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A MANUAL

OF

QUALITATIVE ANALYSIS.

A MANUAL

OF

QUALITATIVE ANALYSIS.

BY

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LONDON:

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MDCCCL.

PREFACE.

THE increased attention, which has of late years been given to Chemistry in this country, has caused the production of several excellent works on Qualitative Analysis. The majority of these works have, however, been found better adapted for the advanced student than for the beginner. To supply the latter with a suitable elementary work is the object aimed at in the present Treatise.

The Author having had ample opportunities, for some years past, of ascertaining the difficulties which oppose the student's progress in the study of Analysis, has endeavoured in the present little work to obviate these, as much as possible, by simplifying the course of study. The peculiar arrangement adopted, whilst simplifying the study of this particular branch of Chemical Science, will afford the student the means of increasing his knowledge of General Chemistry.

Although the work professes to be a mere introduction to the study of Analysis, several new

processes have been described, when they appeared
to be an improvement on those usually employed.
Thus, a new method is given for the detection of
Magnesia, and its separation from the fixed Alkalies.
The separation of Phosphoric and Oxalic Acids from
the Alkaline Earths, is rendered easier or more
secure to the unpractised student, by the new
process here recommended ; and the determination
of Tin and Antimony is facilitated by a modi-
fication of the process usually adopted.   But in
improving processes, which appeared to be de-
fective, the Author has not forgotten that the main
object of the work is to present to the Student a
simple Introduction to Qualitative Analysis.

QUEENWOOD COLLEGE ;
    October, 1850.

TABLE OF CONTENTS.

REAGENTS EMPLOYED IN THE DRY STATE.

CHAPTER V.

PROPERTIES OF THE ACIDS.

GENERAL PROPERTIES OF THE INORGANIC ACIDS.

SPECIAL PROPERTIES OF THE INORGANIC ACIDS.

SPECIAL PROPERTIES OF THE ORGANIC ACIDS.

CHAPTER VI.

EXAMINATION OF LIQUIDS AND SOLIDS.

QUALITATIVE ANALYSIS.

INTRODUCTION.

IT has been discovered, by the aid of CHEMICAL SCIENCE, that all the material matter of the globe is made up of a certain number of *simple* bodies, which, being incapable of being divided into two or more parts, are called *elements*. The number of these elementary substances amounts at the present time to about sixty, but it is not improbable that many of them will, as the science progresses, be resolved into more simple forms.

The breaking up of compound substances into their elements is called ANALYSIS, and this is divided into two kinds— QUALITATIVE and QUANTITATIVE. By the first we ascertain the simple bodies in a compound, and by the second we estimate their respective quantities. It is evident that the study of the former must always precede that of the latter, because it is absolutely necessary to know what substances are present in a compound, before an attempt can be made to estimate their quantities.

It is seldom that the reduction of compounds into their *ultimate* elements, is resorted to in Qualitative Analysis. More frequently the *proximate* elements are made to combine with other substances, producing appearances which distinguish them

1

from all other bodies. Thus, the proximate elements of sulphate of potash are sulphuric acid and potash; the presence of the former is ascertained by adding chloride of barium, which produces a precipitate insoluble in all acids, whilst the potash is detected by forming with tartaric acid a white crystalline powder.

Chloride of barium and *tartaric acid* are types of a class of substances employed for the detection of other bodies. These substances are distinguished by the term TESTS or REAGENTS, whilst the phenomena produced by them are termed *Reactions*.

The processes employed in Qualitative Analysis are exceedingly simple, and do not require much apparatus for their execution. The small amount actually requisite is described in the following list, and may be procured in the shops of operative chemists.

1½ doz. test-tubes.	3 small glass funnels.
Test-tube stand.	2 porcelain crucibles.
2 small evaporating dishes.	½ lb. glass tubing.
Washing bottle.	¼ lb. glass rod.
Spirit-lamp.	Small mortar and pestle.
2 watch-glasses.	1 quire filtering paper.
Rat-tail and triangular file.	Crucible tongs.
2 iron spoons.	Brass blowpipe.
Platinum wire and foil.	Tube cleaner.
Sulphuretted hydrogen apparatus.	

CHAPTER I.

OPERATIONS.

The following are the principal operations occurring in *Qualitative Analysis.*

1. SOLUTION.

Many solid bodies, when placed in contact with a liquid, possess the property of becoming thoroughly incorporated with it, by passing into the fluid state. This change is expressed by the term *solution*, and the liquid in which the solid dissolves is called the *solvent.*

Solutions are of two kinds, *simple* and *chemical.* A *simple* or *mechanical solution*, is the mere dissolving of a solid in a liquid, no chemical change occurring in either ; on the removal, therefore, of the liquid by evaporation, the solid is obtained in its original condition. Common salt dissolved in water affords an illustration of a simple solution.

In a *chemical* solution the solid and fluid combine together, forming an entirely new substance, from which the original solid and fluid can no longer be extracted by mere mechanical operations. Chalk dissolved in hydrochloric acid affords an example of a chemical solution.

The solution is said to be *saturated*, when the solvent is incapable of dissolving any more of the solid.

The solution of a solid is always much facilitated by its being in a fine state of division, and the application of heat generally accelerates it.

The process of solution is conducted either in evaporating dishes or test-tubes. The latter are generally employed when the quantity of the solid operated upon is small.

2. PRECIPITATION.

Precipitation is the conversion of a soluble into an insoluble solid substance, which being generally specifically heavier than the surrounding liquid falls down.   Occasionally, however, it is lighter, and floats upon the surface.   In both cases the insoluble substance is called the *precipitate*, and the substance producing the precipitation is termed the *precipitant*.

Precipitates are classified, according to their appearances, into crystalline, pulverulent, flocculent, curdy, and gelatinous.   The terms *turbid* and *turbidity* are applied when the precipitate is so small that it cannot be distinguished, except by impairing the transparency of the fluid.

The separation of precipitates from the solutions is, with some few exceptional cases, much assisted by the application of heat and agitation.   This operation is therefore conducted in test-tubes, which, from their transparency, admit of an inspection of the process.

3. FILTRATION AND DECANTATION.

These terms are applied to a modification of the same operation, viz., the mechanical separation of fluids from solid matter mixed with them.

FILTRATION.

In filtration the separation of the fluid from the solid matter, is accomplished by passing it through filtering paper, of a proper size and shape, supported in a funnel.   The pores of the paper permit the fluid to pass through, whilst the solid matter being prevented remains behind.

The liquid which passes through the filter is called the *filtrate*.

DECANTATION.

When the solid particles are very heavy the supernatant liquid be perfectly separated, without passing it through a filter, imply inclining the vessel, so as to allow the fluid to pass

away unattended by the precipitate, or by removing the fluid by a syphon.

The separation in this way of a solid from a fluid is called *decantation*.

Too great attention cannot be paid to the washing of precipitates when they are required for further examination. After the precipitate has been thrown upon the filter, a stream of water must be projected from the wash bottle upon it, from time to time, until it is perfectly freed from *soluble matter;* this is sooner accomplished if hot water be employed. Hot water may therefore be used in all cases unless the contrary be expressly stated.

4. EVAPORATION.

This process is used for the purpose of obtaining matter in a solid state from solutions. By the aid of heat, the volatile fluid passes off in the gaseous form whilst the non-volatile matter remains behind.

If the evaporation be conducted slowly, the solid matter will frequently, on being deposited, assume a crystalline form. The operation is then termed *crystallization*.

This operation is frequently conducted for the purpose of obtaining a liquid in a more concentrated form, by volatilizing a portion only of the fluid. Vessels.are constructed expressly for the purpose, called evaporating dishes.

5. DISTILLATION.

This operation like the former one consists in the separation of a *volatile* from a *less volatile* fluid, or in the separation of a *liquid* from a *solid*. But in evaporation no attention is paid to the volatilized fluid, whilst in distillation it is frequently the only substance required. A distilling apparatus is therefore so constructed as to allow the evaporated fluid to be collected, which is called the *Distillate*. It consists of three parts. 1. A vessel in which the liquid to be distilled is heated. 2. An apparatus

in which the vapour is cooled and condensed. 3. A vessel for receiving the distillate.

On a small scale glass retorts are employed, but in the distillation of large quantities, copper stills are usually substituted for them.

6. IGNITION.

By this operation, volatile is separated from non-volatile solid matter, it requires the application of a high temperature and must be conducted in crucibles.

7. SUBLIMATION.

By sublimation we effect not only the separation of volatile from less volatile solid matter, but by cooling we bring the volatile matter back to the solid state, and in this state it is called the *sublimate*.

This process is therefore a *distillation of solid bodies*.

8. FUSION.

This term is applied to the liquefaction of a solid, by the mere application of heat. It is also used for the decomposition of solids in the " dry way."

By this operation we are able to resolve insoluble substances into forms which admit of solution. This is accomplished by causing their proximate elements to unite with bodies the compounds of which will be capable of solution. Thus sulphate of baryta, which, from its insolubility both in water and acids, resists the action of reagents in the fluid state, is decomposed in this way. It is mixed with three or four times its own weight of dry carbonate of soda, and the mixed mass exposed in a crucible, for some time, to a high temperature. The two salts mutually suffer decomposition when placed in these conditions, the sulphuric acid passing over to the soda whilst the carbonic acid unites with the baryta. If the fused mass be treated with water, the sulphate of soda dissolves in that liquid, whilst the carbonate of baryta

being insoluble remains behind. This substance after being well-washed may be dissolved in hydrochloric or nitric acid. The decomposition of substances in the dry way, requires in most cases a higher temperature than that which a small spirit lamp affords. When a limited amount of heat can only be obtained, it is better to employ a mixture of equal parts of carbonate of soda and carbonate of potash, instead of the former salt alone.

9. DEFLAGRATION.

This term is applied to all decompositions attended with noise. It also includes the oxidation of a substance by a reagent, in the dry way, on account of the slight explosions which frequently attend this kind of oxidation.

10. THE BLOWPIPE.

The mouth blowpipe is a small instrument which is employed for directing a fine and continuous stream of air into the flame of a wax candle or oil lamp. By the flame thus produced, two reverse chemical operations may be performed, viz, *oxidation* and *reduction*. The flame is therefore distinguished by these properties, into the outer or *oxidizing* flame and the inner or *reducing* flame.

In the *oxidizing* flame, the inflammable vapour is in a state of complete combustion, being supplied and mixed with an excess of atmospheric air. From the high temperature resulting from the perfect combustion of the inflammable vapour and likewise from the excess of oxygen, all the requisite conditions are present, for causing substances with an affinity for that element, to enter into union with it.

In the *reducing* or *deoxidizing* flame, the inflammable vapour is in an incomplete state of combustion, due to a deficiency of atmospheric air. Hence any metallic oxide placed in this portion of the flame is robbed of its oxygen by the inflammable vapour, which requires that element for its combustion. This portion of the flame is most luminous, whilst the outer flame yields little light, but a large amount of heat.

CHAPTER II.

REAGENTS.

REAGENTS may be divided into two classes—*general* and *special*. The general reagents are employed to divide substances into *families* or *groups*, and the special reagents to detect the *individual members* of a group. A special reagent is said to be *characteristic*, when it produces a reaction so decisive that it admits of no mistake.

The reagents must, in most cases, be chemically pure; a list of the impurities usually found in them is therefore given. But the methods to be employed for their detection are not stated here, as they can be all gathered from the body of the work, and the selection of them will prove a good analytical exercise for the student. The methods of preparing reagents are not given except in one or two simple cases. Fluid tests employed are generally diluted with a certain quantity of water. *The diluted reagent* is in all cases to be employed, except where the contrary is stated.

LIST OF THE REAGENTS EMPLOYED IN THE FLUID STATE.

1. *Hydrochloric acid* (muriatic acid), if perfectly pure, leaves no residue when evaporated. The substances with which it is generally contaminated are iron, arsenic, and sulphuric acid.

Dilute one part of the concentrated acid with four parts of water.

2. *Nitric acid* (aqua fortis), when free from non-volatile matter,

leaves no residue on evaporation. The impurities often found in it are hydrochloric and sulphuric acids.

Dilute one part of the concentrated acid with five of water.

3. *Nitrohydrochloric acid* (aqua regia) is prepared, by adding four parts of concentrated hydrochloric acid to one of concentrated nitric acid.

This test is employed in an undiluted state.

4. *Sulphuric acid* (oil of vitriol) frequently contains both arsenic and lead, and not unfrequently nitrous acid. The lead is deposited to a great extent when the acid is diluted, sulphate of lead being less soluble in dilute than in concentrated sulphuric acid.

The dilute acid is prepared by adding four parts of water to every one of the concentrated acid.

5. *Tartaric acid* is generally sufficiently pure for analytical purposes. As it undergoes decomposition in solution, a small quantity only should be prepared at a time.

For use, dissolve one part, by weight, of acid, in two parts, by measure, of water.

6. *Acetic acid*, when employed in analysis, ought to be free from non-volatile matter and sulphuric acid.

Dilute one part of the acid with four parts of water.

7. *Hydrosulphuric acid* (sulphuretted hydrogen) is prepared by adding to sulphide of iron, in an appropriate apparatus, dilute sulphuric or hydrochloric acid. The sulphuretted hydrogen is liberated in its gaseous state, and may be passed through any solution under examination; or a solution of the gas may be obtained by passing it through pure water. As this solution very soon decomposes by contact with the atmosphere, it ought to be prepared very frequently, and kept in well-stoppered bottles.

Sulphide of iron, from which hydrosulphuric acid is obtained, is prepared by projecting a mixture of thirty parts of iron filings with twenty-one of flower of sulphur, in small portions at a time, into a red-hot crucible, replacing the cover after each addition.

1 §

When the whole has been added, the ignition must be continued for a short time, until the excess of sulphur has been dissipated.

8. *Sulphurous acid* is prepared by acting upon copper or charcoal with sulphuric acid. For this purpose small pieces of charcoal are introduced into a flask, with from six to eight times their weight of sulphuric acid, and a moderate heat applied. The evolved gas must be conducted into cold water until it is no longer absorbed. On account of the great tendency which this reagent has to absorb more oxygen, and become converted into sulphuric acid, it must be preserved in well-stoppered bottles.

9. *Chlorine gas* is prepared by introducing into a flask one part of peroxide of manganese along with four parts of hydrochloric acid; the liberation of the chlorine is assisted by a gentle heat. A solution of the gas may be prepared by passing it into cold water. Chlorine water must be kept in well-stoppered bottles, and excluded from the light.

10. *Oxalic acid.* Dissolve one part, by weight, of the acid, in twenty parts, by measure, of water.

11. *Oxalate of ammonia* must be free from sulphuric acid.

Dissolve one part, by weight, of the salt, in twenty parts, by measure, of water.

12. *Ammonia* ought to be free from non-volatile matter, and also from carbonic, sulphuric, and hydrochloric acid.

Dilute one part of the strong ammonia with four of water.

13. *Chloride of ammonium* is frequently contaminated with iron, from which it ought to be entirely free.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

14. *Sulphide of ammonium* (hydrosulphuret of ammonia) is prepared by passing hydrosulphuric acid through liquid ammonia until it no longer produces a precipitate in a solution of magnesia.

Dilute one part, with three of water.

15. *Carbonate of ammonia* must be free from non-volatile matter, and likewise from sulphuric acid.

Dissolve one part, by weight, of the salt, in four parts, by measure, of water, and add one measure of ammonia.

16. *Arseniate of ammonia* is prepared by neutralising arsenic acid with carbonate of ammonia, and evaporating to dryness.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

17. *Arsenic acid* is prepared by dissolving arsenious acid in nitric acid, mixed with a little hydrochloric acid, evaporating the solution to dryness, and igniting somewhat below a *low* red heat, until all nitric acid is expelled.

18. *Sulphate of potash.* Dissolve one part, by weight, of the salt, in twenty-four parts, by measure, of water.

19. *Ferrocyanide of potassium* (yellow prussiate of potash).

Dissolve one part, by weight, in twelve, by measure, of water.

20. *Ferricyanide of potassium* (red prussiate of potash).

Dissolve one part, by weight, of the salt, in twelve parts, by measure, of water.

21. *Chromate of potash* must be free from sulphuric acid.

Dissolve one part, by weight, in eight parts, by measure, of water.

22. *Caustic soda* is prepared by dissolving one part, by weight, of carbonate soda, in twelve parts, by measure, of water, and boiling the solution in a clean iron pan. Hydrate of lime must be added in small portions to the boiling liquid, until hydrochloric acid causes no effervescence in a portion of the liquid. When this point has been attained, the pan must be removed from the fire, and the precipitate allowed to subside. The supernatant liquid must then be drawn off by means of a syphon, or passed through a filter of bleached linen, and the filtrate evaporated rapidly over a quick fire until it has been reduced to half its original bulk. On supersaturating a portion of the liquid with hydrochloric acid, no, or only a slight, effervescence

should take place. The solution must be kept in well-stoppered bottles.

23. *Carbonate of soda* must contain no sulphuric or hydrochloric acid.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of the water.

24. *Phosphate of soda* must form no precipitate with ammonia.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

25. *Acetate of soda* is made by adding acetic acid to a concentrated solution of carbonate of soda until all effervescence ceases.   This solution must be free from sulphuric acid.

Dilute one part of the concentrated solution with four parts of water.

26. *Chloride of barium.*   Dissolve one part of this salt in ten parts of water.

27. *Nitrate of baryta.*   Dissolve one part of this salt in ten parts of water.

28. *Lime water* is made by digesting recently-prepared hydrate of lime for some time with cold distilled water, with frequent agitation of the mixture; allow the undissolved portion of the lime to subside, decant subsequently, and keep the clear fluid in well-stoppered bottles.

29. *Chloride of calcium* is made by dissolving pure carbonate of lime in dilute hydrochloric acid, the solution thus obtained must be neutral to test paper.

Dilute one part of the concentrated solution with five parts of water.

30. *Sulphate of lime* (gypsum).   Dissolve as much of the salt as the water will take up.

31. *Sulphate of magnesia* (Epsom salts).   Dissolve one part in eight of water.

32. *Perchloride* (sesquichloride) of iron is prepared by dis-

solving recently-precipitated and well-washed peroxide of iron in hydrochloric acid. It must not contain any free acid.

33. *Acetate of lead.* Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

34. *Protonitrate of mercury* is made by heating gently in a small flask nine parts of nitric acid in conjunction with ten parts of mercury, until the disengagement of nitrous fumes ceases; the solution is then boiled for some time with the undissolved portion of the mercury, care being taken to replace the water lost by evaporation. The crystals, which separate on the cooling of the liquid, are dissolved in twenty parts of cold water, slightly acidulated with nitric acid. The fluid is then filtered if necessary, and the filtrate kept in a glass bottle, the bottom of which is covered with mercury.

35. *Nitrate of silver.* Dissolve one part, by weight, of the salt, in twenty parts, by measure, of water.

36. *Nitrate of cobalt.* Dissolve one part in ten parts of water.

37. *Distilled water* ought always to be employed in all the above solutions and in all analytical operations. It should leave no residue on evaporation, and should give no precipitate or even turbidity with chloride of barium, nitrate of silver, oxalate of ammonia or lime water.

38. *Reagent papers.* Blue litmus paper serves to detect the presence of free acids in fluids, since they change the blue colour to red. Reddened litmus paper serves to detect the presence of free alkalies, and of earths and salts possessing an alkaline reaction, by changing the red colour to blue. Turmeric paper aids, like reddened litmus paper, in the detection of free alkalies, &c., by changing its yellow colour to brown.

