity which the fixed alkalies possess for acids renders these substances powerful agents to effect the decomposition of the salts of most bases, and consequently the precipitation of those bases which are insoluble in water. Many of the so precipitated oxides redissolve in an excess of the precipitant, as, for instance, alumina, sesquioxide of chromium, and oxide of lead; whilst others remain undissolved, *e. g.* sesquioxide of iron, teroxide of bismuth, &c. The fixed alkalies serve therefore also as a means to separate the former from the latter. Potassa and soda dissolve also many salts (*e. g.* chromate of lead), sulphides, &c., and serve thus to separate and distinguish them from other substances. Many of the oxides precipitated by the action of potassa or soda exhibit a peculiar color, or possess other characteristic properties which may serve to lead to the detection of the individul metal which they respectively contain; such are, for instance, the precipitates of protoxide of manganese, hydrate of protoxide of iron, suboxide of mercury, &c. The fixed alkalies expel ammonia from its salts, and enable us thus to detect the latter substance by its odor, its reaction on vegetable colors, &c.

§ 30.

7. CARBONATE OF SODA (NaO, CO_2).

Preparation.—Triturate bicarbonate of soda of commerce, put the powder into a funnel stopped loosely with some cotton, make the surface even, cover it with a disc of difficulty permeable paper with turned up edges, and wash by pouring small quantities of water on the paper disc, until the filtrate, when acidified with nitric acid, is not rendered turbid by solution of nitrate of silver, nor by solution of chloride of barium. Let the salt dry, and then convert it by gentle ignition into the simple carbonate. This is effected best in a crucible or dish of silver or platinum; but it may be done also in a perfectly clean vessel of cast iron, or, on a small scale, in a porcelain dish. For use, dissolve one part of the salt in five parts of water.

Tests.—Carbonate of soda intended for analytical purposes 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; nor must addition of sulphocyanide of potassium impart a red, or boiling with molybdate of ammonia, a yellow tint to it; the residue which remains upon evaporating its solution to dryness, after previous supersaturation with hydrochloric acid, must leave no silica behind when redissolved in water.

Uses.—With the exception of the alkalies, carbonate of soda precipitates the whole of the bases, most of them as carbonates, but some also as hydrated oxides. Those bases which are soluble in water as bicarbonates require boiling for their complete precipitation from acid solutions. Many of the precipitates produced by the action of carbonate of soda exhibit a characteristic color which may lead to the detection of the individual metals which they respectively contain. Solution of carbonate of soda serves moreover for the decomposition of many insoluble salts of the alkaline earths, or of the metals, more particularly with organic acids. Upon boiling with carbonate of soda, these salts are converted into insoluble carbonates, whilst the acids combine with the soda, and are thus obtained in solution in the form of salts of soda. Carbonate of soda is often used also to saturate free acids.

§ 31.

8. AMMONIA (NH_4O).

Preparation.—The apparatus illustrated by Fig. 7 (see § 26) may also serve for the preparation of solution of ammonia, with this modification however, that no funnel tube being required in this process, the cork upon the flask, *a*, has only one perforation for the reception of the tube which serves to conduct the evolved ammonia into the washing bottle. Introduce into *a* four parts of chloride of ammonium in pieces about the size of a pea, and a quantity of dry hydrate of lime, prepared from five parts of lime; mix by shaking the flask, and add cautiously a sufficient quantity of water to make the powder into lumps. Put a small quantity of water only into the washing bottle (which should be rather capacious); but pour ten parts of water in the flask which is intended for the final reception of the washed gas. Connect the flask *a* now with the rest of the apparatus, and place in a sand-bath, and the flask *d* in a vessel of cold water. The evolution of gas speedily commences. Continue to heat until no more bubbles appear. Open the cork of the flask *a*, to prevent the receding of the fluid. The solution of ammonia contained in the washing bottle is impure, but that contained in the receiver *d* is perfectly pure; dilute it with water until the specific gravity is about 0·96=9 or 10 per cent of ammonia. Keep the fluid in bottles closed with ground stoppers.

Tests.—Solution of ammonia must be colorless, and ought not to leave the least residue when evaporated on a watch-glass, nor should it cause the slightest turbidity in lime water (carbonic acid). When supersaturated with nitric acid, solution of nitrate of baryta, or nitrate of silver, must not render it turbid, nor must sulphuretted hydrogen impart to it the slighest color.

Uses.—Ammonia is one of the most frequently used reagents. It is especially applied for the saturation of acid fluids, and also to effect the precipitation of a great many metallic oxides and earths; many of these precipitates redissolve in an excess of ammonia, as, for instance, the oxides of zinc, cadmium, silver, copper, &c., whilst others are insoluble in free ammonia. This reagent may serve, therefore, to separate and distinguish the former from the latter. Some of these precipitates, as well as their solutions in ammonia, exhibit a peculiar color, which may at once lead to the detection of the individual metal which they respectively contain.

Many of the oxides which are precipitated by ammonia from neutral solutions, are not precipitated by this reagent from acid solutions, their precipitation from the latter being prevented by the formation of an ammoniacal salt. Compare § 23, chloride of ammonium.*

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* The explanation of many chemical transformations into which the ammoniacal compounds enter, is greatly facilitated by assuming, both as regards its oxygen salts and also the aqueous solution of chloride of ammonium, that it exists as oxide of ammonium, NH_4O, instead of ammonia NH_3, which has no analogy with other bases. In the present edition, ammonia signifies oxide of ammonium NH_4O, and corresponds to the oxides of potassium and sodium, or potassa and soda.

§ 32.

9. Carbonate of ammonia (NH_4O, CO_2).

Preparation.—We use for the purposes of chemical analysis purified sesquicarbonate of ammonia, entirely free from any smell of animal oil, such as is prepared on a large scale from chloride of ammonium and chalk by sublimation. The outer and the inner surface of the mass are carefully scraped. One part of the salt is dissolved by digestion with four parts of water, to which one part of caustic solution of ammonia has been added.

Tests.—Pure carbonate of ammonia must completely volatilize. Neither solution of nitrate of baryta nor nitrate of silver, nor sulphuretted hydrogen, must color or precipitate it, after supersaturation with nitric acid.

Uses.—Carbonate of ammonia precipitates, like carbonate of soda, most metallic oxides and earths. The complete precipitation of many of these takes place likewise only on boiling. Several of the precipitates redissolve again in an excess of the precipitant. In like manner, carbonate of ammonia dissolves many hydrated oxides, and thus enables us to distinguish and separate them from others which are insoluble in this reagent.

Carbonate of ammonia, like caustic ammonia, and for the same reason, fails to precipitate from acid solutions many oxides which it precipitates from neutral solutions. (Compare § 31.) We use carbonate of ammonia in chemical analysis principally to effect the precipitation of baryta, strontia, and lime, and the separation of these substances from magnesia, since the latter is not preciptated by this reagent in the presence of salts of ammonia.

§ 33.

10. Chloride of barium ($Ba Cl$).

Preparation.—Mix six parts of finely pulverized sulphate of baryta with one part of powdered charcoal and one and a half part of flour, or eight parts of baryta, two parts of charcoal, and one part of resin. Introduce the mixture into a crucible, and expose this in a wind furnace to a long continued red heat. Let the mass cool, and then triturate it. Boil about nine-tenths of the powder with four times the quantity of water, and add hydrochloric acid until all effervescence of sulphuretted hydrogen ceases, and the fluid manifest a feebly acid reaction. Add now the last tenth of the powder, and continue to boil for some time longer. Filter the alkaline fluid, and let the filtrate crystallize. Redissolve the dried crystals in water, and crystallize again. For use dissolve one part of the crystals in ten parts of water.

Tests.—Pure chloride of barium must not alter vegetable colors; its solution must not be colored or precipitated by hydrosulphuric acid, nor by sulphide of ammonium. Pure sulphuric acid must precipitate every fixed particle from it, so that the fluid filtered from the precipitate formed upon the addition of that reagent, leaves not the slightest residue when evaporated on platinum foil.

Uses.—Baryta forms with many acids soluble, with others insoluble compounds. This property of baryta affords us a means of distinguishing the former acids, which are not precipitated by chloride of barium, from the latter in the solution of the salts of which this reagent produces a precipitate. The precipitated salts of baryta respectively manifest with other substances (acids) a different deportment. By subjecting these salts, therefore, to the action of such substances, we are enabled to subdivide the group of precipitate acids, and even to detect certain individual acids, and more particularly sulphuric acid. This renders chloride of barium one of our most important reagents.

In cases where it may be desirable to avoid the presence of a metallic chloride, nitrate of baryta is substituted for chloride of barium; this reagent may be readily prepared by dissolving carbonate of baryta (§ 49) in dilute nitric acid.

§ 34.

11. Chloride of calcium ($CaCl$).

Preparation.—Add chalk to warmed dilute hydrocholoric acid until all acid reaction ceases; filter the solution, and add some ammonia to the filtrate; let the mixture stand twenty-four hours at a moderate heat. Filter, heat the filtrate to boiling, add carbonate of ammonia until the lime is completely precipitated, and wash the precipitated carbonate of lime thoroughly. Heat now a mixture of one part of pure hydrocholoric acid with five parts of water, and add the washed carbonate of lime until the last portions remain undissolved, and the fluid is no longer acid. Boil up the solution several times, filter, and keep for use.

Tests.—Solution of chloride of calcium must be perfectly neutral, and neither be colored nor precipitated by sulphide of ammonium; nor ought it to evolve ammonia when mixed with hydrate of potassa or hydrate of lime.

Uses.—Chloride of calcium is, in its action and application, analogous to chloride of barium. For, as the latter reagent is used to divide the *inorganic* acids into groups, so chloride of calcium serves in the same manner to effect the separation of the *organic* acids into groups, since it precipitates some of them, whilst it forms soluble compounds with others. And, as is the case with the baryta precipitates, the different conditions under which the various insoluble lime salts are thrown down, enable us to subdivide the group of precipitable acids, and even to detect certain individual acids.

§ 35.

12. NITRATE OF SILVER ($Ag\,O, N\,O_5$).

Preparation.—Dissolve silver alloyed with copper, a piece of standard coin for instance, in nitric acid, precipitate with solution of chloride of sodium, and allow it to deposit, wash the precipitate by decantation, pour over it in a porcelain dish about an equal volume of very strong solution of potassa or soda, add a quantity of white sugar about equal to the amount of the dissolved silver, heat to boiling, keep boiling for some time, and wash the metallic silver obtained in form of a gray powder most thoroughly by decantation; dissolve the washed silver in dilute nitric acid, filter off the small remaining quantity of undecomposed chloride of silver, evaporate to dryness, and dissolve for use one part of the salt in twenty parts of water.

Tests.—Solution of nitrate of silver must be completely precipitated by dilute hydrochloric acid, so that the fluid filtered from the precipitated chloride of silver leaves no residue when evaporated on a watch-glass, and is neither precipitated nor colored by hydrosulphuric acid.

Uses.—Oxide of silver forms with many acids soluble, with others insoluble, compounds. Nitrate of silver may, therefore, serve, like chloride of barium, to effect the separation and arrangement of acids into groups.

Most of the insoluble compounds of silver dissolve in dilute nitric acid; chloride, bromide, iodide, and cyanide of silver are insoluble in that menstruum. Nitrate of silver is therefore a most excellent agent to distinguish and separate from all other acids, the hydracids corresponding to the last-enumerated four compounds of silver. Many of the insoluble salts of silver exibit a peculiar color (chromate of silver, arseniate of silver), or manifest a characteristic deportment with other reagents or upon the application of heat (formiate of silver); nitrate of silver is therefore an important agent for the direct detection of certain acids.

§ 36.

13. SESQUICHLORIDE OF IRON ($Fe_2\,Cl_3$).

Preparation.—Heat two parts of hydrochloric acid diluted with double the volume of water, with an excess of fine iron wire free from rust, until the evolution of hydrogen ceases; filter the solution into a very capacious porcelain dish, add one part of hydrochloric acid, heat to boiling, and add nitric acid cautiously and gradually in small portions to the boiling fluid until the brownish-green color of the solution changes to a dark yellow, which change of color is attended with violent effervescence caused by the sudden escape of the liberated nitric oxide gas. Whether the operation is really terminated, may be ascertained by diluting a portion of the solution with some water, and then testing with solution of ferricyanide of potassium, which must not produce a blue precipitate. Take now a small portion (about one twenty-fourth part) of the solution, and put it aside; evaporate the remainder in the water-bath to the consistence of syrup. Dilute the small portion which you have put aside with water, heat to boiling, precipitate with ammonia, and wash the precipitated hydrated sesquioxide of iron with boiling water. Dilute the contents of the evaporating dish with twelve parts of water, heat, add the hydrated sesquioxide of iron, heat to ebullition, keep boiling for some time, and then filter.

Tests.—Solution of sesquichloride of iron must not contain an excess of acid; this may be readily ascertained by stirring a sample of it with a glass rod dipped in ammonia, when the absence of any excess of acid will be proved by the formation of a precipitate which shaking of the vessel and agitation of the fluid fail to redissolve. Ferricyanide of potassium must not impart a blue color to it.

Uses.—Sesquichloride of iron serves to subdivide the group of organic acids which chloride of calcium fails to precipitate; as it produces precipitates in solutions of benzoates and succinates, but not in solutions of acetates and formiates. The aqueous solutions of the neutral acetate and formiate of sesquioxide of iron exhibit an intensely red color; sesquichloride of iron is therefore a useful agent for detecting acetic acid and formic acid. Sesquichloride of iron is exceedingly well adapted to effect the decomposition of phosphates of the alkaline earths (see § 135). It serves also for the detection of hydroferrocyanic acid, with which it produces Prussian blue.

II. SPECIAL REAGENTS IN THE HUMID WAY.

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

§ 37.

1. SULPHATE OF POTASSA (KO, SO_3).

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

Uses.—Sulphate of potassa precipitates from solutions of salts of baryta and strontia the insoluble sulphates of these oxides; it serves, therefore, to effect their detection and separation of baryta and strontia. It produces likewise a precipitate in very highly concentrated solutions of lime; but in most cases, this precipitate forms only after the lapse of some time; it fails to precipitate dilute solutions of lime. The action of sulphate of potassa is analogous to that of dilute sulphuric acid; the former reagent is, however, in many cases preferable to the latter, since it does not disturb the neutrality of the solution.

§ 38.

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

Preparation.—The phosphate of soda of commerce is purified by recrystallization, and one part of the pure salt is dissolved in ten parts of water for use.

Tests.—Solution of phosphate of soda must not become turbid when heated with ammonia. The precipitates which solution of nitrate of baryta and solution of nitrate of silver produce in it, must completely redissolve upon 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 baryta, strontia, and lime, as a special test for the detection of magnesia, for which latter purpose it is used in conjunction with ammonia, the magnesia precipitating under these circumstances, as basic phosphate of magnesia and ammonia.

§ 39.

3. ANTIMONIATE OF POTASSA (KO, SbO_5).

Preparation.—Mix four parts of metallic antimony of commerce with nine parts of nitrate of potassa; introduce the mixture gradually into a red hot hessian crucible, and keep this for some time in a state of ignition. Boil the fused mass with water until the soluble part is completely extracted; dry the residue, mix fifty parts of it with twenty-four parts of dry carbonate of potassa, introduce the mixture into a hessian crucible, and expose the latter for thirty minutes to a red heat; keep the friable mass produced in a stoppered bottle. For use, digest one part of the triturated mass with twenty parts of water at a gentle heat; allow the solution to cool, and filter it when quite cold. The solution obtained upon boiling the *antimonium diaphoreticum non ablutum* (*Phar. Bor.*) may also be used, as the salts which this solution contains in admixture scarcely impair the delicacy of the reaction.

Uses.—Antimonic acid forms with soda a salt of very difficult solubility. Antimoniate of potassa affords us therefore a means of detecting the presence of soda. For certain conditions and precautions to be observed in its application, I refer to § 87.

§ 40.

4. NEUTRAL CHROMATE OF POTASSA (KO, CrO_3).

Preparation.—Dissolve the bichromate of potassa of commerce in hot water and add to 100 parts of the salt forty-seven parts of dry carbonate of potassa. Crystallize the yellow fluid produced; wash the crystals thoroughly, and dissolve one part of the salt in ten parts of water.

Uses.—Chromate of potassa decomposes most of the soluble salts of metallic oxides, by double affinity. Most of the precipitated chromates are very difficultly soluble, and many of them exhibit characteristic colors which lead readily to the detection of the particular metal which they respectively contain. We use chromate of potassa principally as a test for lead.

§ 41.

5. CYANIDE OF POTASSIUM ($K Cy$).

Preparation.—Heat ferrocyanide of potassium of commerce (perfectly free from sulphate of potassa) gently, with stirring, until the crystallization water is completely expelled; triturate the anhydrous mass, and mix eight parts of the dry powder with three parts of perfectly dry carbonate of potassa; fuse the mixture in a covered hessian, or, better still, in a covered iron crucible, at a low red heat, until it becomes clear, and a sample of it, taken out with an iron spatula, looks perfectly white. Take the crucible now from the fire and tap it gently; pour the fused cyanide of potassium into a heated porcelain or silver dish, or upon a clean iron plate, with proper care, to prevent the running out of any of the minute particles of iron which have separated in the process of fusion and have subsided to the bottom of the crucible. The cyanide of potassium so prepared is exceedingly well adapted for analytical purposes, although it contains cyanate of potassa which, upon solution in water, is transformed into carbonate of ammonia and carbonate of potassa ($KO, C_2NO + 4\,HO = KO, CO_2 + NH_4O, CO_2$). The proper formula for the cyanide of potassium is therefore $5\,K Cy + KO, CyO$. Keep it in the solid form in a well stoppered bottle, and when you wish to use it dissolve one part in four parts of distilled water, without application of heat.

Tests.—Cyanide of potassium must be of a milk-white color, and quite free from particles of iron. The aqueous solution must be perfectly clear. It must contain neither silicic acid nor sulphide of potassium; the precipitate which salts of lead produce in its solution must accordingly be of a white color, and the residue which its solution leaves upon evaporation, after previous supersaturation with hydrochloric acid, must completely dissolve in water to a clear fluid.

Uses.—Cyanide of potassium (containing cyanate of potassa) produces in the solutions of most of the salts with metallic oxides, precipitates of metallic cyanides, of oxides or carbonates, which are insoluble in water. The precipitated cyanides are soluble in cyanide of potassium, and may therefore be separated from the oxides or carbonates by further addition of this reagent. Some of the metallic cyanides redissolve in the cyanide of potassium, even in presence of free hydrocyanic acid, and upon boiling, invariably as double cyanides; whilst others combine with cyanogen, forming new radicals, which remain in solution in combination with the potassium. The most common compounds of this nature are cobalticyanide of potassium, and ferro and ferricyanide of potassium. These differ from the double cyanides of the other descriptions particularly in this, that dilute acids fail to precipitate the metallic cyanides which they contain. Cyanide of potassium may accordingly serve also to separate the metals which form compounds of the latter description from others, the cyanides of which are precipitated by acids from their solution in cyanide of potassium. In the course of analysis, this reagent serves to effect the separation of cobalt from nickel, and also of copper from cadmium (compare §§ 108 and 119).

§ 42.

6. Ferrocyanide of potassium ($2\ K\ C_6\ N_3\ Fe, = 2\ K, Cfy$).

Preparation.—The ferrocyanide of potassium is found in commerce sufficiently pure for the purposes of chemical analysis. One part of the salt is dissolved in twelve parts of water for use.

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

§ 43.

7. Ferricyanide of potassium ($3\ K\ C_{12}\ N_6\ Fe_2, = 3\ K\ 2\,Cfdy$).

Preparation.—Conduct chlorine gas slowly into a solution of one part of ferrocyanide of potassium in nine parts of water, until the solution exhibits a fine deep red color by transmitted light (the light of a candle answers best), and a portion of the fluid produces no longer a blue precipitate, or a blue color, in a solution of sesquichloride of iron; evaporate to dryness; finally, in a water-bath, dissolve the residue in four parts of water; filter the solution, evaporate it rapidly to half its bulk, and crystallize. Dissolve the crystals obtained in three parts of water, evaporate the solution rapidly to half its volume, and crystallize again. Dissolve one part of the crystals, which are of a splendid red color, in ten parts of water. The solution, as already remarked, must neither produce a blue precipitate nor a blue color, when added to a solution of sesquichloride of iron.

Uses.—Ferricyanide of potassium decomposes with solutions of metallic oxides in the same manner as ferrocyanide of potassium. Of the metallic ferricyanides, the ferriprotocyanide of iron is more particularly characterized by its color, and we apply ferricyanide of potassium therefore principally as a test for protoxide of iron.

§ 44.

8. SULPHOCYANIDE OF POTASSIUM ($K, Cy S_2$).

Preparation.—Mix forty-six parts of anhydrous ferrocyanide of potassium, seventeen parts of carbonate of potassa, and thirty-two parts of sulphur; introduce the mixture into an iron pan covered with a lid, and fuse at a gentle heat; maintain the same temperature until the swelling of the mass which ensues at first has completely subsided and given place to a state of tranquil and clear fusion; increase the temperature now, towards the end of the operation, to dull redness, in order to decompose the hyposulphite of potassa which has been formed in this process. Remove the half refrigerated and still soft mass from the pan, pulverize it, and boil with alcohol. From the alcoholic solution obtained, part of the sulphocyanide of potassium will separate in colorless crystals, upon cooling; the rest is obtained by distilling the alcohol from the mother liquor. One part of the salt is dissolved in ten parts of water for use.

Uses.—Sulphocyanide of potassium serves for the detection of sesquioxide of iron; it is for that substance at once the most characteristic and the most delicate test.

§ 45.

9. HYDROFLUOSILICIC ACID ($Si Fl_2, H Fl$).

Preparation.—Pour six parts of concentrated sulphuric acid over a mixture of one part of sand and one part of fluor-spar in powder, in a strong glass flask, closed with a perforated cork into which the one end of a bent tube is fitted air-tight; the other limb reaching to the bottom of a tall flat-bottomed glass jar, containing a small amount of mercury, just sufficient to let the end of the tube dip into it to the extent of several lines; the mercury in the jar is covered with four parts of water. Promote the disengagement of fluosilicic gas, which commences even in the cold, by exposing the flask to a gentle heat in the sand-bath. Every gas bubble ascending through the mercury produces in the water a precipitate of hydrated silicic acid. The rationale of this process is, that of every three equivalents of fluoride of silicon ($Si\,Fl_2$) one equivalent decomposes with two equivalents of water into silicic acid ($Si\,O_2$), which separates, and hydrofluoric acid, which combines with the two undecomposed equivalents of fluoride of silicon, forming hydrofluosilicic acid.

$$[3\,Si\,Fl_2 + 2\,H\,O = 2\,(Si\,Fl_2,\,H\,Fl) + Si\,O_2].$$

The precipitated hydrate of silicic acid renders the liquid gelatinous, and it is for this reason that the aperture of the exit tube must be placed under mercury, since 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 channels of silica in the gelatinous liquid, through which it gains the surface without undergoing decomposition, if they are not occasionally broken by stirring the liquid. When the evolution of gas has completely ceased, throw the gelatinous paste upon a linen cloth, squeeze the fluid through, and filter it afterwards. Keep the filtrate for use.

Tests.—Hydrofluosilicic acid, mixed with two parts of water, must produce no precipitate in solutions of salts of strontia.

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

§ 46.

10. OXALATE OF AMMONIA ($N\,H_4O,\,\bar{O}$).

Preparation.—Dissolve commercial oxalic acid in twenty parts of water, add caustic or carbonate of ammonia until the fluid begins to manifest a feebly alkaline reaction; let it stand at rest for twelve hours, filter, and evaporate to crystallization. Dissolve one part of the salt in twenty-four parts of water for use.

Tests.—The solution of oxalate of ammonia must not be precipitated nor rendered turbid by hydrosulphuric acid, nor by sulphide of ammonium.

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

§ 47.

11. TARTARIC ACID ($C_4 H_2 O_5 = \bar{T}$).

The tartaric acid of commerce is sufficiently pure for the purpose of chemical analysis. It is best preserved in powder, since its solution, after some time, suffers decomposition, a white film forming upon its surface. For use, it is dissolved in water, with the aid of heat.

Uses.—The addition of tartaric acid to solution of sesquioxide of iron, protoxide of manganese, alumina, and several other metallic oxides, prevents the usual precipitation of these metals by an alkali: their non-precipitation is owing to the formation of double tartrates, which are not decomposed by alkalies.

Tartaric acid may serve therefore to effect the separation of these metals from others, the precipitation of which it fails to prevent. Tartaric acid forms a difficultly soluble acid salt with potassa, but not so with soda; it is therefore one of our best reagents to distinguish between these alkalies.

§ 48.

12. CAUSTIC BARYTA ($Ba O$).

Preparation.—Boil crude sulphide of barium (compare § 33), for some time with water, filter hot when the crystallization point is attained, cover the vessel with the filtrate closely, and let the liquid cool. Pour the mother-liquor off,* and boil the crystals with a quantity of water just sufficient to dissolve them; keep boiling (renewing occasionally the evaporating water), and add finely triturated and sifted copper scales in small portions at a time, until a filtered sample of the fluid gives a pure white precipitate, when mixed with a small quantity of solution of acetate of lead. Filter while boiling into a vessel closely covered with a glass plate. When the liquid has somewhat cooled, place the vessel in a dish containing some milk of lime, invert a bell glass or a large basin over it, and let it stand several days in a cool place. Then pour the fluid (water of baryta) off, let the crystals drain in a well-covered funnel, dry rapidly between sheets of blotting-paper, and keep in well-stoppered bottles. When you wish to use the reagent, dissolve one part of the crystals in twenty parts of water.

Tests.—Water of baryta must, after precipitation of the baryta by sulphuric acid, give a filtrate which leaves no fixed residue upon evaporation in a platinum crucible.

Uses.—Caustic baryta is a strong base, and acts in a similar manner to

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* This and the residue of the first operation may be used for the preparation of chloride of barium.

lime, that is, it precipitates the alkaline earths and metallic oxides which are insoluble in water, from the solution of their salts. We use baryta in the course of analysis simply for the precipitation of magnesia, and for this purpose solution of sulphide of barium will serve as well, if it contains caustic baryta, which it always does except when prepared at an exceeding high temperature. Water of baryta may also be applied like chloride of barium and nitrate of baryta, to effect the precipitation of those acids which form insoluble compounds with baryta; it is principally, however, employed for the detection of carbonic acid.

§ 49.

13. CARBONATE OF BARYTA (BaO, CO_2).

Preparation.—Dissolve crystallized chloride of barium in water, heat to boiling, and add a solution of carbonate of ammonia, mixed with some caustic ammonia, or of pure carbonate of soda, as long as a precipitate forms; let deposit, decant repeatedly, transfer the precipitate to a filter, and wash until the washing water is no longer rendered turbid by solution of nitrate of silver. Stir the precipitate with water to the consistence of thick milk, and keep the mixture in a stoppered bottle. It must of course be shaken every time it is intended to use it.

Tests.—Pure sulphuric acid must precipitate every fixed particle from a hydrochloric acid solution of carbonate of baryta (compare caustic baryta).

Uses.—Carbonate of baryta completely decomposes the solutions of many metallic oxides, *e. g.* sesquioxide of iron, alumina, precipitating from them the whole of the oxide as hydrate and a basic salt, whilst some other metallic salts are not precipitated by it. It serves therefore to separate the former from the latter, and is an excellent means to effect the separation of sesquioxide of iron and alumina from protoxide of mangenese, oxide of zinc, &c., and also from lime and magnesia.

§ 50.

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

Preparation.—Reduce English tin to powder by means of a rasp, or fuse it in an iron spoon, remove from the fire, and triturate the liquid fused mass with a pestle until it has completely solidified. Boil the powder in a flask for some time with concentrated hydrochloric acid (taking care always that there is an excess of tin), until no more hydrogen gas is evolved; dilute the solution with four times its amount of water, slightly acidulated with hydrochloric acid, and filter. Pour the filtrate into a bottle containing small bits of metallic tin or some pure tin-foil, and close the mouth carefully. If these precautions be neglected, the protochloride will soon change to bichloride, which, of course, will render the reagent totally unfit for the purpose for which it is intended.

Tests.—Solution of protochloride of tin, when add to a solution of chloride of mercury, must immediately produce a white precipitate of subchloride of mercury; when treated with hydrosulphuric acid it must give a dark brown precipitate; it must not be precipitated nor rendered turbid by sulphuric acid.

Uses.—The great tendency of protochloride of tin to absorb oxygen, and thus to form binoxide, or rather bichloride,—as the binoxide, in the moment of its formation, decomposes with the free hydrochloric acid present,—render this substance one of our most powerful reducing agents. We employ it in the course of analysis as a test for mercury, and also to effect the detection of gold, for which latter purpose it is previously mixed with some nitric acid, without heating.

§ 51.

15. TERCHLORIDE OF GOLD ($Au\ Cl_3$).

Preparation.—Take fine shreds of gold, which may be alloyed either with silver or copper, treat them in a flask with an excess of nitrohydrochloric acid, and apply a gentle heat until no more of the metal dissolves. If the gold was alloyed with copper, which is known by the brownish-red precipitate produced by ferrocyanide of potassium in a portion of the solution diluted with water, mix the solution with solution of sulphate of protoxide of iron in excess; this will reduce the terchloride to metallic gold, which will separate in the form of a fine brownish-black powder. Wash the powder in a small flask, and redissolve it in nitrohydrochloric acid, evaporate the solution to dryness in the water-bath, and dissolve the residue in thirty parts of water. If the gold was alloyed with silver, the latter metal remains as chloride of silver upon treating the alloy with nitrohydrochloric acid. In that case evaporate the solution at once to dryness, and dissolve the residue in thirty parts of water.

Uses.—Terchloride of gold has a great tendency to yield up its chlorine; it readily converts, therefore, protochlorides into higher chlorides, protoxides into higher oxides and chlorides, &c. These peroxidations are usually indicated by the precipitation of pure metallic gold in the form of a blackish-brown powder. In the course of analysis, this reagent is used only for the detection of protoxide of tin, in the solution of which it produces a purple color, or a purple precipitate (see § 125).

§ 52.

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

Preparation.—Treat platinum filings purified by boiling with nitric acid, with concentrated hydrochloric acid and some nitric acid, in a narrownecked flask, and apply a gentle heat, adding occasionally fresh portions of nitric acid, until the platinum is completely dissolved. Evaporate the solution to dryness in the water-bath, with addition of hydrochloric acid, and dissolve the residue in ten parts of water.

Tests.—Bichloride of platinum must upon evaporation to dryness in the water-bath leave a residue which dissolves completely in spirit of wine.

Uses.—Bichloride of platinum forms very sparingly soluble double salts with chloride of potassium and chloride of ammonium, but not with chloride of sodium. It serves therefore to detect ammonia and potassa, and is indeed our most delicate reagent for the latter substance.

§ 53.

17. ZINC (Zn).

Select the sublimed zinc of good quality, and, above all, perfectly free from arsenic. The method described § 25 will serve to detect the presence of the slightest trace of this substance. Fuse the metal, and pour the fused mass in a thin and broken stream into a large vessel with water. The remainder is to be cast into small cylinders, by pouring the fused metal into wooden moulds, coated with chalk.

Uses.—Zinc serves in qualitative analysis for the evolution of hydrogen, and also of arsenetted and antimonetted hydrogen gas (compare § 124 and § 127).

§ 54.

18. IRON (Fe).

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

§ 55.

19. COPPER (Cu).

We use copper exclusively to effect the reduction of mercury, which precipitates upon it as a white coating which shines with silvery lustre when rubbed. A copper coin scoured with fine sand, or in fact any clean surface of copper, may be employed for this purpose.

b. Special reagents which are principally applied for the detection or separation of individual acids.

§ 56.

1. ACETATE OF SODA (Na O, $\bar{A}$).

Preparation.—Mix one part of purified bicarbonate of soda (§ 30) with four parts of water, add acetic acid to exact neutralization, and expel the carbonic acid by the application of heat.

Tests.—Acetate of soda when boiled with a solution of molybdate of ammonia mixed with hydrochloric acid must not impart a yellow color to it.

Uses.—Acetate of soda when brought into contact with a stronger free acid is decomposed; the stronger acid combines with the soda, and the acetic acid is liberated. In the course of analysis, acetate of soda is used principally to precipitate phosphate of sesquioxide of iron (which is insoluble in acetic acid) from its solution in hydrochloric acid.

§ 57.

2. MOLYBDATE OF AMMONIA.

Preparation.—Expose finely triturated pure sulphide of molybdenum to the action of a moderate heat, until the black sulphide is converted entirely, or at all events to the greater extent, into white molybdic acid (which looks yellow as long as it still remains hot). The process occupies much time, but presents no difficulties in other respects. As the reagent must be perfectly free from phosphoric acid, it is advisable to conduct the operation with small quantities in a platinum crucible* placed in an oblique position; with large quantities, in a muffle protected against the dust of the ashes. Digest the molybdic acid in ammonia until complete solution is effected. Filter the colorless fluid. Keep the residuary sulphide of molybdenum for the next operation.

Tests.—Solution of molybdate of ammonia mixed with nitric acid or hydrochloric acid until the precipitate of molybdic acid which forms at first is redissolved, must remain colorless upon boiling. If it acquires a yellow tint, the reagent contains phosphoric acid, and is unfit for use (supposing always, of course, that the hydrochloric or nitric acid was perfectly pure).

Uses.—Molybdic acid forms with phosphoric acid and ammonia a peculiar compound which is very difficultly soluble in water and acids. The hot solution of this compound has an intensely yellow color. Molybdate of ammonia affords therefore an excellent means to detect minute quantities of phosphoric acid (compare § 135).

§ 58.

3. CAUSTIC LIME ($Ca\,O$).

Preparation.—Digest recently prepared hydrate of lime for some time with cold distilled water, shaking the mixture occasionally; allow the undissolved portion of the lime to subside, decant, and keep the clear fluid in well-stoppered bottles. Besides lime-water, hydrate of lime prepared by slacking quicklime with half its volume of water, should also be kept.

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* Platinum is not injuriously affected by the process.

Tests.—Lime-water must impart a deep brown color to turmeric paper, and give with carbonate of potassa a rather abundant precipitate. It is totally unfit for use as soon as it loses these properties, which takes place speedily on exposure to the air.

Uses.—Lime forms with many acids insoluble, with others soluble salts. Lime-water may therefore serve to distinguish the former acids from the latter. Many of the precipitable acids are thrown down only under certain circumstances, *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 principally to effect the detection of carbonic acid, and also to distinguish tartaric acid and citric acid from one another. Hydrate of lime serves, like caustic potassa, to liberate ammonia, and is in many cases preferable to the latter reagent.

§ 59.

4. SULPHATE OF LIME (CaO, SO_3).

Preparation.—Mix a concentrated solution of chloride of calcium with dilute sulphuric acid, wash the precipitate formed thoroughly, digest, and shake it for some time with water; let the undissolved particles subside, decant, and keep the clear fluid for use.

Uses.—Sulphate of lime being a difficultly soluble salt is a very convenient agent in cases where it is wished to apply a solution of a lime salt or of a sulphate of a definite degree of dilution. As dilute solution of a lime salt it is used in the detection of oxalic acid; as dilute solution of a sulphate, it affords an excellent means of distinguishing between baryta, strontia, and lime (§ 96).

§ 60.

5. SULPHATE OF MAGNESIA (MgO, SO_3).

Preparation.—Dissolve one part of sulphate of magnesia of commerce in ten parts of water; if the salt is not perfectly pure, subject it to recrystallization.

Uses.—Sulphate of magnesia serves almost exclusively for the detection of phosphoric acid, which it precipitates from aqueous solutions of phosphates in presence of ammonia, in the form of a double salt (basic phosphate of magnesia and ammonia) which is nearly insoluble, and has highly characteristic properties. Sulphate of magnesia is moreover employed to test the purity of sulphide of ammonium (see § 27).

§ 61.

6. SULPHATE OF PROTOXIDE OF IRON (FeO, SO_3).

Preparation.—Heat an excess of iron nails free from rust, or of iron wire, with dilute sulphuric acid, until the evolution of hydrogen ceases; filter the sufficiently concentrated solution, add a few drops of dilute sulphuric acid to the filtrate, and allow it to cool. Wash the crystals with water very slightly acidulated with sulphuric acid, dry, and keep for use. The sulphate of protoxide of iron may also be prepared from the solution of sulphide of iron in dilute sulphuric acid, which is obtained in the process of evolving hydrosulphuric acid.

Uses.—Sulphate of protoxide of iron has a great disposition to absorb oxygen, and to be converted into the sulphate of the sesquioxide. It acts therefore as a powerful reducing agent. We employ it principally for the reduction of nitric acid, from which it separates nitric oxide, by withdrawing three atoms of oxygen from it. The decomposition of the nitric acid being attended, in this case, with the formation of a very peculiar intensely brownish-black compound of nitric oxide with an undecomposed portion of the iron salt, this reaction affords a particularly characteristic and delicate test for the detection of nitric acid. Sulphate of protoxide of iron serves moreover for the detection of hydro-ferricyanic acid, with which it produces a kind of Prussian blue, and also to effect the precipitation of metallic gold from solutions of the salts of that metal.

§ 62.

7. SOLUTION OF MAGNETIC OXIDE OF IRON (PROTOSESQUIOXIDE) ($Fe\,O, S\,O_3 + Fe_2\,Cl_3$).

This reagent is not kept in the laboratory, but prepared, when required, by mixing solution of sulphate of protoxide of iron with some sesquichloride of iron. It serves for the detection of hydrocyanic acid (§ 146).

§ 63.

8. SODIO-PROTOCHLORIDE OF PALLADIUM.

Dissolve five parts of palladium in nitrohydrochloric acid (compare § 52), add six parts of pure chloride of sodium, evaporate in the water-bath to dryness, and dissolve one part of the residuary double salt in twelve parts of water. The yellow solution affords an excellent means of detecting and separating iodine (§ 145.).

§ 64.

9. NEUTRAL ACETATE OF LEAD ($Pb\,O, \overline{A}$).

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

Uses.—Oxide of lead forms with a great many acids compounds which are insoluble in water, and are marked either by their peculiar color or characteristic deportment. The acetate of lead therefore produces precipitates in the solutions of these acids or of their salts, and contributes essentially to the detection of several of them. Chromate of lead, for instance, is characterized by its yellow color, phosphate of lead by its peculiar deportment before the blowpipe, and malate of lead by its ready fusibility.

§ 65.

10. Hydrate of teroxide of bismuth.*

Preparation.—Dissolve bismuth, freed from arsenic by fusion with hepar sulphuris or nitrate of potassa, in dilute nitric acid, dilute the solution as much as is practicable without producing a permanent precipitate, filter, and evaporate the filtrate to crystallization. Wash the crystals with water containing nitric acid, triturate them with water, add ammonia in excess, and let the mixture digest for some time; then filter, wash, and dry the white precipitate, and keep it for use.

Tests.—Hydrosulphuric acid must throw down from a solution of this reagent in dilute nitric acid, a white precipitate insoluble in ammonia and sulphide of ammonium; and, accordingly, the ammonia filtered off from this precipitate must remain perfectly clear upon addition of hydrochloric acid, whilst in the sulphide of ammonium filtered off from it, that acid must only produce a pure white turbidity (sulphur).

Uses.—Teroxide of bismuth, when boiled with alkaline solutions of metallic sulphides, decomposes with the latter, giving rise to the formation of metallic oxides, and sulphide of bismuth. It is better adapted to effect decompositions of this kind than oxide of copper, since it enables the operator to judge immediately upon the addition of a fresh portion whether the decomposition is complete or not. It has still another advantage over oxide of copper, viz., it does not, like the latter, dissolve in the alkaline fluid, in presence of organic substances, nor does it act as a reducing agent upon reducible oxygen compounds. We use it principally to convert tersulphide and pentasulphide of arsenic into arsenious and arsenic acids, for which purpose oxide of copper is altogether inapplicable, since it converts the arsenious acid immediately into arsenic acid, being itself reduced to the state of suboxide.

§ 66.

11. Sulphate of copper (CuO, SO_3).

Preparation.—This reagent may be obtained in a state of great purity, by treating the residue remaining in the retort in the process of preparing sulphite of soda (§ 70) with water, applying heat, filtering, and allowing to crystallize.

Tests.—Pure sulphate of copper must be precipitated completely from

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* The basic nitrate of bismuth of commerce, if perfectly free from arsenic and antimony, may also be used instead of the hydrate of teroxide.

its solutions by hydrosulphuric acid; ammonia and sulphide of ammonium must accordingly leave the filtrate unaltered.

Uses.—Sulphate of copper is employed in qualitative analysis, to effect the precipitation of hydriodic acid in the form of subiodide of copper. For this purpose it is necessary to mix the solution of one part of the sulphate of copper with two and a half parts of sulphate of protoxide of iron, otherwise half of the iodine will separate in the free state. The protoxide of iron changes in this process to sesquioxide at the expense of the oxygen of the oxide of copper, which latter is thus reduced to the state of suboxide. Sulphate of copper is used also as a test for arsenious and arsenic acids, for which purpose it is a very *delicate*, but by no means a *characteristic* reagent. For this purpose it is best to convert the sulphate into ammonio-sulphate of copper, by adding ammonia to its solution until the precipitate which forms at first is just redissolved. Applied jointly with potassa, sulphate of copper is a most excellent means to distinguish arsenious acid from arsenic acid, since the presence of the former acid is indicated at once by the separation of red oxide (suboxide) of copper. Compare § 127. Sulphate of copper may also serve as a test to detect the presence of hydroferrocyanic acid.

§ 67.

12. NITRATE OF SUBOXIDE OF MERCURY. (Hg_2O, NO_5).

Preparation.—Treat one part of mercury, in a porcelain dish, with one part of pure nitric acid, and let the mixture stand twenty-four hours in a cool place; separate the crystals formed from the undissolved mercury and the mother-liquor, and dissolve them in water mixed with one-sixteenth part of nitric acid, by trituration. Filter the solution and keep the filtrate in a bottle, over metallic mercury.

Uses.—The nitrate of suboxide of mercury acts in an analogous manner to the nitrate of silver. In the first place, it precipitates many acids, especially the hydracids; and secondly, it serves for the detection of several readily oxidizable substances, *e. g.* of formic acid; since the oxidation of such substances, at the expense of the oxygen of the suboxide of mercury, is attended with the highly characteristic separation of metallic mercury.

§ 68.

13. OXIDE OF MERCURY (HgO).

Preparation.—Moisten oxide of mercury of commerce with alcohol and reduce the moistened oxide to very fine powder. Keep the powder for use.

Uses.—Oxide of mercury is an excellent test for hydrocyanic acid, since it dissolves in alkaline fluids only when this acid is present. Compare § 146. It serves also to effect the separation of magnesia from soda and potassa, as it completely decomposes chloride of magnesium (with formation of chloride of mercury and magnesia), when it is evaporated with a solution of that salt, and the residue gently ignited.

§ 69.

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

The commercial chloride of mercury is sufficiently pure for the purposes of chemical analysis. One part of the salt is dissolved in sixteen parts of water.

Uses.—Chloride of mercury gives with several acids, *e. g.* with hydriodic acid, precipitates of characteristic color; but it is, nevertheless, one of the least essential reagents for the determination of individual acids. It serves also as an oxidizing agent, and enables us to detect the presence of readily oxidizable bodies, *e. g.* of protoxide of tin, by the separation of protochloride of mercury, attendant upon their oxidation.

§ 70.

15. SULPHITE OF SODA.

Preparation.—Heat five parts of copper shreds with twenty parts of concentrated sulphuric acid in a flask, and conduct the sulphurous acid gas evolved, first through a washing bottle containing some water, then into a flask containing four parts of purified bicarbonate of soda (§ 30), and from twenty to thirty parts of water, and which is not much more than half full; continue the transmission of the gas until the evolution of carbonic acid ceases. Keep the solution in a well-stoppered bottle.

Tests.—Sulphite of soda, when evaporated to dryness with pure sulphuric acid, must leave a residue,* the aqueous solution of which is not altered by hydrosulphuric acid, nor colored yellow by boiling with a solution of molybdate of ammonia mixed with hydrochloric acid.

Uses.—Sulphurous acid has a great tendency to absorb oxygen, and thus to be converted into sulphuric acid. It is therefore one of our most powerful reducing agents. Sulphite of soda, which has the advantage of being less readily decomposed than sulphurous acid, acts in an analogous manner, upon addition of acid. We employ sulphite of soda principally to reduce arsenic acid to arsenious acid, chromic acid to sesquioxide of chromium, and sesquioxide of iron to protoxide.

§ 71.

17. CHLORINE (Cl).

Preparation.—Fill a glass-flask to the neck with fragments of binoxide of manganese of the size of a bean, freed from powder by sifting, add a quantity of hydrochloric acid corresponding to the amount of chlorine which you wish to evolve,† and heat gently in the water-bath. Conduct

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* The evaporation is attended with copious evolution of sulphurous acid.

† However, the acid must not more than half fill the flask

the chlorine gas evolved, first through a washing bottle, then into a flask filled with cold water, and continue the process until the water is saturated. The chlorine water must be kept in a cellar, and carefully protected from the action of light; since, if this precaution is neglected, it speedily suffers complete decomposition, being converted into dilute hydrochloric acid, with evolution of oxygen (proceeding from the decomposition of water). Smaller quantities, intended for use in the laboratory, are best kept in a stoppered bottle, protected from the influence of light by a case of pasteboard. Chlorine water which has lost its strong peculiar odor is unfit for use.

Uses.—Chlorine has a greater affinity than iodine and bromine for metals and for hydrogen. Chlorine water is therefore an efficient agent to effect the expulsion of iodine and bromine from their compounds. As free chlorine forms with bromine, chloride of bromine, and with iodine, chloride of iodine, and as these compounds present a different deportment from that of the free metalloids, the greatest care must be taken, in certain cases, *e. g.* when testing for iodine by means of starch (§ 145), to avoid adding chlorine water in excess. Chlorine serves moreover to convert sulphurous acid into sulphuric acid, protoxide of iron into sesquioxide, &c.; and also to effect the destruction of organic substances, in presence of water, as it withdraws hydrogen from the latter, enabling thus the liberated oxygen to combine with the vegetable matters and to effect their decomposition. For this latter purpose it is most advisable to *evolve* the chlorine in the fluid which contains the organic substances; this is effected by adding hydrochloric acid to the fluid, heating the mixture to boiling, and then adding chlorate of potassa. This gives rise to the formation of chloride of potassium, water, free chlorine, and bichlorate of chlorous acid, which acts in a similar manner to chlorine.

§ 72.

17. SOLUTION OF INDIGO.

Preparation.—Heat one part of indigo in powder, with seven parts of fuming sulphuric acid. For use, dilute the solution obtained with just sufficient water to make the fluid appear of a light blue color.

Uses.—Indigo is decomposed upon boiling with nitric acid, and this decomposition is attended with the formation of oxidation products of a yellow color. Solution of indigo serves therefore for the detection of nitric acid. It is equally well adapted also for the detection of chloric acid (compare § 150) and of free chlorine.

§ 73.

18. STARCH-PASTE.

Triturate common starch with cold water, and heat the mixture to boiling, with stirring. The paste must be uniform and almost fluid.

Uses.—Starch, when brought into contact with free iodine, forms with the latter substance a peculiar bluish-black compound, the color of which is so intense that it remains distinctly perceptible, even though the two substances be brought together in a highly dilute state. Starch-paste is therefore a most excellent and delicate test for free iodine. As a test for bromine, it is far less sensitive, the fiery yellow color of bromide of starch being by no means so characteristic and intense as the blue color of iodide of starch.

B. REAGENTS IN THE DRY WAY.

I. FLUXES AND DECOMPOSING AGENTS.

§ 74.

1. MIXTURE OF CARBONATE OF SODA AND CARBONATE OF POTASSA

$$(NaO, CO_2 + KO, CO_2).$$

Preparation.—Digest ten parts of purified bitartrate of potassa in powder, with ten parts of water and one part of hydrochloric acid for several hours on the water-bath, with frequent stirring; put the mass into a funnel with a little filter inserted into the pointed end, let it drain, cover with a disc of rather difficultly permeable filtering paper with upturned edges, and pour upon this repeatedly small quantities of cold water; continue this washing process until the fluid running off is no longer rendered turbid by solution of nitrate of silver, after addition of nitric acid. Dry the bitartrate of potassa freed in this manner from lime (and phosphoric acid), and mix two parts of the dry powder with one part of pure nitrate of potassa (§ 77); introduce the perfectly dry mixture in small portions at a time, into a clean-scoured cast-iron pot heated to gentle redness; when the mixture has deflagrated, heat strongly, until a sample taken from the edges gives with water a perfectly colorless solution. Triturate the charred mass with water, filter, wash slightly, and evaporate the filtrate in a porcelain, or, better still, in a silver dish, until the fluid is covered with a persistent pellicle. Let the mixture now cool, with constant stirring, put the crystals of carbonate of potassa on a funnel, let them well drain, wash slightly, dry them thoroughly in a silver or porcelain dish, and keep the crystals in a well-stoppered bottle. The mother-liquor leaves upon evaporation a salt which, though containing traces of alumina and silicic acid, may still be turned to account for many purposes. Mix thirteen parts of the pure carbonate of potassa prepared in the manner just now described, with ten parts of pure anhydrous carbonate of soda, and keep the mixture in a well-stoppered bottle. The mixture of carbonate of potassa and carbonate of soda may also be prepared by deflagrating twenty parts of pure bitartrate of potassa with nine parts of pure nitrate of soda, treating with water, and evaporating the solution to dryness.

Tests.—The purity of the mixed salt is tested as directed § 30.

Uses.—If silicic acid or silicates are fused with about four parts (consequently with an excess) of carbonate of potassa or soda, carbonic acid escapes with effervescence, and a basic alkaline silicate is formed, which, being soluble in water, may be readily separated from such metallic oxides as it may contain in admixture; from this basic alkaline silicate hydrochloric acid separates the silicic acid as a hydrate. If a fixed alkaline carbonate is fused together with sulphate of baryta, strontia, or lime, there are formed carbonates of the alkaline earths and sulphate of the alkali, in which new compounds both the base and the acid of the originally insoluble salt may now be readily detected. However, we do not employ carbonate of potassa separately, nor carbonate of soda, to effect the decomposition of the insoluble silicates and sulphates; but we apply for this purpose the above described mixture of both, because this mixture requires a far lower degree of heat for fusion than either of its two components, and thus enables us to conduct the operation over a *Berzelius* lamp. The fusion with alkaline carbonates is invariably effected in a platinum crucible, provided no reducible metallic oxides be present.

§ 75.

2. HYDRATE OF BARYTA (BaO, HO).

Preparation.—The crystals of baryta prepared in the manner directed § 48, are heated gently in a porcelain crucible until the water of crystallization is completely expelled. The residuary white mass is pulverized, and kept for use in a well-closed bottle.

Uses.—Hydrate of baryta fuses at a gentle red heat without losing its water. Upon fusing silicates with about four parts of hydrate of baryta, a basic silicate of baryta is formed, and the oxides are liberated. If the fused mass is treated with hydrochloric acid, the solution evaporated to dryness, and the residue digested with hydrochloric acid, the silicic acid is left behind, and the oxides are obtained in solution in the form of chlorides. We use hydrate of baryta as a flux when we wish to test silicates for alkalies. This reagent is preferable as a flux to the carbonate or nitrate of baryta, since it does not require a very high temperature for its fusion, as is the case with the carbonate, nor does it cause any spirting in the fusing mass, arising from disengagement of gas, as is the case with the nitrate. The operation is effected in a silver or platinum crucible.

§ 76.

2. FLUORIDE OF BARIUM ($BaFl$).

Preparation.—Introduce into a leaden box of greater depth than width one part of fluoride of calcium in powder, and two parts of strong sulphuric acid (the space occupied by the mixture must not exceed one-third of the box); stir with a leaden rod; put on a leaden cover, bearing a delivering tube (the cover is best fitted conically into the box), lute the joinings, expose to the heat of a gentle charcoal fire, and conduct the hydrofluoric gas evolved into a leaden bottle containing about three parts of water, and standing in a vessel with cold water. Pour the hydrofluoric acid obtained, which is not perfectly pure, into a solution of two and a half parts of chloride of barium in ten times the quantity of water, add ammonia to neutralization, and let the precipitate deposit. If chloride of barium still produce a precipitate in the supernatant fluid, add some more of the solution of that salt, until the formation of a precipitate ceases. Wash the precipitate of fluoride of barium by decantation, ultimately on a filter, and dry.

Uses.—I have found fluoride of barium a very convenient means of decomposing silicates insoluble in acids. The decomposition is effected as follows. Mix in a platinum crucible or dish one part of the most finely pulverized silicate with five parts of fluoride of barium, add pure sulphuric acid in sufficient quantity to form a thick paste, and heat, first gently, finally strongly, until no more fumes escape (neither of fluoride of silicon, and hydrofluoric acid, nor of hydrate of sulphuric acid. Compare § 138. We employ fluoride of barium principally to detect alkalies in insoluble silicates, for which purpose it is preferable to hydrate of baryta. Instead of fluoride of barium, finely pulverized pure fluoride of calcium may also be used; but less conveniently, since the sulphate of lime formed offers a greater impediment to the operation than the absolutely insoluble sulphate of baryta.

§ 77.

3. NITRATE OF SODA (NaO, NO_5).

Preparation.—Dissolve commercial nitrate of soda in the least possible quantity of boiling water, pass the solution through a readily permeable filter, placed in a hot porcelain funnel; receive the filtrate in a porcelain dish, and stir the fluid till cold. Transfer the crystalline powder to a funnel loosely stopped with cotton, let it drain, press it down, make the surface even, cover it with a disc of difficultly permeable filtering paper, and pour water on this disc, in small portions at a time, and at proper intervals, until the washings are no longer rendered turbid by nitrate of silver. Dry the powder, and keep it in a bottle.*

Tests.—A solution of nitrate of soda must not be rendered turbid by solution of nitrate of silver or nitrate of baryta, nor precipitated by carbonate of soda.

Uses.—Nitrate of soda serves as a very powerful oxidizing agent, by

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* The nitrate of potassa of commerce used for the preparation of pure carbonate of potassa, is purified in the same manner.

yielding oxygen to combustible substances when heated with them. We use this reagent principally to convert several metallic sulphides, and more particularly the sulphides of tin, antimony, and arsenic, into oxides and acids; and also to effect the rapid and complete combustion of organic substances; for the latter purpose, however, nitrate of ammonia is in many cases preferable; this reagent is prepared by saturating nitric acid with carbonate of ammonia.

II. BLOWPIPE REAGENTS.

§ 78.

1. CHARCOAL (C).

Any kind of thoroughly burnt wood-charcoal may be used for blowpipe experiments. However, the charcoal of pine or linden-wood is preferable to any other sort. Smooth pieces ought to be selected, as when knotty they split on heating, and thus throw off portions of the matter under examination.

Uses.—Charcoal is chiefly employed in blowpipe experiments as a support for the substance under examination (see § 13). The following are the properties which render it so valuable in this respect. 1st, its infusibility; 2nd, its low conducting power for heat, which admits of substances being heated more strongly upon a charcoal than upon any other support; 3rd, its porosity, by means of which it imbibes readily fusible substances, such as borax, carbonate of soda, &c., whilst infusible bodies remain on its surface; 4th, its property of reducing oxidized bodies, by which it greatly assists the reduction of oxides by the inner flame of the blowpipe; charcoal serves also to effect the reduction of arsenious acid, which it deprives of its oxygen, at a red heat. For this purpose it is used in the form of small splinters, which, as they must contain no moisture, are obtained by breaking a piece of recently burnt charcoal.

§ 79.

2. CARBONATE OF SODA (NaO, CO_2).

Preparation.—See § 30.

Uses.—Carbonate of soda serves, in the first place, to promote the reduction of oxidized substances in the inner flame of the blowpipe. In fusing it brings the oxides into the most intimate contact with the charcoal support, and enables the flame to embrace every part of the substance under examination. It co-operates in this process also chemically by the transposition of its constituents (according to *R. Wagner*, in consequence of the formation of cyanide of sodium). If the quantity operated upon was very minute, the reduced metal is often found in the pores of the charcoal. In such cases, the parts surrounding the little cavity which contained the sample are dug out with a knife, triturated in a small mortar, and the charcoal is washed off from the metallic particles, which then become visible, either in form of powder or as small flat spangles, according to the nature of the particular metal or metals present.

In many cases, *e. g.* in the reduction of binoxide of tin, some borax may be advantageously added to the carbonate of soda, in order to render the mass more readily fusible. Carbonate of soda serves, in the second place, as a solvent. Platinum wire is the most convenient support for testing the solubility of substances in fusing carbonate of soda. The sample to be examined is made into a paste with some carbonate of soda and water, and this paste is placed upon the loop of a platinum wire and heated. A few only of the bases dissolve in fusing carbonate of soda, but acids dissolve with facility. Silicic acid differs from all other acids, inasmuch as the glass which it forms with carbonate of soda remains clear upon cooling, provided the two constituents be present in the proper proportions. Carbonate of soda is moreover applied as a decomposing agent and flux, and more particularly to effect the decomposition of the insoluble sulphates, with which it exchanges acids, whilst, at the same time, the newly formed sulphate of soda is reduced to sulphide of sodium; and of sulphide of arsenic, with which it forms a double sulphide of arsenic and sodium, and arsenite or arseniate of soda, thus converting it to a state which permits its subsequent reduction by hydrogen. Finally, carbonate of soda is the most sensitive reagent in the dry way for the detection of manganese, since when fused in the outer flame of the blowpipe, with a substance containing manganese, it produces a green opaque bead, owing to the formation of manganate of soda.

§ 80.

3. CYANIDE OF POTASSIUM (K Cy).

Preparation.—See § 41.

Uses.—Cyanide of potassium is an exceedingly powerful reducing agent in the dry way; indeed it excels in its action almost all other reagents of the same class, and separates the metals not only from most oxygen compounds, but also from sulphur compounds; this reduction is attended, in the first case, with formation of cyanate of potassa, by the absorption of oxygen, and, in the latter case, with the formation of sulphocyanide of potassium. By means of this reagent we may effect the reduction of metals from their compounds with the greatest possible facility; thus we may, for instance, produce metallic antimony from antimonious acid or from sulphide of antimony, metallic iron from sesquioxide of iron, &c. The readiness with which cyanide of potassium enters into fusion facilitates the reduction of the metals greatly; the process may usually be conducted even in a porcelain crucible over a spirit-lamp. Cyanide of potassium is a most valuable and important agent to effect the reduction of arsenites and arseniates, and more particularly of tersulphide of arsenic (see § 127). Cyanide of potassium is equally important as a blowpipe reagent. Its action is exceedingly energetic; substances like binoxide of tin, bisulphide of tin, &c., the reduction of which by means of carbonate of soda requires a tolerably strong flame, are reduced by cyanide of potassium with the greatest facility. In blowpipe experiments we invariably use a mixture of equal parts of carbonate of soda and cyanide of potassium; the admixture of carbonate of soda is intended here to check in some measure the excessive fusibility of the cyanide of potassium. This mixture of cyanide of potassium with carbonate of soda, besides being a far more powerful reducing agent than the simple carbonate of soda, has moreover this great advantage over the latter, that it is absorbed by the pores of the charcoal with extreme facility, and thus permits the production of the metallic globules in a state of the greatest purity.

§ 81.

4. BIBORATE OF SODA (*Borax*) ($Na\,O, 2\,B\,O_3$).

The purity of commercial borax may be tested by adding to its solution carbonate of potassa, or after previous addition of nitric acid, solution of nitrate of baryta or of nitrate of silver. The borax may be considered pure if these reagents fail to produce any alteration in the solution; but if either of them causes the formation of a precipitate, or renders the fluid turbid, recrystallization is necessary. The pure borax is exposed to a gentle heat, in a platinum crucible, until it ceases to swell; when cool it is pulverized and kept for use.

Uses.—Boracic acid manifests a great affinity for oxides when brought into contact with them in a state of fusion. This affinity enables it, in the first place, to combine directly with oxides; secondly, to expel weaker acids from their salts; and, thirdly, to predispose metals, sulphides, and haloid compounds to oxidize in the outer flame of the blowpipe, that it may combine with the oxides. Most of the thus produced borates fuse readily, even without the aid of a flux, but far more so in conjunction with borate of soda; the latter salt acts in this operation either as a mere flux, or by the formation of double salts. Now, in the biborate of soda, we have both free boracic acid and borate of soda; the union of these two substances renders it one of our most important blowpipe reagents. In the process of fluxing with borax, we usually select platinum wire for a support; the loop of the wire is ignited, dipped into the powder, and then exposed to the outer flame; a colorless bead of fused borax is thus produced. A small portion of the substance under examination is then attached to the bead, by bringing the latter into contact with it, either whilst still hot or having previously moistened it. The bead with the sample of the substance intended for analysis adhering to it is now again exposed, first to the flame of a spirit-lamp, and finally to the blowpipe flame, and the phenomena to the manifestation of which this process gives rise are carefully observed and examined. The following points ought to be more particularly watched. 1. Whether or not the sample under examination dissolves to a transparent bead, and whether or not it retains this transparency on cooling. 2. Whether the bead exhibits a distinct and definite color, since this, in many instances, at once clearly indicates the individual metal which the analyzed compound contains; such is the case, for instance, with cobalt. And 3, whether the bead manifests the same or a different deportment in the outer and in the inner flame. Phenomena of the latter kind arise from the ensuing reduction of higher to lower oxides, or even to the metallic state, and are for some substances particularly characteristic.

§ 82.

5. PHOSPHATE OF SODA AND AMMONIA (*Microcosmic salt*) (NaO, NH_4O, HO, PO_5).

Preparation.—Heat to boiling, six parts of phosphate of soda and one part of pure chloride of ammonium with two parts of water, and allow the solution to cool. Free the crystals of the double phosphate of soda and ammonia by recrystallization from the chloride of sodium which adheres to them. Dry the purified crystals, and pulverize them for use.

Uses.—When phosphate of soda and ammonia is subjected to the action of heat, the ammonia escapes with the water of crystallization, and a compound of similar composition to borax remains, viz., a compound which contains both a free acid and a readily fusible salt. The action of microcosmic salt is therefore analogous to that of biborate of soda. We prefer it, however, in some cases to borax as a solvent or flux, the beads which it forms with many substances being more beautifully and distinctly colored than those of borax. Platinum wire is also used for a support in the process of fluxing with microcosmic salt; the loop of the wire must be made small and narrow, otherwise the bead will not adhere to it. The operation is conducted as directed in the preceding paragraph.

§ 83.

6. NITRATE OF PROTOXIDE OF COBALT (CoO, NO_5).

Preparation.—Heat finely pulverized cobalt ore with nitric acid until the residue appears perfectly white, evaporate in the water-bath to dryness, and treat the residue with water; filter, add to the filtrate some acetic acid, and then carbonate of potassa, until the cobalt begins to precipitate, which may be known from the red color of the precipitate; heat to boiling, keep boiling some time, and filter off the arsenite and arseniate of sesquioxide of iron; mix the filtrate with a hot saturated solution of binoxalate of potassa, and let it stand at a gentle heat until the fluid appears colorless. Wash the precipitated oxalate of protoxide of cobalt thoroughly, boil it with solution of carbonate of potassa (whereby it is immediately decomposed); filter the carbonate of protoxide of cobalt produced, wash most carefully with boiling water, and dissolve in dilute nitric acid, avoiding the use of the solvent in great excess. Treat the solution, if necessary—which you may learn by testing a portion of it—with hydrosulphuric acid, let the fluid stand some time, then filter, boil the filtrate, and keep the solution, which is now pure, containing at the most, perhaps, a trace of nickel.

Uses.—Protoxide of cobalt forms upon ignition with certain infusible bodies peculiarly colored compounds, and may accordingly serve for the detection of these bodies (oxide of zinc, alumina, and magnesia; see the paragraph treating of these substances.

SECTION III.

ON THE DEPORTMENT OF THE VARIOUS SUBSTANCES WITH REAGENTS.

§ 84.

I stated in my introductory remarks that the operations and experiments of qualitative analysis have for their object the conversion of the *unknown* constituents of any given compound into forms of which we *know* the deportment, relations, and properties, and which will accordingly permit us to draw correct inferences regarding the individual constitutents of which the analyzed compound consists. The greater or less value of such analytical experiments, like that of all other inquiries and investigations, depends upon the greater or less degree of certainty with which they lead to definite results, no matter whether of a positive or negative nature. But as a question does not render us any the wiser if we do not know the language in which the answer is returned, so, in like manner, will analytical investigations prove unavailing if we do not understand the mode of expression in which the desired information is conveyed to us; in other words, if we do not know how to interpret the phenomena produced by the action of our reagents upon the substance examined.

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

The method usually adopted in elementary works on chemistry is to treat of the various substances and their deportment with reagents 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 arrange those substances which are in many respects analogous, into groups, and thus, by confronting their analogies with their differences, to place the latter in the clearest possible light.

A.—DEPORTMENT AND PROPERTIES OF THE METALLIC OXIDES AND OF THEIR RADICALS.*

§ 85.

First Group.

POTASSA, SODA, AMMONIA.

Properties of the Group.—The alkalies are readily soluble in water, as well in the pure or caustic state as in the form of sulphides and carbonates. Accordingly they do not precipitate one another in the pure state or as carbonates, nor are they precipitated by hydrosulphuric acid under any condition whatever. The solutions of the pure alkalies, as well as of their sulphides and carbonates, restore the blue color of reddened litmus-paper, and impart an intensely brown tint to turmeric paper.

Special reactions.

§ 86.

a. POTASSA (KO).

1. The ordinary heat of a spirit-lamp fails to volatilize potassa, its hydrate and salts. Potassa and its hydrate deliquesce in the air; the oily liquids formed do not solidify by absorption of carbonic acid.

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* The deportment and properties of the metals I have given only in the case of such bodies as occur frequently in the metallic state in analytical investigations.

2. Nearly the whole of the salts of potassa are readily soluble in water. They are colorless, if the constituent acid is so. The neutral salts of potassa with strong acids do not alter vegetable colors. Carbonate of potassa crystallizes with difficulty, and deliquesces in the air. Sulphate of potassa is anhydrous, and suffers no alteration in the air.

3. *Bichloride of platinum* produces in the neutral and acid solutions of the salts of potassa a yellow crystalline heavy precipitate of BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM (*Potassio-bichloride of platinum*) ($K\,Cl, Pt\,Cl_2$). In concentrated solutions, this precipitate separates immediately upon the addition of the reagent: in dilute solutions it forms only after some time. Alkaline solutions must be acidified with hydrochloric acid before the bichloride of platinum is added. The precipitate is difficultly soluble in water; the presence of free acids does not greatly increase its solubility; it is insoluble in alcohol. Bichloride of platinum is therefore a particularly delicate test for salts of potassa, when dissolved in spirit of wine. The best method of applying this reagent is, to evaporate the aqueous solution of the potassa salt with bichloride of platinum nearly to dryness on the water-bath, and to treat the residue with spirit of wine; the potassio-bichloride of platinum is left undissolved. Care must be taken not to confound this double salt with ammonio-bichloride of platinum, which greatly resembles it (see § 88, 4).

4. *Tartaric acid* produces in neutral or alkaline* solutions of salts of potassa—a white, quickly subsiding, *granular* crystalline precipitate of BITARTRATE OF POTASSA. ($K\,O, \overline{T} + H\,O, \overline{T}$.) In concentrated solutions this precipitate separates immediately; in dilute solutions, often only after the lapse of some time. Vigorous shaking or stirring of the fluid promotes its formation considerably. Free alkalies and free mineral acids dissolve the precipitate; it is difficultly soluble in cold, but pretty readily soluble in hot water. In the case of acid solutions, the free acid must, if practicable, first be expelled by evaporation and ignition, or the solution must be neutralized with soda or carbonate of soda, before we can proceed to test for potassa with tartaric acid.

5. If a salt of potassa, more particularly chloride of potassium, is placed, by means of a platinum wire, in the apex of the *inner blowpipe flame*, the outer flame acquires a VIOLET color; this arises from reduction of the potassa and subsequent re-oxidation of the reduced potassium. The tint which phosphate and borate of potassa impart to the outer blowpipe flame is scarcely perceptible. Presence of soda obscures this reaction completely. Decrepitating salts are pulverized and made to adhere to the wire with water.

6. If a salt of potassa (more particularly chloride of potassium) is heated

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* In the case of alkaline solutions, the reagent must be added until the fluid shows a strongly acid reaction.

with a small quantity of water, alcohol added, and the latter heated and then ignited, the flame appears VIOLET. The presence of soda obscures this reaction also.

§ 87.

b. SODA (Na O).

1. Soda, its hydrate, and salts present in general the same deportment and properties as potassa and its corresponding compounds. The oily fluid which soda forms by deliquescing in the air, resolidifies speedily by absorption of carbonic acid. Carbonate of soda crystallizes readily, and effloresces rapidly when exposed to the air. The same applies to sulphate of soda.

2. *Antimoniate of potassa* produces in neutral or alkaline solutions of salts of soda a white crystalline precipitate of ANTIMONIATE OF SODA ($Na\,O,\ Sb\,O_5$). In concentrated solutions, this precipitate is formed immediately; but from dilute solutions it separates only after the lapse of some time. Vigorous shaking of the mixture promotes the formation of the precipitate. If the fluid, after the addition of the reagent, be stirred with a glass rod, moving the latter along the sides of the vessel, the lines described will, even in very dilute solutions, speedily becomes visible, since the precipitate forms first on the parts touched by the rod. The presence of neutral salts of potassa does not interfere with the formation of the precipitate. Carbonate of potassa, however, prevents its separation wholly or partially, according to the greater or less proportion in which it is present. In cases therefore where the solution under examination contains this salt, it is necessary to precede the application of the antimoniate of potassa by addition of hydrochloric or acetic acid until the reaction of the solution remains only feebly alkaline. Acid solutions must first be neutralized with potassa, since otherwise the reagent would suffer decomposition, and hydrated antimonic acid or acid antimoniate of potassa be precipitated from it.

3. Salts of soda (more particularly chloride of sodium) when exposed on a platinum wire to the *inner blowpipe flame,* color the outer flame INTENSELY YELLOW, owing to reduction of the soda and subsequent reoxidation of the reduced sodium. This reaction remains clearly perceptible, even if the soda contains a considerable admixture of potassa.

4. If a salt of soda (more particularly chloride of sodium) is heated with a small quantity of water, *alcohol* added, and the latter heated and then ignited, the flame appears strongly YELLOW. The presence of a salt of potassa does not impair the distinctness of this reaction.

5. *Bichloride of platinum* produces no precipitate in solutions of salts of soda; *tartaric acid* only when a highly concentrated solution of soda or carbonate of soda is mixed with a saturated solution of tartaric acid in

excess. The BITARTRATE OF SODA which, in such cases, crystallizes out after the lapse of some time, appears invariably in the shape of small needles and columns, and not, like the corresponding salt of potassa, in the form of a granular crystalline precipitate.

§ 88.

c. AMMONIA (NH_4O).

1. Pure ammonia is gaseous at common temperatures; but we have most frequently to deal with it in its aqueous solution, in which it may be at once detected by its penetrating odor. It is expelled from this solution by the application of heat.

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

3. If salts of ammonia are triturated with *hydrate of lime*, with the addition of a few drops of water, or are, either in a solid form or in solution, heated with solution of potassa or of soda, the ammonia is liberated in the gaseous state, and manifests itself, 1, by its characteristic *odor;* 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, or any of the volatile acids, is brought into contact with it. These fumes arise from the formation of solid ammoniacal salts produced by the contact of the gases in the air. Hydrochloric acid is the most delicate test in this respect; acetic acid, however, admits less readily of a mistake.

4. *Bichloride of platinum* manifests the same deportment with salts of ammonia as with salts of potassa; the yellow precipitate of BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM ($NH_4Cl, PtCl_2$) is, however, of a somewhat lighter color than potassio-bichloride of platinum.

5. *Tartaric acid* added in excess to a solution of ammonia or carbonate of ammonia, produces a precipitate of BITARTRATE OF AMMONIA ($NH_4O, \overline{T} + HO, \overline{T}$). In concentrated solutions this precipitate forms immediately; in dilute solutions only after some time. The solutions of other ammoniacal salts (chloride of ammonium, nitrate of ammonia, &c.) are not precipitated by this reagent, even when highly concentrated; or a trifling precipitate only separates from them after long standing. Bitartrate of ammonia comports itself with solvents like the corresponding salt of potassa; however, it is somewhat more readily soluble in water and acids than the latter.

§ 89.

Recapitulation and remarks.—The salts of potassa and soda are not volatile at a common red heat, whilst the salts of ammonia volatilize readily;

the latter may therefore be easily separated from the former by ignition. —The expulsion of ammonia from its compounds, by hydrate of lime, affords the surest means of ascertaining the presence of this substance. Salts of potassa can be detected *positively* only after the removal of the ammoniacal salts which may be present, since both classes of salts manifest the same or a similar deportment with bichloride of platinum and tartaric acid.—After the removal of the ammonia, the potassa is clearly and positively characterized by either of these two reagents. The most simple way of detecting the potassa in the potassio-bichloride of platinum and bitartrate of potassa, is to decompose these salts by ignition; the former yields the potassa in the form of chloride of potassium, the latter in the form of carbonate of potassa. With respect to soda, the yellow tint which its salts impart to the blow-pipe flame and to the flame of alcohol, is a safe and mostly in itself sufficient proof of its presence, provided always a fixed alkali alone be present.* Antimoniate of potassa gives decisive results only when applied with a careful and attentive consideration of the attendant circumstances. The most indispensable condition of its applicability is, that besides soda or potassa, no other bases be present in the solution, since the salts of the heavy metallic oxides, those of the earths proper and of the alkaline earths, and finally those of ammonia, are also precipitated by antimoniate of potassa.

§ 90.

APPENDIX TO THE FIRST GROUP.

Lithia ($Li\,O$).

Lithia dissolves with difficulty in water; it does not attract moisture from the air. Most of its salts are soluble in water; some of them are deliquescent (chloride of lithium). Carbonate of lithia is difficultly soluble, particularly in cold water. *Phosphate of soda* (but not phosphate of potassa) produces in solutions of salts of lithia, upon boiling, a white pulverulent precipitate of phosphate of soda and lithia. If the solution is evaporated to dryness, and the residue treated with water, this salt remains in form of a white powder; this deportment is characteristic of lithia. The precipitate fuses before the blowpipe, and gives upon fusion with soda on the platinum wire a clear bead; when fused upon charcoal, it is absorbed by the pores of the latter body (difference between it and phosphate of lime and magnesia). *Tartaric acid* and *bichloride of platinum* fail to precipitate even concentrated solutions of salts of lithia. If a salt of lithia (more particularly chloride of lithium) is exposed on a platinum wire to the *inner blowpipe flame*, the outer flame shows a strong CARMINE tint. Presence of salts of soda (but not of salts of potassa) conceals this

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* In form of chlorides, $\frac{1}{100}$th part of soda may by this means be detected in presence of potassa.

reaction. If *spirit of wine* is poured over a salt of lithia (more particularly chloride of lithium), and then ignited, the flame appears of a CRIMSON color; presence of salts of soda conceals this reaction also.

§ 91.

SECOND GROUP.

BARYTA—STRONTIA—LIME—MAGNESIA.

Properties of the group.—The alkaline earths are soluble in water in the pure (caustic) state and as sulphides. (Magnesia, however, dissolves but very sparingly in water.) The solutions manifest alkaline reaction; with magnesia this is most clearly shown when placed upon moistened test-paper. The neutral carbonates and phosphates of the alkaline earths are insoluble in water. The solutions of the salts of the alkaline earths are therefore precipitated by alkaline carbonates and phosphates; whilst hydrosulphuric acid fails to precipitate them under any condition. This deportment distinguishes the oxides of the second group from those of the first. The alkaline earths and their salts are non-volatile and colorless; their solutions are not precipitated by sulphide of ammonium, nor by carbonate of baryta.

Special Reactions.

§ 92

a. BARYTA ($Ba O$).

1. Caustic baryta is pretty readily soluble in hot water, but rather difficultly so in cold water; it dissolves easily in dilute hydrochloric or nitric acid. Hydrate of baryta does not lose its water upon ignition.