LIST OF THE REAGENTS EMPLOYED IN THE DRY STATE.

1. *Nitrate of ammonia* is made by neutralizing nitric acid with carbonate of ammonia. The solution is evaporated until crystals

begin to be deposited, and is then allowed to cool. The crystals are collected and placed in well-stoppered bottles.

2. *Cyanide of potassium* must be of a milk-white colour, and perfectly free from any admixture of iron.

3. *Sulphate of iron* is principally employed for the detection of nitric acid.

4. *Copper turnings* are likewise employed for the detection of nitric acid.

5. *Carbonate of soda* must not contain any sulphuric or hydrochloric acid.

6. *Biborate of soda* (borax) is employed in blowpipe analysis.

7. *Phosphate of soda and ammonia* (microcosmic salt) is likewise employed as a reagent in blowpipe analysis.

CHAPTER III.

REMARKS ON THE STUDY OF QUALITATIVE ANALYSIS.

1. In the present chapter it is proposed to lay before the student a general view of analysis and the methods employed in its study, together with a few remarks of a miscellaneous and introductory character.

2. It has been already stated, that in chemical analysis we either resolve compounds into their simple elements directly, or separate them into their proximate elements, by causing these to unite with other substances with which they form new combinations, the properties and appearances of which are previously well known to us. By the aid therefore of analytical chemistry, we convert substances at first *unknown* to us into known forms which admit of a correct interpretation. To learn the mode of asking these chemical questions, the order and succession in which they are to be put, and the language in which the answers will be returned, are the first things to be studied.

3. The student gains this preparatory knowledge by performing the different experiments pointed out in the SPECIAL TABLES, carefully noting the reactions which the reagents give with each individual member, and explaining by diagrams the decompositions produced.

4. These remarks may be illustrated by an example. The first group, and therefore the one which first claims the attention of the student, is made up of three members, viz., POTASH, SODA, and AMMONIA. In *the first paragraph*, under the head AMMONIA, it is stated that this substance and its salts are *volatile*, i. e. they can be converted by heat into vapour. In the second paragraph it is stated that all salts of ammonia are decomposed on the

addition of a stronger base, gaseous ammonia being given off, In the third, that *tartaric acid* produces, in neutral and alkaline solutions of ammonia, a white crystalline precipitate of bitartrate of ammonia.   He has, therefore, to perform and verify these experiments, to notice those conditions which favour the reactions and those which prevent their development.

5. Let *bitartrate of ammonia* be taken as an example of what has just been said.   It is stated in the table that this precipitate is produced both in neutral and alkaline solutions, but that free alkalies and free mineral acids dissolve it.   Hence it follows that though tartaric acid produces a precipitate in alkaline solutions, it can do so only when it is added in excess, because as free alkalies dissolve the precipitate, they must when present prevent its formation.   It is also evident, that tartaric acid cannot detect ammonia in the presence of free mineral acids for the same reason.

6. The conditions which favour or prevent precipitation, together with the appearances of the precipitates, must therefore be carefully remembered by the student.   This is best accomplished by recording them in a note-book at the time the experiments are made, together with diagrams of the decompositions which the different substances experience on the addition of the reagents.

7. To exemplify what we wish to convey respecting decompositions, we select chloride of ammonium, and show by a diagram the change which this salt undergoes when tartaric acid is added to it, thus :—
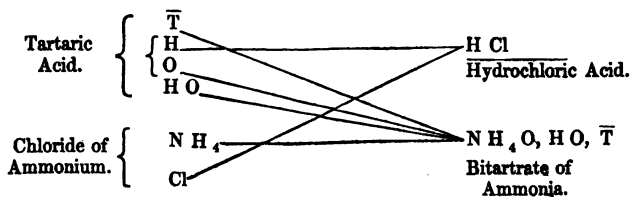
8. The student having performed all the experiments under
ammonia, potash, and soda, must found upon them a method
for detecting these three substances, when they occur together,
and then compare it with the one given in the text. By adopt-
ing this plan, a more extensive and accurate knowledge will be
acquired, than if the method given in the work be immediately
consulted. Several solutions are then given to him, each of
which he must examine for the members of this group. When
he can perform these practical exercises correctly, he may pass
on to the second group, performing the experiments given in
that table in the same manner. He must deduce from them the
method for separating the members of this group from each
other, and again test his acquired knowledge by practical
exercises. When he thoroughly comprehends the way of sepa-
rating them from one another, he will find, by the aid of the
general table, the method to be employed for separating this
group from the first. He should then examine various so-
lutions, which may contain all the members of the first two
groups. When he has completed all the basic groups in
the manner described, he should analyse about twenty different
solutions and look for all the bases given. After which the
experiments given under the different acids must be per-
formed. The student is then in a condition to go through
a complete course of *qualitative analysis*, commencing with
substances already in a state of solution, and concluding with
the examination of solids. Both in the solutions and solids
he must look for all the acids and bases treated of in the
work.

He who would study Analytical Chemistry with success, must
support his determination by unwearying industry, regularity, and
neatness. At the commencement he has, on the one hand, to
guard against a too liberal, and, on the other, a too sparing

addition [1] of the reagents, both being objectionable. He must be very particular in always mixing thoroughly the re-agent with the solution to which he has added it, and not simply content himself by adding it (as is generally the case with beginners) without attempting by agitation to incorporate the two fluids. He has carefully to distinguish between the terms *precipitate* and *filtrate*, and be very particular in thoroughly freeing precipitates required for further examination from all soluble matter by washing. The wash-water must not be collected with the filtrate, if this last should be required for further examination. But all these cautions will have been attended to in vain should the experiments be performed in dirty apparatus, this being sufficient of itself to nullify all satisfactory results.

[1] Imperfect precipitation results from a too sparing addition of the reagent : this error being frequently committed, the mode of rectifying it requires to be pointed out, which simply consists in adding to the filtrate a little more of the reagent with which the precipitation was effected. If this produces no further precipitate the substance has been fully precipitated. Should a further precipitate be produced it must be removed by filtration before attempting to throw down any other substance.

CHAPTER IV.

THE GENERAL PROPERTIES OF THE GROUPS.

THE bases are divided into the five following groups.

GROUP I.	GROUP II.
Ammonia.	Baryta.
Potash.	Strontia.
Soda.	Lime.
	Magnesia.

GROUP III.	GROUP IV.
Alumina.	Arsenious Acid.
Oxide of Chromium.	Arsenic Acid.
Protoxide of Iron.	Oxide of Antimony.
Peroxide of Iron.	Protoxide of Tin.
Oxide of Zinc.	Peroxide of Tin.
Protoxide of Manganese.	Peroxide of Gold.
Oxide of Nickel.	Peroxide of Platinum.
Oxide of Cobalt.	

GROUP V.

Oxide of Silver.
Protoxide of Mercury.
Oxide of Lead.
Peroxide of Mercury.
Oxide of Bismuth.
Oxide of Cadmium.
Oxide of Copper.

The separation into groups is effected by observing some property common to several substances and peculiar to them, by which means a group is formed possessing distinctive characteristics, which distinguish its members from those of every other

group.   (*Ex.* The third is distinguished from the two preceding
ones by its members being precipitated from their solutions by
sulphide of ammonium.   This general property separates the
members of this group from those of the first and second, as they
form no insoluble compound with that reagent.)

Most important advantages are gained by a distribution of
this kind, as it would be impossible to analyse complex sub-
stances accurately without some such division.   For as many of
the reagents precipitate more than one substance, it would be
difficult to decide in such cases what the particular substances
were which had been precipitated, and whether they had all been
detected.   Another important advantage arising from this
arrangement is, that it is as easy to discover a group as an
individual substance, and the absence of a group being proved,
it is unnecessary to examine further for any member contained
in it.

It will be seen by consulting the general table that some of the
tests produce a precipitate with more than one of the groups, the
analysis must therefore be commenced by removing those sub-
stances, the general reagent of which produces no precipitate with
the members of any other group, under the same circumstances.
Such a course will be adopted if the tests are employed in the
order observed in the following Table.

BEHAVIOUR OF THE FIRST GROUP WITH THE GENERAL REAGENTS.

1. *Hydrochloric Acid* .
2. *Hydrosulphuric Acid* .
3. *Alkaline Sulphides* . . . . *do not precipitate the members of this group* . .
4. *Alkaline Carbonates* .
5. *Alkaline Arseniates* .

THEIR CHLORIDES
THEIR SULPHIDES
THEIR CARBONATES *being soluble.*
THEIR ARSENIATES

BEHAVIOUR OF THE SECOND GROUP WITH THE GENERAL REAGENTS.

1. *Hydrochloric Acid* .
2. *Hydrosulphuric Acid* . . . . *do not precipitate the members of this group* . .
3. *Alkaline Sulphides* .

THEIR CHLORIDES *being soluble.*
THEIR SULPHIDES

4. *Carbonate of Ammonia precipitates* BARYTA, STRONTIA, and LIME, from their solutions, as CARBONATES.
   But it precipitates only partly MAGNESIA, and the *presence of Salts of Ammonia prevents the precipitation altogether.*
5. *Alkaline Arseniates precipitate* MAGNESIA from its *neutral* and *alkaline* solutions, as ARSENIATES.

BEHAVIOUR OF THE THIRD GROUP WITH THE GENERAL REAGENTS.

1. *Hydrochloric Acid does not precipitate the members of this group*, THEIR CHLORIDES *being soluble.*
2. *Hydrosulphuric Acid* causes no precipitate in *acid* solutions of this group, THEIR SULPHIDES *being soluble in acids.*
3. *Sulphide of Ammonium precipitates* all the members {ALUMINA and OXIDE of CHROMIUM as OXIDES.
   from their solutions . . . . . {ZINC, IRON, MANGANESE, NICKEL, and COBALT, as SULPHIDES.
4. The *fixed Alkaline Carbonates precipitate* all the members, *some* as OXIDES, the *rest* as CARBONATES.
5. *Alkaline Arseniates precipitate* all the members from *neutral* solutions, as ARSENIATES.

BEHAVIOUR OF THE FOURTH GROUP WITH THE GENERAL REAGENTS.

1. *Hydrochloric Acid does not precipitate the members of this group*, THEIR CHLORIDES *being soluble.*
2. *Hydrosulphuric Acid precipitates* all the members from *acid* solutions, as SULPHIDES.
3. *Alkaline Sulphides do not precipitate them*, their SULPHIDES *being soluble* in these reagents.
4. *Alkaline Carbonates precipitate some of the members*, as OXIDES.
5. *Alkaline Arseniates precipitate some of the members*, as ARSENIATES.

BEHAVIOUR OF THE FIFTH GROUP WITH THE GENERAL REAGENTS.

1. *Hydrochloric Acid precipitates some of the members*, viz., LEAD, SILVER, and PROTOXIDE of MERCURY, as CHLORIDES.
2. *Hydrosulphuric Acid precipitates* all the members both from *Neutral, Acid,* and *Alkaline* solutions, as SULPHIDES.
3. *Alkaline Sulphides precipitate* all the members from *Neutral* and *Alkaline* solutions, as SULPHIDES.
4. *Alkaline Carbonates precipitate* them from *Neutral* solutions, as CARBONATES.
5. *Alkaline Arseniates precipitate* them from *Neutral* solutions, as ARSENIATES.

The analysis must be commenced by adding to the solution *hydrochloric acid*, which precipitates the first section of the fifth group. To the filtrate from this precipitate or to the solution with which it has failed to give a precipitate, is to be added *hydrosulphuric acid* which precipitates the remaining members of the fifth and all the members of the fourth group. *Chloride of ammonium, ammonia*, and *sulphide of ammonium*, being added to this filtrate, precipitate all the members of the third group. *Carbonate of ammonia*, being added to the solution from which the third group has been precipitated, throws down BARYTA, STRONTIA and LIME, whilst MAGNESIA remains in solution along with the members of the first group and the ammoniacal salts which have been added in the course of the analysis. To detect the MAGNESIA, the filtrate from the carbonate of ammonia precipitate must be divided into two portions. To one portion is to be added *arseniate of ammonia*. If a precipitate be produced by this reagent MAGNESIA is present. In this case the remainder of the solution is at once mixed with the portion to which arseniate of ammonia has been added, and the liquid filtered after it has been well agitated. To the filtrate must be added a drop or two more of the arseniate of ammonia. Should this cause no further precipitate all the magnesia has been thrown down. The filtrate must then be evaporated to dryness along with some sulphide of ammonium and ignited until all fuming has ceased. If a residue remain, POTASH AND SODA must be examined for according to the second Table.

Should *arseniate of ammonia* cause no precipitate in the first portion of the solution, MAGNESIA is absent. The other portion of the filtrate can in this case be at once evaporated to dryness to expel ammoniacal salts, and the residue, if any remain after ignition, be examined for POTASH and SODA.

Although the above is the usual course I prefer the following modification, as it renders the plan of analysis taught in the

laboratory more consonant with the methods adopted in general practice. It will be seen, by examining the *special table* of the third group, that some of the oxides belonging to that group are soluble whilst the rest are insoluble in excess of ammonia in the presence of ammoniacal salts. This property may therefore be employed to divide this group into two sections. If this scheme be followed, after boiling the filtrate from the sulphuretted hydrogen precipitate, to expel the excess of that gas, the solution must be filtered to free it from the sulphur which has separated, and be again boiled with the addition of a few drops of *nitric acid,* to convert the IRON if present into PEROXIDE. *Chloride of ammonium* and *ammonia,* being added to the solution, precipitate ALUMINA, OXIDE OF CHROMIUM, PEROXIDE OF IRON, PHOS- PHATE OF ALUMINA, PHOSPHATE OF IRON, and the PHOSPHATES AND OXALATES OF THE ALKALINE EARTHS. The precipitate after being well washed, may then be examined according to Table V.

MANGANESE, NICKEL, COBALT, and ZINC are thrown down from the filtrate by *sulphide of ammonium.* The examination of this precipitate must be conducted according to Table IV. Whilst the filtrate from the sulphide of ammonium precipitate, must be investigated for the second and first groups according to the methods previously given.

PARTICULAR OBSERVATIONS REGARDING THE PRECIPITATES PRODUCED BY THE GENERAL REAGENTS AND THE PRECAUTIONS TO BE ATTENDED TO IN EXAMINING THE SOLUTIONS.

Before adding *hydrochloric acid* to any solution under ex- amination, it is necessary to ascertain by test-papers whether it be acid, neutral, or alkaline. If it be one of the two former, a few drops of the acid will generally be found sufficient; if alkaline, the acid must be added until it is decidedly in excess.

As a precipitate may be produced on the addition of *hydrochloric*

acid, in the absence of the OXIDES OF SILVER, LEAD, and PROTOXIDE OF MERCURY, it is requisite to notice the substances which may be precipitated and under what conditions the precipitation takes place. The precipitate [1] may be occasioned by the presence of some SALT OF ANTIMONY or BISMUTH, as the CHLORIDES of these metals are decomposed by much water into soluble acid and insoluble basic salts. This precipitate may also arise from the presence of some substance insoluble in water but soluble in the caustic or carbonated alkalies. *Ex. gr.* PHOSPHATE OF ALUMINA dissolved in *caustic soda ;* or from the presence of some ALKALINE SILICATE. If the precipitate arise from either of the first two causes, it will generally redissolve on the further addition of acid. When silicic acid is the substance thrown down, the precipitate will present a very gelatinous appearance, and will remain undissolved on the further addition of acid. A fresh portion of the original solution must therefore be acidulated with nitric acid and evaporated to dryness to render the silicic acid insoluble; the ignited mass may then be digested with dilute nitric acid, and filtered. [2] The analysis of the filtrate is to be conducted in the regular way.

As the CHLORIDES OF LEAD, SILVER, and PROTOCHLORIDE OF MERCURY are very heavy, they easily separate from the solution; there is therefore no need to warm the fluid to effect this object. Indeed it would be disadvantageous to do so, as a portion of the protochloride of mercury would be converted into perchloride, and the greater portion if not all the chloride of lead would be dissolved. The precipitate, after being twice

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[1] If the hydrochloric acid employed contain a trace of sulphuric acid, and baryta be present in the fluid under examination, a slight trace of insoluble sulphate of baryta will be formed, which may be distinguished by the difficulty experienced in separating it from the fluid by filtration.

[2] The precipitate left upon the filter must be examined for silicic acid, according to the method described under the head of that acid.

washed with cold water, is to be examined according to first section of Table VI.

The precipitate thrown down by *sulphuretted hydrogen* from the hydrochloric-acid filtrate, may consist of the remaining members of the fifth, and all the members of the fourth group.   The method for separating these two groups will be explained in another paragraph.   Before passing the hydrosulphuric acid through the solution it will be necessary to dilute it with water, if it be very acid, as many of the sulphides will not readily precipitate from very acid solutions.   Should the liquid, on being diluted, become turbid, it arises from the presence of some salt of antimony or bismuth.   A few drops of acid will re-dissolve this precipitate.

If, on the addition of *hydrosulphuric acid,* no precipitate be produced, it proves the absence of the remaining members of the fifth and all the members of the fourth group.   If a precipitate be produced, the colour of which is white,[3] this likewise proves the absence of these groups, as the white precipitate is merely due to a separation of the sulphur, occasioned by the reduction of some higher oxide to a lower degree of oxidation.   If the colour of the solution, originally *orange* or *yellow,* change to a *green,* after the gas is passed through it, the separation of sulphur is due to the reduction of CHROMIC ACID to the state of OXIDE OF CHROMIUM.   If the separation of sulphur be not attended with *any change* in colour, it is (probably) attributable to the reduction of PEROXIDE OF IRON to the state of PROTOXIDE, chromic acid and peroxide of iron being both found in their lowest degree of oxidation, after hydrosulphuric acid, or any other reducing agent, has been added to their solutions.

[3] If nitric acid be present in the solution, a thick, tenacious yellow mass of sulphur will separate, occasioned by the decomposition of the sulphuretted hydrogen by the acid.   When such is the case the gas has to be passed through the solution for some time before its characteristic odour will be imparted to the liquid, showing that a sufficient quantity has been added.

ARSENIC ACID is precipitated, with very great difficulty, by *hydrosulphuric acid*. When this substance is present, the addition of *sulphurous acid*, assisted by a gentle degree of heat, reduces it to a lower oxide (*arsenious acid*). This must be done before passing hydrosulphuric acid through the solution. If on the first transmission of hydrosulphuric acid through the solution a *white* precipitate be formed, which, on a further addition of the reagent, acquires an *orange colour*, and becomes finally *black*, it points out that some salt of the peroxide of mercury is present. If the precipitate, on its first formation, assumes a *red* or *brownish-red* colour, and becomes finally *black*, it indicates the probable presence of some salt of lead.

To separate the two groups thrown down by hydrosulphuric acid, the precipitate produced by that reagent must be collected upon a filter, and washed with water. Boiling *caustic soda* is then poured upon it, and dissolves out the members of the fourth group, whilst the members of the fifth, being insoluble, remain behind upon the filter. This residue, after being well washed, must be examined according to the second section of Table VI. On the addition of *hydrochloric acid* to the alkaline solution, the members of the fourth group, if present, are re-precipitated. If the precipitate produced on the addition of the acid to the alkaline solution be white, this arises merely from the separation of sulphur; if it possess a *yellow* or *orange colour*, ANTIMONY, TIN, and ARSENIC can only be present. If *black*, then all the members of the group must be sought for. The analysis of this precipitate must be conducted according to directions given under the fourth group.