2. Most of the salts of baryta are insoluble in water. The soluble salts do not affect vegetable colors, and are decomposed upon ignition, with the exception of chloride of barium. The insoluble salts dissolve in hydrochloric acid, except the sulphate of baryta.—Nitrate of baryta and chloride of barium are insoluble in alcohol, and do not deliquesce in the air.

3. *Ammonia* produces no precipitate in the aqueous solutions of salts of baryta; *potassa* (free from carbonic acid) only in highly concentrated solutions. Water redissolves the bulky precipitate of CRYSTALS OF BARYTA ($Ba O, H O + 9 aq$) produced by potassa.

4. *Alkaline carbonates* throw down from solutions of baryta CARBONATE OF BARYTA ($Ba O, C O_2$) in the form of a white precipitate. When carbonate of ammonia is used as the precipitant, or if the solution was previously acid, complete precipitation takes place only upon heating the fluid. In chloride of ammonium the precipitate is soluble to a trifling, yet clearly perceptible extent; in very dilute solutions of baryta therefore, which contain much chloride of ammonium, carbonate of ammonia produces no precipitate.

5. *Sulphuric acid* and all the soluble *sulphates*, also solution of sulphate of lime, immediately produce, even in very dilute solutions of baryta, a finely pulverulent white precipitate of SULPHATE OF BARYTA ($Ba\,O, S\,O_3$), which is insoluble in acids, alkalies, and salts of ammonia.

6. *Hydrofluosilicic acid* throws down from solutions of baryta SILICOFLUORIDE OF BARIUM ($Ba\,Fl + Si\,Fl_2$), in the form of a colorless, crystalline, quickly subsiding precipitate. In dilute solutions this precipitate is formed only after the lapse of some time; it is perceptibly soluble in hydrochloric acid and nitric acid. Addition of an equal volume of alcohol renders the precipitation rapid, and so complete that the filtrate remains clear upon addition of sulphuric acid.

7. *Phosphate of soda* produces in neutral or alkaline solutions of baryta a white precipitate of PHOSPHATE OF BARYTA ($2\,Ba\,O, H\,O, P\,O_5$), which is soluble in free acids. Addition of ammonia increases the quantity of this precipitate; but even a small quantity of chloride of ammonium dissolves it to a clearly perceptible extent.

8. *Oxalate of ammonia* produces in moderately dilute solutions of baryta a white pulverulent precipitate of OXALATE OF BARYTA ($Ba\,O, \overline{O}$), which is soluble in hydrochloric acid and nitric acid. When recently thrown down, this precipitate dissolves also in oxalic acid and acetic acid; but the solutions speedily deposit binoxalate of baryta in the form of a crystalline powder.

9. Salts of baryta in powder, when heated with dilute *spirit of wine*, impart to the flame of the latter a YELLOWISH-GREEN color, which, however, is not very characteristic.

§ 93.

b. STRONTIA ($Sr\,O$).

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

2. The salts of strontia manifest with *ammonia* and *potassa*, and also with the *alkaline carbonates* and with *phosphate of soda*, nearly the same deportment as the salts of baryta. Carbonate of strontia dissolves somewhat more difficultly in chloride of ammonium than is the case with carbonate of baryta.

3. *Sulphuric acid* and *sulphates* precipitate from solutions of strontia SULPHATE OF STRONTIA ($Sr\,O, S\,O_3$), in form of a white powder, which is insoluble in dilute acids and alkalies. Application of heat promotes the

precipitation considerably. Sulphate of strontia is far more soluble in water than sulphate of baryta; owing to this readier solubility, the precipitated sulphate of strontia separates from rather dilute solutions in general only after the lapse of some time; and this is invariably the case (even in concentrated solutions) if *solution of sulphate of lime* is used as precipitant. In boiling hydrochloric acid sulphate of strontia dissolves perceptibly, a solution of the kind showing, after dilution with water, a distinct turbidity upon the addition of a drop of solution of chloride of barium.

4. *Hydrofluosilicic acid* fails to produce a precipitate, in concentrated solutions of strontia; even upon addition of an equal volume of alcohol no precipitation takes place, except in most highly concentrated solutions.

5. *Oxalate of ammonia* precipitates even from rather dilute solutions, **OXALATE OF STRONTIA** ($\mathrm{Sr\ O}, \bar{\mathrm{O}}$), in the form of a white powder, which dissolves readily in hydrochloric acid and nitric acid, but is only sparingly soluble in oxalic acid and acetic acid.

6. If salts of strontia soluble in water or alcohol are heated with dilute spirit of wine, and the latter ignited, the flame appears of an intense **CRIMSON** color, more particularly upon stirring the alcoholic mixture.

§ 94.

c. LIME (Ca O).

1. Lime, its hydrate, and salts, present, in their general deportment and properties, a great similarity to baryta and strontia and their corresponding compounds. Hydrate of lime is far more difficultly soluble in water than the hydrates of baryta and strontia; it dissolves, besides, more sparingly in hot than in cold water. Hydrate of lime loses its water upon ignition. Chloride of calcium and nitrate of lime are soluble in absolute alcohol, and deliquesce in the air.

2. *Ammonia, potassa, alkaline carbonates,* and *phosphate of soda,* present nearly the same deportment with salts of lime as with salts of baryta. Recently precipitated carbonate of lime dissolves pretty readily in solution of chloride of ammonium; but the solution speedily becomes turbid, and deposits the greater part of the dissolved salt in a crystalline form.

3. *Sulphuric acid* and *sulphate of soda* produce immediately in very concentrated solutions of lime white precipitates of **SULPHATE OF LIME** ($\mathrm{Ca\ O, S\ O_3}$), which redissolve completely in a large proportion of water, and are still far more soluble in acids. In less concentrated solutions the precipitates are formed only after the lapse of some time; and no precipitation whatever takes place in dilute solutions. Solution of sulphate of lime, of course, cannot produce a precipitate in salts of lime; but even a cold saturated solution of sulphate of potassa, mixed with three parts of water,

produces a precipitate only after standing from twelve to twenty-four hours. In solutions of lime which are so very dilute that sulphuric acid has no apparent action on them, a precipitate will immediately form upon the addition of alcohol with the sulphuric acid.

4. *Hydrofluosilicic acid* does not precipitate salts of lime.

5. *Oxalate of ammonia* produces, even in very dilute solutions of lime, a white precipitate of OXALATE OF LIME ($\text{Ca O}, \overline{\text{O}}$). In very dilute solutions the precipitate forms only after some time. It is readily soluble in hydrochloric and nitric acids, but not perceptibly so in acetic acid or oxalic acid.

6. Soluble salts of lime, when heated with dilute *spirit of wine*, impart to the flame of the latter a YELLOWISH-RED color, which is often confounded with that communicated to the flame of alcohol by salts of strontia.

§ 95.

d. MAGNESIA (Mg O).

1. Magnesia and its hydrate are white powders of far greater bulk than the other alkaline earths and their hydrates. Magnesia and hydrate of magnesia are nearly insoluble both in cold and hot water. Hydrate of magnesia loses its water upon ignition.

2. Some of the salts of magnesia are soluble in water, others are insoluble. The soluble salts of magnesia have a nauseous bitter taste; in the neutral state they do not alter vegetable colors; with the exception of sulphate of magnesia, they undergo decomposition when ignited, and the greater part of them even upon simple evaporation of their solutions. Nearly all the salts of magnesia which are insoluble in water dissolve in hydrochloric acid.

3. *Ammonia* throws down from the solutions of neutral salts of magnesia a part of the magnesia as hydrate (Mg O, H O), in the form of a white bulky precipitate. The rest of the magnesia remains in solution as a double salt, viz. in combination with the ammoniacal salt which forms upon the decomposition of the salt of magnesia; these double salts of ammonia and magnesia are not decomposable by ammonia. It is owing to this tendency of salts of magnesia to form such double salts with ammoniacal compounds, that ammonia fails to precipitate them in presence of ammoniacal salts, or, what is the same, that ammonia produces no precipitate in acid solutions of magnesia; and that precipitates produced by ammonia in neutral solutions of magnesia are redissolved upon the addition of an ammoniacal salt.

4. *Potassa* and *caustic baryta* throw down from solutions of magnesia, HYDRATE OF MAGNESIA. The separation of this precipitate is greatly promoted by boiling the mixture. Salts of ammonia redissolve the precipitated hydrate of magnesia, and prevent its formation altogether when

added in sufficient quantity to the magnesia solution, previously to the addition of the precipitant. However, if the solution be afterwards boiled with an excess of potassa, the precipitate will of course make its appearance, since this process causes the decomposition of the ammoniacal salt, removing thus the agent which retains the hydrate of magnesia in solution.

5. *Carbonate of potassa* and *carbonate of soda* produce in neutral solutions of magnesia a white precipitate of BASIC CARBONATE OF MAGNESIA ($3\,[MgO, CO_2, + aq] + MgO, HO$). One fourth of the carbonic acid of the decomposed alkaline carbonate is liberated in the process, and combines with a portion of the carbonate of magnesia to bicarbonate, which remains in solution. This carbonic acid escapes upon ebullition; the application of heat will therefore promote the separation and increase the quantity of the precipitate. Salts of ammonia prevent this precipitation, and redissolve the precipitates already formed.

6. *Carbonate of ammonia* does not precipitate solutions of magnesia in the cold (at least never immediately, nor even after a short time); upon boiling, it precipitates them only incompletely. Addition of salts of ammonia, in sufficient quantity, entirely prevents the formation of a precipitate.

7. *Phosphate of soda* precipitates from solutions of magnesia, if they are not too dilute, PHOSPHATE OF MAGNESIA ($2\,MgO, HO, PO_5$), as a white powder. The separation of the precipitate is greatly promoted by ebullition. But if the addition of the precipitant is preceded by that of chloride of ammonium and ammonia, a white crystalline precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA ($2\,MgO, NH_4O, PO_5$) will separate, even from very dilute solutions of magnesia; its separation may be greatly promoted and accelerated by vigorous stirring with a glass rod: even should the solution be so extremely dilute as to forbid the formation of a precipitate, yet the lines of direction in which the glass rod has moved along the side of the vessel, will after the lapse of some time appear distinctly as white streaks. Water and solutions of salts of ammonia dissolve the precipitate but very slightly; but it is readily soluble in acids, even in acetic acid. In water containing ammonia it may fairly be said to be insoluble.

8. *Oxalate of ammonia* fails to precipitate even concentrated solutions of magnesia; or, at the most, it produces after long standing only a trifling precipitate of OXALATE OF MAGNESIA ($MgO, \bar{O}$). Salts of ammonia prevent its formation altogether.

9. *Sulphuric acid* and *hydrofluosilicic acid* do not precipitate salts of magnesia.

10. If magnesia or a salt of magnesia is moistened with solution of *nitrate of protoxide of cobalt*, and then exposed some time upon a charcoal support to the action of a strong *blowpipe flame*, a pinkish mass is pro-

duced, the color of which becomes distinct only upon cooling, but is never very intense.

§ 96.

Recapitulation and remarks.—The difficult solubility of the hydrate of magnesia, the ready solubility of the sulphate, and the disposition of salts of magnesia to form double salts with ammoniacal compounds, are the three principal points in which magnesia differs from the other alkaline earths. We invariably select for its positive detection the reaction with phosphate of soda, applied in conjunction with ammonia. If baryta, strontia, or lime is present, these earths are removed first, before proceeding to apply the special tests for magnesia. In cases requiring no very high degree of accuracy, and where the quantity of salts of ammonia present in the solution is inconsiderable, this removal may be effected by means of carbonate of ammonia and ammonia; but the separation is never perfect, owing to the solvent action which salts of ammonia exercise more especially upon carbonate of baryta and lime; indeed, minute traces of baryta and lime can rarely be precipitated in this manner. Baryta is separated the most completely by sulphuric acid or a sulphate; lime, by oxalate of ammonia, in presence of ammonia and some chloride of ammonium; strontia, same manner as lime, or by ammonia and carbonate of ammonia, in presence of chloride of ammonium. After the removal of the other alkaline earths, the magnesia may be readily detected in the filtrate by phosphate of soda, in conjunction with ammonia. The detection of baryta is an easy task under any circumstances; since the precipitate of sulphate of baryta, which separates from baryta solutions immediately upon the addition of sulphate of lime, and the reaction of baryta with hydrofluosilicic acid are indubitable proofs of the presence of this earth. Strontia may likewise readily be detected by its deportment with solution of sulphate of lime, provided, of course, no baryta be present. If baryta is present, the detection of the strontia may be effected by converting the two earths into dry chlorides, and digesting the latter with absolute alcohol; the greater part of the chloride of barium is left undissolved, whilst the chloride of strontium dissolves; if the alcohol is now heated, and then ignited, the crimson tint of the flame will indicate the presence of strontia. However, the results obtained in this way can only be considered satisfactory if the quantity of the strontia is not too minute, and if there is not much lime present; since in the latter case, the yellowish-red flame of the lime will mask the crimson flame of the strontia, and thus prevent the distinct perception of the latter. In cases of this kind, strontia is detected best by the following process. Mix the solution (which contains baryta, strontia, and lime) with hydrofluosilicic acid and a volume of alcohol equal to that of the fluid present; let the mixture stand several hours; filter off the silicofluoride of barium, and mix the filtrate with sulphuric acid; filter the precipitate formed, wash, and convert the sulphates into carbonates by fusion with carbonate of potassa and soda; wash the carbonates, dissolve them in a small quantity of hydrochloric acid, and test the solution for strontia with solution of sulphate of lime.—For the detection of lime we invariably select oxalate of ammonia. Before applying this test, however, baryta and strontia must be removed, as they are equally precipitated by it. This removal is effected best by adding to the solution sulphate of potassa in excess, and heating the mixture some time to boiling. If there is much lime present, a portion of the latter earth precipitates with the baryta and strontia; this is, however, a matter of indifference, since there remains always a sufficient amount of lime in solution to permit the positive and indubitable detection of this substance in the filtrate by oxalate of ammonia.—The best way of effecting the detection of the alkaline earths when in the form of phosphates, is to decompose these by means of sesquichloride of iron in conjunction with acetate of soda (§ 135).—The oxalates of the alkaline earths are converted into carbonates by ignition, preparatory to the detection of the individual earths which they contain.—Sulphate of baryta and sulphate of strontia are fused with alkaline carbonates, to effect the detection of the baryta and strontia (compare § 134).

§ 97.

THIRD GROUP.

ALUMINA. SESQUIOXIDE OF CHROMIUM.

Properties of the group.—Alumina and sesquioxide of chromium are insoluble in water, both in the pure state and as hydrates. They form no neutral salts with carbonic acid. Their sulphides cannot be produced in the humid way. Hydrosulphuric acid therefore fails to precipitate solutions of alumina and sesquioxide of chromium; sulphide of ammonium precipitates the hydrated oxides from these solutions. This deportment with sulphide of ammonium distinguishes the oxides of the third from those of the two preceding groups.

Special Reactions.

§ 98.

a. ALUMINA ($Al_2\ O_3$).

1. Alumina is non-volatile and colorless; the hydrate is also colorless. Alumina dissolves in acids slowly and with very great difficulty; the hydrate in an amorphous state is readily soluble in acids; but its crystals dissolve with very great difficulty in these menstrua. After previous ignition with alkalies, alumina is readily dissolved by acids.

2. The salts of alumina are colorless, and most of them are non-volatile:

some of them are soluble, others insoluble. The soluble salts have a sweetish astringent taste, redden litmus-paper, and lose their acids upon ignition. The insoluble salts are dissolved by hydrocholoric acid, with the exception of certain native compounds of alumina; the compounds of alumina which are insoluble in hydrochloric acid are decomposed by ignition with carbonate of soda or bisulphate of potassa.

3. *Potassa* and *soda* throw down from solutions of alumina a bulky precipitate of HYDRATE OF ALUMINA (Al_2O_3, 3 H O), which contains alkali, and generally also an admixture of basic salt; this precipitate redissolves readily and completely in an excess of the precipitant, but from this solution it is reprecipitated by addition of chloride of ammonium, even in the cold, but more completely still upon application of heat (compare § 23). The presence of salts of ammonia does not prevent the precipitation by potassa.

4. *Ammonia* also produces in solutions of alumina a precipitate of HYDRATE OF ALUMINA, containing ammonia and an admixture of basic salt; this precipitate also redissolves in a very considerable excess of the precipitant, but with difficulty only, which is the greater, the larger the quantity of salts of ammonia contained in the solution. It is this deportment which accounts for the complete precipitation of hydrate of alumina from solution in potassa, by an excess of chloride of ammonium.

5. If the solution of a salt of alumina is digested with finely pulverized carbonate of baryta, the greater part of the acid of the alumina salt combines with the baryta, the liberated carbonic acid escapes, and the alumina precipitates completely as HYDRATE mixed with BASIC SALT OF ALUMINA; even digestion in the cold suffices to produce this reaction.

6. If alumina or one of its compounds is ignited upon charcoal, before the blowpipe, and afterwards moistened with a solution of *nitrate of protoxide of cobalt*, and then again strongly ignited, an infusible mass of a deep SKY-BLUE color is produced, which consists of a compound of the two oxides. The blue color becomes distinct only upon cooling. By candle-light it appears violet. This reaction is decisive only in the case of infusible or difficultly fusible compounds of alumina, as solution of cobalt imparts a blue tint to readily fusible salts, even though no alumina be present.

§ 99.

b. SESQUIOXIDE OF CHROMIUM (Cr_2O_3).

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

2. The salts of sesquioxide of chromium have a green or a violet color. Many of them are soluble in water. Most of them dissolve in hydrochloric acid. The solutions exhibit a fine green color. Many of the

double salts of the sesquioxide of chromium (*e. g.* sulphate of sesquioxide of chromium and potassa, chrome alum) have a deep violet color, and give with cold water bluish-violet solutions, which, however, acquire a green tint when even moderately heated. The salts of sesquioxide of chromium with volatile acids are decomposed upon ignition, the acid being expelled. The salts of sesquioxide of chromium which are soluble in water, redden litmus.

3. *Potassa and soda* produce in solutions of salts of sesquioxide of chromium a bluish-green precipitate of HYDRATE OF SESQUIOXIDE OF CHROMIUM ($Cr_2O_3, 5 HO$), which dissolves readily and completely in an excess of the precipitant, imparting an emerald-green tint to the fluid. Upon *long-continued* ebullition of this solution, the whole of the hydrated sesquioxide separates again, and the supernatant fluid appears perfectly colorless. The same reprecipitation takes place if chloride of ammonium is added to the alkaline solution, and the mixture heated.

4. *Ammonia* produces in solutions of salts of sesquioxide of chromium the same precipitate of HYDRATED SESQUIOXIDE OF CHROMIUM as potass aand soda; a small portion of the precipitate redissolves in an excess of the precipitant in the cold, imparting to the fluid a peach-blossom red tint; but if, after the addition of ammonia in excess, heat is applied to the mixture, the precipitation is complete.

5. *Carbonate of baryta* precipitates from solutions of sesquioxide of chromium the whole of the sesquioxide, as HYDRATE mixed with BASIC SALT. The precipitation takes place in the cold, but is complete only after long continued digestion.

6. The fusion of sesquioxide of chromium, or of any of its compounds, with *nitrate of soda and some carbonate of soda,* invariably gives rise to the formation of yellow CHROMATE OF SODA, part of the oxygen of the nitric acid separating from the nitrate of soda, and converting the sesquioxide of chromium into chromic acid, which then combines with the soda present. For the reactions of chromic acid, see § 132.

7. *Phosphate of soda and ammonia* dissolves sesquioxide of chromium and its salts, both in the *oxidizing* and *reducing* flame of the blowpipe, to clear beads of a faint YELLOWISH-GREEN tint, which, upon cooling, changes to EMERALD-GREEN. The sesquioxide of chromium and its salts show a similar deportment with *biborate of soda.*

§ 100.

Recapitulation and remarks.—The solubility of hydrate of alumina in solutions of potassa and soda, and its reprecipitation from the alkaline solutions by chloride of ammonium, affords a safe means of detecting alumina, in the absence of sesquioxide of chromium. If the latter is present, therefore, which is seen either from the color of the solution, or by the reaction with phosphate of soda and ammonia, it must be removed, before we can proceed to test for alumina. The separation of sesquioxide of chromium from alumina is effected the most completely by fusing one part of the mixed oxides together with two parts of carbonate and two parts of nitrate of soda, which may be done in a platinum crucible. The yellow mass obtained is boiled with water; by this process the whole of the chromium dissolves as chromate of soda, and part of the alumina as alumina-soda, the rest of the alumina remaining undissolved. If the solution is acidified with nitric acid, it acquires a reddish tint; if ammonia is then added to feebly alkaline reaction, the dissolved portion of the alumina separates. The precipitation of sesquioxide of chromium by boiling its solution in solution of potassa or soda, is also nearly accurate, if the ebullition is continued a sufficient length of time; still it is often liable to mislead in cases where only little sesquioxide of chromium is present, or where the solution contains organic matter, even though in small proportion only. Finally, it must be borne in mind that alkalies produce no precipitates in the solutions of alumina if non-volatile organic substances are present, such as sugar, tartaric acid, &c.; whilst the presence of such bodies hardly interferes with the precipitation of sesquioxide of chromium.

§ 101.

FOURTH GROUP.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—SESQUIOXIDE OF IRON.

Properties of the group.—The solutions of the oxides of the fourth group, when containing a stronger free acid, are not precipitated by hydrosulphuric acid; neutral solutions also are not, or only very incompletely, precipitated by that reagent; but alkaline solutions are completely precipitated by hydrosulphuric acid; and other solutions also, if an alkaline sulphide is used as the precipitant, instead of hydrosulphuric acid. The precipitated metallic sulphides, corresponding to the respective oxides, are insoluble in water; some of them are readily soluble in dilute acids; others (sulphide of nickel and sulphide of cobalt) dissolve only with very great difficulty in these menstrua. Some of them are insoluble in sulphides of the alkali metals; others are sparingly soluble in them, under certain circumstances.

Special Reactions.

§ 102.

a. OXIDE OF ZINC (ZnO).

1. Metallic zinc is bluish-white, and very bright; when exposed to the air, a thin coating of basic carbonate of zinc forms on it. It is of medium hardness, ductile at a temperature of between 212° and 292°, at a lower temperature more or less brittle; it fuses readily on charcoal before

the blowpipe, melts afterwards, and burns with a bluish-green flame, filling the air with white fumes, and coating the charcoal support with oxide. Zinc dissolves in hydrochloric acid and sulphuric acid, with evolution of hydrogen gas; in dilute nitric acid, with evolution of nitrous oxide; in more concentrated nitric acid, with evolution of nitric oxide.

2. The oxide of zinc and its hydrate are white powders, which dissolve readily in hydrochloric acid, nitric acid, and sulphuric acid. The oxide of zinc acquires a lemon-yellow tint when heated, but it re-assumes its original white color upon cooling.

3. The compounds of oxide of zinc are colorless; part of them are soluble in water, the rest in acids. The neutral salts of zinc which are soluble in water redden litmus-paper, and are readily decomposed by heat, with the exception of sulphate of zinc, which can bear a dull red heat, without undergoing decomposition.

4. *Hydrosulphuric acid* precipitates from neutral solutions of salts of zinc a portion of the metal as white hydrated SULPHIDE OF ZINC ($Zn\,S, H\,O$). In acid solutions this reagent fails altogether to produce a precipitate, if the free acid present is one of the stronger acids; but from a solution of oxide of zinc in acetic acid, it throws down the whole of the zinc, even if the acid is present in excess.

5. *Sulphide of ammonium* throws down from *neutral*, and *hydrosulphuric acid* from *alkaline* solutions of salts of zinc, the whole of the metal as hydrated SULPHIDE OF ZINC, in the form of a white precipitate. This precipitate is not redissolved by an excess of sulphide of ammonium, nor by potassa or ammonia; but it dissolves readily in hydrochloric acid, nitric acid, and dilute sulphuric acid.

6. *Potassa, soda, and ammonia* throw down from solutions of salts of zinc HYDRATED OXIDE OF ZINC ($Zn\,O, H\,O$), in the form of a white gelatinous precipitate, which is readily and completely redissolved by an excess of the precipitant.

7. *Carbonate of soda* produces in solutions of salts of zinc a precipitate of BASIC CARBONATE OF ZINC ($3\,[Zn\,O, H\,O] + 2\,[Zn\,O, C\,O_2]$), which is insoluble in an excess of the precipitant. Salts of ammonia prevent the formation of this precipitate, or redissolve the precipitate already formed, combining with the oxide of zinc to soluble double salts of oxide of zinc and ammonia.

8. *Carbonate of ammonia* also produces in solutions of salts of zinc a precipitate of BASIC CARBONATE OF ZINC, but this precipitate redissolves upon further addition of the precipitant.

9. *Carbonate of baryta* fails to precipitate, in the cold, oxide of zinc from its solutions.

10. If a mixture of oxide of zinc, or one of its salts, with *carbonate of soda* is exposed to the *reducing flame* of the blowpipe, the charcoal support becomes covered with a slight coating of OXIDE OF ZINC, which presents

a yellow color whilst hot, and turns white upon cooling. This coating is produced by the reduced metallic zinc volatilizing at the moment of its reduction, and reoxidizing in passing through the outer flame.

11. If oxide of zinc, or one of the salts of zinc, is moistened with solution of *nitrate of protoxide of cobalt,* and then heated before the blowpipe, an unfused mass is obtained, of a beautiful GREEN color; this mass is a compound of oxide of zinc with protoxide of cobalt. If, therefore, in the experiment described in 10, the charcoal is moistened, around the little cavity, with solution of cobalt, the coating appears *green* when *cold.*

§ 103.

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

1. Manganese metal has a whitish-gray color, and but little lustre; it is brittle, and fuses with very great difficulty; it oxidizes slowly in cold water, rapidly in boiling water, and dissolves readily in acids. The solutions contain protoxide.

2 Protoxide of manganese exhibits a greenish-gray color; the hydrated protoxide is white. Both the protoxide and its hydrate absorb oxygen from the air, and are converted into the brown sesquioxide. They are readily soluble in hydrochloric acid, nitric acid, and sulphuric acid.

3. The salts of protoxide of manganese are colorless or of a pale red color; part of them are soluble in water, the rest in acids. The salts soluble in water are readily decomposed by a red heat, with the exception of the sulphate. The solutions do not alter vegetable colors.

4. *Hydrosulphuric acid* does not precipitate acid solutions of salts of protoxide of manganese; neutral solutions also it fails to precipitate, or precipitates them only very imperfectly.

5. *Sulphide of ammonium* throws down from neutral, and *hydrosulphuric acid* from alkaline solutions of salts of protoxide of manganese, the whole of the metal as hydrated SULPHIDE OF MANGANESE ($Mn\,S$), in the form of a light flesh-colored* precipitate, which acquires a dark-brown color in the air; this precipitate is insoluble in sulphide of ammonium and in alkalies, but readily soluble in hydrochloric acid and nitric acid. From very dilute solutions the precipitate separates only after standing a certain time in a warm place.

6. *Potassa, soda,* and *ammonia* produce whitish precipitates of HYDRATE OF PROTOXIDE OF MANGANESE ($Mn\,O, H\,O$), which, upon exposure to the air, speedily acquire a brownish, and, finally, a deep blackish-brown color, owing to the conversion of the hydrated protoxide into hydrated sesquioxide, by the absorption of oxygen from the air. Ammonia and carbonate of ammonia do not redissolve this precipitate;

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

but the presence of chloride of ammonium prevents the precipitation by ammonia altogether, and that by potassa partly. Of *already formed* precipitates solution of chloride of ammonium redissolves only those parts which have not yet undergone peroxidation. The solution of the hydrated protoxide of manganese in chloride of ammonium is owing to the disposition of the salts of protoxide of manganese to form double salts with salts of ammonia. The clear solutions of those doublesalts of manganese and ammonia acquire a brown color in the air, and deposit dark-brown hydrate of sesquioxide of manganese ($Mn_2 O_3$, $2 H O$).

7. *Carbonate of baryta* does not precipitate protoxide of manganese from its solutions, upon digestion in the cold.

8. If a compound of manganese, no matter which, is fused with *carbonate of soda* in the *outer* flame of the blowpipe, upon a platinum wire, MANGANATE OF SODA ($Na O$, $Mn O_3$) is formed, which makes the fused mass appear GREEN while hot, and of a BLUEISH-GREEN tint after cooling, the bead at the same time becoming turbid. This reaction enables us to detect the smallest quantities of manganese. The delicacy of the test may be still further increased by the addition of a minute quantity of nitrate of potassa to the carbonate of soda.

9. *Borax* and *phosphate of soda and ammonia* dissolve manganese compounds, in the *outer* flame of the blowpipe, to clear VIOLET-RED beads, which, upon cooling, acquire an AMETHYST-RED tint: they lose their color in the *inner* flame, owing to an ensuing reduction of the sesquioxide to protoxide. The bead which borax forms with manganese compounds appears black when containing a considerable portion of sesquioxide of manganese, but that formed by phosphate of soda and ammonia never loses its transparency. The latter loses its color in the inner flame of the blowpipe far more readily than the former.

§ 104.

c. PROTOXIDE OF NICKEL ($Ni O$).

1. Metallic nickel is, in the fused state, silvery white, inclining to gray, bright, hard, ductile, difficultly fusible; it does not oxidize in the air at common temperatures, but it oxidizes slowly upon ignition; it is attracted by the magnet, and may itself become magnetic. It dissolves in hydrochloric acid and dilute sulphuric acid slowly, upon the application of heat, the solution being attended with evolution of hydrogen gas. It dissolves readily in nitric acid.

2. Protoxide of nickel is a gray, its hydrate a green powder. Both the protoxide and its hydrate are unalterable in the air, and readily soluble in hydrochloric acid, nitric acid, and sulphuric acid.

3. The other salts of protoxide of nickel are for the most part, yellow in

the anhydrous, green in the hydrated state; their solutions are of a light green color. The soluble neutral salts redden litmus paper, and are decomposed at a red heat.

4. *Hydrosulphuric acid* does not precipitate acid solutions of salts of nickel; it fails also to precipitate neutral solutions of salts of nickel with the stronger acids, or it precipitates them only very imperfectly.

5. *Sulphide of ammonium* produces in neutral, and *hydrosulphuric acid*, in alkaline solutions of salts of protoxide of nickel, a black precipitate of hydrated SULPHIDE OF NICKEL ($Ni\,S$), which is not altogether insoluble in sulphide of ammonium containing an admixture of free ammonia or of pentasulphide of ammonium; the fluid from which the precipitate has been thrown down exhibits therefore usually a brownish color. Sulphide of nickel dissolves with great difficulty in hydrochloric acid, but readily in nitrohydrochloric acid, upon application of heat.

6. *Potassa* and *soda* produce a light green precipitate of HYDRATE OF PROTOXIDE OF NICKEL ($Ni\,O, H\,O$), which is insoluble in potassa, and unalterable in the air. Carbonate of ammonia dissolves this precipitate to a greenish-blue fluid, from which potassa reprecipitates the nickel as a yellowish-green hydrate of protoxide of nickel.

7. *Ammonia*, added in small quantity to solutions of protoxide of nickel, produces in them a trifling greenish turbidity; upon further addition of the reagent, this redissolves readily to a blue fluid, containing a compound of protoxide of nickel and ammonia. Potassa precipitates from this solution hydrate of protoxide of nickel. Solutions containing salts of ammonia or a free acid are not rendered turbid by ammonia.

8. *Cyanide of potassium* produces a yellowish-green precipitate of CYANIDE OF NICKEL ($Ni\,Cy$), which redissolves readily in an excess of the precipitant as a double cyanide of nickel and potassium ($K\,Cy + Ni\,Cy$); the solution is brownish-yellow. If sulphuric acid or hydrochloric acid is added to this solution, the cyanide of potassium is decomposed, and the cyanide of nickel reprecipitated; the latter substance is very difficultly soluble in an excess of these acids in the cold, but more readily upon boiling.

9. *Carbonate of baryta* does not precipitate protoxide of nickel from its solutions, upon digestion in the cold.

10. *Borax* and *phosphate of soda and ammonia* dissolve compounds of protoxide of nickel in the *outer* flame of the blowpipe, giving clear beads of a dark yellow color, with a shade of reddish-brown; the color fades upon cooling, and finally disappears almost entirely. The bead which phosphate of soda and ammonia forms with salts of protoxide of nickel, remains unaltered in the *inner* flame of the blowpipe, but that formed in the borax turns gray and turbid from reduced metallic nickel.

§ 105.

d. PROTOXIDE OF COBALT (Co O).

1. Metallic cobalt is reddish-gray, slightly lustrous, tolerably hard, and difficultly fusible; it possesses but very little malleability; it does not oxidize in the air at the common temperature and only slowly at a red heat; with acids it comports itself like nickel.

2. Protoxide of cobalt is a grayish-green, its hydrate a pale red powder. Both dissolve readily in hydrochloric acid, nitric acid, and sulphuric acid.

3. The salts of protoxide of cobalt are light red, violet, or blue. Their solutions show a light red color even though considerably diluted. The soluble neutral salts redden litmus paper slightly, and are decomposed at a red heat; sulphate of protoxide of cobalt alone can bear a moderate red heat, without suffering decomposition. If a solution of chloride of cobalt is evaporated, the light red color changes, towards the end of the operation, to blue; addition of water restores the red color.

4. *Hydrosulphuric acid* does not precipitate acid solutions of cobalt; it also fails to precipitate neutral solutions of salts of protoxide of cobalt with the stronger acids, or it precipitates them only very imperfectly.

5. *Sulphide of ammonium* precipitates from neutral, and *hydrosulphuric acid* from alkaline solutions of salts of protoxide of cobalt, the whole of the metal as black hydrated SULPHIDE OF COBALT (Co S). This substance is insoluble in alkalies and sulphide of ammonium, very difficultly soluble in hydrochloric acid, but readily so in nitrohydrochloric acid upon application of heat.

6. *Potassa* and *soda* produce in solutions of cobalt BLUE precipitates of basic salts of cobalt, which turn GREEN upon exposure to the air, owing to the absorption of oxygen, and are, upon boiling, converted into the pale red hydrate of protoxide of cobalt, which generally appears rather discolored from an admixture of sesquioxide formed in the process. These precipitates are insoluble in potassa; but neutral carbonate of ammonia dissolves them completely to intensely violet-red fluids, in which potassa produces no precipitate, or only a slight one.

7. *Ammonia* produces the same precipitate as potassa, but this redissolves in an excess of the ammonia to a reddish-brown fluid, in which potassa produces no precipitate, or, at all events, only a slight one. Ammonia fails to precipitate solutions of protoxide of cobalt containing salts of ammonia or a free acid.

8. The addition of *cyanide of potassium* to a solution of cobalt gives rise to the formation of a brownish-white precipitate of PROTOCYANIDE OF COBALT (Co Cy), which dissolves readily as a double cyanide of cobalt and potassium in an excess of solution of cyanide of potassium. Acids precipitate from this solution cyanide of cobalt. But if the solution is boiled with

cyanide of potassium in excess, in presence of free hydrocyanic acid, (liberated by addition of one or two drops of hydrochloric acid), a double compound of sesquicyanide of cobalt and cyanide of potassium ($3\,K + Co_2\,Cy_6 = 3\,K\,Cky$) is formed, in the solution of which acids *produce no precipitate.*

9. *Carbonate of baryta* does not precipitate solution of protoxide of cobalt in the cold.

10. *Borax* dissolves compounds of cobalt both in the *inner* and *outer* flame of the blowpipe, giving clear beads of a magnificent BLUE color, which appear violet by candle-light, and almost black if the cobalt is present in considerable proportion. This test is as delicate as it is characteristic. *Phosphate of soda and ammonia* manifests with salts of cobalt before the blowpipe, an analogous but less intense reaction.

§ 106.

e. PROTOXIDE OF IRON ($Fe\,O$).

1. Metallic iron in the pure state has a light whitish gray color (iron containing carbon is more or less gray) ; the metal is hard, lustrous, malleable, exceedingly difficult to fuse, and is attracted by the magnet. In contact with air and moisture a coating of rust (hydrate of sesquioxide of iron) forms on its surface ; upon ignition in the air, a coating of black protosesquioxide. Hydrochloric acid and dilute sulphuric acid dissolve iron with evolution of hydrogen gas ; if the iron contains carbon, the hydrogen is mixed with carbide of hydrogen. The solution contains protoxide. Dilute nitric acid dissolves iron in the cold to nitrate of protoxide, with evolution of nitrous oxide ; at a high temperature, to nitrate of sesquioxide, with evolution of nitric oxide ; if the iron contains carbon, some carbonic acid is also evolved, and there is left undissolved a brown substance resembling humus, which is soluble in alkalies.

2. Protoxide of iron is a black powder ; its hydrate is a white powder, which in the moist state absorbs oxygen and speedily acquires a grayish-green, and finally a brownish-red color. Both the protoxide and its hydrate are dissolved by hydrochloric acid, sulphuric acid, and nitric acid.

3. The salts of protoxide of iron have in the anhydrous state a white, in the hydrate state a greenish color ; their solutions appear colored only when very concentrated. Exposed to the air, they absorb oxygen, and become converted into salts of the protosesquioxide. The soluble neutral salts redden litmus paper, and are decomposed at a red heat.

4. Acid solutions of salts of protoxide of iron are not precipitated by *hydrosulphuric acid;* neutral solutions of salts with weak acids, are precipitated by this reagent at the most but incompletely ; the precipitates are of a black color.

5. *Sulphide of ammonium* precipitates from neutral, and hydrosulphuric acid from alkaline solutions of salts of protoxide of iron, the whole of the metal as black hydrated SULPHIDE OF IRON ($Fe\,S$), which is insoluble in alkalies and alkaline sulphides, but dissolves readily in hydrochloric acid and nitric acid.

6. *Potassa* and *ammonia* produce a precipitate of HYDRATE OF PROTOXIDE OF IRON ($Fe\,O, H\,O$), which in the first moment looks almost white, but acquires after a very short time a dirty green, and finally a reddish-brown color, owing to absorption of oxygen from the air. The presence of salts of ammonia prevents the precipitation by potassa partly, and that by ammonia altogether. If the alkaline solutions of protoxide of iron thus obtained by the agency of salts of ammonia are exposed to the air, hydrate of sesquioxide of iron precipitates.

7. *Ferrocyanide of potassium* produces in solutions of protoxide of iron a bluish-white precipitate of FERROCYANIDE OF POTASSIUM AND IRON ($3\,Fe, K, 2\,Cfy$), which, by absorption of oxygen from the air, speedily acquires a blue color. Nitric acid or chlorine convert it immediately into Prussian blue ($3\,[3\,Fe, K, 2\,Cfy] + 4\,Cl = 3\,K\,Cl + Fe\,Cl + 2\,[Fe_4\,Cfy_3]$).

8. *Ferricyanide of potassium* produces a magnificently blue precipitate of FERRICYANIDE OF IRON ($3\,Fe, Cfdy$). This precipitate does not differ in color from Prussian blue. It is insoluble in hydrochloric acid, but is readily decomposed by potassa. In highly dilute solutions of salts of protoxide of iron, the reagent produces simply a deep bluish-green coloration.

9. *Sulphocyanide of potassium* does not alter solutions of protoxide of iron free from sesquioxide.

10. *Carbonate of baryta* does not precipitate solutions of protoxide of iron in the cold.

11. *Borax* dissolves salts of protoxide of iron in the *oxidizing* flame, giving DARK RED BEADS, the color of which changes to bottle green in the *inner* flame, owing to the reduction of the newly-formed sesquioxide to protosesquioxide. Both tints disappear totally, or in a great measure, upon cooling. *Phosphate of soda and ammonia* manifest a similar deportment with the salts of protoxide of iron; the beads produced by the latter reagent lose their color, upon cooling, more completely than is the case with those produced by borax.

§ 107.

f. SESQUIOXIDE OF IRON ($Fe_2\,O_3$).

1. The native crystalline sesquioxide of iron has a steel-gray color; native as well as the artificially prepared sesquioxide of iron, gives upon trituration a brownish-red powder; the color of hydrate of sesquioxide of iron is more inclined to reddish-brown. Both the sesquioxide and its

hydrate dissolve in hydrochloric acid, nitric acid, and sulphuric acid; the hydrate dissolves readily in these acids, but the anhydrous sesquioxide dissolves with greater difficulty, and completely only after long exposure to heat.

2. The neutral anhydrous salts of sesquioxide of iron are nearly white; the basic salts are yellow, or reddish-brown. The color of the solution is brownish-yellow, and becomes reddish-yellow upon the application of heat. The soluble neutral salts redden litmus paper, and are decomposed by heat.

3. *Hydrosulphuric acid* produces in neutral and acid solutions of salts of sesquioxide of iron a milky turbidity, proceeding from separated SULPHUR. This reaction is caused by a mutual decomposition of the sesquioxide of iron and the hydrosulphuric acid, in which the former is deprived of one-third of its oxygen, and thus reduced to the state of protoxide; the oxygen forms water with the hydrogen of the hydrosulphuric acid, and the liberated sulphur separates. Hydrosulphuric acid water, rapidly added to neutral solutions, imparts to the fluid a transitory blackening.

4. *Sulphide of ammonium* precipitates from neutral, and *hydrosulphuric acid* from alkaline solutions of salts of sesquioxide of iron, the whole of the metal as black hydrated SULPHIDE OF IRON ($Fe\,S$). This precipitation is preceded by the reduction of the sesquioxide to protoxide. In very dilute solutions, the reagent produces only a blackish-green coloration. The minutely divided protosulphide of iron subsides in such cases only after long standing. Protosulphide of iron, as already stated (*e.* 5), is insoluble in alkalies and alkaline sulphides, but dissolves readily in hydrochloric acid and nitric acid.

5. *Potassa* and *ammonia* produce bulky reddish-brown precipitates of HYDRATE OF SESQUIOXIDE OF IRON ($F_2\,O_3$, $H\,O$), which are insoluble in an excess of the precipitant as well as in salts of ammonia.

6. *Ferrocyanide of potassium* produces, even in highly dilute solutions, a magnificently blue precipitate of FERROCYANIDE OF IRON, or Prussian blue ($Fe_4\,Cfy_3$), which is insoluble in hydrochloric acid, but is readily decomposed by potassa, with separation of sesquioxide of iron.

7. *Ferricyanide of potassium* changes the color of solutions of salts of sesquioxide of iron to brownish-green; but it fails to produce a precipitate.

8. *Sulphocyanide of potassium* imparts to neutral or slightly acid solutions of salts of sesquioxide of iron a very intense blood-red color, arising from the formation of a soluble SULPHOCYANIDE OF IRON. This test is the most delicate of all; it will indicate the presence of sesquioxide of iron even in fluids which are so highly dilute that every other reagent fails to produce the slightest visible alteration. The red coloration may in such cases be detected most distinctly, by resting the test-tube upon a sheet of white paper, and looking through it from the top.

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

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

§ 108.

Recapitulation and Remarks.—On observing the behavior of the oxides of the fourth group with solution of potassa, it would appear that the separation of the oxide of zinc, which is soluble in an excess of this reagent, might be readily effected; however, in the actual experiment, we find that in the presence of sesquioxide of iron, protoxide of cobalt, &c., some of the oxide of zinc precipitates with these oxides; and if only a small quantity of oxide of zinc is present, it frequently occurs that no trace of this metal can be detected in the alkaline filtrate. Again, from the behaviour of the different oxides with chloride of ammonium and an excess of ammonia, one would conclude that the separation of sesquioxide of iron from the protoxides of cobalt, nickel, and manganese, and from oxide of zinc, might be readily effected by these agents. But this method also is inaccurate, since greater or smaller portions of the other oxides will always precipitate with the sesquioxide of iron: and it may accordingly happen that with the application of this process small quantities of cobalt, manganese, &c., may altogether escape detection. It is far safer, therefore, to separate the other oxides of the fourth group from sesquioxide of iron by carbonate of baryta, as in this case the iron is precipitated free from oxide of zinc and protoxides of manganese and nickel, and mixed only with a very trifling quantity of protoxide of cobalt. Protoxide of manganese may be separated from the protoxides of cobalt and nickel and from oxide of zinc, by treating the precipitated sulphides with moderately diluted acetic acid, which dissolves the sulphides of manganese, leaving the other sulphides unacted on. If the acetic acid solution is now mixed with solution of potassa, the least trace of a precipitate will be sufficient to detect the manganese before the blowpipe with carbonate of soda.

If the undissolved sulphides are now treated with very dilute hydrochloric acid, the sulphide of zinc dissolves, leaving almost the whole of the sulphides of cobalt and nickel behind. If the fluid is then boiled, to expel the hydrosulphuric acid, and afterwards treated with solution of potassa in excess, the zinc is sure to be detected in the filtrate by hydrosulphuric acid.

Cobalt may be readily and safely detected in presence of nickel by the reaction with borax in the inner flame of the blowpipe. The detection of nickel in presence of cobalt is a less easy task, which may, however, be effected with great accuracy by two different methods. The process of the *first* of these methods is as follows: saturate the very dilute solution of the two metals in hydrochloric acid, containing a little free acid, with chlorine, add carbonate of baryta in excess, and let the fluid stand twenty-four hours. The cobalt is entirely precipitated in this process, as black sesquioxide, whilst the nickel remains in solution, and may, after the removal of the baryta by sulphuric acid, be thrown down with solution of soda. The *second* method is based upon the application of cyanide of potassium. Both cyanide of nickel and cyanide of cobalt dissolve in cyanide of potassium; but cyanide of nickel is precipitated from this solution by acids, whilst cyanide of cobalt is not precipitated if the solution contains free hydrocyanic acid, and has been exposed to the action of heat.* This reaction, *i. e.* the formation of a precipitate upon adding hydrochloric acid or dilute sulphuric acid to the solution of the two cyanides in cyanide of potassium, prepared under the conditions stated, indicates the presence of nickel with positive certainty. Whether the precipitate be cyanide of nickel, or cobalticyanide of nickel, is quite immaterial as far as the *detection of nickel* is concerned: all we have to bear in mind is simply this, that no precipitate will form if cobalt alone is present in the solution, since cobalticyanide of potassium is not decomposed by hydrochloric acid. In order to get at the composition of the various precipitates which are formed by hydrochloric acid in solutions of the mixed cyanides of nickel and cobalt, and to comprehend the general process of their formation, we have to assume and consider three special and distinct cases, differing from one another in the relative proportions of nickel and cobalt which the solutions under examination respectively contain.

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

The solution will accordingly, in the first case, contain one eq. of cobalticyanide of potassium ($3\ K,\ Co_2\ Cy_6$) and 3 eq. of double cyanide of nickel and potassium, 3 (K Cy, Ni Cy); now upon the addition of hydrochloric acid in excess to this solution, the double cyanide of nickel and potassium suffers decomposition, and the potassium of the cobalticyanide of potassium transposes with the nickel of the cyanide of nickel; the products of this process of double decomposition and transposition are chloride of potassium, hydrocyanic acid, and cobalticyanide of nickel ($3\ Ni,\ Cy_6\ Co_2$), which latter separates in the form of a dirty green precipitate containing the *whole* of the nickel and cobalt present in the solution. In the second case we obtain equally a precipitate of cobalticyanide of nickel; but this precipitate, though containing the whole of the *nickel*, does *not* contain *all* the *cobalt* of the solution, since the excess of cobalticyanide of potassium is not decomposed. In the third case, we obtain a precipitate of

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* In this process the double cyanide of cobalt and potassium (K Cy, Co Cy), which forms at first, is converted by the aid of the free hydrocyanic acid and the excess of cyanide of potassium, into cobalticyanide of potassium ($3\ K,\ Co_2\ Cy_6$). $2(K\ Cy,\ Co\ Cy), + K\ Cy + H\ Cy = (3\ K,\ Co_2\ Cy_6) + H$.

cobalticyanide of nickel, which contains the *whole* of the *cobalt* and a *portion* of the *nickel*, mixed with insoluble cyanide of nickel which contains the rest of the nickel. The cobalticyanide of nickel has been formed here in the same manner as in the first case, whilst the cyanide of nickel owes its formation to the decomposition of the *excess* of the double cyanide of nickel and potassium. Hence it is evident that the presence of nickel is indispensable to the formation of a precipitate, and consequently, that the production of a precipitate is the most positive proof of the presence of this metal.

Protoxide and sesquioxide of iron may be detected in presence of each other, by testing for the former with ferricyanide of potassium, for the latter with ferrocyanide of potassium, or, better still, with sulphocyanide of potassium.

Finally, it is necessary to mention, that alkalies fail to precipitate the oxides of the fourth group in presence of non-volatile organic substances (such as sugar, tartaric acid, &c.). We have already seen that the same applies to alumina.

§ 109.

APPENDIX TO THE FOURTH GROUP.

SESQUIOXIDE OF URANIUM (U_2O_3).

Sesquioxide of uranium is brick red-color, the hydrate is yellow. Upon ignition both are converted into the dark blackish-green protosesquioxide. The solutions of sesquioxide of uranium in acids are yellow; hydrosulphuric acid does not alter them; sulphide of ammonium throws down from them, after neutralization of the free acid, a dark brown precipitate of SULPHIDE OF URANIUM, which subsides slowly, and is readily soluble in acids, even in acetic acid, but does not dissolve in an excess of the precipitant. Ammonia, potassa, and soda produce yellow precipitates of sesquioxide of uranium and alkali, insoluble in excess of the precipitants. Carbonate of ammonium produces a yellow precipitate of carbonate of sesquioxide of uranium and ammonia, which *dissolve readily in an excess of the precipitant*. Potassa and soda throw down from the solution the whole of the sesquioxide of uranium. Carbonate of baryta completely precipitates solutions of sesquioxide of uranium, even in the cold. Ferrocyanide of potassium produces a reddish-brown precipitate: this is a very delicate test for uranium. Borax and phosphate of soda and ammonia give with sesquioxide of uranium in the inner flame of the blowpipe green beads, in the outer flame yellow beads, which upon cooling acquire a yellowish-green tint.

§ 110.

FIFTH GROUP.

OXIDE OF SILVER—SUBOXIDE OF MERCURY—OXIDE OF MERCURY—OXIDE OF LEAD—TEROXIDE OF BISMUTH—OXIDE OF COPPER—OXIDE OF CADMIUM.

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

For the sake of greater clearness and simplicity, we divide the oxides of this group into two sections, and distinguish,

1. OXIDES PRECIPITABLE BY HYDROCHLORIC ACID, viz.: oxide of silver, suboxide of mercury, oxide of lead.

2. OXIDES NOT PRECIPITABLE BY HYDROCHLORIC ACID, viz.: oxide of mercury, oxide of copper, teroxide of bismuth, oxide of cadmium.

Lead must be considered in both sections, since the sparing solubility of its chloride might lead to confounding its oxide with suboxide of mercury and oxide of silver, without affording us, on the other hand, any means of effecting its perfect separation from the oxides of the second section.

FIRST SECTION OF THE FIFTH GROUP: OXIDES WHICH ARE PRECIPITATED BY HYDROCHLORIC ACID.

Special Reactions.

§ 111.

a. OXIDE OF SILVER (Ag O).

1. Metallic silver is white, very lustrous, moderately hard, highly malleable, rather difficultly fusible. It is not oxidized by ignition in the air. Nitric acid dissolves silver readily; the metal is insoluble in dilute sulphuric acid and in hydrochloric acid.

2. Oxide of silver is a dark brown powder; it dissolves readily in dilute nitric acid. It forms no hydrate. It is decomposed by heat into metallic silver and oxygen gas.

3. The salts of oxide of silver are non-volatile and colorless; most of them acquire a black tint upon exposure to light. The soluble neutral salts do not alter vegetable colors, and are decomposed at a red heat.

4. *Hydrosulphuric acid* and *sulphide of ammonium* precipitate from solutions of salts of silver black SULPHIDE OF SILVER (Ag S), which is insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potas-

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* Consult, however, the paragraph on oxide of copper and suboxide and oxide of mercury, as the latter remark applies only partially to them.

sium. Boiling concentrated nitric acid decomposes and dissolves this precipitate readily, with separation of sulphur.

5. *Potassa* and *ammonia* precipitate from solutions of salts of silver the oxide of this metal in the form of a LIGHT BROWN POWDER, which is insoluble in potassa, but dissolves readily in ammonia. The presence of salts of ammonia prevents this precipitation totally or partly.

6. *Hydrochloric acid* and *soluble metallic chlorides* produce in solutions of salts of silver a white curdy precipitate of CHLORIDE OF SILVER ($Ag\,Cl$). In very dilute solutions, these reagents impart simply a bluish-white opalescent appearance to the fluid. By the action of light, chloride of silver acquires first a violet tint, and then turns black; it is insoluble in nitric acid, but dissolves readily in ammonia as ammonio-chloride of silver, from which double compound the chloride of silver is separated again by acids. Concentrated hydrochloric acid, and concentrated solutions of chlorides of the alkali metals dissolve some chloride of silver, more particularly upon application of heat; but the dissolved chloride separates again upon dilution of the solution. Upon exposure to heat, chloride of silver fuses without decomposition, giving upon cooling a transparent horny mass.

7. If compounds of silver, mixed with *carbonate of soda*, are exposed on a charcoal support to the *inner* flame of the blowpipe, WHITE BRILLIANT AND MALLEABLE METALLIC GLOBULES are produced, unattended with any incrustation of the charcoal.

§ 112.

b. SUBOXIDE OF MERCURY ($Hg_2\,O$).

1. Metallic mercury is grayish-white, brilliant, fluid at the common temperature; it solidifies at — 40°, and boils at 680°. It is insoluble in hydrochloric acid; in dilute cold nitric acid it dissolves to nitrate of suboxide, in more concentrated hot nitric acid to nitrate of oxide.

2. Suboxide of mercury is a black powder which is readily soluble in nitric acid, and is decomposed by the action of heat, the mercury volatilizing in the metallic state. It forms no hydrate.

3. The salts of suboxide of mercury, and also the corresponding haloid compounds, volatilize upon ignition, either unaltered, or they are decomposed, and the mercury volatilizes in the metallic state. Most of the salts of suboxide of mercury are colorless. The soluble salts in the neutral state, redden litmus paper. Nitrate of suboxide of mercury is decomposed by addition of much water into an insoluble basic and a soluble acid salt.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce black precipitates of SUBSULPHIDE OF MERCURY ($Hg_2\,S$), which are insoluble in dilute acids, sulphide of ammonium, and cyanide of potassium. Protosulphide of potassium converts this subsulphide into sulphide which dissolves, and globules of metallic mercury, which separate. Bisulphide of

potassium converts the subsulphide into sulphide, without separation of metallic mercury. Subsulphide of mercury is readily decomposed and dissolved by nitrohydrochloric acid, but not by boiling concentrated nitric acid.

5. *Potassa* and *ammonia* produce in solutions of salts of suboxide of mercury black precipitates, which are insoluble in an excess of the precipitants. The precipitates produced by potassa consist of SUBOXIDE OF MERCURY; whilst those produced by ammonia consist of a BASIC DOUBLE SALT OF SUBOXIDE OF MERCURY AND AMMONIA, *e.g.* $(NH_4O, NO_5 + 3Hg_2O)$.

6. *Hydrochloric acid*, and *soluble metallic chlorides* precipitate from solutions of salts of suboxide of mercury SUBCHLORIDE OF MERCURY (Hg_2Cl), as a fine powder of dazzling whiteness. Cold hydrochloric acid and cold nitric acid fail to dissolve this precipitate; it dissolves, however, although very difficultly and slowly, upon long protracted boiling with these acids, being resolved by hydrochloric acid into chloride of mercury and metallic mercury, which separates; and converted by nitric acid into chloride of mercury and nitrate of oxide of mercury. Nitrohydrochloric acid and chlorine water dissolve the subchloride of mercury readily, converting it into chloride. Ammonia and potassa decompose the subchloride of mercury, and separate black suboxide from it.

7. If a drop of a neutral or slightly acid solution of suboxide of mercury is put on a *clean and smooth surface of copper*, and washed off after some time, the spot will afterwards upon rubbing with cloth, paper, &c., appear WHITE and LUSTROUS like silver. The application of a gentle heat to the copper causes the metallic mercury precipitated on its surface to volatilize, and thus removes the silvering.

8. *Protochloride of tin* produces in solutions of suboxide of mercury a gray precipitate of METALLIC MERCURY, which may be united into globules by heat and agitation, but most readily by boiling the metallic deposit, after decantation of the fluid, with hydrochloric acid.

9. If an intimate mixture of a compound of mercury with anhydrous *carbonate of soda* is introduced into a drawn-out glass tube, and covered with a layer of carbonate of soda, and the tube is then heated before the blowpipe, the mercurial compound invariably undergoes decomposition, and metallic mercury separates, forming a coat of gray sublimate above the heated part of the tube. The minute particles of mercury may be united into larger globules by rubbing this coating with a glass rod.

§ 113.

c. OXIDE OF LEAD (Pb O).

1. Metallic lead is bluish-gray; its surface recently cut exhibits a metallic lustre; it is soft, malleable, readily fusible. Fused upon charcoal before the blowpipe, it form a coating of yellow oxide on the charcoal.

Hydrochloric acid and moderately concentrated sulphuric acid act upon it but little, even with the aid of heat; but dilute nitric acid dissolves it readily, more particularly on heating.

2. Oxide of lead is a yellow or reddish-yellow powder which upon exposure to heat fuses to a vitreous mass. Hydrate of oxide of lead is white. Both the oxide and its hydrate dissolve readily in nitric acid and acetic acid.

3. The salts of oxide of lead are colorless and non-volatile; the neutral soluble salts redden litmus paper, and are decomposed at a red heat.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in solutions of salts of lead, black precipitates of SULPHIDE OF LEAD ($Pb S$), which are insoluble in *cold* dilute acids, in alkalies, alkaline sulphides, and cyanide of potassium. Sulphide of lead is decomposed by boiling concentrated nitric acid; the whole of the lead is converted, at first, into nitrate of lead, and the greater portion of the sulphur separates, whilst another portion is converted into sulphuric acid. The sulphuric acid thus formed decomposes a portion of the nitrate of lead, and forms sulphate of lead, which remains undissolved in the form of a white powder, mixed with the separated sulphur. In solutions of salts of lead containing an excess of a concentrated mineral acid, hydrosulphuric acid produces a precipitate only after the addition of water or after neutralization of the free acid by an alkali. If a solution of lead is precipitated by hydrosulphuric acid, in presence of a large quantity of free hydrochloric acid, a reddish precipitate is formed, consisting of chloride and sulphide of lead, which, however, is converted by an excess of hydrosulphuric acid into black sulphide of lead.

5. *Potassa* and *ammonia* throw down BASIC SALTS OF LEAD in the form of white precipitates, which are insoluble in ammonia, and of difficultly soluble in potassa. In solutions of acetate of lead, ammonia does not immediately produce a precipitate, owing to the formation of a soluble trisacetate of lead.

6. *Carbonate of potassa* throws down from solutions of salts of lead a white precipitate of CARBONATE OF LEAD ($Pb O, C O_2$), which is insoluble in an excess of the precipitant and also in cyanide of potassium.

7. *Hydrochloric acid* and *soluble chlorides* produce in concentrated solutions of salts of lead heavy white precipitates of CHLORIDE OF LEAD ($Pb Cl$), which are soluble in a large amount of water, especially upon the application of heat. This chloride of lead is converted by ammonia into basic chloride of lead ($Pb Cl, 3 Pb O + H O$), which is also a white powder, but is almost absolutely insoluble in water. In dilute nitric acid and hydrochloric acid, chloride of lead is more difficultly soluble than in water.

8. *Sulphuric acid* and *sulphates* produce in solutions of salts of lead white precipitates of SULPHATE OF LEAD ($Pb O, S O_3$), which are nearly insoluble in water and dilute acids. From dilute solutions, and especially

from those which contain much free acid, the sulphate of lead precipitates only after some, often after a long time. It is advisable under all circumstances to add a considerable *excess* of dilute sulphuric acid, since sulphate of lead is far more insoluble in this menstruum than in water. The separation of small quantities of sulphate of lead is effected best by evaporating, after the addition of the sulphuric acid, as far as practicable on the water-bath, and then treating the residue with water. Sulphate of lead is slightly soluble in concentrated nitric acid; it dissolves with difficulty in boiling concentrated hydrochloric acid, but more readily in solution of potassa.

9. *Chromate of potassa* produces in solutions of salt of lead a yellow precipitate of CHROMATE OF LEAD (PbO, CrO_3), which is readily soluble in potassa, but difficultly so in dilute nitric acid.

10. If a mixture of a compound of lead with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, soft and malleable METALLIC GLOBULES OF LEAD are readily produced, the charcoal becoming covered at the same time with a slight yellow incrustation of OXIDE OF LEAD.

§ 114.

Recapitulation and Remarks.—The metallic oxides of the first section of the fifth group are most distinctly characterized in their corresponding chlorides; since the different respective deportment of these chlorides with water and ammonia affords us a simple means both of detecting and of separating them from one another. For if the precipitate containing the three metallic chlorides is boiled with a somewhat large quantity of water, or boiling water is repeatedly poured over it on the filter, the chloride of lead dissolves, whilst the chloride of silver and the subchloride of mercury remain undissolved. If these two chlorides are then treated with ammonia, the subchloride of mercury is converted into a black basic salt, insoluble in an excess of the ammonia; whilst the chloride of silver dissolves readily in that agent, and precipitates from this solution again upon addition of nitric acid. When operating upon small quantities, it is advisable, first to expel the greater part of the ammonia by heat. In the aqueous solution of chloride of lead, the metal may be readily detected by sulphuric acid.

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

Special Reactions.

§ 115.

a. OXIDE OF MERCURY (HgO).

1. Oxide of mercury is generally crystalline and of a bright red color, inclining sometimes to orange; which when pulverised has a yellowish-red

color. Upon exposure to heat it transiently acquires a deeper tint; at a faint red heat it is resolved into metallic mercury and oxygen. The hydrate of oxide of mercury is yellow. Both the oxide and its hydrate dissolve readily in hydrochloric acid and nitric acid.

2. The salts of oxide of mercury, and also the corresponding haloid compounds, volatilize upon ignition; part of them suffer decomposition in this process, whilst others remain unaltered. Most of the salts of oxide of mercury are colorless. The soluble salts, in the neutral state, redden litmus paper. The nitrate and sulphate of oxide of mercury are decomposed by water added in large quantity, into soluble acid and insoluble basic salts.

3. Addition of a very small quantity of *hydrosulphuric acid*, or *sulphide of ammonium* produces in solutions of oxide of mercury, after shaking, a perfectly white precipitate. Addition of somewhat larger quantities of these reagents causes the precipitate to acquire a yellow, orange, or brownish-red color, according to the less or greater proportion added; an excess of the reagent produces a purely black precipitate of SULPHIDE OF MERCURY ($Hg\,S$). This progressive variation of color from white to black, which depends on the proportion of the hydrosulphuric acid or sulphide of ammonium added, distinguishes the oxide of mercury from all other bodies. The white precipitate which forms at first consists of a double compound of sulphide of mercury with the still undecomposed portion of the salt of oxide of mercury (in a solution of chloride of mercury, for instance, $Hg\,Cl + 2\,Hg\,S$); the gradually increasing admixture of black sulphide causes the precipitate to pass through the several gradations of color which I have mentioned. Sulphide of mercury is not dissolved by sulphide of ammonium, nor by potassa nor by cyanide of potassium; it is altogether insoluble in hydrochloric acid and in nitric acid, even upon boiling. It dissolves completely in sulphide of potassium, and is readily decomposed and dissolved by nitrohydrochloric acid.

4. *Potassa*, added in small quantity, produces in neutral or slightly acid solutions of oxide of mercury a reddish-brown precipitate, which acquires a yellow tint if the reagent is added in excess. The *reddish-brown* precipitate is a BASIC SALT; the *yellow* precipitate consists of HYDRATE OF OXIDE OF MERCURY ($Hg\,O,\ 3\ H\,O$). An excess of the precipitant does not redissolve these precipitates. In very acid solutions this reaction does not take place at all, or at least only incompletely. In presence of salts of ammonia, potassa produces in solutions of salts of oxide of mercury *white* precipitates, consisting of double compounds of the salts of oxide of mercury with amide of mercury. Thus, for instance, from a solution of chloride of mercury containing an excess of chloride of ammonium, potassa throws down a compound of chloride of mercury with amide of mercury and chloride of ammonium ($Hg\,Cl,\ Hg\,N\,H_2 + N\,H_4\,Cl$).

5. *Ammonia* produces in solutions of salts of oxide of mercury the same white precipitates as potassa does in presence of chloride of ammonium; thus, for instance, ammonia precipitates from solutions of chloride of mercury a double compound of chloride of mercury and amide of mercury ($Hg\ Cl + Hg\ N\ H_2$).

6. *Protochloride of tin*, added in small quantity to salts of oxide of mercury, reduces the oxide to suboxide, thus giving rise to the formation of a white precipitate of SUBCHLORIDE OF MERCURY ($Hg_2\ Cl$); but if added in excess, this reagent deprives the mercury completely of the oxygen and acid, or of the salt-radical, and throws it down in the metallic state, the same as in the case of the suboxide of mercury. The precipitate, which was white at first, acquires therefore now a gray tint, and may be readily united into globules of metallic mercury by boiling with hydrochloric acid.

7. The salts of oxide of mercury present the same deportment as the salts of the suboxide, both with metallic *copper* and when heated, mixed with *carbonate of soda*, in a glass tube before the blowpipe.

§. 116.

b. OXIDE OF COPPER ($Cu\ O$).

1. Metallic copper has a peculiar red color, and a strong lustre; it is moderately hard, malleable, rather difficultly fusible; in contact with water and air it becomes covered with green basic carbonate of copper; upon ignition in the air it becomes coated over with black oxide. If copper is ignited in the flame of a candle or of spirit of wine, it imparts a green tint to the flame. In hydrochloric acid and dilute sulphuric acid it is insoluble or nearly so, even upon boiling. Nitric acid dissolves the metal readily. Concentrated sulphuric acid converts it into sulphate of copper, with evolution of sulphurous acid.

2. Oxide of copper is a black, fixed powder; its hydrate is of a light blue color. Both the oxide of copper and its hydrate dissolve readily in hydrochloric acid, sulphuric acid, and nitric acid.

3. Most of the neutral salts of oxide of copper are soluble in water; the soluble salts redden litmus, and suffer decomposition when heated to gentle redness, with the exception of the sulphate, which can bear a somewhat higher temperature. They are usually white in the anhydrous state; the hydrated salts are usually of a blue or green color, which their solutions continue to exhibit, even when much diluted.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in alkaline, neutral, and acid solutions of salts of oxide of copper, blackish-brown precipitates of SULPHIDE OF COPPER ($Cu\ S$). This sulphide is insoluble in dilute acids and caustic alkalies. Hot solutions of sulphide of potassium

and sulphide of sodium fail also to dissolve it, or dissolve it only to a very trifling extent; but it is a little more soluble in sulphide of ammonium. The latter reagent is, therefore, not adapted to effect the perfect separation of sulphide of copper from other metallic sulphides. Sulphide of copper is readily decomposed and dissolved by boiling concentrated nitric acid; it dissolves completely in solution of cyanide of potassium. In solutions of salts of copper which contain an excess of a concentrated mineral acid, hydrosulphuric acid produces a precipitate only after the addition of water.

5. *Potassa* produces in solutions of salts of oxide of copper a light blue, bulky precipitate of HYDRATE OF OXIDE OF COPPER ($Cu\,O, HO$). If the solution is highly concentrated, and the potassa added in excess, the precipitate turns black, after the lapse of some time, and loses its bulkiness, even in the cold; but the change takes place immediately if the precipitate is boiled with the fluid in which it is suspended (and which may, if necessary, be diluted for this purpose). In this process the hydrated oxide is converted into simple oxide.

6. *Carbonate of potassa* produces in solutions of salts of copper a greenish-blue precipitate of HYDRATED BASIC CARBONATE OF COPPER ($Cu\,O, C\,O_2 + Cu\,O, H\,O$), which, upon boiling, changes to brownish-black oxide of copper, and dissolves in ammonia to an azure-blue, and in cyanide of potassium to a brownish fluid.

7. *Ammonia* added in small quantity to solutions of salts of copper, produces a GREENISH-BLUE precipitate, consisting of a BASIC SALT OF COPPER. This precipitate redissolves readily upon further addition of ammonia, giving a perfectly clear solution of a magnificent azure-blue, which owes its color to the formation of a BASIC DOUBLE SALT OF AMMONIO-OXIDE OF COPPER. Thus, for instance, in a solution of sulphate of copper, ammonia produces a precipitate of $N\,H_3, Cu\,O + N\,H_4\,O, S\,O_3$. The blue color ceases to be perceptible only in very dilute solutions. Potassa produces in such blue solutions in the cold, after the lapse of some time, a precipitate of blue hydrate of oxide of copper; but, upon boiling, this reagent precipitates the whole of the copper as black oxide. Carbonate of ammonia presents the same deportment with salts of copper as pure ammonia.

8. *Ferrocyanide of potassium* produces even in highly dilute solutions a reddish-brown precipitate of FERROCYANIDE OF COPPER ($2\,Cu, Cfy$) which is insoluble in dilute acids, but suffers decomposition when acted upon by potassa.

9. *Metallic iron*, when brought into contact with concentrated solutions of salts of copper, is almost immediately covered with a COPPERY-RED COATING OF METALLIC COPPER; very dilute solutions produce this coat-

ing only after some time. This test is extremely delicate; the reaction takes place most speedily in presence of a free acid (hydrochloric acid).

10. If a mixture of a compound of copper with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, METALLIC COPPER is obtained, without simultaneous incrustation of the charcoal. The best method of freeing this copper from the surrounding particles of charcoal, is to triturate the whole mass in a small mortar with some water, and to wash off the charcoal powder; when the coppery-red metallic particles will be left behind.

§ 117.

c. TEROXIDE OF BISMUTH ($Bi\ O_3$).

1. Bismuth has a reddish tin-white color and moderate metallic lustre; it is of medium hardness, brittle, readily fusible; when fused upon a charcoal support, it forms a coating of yellow teroxide on the surface of the charcoal. It dissolves readily in nitric acid, but is nearly insoluble in hydrochloric acid, and altogether so in dilute sulphuric acid. Concentrated sulphuric acid converts it into sulphate of teroxide of bismuth, with evolution of sulphurous acid.

2. The teroxide of bismuth is a yellow powder; when heated, it transiently acquires a deeper tint; it fuses at a red heat. Hydrate of teroxide of bismuth is white. Both the teroxide and its hydrate dissolve readily in hydrochloric acid, sulphuric acid, and nitric acid.

3. The salts of bismuth are non-volatile, with the exception of a few (terchloride of bismuth). Most of them are decomposed at a red heat. They are colorless; some of them are soluble in water, whilst others are insoluble in this menstruum. The soluble salts, in the neutral state, redden litmus paper, and are decomposed into soluble acid and insoluble basic salts when treated with a large amount of water.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in neutral and acid solutions of salts of bismuth black precipitates of TERSULPHIDE OF BISMUTH ($Bi\ S_3$), which are insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium, but are readily decomposed and dissolved by boiling concentrated nitric acid. In solutions of salts of bismuth which contain an excess of concentrated hydrochloric or nitric acid, hydrosulphuric acid produces a precipitate only after the addition of water.

5. *Potassa* and *ammonia* throw down from solutions of salts of bismuth HYDRATE OF TEROXIDE OF BISMUTH as a white precipitate, which is insoluble in an excess of the precipitants.

6. *Carbonate of potassa* throws down from solutions of salts of bismuth BASIC CARBONATE OF BISMUTH ($Bi\ O_3$, $C\ O_2$) as a white bulky precipitate,

which is insoluble in an excess of the precipitant, and equally so in cyanide of potassium.

7. *Chromate of potassa* precipitates from solutions of salts of bismuth CHROMATE OF BISMUTH as a yellow powder. This substance differs from chromate of lead in this, that it is soluble in dilute nitric acid, and insoluble in potassa.

8. The reaction which characterizes the teroxide of bismuth more particularly, is the decomposition of its neutral salts by *water* into soluble acid and insoluble basic salts. The addition of a large amount of water to solutions of salts of bismuth causes the immediate formation of a white precipitate, provided there be not too much free acid present. This reaction is the most sensitive with terchloride of bismuth, as the basic chloride of bismuth ($Bi\ Cl_3, 2\ Bi\ O_3$) is nearly insoluble in water. If water fails to produce a precipitate in nitric acid solutions of bismuth, owing to the presence of too much free acid, the excess of the acid must be removed by evaporation, before the water is added. From the basic salts of antimony which are formed under analogous circumstances, the precipitated basic salts of bismuth may be readily distinguished by their insolubility in tartaric acid.

9. If a mixture of a compound of bismuth with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, brittle GLOBULES OF BISMUTH are obtained, which fly into pieces under the stroke of a hammer. The charcoal becomes covered at the same time, with a slight yellow incrustation of TEROXIDE OF BISMUTH.

§ 118.

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

1. Metallic cadmium has a tin-white colour; it is lustrous, not very hard, malleable; it fuses at a temperature below red heat, and volatilizes at a temperature somewhat above the boiling point of mercury. Heated on charcoal before the blowpipe, it takes fire and burns, emitting brown fumes of oxide of cadmium, which form a coating on the charcoal. Hydrochloric acid and dilute sulphuric acid dissolve it, with evolution of hydrogen; but nitric acid dissolves it most readily.

2. Oxide of cadmium is a yellowish-brown fixed powder; its hydrate is white. Both the oxide and its hydrate dissolve readily in hydrochloric acid, nitric acid, and sulphuric acid.

3. The salts of oxide of cadmium are colorless or white; most of them are soluble in water. The soluble salts, in the neutral state, redden litmus paper, and are decomposed at a red heat.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in alkaline, neutral, and acid solutions of salts of cadmium, bright yellow precipitates

of SULPHIDE OF CADMIUM ($Cd\,S$), which are insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium. They are readily decomposed and dissolved by boiling concentrated nitric acid. In solutions of salts of cadmium which contain a considerable excess of acid, hydrosulphuric acid produces a precipitate only after dilution with water.

5. *Potassa* produces in solutions of salts of cadmium a white precipitate of HYDRATE OF OXIDE OF CADMIUM ($Cd\,O, H\,O$), which is insoluble in an excess of the precipitant.

6. *Ammonia* likewise precipitates from solutions of salts of cadmium white HYDRATE OF OXIDE OF CADMIUM, which, however, redissolves readily to a colorless fluid in an excess of the precipitant.

7. *Carbonate of potassa* and *carbonate of ammonia* produce white precipitates of CARBONATE OF CADMIUM ($Cd\,O, C\,O_2$), which are insoluble in an excess of the precipitants. The presence of salts of ammonia does not prevent the formation of these precipitates. The precipitated carbonate of cadmium dissolves readily in solution of cyanide of potassium. From dilute solutions the precipitate separates only after some time.

8. If a mixture of a compound of cadmium with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, the charcoal becomes covered with a reddish-brown coating of OXIDE OF CADMIUM, owing to the volatilization of the reduced metal and its subsequent re-oxidation in passing through the oxidizing flame. The coating is seen most distinctly after cooling.

§ 119.

Recapitulation and remarks.—The perfect separation of the metallic oxides of the second section of the fifth group from suboxide of mercury and oxide of silver may, as already stated, be effected by means of hydrochloric acid; but this agent fails to separate them completely from oxide of lead. The oxide of mercury is distinguished from the other oxides of this section by the insolubility of the corresponding sulphide 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, will, after the previous removal of the suboxide, always readily indicate the presence of oxide of mercury.

From the still remaining oxides the oxide of lead is separated by addition of sulphuric acid; the separation is the most complete if the fluid, after the addition of the sulphuric acid, is evaporated on the water-bath, and the residue diluted with water. Teroxide of bismuth may be separated from oxide of copper and oxide of cadmium by addition of ammonia in excess, as the latter two oxides are soluble in an excess of this agent. If the filtered precipitate is dissolved in the least possible quantity of hydrochloric acid, and water added, the appearance of a milky turbidity gives confirmation of the presence of teroxide of bismuth.—The presence of a notable quantity of oxide of copper is revealed by the color of the ammoniacal solution; smaller quantities are detected by evaporating the ammoniacal solution, dissolving the residue in hydrochloric acid and water, and then adding ferrocyanide of potassium. The separation of oxide of copper from oxide of cadmium may be effected by means of carbonate of ammonia; however, in this method, minute quantities of cadmium might readily escape detection. The separation by means of cyanide of potassium is safer. The neutral or acid solution is mixed with carbonate of soda until a precipitate forms; cyanide of potassium is added, until this precipitate is redissolved; hydrosulphuric acid is then added, the mixture heated, and, if necessary, some more cyanide of potassium added, to redissolve the sulphide of copper which might perchance have been thrown down. The separation of the yellow sulphide of cadmium shows the presence of cadmium; the copper may be precipitated from the filtrate by hydrochloric acid as sulphide of copper.

§ 120.

SIXTH GROUP.

TEROXIDE OF GOLD—BINOXIDE OF PLATINUM—TEROXIDE OF ANTIMONY—BINOXIDE OF TIN—PROTOXIDE OF TIN—ARSENIOUS ACID AND ARSENIC ACID.*

Properties of the group.—The sulphides corresponding to the oxides of the sixth group are insoluble in dilute acids. These oxides combine with alkaline sulphides, forming soluble sulphur salts, in which they perform the part of the acid. Hydrosulphuric acid precipitates these oxides therefore completely from acidified solutions, but fails to precipitate them from alkaline solutions. The precipitated sulphides dissolve in sulphide of ammonium, sulphide of potassium, &c., and are reprecipitated from these solutions on the addition of acids.

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

1. OXIDES WHOSE CORRESPONDING SULPHIDES ARE INSOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID, and are reduced to the metallic state, upon fusion in conjunction with nitrate and carbonate of soda, viz.: teroxide of gold and binoxide of platinum.

2. OXIDES WHOSE CORRESPONDING SULPHIDES ARE SOLUBLE IN BOILING HYDROCHLORIC ACID OR NITRIC ACID, and are, upon fusion with nitrate and carbonate of soda, converted into oxides or acids, which

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* I have placed the two acids of arsenic with the metallic oxides, since the deportment of the sulphides of arsenic might readily lead to their being confounded with some of the oxides of the sixth group, and because in the systematic course of analysis the sulphide of arsenic is invariably obtained in the same precipitate with the sulphide of antimony the sulphide of tin, &c.

combine with the soda, viz-: Teroxide of antimony, protoxide and binoxide of tin, arsenious and arsenic acids.

FIRST SECTION.

Special Reactions.

§ 121.

a. TEROXIDE OF GOLD ($Au\,O_3$).

1. Metallic gold has a yellow color, and a high metallic lustre: it is rather soft, exceedingly malleable, difficultly fusible; it does not oxidize upon ignition in the air, and is insoluble in hydrochloric acid, nitric acid, and sulphuric acid; but it dissolves in fluids containing or evolving chlorine, *e. g.* in nitro-hydrochloric acid. The solution contains terchloride of gold.

2. Teroxide of gold is a blackish-brown, its hydrate a chesnut-brown powder. Both are reduced by light and heat, and dissolve readily in hydrochloric acid, but not in dilute oxygen acids. Concentrated nitric and sulphuric acids dissolve a little teroxide of gold; water reprecipitates it from these solutions.

3. Salts of gold with oxygen acids are nearly unknown. The haloid salts of gold are yellow, and their solutions continue to exhibit this color up to a high degree of dilution. The whole of them are readily decomposed upon ignition. Neutral solutions of terchloride of gold redden litmus paper.

4. *Hydrosulphuric acid* precipitates from neutral and acid solutions of salts of gold the whole of the metal as black TERSULPHIDE OF GOLD ($Au\,S_3$), which is insoluble in either of the acids, partly soluble in potassa, and perfectly so in sulphuretted alkaline sulphides and in nitro-hydrochloric acid.

5. *Sulphide of ammonium* produces the same precipitate. This redissolves in an excess of the precipitant only if the latter contains an excess of sulphur.

6. *Ammonia* produces, but only in tolerably concentrated solutions of salts of gold, reddish-yellow precipitates of AURATE OF AMMONIA (fulminating gold). The more acid the solution and the greater the excess of ammonia added, the more gold remains in solution.

7. *Protochloride of tin* containing an admixture of bichloride produces even in extremely dilute solutions of gold, a purple-red precipitate (or coloration at least), which sometimes inclines rather to violet or to brownish-red. This precipitate, which has received the name of PURPLE OF CASSIUS, is insoluble in hydrochloric acid. It is assumed to be a hydrated compound of binoxide of tin and protoxide of gold with protoxide and binoxide of tin ($Au\,O,\ Sn\,O_2 + Sn\,O,\ Sn\,O_2 + 4\,H\,O$).

8. *Salts of protoxide of iron* reduce the teroxide of gold, when added to its solutions, and precipitate metallic gold in the form of a very fine brown powder, which acquires metallic lustre when pressed with the blade of a knife, or when rubbed. The fluid in which the precipitate is suspended appears of a blackish-blue color, by transmitted light.

§ 122.

b. BINOXIDE OF PLATINUM ($Pt\,O_2$).

1. Metallic platinum has a light steel-gray color; it is very lustrous, moderately hard, very difficultly fusible; it does not oxidize upon ignition in the air, and is insoluble in hydrochloric acid, nitric acid, and sulphuric acid. It dissolves in nitro-hydrochloric acid, especially upon heating. The solution contains bichloride of platinum.

2. Binoxide of platinum is a blackish-brown, its hydrate a reddish-brown powder. Both are reduced by heat; they are both readily soluble in hydrochloric acid, and difficultly soluble in oxygen acids.

3. The salts of binoxide of platinum are decomposed at a red-heat. They are of a reddish-brown color, which their solutions continue to exhibit up to a high degree of dilution. The soluble salts, in the neutral state, redden litmus paper.

4. *Hydrosulphuric acid* throws down from acid and neutral solutions—(but not from alkaline solutions, or, at all events, not completely)—after the lapse of some time, a blackish-brown precipitate of BISULPHIDE OF PLATINUM ($Pt\,S_2$). If the solution is heated, after the addition of the hydrosulphuric acid, the precipitate forms *immediately*. It dissolves in a great excess of alkaline sulphides, more particularly of the higher degrees of sulphuration. Bisulphide of platinum is insoluble in hydrochloric acid and in nitric acid; but it dissolves in nitrohydrochloric acid.

5. *Sulphide of ammonium* produces the same precipitate; this redissolves completely in a large excess of the precipitant, if the latter contains an excess of sulphur. Acids reprecipitate the bisulphide of platinum unaltered from this solution.

6. *Potassa and ammonia* produce in not too highly dilute solutions of salts of platinum, mixed with some hydrochloric acid, yellow crystalline precipitates of POTASSIO- and AMMONIO-BICHLORIDE OF PLATINUM, which are insoluble in acids, but dissolve in an excess of the precipitants, upon the application of heat. From dilute solutions these precipitates are obtained by evaporating the fluid mixed with potassa or ammonia (or chloride of potassium or chloride of ammonium), but remaining still acid, in the water-bath to dryness, and treating the residue with dilute spirit of wine, until the alkaline chlorides are dissolved.

7. *Protochloride of tin* imparts to solutions of salts of binoxide of platinum which contain much free hydrochloric acid an INTENSELY DARK

BROWNISH-RED COLOR, owing to a reduction of the binoxide or bichloride of platinum, to protoxide or simple chloride. But the reagent produces no precipitate in such solutions.

§ 123.

Recapitulation and Remarks.—The reactions of gold and platinum enables us, at least partially, to detect these two metals in the presence of many other oxides, and also when they are present in the same solution. In the latter case, the solution is either evaporated to dryness with chloride of ammonium, and the residue treated with spirit of wine, in order to obtain the gold in solution, and the platinum in the residue; or the gold is precipitated with protochloride of iron, and the fluid filtered off after some time. The presence of the platinum in the filtrate may then be proved by means of chloride of ammonium, after previous evaporation and addition of spirit of wine. The latter method is applicable only in cases where both metals are in solution as chlorides.

SECOND SECTION OF THE SIXTH GROUP.

Special Reactions.

§ 124.

a. TEROXIDE OF ANTIMONY ($Sb\,O_3$).

1. Metallic antimony has a bluish tin-white color, lustrous, hard, brittle, readily fusible. When heated on charcoal before the blowpipe, it emits thick white fumes of teroxide of antimony which form a coating on the charcoal; this combustion continues for some time, even after the removal of the metal from the flame; it is the most distinctly visible, if a current of air is directed with the blowpipe right upon the sample on the charcoal. But if the sample on the charcoal support is kept steady, that the fumes may ascend straight, the metallic grain becomes surrounded with a net of brilliant crystalline needles of teroxide of antimony. Nitric acid, oxidizes antimony readily: the dilute acid converts it almost entirely into teroxide, the more concentrated acid into antimonic acid; both are nearly insoluble in nitric acid, still, in the acid fluid filtered from the precipitate there are always found traces of antimony. Hydrochloric acid, even boiling, does not act upon antimony. In nitrohydrochloric acid the metal dissolves readily. The solution contains terchloride of antimony ($Sb\,Cl_3$), or pentachloride of antimony ($Sb\,Cl_5$), according to the degree of concentration of the acid, and the duration of the action.

2. The teroxide of antimony according to the mode of its preparation, occurs either as white, brilliant, crystalline needles, or as a grayish-white powder. It fuses at a moderate red heat, and when exposed to a higher temperature, it volatilizes unaltered. It is almost insoluble in nitric acid, but dissolves readily in hydrochloric and tartaric acids. Teroxide of antimony is easily reduced to the metallic state by fusion with cyanide of potassium.

3. Part of the salts of teroxide of antimony are decomposed upon ignition; the haloid salts volatilize readily and unaltered. The soluble neutral salts of antimony redden litmus paper. When treated with a large amount of water, they are decomposed into insoluble basic, and soluble acid salts. Thus, for instance, water throws down from solutions of terchloride of antimony in hydrochloric acid, a white bulky precipitate of basic terchloride of antimony (powder of Algaroth) $Sb\,Cl_3, 5\,Sb\,O_3$, which after some time becomes heavy and crystalline. Tartaric acid dissolves this precipitate readily, and accordingly prevents its formation if mixed with the solution previously to the addition of the water. It is by this property that the basic terchloride of antimony is distinguished from the basic salts of bismuth formed under similar circumstances.

4. *Hydrosulphuric acid* precipitates from acid solutions of teroxide of antimony the whole of the metal as orange-red TERSULPHIDE OF ANTIMONY ($Sb\,S_3$), In alkaline solutions this reagent fails to produce a precipitate, or, at least, it precipitates them only imperfectly; neutral solutions also are only imperfectly precipitated by it. The tersulphide of antimony produced is readily dissolved by potassa and by alkaline sulphides, especially if the latter contain an excess of sulphur; it is but sparingly soluble in ammonia, and—if it contains no free sulphur nor tetra- or pentasulphide of antimony —almost insoluble in bicarbonate of ammonia. It is insoluble in dilute acids. Concentrated boiling hydrochloric acid dissolves it, with evolution of hydrosulphuric acid gas. When heated in the air, it is converted into a mixture of antimonious acid and tersulphide of antimony. When deflagrated with nitrate of soda, it gives sulphate of soda and antimoniate of soda. If a potassa solution of tersulphide of antimony is boiled with teroxide of bismuth, tersulphide of bismuth precipitates, and teroxide of antimony dissolved in potassa remains in the solution. On fusing tersulphide of antimony with cyanide of potassium, metallic antimony and sulphocyanide of potassium are produced. If the operation is conducted in a small tube expanded into a bulb at the lower end, or in a stream of carbonic acid gas (see § 127, 11), no sublimate of antimony is produced. But if a mixture of tersulphide of antimony with carbonate of soda, or with cyanide of potassium and carbonate of soda, is heated in a glass tube in a stream of hydrogen gas (compare § 127, 4), a mirror of antimony is deposited on the inner surface of the tube, immediately behind the spot occupied by the mixture.

5. *Sulphide of ammonium* produces an orange-red precipitate of TERSULPHIDE OF ANTIMONY, which readily redissolves in an excess of the precipitant, if the latter contains an excess of sulphur. Acids throw down from this solution pentasulphide of antimony ($Sb\,S_5$). However, the orange color appears in that case usually of a lighter tint, owing to an admixture of free sulphur.

6. *Potassa, ammonia, carbonate of potassa,* and *carbonate of ammonia,* throw down from solutions of terchloride of antimony, and also of simple

salts of antimony—but not, or at least not immediately, from solutions of tartar emetic or analogous compounds—a white, bulky precipitate of TEROXIDE OF ANTIMONY, which redissolves pretty readily in an excess of potassa, but requires the application of heat for its re-solution in carbonate of potassa and is altogether insoluble in ammonia.

7. *Metallic zinc* precipitates from all solutions of salts of teroxide of antimony, if they contain no free nitric acid, METALLIC ANTIMONY as a black powder. But if the solution contains free nitric acid, teroxide of antimony precipitates together with the metal.

8. If a solution of teroxide of antimony is brought into contact 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 teroxide of antimony, and the antimony separates accordingly in the metallic state; but a portion of the metal combines in the moment of its separation with the liberated hydrogen of the water, forming ANTIMONIETTED HYDROGEN ($Sb\ H_3$). If this operation is conducted in a gas-evolution flask, connected by means of a perforated cork with the limb of a bent tube, of which the other limb ends in a finely drawn-out point, pinched off at the top,* and the hydrogen passing through the fine aperture of the tube, is ignited when the atmospheric air is completely expelled, the flame appears of a bluish-green tint, which is imparted to it by the antimony separating in a state of intense ignition upon the combustion of the antimonietted hydrogen; white fumes of teroxide of antimony rise from the flame, which condense readily upon cold substances, and are not dissolved by water. If a cold body, a porcelain dish, for instance, is now depressed upon the flame, METALLIC ANTIMONY deposits upon the surface of the plate, in a state of the most minute division, forming a deep black and almost lustreless spot. If the tube through which the gas is passing is heated to redness, in the middle, the bluish-green tint of the flame decreases in intensity, and a metallic mirror of antimony of silvery lustre is formed within the tube on both sides of the heated part. As the acids of arsenic give, under the same circumstances, similar spots of metallic arsenic, it is always necessary to examine the spots produced, in order to ascertain whether they really consist of antimony or contain any of that metal. With spots on a porcelain dish the object in view is most readily attained, by treating them with a solution of chloride of soda (a compound of hypochlorite of soda with chloride of sodium, prepared by mixing a solution of chloride of lime with carbonate of soda in excess, and filtering); which will immediately dissolve arsenical spots, leaving the spots proceeding from antimony untouched, or removing them at least only after a very protracted action upon

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* In accurate experiments it is necessary to transmit the gas first through another tube, loosely filled with cotton or with chloride of calcium, to prevent any moisture being carried into the exit tube. Compare the engraving of Marsh's apparatus, § 127, 9.

them. A mirror within the glass tube, on the other hand, is examined best by conducting through the tube a *very slow* stream of dry hydrosulphuric acid gas, and heating the mirror, by means of a spirit-lamp, proceeding from the outer to the inner border, and accordingly in an opposite direction to that of the gaseous current. The antimonial mirror is by this means converted into tersulphide of antimony, which appears of a more or less reddish-yellow color, and almost black when in thick layers. If a feeble stream of dry hydrochloric acid gas is now transmitted through the same glass tube, the tersulphide of antimony, if present in thin layers only, disappears immediately; if the incrustation is somewhat thicker it takes a few seconds to dissipate it. The reason for this is, that the tersulphide of antimony decomposes readily with hydrochloric acid, and the terchloride of antimony formed is exceedingly volatile in a stream of hydrochloric acid gas. If the gaseous current is now conducted into some water, the presence of antimony in the latter fluid may readily be proved by means of hydrosulphuric acid. By this combination of reactions, antimony may be distinguished with positive certainty from all other metals.

9. If a mixture of a compound of antimony with *carbonate of soda and cyanide of potassium* is exposed on a charcoal support to the *reducing flame of the blowpipe*, brittle globules of METALLIC ANTIMONY are produced, which may be readily recognized by the peculiar appearances attendant upon their oxidation (compare § 124, 1).

§ 125.

b. PROTOXIDE OF TIN ($Sn O$).

1. Tin has a light grayish-white color and a high metallic lustre; it is soft and malleable; when bent, it produces a crackling sound. When heated in the air, it absorbs oxygen, and is converted into grayish-white binoxide; heated on charcoal before the blowpipe, it forms a white coating on the support. Concentrated hydrochloric acid dissolves tin to protochloride, with evolution of hydrogen gas; nitrohydrochloric acid dissolves it, according to circumstances, either to bichloride, or to a mixture of proto- and bichloride. It dissolves with difficulty in dilute sulphuric acid; concentrated sulphuric acid converts it, with the aid of heat, into sulphate of binoxide, moderately concentrated nitric acid oxidizes it readily, particularly with the aid of heat; the white binoxide formed does not redissolve in an excess of the acid.

2. Protoxide of tin is a black or grayish-black powder; its hydrate is white. Protoxide of tin is reduced by fusion with cyanide of potassium. It is readily soluble in hydrochloric acid. Nitric acid converts it into binoxide of tin, which is insoluble in an excess of the acid.

3. The salts of protoxide of tin are colorless, and are decomposed by heat. The soluble salts, in the neutral state, redden litmus paper. The

salts of protoxide of tin rapidly absorb oxygen from the air, and are partially or entirely converted into salts of binoxide; hence a solution of protochloride of tin turns speedily turbid, if the glass is often opened and there is only little free acid present;—hence quite recently prepared protochloride of tin only will completely dissolve in water free from air, &c.

4. *Hydrosulphuric acid* throws down from neutral and acid solutions of salts of protoxide of tin a dark brown precipitate of hydrated PROTOSULPHIDE OF TIN ($Sn\,S$), which is insoluble, or nearly so, in protosulphide of ammonium, but dissolves readily in the higher yellow sulphide. Acids precipitate from this solution yellow bisulphide of tin, mixed with sulphur. Protosulphide of tin dissolves also in solution of soda or potassa. Acids precipitate from these solutions brown protosulphide. Boiling hydrochloric acid dissolves it, with evolution of hydrogen; boiling nitric acid converts it into insoluble binoxide of tin. Alkaline solutions of protosalts of tin are not, or at least only imperfectly, precipitated by hydrosulphuric acid.

5. *Sulphide of ammonium* produces the same precipitate of hydrated PROTOSULPHIDE OF TIN.

6. *Potasssa, ammonia, carbonate of potassa,* and *carbonate of ammonia,* produce in solutions of salts of protoxide of tin a white bulky precipitate of HYDRATE OF PROTOXIDE OF TIN ($Sn\,O, H\,O$), which redissolves readily in an excess of potassa, but is insoluble in an excess of the other three precipitants. If the solution of hydrate of protoxide of tin in potassa is heated in the concentrated state, or is concentrated by evaporation, anhydrous protoxide of tin separates in the form of brown flakes.

7. *Terchloride of gold* produces in solutions of protochloride or protoxide of tin, upon the addition of some nitric acid (without application of heat), a precipitate or coloration of PURPLE OF CASSIUS. (Compare § 121, 7.)

8. Solution of *chloride of mercury*, added in excess, produces in solutions of protochloride or protoxide of tin a white precipitate of SUBCHLORIDE OF MERCURY, owing to the protosalt of tin withdrawing from the chloride of mercury half of its chlorine.

9. If a compound of protoxide of tin, mixed with *carbonate of soda* and some *borax*, or, better still, with equal parts of *carbonate of soda* and *cyanide of potassium*, is exposed on a charcoal support to the *inner blowpipe flame*, malleable grains of METALLIC TIN are obtained. The best way of making quite sure in this respect, is to triturate the sample and the surrounding parts of charcoal with water in a small mortar, pressing heavily upon the mass; and then to wash the charcoal off from the metallic particles. Upon strongly heating the grains of metallic tin on the charcoal support, the latter becomes covered with a coating of white binoxide.

§ 126.

c. Binoxide of tin ($Sn\,O_2$).

1. Binoxide of tin is a powder varying in color from white to straw-yellow, and which upon heating transiently assumes a brown tint. It forms two different series of salts with acids, bases, and water. The hydrate precipitated by alkalies from solution of bichloride of tin dissolves readily in hydrochloric acid; whilst that formed by the action of nitric acid upon tin—hydrate of metastannic acid—remains undissolved. But if it is boiled for some time with hydrochloric acid, and a large quantity of water added, a clear solution is obtained. Upon boiling this solution, hydrate of metastannic acid separates from it; whilst from a solution of bichloride, largely diluted with water, common hydrate of binoxide separates upon boiling.

2. The salts of binoxide of tin are colorless, and are decomposed at a red heat. The soluble salts of binoxide of tin, in the neutral state, redden litmus paper.

3. *Hydrosulphuric acid,* added in sufficient quantity, throws down from acid and neutral solutions of salts of binoxide of tin a *white* precipitate; if applied *in excess,* a *faintly yellow* precipitate. The former (the white precipitate) may safely be assumed, in the case of a solution of bichloride of tin, to consist of a mixture of bichloride and bisulphide of tin (however, it has not as yet been analysed); the latter (the yellow precipitate) consists of hydrated BISULPHIDE OF TIN ($Sn\,S_2$). Application of heat promotes the formation of the precipitate. Alkaline solutions are not precipitated by hydrosulphuric acid. The bisulphide of tin dissolves readily in potassa, alkaline sulphides, and concentrated boiling hydrochloric acid. It dissolves with some difficulty in pure ammonia and in carbonate of ammonia. Nitric acid converts it into insoluble binoxide of tin. Upon deflagrating bisulphide of tin with nitrate and carbonate of soda, sulphate of soda and binoxide of tin are obtained. If a solution of bisulphide of tin in potassa is boiled with teroxide of bismuth, tersulphide of bismuth and binoxide of tin are formed, which latter substance remains dissolved in the potassa solution.

4. *Sulphide of ammonium* produces the same precipitate of hydrated BISULPHIDE OF TIN; the precipitate redissolves readily in an excess of the precipitant. From this solution acids reprecipitate the bisulphide of tin unaltered.

5. *Potassa, ammonia, carbonate of potassa,* and *carbonate of ammonia,* produce in solutions of salts of binoxide of tin white precipitates, which, according to the nature of the solutions, consist of hydrate of binoxide of tin or of hydrate of metastannic acid. Both dissolve readily in an excess of potassa.

6. *Metallic zinc* precipitates from solutions of bichloride or of salts of

binoxide of tin, in the absence of free acid, gelatinous hydrate of binoxide, but in presence of a sufficient quantity of free hydrochloric acid, **METALLIC TIN**, in the shape of small gray scales, or as a spongy mass.

7. The compounds of the binoxide of tin manifest the same deportment before the blowpipe as the compounds of the protoxide.

§ 127.

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

1. Metallic arsenic has a blackish-gray color and metallic lustre, which it retains in dry air, but loses in moist air, becoming covered with suboxide ; the metallic arsenic of commerce looks therefore rather dull, the planes of crystallization appearing bronze colored and feebly shining. Arsenic is not very hard, but very brittle ; at a dull red heat it volatilizes without previous fusion. The fumes have a most characteristic odor of garlic, which proceeds from the suboxide of arsenic formed. Heated with free access of air, arsenic burns—at an intense heat with a bluish flame—emitting white fumes of arsenious acid, which condense on cold bodies. If arsenic is heated in a glass tube sealed at the lower end, the greater part of it volatilizes unoxidized, and recondenses above the heated spot as a lustrous black sublimate (arsenical mirror) ; a very thin coating of the sublimate appears of a brownish-black color. In contact with air and water arsenic oxidizes slowly to arsenious acid. Weak nitric acid converts it, with the aid of heat, into arsenious acid, which dissolves only sparingly in an excess of the acid ; strong nitric acid converts it partially into arsenic acid. It is insoluble in hydrochloric acid and dilute sulphuric acid ; concentrated boiling sulphuric acid oxidizes it to arsenious acid, with evolution of sulphurous acid.

2. Arsenious acid generally appears either as a transparent vitreous, or as a white porcelain-like mass. When pulverized, it forms a heavy, white powder. When heated, it volatilizes in white inodorous fumes. If the operation is conducted in a glass tube, a sublimate is obtained consisting of small brilliant octahedrons and tetrahedrons. Arsenious acid is only difficultly moistened by water ; it comports itself in this respect like a fatty substance. It is difficultly soluble in cold, but more readily in hot water. It is copiously dissolved by hydrochloric acid, and by solution of soda and potassa. Upon boiling with nitrohydrochloric acid it dissolves to arsenic acid. It is highly poisonous.

3. The arsenites are mostly decomposed upon ignition either into arseniates and metallic arsenic, which volatilizes, or into arsenious acid and the base with which it was combined. Of the arsenites those only with alkaline bases are soluble in water. The insoluble arsenites are dissolved, or at least decomposed by hydrochloric acid.

4. *Hydrosulphuric acid* precipitates the solutions of arsenious acid and

of neutral arsenites slowly and imperfectly, except a free acid be present, in which case the precipitation is immediate and perfect. Alkaline solutions are not precipitated. The precipitates are of a bright yellow color; they consist of TERSULPHIDE OF ARSENIC ($As\ S_3$), and are readily and completely dissolved by pure alkalies, alkaline carbonates and bicarbonates, and also by alkaline sulphides; but they are nearly insoluble in hydrochloric acid. Boiling nitric acid decomposes and dissolves them readily. The deflagration of tersulphide of arsenic with carbonate of soda and nitrate of soda gives rise to the formation of arseniate and sulphate of soda. If a solution of tersulphide of arsenic in potassa is boiled with oxide of copper, sulphide of copper and arseniate of potassa are formed. Upon boiling a similar solution with hydrated carbonate or basic nitrate of bismuth, tersulphide of bismuth and arsenite of potassa are produced.

If a mixture of tersulphide of arsenic with from three to four parts of carbonate of soda is made into a paste with some water, and this spread over some small pieces of glass, and after being well dried, rapidly heated to redness in a glass tube through which dry hydrogen gas is transmitted, the whole of the arsenic present is reduced to the metallic state, and expelled, provided always the temperature applied be sufficiently high. Part of the reduced arsenic forms a metallic mirror on the inner surface of the tube, the rest is carried away, suspended in the hydrogen gas; the minute particles of arsenic impart a bluish tint to the latter when kindled, and form stains of arsenic upon the surface of a porcelain dish depressed upon the flame. It is erroneous to suppose that arsenietted hydrogen is formed in this process, although such might seem to be the case from the circumstance that, upon heating another part of the tube to redness, a fresh metallic mirror is produced behind the heated spot, but this is simply owing to the suspended particles of arsenic being reconverted into arsenical fumes, which recondense upon the cold part of the tube. That this is in reality the case, may be readily ascertained by conducting the hydrogen gas charged with the particles of arsenic through water, and afterwards through a long tube filled with moistened cotton; pure hydrogen gas will now escape from the end of the tube, and all the arsenic will be retained by the water and the cotton in the form of a black powder. The fusion of a mixture of two equivalents of tersulphide of arsenic with four equivalents of carbonate of soda gives rise at first to the formation of a double sulphide of arsenic and sodium, and of arsenite of soda. Upon heating these products in hydrogen gas, at first the arsenious acid alone undergoes reduction; but upon the application of a more intense heat, the sulphide of arsenic also is reduced to the metallic state. This method of reduction gives indeed very accurate results, but it does not enable us to distinguish arsenic from antimony with a sufficient degree of certainty, nor to detect the one in presence of the other. (Compare § 124, 4.)

The operation is conducted in the apparatus illustrated by

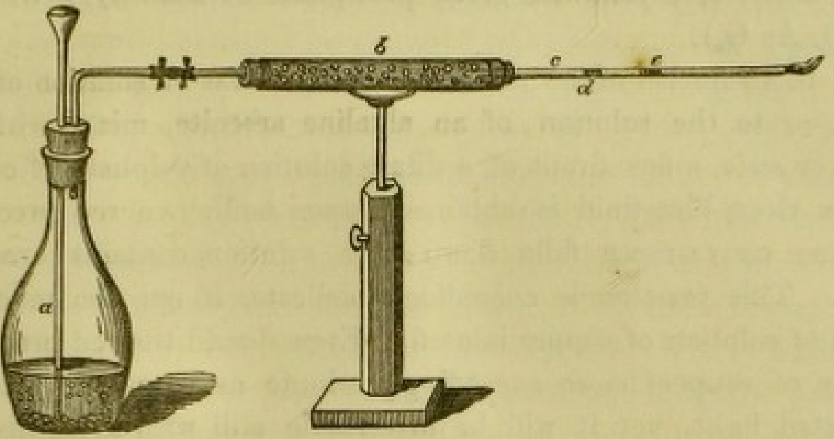

Fig. 9.

a is the evolution flask, *b* a tube containing chloride of calcium, *c* the tube in which, at the point *d*, the pieces of glass with the mixture of tersulphide of arsenic and carbonate of soda is placed. When the apparatus is completely filled with pure hydrogen gas, *d* is exposed to a gentle heat at first, in order to expel all the moisture which may still be present, and then suddenly to a very intense heat,* to prevent the sublimation of undecomposed tersulphide of arsenic. The metallic mirror is deposited near the point *e*. Another method of effecting the reduction of tersulphide of arsenic to the metallic state, and which combines with the very highest degree of delicacy the advantage, that it precludes the possibility of confounding arsenic with antimony, will be found in number 11 of this paragraph.

5. *Sulphide of ammonium* also causes the formation of TERSULPHIDE OF ARSENIC. In neutral and alkaline solutions, however, the tersulphide formed does not precipitate, but remains dissolved as a double sulphide of arsenic and ammonium (tersulphide of arsenic and sulphide of ammonium). From this solution it precipitates immediately upon the addition of a free acid.

6. *Nitrate of silver* leaves aqueous solutions of arsenious acid quite clear, or at least produces only a trifling yellowish-white turbidity in them; but if a little ammonia is now added, a yellowish precipitate of ARSENITE OF SILVER ($2\,Ag\,O, As\,O_3$) separates. The same precipitate forms of course immediately upon the addition of nitrate of silver to the solution of a neutral arsenite. The precipitate dissolves readily in nitric acid and in ammonia, and is not insoluble in nitrate of ammonia; accordingly, if a small quantity of the precipitate is dissolved in a large amount of nitric acid, and the latter is afterwards neutralized with ammonia, the precipitate does not make its appearance again, as it remains dissolved in the nitrate of ammonia formed.

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* The flame of the blowpipe answers the purpose best.

7. *Sulphate of copper* produces, under the same circumstances as the nitrate of silver, a yellowish-green precipitate of **ARSENITE OF COPPER** ($2\ CuO, AsO_3$).

8. If to a solution of arsenious acid in an excess of solution of soda or potassa, or to the solution of an alkaline arsenite, mixed with *caustic potassa* or *soda*, a few drops of a dilute solution of sulphate of copper are added, a clear, blue fluid is obtained; upon boiling, a red precipitate of **SUBOXIDE OF COPPER** falls down; the solution contains arseniate of potassa. This reaction is exceedingly delicate, if not too much of the solution of sulphate of copper is used. Even should the red precipitate of suboxide of copper be so exceedingly minute as to escape detection in transmitted light, yet it will be discernible still with great distinctness upon looking in at the top of the test tube. Of course this reaction, although really of great importance in certain instances, as a confirmatory proof of the presence of arsenious acid, and more particularly also as a means of distinguishing that acid from arsenic acid, is yet utterly inapplicable for the *direct detection* of arsenic, since grape sugar and other organic substances also separate suboxide of copper from salts of copper in the same manner.

9. If an acid or neutral solution of arsenious acid, or of any of its compounds, is mixed with *zinc*, *water*, and *sulphuric acid*, **ARSENIETTED HYDROGEN** (AsH_3) is formed, in the same manner as compounds of antimony give under analogous circumstances antimonietted hydrogen. (Compare § 124, 8.) This deportment of arsenic affords us a most delicate test for the detection of this substance, and likewise a very valuable means to effect its isolation.

No matter which of the two purposes it is intended to effect, the process is conducted in the apparatus illustrated by Fig. 10, and which has already been mentioned in § 124, 8.

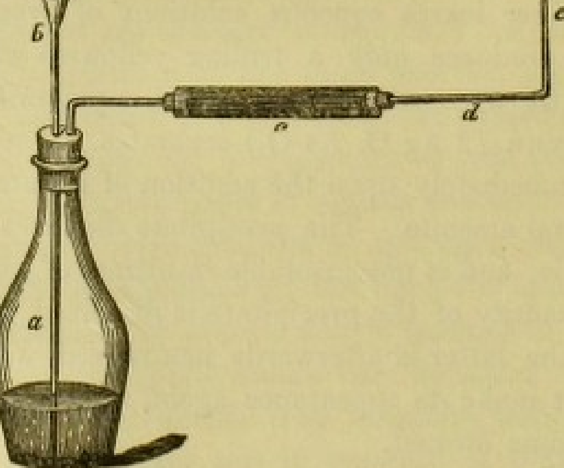

Fig. 10.

a is the evolution flask, containing water and fragments of metallic zinc; *b* is a funnel-tube, through which the sulphuric acid, and afterwards the fluid to be tested for arsenic, are poured into the flask; *c* is a glass tube, loosely filled with cotton, or, better still, with fragments of fused chloride of calcium, and to which a bent tube (*d e*) of DIFFICULTLY FUSIBLE GLASS is fitted by means of a perforated cork; the limb *e* of this tube is drawn out to a point and pinched off at the top. When the evolution of hydrogen has proceeded for a considerable time, so that it may safely be concluded that all atmospheric air has been expelled from the apparatus, the gas is kindled at the aperture of the tube *d e*. (It is advisable to envelope the flask with a piece of cloth before kindling the gas, as an effectual means of preventing accidents should an explosion take place.) It is now absolutely necessary first to ascertain whether the zinc and the sulphuric acid are quite free from any admixture of arsenic. This is effected, 1st, by depressing a porcelain plate or dish upon the flame; and, 2nd, by heating the central part of the tube *d e* to redness, for which purpose the limb *e* is to be turned into a horizontal position. If no coating appears on the plate nor inside the tube, this may be considered a proof of the perfect freedom of the zinc and sulphuric acid from the slightest admixture of arsenic. The fluid to be tested is now introduced into the flask through the funnel-tube. If it contains arsenic, arsenietted hydrogen is immediately evolved along with the hydrogen, imparting at once a bluish tint to the flame, caused by the ignition of the particles of arsenic separating upon the combustion of the arsenietted hydrogen. At the same time white fumes of arsenious acid arise, which condense upon cold objects. If a porcelain plate is now depressed upon the flame, the separated and not yet re-oxidized arsenic condenses upon the plate in the form of black stains (see antimony, § 124, 8). The stains formed by arsenic are of a rather blackish-brown color, and bright metallic lustre; whilst those of antimony are of a deep black color, and but feebly lustrous. The arsenical stains may be distinguished, moreover, from the antimonial stains by pouring a solution of chloride of soda over them (compare § 124, 8), which dissolves the arsenical spots immediately, whilst it leaves the antimonial spots unaffected, or removes them only after a considerable time. If the tube *d*, or, better still, a straight tube substituted for it, about two or three feet long, and drawn out to a fine point at the anterior end, is heated in one or several places to gentle redness, by means of lamps, there is formed behind the heated parts of the tube fine and distinct metallic mirrors, of a darker and less silvery white hue than those produced by antimony under similar circumstances, and which may moreover be distinguished from the latter by the characteristic odor of garlic, emitted when the tube is cut off close to one of the mirrors, and the latter is dissipated in the air by heating. If the formation of a metallic stain upon the porcelain plate seems to indicate the presence of arsenic, it is necessary still to ascertain beyond the possibility of a doubt whether these spots consist in reality of arsenic, or contain that body—in presence of antimony perhaps. Now, although the properties and reactions just mentioned suffice to distinguish pure arsenical stains and mirrors from antimonial stains and mirrors, yet they do not fully enable us to detect arsenic with positive certainty in presence of antimony. However, all doubt upon the point may be removed by the following process: heat the straight tube through which the arsenietted hydrogen passes to redness in several parts, to produce distinct metallic mirrors. Transmit now a very feeble stream of dry hydrosulphuric acid gas through the tube, and heat the metallic mirrors by means of a common spirit-lamp, proceeding from the outer towards the inner border of the mirrors. If arsenic alone is present, yellow tersulphide of arsenic is formed inside the tube; if antimony alone is present, an orange-red or black tersulphide of antimony is produced; and if the mirror consists of both metals, the two sulphides appear side by side, the sulphide of arsenic as the more volatile lying invariably before the sulphide of antimony. If you now transmit through the tube containing the sulphide of arsenic, sulphide of antimony, or both sulphides together, dry hydrochloric gas, without applying heat, no alteration will take place if sulphide of arsenic alone is present, even though the gas be transmitted through the tube for a considerable time. If sulphide of antimony alone is present, this will entirely disappear, as already stated, and if both sulphides are present, the sulphide of antimony will immediately volatilize, whilst the yellow sulphide of arsenic will remain. If a small quantity of ammonia is now drawn into the tube, the sulphide of arsenic is dissolved, and may thus be readily distinguished from sulphur which perhaps may have separated. My personal experience has convinced me of the infallibility of these combined tests for the detection of arsenic.

Marsh was the first who suggested the method of detecting arsenic by the production of arsenietted hydrogen.

10. If a little lump of arsenious acid (*a*) is introduced into the pointed end of a drawn out glass tube (Fig. 11), and a small fragment of very recently burnt charcoal (*b*) is pushed down the tube to within a short distance of the arsenious acid, and the flame of a spirit-lamp applied, first to the piece of charcoal, then to the arsenious acid, a MIRROR OF METALLIC ARSENIC will form at *c*, owing to the reduction of the arsenious acid vapor by the red-hot charcoal. If the tube is now cut between *b* and *c*, and then heated, with the cut end *c* turned upwards, the metallic mirror will volatilize, emitting the characteristic odor of garlic. This is both the simplest and safest way of detecting the pure arsenious acid.

11. If arsenites, or arsenious acid, or tersulphide of arsenic are fused

together with a mixture of equal parts of dry *carbonate of soda* and *cyanide of potassium*, the whole of the arsenic is reduced to the metallic state,

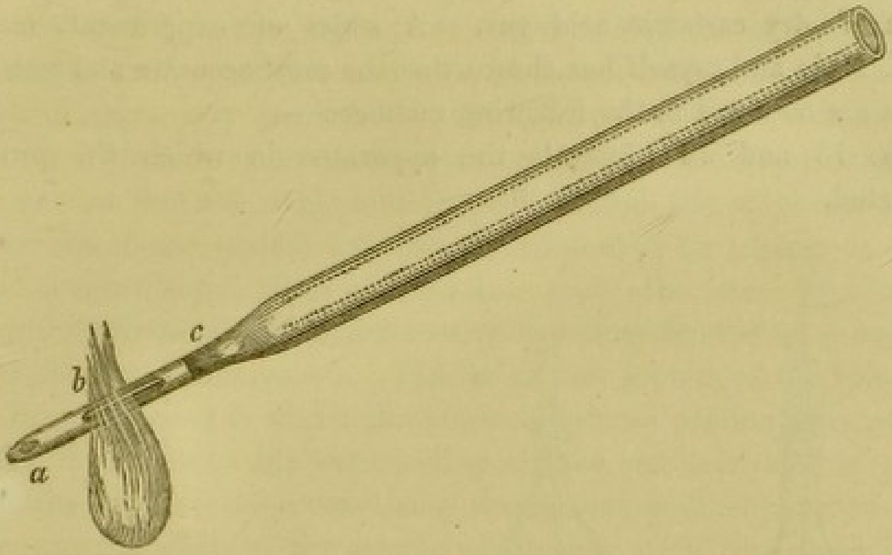

Fig. 11.

and, if an easily reducible base, the latter also ; the eliminated oxygen converts part of the cyanide of potassium into cyanate of potassa. In the reduction of tersulphide of arsenic, sulphocyanide of potassium is formed. The operation is conducted as follows :—introduce the perfectly dry arsenical compound into the bulb of a small bulb tube (Fig. 12), and

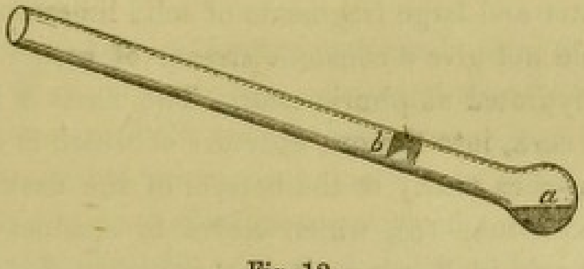

Fig. 12.

cover it with six times the quantity of a perfectly dry mixture of carbonate of soda and cyanide of potassium. The whole quantity must not more than half-fill the bulb, otherwise the fusing cyanide of potassium is likely to ascend into the tube. Apply the heat of a spirit-lamp to the bulb, and continue this for a while, as the arsenic frequently requires some time for its complete sublimation. The mirrors are deposited at *b* ; they are of exceeding purity. They are obtained from all arsenites whose bases remain either altogether untouched, or are reduced to such metallic arsenides as lose their arsenic partly or totally upon the simple application of heat. This method deserves to be particularly recommended on account of its simplicity and neatness, as well as for the accuracy of the results attainable by its application, even in cases where only very minute quantities of arsenic are present. It is more especially adapted for the direct production of arsenic from tersulphide of arsenic, and is in this respect superior to all other methods hitherto suggested. The delicacy of the reaction may be very much heightened by heating the mixture in a stream of dry carbonic acid gas. A series of experiments made by *Dr. V. Babo* and myself has shown that the most accurate and satisfactory results are obtained in the following manner :—

Figs. 13 and 14 illustrate the apparatus in which the process is conducted.

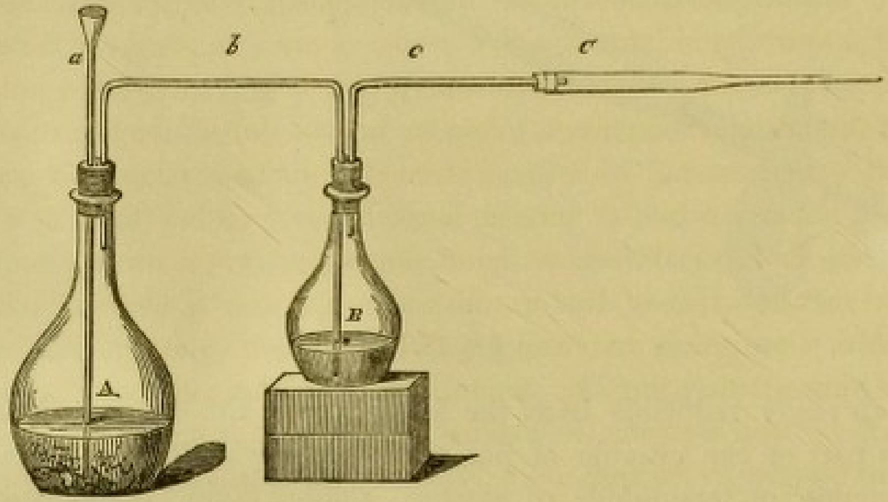

Fig. 13.

A is a capacious flask intended for the evolution of carbonic acid ; it is half-filled with water and large fragments of solid limestone or marble (not chalk, as this would not give a constant stream of gas). *B* is a smaller flask containing hydrated sulphuric acid. The flask *A* is closed with a doubly perforated cork, into the one aperture of which is inserted a funnel-tube (*a*), which reaches nearly to the bottom of the flask ; into the other perforation is fitted a tube (*b*), which serves to conduct the evolved gas into the sulphuric acid in *B*, where it is thoroughly freed from moisture. The tube *c* conducts the dried gas into the reduction-tube *C*, of which Fig. 14 gives a representation on the scale of one-third of the actual length.

Fig. 14.

When the apparatus is fully prepared for action, triturate the perfectly dry sulphide of arsenic or arsenite in a slightly heated mortar with about twelve parts of a well-dried mixture consisting of three parts of carbonate of soda and one part of cyanide of potassium. Put the powder upon a narrow slip of card-paper bent into the shape of a gutter, and push this into the reduction tube down to *e*; turn the tube now half-way round its axis, which will cause the mixture to drop into the tube between *e* and *d*, every other part remaining perfectly clean. Connect the tube now with the gas evolution apparatus, and evolve a moderate stream of carbonic acid, by pouring some hydrochloric acid into the funnel-tube *a*. Heat the tube in its whole length very gently with a spirit-lamp, until the mixture in it is quite dry; when every trace of water is expelled, and the gas-stream has become so slow that the single bubbles pass through the sulphuric acid in *B* at intervals of one second, heat the reduction-tube to redness at *g*, by means of a spirit-lamp; when *g* is red-hot, apply the flame of a second and larger spirit-lamp to the mixture, proceeding from *d* to *e*, until the whole of the arsenic is expelled. The far greater portion of the volatilized arsenic recondenses at *h*, whilst an extremely minute portion only escapes through *i*, imparting to the surrounding air the peculiar odor of garlic. Advance the flame of the second lamp slowly and gradually up to *g*, by which means the whole of the arsenic which may have condensed in the wide part of the tube is driven to *h*. When you have attained this end, close the tube at the point *i* by fusion, and apply heat, proceeding from *i* towards *h*, by which means the extent of the mirror is narrowed, whilst its beauty and lustre are correspondingly increased. In this manner perfectly distinct mirrors of arsenic may be produced from as little as the $\frac{1}{300}$th part of a grain of tersulphide of arsenic. No mirrors are obtained by this process from tersulphide of antimony, nor from any other compound of antimony.

12. If to arsenious acid, no matter whether in solid form or in solution, some *acetic acid* is added, and then *potassa* in slight excess, the mixture evaporated to dryness, and the residue heated to redness in a small tube—or if a trace of arsenious acid is introduced into a narrow test tube, and then covered with a somewhat larger quantity of acetate of soda, and heat applied—part of the arsenious acid is reduced, but there forms at the same time ALKARSIN (oxide of cacodyl, $C_4\ H_6\ As+O$), which makes its presence immediately known by its equally characteristic and formidable odor, which somewhat resembles that of sharp onions. This changes speedily to the not less characteristic odor of chloride of cacodyl, if the ignited contents of the tube are heated with a few drops of protochloride of tin (*Bunsen*).

13. If arsenious acid or one of its compounds is exposed on a charcoal support to the *reducing flame of the blowpipe*, a highly characteristic garlic odor is emitted, more especially if some carbonate of soda is added to the examined sample. This odor has its origin in the reduction and re-oxidation of the arsenic, and enables us to detect very minute quantities. This test, however, like all others that are based upon the mere indications of the sense of smell, cannot be implicitly relied on.

§ 128.

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

1. Arsenic acid is a transparent or white mass, which gradually deliquesces in the air, and dissolves slowly in water. It fuses at a gentle red heat without suffering decomposition; but at a higher temperature it is resolved into oxygen and arsenious acid, which volatilizes. It is highly poisonous.

2. Most of the arseniates are insoluble in water. Of the so-called neutral arseniates those with alkaline bases alone are soluble in water. Most of the neutral and basic arseniates can bear a strong red heat without suffering decomposition. The acid arseniates lose their excess of acid upon ignition, the free acid being decomposed into arsenious acid and oxygen.

3. *Hydrosulphuric acid* fails to precipitate alkaline and neutral solutions of arseniates; but in acidified solutions it produces a yellow precipitate of PENTASULPHIDE OF ARSENIC ($As\,S_5$). This precipitate never forms instantaneously, and in dilute solutions frequently only after the lapse of a considerable time (twenty-four hours). Heat promotes its separation. The pentasulphide of arsenic manifests the same deportment as the tersulphide with the various solvents and decomposing agents mentioned in the preceding paragraph. If a solution of arsenic or of an arseniate is mixed with sulphurous acid, or with sulphite of soda and some hydrochloric acid, the sulphurous acid is converted into sulphuric acid, and the arsenic acid reduced to arsenious acid; application of heat promotes the change. If hydrosulphuric acid is now added, the whole of the arsenic is thrown down as tersulphide.

4. *Sulphide of ammonium* converts the arsenic acid in neutral and alkaline solutions of arseniates into pentasulphide of arsenic, which remains in solution as ammonio-pentasulphide of arsenic (pentasulphide of arsenic and sulphide of ammonium). Upon the addition of an acid to the solution, this double sulphide is decomposed, and pentasulphide of arsenic precipitates. The separation of this precipitate proceeds more rapidly than is the case when acid solutions of arseniates are precipitated with hydrosulphuric acid. It is promoted by heat.

5. *Nitrate of silver* produces under the circumstances stated § 127, 6, a highly characteristic reddish-brown precipitate of ARSENIATE OF SILVER ($3\,Ag\,O, As\,O_5$), which is readily soluble in dilute nitric acid and in ammonia, and dissolves also slightly in nitrate of ammonia. Accordingly, if a little of the precipitate is dissolved in a large proportion of nitric acid, neutralization with ammonia often fails to reproduce the precipitate.

6. *Sulphate of copper* produces under the circumstances stated § 127, 7, a greenish-blue precipitate of ARSENIATE OF COPPER ($2\,Cu\,O, H\,O, As\,O_5$).

7. With *hydrogen*, *cyanide of potassium*, and before the *blowpipe*, the compounds of arsenic acid comport themselves in the same way as those of arsenious acid.

§ 129.

Recapitulation and remarks.—The separation and positive detection of the oxides belonging to the second section of the sixth group was formerly —more especially with regard to tin—an imperfectly solved problem ; the more recent researches of *H. Rose* have considerably advanced us in this respect. The protoxide of tin may be readily detected by its reaction with terchloride of gold or chloride of mercury, even in the presence of other oxides. The separation of binoxide of tin from teroxide of antimony may be effected with tolerable accuracy in the humid way, by means of a hot solution of bitartrate of potassa, or of a solution of free tartaric acid ; but this method is applied with success only if the binoxide of tin exists in the state of hydration in which it is obtained by the action of nitric acid on metallic tin. It is necessary, therefore, if the substance under examination is not an alloy, to reduce the compound of tin to the metallic state, either in the humid way, by means of zinc, the presence of nitric acid being carefully avoided—or, in the dry way, by means of cyanide of potassium. Complete separation of the two metals is effected best by oxidizing them with nitric acid, fusing the oxides produced in a silver crucible in conjunction with an excess of hydrate of soda, moistening the mass with water, and adding one-third (by volume) of spirit of wine. The dilute spirit of wine holds the sodio-binoxide of tin in solution, whilst the antimoniate of soda remains undissolved (*H. Rose*). The modifications which this process requires to adapt it to effect the separation of tin from antimony in cases where the two metals are present in the form of sulphides, will be found below. The only *positive* proof of the presence of binoxide of tin is the production of a malleable globule of tin in the reducing flame of the blowpipe, since the malleability of tin distinguishes this metal amply and sufficiently from antimony. This reduction is very readily effected before the blowpipe by means of a mixture of equal parts of cyanide of potassium and carbonate of soda ; but care must be taken that the binoxide of tin be not mixed with nitrate of potassa—since this would cause deflagration—nor with any other substance of that description. Whether the malleable globule produced in the process be *really* tin, may be ascertained and confirmed by the following direct experiment :— flatten the metallic globule, then boil it with some concentrated hydrochloric acid, add water to the solution, and test the fluid with chloride of mercury. (See § 125, 8.)

Binoxide of tin and teroxide of antimony may also be distinguished in presence of each other before the blowpipe, as the antimony is characterized by the peculiar incrustation with which its oxide covers the charcoal support, and the binoxide of tin may, after the volatilization of the antimony, be readily recognized by the malleability of the globule of metallic tin produced in the process. I have however found that inexperienced students generally fail in their attempts at detecting by this means binoxide of tin and teroxide of antimony in presence of each other. Antimony may be recognized, moreover, by the decomposition which its terchloride suffers by the action of water, and likewise by the color of its tersulphide. The latter test, however, is uncertain, if the sulphide of antimony contains a very large admixture of sulphide of arsenic. The best way of arriving at a positive conclusion in such cases, is to heat the mixed sulphides to redness whereupon the sulphide of arsenic will volatilize—to dissolve the residue in hydrochloric acid, and to test the solution again with hydrosulphuric acid.

The detection of arsenic cannot be called difficult upon the whole ; yet errors will frequently arise, especially if positive and definite conclusions are drawn from isolated reactions, such as the characteristic odor, for instance, which arsenical compounds exhale when heated on charcoal. It must therefore be laid down as a rule that the presence of arsenic is to be considered positively proved only by a concurrence of the various reactions, and particularly by the production of metallic arsenic. The separation of arsenic from tin and antimony is effected best by fusing the sulphides of the metals together with one part of carbonate and three parts of nitrate of soda, treating the fused mass with cold water, filtering, and washing the residue with dilute spirit of wine (one volume of alcohol to one volume of water). The filtrate contains the arsenic as arseniate of soda, the residue the tin as binoxide, and the antimony as antimoniate of soda. The tin and antimony may then be separated by boiling with concentrated solution of soda, which dissolves the binoxide of tin and leaves the antimoniate of soda undissolved. After boiling, about one-third of the volume of the fluid of spirit of wine must be added, to prevent the solution of the antimoniate of soda. The precipitate is washed with a mixture of equal volumes of water and alcohol.

How very carefully the confounding antimony with arsenic has to be guarded against in the detection of the latter by *Marsh's* method, will readily be understood from what has been said upon the subject, § 124, 8, and § 127, 9.

A tolerably complete separation of arsenic from antimony may be effected also by means of bicarbonate of ammonia, as the tersulphide of antimony is nearly insoluble in that substance, whilst the tersulphide of arsenic dissolves readily in it. But this method of distinguishing between arsenic and antimony gives reliable results in few cases only, viz., in those alone in which it is known to a certainty that the tersulphide of antimony contains no higher sulphide of antimony, nor free sulphur, and where the proportion of tersulphide of arsenic present is not too inconsiderable. In all other cases this method is apt to mislead.

The presence of antimony does not interfere with the accuracy of the results obtained by the reduction of arsenites or arseniates with *cyanide of potassium* and *carbonate of soda.*—Arsenious acid and arsenic acid in aqueous solution may be most readily and positively distinguished from each other by means of nitrate of silver. In cases where the presence of other substances interferes with the direct application of that test, precipitate the solution completely with hydrosulphuric acid, dissolve the precipitated sulphides in solution of potassa, and boil the fluid with hydrated teroxide of bismuth, or with carbonate or basic nitrate of bismuth ; filter from the precipitated tersulphide of bismuth, and test a portion of the filtrate for arsenious acid, by means of sulphate of copper in the manner directed § 127, 8 ; neutralize another portion of the filtrate with nitric acid, and test for arsenic acid by means of nitrate of silver.

B.—DEPORTMENT OF THE ACIDS AND THEIR RADICALS* WITH REAGENTS.

§ 130.

The reagents which serve for the detection of the acids are divided, like those used for the detection 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 serve to effect the detection of the INDIVIDUAL ACIDS. The groups into which we classify the various acids can scarcely be defined and limited with the same degree of precision as those into which the bases are divided.

The two principal groups into which acids are divided are those of INORGANIC and ORGANIC ACIDS. We base this division upon those characteristics by which, irrespectively of theoretical considerations, the ends of analysis are most easily attained. We select, therefore, here, as the characteristic mark to guide us in the classification into organic and inorganic acids, the deportment which the various acids manifest at a high temperature, and call *organic* those acids of which the salts—(particularly those which have an alkali or an alkaline earth for base)—are decomposed upon ignition, the decomposition being attended with separation of carbon.

By selecting this deportment at a high temperature as the distinctive characteristic of organic acids, we are enabled to determine at once by a most simple preliminary experiment the class to which the acid or acids

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* The properties and deportment of those radicals which form acids both with oxygen and with hydrogen are given with their hydracids.

under examination belong. The salts of organic acids with alkalies or alkaline earths are converted into carbonates, upon ignition.

I. Inorganic Acids.

§ 131.

First Group.

Acids which are precipitated from neutral solutions by chloride of barium: *Arsenious Acid—Arsenic Acid— Chromic Acid—Sulphuric Acid—Phosphoric Acid—Boracic Acid—Oxalic Acid —Hydrofluoric Acid—Carbonic Acid—Silicic Acid.*

This group is again subdivided into four classes, viz.:

1. Acids which are decomposed in an acid solution by hydrosulphuric acid, and to which attention has been accordingly directed already in the testing for bases, viz., ARSENIOUS ACID, ARSENIC ACID, and CHROMIC ACID (in an appendix we give sulphurous acid and hyposulphurous acid, the latter because it is decomposed and detected by the mere addition of hydrochloric acid to the solution of one of its salts.
2. Acids which are not decomposed in an acid solution by hydrosulphuric acid, and the baryta compounds of which are insoluble in hydrochloric acid. Of the acids claiming our attention here, SULPHURIC ACID alone belongs to this class.
3. Acids which are not decomposed in an acid solution by hydrosulphuric acid, and the baryta compounds of which dissolve in hydrochloric acid, apparently WITHOUT DECOMPOSITION, inasmuch as the acids cannot be completely separated from the hydrochloric acid solution by heating or evaporation; these are PHOSPHORIC ACID, BORACIC ACID, OXALIC ACID, and HYDROFLUORIC ACID. (Oxalic acid belongs more properly to the organic group. We consider it, however, here with the acids of the inorganic class, as the property of its salts to be decomposed upon ignition without actual carbonization, may lead to its being overlooked as an organic acid.)
4. Acids which are not decomposed in an acid solution by hydrosulphuric acid, and the baryta salts of which are soluble in hydrochloric acid, WITH DECOMPOSITION (separation of the acid): CARBONIC ACID, SILICIC ACID.

First Section of the First Group of the Inorganic Acids.

§ 132.

a. ARSENIOUS ACID and ARSENIC ACID are, as we have seen above, decomposed by hydrosulphuric acid, and are precipitated by that reagent respectively as ter- and pentasulphide of arsenic. Since this would lead to confounding them rather with the metallic oxides than with other acids, it has been deemed more judicious to class these two acids with the oxides of the sixth group, see § 127 and § 128.

b. Chromic acid ($Cr\,O_3$).

1. Chromic acid forms a scarlet-red crystalline mass, or distinct needle-shaped crystals. Upon ignition it is resolved into sesquioxide of chromium and oxygen. It deliquesces rapidly upon exposure to the air. It dissolves in water, imparting to the fluid a deep reddish-brown tint, which remains still visible in very dilute solutions.

2. The chromates are all red or yellow, and for the most part insoluble in water. Part of them are decomposed upon ignition ; those with alkaline bases are fixed, and soluble in water ; the solutions of the neutral alkaline chromates are yellow, those of the alkaline bichromates are red. These tints are still visible in highly dilute solutions. The yellow color of the solution of a neutral salt changes to red on the addition of a mineral acid, owing to the formation of an acid chromate.

3. *Hydrosulphuric acid* reduces chromic acid, no matter whether present in the solution in the free state or as a chromate ; sesquioxide of chromium, water, and sulphuric acid are formed in this process, and sulphur precipitates. Heat promotes this decomposition. If no free acid is present, a greenish-gray precipitate is produced consisting of a mixture of hydrated sesquioxide of chromium and sulphur. But if free acid is present, the precipitate is far less considerable, and consists of pure sulphur. In the latter case, the salt of sesquioxide of chromium formed imparts a green tint to the fluid, which may lead to the erroneous impression that the precipitate itself is green.

4. Chromic acid may also be reduced to sesquioxide of chromium by means of many other substances, and more particularly by *sulphurous acid*, or by heating with *hydrochloric acid*, especially upon the addition of alcohol (in which case chloride of ethyle and aldehyde are evolved) ; also by *metallic zinc*, or by heating with *tartaric acid, oxalic acid*, &c. All these reactions are clearly characterized by the change of the red or yellow color of the solution, to the green tint of the salt of sesquioxide of chromium.

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

6. *Nitrate of silver* produces a dark purple-red precipitate of CHROMATE OF SILVER ($Ag\,O, Cr\,O_3$), which is soluble in nitric acid and in ammonia.

7. *Acetate of lead* produces a yellow precipitate of CHROMATE OF LEAD

(PbO, CrO_3), which is soluble in potassa, but only difficultly soluble in dilute nitric acid. The yellow color of this precipitate changes to red upon heating with ammonia.

8. If insoluble chromates are fused together with *carbonate of soda* and *nitrate of soda,* and the fused mass is treated with water, the fluid produced appears YELLOW from the alkaline chromate which it holds in solution; upon the addition of an acid the yellow color inclines more to red. The oxides remain behind either in the pure state or as carbonates, if they are not soluble in the caustic soda formed from the nitrate.

Remarks.—When testing for bases, we always find the chromic acid as sesquioxide of chromium, since hydrosulphuric acid reduces it to that state. The characteristic color of the solution frequently renders the application of any further test unnecessary. If there is reason to suppose that chromic acid is present in a solution, metallic oxides being also present, it is preferable to effect the reduction of the chromic acid by means of hydrochloric acid and alcohol, or by sulphurous acid, instead of reducing it by hydrosulphuric acid. The reactions with salts of silver and salts of lead afford positive and confirmatory proofs of the presence of chromic acid in aqueous solutions.

§ 133.

Appendix to the First Section of the First Group.

a. SULPHUROUS ACID (SO_2) is a colorless non-inflammable gas, which exhales the stifling odor of burning sulphur. It dissolves copiously in water. The solution has the odor of the gas, reddens litmus paper and blanches Brazil-wood paper. It absorbs oxygen from the air, and is thereby converted into sulphuric acid. The salts of sulphurous acid are colorless. Of the neutral sulphites those with alkaline base only are readily soluble in water; many of the sulphites insoluble or difficultly soluble in water, dissolve in an aqueous solution of sulphurous acid, but fall down again upon boiling. All the sulphites evolve sulphurous acid when treated with *sulphuric acid* or *hydrochloric acid. Chlorine water* dissolves most sulphites to sulphates. *Chloride of barium* precipitates neutral sulphites, but not free sulphurous acid. *Hydrosulphuric acid* decomposes free sulphurous acid, water being formed and free sulphur eliminated, which latter separates from the fluid. If a trace of sulphurous acid or of a sulphite is introduced into a flask in which hydrogen is being evolved from *zinc* and *hydrochloric acid,* hydrosulphuric acid is immediately evolved along with the hydrogen, and the gas now produces a black coloration or a black precipitate in a solution of acetate of lead, mixed with solution of soda until the precipitate which forms at first is redissolved.

b. Hyposulphurous acid (S_2O_2). This acid does not exist in the free state. Its salts are mostly soluble in water. The solutions of most hyposulphites may be boiled without suffering decomposition; hyposulphite of lime is decomposed upon boiling into sulphite of lime and sulphur. If *hydrochloric acid* or *sulphuric acid* is added to the solution of a hyposulphite, the fluid remains at first clear and inodorous, but after a short time—the shorter the more concentrated the solution—it becomes more and more turbid, owing to the separation of sulphur, and exhales the odor of sulphurous acid. Application of heat promotes this decomposition. *Nitrate of silver* produces a white precipitate of hyposulphite of silver, which is soluble in an excess of the hyposulphite; after a little while (upon heating almost immediately) the precipitate becomes black, being decomposed into sulphide of silver and sulphuric acid. Hyposulphite of soda dissolves chloride of silver; upon the addition of an acid the solution remains clear at first, but some time after, and upon boiling, immediately, sulphide of silver separates. *Chloride of barium* produces a white precipitate, which is soluble in much water, more especially hot water, and is decomposed by hydrochloric acid.

Second Section of the First Group of the Inorganic Acids.

§ 134.

SULPHURIC ACID (SO_3).

1. Anhydrous sulphuric acid is a white feathery-crystalline mass, which emits strong fumes upon exposure to the air; hydrated sulphuric acid forms an oily liquid, colorless and transparent like water. Both the anhydrous and hydrated acid char organic substances, and combine with water in all proportions, the process of combination being attended with considerable elevation of temperature, and in the case of the anhydrous acid, with a hissing noise.

2. Most of the sulphates are soluble in water; the insoluble sulphates are generally white; the soluble sulphates are for the mose part colorless, in the crystalline state. The sulphates of the alkalies and alkaline earths are not decomposed upon ignition.

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

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

5. The salts of sulphuric acid with the alkaline earths which are inso-

luble in water and acids are converted into CARBONATES, by fusion with *alkaline carbonates*. But the sulphate of lead is reduced to the state of PURE OXIDE when treated in this manner. Both the conversion of the former into carbonates, and the reduction of the latter to the state of oxide, are attended with the formation of an alkaline sulphate.

6. Upon fusing sulphates with *carbonate of soda* on charcoal, in the inner flame of the blowpipe, the sulphuric acid is reduced, and sulphide of sodium formed, which may be readily recognized by the odor of hydrosulphuric acid emitted upon moistening the sample and the part of the charcoal into which the fused mass has soaked, and adding some acid. If the fused mass is transferred to a clean silver plate, or a polished silver coin, and then moistened with water and some acid, a black stain of sulphide of silver is immediately formed.

Remarks.—The characteristic and exceedingly delicate reaction of sulphuric acid with salts of baryta renders the detection of this acid an easier task than that of almost any other. It is simply necessary to take care not to confound with sulphate of baryta, precipitates of chloride of barium, and particularly of nitrate of baryta, which are formed upon mixing aqueous solutions of these salts 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 baryta, since they redissolve immediately upon diluting the acid fluid with water. The deportment of sulphuric acid with baryta might, however, possibly lead to confounding this acid with hydrofluosilicic acid, as the crystalline precipitate of silicofluoride of barium is only sparingly soluble in hydrochloric acid. Although we do not treat of hydrofluosilicic acid in the present work, yet it may be as well to remark that, should any doubt arise as to the real nature of a precipitate of baryta, this may be easily set at rest by fusing the precipitate in question in the inner flame of the blowpipe, with carbonate of soda upon charcoal (compare § 134, 6).

Third Section of the First Group of the Inorganic Acids.

§ 135.

a. PHOSPHORIC ACID (PO_5).

1. Phosphorus is a colorless, transparent, solid body, of 2·089 specific gravity; it has a greasy gloss. Taken internally it acts as a virulent poison. It fuses at 113°, and boils at 554° Fahr. By the influence of light phosphorus kept under water turns first yellow, then red, and is finally covered with a white crust. If phosphorus is exposed to the air, at the common temperature, it exhales a garlic odor, shines in the dark,

and emits fumes of phosphorous acid, into which substance it is gradually entirely converted. Phosphorus very readily takes fire spontaneously, and burns with a luminous flame, being converted into phosphoric acid, which is dissipated for the most part in white fumes through the surrounding air. Nitric acid and nitrohydrochloric acid dissolve phosphorus pretty readily upon heating. The solutions contain at first, besides phosphoric acid, also phosphorous acid. Hydrochloric acid does not dissolve phosphorus; if phosphorus is boiled with solution of soda or potassa, or with milk of lime, hypophosphites and phosphates are formed, whilst spontaneously inflammable phosphuretted hydrogen gas escapes.

2. Anhydrous phosphoric acid is a white, snowlike mass, which rapidly deliquesces in the air, and dissolves in water with a hissing noise. It forms with water and bases three different series of compounds, viz.; with three equivalents of water or base, hydrate of common phosphoric acid or common phosphates; with two equivalents of water or base, hydrate of pyrophosphoric acid or pyrophosphates; with one equivalent of water or base, hydrate of metaphosphoric acid or metaphosphates.

We shall treat here exclusively of the tribasic compounds, as these only occur frequently in nature, in pharmacy, &c.

3. The hydrate of common phosphoric acid ($3\,HO, PO_5$) forms colorless and transparent crystals which deliquesce rapidly in the air, forming a syrupy non-caustic fluid. The action of heat changes it into hydrated pyro- or metaphosphoric acid, according as either one or two equivalents of water are expelled. Heated in an open platinum dish, the hydrate of common phosphoric acid, if pure, volatilizes completely, though with difficulty, in white fumes.

4. The action of heat fails to decompose the phosphates with fixed bases, but converts them into pyrophosphates, if they contain one equivalent of basic water or ammonia, and into metaphosphates, if they contain two equivalents. The phosphates with alkaline bases only are soluble in water, in the neutral state. The solutions manifest an alkaline reaction. If pyro- or metaphosphates are fused with carbonate of soda, the fused mass contains the phosphoric acid invariably in the tribasic state.

5. *Chloride of barium* produces in aqueous solutions of the neutral or basic phosphates a white precipitate of PHOSPHATE OF BARYTA [$2\,BaO, HO, PO_5$; or $3\,BaO, PO_5$],* which is soluble in hydrochloric acid and in nitric acid, but difficultly soluble in chloride of ammonium.

6. *Solution of sulphate of lime* produces in neutral or alkaline solutions of phosphates a white precipitate of PHOSPHATE OF LIME ($2\,CaO, HO, PO_5$

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* Precipitates of the first composition are formed in solutions containing an alkaline phosphate with two equivalents of a fixed base or ammonia; whilst precipitates of the latter composition are formed in solutions which contain an alkaline phosphate with three equivalents of a fixed base or ammonia.

or $3\,CaO, PO_5$), which dissolves readily in acids, even in acetic acid, but with difficulty in chloride of ammonium.

7. *Sulphate of magnesia* produces in neutral solutions of phosphates a white precipitate of PHOSPHATE OF MAGNESIA ($2\,MgO, HO, PO_5$), which, however, is visible only in rather concentrated solutions, and particularly upon the application of heat. But if *sulphate of magnesia*, mixed with a sufficient quantity of chloride of ammonium to leave the solution clear upon addition of ammonia (which must be in excess), is added to a solution of free phosphoric acid or of an alkaline phosphate, a white, crystalline, and quickly subsiding precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA ($2\,MgO, NH_4O, PO_5$), is formed, even in highly dilute solutions. This precipitate is insoluble both in ammonia and chloride of ammonium, but dissolves readily in acids, even in acetic acid. It appears often only after the lapse of some time; stirring promotes its separation (see § 95, 7). In aqueous solutions of phosphates with three equivalents of fixed base, salts of magnesia produce immediately a precipitate of basic phosphate of magnesia ($3\,MgO, PO_5$); this precipitate is produced even in dilute solutions.

8. *Nitrate of silver* throws down from solutions of neutral and basic alkaline phosphates a light yellow precipitate of PHOSPHATE OF SILVER ($3\,AgO, PO_5$), which is readily soluble in nitric acid and in ammonia. If the solution contained a basic phosphate, the fluid in which the precipitate is suspended, manifests a neutral reaction; whilst the reaction is acid, if the solution contained a neutral phosphate. The acid reaction in the latter case arises from the circumstance that the nitric acid receives for the three equivalents of oxide of silver, which it yields to the phosphoric acid, only 2 eq. of alkali and 1 eq. of water; and as the latter does not neutralize the acid properties of the nitric acid, the solution becomes acid.

9. *Acetate of lead* produces in neutral and alkaline solutions of phosphates a white precipitate of PHOSPHATE OF LEAD ($3\,PbO, PO_5$), which is readily soluble in nitric acid, but nearly insoluble in acetic acid. This reaction acquires a great value as a test for phosphoric acid, from the peculiar deportment which the precipitated phosphate of lead exhibits before the blowpipe. For, in the first place, even the inner flame of the blowpipe fails to reduce it, or effects its reduction only with the greatest difficulty; and, in the second place, the colorless and transparent bead which it gives in the oxidizing flame crystallizes upon cooling, and becomes opaque, showing generally perfectly distinct dodecahedrons.

10. If to a solution containing phosphoric acid and the *least possible excess* of hydrocholic or nitric acid, a tolerably large amount of acetate of soda is added, and then a drop of *sesquichloride of iron*, a yellowish white, flocculent-gelatinous precipitate of PHOSPHATE OF SESQUIOXIDE OF IRON

is formed. An excess of sesquichloride of iron must be avoided, as acetate of sesquioxide of iron (of red color) would thereby be formed, in which the precipitate is not insoluble. This reaction is of importance, as it enables us to detect the phosphoric acid in phosphates of the alkaline earths; to effect the complete separation of the phosphoric acid from the alkaline earths, a sufficient quantity of sesquichloride of iron is added to impart a reddish color to the solution which is then boiled (whereby the whole of the sesquioxide of iron is thrown down, partly as phosphate, partly as basic acetate), and filtered hot. The filtrate contains the alkaline earths as chlorides. If you wish to detect, by means of this reaction, phosphoric acid in presence of a large proportion of sesquioxide of iron, boil the hydrochloric acid solution with sulphite of soda, until the sesquichloride is reduced to protochloride, which reduction is indicated by the decoloration of the solution; add carbonate of soda, until the fluid is nearly neutral, then acetate of soda, and finally one drop of sesquichloride of iron. The reason for this proceeding is, that acetate of protoxide of iron does not dissolve phosphate of sesquioxide of iron.

11. If some *molybdate of ammonia* is mixed in a test-tube with hydrochloric acid or nitric acid in sufficient quantity to redissolve the precipitate which forms at first, and a little of a very dilute fluid containing phosphoric acid is then added, and the mixture boiled, the fluid acquires an intensely yellow color, and after some time a yellow precipitate separates, which is insoluble in hydrochloric acid. The exact composition of this precipitate is not yet ascertained; we only know that it contains MOLYBDIC ACID, AMMONIA, AND A LITTLE PHOSPHORIC ACID. This reaction is so delicate that the phosphoric acid may be detected by its means in almost all salts and most minerals containing it. As the yellow compound is decomposed by free phosphoric acid, an excess of the fluid containing the phosphoric acid must be carefully avoided. The yellow precipitate may, when it has subsided, be perceived even in dark-colored fluids.

12. In phosphate of alumina the phosphoric acid may be detected also by one of the two following methods:

a. Add carbonate of soda to the hydrochloric acid solution until the free acid is nearly neutralized; mix with carbonate of baryta in excess, add solution of soda or potassa, and boil. This process gives the alumina in solution, the phosphoric acid in a precipitate of phosphate of baryta. Dissolve this precipitate in hydrochloric acid, decompose by sulphuric acid, filter, and test the filtrate with sulphate of magnesia, with addition of chloride of ammonium and ammonia.

b. Mix the hydrochloric acid solution with tartaric acid, add ammonia in excess, and finally to the clear solution chloride of ammonium and sulphate of magnesia. If a precipitate forms only after some time, this cannot be considered a safe indication of the presence of phosphoric acid, as, under the circumstances named, a precipitate of tartrate of magnesia, resembling the phosphate of magnesia and ammonia, may form in a solution of the proper degree of concentration, though no phosphoric acid is present. The precipitate must therefore be tested for phosphoric acid; which is done by dissolving it in nitric acid, evaporating the solution, with addition of some pure nitrate of potassa or soda, to dryness, igniting the residue, then heating it with hydrochloric acid, filtering the solution, and mixing the filtrate with ammonia in excess. The formation of a crystalline precipitate of phosphate of magnesia and ammonia confirms the presence of phosphoric acid.

§ 136.

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

1. Boracic acid, in the anhydrous state, is a colorless fixed glass, fusible at a red heat; hydrate of boracic acid ($2\,B\,O_3, 3\,H\,O$) is a porous white mass; in the crystalline state ($2\,B\,O_3, 3\,H\,O + 3$ aq.) it presents small scaly laminæ. It is soluble in water and in spirit of wine; upon evaporating the solutions, a large proportion of boracic acid volatilizes along with the aqueous and alcoholic vapors. The solutions redden litmus paper, but impart also a faint brown tint to turmeric paper. The borates are not decomposed upon ignition; those with alkaline bases alone are readily soluble in water. The solutions are colorless, and all of them, even those of the acid salts, manifest alkaline reaction.

2. *Chloride of barium* produces in solutions of borates, if not too highly dilute, a white precipitate of BORATE OF BARYTA ($Ba\,O, B\,O$), 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 ammonia.

4. If *sulphuric acid* or *hydrochloric acid* is added to highly concentrated, hot solutions of alkaline borates, the BORACIC ACID separates upon cooling, in the form of shining crystalline scales.