To the filtrate from the hydrosulphuric-acid precipitate is to be added *chloride of ammonium*,[4] *ammonia*, and *sulphide of*

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[4] No chloride of ammonium need be added to solutions which contain a considerable quantity of free acid, as a sufficient quantity of ammoniacal salt will be formed on neutralising the acid with ammonia.

ammonium. Chloride of ammonium is employed to prevent the precipitation of the MAGNESIA by the ammonia, and this alkali is added to neutralise the acid solution, and thus prevent the decomposition of the sulphide of ammonium.

The precipitate produced by sulphide of ammonium may consist, in addition to the members of the third group, of the following salts: ALUMINA, BARYTA, STRONTIA, LIME, and MAGNESIA, when in combination with PHOSPHORIC ACID; and BARYTA, STRONTIA, and LIME, when in combination with OXALIC ACID. The precipitate produced by sulphide of ammonium may therefore be composed of SULPHIDES, OXIDES, and SALTS. The substances contained in the second and third classes do not, like those contained in the first, give up their oxygen for the sulphur contained in the alkaline sulphide. It is therefore the ammonia in the sulphide of ammonium which determines their precipitation, and consequently hydrosulphuric acid is always evolved when the alkaline sulphide is added to a solution containing any or all of the substances contained in these classes. One reason why the alkaline sulphide is restricted in the Table to sulphide of ammonium, is that alumina and oxide of chromium are soluble in the fixed alkalies, and consequently the sulphides of potassium or sodium would cause no precipitate in their solutions. The substances composing the first class are not only precipitated by all soluble sulphides, but also form neutral or alkaline solutions by *hydrosulphuric acid.*

The precipitate produced by sulphide of ammonium, after being well washed, must be examined according to Table IV.

If the filtrate from the sulphide of ammonium precipitate be very dark and turbid, it is occasioned by the presence of NICKEL, the sulphide of that metal being slightly soluble in sulphide of ammonium. When a considerable portion of this substance has passed into solution, the filtrate must be evaporated to dryness, and the residue treated with water. The substance which is

insoluble in water must be added to the precipitate produced by sulphide of ammonium, whilst the solution is to be investigated for the first and second groups.

To the solution, which may contain the members of the first and second groups, is to be added *chloride of ammonium, ammonia* (if these reagents are not already present in the solution), and *carbonate of ammonia*. BARYTA, STRONTIA, and LIME are completely precipitated from their solutions by the alkaline carbonate; but this reagent precipitates MAGNESIA only partly, even under the most favourable circumstances, and this partial precipitation is altogether prevented if a salt of ammonia be present.   It is for this reason that chloride of ammonium[5] is directed to be added along with the alkaline carbonate.   The carbonate of ammonia employed being generally a sesquicarbonate, a portion of the alkaline earths is apt to be dissolved by the excess of carbonic acid.   To prevent this, a little ammonia should be added along with that reagent.

The solution, after the addition of the carbonate of ammonia, should be gently warmed, and the precipitate, if any be formed, examined according to Table III, for BARYTA, STRONTIA, and LIME.

The separation of MAGNESIA from the FIXED ALKALIES is effected by precipitating it from its solutions by means of arseniate of ammonia.   To get rid of the excess of arseniate of ammonia in the filtrate, *sulphide of ammonium* (containing an excess of sulphur) must be added, and the solution evaporated to dryness and ignited.   By this means the whole of the arsenic will be expelled, along with the ammoniacal salts, in the state of SULPHARSENIC ACID.   This mode of getting rid of the arsenic is open to two objections:—1. It would be ineffectual when nitrates were present, as the sulpharsenic acid formed by

[5] Any ammoniacal salt may be employed, the acid of which forms no insoluble compound with magnesia or the other members.

the sulphide of ammonium would be again converted, during the process of ignition, into arsenic acid. 2. It would be dangerous, in ill-ventilated laboratories, to volatilise any compound of arsenic into the atmosphere. By adopting the following modification the two objections will be removed. After sulphide of ammonium has been added to the filtrate from the magnesia precipitate, and the solution evaporated to one half its bulk, hydrochloric acid must be added slightly in excess. The solution must then be filtered off from the precipitated SULPH-ARSENIC ACID, evaporated to dryness, and heated to expel ammoniacal salts. If a residue remain, it must be examined for the NON-VOLATILE ALKALIES.

FIRST GROUP.

POTASH. SODA. AMMONIA.

The members of this group are called alkalies. They are readily soluble in water in their pure (caustic) state. The solution restores the blue colour of reddened litmus paper, and imparts an intensely brown colour to turmeric paper; the solution of their sulphides and carbonates act in a similar manner upon vegetable colours.

Potash and soda are oxides of the metals *potassium* and *sodium;* these metals are lighter than water, and decompose it at the ordinary temperature. Ammonia (NH_3) being a gas of a very pungent odour, is readily distinguished from all other substances; it dissolves freely in water, and may be again expelled on boiling the solution. Ammonia, when dissolved in an aqueous solution, unites with one atom of water forming NH_4O, the oxide of an hypothetical compound metal *ammonium* (NH_4).

Potash cannot be detected in the presence of ammonia or any of its salts: because the same reagents which precipitate potash from its solutions, form also with ammonia a corresponding class of insoluble substances; the latter must therefore be separated from the substance before proceeding to test for the former.

When a solution is to be examined, containing only THE ALKALIES, it must be divided into two parts. In one portion an examination for AMMONIA is to be made according to the method described in the second paragraph of the Table for this group. If that alkali be present, the other portion of the solution must be evaporated to dryness, and ignited in order to volatilise the ammoniacal salts; if a residue remain,[6] one or both of the FIXED ALKALIES may be present. A portion of this residue is to be placed upon the loop of a platinum wire, and exposed to the inner blowpipe flame. If the flame be coloured *yellow*, SODA is present; if *violet*, it proves the absence of soda, and the probable presence of POTASH. The remainder of the substance is to be dissolved in the smallest possible quantity of water, and examined for potash by adding *tartaric acid* to the solution, which produces, in solutions of that alkali, a crystalline precipitate. In the absence of ammonia, the other portion will not require to be evaporated to dryness before proceeding to test for potash and soda.

When the examination is not confined to the alkalies, the solution, after having been freed from all other substances, must be evaporated to dryness, and ignited, to expel the ammoniacal salts, which have been added in the course of the analysis. If a residue remain after the vapours of the ammoniacal salts have ceased, it must be examined for potash and soda. In this case, ammonia is to be tested for in the original solution.

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[6] A fixed residue is not a certain proof of the presence of potash or soda, as it may arise from the presence of one of the non-volatile acids, viz., phosphoric, boracic, or silicic acid.

TABLE II.

BEHAVIOUR OF THE FIRST GROUP WITH THE SPECIAL REAGENTS.

AMMONIA (N H $_4$ O).	POTASH (K O).	SODA (Na O).
1. Ammonia and its salts are *volatile.*	1. Potash and its salts are *not volatile.*	˙1. Soda and its salts are *not volatile.*
2. All salts of ammonia are *decomposed* with the liberation of free ammonia, when any stronger base, such as *lime, potash,* or *soda,* is added to their solutions. If the liquid be gently heated, the ammonia is volatilised, and its presence may then be recognised in three distinct ways. *a.* By its pungent *odour.* *β.* By turning *red* litmus paper *blue.* *γ.* By forming *white fumes,* when any volatile acid, as hydrochloric acid, is brought into contact with it.[7]	2. When salts of potash are decomposed by a stronger base, the potash which is liberated *not being volatile* like ammonia, cannot be detected in a similar way.	2. When soda salts are decomposed by a stronger base, the soda which is liberated *not being volatile* like ammonia, cannot be detected in a similar manner.
3. *Tartaric acid* (2 H O, $C_8 H_4 O_{10}$ = 2 H O, $\overline{T}$) produces in neutral or alkaline solutions of ammonia, a white crystalline precipitate of BITARTRATE OF AMMONIA (N H $_4$ O, H O, $\overline{T}$), which is rather more soluble in water than the corresponding potash salt.	3. *Tartaric acid* throws down from neutral or alkaline solutions of potash a white crystalline precipitate of BITARTRATE OF POTASH (KO, HO, $\overline{T}$). This salt and the corresponding one of ammonia, are soluble in free alkalies and free mineral acids.	3. *Tartaric acid* produces no precipitate in solutions of soda, bitartrate of soda being soluble.
4. Ammonia and its salts impart to the blowpipe flame *no* characteristic colour.	4. Potash and its salts tinge the outer blowpipe flame VIOLET.	4. Soda and its salts impart to the exterior blowpipe flame an intense YELLOW colour. Small quantities of soda can by this means be detected in the presence of much potash, the yellow flame overpowering the violet.

[7] This experiment is best performed by inserting a glass rod moistened with hydrochloric acid into the mouth of the test-tube in which the decomposition of the ammonia salt has been effected. The hydrochlorid acid employed should not be concentrated, but should be diluted with an equal volume of water.

The following precautions are to be attended to in the analysis of this group. In testing for ammonia, one error frequently committed is that of allowing the glass rod to remain so long in the heated atmosphere of the test-tube, that on its removal a *sensible evaporation* takes place from its surface, which is mistaken for the white fumes which are formed when any volatile acid is brought in contact with ammonia. To avoid this error the solution which is under examination should be heated until it approaches the boiling point, but should not actually be boiled, and the moistened glass rod should, immediately after its insertion into the test-tube, be withdrawn. If any fuming should then arise, it can only proceed from the presence of ammonia, which must be confirmed by the other appropriate tests. The detection of potash by tartaric acid requires in the first place that the solution be neutral, and as concentrated as possible. The reagent must then be added in excess, and the fluid well agitated. The application of heat must be avoided, and time allowed for the appearance of the precipitate, as it becomes visible only after the lapse of some hours, when small quantities of potash are present. In testing for potash or soda by the blowpipe flame, it is necessary that the platinum wire should be perfectly clean. This can only be secured by directing the blowpipe flame upon it until it ceases to impart a colour; care should then be taken not to touch, even with the fingers, that end of it on which the substance is to be placed.

SPECIAL REMARKS.

1. AMMONIA. This substance is a gas, transparent and colourless, of a very pungent and peculiar smell and taste. It is instantly absorbed by water, forming the solution of the gas called *aqua ammoniæ*. When organic substances containing nitrogen decay and putrefy, carbonate of ammonia is constantly produced. The same salt is likewise formed when

nitrogenised organic substances are submitted to destructive distillation.

When any volatile acid is brought into an atmosphere of ammonia, they unite together, forming a solid *salt ;* this is the white fumes observed on testing ammonia.

Bichloride of platinum (Pt Cl₂) produces in neutral and acid solutions of ammonia, a yellow crystalline precipitate, which is a double salt of CHLORIDE OF AMMONIUM and CHLORIDE OF PLATINUM (NH₄ Cl, Pt Cl₂).

2. POTASH. This alkali and its hydrate when exposed to the air absorb moisture and carbonic acid, the carbonate formed dissolving in the absorbed water. Almost all the salts of this base are readily soluble in water. They are colourless provided the constituent acid be so. This alkali is an important constituent in many of our crystalline rocks. It exists there, in combination with SILICIC ACID, ALUMINA and IRON, as a double salt of SILICATE OF POTASH and SILICATE OF ALUMINA or IRON. The decay of these rocks is occasioned by the carbonic acid in the atmosphere decomposing the alkaline silicate. It is also found in the mineral kingdom as SULPHATE and NITRATE OF POTASH; the latter being *saltpetre.*

Bichloride of platinum produces in neutral and acid solutions of potash, a yellow crystalline precipitate, a double salt of CHLORIDE OF POTASSIUM and CHLORIDE OF PLATINUM (KCl, Pt Cl₂). The presence of free hydrochloric acid promotes the formation of this precipitate. It is slightly soluble in water but wholly insoluble in alcohol.

3. SODA. This alkali and its hydrate on exposure to the air attract moisture and become fluid, but absorbing carbonic acid again solidifies. The salts of this base, with a few exceptions, are very soluble. The means we have of detecting it are there-

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fore limited. It exists in the mineral kingdom as CHLORIDE (*kitchen salt*), SULPHATE (*Glauber's salt*), BORATE (*borax or tincal*), NITRATE and CARBONATE. It likewise forms a constituent of many SILICEOUS MINERALS.

The best test for soda is the blowpipe flame, to which it imparts a yellow colour, caused by the reduction of the soda and the subsequent re-oxidation of the sodium.

Antimoniate of potash (KO, SbO_5) produces in neutral or alkaline solutions of salts of soda, a white crystalline precipitate of ANTIMONIATE OF SODA (NaO, SbO_5). In concentrated solutions the precipitate is formed immediately; but from dilute solutions it separates only after the lapse of some time. Violent agitation of the fluid promotes the separation of the precipitate. Acid solutions decompose antimoniate of potash, antimonic acid being precipitated; free acids must therefore be first neutralised with potash before this test can be applied. Antimoniate of soda is soluble in carbonate of potash; if this substance be present in the solution it must be nearly saturated with acetic acid.

SECOND GROUP.

BARYTA. STRONTIA. LIME. MAGNESIA.

The members of this group are called alkaline earths. They are soluble in water in their pure (caustic) state, also as sulphides. Magnesia however is very sparingly soluble in water. Their solutions exhibit an alkaline reaction.

The metallic radicals of these oxides are *barium, strontium, calcium,* and *magnesium,* all of which decompose water at the ordinary temperature.

As magnesia differs so entirely from the other members of the group in its behaviour with reagents it has not been included in

the *special table.* The group is therefore subdivided, the first division comprising BARYTA, STRONTIA, and LIME, the second containing MAGNESIA.

FIRST DIVISION.

The precipitate produced by the general reagent must be dissolved in *acetic acid*, and the solution divided into two parts, which we will call A and B.

If the addition of a solution of *sulphate of lime* to the A portion produce an immediate precipitate, BARYTA is present. In the B solution the BARYTA must be separated, in order that an examination may be made for STRONTIA and LIME ; for this purpose *chromate of potash* is to be added to the B solution, and it precipitates the BARYTA as CHROMATE ; to the filtrate from this precipitate must be added *ammonia* and *oxalate of ammonia ;* if a precipitate be produced, it may be due to the presence both of STRONTIA and LIME ; filter off, and after having washed the precipitate with water dissolve it in *hydrochloric acid,* dilute the acid solution with three or four times its volume of water, then add a small quantity of *sulphate of potash.* If a precipitate be formed after the lapse of a short time STRONTIA is present ; filter off, and to the filtrate add *ammonia* in excess ; if a precipitate be produced, LIME is present.

If the addition of *sulphate of lime* to the A portion caused a precipitate only after the lapse of some time, it is probable that STRONTIA is present, and BARYTA absent. In this case dilute *sulphuric acid* is to be added to the B solution to precipitate the STRONTIA, and to the filtrate must be added *ammonia* and *oxalic acid* to precipitate the LIME.

TABLE III.

BEHAVIOUR OF THE SECOND GROUP WITH THE SPECIAL REAGENTS.

BARYTA (Ba O).	STRONTIA (Sr O).	LIME (Ca O).
1. *Sulphate of lime* (CaO, SO$_3$) precipitates baryta *immediately,* from its solutions in the form of SULPHATE (Ba O, SO$_3$), insoluble in acids and alkalies.	1. *Sulphate of lime* precipitates strontia *after* the *lapse of some time* from its solutions in the form of SULPHATE (Sr O, SO$_3$), almost absolutely insoluble in acids and alkalies.	1. *Sulphate of lime* produces no precipitate in solutions of lime.
2. *Chromate of potash* (K O, Cr O$_3$) produces in neutral and alkaline solutions of baryta, a pale yellow precipitate of CHROMATE OF BARYTA (Ba O, Cr O$_3$), insoluble in the alkalies and acetic acid.	2. *Chromate of potash* produces no precipitate in solutions of strontia, CHROMATE of STRONTIA being soluble.	2. *Chromate of potash* produces no precipitate in solutions of lime, CHROMATE OF LIME being soluble.
3. *Sulphuric acid* and *the soluble sulphates* behave in the same manner in solutions of baryta as sulphate of lime.	3. *Sulphuric acid* and the *soluble sulphates* precipitate strontia completely from its solutions in the form of SULPHATE. The precipitate will not appear immediately, unless the solution be very concentrated.	3. *Sulphuric acid* and the *alkaline sulphates* cause only in concentrated solutions of lime a partial precipitate of SULPHATE OF LIME, which redissolves completely in a large amount of water.
4. *Oxalic acid* (H O, C$_2$ O$_3$ = H O, $\overline{O}$) produces only in concentrated solutions of baryta, a white precipitate of Oxalate of Baryta (Ba O, $\overline{O}$), soluble in acids. The addition of ammonia renders this reaction therefore more susceptible.	4. *Oxalic acid* precipitates even from dilute solutions of strontia a white precipitate of Oxalate of Strontia. The addition of ammonia promotes the formation of the precipitate.	4. *Oxalic acid* throws down from neutral solutions of lime, even if highly diluted, a precipitate of Oxalate of Lime. The addition of ammonia renders this reaction more delicate.

The following precautions are to be attended to in the analysis of this group. The solution of sulphate of lime must always be added in the cold, as this reagent is less soluble in hot than cold water. Time must be allowed for the formation of the precipitate produced by this reagent in solutions of strontia, the formation of which is much promoted by agitation. In separating strontia from a solution by sulphate of potash, the liquid ought not to be filtered immediately, but a due time allowed for the complete separation of the precipitate from the solution.

<center>SPECIAL REMARKS.</center>

1. BARYTA. This oxide is of a grayish-white colour, it combines with water, forming a hydrate (Ba O, HO). Both the oxide and its hydrate are soluble in water. The solution reacts strongly alkaline, and when exposed to the air absorbs carbonic acid, and becomes covered with a film of carbonate of baryta, the absorption continuing until all the baryta has been precipitated as carbonate.

The salts of baryta are colourless provided the constituent acid be so. Most of them are insoluble in water, but they are all, with the exception of the sulphate, soluble in hydrochloric and nitric acid. The salts which are soluble in water do not affect vegetable colours, and are decomposed upon ignition, with the exception of chloride of barium. The SULPHATE (*heavy spar*) and the CARBONATE (*witherite*) are the principal minerals of this oxide.

Hydrofluosilicic acid (HF, Si F$_2$) throws down, both from neutral and alkaline solutions of baryta, a white precipitate of SILICOFLUORIDE OF BARIUM (Ba F, Si F$_2$) which appears only after much agitation.

2. STRONTIA. This oxide and its salts resemble, in their colour, solubility, and other properties, the corresponding com-

pounds of baryta. The hydrate of this oxide is however less soluble in water than the hydrate of baryta. The SULPHATE (*celestine*) and the CARBONATE (*strontianite*) are the principal minerals of strontia.

The CHLORIDE and NITRATE of STRONTIA are soluble in alcohol, the corresponding salts of baryta are insoluble. If an alcoholic solution of either of these salts be ignited it will burn with a *beautiful crimson flame* which becomes more apparent on stirring the solution.