5. If alcohol is poured over free boracic acid or a borate—(in the latter case *a sufficient quantity of concentrated sulphuric acid* must be added, to liberate the boracic acid)—and the alcohol is kindled, the flame appears of a very distinct YELLOWISH-GREEN color, especially upon stirring the mixture; this tint is imparted to the flame by the ignited boracic acid which evaporates with the alcohol. The delicacy of this reaction may be considerably heightened by heating the dish which contains the alcoholic mixture, kindling the alcohol, allowing it to burn for a short time, then extinguishing the flame, and afterwards rekindling it. At the

first flickering of the flame its borders will now appear green, even though the quantity of the boracic acid be so minute that it fails to produce a perceptible coloring of the flame, when treated in the usual manner.

§ 137.

c. Oxalic acid ($C_2 O = \bar{O}$).

1. The hydrate of oxalic acid ($C_2 O_3$, $H O$) is a white powder; the crystallized acid ($C_2 O_3$, $H O + aq.$) forms colorless rhombic columns. Both dissolve readily in water and in spirit of wine. When heated rapidly in open vessels, part of the hydrated acid undergoes decomposition, whilst another portion volatilizes unaltered. The fumes of the volatilizing acid are very irritating and provoke coughing. If the hydrate is heated in a test-tube, the greater part of it sublimates unaltered.

2. The whole of the oxalates undergo decomposition at a red heat, the oxalic acid being converted into carbonic acid and carbonic oxide. Those with an alkali or an alkaline earth for base are in this process converted into carbonates (if pure, almost without separation of charcoal); those with metallic base leave either the pure metal or the oxide behind, according to the greater or less degree of reducibility of the metallic oxide. The alkaline oxalates, and also some of the oxalates with metallic bases, are soluble in water.

3. *Chloride of barium* produces in neutral solutions of oxalates a white precipitate of OXALATE OF BARYTA ($Ba O$, $\bar{O}$), which is soluble in nitric acid and in hydrochloric acid, but dissolves more sparingly in ammoniacal salts than borate of baryta.

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

5. *Lime-water* and all the *soluble salts of lime*, and consequently also *solution of sulphate of lime*, produce in even highly dilute solutions of free oxalic acid or of oxalates, white finely pulverulent precipitates of OXALATE OF LIME ($Ca O$, $\bar{O}$), which dissolve readily in hydrochloric acid and in nitric acid, but are nearly insoluble in oxalic acid and in acetic acid. The presence of salts of ammonia does not interfere with the formation of these precipitates. Addition of ammonia considerably promotes the precipitation of the free oxalic acid by salts of lime.

6. If hydrated oxalic acid (or an oxalate), in the dry state, is heated with an excess of *concentrated sulphuric acid*, the latter withdraws from the oxalic acid its constitutional water, and thus causes its decomposition into CARBONIC ACID and CARBONIC OXIDE ($C_2 O_3 = C O + C O_2$), which two 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. Should the sulphuric acid acquire a dark tint

in this reaction, this is a sign that the oxalic acid examined contained some organic substance in admixture.

7. If oxalic acid, or an oxalate, is mixed with some finely pulverized binoxide of manganese (which must be free from carbonates), a little water added and a few drops of sulphuric acid, a lively effervescence ensues, caused by the escaping carbonic acid ($\mathrm{Mn\,O_2 + C_2\,O_3 + S\,O_3 = Mn\,O,\ S\,O_3 + 2\ C\,O_2}$).

8. If oxalate of lime or any other insoluble oxalate is boiled with a concentrated solution of *carbonate of soda*, and the fluid is filtered, the oxalic acid is obtained in the filtrate in combination with soda, whilst the precipitate contains the base, as oxide, or as carbonate.

§ 138.

Hydrofluoric acid (H Fl).

1. Hydrofluoric acid is a colorless, highly volatile fluid of pungent odor; it emits fumes when exposed to the air, and is miscible with water in all proportions. Hydrofluoric acid is distinguished from all other acids by the exclusive property it possesses of dissolving crystallized silicic acid, and also the silicates which are insoluble in hydrochloric acid. Fluoride of silicon and water are formed in the process of solution ($\mathrm{Si\,O_2 + 2\ H\,Fl = Si\,Fl_2 + 2\ H\,O}$). Hydrofluoric acid decomposes with metallic oxides in the same manner, metallic fluorides and water being formed.

2. The fluorides of the alkali metals are soluble in water; the solutions have an alkaline reaction. The fluorides of the metals of the alkaline earths are either altogether insoluble in water, or they dissolve in that menstruum only with very great difficulty. Fluoride of aluminium is readily soluble. Most of the fluorides corresponding to the oxides of the heavy metals are very difficultly soluble in water, for instancs, fluoride of copper, fluoride of lead, fluoride of zinc; many other of the fluorides of the heavy metals dissolve in water without difficulty, as, for instance, the sesquifluoride of iron, protofluoride of tin, fluoride of mercury, &c. Many of the fluorides insoluble or difficultly soluble in water dissolve in free hydrofluoric acid, others do not. Most of the fluorides bear ignition in a crucible without suffering decomposition.

3. *Chloride of barium* precipitates free hydrofluoric acid incompletely, but upon addition of ammonia a copious white precipitate of FLUORIDE OF BARIUM (Ba Fl) forms immediately, which is soluble in hydrochloric acid, and not insoluble in chloride of ammonium.

4. *Chloride of calcium* produces in aqueous solutions of hydrofluoric acid or of fluorides a gelatinous precipitate of FLUORIDE OF CALCIUM (Ca Fl), which is so transparent, as at first to induce the belief, that the fluid has remained perfectly clear. Addition of ammonia promotes the complete separation of the precipitate. The precipitated fluoride of calcium is very little soluble in hydrochloric acid and nitric acid, in the

cold; it dissolves a little more largely upon boiling with hydrochloric acid. Ammonia produces no precipitate in the solution, or only a very trifling one, as the salt of ammonia formed retains it in solution. It is scarcely more soluble in free hydrofluoric acid than in water. It is insoluble in alkaline fluids.

5. If a finely pulverized fluoride, no matter whether soluble or insoluble, is treated in a platinum crucible with concentrated sulphuric acid, the crucible covered with the convex face of a watch glass, coated on that side with bees-wax, which has been removed again in some places by tracing lines in it with some pointed instrument,* the hollow of the glass filled with water, and the crucible gently heated for the space of half an hour or an hour, the exposed lines will, upon the removal of the wax, be found etched into the glass. If the quantity of hydrofluoric acid disengaged by the sulphuric acid was very minute, the etching is often invisible upon the removal of the wax; it will, however, in such cases reappear when the plate is breathed upon. This reappearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess.

This reaction (5) fails if there is too much silicic acid present, or if the body under examination is not decomposed by sulphuric acid. In such cases the one or the other of the two following methods is resorted to, according to circumstances.

6. If we have to deal with a fluoride *decomposable by sulphuric acid*, but mixed with a large proportion of silicic acid, the fluorine in it may be detected by heating the mixture in a test-tube with *concentrated sulphuric acid*. FLUOSILICIC GAS is evolved in this process, which forms dense white fumes in moist air. If the gas is conducted into water, through a bent tube moistened inside, the latter has its transparency more or less impaired, by the separation of silicic acid. If the quantity operated upon is rather considerable, hydrate of silicic acid separates in the water, and the fluid is rendered acid by hydrofluosilicic acid. This reaction may be tried also in the following very simple manner: Put the mixture into a small beaker, stir with concentrated sulphuric acid into a paste, and cover the beaker with a watch-glass having a small slip of moist blue litmus paper pasted on the lower surface. After a short time the color of the litmus-paper changes to red, whilst the glass round the paper, which is wetted by its moisture, becomes dim, owing to the ensuing separation of

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* The coating with the wax may be readily effected by heating the glass cautiously, putting a bit of wax upon the convex face, and spreading the fused mass equally over it. The instrument used for tracing the exposed lines should not be too hard; a pointed piece of wood answers best. The removal of the wax coating is effected by heating the glass gently, and wiping the wax off with a cloth.

silicic acid. The following process is less simple indeed, but much safer in its results: Add to the substance under examination some coarse pieces of marble (to ensure a continuous slight evolution of gas), boil the mixture in a flask with concentrated sulphuric acid, conduct the gases evolved into solution of ammonia, heat, filter, evaporate in a platinum crucible to dryness, and examine the residue by the method described in 5.—In the case of more difficultly decomposable substances bisulphate of potassa is used instead of sulphuric acid, and the mixture, to which some marble is likewise added, heated to fusion, and kept in that state for some time.

7. Compounds not decomposable by sulphuric acid must first be fused with four parts of carbonate of soda and potassa. The fused mass is treated with water, the solution filtered, the filtrate concentrated by evaporation, allowed to cool, transferred to a platinum or silver vessel, hydrochloric acid added to feebly acid reaction, and the fluid let stand until the carbonic acid has escaped. It is then supersaturated with ammonia, heated, filtered into a bottle, chloride of calcium added to the still hot fluid, the bottle closed, and allowed to stand at rest. If a precipitate separates after some time, it is collected on a filter, dried, and examined by the method described in 5. (*H. Rose*).

§ 139.

Recapitulation and remarks.—The third section embraces phosphoric acid, boracic acid, oxalic acid, and hydrofluoric acid. We have seen that the baryta compounds of these acids are dissolved by hydrochloric acid, apparently without undergoing decomposition; alkalies therefore reprecipitate them unaltered, by neutralizing the hydrochloric acid. The baryta compounds of arsenious acid, arsenic acid, and chromic acid present, however, the same deportment; these acids must therefore, if present, be removed before any conclusion regarding the presence of phosphoric acid, boracic acid, oxalic acid, or hydrofluoric acid, can be drawn from the reprecipitation of a salt of baryta by alkalies. But even leaving this point altogether out of the question, no great value is to be placed on this reaction, not even so far as the simple detection of these acids is concerned, and far less still as regards their separation from other acids, since ammonia fails to reprecipitate from hydrochloric acid solutions the salts of baryta in question, and more particularly the borate of baryta and the fluoride of barium, if the solution contains any considerable proportion of free acid, or of an ammoniacal salt. Boracic acid may be invariably detected by the characteristic tint which it communicates to the flame of alcohol, provided care be taken to concentrate the solution sufficiently before adding the alcohol, and in the case of borates, to mix the solution with a sufficient amount of concentrated sulphuric acid. Upon evaporating solutions of boracic acid, it must be combined with an alkali, otherwise a large portion of it will volatilize along with the aqueous vapors.

The detection of phosphoric acid in compounds soluble in water is not difficult; the reaction with sulphate of magnesia is the best adapted to effect the purpose. The detection of phosphoric acid in insoluble compounds is much more difficult; but even here we have now some excellent tests, in the reaction with sesquichloride of iron and acetate of soda, and in that with molybdate of ammonia. With regard to the former of these two tests, I repeat here once more, that a sensitive reaction is not to be expected in a fluid colored red by acetate of sesquioxide of iron, as the latter (as well as acetate of alumina) dissolves phosphate of sesquioxide of iron; the directions given in § 135, 10, must therefore be strictly attended to. As regards the reaction with molybdate of ammonia, I must not omit to remark that, on account of its extraordinary sensitiveness, the greatest possible care and caution must be observed in the application of the test; not that we may not almost always, or, at all events, in most cases assume the yellow color of the solution or the formation of the yellow precipitate, to indicate the presence of phosphoric acid (although arsenic acid shows the same deportment), but that the reagent used may contain a trace of phosphoric acid, very slight perhaps, yet sufficient to be brought to light by this most delicate test; the purity of the reagents used in the process must therefore always be ascertained with the utmost care, otherwise it may happen that the presence of phosphoric acid is erroneously assumed in a substance simply because one or other of the reagents employed contained a trace of that acid. It must also be borne in mind that the reaction is manifest only in presence of an *excess* of molybdic acid. If this point is lost sight of, the phosphoric acid may be overlooked most readily in the very cases where it is present in the largest proportion. Oxalic acid may always be easily detected in aqueous solutions by solution of sulphate of lime. The formation of a finely pulverulent precipitate, insoluble in acetic acid, leaves hardly a doubt on the point, as racemic acid alone, which occurs so very rarely, gives the same reaction. In case of doubt, the oxalate of lime may be readily distinguished from the paratartrate, or racemate, by simple ignition, with exclusion of the air, as the decomposed paratartrate leaves a considerable proportion of charcoal behind; the paratartrate dissolves moreover in cold solution of potassa or soda, in which oxalate of lime is insoluble. The deportment of the oxalates with sulphuric acid, or with binoxide of manganese and sulphuric acid, affords also sufficient means to confirm the results of other tests. In insoluble salts the oxalic acid is detected most safely by decomposing the insoluble compound first by boiling with solution of carbonate of soda. In salts decomposable by sulphuric acid, the hydrofluoric acid is readily detected; only, it must be borne in mind that the glass cannot be distinctly etched, if, instead of hydrofluoric gas, fluosilicic gas alone is evolved; and therefore, in the case of compounds abounding in silica, the safer way is to try, besides the reaction given § 138, 5, also the one given in § 138, 6. In silicates which are not decomposed by sulphuric acid, the presence of fluorine is often overlooked, because the analyst omits to examine the compound carefully by the method given § 138, 7.

Fourth Section of the First Group of the Inorganic Acids.

§ 140.

a. Carbonic acid ($C O_2$).

1. Carbon is a solid, tasteless and inodorous body. The very highest degrees of heat alone can effect its fusion and volatilization (*Despretz*). Carbon is combustible, and yields carbonic acid when burnt with a sufficient supply of oxygen or atmospheric air. In the diamond the carbon is crystallized, transparent, exceedingly hard, difficultly combustible; in the form of graphite, it is opaque, blackish-gray, soft, greasy to the touch, difficultly combustible, and stains the fingers; as carbon, produced by the decomposition of organic matters, it is black, opaque, noncrystalline—often dense, shining, difficultly combustible—often porous, dull, readily combustible.

2. Carbonic acid, at the common temperature and common atmospheric pressure, is a colorless gas of far higher specific gravity than atmospheric air, so that it may be poured from one vessel into another. It is almost inodorous, has a sourish taste, and reddens moist litmus-paper; but the red tint disappears again upon drying. Carbonic acid is readily absorbed by solution of potassa; it dissolves pretty copiously in water.

3. The aqueous solution of carbonic acid has a feebly acid, pungent taste; it transiently imparts a red tint to litmus-paper, and loses its carbonic acid upon the application of heat, and also when shaken with air in a half-filled bottle. Part of the carbonates lose their carbonic acid upon ignition; those with colorless oxides are white or colorless. Of the neutral carbonates, only those with alkaline bases are soluble in water. The solutions manifest a very strong alkaline reaction. The bicarbonates with alkaline bases are very soluble in water; those of the alkaline earths and some of the bicarbonates with metallic bases, slightly so.

4. The carbonates are decomposed by all *free* acids soluble in water, with the exception of hydrocyanic acid and hydrosulphuric acid. The decomposition of the carbonates by acids is attended with EFFERVESCENCE, the carbonic acid being disengaged as a colorless an almost inodorous gas, which transiently imparts a reddish tint to litmus-paper. It is necessary to apply the decomposing acid in excess, especially when operating upon carbonates with alkaline bases, since the formation of

bicarbonates will frequently prevent effervescence, if too little of the decomposing acid be added. Substances which it is intended to test for carbonic acid, by this method, should first be drenched with water, to prevent any mistake which might arise from the escape of air-bubbles upon treating the dry substances with the test-acid. If it is wished to determine by a direct experiment whether the disengaged gas is really carbonic acid or not, this may be readily accomplished by transferring some of the disengaged gas (but none of the fluid) from the test-tube into another tube, adding some lime-water to it, and shaking the mixture. The formation of a copious precipitate will prove that the evolved gas is really carbonic acid, since

4. *Lime-water* and *water of baryta*, when brought into contact with carbonic acid or with soluble carbonates, produce white precipitates of neutral CARBONATE OF LIME ($Ca\,O, C\,O_2$), or neutral CARBONATE OF BARYTA ($Ba\,O, C\,O_2$). When testing for free carbonic acid, these reagents ought always to be added in excess, as the *acid* carbonates of the alkaline earths are soluble in water. The precipitated carbonates of lime and baryta dissolve in acids, with effervescence, and are not reprecipitated from such solutions by ammonia, after the complete expulsion of the carbonic acid by ebullition.

5. *Chloride of calcium* and *chloride of barium* immediately produce in solutions of neutral alkaline carbonates, precipitates of CARBONATE OF LIME or of CARBONATE OF BARYTA; in dilute solutions of bicarbonates these precipitates are formed only upon ebullition; with free carbonic acid these reagents give no precipitate.

§ 141.

b. SILICIC ACID ($Si\,O_2$).

1. Silicic acid is colorless or white, even in the hottest blowpipe flame unalterable and infusible. It fuses in the flame of the oxyhydrogen blowpipe. It is met with in two modifications, crystalline and amorphous. It is insoluble in water and acids, excepting the hydrofluoric acid; whilst its hydrate is soluble in acids, but only at the moment of its separation. The amorphous silicic acid and the hydrate dissolve in hot aqueous solutions of caustic alkalies and of fixed alkaline carbonates; but the crystallized acid is insoluble or nearly so in these fluids. If the crystalline acid is fused with pure alkalies or alkaline carbonates, a basic silicate of the alkali is obtained, which is soluble in water, and from which acids again separate hydrated silicic acid. The alkaline silicates alone are soluble in water.

2. The solutions of the alkaline silicates are decomposed by all *acids*. If the solutions are highly concentrated, the hydrate of SILICIC ACID separates in the form of gelatinous flakes; from more dilute solutions, the

acid separates only after some time, and in very dilute solutions it remains dissolved. If a dilute solution of an alkaline silicate, mixed with an acid (hydrochloric acid or nitric acid), is evaporated to dryness, silicic acid separates, in proportion as the acid escapes; upon treating the residue with hydrochloric acid and water, the silicic acid remains in the free state (or, if the temperature in the process of drying was restricted to 212° as hydrate, $4\ Si\,O_2,\ H\ O$), as an insoluble white powder. Chloride of ammonium produces in rather concentrated solutions of alkaline silicates precipitates of hydrate of silicic acid.

3. Part of the silicates insoluble in water are decomposed by hydrochloric acid or nitric acid, part of them are not affected by these acids, even upon boiling. In the decomposition of the former, the greater portion of the silicic acid separates usually as gelatinous, more rarely as a pulverulent hydrate. To effect the complete separation of the silicic acid, the hydrochloric acid solution, with the precipitated hydrate of silicic acid suspended in it, is evaporated to dryness, the residue heated at a temperature above the boiling point of water, until no more acid fumes escape, then moistened with hydrochloric acid, heated with water, and the fluid containing the bases filtered from the residuary insoluble silicic acid.

4. Of the silicates not decomposed by hydrochloric acid, many, *e. g.* Kaolin, are completely decomposed by heating with hydrate of sulphuric acid, the decomposition being attended with separation of silicic acid in the pulverulent form; many others are acted upon to some extent by hydrated sulphuric acid, upon heating.

5. The silicates which are not acted upon by acids, are decomposed, *a* by fusion with alkaline carbonates; *b* by fusion with hydrate of baryta; *c* by heating with hydrofluoric acid, or with a metallic fluoride and sulphuric acid. In *a* and *b* basic silicates are formed, which are readily decomposed by hydrochloric acid; in *c* the silicic acid escapes as fluosilicic gas. Respecting the application of these several methods of decomposition, compare §§ 193—196.

6. *Carbonate of soda* dissolves a copious amount of silicic acid in the flame of the blowpipe to a colorless glass of SILICATE OF SODA, which remains transparent on cooling; the carbonic acid escapes with effervescence in this process. Inexperienced students often fail to produce a clear bead, because they use too much carbonate of soda in proportion to the quantity of the test-specimen.

7. *Phosphate of soda and ammonia* fails nearly altogether to dissolve silicic acid. The silicic acid floats about in the transparent bead as an opaque mass, and may therefore be seen better in the ignited than in the cold bead. The same reaction is shown by the silicates, from which the phosphate of soda and ammonia withdraw the base with separation of silicic acid. The bases are generally dissolved; the silicic acid remains undissolved.

§ 142.

Recapitulation and remarks.—Free carbonic acid is readily known by its deportment with lime-water; the carbonates are easily detected by the evolution of a nearly inodorous gas, which takes place when they are treated with acids. When operating upon compounds which, besides carbonic acid, evolve other gases, the disengaged gas is to be tested with lime-water or with water of baryta. Silicic acid, in the free state and in silicates, may usually be readily detected by the reaction with phosphate of soda and ammonia. It differs moreover from all other bodies, in the form in which it is always obtained in analyses, by its insolubility in acids (except hydrofluoric acid), and its solubility in boiling solutions of pure alkalies and alkaline carbonates.

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.*

§ 143.

The silver compounds corresponding to the acids of this group are insoluble in dilute nitric acid. The acids of this group decompose with metallic oxides, the metals combining with the chlorine, bromine, cyanogen, iodine, or sulphur, whilst the oxygen of the metallic oxide forms water with the hydrogen of the hydracid.

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

1. Chlorine is a heavy, yellowish-green gas of a disagreeable stifling odor, and which has a most injurious action upon the respiratory organs; it destroys vegetable color (litmus, indigo-blue, &c.); it is not inflammable, and supports the combustion of few bodies only. Minutely divided antimony, tin, &c., kindle in it and burn, being converted into chlorides. It dissolves pretty largely in water; the chlorine water formed has a faint yellowish-green color, smells strongly of the gas, bleaches vegetable colors, is decomposed by the action of light (§ 71), and loses its odor when shaken with mercury; in this process the latter is converted into a mixture of subchloride and metallic mercury. Small quantities of chlorine may be readily detected in a fluid, by adding the latter to a solution of pure protoxide of iron, mixed with sulphocyanide of potassium: the solution is at once colored red by the action of free chlorine;—or, in the absence of nitric acid, by adding it to a dilute solution of iodide of potassium, mixed with starch-paste. (See § 145, 10.)

2. Hydrochloric acid, at the common temperature and common atmospheric pressure, is a colorless gas which forms dense fumes in the air, is

suffocating and very irritant, and dissolves in water with exceeding facility. The more concentrated solution (common hydrochloric acid) loses a large portion of its gas upon heating.

3. The neutral metallic chlorides are readily soluble in water, with the exception of chloride of lead, chloride of silver, and subchloride of mercury; most of the chlorides are white or colorless. Many of them volatilize at a high temperature, without suffering decomposition; others are decomposed upon ignition, and but few of them are fixed.

4. *Nitrate of silver* produces in even highly dilute solutions of free hydrochloric acid or of metallic chlorides white precipitates of **CHLORIDE OF SILVER** ($Ag\ Cl$), which, upon exposure to light, change first to violet, then to black; they are insoluble in nitric acid, but dissolve readily in ammonia, and fuse without decomposition, when heated. (Compare § 111, 6.)

5. *Nitrate of suboxide of mercury* and *acetate of lead* produce in solutions containing free hydrochloric acid or metallic chlorides precipitates of **SUBCHLORIDE OF MERCURY** ($Hg_2\ Cl$) and **CHLORIDE OF LEAD** ($Pb\ Cl$). For the properties of these precipitates, see § 112, 6, and § 113, 7.

6. If hydrochloric acid is heated with *binoxide of manganese,* or a chloride with *binoxide of manganese* and *sulphuric acid,* chlorine gas is evolved, which may be readily recognized by its odor and **YELLOWISH-GREEN** color.

7. If a metallic chloride is triturated together with *chromate of potassa,* the mixture treated with *concentrated sulphuric acid,* in a tubulated retort, and a gentle heat applied, a deep brownish-red gas will be copiously evolved (**CHROMATE OF TERCHLORIDE OF CHROMIUM**, $Cr\ Cl_3,\ 2\ Cr\ O_3$), which condenses into a fluid of the same color, and passes over into the receiver. If this chromate of terchloride of chromium is mixed with ammonia in excess, a yellow-colored liquid is produced; the yellow tint is imparted to the fluid by the chromate of ammonia which forms in this process; upon the addition of an acid, the color of the solution changes to a reddish-yellow, owing to the formation of acid chromate of ammonia.

8. In the metallic chlorides insoluble in water and nitric acid, the chlorine is detected by fusing them with carbonate of soda and potassa, and treating the fused mass with water, which will dissolve, besides the excess of the alkaline carbonate, the chloride of the alkali metal formed in the process of fusion.

§ 144.

b. HYDROBROMIC ACID ($H\ Br$).

1. Bromine is a heavy, reddish-brown fluid, of a very disagreeable, chlorine-like odor; it boils at 116°, and volatilizes rapidly even at the common temperature. The vapor of bromine is brownish-red. Bromine bleaches vegetable colors like chlorine; it is rather difficultly soluble in

water, but dissolves more easily in alcohol, and very readily in ether. The solutions are yellowish-red.

2. Hydrobromic acid gas, its aqueous solution, and the metallic bromides, offer in their general deportment a great analogy to the corresponding chlorides.

3. *Nitrate of silver* produces in aqueous solutions of hydrobromic acid or of bromides a yellowish-white precipitate of BROMIDE OF SILVER ($Ag\,Br$), which changes to violet upon exposure to the light; this precipitate is insoluble in dilute nitric acid, and somewhat sparingly soluble in ammonia.

4. *Nitrate of protoxide of palladium*, but not protochloride of palladium, produces in neutral solutions of metallic bromides a reddish-brown precipitate of PROTOBROMIDE OF PALLADIUM ($Pd\,Br$). In more concentrated solutions this precipitate is formed immediately, in more dilute solutions it makes its appearance only after standing some time.

5. *Nitric acid* decomposes hydrobromic acid and the bromides, with the exception of bromide of silver and bromide of mercury, upon the application of heat, and liberates the bromine, by oxidizing the hydrogen or the metal. The liberated bromine colors the solution yellowish-red. When operating upon bromides in the solid state, brownish-red (if diluted, yellowish-red) vapors of bromine gas escape, emitting the odor of chlorine; these vapors, when evolved in sufficient quantity, condense in the cold part of the test-tube into small drops.

6. *Chlorine*, in the *gaseous* state or in *solution*, liberates bromine also in the solutions of its compounds; the fluid assuming a yellowish-red tint, if the quantity of the bromine present is not too minute. If a solution of this kind is shaken together with some *ether*, it loses its yellow color, the whole of the bromine present dissolving in the ether, which appears now distinctly yellow, even though but a very minute quantity of bromine be present. If the ethereal solution of bromine is mixed with some solution of potassa, and the mixture shaken, the yellow tint disappears again, and the solution now contains bromide of potassium and bromate of potassa. Upon evaporation and subsequent ignition of the residue, the bromate of potassa is converted into bromide of potassium, and this may then be further tested as directed in 7.

7. If bromides are heated with *binoxide of manganese* and *hydrate of sulphuric acid*, BROWNISH-RED VAPORS OF BROMINE are evolved. If the bromine is present only in a very minute quantity, the color of these vapors is not visible. The experiment is, in that case, to be conducted in a small retort, and the evolved vapors are to be transmitted through a long condensing glass tube, and finally received into small test-glasses, containing some moistened starch.

8. If moistened *starch* is brought into contact with free bromine, no

matter whether in solution or in the gaseous state, **YELLOW BROMIDE OF STARCH** is formed. The coloration is not always instantaneous. The reaction is rendered most delicate by hermetically closing the test-tube which contains the moistened starch and the fluid under examination, and then inverting it, so as to cause the moist starch to occupy the upper part of the tube whilst the fluid occupies the bottom. The presence of even the slightest trace of bromine will now, in the course of from twelve to twenty-four hours, impart a yellow tint to the starch, which, however, after some time disappears.

9. If sulphuric acid is poured over a mixture of a bromide with *chromate of potassa*, and heat is then applied, a brownish-red gas is evolved, exactly as in the case of chlorides. But this gas consists of pure **BROMINE**, and therefore the fluid passing over does not turn yellow, but becomes colorless, upon supersaturation with ammonia.

10. In the metallic bromides which are insoluble in water and nitric acid, the bromine is detected in the same way, as the chlorine in the corresponding chlorides.

§ 145.

c. HYDRIODIC ACID ($H\,I$).

1. Iodine is a solid, soft body, of a peculiarly disagreeable odor. It is generally seen in the form of black, shining, crystalline scales. It fuses at a gentle heat; at a somewhat higher temperature, it is converted into iodine vapor, which has a beautiful violet-blue color, and condenses upon cooling to a black sublimate. It is very sparingly soluble in water, but readily in alcohol and ether; the aqueous solution is of a light-brown color, the alcoholic and ethereal solutions are a deep reddish-brown. Iodine destroys vegetable colors only slowly; it stains the skin brown; with starch it forms a compound of an intensely deep blue color. This compound is formed invariably when iodine vapor, or a solution containing free iodine comes in contact with starch, best with starch-paste. It is decomposed by alkalies and also by chlorine and bromine.

2. Hydriodic acid gas resembles hydrochloric and hydrobromic acid gas; it dissolves copiously in water. The colorless hydrated hydriodic acid turns speedily to a reddish-brown when in contact with the air; this is owing to the formation of hydriodous acid ($H\,I_2$) and water.

3. The iodides also correspond in many respects with the chlorides. Of the iodides of the heavy metals, however, many more are insoluble in water than is the case with the corresponding chlorides. Many iodides have characteristic colors.

4. Nitrate of silver produces in aqueous solutions of hydriodic acid and of iodides yellowish-white precipitates of **IODIDE OF SILVER** ($Ag\,I$), which blacken on exposure to light; these precipitates are insoluble in dilute nitric acid, and but very sparingly soluble in ammonia.

5. *Protochloride of palladium* and *nitrate of protoxide of palladium* produce even in very dilute solutions of hydriodic acid or metallic iodides a brownish-black precipitate of PROTIODIDE OF PALLADIUM, which dissolves to a trifling extent in saline solutions (solution of chloride of sodium, chloride of magnesium, &c.), but is insoluble or nearly so in dilute cold hydrochloric and nitric acids.

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

7. *Nitric acid* decomposes the hydriodic acid and the iodides in the same manner as the corresponding compounds of bromine. Nitric acid imparts therefore to colorless solutions of hydriodic acid or of the iodides, even in the cold, a yellowish tint, which upon the application of heat changes to a brownish-red; from more concentrated solutions the IODINE separates under these circumstances, in the form of small black plates, whilst nitric oxide gas and iodine vapors escape. The latter reaction is observed also when solid or metallic iodides are heated with nitric acid.

8. *Chlorine*, in the *gaseous* state or in *solution*, liberates iodine also in the solutions of its compounds, but in presence of an excess of chlorine the free iodine combines with the latter, forming colorless chloride of iodine. If to even a very dilute solution of a metallic iodide a little chlorine water is added, then some ether, and the mixture shaken, the ether dissolves the liberated iodine, and acquires thereby a reddish-brown or reddish-yellow color. The color imparted to the ether by iodine is much more intense than that imparted to that fluid by an equal quantity of bromine.

9. If iodides are heated with concentrated *sulphuric acid*, or with *sulphuric acid* and *binoxide of manganese*, IODINE is liberated, which may be readily recognized by the violet color of its vapor. If concentrated sulphuric acid alone is used, sulphurous acid is evolved along with the iodine. If the quantity of iodine present is very minute, the characteristic color of its vapor does not distinctly appear; in such cases a little slip of paper or cotton cloth, coated with starch-paste, is fixed to the cork with which the flask containing the mixture is loosely closed. The slip appears after some time blue, if the least trace of iodine is present.

10. If to a solution of hydriodic acid, or to that of an iodide in water, starch-paste is added, the fluid remains colorless; but if nitric acid is now added, iodide of starch forms immediately, which imparts a deep dark-blue tint to the fluid, and gradually separates in part as a precipitate of the same color. Even a considerable excess of nitric acid does not destroy

the color in the cold. If metallic chlorides are also present, the nitric acid must be added more cautiously. The delicacy of the reaction is heightened by substituting chlorine water for nitric acid. If the fluid is alkaline, it is previously acidified with a little dilute sulphuric acid. But great caution must be observed in the addition of the chlorine water, in cases where it is intended to detect minute traces of iodine; since an excess of chlorine will immediately destroy the blue color of the iodide of starch. It is advisable therefore, in such cases, to use dilute chlorine water, and to add this in small portions at a time, by means of a glass rod.

11. The iodides manifest with sulphuric acid used in conjunction with chromate of potassa (compare § 143, 7) the same deportment which they exhibit with sulphuric acid alone. The iodides which are insoluble in water and nitric acid comport themselves upon fusion with carbonate of soda and potassa, in the same manner as the corresponding chlorides.

§ 146.

d. Hydrocyanic acid (H Cy).

1. Cyanogen is a colorless gas of a peculiar and penetrating odor; it burns with a crimson flame, and is pretty soluble in water.

2. Hydrocyanic acid is a colorless, volatile, inflammable liquid, the odor of which resembles that of bitter almonds; it is miscible with water in all proportions; and in the pure state, it speedily suffers decomposition. It is extremely poisonous.

3. The cyanides with alkalies or alkaline earths are soluble in water; the solutions smell of hydrocyanic acid. They are readily decomposed by acids, even by carbonic acid; but ignition fails to decompose them, if the access of air is precluded. When fused with oxides of lead, copper, antimony, tin, &c., the cyanides reduce these oxides, and are converted into cyanates. Only a few of the cyanides with heavy metals are soluble in water; all of them are decomposed upon ignition, the cyanides of the noble metals being converted into cyanogen gas and metal, the cyanides of the other heavy metals into nitrogen gas and carbides. Many of the cyanides with heavy metals are not decomposed by dilute oxygen acids, and only with difficulty by concentrated nitric acid. But hydrochloric acid and hydrosulphuric acid decompose most of them readily and completely.—Cyanogen combines with several metals (iron, manganese, cobalt, chromium), forming with them compound radicals, which combine with hydrogen to acids, with metals to haloid salts, and indeed comport themselves in general like salt-radicals. From compounds of this nature the metals named cannot be separated by alkalies and alkaline sulphides.

4. *Nitrate of silver* produces in solutions of free hydrocyanic acid and of cyanides of the alkali metals white precipitates of CYANIDE OF SILVER (Ag Cy), which are readily soluble in cyanide of potassium, dissolve with

some difficulty in ammonia, and are insoluble in nitric acid; these precipitates are decomposed upon ignition, leaving metallic silver with some paracyanide of silver.

5. If solution of *sulphate of protoxide of iron* which has been for some time in contact with the air is added to a solution of free hydrocyanic acid, no alteration takes place; but if *solution of potassa* or *soda* is now added, a bluish-green precipitate forms, which consists of a mixture of Prussian-blue ($Fe_4\ Cfy_3$), and hydrate of protosesquioxide of iron. Upon addition of hydrochloric acid (best after previous application of heat), the latter dissolves, whilst the PRUSSIAN-BLUE remains undissolved. If only a very minute quantity of hydrocyanic acid is present, the fluid simply appears green after the addition of the hydrochloric acid, and it is only after long standing that a trifling blue precipitate separates from it. The same reactions are observed when sulphate of protoxide of iron is added to the solution of an alkaline cyanide.

6. If to a solution of hydrocyanic acid potassa is added in excess, and then finely pulverized *oxide of mercury*, the latter dissolves as readily as it would in free hydrocyanic acid. Since oxide of mercury is soluble in alkaline fluids *only in presence of hydrocyanic acid*, this reaction may be looked upon as a positive test for that acid.

7. If a liquid containing hydrocyanic acid is mixed with a small quantity (one or two drops) of yellow sulphide of ammonium and a trace of ammonia, and the mixture warmed in a porcelain dish until it becomes colorless, sulphocyanide of ammonium is formed, and the fluid acquires a deep blood-red tint upon addition of sesquichloride of iron (*Liebig*). This reaction is exceedingly delicate. The following formula expresses the transformation of hydrocyanic acid into sulphocyanide of ammonium: $N\ H_4,\ S_5 + 2\ (N\ H_4,\ O) + 2\ H\ Cy = 2\ (N\ H_4,\ Cy\ S_2) + N\ H_4,\ S + 2\ H\ O$. If an acetate is present, the reaction takes place only upon addition of hydrochloric acid.

8. Neither of the above methods will serve to effect the detection of cyanogen in cyanide of mercury. To detect cyanogen in that compound the solution is mixed with hydrosulphuric acid: sulphide of mercury precipitates, the solution contains free hydrocyanic acid. In solid cyanide of mercury the cyanogen is most readily detected by heating in a glass tube. Compare 3.

9. In the ferro- and ferricyanides with alkaline bases, the ferro- and ferricyanogen may be readily detected, the former by means of *solution of sesquioxide of iron* or *solution of copper*, and the latter by means of solution of *protoxide of iron*. The distillation of these double cyanides with sulphuric acid gives rise to the evolution of free hydrocyanic acid. The insoluble ferrocyanides and ferricyanides undergo decomposition, when heated with a solution of carbonate of soda or caustic soda; ferro-

cyanide of sodium is formed, and the metals separate as pure oxides or as carbonates.

§ 147.

e. HYDROSULPHURIC ACID ($H S$).

Sulphuretted Hydrogen Gas.

1. Sulphur is a solid, brittle, friable, tasteless body, insoluble in water. It occurs occasionally in the form of yellow or brownish crystals, or crystalline masses of a yellow or brownish color, and occasionally in that of a yellow or yellowish-white or grayish-white powder. It melts at a moderate heat; upon the application of a stronger heat it is converted into brownish-yellow vapors, which, in cold air, condense to a yellow powder, and on the sides of the vessel, to drops. Heated in the air, it burns with bluish flame to sulphurous acid, which manifests its presence in the air at once by its suffocating odor. Concentrated nitric acid, nitrohydrochloric acid, and a mixture of chlorate of potassa and hydrochloric acid dissolve sulphur gradually, with the aid of a moderate heat, and convert it into sulphuric acid; in boiling solution of soda sulphur dissolves to a yellow fluid, which contains sulphide of sodium and hyposulphite of soda; in ammonia sulphur is insoluble.

2. Hydrosulphuric acid, at the common temperature and under common atmospheric pressure, is a colorless, inflammable gas, soluble in water, and which may be readily recognized by its characteristic smell of rotten eggs; it transiently imparts a red tint to litmus paper.

3. Of the sulphides only those with alkalies and alkaline earths are soluble in water. These, and the sulphides of metals of the fourth group, such as the sulphides of iron, manganese, and zinc, for instance, are decomposed by dilute mineral acids, with evolution of hydrosulphuric acid gas, which may be readily detected by its peculiar smell, and by its action upon solution of lead (see 4). The decomposition of higher sulphides is attended also with separation of sulphur in a highly divided state; the white precipitate may be readily distinguished from similar precipitates by its deportment on heating. Part of the sulphides of the metals of the fifth and sixth group are decomposed by concentrated and boiling hydrochloric acid, with evolution of hydrosulphuric acid gas, whilst others are not dissolved by hydrochloric acid, but by concentrated and boiling nitric acid. The compounds of sulphur with mercury resist the action of both acids, but dissolve readily in nitrohydrochloric acid. Upon the solution of sulphides in nitric acid, and in nitrohydrochloric acid, sulphuric acid is formed, and the process of solution is moreover attended, in most cases, with separation of sulphur, which is readily recognized by its color and by its deportment upon heating. Many metallic sulphides, more especially

of a higher degree of sulphuration, give a sublimate of sulphur, when heated in a glass-tube closed at one end.

4. If hydrosulphuric acid, in the gaseous state or in solution, is brought into contact with *nitrate of silver* or *acetate of lead*, black precipitates of SULPHIDE OF SILVER OR SULPHIDE OF LEAD are formed (see § 111 and §113). In cases, therefore, where the odor of the gas fails to afford sufficient proof of the presence of hydrosulphuric acid, these reagents will remove all doubt. If the hydrosulphuric acid is present in the gaseous form, the air suspected to contain it is tested by placing in it a small slip of paper, moistened with solution of neutral acetate of lead and a little ammonia; if the gas is present, the slip becomes covered with a thin, brownish-black, shining film of sulphide of lead.

5. If metallic sulphides are exposed to the *oxidizing flame of the blowpipe*, the sulphur burns with a blue flame, emitting at the same time the well-known odor of sulphurous acid. If a metallic sulphide is heated in a glass-tube open at both ends, in the upper part of which a slip of blue litmus paper is inserted, and the tube is held in a slanting position during the operation, the escaping sulphurous acid reddens the litmus paper.

6. If a finely-pulverized metallic sulphide is boiled in a porcelain dish with solution of potassa, and the mixture heated to incipient fusion of the hydrate of potassa, or if the test specimen is fused in a platinum spoon with hydrate of potassa, and the mass is, in either case, dissolved in a little water, a piece of bright silver (a polished coin) put into the solution, and the fluid warmed, a brownish-black film of sulphide of silver forms on the metal. This film may be removed afterwards by rubbing the metal with leather and quick-lime (*v. Kobell*).

§ 148.

Recapitulation and remarks.—Most of the acids of the first group are also precipitated by nitrate of silver, but the precipitates cannot well be confounded with the silver compounds of the acids of the second group, since the former are *soluble* in dilute nitric acid, whilst the latter are *insoluble* in that menstruum. The presence of hydrosulphuric acid interferes more or less with the testing for the other acids of the second group; this acid must, therefore, if present, be removed first, before the testing for the other acids can be proceeded with. The removal of the hydrosulphuric acid, when present in the free state, may be effected by simple ebullition, and when present in the form of an alkaline sulphide, by the addition of a metallic salt, such as will not precipitate any of the other acids, or at least will not precipitate them from acid solutions. Hydriodic and hydrocyanic acids may be detected, even in presence of hydrochloric or hydrobromic acid, by the equally characteristic and delicate reactions with starch and with solution of protosesquioxide of iron. But the detection of chlorine and bromine is more or less difficult in presence of iodine and cyanogen. These latter must therefore, if present, be removed first, before the proper tests for chlorine and bromine can be applied. The separation of the cyanogen may be readily effected by converting the whole of the radicals present into salts of silver, and igniting the mixed compound produced: the cyanide of silver is decomposed in this process, whilst the chloride, bromide, and iodide of silver remain unaltered. Upon fusing the ignited residue with carbonate of soda and potassa, and boiling the fused mass with water, chloride, bromide, and iodide of the alkali metals are obtained in solution. The iodine may be separated from the chlorine and bromine, by treating the mixed silver compound with ammonia, but more accurately by precipitating the iodine as protiodide of copper. From bromine the iodine is separated most accurately by protochloride of palladium, which only precipitates the iodine; from chlorine it is separated by nitrate of protoxide of palladium. Metallic bromides are detected in presence of metallic chlorides by means of chlorine water and ether. This reaction, however, affords a safe test for bromine only in the absence of iodine. Metallic chlorides are detected in presence of metallic bromides by the reaction with chromate of potassa and sulphuric acid.

THIRD GROUP OF THE INORGANIC ACIDS.

ACIDS WHICH ARE NOT PRECIPITATED BY SALTS OF BARYTA NOR BY SALTS OF SILVER: *Nitric Acid—Chloric Acid.*

§ 149.

a. NITRIC ACID ($N O_5$).

1. Anhydrous nitric acid crystallizes in six-sided prisms. It fuses at 85·2°, and boils at 113° (*Deville*, Compt. Rendus, xxviii. 257). Its hydrate is a colorless, exceedingly caustic fluid, which emits fumes in the air, exercises a rapidly destructive action upon organic substances, and colors nitrogenous matter intensely yellow. Admixture of nitrous acid imparts to hydrated nitric acid a red color.

2. All the neutral salts of nitric acid are soluble in water; only some of the basic nitrates are insoluble in this menstruum. All nitrates without exception undergo decomposition at an intense red heat. Those with alkaline bases yield oxygen and nitrogen; the others yield oxygen and nitrous or hyponitric acid.

3. If a nitrate is thrown upon *red-hot charcoal*, or if charcoal or some organic substance, paper for instance, is brought into contact with a nitrate in fusion, DEFLAGRATION takes place, *i. e.* the charcoal burns at the

expense of the oxygen of the nitric acid, the combustion being attended with vivid scintillation.

4. If a mixture of a nitrate with *cyanide of potassium* in powder is heated on a platinum plate, a vivid DEFLAGRATION will ensue, attended with distinct ignition and detonation. Even very minute quantities of nitrates may be detected by this reaction.

5. If the solution of a nitrate is mixed with one-fourth part of its amount of concentrated sulphuric acid, and a crystal of *sulphate of protoxide of iron* thrown into the cooled mixture, the fluid immediately surrounding the crystal acquires a DARK BROWN COLOR, which generally disappears upon simple agitation of the fluid, and invariably upon the application of heat. In this process, the nitric acid is decomposed by the protoxide of iron, three-fifths of its oxygen combining with the protoxide and converting a portion of it into sesquioxide, whilst the remaining nitric oxide combines with the remaining portion of the protoxide of iron, and forms with it a peculiar compound, which dissolves in water, imparting a brownish-black color to the fluid.

6. If to the solution of a nitrate some sulphuric acid is added, and as much *solution of indigo* in sulphuric acid as will impart a faint light blue tint to the fluid, and the mixture is heated to boiling, the blue color changes to a faint yellowish tint, or the fluid becomes colorless. This change of color is owing to the oxidation of the indigo at the expense of the oxygen of the nitric acid which is liberated by the sulphuric acid. It must be borne in mind, however, that several other substances also cause decoloration of solution of indigo—free chlorine more particularly produces this effect.

7. If concentrated sulphuric acid is poured over a mixture of a nitrate with *copper-filings*, in a test-tube, the air in the latter acquires a yellowish-red tint, owing to the nitric oxide gas which is liberated upon the oxidation of the copper by the nitric acid, combining with the oxygen of the air and forming nitrous acid. This coloration may be observed most distinctly by looking lengthways through the tube.

§ 150.

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

1. Chloric acid, in its most highly concentrated solution, is a yellow oily fluid; its odor resembles that of nitric acid. It first reddens litmus and then bleaches it. Dilute chloric acid is colorless and inodorous.

2. All chlorates are soluble in water. When chlorates are heated to redness, the whole of their oxygen escapes and metallic chlorides remain.

3. Heated with *charcoal* or some organic substance, the chlorates DEFLAGRATE, and this with far greater violence than the nitrates.

4. If a mixture of a chlorate with *cyanide of potassium* is heated on a

platinum foil, **DEFLAGRATION** takes place, attended with strong detonation and ignition, even though the chlorate be present only in very small quantity. (This experiment should be made with minute quantities only.

5. Free chloric acid oxidizes and decolorizes *indigo* in the same manner as nitric acid; consequently if the solution of a chlorate is mixed with sulphuric acid and solution of indigo, and the mixture heated to boiling, the same reaction is observed as with nitric acid (see § 149, 6).

6. If the solution of a chlorate is colored light blue with some *solution of indigo* in sulphuric acid, a little dilute sulphuric acid added, and a solution of sulphite of soda dropped cautiously into the blue fluid, the color of the indigo disappears immediately. The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric acid of its oxygen, and the liberated chlorine decolorizes the indigo.

7. Upon heating chlorates with *hydrochloric acid*, the constituents of the two acids decompose, forming water, chlorine, and bichlorate of chlorous acid ($Cl\,O_3, 2\,Cl\,O_5$). The test-tube in which the experiment is made becomes filled in this process with a greenish-yellow gas of a very disagreeable odor resembling that of chlorine; the hydrochloric acid acquires a greenish-yellow color.

8. *Concentrated sulphuric acid*, poured over a chlorate, converts two-thirds of the metallic oxide into a sulphate and the remaining one-third into perchlorate; this conversion is attended, moreover, with liberation of chlorate of chlorous acid, which imparts an intensely yellow tint to the sulphuric acid, and manifests its presence by its odor and the greenish color of the evolved gas. $[3\,(K\,O, Cl\,O_5) + 4\,S\,O_3 = 2\,(K\,O, 2\,S\,O_3) + K\,O, Cl\,O_7 + (Cl\,O_3, Cl\,O_5)]$. The application of heat must be avoided in this experiment, and the quantities operated upon should be very minute, since otherwise the decomposition might take place with such force as to cause an explosion.

§ 151.

Recapitulation and remarks.—Of all the reactions which have been suggested to effect the detection of nitric acid, those with sulphate of protoxide of iron and sulphuric acid, and with copper filings and sulphuric acid, give the most positive results; with regard to deflagration with charcoal, detonation with cyanide of potassium, and decoloration of solution of indigo, we have seen that these reactions belong equally to chlorates as to nitrates, and are consequently decisive only when no chloric acid is present. The best way to ascertain whether chloric acid is present or not, is to ignite the sample under examination, dissolve the mass, and test the solution with nitrate of silver. If a chlorate is present, this is converted into a chloride upon the ignition of the sample, and nitrate of silver will now precipitate chloride of silver from the solution. However, the process is thus simple only if no chloride is present along with the chlorate. But in presence of a chloride, the latter must be removed first by adding nitrate of silver to the solution as long as a precipitate continues to form, and filtering the fluid from the precipitate; the filtrate is then evaporated to dryness, and the residue ignited. It is, however, generally unnecessary to pursue this circuitous way, since the reactions with concentrated sulphuric acid, and with indigo and sulphurous acid, are sufficiently marked and characteristic to afford positive proof of the presence of chloric acid.

II. Organic Acids.

FIRST GROUP.

ACIDS WHICH ARE INVARIABLY PRECIPITATED BY CHLORIDE OF CALCIUM: *Oxalic Acid—Tartaric Acid—Citric Acid—Malic Acid—Paratartaric or Racemic Acid.*

§ 152.

a. Oxalic acid.

For the reactions of oxalic acid I refer to § 137.

b. Tartaric acid* ($C_4 H_2 O_5 = \bar{T}$).

1. The hydrate of tartaric acid ($C_4 H_2 O_5, H O$) forms colorless crystals of an agreeable acid taste, which are persistent in the air, and soluble in water and in spirit of wine. Tartaric acid when heated fuses at first, and afterwards becomes carbonized, emitting during the process a very peculiar and highly characteristic odor, which resembles that of burnt sugar.

2. The tartrates with alkaline bases are soluble in water, and so are those with the metallic oxides of the third and fourth group; those of the tartrates which are insoluble in water dissolve in hydrochloric or nitric acid. The tartrates suffer decomposition when heated to redness; charcoal separates, and the same peculiar odor is emitted as attends the carbonization of free tartaric acid.

3. If to a solution of tartaric acid, or to that of a tartrate, solution of *sesquioxide of iron, protoxide of manganese* or *alumina* is added, and then ammonia or potassa, no precipitation of sesquioxide of iron, protoxide of manganese or alumina will ensue, since the double tartrates formed are not decomposed by alkalies. Tartaric acid prevents also the precipitation of several other oxides by alkalies.

4. Free tartaric acid produces with *salts of potassa,* and more particularly with the acetate, a difficultly soluble precipitate of BITARTRATE

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* It will be observed that some of the formulæ for the organic acids differ from those in use in English works; but as this does not affect the results, it has been deemed best to adhere to the German text.

OF POTASSA. A similar precipitate is formed, when acetate of potassa and free acetic acid are added to the solution of a neutral tartrate. The acid tartrate of potassa dissolves readily in alkalies and mineral acids; tartaric acid and acetic acid do not increase its solubility in water. The separation of the bitartrate of potassa precipitate may be greatly promoted by shaking, or by rubbing the sides of the vessel with a glass rod.

5. *Chloride of calcium* throws down from the solutions of neutral tartrates a white precipitate of TARTRATE OF LIME ($Ca\,O, \bar{T}$). Presence of ammoniacal salts retards the formation of this precipitate for a more or less considerable space of time. Agitation of the fluid, or friction on the sides of the vessel, promotes the separation of the precipitate. Tartrate of lime dissolves in a cold solution of potassa or soda to a clear fluid. But upon boiling this solution, the dissolved tartrate of lime separates again in the form of a gelatinous precipitate, which redissolves upon cooling.

6. *Lime-water* produces in solutions of neutral tartrates, and also in a solution of free tartaric acid, if added to alkaline reaction, white precipitates which dissolve readily in tartaric acid, and also in solution of chloride of ammonium. From these solutions the tartrate of lime separates again, after the lapse of several hours, in the form of small crystals deposited upon the sides of the vessel.

7. *Solution of sulphate of lime* fails to produce a precipitate in a solution of tartaric acid; in solutions of neutral tartrates it produces a trifling precipitate after the lapse of some time.

8. Upon heating hydrate of tartaric acid, or a tartrate, with hydrate of sulphuric acid, the sulphuric acid acquires a brown color almost simultaneously with the evolution of gas.

§ 153.

c. Citric acid ($C_4\,H_2\,O_4 = \overline{Ci}$).

1. Crystallized citric acid, obtained by the cooling of its solution, has the formula, $3\,\overline{Ci}, 4\,H\,O$. It crystallizes in transparent, colorless, and inodorous crystals of an agreeable acid taste, which dissolve readily in water and in spirit of wine, and are unalterable in the air. When subjected to the action of heat, citric acid fuses at first, and afterwards carbonizes, with evolution of pungent acid fumes, the odor of which may be readily distinguished from that emitted by tartaric acid upon carbonization.

2. The citrates with alkaline bases are readily soluble in water, both in the neutral and acid state; the same applies to the compounds of citric acid with such of the metallic oxides as are weak bases, sesquioxide of iron, for instance. Citrates, like tartrates, and for the same reason, prevent the precipitation of sesquioxide of iron, protoxide of manganese, alumina, &c., by alkalies.

3. *Chloride of calcium* fails to produce a precipitate in solution of free citric acid, even upon boiling; but a precipitate of NEUTRAL CITRATE OF LIME ($CaO, \overline{Ci}$) forms immediately upon saturating the free citric acid with potassa or soda. This precipitate is insoluble in potassa, but it dissolves readily in solution of chloride of ammonium; upon boiling this solution, neutral citrate of lime separates again in the form of a white crystalline precipitate. If a solution of citric acid mixed with chloride of calcium is saturated with ammonia, a precipitate will form in the cold only after many hours' standing, but upon boiling the clear fluid, neutral citrate of lime will suddenly precipitate.

4. *Lime-water* produces no precipitate in cold solutions of citric acid or of citrates. But upon heating the solution to boiling, with a tolerable excess of hot lime-water, a white precipitate of CITRATE OF LIME is formed, of which the greater portion redissolves upon cooling.

5. *Acetate of lead*, when added in excess to a solution of citric acid, produces a white precipitate of CITRATE OF LEAD ($PbO, \overline{Ci}$), which is very difficultly soluble in ammonia, but dissolves readily in citrate of ammonia. The addition of citric acid in excess to a solution of neutral acetate of lead also gives rise to the formation of a precipitate of citrate of lead; but this precipitate redissolves readily upon the addition of ammonia. We have just now seen that the citrate of lead is but very sparingly soluble in ammonia; the solution therefore is caused here by the citrate of ammonia which the excess of the acid forms with the ammonia added.

6. Upon heating citric acid or citrates with concentrated sulphuric acid carbonic oxide and carbonic acid escape at first, the sulphuric acid retaining its natural color; upon continued ebullition, however, the solution acquires a dark color, and sulphurous acid is evolved.

§ 154.

d. MALIC ACID ($C_4 H_2 O_4 = \overline{M}$).

1. Hydrate of malic acid ($\overline{M}, HO$) crystallizes with great difficulty, forming crystalline crusts, which deliquesce in the air, and dissolve readily in water and in alcohol. Exposed to a temperature of 392°, malic acid is resolved into MALEIC ACID ($C_4 H O_3$) and FUMARIC ACID ($C_4 H O_3$), which latter is upon continued application of heat also converted into the former. This deportment of malic acid is highly characteristic. If the experiment is made in a small spoon, pungent acid vapors of maleic acid are evolved with effervescence. If the experiment is made in a small tube, these fumes condense to crystals in the colder part of the tube.

2. Malic acid forms with most bases, salts soluble in water. The acid malate of potassa is not difficultly soluble in water. Malic acid prevents, like tartaric acid, the precipitation of sesquioxide of iron, &c., by alkalies.

3. *Chloride of calcium* fails to produce a precipitate in solutions of free malic acid. Even after saturation with potassa or soda no precipitate is formed. But upon boiling, a precipitate of malate of lime separates from concentrated solutions. If the precipitated malate of lime is dissolved in a very little hydrochloric acid, ammonia added to the solution, and the fluid boiled, the malate of lime separates again; but if it is dissolved in a somewhat larger quantity of hydrochloric acid, it will not reprecipitate, after addition of ammonia in excess, even upon continued boiling. Alcohol precipitates it immediately from a solution of the kind.

4. *Lime-water* produces no precipitate, either in solutions of free malic acid or in solutions of malates.

5. *Acetate of lead* throws down from solutions of malic acid and of malates, a white precipitate of MALATE OF LEAD ($PbO, \overline{M}$). The precipitation is the most complete, if the fluid is neutralized by ammonia, as the precipitate is soluble in free malic acid and acetic acid, and also in ammonia. If the fluid in which the precipitate is suspended is heated to boiling, the precipitate fuses to a mass resembling resin melted under water. This reaction is distinctly marked only when the malate of lead is tolerably pure; if it is mixed with other salts of lead—if, for instance, ammonia is added to alkaline reaction, it is only imperfect or fails altogether to make its appearance.

6. Upon heating malic acid with concentrated sulphuric acid carbonic acid and carbonic oxide gas are evolved at first; the fluid then acquires a brown and black tint, and sulphurous acid is given off.

§ 155.

Recapitulation and remarks.—Of the organic acids of this group, the oxalic acid is most strongly characterized by the insolubility of its lime-salt in solution of chloride of ammonium or in free acetic acid, and also by the immediate precipitation of its solution by solution of sulphate of lime. Tartaric acid is characterized by the difficult solubility of the acid potassa salt, the solubility of the lime salt in cold solution of soda and of potassa, and the peculiar odor which the acid and its salts emit upon heating. Citric acid is most strongly characterized by its deportment with lime-water, or with chloride of calcium and ammonia in presence of chloride of ammonium. Malic acid would be sufficiently characterized by the deportment of malate of lead when heated under water, were this reaction more sensitive, and not so easily prevented by the presence of other acids. The safest means of detecting malic acid, is to convert it into maleic acid by heating in a glass tube; but this conversion can be effected successfully only with pure hydrate of malic acid. If only one of the four acids is present in a solution, lime-water will suffice to indicate which of the four is present; since malic acid is not precipitated by this reagent, citric acid only upon boiling, tartaric acid and oxalic acid already in the cold; and the tartrate of lime redissolves upon addition of chloride of ammonium, whilst the oxalate does not. If all four acids together are present in a solution, the oxalic acid and tartaric acid are precipitated first by chloride of calcium and ammonia, in presence of chloride of ammonium (the tartrate of lime separates under these circumstances completely only after some time; it is separated from the oxalate by treating with solution of potassa); the citrate of lime is then thrown down by boiling, and the malate finally by means of spirit of wine. The precipitate produced by spirit of wine must never be taken positively for malate of lime, without further proof, since the sulphate and other salts of lime are also precipitated by that agent under the same circumstances. Positive conviction can only be attained by the production of hydrate of malic acid from the lime-salt. To effect this, the precipitate is dissolved in acetic acid, spirit of wine added, and the fluid filtered, if necessary. The filtrate is precipitated with acetate of lead, the fluid neutralized with ammonia, the precipitate washed, stirred in water, decomposed by hydrosulphuric acid, and the filtrate evaporated to dryness.

§ 156.

Appendix: RACEMIC ACID, OR PARATARTARIC ACID ($C_4H_2O_5=\overline{R}$).

The formula of crystallized racemic acid is, $\overline{R}, HO+aq$. The crystallization water escapes slowly in the air, but rapidly at 212° (difference between racemic acid and tartaric acid). To solvents the racemic acid comports itself like the tartaric acid. The racemates also show very similar deportment to that of the tartrates. However, many of them differ in the amount of water, in form and solubility from the corresponding tartrates. *Chloride of calcium* precipitates from the solutions of free racemic acid and of racemates **racemate of lime** ($CaO, \overline{R}$), as a white powder. The precipitate is insoluble in chloride of ammonium, soluble in solution of soda and of potassa, from which solutions it falls down again upon boiling (difference between racemic acid and oxalic acid). *Lime-water* added in excess, produces immediately a white precipitate insoluble in chloride of ammonium (difference between racemic acid and tartaric acid). *Solution of sulphate of lime* does not immediately produce a precipitate in a solution of racemic acid (difference between racemic acid and oxalic acid); however, after ten or fifteen minutes racemate of lime separates (difference between racemic acid and tartaric acid); in solutions of neutral racemates the precipitate forms immediately. With *salts of potassa* racemic acid comports itself like tartaric acid.

SECOND GROUP OF THE ORGANIC ACIDS.

ACIDS WHICH CHLORIDE OF CALCIUM FAILS TO PRECIPITATE UNDER ANY CIRCUMSTANCES, BUT WHICH ARE PRECIPITATED FROM NEUTRAL SOLUTIONS BY SESQUICHLORIDE OF IRON: *Succinic Acid —Benzoic Acid.*

§ 157.

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

1. Succinic acid forms colorless and inodorous crystalline scales or prisms, of feebly acid taste, which are readily soluble in water, alcohol, and ether, and volatilize without residue when exposed to the action of heat. The officinal acid has an empyreumatic odor, and leaves a small carbonaceous residue upon volatilization.

2. The succinates are decomposed at a red heat, with the exception of succinate of ammonia; those which have an alkali or alkaline earth for base, are converted into carbonates in this process. Most of the succinates are soluble in water.

3. *Sesquichloride of iron* produces in solutions of neutral succinates of the alkalies a brownish pale red bulky precipitate of SUCCINATE OF SESQUIOXIDE OF IRON ($Fe_2 O_3, \overline{S}_2$). This precipitate dissolves readily in acids; ammonia decomposes it, causing the separation of a less bulky precipitate of a highly basic succinate of sesquioxide of iron, and combining with the greater portion of the acid, forms succinate of ammonia, which dissolves.

4. *Acetate of lead* gives with succinic acid a white precipitate of neutral SUCCINATE OF LEAD ($Pb O, \overline{S}$), which is soluble in an excess of succinic acid, in solution of acetate of lead, in nitric acid, and also though less readily, in acetic acid. Treated with ammonia the neutral succinate of lead is converted into a basic salt ($3\ Pb O, \overline{S}$.)

5. A mixture of *alcohol*, *ammonia*, and *solution of chloride of barium* produces in solutions of free succinic acid and of succinates a white precipitate of SUCCINATE OF BARYTA ($Ba O, \overline{S}$).

6. *Nitrate of suboxide of mercury* and *nitrate of silver* also precipitate the succinates; the precipitates, however, are not possessed of any characteristic properties.

§ 158.

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

1. Pure hydrate of benzoic acid forms white scales or needles, or simply a crystalline powder. It volatilizes completely when heated. The fumes

of benzoic acid cause a peculiar, irritating sensation in the throat, and provoke coughing. The common officinal hydrate of benzoic acid has the odor of benzoin, and leaves a small carbonaceous residue upon volatilization. Hydrate of benzoic acid is very sparingly soluble in cold water, but it dissolves pretty readily in hot water and in alcohol.

2. Most of the benzoates are soluble in water; only those with weak bases, *e. g.* sesquioxide of iron, are insoluble. The soluble benzoates have a peculiar, pungent taste. The addition of a *strong acid* to aqueous solutions of benzoates displaces the benzoic acid, which separates as hydrate in the form of a dazzling white, sparingly soluble powder. Benzoic acid is expelled in the same way from the insoluble benzoates, by such strong acids as form soluble salts with the bases with which the benzoic acid is combined.

3. Benzoic acid comports itself with *sesquichloride of iron* like succinic acid. The BENZOATE OF SESQUIOXIDE OF IRON ($Fe_2O_3, 3\,Bz\,O$), however, is of a far lighter and more yellow color than the succinate. It is decomposed by ammonia in the same manner as the latter.

4. *Acetate of lead* fails to precipitate free benzoic acid and benzoate of ammonia, at least immediately; but it produces white flocculent precipitates in solutions of benzoates with fixed alkaline bases.

5. A mixture of *alcohol, ammonia,* and *solution of chloride of barium* produces NO precipitate in solutions of free benzoic acid or of the alkaline benzoates.

§ 159.

Recapitulation and remarks.—Succinic and benzoic acids are distinguished from all other acids by their ready volatility and their deportment with sesquichloride of iron. They are distinguished from one another by the different color of their salts with sesquioxide of iron, and also by their different deportment with chloride of barium and alcohol, but principally by their different degrees of solubility, succinic acid being readily soluble in water, whilst benzoic acid is very difficult of solution. Succinic acid is seldom perfectly pure, and may therefore often be detected by the odor of oil of amber which it emits.

The detection of the two acids, when present in the same solution with other acids may be effected as follows: precipitate with sesquichloride of iron, warm the precipitate with ammonia, filter, concentrate the solution, divide it into two parts, and mix one part with hydrochloric acid, the other with chloride of barium and alcohol.

Succinic acid and benzoic acid do not prevent the precipitation of sesquioxide of iron, alumina, &c., by alkalies.

THIRD GROUP OF THE ORGANIC ACIDS.

ACIDS WHICH ARE NOT PRECIPITATED BY CHLORIDE OF CALCIUM NOR BY SESQUICHLORIDE OF IRON: *Acetic Acid—Formic Acid.*

§ 160.

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

1. The hydrate of acetic acid forms transparent crystalline scales, which fuse at 62·6° to a colorless fluid of a peculiar pungent odor, and exceedingly acid taste. When exposed to the action of heat, it volatilizes completely, forming pungent inflammable vapors, which burn with a blue flame. It is miscible with water in all proportions; it is to such mixtures of the acid with water that the name of acetic acid is commonly applied. The hydrate of acetic acid is also soluble in alcohol.

2. The acetates undergo decomposition at a red heat; among the products of this decomposition we generally find hydrate of acetic acid, and almost invariably acetone ($C_3 H_3 O$). The acetates of the alkalies and alkaline earths are converted into carbonates in this process; of the acetates with metallic bases many leave the metal behind in the pure state, others in the form of oxide. Most of the residues which the acetates leave upon ignition are carbonaceous. Nearly all acetates dissolve in water and in alcohol; most of them are readily soluble in water, a few only are difficult of solution in that menstruum.

3. If *sesquichloride of iron* is added to acetic acid, and the acid is then saturated with ammonia, or if a neutral acetate is mixed with sesquichloride of iron, the fluid acquires a deep dark red color, owing to the formation of ACETATE OF SESQUIOXIDE OF IRON. Upon boiling, the fluid becomes colorless, if it contains an excess of acetate, the whole of the sesquioxide of iron precipitating as a hyperbasic acetate, in the form of brownish-yellow flakes. Ammonia precipitates from it the whole of the sesquioxide of iron as hydrate.

4. Neutral acetates (but not free acetic acid) give 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 easily in hot water, but separate again upon cooling, in the form of very fine crystals. Ammonia dissolves them readily; free acetic acid does not increase their solubility in water.

5. *Nitrate of suboxide of mercury* produces in solutions of acetic acid, and more readily still in solutions of acetates, white scaly crystalline precipitates of ACETATE OF SUBOXIDE OF MERCURY ($Hg_2 O, \bar{A}$), which are sparingly soluble in water and acetic acid in the cold, but dissolve without difficulty in an excess of the precipitant. The precipitates dissolve in water

upon heating, but separate again upon cooling, in the form of small crystals; in this process, the salt undergoes partial decomposition: a portion of the mercury separates in the metallic state, and imparts a gray color to the precipitate. If the acetate of suboxide of mercury is boiled with dilute acetic acid instead of water, the quantity of the metallic mercury which separates is exceedingly minute.

6. When acetates are heated with *dilute sulphuric acid,* ACETIC ACID is evolved, and may be detected by its pungent odor. But if the acetates are heated with a mixture of equal portions of *concentrated sulphuric acid* and *alcohol,* ACETIC ETHER ($C_4 H_5 O, \bar{A} = Ae O, \bar{A}$) is formed. The odor of this ether is highly characteristic and agreeable; it is most distinct upon shaking the mixture when somewhat cooled, and is less liable to lead to mistakes than the pungent odor of the free acetic acid.

7. If acetates are distilled with dilute sulphuric acid, and the distillate digested with an excess of oxide of lead, part of the latter dissolves as basic acetate of lead, which may be readily detected by its alkaline reaction.

§ 161.

b. FORMIC ACID ($C_2 H O_3 = Fo O_3$).

1. The hydrate of formic acid is a transparent, colorless, slightly fuming liquid, of a characteristic and exceedingly penetrating odor. When cooled to below 32°, it crystallizes in colorless plates. It is miscible in all proportions with water and with alcohol. When exposed to the action of heat, it volatilizes completely; the vapors are inflammable and burn with a blue flame.

2. The formiates, like the corresponding acetates, leave upon ignition, either carbonates, oxides, or metals behind, the process being attended with separation of charcoal, and escape of carbide of hydrogen, carbonic acid, and water. All the compounds of formic acid with bases are soluble in water; alcohol likewise dissolves some of them.

3. Formic acid presents the same deportment with *sesquichloride of iron* as acetic acid.

4. *Nitrate of silver* fails to precipitate free formic acid, and decomposes the alkaline formiates only in concentrated solutions. The white, sparingly soluble, crystalline precipitate of FORMIATE OF SILVER ($Ag O, Fo O_3$) acquires very rapidly a darker tint, owing to the separation of metallic silver. This reduction of the oxide of silver to the metallic state takes place, even in the cold, after the lapse of some time, but immediately, upon applying heat to the fluid containing the precipitated formiate of silver. The same reduction of the oxide of silver to the metallic state takes place in a solution of free formic acid, and also in solutions of formiates so dilute that the addition of the nitrate of silver has failed to produce a precipitate. The rationale of this reduction is as follows: the

formic acid, which may be looked upon as a compound of carbonic oxide with water, deprives the oxide of silver of its oxygen, thus causing the formation of carbonic acid, which escapes, and of water, whilst the reduced silver separates in the metallic state.

5. *Nitrate of suboxide of mercury* gives no precipitate with free formic acid; but in concentrated solutions of alkaline formiates this reagent produces a white, sparingly soluble precipitate of FORMIATE OF SUBOXIDE OF MERCURY (Hg_2 O, Fo O_3), which rapidly becomes gray, owing to the separation of metallic mercury. Complete reduction ensues, even in the cold, after the lapse of some time, but is immediate upon application of heat. This reduction is also attended with the formation of carbonic acid and water, and takes place both in solutions of free formic acid, and in fluids so highly dilute that the formiate of suboxide of mercury is retained in solution, instead of precipitating.

6. If formic acid or an alkaline formiate is heated to from 140° to 158°, with *chloride of mercury*, SUBCHLORIDE OF MERCURY precipitates. If the mixture is heated to 212°, metallic mercury separates along with the subchloride.

7. If formic acid or a formiate is heated with *concentrated sulphuric acid*, the formic acid is resolved into water, and carbonic oxide gas, which escapes with effervescence, and if kindled, burns with a blue flame. The fluid does not turn black in this process. The rationale of this decomposition of the formic acid is this: the sulphuric acid withdraws from the formic acid the water or the oxide necessary for the existence of the latter acid, and thus occasions a transposition of its elements ($C_2\,H\,O_3 = 2\,C\,O + H\,O$). Upon heating a formiate with dilute sulphuric acid formic acid escapes, and may be readily detected by its odor. Upon heating a formiate with a mixture of sulphuric acid and alcohol, formic ether is evolved, which is characterized by its peculiar arrack-like smell.

§ 162.

Recapitulation and remarks.—Acetic acid and formic acid may be distilled over with water, and form with sesquioxide of iron soluble neutral salts which dissolve in water, imparting to the fluid a blood-red color, and are decomposed upon boiling. These reactions distinguish the two acids of the third group from the other organic acids. From each other the two acids are distinguished by the odor of their hydrates and ethyle compounds, and by their different deportment with salts of silver and salts of mercury, oxide of lead, and concentrated sulphuric acid. The separation of acetic acid from formic acid is effected by heating the mixture of the two acids with an excess of oxide of mercury or oxide of silver. Formic acid reduces the oxides, and suffers decomposition, being resolved into carbonic oxide and water; whilst the acetic acid combines with them, forming acetates which remain 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 PART OF THE PRESENT WORK IN PARTICULAR.

THE knowledge of reagents and of the deportment which other bodies exhibit with them, enables us to ascertain at once whether a compound, of which the physical properties permit an inference as to its nature, is in reality what we suspect it to be. Thus, for instance, by a few simple reactions we prove whether a body which appears to be calcareous spar, is really carbonate of lime, and that another, which we deem gypsum, is sulphate of lime. This knowledge usually suffices to ascertain whether a certain body is present or not in a compound; for instance, whether or not a white powder contains subchloride of mercury. But if our design is to ascertain the chemical nature of a substance entirely unknown to us—if we wish to discover *all* the constituents of a mixture or chemical compound—if we intend to prove that, besides certain bodies which we have detected in a mixture or compound, no other substance *can* be present—consequently, if a *complete qualitative analysis* is our object, the mere knowledge of the reagents, and of the reactions of other bodies with them, will not suffice for the attainment of this end; this requires the additional knowledge of a systematic and progressive course of analysis, in other words, the knowledge of the *order* and *succession* in which solvents, and general and special reagents, are to be applied, both to effect the speedy and perfect detection of every component element of a compound or mixture, and to prove with certainty the absence of all other substances. If we do not possess the knowledge of this systematic course, or if, in the hope of attaining our object more rapidly, we adhere to no method whatever in our investigations and experiments, analyzing becomes (at least in the hands of a novice) mere guess work, and the results obtained are no longer the fruits of scientific calculation, but mere matters of accident, which sometimes may prove lucky hits, and at others total failures.

Every analytical investigation must therefore be based upon a definite method. But it is not by any means necessary that this method should be the same in all cases. Practice, reflection, and a due attention to circumstances will, on the contrary, generally lead to the adoption of different methods for different cases. However, all analytical methods agree in this, that the substances present, or supposed to be present, in a compound or mixture, are in the first place classed into certain groups, which are then again subdivided, until the individual detection of the various substances present is finally accomplished. The diversity of analytical methods depends partly on the order and succession 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 imaginable case, so that afterwards, when we have acquired some practice in analysis, we may be able to determine which modification of the general method will, in certain given cases, most readily 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 simplicity with the greatest possible security, is the object of the *First Section* of the second part of this work.

The elements and compounds comprised in it are the same which we have studied in Part I., with the exception of the four substances given in that part simply by way of appendix.

The *First Section* of the Second Part consists of PRACTICAL INSTRUCTIONS IN ANALYSIS, wherein I have laid down a systematic course which, with due care and attention, will, by progressive steps, lead speedily and safely to the attainment of the end in view.

The subdivisions of this practical course are, 1. Preliminary examination; 2. Solution; 3. Actual examination.

The third subdivision (the *actual examination*) is again subdivided into, 1. Examination of compounds in which but one base and one acid are assumed to be present; and, 2. Examination of mixtures or compounds in which all the substances treated of in the present work are assumed to be present. With respect to the latter section, I have to remark that where the preliminary examination has not afforded the most positive conviction of the absence of certain groups of substances, the student cannot safely disregard any of the paragraphs referred to. In cases where the intention is simply to test a compound or mixture for certain substances, and not to ascertain all its constituents, it will be easy to select the particular numbers which ought to be attended to.

As the construction of a universally applicable systematic course of analysis requires due regard to, and provision for, every contingency that may possibly arise, it is self-evident that the various bodies here treated of may indeed be combined or mixed in every imaginable way, but must invariably be assumed to be free from the least trace of extraneous organic matter, as the presence of such matter might prevent or obscure many reactions, and variously modify others.

Although the general analytical course laid down here is devised and arranged in a manner to suit all possible contingencies, with a very few exceptions, still there are special cases in which it may be advisable to modify it. A preliminary treatment of the substance is also sometimes necessary, before the actual analysis can be proceeded with ; the presence of coloring, slimy, organic matters more especially, demand some preliminary operations.

The *Second Section* of this Part will be found to contain a detailed description of the special methods employed to effect the analysis of a few important compounds and mixtures which chemists are frequently called upon to examine. Some of these methods show how the analytical processes become simplified as the number of substances decrease to which regard must be had in the analysis.

In conclusion, as an intelligent and successful pursuit of analysis is possible only with an accurate knowledge of the principles whereon the detection and separation of bodies depends, since this knowledge alone can furnish the student with a guide to the selection of the proper reagents, and the order in which they ought to be applied, I have given in the *Third Section* of the Second Part an explanation and elucidation of the general analytical process, with numerous additions to the practical operations. As this third section may properly be regarded as the key to the first and second sections, I strongly recommend students to make themselves early and thoroughly acquainted with it. I have devoted a special section to the theoretical explanation of the process, as I think it will be understood better in a connected form, than it would have been by explanatory additions to several paragraphs, which, moreover, might have materially interfered with the plainness and perspicuity of the plan of the practical process.

SECTION I.

PRACTICAL PROCESS.*

I. PRELIMINARY EXAMINATION.

§ 163.

1. Examine, in the first place, the physical properties—(color, shape, hardness, gravity, odor, &c.)—of the substance intended for analysis,

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* Consult also the observations and additions in the Third Section.

since these will often enable you in some measure to infer the nature of the substance. Before proceeding to the application of any chemical process, you must always consider how much of the substance to be analyzed you have at command, since it is necessary, at this early period of the examination, to calculate the quantity which may be used in the preliminary investigation. A reasonable economy is in all cases advisable, even though you may possess the substance in large quantities; and lay it down as a fixed rule, never to use at once the whole of what you possess of a substance, but always to keep a portion of it for unforeseen contingencies, and for confirmatory experiments.

A. THE BODY UNDER EXAMINATION IS SOLID.

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

§ 164.

1. The substance is fit for examination if in powder or in minute crystals; but if in larger crystals or in solid pieces, it is necessary in the first place to reduce a portion of it to powder, if practicable. Bodies of the softer kind may be triturated in a porcelain mortar; those of a harder kind must first be broken into small pieces in a steel mortar, or upon a steel anvil, and the pieces then be triturated in an agate mortar. 2*

2. Heat some of the powder on a slip of platinum foil, or in a small iron spoon, over a spirit-lamp: the resulting reactions may lead to many positive or probable conclusions regarding the nature of the substance. 3

a. THE SUBSTANCE REMAINS UNALTERED: absence of organic matters, salts containing water, readily fusible matters, and volatile bodies. 4

b. IT FUSES READILY AND RE-SOLIDIFIES WITH EXPULSION OF AQUEOUS VAPOR: salts which contain water of crystallization. If the solidified residue fuses again upon the application of an increased heat *c* must be had regard to. 5

c. IT FUSES WITHOUT EXPULSION OF AQUEOUS VAPOR. A small piece of paper is added to the melted mass; if deflagration takes place, this indicates the presence of NITRATES, or also of CHLORATES. 6

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. 7

α. No odor is emitted. In this case you have to look more particularly for compounds of AMMONIA, MERCURY, and ARSENIC.

β. An odor is emitted. If of sulphurous acid, SULPHUR is

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[*] These marginal numbers are simply intended to facilitate references.

present; whilst the smell of iodine, with violet vapors, denotes the presence of free IODINE. Free BENZOIC ACID, and many other substances, may also be detected by the odor of their vapor.

8 *e.* THE SUBSTANCE IS A WHITE POWDER, TURNING YELLOW UPON THE APPLICATION OF HEAT: this indicates OXIDE OF ZINC, BINOXIDE OF TIN, OXIDE OF LEAD, or TEROXIDE OF BISMUTH; the two latter retain the yellow color upon cooling, whilst the oxide of zinc resumes its white color, and the binoxide of tin, which acquires a brownish tint upon the application of heat, appears, when cold again, of a dirty light yellow color.

9 *f.* CARBONIZATION TAKES PLACE: organic substances. If the residue effervesces with acids, whilst the original substance does not, this indicates the presence of ORGANIC ACIDS combined with alkalies or alkaline earths. Odor of cyanogen indicates the presence of a CYANIDE.

Many substances swell up considerably upon the application of heat; as for instance, borax, sulphate of alumina, &c.; others decrepitate, *e. g.* chloride of sodium, chloride of potassium, &c.; these phenomena, however, are of a less conclusive nature than the preceding.

10 3. Put a small portion of the substance on a charcoal support, and expose to the reducing flame of the blowpipe.

Since most of the reactions described in § 164, 2 (3), are also produced by this process, I will enumerate here only those which result more particularly and exclusively from its application.

11 *a.* THE SUBSTANCE VOLATILIZES PARTLY OR COMPLETELY. This indicates, besides the substances mentioned in § 164, 2, *d.* (7), also TEROXIDE OF ANTIMONY, and several other oxides (compare § 164, 3, *d.* *β.*) (16). The teroxide of antimony fuses, previously to volatilizing in the form of a white vapor. The presence of ARSENIOUS or ARSENIC ACID is indicated by the characteristic odor of garlic, which is rendered more strongly perceptible by adding carbonate of soda to the sample before exposing it to the blowpipe flame.

12 *b.* THE BODY FUSES, AND IS ABSORBED BY THE CHARCOAL; this indicates the presence of ALKALIES. In this case, put a portion of the pulverized substance upon the moistened loop of a platinum wire, and direct the point of the inner flame of the blowpipe upon it. If the oxidizing flame assumes a violet tint, this indicates the presence of POTASSA alone; if a yellow tint, the presence of SODA, with which potassa may however be mixed, even in considerable proportion, as the flame appears invariably yellow when both these alkalies are present.

c. **THE SUBSTANCE LEAVES AN INFUSIBLE WHITE RESIDUE ON THE CHARCOAL, EITHER AT ONCE, OR AFTER PREVIOUS MELTING IN THE WATER OF CRYSTALLIZATION.** This indicates more particularly the presence of baryta, strontia, lime, magnesia, alumina, oxide of zinc, and silicic acid. Among these substances, STRONTIA, LIME, MAGNESIA, and OXIDE OF ZINC, are distinguished by strong luminosity in the blowpipe flame. Moisten the white residue with a drop of solution of nitrate of protoxide of cobalt, and ignite again strongly. If the mass assumes a fine blue tint, this indicates the presence of ALUMINA; if a reddish tint, of MAGNESIA; if a green color, of ZINC. When SILICIC ACID is present, the mass also assumes a faint bluish tint, which must not be confounded with that proceeding from the presence of alumina. Silicic acid is characterized moreover by the formation of a clear bead, attended with effervescence, upon exposing the acid, in conjunction with carbonate of soda, to a strong blowpipe flame (§ 141). 13

d. **THE SUBSTANCE LEAVES AN INFUSIBLE RESIDUE OF A DIFFERENT COLOR, OR A REDUCTION TO THE METALLIC STATE TAKES PLACE, WITH OR WITHOUT INCRUSTATION OF THE CHARCOAL.** Mix a portion of the powder with carbonate of soda, and heat on charcoal in the reducing flame. 14

α. The continued application of a strong flame produces a metallic bead, without incrustation of the charcoal; this indicates the presence of GOLD, SILVER, TIN, or COPPER. The compounds of platinum, iron, cobalt, and nickel, are likewise reduced, but yield no metallic beads. 15

β. The charcoal support is coated with an incrustation, either with or without simultaneous formation of a metallic bead; this indicates the presence of BISMUTH, LEAD, CADMIUM, ANTIMONY, or ZINC. 16

aa. If, after cooling, the incrustation is white, ANTIMONY or ZINC may be supposed to be present. The coating produced by zinc appears yellow as long as it remains hot. The pure metallic bead of antimony continues to evolve white vapors, even for a long time after all application of heat has been withdrawn, and upon cooling generally becomes surrounded with crystals of teroxide of antimony. It is brittle under the stroke of the hammer. 17

bb. The incrustation, after cooling, is more or less yellow or brown; this indicates the presence of BISMUTH, LEAD, or CADMIUM. The yellow incrustation of oxide of cadmium inclines slightly to orange; the brownish-yellow incrustations of oxide of lead and teroxide of bismuth change to a light 18 yellow upon cooling. Upon reduction, cadmium volatilizes immediately. The globules of lead are very malleable, whilst those of bismuth are brittle under the stroke of the hammer.

4. Fuse a small portion with a bead of microcosmic salt, and expose for some time to the outer flame of the blowpipe. 19

a. THE SUBSTANCE DISSOLVES READILY AND IN CONSIDERABLE QUANTITY, FORMING A CLEAR BEAD (WHILST HOT).

α. *The hot bead is colored:* 20

- BLUE, by candlelight inclining to violet—COBALT ;
- GREEN, upon cooling blue, in the reducing flame red—COPPER ;
- GREEN, very bright on cooling, unaltered in the reducing flame—CHROMIUM ;
- REDDISH-BROWN, on cooling light-yellow or colorless, in the reducing flame bottle-green—IRON ;
- DARK-YELLOW to REDDISH, becoming lighter or altogether colorless on cooling, when heated some time in the reducing flame gray—NICKEL ;
- YELLOWISH-BROWN, becoming of a lighter yellow or losing its color altogether on cooling, almost colorless in the reducing flame (especially after mixing with some tin), blackish-gray on cooling—BISMUTH ;
- BRIGHT YELLOW to OPAL, when cold rather dull, in the reducing flame whitish-gray—SILVER ;
- AMETHYST-RED, especially on cooling, colorless in the reducing flame, not quite clear—MANGANESE.

β. *The hot bead is colorless:* IT REMAINS CLEAR ON COOLING—ANTIMONY, ALUMINA, ZINC, CADMIUM, LEAD, LIME, MAGNESIA ; the latter five metals, when present in a somewhat large proportion, give enamel-white beads ; the bead of oxide of lead is yellow when saturated ; 21

IT BECOMES ENAMEL-WHITE ON COOLING, even though present only in small proportion—BARYTA, STRONTIA.

b. THE SUBSTANCE DISSOLVES SLOWLY AND ONLY IN SMALL QUANTITY : 22

α. The bead is colorless, even after cooling ; upon addition of a little sesquioxide of iron, it acquires the characteristic color of an iron bead—SILICA ;

β. The bead is colorless, and remains so after the addition of some sesquioxide of iron—TIN.

c. THE SUBSTANCE DOES NOT DISSOLVE, BUT FLOATS (IN THE METALLIC STATE) IN THE BEAD—GOLD, PLATINUM. 23

As the body under examination may consist of a mixture of the most heterogeneous elements, it is impossible to give here rigorously defined cases that shall offer at the same time the advantage of general applicability. If, therefore, reactions are observed in an experiment which proceeds from a combination of two or several substances, the conclusions drawn from these reactions must of course be modified accordingly.

§ 165.

II. THE SUBSTANCE IS A METAL OR AN ALLOY.

1. Heat a small portion of the substance with water, acidulated with acetic acid. 24

a. HYDROGEN GAS IS EVOLVED: this indicates the presence of a light metal (possibly also of manganese in the metallic state). The presence of alkalies and of alkaline earths must be had regard to in the actual examination.

b. NO HYDROGEN IS EVOLVED: this indicates the absence of light metals. Alkalies and alkaline earths may be altogether disregarded in the course of the special investigation.

2. Heat a portion of the substance on charcoal in the reducing flame of the blowpipe, and watch the reactions; for instance, whether the substance fuses, whether an incrustation is formed, or an odor emitted, &c. 25

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, NICKEL, or COBALT.

b. THE SUBSTANCE FUSES WITHOUT SIMULTANEOUS INCRUSTATION, AND WITHOUT ODOR: absence of antimony, zinc, lead, bismuth, cadmium, and arsenic; presence of GOLD, SILVER, or COPPER.

c. THE SUBSTANCE FUSES, AND AN INCRUSTATION IS FORMED, BUT NO ODOR EMITTED: absence of arsenic, and presence of ANTIMONY, ZINC, BISMUTH, LEAD, or CADMIUM (compare § 164, I. 3, *d.* β). (16).

d. THE SUBSTANCE EMITS THE ODOR OF GARLIC; ARSENIC is present. As regards the other reactions which may manifest themselves, I refer to *a.* *b.* or *c.* (25).

3. Heat a portion of the substance before the blowpipe in a glass tube, sealed at one end. 26

a. NO SUBLIMATE IS FORMED IN THE COLDER PART OF THE TUBE: absence of mercury.

b. A SUBLIMATE IS FORMED; presence of MERCURY, CADMIUM, or ARSENIC. The sublimate of mercury, which consists of small globules, cannot possibly be confounded with that of cadmium or arsenic.

§ 166.

B. THE SUBSTANCE UNDER EXAMINATION IS A FLUID.

1. Evaporate a small portion of the fluid in a platinum spoon, or in a small porcelain crucible, to ascertain whether it contains any matter in solution; if a residue remains examine it as directed § 164. 27

2. Test with litmus papers (blue and red). 28

a. THE FLUID REDDENS BLUE LITMUS PAPER. This reaction may be caused by a free acid or an acid salt, as well as by a soluble metallic salt. To distinguish between these two cases, pour a small quantity of the fluid into a watch-glass, and dip into it a small glass rod, the point of which has previously been moistened with dilute solution of carbonate of soda; if the fluid remains clear, or if the precipitate which may form at first, redissolves upon stirring the liquid, this proves the presence of a free acid or of an acid salt; but if the fluid becomes turbid and remains so, this generally denotes the presence of a soluble metallic salt. As a matter of course, a solution which contains a free acid or an acid salt can no longer be considered simply aqueous, and the subsequent examination must accordingly be conducted with due regard to the possible presence of substances insoluble in water but soluble in acids.

b. REDDENED LITMUS PAPER TURNS BLUE: this indicates the presence of free alkalies or alkaline carbonates, free alkaline earths, alkaline sulphides, and of a number of other salts which show this reaction. In presence of a free alkali, a body dissolved in a fluid is as likely to belong to the class of substances soluble, as to that of bodies insoluble in water. For the way to settle this point and also for further information on the subject of alkaline solutions in general, I refer to § 177, I. 2 (104). 29

3. Smell the fluid, or, should this fail to give satisfactory results, distil, to ascertain whether the simple solvent present is water, alcohol, ether, &c. If you find it is not water, evaporate the solution to dryness, and treat the residue as directed § 164. 30

4. If the solution is aqueous, and manifests an acid reaction, dilute a portion of it largely with water. Should this impart a milky and turbid appearance to it, the presence of ANTIMONY, BISMUTH, or TIN, may be inferred. If the precipitate disappears upon the addition of tartaric acid, there is reason to believe it consists of antimony; if it is not redissolved by tartaric acid, but by acetic acid, you may assume the presence of bismuth. Treat the original fluid either as directed § 170, or as directed § 177, according as you have reason to suppose it to be the solution of a simple or a compound (mixed) substance. 31

II. Solution of Bodies, or Classification of Substances according to their Deportment with Certain Solvents.[*]

§ 167.

32 Water, hydrochloric acid, and in certain cases nitric acid, are the solvents used to classify simple or compound substances, and to isolate the component parts of mixtures. We divide the various substances into three classes, according to their respective behavior with 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 DIFFICULTLY SOLUBLE IN WATER AND IN HYDROCHLORIC OR NITRIC ACID.

The solution of alloys being more appropriately effected in a different manner from that pursued with other bodies, I shall give a special method for these substances (see § 169) (43).

The process of solution is conducted in the following manner.

A. THE SUBSTANCE UNDER EXAMINATION IS NEITHER A METAL NOR AN ALLOY.

§ 168.

33 1. Put about a gramme (15·5 grains) of the finely pulverized substance under examination into a test-tube, add from ten to twelve times the amount of distilled water, and heat to boiling.

a. THE SUBSTANCE DISSOLVES COMPLETELY. In this case it belongs to the first class; regard must be had to what has been stated in § 166, 2 (28), concerning the reactions with test-papers. Treat the solution either as directed § 170, or as directed § 177, according as either one or several acids and bases are supposed to be present.

34 *b.* AN INSOLUBLE RESIDUE REMAINS, EVEN AFTER PROTRACTED BOILING. Allow the residue to subside, and filter the fluid off, if practicable in such a manner as to retain the residue in the test-tube; evaporate a few drops of the clear filtrate on platinum foil; if nothing remains, the substance is completely insoluble in water; in which case proceed as directed § 168, 2 (35). But if a residue remains, the substance is at least partly soluble; in which case boil again with water, filter, add the filtrate to the original solution, and treat the fluid, according

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[*] Consult the remarks in the Third Section.

to circumstances, either as directed § 170, or according to § 177. Wash the residue with water, and proceed as directed § 168, 2 (35).

2. Treat the residue of *b.* (34) with dilute hydrochloric acid. If it does not dissolve, heat to boiling, and if this fails to effect complete solution, decant, and boil the residue with concentrated hydrochloric acid. 35

The reactions 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 hydrosulphuric acid; see § 171, 2 (68); *β.* Evolution of chlorine, which indicates the presence of peroxides, chromates, &c.; *γ.* Evolution of the odor of hydrocyanic acid, which indicates the presence of insoluble cyanides. To the decomposition of the latter, a special paragraph will be devoted (see § 192).

a. THE RESIDUE IS COMPLETELY DISSOLVED BY THE HYDROCHLORIC ACID (except perhaps that sulphur separates, which may be known by its color and light specific gravity, and may, after boiling some time longer, be removed by filtration; or that gelatinous hydrate of silicic acid separates). Proceed, according to circumstances, either as directed § 173, or according to § 178. The substance belongs to the second class.—If you know, or suspect, silica to be present (§ 164, 4, *b.*) (22), evaporate first to dryness, treat the residue with hydrochloric acid at a gentle heat, then with water, filter from the now insoluble silica, and treat the filtrate, according to circumstances, either as directed § 173, or according to § 178. Examine the silica as directed § 141. 36

b. THERE IS STILL A RESIDUE LEFT. In this case put the test-tube containing the specimen which has been boiled with the hydrochloric acid aside, and try to dissolve another sample of the substance under examination, by boiling in nitric acid, and subsequent addition of water. 37

α. The specimen is completely dissolved, or leaves no other residue but sulphur or the gelatinous hydrate of silicic acid; in this case also the body belongs to the second class. Use this solution to test further for bases, proceeding, according to circumstances, either as directed § 173, or as directed § 177, III. (109); if silicic acid is known or suspected to be present, first remove this by evaporating to dryness (see § 168, 2, *a.*) (36). 38

β. After boiling with nitric acid there is still a residue left. 39

aa. THERE IS REASON TO ASSUME THAT THE SUBSTANCE UNDER EXAMINATION CONTAINS ONLY *one* BASE

AND *one* ACID. Pour nitrohydrochloric acid over the substance, and apply heat.

aa. The substance dissolves. Treat the solution as directed § 173.

ββ. The substance does not dissolve. Proceed as directed § 176.

bb. THERE IS REASON TO SUPPOSE THAT THE SUBSTANCE UNDER EXAMINATION IS A COMPLEX COMPOUND OR MIXTURE. In this case use the reserved hydrochloric solution (§ 168, 2, *b.*) (37) to test for the bases, for which purpose heat it once more to boiling, with the insoluble residue—(which latter treat afterwards as directed § 168, 3 (42)—and filter hot into a tube containing some water; boil the residue with water, filter hot, and add the filtrate to the hydrochloric acid solution. (If the presence of silica is suspected, evaporate the solution first to dryness, heat the residue with a little hydrochloric acid, then with water, and filter into a tube containing some water.) 40

aa. The filtrate becomes turbid and milky; this indicates ANTIMONY and BISMUTH; or it deposits fine crystals; this indicates the presence of LEAD. Heat the filtrate (if necessary, with addition of some hydrochloric acid) until it appears clear again, and then proceed as directed § 178. 41

ββ. The filtrate remains clear. Evaporate a few drops of it to ascertain beyond doubt whether the hydrochloric acid has really dissolved anything. If a residue is left, treat the filtrate according to the directions at § 178.

3. If the boiling concentrated hydrochloric acid has left a residue, wash this with water, and proceed as directed § 191. 42

B. THE SUBSTANCE UNDER EXAMINATION IS A METAL OR AN ALLOY. 43

§ 169.

The metals are best classed according to their respective behaviour with nitric acid: this gives us,

I. METALS WHICH ARE NOT AFFECTED BY NITRIC ACID: gold, platinum.

II. METALS WHICH ARE OXIDIZED BY NITRIC ACID, BUT OF WHICH THE OXIDES DO NOT DISSOLVE IN AN EXCESS OF THE ACID, NOR IN WATER: antimony, tin.

III. METALS WHICH ARE OXIDIZED BY NITRIC ACID, AND CON-

VERTED INTO NITRATES, WHICH DISSOLVE IN AN EXCESS OF THE ACID, OR IN WATER: all other metals.

Accordingly, pour nitric acid of 1·25 sp. gr. over a small portion of the metal or alloy under examination, and apply heat.

1. COMPLETE SOLUTION TAKES PLACE EITHER AT ONCE OR UPON ADDITION OF WATER; this proves the absence of platinum,* gold, antimony,† and tin. Proceed, according to circumstances, either as directed § 173, or as instructed § 177, III. 44

2. A RESIDUE IS LEFT. 45

a. A metallic residue. Filter, and treat the filtrate as directed § 177, III., after having examined, in the first place, whether anything has really been dissolved. Wash the residue thoroughly, dissolve in nitrohydrochloric acid, and add to a portion of the solution chloride of potassium and alcohol; to another portion, sulphate of protoxide of iron; a yellow precipitate in the first portion indicates the presence of PLATINUM, a black precipitate in the second, the presence of GOLD.

b. A white pulverulent residue; this indicates the presence of ANTIMONY or TIN. Filter, ascertain whether anything has been dissolved, and if so treat the filtrate as directed § 177, III. Wash the residue thoroughly, and heat it with a hot saturated solution of bitartrate of potassa, or with a solution of tartaric acid. 46

α. Complete solution ensues; this indicates the presence of oxide of ANTIMONY alone; test the solution with hydrosulphuric acid after addition of some hydrochloric acid. 47

β. A white precipitate remains, even after boiling with a fresh portion of solution of bitartrate of potassa or tartaric acid; this indicates the probable presence of TIN. Filter, and mix the filtrate with some hydrochloric acid, then with solution of hydrosulphuric acid. If an orange-red precipitate is formed, TEROXIDE OF ANTIMONY is present. It is invariably necessary to satisfy yourself whether the residue consists really of binoxide of tin: which is done by mixing it with cyanide of potassium and carbonate of soda, and reducing it before the blowpipe (compare § 126, 7).

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[*] Alloys of silver and platinum, with the latter metal present in small proportion only, dissolve in nitric acid.

[†] Very minute traces of antimony, however, are often completely dissolved by nitric acid.

III. Actual Examination.

Simple compounds.[*]

A. Substances soluble in water.

Detection of the base.[†]

§ 170.

1. Add some hydrochloric acid to a portion of the aqueous solution. 48

a. No precipitate is formed; this is a positive proof of the absence of silver and suboxide of mercury, and is likewise an indication of the probable absence of lead. Pass on to § 170, 2 (50).

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. 49

a. *The precipitate redissolves, and the fluid becomes clear;* this shows the precipitate to have consisted of chloride of silver, and is consequently indicative of the presence of silver. To arrive at a positive conviction on this point, the original solution must be tested with chromate of potassa, and with hydrosulphuric acid (see § 111, 4, and § 132, *b.* 6).

β. *The precipitate becomes black:* this shows the precipitate to have consisted of subchloride of mercury, which has now been converted by the ammonia into suboxide of mercury; it is consequently indicative of the presence of suboxide of mercury. To set all doubt on this point at rest, test the original solution with protochloride of tin, and with metallic copper (see § 112).

γ. *The precipitate remains unaltered;* it consists in this case of chloride of lead, which is not dissolved by ammonia; this reaction is accordingly indicative of the presence of lead. Whether the precipitate consists really of chloride of lead or not is conclusively ascertained: 1st, by diluting the second portion of the fluid in which the precipitate produced by hydrochloric acid is suspended, with a large amount of water, and applying heat; the precipitate must dissolve if it consists really of chloride of lead; and 2nd, by adding dilute sulphuric acid to the original solution (§ 113).

2. Add to the fluid acidified with hydrochloric acid (1) solution of 50

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[*] This term is used here, and wherever it happens to occur hereafter in the present work, to designate compounds supposed to contain only *one* base and *one* acid, or *one* metal and *one* metalloid.

[†] Arsenious acid and arsenic acid are included here.

hydrosulphuric acid until it smells distinctly of that gas, even after shaking, and heat the mixture.

a. THE FLUID REMAINS CLEAR. Pass on to 3 (56), since this is a proof that lead, bismuth, copper, cadmium, oxide of mercury, gold, platinum, tin, antimony, arsenic, and sesquioxide of iron, are not present.

b. A PRECIPITATE IS FORMED.

α. THIS PRECIPITATE IS WHITE; it consists in this case of separated sulphur, and is indicative of the presence of SESQUIOXIDE OF IRON (§ 107). However, as the separation of sulphur may also be caused by other substances, it is indispensable that you should satisfy yourself whether the substance present is really sesquioxide of iron or not. For this purpose test the original solution with ammonia, and with ferrocyanide of potassium (§ 107). 51

β. THE PRECIPITATE IS YELLOW; in this case it may consist either of sulphide of cadmium, sulphide of arsenic, or bisulphide of tin; it indicates accordingly the presence of either cadmium, arsenic, or binoxide of tin. To distinguish between them, mix a portion of the fluid wherein the precipitate is suspended with ammonia in excess, add sulphide of ammonium, and heat. 52

aa. The precipitate does not dissolve; it consists of CADMIUM; for sulphide of cadmium is insoluble in ammonia and sulphide of ammonium. The blowpipe is resorted to as a confirmatory test (§ 118).

bb. The precipitate dissolves. It consists either of binoxide of tin or of arsenic; add ammonia to a small portion of the original solution.

αα. A white precipitate is formed. BINOXIDE OF TIN is the substance present. Positive conviction is obtained by reducing the precipitate before the blowpipe, with cyanide of potassium and carbonate of soda (§ 126).

ββ. No precipitate is formed. This indicates the presence of ARSENIC. Positive conviction may be arrived at by the production of an arsenical mirror, which is effected by reducing the original substance, or the precipitated sulphide of arsenic, either with cyanide of potassium and carbonate of soda, or in some other way; and moreover by exposing the original substance with carbonate of soda to the inner flame of the blowpipe (§ 127). If the solution (50) contained *arsenious* acid, the yellow precipitate (52) formed immediately; if *arsenic* acid, it formed only upon the application of heat, or after long standing. For further information respecting the means of distinguishing between the two acids see § 129.

γ. THE PRECIPITATE IS ORANGE COLORED; in this case it consists of tersulphide of antimony, and indicates the presence of TEROXIDE OF ANTIMONY. Reduction before the blowpipe is resorted to for confirmation (§ 124). 53

δ. THE PRECIPITATE IS BROWN. It consists of protosulphide of tin, and indicates the presence of PROTOXIDE OF TIN. To remove all doubt, test a portion of the original solution with solution of chloride of mercury, and another portion with solution of terchloride of gold (§ 125). 54

ε. THE PRECIPITATE IS BLACK. It may in this case consist of sulphide of lead, sulphide of copper, tersulphide of bismuth, tersulphide of gold, bisulphide of platinum, or sulphide of mercury. To distinguish between these different sulphides, the following experiments are resorted to. 55

aa. Add dilute sulphuric acid to a portion of the original solution; if a white precipitate is formed, this indicates LEAD. To dispel all doubt, test with chromate of potassa (§ 113).

bb. Add ammonia in excess to a portion of the original solution; if a bluish precipitate is formed which redissolves in an excess of the precipitant, imparting an azure color to the fluid, this indicates COPPER. To remove all doubt, test with ferrocyanide of potassium (§ 116).

cc. Add solution of soda to a portion of the original solution; if a yellow precipitate is formed this indicates OXIDE OF MERCURY. The reaction with protochloride of tin and metallic copper afford positive certainty on the point (§ 115).

The presence of oxide of mercury is usually sufficiently indicated by the several changes of color through which the precipitate produced by the solution of hydrosulphuric acid in the fluid under examination is observed to pass; this precipitate is white at first, but changes upon the addition of an excess of the precipitant to yellow, then to orange, and finally to black (§ 115, 3).

dd. Evaporate a portion of the original solution nearly to dryness, in a porcelain crucible, and rinse the residue into a test-tube, half filled with water. If the solution becomes milky, a basic salt of bismuth is present: this reaction, consequently, indicates BISMUTH. The blowpipe is resorted to as a conclusive test (§ 117).

ee. Add solution of sulphate of protoxide of iron to a portion of the original solution. A fine black precipitate is indicative of the presence of GOLD. To remove all doubt as to the nature of the precipitate, expose it to the flame of the blowpipe, or test the original solution with protochloride of tin (§ 121).

ff. Add chloride of potassium and alcohol to a portion of the original solution; the formation of a yellow crystalline precipitate is indicative of the presence of PLATINUM. To remove all doubt, heat the precipitate to redness (§ 122).

3. Mix a portion of the original solution with chloride of ammonium, add ammonia to alkaline reaction, and then, no matter whether the latter reagent has produced a precipitate or not, a little sulphide of ammonium. 56

a. NO PRECIPITATE IS FORMED; pass on to § 170. 4, (62); 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. Mix a portion of the original solution with some solution of potassa or soda. 57

aa. A dirty greenish-white precipitate is formed, which soon changes to reddish-brown, upon exposure to the air: PROTOXIDE OF IRON. To remove all doubt, test with ferricyanide of potassium (§ 106).

bb. A precipitate of a light greenish tint is produced, which does not change its color: NICKEL. The reaction with ammonia, and the precipitation of the ammoniacal solution by potassa, will afford positive certainty on the point (§ 104).

cc. A sky-blue precipitate is formed, which is discolored upon boiling, and acquires a dark tint: COBALT. The blowpipe is resorted to as a conclusive test (§ 105).

β. *The precipitate is not black.* 58

aa. If the precipitate is distinctly flesh-colored, it consists of sulphide of manganese, and is consequently indicative of the presence of PROTOXIDE OF MANGANESE. To remove all doubt, add potassa to the original solution, or try before the blowpipe (§ 103).

bb. If the precipitate is bluish-green, it consists of hydrated SESQUIOXIDE OF CHROMIUM. To dispel all doubt, test the original solution with potassa, and apply the blowpipe tests (§ 99).

cc. If the precipitate is white, it may consist of hydrate of 59 alumina or sulphide of zinc, and thus indicate the presence of either alumina or oxide of zinc. To distinguish between these two oxides, add to a portion of the original fluid solution of soda, drop by drop, until the precipitate which forms is redissolved ; and

αα. Add hydrosulphuric acid water to a portion of the alkaline solution ; the formation of a white precipitate indicates the presence of ZINC. The reaction with solution of nitrate of protoxide of cobalt before the blowpipe will afford conclusive proof (§ 102).

ββ. Add to another portion of the alkaline solution chloride of ammonium. The formation of a white precipitate indicates the presence of ALUMINA. The reaction with solution of protonitrate of cobalt before the blowpipe will afford conclusive proof (§ 98).

Note to § 170, 3. *b. β.* (58). 60

As very slight contaminations may impair the distinctness of the tints exhibited by the precipitates considered in § 170, 3, *b. β.* (58), it is advisable, in all cases where the least impurity is suspected, to adopt the following method for the detection of manganese, chromium, zinc, and alumina.

Add solution of soda in excess to a portion of the original solution.

aa. A whitish precipitate is formed, which does not redissolve in an excess of the precipitant, and changes its color speedily to a blackish-brown upon exposure to the air: MANGANESE. The blowpipe is resorted to as a conclusive test (§ 103).

bb. A precipitate is formed which redissolves in an excess of the precipitant: SESQUIOXIDE OF CHROMIUM, ALUMINA, OXIDE OF ZINC. 61

αα. Add hydrosulphuric acid water to a portion of the alkaline solution. The formation of a white precipitate indicates the presence of ZINC.

ββ. If the original solution, or the alkaline solution, is green, and if the precipitate produced by potassa and redissolved by an excess of the precipitant, was of a bluish color, SESQUIOXIDE OF CHROMIUM is present. To remove all doubt, heat the alkaline solution to boiling, or try the reaction before the blowpipe (§ 99).

γγ. Add chloride of ammonium to the alkaline solution. The formation of a white precipitate indicates the presence of

ALUMINA. The reaction with solution of cobalt before the blowpipe will afford conclusive proof (§ 98).

4. Add to a portion of the original solution chloride of ammonium and carbonate of ammonia, mixed with some caustic ammonia, and heat. 62

a. NO PRECIPITATE IS FORMED: absence of bartya, strontia, and lime. Pass on to § 170, 5 (64).

b. A PRECIPITATE IS FORMED: presence of baryta, strontia, or lime. 63

Add solution of sulphate of lime in considerable quantity to a portion of the original solution.

α. *The solution does not become turbid; not even after the lapse of from five to ten minutes:* LIME. To remove all doubt test with oxalate of ammonia (§ 94).

β. *The solution becomes turbid after the lapse of some time:* STRONTIA. The alcohol flame will afford conclusive proof (§ 93).

γ. *A precipitate is immediately formed:* BARYTA. To remove all doubt, test with hydrofluosilicic acid (§ 92).

5. Mix that portion of the solution of 4, in which carbonate of ammonia has failed to produce a precipitate, after previous addition of chloride of ammonium (*a.* 62), with phosphate of soda, add some more ammonia, and rub the sides of the vessel with a glass rod. 64

a. NO PRECIPITATE IS FORMED: absence of magnesia. Pass on to § 170, 6 (65).

b. A CRYSTALLINE PRECIPITATE IS FORMED: MAGNESIA.

6. Evaporate a drop of the original solution on a platinum knife as slowly as possible, and gently ignite the residue. 65

a. THERE IS NO FIXED RESIDUE LEFT. Test for ammonia, by adding to the original solution hydrate of lime, and observing the odor and reaction of the escaping gas, and the fumes which it forms with acetic acid (§ 88).

b. THERE IS A FIXED RESIDUE LEFT: potassa or soda. Mix a portion of the original solution with tartaric acid, and shake vigorously. If the original solution is very dilute, concentrate it first by evaporation. 66

α. *No precipitate is formed, not even after the lapse of ten or fifteen minutes:* SODA. The blowpipe flame and alcohol flame are selected as conclusive tests (§ 87).

β. *A crystalline granular precipitate is formed:* POTASSA.

Bichloride of platinum, the blowpipe flame and alcohol flame are selected as conclusive tests (§ 86).

Simple compounds.

A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACID.

I. *Detection of inorganic acids.*

§ 171.

Reflect in the first place *which* of the inorganic acids form soluble compounds with the detected base, and bear this in mind in your subsequent operations.

1. ARSENIOUS ACID and ARSENIC ACID have already been considered in the preceding paragraph (detection of the base). These two acids are distinguished from each other by their respective behaviour with nitrate of silver, or with potassa and sulphate of copper (see § 129). 67

2. The presence of CARBONIC ACID, HYDROSULPHURIC ACID, and CHROMIC ACID, is also indicated already in the course of the process pursued for the detection of the bases. The two former betray their presence by effervescing upon the addition of hydrochloric acid; they may be distinguished from one another by their odor. Should additional proof be required, the presence of carbonic acid may be ascertained beyond a doubt by the reaction with lime-water (see § 140), and that of hydrosulphuric acid by the reaction with solution of acetate of lead (§ 147). The presence of chromic acid is invariably indicated by the yellow or red tint of the solution, and likewise by the transition of the red or yellow color to green, accompanied by the separation of sulphur upon the addition of hydrosulphuric acid water. To remove all doubt, try the reactions with solutions of acetate of lead and of nitrate of silver (§ 132, *b*). 68

3. Add chloride of barium to a portion of the solution: if the reaction is acid, neutralize previously, or make slightly alkaline, by means of ammonia. 69

a. THE FLUID REMAINS CLEAR. Pass on to § 171, 4 (71). The absence of sulphuric acid, phosphoric acid, and silicic acid is certain, that of oxalic acid and boracic acid probable; as the baryta compounds of the two latter acids are kept in solution by ammoniacal salts, whilst borate of baryta does not separate from *dilute* solutions, even in the absence of ammoniacal salts.

b. A PRECIPITATE IS FORMED. Add dilute hydrochloric acid in excess. 70

a. The precipitate dissolves: absence of sulphuric acid. Pass on to 4 (71).

β. The precipitate remains undissolved, even on the addition of a large quantity of water: SULPHURIC ACID.

4. Add solution of sulphate of lime to another portion of the solution (which, if it has an acid reaction, must first be neutralized, or made slightly alkaline, by means of ammonia). If no salt of ammonia is present, add some chloride of ammonium before adding the solution of sulphate of lime. 71

a. NO PRECIPITATE IS FORMED: absence of oxalic acid and phosphoric acid. Pass on to 5 (73).

b. A PRECIPITATE IS FORMED. Add acetic acid in excess. 72

a. The precipitate is redissolved: PHOSPHORIC ACID. To remove all doubt, try the reactions with sulphate of magnesia and ammonia, and with solution of nitrate of silver (§ 135).

β. The precipitate remains undissolved, but is readily dissolved by hydrochloric acid: OXALIC ACID. To remove all doubt, try the reaction with concentrated sulphuric acid (§ 137).

5. Acidify a fresh portion of the original solution with nitric acid, and add solution of nitrate of silver. 73

a. THE FLUID REMAINS CLEAR. This is a proof of the absence of chlorine and iodine; the absence of cyanogen is also probable. (Of the soluble metallic cyanides, cyanide of mercury is not precipitated by nitrate of silver; if, therefore, in the analytical process for the detection of the bases, mercury has been found, cyanide of mercury may be present. For the manner of detecting the cyanogen in the latter, see § 146. Pass on to 6 (75).

b. A PRECIPITATE IS FORMED. Add ammonia in excess. 74

a. The precipitate does not dissolve: IODINE. To remove all doubt, try the reaction with starch. (§ 145.)

β. The precipitate redissolves. If it dissolves readily, there is reason to suppose that CHLORINE is present; if it dissolves with difficulty, and only upon the addition of a large quantity of ammonia, it is probably a CYANIDE. The question as to the presence of chlorine may be settled beyond doubt, by testing the original solution with nitrate of suboxide of mercury, and by the deportment of the silver precipitate at a high temperature (§ 143); the presence of cyanogen may be ascertained by adding soda, solution of proto-sesquioxide of iron, and hydrochloric acid to the original solution. (§ 146.)

6. Pour some sulphuric acid over a portion of the solid substance (or, if you have a fluid, over *the residue left upon evaporation*), add 75

alcohol, and ignite. If the flame appears green upon stirring, **BORACIC ACID** is present. As a confirmatory test try turmeric paper, § 136.

7. With regard to the presence of nitric acid, this is usually discovered already in the course of the preliminary examination (see § 164, 2, *c.*) (6). The reaction with sulphate of protoxide of iron and sulphuric acid, or that with solution of indigo, will afford conclusive evidence of the presence of that acid (§ 149). 76

8. For the detection of chloric acid, hydrofluoric acid, silicic acid, which occur more rarely in the free state or in soluble compounds, and that of bromine, I refer to § 187, end. 77

Simple compounds.

A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACID.

II. *Detection of organic acids.*

§ 172.

1. Add ammonia to a portion of the aqueous solution of the compound under examination to slight alkaline reaction, and then chloride of calcium. If the solution was neutral, or only slightly acid, add chloride of ammonium, before adding the chloride of calcium. 78

a. **NO PRECIPITATE IS FORMED, NEITHER AFTER SHAKING THE FLUID, NOR AFTER THE LAPSE OF A FEW MINUTES:** absence of oxalic acid and tartaric acid. Pass on to § 172, 2 (80).

b. **A PRECIPITATE IS FORMED.** Add lime-water in excess to a fresh portion of the original solution, and then to the precipitate formed add solution of chloride of ammonium. 79

α The precipitate redissolves: **TARTARIC ACID.** The reaction with acetate of potassa may be resorted to as a confirmatory test; but a still more positive proof will be afforded by the deportment which the precipitate produced by the chloride of calcium exhibits with solution of soda or of potassa (§ 152).

β. The precipitate does not redissolve: **OXALIC ACID.** To remove all doubt, try the reaction with concentrated sulphuric acid (§ 137).

2. Heat the fluid of 1, *a.* (78) to boiling, keep at that temperature for some time, and add some more ammonia to the boiling fluid. 80

a. **IT REMAINS CLEAR:** absence of citric acid. Pass on to § 172, 3 (81).

b. **IT BECOMES TURBID, AND DEPOSITS A PRECIPITATE: CITRIC ACID.**

3. Mix the fluid of 2, *a* (80) with alcohol. 81

a. IT REMAINS CLEAR: absence of malic acid. Pass on to § 172, 4 (82).

b. A PRECIPITATE IS FORMED: MALIC ACID. To remove all doubt, it is *invariably* necessary to try the reaction with acetate of lead (§ 154).

4. Neutralize a portion of the original solution *completely* (if not already absolutely neutral) with ammonia or with hydrochloric acid, and add solution of sesquichloride of iron. 82

a. A BULKY PRECIPITATE FORMS, OF A CINNAMON OR DIRTY YELLOW COLOR. Wash the precipitate, heat it with ammonia, filter, concentrate the filtrate by evaporation, divide into two parts, and add to the one some hydrochloric acid, to the other alcohol and chloride of barium. The formation of a precipitate in the first portion indicates the presence of BENZOIC ACID, a precipitate in the second denotes the presence of SUCCINIC ACID. Compare § 157 and § 158.

b. THE LIQUID ACQUIRES AN INTENSE DEEP RED TINT, AND, UPON PROTRACTED BOILING, A LIGHT REDDISH-BROWN PRECIPITATE SEPARATES: acetic acid or formic acid. Heat a portion of the solid salt under examination, or, if the substance is in the fluid state, of the residue left upon evaporating the fluid (which, if acid, you must neutralize first with soda), with sulphuric acid and alcohol (§ 160). The characteristic odor of acetic ether indicates the presence of ACETIC ACID. 83

If you do not detect acetic acid in the fluid, you may conclude that the substance under examination contains FORMIC ACID: to remove all doubt, try the reactions with nitrate of silver and chloride of mercury (§ 161).

Simple compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

Detection of the base.[*]

§ 173.

Dilute a portion of the solution in hydrochloric acid, nitric acid, or nitrohydrochloric acid with water,[†] and proceed exactly as directed at 84

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[*] Regard is also had here to certain salts, as this course of examination leads directly to their detection.

[†] If upon the addition of the water the liquid becomes white and turbid, or deposits a white precipitate, this indicates the presence of antimony, bismuth, or tin. Compare § 166, 4 (31). Heat with hydrochloric acid until the fluid has become clear again, and then pass on to § 170, 2 (50).

§ 170, beginning at 1 (48), in cases where the substance is dissolved in nitric acid, and at 2 (50), if the solution already contains hydrochloric acid. Particular regard must be had in this to the following: we have seen § 170, 3, *b. β. cc.* (59), that, if in cases where we have A SUBSTANCE SOLUBLE IN WATER, we obtain, in the course of the examination, a white precipitate upon testing with sulphide of ammonium—(after having neutralized with ammonia the free acid either originally present in, or previously added to, the solution under examination)—this precipitate can consist only of sulphide of zinc, or of alumina. But the case is different if the body is INSOLUBLE IN WATER, but dissolves in hydrochloric acid; for in that case a white precipitate produced by sulphide of ammonium, in presence of chloride of ammonium, may consist also of a PHOSPHATE OF AN ALKALINE EARTH, and likewise of OXALATE OF LIME, BARYTA, and STRONTIA, possibly, also of the FLUORIDE* of a metal of an alkaline earth. If, therefore, a white precipitate is produced upon testing an acid solution, under the circumstances stated, and according to the directions of § 170, 3, *b. β. cc.* (59), the following method is resorted to: add to a portion of the original hydrochloric acid solution some tartaric acid, and after this ammonia in excess.

1. NO PERMANENT PRECIPITATE IS FORMED: absence of the salts of the alkaline earths;—mix another portion of the original solution with solution of soda in excess, and add to the one half of the clear fluid chloride of ammonium, to the other half, hydrosulphuric acid. The formation of a precipitate in the former indicates the presence of ALUMINA; in the latter, the presence of ZINC. Whether the alumina or the oxide of zinc was combined with PHOSPHORIC ACID, may be ascertained by adding to a portion of the clear fluid mixed with tarraric acid and ammonia, some solution of sulphate of magnesia; if a precipitate forms, phosphoric acid is present. (Compare, however, § 135, 12, *b.*). 85

2. A PERMANENT PRECIPITATE IS FORMED: presence of a salt of an alkaline earth.—Take a portion of the original solution in hydrochloric acid, neutralize the greater part of the free acid with soda, mix with acetate of soda, add some solution of chloride of calcium, and, if a precipitate forms, some free acetic acid. 86

a. A permanent precipitate is formed: presence of an OXALATE. Heat a portion of the original substance to gentle redness, dissolve the residue in hydrochloric acid (effervescence confirms the presence of oxalic acid), and test the solution, for baryta and strontia, with solution of sulphate of lime; for lime, with oxalate of ammonia (§ 170, 4) (62). 87

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* With regard to the fluorides, see § 187, at the end; no further notice is taken of them in this paragraph.

b. No permanent precipitate is formed.—Add to a portion of the fluid mixed with acetate of soda, a drop of solution of sesquichloride of iron. The formation of a flocculent, white or yellowish-white precipitate confirms the presence of PHOSPHORIC ACID. Test the original solution for baryta and strontia, with solution of sulphate of lime; for lime, with oxalate of ammonia (which must be added in sufficient quantity, and after previous neutralization of the greater part of the free acid present); for magnesia, with ammonia (as phosphoric acid is already present). 88

Simple compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

DETECTION OF THE ACID.

I. *Detection of inorganic acids.*

§ 174. 89

1. CHLORIC ACID cannot be present, since all chlorates without exception are soluble in water; the nitrates also, with the exception of a few, being soluble in that menstruum, the presence of NITRIC ACID may usually be disregarded. The basic nitrate of bismuth forms the most frequently occurring exception from the general rule of the solubility of the nitrates in water. The presence of nitric acid in *insoluble* nitrates may be most readily ascertained by heating with copper filings and concentrated sulphuric acid (§ 149). For the analysis of the insoluble metallic CYANIDES, see § 192.

2. The course of examination laid down here for the detection of the bases leads likewise to that of ARSENIOUS and ARSENIC ACIDS, CARBONIC ACID, HYDROSULPHURIC ACID, and CHROMIC ACID. With regard to the latter acid, I repeat that its presence is indicated by the yellow or red color of the compound, the evolution of chlorine which ensues upon boiling with hydrochloric acid, and the subsequent presence of sesquioxide of chromium in the solution. Fusion of the compound under examination with some carbonate of soda and potassa is, however, the most conclusive test for chromic acid. Upon treating the fused mass with water, a yellow solution of alkaline chromate is obtained, in which the chromic acid may be readily detected by means of solution of acetate of lead or of nitrate of silver (§ 132). 90

3. Boil a portion of the substance with nitric acid. 91

a. If nitric oxide gas is evolved—which may be readily recognized by the red fumes of nitrous acid forming in the air—this indicates the presence of a metallic SULPHIDE; whilst the evolution of carbonic acid is indicative of the presence of a CARBONATE. The positive proof of the presence of a sulphide may then be readily obtained by testing the nitric acid solution with chloride of barium, with which reagent it must yield a precipitate of sulphate of baryta, which even a large proportion of water fails to dissolve. Metallic sulphides may also be detected with certainty by the methods given in § 147.

b. If violet vapors escape, the compound may be supposed to be a metallic IODIDE. A slip of paper, covered with starch-paste, is the most conclusive test for iodine (§ 145).

4. Dilute a portion of the solution obtained by boiling with nitric acid (3—91)—or of the filtrate of this solution, should the nitric acid have left an undissolved residue—with water, and add solution of nitrate of silver to the fluid. The formation of a white precipitate, soluble in ammonia, and fusing without decomposition when heated, indicates the presence of CHLORINE. 92

5. Boil a portion of the substance with hydrochloric acid, filter, if necessary, dilute with water, and add chloride of barium. The formation of a white precipitate, which does not redissolve, even upon addition of a large quantity of water, indicates the presence of SULPHURIC ACID. 93

6. Test for BORACIC ACID as directed § 171, 6 (75).

7. If none of the acids enumerated from 1 to 6 are present, there is reason to suspect the presence of PHOSPHORIC ACID or OXALIC ACID, or the total absence of acids. If the phosphoric acid had been combined with an alkaline earth, or with alumina, or oxide of zinc, and the oxalic acid with lime, baryta, or strontia, they would have been already detected in the process of testing for these bases (§ 173). The presence of either of these two acids is therefore to be suspected only if the examination for bases has revealed the presence of another base than any of those just now named. Should this be the case, the fluid freed from the heavy metals, no matter whether the latter have been precipitated from acid solutions by hydrosulphuric acid, or from alkaline solutions by sulphide of ammonium, is tested for the two acids as directed § 171, 4 (71). If you have precipitated with sulphide of ammonium, filter and wash the precipitate which may be produced by sulphate of lime, before treating with acetic acid. 94

8. For the detection of BROMINE and FLUORINE, see § 187 at the end.

Simple compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

DETECTION OF THE ACID.

II. *Detection of organic acids.*

§ 175.

95

1. Dissolve a portion of the substance under examination in the least possible quantity of hydrochloric acid. If a residue is left, test this for BENZOIC ACID, by exposing it to the action of heat, add to the solution, or filtrate, carbonate of soda in excess, boil the mixture for some time, and filter. Saturate the alkaline filtrate, which now contains the organic acid, exactly with hydrochloric acid, and then examine the fluid as directed § 172. No regard need be had to formic acid, as all the formiates are soluble in water.

2. ACETIC ACID is most readily detected in such compounds by means of sulphuric acid and alcohol (§ 160).

Simple compounds.

C. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC.

DETECTION OF THE BASE AND THE ACID.

§ 176.

Under this head we have to consider, SULPHATE OF BARYTA, SULPHATE OF STRONTIA, 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 insoluble compounds, I refer to § 191, and for the simple silicates, to § 193. 96

Sulphate of lime and chloride of lead are not altogether insoluble in water, and sulphate of lead may be dissolved in hydrochloric acid. However, as these compounds are so difficultly soluble that complete solution of them is seldom effected, they are included here also among the class of insoluble substances, to insure their detection, should they have been overlooked in the course of the examination of the aqueous or acid solution of the body to be analyzed.

1. Pour sulphide of ammonium over a very small quantity of the substance under examination.

a. IT BECOMES BLACK; this indicates the presence of a SALT OF LEAD, or of CHLORIDE OF SILVER. Digest a somewhat 97 larger portion of the substance for some time with sulphide of ammonium. This effects the decomposition of the metallic salt and the formation of a sulphide, which latter remains undissolved, whilst the solution now contains the acid of the metallic salt, combined with the ammonia of the sulphide of ammonium. Filter, wash the sulphide, dissolve in nitric acid, and test the solution for LEAD, with sulphuric acid, and for SILVER, with hydrochloric acid and ammonia. Test a portion of the filtrate for SULPHURIC ACID, with chloride of barium, after having previously decomposed the excess of the sulphide of ammonium, by adding hydrochloric acid and boiling the mixture; and another portion for HYDROCHLORIC ACID, with solution of nitrate of silver, after previous acidification of the liquid with nitric acid, and boiling the mixture.

b. IT REMAINS WHITE. Absence of a heavy metallic oxide. Mix a small portion of the very finely pulverised substance under examination with four times the quantity of carbonate of soda and potassa, put the mixture in a small platinum crucible, and fuse over a Berzelius spirit-lamp or gas-lamp. Boil the fused mass with water. 98

α. Complete solution ensues : SILICA. All doubts regarding the presence of this substance may be removed by saturating the solution with hydrochloric acid, and evaporating to dryness. This operation serves to convert the silicic acid into the insoluble modification. It will, accordingly, now remain undissolved upon treating the residue with water. If the residuary silicic acid is then mixed with carbonate of soda, and exposed to a strong blowpipe flame, a clear bead is produced (§ 141). 99

β. A white residue is left : this indicates the presence of a SULPHATE OF ONE OF THE ALKALINE EARTHS. Filter the solution, acidify the filtrate with hydrochloric acid, dilute with water, and test for SULPHURIC ACID, with chloride of barium. Wash the white residue, which contains the alkaline earth in the form of a carbonate, carefully dissolve in a small quantity of dilute hydrochloric acid, and test the solution for BARYTA, STRONTIA, and LIME, as directed § 170, 4 (62). 100

Complex compounds.[*]

A. SUBSTANCES SOLUBLE IN WATER, AND ALSO SUCH AS ARE INSOLUBLE IN WATER, BUT DISSOLVE IN HYDROCHLORIC ACID OR NITRIC ACID.

Detection of the bases.[†]

§ 177.[‡] 101

The compounds of classes I. and II. (see § 167) are here considered jointly, as the analytical course is in most cases the same for the compounds of the two classes. Those parts which refer only to substances insoluble in water, but soluble in hydrochloric acid or nitric acid, are enclosed between inverted commas, and may therefore be passed over in the examination of substances soluble in water.

I. SOLUTION IN WATER.

Mix with some hydrochloric acid.

1. THE SOLUTION HAD AN ACID OR NEUTRAL REACTION PREVIOUSLY TO THE ADDITION OF THE HYDROCHLORIC ACID. 102

a. NO PRECIPITATE IS FORMED, this indicates the absence of silver and suboxide of mercury. Pass on to § 178.

b. A PRECIPITATE IS FORMED. Add hydrochloric acid drop by drop until the precipitate ceases to increase; then add about six or eight drops more of hydrochloric acid, shake the mixture, and filter.

The precipitate produced by hydrochloric acid may consist of chloride of silver, subchloride of mercury, chloride of lead, a basic salt of antimony, possibly also of benzoic acid. The basic salt of antimony, however, redissolves in the excess of hydrochloric acid; consequently, if the instructions given have been strictly followed, the precipitate collected upon the filter can consist only of chloride of silver, subchloride of mercury, or chloride of lead—(possibly also of benzoic acid, which, however, is altogether disregarded here).

Wash the precipitate collected upon the filter twice with water, add the washings to the filtrate, and examine the solution as directed § 178, even though the addition of the washings to the acid filtrate should produce turbidity in the fluid (which indicates

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[*] I use this term here, and hereafter in the present work, to designate compounds in which all the more frequently occurring bases, acids, metals, and metalloids are supposed to be present.

[†] Consult the explanations in the Third Section. The acids of arsenic, and the phosphates of the alkaline earths are also included here, as this course of analysis leads to their detection.

[‡] Consult the remarks in the Third Section.

the presence of compounds of antimony, bismuth, or protoxide of tin).

Treat the washed precipitate in the filter as follows:

a. Pour hot water over it upon the filter, and test the fluid running off with sulphuric acid for LEAD. The non-formation of a precipitate upon the addition of the sulphuric acid simply proves that the precipitate produced by hydrochloric acid contains no lead, and does not by any means establish the total absence of this metal, as hydrochloric acid fails to precipitate lead from dilute solutions. 103

β. Pour over the now thrice-washed precipitate upon the filter solution of ammonia. If this changes its color to black or gray, it is a sign of the presence of SUBOXIDE OF MERCURY.

γ. Mix the ammoniacal fluid running off in *β* with nitric acid. The formation of a white, curdy precipitate indicates the presence of SILVER. (If the precipitate did contain lead, the ammoniacal solution generally appears turbid, owing to the separation of a basic salt of lead. This, however, does not interfere with the testing for silver, since the basic salt of lead redissolves upon the addition of nitric acid.)

2. **THE ORIGINAL AQUEOUS SOLUTION HAD AN ALKALINE REACTION.** 104

a. **THE ADDITION OF HYDROCHLORIC ACID TO STRONGLY ACID REACTION FAILS TO PRODUCE EVOLUTION OF GAS OR A PRECIPITATE, OR THE PRECIPITATE WHICH FORMS AT FIRST REDISSOLVES UPON CONTINUED ADDITION OF HYDROCHLORIC ACID**: pass on to § 178. The parts between inverted commas (referring to bodies insoluble in water, but soluble in acids) must be attended to.

b. **THE ADDITION OF HYDROCHLORIC ACID TO THE ORIGINAL SOLUTION PRODUCES A PRECIPITATE WHICH DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECIPITANT, EVEN UPON BOILING.**

a. *The formation of the precipitate is attended neither with evolution of hydrosulphuric acid nor of hydrocyanic acid.* Filter, and treat the filtrate as directed § 178. 105

aa. THE PRECIPITATE IS WHITE. It can, in that case, consist only of CHLORIDE OF LEAD, SULPHATE OF LEAD, or CHLORIDE OF SILVER. Test for the bases and acids of these three compounds as directed § 191, bearing in mind that the chloride of lead or chloride of silver which may be present may perchance have been formed in the process.

bb. THE PRECIPITATE IS YELLOW OR ORANGE. In this case it may consist of TERSULPHIDE OF ARSENIC (and if the fluid from which it has separated was not boiled long, or only with very dilute hydrochloric acid, also of tersulphide of antimony or bisulphide of tin), which substances were originally dissolved in solution of ammonia, borax, phosphate of soda, or some other alkaline fluid, with the exception of solutions of alkaline sulphides and cyanides. Examine the precipitate as directed § 180.

*β. The formation of the precipitate is attended with evolution of hydrosulphuric acid gas, but not of hydrocyanic acid.** 106

aa. THE PRECIPITATE IS PURE WHITE, AND CONSISTS OF SEPARATED SULPHUR. In this case a SULPHURETTED ALKALINE SULPHIDE is present. Filter the solution and pass on to § 182, bearing in mind that of the substances considered in that paragraph the heavy metals cannot be present if the solution was colorless.

bb. THE PRECIPITATE IS COLORED. In this case you may conclude that a metallic sulphur salt is present, *i. e.* a combination of an alkaline sulphur base with an electronegative sulphide. The precipitate may accordingly consist of TERSULPHIDE OF GOLD, BISULPHIDE OF PLATINUM, BISULPHIDE OF TIN, TERSULPHIDE OF ARSENIC, or TERSULPHIDE OF ANTIMONY. It might, however, consist also of SULPHIDE OF MERCURY or of SULPHIDE OF COPPER, or contain these substances, as the former is readily soluble in sulphide of potassium, and the latter slightly soluble in sulphide of ammonium. Filter, and treat the filtrate as in *aa.*, the precipitate as directed § 179.

γ. The formation of the precipitate is attended with evolution of hydrocyanic acid, with or without simultaneous disengagement of hydrosulphuric acid. This indicates the presence of an ALKALINE CYANIDE, and, if the evolution of the hydrocyanic acid is attended with that of hydrosulphuric acid, also of an alkaline SULPHIDE. In this case the precipitate may, besides the compounds enumerated in *α.* (105) and *β.* (106), contain many other substances (*e. g.* sulphide of nickel, cyanide of nickel, cyanide of silver, &c.). Boil, with further addition of hydrochloric acid, until the whole of the hydrocyanic acid is expelled, and treat the solution, or, if an 107

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* Should the odor of the evolved gas leave any doubt regarding the actual presence or absence of hydrocyanic acid, you need simply add some chromate of potassa to a portion of the fluid, previously to the addition of the hydrochloric acid.

undissolved residue has been left, the filtrate, as directed § 178; and the residue (if any) according to § 191.

c. THE ADDITION OF HYDROCHLORIC ACID FAILS TO PRODUCE A PERMANENT PRECIPITATE, BUT CAUSES EVOLUTION OF GAS. 108

a. The escaping gas smells of hydrosulphuric acid ; this indicates the presence of a SIMPLE ALKALINE SULPHIDE. Proceed as in *b. β. aa.* (106).

β. The escaping gas is inodorous ; in this case it is carbonic acid which was combined with an alkali. Pass on to § 178.

γ. The escaping gas smells of hydrocyanic acid (no matter whether hydrosulphuric acid or carbonic acid is evolved at the same time or not). This indicates the presence of an ALKALINE CYANIDE. Boil until the whole of the hydrocyanic acid is expelled, and then pass on to § 178.

II. SOLUTION IN HYDROCHLORIC ACID.

Proceed as directed § 178.

III. SOLUTION IN NITRIC ACID.

Dilute a small portion of it largely with water.

1. IT REMAINS CLEAR ; add hydrochloric acid. 109

a. No precipitate is formed. Absence of silver and suboxide of mercury. Treat the original solution as directed § 178.

b. A precipitate is formed. Dilute a larger portion of the solution with much water, and proceed as directed § 177, I. 1, *b.* (102).

2. THE SOLUTION BECOMES MILKY: BISMUTH OR ANTIMONY. Add tartaric acid or acetic acid, or both, until the fluid becomes clear again (compare § 166, 4) (31), and then proceed as directed § 177, III. 1. (109).

§ 178.*

(*Treatment with hydrosulphuric acid, precipitation of the metallic oxides of Group* V. *2nd Section, and of Group* VI.)

ADD TO A SMALL PORTION OF THE CLEAR ACID SOLUTION HYDROSULPHURIC ACID WATER, UNTIL THE ODOR OF HYDROSULPHURIC ACID IS DISTINCTLY PERCEPTIBLE AFTER SHAKING THE MIXTURE, AND WARM GENTLY. 110

1. NO PRECIPITATE IS FORMED, even after the lapse of

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* Consult the remarks in the third section.

some time. Pass on to § 182, for lead, bismuth, cadmium, copper, mercury, gold, platinum, antimony, tin, and arsenic,[*] are not present;[†] the absence of sesquioxide of iron and of chromic acid is also indicated by this negative reaction.

2. A PRECIPITATE IS FORMED.

a. The precipitate is pure white, light and pulverulent, and does not redissolve on addition of hydrochloric acid. It consists of separated sulphur, and indicates the presence of SESQUIOXIDE OF IRON.[‡] None of the other metals enumerated at § 178, 1, can be present. Treat the original solution as directed § 182. **111**

b. The precipitate is colored. **112**

Add to the larger proportion of the acid or acidified solution hydrosulphuric acid water in excess, *i. e.* until the fluid smells distinctly of it, and the precipitate ceases to increase upon continued addition of the reagent; apply a gentle heat, shake vigorously for some time, filter, keep the filtrate (which contains the oxides present of Groups I.—IV.) for further examination, according to the instructions of § 182, and thoroughly wash the precipitate, which contains the sulphides of the metals present of Groups V. and VI.

In some cases, and more particularly when there is any reason to suspect the presence of arsenic, it will be found more convenient to transmit hydrosulphuric acid gas through the diluted solution, instead of adding hydrosulphuric acid water.

If the precipitate is yellow, it consists principally of tersulphide of arsenic, bisulphide of tin, or sulphide of cadmium; if orange-colored, this indicates tersulphide of antimony; if brown or black, one at least of the following oxides is present: oxide of lead, teroxide of bismuth, oxide of copper, oxide of mercury, teroxide of gold, binoxide of platinum, prot-

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[*] Should the preliminary examination have led you to suspect the presence of arsenic acid, you must endeavor to obtain the most conclusive evidence of the absence of this acid; this may be done by allowing the fluid to stand for some time, or by adding sulphurous acid previous to the addition of the hydrosulphuric acid. (Compare § 128.)

[†] In solutions containing much free acid, the precipitates are frequently formed only after dilution with water.

[‡] Sulphur will precipitate also if sulphurous acid, iodic acid, or bromic acid are present (which substances are not included in our analytical course), and also if chromic acid, chloric acid, or free chlorine are present. In presence of chromic acid, the separation of the sulphur is attended with reduction to the sesquioxide of chromium, in consequence of which the reddish-yellow color of the solution changes to green. (Compare § 132.) The white sulphur suspended in the solution, appears at first like a green precipitate, which frequently tends to mislead beginners.

oxide of tin. However as a yellow precipitate may contain small admixtures of an orange-colored, a brown, or even a black precipitate, and yet its color not be very perceptibly altered thereby, it will always prove the safest way to assume the presence of all the metals named in § 178, 1, in any precipitate produced by hydrosulphuric acid, and to proceed accordingly as (§ 179) directs.

§ 179.

(*Treatment of the precipitate produced by hydrosulphuric acid with sulphide of ammonium; separation of the 2nd Section of Group* V. *from Group* VI.)

INTRODUCE A SMALL PORTION OF THE PRECIPITATE PRODUCED IN THE ACIDIFIED SOLUTION BY HYDROSULPHURIC ACID INTO A TEST-TUBE,* ADD A LITTLE WATER, AND THREE OR FOUR DROPS OF YELLOW SULPHIDE OF AMMONIUM, AND HEAT FOR A SHORT TIME VERY GENTLY.†

1. THE PRECIPITATE DISSOLVES COMPLETELY IN SULPHIDE 113
OF AMMONIUM (OR SULPHIDE OF SODIUM): absence of the metals of Group V.—cadmium, lead, bismuth, copper, mercury. Treat the remainder of the precipitate (of which you have digested a portion with sulphide of ammonium) as directed § 180.—If the precipitate produced by hydrosulphuric acid was so trifling that you have used the whole of it in treating with sulphide of ammonium, precipitate the solution obtained in that process by addition of hydrochloric acid, filter, wash the precipitate, and treat the latter as directed § 180.

2. THE PRECIPITATE IS NOT REDISSOLVED, OR AT LEAST NOT 114
COMPLETELY.

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* If there is a somewhat large precipitate, you may effect this readily by means of a small spatula of platinum or horn; but if you have only a very trifling precipitate, make a hole in the bottom of the filter, insert the perforated point into the mouth of the test-tube, and rinse the precipitate into the latter by means of the washing bottle.

† If the solution contains copper, which is generally revealed by the color of the fluid, and may be ascertained positively by testing with a clean iron rod (see § 116, 9), use solution of sulphide of sodium instead of sulphide of ammonium (in which sulphide of copper is not absolutely insoluble, see § 116, 4), and boil the mixture. But if the fluid, besides copper, also contains oxide of mercury (the presence of which is generally sufficiently indicated by the several changes of color exhibited by the precipitate forming upon the addition of the hydrosulphuric acid (§ 115, 3), and which, in doubtful cases, may be detected with positive certainty by testing a portion of the original solution acidified with hydrosulphuric acid, with protochloride of tin), sulphide of ammonium must be used, although the separation of the sulphides of the antimony group from the sulphide of copper is not fully effected in such cases; since were sulphide of sodium used, the sulphide of mercury would dissolve in this reagent, and this would impede the ulterior examination of the sulphides of the antimony group.

Dilute with four or five parts of water, filter, and mix the filtrate with hydrochloric acid in slight excess.

a. The fluid simply turns milky, owing to the separation of sulphur. Absence of Group VI.—gold, platinum, tin, antimony, and arsenic.* Treat the rest of the precipitate of which you have digested a portion with sulphide of ammonium, according to the directions of § 181. 115

b. A colored precipitate is formed. Treat the entire precipitate produced by hydrosulphuric acid the same as you have treated a portion of it, *i. e.* digest it with yellow sulphide of ammonium, or, as the case may be, sulphide of sodium, let it subside, pass the supernatant liquid through a filter, digest the residue in the tube once more with yellow sulphide of ammonium (or sulphide of sodium), and filter. Wash the residue † (the sulphides of Group V.), and treat afterwards as directed § 181. Dilute the filtrate—which contains the metals of Group VI. in the form of sulphur salts—with water, add hydrochloric acid to slightly acid reaction, heat gently, filter the precipitate formed—which contains the sulphides of the metals of Group VI. mixed with sulphur—wash thoroughly, and proceed as directed next paragraph, § 180. 116

§ 180.

(*Detection of the metals of Group* VI. : *arsenic, antimony, tin, gold, platinum.*)

If the precipitate produced by hydrochloric acid in the solution containing sulphide of ammonium or sulphide of sodium, has a PURE YELLOW COLOR, this indicates principally arsenic and tin; if it is distinctly ORANGE-YELLOW, antimony is present; if it is BROWN OR BLACK, this denotes the presence of platinum or gold.

Beyond these general indications, the color of the precipitate affords no safe guidance. It is therefore always advisable to test

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* That this inference becomes uncertain if the precipitate produced by hydrosulphuric acid, instead of being digested with a small quantity of sulphide of ammonium, has been treated with a larger quantity of that reagent, is self-evident; for the large quantity of sulphur which separates in that case will, of course, completely conceal any slight traces of tersulphide of arsenic or bisulphide of tin which may have been thrown down.

† If the insoluble residue suspended in the fluid containing sulphide of ammonium subsides readily, it is not transferred to the filter, but washed in the tube by decantation. But if its subsidence proceeds slowly and with difficulty, it is transferred to the filter, and washed there; a hole is then made in the bottom of the filter, and the residue rinsed into a small porcelain basin by means of a washing-bottle; the application of a gentle heat will now materially aid the subsidence of the residue, and the supernatant water may then be decanted.

yellow precipitate also for antimony, gold, and platinum, since minute quantities of the sulphides of these metals are completely hid by a large quantity of bisulphide of tin or sulphide of arsenic. Proceed accordingly as follows:

Heat a little of the precipitate on the lid of a porcelain crucible, or on a broken piece of porcelain or glass.*

1. *Complete volatilization ensues.* Probable presence of arsenic, absence of the other metals of Group VI. Reduction of the filtered precipitate with cyanide of potassium and carbonate of soda (§ 127) will afford positive proof of the presence or absence of arsenic. Whether that metal was present in the form of arsenious acid or in that of arsenic acid, may be ascertained by the method described § 129.

2. *A fixed residue is left.* In this case all the metals of Group VI. must be sought for. Dry the remainder of the precipitate thoroughly upon the filter, triturate it together with about one part of anhydrous carbonate of soda and one part of nitrate of soda, and transfer the mixture in small portions at a time to a little porcelain crucible, in which you have previously heated two parts of nitrate of soda to fusion. †

After cooling digest the fused mass in cold water, filter the insoluble residue—which will remain if the mass contained antimony, tin, gold, or platinum—and well wash with a mixture of about equal parts of water and alcohol. (The alcohol is added to prevent the decomposition and solution of the antimoniate of soda. The washings are not added to the filtrate.) The filtrate and the residue are now examined as follows:

a. EXAMINATION OF THE FILTRATE FOR ARSENIC (which **119**
must be present in it in the form of arseniate of soda).

Divide the filtrate into two portions, add highly dilute nitric acid cautiously to the one portion to feebly acid reaction, and apply heat.‡ Add to the acidified solution nitrate of silver in

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* That this preliminary examination may be omitted if the precipitate has any other color than yellow is self-evident.

† Should the amount of the precipitate be so minute that this operation cannot be conveniently performed, cut the filter, with the dried precipitate adhering to it, into small pieces, triturate these together with some carbonate of soda and nitrate of soda, and throw both the powder and the paper into the fusing nitrate of soda. It is *perferable*, however, in such cases, at once to procure a sufficiently large amount of the precipitate, as otherwise there will be but little hope of effecting the positive detection of all the metals of Group VI. Supposing all the metallic sulphides of the sixth group to have been present, the fused mass would consist of antimoniate and arseniate of soda, binoxide of tin, metallic gold and platinum, sulphate, carbonate, and nitrate of soda.

‡ In some cases where a somewhat larger proportion of carbonate of soda had been used, or a

not too small a quantity, filter, in case some chloride of silver should have separated (which will invariably happen if the reagents were not perfectly pure, and the precipitate has not been thoroughly washed), pour upon the filtate, along the side of the tube held obliquely, a layer of very dilute solution of ammonia, —twenty parts of water to one part of solution of ammonia—and let the mixture stand for some time without shaking. The formation of a reddish-brown precipitate, which appears hovering cloud-like between the two layers (and may be seen far more readily and distinctly by reflected than by transmitted light), denotes the presence of ARSENIC. If the arsenic is present in some quantity, and the free nitric acid of the solution is exactly saturated with ammonia, the fluid being stirred during this process, the precipitate of arseniate of silver which forms imparts a brownish-red tint to the entire fluid. To gain more positive information respecting the presence or absence of arsenic, precipitate the second portion of the filtrate with solution of neutral acetate of lead, filter the precipitate (which consists of sulphate, carbonate, and—if arsenic is really present—arseniate of lead), dry between blotting paper, and then expose on charcoal to the inner flame of the blowpipe. If arsenic is really present, a globule of metallic lead containing arsenic will be produced, which will long continue to exhale the odor of garlic, when it is exposed to the inner flame of the blowpipe. The only *positive proof* of the presence of arsenic, however, is the exhibition of this substance in the metallic state. (Compare § 127 and § 128.) Whether the arsenic was present in the form of arsenious acid, or in that of arsenic acid, may be ascertained by the method described at the end of § 129.

b. EXAMINATION OF THE RESIDUE FOR ANTIMONY, TIN, GOLD, PLATINUM. (As the antimony, if present in the residue, must be so in the form of white, pulverulent antimoniate of soda, the tin as white, flocculent binoxide, the gold and platinum in the metallic state, the appearance of the residue is in itself indicative of its nature). Boil the residue with concentrated solution of soda, then add about an equal quantity by volume of alcohol, and let the mixture stand half an hour. Under these circumstances antimoniate of soda, gold, and platinum remain undissolved, whilst the binoxide of tin which may be present dissolves in the alkaline fluid. 120

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very strong heat applied, a trifling precipitate (hydrated binoxide of tin) will separate upon the acidification of the filtrate with nitric acid. This may be filtered off, and then treated in the same manner as the undissolved residue.

Filter, wash with a mixture of equal volumes of water and alcohol (keeping the washings separate from the filtrate), and,

a. Test the alkaline filtrate for tin, by acidifying with hydrochloric acid, evaporating the alcohol, adding solution of hydrosulphuric acid, and heating. A yellow precipitate forms: TIN. To remove all doubt, reduce the precipitated sulphide of tin to the metallic state, by exposing it in conjunction with cyanide of potassium and carbonate of soda to the inner flame of the blowpipe. Whether the tin was present in the analyzed substance in the state of protoxide, you may ascertain by testing the original solution in water or hydrochloric acid with chloride of mercury (§ 125). **121**

β. Boil *the insoluble residue* with hydrochloric acid, with addition of some tartaric acid, add to the fluid (previously filtered, if necessary) solution of hydrosulphuric acid, and warm. An orange-red precipitate denotes antimony. If upon boiling the residue with hydrochloric acid, an insoluble, heavy residue remains, this is to be tested for gold and platinum. For this purpose heat it with nitrohydrochloric acid, and **122**

aa. Mix a portion of the solution with protochloride of tin. The formation of a reddish-brown or purple colored precipitate denotes GOLD. The presence of this metal may be positively demonstrated by testing another portion of the fluid, or some of the original solution of the substance, with sulphate of protoxide of iron (§ 11). **123**

bb. Evaporate the remainder of the solution, with addition of some chloride of potassium, and add alcohol to the residue. The formation of a yellow precipitate indicates the presence of PLATINUM. **124**

§ 181.

(*Detection of the metallic oxides of Group* V. *2nd Section:—Oxide of lead.—Teroxide of bismuth.—Oxide of copper.—Oxide of cadmium.—Oxide of mercury.*)

WASH THE PRECIPITATE WHICH HAS NOT BEEN DISSOLVED BY SULPHIDE OF AMMONIUM, AND BOIL WITH NITRIC ACID. This operation is performed best in a small porcelain dish; the boiling mass must be constantly stirred with a glass rod during the process. A great excess of acid must be avoided. **125**

1. THE PRECIPITATE DISSOLVES, AND THERE REMAINS FLOATING IN THE FLUID ONLY THE SEPARATED, LIGHT FLOCCULENT, YELLOW SULPHUR; this indicates the absence of mercury. CADMIUM, COPPER, LEAD, and BISMUTH, may be present. **126**

Filter the fluid from the separated sulphur, and treat the filtrate as follows (should there be too much nitric acid present, the greater part must first be driven off by evaporation): add to a portion of the filtrate dilute sulphuric acid in moderate quantity, heat gently, and let the fluid stand some time.

a. No precipitate forms; absence of lead. Mix the remainder of the filtrate with ammonia in excess, and gently heat. 127

α. *No precipitate is formed;* absence of bismuth. If the liquid is blue, copper is present; very minute traces of copper, however, might be overlooked, if the color of the ammoniated fluid alone were consulted. To be quite safe, and also to test for cadmium, evaporate the ammoniated solution nearly to dryness, add a little acetic acid, and, if necessary, some water, and 128

aa. Test a small portion of the fluid for copper with ferrocyanide of potassium. The formation of a reddish-brown precipitate, or a light brownish-red turbidity, indicates the presence of copper (in the latter case only to a very trifling amount). 129

bb. Mix the remainder of the fluid with solution of hydrosulphuric acid in excess. The formation of a yellow precipitate denotes cadmium. If, on account of the presence of copper, the sulphide of cadmium cannot be distinctly recognized, allow the precipitate produced by the hydrosulphuric acid to subside, decant the supernatent fluid, and add to the precipitate solution of cyanide of potassium until the sulphide of copper is dissolved. If a yellow residue is left undissolved, cadmium is present; in the contrary case, not. 130

β. *A precipitate is formed.* Bismuth is present. Filter the fluid, and test the filtrate for copper and cadmium, as directed in *α*. (128, 129, 130). To test the washed precipitate more fully for bismuth, slightly dry the filter containing it between blotting-paper, remove the moist precipitate with a platinum spatula, dissolve in a watch-glass in the least possible quantity of hydrochloric acid, and then add a large quantity of water. The appearance of a milky turbidity confirms the presence of bismuth. 131

b. A precipitate is formed. Presence of lead. Filter, treat the entire fluid the same as you have treated the sample, filter off the precipitate of sulphate of lead, and test the filtrate for bismuth, copper, and cadmium, as directed in *a*. (128—131).[*] 132

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[*] For another method of distinguishing cadmium, copper, lead, and bismuth from each other, I refer to the Third Section (additions and remarks to § 181).