Salts of strontia when heated on the platinum wire in the inner blowpipe flame impart a *crimson colour* to the outer flame.

3. LIME. This oxide and its salts resemble in their general behaviour the corresponding compounds of baryta and strontia. The hydrate of lime is less soluble in water than the hydrates of strontia or baryta; it is also more sparingly soluble in hot than cold water. The solution absorbs carbonic acid from the air, the lime becoming converted into carbonate. The principal minerals of lime are the SULPHATE (*gypsum, selenite* $CaO, SO_3 + 2$ aq) and (*anhydrite* CaO, SO_3), the CARBONATE (*chalk, limestone, calcareous spar*), the double CARBONATE OF LIME and MAGNESIA (*dolomite*) $(CaO, CO_2) + 3 (MgO, CO_2)$, and the FLUORIDE OF CALCIUM (*fluor spar* CaF).

CHLORIDE OF CALCIUM and NITRATE OF LIME are soluble in alcohol. The alcoholic solution of these salts when ignited burn with a *yellowish-red coloured flame*.

Arsenite of ammonia produces in aqueous solutions of chloride of calcium, an immediate precipitate of ARSENITE OF LIME. In solutions of chloride of barium or strontium a precipitate is produced by this reagent only after the lapse of some time Should this test be resorted to for confirming the presence of lime, ammoniacal salts if present must first of all be removed from

the solution; because all the salts of arsenious acid which are insoluble in water, dissolve in it if ammoniacal salts are present.

SECOND DIVISION.

MAGNESIA. This oxide differs from the other members of this group, not only by its non-precipitation by *carbonate of ammonia* in the presence of *ammoniacal salts*, but likewise from the difficult solubility of its hydrate and the ready solubility of its sulphate. The oxalate and chromate as well as some other salts of magnesia are soluble in water. The soluble magnesian salts have a nauseous bitter taste; they do not alter vegetable colours when in a neutral state, and, with the exception of sulphate of magnesia, they undergo decomposition when ignited. All the salts of magnesia which are insoluble in water dissolve readily in hydrochloric acid. Magnesia is found in the mineral kingdom, principally in the state of SULPHATE (*epsom salts* MgO, $SO_3 + HO + 6$ aq), of CARBONATE, and in combination with SILICIC ACID in various proportions, forming the *meerschaum*, *serpentine*, &c.

Ammonia precipitates from aqueous solutions of salts of magnesia, a portion as HYDRATE (MgO, HO). The rest of the magnesia remains in solution, with the salt of ammonia formed as a double salt. The presence of salts of ammonia prevents the precipitation altogether.

The *fixed alkalies* and the other *alkaline earths* precipitate magnesia from its solutions in the form of HYDRATE. This precipitate is soluble in salts of ammonia; the addition therefore of these substances, either before or after the precipitation, prevents or re-dissolves the precipitate formed.

Arseniate of ammonia ($3NH_4O$, AsO_5), produces, in solutions of magnesia, a white precipitate of ARSENIATE OF MAGNESIA

AND AMMONIA (2 MgO, NH$_4$O, AsO$_5$) which is soluble in acetic and other weak acids.

Phosphate of soda (2 NaO, HO, PO$_5$) produces, in concentrated solutions of magnesia, a precipitate of PHOSPHATE OF MAGNESIA (2 MgO, HO, PO$_5$). A more insoluble magnesian salt may be produced by adding along with the *phosphate of soda, chloride of ammonium and ammonia.* The precipitate in this case being PHOSHATE OF MAGNESIA AND AMMONIA (2 MgO, NH$_4$O, PO$_5$), which is soluble in free acids.

Phosphate of magnesia and ammonia, and arseniate of magnesia and ammonia, are the only magnesian salts which are insoluble in aqueous solutions containing salts of ammonia.

If magnesia or any of its compounds, after being ignited strongly by the blowpipe flame upon a charcoal support, be moistened with *nitrate of cobalt*, and again ignited, the mass assumes, on cooling, a *pale flesh colour*.

THIRD GROUP.

ALUMINA.   OXIDE   OF   CHROMIUM.   PROTOXIDE   OF   IRON.
PEROXIDE   OF   IRON.   OXIDE   OF   ZINC.   OXIDE   OF   MAN-
GANESE.   OXIDE   OF   NICKEL.   OXIDE   OF   COBALT.

All the members belonging to this group are insoluble in water, but they dissolve readily in the dilute mineral acids.[8] After ignition ALUMINA, OXIDE OF CHROMIUM, and the OXIDES OF IRON, dissolve with great difficulty, even in the concentrated mineral acids. In the state of sulphides they are insoluble, not only in water, but also in the alkalies and alkaline sulphides; but they are soluble (with decomposition) in hydrochloric acid,

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[8] Sulphuric, nitric, and hydrochloric acids.

with the exception of the SULPHIDES OF NICKEL AND COBALT, which are almost totally insoluble in that acid, but dissolve readily in *aqua regia*. The SULPHIDES OF MANGANESE AND IRON are soluble in acetic and other weak acids.

The metallic radicals of these oxides possess the following properties: *aluminum* and *manganese* decompose water at 212° F., and *chromium, iron, zinc, nickel,* and *cobalt* decompose it at a red heat, and at common temperatures in contact with strong acids.

It has been shown, in treating of the general properties of this extensive group, that it may be classified in two distinct ways—the first method of division depending upon the precipitation of the members as SULPHIDES or OXIDES—the other, on the solubility or insolubility of some of the members in an excess of ammonia, when ammoniacal salts are present.

If the group has been precipitated by *sulphide of ammonium*, the precipitate, according to its colour, must be examined by one of the two following methods.

A. If the precipitate produced be *black*, all the substances must be sought for. Since black will obscure every other colour, *aqua regia* is employed as the solvent for this precipitate, for two reasons: first, to dissolve the SULPHIDES OF COBALT AND NICKEL; lastly, to convert the PROTOXIDE OF IRON into PEROXIDE. In whatever state iron may have existed in the original solution, it is always precipitated by *sulphide of ammonium* as PROTOSULPHIDE. To the acid solution, after it has been well boiled to expel the hydrosulphuric acid, are to be added *chloride of ammonium* and *ammonia*, which precipitate ALUMINA, OXIDE OF CHROMIUM, and PEROXIDE OF IRON, whilst the OXIDES OF ZINC, MANGANESE, NICKEL, and COBALT remain in solution. The precipitate and solution must then be separately examined.

a. The precipitate, after being well washed to free it from

the ammonia, must be dissolved in *hydrochloric acid.* A cold solution of *caustic soda* or *potash* being then added in excess, determines the precipitation of the IRON. On *boiling* the filtrate from this precipitate, or the solution which has failed to give a precipitate, OXIDE OF CHROMIUM is thrown down. To the filtrate from this precipitate, which may still contain ALUMINA is to be added *chloride of ammonium,* or, what is better, after neutralising the alkaline solution by *hydrochloric acid* add *ammonia* in excess; ALUMINA, if present, will be thrown down, on gently warming the solution after the addition of these reagents.

b. Before examining the ammoniacal solution for the OXIDES OF ZINC, MANGANESE, NICKEL, and COBALT, a trial experiment should be first made to ascertain whether any of these oxides are present. For this purpose add *sulphide of ammonium* to a small portion of the ammoniacal solution. If no precipitate be produced they are all absent. If a precipitate be formed we ascertain by the *black colour* whether NICKEL and COBALT are present. When a precipitate has been produced *caustic soda* must be added to the remainder of the ammoniacal solution, and the whole boiled until all the ammonia has been expelled. The OXIDES OF MANGANESE, NICKEL, and COBALT, being insoluble in the fixed alkalies, are precipitated, whilst OXIDE OF ZINC, being soluble, remains in solution; from which solution it will be precipitated on the addition of *hydrosulphuric acid.* The precipitate produced by the fixed alkalies, after being well washed, may be dissolved in *hydrochloric acid; ammonia* and *carbonate of ammonia,* being then added, throw down the MANGANESE, whilst the NICKEL and COBALT remain in solution; to effect their separation, acidulate the liquid with *hydrochloric acid,* add *cyanide of potassium* in excess, and boil for some time. Filter, if necessary, and add *dilute sulphuric acid.* If a light greenish precipitate form, either immediately, or after the lapse of some time, it is a proof that NICKEL is present. COBALT should be tested for

in the precipitate obtained by sulphide of ammonium in the trial experiment, with *borax* in the inner blowpipe flame. OXIDE OF MANGANESE might likewise be tested for in the same precipitate, with *carbonate of soda* in the outer blowpipe flame. Should MANGANESE be absent, to the hydrochloric solution of the oxides precipitated by caustic soda might be added at once *cyanide of potassium*, and the investigation conducted in the manner described for NICKEL.

B. If the precipitate produced by *sulphide of ammonium* be *white* or *flesh-coloured*, IRON, NICKEL, and COBALT must be absent. Hydrochloric acid is to be employed as the solvent of this precipitate. To the acid solution, after it has been well boiled to expel the hydrosulphuric acid, is to be added a cold solution of *caustic soda* in excess to precipitate the MANGANESE, if present. On *boiling* the filtrate from this precipitate, or the solution which has failed to give a precipitate, OXIDE OF CHROMIUM is thrown down. On adding to the liquid, which has been freed from the manganese and chromium, *hydrosulphuric acid*, ZINC, if present, will be precipitated. *Chloride of ammonium* produces in this filtrate a precipitate, if ALUMINA be present.

If the group has been divided by precipitating, first of all ALUMINA, OXIDE OF CHROMIUM, and PEROXIDE OF IRON, by *ammonia*, and afterwards throwing down the rest of the members by *sulphide of ammonium*, the precipitate produced by *ammonia* must be treated according to A. *a.*, and the precipitate by *sulphide of ammonium*, after being dissolved in acid according to A. *b.*

TABLE IV.

BEHAVIOUR OF THE THIRD GROUP

ALUMINA ($Al_2 O_3$).	OXIDE OF CHROMIUM ($Cr_2 O_3$).	OXIDES OF IRON.	
1. This oxide and its hydrate ($Al_2 O_3$, 3 H O) are *colourless*.	1. This oxide is green and its hydrate ($Cr_2 O_3$, 3 H O) a *bluish green powder*.	1. Protosulphide of Iron (Fe S) is always formed when sulphide of Ammonium is added to any per-or protosalt of Iron. It is of a *black colour*, which rapidly becomes *brown* on exposure to the air.	
		PEROXIDE OF IRON ($Fe_2 O_3$).	PROTOXIDE OF IRON (Fe O).
2. *Ammonia, even* in the presence of its salts, precipitates Alumina, in the form of HYDRATE, which an excess of the reagent *does not* redissolve.	2. *Ammonia, even* in the presence of its salts, precipitates this oxide in the state of HYDRATE, which an excess of the reagent *does not* redissolve.	2. *Ammonia, even* in the presence of its salts, precipitates this oxide from its solutions, in the form of the *red brown* HYDRATE (Fe_2O_3, H O), which an excess of the reagent *does not* redissolve.	2. *Ammonia, but not* in the presence of its salts, precipitates the HYDRATED PROTOXIDE (Fe O, H O) from solutions of the protosalts of iron, which an excess of the reagent *does not* redissolve.
3. *The fixed Alkalies* throw down Alumina from its solutions, in the form of HYDRATE, which *is soluble* in an excess of reagent, from which solution it may be again precipitated on the addition of *Chloride of Ammonium*.	3. The *fixed Alkalies* throw down, from solutions of this oxide the HYDRATE, which is *soluble* in an excess of the reagent in the *cold*, but on *boiling* the solution, it is again precipitated.	3. *The fixed Alkalies* precipitate from solutions of this oxide the HYDRATE, *insoluble* in an excess of the reagent.	3. The *fixed Alkalies* precipitate from solutions of this oxide the HYDRATE, *insoluble* in an excess of the reagent.
4. *Carbonate of Ammonia* precipitates from solutions of Alumina the HYDRATE. This precipitation is attended with an evolution of carbonic acid.	4. *Carbonate of Ammonia* precipitates from solutions of this oxide the HYDRATE, carbonic acid being given off.	4. *Carbonate of Ammonia* precipitates from solutions of this oxide the HYDRATE, carbonic acid being given off.	4. *Carbonate of Ammonia* precipitates from solutions of this oxide the PROTOCARBONATE (Fe O, C O$_2$), soluble in chloride of ammonium.

The fixed alkaline carbonates throw down from their solutions all the members of this group, some as oxides, the rest as carbonates. An excess of the reagent does not redissolve the precipitate.

TABLE IV.

WITH THE SPECIAL REAGENTS.

OXIDE OF ZINC (Zn O).	OXIDE OF MANGA-NESE (Mn O).	OXIDE OF NICKEL (Ni O).	OXIDE OF COBALT (Co O).
1. Sulphide of Zinc (ZnS), like the oxide, is *colourless*.	1. Sulphide of Manganese (Mn S) is *flesh - coloured*, but becomes *brown* on exposure to the air.	1. Sulphide of Nickel (Ni S) is *black*.	1. Sulphide of Cobalt (Co S) is *black*.
2. *Ammonia* precipitates from solutions of Zinc the HYDRATED OXIDE (Zn O, H O), which *is soluble* in an excess of the reagent.	2. *Ammonia, but not* in the presence of its salts, precipitates this oxide from its solutions in the form of HYDRATE (Mn O, H O), which an excess of the reagent *does not* redissolve.	2. *Ammonia* precipitates from solutions of Nickel the GREEN HYDRATE (NiO, H O), which is *easily soluble* in an excess of the reagent.	2. *Ammonia* precipitates, from solutions of Cobalt, a LIGHT BLUE PRECIPITATE, which is *easily soluble* in an excess of the reagent.
3. The *fixed Alkalies* precipitate from solutions of this oxide the HYDRATE, *soluble* in an excess of the reagent.	3. The *fixed Alkalies* precipitate from solutions of Manganese the HYDRATE, *insoluble* in an excess of the reagent.	3. The *fixed Alkalies* precipitate from solutions of Nickel the HYDRATE, *insoluble* in an excess of the reagent.	3. The *fixed Alkalies* produce, in solutions of Cobalt, a BLUISH GREEN PRECIPITATE, which becomes red on boiling; an excess of the reagent *does not* re-dissolve it.
4. *Carbonate of Ammonia* produces a PRECIPITATE in solutions of Zinc, easily *soluble* in an excess of the reagent.	4. *Carbonate of Ammonia* produces, in solutions of Manganese, a precipitate of the white PROTO-CARBONATE (Mn O C O₂), *insoluble* in an excess of the reagent.	4. *Carbonate of Ammonia* produces, in solutions of Nickel, a pale yellow coloured PRECIPITATE, readily *soluble* in an excess of the reagent.	4. *Carbonate of Ammonia* produces, in solutions of this oxide, a pink PRECIPITATE, readily *soluble* in an excess of the reagent.

The alkalies fail to precipitate the members of this group in the presence of non-volatile organic matter, such as starch, sugar, tartaric acid, &c.

The following precautions are to be attended to in the analysis of this group. Dissolve the precipitates in as little acid as possible; for this purpose, pour the acid, small quantities at a time, in a boiling state upon the precipitate collected upon the filter. If the precipitate be very large, remove it from the filter into an evaporating dish, before adding the acid. When sulphides are dissolved in hydrochloric acid, hydrosulphuric acid is produced; before adding any alkali to the solution, this gas must be removed by boiling. If this be neglected, an alkaline sulphide will be produced, which will precipitate the substances present as sulphides. To ascertain when all the gas has been expelled, hold a paper, moistened with a solution of a salt of lead, over the mouth of the tube. If the paper be not blackened, all the gas has been volatilised. The solution, after the addition of chloride of ammonium and ammonia, ought to be warmed. When much oxide of chromium is present, a small quantity will dissolve in the ammonia, and will impart to the fluid a puce-red tint. When this occurs, it is difficult to remove the last traces of chromium from the solution. If warming the solution fail, it must be evaporated until the separation takes place. Frequently a greater or less quantity of oxide of manganese will precipitate along with the alumina, oxide of chromium, and peroxide of iron. This precipitate is occasioned by the solution of the protoxide of manganese absorbing oxygen from the air, and becoming converted into a higher oxide, which is insoluble in ammonia in the presence of ammoniacal salts; this oxide is likewise insoluble in the fixed alkalies. On re-dissolving the precipitate by ammonia in hydrochloric acid, and then adding caustic soda, if a precipitate be produced, it is necessary to ascertain by further tests whether it be due to the presence of iron or manganese. On adding caustic soda to the ammoniacal solution, which may contain the oxides of manganese, nickel, cobalt, and zinc, and boiling, a small precipitate will fre-

quently be formed, if only zinc be present. This is occasioned by the caustic alkali having absorbed some carbonic acid from the atmosphere and become partially converted into carbonate, which causes a partial precipitation of the zinc.

SPECIAL REMARKS.

1. ALUMINA. This substance is very abundant in nature. It forms, not only the basis of common clay, but is likewise a principal ingredient in many of the precious stones. Along with slight traces of silica and peroxide of iron, it forms the CORUNDUM, SAPPHIRE, RUBY, DIAMANT SPAR, &c. As hydrate, it is known under the names of DIASPORE and GIBBSITE. Combined with silica and glucina, it forms the EMERALD, BERYL, EUCLASE, and CHRYSOBERYL. When pure it is white, but it frequently possesses a yellowish tint when obtained by drying the hydrate. Its salts are colourless, the soluble ones redden litmus paper, and lose their acids upon ignition. The SULPHIDE OF ALUMINUM cannot exist in contact with water, being decomposed into alumina and hydrosulphuric acid.

If alumina or any of its compounds be ignited upon charcoal by the blowpipe flame, afterwards moistened with a few drops of *protonitrate of cobalt*, and again strongly heated, the mass assumes a BLUE COLOUR on cooling, which is characteristic of alumina.

2. OXIDE OR SESQUIOXIDE OF CHROMIUM. The colour of this oxide is green; its hydrate is bluish grey. The solution of its salts possess a beautiful green colour by reflected, and reddish-violet colour by transmitted light. Sulphide of chromium is decomposed in contact with water into oxide of chromium and hydrosulphuric acid. The principal mineral from which this oxide is extracted is the CHROME IRON (FeO, Cr_2O_3), which is found principally in Sweden, in the Uralian Mountains, and in America.

When oxide of chromium or any of its compounds are fused with nitrate of potash, it becomes converted into a higher oxide, viz., CHROMIC ACID, which, combining with the potash, forms yellow chromate of potash. This test distinguishes it at once from all other substances.

Borax dissolves oxides of chromium and its salts, both in the inner and outer blowpipe flame; the bead, on cooling, assumes an EMERALD-GREEN COLOUR. *Microcosmic salt* has the same effect.

In the fixed alkalies a small quantity of oxide of chromium in the presence of a large quantity of peroxide of iron is totally insoluble; but a small quantity of the latter dissolves readily when a large quantity of the former is present. Under these circumstances, the two oxides are best separated from each other by fusing the mixed substances with *nitre* and *carbonate of soda*, and treating the fused mass with water; the CHROMATE OF POTASH dissolves in the liquid, whilst the PEROXIDE OF IRON remains behind.