2. THE PRECIPITATE OF THE METALLIC SULPHIDES DOES NOT COMPLETELY DISSOLVE IN THE BOILING NITRIC ACID, AND LEAVES A RESIDUE, BESIDES THE LIGHT FLAKES OF SULPHUR THAT FLOAT IN THE FLUID. Probable presence of OXIDE OF MERCURY (which may be pronounced almost certain, if the precipitate is heavy and black). Allow the precipitate to subside, filter the fluid from it, and examine the filtrate for CADMIUM, COPPER, LEAD, and BISMUTH, for that purpose mix first a small portion of it with a large amount of solution of hydrosulphuric acid, and, should a precipitate form, or a coloration become visible, treat the remainder according to the directions of § 181, 1 (126). 133

Wash the residue, dissolve by heating with some nitrohydrochloric acid, add ammonia until the solution retains only a feebly acid reaction, and put a drop of the fluid on a clean copper plate. If MERCURY be present, the surface of the copper will, after the lapse of some time, exhibit a white stain, which presents a metallic lustre when rubbed, and disappears upon heating. Or evaporate the solution in nitrohydrochloric acid nearly to dryness, adding some hydrochloric acid during the operation; dilute the residuary mass with water, and add protochloride of tin. The formation of a precipitate, which appears white at first, but changes to gray upon the addition of an excess of protochloride of tin, is a positive proof of the presence of mercury.*

§ 182.

(*Precipitation with sulphide of ammonium, detection and separation of the oxides of Groups* III. *and* IV: *alumina, sesquioxide of chromium; —oxide of zinc, protoxide of manganese, protoxide of nickel, protoxide of cobalt, proto- and sesquioxide of iron;—and also of the phosphates of the alkaline earths.*)

MIX A SMALL PORTION OF THE FLUID IN WHICH SOLUTION OF HYDROSULPHURIC ACID HAS FAILED TO PRODUCE A PRECIPITATE (§ 178, 1), OR OF THE FLUID WHICH HAS BEEN FILTERED FROM THE PRECIPITATE FORMED, WITH AMMONIA TO ALKALINE REACTION, AND ADD SULPHIDE OF AMMONIUM (whether the ammonia has produced a precipitate or not). 134

In cases where only a small quantity of hydrochloric acid is present, so that but little chloride of ammonium has been formed, you must

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* If you have an aqueous solution, or a solution in very dilute hydrochloric acid, the mercury was present in the original substance in the form of oxide; but if the solution has been prepared by boiling with concentrated hydrochloric acid, or by heating with nitric acid, the mercury may have been originally present in the state of suboxide.

add a proper amount of solution of chloride of ammonium to the fluid, before mixing with ammonia and sulphide of ammonium.

a. No precipitate is formed. Pass on to § 183, for iron, manganese, cobalt, zinc, nickel, sesquioxide of chromium, alumina, are not present; nor are "phosphates of the alkaline earths, nor oxalates of lime, baryta, and strontia; nor fluorides of the metals of the alkaline earths." * 135

b. A precipitate is formed. Treat the whole fluid the same as you have the sample.

1. The precipitate is perfectly white; absence of iron, cobalt, and nickel. All the metals and "compounds" enumerated in § 182, *a.* (135) must be searched for, as the faint tints of sulphide of manganese and hydrate of sesquioxide of chromium are completely hidden in a somewhat large bulk of a white precipitate. Filter, and set aside the filtrate for ulterior examination, according to the directions of § 183. Wash the precipitate, dissolve in a small dish by heating with the least possible quantity of hydrochloric acid, boil—if hydrosulphuric acid is thereupon evolved—until that gas has completely escaped, neutralize with carbonate of soda, add an excess of solution of soda, heat to boiling, and keep at that temperature for some time. 136

a. The precipitate formed dissolves completely in the excess of solution of soda. Absence of the phosphates of the alkaline earths, and of manganese and chromium; presence of alumina ("perhaps as phosphate") or oxide of zinc. Test a small portion of the alkaline fluid with solution of hydrosulphuric acid for zinc; acidify the remainder with hydrochloric acid, and add ammonia in moderate excess. The formation of a white precipitate indicates alumina. Whether the alumina is combined with phosphoric acid, is ascertained in the most simple way, by dissolving the precipitate in hydrochloric acid, and adding the solution, in small portions at a time, to a colorless and clear solution of molybdate of ammonia, heated with hydrochloric acid to boiling. The formation of a yellow precipitate, or the appearance of a yellow tint in the fluid, is indicative of the presence of phosphoric acid.† 137

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* In order to simplify the following course, no special notice is taken of the fluorides, nor of the oxalates of the alkaline earths. If there is reason to suspect the presence of fluorides of the metals of the alkaline earths, the reactions described § 138, 5 and 6, will give positive information on the point. The simplest way to test for oxalic acid, is boiling a sample of the original substance, for some time, with solution of carbonate of soda, filtering hot, acidifying the filtrate with acetic acid, and testing with solution of sulphate of lime, see § 137, 5.

† From the extraordinary sensitiveness of the reaction, this conclusion can only be positively arrived at, if the perfect absence of phosphoric acid from the solutions of soda and

b. THE PRECIPITATE DOES NOT DISSOLVE, AT LEAST NOT COMPLETELY IN THE EXCESS OF SOLUTION OF SODA. Filter, test the filtrate, as directed in *a.* for oxide of zinc and alumina, and, in case the latter is present, also for "phosphoric acid." 138

Treat the *precipitate* as follows:

α. Test a small portion of it for MANGANESE, with carbonate of soda, before the blowpipe (§ 103, 8).

β. Test another portion for CHROMIUM (if the original solution was green, yellow, violet, or red), by fusion in conjunction with carbonate of soda and nitrate of potassa or soda (§ 99, 6).

γ. "Dissolve the remainder in the least possible quantity of hydrochloric acid—(should you have used too much acid nearly neutralize by carbonate of soda)—and add to a portion of the fluid a trace of solution of sesquichloride of iron, by means of a glass rod dipt in that liquid, and then acetate of soda in excess." *

aa. The fluid remains clear: absence of phosphoric acid. Add the remainder of the fluid,† after supersaturating it with ammonia, to the filtrate from the precipitate produced by sulphide of ammonium, and proceed as directed § 183. (If sesquioxide of chromium is present, this must be filtered off after the addition of the ammonia, and after previously heating the fluid; and if manganese is present, this must be removed, by precipitation with sulphide of ammonium.) 139

bb. "A flocculent, yellowish-white precipitate is formed: phosphoric acid. Treat the entire solution the same as you have the sample, and add sesquichloride of iron until the liquid (from the formation of acetate of sesquioxide of iron) becomes slightly red; boil, filter off the phosphate of sesquioxide of iron, which is mixed with basic acetate of ses- 140

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carbonate of soda has been established beyond doubt, by testing these solutions also with molybdate of ammonia. If they are not perfectly free from the least trace of phosphoric acid, or if the analyst has no molybdate of ammonia at his command, the phosphoric acid in the phosphate of alumina is detected by one of the two methods given in § 135.

* That the molybdate of ammonia may be used here also with advantage for the detection of phosphoric acid need not be repeated.

† This fluid may very possibly contain a small quantity of the alkaline earths, even though phosphoric acid, oxalic acid, &c. are not present, as some magnesia (and if only a trace of it be present, frequently the whole) invariably falls down along with the alumina; and as owing to the action of the carbonic acid of the air, traces of the other alkaline earths may also possibly be present in the precipitate produced by sulphide of ammonium.

quioxide of iron, and test the filtrate for the alkaline earths which were combined with the phosphoric acid, by the method given in § 183, after having previously removed the manganese, if any of that metal happens to be present, by precipitating with sulphide of ammonium after addition of ammonia. In the precipitate containing the phosphoric acid in combination with sesquioxide of iron, the acid may be readily detected by dissolving the precipitate in hydrochloric acid, adding ammonia, then sulphide of ammonium, filtering, and testing the filtrate with sulphate of magnesia."

2. THE PRECIPITATE PRODUCED BY SULPHIDE OF AMMONIUM IS NOT WHITE; it may be chromium, manganese, iron, cobalt, or nickel. If it is black or blackish, one of the three last-mentioned metals is sure to be present. Under all circumstances, the metals and "compounds" mentioned in § 182, *a.* (135) must be had regard to. Filter—reserving the filtrate which contains the oxides of Groups I. and II., for further examination according to § 183— carefully wash the precipitate with water containing some sulphide of ammonium, remove it from the filter with a spatula, or by rinsing it, with the aid of a washing-bottle, into a test-tube, through a hole made in the bottom of the filter, and then treat it with a moderate excess of rather dilute cold hydrochloric acid. 141

a. IT DISSOLVES COMPLETELY (except perhaps a little sulphur, which may separate); probable absence of cobalt and nickel. 142

Filter, if necessary, then boil until the hydrosulphuric acid is *completely* expelled; neutralize with carbonate of soda, then add solution of potassa or soda in excess, boil, filter the fluid from the insoluble precipitate which is sure to remain, wash the latter, and then proceed first to examine the filtrate, afterwards the precipitate.

α. Of the *filtrate* test a small portion with hydrosulphuric acid for ZINC, the remainder, after acidifying with hydrochloric acid and boiling with a little chlorate of potassa,* with ammonia for ALUMINA. "Whether the alumina which may have been found, is combined with phosphoric acid, can be ascertained in the manner directed § 182, 1, *a.* (137.)" 143

β. The treatment of the *precipitate* differs according to whether the original solution was or was not green, yellow, violet, or red, and, consequently, whether, from this circum- 144

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* The boiling with chlorate of potassa is intended to destroy the organic matter which is absorbed from the filter by the alkaline fluid, and which would partially (and in the case of minute quantities, totally) prevent the precipitation of the alumina.

stance, or from the results of the preliminary examination, any grounds exist for suspecting the presence of chromium.

aa. THERE IS NO REASON TO SUSPECT THE PRESENCE OF CHROMIUM IN THE PRECIPITATE. 145

Examine a small portion in the outer blowpipe flame with carbonate of soda for MANGANESE, dissolve the remainder in hydrochloric acid, take a little of the solution, add a drop of nitric acid, boil, and then test for IRON, with sulphocyanide or ferrocyanide of potassium. "Heat another portion of the solution—if it appears of a yellow color, from the presence of sesquichloride of iron—with sulphite of soda* until complete decolorization (reduction of the sesquichloride to protochloride) is effected; then nearly neutralize with carbonate of soda, and add acetate of soda in not too small a quantity, and finally a trace of sesquichloride of iron."

aa. No precipitate is formed; absence of phosphoric acid. The analysis of the precipitate may now be considered finished, unless very great accuracy is required; in which case you have to look for traces of cobalt, nickel, and zinc, as well as minute quantities of magnesia, which may have been thrown down along with the precipitate produced by sulphide of ammonium. 146

For this purpose boil the remainder of the hydrochloric acid solution with nitric acid, nearly saturate with carbonate of soda, add carbonate of baryta in excess, and allow the mixture to digest some time at a very gentle heat and with repeated stirring. Then filter off the precipitate, which contains all the iron thrown down, and precipitate the baryta from the filtrate, by means of sulphuric acid; filter, supersaturate with ammonia, and test a small portion of the fluid with sulphide of ammonium; if this reagent produces a precipitate, treat the entire fluid with it, and filter. Then test the filtrate, or, if the sulphide of ammonium has failed to produce a precipitate, the remainder of the fluid, with phosphate of soda for magnesia. Treat the precipitate produced by the sulphide of ammonium (that is, of course, if any precipitate has been produced by that reagent) with very dilute hydrochloric acid, and if this leaves no black residue, the absence of

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* The sesquichloride of iron present may also be reduced, instead of with sulphite of soda, by boiling with solution of hydrosulphuric acid; in which case filter off the separated sulphur, before proceeding with the examination.

cobalt and nickel is certain. If a residue remains, examine this as directed § 182, 2, *b*. (149). Boil the hydrochloric acid solution, which must contain all the manganese present, and may also contain traces of zinc, until the hydrosulphuric acid is completely expelled; mix with solution of soda in excess, boil, and examine the insoluble residue before the blow-pipe for manganese (supposing that metal has not been previously detected), the solution with hydrosulphuric acid for zinc.

ββ. "*A precipitate is formed:* PHOSPHORIC ACID. 147
Treat the entire solution in the same manner as you have treated the sample, then add more sesquichloride of iron until the fluid begins to acquire a red color, boil, filter the precipitate, which contains all the phosphoric acid and in which the presence of that acid may, if required, be demonstrated once more, by the method described, § 182, 1, *b*. *γ*. *bb*. (140), treat the filtrate, after addition of ammonia, with sulphide of ammonium, and examine the fluid filtered from the precipitate (if any has been formed) for the alkaline earths which were combined with phosphoric acid, as directed § 183. The precipitate (if any) produced by sulphide of ammonium—and which contains that iron which existed in the fluid boiled with acetate of soda as protoxide, together with all the manganese, and, besides, possibly traces of cobalt, nickel, and zinc—must, in very exact and minute analyses be treated as directed in *aa*. (146). You must accordingly first warm it with hydrochloric acid, then boil with nitric acid, and after nearly neutralizing the solution with carbonate of soda, precipitate the iron with carbonate of baryta in excess," &c.

bb. THERE IS REASON TO SUSPECT THE PRESENCE 148
OF CHROMIUM. In this case triturate the precipitate together with one part of soda and three parts of nitrate of potassa or nitrate of soda, fuse the mixture in a porcelain crucible, or on a piece of broken procelain, let the mass cool, then boil with water and filter. Wash the insoluble portion, and examine it as directed in *aa*. (145). The yellow color of the solution indicates the presence of CHROMIC ACID, which may be further demonstrated by acidifying a sample with acetic acid, and adding solution of acetate of lead (§ 132). As this alkaline solution may also contain alumina (compare § 100), respectively "phosphate of alumina, as well as phosphoric acid, proceeding from a

phosphate of an alkaline earth," it must be further examined. For this purpose acidify with nitric acid, expel the carbonic acid by boiling, and add ammonia. The formation of a white precipitate indicate ALUMINA, respectively "phosphate of alumina (compare § 182, 1, *a* (137); filter, and add solution of sulphate of lime: the formation of a white precipitate indicates PHOSPHORIC ACID, proceeding from a phosphate of an alkaline earth."

b. THE PRECIPITATE IS NOT COMPLETELY DISSOLVED, A BLACK RESIDUE BEING LEFT; this indicates the presence of cobalt and nickel. Filter, wash the residue, and examine the filtrate as directed § 182, 2 *a*. (142). 149

α. Expose a small portion of it, in conjunction with borax, to the inner flame of the blowpipe; a blue bead denotes the presence of COBALT.—A dark yellow bead, which becomes gray and dull in the inner flame, indicates NICKEL.

β. Dissolve the remainder of the precipitate in nitrohydrochloric acid, evaporate almost to dryness, add cyanide of potassium in excess; then, after boiling for some time, dilute sulphuric acid; avoid using a notable excess of the latter reagent. The formation of a whitish precipitate (cyanide of nickel or cobalticyanide of nickel, § 104 and § 108) indicates NICKEL.

§. 183.

(*Separation and detection of the oxides of Group II., which are precipitated by carbonate of ammonia, in presence of chloride of ammonium, viz. baryta, strontia, lime*).

ADD TO A PORTION OF THE FLUID IN WHICH SULPHIDE OF AMMONIUM HAS FAILED TO PRODUCE A PRECIPITATE, OR OF THE FLUID FILTERED FROM THE PRECIPITATED SULPHIDES, PHOSPHATE OF SODA, AND ALSO AMMONIA, IF THE FLUID DOES NOT ALREADY CONTAIN THE LATTER REAGENT IN THE FREE STATE, AND SHAKE THE MIXTURE VIGOROUSLY. 150

a. NO PRECIPITATE IS FORMED: absence of the alkaline earths. Evaporate another sample of the fluid to dryness, and ignite the residue; if it completely volatilizes, neither potassa nor soda is present: pass on to § 186. If a residue is left, evaporate the entire fluid to dryness, ignite the residue, and proceed as directed § 185. 151

b. A PRECIPITATE IS FORMED. 152

Mix the remainder of the fluid with chloride of ammonium, if this salt is not present already, add a mixture of carbonate of ammonia with some caustic ammonia, and heat for some time gently (not to boiling).

1. NO PRECIPITATE IS FORMED. Pass on to § 184. Lime, baryta, and strontia are not present, or if so, only in very minute quantity.

2. A PRECIPITATE IS FORMED. Presence of LIME, BARYTA, or STRONTIA. Filter, and put aside the filtrate (which has still to be examined for magnesia and the alkalies), to proceed with it afterwards as directed § 184; wash the precipitate, dissolve in the least possible amount of dilute hydrochloric acid, and add to a small portion of the fluid some solution of sulphate of lime. 153

a. No precipitate is formed, NOT EVEN AFTER THE LAPSE OF SOME TIME. Absence of baryta and strontia; presence of LIME. To remove all doubt, mix another sample with oxalate of ammonia.

b. A precipitate is formed.

α. It is formed immediately upon addition of the solution of sulphate of lime; this indicates BARYTA. Besides this substance, strontia and lime may also be present. 154

Evaporate the remainder of the hydrochloric acid solution of the precipitate produced by carbonate of ammonia to dryness, digest the residue with strong alcohol, decant the fluid from the undissolved chloride of barium, dilute with an equal volume of water, mix with a few drops of hydrofluosilicic acid—which throws down the small portion of baryta that had dissolved in form of chloride of barium—allow the mixture to stand for some time; filter, evaporate the alcoholic solution to dryness, dissolve the residue in water, and test a portion of the fluid with a dilute solution of sulphate of potassa (§ 93, 3). If a precipitate forms immediately, or in the course of half an hour, the presence of STRONTIA is demonstrated. In that case, let the fluid with the precipitate in it stand at rest for some time, then filter, and add ammonia and oxalate of ammonia to the filtrate. The formation of a white precipitate indicates LIME. If sulphate of potassa has failed to produce a precipitate, the remainder of the solution of the residue left upon evaporation of the alcoholic fluid is tested at once with ammonia and oxalate of ammonia for lime.

β. It is formed only after some time. Absence of baryta, presence of STRONTIA. Mix the remainder of the hydrochloric acid solution with sulphate of potassa, let the mixture stand for some time, then filter, and test the filtrate with ammonia and oxalate of ammonia for lime.

§ 184.

(*Examination for Magnesia.*)

156 TAKE TWO SMALL PORTIONS OF THE FLUID IN WHICH CARBONATE OF AMMONIA HAS FAILED TO PRODUCE A PRECIPITATE, OR OF THAT WHICH HAS BEEN FILTERED FROM THE PRECIPITATE FORMED (§ 183, 2 (153), ADD SOME SULPHATE OF POTASSA TO ONE PORTION, AND OXALATE OF AMMONIA TO THE OTHER.

157 1. BOTH REAGENTS FAIL TO PRODUCE ANY FURTHER PRECIPITATE OR TURBIDITY. This is a positive proof that the fluid no longer contains a trace of baryta, strontia, or lime, and now test for magnesia, by adding to a third portion of the fluid, PHOSPHATE OF SODA, and some ammonia, and stirring with a glass rod. The formation of a crystalline precipitate demonstrates the presence of MAGNESIA. No matter whether magnesia has been detected or not, evaporate the remainder of the fluid to dryness, and heat the residue till all ammoniacal salts are expelled. If no residue is left, pass on to § 186, if one is left to § 185.

158 2. ONE OR BOTH OF THE REAGENTS STILL PRODUCE A PRECIPITATE. In that case the carbonate of ammonia has not completely removed the whole of the baryta, strontia, and lime.* Add therefore to the remainder of the fluid a little sulphate of ammonia †—if sulphate of potassa had rendered the test specimen turbid, or oxalate of ammonia, if there is still a trace of lime present—or if necessary, both reagents together; heat, filter, and proceed as directed in 1 (157).

§ 185.

(*Examination for Potassa and Soda.*)

The presence of magnesia renders certain modifications necessary in the method of examining for potassa and soda; we have therefore to distinguish two cases, viz:—

159 1. MAGNESIA IS NOT PRESENT. Dissolve the ignited residue (§ 183, *a.* (151), or § 184, 1 (157), in a little water, add alcohol to the solution, heat the mixture to boiling, and kindle the alcohol.

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* The precipitation of baryta, strontia, and lime, by carbonate of ammonia is incomplete more particularly in cases where a large proportion of chloride of ammonium is present, which dissolves small quantities of the carbonates of the alkaline earths, more especially carbonate of baryta.

† To be prepared by supersaturating dilute sulphuric acid with ammonia.

a. The flame is violet. Absence of soda; probable presence of POTASSA

b. The flame is yellow. Presence of SODA. In either case evaporate to dryness, dissolve the residue in a little water, and test separate portions of the solution with bichloride of platinum, and tartaric acid for potassa; with antimoniate of potassa for soda. This final examination for potassa and soda is the more indispensable in cases where these bodies are not present in the form of chlorides or nitrates, but in that of sulphates, phosphates, borates, &c. (which may be immediately learnt from the formation of a precipitate upon the addition of chloride of barium to a portion of the fluid)—as these latter salts impart a much fainter tint to the flames of alcohol and the blowpipe than the chlorides and nitrates. The safest way, in such cases, however, is to convert the alkalies into chlorides. This is done by cautiously adding chloride of barium to the boiling solution, as long as a precipitate continues to form, then carbonate of ammonia and ammonia to precipitate the excess of the reagent. If the filtered fluid is now evaporated and the residue heated to redness, the alkalies will remain as chlorides. If too much chloride of barium is used, a large quantity of chloride of ammonium will form, which will retain a part of the carbonate of baryta in solution. As the latter, upon evaporation with chloride of ammonium, is again converted into chloride of barium, the analyst must in such cases redissolve the ignited chlorides of the alkali metals in water, and mix the solution again with ammonia and carbonate of ammonia, if he wishes to obtain them perfectly free from baryta.

2. MAGNESIA IS PRESENT. Dissolve the ignited residue of § 184, 1 (157), in water, and add baryta water prepared from crystals of baryta, as long as a precipitate continues to form; boil, filter, add to the filtrate a slight excess of a mixture of carbonate of ammonia with some caustic ammonia, heat gently for some time, filter, evaporate the filtrate to dryness, and heat the residue to redness, to remove the salts of ammonia; dissolve the residue in a little water, precipitate, if necessary, once more with ammonia and carbonate of ammonia, evaporate again, and, if a residue remains, heat this to redness, dissolve in a little water, and treat the solution as directed § 185, 1 (159). 160

§ 186.

(*Examination for Ammonia.*)

There remains still the examination for ammonia. Triturate some of the substance under examination, or, if a fluid, a portion of the 161 latter, together with an excess of hydrate of lime, and, if necessary, a little water. If the escaping gas smells of ammonia; if it restores the blue color of reddened litmus paper, and forms white fumes with hydrochloric acid, brought into contact with it by means of a glass rod, AMMONIA is present. The reaction is the most sensitive, if the trituration is made in a small beaker, and the latter covered with a glass plate, on the lower side of which adheres a small piece of moist tumeric or moist reddened litmus paper.

Complex compounds.

A. 1. SUBSTANCES SOLUBLE IN WATER. DETECTION OF ACIDS.

I. *In the absence of Organic Acids.*

§ 187.

1. For the detection of the ACIDS, of ARSENIC, CARBONIC ACID,[*] HYDROSULPHURIC ACID, and CHROMIC ACID, compare § 171, 1 (67) and 2 (68).

2. Add to a portion of the solution nitrate of baryta,[†] and neutralize with ammonia, if necessary. 162

a. NO PRECIPITATE IS FORMED. Absence of sulphuric acid, phosphoric acid, boracic acid, chromic acid, silicic acid, oxalic acid, arsenious and arsenic acids.[‡] Pass on to 3.

b. A PRECIPITATE IS FORMED. Dilute the fluid, and add hydrochloric acid; if the precipitate does not redissolve, or at least not completely, SULPHURIC ACID is present. 163

3. Add nitrate of silver to a portion of the solution, having previously EXACTLY neutralized it, if acid, by means of ammonia, and if alkaline, by means of nitric acid.[§] 164

a. NO PRECIPITATE IS FORMED. Pass on to 4 (168); there is no chlorine, iodine, or cyanogen,[||] no phosphoric acid, silicic acid, oxalic acid, or chromic acid present; nor boracic acid, if the solution was not too dilute.

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[*] Consult also Section III.

[†] Chloride of barium may always be used instead of nitrate of baryta, if no silver, suboxide of mercury, or lead, is present.

[‡] Should an ammoniacal salt be present in the fluid under examination, the nonformation of a precipitate cannot be considered a conclusive proof of the absence of oxalic acid, arsenious and arsenic acids, and more particularly of boracic acid, since the baryta salts of these acids are not insoluble in water, in presence of ammoniacal salts.

[§] This operation presents no difficulty, and requires but little time for its performance, if the analyst takes care to largely dilute the nitric acid or ammonia.

[||] That the cyanogen in cyanide of mercury is not indicated by nitrate of silver has been mentioned § 146.

b. A PRECIPITATE IS FORMED. Observe the color of the precipitate, and then treat it with nitric acid. 165

α. The precipitate redissolves completely. Pass on to 4 (168); for there is no chlorine, iodine, or cyanogen present.

β A residue is left: CHLORINE, IODINE, or CYANOGEN. Wash the residue, and digest it with ammonia.

aa. A yellowish residue is left: IODINE. To remove all doubt, try the reaction with starch (see § 145). Filter, and mix the filtrate with nitric acid in excess; if a precipitate is formed, it indicates the presence of chlorine or cyanogen; treat it as directed in *bb* (167). 166

bb. No residue is left: presence of CHLORINE or CYANOGEN; absence of iodine. Precipitate the solution again with nitric acid. Before proceeding to distinguish between the chloride and cyanide of silver, ascertain whether cyanogen is present or not. For this purpose add to a small portion of the original solution some solution of soda, then a little solution of sulphate of protoxide of iron, shake the mixture some time, heat gently, and add hydrochloric acid in excess. The formation of a blue precipitate indicates the presence of CYANOGEN. If no precipitate remains, nor even a blue tint given to the fluid, the precipitate dissolved by the ammonia consists of chloride of silver alone, and there is no necessity to proceed further. But if this preliminary examination has revealed the presence of cyanogen, wash the silver precipitate, remove it from the filter while still moist, dry in a small porcelain crucible, and heat to redness; the chloride of silver will simply fuse, whilst the cyanide will suffer reduction, attended with formation of some paracyanide of silver. The presence of chlorine may now be readily demonstrated by placing a fragment of zinc upon the residual mass, pouring over it water, containing some sulphuric acid, filtering when the evolution of hydrogen has ceased, diluting the filtrate largely with water, mixing with nitric acid, and finally adding solution of nitrate of silver. The end in view may also be attained by fusing the ignited silver precipitate together with some carbonate of soda and potassa: the chloride of silver is thereby reduced to the metallic state, and a chloride of the alkali metals formed. 167

4. Test the aqueous solution for NITRIC ACID, by mixing with solution of indigo until the fluid acquires a light blue tint, adding some sulphuric acid, and applying heat; also by treating the solution with 168

one-third its amount of concentrated sulphuric acid, and throwing a crystal of sulphate of protoxide of iron into the mixture. The presence of nitric acid is demonstrated, in the first case, by the decoloration of the blue solution, and, in the second case, by the formation of a layer of brown fluid around the crystal (§ 149).

There remain still the examinations for phosphoric acid, boracic acid, silicic acid, oxalic acid, and chromic acid. Testing for these acids is necessary only in cases where both chloride of barium and nitrate of silver have produced precipitates in neutral solutions. (Compare note to § 187, 2, *a*. (162).

169 5. If the precipitate produced by nitrate of silver was of a yellowish color, the analyst has to look more particularly for the presence of phosphoric acid. To detect this acid, add to a portion of the fluid ammonia in excess, then chloride of ammonium and sulphate of magnesia, and stir with a glass rod. The formation of a crystalline precipitate demonstrates the presence of PHOSPHORIC ACID. The reaction with sesquichloride of iron and acetate of potassa, described § 135, 10, may also be resorted to. Exceedingly minute traces, however, are detected most readily by means of molybdate of ammonia.

170 6. Pour alcohol over a small portion of the substance under examination, add sulphuric acid, heat the mixture to boiling in a small crucible, and set fire to the alcohol. If the flame presents a green tint, BORACIC ACID is present. Should copper be present, this must first be removed either by means of hydrosulphuric acid or by boiling the fluid with an excess of potassa.*

171 7. If the fluid was red, or yellow changing to red upon the addition of hydrochloric acid, and if the precipitate produced by nitrate of silver in the neutral solution had a purple-red color, the presence of CHROMIC ACID is thereby indicated.

8. For SILICIC ACID test as § 141, 2, directs.

172 9. To effect the detection of OXALIC ACID, add solution of sulphate of lime to a portion of the fluid under examination; in case of acid reaction, neutralize first with ammonia, before adding the reagent. The formation of a white precipitate, insoluble in acetic acid, demonstrates the presence of oxalic acid.

173 CHLORATES, BROMIDES, and FLUORIDES, are of less frequent

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* If the substance under examination is in the fluid state, first evaporate to dryness—if acid, after addition of solution of soda—and then treat the residue with sulphuric acid and alcohol in the manner directed in the text, since where the fluid is treated at once with the acid and alcohol, the boracic acid is almost invariably overlooked.

occurrence. The presence of chlorates is already indicated by the violent deflagration which ensues upon addition of charcoal to the fusing salt (see § 164, 2, *c.*) (6). To remove all doubt, heat a sample of the solid salt in a glass tube sealed at one end, and introduce into the open end a smouldering wood splinter; when the presence of CHLORIC ACID will be confirmed by the kindling of the splinter. Nitrate of silver will, in that case, produce a copious precipitate of chloride of silver in the aqueous solution of the residue. The reaction with concentrated sulphuric acid (§ 150, 8) may likewise be resorted to. The detection of BROMIDES is simple, if iodides are not present at the same time. I refer to § 148, for the manner of effecting the positive detection of bromine in either case. With regard to the detection of FLUORIDES, the methods described § 138, 5 and 6, are the most efficient under all circumstances.

Complex compounds.

A. 1. SUBSTANCES SOLUBLE IN WATER. DETECTION OF ACIDS.

II. *In presence of Organic Acids.*

§ 188.

1. CHROMIC ACID, ARSENIOUS and ARSENIC ACIDS, have already been detected in the course of testing for the bases; concerning the distinction of arsenious from arsenic acid, compare § 129. 174

2. Add hydrochloric acid to a portion of the solution. The formation of a precipitate, which, when heated on platinum foil, volatilizes partly or totally, exhaling the characteristic odor of BENZOIC ACID, indicates the presence of the latter acid. Effervescence upon the addition of hydrochloric acid may be caused by the presence of CARBONIC ACID, or by that of HYDROSULPHURIC ACID (see § 171, 2 (68). 175

3. Add ammonia to a portion of the solution until the fluid acquires a feebly alkaline reaction; filter, if necessary, add chloride of barium and heat to boiling. 176

Should hydrochloric acid have produced a precipitate in the original solution, you must use the filtrate of this for the present experiment.

a. NO PRECIPITATE IS FORMED. Absence of sulphuric acid, phosphoric acid, chromic acid, silicic acid, boracic acid, arsenic acid, arsenious acid, oxalic acid, tartaric acid, citric acid; these acids may therefore be disregarded in the subsequent course of examination. The remarks made in the note to § 187, 2, *a.* (162) apply equally here to the last six of these acids.

b. A PRECIPITATE IS FORMED. Add dilute hydrochloric acid. 177

α. The precipitate redissolves : absence of sulphuric acid.

β. A residue is left : SULPHURIC ACID.

4. Add nitrate of silver to a portion of the solution, after having EXACTLY neutralized it with nitric acid, if alkaline, and with ammonia, if acid. (Compare note to § 187, 3 (164). 178

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 white or yellow. Boil a portion of the fluid, with the precipitate suspended in it. Speedy and complete reduction indicates FORMIC ACID. The reaction with nitrate of suboxide of mercury may be had recourse to as a conclusive test (§ 161) ; however, regard must be had also to the remark at the end of this number (4). Add nitric acid to the rest of the precipitate suspended in the fluid. If it dissolves, neither CHLORINE, IODINE, nor CYANOGEN, is present ; but if the nitric acid fails to effect its complete solution, test the residue for these salt radicals according to the directions of § 187, 3, *b. β.* (166). 179

β. The precipitate produced by nitrate of silver is *purple-red :* CHROMIC ACID. Should arsenic acid be present, acetate of lead must be added to a fresh sample of the solution ; the formation of a yellow precipitate removes all doubt as to the presence of chromic acid. CHLORINE, IODINE, and CYANOGEN, may likewise be present in the red silver precipitate : test for these salt radicals as directed § 187, 3, *b.* (165). 180

Remark.—In presence of chromic acid the reduction of oxide of silver and of suboxide of mercury is not a positive proof of the presence of formic acid. In cases where the two acids are present, the following method must be resorted to :—Mix the original solution with nitric acid, add oxide of lead in excess, shake the mixture, filter, add to the filtrate dilute sulphuric acid in excess, and distil. Test the distillate as directed § 161.

5. If chloride of barium and nitrate of silver have produced precipitates, test for PHOSPHORIC ACID as directed § 187, 5 (169), and for SILICIC ACID as directed § 141. 181

6. Evaporate a portion of the solution to dryness—if acid, after previous saturation with soda—introduce the residue, or a portion of 182

the original dry substance, into a small tube, pour some alcohol over it, add about an equal volume of concentrated sulphuric acid, and heat to boiling. Evolution of the odor of acetic ether demonstrates the presence of ACETIC ACID. This odor becomes in many instances more distinctly perceptible on agitating the cooling or cold mixture. Pour the contents of the tube into a small crucible, apply heat, and kindle. A green flame denotes the presence of BORACIC ACID.* (Compare § 194, 2, ε., foot-note.)

183 7. Make a portion of the fluid feebly alkaline by addition of ammonia, filter, if necessary, add some chloride of ammonium, then chloride of calcium, shake vigorously, and let the mixture stand at rest from ten to twenty minutes.

a. NO PRECIPITATE IS FORMED, NOT EVEN AFTER THE LAPSE OF SOME TIME. Absence of oxalic acid and tartaric acid; pass on to 8.

b. A PRECIPITATE IS FORMED IMMEDIATELY, OR AFTER SOME TIME. Filter, wash, and keep the filtrate for further examination according to the directions of 8.

Digest and shake the precipitate with solution of soda, without applying heat, then dilute with water, filter, and boil the filtrate some time. If a precipitate separates, TARTARIC ACID is present.

Add solution of sulphate of lime to a portion of the original solution—if acid, after previous neutralization with ammonia. The formation of a precipitate, which does not disappear upon addition of acetic acid, but is redissolved by hydrochloric acid, demonstrates the presence of OXALIC ACID.

184 8. Mix the fluid in which chloride of calcium has failed to produce a precipitate, or that which has been filtered from the precipitate—in which latter case some more chloride of calcium is to be added—with alcohol.

a. NO PRECIPITATE IS FORMED. Absence of citric acid and of malic acid. Pass on to 9.

b. A PRECIPITATE IS FORMED. Filter and treat the filtrate as directed in 9. As regards the precipitate, treat this as follows:—

After washing with some alcohol, dissolve it on the filter in a little dilute hydrochloric acid, add ammonia to the filtrate to feebly alkaline reaction, and then boil for some time.

185 *α.* THE FILTRATE REMAINS CLEAR. Absence of citric acid. Probable presence of MALIC ACID. Add alcohol again

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* As regards the removal of oxide of copper which may happen to be present, compare § 187, 6 (170).

to the fluid, and test the lime precipitate in the manner directed § 155, to make sure whether malic acid is really present or not.

β. A HEAVY, WHITE PRECIPITATE IS FORMED. Presence of CITRIC ACID. Filter boiling, and test the filtrate for malic acid in the same manner as in α. To remove all doubt as to whether the precipitate is really citrate of lime or not, it is advisable to dissolve once more in some hydrochloric acid, supersaturate again with ammonia, and boil; if the precipitate consisted really of citrate of lime it will now be thrown down again. (Compare § 154, 3.)

9. Heat the filtrate of 8, *b.* (or the fluid in which addition of alcohol has failed to produce a precipitate, 8, *a.*), to expel the alcohol, neutralize exactly with hydrochloric acid, and add sesquichloride of iron. If this fails to produce a light brown, flocculent precipitate, neither succinic nor benzoic acid is present. If a precipitate of the kind is formed, filter, digest, and heat the washed precipitate with ammonia in excess; filter, evaporate the filtrate nearly to dryness, and test a portion for SUCCINIC ACID with chloride of barium and alcohol; the remainder for BENZOIC ACID with hydrochloric acid. (Compare § 159.) 186

10. Test for NITRIC ACID as directed § 187, 4 (168).

Complex compounds.

A. 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID OR IN NITRIC ACID. DETECTION OF THE ACIDS.

1. *In the absence of Organic Acids.*

§ 189.

In the examination of these compounds attention must be directed to all the acids mentioned in § 187, with the single exception of chloric acid. Cyanogen compounds are not examined by this method. (Compare § 192.) 187

1. The remarks made § 174, 2 (90) respecting ARSENIOUS and ARSENIC ACIDS, HYDROSULPHURIC ACID, CARBONIC ACID, and CHROMIC ACID apply equally here.

2. Boil a portion of the substance with nitric acid, and filter, if necessary. 188

a. Effervescence takes place; this may be caused by CARBONIC ACID, or NITRIC OXIDE GAS; the former is recognized by the directions given in § 140; evolution of the latter generally indicates the presence of a sulphur compound.

b. Violet fumes escape, which impart a blue tint to starch: IODINE.

3. Add nitrate of silver to a portion of the nitric acid solution. 189

a. NO PRECIPITATE IS FORMED: absence of chlorine; pass on to 4.

b. A PRECIPITATE IS FORMED. Filter the fluid from the precipitate, wash the latter, and digest with ammonia. If it is redissolved completely, or partly (*i. e.* if a precipitate is formed again in the filtrate upon addition of nitric acid), CHLORINE is present.

4. Boil some of the substance under examination with hydrochloric acid, filter, if necessary, dilute with water, and mix a portion of the fluid with chloride of barium. The formation of a precipitate indicates SULPHURIC ACID.

5. Heat a small portion of the substance under examination with some copper filings and concentrated sulphuric acid. If nitric oxide gas escapes—which, in contact with the air, is immediately converted into nitrous acid—NITRIC ACID is present. In this experiment the presence of OXALIC ACID is also demonstrated (in absence of carbonates) by the evolution, with effervescence, of carbonic oxide gas and carbonic acid, which latter may be readily detected by means of lime water (§ 140).* 190

6. Test for BORACIC ACID, by treating a sample of the substance with sulphuric acid and alcohol. (See § 136). 191

7. Examine, if necessary, the hydrochloric solution from which the metallic oxides have been removed by means of hydrosulphuric acid, and sulphide of ammonium (see § 174, 7) (94), for PHOSPHORIC ACID. If baryta, strontia, lime, magnesia, or alumina, is present, the phosphoric acid has been discovered already in the course of the examination of the bases; as, in that case, a quantity of the acid corresponding to that of the bases named, is found in the precipitate produced by sulphide of ammonium. 192

8. For SILICIC ACID—which has mostly been discovered already in the preliminary examination with microcosmic salt, and upon dissolving the body to be analyzed—test, if necessary, as directed § 141. With regard to the more rarely occurring BROMINE and FLUORINE compounds, compare § 187, at the end.

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* Very minute quantities of oxalic acid are more safely detected by boiling the substance with carbonate of soda, filtering, acidifying the filtrate with acetic acid, and adding solution of sulphate of lime (§ 137).

Complex compounds.

A. 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, OR IN NITRIC ACID.

DETECTION OF THE ACIDS.

II. *In presence of Organic Acids.*

§ 190.

1. Test for CARBONIC ACID, ARSENIC ACID, ARSENIOUS ACID, SULPHURIC ACID, NITRIC ACID, BORACIC ACID, CHROMIC ACID, SILICIC ACID, CHLORINE, IODINE, and SULPHUR, as directed § 189; and for ACETIC ACID as directed § 188, 6 (182). CYANOGEN compounds are not examined by this method; compare commencement of § 189. 193

2. Dissolve a portion of the compound under examination in the least possible amount of hydrochloric acid, filter, if necessary, and test the undissolved residue which may remain, for BENZOIC ACID as directed § 188, 2 (175). Add solution of carbonate of soda in considerable excess to the filtrate, and boil the mixture some time. Filter the fluid from the precipitate formed, saturate the filtrate with dilute hydrochloric acid, and test for PHOSPHORIC ACID and OXALIC ACID as directed § 187, 5 (169), and 9 (172); and for TARTARIC ACID, CITRIC ACID, MALIC ACID, SUCCINIC ACID, and BENZOIC ACID, strictly according to the directions of § 188, 7, 8, and 9, (183—186). 194

Complex compounds.

B. SUBSTANCES INSOLUBLE, OR SPARINGLY SOLUBLE, BOTH IN WATER AND IN HYDROCHLORIC ACID.

DETECTION OF THE BASES, ACIDS, AND METALLOIDS.

§ 191.

The following substances and compounds belong to this class:— 195
SULPHATE OF BARYTA, SULPHATE OF STRONTIA, SULPHATE OF LIME, CHLORIDE OF SILVER, CHLORIDE OF LEAD, SULPHATE OF LEAD, SUBSULPHIDE and SULPHIDE OF MERCURY, SUBCHLORIDE OF MERCURY, SEVERAL METALLIC SULPHIDES, SILICIC ACID, SULPHUR AND CARBON.*

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* The solution of a body in nitric acid, upon long continued boiling, is no proof of the absence of subchloride of mercury, since this compound, as has been already stated, is in this pro-

Besides the above, there belong to this class most silicates, native alumina, many native aluminates, chrome-iron-ore (a compound of sesquioxide of chromium and protoxide of iron) ignited and native binoxide of tin (tin-stone), ignited sesquioxide of chromium, fluoride of calcium, some acid arseniates, some metallic ferro- and ferricyanides, &c. It must also be borne in mind that many metallic sulphides and iodides are decomposed only by long continued boiling with concentrated hydrochloric acid. For the sake of greater clearness the systematic course given in this paragraph embraces only those of the above bodies and compounds which are printed in capitals; the deportment and detection of the others is glanced at in a short appendix. As the silicates perform a very important part in mineral analysis, a separate chapter (§§ 193—196) is devoted to them. The same with regard to the cyanides, see § 192.

A. THE RESIDUE IS WHITE. It may in that case contain of the **196** substances above enumerated, and comprised within the systematic course, **SULPHATE OF BARYTA, SULPHATE OF STRONTIA, SULPHATE OF LIME, SULPHATE OF LEAD, CHLORIDE OF LEAD, CHLORIDE OF SILVER, SUBCHLORIDE OF MERCURY, SILICIC ACID, SULPHUR.**

No attention need be paid to the presence of sulphate of lime, unless this substance has been already detected in the aqueous solution. The lead compounds also may be disregarded, if the previous examination has not already revealed their presence.

1. Heat a small portion on platinum foil, and let the flame play **197** upon it. Evolution of the odor of sulphurous acid demonstrates the presence of SULPHUR. If no residue is left, sulphur alone is present. If, however, the heat applied was very intense, subchloride of mercury may also have volatilized. The appearance of the residue will show whether there is reason to apprehend this.

2. Add to a small portion sulphide of ammonium.

a. It remains white. Absence of compounds of heavy metals. Pass on to 3 (**201**).

cess converted into nitrate of oxide of mercury and chloride of mercury, and is thus dissolved. As regards the chlorides named in the text (chloride of silver, subchloride of mercury, and chloride of lead), they may have been present as such in the original substance; but they may also have been formed by the treatment with hydrochloric acid. The presence of chloride of lead has in the former case been discovered already in the aqueous solution; the original presence of chloride of silver and subchloride of mercury may be ascertained by the following process: Treat the substance insoluble in water with dilute nitric acid until the part soluble in that acid is completely dissolved. By this operation all the salts of suboxide of mercury and oxide of silver are dissolved, whilst the chlorides named, and iodide of silver, are left in the residue. These latter compounds are then separated by ammonia, which at once reveals the presence of the subchloride of mercury.

b. It turns black. This is a positive proof of the presence of a metallic salt, which may be either subchloride of mercury, chloride of silver, chloride of lead, or sulphate of lead. Moreover, all the other compounds enumerated under A. may be present. Boil the residue with pure solution of potassa or soda, for a considerable time; after this, dilute, filter, wash, and examine the filtrate and the precipitate as follows :[*] 198

a. Add solution of hydrosulphuric acid to a portion of the *filtrate*. The formation of a black precipitate, insoluble in an excess of dilute hydrochloric acid, indicates the presence of 199

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[*] By boiling with solution of potassa, the lead compounds and the amorphous silicic acid are dissolved, the subchloride of mercury and the chloride of silver are converted into oxides; the sulphates of the alkaline earths remain unaltered. But if the solution of potassa contains carbonate of potassa, they may also suffer partial decomposition. Should the body under examination, insoluble in hydrochloric acid, not be in a fine powder, or even fused, substitute the following method for the one given in the text :—

a. Fuse the greater portion of the residue (which, if moist, must first be dried) with three parts of dry carbonate of soda and three parts of cyanide of potassium, in a small porcelain crucible, over a spirit-lamp. The mass fuses readily; maintain it in this state for some time. After cooling, boil with water, filter, and wash the insoluble residue very carefully. Supersaturate the greater portion of the filtrate with hydrochloric acid—with proper caution, on account of the escaping hydrocyanic acid—and test a small quantity of the acidified portion with chloride of barium. The formation of a precipitate indicates the presence of a SULPHATE. (Should a precipitate [hydrate of silicic acid] be formed upon supersaturating the filtrate with hydrochloric acid, dilute the fluid, filter, and then test the filtrate for sulphuric acid). Evaporate the remainder of the acidified portion of the filtrate to dryness, and treat the residue with water. If a residue is left, this consists of SILICIC ACID. All doubt may be set at rest by the reaction with microcosmic salt or carbonate of soda before the blowpipe. Mix the remainder of the first filtrate of *a.*—the portion which has not been acidified with hydrochloric acid—with a solution of oxide of lead in solution of potassa. The formation of a black precipitate of sulphide of lead indicates equally the presence of a SULPHATE, as the latter may have been completely reduced to a metallic sulphide by the cyanide of potassium.

Pour dilute nitric acid over the insoluble part, and apply heat until complete solution is effected (if, notwithstanding the long continued application of heat, a residue is still left, this proceeds from undissolved silicic acid, or else from a sulphate of an alkaline earth which is not completely decomposed); mix the fluid with hydrochloric acid. If a white precipitate is formed—chloride of silver and chloride of lead—examine this as directed § 177, I. 1, *b.* Mix the fluid now, or, as the case may be, the filtrate, with solution of hydrosulphuric acid; if a precipitate forms, this is sulphide of lead. Filter; the precipitate may be further examined according to the directions of § 181. Test the filtrate, or the fluid in which hydrosulphuric acid has failed to produce a precipitate, for baryta, strontia, and lime, as directed § 183.

b. Boil the remainder of the residue with solution of soda, free from chlorine. If it becomes black or gray, SUBCHLORIDE OF MERCURY is present. Filter, dilute largely, supersaturate the filtrate with nitric acid, and test with nitrate of silver. The formation of a white precipitate, or the appearance of a white turbidity, shows the presence of chlorine. In confirmation, the residue blackened by the presence of the suboxide of mercury which has been eliminated in the process of boiling with solution of soda, may be examined, by mixing it, when dry, with carbonate of soda, and heating the mixture in a glass tube (§ 112).

LEAD. To remove all doubt, dissolve the precipitate in nitric acid, and test the solution with sulphuric acid.

Dilute another portion of the filtrate largely with water, and add a few drops of chloride of barium, and then hydrochloric acid in moderate excess. The formation of a white precipitate indicates the presence of SULPHURIC ACID.

To a third portion of the filtrate add nitric acid in excess, then (if necessary, after previous filtration) nitrate of silver. The formation of a white precipitate indicates the presence of CHLORINE.

Acidify the remainder of the filtrate with hydrochloric acid, evaporate to dryness, and treat the residue with water. If a residue remains, which dissolves only very sparingly upon fusion with microcosmic salt, this shows the presence of SILICIC ACID. In case you have found lead, use the fluid filtered from the sulphide of that metal, for the process of separating the silicic acid.

β. Treat the residue—which appears black or gray, if suboxide of mercury is present—with dilute nitric acid, and test the solution with hydrochloric acid for SILVER and SUBOXIDE OF MERCURY (compare § 177, I. 1, *b*.); and the filtrate, for security, with sulphate of potassa and with oxalate of ammonia, for baryta, strontia, and lime.

If the nitric acid has failed to dissolve the whole of the residue, treat the undissolved part as directed in 3—after treating a portion of it with sulphide of ammonium, to make sure of the absence of compounds of the heavy metals. 200

3. Fuse the residue free or freed from compounds of the heavy metals, in a platinum crucible, over a spirit-lamp with double draught, together with four parts of carbonate of soda and potassa, treat the fused mass with water, boil, filter, and *wash the residue which may remain, until chloride of barium ceases to produce a precipitate in the washing water*. (This water must not be added to the first filtrate.) Supersaturate the filtrate with hydrochloric acid, and test a small portion of it with chloride of barium; the formation of a precipitate indicates the presence of SULPHATES OF THE ALKALINE EARTHS. Evaporate the remainder of the filtrate to dryness, and treat the residue with water; should anything remain undissolved, this consists of SILICIC ACID. 201

4. If a residue has been left upon boiling the fused mass with water (see 3), this denotes the presence of SULPHATES OF THE ALKALINE EARTHS. Wash this residue thoroughly, and treat it 202

with hydrochloric acid. If it dissolves, completely or partly, with effervescence, this is a positive proof of the presence of sulphates of the alkaline earths. Test the hydrochloric acid solution as directed § 183, beginning at 2, *a*. (153). Should the hydrochloric acid leave a residue, this consists of silicic acid, or of an imperfectly decomposed sulphate of one of the alkaline earths.

B. THE RESIDUE IS NOT WHITE. The presence of some substances (cinnabar, sulphide of arsenic) may in that case sometimes be inferred from the color of the residue.

1. Test for SULPHUR as directed § 147, 5.

2. Pour over the greater portion of the residue nitrohydrochloric acid, boil, and filter hot; should a residue be left, besides the sulphur which may have separated, boil this once more with water, filter, and add this second filtrate to the first. Evaporate the whole nearly to dryness, redissolve the residual mass in some water, and test a small portion of the solution for LEAD, with sulphuric acid, and another portion for MERCURY, with a clean piece of copper. If hydrochloric acid has been used as a solvent in the examination for the bases (§ 167), the solution in nitrohydrochloric acid must be tested for the metals in the usual way, since various other metallic sulphides, insoluble or sparingly soluble in hydrochloric acid, might be present. 203

3. If nitrohydrochloric acid has left a residue, besides the sulphur which may have separated and remained undissolved, wash this well—should a compound of lead have been present, with hot water until the filtrate is no longer blackened by sulphide of ammonium. 204

a. THE RESIDUE IS WHITE; test a portion of it with sulphide of ammonium. 205

α. *It becomes black.* Treat the remainder as directed § 191, A. 2, *b*. (198).

β. *It remains white.* Treat the residue as directed § 191, A. 3. (201).

b. THE RESIDUE IS BLACK; this indicates the presence of carbon in some form: wood-charcoal, coal, bone-black, graphite, &c. Burn a portion of the residue in a small platinum spoon, or in the blowpipe flame. If it is entirely consumed, this is a proof of the exclusive presence of carbon; but if there is a residue left, or if the combustion is not complete (graphite), you have to look also for CHLORIDE OF SILVER, SULPHATES OF THE ALKALINE EARTHS, and SILICIC ACID; treat the remainder of the residue in that case as directed § 191, A. 2, *b*. (198.) 206

207 *Appendix:* The insoluble BINOXIDE OF TIN and SESQUIOXIDE OF CHROMIUM may be detected before the blowpipe. The former, when exposed on charcoal, together with carbonate of soda and cyanide of potassium, to the reducing flame of the blowpipe, gives a soft metallic globule without incrustation of the charcoal, or with a very trifling coating; sesquioxide of chromium, which is distinguished also by its green color, is treated with phosphate of soda and ammonia (see § 99, 7), or fused together with carbonate of soda and nitrate of potassa (§ 99, 6). The latter is also the best way to effect the decomposition of chrome-iron ore. Alumina and aluminates are dissolved by fusion with bisulphate of potassa; insoluble acid arseniates, and fluoride of calcium are decomposed by heating with concentrated sulphuric acid.

SECTION II.

PRACTICAL COURSE.

IN PARTICULAR CASES.

I. SPECIAL METHOD OF EFFECTING THE DECOMPOSITION OF CYANIDES, FERROCYANIDES, ETC., INSOLUBLE IN WATER.*

§ 192.

The analysis of these compounds by the common method is often attended with the manifestation of such abnormal reactions as easily to mislead the analyst. Moreover, acids often fail to effect their complete solution. For these reasons it is advisable to analyse them by the following special method:

Treat the substance with water until the soluble parts are entirely removed, and boil the residue with strong solution of potassa or soda; after a few minutes ebullition add some carbonate of soda and boil again.

a. COMPLETE SOLUTION IS EFFECTED. Absence of alkaline earths, nickel, cadmium, bismuth, and silver. Add to the alkaline solution hydrosulphuric acid water in excess.

α. *No permanent precipitate is formed.* Absence of zinc, lead, copper.† Add to the alkaline fluid nitric acid in excess, and should the mixture

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* Before commencing this course of analysis, consult the explanatory remarks to the paragraph (§ 192), in the Third Section.

† Oxide of copper is here included among the oxides soluble in potassa, since the hydrated oxide of copper remains suspended in a concentrated solution of potassa in a state of exceedingly minute division, and is not thrown down even upon boiling: the blue fluid thus produced looks so like an actual solution, that it can scarcely be distinguished from one.

not yet smell strongly of hydrosulphuric acid, add some more of the latter reagent

aa. No precipitate is formed. Absence of mercury, tin, arsenic, antimony, gold, and platinum. The solution can now contain only alumina, and those metals which form compound radicals with cyanogen. Test a portion of the fluid for CYANOGEN, by the successive addition of soda or potassa, solution of protosesquioxide of iron, and hydrochloric acid. Evaporate the remainder of the fluid to dryness, and heat the residue to fusion. Pour the fused mass upon a broken piece of porcelain, boil with water, filter, and examine the residue for IRON, MANGANESE, COBALT, and ALUMINA. Test the filtrate, after addition of acetic acid, with acetate of lead, for CHROMIC ACID (in which form you will obtain the whole of the chromium present) ; for the other acids which may be present, according to the directions of § 187 ; and for ALUMINA—which may be partly or entirely in solution—with chloride of ammonium.

bb. A precipitate is formed. Filter, and examine the precipitate for mercury and the metals of the sixth group, according to the directions of § 179. Examine the filtrate for cyanogen, alumina, iron, manganese, cobalt, chromium, and the acids, as directed in *aa.*

β. A precipitate is formed. Filter, dissolve the precipitate in nitric acid, and treat the solution according to the directions of § 177. III. (109), bearing in mind that only ZINC, LEAD, COPPER, and MERCURY can be present. Treat the filtrate as directed in *α.*

b. A RESIDUE INSOLUBLE IN POTASSA IS LEFT. Add water, boil again, and filter. Dissolve and examine the residue as directed § 168, 2. Treat the alkaline solution according to § 192, *a.*

II. ANALYSIS OF SILICATES.

§ 193.

Whether the body to be analyzed contains a silicate, is ascertained by the preliminary examination with phosphate of soda and ammonia before the blowpipe ; since, in the process of fusion, the metallic oxides dissolve, whilst the separated silicic acid floats about in the liquid bead as a transparent, swollen mass.

The analysis of the silicates differs from the common course only in so far as the preliminary treatment is concerned, which is required to effect the separation of the silicic acid from the bases, and the solution of the latter.

The silicates and double silicates are divided into two distinct classes, which require respectively a different method of analysis ; viz. 1, silicates decomposable by acids (hydrochloric acid, nitric acid, sulphuric acid), and 2, silicates which are not decomposed by acids.

To ascertain to which of these two classes a silicate belongs, reduce it to a very fine powder, and boil a portion with hydrochloric acid. If this fails to decompose it, try another portion with tolerably concentrated sulphuric acid, and apply heat. If this also fails, after some time, to produce the desired effect, the silicate belongs to the second class. Whether decomposition has been effected by the acid or not, is generally learned from external appearances, as a colored solution forms almost invariably, and the separated gelatinous, flocculent, or finely-pulverulent hydrate of silicic acid takes the place of the original heavy powder which grated under the glass rod with which it was stirred; the separated hydrate of silicic acid will, after filtering and washing, dissolve in boiling solution of potassa or soda.

Before proceeding further, test a portion of the pulverized compound also for water, by heating it in a perfectly dry glass tube. If the result shows the substance to contain hygroscopic moisture, dry it by protracted exposure to a temperature of 212°, before proceeding with the analysis.

A. SILICATES DECOMPOSABLE BY ACIDS.

§ 194.

a. Silicates decomposable by Hydrochloric Acid or by Nitric Acid.[*]

1. Heat the finely pulverized silicate with hydrochloric acid until complete decomposition is effected, evaporate to dryness, and expose the residue to a temperature somewhat exceeding 212°, with constant stirring, until no more, or very few, hydrochloric acid vapors escape; allow it to cool, moisten the residue with hydrochloric acid, or as the case may be, with nitric acid, afterwards add a little water, and heat for some time.

This operation effects the separation of the silicic acid, and the solution of the bases in the form of chlorides. Filter, well wash the residue, and examine the solution by the common method, beginning at § 177. The residuary silicic acid may, for precaution be digested with ammonia, filtered, and the filtrate tested for silver, by supersaturation with nitric acid.

2. As in silicates, and more particularly in those decomposed by hydrochloric acid, there are often found other acids, as well as metalloids, the following observations and instructions must be attended to:

α. PHOSPHORIC ACID is detected in the examination for bases, in the precipitate produced by sulphide of ammonium, which always contains it in combination with alumina or the alkaline earths. If you wish, however, to make a special experiment to ascertain whether phosphoric acid is present or not, proceed as directed in *ε.*, and test the filtrate, acidified with nitric acid, with molybdate of ammonia.

β. SULPHIDES and CARBONATES are detected in the process of treating with hydrochloric acid.

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[*] Nitric acid is preferable to hydrochloric acid in cases where compounds of silver or lead are present.

γ. SULPHURIC ACID is detected by means of chloride of barium in the hydrochloric acid solution filtered from the silicic acid, provided the temperature at which the separation of the silicic acid has been effected was not too high.

δ. If the silicic acid which has separated looks black, but becomes white upon ignition in the air, this indicates the presence of CHARCOAL or of an ORGANIC substance. If organic substances are present, the silicate exhales an empyreumatic odor when heated in a glass tube.

ε To detect the BORACIC ACID which may be present, fuse a portion of the substance in a platinum spoon with carbonate of soda and potassa, boil the fused mass with water, filter, and,—

a. Add to a small portion of the filtrate hydrochloric acid until the reaction is distinctly acid, dip a slip of turmeric paper half into the fluid, and dry at a gentle heat. If boracic acid is present, the part of the slip which has been immersed in the fluid appears brownish-red.*

b. Neutralize the remainder of the filtrate nearly with sulphuric acid, evaporate to dryness, and test the residue with alcohol and sulphuric acid, as directed § 136, 5.

ζ. With many silicates boiling with water will suffice to dissolve the metallic CHLORIDES present, which may then be readily detected in the filtrate by means of solution of nitrate of silver; but the safest way is to dissolve the mineral in dilute nitric acid, and test the solution with nitrate of silver.

η. Metallic FLUORIDES, which often occur in silicates in greater or smaller proportion, are detected by the methods described § 138, 6.

b. *Silicates which resist the action of hydrochloric acid, but are decomposed by concentrated sulphuric acid.*

Heat the finely pulverized mineral with moderately concentrated pure sulphuric acid (best in a platinum dish), finally drive off the sulphuric acid, boil the residue with hydrochloric acid, dilute, filter, and treat the filtrate as directed § 178; and the residue, which, besides the separated silicic acid, may contain also sulphates of the alkaline earths, &c., according to the directions of § 191.

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* This method of detecting boracic acid, which *H. Rose* gives in the additions and corrections to the first volume of his Manual, page 946, recommends itself equally by its simplicity and delicacy. A solution of one part of borax in 1000 parts of water, acidified with hydrochloric acid, imparts to turmeric paper, after drying, a distinctly brown tint. This method may, therefore, be employed advantageously also in the general course of analysis to effect the detection of minute traces of boracic acid, which might escape notice by the common method.

B. SILICATES WHICH ARE NOT DECOMPOSED BY ACIDS.

§ 195.

As the silicates of this class are most conveniently decomposed by fusion with carbonate of soda and potassa, the portion so treated cannot, of course, be examined for alkalies. The analytical process is therefore properly divided into two principal parts, viz. a portion of the mineral is examined for the silicic acid and the bases, with the exception of the alkalies, whilst another portion is specially examined for the latter.—Besides these, there are some experiments required, to obtain information as to the presence or absence of other acids.

1. *Detection of the silicic acid and the bases, with the exception of the alkalies.—Examination for phosphoric acid, sulphuric acid, and metallic sulphides.*

Reduce the mineral to a very fine powder, mix this with four parts of carbonate of soda and potassa, and heat the mixture in a platinum crucible over a *Berzelius*' spirit-lamp, until the mass is in a state of calm fusion. Put the crucible with its contents into a porcelain dish, pour water over it, add hydrochloric acid, and heat until the mass is dissolved, with the exception of the silicic acid, which separates in flakes. Remove the crucible from the dish, evaporate the contents of the latter to dryness, and treat the residue as directed § 194, 1, or, as the case may be, according to 2.

2. *Detection of the alkalies.*

To effect this, the silicates under examination must be decomposed by means of a substance free from alkalies. Hydrofluoric acid or a metallic fluoride answers this purpose best; but fusion with hydrate of baryta will also accomplish the end in view.

a. DECOMPOSITION BY MEANS OF A METALLIC FLUORIDE.—Mix one part of the very finely pulverised mineral with five parts of fluoride of barium, or pure, finely pulverized fluoride of calcium, stir in a platinum crucible with concentrated sulphuric acid to a thickish paste, and heat gently for some time in a place affording a free escape to the vapors; finally heat a little more strongly, until the excess of sulphuric acid is completely expelled. Boil the residue now with water, add chloride of barium cautiously as long as a precipitate continues to form, then baryta-water to alkaline reaction, boil, filter, mix with carbonate of ammonia and some ammonia as long as a precipitate forms, and proceed exactly as directed § 185, 2.

b. DECOMPOSITION BY MEANS OF HYDRATE OF BARYTA. Mix one part of the very finely pulverized substance with four parts of hydrate of baryta, expose the mixture for half an hour in a platinum crucible to the strongest possible heat of a good *Berzelius'* lamp, and treat the fused or agglutinated mass with hydrochloric acid and water until it is dissolved; precipitate the solution with ammonia and carbonate of ammonia, filter, evaporate to dryness, ignite, dissolve the residue in water, precipitate again with ammonia and carbonate of ammonia, filter, evaporate, ignite, and test the residue for potassa and soda as directed § 185. If the residue still contains magnesia, this may be readily removed, by adding to its aqueous solution a little finely pulverized oxide of mercury, evaporating to dryness, igniting the dry mass, and then treating it with water, which will dissolve the chlorides of the alkalies, and leave the magnesia undissolved.

3. *Examination for fluorine, chlorine, boracic acid, and phosphoric acid.*

Fuse the very finely pulverized substance with four parts of pure carbonate of soda and potassa until the mass flows calmly; boil the fused mass with water, filter the solution, which contains all the fluorine as fluoride of sodium, all the chlorine as chloride of sodium, all the boracic acid as borate of soda, and at least a part of the phosphoric acid as phosphate of soda, and treat the filtrate as follows:—

a. Acidify a small portion of it with nitric acid, and test for chlorine with nitrate of silver;

b. Test another portion for boracic acid as directed § 195, 2, ε.;

c. Test a third portion, after addition of nitric acid, with molybdate of ammonia for phosphoric acid (which has already been mentioned in 1);

d. To effect the detection of the fluorine, treat the remainder of the filtrate as directed § 138, 7.

That the filtrate may be tested also for sulphuric acid, need hardly be mentioned.

C. SILICATES WHICH ARE PARTIALLY DECOMPOSED BY ACIDS.

§ 196.

Most of the native minerals are mixtures of several silicates, of which the one is often decomposed by acids, the other not. If such minerals were analyzed by the same method as the absolutely insoluble silicates, the analyst would indeed detect all the elements present, but it would not afford a satisfactory insight into the actual composition of the mineral.

It is, therefore, advisable to examine separately those parts which show a different deportment with acids. For this purpose digest the very finely pulverized mineral for some time with hydrochloric acid at a gentle heat, evaporate to dryness, and expose to a temperature somewhat exceeding 212°, with stirring, until no more or very few hydrochloric acid vapors are evolved; let the residue cool, moisten with hydrochloric acid, heat with water, and filter.

The filtrate contains the bases of the decomposed part of the mixed mineral; examine this as directed § 194. The residue contains, besides the silicic acid separated from the base by the action of the hydrochloric acid, that part of the mixed mineral which has resisted the action of the acid. Boil this residue with an excess of solution of carbonate of soda, filter hot, and wash, first with hot solution of carbonate of soda, finally with boiling water.—Test the residuary undecomposed part of the mineral, from which the admixed free silicic acid has thus been removed, according to the instructions given § 195.

III. Analysis of waters.

§ 197.

In the examination of natural waters the analytical process is simplified by the circumstance that we know from experience the elements and compounds which are usually found in them. Now, although a quantitative analysis alone can properly inform us as to the true nature and character of a water, since the differences between the various waters are principally caused by the different proportions in which the several constituents are respectively present, a qualitative analysis may yet render very good service, especially if the analyst notes with proper care, whether a reagent produces a faint or a distinctly marked turbidity, a slight or a copious precipitate, since these circumstances will enable him to make an approximate estimation of their relative proportions in which the several constituents are present.

I separate here the analysis of the common fresh waters (spring-water, well-water, brook-water, river-water, &c.) from that of the mineral waters, in which we also include sea water; for, although no well defined limit can be drawn between the two classes, still the analytical examination of the former is necessarily far more simple than that of the latter, as the number of substances to be looked for is much more limited than in the case of mineral waters.

A. Analysis of the fresh waters (spring-water, well-water, brook-water, river-water, &c.)

§ 198.

We know from experience that the substances to be found in the analysis of such waters are the following:—

a. Bases: Potassa, soda, ammonia, lime, magnesia, protoxide of iron.

b. Acids, &c.: Sulphuric acid, phosphoric acid, silicic acid, carbonic acid, nitric acid, chlorine.

c. Organic matters.

d. Mechanically suspended substances: Clay, &c.

The fresh waters contain indeed also other constituents, besides those enumerated here, as may be inferred from the origin and formation of springs, &c., and has moreover been established by the results of analytical investigations;* but the quantity of such constituents is so trifling that they escape detection, unless hundreds of pounds of the water are subjected to the analytical process. The detection of these constituents has therefore no value for the practical purposes of life, although it may still be of great interest in a scientific point of view.

1. Evaporate the carefully collected water in a glass flask or retort to one half. This generally produces a precipitate. Pass the fluid through a perfectly clean filter (free from iron and lime), wash the precipitate well, after having removed the filtrate, and then examine both as follows:—

a. Examination of the precipitate.

The precipitate contains the constituents which were only kept in solution through the agency of free carbonic acid, or, as the case may be, in the form of bicarbonates, viz., carbonate of lime, carbonate of magnesia, hydrated sesquioxide of iron (which was in solution as bicarbonate of protoxide of iron, and precipitates upon boiling as sesquioxide; if phosphoric acid is present, also in combination with that acid), phosphate of lime,—and besides, silicic acid, and sometimes also sulphate of lime, if that substance is present in large proportion—and clay which was mechanically suspended in the water.

Dissolve the precipitate in the filter in the least possible quantity of dilute hydrochloric acid—effervescence indicates the presence of CARBONIC ACID—and mix separate portions of the solution:—

α. With sulphocyanide of potassium, red coloration: IRON;

β. With ammonia; heat, filter, if necessary, mix the filtrate with oxalate of ammonia, and let the mixture stand for some time in a warm place. The formation of a white precipitate indicates the presence of LIME—in the form of carbonate, or sulphate if sulphuric acid is detected in *γ*.—Filter, mix the filtrate again with ammonia, add some phosphate of soda, stir with a glass rod, and let the mixture stand for twelve hours. The formation of a white, crystalline precipitate, which is often visible only on the sides of the vessel when the fluid is poured off, indicates the presence of MAGNESIA (carbonate of);

γ. With chloride of barium, and let the mixture stand for twelve hours in a warm place. The formation of a precipitate—which, when very incon-

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* *Chatin* (Journ. de Pharm. et de Chim. 3 Sér. T. XXVII. p. 418) found iodine in all fresh water plants, but not in land plants, a proof that the water of rivers, brooks, ponds, &c. contains traces, even though infinitely minute ones, of metallic iodides. According to *Marchand* (Compt. rend. T. XXXI., p. 495) all waters contain iodine, bromine, and lithia. And it may be affirmed with the same certainty that all, or at all events most waters contain compounds of strontia, fluorine, &c.

siderable, is best seen if the supernatant clear fluid is cautiously decanted, and the small quantity remaining shaken about in the glass—indicates the presence of SULPHURIC ACID.

δ. Add some of the fluid to a solution of molybdate of ammonia, acidified with hydrochloric acid, and boil. The appearance of a yellow color, or the formation of a yellow precipitate, indicates the presence of PHOSPHORIC ACID.*

b. Examination of the filtrate.

α. Mix a portion of the filtrate with a little hydrochloric acid and chloride of barium. The formation of a white precipitate, which makes its appearance at once, or perhaps only after standing some time, indicates SULPHURIC ACID.

β. Mix another portion with nitric acid, and add nitrate of silver. The formation of a white precipitate, or a white turbidity, indicates the presence of CHLORINE.

γ. Evaporate a third larger portion nearly to dryness, and test the residue, first with reddened litmus, or turmeric paper, then, after addition of hydrated sulphuric acid, with solution of sulphate of protoxide of iron, for NITRIC ACID (§ 149). If the evaporated fluid had an alkaline reaction, and CARBONIC ACID escaped upon the addition of the sulphuric acid, an alkaline carbonate is present. If the color of the reddened litmus-paper has changed to blue, test another portion of the filtrate for PHOSPHORIC ACID, by one of the methods given in *a.* (Examination of the precipitate.)

δ. Mix the remainder of the filtrate with some chloride of ammonium, add ammonia and oxalate of ammonia, and let the mixture stand for some time in a warm place. The formation of a precipitate indicates the presence of LIME. Filter, and test,—

> *aa.* A small portion with ammonia and phosphate of soda, for MAGNESIA.
>
> *bb.* Evaporate the remainder to dryness, heat the residue to redness, and examine it for POTASSA and SODA, according to the directions of § 185.

2. Acidify a tolerably large portion of the filtered water with hydrochloric acid, and evaporate nearly to dryness; divide the residue into two parts, and,—

a. Test the one with hydrate of lime, for AMMONIA (compare § 186.)

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* In default of molybdate of ammonia, evaporate the remainder of the hydrochloric acid solution of the precipitate to dryness, redissolve the residue in a little hydrochloric acid and water, filter the solution, and mix the filtrate with carbonate of soda until it is nearly neutralized, then with acetate of soda and a very trifling quantity of sesquichloride of iron. The formation of a white precipitate, which generally becomes visible only after long standing, indicates the presence of PHOSPHORIC ACID.

b. Evaporate the other to dryness, moisten the residue with hydrochloric acid, add water, heat, and filter, if a precipitate remains. The precipitate may consist of SILICIC ACID and of CLAY which have been mechanically suspended in the water; these two substances may be separated from each other by boiling with solution of carbonate of soda. The precipitate is often dark-colored from the presence of organic substances; but it becomes perfectly white upon ignition.

3. Mix another portion of the water, fresh taken from the well, &c., with lime-water. If a precipitate is thereby produced, FREE CARBONIC ACID or a BICARBONATE is present. If the former is present (free carbonic acid), no permanent precipitate is obtained when a larger portion of the water is mixed with only a small amount of lime-water, since in that case soluble bicarbonate of lime is formed.

4. To detect the presence of ORGANIC MATTERS, evaporate a portion of the water to dryness, and gently ignite the residue: blackening of the mass denotes the presence of organic substances. If this experiment is to give conclusive results, the evaporation of the water, as well as the ignition of the residue, must be conducted in a glass flask or a retort.

5. If you wish to examine the MATTERS MECHANICALLY SUSPENDED in a water (in muddy brook or river-water, for instance), fill a large glass bottle with the water, cork securely, and let it stand at rest for several days, until the matter has deposited; remove now the clear supernatant fluid with the aid of a syphon, filter the remainder, and examine the sediment in the filter. As this sediment may consist of the finest dust of various minerals, treat it first with hydrochloric acid, and examine the part insoluble in that menstruum in the manner directed § 193 (Examination of silicates).

B. ANALYSIS OF MINERAL WATERS.

§ 199.

The analysis of mineral waters embraces a larger number of constituents than that of fresh water. The following are the principal of the additional elements to be looked for:—

LITHIA, BARYTA, STRONTIA, ALUMINA, PROTOXIDE OF MANGANESE, BROMINE, IODINE, FLUORINE, HYDROSULPHURIC ACID, CRENIC ACID, and APOCRENIC ACID.

The analyst has, moreover, to examine the muddy ochreous or hard sinter-deposits of the spring, for ARSENIOUS ACID, ARSENIC ACID, OXIDE OF COPPER, OXIDE OF LEAD, and the oxides of other heavy metals. The greatest care is required in this examination, to ascertain whether these oxides come really from the water, and do not perhaps proceed from metal pipes, stopcocks, &c.* The absolute purity of the reagents employed in these delicate investigations must also be ascertained with the greatest care.

1. EXAMINATION OF THE WATER.

a. OPERATIONS AT THE SPRING.

§ 200.

1. Filter the water, if not perfectly clear, through Swedish filter paper, and collect the filtrate in large bottles with glass stoppers. The sediment remaining in the filter, which contains, besides the suspended flocculent matter, also the constituents which separate at once upon contact with the air (hydrate of sesquioxide of iron, and compounds of sesquioxide of iron with phosphoric acid, silicic acid, arsenic acid), is taken to the laboratory, to be examined afterwards according to the directions of § 201, 2, *b. β. bb.*

2. The presence of FREE CARBONIC ACID is usually sufficiently visible to the eye. However, to convince yourself by positive reactions, test the water with sensitive blue litmus-paper, and with lime-water. If carbonic acid is present, the former acquires a red color, which disappears again upon drying; the latter produces turbidity, which must disappear again upon addition of the mineral water in excess.

3. Free HYDROSULPHURIC ACID is most readily detected by the smell. For this purpose half fill a bottle with the mineral water, cover with the hand, shake, take off the hand, and smell the bottle. In this way distinct traces of hydrosulphuric acid are often found, which would escape detection by reagents. However, if you wish to have some visible reactions, fill a large white bottle with the water, add a few drops of solution of acetate of lead, place the bottle on a white surface, and look in at the top, to see whether the water acquires a brownish color or deposits a blackish precipitate ;—or half fill a large bottle with the water, and close with a cork to which is attached a small slip of paper, previously steeped in solution of acetate of lead and moistened with a little solution of carbonate of ammonia; shake the bottle gently from time to time, and observe whether the paper slip acquires a brownish tint in the course of a few hours. If the addition of acetate of lead to the water has imparted a brown color to the fluid, or produced a precipitate in it, whilst the reaction with the paper slip gives no result, this indicates that the water contains an alkaline sulphide, but no free hydrosulphuric acid.

4. Mix a wineglass-full of the water with some tannic acid, another

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* Compare "Chemische Untersuchung der wichtigsten Mineralwasser des Herzogthums Nassau, von Professor Dr. *Fresenius;* I. Der Kochbrunnen zu Wiesbaden; II. Die Mineralquellen zu Ems, III. die Quellen zu Schlangenbad, Wiesbaden, bei *C. W. Kreidel.* 1850—1852."

wineglass-full with some gallic acid. If the former imparts a blue violet color, the latter a red violet color to the water, **PROTOXIDE OF IRON** is present. Instead of the two acids, you may employ infusion of galls, which contains them both.

5. OPERATIONS IN THE LABORATORY.

§ 201.

As it is always desirable to obtain even in the qualitative examination some information as to the quantitative composition of a mineral water *i. e.* as to the proportions in which the several constituents are contained in it, it is advisable to analyse a comparatively small portion for the principal constituents, and to ascertain, as far as may be practicable, the relative proportions in which these constituents exist, and thereby also the character of the water; and then to examine a very large amount of the water for those elements which are present only in minute quantities. For this purpose proceed as follows:—

1. Boil about two pounds of the clear water, or of the filtrate, which you have brought from the spring, in a glass flask for one hour, taking care, however, to add from time to time some distilled water, that the quantity of liquid may remain undiminished, and thus the separation of any but *those* salts be prevented which owe their solution to the presence and agency of carbonic acid. Filter after an hour's ebullition, and examine the precipitate and the filtrate as directed § 198.

2. Evaporate a large quantity (about twenty pounds) of the water in a covered porcelain dish to dryness on the water or sand bath; conduct this operation with the most scrupulous cleanliness in a place as free as possible from dust.

a. Introduce a small quantity of the dry residue into a little retort, or into a test-tube, and heat cautiously over the lamp. If the residue becomes black or brown, this denotes the presence of organic matters.*

b. Triturate two-thirds of the remainder of the residue with strong and pure spirit of wine, with the aid of a pestle; let the mixture digest for some time, and filter.

α. The alcoholic filtrate contains all the iodine and bromine present, combined, according to circumstances, with sodium, calcium, or magnesium. Evaporate it to dryness, in which process much chloride of sodium usually remains. Triturate this residue again with spirit of wine, digest, filter, evaporate the filtrate again to dryness, dissolve the residue in very little water, and test,—

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* This inference is, however, correct only if the water has been effectually protected from dust during the process of evaporation; if this has not been the case, and you yet wish to ascertain beyond doubt whether organic matters are present, evaporate a separate portion of the water in a retort. If you have found organic matter, and wish to know whether it consists of crenic acid or of apocrenic acid, treat a portion of the residue as directed § 202, 2.

aa. A portion of the solution for IODINE with starch-paste and chlorine water (§ 145).

bb. If no iodine has been found, the remainder with chlorine water and ether for BROMINE (§ 144). But if iodine has been detected, mix the remainder of the solution with some sodio-protochloride of palladium, let the mixture stand at rest for some time, filter the fluid from the precipitated iodide of palladium, and test the filtrate for bromine with chlorine water and ether.

β. Mix the residue with water, add hydrochloric acid sufficient to impart a slightly acid reaction to the fluid (if you add more of the acid than is absolutely necessary for this purpose, fluorine may escape upon the subsequent evaporation of the fluid), and evaporate to dryness. Should the water contain no sulphuric acid, which, however, is only very rarely the case, you must previously add a little sulphate of soda. Treat the residue with water at a gentle heat, with addition of a little hydrochloric acid, and then filter the fluid from the undissolved part, which consists principally of silicic acid, but may contain besides small quantities of sulphate of baryta, strontia, and lime, and also of fluoride of calcium.

aa. Examination of the precipitate. Boil with solution of soda in excess, until the silicic acid is dissolved ; dilute slightly, and filter. If a residue remains in the filter, wash this, dry the filter, incinerate in a platinum crucible, add, after cooling, some concentrated sulphuric acid, cover the crucible with a watch-glass coated with wax, and arranged in the proper manner (§ 138), and let it stand for several hours in a warm place. If the parts of the glass exposed appear etched after the removal of the wax coating, the residue contained a compound of FLUORINE (fluoride of calcium). Heat now the contents of the crucible more strongly over the lamp, until all free sulphuric acid is expelled, put some carbonate of soda and potassa into the crucible, heat for some time to fusion, boil the residue with water, filter, wash thoroughly, dissolve the residue—which must remain if sulphates of alkaline earths are present—on the filter in the least possible quantity of dilute hydrochloric acid, add an equal volume of spirit of wine, then some pure hydrofluosilicic acid, and let the mixture stand for twelve hours. If a precipitate has made its appearance after this time, this shows the presence of BARYTA. Filter, warm the filtrate in a small platinum dish, adding from time to time some water, until all the alcohol is expelled, and mix the fluid finally with a saturated solution of sulphate of lime. If a precipitate is thereby produced, even though only after several hours' standing, it consists of sulphate of STRONTIA. To make sure, boil the washed precipitate with moderately dilute hydrochloric acid, filter hot, and test the solution with chloride of barium, which must produce turbidity. Compare also § 96.

bb. Examination of the filtrate. Mix the filtrate in a flask with chlorine water, then with ammonia in excess, close the flask, and let it stand for twelve hours in a warm place.* Filter, wash the precipitate, pierce the point of the filter, rinse the precipitate through, dissolve it in a little hydrochloric acid, mix the unfiltered solution with some tartaric acid, then with ammonia in excess, and let the mixture stand for twelve hours. If a trifling precipitate makes its appearance, filter, incinerate the filter, and test the ash for FLUORINE as directed § 138, 5. Pour the filtrate, or the clear fluid, as the case may be, into a small flask, add cautiously, and drop by drop, sulphide of ammonium in moderate excess. Close the flask, let it stand, until the fluid over the precipitate looks yellowish (but not greenish), and then filter rapidly. Test the precipitate before the blowpipe with carbonate of soda for MANGANESE ; mix the filtrate with hydrochloric acid in excess, heat the fluid to 158°—176°, and allow it to stand in a warm place for twelve hours. If the precipitate contained ARSENIC ACID, the separated sulphur contains sulphide of arsenic. Examine it for the latter substance, by digesting with some ammonia, filtering, evaporating the filtrate to dryness, with addition of a minute quantity of carbonate of soda, and treating the residue with cyanide of potassium and carbonate of soda in a stream of carbonic acid (§ 127). Mix the fluid filtered from the sulphur precipitate—and which must contain all the alumina and phosphoric acid present—with some perfectly pure nitrate of potassa or soda, evaporate in a small platinum dish to dryness, and heat the residue until all the salts of ammonia are expelled and the tartaric acid is completely destroyed ; heat the residue after this with hydrochloric acid and water, filter, mix one half of the filtrate with ammonia just to alkaline reaction, and allow the fluid to stand in a warm place for several hours. The formation of a flocculent precipitate demonstrates the presence of ALUMINA. Test the other half for PHOSPHORIC ACID with molybdate of ammonia, if you have not already detected that acid in 1.

c. Use the remainder of the residue left upon evaporation of the twenty pounds of the mineral water to examine for lithia. For this purpose boil with water and add as much hydrochloric acid as will impart a distinctly acid reaction to the solution ; add ammonia, carbonate of ammonia, and some oxalate of ammonia, allow the mixture to stand for some time in a warm place, and then filter the fluid from the precipitate of carbonate of lime, &c., which is usually copious. Evaporate the filtrate to dryness, heat the residue to redness, to expel the salts of ammonia, redissolve in water and some hydrochloric acid, add solution of soda in excess, let the mixture stand some time, and then filter the fluid from the precipitated

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* If the water contains no iron, a little sesquichloride of iron must be added to it after the addition of the chlorine water.

magnesia, and evaporate the filtrate to dryness, with addition of phosphate of soda. Treat the residue with water; if this leaves a white powder undissolved, the presence of LITHIA is indicated. For the ulterior examination of this powder, compare § 90.

3. Concentrate a large portion of the water to a considerable extent by boiling, with addition of some carbonate of soda in excess; filter, nearly saturate the filtrate with hydrochloric acid, and boil almost to dryness, filter the little remaining fluid from the chloride of sodium which separates; acidify a portion with hydrochloric acid, and test this with turmeric paper for BORACIC ACID (§ 194, 2, ε.). If boracic acid is present—which will be found to be the case more particularly in hot springs*—test the remainder of the fluid, after evaporation to dryness, as directed § 136, 6.

4. If you have not already clearly detected ammonia in 1, add to a larger quantity of water hydrochloric acid to acid reaction, and concentrate the fluid considerably by boiling in a retort. Add now, through the tubular neck of the retort, an excess of milk of lime, prepared with recently ignited hydrate of lime, boil, and conduct the vapor into a flask containing very dilute hydrochloric acid, and which must be kept cool, by surrounding it with ice or very cold water; finally evaporate the contents of the flask almost to dryness, and test for ammonia with hydrate of lime or with bichloride of platinum.

2. EXAMINATION OF THE SINTER-DEPOSITS.

§ 202.

1. Free the ochreous or sinter-deposit from impurities, by sifting, elutriation, &c. and from the soluble salts adhering to it, by washing with water; digest a large quantity (about 200 grammes) of the residue with water and hydrochloric acid, until the soluble part is completely dissolved; dilute, cool, filter, and wash the residue.

a. Examination of the filtrate.

α. Saturate one-half of the filtrate nearly with carbonate of soda, add some sulphate of soda or of potassa, and allow the mixture to stand for twenty-four hours at a gentle heat. If a precipitate is found to have formed after this time, filter, wash the precipitate, pour hydrosulphuric acid over it, that you may not overlook the possible presence of sulphate of lead, and test for BARYTA and STRONTIA as directed § 201, 2, *b. β. aa.* Boil the fluid filtered from this precipitate with sulphite of soda—if necessary, with addition of some hydrochloric acid as the fluid must always remain acid—to reduce the sesquioxide of iron to protoxide, and the arsenic acid, which may be present, to arsenious acid; heat finally, until all sulphurous acid is expelled, and conduct for some hours a slow stream of washed hydrosulphuric acid gas into the fluid; allow the latter now to

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* I detected it in the Kochbrunnen at Wiesbaden.

stand in a moderately warm place until the smell of hydrosulphuric acid has become quite faint: if a precipitate has formed, filter, wash, and digest the precipitate with dilute solution of soda and some sulphide of sodium; filter, and mix the filtrate with hydrochloric acid to acid reaction. If a precipitate is thereby produced, test,—

aa. A portion of it for ARSENIC, with cyanide of potassium and carbonate of soda in a stream of carbonic acid.

bb. Treat the remainder as directed § 180, that traces of ANTIMONY and TIN, which may happen to be present, may not be overlooked.

If a residue has been left upon treating the precipitate produced by hydrosulphuric acid with solution of soda and sulphide of sodium, boil this residue, together with the filter, with a very little dilute nitric acid, filter, wash the filter thoroughly, and pour solution of hydrosulphuric acid over it, that you may not overlook the sulphate of lead which may have separated; mix the filtrate with some pure sulphuric acid, evaporate to dryness in the water bath, and treat the residue with water. If this leaves an undissolved residue, the latter consists of SULPHATE OF LEAD. To make quite sure, filter, wash the residue, treat it with hydrosulphuric acid water, and observe whether that reagent imparts a black color to it. Test the fluid filtered from the sulphate of lead which may have separated, *a* with ammonia, *b* with ferrocyanide of potassium, for COPPER.

Oxidize the fluid filtered from the precipitate produced by hydrosulphuric acid, with nitric acid, saturate nearly with carbonate of soda, then add to the tepid fluid carbonate of baryta, let the mixture stand for twenty-four hours, and filter.—Wash the precipitate thoroughly, dissolve in hydrochloric acid, remove the baryta by means of sulphuric acid, and then test for ALUMINA and PHOSPHORIC ACID in the manner directed § 201, 2, *b. β. bb.* (the presence of IRON is usually sufficiently visible to the eye).

Boil the fluid filtered from the precipitate produced by carbonate of baryta, and, whilst boiling, add sulphuric acid to precipitate the baryta; filter, mix the filtrate in a flask with ammonia and sulphide of ammonium, and let the mixture stand for twelve hours in a warm place. If a precipitate forms, examine this for MANGANESE and ZINC (§ 182). Test the fluid filtered from this precipitate for LIME* and MAGNESIA in the usual way.

β. Mix a portion of the hydrochloric acid solution with chloride of barium, and let the mixture stand for twelve hours in a warm place. The formation of a white precipitate indicates the presence of SULPHURIC ACID.

γ. Precipitate the remainder in a flask with ammonia, close the flask, and let it stand for twelve hours, filter, dry the precipitate, triturate it, and test with sulphuric acid, in a platinum crucible, for FLUORINE

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* Of course all the lime is not found here, but only a quantity corresponding to the degree of solubility of sulphate of lime.

(§ 138, 5 and 6). (Upon treating the sinter with hydrochloric acid the fluorine may have dissolved as silicofluoride of calcium, in which case it must be present in the ammonia precipitate as fluoride of calcium). Upon heating the residue until the sulphuric acid is completely expelled, and then digesting it with hydrochloric acid, the SILICIC ACID which had dissolved in the hydrochloric acid will be left behind.

b. Examination of the residue.

This consists usually of silicic acid, clay, and organic matters, but it may contain also sulphate of baryta and sulphate of strontia, as well as fluoride of calcium. Boil in the first place with solution of soda or potassa, to dissolve the silicic acid; then test the residue for FLUORINE in the manner directed § 138, 5 or 6, evaporate the sulphuric acid, and fuse the residue with carbonate of soda and potassa. Dissolve the residue which remains upon boiling with water, in some hydrochloric acid, boil, add ammonia, filter the fluid from the alumina which may precipitate, evaporate the filtrate to dryness, ignite the residue, redissolve it in very little water, with addition of a drop of hydrochloric acid, and test for BARYTA and STRONTIA as directed § 201, 2, *b. β.*

2. Boil the ochreous or sinter deposit for a considerable time with concentrated solution of potassa or soda, and filter.

a. Acidify a portion of the filtrate with acetic acid, add ammonia, let the mixture stand for twelve hours, and then filter the fluid from the precipitate of alumina and hydrated silicic acid, which usually forms, again add acetic acid to acid reaction, and then a solution of neutral acetate of copper. If a brownish precipitate is formed, this consists of APOCRENATE OF COPPER. Mix the fluid filtered from the precipitate with carbonate of ammonia, until the green color has changed to blue, and heat. If a bluish-green precipitate is formed, this consists of CRENATE OF COPPER.

b. If you have detected arsenic, use the remainder of the alkaline fluid to ascertain whether the arsenic existed in the sinter as arsenious acid of as arsenic acid. Compare § 129.

IV. ANALYSIS OF SOILS.

§ 203.

Soils must necessarily contain all the constituents which are found in the plants growing upon them, with the exception of those supplied by the atmosphere and the rain. When we find, therefore, a plant, the constituent elements of which are known, growing in a certain soil, the mere fact of its growing there gives us some insight into the composition of that soil, and may accordingly save us, to some extent, the trouble of a qualitative analysis.

It may, therefore, appear quite superfluous to make qualitative analysis of soils on which plants are growing; for it is well known that the ashes of plants contain almost invariably the same constituents, and the differences between them are caused principally by differences in their relative proportions. But in order to a correct appreciation of the quality and condition of soils, the form and composition under which their constituents exist, must be ascertained; they must be mechanically divided into their component parts, and the physical properties[*] of each must be known. When these points are correctly ascertained, they will enable the analyst to deduce inferences which may in many cases supersede the necessity for a *quantitative* analysis, which is a far more tedious and difficult task.

As plants can only absorb substances in a state of solution, it is a matter of especial importance, in the qualitative analysis of a soil, to know which are the constituents that are soluble in water, which those that require an acid for their solution (in nature principally carbonic acid), and finally which those that are neither soluble in water nor in acids, and are not, accordingly, in a position for the time being to afford nutriment to the plant. With regard to the insoluble substances, another interesting question to answer is, whether they suffer disintegration readily, or slowly and with difficulty, or whether they altogether resist the action of disintegrating agencies;—and also what are the products which they yield upon their disintegration.[†]

In the analysis of soils, the constituents soluble in water, those soluble in acids, and the insoluble constituents must be examined separately. The examination of the organic portion also demands a separate process.

The analysis is therefore properly divided into the following four parts:

1. *Preparation and examination of the aqueous extract.*

§ 204.

About two pounds (1000 grammes) of the air-dried soil are used for the preparation of the aqueous extract. To prepare this extract quite clear is a matter of some difficulty; in following the usual course, viz. digesting or boiling the earth with water, and then filtering, the fine particles of clay are speedily found to impede the operation, by choking up the pores of the filter; they also almost invariably render the filtrate turbid, at least the portion which passes through first. I found the following method the

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[*] With regard to the mechanical separation of the component parts of a soil, and the examination of its physical properties and chemical condition and quality, compare *Fr. Schulze's* paper "Anleitung zur Untersuchung der Ackererden auf ihre wichtigsten physikalischen Eigenschaften und Bestandtheile."—Journal f. prakt. Chemie, Bd. 47, p. 241.

[†] For more ample information on this subject I refer the reader to *Fresenius* "Chemie für Landwirthe, Forstmänner und Cameralisten," Braunschweig bei *Vieweg*, 1847, p. 485.

most practical.* Close the neck of several middle-sized funnels with small filters of coarse blotting paper, moisten the paper, press it close to the sides of the funnels, and then introduce the air-dried soil, in small lumps ranging from the size of a pea to that of a walnut, but not pulverized or even crushed; fill the funnels with the soil to the extent of about two-thirds. Pour distilled water into them, in sufficient quantity to cover the soil; if the first portion of the filtrate is turbid, pour it back on the filter. Let the operation proceed quietly. When the first quantity of the fluid has passed, fill the funnels a second, and after this a third time. Collect the several filtrates in one vessel. Treat the contents of the funnels repeatedly with hot water, in order to remove all the soluble matter, the lixiviated soil being required for the preparation of the acid extract.

a. Concentrate two-thirds of the aqueous solution by cautiously evaporating in a porcelain dish, filter off a portion, and test its reaction; put aside a portion of the filtrate for the subsequent examination for organic matters, according to the directions of 4. Heat the remainder, and add nitric acid. Evolution of gas indicates the presence of an ALKALINE CARBONATE. Then test with nitrate of silver for CHLORINE. *b.* Transfer the remainder of the concentrated fluid, together with the precipitate which usually forms in the process of concentration, to a small porcelain or, which is preferable, platinum dish, evaporate to dryness, and cautiously heat the brownish residue over the lamp until complete destruction of the organic matter is effected. In presence of NITRATES this operation is attended with deflagration, which is more or less violent, according to the greater or smaller proportion in which these salts are present. *c.* Test a small portion of the gently ignited residue with carbonate of soda before the blowpipe for MANGANESE. *d.* Heat the remainder with water, add some hydrochloric acid (effervescence indicates the presence of CARBONIC ACID), evaporate to dryness, heat a little more strongly, to effect the complete separation of the silicic acid, moisten with hydrochloric acid, add water, heat, and filter. The washed residue generally contains some charcoal, and also a little clay—if the aqueous extract was not perfectly clear—and SILICIC ACID. To detect the latter, make a hole in the point of the filter, rinse the residue through, boil with solution of carbonate of soda, filter, saturate with hydrochloric acid, evaporate to dryness, and treat the residue with water, which will leave the silicic acid.

e. Test a small portion of the hydrochloric acid solution with chloride of barium for SULPHURIC ACID; mix the remainder with ammonia, filter the fluid from the precipitate which forms, throw down the LIME from the

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* Recommended by *Fr. Schulze* "Anleitung zur Untersuchung der Ackererden auf ihre wichtigsten physikalischen Eigenschaften und Bestandtheile." Journ. f. prakt. Chemie, Bd. 47, p. 241.

filtrate by means of oxalate of ammonia, and proceed for the detection and separation of MAGNESIA, and for the detection of POTASSA and SODA, exactly as directed § 185.

f. Dissolve the precipitate produced by ammonia (*e*) in some hydrochloric acid, and test a small portion of the solution with ferrocyanide of potassium or sulphocyanide of potassium for IRON; mix the remainder with ammonia to moderate predominance, then with acetic acid in slight excess. If a white precipitate remains, this consists of PHOSPHATE OF SESQUIOXIDE OF IRON).[*] Filter, mix the filtrate with oxalate of ammonia, and let the mixture stand some time. If a precipitate is formed, this proceeds from LIME, which had passed into the ammonia precipitate in combination with phosphoric acid. Filter, mix with ammonia in excess, and stir. The formation of a crystalline precipitate immediately or after some time, indicates the presence of PHOSPHATE OF MAGNESIA. The PHOSPHORIC ACID which was in combination with the lime may then be found by adding some solution of sulphate of magnesia to the filtrate.

g. If you have detected iron, test a portion of the remaining third of the aqueous extract with ferricyanide of potassium, another with sulphocyanide of potassium, both after previous addition of some hydrochloric acid: this will indicate the degree of oxidation in which the iron is present. Mix the remainder of the aqueous extract with a little hydrochloric acid, evaporate on the water-bath nearly to dryness, and test the residue for AMMONIA, by adding hydrate of lime.

2. *Preparation and examination of the acid extract.*

§ 205.

a. Heat about fifty grammes of the soil from which the part soluble in water has been removed as far as practicable[†] (see § 204), with moderately strong hydrochloric acid (effervescence indicates CARBONIC ACID) for several hours on the water-bath, filter, and test small portions of the filtrate for SULPHURIC ACID, PROTOXIDE and SESQUIOXIDE OF IRON in the manner directed in 1. *b.* Evaporate the remainder in a porcelain dish to dryness, heat a little more strongly, with stirring, moisten with hydrochloric acid, treat with water, and filter. *c.* Wash the residue, and then ignite in a platinum crucible, to detect the SILICIC ACID remaining after the combustion of the organic matters. *d.* Mix the filtrate with ammonia until the free acid is neutralized, then with sulphide of ammonium, filter, and test the filtrate for LIME, MAGNESIA, POTASSA, and SODA, as in 1. *e.* Wash the precipitate, which is usually black from sulphide of

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[*] Alumina is hardly ever found in the aqueous extract; *Fr. Schulze* never detected any of that substance in it.

[†] Complete lixiviation is generally impracticable.

iron, with water containing some sulphide of ammonium, pierce the filter, rinse the contents into a porcelain dish, add hydrochloric acid, and boil until the precipitate is dissolved—with the exception of the separated sulphur—and the fluid smells no longer of hydrosulphuric acid. Filter, add carbonate of soda* to alkaline reaction, then solution of soda in sufficient quantity, boil some time, and filter. *f.* Examine the filtrate for ALUMINA and PHOSPHORIC ACID in the manner directed § 182, 1, *a.*,—the residue for MANGANESE, IRON, PHOSPHORIC ACID, and also for the LIME and MAGNESIA combined with the phosphoric acid, exactly as instructed § 182, 2, *a.*, *β.*, *aa.*

3. *Examination of the inorganic constituents insoluble in water and acids.*

§ 206.

The operation of heating the lixiviated soil with hydrochloric acid (§ 205, *a*) leaves still the greater portion of it undissolved. If you wish to subject this undissolved residue to a chemical examination, wash, dry, and sift, to separate the large and small stones from the clay and sand; moreover, separate the two latter from each other by elutriation. Subject the several portions separated to the analytical process given for the silicates (§ 193).

4. *Examination of the organic constituents of the soil.*†

§ 207.

The organic constituents of the soil, which exercise so great an influence upon its fertility, both by their physical and chemical action, are partly portions of plants in which the structure may still be recognised (fragments of straw, roots, seeds of weeds, &c.), partly products of vegetable decomposition, which are usually called by the general name of HUMUS, but differ in their constituent elements and properties, according to whether they proceed from nitrogenous or non-nitrogenous parts of plants,—whether alkalies or alkaline earths have or have not had a share in their formation—whether they are in the incipient or in a more advanced stage of decomposition. To separate these several component parts of humus would be an exceedingly difficult task; the following operations are amply sufficient to answer all the purposes of a qualitative analysis of the organic constituents of a soil.

a. Examination of the organic substances soluble in water.

Evaporate the portion of the filtrate of 204, *a*, which has been put aside

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* Dry carbonate of soda answers the purpose best.

† Compare *Fresenius'* "Chemie für Landwirthe, Forstmänner und Cameralisten," Braunschweig bei *Vieweg*, 1847, §§ 282—285.

for the purpose of examining the organic constituents, on the water-bath to perfect dryness, and treat the residue with water. The ulmic, humic, and geïc acids, which were in the solution in combination with bases, remain undissolved, whilst crenic acid and aporcrenic acid are dissolved in combination with ammonia; for the manner of detecting the latter acids, see § 202, 2.

b. Treatment with an alkaline carbonate.

Dry a portion of the lixiviated soil with water, and sift to separate the fragments of straw, roots, &c., together with the little stones, from the finer parts; digest the latter for several hours, at a temperature of 176°—194°, with solution of carbonate of soda, and filter. Mix the filtrate with hydrochloric acid to acid reaction. If brown flakes separate, these proceed from ulmic acid, humic acid, or geïc acid. The larger the quantity of ulmic acid present the lighter, the larger that of humic acid or geïc acid, the darker the brown color of the flakes.

c. Treatment with caustic alkali.

Wash the soil boiled with solution of carbonate of soda (*b*) with water, boil several hours with solution of potassa, replacing the water in proportion as it evaporates, dilute, filter, and wash. Treat the brown fluid as in *b*. The ulmic and humic acids which separate in this process, have only been formed from ulmine and humine by boiling with solution of potassa.

V. DETECTION OF INORGANIC SUBSTANCES IN PRESENCE OF ORGANIC SUBSTANCES.

§ 208.

The impediments which the presence of coloring, slimy, and other organic substances throw in the way of the detection of inorganic bodies, and that the latter can often be effected only after the total destruction of the organic admixture, will be readily conceived, if we reflect that changes of color or the formation of precipitates in dark colored fluids escape the eye, that slimy fluids cannot be filtered, &c. Now, as these difficulties are very often met with in the analysis of medicinal substances, and more especially in the detection of inorganic poisons in articles of food or in the contents of the stomach, and, lastly, also in the examination of plants and animals, or parts of them, for their inorganic constituents, I will here point out the processes best adapted to lead to the attainment of the object in view, both in the general way and in special cases.

1. *General rules for the detection of inorganic substances in presence of organic matters, which by their color, consistence, &c., impede the application of the reagents, or obscure the reactions produced.*

§ 209.

We confine ourselves here, of course, to the description of the most generally applicable methods, leaving the adaptation of the modifications which circumstances may require in special cases, to the discretion of the analyst.

1. THE SUBSTANCE UNDER EXAMINATION DISSOLVES IN WATER, BUT THE SOLUTION IS DARK COLORED OR OF SLIMY CONSISTENCE.

a. Boil a portion of the solution with hydrochloric acid, and gradually add chlorate of potassa, until the mixture is decolorized and perfectly fluid; heat until the fluid exhales no longer the odor of chlorine, then dilute with water, and filter. Examine the filtrate in the usual way, commencing at § 178.

b. Boil another portion of the solution for some time with nitric acid, filter, and test the filtrate for SILVER, POTASSA, and HYDROCHLORIC ACID. If the nitric acid succeeds in effecting the ready and complete destruction of the coloring and slimy matters, &c., this method is often preferable to all others.

c. ALUMINA and SESQUIOXIDE OF CHROMIUM might escape detection by this method, because ammonia and sulphide of ammonium fail to precipitate these oxides from fluids containing non-volatile organic substances. Should you have reason to suspect the presence of these oxides, deflagrate a third portion of the substance with nitrate of potassa, and some carbonate of soda, and boil the fused mass with solution of soda. The alumina is now found by acidifying with nitric acid, and then adding ammonia; the chromium—as alkaline chromate—in the filtrate, by means of acetate of lead, after addition of acetic acid.

2. BOILING WATER FAILS TO DISSOLVE THE SUBSTANCE, OR EFFECTS ONLY PARTIAL SOLUTION; THE FLUID ADMITS OF FILTRATION.

Filter, and treat the filtrate either as directed § 177, or, should it require decolorization, according to the directions of § 209, 1. The residue may be of various kinds.

a. IT IS FATTY. Remove the fatty matters by means of ether, and should a residue be left, treat this as directed § 167.

b. IT IS RESINOUS. Use alcohol instead of ether, or apply both liquids successively.

c. IT IS OF A DIFFERENT NATURE, *e.g.* woody fibre, &c. Dry, and ignite a portion of the dried residue in a porcelain or platinum vessel, until total or partial incineration is effected; boil the residue with nitric acid and water, and examine the solution as directed § 177, III.; if a residue has been left, treat this according to the directions of § 191.

β. Examine another portion for the heavy metals, in the manner directed § 209, 1, *a*; as in *a* not only the compounds of mercury which may be present will volatilize, but also arsenic, cadmium, zinc, &c.

γ. Test the remainder for ammonia, by triturating it together with hydrate of lime.

3. THE SUBSTANCE DOES NOT ADMIT OF FILTRATION OR ANY OTHER MEANS OF SEPARATING THE DISSOLVED FROM THE UNDISSOLVED PART.

Treat the substance in the same manner as the residue in 2. As regards the ignited mass (2, *a*.), it is often desirable to boil the mass carbonized at a gentle heat, with water, filter, examine the filtrate, wash the residue, incinerate it, and examine the ashes.

2. *Detection of inorganic poisons in articles of food, in dead bodies, &c., in chemico-legal cases.*[*]

§ 210.

The chemist is sometimes called upon to examine an article of food, the contents of the stomach of an individual, a dead body, &c., with a view to detect the presence of some poison, and thus to establish the fact of a voluntary or accidental poisoning;—but it is more frequently the case that a more special question is put to him, viz., to determine whether a certain substance placed before him contains a metallic poison or not;—or particularly, whether it contains arsenic, hydrocyanic acid, or some other distinctly named poison; as it may be, either that the symptoms point clearly in the direction of that poison, or that the examining magistrate has, or believes he has, some other reason to put this question.

It is obvious that the task of the chemist will be the easier, the more special and pointed the question which is put to him. However, the analyst will always act most wisely, even in cases where he is simply requested to state whether *a certain poison*, *e. g.* arsenic, is present or not, if he adopts a course of proceeding which will not only permit the detection of the *one* poison specially named, the presence of which may perhaps be suspected on insufficient grounds, but will moreover inform him as to the presence or absence of other similar poisons.

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[*] Compare: *a*. *Fresenius*, "die Stellung des Chemikers bei gerichtlich chemischen Untersuchungen, &c.," Annal. der Chemie und Pharm. 49, 275; and *b*. *Fresenius* and *v. Babo's* "Abhandlung über ein neues, unter allen Umständen sicheres Verfahren zur Ausmittelung und quantitativen Bestimmung des Arsens bei Vergiftungsfällen."— Annal. der Chemie und Pharmacie, 49, 287.

But we must not go too far in this direction either; if we were to attempt to devise a method that should embrace *all* poisons, we might unquestionably succeed in elaborating such a method at the writing desk; but practical experience would but too speedily convince us that the intricate complexity inseparable from such a course, must necessarily impede the easy execution of the process, and impair the certainty of the results, to such an extent, indeed that the drawbacks would be greater than the advantages derivable from it.

Moreover, the attendant circumstances permit usually at least a tolerably safe inference as to the group to which the poison belongs. Acting on these views, I give here,

1. A method which ensures the detection of the minutest traces of arsenic, allows of its quantitative determination, and permits at the same time the detection of all other metallic poisons.

2. A method to effect the detection of hydrocyanic acid, which leaves the substance still fit to be examined both for metallic poisons and for vegeto-alkalies.

This Section does not, therefore, profess to supply a complete guide in every possible case or contingency of chemico-legal investigations. But the instructions given in it are the tried and proved results of my own practice and experience. Moreover, they will be found sufficient in most cases, the more so as I shall append to the Section on the vegeto-alkalies the description of a process by which the detection of these latter poisons in criminal cases may be effected.

A. METHOD FOR THE DETECTION OF ARSENIC.

§ 211.

Of all metallic poisons arsenic is the most dangerous, and at the same time the one most frequently used, more particularly for the wilful poisoning of others. And again, among the compounds of arsenic arsenious acid (white arsenic) occupies the first place, because, 1. It kills even in small doses; 2. It does not betray itself, or at least very slightly, by the taste; and 3. It is but too readily procurable.

As arsenious acid dissolves in water only sparingly and—on account of the difficulty with which it is moistened by water—very slowly, the greater portion of the quantity swallowed exists usually in the body still in the undissolved state. As, moreover, the smallest grains of it may be readily detected by means of an exceedingly simple experiment; and lastly, as—no matter what opinion may be entertained about the normal presence of arsenic in the bones, &c.—this much is certain, that at all events, *arsenious acid in grains or powder* is never normally present in the body, the particular care and efforts of the analyst ought always to be directed to the detection of the arsenious acid in substance—and this end may indeed usually be attained.

a. Method for the detection of undissolved arsenious acid.

§ 212.

1. If you have to examine some article of food, substances rejected from the stomach, or some other matter of the kind, mix the whole as uniformly as may be practicable, put aside one-third for unforeseen contingencies, and mix the other two-thirds in a porcelain dish with distilled water, with a stirring rod; let the mixture stand a little, and then pour off the fluid, together with the lighter suspended particles, into another porcelain dish. Repeat this latter operation several times, and, if possible, with the same fluid, pouring it from the second dish back into the first, &c. Finally, wash once more with pure water, remove the fluid, as far as practicable, and try whether you can find in the dish small, white, hard grains which feel gritty and grate under the glass rod. If not, proceed as directed § 213. But if so, put the grains, or part of them, on blotting-paper, removing them from the dish with the aid of pincers, and try the deportment of one or several grains upon heating in a glass tube, and of some other grains upon ignition with a splinter of charcoal (compare § 127).—If you obtain in the former experiment a white crystalline sublimate, in the latter a lustrous arsenical mirror, the fact is clearly demonstrated that the grains selected and examined consisted really of arsenious acid. If you wish to determine the quantity of the poison, unite the contents of both dishes, and proceed as directed § 213.

2. If a stomach is submitted to you for analysis, empty the contents into a porcelain dish, turn the stomach inside out, and, *α.*, search the inside coat for small, white, hard, sandy grains. The spots occupied by such grains are often reddened; they are also frequently found firmly imbedded in the membrane. *β.* Mix the contents in the dish uniformly, put aside one-third for unforeseen contingencies, and treat the other two-thirds as in 1.—The same course, as with a stomach, is pursued also with intestines. In other parts of the body—with the exception perhaps of the pharynx and œsophagus—arsenious acid cannot be found in grains, if the poison has been introduced through the mouth. If you have found grains of the kind described, examine them as directed in 1;—if not, proceed according to the instructions of § 213.

b. Method for the detection of arsenic in whatever form of combination it may exist, which allows also a quantitative determination of that poison, and permits, at the same time, the detection of other metallic poisons which may be present.[*]

§ 213.

If you have found no arsenious acid by the method described in *a.*, evaporate the mass in the porcelain dish, which has been diluted by washing with water (see *a*, 1), on the water-bath, to a pasty consistence. If you have to analyze a stomach, intestinal tube, &c., cut this into pieces, and add two-thirds to the mass in the dish.

In examining other parts of the body (the lungs, liver, &c.), cut them also into pieces, and use two-thirds for the analysis. The process is divided into the following parts.[†]

aa. Decolorization and solution.

Add to the matters in the porcelain dish an amount of pure hydrochloric acid about equal to, or somewhat exceeding the weight of the dry substance present, and sufficient water to give to the whole mixture the consistence of a thin paste. Heat the dish now on the water-bath, adding every five minutes about two grammes (half a drachm) of chlorate of potassa to the hot fluid, with stirring, and continue the same operation until the contents of the dish show a light-yellow color and a perfectly homogeneous appearance, and are quite fluid. When this point is attained, add again a portion of chlorate of potassa, and then remove the dish from the water-bath. When the contents are quite cold, transfer them cautiously to a linen strainer or to a white filter, according to the greater or less quantity of substance; allow the whole of the fluid to pass through, and put the filtrate aside. Wash the residue well with hot water, evaporate the washings on the water-bath to about three or four ounces, put this to the filtrate, and then add to the united fluid, which is still very acid, some solution of sulphite of soda, with stirring, until the odor of sulphurous acid becomes distinctly perceptible. Then heat the mixture again gently on the water-bath until the excess of the sulphurous acid is expelled, which will take about an hour.

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[*] This method is essentially the same as that which I elaborated and published in 1844, jointly with *L. v. Babo;* compare Annal. der Chemie und Pharmacie, Bd. 49, p. 308. I have since that time had frequent occasion to apply it; I have also had it tried by others, under my own inspection, and *I have invariably found it to answer the purpose to the fullest extent.*

[†] I think, I need hardly observe that in such extremely delicate experiments the vessels and reagents used in the process must be perfectly free from arsenic, from heavy metals in general, and indeed from every impurity.

bb. Separation of the arsenic as tersulphide.

When the fluid obtained in *aa.*, and which amounts to about twice or three times the quantity of hydrochloric acid used, is quite cold, introduce it into a beaker, transmit through it, for about twelve hours, a slow stream of washed hydrosulphuric acid gas, rinse the delivery pipe with some ammonia, add the ammoniated solution thus obtained to the principal fluid, cover the beaker lightly with unsized paper, and put it in a moderately warm place (about 86°), until the odor of hydrosulphuric acid has nearly disappeared. Collect the precipitate obtained in this manner on a moderately sized filter, and wash.

cc. Purification of the crude tersulphide of arsenic.

Thoroughly dry the precipitate of *bb.*—which contains, besides organic matters, the whole of the arsenic present in the analyzed substance, and may contain moreover some other metallic sulphides—together with the filter, in a small porcelain dish, heated on the water-bath; add fuming nitric acid drop by drop, until the mass is completely moistened, and then evaporate on the water-bath to dryness. Moisten the residue uniformly all over with pure hydrate of sulphuric acid, previously warmed; then heat for two or three hours on the water-bath, and finally in the sand-bath at a somewhat higher though still moderate temperature (302°), until the carbonized mass becomes friable. Treat the residue with from ten to twenty parts of distilled water on the water-bath, filter, wash the undissolved part with hot, distilled water, until the last drops show no longer acid reaction, and add the washings to the filtrate.

dd. Determination of the weight of the tersulphide of arsenic.

Mix the clear fluid obtained in *cc.* with some hydrochloric acid, and then precipitate with hydrosulphuric acid, exactly in the manner directed in *bb.* When the odor of hydrosulphuric acid has nearly disappeared, filter the precipitate on a small filter (as small as may be practicable), wash carefully, pour upon the still moist precipitate on the filter solution of ammonia, wash the filter with dilute ammonia as long as the latter agent continues to dissolve the least particle of the precipitate, evaporate the ammoniacal fluid in a small accurately weighed porcelain dish on the water-bath, dry the residue at 212°, until its weight suffers no further diminution, and weigh. If it turns out afterwards, upon reduction, that the residue consists exclusively of tersulphide of arsenic, calculate for every one part of it 0·8047 of arsenious acid, or 0·6095 of arsenic. If the ammonia has left an undissolved residue on the filter, examine this for bismuth, copper, &c. Lead, tin, and mercury, may besides be contained in the carbonized residue of *cc.*, and silver and lead in the residue of *aa.*; these residues must accordingly be subjected to examination.*

ee. Reduction of the tersulphide of arsenic.

The production of metallic arsenic from the tersulphide, which may be regarded as the key-stone of the whole process, demands the greatest care and attention. The method recommended § 127, 11, viz., to fuse the tersulphide of arsenic with cyanide of potassium and carbonate of soda, in a slow stream of carbonic acid gas, answers the purpose best. That method affords, besides the advantage of great accuracy, also a positive guarantee against the chance of confounding the arsenic with some other body, more particularly antimony, on which account it is more especially adapted for medico-legal investigations.

The entire quantity of the residue in the dish, obtained by the evaporation of the ammoniacal solution, must not be employed for the process of reduction, but only a portion of it, so that the process may be repeated several times, if necessary.

If sulphide of tin or of antimony were present along with the sulphide of arsenic, the metals of these sulphides would remain in the metallic state upon washing the residue in the reduction tube. Antimony would be found besides in the solution in the form of a sulphur salt. The determination of the weight of the arsenic would in that case require a quantitative separation of the mixed sulphides, with which, of course, we cannot occupy ourselves here.

B. METHOD FOR THE DETECTION OF HYDROCYANIC ACID.

§ 214.

In cases of actual or suspected poisoning with hydrocyanic acid, where it is required to separate that acid from articles of food or from the contents of the stomach, and thus to prove its presence, it is above all necessary to act with the greatest expedition, as the hydrocyanic acid speedily

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* To examine the residue which boiling with hydrochloric acid and chlorate of potassa has left undissolved, for silver and for compounds of lead, which may have remained undissolved, dry it, triturate with an equal amount of carbonate of soda, and as much nitrate of soda or potassa, and add the mixture in portions to fusing nitrate of soda or potassa in a porcelain dish. Boil the mass with water, filter, and treat the filtrate with hydrosulphuric acid; if the boiling water has left a residue, dissolve this in nitric acid and test the solution for silver and lead in the usual way. As regards the carbonized residue of *cc.*, which has been left undissolved upon treating the mass carbonized by sulphuric acid with distilled water, boil this first with solution of soda or potassa, then with nitrohydrochloric acid. Treat the filtrates separately with hydrosulphuric acid. Ignite the washed residue finally in a platinum crucible, to ascertain whether anything will remain. If the hydrosulphuric acid fails to produce a precipitate in the alkaline filtrate—which after washing is insoluble in dilute acids (lead)—acidify with hydrochloric acid, and see whether this will produce a precipitate (tin).

undergoes decomposition. Still this decomposition is not quite so rapid as is generally supposed, and indeed it requires some time before the *complete* decomposition of the *whole* of the acid present is effected.*

Although hydrocyanic acid betrays its presence, even in minute quantities, by its peculiar odor, still this sign must never be looked upon as conclusive. On the contrary, to adduce positive proof of the presence of the acid, it is always indispensable to separate it, and to convert it into certain known compounds.

For this purpose test, in the first place, the reaction of the mass under examination; if necessary, after mixing and stirring it with water. If it is not strongly acid, add solution of tartaric acid until the fluid reddens litmus paper; introduce the mixture into a retort, add some spirit of wine, and place the body of the retort, with the neck pointing upwards, in an iron or copper kettle, but so that it does not touch the bottom, which should, moreover, by way of precaution, be covered with a cloth; fill the kettle with a solution of chloride of calcium, and apply heat, so as to cause gentle ebullition of the contents of the retort. Conduct the vapors passing over, with the aid of a tight-fitting tube, bent at a very obtuse angle, through a *Liebig's* condensing apparatus, and receive the distillate in a flask, fitted tightly to the lower end of the cooling tube by means of a perforated cork, which bears also a narrow double-limbed tube, to afford egress to the air; the exterior end of this tube is made to dip into a little water. When about one-sixth of the fluid in the retort has passed over, change the receiver, weigh the contents of the flask removed, and treat as follows:—

a. Mix one-fourth of the contents of the flask with solution of potassa or soda, then add a small quantity of solution of sulphate of protoxide of iron, mixed with a little sesquichloride of iron, and lastly, add hydrochloric acid. Compare § 146.

b. Treat another fourth as directed § 146, 7, to convert the hydrocyanic acid into sulphocyanide of iron. As the distillate might, however, contain acetic acid, do not neglect to add hydrochloric acid after the sesquichloride of iron, in order to neutralize the adverse influence of the acetate of ammonia. Compare § 146, 7.

c. If the experiments *a.* and *b.* have demonstrated the presence of hydrocyanic acid, and you wish now also to approximately determine its quantity, continue the distillation, until the fluid passing over contains no longer the least trace of hydrocyanic acid; add one-half of the con-

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* Thus I succeeded in separating a notable quantity of hydrocyanic acid from the stomach of a man who had poisoned himself with that acid in very hot weather, and whose intestines were handed to me full thirty-six hours after death.—A dog was poisoned with hydrocyanic acid, and the contents of the stomach, mixed with the blood, were left for twenty-four hours exposed to an intense summer-heat, and then examined: the acid was still detected.

tents of the second receiver to the remaining half of the contents of the first, mix the fluid with nitrate of silver, then with ammonia until it predominates, and finally with nitric acid to strong acid reaction. Allow the precipitate which forms to subside, filter on a weighed filter, dried at 212°, wash the precipitate, dry it thoroughly at 212°, and weigh. Ignite the weighed precipitate in a little porcelain crucible, to destroy the cyanide of silver, fuse the residue with carbonate of soda and potassa—to effect the decomposition of the chloride of silver which it may contain—boil the mass with water, filter, acidify the filtrate with nitric acid, and precipitate with nitrate of silver; determine the weight of the chloride of silver which may precipitate, and deduct the amount found from the total weight of the chloride and cyanide of silver: the difference gives the quantity of the latter; by multiplying the quantity found of the cyanide of silver by 0·2017, you find the corresponding amount of anhydrous hydrocyanic acid; and by multiplying this again by 2—as only one-half of the distillate has been used—you find the total quantity of hydrocyanic acid which was present in the examined mass.

3. *Examination of the inorganic constituents of plants, animals, or parts of the same, of manures, &c.* (*Analysis of ashes.*)

§ 215.

A. PREPARATION OF THE ASH.

It is sufficient for the purposes of a qualitative analysis to incinerate a comparatively small quantity of the substance which it is intended to examine for its inorganic constituents; the substance must previously be most carefully cleaned. The incineration is effected best in a small clay muffle, but it may be conducted also in a Hessian crucible placed in a slanting position, or, under certain circumstances, even in a small porcelain or platinum dish. The heat must always be moderate to guard against the volatilization of certain constituents, more especially of metallic chlorides. It is not always necessary to continue the combustion until all the charcoal is consumed. With ashes containing a large proportion of fusible salts, as, *e. g.* the ash of beet-root molasses, it is even advisable to effect, in the first place, complete carbonization, then to boil the charred mass with water, and finally to incinerate the washed and dried residue.

B. EXAMINATION OF THE ASH.

As the qualitative analysis of the ash of a vegetable substance is usually undertaken, either as a practical exercise, or for the purpose of determining the general character of an ash, and the state or condition in which any given constituent may happen to be present, or also with a view to make, as far as practicable, an approximate estimation of the respective quantities of the several constituents, it is usually the best way to examine separately; 1, the part soluble in water; 2, the part soluble in hydrochloric acid; and, 3, the residue which is insoluble in either menstruum. This can be done the more readily, as the number of bodies to which regard must be had in the analysis is only small, and the several processes may accordingly be expeditiously performed.

a. Examination of the part soluble in water.

Boil the ash with water, filter, and whilst the residue is being washed, examine the solution as follows :—

1. Add to a portion, after heating it, hydrochloric acid in excess, heat, and allow the fluid to stand at rest. Effervescence indicates CARBONIC ACID combined with alkalies; odor of hydrosulphuric acid indicates the SULPHIDE of an ALKALI METAL, formed from an alkaline sulphate by the reducing action of the charcoal. Turbidity from separation of sulphur, with odor of sulphurous acid, denotes a HYPOSULPHITE (which occurs occasionally in the ash of pit-coal). Filter, if necessary, and add to the filtrate—or to the fluid if no filtration is required—some chloride of barium; the formation of a white precipitate indicates the presence of SULPHURIC ACID.

2. Evaporate another portion of the solution until it is reduced to a small volume, add hydrochloric acid to acid reaction—effervescence indicates the presence of CARBONIC ACID—evaporate now to dryness, and treat the residue with hydrochloric acid and water. The portion left undissolved consists of SILICIC ACID. Filter, add ammonia, chloride of ammonium, and sulphate of magnesia; the formation of a white precipitate indicates the presence of PHOSPHORIC ACID. Instead of this reaction you may also mix the fluid filtered from the silicic acid with acetate of soda, and then cautiously add, drop by drop, sesquichloride of iron (see § 135).

3. Add to another portion of the solution nitrate of silver as long as a precipitate continues to form; heat gently, and then cautiously add ammonia; if a black residue is left, this consists of sulphide of silver, proceeding from the sulphide of an alkali metal, or from a hyposulphite. Mix the ammoniacal solution now—after previous filtration, if necessary—cautiously with nitric acid until it is exactly neutralized. If this produces a *light yellow* precipitate, the phosphoric acid found in 2 was present in the *tribasic*, if a *white* precipitate, it was present in the bibasic form. Add more nitric acid. This effects the solution of the phosphate of silver precipitate. But if CHLORINE (iodine,* bromine) is present, a portion of the precipitate remains undissolved, or the fluid appears turbid.

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* To detect the iodine in aquatic plants, dip the plant in solution of potassa (*Chatin*), dry, incinerate, treat with water, and examine the aqueous solution as directed § 201, 2.

4. Acidify a portion of the solution with hydrochloric acid, and then make it alkaline with ammonia; mix the alkaline fluid with oxalate of ammonia, and allow it to stand at rest. The formation of a white precipitate indicates LIME. Filter, and mix the filtrate with ammonia and phosphate of soda; the formation of a crystalline precipitate, which often becomes visible only after long standing, indicates MAGNESIA.—Magnesia is often found in notable, lime in exceedingly minute, quantity, even when alkaline carbonates and phosphates are present.

5. For POTASSA and SODA examine as directed § 185.

b. Examination of the part soluble in hydrochloric acid.

Heat the residue left undissolved by water with hydrochloric acid* —effervescence indicates CARBONIC ACID, combined with alkaline earths; evolution of chlorine denotes OXIDES OF MANGANESE—evaporate to dryness, heat a little more strongly, to effect the separation of the silicic acid, and moisten the residue with hydrochloric acid and some nitric acid, add water, heat, and filter.

1. Test with hydrosulphuric acid. If this produces any other than a perfectly white precipitate, you must examine in the usual way. The ashes of plants occasionally contain COPPER; if the plant has been manured with excrements deodorized by nitrate of lead, they may contain LEAD; other metals are also occasionally found.

2. Mix a portion of the original solution with carbonate of soda, as long as the precipitate formed redissolves upon stirring; then add acetate of soda, and some acetic acid. This produces, in most cases, a white precipitate of PHOSPHATE OF SESQUIOXIDE OF IRON. If the fluid in which this precipitate is suspended is reddish, there is more sesquioxide of iron present than corresponds to the phosphoric acid; if it is colorless, add sesquichloride of iron, drop by drop, until the fluid looks reddish. (From the quantity of the precipitate formed of phosphate of sesquioxide of iron you may estimate the PHOSPHORIC ACID present.) Heat to boiling,† filter hot, precipitate the filtrate, after addition of a sufficient quantity of chlorine water, with ammonia, examine the precipitate which may form before the blowpipe for MANGANESE, and the fluid filtered from it for LIME and MAGNESIA, in the usual way (§ 215, B. *a*, 4).

c. Examination of the residue insoluble in hydrochloric acid.

The residue insoluble in hydrochloric acid contains,

1. The silicic acid, which has separated on treating with hydrochloric acid.

2. Those ingredients of the ash which are insoluble in hydrochloric acid.

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* If the residue still contains much charcoal, after further incineration.

† If this should fail to decolorize the fluid, add some more acetate of soda.

These are, in most ashes, sand, clay, charcoal; substances therefore, which are present in consequence of defective cleaning or imperfect combustion of the plants, or matter derived from the crucible. It is only the ashes of the stems of cereals and others abounding in silicic acid, that are not completely decomposed by hydrochloric acid.

Boil the washed residue with solution of carbonate of soda in excess, filter hot, wash with boiling water, and test for silicic acid in the filtrate by evaporation with hydrochloric acid. If the ash was of a kind to be completely decomposed by hydrochloric acid, the analysis may be considered as finished—for the accidental admixture of clay and sand will rarely interest the analyst sufficiently to warrant their decomposition and examination. But, if the ash abounded in silicic acid, and it may therefore be supposed that the hydrochloric acid has failed to effect complete decomposition, evaporate half of the residue insoluble in solution of carbonate of soda, with pure solution of soda in excess, in a silver or platinum dish, to dryness. This decomposes the silicates of the ash, whilst but little affecting the sand. Acidify now with hydrochloric acid, evaporate to dryness, &c., and proceed as in *b*. For the detection of the alkalies use the other half of the residue. Compare § 195, 2.

SECTION III.

EXPLANATORY NOTES AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

I. ADDITIONAL REMARKS TO THE PRELIMINARY EXAMINATION.

To §§ 163—165.

THE inspection of the physical properties of a body may, as already stated § 163, in many cases enable the analyst to draw certain general—if not positive at least negative—inferences as to its nature. Thus, for instance, if the analyst has a white substance before him, he may at once conclude that it is not cinnabar, or if a light substance, that it is not a compound of lead, &c.

Inferences of this kind are quite admissible to a certain extent; but if carried too far, they are apt to mislead the operator, by blinding him to every reaction not exactly in accordance with his preconceived notions.

As regards the examination of substances at a high temperature, I may remark that small test-tubes, from two to three inches in length, may, in many cases, be substituted for iron spoons. They afford this advantage over the latter, that volatile bodies, organic substances, &c., are less likely to escape detection, and that a more correct and precise notion can be formed of the nature of the heated substance, than exposure in an iron spoon will permit. However, as every experiment would require a fresh tube, a spoon will be found more convenient and economical in experiments for practice. To ascertain the products of oxidation of a body, it is sometimes advisable also to heat it in a short glass-tube, open at both ends, and held in a slanting position; small quantities of a metallic sulphide, for instance, may be readily detected by this means. (Compare § 147.)

With respect to the preliminary examination by means of the blowpipe, I have to remark that the student must avoid drawing positive conclusions from pyrochemical experiments, until he has acquired some practice in this branch of analytical chemistry. A slight incrustation of the charcoal support, which may *seem* to denote the presence of a certain metal, is not always a *conclusive* proof of the presence of that metal, nor would it be safe to assume the absence of a substance simply because the blowpipe flame has failed to effect reduction, &c. The blowpipe reactions are, indeed, in most cases unerring, but it is not always easy to produce them and they are moreover liable to suffer modification by accidental circumstances.

The student should never omit the preliminary examination; the notion that this omission will save time and trouble, is very erroneous.

II. ADDITIONAL REMARKS TO THE SOLUTION OF SUBSTANCES, ETC.

To §§ 167—169.

It is a task of some difficulty to fix the exact limit between substances which are soluble in water and those that are insoluble in that menstruum, since the number of bodies which are sparingly soluble in water is very considerable, and the transition from *sparingly* soluble to *insoluble* is very gradual. Sulphate of lime, which is soluble in 430 parts of water, might perhaps serve as a limit between the two classes, since this salt may still be positively detected in aqueous solution, by the delicate reagents which we possess for lime and sulphuric acid.

When examining an aqueous fluid by evaporating a few drops of it upon platinum foil, a very minute residue sometimes remains, which leaves the analyst in doubt respecting the nature of the substance; in cases of the kind test, in the first place, the reaction of the fluid with litmus papers; in the second place, add to a portion of it a drop of solution of chloride of barium; and lastly, to another portion some carbonate of soda. Should the fluid be neutral, and remain unaltered upon the addition of these reagents, the analyst need not examine it any further for bases or acids;

since if the fluid contained any of those bases or acids which principally form sparingly soluble compounds, the chloride of barium and the carbonate of soda would have revealed their presence. The analyst may therefore feel assured that the detection of the substance of which the residue left upon evaporation consists, will be more readily effected in the class of bodies insoluble in water.

If water has dissolved any part of the substance under examination, the student will always do well to examine the solution both for acids and bases, since this will lead more readily to a correct apprehension of the nature of the compound—an advantage which will amply connterbalance the drawback of sometimes meeting with the same substance both in the aqueous and in the acid solution.

The following substances (with few exceptions) are insoluble in water, but soluble in hydrochloric acid or in nitric acid : the phosphates, arseniates, arsenites, borates, carbonates, and oxalates of the earths and metals ; and also several tartrates, citrates, malates, benzoates, and succinates, the oxides and sulphides of the heavy metals, alumina, magnesia, many of the metallic iodides and cyanides, &c. Nearly the whole of these compounds are decomposed, if not by dilute, by boiling concentrated hydrochloric acid ;* 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 suboxide of mercury and lead. This is not the case with nitric acid, and accordingly the latter effects complete solution in many cases where hydrochloric acid has left a residue. But, on the other hand, nitric acid leaves, besides the bodies insoluble in any simple acid, teroxide of antimony, binoxide of tin, binoxide of lead, &c., undissolved, and fails also to effect the complete solution of many other substances. When, therefore, the compound under examination is not completely dissolved by nitric acid, but leaves an undissolved residue, besides sulphur—which may separate in the case of sulphur compounds—and hydrate of silicic acid, the analyst is again referred to the hydrochloric acid solution, and thus exact limits are in some measure assigned to the third class of substances, viz. those which are insoluble in water and simple acids.

With regard to the solution of metals and alloys, I have to remark that, upon boiling them with nitric acid, white precipitates will frequently form, although neither tin nor antimony be present. Inexperienced students often confound such precipitates with the oxides of these two metals, although their appearance is quite different. These precipitates consist simply of nitrates sparingly soluble in the nitric acid present, but readily soluble in water. Consequently the analyst should ascertain whether these white precipitates will dissolve in water or not, before he concludes them to consist of tin or antimony.

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* For the exceptions, see § 191.

III. ADDITIONAL REMARKS TO THE ACTUAL EXAMINATION.

To §§ 170—191.

A. GENERAL REVIEW AND EXPLANATION OF THE ANALYTICAL COURSE.

a. DETECTION OF THE BASES.

The classification of the bases into groups, and the methods which serve to detect and isolate them individually, have been fully explained in Part I., Section III. The systematic course of analysis, from § 168 to § 177, is based upon this classification of the bases; and as a correct apprehension of it is of primary importance, I will here subjoin a brief explanation of the grounds upon which this division rests. Respecting the detection of the several bases individually, I refer the student to the recapitulations and remarks in §§ 89, 96, 100, 108, 114, 119, 123, and 129.

The general reagents which serve to divide the bases into principal groups are—HYDROCHLORIC ACID, HYDROSULPHURIC ACID, SULPHIDE OF AMMONIUM, and CARBONATE OF AMMONIA; this is likewise the order of succession in which they are applied. Sulphide of ammonium performs a *double* part.

Let us suppose we have in solution the whole of the bases, together with arsenious and arsenic acids, and also phosphate of lime—which latter may serve as a type for the salts of the alkaline earths, soluble in acids, and reprecipitated unaltered by ammonia.

Chlorine forms insoluble compounds only with silver and mercury; chloride of lead is sparingly soluble in water. The insoluble subchloride of mercury corresponds to the suboxide of that metal. If, therefore, we add to our solution:

1. *Hydrochloric acid,*

we remove from it the metallic oxides of the first section of the fifth group, viz., the whole of the OXIDE OF SILVER and the whole of the SUBOXIDE OF MERCURY. From concentrated solutions, a portion of the LEAD may likewise precipitate as chloride; this is, however, immaterial, as a sufficient quantity of the lead remains in the solution to permit the subsequent detection of this metal.

Hydrosulphuric acid completely precipitates the oxides of the fifth and sixth group from solutions containing a free mineral acid, since both the affinity of the metallic radicals of these oxides for sulphur, and of the hydrogen for oxygen, are sufficiently powerful to overcome that between the metal and the oxygen, and between the oxide and a strong acid, EVEN

THOUGH THE ACID BE PRESENT IN EXCESS. But none of the other bases are precipitated under these circumstances, since those of the first, second, and third group, form no sulphur compounds insoluble in water; and the affinity which the metallic radicals of the oxides of the fourth group possess for sulphur, combined with that manifested by hydrogen for oxygen, is not sufficiently powerful to overcome the affinity either of the metal for oxygen or of the oxide for a strong acid, IF THE LATTER IS PRESENT IN EXCESS.

If, therefore, after the removal of the oxide of silver and suboxide of mercury, by means of hydrochloric acid, we add to the solution, which still contains free hydrochloric acid,

2. *Hydrosulphuric acid*,

we remove from it the remainder of the oxides of the fifth, together with those of the sixth group, viz., OXIDE OF LEAD, OXIDE OF MERCURY, OXIDE OF COPPER, TEROXIDE OF BISMUTH, OXIDE OF CADMIUM, TEROXIDE OF GOLD, BINOXIDE OF PLATINUM, PROTOXIDE OF TIN, BINOXIDE OF TIN, TEROXIDE 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.* sesquioxide of iron to protoxide; chromic acid to sesquioxide of chromium, &c.

The sulphides corresponding to the oxides of the sixth group combine with basic metallic sulphides (the sulphides of the alkali metals), and form with them sulphur salts soluble in water; while the sulphides corresponding to the oxides of the fifth group do not possess this property, or possess it only to a limited extent.* If, therefore, we treat the whole of the sulphides precipitated by hydrosulphuric acid from an acid solution, with—

3. *Sulphide of ammonium* (or, in certain cases, *sulphide of sodium*),

the sulphides of mercury, lead, copper, bismuth, and cadmium, remain undissolved, whilst the other sulphides dissolve as double compounds of sulphide of GOLD, PLATINUM, ANTIMONY, TIN, ARSENIC, with SULPHIDES OF AMMONIUM (or, as the case may be, SULPHIDE OF SODIUM), and precipitate again from this solution upon the addition of an acid, either unaltered, or, as regards the protosulphide of tin, and the tersulphide of antimony, in a state of higher sulphuration—these two compounds taking up sulphur from the sulphide of ammonium. The rationale of this precipitation is as follows:—The acid decomposes the sulphur salt formed. The sulphur base (sulphide of ammonium or sodium) transposes with the constituents

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* Sulphide of mercury combines with sulphide of potassium and sulphide of sodium, but not with sulphide of ammonium; sulphide of copper dissolves a little in sulphide of ammonium, but not in sulphide of potassium or sulphide of sodium.

of the water, forming an oxygen base (oxide of ammonium or soda) and hydrosulphuric acid; the former combines with the acid added, the latter escapes, and the liberated electronegative sulphide (sulphur acid) precipitates. If the acid is an hydracid, its radical combines with the ammonium, its hydrogen with the sulphur. Sulphur precipitates at the same time, the sulphide of ammonium containing generally an excess of that element. The analyst must bear in mind that this eliminated sulphur makes the precipitated sulphides appear of a lighter color than they are naturally.

The alkalies, the alkaline earths, alumina, and sesquioxide of chromium have remained in solution, because either their sulphur compounds are soluble in water, or their salts are not affected in the least by hydrosulphuric acid; the sulphides corresponding to the oxides of the fourth group are insoluble in water, and would have been precipitated accordingly by hydrosulphuric acid, but for the free acid present. If, therefore, this free acid is removed, *i. e.* if the solution is made alkaline, and then treated with hydrosulphuric acid, or, what answers both purposes at once, if

4. *Sulphide of ammonium,*

is added to the solution,* the sulphides corresponding to the oxides of the fourth group will precipitate, viz.: the **SULPHIDES OF IRON, MANGANESE, COBALT, NICKEL,** and **ZINC.** But in conjunction with them, **ALUMINA, SESQUIOXIDE OF CHROMIUM,** and **PHOSPHATE OF LIME,** are thrown down, because the affinity which the oxide of ammonium possesses for the acid of the salt of alumina or of sesquioxide of chromium, or for that which keeps the phosphate of lime in solution, causes the elements of the sulphide of ammonium to transpose with those of the water, thus giving rise to the formation of oxide of ammonium and of hydrosulphuric acid. The former combines with the acid, the latter escapes, being incapable of entering into combination with the liberated oxides or with the phosphate of lime,—the oxides and the lime-salt precipitate.

There remain now 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 in that menstruum. If, therefore, we now add,

5. *Carbonate of ammonia,*

and apply heat, in order to decompose the bicarbonates which may have formed, the whole of the alkaline earths ought to precipitate. This is,

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* After previous neutralization of the free acid by ammonia, to prevent unnecessary evolution of hydrosulphuric acid.

however, the case only as regards **BARYTA, STRONTIA**, and **LIME**; of magnesia we know that, owing to its disposition to form double compounds with salts of ammonia, it precipitates only in part; and that the presence of an additional salt of ammonia will altogether prevent its precipitation. To guard against any uncertainty arising from this cause, chloride of ammonium is added previously to the addition of the carbonate of ammonia, and thus the precipitation of the magnesia is altogether prevented.

We have now in solution magnesia and the alkalies. The detection of magnesia may be effected by means of phosphate of soda and ammonia; but its separation requires a different method, since the presence of phosphoric acid would impede the further progress of the analysis. The process which serves to effect the removal of the magnesia is based upon the insolubility of that earth in the pure state. The substance under examination is accordingly ignited in order to expel the salt of ammonia, and the magnesia is then precipitated by means of baryta, the alkalies, together with the newly formed salt of baryta and the excess of the caustic baryta added, remaining in solution. By the addition of carbonate of ammonia the compounds of baryta are removed from the solution, which now only contains the fixed alkalies, the salt of ammonia formed, and the excess of the carbonate of ammonia added. If the salts of ammonia are then removed by ignition, the residue consists of the fixed alkalies alone. This method of separating the baryta affords the advantage over that of effecting the removal of that earth by means of sulphuric acid, that the alkalies are obtained in the most convenient form for their subsequent individual detection and isolation, viz., as chlorides. But as the carbonate of baryta is slightly soluble in salts of ammonia, some baryta often remains in solution, the removal of which, after the expulsion of the salts of ammonia, often requires another precipitation with carbonate of ammonia. Lastly, to effect the detection of the ammonia, a fresh portion of the substance must of course be taken.

b. DETECTION OF THE ACIDS.

Before passing on to the examination for acids and salt-radicals, the analyst should first ask himself *which* of these substances may be expected to be present, from the nature of the detected bases and the class to which the substance under examination belongs with respect to its solubility in water or acids, since this will save him the trouble of unnecessary experiments. Upon this point I refer the student to the table in the appendix (p. 296), in which the various compounds are arranged according to their several degrees of solubility in water and acids.

The general reagents applied for the detection of the acids are, for the inorganic acids **CHLORIDE OF BARIUM** and **NITRATE OF SILVER**, for the organic acids CHLORIDE OF CALCIUM and SESQUICHLORIDE OF IRON. It is therefore indispensable that the analyst should first assure himself whether the substance under examination contains only inorganic acids, or whether the presence of organic acids must also be looked for. The latter is invariably the case, if the body, when ignited, becomes black from separated charcoal.—In the examination for bases the different reagents serve to effect the actual separation of the several groups of bases from each other; but in the examination for acids they serve simply to demonstrate the presence or absence of the acids belonging to the different groups.

Let us suppose we have an aqueous solution containing the whole of the acids, in combination with soda, for instance.

Baryta forms insoluble compounds with sulphuric 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 baryta. If therefore to a portion of our neutral or, if necessary, neutralized solution, we add,

1. *Chloride of barium*,

the formation of a precipitate will denote the presence of at least one of these acids. By treating the precipitate with hydrochloric acid, we learn at once whether sulphuric acid is present or not, as all the salts of baryta being soluble in this menstruum, with the exception of the sulphate, a residue left undissolved by the hydrochloric acid can consist only of the latter salt. When sulphate of baryta is present, the reaction with chloride of barium fails to effect the positive detection of the whole of the other acids enumerated. For upon filtering the hydrochloric solutions of the precipitates and supersaturating the filtrate with ammonia, the borate, tartrate, citrate, &c., of baryta do not fall down again, being kept in solution by the chloride of ammonium formed. For this reason, chloride of barium cannot serve to effect the actual separation of the several acids from one another, and except as regards sulphuric acid, we set no value upon this reagent as a means of effecting their individual detection. Still it is of great importance as a reagent, since the non-formation of a precipitate upon its application in neutral or alkaline solutions, proves at once the absence of so considerable a number of acids.

The compounds of silver with chlorine, iodine, bromine, and cyanogen; and of the oxide of silver with phosphoric acid, arsenious acid, arsenic acid, boracic acid, chromic acid, silicic acid, oxalic acid, tartaric acid, and citric acid, are insoluble in water. The whole of these compounds are soluble in ammonia, with the exception of iodide of silver, and in nitric acid, excepting the iodide, chloride, bromide, and cyanide of silver. If, therefore, we added to our solution, which, for the reason just now stated, must be perfectly neutral,

2. *Nitrate of silver,*

and precipitation ensues, it proves at once the presence of one or several of the acids enumerated; chromic acid, arsenic acid, and several others, of which the silver salts are colored, may even from the latter circumstance be individually recognized with tolerable certainty. By treating the precipitate now with nitric acid, we see whether it contains any of the haloid compounds of silver, as these latter remain undissolved, whilst all the oxide salts dissolve.—Nitrate of silver fails to effect the complete separation of those acids which form insoluble compounds with oxide of silver, from the same cause which renders the separation of acids by chloride of barium uncertain, viz. the ammoniacal salt formed prevents the reprecipitation of several of the salts of silver by ammonia, from the acid solution. Nitrate of silver, besides effecting the separation of chlorine, iodine, bromine, and cyanogen, and indicating the presence of chromic acid, &c., serves, like the chloride of barium, to demonstrate at once the absence of a great many acids, where it produces no precipitate in neutral solutions.

The deportment which the solution under examination exhibits with chloride of barium and with nitrate of silver, indicates therefore at once the further course of the investigation. Thus, for instance, where chloride of barium has produced a precipitate, whilst nitrate of silver has failed to do so, 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 the solution contains no salts of ammonia. The same is the case if we obtain a precipitate by nitrate of silver, but none by chloride of barium.

Returning to the supposition which we have assumed here, viz., that the whole of the acids are present in the solution under examination, we should now have detected CHLORINE, BROMINE, IODINE, and CYANOGEN,* and also SULPHURIC ACID; and there would be reason to test for all the other acids precipitated by these two reagents. The detection of these acids is based upon the results of a series of special experiments, which have already been fully described and explained in the course of the present work: the same remark applies to the rest of the inorganic acids, viz. nitric acid and chloric acid.

Of the organic acids, oxalic acid, paratartaric acid, and tartaric acid, are precipitated by chloride of calcium in the cold, in presence of chloride of ammonium; the two former immediately, the latter often only after some

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* For the separation and detection of these substances, I refer to § 148.

time; but the precipitation of citrate of lime is prevented by the presence of salts of ammonia, and ensues only upon ebullition or upon mixing the solution with alcohol; the latter agent serves also to effect the separation of malate of lime from aqueous solutions. If, therefore, we add to our fluid,—

3. *Chloride of calcium* and chloride of ammonium,

OXALIC ACID, TARTARIC ACID, and PARATARTARIC ACID are precipitated, but the lime-salts of several inorganic acids, which have not yet been separated, phosphate of lime for instance, precipitate along with them. We must therefore select for the individual detection of the precipitated organic acids such reactions only as preclude the possibility of confounding the organic acids with the inorganic acids that have been thrown down along with them. For the detection of oxalic acid we select solution of sulphate of lime, with acetic acid (§ 137); to effect the detection of the tartaric and paratartaric acids, we treat the precipitate produced by chloride of calcium with solution of soda, since the lime-salts of these two acids only are soluble in this menstruum in the cold, but insoluble upon ebullition.

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 addition of alcohol to the fluid filtered from the oxalate, tartrate, &c., of lime, and which still contains an excess of chloride of calcium. Sulphate and borate of lime invariably precipitate along with the malate and citrate of lime, if sulphuric acid and boracic acid happen to be present; the analyst must therefore carefully guard against confounding the lime precipitates of these acids with those of citric acid and malic acid. The alcohol is now removed by evaporation, and,—

4. *Sesquichloride of iron*

added. This reagent precipitates SUCCINIC ACID and BENZOIC ACID in combination with sesquioxide of iron, whilst FORMIC ACID and ACETIC ACID remain in solution. The methods which serve to effect the separation of the several groups from each other, and the individual detection of the various acids, have been fully described and explained in the former part of this work.

B. SPECIAL REMARKS AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

To § 177.

At the commencement of § 177, the analyst is directed to mix neutral or acid aqueous solutions with hydrochloric acid. This should be done drop by drop. If no precipitate forms, a few drops are sufficient, since the only object in that case is to acidify the fluid in order to prevent the subsequent precipitation of the metals of the iron group, by hydrosulphuric acid. In the case of the formation of a precipitate, some chemists recommend that a fresh portion of the solution should be acidified with nitric acid. However, even leaving the fact out of consideration that nitric acid also produces precipitates in many cases—in a solution of potassio-tartrate of antimony, for instance—I prefer the use of hydrochloric acid, *i. e.* the complete precipitation by that acid of all that is precipitable by it, for the following reasons:—1. Metals are more readily precipitated by hydrosulphuric acid, from solutions acidified with hydrochloric acid, than from those acidified with nitric acid;—2. In cases where the solution contains silver, suboxide of mercury, or lead, the further analysis is matertally facilitated by the total or partial precipitation of these three metals in the form of chlorides;—and 3. This latter form is the best adapted for the individual detection of these three metals when present in the same solution. Besides, the application of hydrochloric acid saves the necessity of examining whether the mercury, which may be subsequently detected with the other metals of the fifth group, was originally present in the form of oxide or in that of suboxide. That part of the lead is obtained in the form of a chloride, and the rest in the precipitate produced by hydrosulphuric acid in the acid solution, can hardly be thought an objection to the application of this method, as the further examination for lead may of course be omitted, if that metal has already been found in the precipitate produced by hydrochloric acid.

As already remarked, a basic salt of antimony may separate from potassio-tartrate of antimony, for instance, or from some other analogous compound, and precipitate along with the insoluble chloride of silver and subchloride of mercury, and the sparingly soluble chloride of lead. This precipitate, however, is readily soluble in the excess of hydrochloric acid which is subsequently added, and exercises therefore no influence whatever upon the further process. The application of heat to the fluid mixed with hydrochloric acid is neither necessary nor even advisable, since it might cause the conversion of a little of the precipitated subchloride of mercury into chloride.

Should bismuth or chloride of antimony be present, the addition of the washings of the precipitate produced by hydrochloric acid to the first filtrate will cause turbidity, if the amount of free hydrochloric acid present is not sufficient to prevent the separation of the basic salts. This turbidity exercises, however, no influence upon the further process, since hydrosulphuric acid as readily converts these finely-divided precipitates into sulphides, as if the metals were in actual solution.

In the case of alkaline solutions, the addition of hydrochloric acid must be continued until the fluid shows a strongly acid reaction. The substance which causes the alkaline reaction of the fluid combines with the hydrochloric acid, and the bodies originally dissolved in that acid separate. Thus, if the alkali was present in the free state, oxide of zinc, for instance, or alumina, &c., may precipitate. But these oxides redissolve in an excess of hydrochloric acid, whereas chloride of silver would not redissolve, and chloride of lead only with difficulty. If a metallic sulphur salt is the cause of the alkaline reaction, the sulphur acid, *e.g.* tersulphide of antimony, precipitates upon the addition of the hydrochloric acid, whilst the sulphur base, *e. g.* sulphide of sodium, transposes with the constituents of the hydrochloric acid, forming chloride of sodium and hydrosulphuric acid. If an alkaline carbonate, a cyanide, or the sulphide of an alkali metal is the cause of the alkaline reaction, carbonic acid, hydrocyanic acid, or hydrosulphuric acid escapes. All these phenomena should be carefully observed by the analyst, since they not only indicate the presence of certain substances, but demonstrate also the absence of certain groups of bodies.