3. PROTOXIDE OR OXIDE OF IRON. The colour of this oxide is black; its hydrate is white, but when moist absorbs oxygen, and is converted into the peroxide. The salts of the protoxide are green, but their solutions exhibit this colour only when very concentrated. They turn blue litmus paper red, and are decomposed at a red heat. When dissolved, they absorb oxygen from the air, the oxide being thereby converted into peroxide, which in a neutral solution is deposited as a yellow basic salt. Oxidising agents, such as chlorine and nitric acid, effect this conversion more speedily.

Ferrocyanide of potassium produces, in solutions of protoxide of iron, a white precipitate of FERROCYANIDE OF IRON AND POTASSIUM (2 Cfy, K, 3 Fe), which speedily becomes *blue* by absorbing oxygen from the air.

Ferricyanide of potassium produces a beautiful blue-coloured precipitate of FERRICYANIDE OF IRON (2 Cfy + 2 Fe), which is

insoluble in hydrochloric acid, but is decomposed with precipitation of oxide of iron by potash.

4. PEROXIDE or SESQUIOXIDE OF IRON. This oxide, which is abundantly spread through nature, has received from mineralogists the name of HÆMATITE. It is of a brownish-red colour, and is well known as rust of iron. Its salts usually possess a reddish-yellow colour. The soluble neutral salts of mineral acids redden litmus paper, and are decomposed by heat.

Soluble SULPHOCYANIDES give to neutral and acid solutions of persalts of iron an intense blood-red colour.

Ferrocyanide of potassium throws down, even from highly dilute solutions, a beautiful blue precipitate of FERROCYANIDE OF IRON (Prussian blue, Fe_4, Cfy_3), which is insoluble in acids, but is decomposed by potash.

Ferricyanide of potassium deepens the colour of the solution to a ruddy-brown, if much peroxide of iron be present; if only small traces be present, it renders the solution green. In no case does a solution of peroxide of iron yield a precipitate with this reagent.

The ferrocyanides are decomposed by the mineral acids, forming green-coloured solutions. In testing, therefore, for iron in acid solutions, it is necessary to avoid this error by the previous addition of an alkaline acetate.

5. OXIDE OF ZINC. The colour of this oxide is white, but becomes yellow on being heated, regaining its original colour on cooling. The salts of zinc are colourless. The soluble ones redden litmus paper, and are decomposed by heat. The principal minerals of this metal are the anhydrous CARBONATE (*calamine* ZnO, CO_2) and the SULPHIDE (*zinc blende* ZnS).

When compounds of zinc, mixed with *carbonate of soda*, are subjected upon a charcoal support to the inner blowpipe flame,

metallic zinc is produced, which volatilises, and on passing through the oxidising flame becomes again converted into oxide. The charcoal support becomes incrusted with this oxide, which is of a yellow colour while hot, and turns white on cooling.

If a compound of zinc be moistened with *protonitrate of cobalt* and exposed to the outer blowpipe flame, a mass of beautiful GREEN COLOUR will be produced.

6. PROTOXIDE OF MANGANESE. Numerous oxides of manganese exist as natural productions, and a still larger number can be formed artificially. The only one treated of in this work is the first or lowest compound of oxygen with manganese. All the others are reduced to this state by adding to their solutions hydrosulphuric acid or any other reducing agent. This oxide is of a greenish-grey colour, and its hydrate is white. Both, however, turn brown when exposed to the air, being converted into higher oxides. Its salts are of a pale rose colour, and are decomposed by heat. The most abundant source of manganese is the PEROXIDE, which exists in nature under a variety of forms.

The smallest quantity of manganese can be detected in any of its compounds, by fusing them in conjunction with *carbonate of soda* and a small quantity of *nitrate of potash*, upon platinum wire, in the outer blowpipe flame; MANGANATE OF SODA (Na O, Mn O$_3$), which is of a bluish-green colour, being produced.

7. OXIDE OF NICKEL. The colour of this oxide is grey, its hydrate is green. Its salts likewise exhibit this latter colour, except when anhydrous; in this state they are mostly yellow. The soluble salts redden litmus paper, and are decomposed at a red heat. The principal minerals of this metal are the

ARSENICAL NICKEL (Ni As) and the NICKEL GLANCE (Ni S₂+
Ni As₂).

Cyanide of potassium throws down from solutions of nickel, a
yellowish-green precipitate of CYANIDE OF NICKEL (Ni Cy)
which re-dissolves in an excess of the precipitant, a double salt
of CYANIDE OF NICKEL and CYANIDE OF POTASSIUM (Ni Cy +
KCy) being formed. On the addition of *hydrochloric* or *sul-
phuric acid* to a solution of this double salt, the CYANIDE OF
NICKEL is re-precipitated, whilst the cyanide of potassium is
decomposed, hydrocyanic acid being evolved.

Oxide of nickel and its compounds give to beads of *borax* in
the outer blowpipe flame a REDDISH-YELLOW tint. The addi-
tion of nitre changes the colour to a BLUISH-PURPLE.

8. OXIDE OF COBALT. The colour of this oxide is grey, its
hydrate being pale red. The salts of cobalt, when anhydrous, are
blue, in the hydrated state they are red. Their solutions exhibit
this colour even when very dilute. The soluble salts redden
litmus paper, and are decomposed by heat. The principal
mineral of this metal is the BRIGHT WHITE COBALT (Co As₂ +
Co S₂).

Cyanide of potassium produces in solutions of cobalt a brown-
ish-yellow precipitate of CYANIDE OF COBALT (Co Cy), which
re-dissolves in an excess of the precipitant; from this solution
it is not re-precipitated on the addition of acids.

The compounds of cobalt impart to beads of *borax*, in both
flames of the blowpipe, a beautiful BLUE COLOUR, which is a
very characteristic test for this oxide.

The following SALTS *being insoluble in Neutral and Alkaline Solutions, are precipitated along with the members of the Third Group when the Filtrate from the Sulphuretted Hydrogen Precipitate is neutralised by Ammonia.*[9]

PHOSPHATE OF ALUMINA, THE PHOSPHATES OF IRON AND THE PHOSPHATES AND OXALATES OF THE ALKALINE EARTHS WITH THE EXCEPTION OF OXALATE OF MAGNESIA.

PHOSPHATE OF ALUMINA behaves in the same way with reagents as pure alumina, with this exception, that it is insoluble in *acetic acid* whilst pure alumina is soluble. The presence of phosphoric acid when combined with alumina may be detected by the following method. After having *dissolved* the alumina compound in a small quantity of hydrochloric acid, *tartaric acid* must be added and then *ammonia* in *excess*. If on the addition of *sulphate of magnesia* to this solution a precipitate be formed, PHOSPHORIC ACID is present. When the quantity of acid present is small, the precipitate will not appear until after the lapse of some time; in all cases the formation of the precipitate is much promoted by agitation.

PHOSPHATE OF IRON behaves in the same way with reagents as the peroxide, with this exception, that it is insoluble in *acetic acid* in which reagent the latter is soluble. *Sulphide of ammonium* decomposes PHOSPHATE OF IRON, precipitating the metal in the state of sulphide whilst the acid remains in solution in combination with the ammonia. The phosphoric acid is therefore sought for in the filtrate and not in the precipitate, when sulphide of

[9] The student will do well to omit this section of the group until he has had some practice in detecting the more simple combinations of acid and base.

ammonium has been employed as the precipitating reagent. The·
same method may be employed for the detection of phosphoric
acid when combined with iron, as is employed when this acid is
in combination with alumina.

PHOSPHATE OF LIME (bone earth 3 CaO, PO₅) is soluble in
acetic acid. This salt may be decomposed in several ways.
The following are those which are most applicable in qualitative
analysis.   1. Dissolve the phosphate in a small quantity of
hydrochloric acid; add to the solution *acetate of potash* and
after that a few drops of *perchloride of iron*. PHOSPHATE OF IRON
will be precipitated, whilst the LIME will remain in solution along
with the excess of the perchloride of iron employed.   To detect
the LIME, throw down the iron by sulphide of ammonium and
add to the filtrate *oxalic acid*.   If a precipitate be produced
lime is present.   2. Dissolve the phosphate in a small quantity
of *nitric acid*, add to this solution *protonitrate of mercury* and
then *ammonia* slightly in excess ; PHOSPHATE OF MERCURY along
with the excess of OXIDE OF MERCURY will be precipitated
whilst the LIME will remain in solution, from which solution it will
be thrown down on the addition of *oxalic acid*.   Boil the mixed
precipitate of phosphate of mercury and oxide of mercury in
sulphide of ammonium ; filter, and to the filtrate add *chloride of
ammonium* and *sulphate of magnesia :* if a precipitate be produced
it proves the presence of phosphoric acid.   The above remarks
upon PHOSPHATE OF LIME will apply to the corresponding salt
of BARYTA, STRONTIA and MAGNESIA.

OXALATE OF LIME is insoluble in *acetic acid*.   By ignition
this salt, like all the other oxalates, is decomposed, a carbonate
being left.   To separate the oxalic acid from the lime, add to a
nitric solution of this salt *protonitrate of mercury*.   OXALATE

OF MERCURY will be precipitated, whilst the lime in the state of nitrate will remain in solution along with the excess of protonitrate of mercury employed. To detect the LIME, precipitate the mercury by ammonia and add to the filtrate *oxalic acid*. OXALATE OF MERCURY is decomposed by boiling it in *sulphide of ammonium*, the metal being precipitated as sulphide whilst the acid remains in combination with ammonia, in which solution it may be detected on the addition of any soluble *lime salt*. The above remarks will apply to the corresponding SALT OF BARYTA and STRONTIA.

·When the insoluble salts contained in this section are to be looked for, the filtrate, from the hydrosulphuric acid precipitate, after being boiled to expel the excess of that gas, must be rendered alkaline by *ammonia*, and the precipitate produced examined according to TABLE V, whilst the ZINC, MANGANESE, NICKEL, and COBALT must be thrown down from the ammoniacal filtrate by *sulphide of ammonium*.

TABLE V.

PRECIPITATE PRODUCED BY AMMONIA IN THE HYDROSULPHURIC ACID FILTRATE.——Add an excess of Caustic Soda in the cold.

FILTRATE
SESQUIOXIDE of CHROMIUM; ALUMINA; PHOSPHATE of ALUMINA. Boil for some time.

- **FILTRATE** — ALUMINA; PHOSPHATE of ALUMINA. Add Acetic Acid in excess.
  - **FILTRATE** — ALUMINA; add Phosphate of Soda.
    - **PRECIPITATE** — PHOSPHATE of ALUMINA.
  - **PRECIPITATE** — PHOSPHATE of ALUMINA.
- **PRECIPITATE** — SESQUIOXIDE of CHROMIUM.

PRECIPITATE
PEROXIDE of IRON, PERPHOSPHATE of IRON, AND WHEN IN COMBINATION WITH OXALIC OR PHOSPHORIC ACIDS, BARYTA, STRONTIA, LIME; ALSO MAGNESIA, WHEN IN COMBINATION WITH PHOSPHORIC ACID.
Dissolve in Hydrochloric Acid, then add Tartaric Acid, and finally Ammonia in excess.

- **FILTRATE** — PERCHLORIDE of IRON; PERPHOSPHATE of IRON. Divide the solution into two parts.
  - *To one part add Acetic Acid, until the solution possesses an acid reaction, then add Ferrocyanide of Potassium.*
    - *If a blue precipitate is formed, it shows the presence of IRON.*
  - *If iron has been found, add to the other part Chloride of Ammonium and Sulphate of Magnesia.*
    - *If a precipitate is formed after agitating the fluid, and allowing it to stand for some time, it shows the presence of PHOSPHORIC ACID.*

  NOTE.—To ascertain whether there was any Iron, uncombined with Phosphoric Acid, add to the original solution Acetate of Soda; filter, and to the filtrate add Ferrocyanide of Potassium. If a blue precipitate is formed, it proves that all the iron did not exist as phosphate.

- **PRECIPITATE** — The PHOSPHATES and OXALATES of the ALKALINE EARTHS. Free the Precipitate completely from the hydrochloric acid by washing. Dissolve in Nitric Acid, and add protonitrate of Mercury.
  - **FILTRATE** — BARYTA, STRONTIA, or LIME, *originally in combination with* OXALIC ACID *and the* PHOSPHATES of the ALKALINE EARTHS, *along with the excess protonitrate of Mercury.* Add Ammonia slightly in excess.
    - *Filtrate* BARYTA, STRONTIA, LIME, and MAGNESIA. *Examine the filtrate for the Alkaline Earths, according to the method already given.*
    - *Precipitate* PHOSPHATE OF MERCURY *along with the excess of Oxide of Mercury. Boil the precipitate in Sulphide of Ammonium; filter, and to the filtrate add Chloride of Ammonium and Sulphate of Magnesia. If a Precipitate is formed after agitating the liquid, and allowing it to stand for some time, it proves the presence of* PHOSPHORIC ACID.
  - **PRECIPITATE** — OXALATE of MERCURY. *Confirm the presence of* Oxalic Acid, *by boiling the Mercury precipitate in Sulphide of Ammonium; filter, and to the filtrate add Sulphate of Lime. If a precipitate is formed which is insoluble in acetic acid, it proves the presence of* OXALIC ACID.

The following precautions are to be attended to in the analysis of this section. Before dissolving the precipitate produced by ammonia, it must be completely freed by washing from all trace of that reagent. Frequently a small precipitate will appear after boiling the caustic soda solution, when oxide of chromium is absent; the presence of this member must therefore in all cases be confirmed by other tests. Alumina and phosphate of alumina are sometimes overlooked by the operator from his neglecting to add acetic acid in excess. The precipitate produced by caustic soda, after being well washed, should be dissolved in as small a quantity of hydrochloric acid as possible, to which solution a moderate quantity of tartaric acid should be afterwards added, and finally ammonia in excess; the solution ought, after the addition of these reagents, to be well agitated, and time allowed for the separation of the precipitate. In testing for phosphoric acid in the ammoniacal solution, a precipitate will frequently be formed on the addition of sulphate of magnesia when phosphoric acid is absent. To distinguish the phosphate precipitate from this, the precipitate produced ought to be dissolved in tartaric acid, and ammonia added in excess. If a precipitate again appears, after agitating the liquid and allowing it to stand, it must be due to the presence of phosphoric acid. The precipitate produced by ammonia in the tartaric-acid solution must be washed until all trace of hydrochloric acid is removed, before dissolving it in dilute nitric acid. A slight turbidness will generally be formed on the addition of nitrate of mercury to the nitric-acid solution, even in the absence of oxalic acid, owing to the nitric acid containing a slight trace of chlorine.

When substances are examined, the nature of which is a sufficient proof that the phosphate and oxalate of baryta and strontia must be absent, as in the case of *natural and artificial manures, soils,* etc., a simpler method may be employed for separating OXALATE OF LIME, PHOSPHATE OF LIME, and PHOS-

PHATE OF MAGNESIA from each other, than the one given in the Table. After separating them from all the other substances, dissolve the precipitate produced by ammonia in the tartaric-acid solution, in a small quantity of hydrochloric acid, and to this solution add *acetate of soda* in excess. OXALATE OF LIME, if present, will be precipitated, whilst the phosphates of lime and magnesia will remain in solution. Filter, and to the filtrate add *oxalic acid,* which will precipitate the LIME existing originally as PHOSPHATE in the state of OXALATE. PHOSPHATE OF MAGNESIA will be precipitated from this filtrate on the addition of *ammonia* in excess.

FOURTH GROUP.

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

All the members of this group possess, in a greater or less degree, the character of acids. Arsenious and arsenic acids are soluble in water, the rest are insoluble, not only in water, but likewise in nitric acid. They are all readily soluble in concentrated hydrochloric acid. In the state of sulphides they behave with different reagents in the following manner: the protosulphide and bisulphide of tin, with the sulphide of antimony, are insoluble in nitric acid, but dissolve readily in concentrated hydrochloric acid; whereas sulpharsenious and sulpharsenic acids are insoluble in hydrochloric acid, but are easily soluble in concentrated nitric acid. These different sulphides are readily dissolved by the alkalies and alkaline sulphides, from which solutions they are again precipitated unaltered on the additon of any acid in excess. The sulphides of gold and platinum are insoluble both in hydro-

§ 3

chloric and nitric acid, but are easily soluble in aqua regia (a mixture of the two acids). They also dissolve with difficulty in the alkalies and alkaline sulphides.

As gold and platinum are seldom met with in ordinary analysis, and as many of their properties render them perfectly distinct from the rest of the members, it has been found of advantage to subdivide the group. The first division comprises the OXIDES of TIN, ANTIMONY, and ARSENIC; the second the OXIDES of GOLD and PLATINUM.

FIRST DIVISION.

The precipitate produced by the general reagent, after having been well washed, must be treated with a dilute solution of *carbonate of ammonia.* Both SULPHIDES of ARSENIC, being soluble in that reagent, will pass into solution, whilst the SULPHIDES of ANTIMONY and TIN, being insoluble, will remain undissolved. The solution must be separated from the insoluble sulphides by filtration. If a *yellow precipitate* be produced on the addition of *hydrochloric acid* to the filtrate, one or both SULPHIDES of ARSENIC must be present. The substance which was insoluble in carbonate of ammonia, after having been well dried, must be mixed with three parts of *nitrate of ammonia,*[10] and the mixture projected in small portions into a porcelain crucible containing two parts of nitrate of ammonia in a state of liquefaction. After all fuming has ceased, the residue should be gently ignited for a short time and then allowed to cool. The residue must be subsequently heated with a saturated solution of *tartaric acid.* If complete solution takes place, OXIDE OF ANTIMONY only can be present. If a portion remain

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[10] When the amount of precipitate is so small that little or nothing can be detached from the filter, the precipitate as well as the filter, after having been cut into small pieces, must be mixed up with the nitrate of ammonia, and subsequently projected into the crucible

undissolved by the tartaric acid, it indicates the probable pre-
sence of TIN. When complete solution does not take place,
the liquid must be filtered, and to the filtrate must be added
hydrochloric acid and subsequently *hydrosulphuric acid*. If an
orange-red coloured precipitate be formed, OXIDE OF ANTIMONY
is present. The substance insoluble in tartaric acid must be
examined for tin by fusing it with *carbonate of soda* and *cyanide
of potassium*, as directed under the special remarks of the per-
oxide of that metal.

*The following precautions must be attended to in analysing this
group.* The mixed precipitate must be agitated in a test-tube
for a few seconds only, with a dilute solution of carbonate of
ammonia,[11] and then quickly filtered. When only a slight trace
of arsenic is present, the carbonate of ammonia solution, on the
addition of hydrochloric acid, will simply assume a slight yellow
colour, no distinct precipitate being formed. When arsenic is
present, the original solution must be examined to ascertain in
what state it exists, whether as arsenious or arsenic acids.

SPECIAL REMARKS.

OXIDE OF TIN (Sn O). This oxide is black, its hydrate being
white. Nitric acid and nitrates in a state of fusion convert it
into the peroxide. The protosalts of tin are colourless, and are
decomposed by heat. The soluble neutral salts redden litmus
paper, and are decomposed, in the presence of much water, into
soluble acid, and insoluble basic salts. The addition of water
therefore to the protosalts of tin produces a milkiness which dis-

[11] According to Blyth, the dilute solution must be prepared by dis-
solving one ounce of solid carbonate of ammonia in twelve fluid ounces of
water. *Vid.* Blyth's Outlines of Chemical Analysis.

appears on the addition of hydrochloric acid.   Sulphide of tin
(SnS), is of a dark-brown colour.