To § 178.

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 cases where the analyst has simply to deal with metallic oxides of the sixth group—*e. g.* teroxide of antimony—and of the fourth or fifth group —*e. g.* the oxides of iron—he need not precipitate the acidified solution with hydrosulphuric acid, but may, after neutralization, at once add sulphide of ammonium in excess. The sulphide of iron, &c., will in that case precipitate, whilst the antimony, &c., will remain in solution, from which they will, upon addition of an acid, at once be thrown down as tersulphide of antimony, &c. This method has the advantage that the fluid is diluted less than is the case where solution of hydrosulphuric acid is employed, and that the operation is performed more expeditiously and conveniently than is the case where hydrosulphuric acid gas is conducted into the fluid. Finally, I must once more remind the student that the perfect purity of the reagents, and their application in correct quantity, rank amongst the most indispensable conditions of successful analysis. This applies more particularly to hydrosulphuric acid, especially when used in the gaseous form. In such cases, students often lose sight of the circumstance that hydrosulphuric acid gas fails to precipitate highly acid solutions unless they be previously diluted with water.

To § 181.

Besides the methods described in the systematic course to distinguish between cadmium, copper, lead, and bismuth, the following process will also be found to give highly satisfactory results. Add carbonate of soda to the nitric acid solution as long as a precipitate continues to form, then solution of cyanide of potassium in excess, and heat. This effects the complete separation of lead and bismuth in the form of carbonates, whilst copper and cadmium are obtained in solution in the form of cyanide of copper and potassium, and cyanide of cadmium and potassium. Lead and bismuth may now be readily separated from one another by means of sulphuric acid. The separation of the copper from the cadmium is effected by adding to the solution of the cyanides of these two metals in cyanide of potassium, hydrosulphuric acid in excess, heating, and then adding some more cyanide of potassium, in order to redissolve the sulphide of copper which may have precipitated along with the sulphide of cadmium. A residuary yellow precipitate (sulphide of cadmium) insoluble in the cyanide of potassium, demonstrates the presence of cadmium. Filter the fluid from this precipitate, and add hydrochloric acid to the filtrate, when the formation of a black precipitate (sulphide of copper) will demonstrate the presence of copper.

To § 182.

The precipitate produced by sulphide of ammonium (§ 182) may, as already stated, consist of sulphides, of oxides, and of phosphates of the alkaline earths, phosphate of alumina, oxalate of lime (baryta and strontia), as well as of fluorides of the metals of the alkaline earths. The borates of the alkaline earths, and the oxalate of magnesia would also be precipitated were they not retained in solution by the chloride of ammonium formed in the fluid or added to it. It is a matter of perfect indifference, as regards the final results of this operation, whether a precipitate forms or not upon the simple addition of ammonia, since sulphide of ammonium decomposes without difficulty the recently precipitated hydrated oxides of iron, &c. Nor can any positive inference respecting the presence or absence of certain metals and compounds be drawn from this reaction, unless the hydrosulphuric acid have been previously altogether removed from the fluid, and a positive assurance of the absence of organic substances obtained.

In § 182 we have distinguished two cases, of which the first—marked by the formation of a white precipitate—requires no further explanation, especially as it is included in the second—marked by the formation of a precipitate of a different color. We proceed therefore at once to the explanation of the process to be adopted in cases where all the substances under consideration here are contained in the precipitate produced by sulphide of ammonium. However, to simplify this explanation as much as possible, we will omit sesquioxide of chromium, which may be done the more readily, as the separation of sesquioxide of chromium by fusion with nitrate of potassa and carbonate of soda is a perfectly independent operation, and which gives a sufficiently characteristic reaction. We will therefore suppose the precipitate to contain :—

Sulphides of cobalt, nickel, iron, manganese, and zinc, along with alumina* and phosphate of lime.

Sulphide of cobalt and sulphide of nickel are difficultly soluble in cold dilute hydrochloric acid, whilst the other bodies readily dissolve in that menstruum. On treating the precipitate therefore with cold dilute hydrochloric acid, the two first-named sulphides remain almost entirely undissolved, whilst the other bodies dissolve along with traces of cobalt and nickel.

If the solution, after being freed from hydrosulphuric acid by boiling, is now treated with solution of soda in excess, the oxide of zinc and the alumina, and also the phosphate of the latter, being soluble in an excess of solution of soda, are obtained in solution, whilst the other bases remain undissolved, the iron as black protosesquioxide, in which form it is most easily separated from alumina ; a small portion of the oxide of zinc is also always found in the insoluble precipitate.

Small portions of the latter are tested for iron and manganese ; the remainder is dissolved in hydrochloric acid, and in order to obtain the iron entirely as protoxide, the solution treated with sulphite of soda, then nearly neutralized, and mixed with acetate of soda. The solution remains still clear ; it contains, at least we may assume it to be so, protoxide of iron and protoxide of manganese, and also traces of protoxides of cobalt and nickel, and oxide of zinc combined with acetic acid ; moreover, phosphate of lime dissolved in the excess of the acetic acid ; and, lastly, sulphate of soda and chloride of sodium, of which latter the constituent elements have been supplied by the hydrochloric acid that had previously been used as the solvent, and by the soda of the carbonate and acetate of soda. On adding now sesquichloride of iron, the elements of that reagent transpose with the constituents of the phosphate of lime, and chloride of calcium and phosphate of sesquioxide of iron are formed, the latter of which being insoluble both in free acetic acid and in acetate of protoxide of iron, separates as a yellowish-white precipitate. If sesquichloride of iron is now added until the fluid acquires a reddish tint, owing to the formation of acetate of sesquioxide of iron, the analyst may rest assured that the phosphoric acid will now completely precipitate upon boiling, and that only a slight excess of sesquioxide of iron will precipitate along with it.

Had we not reduced the solution before adding the acetate of soda, the fluid—always presupposing the quantity of the sesquioxide of iron to pre-

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* Phosphate of alumina comports itself in respect to the process here under consideration exactly like pure alumina.

dominate—would have at once become red, from the formation of acetate of sesquioxide of iron; and as the latter dissolves phosphate of sesquioxide of iron in notable quantity, we should, in the first place, have obtained no precipitate, if only a small portion of phosphoric acid was present; and, in the second place, on boiling the liquid the phosphoric acid would have been thrown down in combination with a large excess of sesquioxide of iron, which would have materially interfered with the recognition of the acid in the precipitate.

We have now in the precipitate all the phosphoric acid in combination with the sesquioxide of iron added, in solution the other above enumerated bodies. Upon the addition of ammonia and sulphide of ammonium, the heavy metals are thrown down, whilst the lime, and the alkaline earths generally, that had been combined with the phosphoric acid, remain dissolved, and may then be detected in the usual way. If we now dissolve the precipitated metallic sulphides in hydrochloric acid—which may again leave undissolved traces of sulphide of cobalt and sulphide of nickel—then boil with nitric acid, nearly saturate with carbonate of soda, and mix with carbonate of baryta, all the sesquioxide of iron will precipitate as a basic salt, so that the least traces of zinc, nickel, and cobalt, may now be detected in the filtrate, after the previous removal of the baryta by means of sulphuric acid.

To § 192.

The analysis of cyanogen compounds is not very easy in certain cases, and it is sometimes extremely difficult even to ascertain whether we have really a cyanide before us or not. However, if the reactions of the substance under examination upon ignition (§ 164, A. I. 2.) (3) be carefully observed, and also whether upon ebullition with hydrochloric acid any odor of hydrocyanic acid is emitted (§ 168, 2), (35) the presence or absence of a cyanide will generally not long remain a matter of doubt.

It must above all be borne in mind that the insoluble cyanogen compounds occurring in pharmacy, &c., belong to two distinct classes. Viz. they are either SIMPLE CYANIDES, or COMPOUNDS OF METALS WITH FERROCYANOGEN or some other analogous compound radical.

All the simple cyanides are decomposed upon boiling with concentrated hydrochloric acid, into metallic chlorides and hydrocyanic acid. Their analysis is therefore never difficult. But the ferrocyanides, &c., to which indeed the method described § 192 more exclusively refers, suffer by acids such complicated decompositions that their analysis by means of acids is a task not so easily accomplished. Their decomposition by potassa or soda is far more simple. The alkali yields its oxygen to the metal combined with the ferrocyanogen, &c., the oxide thus formed precipitates, and the reduced potassium or sodium forms with the liberated radical soluble ferrocyanide, &c. of potassium or sodium. But several oxides are soluble in an excess of potassa, as *e. g.* oxide of lead, oxide of zinc, &c. If, therefore, the double ferrocyanide of zinc and potassium, for instance, is boiled with solution of caustic potassa, it dissolves completely in that menstruum, and we may assume that the solution contains ferrocyanide of potassium, and oxide of zinc dissolved in potassa. Were we to add an acid to this solution, we should of course simply re-obtain the original precipitate of the double ferrocyanide of zinc and potassium, and the experiment would consequently be of no avail. To prevent this, conduct hydrosulphuric acid into the solution in potassa. This serves to convert into sulphides all the heavy metals which the potassa holds in solution as oxides. Those sulphides which are insoluble in potassa, such as sulphide of lead, sulphide of zinc, &c., precipitate, whilst those which are soluble in alkaline sulphides, such as sulphide of tin, sulphide of antimony, &c., remain in solution, and separate only upon the addition of an acid.

The fluid filtered from the precipitated oxides and sulphides accordingly always contains the cyanogen as ferrocyanide, &c., of potassium—provided, of course, the analyzed compound is really a double ferrocyanide, &c. From most of these compounds—ferrocyanide, ferricyanide, chromicyanide, and manganocyanide of potassium—the cyanogen partly separates as hydrocyanic acid, upon boiling the solutions with sulphuric acid, and may thus be readily detected. But the cobalticyanide of potassium is not decomposed by sulphuric acid, and this renders the *direct* demonstration of the presence of cyagogen in this double compound a difficult task. Upon fusion with nitrate of potassa, all these double compounds suffer decomposition, cobalticyanide of potassium not excepted. The reason why the fusion of these double compounds with nitrate of potassa should be preceded by evaporation with an excess of nitric acid, is simply to prevent the occurrence of explosions. Caution is highly advisable in this operation.

If the analyst merely wishes to examine for certain bases in simple or compound cyanides, he may in most cases accomplish his object by igniting the substance for some time, or by fusing it with carbonate of soda and potassa. The metals are thus obtained either in the metallic state or in combination with carbon. If the compound has been fused with alkaline carbonates, cyanide of potassium is found in the slag, if it has not been converted into cyanate of potassa, owing to the adventitious presence of reducible oxides. (Compare § 146, 3.) That the volatile metals (mercury, arsenic, &c.) suffer volatilization in this process, need hardly be mentioned.

APPENDIX.

I.

DEPORTMENT OF THE MOST IMPORTANT OF THE ALKALOIDS WITH REAGENTS, AND SYSTAMATIC METHOD OF EFFECTING THE DETECTION OF THESE SUBSTANCES.

§ 216.

THE detection and separation of the vegeto-alkalies, or alkoloids, is a task of far greater difficulty than that of most of the inorganic bases. Although this difficulty is owing partly to the circumstance that scarcely one of the compounds which the alkaloids form with other substances, is absolutely insoluble or particularly characterized by its color or any striking property, yet the principal cause of this difficulty must be ascribed to the want of accurate and minute investigations of the salts and other compounds of the alkaloids, and of the products of their decomposition. We therefore generally see and apprehend the reactions only in their external manifestation, but without being able to connect them with the causes producing them, which makes it impossible to understand all the conditions which may exercise a modifying influence.

Although therefore, in the present imperfect state of our knowledge of these bodies, an attempt to define their deportment with reagents, and base thereon a method of effecting their separation or, at least, their individual detection, must of necessity fall very short of perfection, yet, having made a great many experiments on the nature and behavior of these substances, I will attempt here, for the benefit of young chemists, and more particularly pharmaceutists, to describe in some measure the reactions which the most important of the alkaloids manifest with other bodies, and to lay down a systematic method of effecting their individual detection.

The classification of the alkaloids into groups, which I have adopted, is based upon their deportment with certain general reagents. I have verified by numerous experiments the whole of the reactions described in the succeeding paragraphs.

FIRST GROUP.

ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA OR SODA FROM THE SOLUTIONS OF THEIR SALTS, AND REDISSOLVE READILY IN AN EXCESS OF THE PRECIPITANT. Of the alkaloids of which I purpose to treat here, *one* only belongs to this group, viz.,

MORPHIA $(C_{34}H_{19}NO_6=\overset{+}{Mo})$

§ 217.

1. Crystallized morphia $(\overset{+}{Mo}+2\,aq.)$ usually appears in the form of colorless, brilliant, four-sided prisms, or, when obtained by precipitation, as a white crystalline powder. It has a bitter taste, and dissolves very sparingly in cold, but somewhat more readily in boiling water. Of cold alcohol it requires ninety parts by weight for solution ; of boiling alcohol from twenty to thirty parts. The solutions of morphia in alcohol, and in hot water manifest distinctly alkaline reaction. This alkaloid is nearly insoluble in ether. At a moderate heat the crystallized morphia loses the two equivalents of water.

2. Morphia neutralizes acids completely, and forms with them the SALTS OF MORPHIA. These salts are readily soluble in water, and in spirit of wine, but insoluble in ether ; their taste is disagreeably bitter. Most of them are crystallizable.

3. *Potassa* and *ammonia* precipitate from the solutions of salts of morphia—generally only after some time—$\overset{+}{Mo}+2\,aq.$, in the form of a white crystalline powder. Stirring and friction on the sides of the vessel promote the separation of the precipitate, which redissolves with great readiness in an excess of potassa, but more difficultly in ammonia. It dissolves also in chloride of ammonium and, though with difficulty only, in carbonate of ammonia.

4. *Carbonate of potassa and carbonate of soda* produce the same precipitate as potassa and ammonia, but fail to redissolve it upon addition in excess. Consequently if a fixed alkaline bicarbonate is added to a solution of morphia in caustic potassa, $\overset{+}{Mo}+2\,aq.$ separates,—especially after previous ebullition—in the form of a crystalline powder. A more minute inspection, particularly through a magnifying glass, shews this powder to consist of small acicular crystals ; seen through a glass which magnifies 100 times, these crystals present the form of four-sided prisms.

5. *Bicarbonate of soda and bicarbonate of potassa* speedily produce in solutions of neutral salts of morphia a precipitate of hydrated morphia, in the form of a crystalline powder. The preccpitate is insoluble in an

excess of the precipitants. These reagents fail to precipitate acidified solutions of salts of morphia in the cold.

6. The action of strong *nitric acid* upon morphia or one of its salts, in the solid state or in concentrated solutions, produces a fluid varying from red to yellowish-red. Dilute solutions do not change their color upon addition of nitric acid in the cold, but upon boiling they acquire a yellow tint.

7. *Neutral sesquichloride of iron* imparts to neutral solutions of salts of morphia a beautiful dark blue color, which disappears upon the addition of an acid. If the solution contains an admixture of animal or vegetable extractive matters, or of acetates, the color will appear clouded and less distinct.

8. If *iodic acid* is added to a solution of morphia or of a salt of morphia, IODINE separates. In concentrated aqueous solutions the separated iodine appears as a kermes-brown precipitate, whilst to alcoholic and dilute aqueous solutions it imparts a brown or yellowish-brown color. The addition of starch-paste to the fluid considerably heightens the delicacy of the reaction, since the blue tint of the iodide of starch remains still perceptible in exceedingly dilute solutions, which is not the case with the brown color imparted by iodine. As other nitrogenous bodies (albumen, caseïne, fibrine, &c.) likewise reduce iodic acid, this reaction has only a relative value.

SECOND GROUP.

ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, BUT DO NOT REDISSOLVE, TO A PERCEPTIBLE EXTENT, IN AN EXCESS OF THE PRECIPITANT, AND ARE PRECIPITATED BY BICARBONATE OF SODA EVEN FROM ACID SOLUTIONS, if the latter are not diluted in a larger proportion than 1 : 100; Narcotina—Quina—Cinchonia.

a. NARCOTINA ($C_{46}H_{25}NO_{14}=\overset{+}{Na}$).

§ 218.

1. Crystallized narcotina ($\overset{+}{Na}+aq.$) appears usually in the form of colorless, brilliant, straight rhombic prisms, or, when precipitated by alkalies, as a white, loose, crystalline powder. It is insoluble in water. Alcohol and ether dissolve it sparingly in the cold, but somewhat more readily upon heating. Solid narcotina is tasteless, but the alcoholic and ethereal solutions are intensely bitter. Narcotina does not alter vegetable colors. At 338° it fuses, with loss of 1 eq. of water.

2. Narcotina dissolves readily in acids, combining with them and forming

salts. These salts have invariably an acid reaction. Those with weak acids are decomposed by a large amount of water, and, if the acid is volatile, even upon simple evaporation. Most of the salts of narcotina are amorphous, and soluble in water, alcohol, and ether; they have a bitter taste.

3. *Pure alkalies,* and *alkaline carbonates* and *bicarbonates,* immediately precipitate from the solutions of salts of narcotina $\overset{+}{\mathrm{Na}}+\mathrm{aq.}$, in the form of a white powder, which seen through a lens magnifying 100 times, appears an aggregate of small crystalline needles. The precipitate is insoluble in an excess of the precipitants. If a solution of narcotina is mixed with ammonia, and ether added in sufficient quantity, the narcotina which has separated upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers. If a drop of the ethereal solution is evaporated on a watch-glass, the residue is seen, upon inspection through a lens magnifying 100 times, to consist of small distinct, elongated, and lance-shaped crystals.

4. *Concentrated nitric acid* dissolves narcotina to a colorless fluid, which acquires a pure yellow tint upon application of heat.

5. *Concentrated sulphuric acid* dissolves narcotina to a yellow fluid, which turns brown upon application of heat. A solution of narcotina in concentrated sulphuric acid containing a *slight* admixture of nitric acid, appears of an intense blood-red color, which disappears altogether upon the addition of a somewhat larger amount of nitric acid.

6. If the solution of a salt of narcotina is mixed with *chlorine water,* it acquires a yellow color, slightly inclining to green; if ammonia is then added, a much more intensely colored, yellowish-red fluid is obtained.

7. If narcotina or one of its salts is dissolved in an excess of dilute *sulphuric acid,* some finely legivated binoxide of manganese added, the mixture heated to boiling, and kept in ebullition for the space of several minutes, the narcotina absorbs oxygen and is converted into opianic acid cotarnina (a base soluble in water), and carbonic acid.

b. QUINA ($C_{40}H_{24}N_2O_4=\overset{+}{\mathrm{Q}}$).

§ 219.

1. Crystallized quina ($\overset{+}{\mathrm{Q}}+2\,\mathrm{aq.}$) appears either in the form of fine crystalline needles of silky lustre, which are frequently aggregated into tufts, or as a loose white powder. It is sparingly soluble in cold, but somewhat more readily in hot water. It is readily soluble in spirit of wine, both cold and hot, but less so in ether. The taste of quina is intensely bitter; the solutions of quina manifest alkaline reaction. Upon exposure to heat it loses the 2 eq. of water.

2. Quina neutralizes acids completely. The salts taste intensely bitter; most of them are crystallizable, and for the greater part readily soluble in water and in spirit of wine. Acid solutions have a bluish tint.

3. *Potassa*, *ammonia*, and the neutral *carbonates of the alkalies*, produce in solutions of salts of quina (if they are not too dilute) a white, loose, pulverulent precipitate of hydrated quina, which immediately after precipitation appears opaque and amorphous under the microscope, but assumes, after the lapse of some time, the appearance of aggregated crystalline needles. The precipitate redissolves only to a scarcely perceptible extent in an excess of potassa, but more readily in ammonia. It is hardly more soluble in fixed alkaline carbonates than in pure water. If a solution of quina is mixed with ammonia, ether added, and the mixture shaken, the quina which has separated upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers. In this point quina differs essentially from cinchonia; by means of this reaction the former may therefore be readily detected in presence of the latter, and separated from it.

4. *Bicarbonate of soda* also produces, and this both in neutral and acid solutions of salts of quina, a white precipitate. In acidified solutions containing one part of quina to 100 parts of acid and water, the precipitate forms immediately;—if the proportion of the quina to the acid and water is as 1:150, the precipitate separates only after an hour or two, in the form of distinct needles, aggregated into groups. If the proportion is as 1 : 200, the fluid remains clear, and it is only after from twelve to twenty-four hours' standing that a slight precipitate makes its appearance. The precipitate is not altogether insoluble in the precipitant, and the separation is accordingly the more complete, the less the excess of the precipitant; the precipitate contains carbonic acid.

5. *Concentrated nitric acid* dissolves quina to a colorless fluid, becoming yellowish upon the application of heat.

6. The addition of *chlorine water* to the solution of a salt of quina fails to impart a color to the fluid, or, at least, imparts to it only a very faint tint; but if ammonia is now added the fluid acquires an intensely emerald-green color.*

7. *Concentrated sulphuric acid* likewise dissolves pure quina and pure salts of quina to a colorless fluid, which does not acquire any coloration upon being heated to the point of incipient evaporation of the sulphuric acid, but becomes afterwards yellow, and finally brown. Sulphuric acid containing an admixture of nitric acid dissolves quina to a colorless or very faint yellowish fluid.

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* *Vogel's* statement, that the solution mixed with chlorine water acquires a dark red color upon addition of concentrated solution of ferrocyanide of potassium in excess, has not been confirmed by the results of my own experiments.

c. CINCHONIA ($C_{40} H_{24} N_2 O_2 = \overset{+}{Ci}$).

§ 220.

1. Cinchonia appears either in the form of pellucid, brilliant, four-sided prisms, fine white crystalline needles, or when precipitated from concentrated solutions, as a loose white powder. At first it appears tasteless, but after some time the bitter taste of the bark becomes perceptible. It is nearly insoluble in cold water, and dissolves only with exceeding difficulty in hot water; it dissolves sparingly in cold dilute spirit of wine, more readily in hot spirit of wine, and the most easily in absolute alcohol. From hot alcoholic solutions the greater portion of the dissolved cinchonia separates upon cooling in a crystalline form. Solutions of cinchonia taste bitter, and manifest alkaline reaction. Cinchonia is insoluble in ether.*

2. Cinchonia neutralizes acids completely. The salts have the bitter taste of the bark; most of them are crystallizable; they are generally more readily soluble in water and in spirit of wine, than the corresponding quina compounds. Ether fails to dissolve them.

3. Cinchonia when heated cautiously fuses at first without loss of water; subsequently white fumes arise which, like benzoic acid, condense upon cold substances, in the form of small brilliant needles, or as a loose sublimate, a peculiar aromatic odor being exhaled at the same time. If the operation is conducted in a stream of hydrogen gas, long, brilliant prisms are obtained (*Hlasiwetz*).

4. *Potassa, ammonia,* and the *neutral carbonates of the alkalies* produce in solutions of salts of cinchonia a white, loose, precipitate of CINCHONIA, which does not redissolve in an excess of the precipitants. If the solution was concentrated, the precipitate does not exhibit a distinctly crystalline appearance, even though viewed through a lens magnifying 200 times; but if the solution was so dilute that the precipitate formed only after some time, it appears under the microscope to consist of distinct crystalline needles aggregated into star-shaped tufts.

5. *Bicarbonate of soda* and *bicarbonate of potassa* precipitate cinchonia in the same form as in 4, both from neutral and acid solutions, but not so completely as the simple carbonates of the alkalies. In solutions containing one part of cinchonia to 200 parts of water and acid, the precipitate still forms immediately; its quantity increases after standing some time.

6. *Concentrated sulphuric acid* dissolves cinchonia to a colorless fluid,

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* The cinchonia of commerce usually contains in admixture another alkaloid, called cinchotina, which is soluble in ether. Cinchotina crystallizes in large rhomboidal crystals of brilliant lustre, which fuse at a high temperature, and cannot be sublimed, even in a stream of hydrogen gas (*Hlasiwetz*).

which upon application of heat first acquires a brown, and finally a black color. Addition of some nitric acid leaves the solution colorless in the cold, but upon application of heat the fluid, after passing through the intermediate tints of yellowish-brown and brown, becomes finally black.

7. The addition of *chlorine water* to the solution of a salt of cinchonia fails to impart a color to the fluid; if ammonia is now added, a yellowish-white precipitate is formed.

Recapitulation and remarks.

§ 221

The alkaloids of the second group are altered or precipitated by various other reagents besides those mentioned above; the reactions are, however, not adapted to effect their individual detection and separation. Thus, for instance, bichloride of platinum produces in solutions of the salts of the three alkaloids belonging to this group, a yellowish-white precipitate, chloride of mercury, a white precipitate, tincture of galls a yellowish-white, flocculent precipitate, &c.

Narcotina and quina being soluble in ether, whilst cinchonia is insoluble in that menstruum, the former may be most readily separated by this means from the latter alkaloid. For this purpose the analyst need simply mix the solution of the three alkaloids with ammonia in excess, then add ether, and separate the solution of quina and narcotina from the undissolved cinchonia. If the ethereal solution is now evaporated, the residue dissolved in hydrochloric acid and a sufficient amount of water to make the dilution as 1 : 200, and bicarbonate of soda is then added, the narcotina precipitates, whilst the quina remains in solution. By evaporating the solution, and treating the residue with water, the quina is obtained in the free state.

THIRD GROUP.

ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, AND DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT; BUT ARE NOT PRECIPITATED FROM ACID SOLUTIONS BY THE BICARBONATES OF THE FIXED ALKALIES: Strychnia, Brucia, Veratria.

a. STRYCHNIA ($C_{44}H_{24}N_2O_4=\overset{+}{Sr}$).

§ 222.

1. Strychnia appears either in the form of white, brilliant octohedrons, or four-sided prisms, or finally, when produced by precipitation or rapid evaporation, as a white powder. It has an exceedingly bitter taste. It is

nearly insoluble in cold, and scarcely soluble in hot water. It is insoluble in absolute alcohol and ether, and difficultly soluble in dilute spirit of wine. It does not fuse when heated. It is exceedingly poisonous.

2. Strychnia neutralizes acids completely. Most of the salts of strychnia are crystallizable, and soluble in water. All the salts of strychnia have an intolerably bitter taste, and are exceedingly poisonous.

3. *Potassa* and *carbonate of soda* produce in solutions of salts of strychnia white precipitates of strychnia, which are insoluble in an excess of the precipitants. Viewed through a lens magnifying one hundred times, the precipitate appears as an aggregate of small crystalline needles. From dilute solutions the strychnia separates only after the lapse of some time, in the form of crystalline needles, which are perfectly visible even to the naked eye.

4. *Ammonia* produces the same precipitate as potassa. The precipitate redissolves in an excess of ammonia, but after a short time—or if the solution is highly dilute, after a more considerable lapse of time—the strychnia crystallizes from the ammoniacal solution in the form of needles, which are distinctly visible to the naked eye.

5. *Bicarbonate of soda* produces in neutral solution of salts of strychnia a precipitate of strychnia, which separates in fine needles shortly after the addition of the reagent, and is insoluble in an excess of the precipitant. But upon adding one drop of acid (so as to leave the fluid still alkaline) the precipitate dissolves readily in the liberated carbonic acid. The addition of bicarbonate of soda to an acid solution of strychnia causes no precipitation, and it is only after the lapse of twenty-four hours, or even a longer period, that strychnia crystallizes from the fluid in distinct prisms, in proportion as the free carbonic acid escapes. If a concentrated solution of strychnia, supersaturated with bicarbonate of soda, is boiled for some time, a precipitate forms immediately; from dilute solutions this precipitate separates only after concentration.

6. *Sulphocyanide of potassium* produces in concentrated solution of salts of strychnia immediately, and in dilute solutions after the lapse of some time, a white crystalline precipitate, which appears under the microscope as an aggregate of flat needles, truncated or pointed, and is but little soluble in an excess of the precipitant.

7. On putting a drop of concentrated sulphuric acid on a watch-glass, and adding to it some strychnia or a little of a salt of strychnia, solution ensues without any particular reaction; but if a drop of solution of chromate of potassa is now added to the fluid, the latter instantly acquires a deep blue color, which speedily changes to red (*Otto*). If the strychnia is rubbed together with binoxide of lead and concentrated sulphuric acid containing one per cent of nitric acid, the mass acquires first a blue, then a violet color, which changes to red, and, finally, to

greenish-yellow (*E. Marchand*). The former reaction (*Otto's*) loses in distinctness, or even altogether fails to manifest itself, if the substance contains admixtures of some other organic compounds, *e. g.* quina, sugar (*Brieger*). But by the second method (*Marchand's*) strychnia may be clearly detected even when mixed with much sugar.

8. *Chloride of mercury* produces in solutions of salts of strychnia a white precipitate, which changes after some time to crystalline needles aggregated into stars, and distinctly visible through a lens. Upon heating the fluid these crystals redissolve, and upon subsequent cooling of the solution the double compound recrystallizes in distinct needles.

9. Strong *chlorine water* produces in solutions of salts of strychnia a white precipitate, which dissolves in ammonia to a colorless fluid.

10. *Concentrated nitric acid* dissolves strychnia to a colorless fluid, which becomes yellow upon the application of heat.

b. BRUCIA ($C_{46}\,H_{26}\,N_2\,O_8=\overset{+}{\mathrm{Br}}$).

§ 223.

1. Crystallized brucia ($\mathrm{Br}+7$ aq.) appears either in the form of transparent, straight rhombic prisms, or in that of crystalline needles aggregated into stars, or as a white powder composed of minute crystalline scales. Brucia is difficultly soluble in cold, but somewhat more readily so in hot water. Both absolute and dilute alcohol dissolve it readily, but it is insoluble in ether. Its taste is intensely bitter. When heated it fuses with loss of its water of crystallization.

2. Brucia neutralizes acids completely. The salts of brucia are readily soluble in water, and of an intensely bitter taste. Most of them are crystallizable.

3. *Potassa* and *carbonate of soda* throw down from solutions of salts of brucia a white precipitate of brucia, which is insoluble in an excess of the precipitant. Viewed under the microscope, immediately after precipitation, it appears to consist of very minute grains, but, upon further inspection, these grains are seen—with absorption of water—to suddenly form into needles, which latter subsequently arrange themselves into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye.

4. *Ammonia* produces a whitish precipitate in solutions of salts of brucia, which appears at first like a number of minute drops of oil, but changes subsequently—with absorption of water—to small needles. The precipitate redissolves, immediately after separation, very readily in an excess of the precipitant, but after a very short time—or, in dilute solutions, after a more considerable lapse of time—the brucia, combined with crystallization water, crystallizes from the ammoniacal fluid in small

concentrically grouped needles, which addition of ammonia fails to redissolve.

5. *Bicarbonate of soda* produces in neutral solutions of salts of brucia a precipitate of brucia, which separates after the lapse of a short time, in form of concentrically aggregated needles of silky lustre, which are insoluble in an excess of the precipitant, but dissolve in free carbonic acid (compare strychnia). Bicarbonate of soda fails to precipitate acid solutions of salts of brucia. But this alkaloid separates after a considerable lapse of time, with the escape of carbonic acid, in regular and comparatively large crystals.

6. *Concentrated nitric acid* dissolves brucia and its salts to intensely red fluids, which subsequently acquire a yellowish-red tint, and become completely yellow upon the application of heat. Upon addition of protochloride of tin or sulphide of ammonium to this yellow fluid, no matter whether concentrated or diluted with water, the faint yellow color changes to a most intense violet.

7. Addition of *chlorine water* to the solution of a salt of brucia imparts to the fluid a fine bright red tint; if ammonia is then added, the red color changes to yellowish-brown.

8. *Concentrated sulphuric acid* dissolves brucia to a faint rose-colored fluid.

9. *Sulphocyanide of potassium* produces in concentrated solutions of salts of brucia immediately, and in dilute solutions after some time, a granular crystalline precipitate, which, when viewed under the microscope, appears composed of variously aggregated polyhedral crystalline grains. Friction applied to the sides of the vessel promotes the separation of the precipitate.

10. *Chloride of mercury* produces also a white granular precipitate, which, when viewed under the microscope, appears composed of small round-shaped crystalline grains.

c. VERATRIA $(C_{34}\,H_{22}\,NO_6)\,\overset{+}{Ve}$.

§ 224.

1. Veratria appears generally as a pure white, yellowish, or greenish white powder, of acrid and burning, but not bitter taste; it is exceedingly poisonous. Veratria acts with great energy upon the membranes of the nose; even the most minute quantity of the powder excites the most violent sneezing. It is insoluble in water; in alcohol it dissolves readily, but more sparingly in ether. At a gentle heat it fuses like wax, and solidifies upon cooling to a transparent yellow mass.

2. Veratria neutralizes acids completely. Some salts of veratria are crystallizable, others dry up into a gummy mass. They are soluble in water, and of acrid and burning taste.

3. *Potassia, ammonia,* and the *simple carbonates of the alkalies* produce in solutions of salts of veratria a flocculent white precipitate, which viewed under the microscope, immediately after precipitation, does not appear crystalline. After the lapse of a few minutes, however, it alters its appearance, and small scattered clusters of short prismatic crystals are observed, instead of the original coagulated flakes. The precipitate does not redissolve in an excess of potassa, and of carbonate of potassa. It is slightly soluble in ammonia, in the cold, but the dissolved portion separates again upon application of heat.

4. With *bicarbonate of soda* and *bicarbonate of potassa,* the salts of veratria comport themselves like those of strychnia and brucia. However, upon boiling, the veratria separates readily, even from dilute solutions.

5. If veratria is acted upon with concentrated nitric acid it agglutinates into small resinous lumps, which afterwards dissolve slowly in the acid. The solution presents a faint reddish-yellow color.

6. If veratria is treated with *concentrated sulphuric acid,* it agglutinates at first into small resinous lumps; but these dissolve with great readiness to a pale yellow fluid, the color of which gradually increases in depth and intensity, and changes afterwards to a reddish-yellow, then to an intense blood-red, subsequently to crimson, and finally to violet.

7. *Sulphocyanide of potassium* produces only in concentrated solutions of salts of veratria flocculent gelatinous precipitates.

8. Addition of *chlorine-water* to the solution of a salt of veratria imparts to the fluid a yellowish tint which, upon addition of ammonia, changes to a faint brownish color. In concentrated solutions chlorine produces a white precipitate.

Recapitulation and remarks.

§ 225.

The alkaloids of the third group are also precipitated by many other reagents besides those above-mentioned, as, for instance, by tincture of galls, bichloride of platinum, &c. But as these reactions are common to all, they are of little importance in an analytical point of view.

Strychnia may be separated from brucia and veratria by means of absolute alcohol, since it is insoluble in that menstruum whilst the two latter alkaloids readily dissolve in it. The identity of strychnia is best established by the reaction with sulphuric acid and chromate of potassa; also by the form of its crystals—when thrown down by alkalies—viewed under the microscope; and lastly, by the form of the precipitate which sulphocyanide of potassium and chloride of mercury produce in solutions of its salts. Brucia and veratria are not readily separated from one another, but may be detected in presence of each other. The identity of brucia is best established by the reactions with nitric acid and protochloride of tin or sulphide of ammonium, or by the form of the precipitate which ammonia produces in solutions of salts of brucia. Veratria is sufficiently distinguished from brucia and the other alkaloids which we have treated of, by its characteristic deportment at a gentle heat, and also by the form of the precipitate which alkalies produce in solutions of its salts. To distinguish veratria in presence of brucia, the reaction with sulphuric acid is employed.

To these alkaloids I will add *salicine*, although this substance does not properly belong to the same class of chemical compounds.

§ 226.

SALICINE ($C_{26}H_{18}O_{14}$).

1. Salicine appears either in the form of white crystalline needles and scales of silky lustre, or, when the crystals are very small, as a powder of silky lustre. It has a bitter taste, is readily soluble in water and in alcohol, but insoluble in ether.

2. No reagent precipitates salicine as such.

3. If salicine is treated with *concentrated sulphuric acid*, it agglutinates into a resinous lump, and acquires an intensely blood-red color, without dissolving in the acid; the color of the sulphuric acid is at first unaltered.

4. If an aqueous solution of salicine is mixed with *hydrochloric acid or dilute sulphuric acid*, and the mixture boiled for a short time, the fluid suddenly becomes turbid, and deposits a finely granular crystalline precipitate (saliretine).

SYSTEMATIC COURSE FOR THE DETECTION OF THE ALKALOIDS TREATED OF IN THE PRECEDING PARAGRAPHS, AND OF SALICINE.

§ 227.

The analytical course which I am now about to describe is based upon the supposition that the analyst has to examine a concentrated aqueous solution—effected by the agency of an acid—of one or several of the alkaloids, which solution is free from any admixture of substances that might tend to obscure or modify the reactions. For the modifications which the presence of coloring or extractive matters, &c. requires, I refer to § 230.

I. DETECTION OF THE ALKALOIDS, AND OF SALICINE, IN SOLUTIONS SUPPOSED TO CONTAIN ONLY ONE OF THESE SUBSTANCES.

§ 228.

1. Add dilute solution of potassa or soda drop by drop to a portion of the aqueous solution, until the fluid acquires a scarcely perceptible alkaline reaction; stir, and let the fluid stand for some time.

a. NO PRECIPITATE IS FORMED; this proves the total absence of the alkaloids, and indicates the presence of SALICINE. To set all doubt at rest, test the original substance with concentrated sulphuric acid, and with hydrochloric acid. Compare § 226.

b. A PRECIPITATE IS FORMED. Add solution of potassa or soda drop by drop until the fluid manifests a strongly alkaline reaction.

> α. *The precipitate redissolves :* MORPHIA. To arrive at a positive conclusion on this point, test another portion of the solution with iodic acid (§ 217, 8), and a portion of the original substance with nitric acid (§ 217, 6).
>
> β. *The precipitate remains undissolved :* Presence of an alkaloid of the second or third group. Pass on to 2.

2. Add to a second portion of the original solution two or three drops of dilute sulphuric acid, and then a saturated solution of bicarbonate of soda until the acid reaction is just neutralized; vigorously rub the inside of the vessel, and allow the mixture to stand for half an hour.

a. NO PRECIPITATE IS FORMED: Absence of narcotina and cinchonia. Pass on to 3.

b. A PRECIPITATE IS FORMED: Narcotina, cinchonia, and perhaps also quina, as the precipitation of the latter substance by bicarbonate of soda depends entirely upon the degree of dilution of the fluid. Add to a portion of the original solution ammonia in excess, then a sufficient quantity of ether, and shake the mixture.

> α. *The precipitate which forms at first upon the addition of the ammonia redissolves in the ether, and the clear fluid presents two distinct layers :* narcotina or quina. To distinguish between the two, test a fresh portion of the original solution with chlorine water and ammonia. If the solution turns green, QUINA, if yellowish-red NARCOTINA is present.
>
> β. *The precipitate which forms upon the addition of ammonia does not redissolve in the ether :* CINCHONIA. The deportment of cinchonia at a high temperature may serve as a conclusive test (§ 220, 3).

3. Put a portion of the original substance, or of the residue remaining upon the evaporation of the solution, into a watch-glass, and treat with concentrated sulphuric acid.

a. A rose-colored solution is obtained, which becomes intensely red upon addition of nitric acid: BRUCIA. The reaction with nitric acid and protochloride of tin is resorted to as a conclusive test (§ 223, 6).

b. A yellow solution is obtained, the color of which changes to a yellowish-red, then to blood-red, and turns finally crimson: VERATRIA.

c. A colorless fluid is obtained, which remains colorless after some standing.

Add to the fluid a drop of chromate of potassa; if this imparts to it a deep blue color, **STRYCHNIA** is present; if it leaves the fluid unaltered, **QUINA** is present. The reaction with chlorine water and ammonia is resorted to as a conclusive test.

II. DETECTION OF THE ALKALOIDS, AND OF SALICINE, IN SOLUTIONS SUPPOSED TO CONTAIN SEVERAL OR ALL OF THESE SUBSTANCES.

§ 229.

1. Add to a portion of the aqueous solution dilute solution of potassa or soda drop by drop, until the fluid acquires a scarcely perceptible alkaline reaction; stir, and let the fluid stand for some time.

a. **NO PRECIPITATE IS FORMED**; this proves the total absence of the alkaloids, and indicates the presence of **SALICINE**. To remove all doubt on the point, test the original substance with concentrated sulphuric acid, and with hydrochloric acid. Compare § 226.

b. **A PRECIPITATE IS FORMED**: add solution of potassa or soda drop by drop until the fluid manifests a strongly alkaline reaction.

> *α. The precipitate redissolves.* Absence of the alkaloids of the second and third group. Presence of **MORPHIA** is indicated. The reactions with iodic acid (§ 217, 8.) and with nitric acid (§ 217, 6.) are resorted to as conclusive tests. Examination for salicine, see 4.
>
> *β. The precipitate does not redissolve, or at least not completely.* Filter, and treat the precipitate as directed in 2. Saturate the filtrate with carbonic acid, or mix it with bicarbonate of soda or bicarbonate of potassa, and boil nearly to dryness. Treat the residue with water; if it dissolves completely, this is a sign that no morphia is present; but if there is an insoluble residue left, this indicates the presence of morphia. The reactions with iodic acid (§ 217, 8.) and with nitric acid (§ 217, 6.) are resorted to as conclusive tests.

2. Wash the precipitate of 1. *b.* *β.* with cold water, dissolve in a slight excess of dilute sulphuric acid and add solution of bicarbonate of soda to the fluid until the acid reaction is neutralized; stir the mixture, vigorously rubbing the sides of the vessel, and allow the fluid to stand at rest for half an hour.

a. **NO PRECIPITATE IS FORMED.** Absence of narcotina and cinchonia. Boil the solution nearly to dryness, and treat the residue with cold water. If it dissolves completely, pass on to 4; but if an insoluble residue is left, examine this for quina—of which a minute quantity might be present—and for strychnia, brucia, and veratria, according to the directions of 3.

b. **A PRECIPITATE IS FORMED.** This may contain narcotina, cinchonia, and also quina, compare § 228, 2, *b*. Filter, and treat the filtrate as directed § 229, 2, *a*. Wash the precipitate with cold water, dissolve in a little hydrochloric acid, add ammonia in excess, and then a sufficient quantity of ether.

a. The precipitate which forms at first upon the addition of the ammonia redissolves completely in the ether, and the clear fluid presents two distinct layers. Absence of cinchonia; presence of quina or narcotina. Evaporate the ethereal solution, dissolve the residue in a little hydrochloric acid and a sufficient amount of water to make the dilution at least as 200 : 1; add bicarbonate of soda to neutralization, and allow the fluid to stand for some time. The formation of a precipitate indicates the presence of NARCOTINA. Filter, and test the precipitate with chlorine water and ammonia (§ 218, 6.). Evaporate the filtrate, or the fluid if no precipitate has been formed, to dryness, and treat the residue with water. If part of it remains undissolved, wash this, dissolve in hydrochloric acid, and add chlorine water and ammonia. Green color: QUINA.

β. The precipitate produced by the ammonia does not redissolve in the ether, or at least not completely: CINCHONIA. Quina or narcotina may also be present. Filter, and examine the filtrate for quina and narcotina as in *a*. The precipitate consists of cinchonia, and may be further examined according to § 220, 3.

3. Wash the insoluble residue of 2, *a*. with water, dry in the water-bath, and digest with absolute alcohol.

a. IT DISSOLVES COMPLETELY: absence of strychnia; presence of (quina) brucia or veratria. Evaporate the alcoholic solution on the water-bath to dryness, and, if quina has already been detected, divide the residue into two portions, and test one of them for BRUCIA, with nitric acid and protochloride of tin (§ 223, 6.), and the other for VERATRIA, by means of concentrated sulphuric acid (§ 224, 6.);—but if no quina has as yet been detected, divide the residue into three portions, *a*, *b*, and *c*; examine *a* and *b* for BRUCIA and VERATRIA in the manner just stated, and *c* for quina, with chlorine water and ammonia.—However, if brucia is present, dissolve *c* in hydrochloric acid, add ammonia and ether, let the mixture stand for some time, evaporate the ethereal solution, and examine the residue for quina.

b. It does not dissolve, or at least not completely: presence of STRYCHNIA; perhaps also of (quina) brucia and veratria. Filter, and examine the filtrate for (QUINA) BRUCIA and VERATRIA as directed § 229, 3. *a*. The identity of the precipitate with strychnia is demonstrated by the reaction with sulphuric acid and chromate of potassa (§ 222, 7.).

4. Mix a portion of the original solution with hydrochloric acid, and boil the mixture for some time. The formation of a precipitate indicates the presence of SALICINE. To set all doubt on this point at rest, test the original substance with concentrated sulphuric acid (§ 226, 3.).

DETECTION OF THE ALKALOIDS, IN PRESENCE OF COLORING AND EXTRACTIVE VEGETABLE OR ANIMAL MATTERS.

§ 230.

The presence of mucilaginous, extractive, and coloring matters renders the detection of the alkaloids a task of considerable difficulty. These matters obscure the reactions so much that we are even unable to determine by a preliminary experiment, whether the substance under examination contains one of the alkaloids we have treated of in the foregoing paragraphs, or not. The best method of preparing substances containing such extraneous matters in admixture, for subsequent analysis in the usual way, is that recommended by MERCK, which I will give here with a few modifications.

Mix the substance under examination with concentrated acetic acid to strongly acid reaction, and let the mixture digest for several hours. Then strain the fluid from the solid part, squeeze the latter, and wash it with water acidified with acetic acid ; evaporate the whole of the fluid obtained to dryness on the water-bath. Boil the residue first with pure spirit of wine then with spirit of wine containing some acetic acid ; evaporate the solutions thus obtained nearly to dryness on the water-bath, dilute again with water, add carbonate of soda to feebly alkaline reaction, evaporate to the consistence of syrup, and allow to stand at rest for twenty-four hours ; then dilute again with water, and filter the fluid from the precipitate formed ; wash the latter with water, digest with concentrated acetic acid, dilute with water, and decolorize with pure animal charcoal. Examine the decolorized fluid in the usual way for the alkaloids, and for salicine.

GENERAL PLAN OF THE ORDER AND SUCCESSION IN WHICH SUBSTANCES OUGHT TO BE ANALYZED FOR PRACTICE.

IT is not a matter of indifference whether the student, in analyzing for the sake of practice, follows no rule or order whatever in the selection of the substances which he intends to analyze, or whether, on the contrary, his investigations and experiments proceed systematically. Many ways indeed may lead to the desired end, but one of them will invariably prove the shortest. I will therefore here point out a course which experience has shown to lead safely and speedily to the attainment of the object in view.

Let the student take 100 compounds, systematically arranged (*see below*) and let him analyze these compounds successively in the order in which they are placed. A careful and diligent examination of these will be amply sufficient to impart to him the necessary 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 for him by a friend who knows their exact composition.

A. *From* 1 *to* 20.

AQUEOUS SOLUTIONS OF SIMPLE SALTS: *e.g.* sulphate of soda, nitrate of lime, chloride of copper, &c. These investigations will serve to teach the student the method of analyzing substances soluble in water, which contain but one base. In these investigations it is only intended to ascertain which base is present in the fluid under examination; but neither the detection of the acid, nor the proof of the absence of all other bases besides the one detected, is required.

B. *From* 21 *to* 50.

SALTS, ETC., CONTAINING ONE BASE AND ONE ACID, OR ONE METAL AND ONE METALLOID (in the form of powder): *e. g.* carbonate of baryta, borate of soda, phosphate of lime, arsenites, chloride of sodium, bitartrate of potassa, acetate of copper, sulphate of baryta, chloride of lead, &c. These investigations will serve to teach the student how to make a preliminary examination of a solid substance, by heating in a spoon or before the blowpipe; how to convert it into a proper form for analysis, *i. e.* how to dissolve or decompose it; how to detect *one* metallic oxide, even in substances *insoluble* in water; and how to demonstrate the presence of *one* acid. The detection of both the base and the acid is required, but it is not necessary to prove that no other constituents are present.

C. *From* 51 *to* 65.

AQUEOUS OR ACID SOLUTIONS OF SEVERAL BASES. These investigations will serve to teach the student the method of separating and distinguishing several metallic oxides from each other. The proof is required that no other bases are present besides those detected. No regard is paid to the acids.

D. *From* 66 *to* 80.

Dry mixtures of every description. A portion of the salts should be organic, another inorganic; a portion of the compounds soluble in water or hydrochloric acid, another insoluble; *e. g.* mixtures of chloride of sodium, carbonate of lime, and oxide of copper;—of phosphate of magnesia and ammonia, and arsenious acid;—of tartrate of lime, oxalate of lime, and sulphate of baryta;—of phosphate of soda, nitrate of ammonia, and acetate of potassa, &c.

These investigations will serve to teach the student how to treat mixtures of different substances with solvents; how to detect several acids in presence of each other; how to detect the bases in presence of phosphates of the alkaline earths;—and they will serve as a general introduction to scientific and practical analyses. All the constituents must be detected, and the nature of the substance ascertained.

E. *From* 81 *to* 100.

Native compounds, articles of commerce, &c.—Mineral and other waters, minerals of every description, soils, potash, soda, alloys, colors, &c.

III.

ARRANGEMENT OF THE RESULTS OF THE ANALYSES PERFORMED FOR PRACTICE.

The manner in which the results of analytical investigations ought to be arranged, is not a matter of indifference. The following examples will serve to illustrate the method which I have found the most suitable in this respect.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, NOS. 1 TO 20.

Colorless fluid of neutral reaction.

HCl	HS	NH_4S, HS	NH_4O, CO_2 and NH_4Cl
no precipitate, consequently no AgO Hg_2O	*no precipitate,* no PbO ,, HgO ,, CuO ,, BiO_3 ,, CdO	*no precipitate,* no FeO ,, MnO ,, NiO ,, CoO ,, ZnO	*a white precipitate,* consequently either BaO, SrO, or CaO, no precipitate by solution of sulphate of lime, consequently **LIME.** Confirmation by means of $\overline{O}$
	,, AsO_3 ,, AsO_5 ,, SbO_3 ,, SnO_2 ,, SnO ,, AuO_3 ,, PtO_2	,, Al_2O_3 ,, Cr_2O_3	
	,, Fe_2O_3		

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, NOS. 21—50.

White powder melting in the water of crystallization upon application of heat, and then remaining unaltered—soluble in water—reaction neutral.

HCl	HS	NH_4S, HS	NH_4O, CO_2, and NH_4, Cl	$2NaO, HO, PO_5$, and NH_4O
no precipitate.	*no precipitate.*	*no precipitate.*	*no precipitate.*	*a white precipitate,* consequently **MAGNESIA.**

The detected base being MgO, and the analyzed substance being soluble in water, Cl, I, Br, SO_3, NO_5, $\overline{A}$, &c., are the only acids or metalloids that can be present. The preliminary examination has proved the absence of the organic acids and of nitric acid.

Ba Cl produces a white precipitate which H Cl fails to dissolve; consequently **SULPHURIC ACID.**

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, Nos. 51—100.

A white powder, acquiring a permanent yellow tint upon application of heat. Before the blowpipe, a ductile metallic globule, and yellow incrustation with white border upon cooling. Insoluble in water, effervescing with hydrochloric acid, incompletely soluble in that acid, readily soluble in nitric acid.

H Cl White precipitate, insoluble in an excess of the precipitant, unaltered by ammonia: LEAD—confirmation by means of SO_3.	HS Black precipitate, insoluble in sulphide of ammonium, readily soluble in nitric acid. Examination for Cu, Bi, and Cd, results negative.	NH_4, S, HS White precipitate; solution of this in hydrochloric acid remains clear upon addition of soda in excess. NH_4, Cl no precipitate. HS white precipitate: ZINC.	NH_4O, CO_2 White precipitate; upon dissolving this in hydrochloric acid, and adding solution of sulphate of lime to the fluid, a white precipitate forms after some time: STRONTIA. Precipitation with sulphate of potassa, filtrate tested for lime with $\bar{O}$, results negative.	No fixed residue upon evaporation.	Hydrate of lime has failed to evolve ammmonia.

Of the acids, CARBONIC ACID has already been found. Of the remaining acids, the following cannot be present:

The preliminary examination has proved the absence of organic acids.

NO_5 and $Cl\,O_5$, and also H Cl, H I, and H Br, cannot be present, because the analyzed substance is insoluble in water.

S and $S\,O_3$ not, because the analyzed substance is readily soluble in nitric acid.

The white color of the analyzed compound proves the absence of $Cr\,O_3$.

PO_5, and $\bar{O}$ not, because the hydrochloric acid solution of the precipitate produced by sulphide of ammonium has given no precipitate insoluble in soda (phosphate or oxalate of strontia).

BO_3 might be present; the examination for it gave a negative result.

The analyzed compounds contain accordingly $\begin{cases}\text{bases: oxide of lead, oxide of zinc, strontia.}\\ \text{acids: carbonic acid.}\end{cases}$

IV.

TABLE

OF THE

MORE FREQUENTLY OCCURRING FORMS AND COMBINATIONS OF THE SUBSTANCES TREATED OF IN THE PRESENT WORK,

ARRANGED

WITH ESPECIAL REGARD TO THE CLASS TO WHICH THEY RESPECTIVELY BELONG ACCORDING TO THEIR SOLUBILITY

IN WATER, IN HYDROCHLORIC ACID, OR IN NITRIC ACID.

PRELIMINARY REMARKS.

The class to which the several compounds respectively belong according to their solubility in water or acids (see § 167), is 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. For those substances which stand 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 of which the solubility is not increased by the addition of the acids; and 2—3 a substance insoluble in water, and difficultly soluble in hydrochloric acid and in nitric acid. Wherever the deportment of a substance with hydrochloric acid differs materially from that which it exhibits with nitric acid, this is stated in the notes.

The roman figures denote officinal and more commonly occurring compounds.

The haloid salts and sulphur compounds are placed in the columns of the corresponding oxides. The salts given are the neutral salts; the basic, acid, and double salts, if officinal, 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 common occurrence in combination with a few bases only, and have therefore been omitted from the table. The most frequently occurring compounds of these substances are: cyanide of potassium I, ferrocyanide of potassium I, ferricyanide of potassium I, sesqui-ferrocyanide of iron (Prussian blue) III, ferrocyanide of zinc and potassium II—III, chlorate of potassa I, the citrates of the alkalies I, the malates of the alkalies I, malate of sesquioxide of iron I, the benzoates of the alkalies I, the succinates of the alkalies I, and the formiates of the alkalies I.

INDEX OF THE SOLUBILITY OF

	KO	O	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	2	2	II	II	II	II
S	I	I	I	I	1	I-II	2		II	II	2	$_{15}$	$_{16}$	2
Cl	I	I	I_{12}	I	I	I	1	1	I	I	I_{12}	I	I	1
I	I	1	1	1	1	1	1		1	1	1			1
SO	I_1	I	I_{13}	III	III	I-III	I	$I_{1\cdot 13}$	I	I	I	1	I	I
NO_5	I	I	I	I	I	1	1	1	1	1	1	I	1	1
PO_5	1	I_{10}	1_{10}	2	2	II_{14}	2		2	2	II	2	2	2
CO_2	I_2	I_{11}	I	II	II	II	II		II	2		2	2	II
C_2O_3	I_3	1	I	2	2	II	2	2	2	1-2	1-2	2		2
BO_3	1_4	I_4	1	2	2	2	2	2	2	2	2	2	2	2
$\overline{A}$	I	I	I	I	1	1	1	1	1	1	I	1	1	I
$\overline{T}$	$I_{4\cdot 9}$	I_7	1_6	2	2	II	1·2	1	1·2	1·2	I_8	1		2
AsO_5	I	1	1	2	2	2	2	2	2	2	2	2	2	
AsO_3	I	1	1	2	2	2				2		2	2	
CrO_3	I	1	1	2	2	2	1	2	1		1	2	2	1

NOTES,

1. Sulphate of potassa and alumina I.
2. Bicarbonate of potassa I.
3. Binoxalate of potassa I.
4. Tartarized borax (Bitartrate of potassa and borate of soda), I.
5. Bitartrate of potassa I-II.
6. Tartrate of potassa and ammonia I.
7. Tartrate of potassa and soda I.
8. Tartrate of potassa and sesquioxide of iron I.
9. Tartrate of antimony and potassa I.
10. Phosphate of soda and ammonia I.
11. Bicarbonate of soda I.
12. Sesquichloride of iron and chloride of ammonium I.
13. Sulphate of alumina and ammonia I.

SUBSTANCES IN WATER OR ACIDS.

	CdO	PbO	SnO	SnO_2	BiO_3	CuO	Hg_2O	HgO	AgO	PtO_2	AuO_3	SbO_3	Cr_2O_3
	2	II_{18}	2	2 & 3	2	II_{22}	II	II	2	2		$_{35}$	II&III
S	2	II	$_{20}$	$_{20}$	2	$_{23}$	III	III	$_{30}$	$_{31}$		II_{36}	
Cl	1	I-III	I	1	I	I_{24}	II-III	I_{28}	III	$\mathrm{I}_{32 \cdot 33}$	I_{34}	I_{37}	I & III
J	1	I-II	2	1			II	II	3				
SO_3	I	II-III	1		1	I_{25}	1-2	1_{29}	I-II	1		2	I & III
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	2	2	1	2	2	2	2	2			1-2	1
BO_3	1-2	2	2		2	2	1						2
$\bar{A}$	1	I_{19}	1	1	1	I_{26}	1-2	1	1			1	1
$\bar{T}$	1-2	2	1-2		2	1	1-2	2	2			I_{38}	1
AsO_5		2			2	2	2	2	2			2	2
AsO_3		2				II	2	2	2			2	
CrO_3		II-III	2		2	2	2	1-2	2			2	2

14. Basic phosphate of lime II.
15. Sulphide of cobalt is pretty readily decomposed by nitric acid, but very difficultly by hydrochloric acid. This substance is not officinal.
16. The same applies to sulphide of nickel.
17. Sulphide of zinc is readily soluble in nitric acid, somewhat more difficultly soluble in hydrochloric acid.
18. Minium is converted by hydrochloric acid into chloride of lead; by nitric acid into oxide, which redissolves in an excess of the acid, and into brown binoxide of lead, which is insoluble in nitric acid.
19. Trisacetate of lead I.
20. Proto and bisulphide of tin are decomposed and dissolved by hydrochloric acid; by nitric acid they are converted into binoxide,

which is insoluble in an excess of the acid. Sublimed bisulphide of tin dissolves only in nitrohydrochloric acid.

21. Basic nitrate of bismuth II.
22. Ammoniated oxide of copper 1.
23. Sulphide of copper is difficultly decomposed by hydrochloric acid, but with facility by nitric acid.
24. Chloride of copper and ammonium I.
25. Sulphate of copper and ammonia I.
26. Basic acetate of copper, partially soluble in water, and completely in acids.
27. Basic nitrate of suboxide of mercury and ammonia II.
28. Chloride of mercury and ammonia II.
29. Basic sulphate of oxide of mercury II.
30. Sulphide of silver soluble only in nitric acid.
31. Bisulphide of platinum is not affected by hydrochloric acid, and but little by boiling nitric acid ; it dissolves in hot nitrohydrochloric acid.
32. Bichloride of platinum and chloride of potassium 1—3.
33. Bichloride of platinum and chloride of ammonium 1—3.
34. Terchloride of gold and chloride of sodium I.
35. Teroxide of antimony is soluble in hydrochloric acid, but not in nitric acid.
36. Tersulphide of antimony and sulphide of calcium I—II.
37. Basic terchloride of antimony II.
38. Tartrate of antimony and potassa I.

SUPPLEMENTARY REMARKS.

I. Detection of arsenic, antimony, and tin, in presence of each other.

To §§ 129 and 180.

On this difficult part of qualitative analysis, some papers have lately been published, the most essential results of which I communicate here, as they are valuable and well suited, in certain cases, to complete and improve the methods given in the above-named paragraphs.

1, *Bloxam*,[*] having carefully investigated the several methods of detecting arsenic, antimony, and tin, in presence of each other, has devised a method which, combining known facts with the results of more recent observations and experiments, is more particularly suited to effect the detection of minute traces of one or two of these metals, in presence of large quantities of the other or others.

I will give, in the first place, those reactions which are new or present some new feature, and then proceed to describe *Bloxam's* method.

a. If a solution of terchloride of antimony is mixed with an excess of solution of sesquicarbonate of ammonia, and boiled, the precipitate at first produced is generally entirely redissolved ; whilst, if the same experiment is made with solution of bichloride of tin, the precipitate is not redissolved, and not the least trace of tin found in the filtrate.

b. Occasionally, however, the precipitate produced by sesquicarbonate of ammonia in solution of terchloride of antimony, does not entirely redissolve in an excess of the precipitant, upon boiling; and, accordingly, the mere fact of a residue being left is by no means a positive proof of the presence of tin. To ascertain whether the residue so left consists really of tin, or contains that metal, the filter, with the white precipitate produced by the sesquicarbonate of ammonia, and which an excess of that reagent has failed to dissolve, must, after washing with solution of sesquicarbonate of ammonia, be dried, incinerated in a porcelain crucible, the ash fused with a little cyanide of potassium, and the mass digested with water. The residue which contains the tin reduced to the metallic state, is then boiled with hydrochloric acid,[†] and the solution tested with chloride of mercury (compare § 125, 8, and § 129).

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[*] Chem. Soc. Quart. Journ. V., 104.

[†] With minute traces of tin, it is quite sufficient to raise the acid to the boiling point. Continued boiling with hydrochloric acid tends to materially interfere with the reaction with chloride of mercury.

c. By this process *Bloxam* succeeded perfectly in detecting the two metals, even in cases where they were mixed in the proportion of 99 to 1, and when only 0·003 grm., or even less, of the metal which was in small quantity, was present. However, the reaction can be fully relied upon only in the absence of arsenic ; since, if the latter metal is present, part or even the whole of the binoxide of tin may dissolve in the sesquicarbonate of ammonia.

d. If tersulphide or pentasulphide of antimony is digested, with or without application of heat, in a solution of sesquicarbonate of ammonia, it dissolves only in very small quantity, whilst the corresponding sulphides of arsenic dissolve at once* (compare § 129). Bisulphide of tin does not dissolve in sesquicarbonate of ammonia, even on boiling; however, in presence of sulphide of arsenic, the bisulphide of tin dissolves partly or entirely in the sesquicarbonate of ammonia.

e. Method based on the reactions a, b, c, and *d.*

Digest the washed precipitate of the sulphides of group VI (see § 179, at the end), at 180°, for about half an hour, with a saturated solution of sesquicarbonate of ammonia.

You have now,—

α. An insoluble residue, which may consist of sulphide of antimony, sulphide of tin, and sulphur.

β. A solution containing all the arsenic, and slight traces of antimony; and which may also contain part or the whole of the tin.

Wash the residue *α* with a solution of sesquicarbonate of ammonia as long as the washings continue to yield a precipitate with hydrochloric acid ; dissolve, with the aid of heat, in the least possible quantity of a mixture of eight volumes of concentrated hydrochloric acid and one volume of concentrated nitric acid, mix the solution in a dish, with a considerable excess of sesquicarbonate of ammonia, and boil for a few minutes. If a permanent precipitate is formed, collect it upon a filter, and examine for TIN, according to the directions of *b.* Acidify the filtrate with hydrochloric acid, and pass hydrosulphuric acid gas through the fluid : the formation of an orange precipitate will at once show the presence of ANTIMONY.

Divide the solution *β.* into two parts, acidify both with hydrochloric acid, precipitate with hydrosulphuric acid, collect the precipitates, which we will call respectively *aa.* and *bb.*, upon small filters, and wash. Examine *aa.* for ARSENIC in the manner directed § 213 *dd.* and *ee.*—Dry *bb.*, put it, together with the filter, cut into strips, into nitrate of potassa in a state of fusion (§180, 2), pour out the mass, boil with water, and add, without filtering, nitric acid to acid reaction; filter, wash, and examine the contents of the filter for TIN, as directed in *b.* In cases where

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* "Pretty readily," would be more correct.

the quantity of tin is very minute, the residues obtained by the incineration of the small filters of α. and β. are collected, and examined for that metal.

2. *G. F. Ansell*[*] has, under the direction of *Dr. A. W. Hofmann*, devised the following method, which is especially suited to effect the detection of small quantities of antimony in presence of arsenic.

Dissolve the precipitated sulphides—bisulphide of tin, pentasulphide of arsenic, and pentasulphide of antimony—in hydrochloric acid, mixed with a little nitric acid, and pour the solution into an apparatus for generating hydrogen gas from zinc and dilute sulphuric acid. Pass the gas evolved through a dilute solution of acetate of lead—which will absorb any hydrochloric acid and hydrosulphuric acid—and conduct the washed mixture of hydrogen and antimonietted and arsenietted hydrogen into a test-tube half filled with concentrated pure nitric acid; it is advisable to heat the acid in the tube a little.

If the gas is evolved with moderate slowness, the hydrides of antimony and arsenic are completely decomposed, and the fluid is rendered turbid by the antimonic acid formed. When the gaseous mixture has been conducted into the tube for about a quarter of an hour, evaporate the nitric acid solution to dryness, and expose the residue to the heat of a sand-bath, to expel the last traces of the nitric acid. Digest the residue, which consists of antimonic acid and the acids of arsenic, with warm water; this will dissolve the arsenious and arsenic acids, leaving the antimonic acid as insoluble residue. On mixing the solution with nitrate of silver and some ammonia, the well-known precipitates will be produced.

To effect the detection of small quantities of arsenic, in presence of a large quantity of antimony, this process may be advantageously modified by passing the washed gases into solution of nitrate of silver, instead of nitric acid: the whole of the antimony is precipitated as antimonide of silver, whilst the arsenic remains in solution as arsenious acid, and may—after the removal of the excess of silver by means of hydrochloric acid—be found in the filtrate, with the aid of the proper reagents (§ 127). For the detection of minute quantities of arsenic *Hofmann* prefers the modified method.

II. METHODS OF EFFECTING THE DETECTION OF ORGANIC BASES IN CASES OF POISONING.

The detection, more especially of minute quantities, of alkaloids in food, or in the contents of the stomach, &c., is no very easy task. I add, therefore, to the method described § 230, two other processes, with which chemical analysis has lately been enriched.

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[*] Chem. Soc. Quart. Journ., V., 210.

1. Stas's method.*

a. If you have to look for the suspected organic bases in the contents of the stomach or intestines, or in articles of food, or in other pappy matter, heat the suspected substance with double the weight of strong alcohol, acidified with from 0·5 grm. to 2 grammes of tartaric acid or oxalic acid, to from 158° to 167°. When quite cold, filter, and wash the undissolved part with strong alcohol, adding the washings to the filtrate.

If you have to deal with the heart, liver, lungs, or similar organs, cut them into fine shreds, moisten with the acidified alcohol, press, and repeat the same operation until the soluble parts are completely dissolved; collect the fluids obtained, and filter.

b. Concentrate the alcoholic fluid at a temperature not exceeding 95°, and, if no insoluble matter separates, continue to evaporate nearly to dryness. Conduct this process, either under a bell-glass over sulphuric acid, with or without rarefaction of the air, or in a tubular retort, into which a stream of air is passed. If fatty or other insoluble matters separate in the process of concentration, pass the concentrated fluid through a moistened filter, and evaporate the filtrate nearly to dryness, conducting the process, as above, either under a bell-glass or in a retort.

c. Digest the residue with cold absolute alcohol, filter, wash the insoluble residue thoroughly with alcohol, and let the alcoholic solution evaporate in the air or in vacuo; dissolve the acid residue in a little water, and add bicarbonate of soda as long as effervescence ensues.

d. Add to the mixture four or five times its volume of ether, and shake; then allow it to stand at rest; let a little of the supernatant ether evaporate spontaneously on a watch-glass. If this leaves only streaks upon the glass, which gradually collect into a drop, and emit, upon the application of a gentle heat, a disagreeable, pungent, and stifling odor, there is reason to infer the presence of a liquid volatile base; whilst a solid residue or a turbid fluid, with solid particles suspended in it, indicates a non-volatile, solid base. In the latter case the base may emit a disagreeable animal smell, but not a pungent odor, as is the case with volatile bases. The blue color of reddened litmus paper is permanently restored. If no residue is left, add to the fluid some solution of soda or potassa, and shake with repeatedly renewed ether, which will now dissolve the base. It follows from the assumption that the bases present will pass into the etherial solution, that *Stas's* method is principally calculated for the detection of the poisonous alkaloids which are soluble in ether, though some of them only difficultly. The following are the vegeto-alkalies which *Stas* enumerates

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* Bulletin de l'académie de médecine de Belgique, IX. 304. Jahrb. f. prakt. Pharm., XXIV, 313. Jahresbericht von *Liebig* und *Kopp*, 1851, p. 640.

as discoverable by his method: Conia, Nicotina, Aniline, Picoline, Petinine, Morphia, Codeia, Brucia, Strychnia, Veratria, Colchicia, Delphia, Emetina, Solania, Aconita, Atropia, and Hyoscyamia.

a. There is reason to infer the presence of a volatile base.

Add to the contents of the vessel from which you have taken the small portion of ether for evaporation on the watch-glass, one or two cubic centimeters of strong solution of potassa or soda, shake the mixture, let it stand at rest, pour the supernatant ether into a flask, and treat the residue again three or four times with ether, until a portion of the ether last poured off leaves no longer a residue upon evaporation. Mix the ethereal fluid now with some dilute sulphuric acid until the well-shaken fluid manifests acid reaction; allow the mixture to stand at rest, decant the supernatant ether from the acid aqueous fluid, and treat the latter once more with ether in the same way.

aa. Mix the residual acid solution (which may contain sulphates of ammonia, nicotina, aniline, picoline, and petinine, indeed which must contain these bases, since their compounds with sulphuric acid are quite insoluble in ether; and in which, if conia is present, the greater part of the latter alkaloid is also found) with concentrated solution of soda or potassa in excess, and treat with ether, which will again dissolve the liberated bases; decant the ether, and leave it to spontaneous evaporation, at the lowest possible temperature; place the dish with the residue in vacuo over sulphuric acid. In this process the ether and ammonia escape, leaving the volatile organic base behind in the pure state. The nature of the organic base is then finally ascertained.

bb. The ether decanted from the acid solution contains the animal matter which it has removed from the alkaline fluid. It leaves therefore, upon spontaneous evaporation, a trifling faint yellow residue of nauseous odor, which contains also some sulphate of conia, if that base was present in the examined matter.

β. There is reason to infer the presence of a solid base.

Add a few drops of alcohol to the etheral solution obtained by treating with ether the previously acid residues mixed either simply with bicarbonate of soda, or first with that reagent and then with solution of soda or potassa (see *c* and *d*), and leave the mixture to spontaneous evaporation. If this fails to give the base in a distinctly crystalline form and sufficiently pure, add a few drops of water feebly acidified with sulphuric acid, which will usually serve to separate the mass into a fatty portion, adhering to the dish, and an acid aqueous solution, which contains the base as a bisulphate. Decant or filter, wash with a little feebly acidified water, and evaporate the solution to a considerable extent, under a jar over sulphuric acid. Mix the residue with a highly concentrated solution of pure carbonate of soda, treat the mixture with absolute alcohol, decant, and let the alcoholic fluid evaporate, which will generally leave the base behind in a state of perfect purity or nearly so.

2. METHOD OF EFFECTING THE DETECTION OF STRYCHNIA IN BEER, BY *Graham* AND *A. W. Hofmann.*[*]

This method, which is based on the known fact that a solution of a salt of strychnia, when mixed and shaken with animal charcoal, yields its strychnia to the charcoal, will undoubtedly be found applicable also for the detection of other alkaloids. The process is conducted as follows :

Shake two ounces of ivory black, or animal charcoal, in half-a-gallon of the aqueous neutral or feebly acid fluid under examination ; let the mixture stand for from twelve to twenty-four hours, with occasional shaking, filter, wash the charcoal twice with water, and then boil for half-an-hour with eight ounces of spirit of wine of 80—90 per cent., avoiding loss of alcohol by evaporation. Filter the spirit of wine hot from the charcoal, and distil the filtrate ; add a few drops of solution of potassa to the residual watery fluid, shake with ether, let the mixture stand at rest, and then decant the supernatant ether. The ethereal fluid leaves, upon spontaneous evaporation, the strychnia in a sufficient state of purity to admit of its further examination by reagents (see § 222.)

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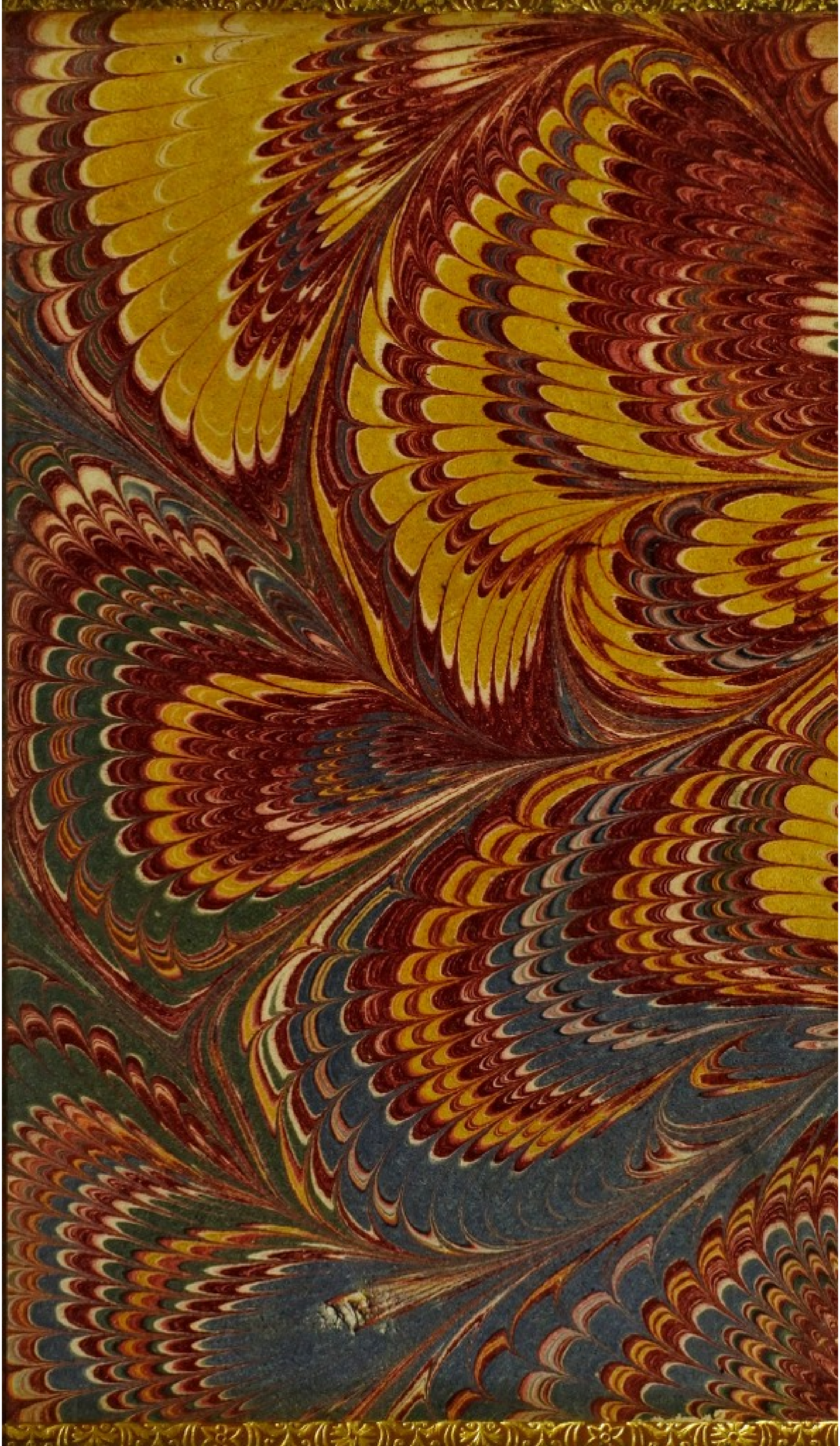
[*] Chem. Soc. Quart. Journ. V. 173.

ALPHABETICAL INDEX.

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