The *alkalies* and their *carbonates* throw down from solutions
of this oxide the HYDRATE (SnO, HO), which is easily soluble in
solutions of the fixed alkalies, but insoluble in ammonia and the
alkaline carbonates.   .

All protosalts of tin are powerful reducing agents, from the
great affinity they have for an additional quantity of oxygen.
Many metallic oxides, such as the oxides of gold, silver, and
mercury, are reduced to the metallic state in their presence, whilst
other oxides, such as peroxide of iron and oxide of copper, are
reduced to a lower degree of oxidation.

Perchloride of gold produces in solutions of protosalts of tin,
containing a small quantity of free nitric acid, a beautiful PURPLE
PRECIPITATE (purple of cassius).

PEROXIDE OF TIN (SnO_2).   This oxide is of a light straw
colour; its hydrate is white.   Nitric acid converts metallic tin
and its protoxide into the hydrated peroxide, which is deposited
in the form of a white powder.   A peroxide of tin is likewise
precipitated from persalts of tin, on the addition of caustic soda
to their solutions.   These hydrates, although they have the same
composition, are perfectly distinct in their chemical properties.
The one formed by the action of nitric acid is insoluble, both
in acids and the fixed alkalies; the other is soluble in these
reagents.   These modifications are capable of being transformed
into each other.   The insoluble one is rendered soluble by fusion
with the carbonated alkalies; the soluble is converted into the
insoluble form by ignition.   Bisulphide of tin (SnS_2), is of a
yellow colour.   The usual mineral of this metal is the peroxide
(*tin stone* Sn O_2).

The *alkalies* and their *carbonates* precipitate from solutions of
persalts of tin the HYDRATE, which is soluble in the fixed

caustic alkalies, but insoluble in ammonia and the alkaline carbonates.

If per- or proto-compounds of tin be mixed with equal parts of *carbonate of soda* and *cyanide of potassium*, and the mixed mass be subjected, upon a charcoal support, to the inner blowpipe flame, *ductile metallic grains of* TIN will be obtained, unaccompanied by any incrustation upon the charcoal.

OXIDE OF ANTIMONY (Sb O_3). This oxide occurs either in the form of white brilliant crystalline needles, or as a greyish-white powder, assuming the one or the other of these forms according to its mode of preparation. It fuses at a gentle red heat, and when exposed to a higher temperature volatilises un-altered. The solubility of this oxide in tartaric acid distinguishes it from the other members of the group. When fused along with nitrates, it is converted into a higher oxide (antimonic acid, Sb O_5).

Some of the salts of antimony are decomposed by ignition; some are volatilised unaltered. The soluble neutral salts redden litmus paper. When treated with a large amount of water, they are decomposed into soluble acid and insoluble basic salts. In this respect they resemble the salts of bismuth, with this exception, that the insoluble basic salts of antimony dissolve in tartaric acid, whilst the corresponding salts of bismuth are insoluble. Sulphide of antimony (Sb S_3) is of an orange-red colour. The principal mineral of this metal is the sulphide.

The *alkalies* and their *carbonates* throw down from solutions of antimony a bulky precipitate of OXIDE OF ANTIMONY, which is soluble in the fixed caustic alkalies and the alkaline carbonates, but insoluble in ammonia.

If compounds of antimony, mixed with *carbonate of soda* and *cyanide of potassium*, be exposed, upon a charcoal support, to the

reducing flame of the blowpipe, *brittle grains* of *metallic antimony* will be formed, accompanied with a white incrustation on the charcoal.

ARSENIOUS ACID (AsO_3). There are two varieties of this acid which are perfectly distinct in their physical characters and chemical properties. One, from its appearance, is termed the vitreous, and the other the milky variety; when heated, they volatilise in white inodorous fumes. Both kinds are more easily soluble in hot than in cold water. This acid is exceedingly poisonous, and being altogether inodorous, almost destitute of taste, and readily obtainable, is frequently employed as a poison. The best antidote is the moist and well-washed hydrated sesqui-oxide of iron.

This acid unites with bases, forming a class of salts called arsenites, which are all insoluble in water, with the exception of the alkaline arsenites. Sulpharsenious acid (AsS_3) is yellow, and soluble, not only in the alkalies and alkaline sulphides, but like-wise in the alkaline carbonates.

Nitrate of silver produces in neutral solutions of the arsenites a yellow precipitate of ARSENITE OF SILVER ($2 AgO, AsO_3$), soluble in nitric acid and ammonia.

Sulphate of copper produces in neutral solutions of the arsenites a yellowish-green precipitate of ARSENITE OF COP-PER ($2 CuO, AsO_3$).

If to a solution of arsenious acid, or an arsenite, *caustic potash* be added in excess, and a few drops only of a dilute solution of *sulphate of copper*, and the liquid subsequently boiled, a red precipitate of *suboxide of copper* (Cu_2O) will fall down, whilst the solution will contain ARSENIATE OF POTASH. This test is particularly appli-cable in distinguishing arsenious from arsenic acid. It cannot be employed with safety as a direct means for detecting arsenious

acid, as many organic substances possess the property of reducing protoxide of copper to the state of suboxide.

If dry arsenious acid be mixed with a little solid *acetate of potash* and *caustic potash*, and subsequently heated in a glass tube, a substance called ALCARSINE (Oxide of cacodyl $C_4 H_6 As, O$) will be formed, which may be detected by its characteristic and disagreeable odour.

Metallic copper, when boiled with an acidified mixture containing arsenious acid, becomes coated with a steel-grey crust of metallic arsenic. As many other metallic oxides are under the same circumstances reduced to their metallic state, it is necessary to submit the crust to further examination.

Antimony and arsenic, in their *nascent* state, combine with hydrogen, forming inflammable gaseous compounds which burn with a bluish-white flame; water and oxide of antimony in the one case, and water and arsenious acid in the other, being formed. When free access of air is prevented, the hydrogen only is oxidized, metallic antimony and arsenic being deposited in a finely divided state. By adding, therefore, metallic zinc, strong sulphuric acid and water to arsenious acid, or to an arsenite in a flask provided with an evolution tube drawn out at the point, the zinc oxidises at the expense of the water and arsenious acid, whilst the metallic arsenic combines with the liberated hydrogen, forming arseniuretted hydrogen ($As H_3$). Before lighting the gas, a reasonable time should be allowed for the expulsion of atmospheric air. To obtain the metallic mirrors, a piece of porcelain should be depressed upon the flame, the mirrors produced by arsenic being of a brown or steel-grey colour soluble in nitric acid. Oxide of antimony and its compounds form, under similar circumstances, antimonuretted hydrogen (SbH_3), which, when burnt in a limited quantity of air, deposits metallic antimony as a black spot without metallic lustre. It would be impossible to decide from the appearance of the mirror whether both

metals were present, or, if one only, which of the two.   To obtain
positive evidence the following method ought to be employed.   The
central part of the glass tube (which ought to be free from lead)
through which the gas passes should be heated to redness; this
effects the decomposition of the gaseous compound, the metal
being deposited in a finely divided state.   A feeble stream of dry
hydrosulphuric-acid gas must now be transmitted through the
tube, the metallic mirror being heated from its outward to its
inward extremity.   If only arsenic be present, the yellow sulphide
of that metal will be formed.   If antimony only be present, the
orange or black sulphide of antimony will be produced; but if
both metals be present, the corresponding sulphides will be
formed; and the sulphide of arsenic being the more volatile of the
two, will be the further removed from the flame.   A stream of
dry hydrochloric acid gas must be passed through the tube without
the application of heat, by this means the sulphide of antimony
will be converted into volatile chloride, which will entirely dis-
appear, whilst the sulphide of arsenic will remain unaltered, and
may be distinguished from any sulphur which may have separated,
by dissolving readily in ammonia.

ARSENIC ACID (As O_5). This oxide is white; it is deliquescent
and strongly acid, forming with bases a class of salts called arse-
niates which are all insoluble in water, with the exception of the
alkaline arseniates.   It fuses at a low red heat without under-
going decomposition, but at a higher temperature is resolved into
oxygen and arsenious acid, which volatilise. Sulphurous acid, aided
by a gentle heat, reduces it likewise to this lower state of oxidation.
The metal arsenic is found in nature principally as sulphide.

Nitrate of silver produces, in neutral solutions of the
arseniates, a reddish-brown precipitate of ARSENIATE OF SILVER
(3 Ag O, As O_5), soluble in dilute nitric acid and in ammonia.

Sulphate of copper produces, in neutral solutions of the arseniates,

a greenish-blue precipitate of ARSENIATE OF COPPER (2 Cu O, HO, AsO_5).

Sulphate of magnesia, in the presence of chloride of ammonium and ammonia, produces, in solutions of the arseniates, a white precipitate of ARSENIATE OF AMMONIA AND MAGNESIA ($2 \text{ MgO, NH}_4\text{O, AsO}_5$), soluble in acids.

SECOND DIVISION.

Gold and platinum produce reactions so decisive—the former with chloride of tin and the latter with chloride of ammonium—that their presence may invariably be detected in the presence of all the other metals. The original solution may therefore in all cases be examined for these substances.

PEROXIDE OF GOLD (Au O_2). This oxide is of a deep brown colour, its hydrate being somewhat lighter in colour. They both dissolve readily in hydrochloric acid, but are insoluble in dilute oxygen acids. Persulphide of gold (Au S_2) is black.

Protochloride of Tin produces, in solutions of gold containing a little free nitric acid, a beautiful PURPLE PRECIPITATE, insoluble in hydrochloric acid.

PEROXIDE OF PLATINUM (PtO_2). This oxide is of a deep brown colour, its hydrate is reddish-brown. Both the oxide and its hydrate dissolve readily in hydrochloric acid, but with difficulty in the oxygen acids. Persulphide of platinum (Pt S_2) is of a blackish-brown colour.

Chloride of potassium or *ammonium* produces, in solutions of platinum, yellow crystalline precipitates of POTASSIO-CHLORIDE OF PLATINUM and AMMONIO-CHLORIDE OF PLATINUM. The presence of free hydrochloric acid promotes the formation of these precipitates.

FIFTH GROUP.

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

The oxides of this group are insoluble in water. They all
combine with nitric acid, forming soluble salts ; many of them
likewise form, with hydrochloric and sulphuric acid, soluble
chlorides and sulphates ; but a few give, particularly with the
former acid, insoluble salts. This character permits of a sub-
division of the group, which is fully exhibited under the head
of its general properties.

In the state of sulphides they are insoluble, not only in the
alkalies and alkaline sulphides, but likewise in the dilute mineral
acids. They are therefore thrown down, both from their neutral
acid and alkaline solutions, by sulphuretted hydrogen. They
are all decomposed and rendered soluble in boiling concentrated
nitric acid, with the exception of PERSULPHIDE OF MERCURY.

The metallic radicals of these oxides possess the following
properties :—*Cadmium* decomposes water at a red heat, and at
common temperatures in contact with strong acids. *Copper*,
lead, and *bismuth* absorb oxygen at a red heat; their oxides
are therefore not decomposed by heat alone. They do not
decompose water but at a very elevated temperature, and even
then very feebly. Neither do they decompose it in the presence
of strong acids or bases. The affinity of *mercury* and *silver* for
oxygen is very feeble, so much so that their oxides are decom-
posed by heat alone, at a more or less elevated temperature.
These metals do not decompose water, under any circumstances ;
they have therefore no tendency to rust when exposed to the air.

This group may, as before noticed, be divided into two sections.

a. OXIDES which are precipitated by hydrochloric acid, viz.,
OXIDE OF SILVER, PROTOXIDE OF MERCURY, and OXIDE OF LEAD.

b. OXIDES which are not precipitated by hydrochloric acid, viz., PEROXIDE OF MERCURY, OXIDE OF BISMUTH, OXIDE OF CADMIUM, and OXIDE OF COPPER.

The slight solubility of chloride of lead in water renders it impossible to confine this member exclusively to the first section, a portion of the chloride, varying according to the amount of liquid present, always remaining dissolved. This is finally precipitated along with the members of the second section on the addition of hydrosulphuric acid. If attention be paid to the following facts, they will frequently remove a source of much confusion. 1. If lead has been discovered in the first section, a precipitate must always be obtained on passing hydrosulphuric acid through the filtrate, even if no other member of the group be present. 2. If only a small quantity of lead be present, hydrochloric acid may cause no precipitate, as a sufficient quantity of water may be present to dissolve the chloride formed. In this case, all the lead will be found in testing for the members of the second section.

First section. Boiling water being poured upon the precipitate produced by hydrochloric acid, will remove the CHLORIDE OF LEAD, if present, which is ascertained by *sulphuric acid* producing in the filtrate a precipitate of SULPHATE OF LEAD. If a residue remain after removing the chloride of lead by adding successively to the mixed chlorides fresh quantities of boiling water, until the last washings give on the addition of sulphuric acid no further precipitate, it proves that either chloride of silver or protochloride of mercury (calomel), or both, must be present. *Ammonia* being added to this residue dissolves the CHLORIDE OF SILVER, whilst the CHLORIDE OF MERCURY is converted into a *black* compound. To detect the CHLORIDE OF SILVER in the ammoniacal solution, *nitric acid* must be added in excess, which, by destroying the solvent, causes the CHLORIDE OF SILVER (if present), to be re-precipitated.

TABLE VI.

BEHAVIOUR OF THE MEMBERS OF THE FIRST SECTION WITH THE SPECIAL REAGENTS.

OXIDE OF LEAD (Pb O).	OXIDE OF SILVER (Ag O).	PROTOXIDE OF MERCURY (Hg_2O).
1. CHLORIDE of LEAD (Pb Cl) is difficultly soluble in cold water; it is much more soluble in boiling water. It is precipitated, by *sulphuric acid*, from its aqueous solutions, as insoluble SULPHATE of LEAD (Pb O, SO$_3$).	1. CHLORIDE of SILVER (Ag Cl) is insoluble in water.	1. PROTOCHLORIDE of MERCURY (Hg_2Cl) is insoluble in water.
2. CHLORIDE of LEAD does not become altered in the least degree by *ammonia*.	2. CHLORIDE of SILVER is easily soluble in *ammonia*. On the addition of any acid it is again precipitated from this solution.	2. PROTOCHLORIDE of MERCURY does not dissolve in *ammonia*, but becomes altered in colour, the *white chloride* being converted into a *black compound*.

BEHAVIOUR OF THE MEMBERS OF THE SECOND SECTION WITH THE SPECIAL REAGENTS.

PEROXIDE OF MERCURY. (Hg O).	OXIDE OF LEAD (Pb O).	OXIDE OF BISMUTH (Bi O$_3$).	OXIDE OF CADMIUM (Cd O).	OXIDE OF COPPER (Cu O).
1. PERSULPHIDE of MERCURY (Hg S) is *black*; it is *insoluble* in concentrated nitric acid, but is easily soluble in aqua regia.	1. SULPHIDE of LEAD is *black*; it is *soluble* in boiling concentrated nitric acid.	1. SULPHIDE of BISMUTH (Bi S$_3$) is *black*: it is *soluble* in boiling concentrated nitric acid.	1. SULPHIDE of CADMIUM is *yellow*; it is *soluble* in boiling concentrated nitric acid.	1. SULPHIDE of COPPER is *black*: it is *soluble* in boiling concentrated nitric acid.

2. Sulphate of the peroxide of mercury is decomposed, in the presence of much water, into an insoluble basic and a soluble acid salt.	2. *Sulphuric Acid* precipitates, from solutions of lead, the SULPHATE (PbO, SO₃), which is *insoluble* in water and dilute acids.	2. *Sulphuric Acid* produces no precipitate in solutions of this oxide, SULPHATE of BISMUTH being *soluble* in water.	2. *Sulphuric Acid* produces no precipitate in solutions of this oxide, the SULPHATE being *soluble* in water.	2. *Sulphuric Acid* produces no precipitate in solutions of this oxide, SULPHATE of COPPER being *soluble* in water.
3. *Ammonia*[1] produces, in solutions of peroxide of mercury, a WHITE PRECIPITATE (Hg N H₂ + Hg Cl), *insoluble* in an excess of the reagent.	3. *Ammonia* throws down, from solutions of lead, the HYDRATE (Pb O, H O), *insoluble* in an excess of the reagent.	3. *Ammonia* throws down, from solutions of bismuth, the HYDRATE, *insoluble* in an excess of the reagent.	3. *Ammonia* precipitates, from solutions of cadmium, the HYDRATE, *soluble* in an excess of the reagent.	3. *Ammonia* produces, in solutions of this oxide, a GREENISH-BLUE precipitate, which *dissolves* with a beautiful azure colour in an excess of the reagent.
4. *Carbonate of Ammonia*[2] behaves in the same way, in solutions of peroxide of mercury, as caustic ammonia.	4. *Carbonate of Ammonia* precipitates, from solutions of lead, the CARBONATE (Pb O, CO₂), *insoluble* in an excess of the reagent.	4. *Carbonate of Ammonia* throws down, from solutions of bismuth, a BASIC WHITE CARBONATE (BiO₃, CO₂), *insoluble* in an excess of the reagent.	4. *Carbonate of Ammonia* throws down, from solutions of cadmium, the CARBONATE (CdO, CO₂), *insoluble* in an excess of the reagent.	4. *Carbonate of Ammonia* behaves in the same way in solutions of copper as caustic ammonia.

[1] The fixed alkalies precipitate all the members of this group from their solutions; the hydrate of lead is difficultly soluble in an excess of the reagents; all the rest are insoluble. The precipitate produced by the fixed alkalies, in solutions of the peroxide of mercury, is the yellow hydrate, unless salts of ammonia are present; in that case the precipitate is the same as that produced by ammonia.

[2] The fixed alkaline carbonates precipitate all the members of this group from their solutions. If added to solutions of copper in the cold, they produce a basic carbonate; but if the solution is boiled, it is converted into the black oxide.

Second section. The precipitate produced by the general re-agent must be boiled in a small quantity of *concentrated nitric acid.* If it all dissolves, with the exception of a light yellow mass of sulphur, PEROXIDE OF MERCURY is absent; but if, after boiling for some time, the undissolved mass presents a black appearance, it points out the probable presence of that member. To the acid solution, after it has been filtered and evaporated nearly to dryness, so as to remove the greater part of the free acid, must be added a little water and then a few drops of *dilute sulphuric acid,* which will precipitate the LEAD as sulphate. *Ammonia* being added in excess to the filtrate throws down the BISMUTH. The ammoniacal filtrate, after being slightly acidu-lated with acetic acid, must be divided into two portions. To one portion is to be added *carbonate of ammonia,* and heat applied; by this means the CADMIUM, if present, will be pre-cipitated. COPPER is discovered, if it has not been already manifested by the blue colour of the ammoniacal solution, by *ferrocyanide of potassium* producing in the other portion of the solution a brownish-red coloured precipitate.

If a black residue remain after boiling the mixed sulphides in nitric acid, it must be collected upon a filter, to separate it from the other members, and specially examined for peroxide of mercury, by one of the two following methods:—1. Dissolve the probable persulphide of mercury in as small a quantity of *aqua regia* as possible. After nearly neutralising this solution with ammonia, place a few drops of it upon a piece of clean copper. If MERCURY be present, the surface of the copper will, after the lapse of some time, exhibit a white stain, which pre-sents a metallic lustre when rubbed, and disappears on heating. 2. The black mass, after being dried, must be mixed with three times its own weight of *carbonate of soda,* and heated in a small glass tube; mercury, if present, will sublime in the form of small metallic globules.

The following precautions must be attended to in analysing this group. The means, both for separating and detecting the members of the first section, are so simple and positive, that no rules can be laid down for the student's guidance. The difficulties, which occur in examining the second section, will be easily overcome by a little attention. Many erroneous conclusions will be formed if the simple yet necessary precaution of washing the sulphuretted hydrogen precipitate be neglected, because a small quantity of the hydrochloric acid employed to precipitate the first section being left behind, will be converted, on the addition of nitric acid, into aqua regia, which, by dissolving the persulphide of mercury, may cause that member to be overlooked; and should the mercury thus pass into solution, a compound of that metal will be precipitated on the addition of ammonia, which may be mistaken for bismuth. It is difficult to free the mass of sulphur, which separates on the addition of nitric acid, entirely from some of the undecomposed sulphides; and which, by communicating to it a black appearance, might lead to the belief that peroxide of mercury was present, even in the absence of that member. An experienced eye can generally distinguish between this mixture of undecomposed sulphide and sulphur, and persulphide of mercury, the former being light and flocculent, whilst the latter is dense and heavy. But a safe and legitimate conclusion can only be arrived at, by examining it specially for mercury. A varying amount of sulphuric acid is always formed in dissolving the sulphides in nitric acid, a portion of the lead will therefore be precipitated as sulphate, and remain behind mixed up with the substance insoluble in nitric acid; it is necessary, on this account, to examine the insoluble mass for this member, if it should not be met with in its proper place. A precipitate will be formed on the addition of ammonia to the nitric solution, if either of these reagents contain a trace of iron, but this precipitate cannot be mistaken for bismuth if a confirmatory test be applied.

SPECIAL REMARKS.

1. OXIDE OF SILVER. The colour of this oxide is brown. It is very soluble in nitric acid; it combines with ammonia, giving rise to a dangerous compound (fulminating silver). Many of the salts of silver are colourless and insoluble. The soluble ones do not affect vegetable colours, and are decomposed at a red heat. Many of them blacken on exposure to light, and they are all decomposed with the precipitation of metallic silver by many metals, such as *zinc, iron, copper*, etc., and other *reducing agents*. The principal minerals of this metal are the SULPHIDE (*silver glance* AgS), the CHLORIDE (*horn silver* AgCl), SULPHIDE OF SILVER and ARSENIC (3 Ag S + As S_3), and SULPHIDE OF SILVER and ANTIMONY (3Ag S + Sb S_3); SILVER is also met with in the metallic state. It is likewise found in small quantities in most lead and some copper ores.

When silver compounds, mixed with *carbonate of soda*, are subjected on charcoal to the inner blowpipe flame, brilliant metallic globules are produced, which are not attended with any incrustation.

2. OXIDE OF LEAD. This oxide is of a yellow or reddish-yellow colour. In commerce it frequently goes under the name of massicot, and when partially fused is called litharge. The hydrated oxide is of a white colour, and it speedily absorbs carbonic acid from the air. The best solvent, both for the oxide and its hydrate, is nitric or acetic acid. The salts of lead are frequently insoluble, and are colourless, if the constituent acids be so. The soluble neutral salts redden litmus paper, and are decomposed at a red heat. The principal minerals of this metal are the SULPHIDE (*galena* or *lead glance* PbS) and the CARBONATE (PbO, CO_2).

Chromate of potash produces, in solutions of lead, a yellow precipitate of CHROMATE OF LEAD (PbO, Cr O_3), soluble in the fixed alkalies, but insoluble in nitric acid.

When lead compounds, mixed with *carbonate of soda*, are exposed upon charcoal to the inner blowpipe flame, ductile metallic globules are formed, accompanied with an incrustation which is yellow whilst hot, but becomes paler on cooling.

3. PROTOXIDE or SUBOXIDE OF MERCURY. This oxide is black; it is decomposed by heat, the mercury volatilising in the metallic state. It forms no hydrate. The salts of the protoxide of mercury, when ignited, volatilise either with or without decomposition. The soluble neutral ones redden litmus paper, some of them are decomposed by much water into soluble acid and insoluble basic salts. The colour of the neutral salts is white, the colour of the basic ones is yellow. They are reduced, like the silver salts, by many metals, such as *zinc, iron, copper,* etc., and by other reducing agents.

4. PEROXIDE or OXIDE OF MERCURY. This oxide is obtained in the form of a crystalline mass, nearly black whilst hot (at a red heat it is decomposed and entirely volatilised) but of a light red when cold. Its hydrate is yellow. Both the oxide and its hydrate are soluble in hydrochloric and nitric acid. The salts of the peroxide of mercury, when ignited, volatilise either with or without decomposition. The soluble neutral ones redden litmus paper. The sulphate and nitrate are decomposed in the presence of much water into soluble acid and insoluble basic salts. The metals and other reducing agents which decompose the protosalts, act in a similar manner upon the persalts of this metal.

These two oxides differ not only in colour, but likewise in their behaviour with alkalies and hydrochloric acid; the latter reagent is especially applicable for separating them when present in the same solution; protochloride of mercury (*calomel*) being insoluble, whilst the perchloride (*corrosive sublimate*) is soluble.

4

The characteristic tests for mercurial compounds have been given, when treating upon the detection of persulphide of mercury. The chief mineral of this metal is the PERSULPHIDE (*cinnabar*); it is likewise met with in the metallic state.

5. OXIDE OF BISMUTH. This oxide is of a yellow colour; when heated, it acquires, for the time, a deeper tint; it fuses at a red heat. Its hydrate is white. They are both readily soluble in the dilute mineral acids. Most of the salts of bismuth are decomposed at a red heat. They are colourless, provided the constituent acid be so. The soluble neutral salts redden litmus paper; and one distinguishing character which they possess is that of being decomposed by water into soluble acid and insoluble basic salts. This property is exhibited in the most decided manner by the chloride. To employ it as a confirmatory test, dissolve the precipitate in a small quantity of hydrochloric acid, evaporate nearly to dryness, and pour this solution into a large quantity of water. If bismuth be present, a milky turbidness will be produced. This metal is found principally in the native state.

Chromate of potash throws down from solutions of bismuth the YELLOW CHROMATE. This salt differs from the corresponding one of lead by its solubility in dilute nitric acid, and its insolubility in potash.

When compounds of bismuth, mixed with *carbonate of soda,* are exposed on charcoal to the inner blowpipe flame, brittle metallic globules are obtained, attended with a yellow incrustation of oxide of bismuth.

6. OXIDE OF CADMIUM. This oxide is of a brown or yellowish-brown colour: its hydrate is white. They are both easily soluble in the dilute mineral acids. The salts of cadmium are colourless, provided the constituent acid be so. Most of

them are soluble in water. The soluble neutral ones redden litmus paper, and are decomposed at a red heat. This metal occurs only in zinc ores. It is found as SULPHIDE in zinc blende, and as OXIDE or CARBONATE in calamine.

When compounds of cadmium, mixed with *carbonate of soda* or other reducing agents, are exposed on charcoal to the inner blowpipe flame, the charcoal becomes covered with a yellow or reddish-yellow incrustation of oxide of cadmium.

7. OXIDE OF COPPER. This oxide is black; its hydrate is of a light blue colour. They are both readily soluble in the dilute mineral acids. Most of the salts of this metal are soluble in water. The soluble ones redden litmus paper, and are decomposed at a red heat. In their anhydrous state the salts are white; in their hydrated state they are of a blue or greenish-blue colour, which their solutions exhibit, even when much diluted.

This metal is sometimes found in the native state, but it chiefly occurs in combination with sulphide of iron, constituting the COPPER PYRITES ($Cu_2S+Fe_2S_3$), and in BLUE COPPER ORE or MALACHITE ($2\ CuO,\ CO_2+HO$).

Ferrocyanide of potassium throws down, even from dilute solutions of copper, a reddish-brown precipitate of FERRO-CYANIDE OF COPPER (Cu, Cfy), which is insoluble in dilute acids, but is decomposed by the fixed alkalies.

If bright *metallic iron* be introduced into a solution of a salt of copper, it becomes coated with a red deposit of that metal, provided the solution be neutral or only very slightly acid.

When any of the compounds of copper, mixed with *carbonate of soda*, are exposed on a charcoal support to the inner blowpipe flame, METALLIC COPPER is obtained, unaccompanied with any incrustation on the charcoal.

CHAPTER V.

THE GENERAL PROPERTIES OF THE ACIDS.

ALL acids belong to one of two grand classes, which are distinguished by the terms *Organic* and *Inorganic*.

The striking characteristic of the organic class of acids is the separation of charcoal, which attends their decomposition by heat, along with the conversion of the bases, with which they were combined (if alkalies or alkaline earths), into carbonates.

Acids do not admit of that accurate classification into groups, as is the case with bases, many of them being members of more than one group.

INORGANIC ACIDS.

The inorganic acids treated of in the present work are divided into six groups.

First Group. The acids in this division are not only gaseous in their free state, but their affinity for bases is likewise feeble; their salts are therefore decomposed by most acids, the decomposition being attended with *effervescence*, owing to the liberated acid assuming the gaseous state. On this account they are always discovered at the very commencement of an analysis; for an evolution of gas must take place when hydrochloric acid is added to the substance under examination, if these acids are present. The evolved gas must be examined: 1, By the smell; 2, by paper moistened with a solution of acetate of lead; 3, by placing the thumb on the mouth of the test-tube, so that the gas may accumulate, and finally decanting it (taking care not to

allow any of the liquid to pass over along with it), into a another test-tube half filled with *lime water*.   If, on agitating the liquid, a precipitate be formed, CARBONIC ACID is present.   The special properties just alluded to will be found detailed in the respective paragraphs of these acids.

Positive proof will thus be afforded of the presence or absence of carbonic and hydrosulphuric acid.   Hydrocyanic acid may, especially in the presence of much hydrosulphuric acid, be overlooked in this way.   The methods to be employed for its detection in all cases will be afterwards stated.

Second Group.   The acids contained in this group are detected in testing for the bases.   ARSENIOUS and ARSENIC ACID, being precipitated by hydrosulphuric acid, are classed amongst the bases; whilst the remaining acid is reduced to a lower state of oxidation, viz., oxide of chromium, which forms a part of the third group of bases.   The change of colour attending this decomposition is so characteristic, that it cannot be overlooked by the most inexperienced student.   The only thing which can cause the least difficulty or perplexity is the mistaking a green solution with a light-coloured precipitate suspended in it for a green precipitate.

Third Group.   It will be seen by referring to the Table that some of the acids already noticed form a part of this group. The examination is commenced by adding to a portion of the original solution *chloride of barium;* if a precipitate be formed which is not entirely soluble in hydrochloric acid, SULPHURIC ACID is present; filter off from the insoluble sulphate of baryta, and to the filtrate add ammonia; if no precipitate ensue, the other acids (boracic acid excepted) in the group cannot be present.   Borate of baryta is soluble in ammoniacal salts, from which solution it is not precipitated on the addition of ammonia.

Arseniate and arsenite of baryta are likewise soluble in ammoniacal salts, from which solutions ammonia fails to precipitate them, but their presence or absence will have been determined already. If any base is present, which is precipitated by ammonia, it must be removed before we can employ the alkali for pointing out whether any other acid is present but sulphuric.

All the baryta salts mentioned in the Table are colourless, with the exception of the CHROMATE, which is of a *pale yellow colour*.

The following precautions must be attended to in examining for this group of acids. The first thing which claims attention is the state of the solution, viz., whether it be acid, alkaline, or neutral. When it is acid, ammonia must be added until it is slightly alkaline; should this cause a precipitate, filter off, and to the filtrate add chloride of barium; if no precipitate ensue on the addition of ammonia, add at once the baryta salt. Should the solution be alkaline, the alkalinity proceeding from one of the fixed alkalies, it would be better to neutralise with hydrochloric acid before adding the chloride of barium. Nitrate of baryta must be substituted for chloride of barium, and the precipitate produced be digested with nitric acid, when lead, silver, or protoxide of mercury are present. The precipitate must not be digested in undiluted acids, because chloride of barium and nitrate of baryta are insoluble in concentrated acids, and would therefore separate from the solution. When carbonic acid is present in the solution, it is better to get rid of it before adding the baryta salt; this is effected by adding to the solution hydrochloric acid, and boiling for a short time; when all the acid has been removed add ammonia to neutralise the solution, and finally the baryta salt.

Fourth Group. This group is merely a section of the last. The examination is commenced by adding to a portion of the

original solution *chloride of calcium;* the precipitate produced by this reagent after being collected upon a filter and washed, must be digested with acetic acid. If complete solution ensue, HYDROFLUORIC ACID and OXALIC ACID are both absent. If the precipitate does not dissolve or at least not entirely, filter, and to the filtrate add ammonia. If a precipitate be formed it points out the probable presence of PHOSPHORIC ACID; should no precipitate be formed that acid must be absent, but BORACIC ACID may still be present, because borate of lime, like borate of baryta, is soluble in ammoniacal salts. A special examination must therefore be made in all cases for boracic acid. Hydrochloric acid must be poured upon the washed precipitate which was insoluble in acetic acid. If it all dissolves, it proves the presence of OXALIC ACID and the absence of HYDROFLUORIC ACID. If the precipitate be not entirely soluble the latter acid must be present; the presence of the former is proved by ammonia producing a precipitate in the filtered liquid.

The precautions to be attended to are very similar to those given in the third group. The same plan must be pursued when the solution is acid or alkaline. Nitrate of lime must also be employed when silver, lead, or protoxide of mercury are present. When carbonic acid is present it is better to get rid of it before adding the reagent. When much sulphuric acid is present, the solution ought to be diluted with water before adding the chloride of calcium, to prevent any sulphate of lime from precipitating. Arsenious and arsenic acids are precipitated by chloride of calcium from neutral solutions free from ammoniacal salts. To avoid the precipitation of these lime salts, add chloride of ammonium along with the chloride of calcium, when these acids are present.

Fifth Group. *Nitrate of silver* precipitates, along with most of

the acids previously noticed, the non-metallic elements CHLORINE, BROMINE, IODINE, and the compound body CYANOGEN from their combinations with hydrogen and the metallic radicals.

To a portion of the original solution must be added *nitrate of silver*. If a precipitate be produced it must be digested with nitric acid, which will dissolve all the silver salts, with the exception of the CHLORIDE, CYANIDE, BROMIDE and IODIDE OF SILVER. To ascertain still further which of these substances are present, the silver precipitate (insoluble in nitric acid) must, after being washed, be digested in *dilute ammonia*, the CHLORIDE and CYANIDE OF SILVER being soluble in that reagent will dissolve, whilst the BROMIDE and IODIDE OF SILVER, being insoluble, will remain undissolved. To the solution, after it has been filtered to free it from the insoluble residue, must be added nitric acid in excess. If no precipitate is formed, it shows the absence of chlorine and cyanogen. If a precipitate is formed, an examination must be made for chlorine and cyanogen, as well as for bromine and iodine according to the methods described at page 98.

Some of the acids give with solutions of silver characteristic coloured precipitates; thus CHROMATE OF SILVER is *red*, SULPHIDE OF SILVER *black*, ARSENIATE OF SILVER *red*, SILICATE OF SILVER *yellow* or *white*, ARSENITE, PHOSPHATE and IODIDE OF SILVER *yellow*, the rest of the acids give, with soluble silver salts, colourless precipitates.

The following precautions must be attended to in analysing this group. The solution must be perfectly neutral: an acid one is neutralised by adding ammonia slightly in excess, and then boiling the solution until all free alkali has been expelled. When a soluble sulphide or free hydrosulphuric acid is present, it is necessary before testing with nitrate of silver, to remove the sulphur compound by adding nitric acid, and warming the solution. When sulphate of the protoxide of iron is present,

the silver salt will be reduced, metallic silver being precipitated. This may be obviated either by converting the iron into peroxide or by removing it from the solution, by ammonia.

The presence of the different acids, which the general reagents, *chloride of barium*, *chloride of calcium*, and *nitrate of silver* have pointed out as existing in the solution, must be confirmed by the *special tests*.

Sixth Group. A *special* examination must always be made for the acids contained in this group.

NOTE.—When hydrocyanic, hydrobromic, and hydriodic acids have to be looked for in a substance insoluble in water, a portion of the original substance should be boiled in a solution of *carbonate of soda ;* by this means the insoluble salts are decomposed, the acid passing into solution along with the soda, whilst the base remains behind in the residue. The soda solution must be rendered perfectly neutral by nitric acid, before testing for these acids.

TABLE VII.

BEHAVIOUR OF THE INORGANIC ACIDS WITH THE GENERAL REAGENTS.

ACIDS WHICH ARE GASEOUS AT THE COMMON TEMPERATURE AND PRESSURE.

CARBONIC ACID, HYDROSULPHURIC ACID, HYDROCYANIC ACID.

These acids are liberated from their combinations by the *stronger acids*; being set free they immediately assume the gaseous state. The decomposition of their salts by acids is therefore attended with *effervescence*.

ACIDS WHICH ARE DECOMPOSED BY SULPHURETTED HYDROGEN.

ARSENIOUS ACID, ARSENIC ACID, CHROMIC ACID.

ARSENIOUS and ARSENIC ACID are converted by *sulphuretted hydrogen* into the corresponding SULPHUR ACIDS, viz., SULPHARSENIOUS and SULPHARSENIC ACID, which are insoluble in the dilute mineral acids. Their presence or absence is therefore proved in testing for the bases—they in fact form a part of the fourth group.

CHROMIC ACID is converted, by the action of the *same reagent*, into a LOWER and BASIC OXIDE (oxide of Chromium), which belongs to the third group. The change of colour which attends this decomposition is very characteristic, *viz.*, the conversion of a *yellow* or *orange coloured* solution to a *green* one; the reduction is likewise attended with a separation of sulphur.

ACIDS WHICH ARE PRECIPITATED FROM A NEUTRAL SOLUTION BY CHLORIDE OF BARIUM OR ANY SOLUBLE SALT OF BARYTA.

CARBONIC ACID, ARSENIOUS ACID, ARSENIC ACID, CHROMIC ACID, SULPHURIC ACID, BORACIC ACID, PHOSPHORIC ACID, OXALIC ACID, HYDROFLUORIC ACID, SILICIC ACID.

The salts which these acids form with baryta are *all soluble* in hydrochloric acid, with the exception of *sulphate of baryta*; the solubility or insolubility of the baryta precipitate in acids is at once characteristic of the *presence* or *absence* of SULPHURIC ACID.

TABLE VII *continued.*

ACIDS WHICH ARE PRECIPITATED FROM A NEUTRAL SOLUTION BY CHLORIDE OF CALCIUM OR ANY SOLUBLE LIME SALT.

BORACIC ACID, PHOSPHORIC ACID, OXALIC ACID, HYDROFLUORIC ACID.

PHOSPHATE of LIME and BORATE of LIME are soluble in *acetic acid,* whilst OXALATE of LIME and FLUORIDE of CALCIUM are insoluble. OXALATE of LIME is soluble in *dilute hydrochloric acid,* in which liquid FLUORIDE of CALCIUM is insoluble.

ACIDS WHICH ARE PRECIPITATED FROM A NEUTRAL SOLUTION BY NITRATE OF SILVER.

HYDROSULPHURIC ACID, ARSENIOUS ACID, ARSENIC ACID, CHROMIC ACID, BORACIC ACID, PHOSPHORIC ACID, OXALIC ACID, SILICIC ACID.

ACIDS WHICH ARE PRECIPITATED BOTH FROM A NEUTRAL AND ACID SOLUTION BY THE SAME REAGENT.

HYDROCHLORIC ACID, HYDROCYANIC ACID, HYDROBROMIC ACID, HYDRIODIC ACID.

All the silver salts of these acids are soluble in *dilute ammonia,* with the exception of BROMIDE and IODIDE of SILVER.

ACIDS WHICH ARE NOT PRECIPITATED BY ANY REAGENT.

NITRIC ACID, CHLORIC ACID.

The salts of these acids *deflagrate* on ignited charcoal.

CARBONIC ACID. (CO_2).

This acid exists at the common temperature and pressure as a colourless, inodorous and non-inflammable gas. Being heavier than the atmosphere in the proportion of 1·5 to 1, it can be decanted from one vessel to another like a liquid. It reddens blue litmus paper, which returns to its original colour as the acid volatilises. It is soluble in *cold* water, but when the solution is heated the gas escapes.

The neutral alkaline carbonates are the only *neutral* salts of this acid which are soluble in pure water. All the carbonates are decomposed in the presence of the other acids (hydrocyanic and hydrosulphuric acids excepted) with evolution of carbonic acid.

To detect carbonic acid add to the solution or solid substance under examination *hydrochloric acid*. Should any gas be evolved allow it to accumulate by placing the thumb on the mouth of the test-tube, and afterwards decant it (taking care not to allow any of the liquid to pass over along with it) into another test-tube half filled with *lime water*. A white precipitate of CARBONATE OF LIME will be produced, if carbonic acid is present.

Many of the insoluble carbonates dissolve in water containing free carbonic acid, from which solutions they are precipitated on boiling, the free acid being expelled. It is in this state that most of the lime and magnesia in spring and river waters exist. The incrustations which are formed in the vessels in which such waters are boiled, are due to the precipitation of these carbonates occasioned by the removal of the free carbonic acid. Carbonic acid is best detected in waters by adding to them *lime water ;* by this means not only is the CARBONATE OF LIME which is formed precipitated, but also that which pre-existed in the solution. This process is employed on a large scale for softening hard waters (waters impregnated with earthy matter).

All the carbonates with the exception of those of the alkalies,

lose their acid upon ignition, the metal being left either in an oxidised or uncombined state, according to its greater or less affinity for oxygen. The alkaline carbonates and bicarbonates affect test-paper in the manner of a free alkali.

The following precautions must be attended to in testing for this acid. When the substance is in the solid state, a little water should be added prior to the acid to displace the air in its pores, otherwise an apparent effervescence will ensue which is due to the expulsion of atmospheric air. In the case of alkaline carbonates, the decomposing acid must be added in excess; otherwise the carbonic acid set free may combine with some of the undecomposed carbonate, forming with it a bicarbonate, and thus prevent any effervescence from taking place.

HYDROSULPHURIC ACID (*Sulphuretted Hydrogen* H S).

This acid exists at the common temperature and pressure, as a colourless inflammable gas possessing a highly offensive odour resembling that of rotten eggs. It burns with a blue flame, the products of combustion being sulphurous acid and water. It is soluble in water, three volumes of which dissolve one volume of the gas : this solution reddens litmus paper, and on exposure to the air is decomposed, water being formed, and sulphur in a highly divided state being separated.

Most metallic sulphides dissolve with decomposition in *hydrochloric acid*, in which case SULPHURETTED HYDROGEN is evolved, which, from its characteristic smell, is easily recognised. When the quantity is so minute that the smell fails to afford a sufficient proof it may be detected by holding a piece of paper moistened with a solution of any soluble SALT OF LEAD over the mouth of the test-tube, as a brown or black coating of SULPHIDE OF LEAD will be formed upon the paper.

When sulphides are dissolved in *nitric* or *nitro-hydrochloric* acid, SULPHURIC ACID is formed along with a separation of sulphur, which may be recognised by its colour, and also its behaviour upon ignition. In the case of sulphides therefore, which, from their insolubility in hydrochloric acid, must be dissolved in nitric or nitro-hydrochloric acids, the sulphur is converted into sulphuric acid, and not given off as sulphuretted hydrogen.

When the sulphides of the heavy metals are heated in contact with air, sulphurous acid is evolved, the metal being left in some cases uncombined, and in others as an oxide. The sulphides of the alkalies and alkaline earths are converted by this process into sulphates.

CHROMIC ACID (CrO₃).

Chromic acid is a solid coloured acid occurring in the form of beautiful crimson needles, which deliquesce rapidly when exposed to the air, the solution possessing a deep red-brown tint. This acid is decomposed, upon ignition, into oxide of chromium and oxygen. All its salts are coloured; the neutral chromates possessing a yellow, and the acid or bichromates a red colour. Most of the salts are insoluble in water; they are nearly all soluble in nitric acid.

Chromic acid, whether in its free or combined state, is reduced by *hydrosulphuric acid* to the state of OXIDE OF CHROMIUM; water and some oxide of sulphur is formed in this decomposition along with a separation of sulphur. The change of colour which attends this decomposition, viz., the conversion of a yellow or red coloured solution to a green one, is so characteristic that it cannot be mistaken.

Alkaline chromates may be prepared from insoluble chromates by fusing the latter in conjunction with alkaline carbonates.

SULPHURIC ACID (*Oil of Vitriol*) (HO, SO₃).

Anhydrous sulphuric acid (SO_3) is a white feathery crystalline mass, which when exposed to the air emits dense white fumes. It is destitute of acid properties until it has combined with water and passed into the hydrated state. The hydrated acid is a heavy, colourless, oily fluid, which possesses a strong affinity for water, producing when mixed with it a great degree of heat. Its affinity for water is so great that it decomposes organic substances when placed in contact with them, removing their hydrogen and oxygen, whilst the carbon is left behind as a black coaly mass, a portion of which dissolves in the acid and communicates to it a brown tint. If heat is applied, the carbon is oxidised at the expense of the sulphuric acid, carbonic acid and sulphurous acid being formed : these facts may be illustrated by pouring some strong sulphuric acid upon white sugar. Sulphuric acid, at temperatures below its boiling point (572 F), displaces all other acids from their combinations with bases, but above that temperature it is itself displaced by the non-volatile acids.

Most of the sulphates, with the exception of the sulphates of baryta, strontia, and lead, are soluble in water. The alkaline sulphates and the three just named are the only salts of this acid which are not decomposed on simple ignition.

Sulphates in dilute solutions containing organic matter are gradually converted into sulphides. Water may therefore, after it has been kept a long time in a bottle, or any closed vessel, be found to contain sulphuretted hydrogen, although originally it was perfectly free from that gas.

Sulphate of baryta, from its insolubility in acids, is at once distinguished from all the other baryta salts; any *soluble salt of baryta* is therefore the best and most delicate test for SULPHURIC ACID.

Insoluble sulphates are completely decomposed by fusion with

alkaline carbonates, an ALKALINE SULPHATE being produced along with a CARBONATE or an OXIDE of the METAL.

When a sulphate, mixed with *charcoal* and *carbonate of soda*, is fused upon a charcoal support by the inner blowpipe flame, sulphide of sodium is produced. If the fused mass moistened with water be placed upon a piece of silver, a brown stain of sulphide of silver will be formed.

BORACIC ACID (BO_3).

This acid is best obtained by adding to a boiling concentrated solution of biborate of soda (borax), strong sulphuric acid until the liquor becomes sour to the taste: on cooling, the greater part of the boracic acid separates from the solution in the form of colourless crystalline scales, containing water. When ignited, they fuse to an anhydrous glassy mass, which, on exposure to the air, absorbs water, swells, and becomes opaque. The hydrated acid is much more soluble in hot than cold water. When an alcoholic or an aqueous solution of this acid is evaporated, a portion of the acid volatilises with the vapours of the solvent, but alone it is perfectly fixed at a red heat. One peculiar property which this acid possesses is that of affecting turmeric paper in the manner of a free alkali; it acts however upon blue litmus paper like other acids. All the borates, with the exception of the alkaline ones, are almost totally insoluble in pure water; they dissolve readily in acids, and in water containing ammoniacal salts. They are not decomposed upon ignition: they are colourless, and all of them, even the acid salts, manifest an alkaline reaction.

An alcoholic solution of boracic acid burns with a *green-coloured flame*, which becomes more distinct upon stirring the mixture. To detect a borate, add to the substance under examination *strong sulphuric acid* and *alcohol* or *wood naphtha*, ignite the mixture subsequently. If a borate be present, the borders of the

flame will appear *green*, which becomes more distinct upon stirring, and the delicacy is further increased by repeatedly extinguishing and rekindling the flame. The only substance which at all interferes with this test is copper, the salts of which impart the same colour to the flame. This metal, if present, must therefore be got rid of by sulphuretted hydrogen, before testing for boracic acid.

PHOSPHORIC ACID (3 HO, PO_5).

Anhydrous phosphoric acid (PO_5) appears under the form of white flakes, which rapidly absorb moisture from the atmosphere. It has a great affinity for water, with which it combines in three different proportions, forming three distinct acids, which have the following constitution—

> Tribasic phosphoric acid (3 HO, PO_5).
> Bibasic phosphoric acid (2 HO, PO_5).
> Monobasic phosphoric acid (HO PO_5).

Each of these acids form with bases a distinct class of salts.

The tribasic acid, which is the most important, is the only one treated of in this work. It appears in the form of colourless crystals, which deliquesce rapidly in the air. When strongly heated in an open platinum vessel it volatilises without a residue.

The neutral phosphates, with the exception of the alkaline ones, are nearly all insoluble in water. The action of heat converts the tribasic phosphates into bibasic or monobasic salts, according to the number of atoms of basic water expelled.

Sulphate of magnesia, or *any soluble magnesian salt,* produces in aqueous solutions of the phosphates, if concentrated, a white precipitate of PHOSPHATE OF MAGNESIA (2 MgO, HO,PO_5). A salt much more insoluble in water is produced by adding *chloride of ammonium, ammonia,* and then the *magnesian salt; in* this way PHOSPHATE OF MAGNESIA AND AMMONIA (2 MgO, NH_4O, PO_5)

is precipitated, which is slightly soluble in pure water, but almost insoluble in water containing ammonia.   In dilute solutions it only appears after much agitation and the lapse of some time.   This test can only be applied when the phosphates are soluble in ammoniacal solutions.

Acetate of lead produces a white precipitate of PHOSPHATE OF LEAD (3 PbO, PO_5) which is soluble in nitric acid.   If this precipitate, after being dried, is heated in the outer flame of the blowpipe, it becomes distinctly crystalline on cooling.   This test is very characteristic, not only on account of the crystalline structure of the bead, but also from the circumstance that the phosphate of lead is the only salt of that metal which is not reduced to the metallic state when heated in the inner blowpipe flame.   It is evident that, to render this test of any value, the phosphate of lead must be freed thoroughly by washing from all acetate of lead.

If a solution containing phosphoric acid be slightly acidulated with hydrochloric acid (if it is not already acid), and afterwards a few drops of *perchloride of iron* be added, and finally *acetate of soda* in excess, a white gelatinous precipitate of PERPHOSPHATE OF IRON (2 Fe_2O_3 3 HO, 3 PO_5) will be produced, which is soluble in free mineral acids, but insoluble in acetic acid. Should the quantity of phosphoric acid be very minute, the precipitate will appear only after the lapse of several hours. Care must be taken not to add too much perchloride of iron, because perphosphate of iron is rather soluble in peracetate of iron.   This test requires therefore the following modification, when large quantities of peroxide exist in the substance under examination.   To the acid solution add *acetate of soda* in *excess.* and then boil; by this means the whole of the iron will be thrown down in combination with acetic and phosphoric acids.   After having filtered and washed the precipitate, digest it in sulphide of ammonium; by this means the iron is converted into insoluble

sulphide, whilst the phosphoric acid passes into solution in combination with ammonia. Test the ammoniacal filtrate for this acid by means of *chloride of ammonium* and *sulphate of magnesia*.

Oxalic Acid (HO, C_2O_3, or HO, $\overline{O}$).

Oxalic acid crystallises from its aqueous solutions in four-sided prisms. These crystals contain three atoms of water, of which one is essential (HO, $C_2O_3 + 2$ aq). When warmed, the 2 atoms of non-essential water (water of crystallisation), are given off, and the hydrate of oxalic acid remains as a white powder, which melts at 350°, and when further heated sublimes, a portion however being decomposed. It is very soluble in water, and highly poisonous. It is usual to place it in the list of organic acids, but since its salts upon ignition leave no carbonaceous residue, it has been included in the list of inorganic acids.

All the oxalates are decomposed at a red heat, the oxalic acid being resolved into carbonic acid and carbonic oxide. If the base with which the acid is combined be an alkali or an alkaline earth, it is left as a carbonate; the other bases are left either in an oxidised or metallic state, according to their greater or less affinity for oxygen.

Lime water and all the soluble *salts of lime* produce in solutions of oxalic acid and the oxalates, even if highly diluted, a white precipitate of OXALATE OF LIME, which is insoluble in acetic acid.

When *concentrated sulphuric acid* is added to dry oxalic acid or an oxalate, it withdraws the constitutional water in the one case and the base in the other from the anhydrous acid (C_2O_3), which, being incapable of existing alone, splits up into CARBONIC ACID and CARBONIC OXIDE. The two gases escape with effervescence, and if a light be applied as they issue from the mouth of the tube, the latter will burn with a blue flame.

HYDROFLUORIC ACID (H F).

This acid is best obtained by the action of concentrated sulphuric acid on fluoride of calcium (fluor spar). The powdered mineral is gently heated with the acid in a retort of lead, and the acid condensed in a receiver of the same metal. It is obtained in the form of a very volatile liquid, strongly acid and corrosive, fuming in the air. It burns the skin like red-hot iron, causing a sore which is not easily healed. It is distinguished from all other acids by dissolving insoluble silicic acid and the silicates; on this account it cannot be prepared or kept in glass vessels.

To detect fluorine in a compound, take a plate of glass coated with bee's wax, which has here and there been removed by means of a pointed instrument, lay it upon a platinum crucible containing the pulverised fluoride and strong sulphuric acid, and then heat the platinum vessel for about a quarter of an hour. Upon removing the wax by means of turpentine, the exposed parts will be found etched into the glass. To keep the wax from melting, the upper surface of the plate should be moistened with water, and the heat applied should not be too great. This method cannot be adopted when *silicic acid* is present.

If *nascent* hydrofluoric acid meet with silicic acid, the two compounds are mutually decomposed, FLUORIDE OF SILICON (Si F_2), and water being formed. Should the compound examined contain therefore silicic acid as well as fluorine, fluoride of silicon, and not hydrofluoric acid, will be disengaged by the sulphuric acid.

To detect fluorine in the presence of silicic acid, the compound under examination must be finely powdered, and treated with strong sulphuric acid in a dry tube. If the evolved gas be transmitted through a tube moistened within, the inner surface will become coated with a deposit of silicic acid, which will

render the tube less transparent. This deposit is occasioned by the decomposition which fluoride of silicon undergoes in the presence of water, viz., into silica and hydrofluosilicic acid (H F, Si F$_2$).

If a fluoride mixed with bisulphate of potash is heated in a test-tube, hydrofluoric acid is disengaged, which is easily detected by the etching of the glass.

SILICIC ACID (*Silica* Si O$_3$).

This acid occurs in two modifications: the one is soluble in water and acids, the other is affected only by hydrofluoric acid. The soluble is converted into the insoluble form by heat, the insoluble modification is made to pass into the soluble by fusion with the carbonated alkalies. On dissolving the fused mass in water, and adding to the solution hydrochloric acid, hydrated silicic acid separates in a gelatinous form, which is soluble in water. The alkaline silicates are the only salts of this acid which are soluble in water.

On adding chloride of ammonium to a solution of an alkaline silicate a gelatinous precipitate [12] takes place.

The separation of silicic acid from an aqueous solution of a silicate on the addition of an acid, depends upon the amount of water present. If there is sufficient to dissolve it no separation takes place. To detect this acid in an aqueous solution a portion of the liquid ought to be evaporated to dryness along with some hydrochloric acid, and the residue treated with water. If a gritty powder remains behind, it must be tested before the blowpipe with carbonate of soda for silica.

The compounds formed by soluble silicic acid, in combination with other bases, are insoluble in water, but are decomposed by

[12] Is this precipitate, which is always looked upon as hydrated silicic acid, a silicate of ammonia, corresponding to the titanate of ammonia discovered by Rose?

boiling hydrochloric or nitric acid, the silicic acid separating as a gelatinous hydrate, whilst the decomposing acid combines with the liberated base.

The combinations of the insoluble silicic acid require to be fused with an alkaline carbonate, or treated with hydrofluoric acid, to effect their decomposition.

When silicic acid is fused with *carbonate of soda* before the blowpipe, a transparent colourless bead is formed, while carbonic acid is expelled. A small quantity of soda ought only to be employed, as an opaque bead is produced when it is added in excess.

HYDROCHLORIC ACID (*Muriatic Acid*, H Cl.)

This acid is a transparent and colourless gas, of a pungent, acid, suffocating smell, and fuming strongly with moist air. It is absorbed in large proportions by water, forming the common liquid hydrochloric acid, which is a mere solution of the gas in water.

When a chloride is heated with *peroxide of manganese* (MnO_2) and *sulphuric acid*, chlorine gas is evolved, which may be recognised by its ODOUR and GREENISH-YELLOW COLOUR.

When a chloride is heated with *chromate of potash* and *concentrated sulphuric acid*, a brown gas is disengaged, which condenses into a blood-red liquid, CHROMATE OF CHLORIDE OF CHROMIUM ($CrCl_3$, $2\ CrO_3$). On the addition of ammonia in excess, the colour changes to a yellow, owing to the formation of neutral chromate of ammonia; upon the addition of an acid, the yellow changes to a reddish-yellow colour, owing to the formation of an acid chromate.

HYDROCYANIC ACID (*Prussic Acid*, H, C_2 N, or H Cy).

This acid is the hydrogen compound of the radical cyanogen (C_2 N), which is itself a compound of carbon and nitrogen.

In its anhydrous state hydrocyanic acid is a colourless, vola-
tile, inflammable liquid, possessing a strong odour resembling
that of bitter almonds. Water dissolves it in all proportions:
both in its concentrated and diluted state it speedily undergoes
decomposition when exposed to the light. Being exceedingly
poisonous, it requires to be used with care.

The compounds of cyanogen with the metals of the alkalies
and alkaline earths, are soluble in water; their solutions possess
an alkaline reaction, and are decomposed, with the liberation of
hydrocyanic acid, by the weakest acid.

If to a solution of free hydrocyanic acid or an alkaline cyanide,
potash and a mixture of a *per- and proto-salt of iron* be added, a
greenish-blue precipitate will be produced, which, on the addition
of hydrochloric acid, will re-dissolve, *Prussian blue* precipitating.

When free hydrocyanic acid is added to sulphide of ammonium
containing an excess of sulphur, the acid seizes upon some of the
ammonia and sulphur, forming with them SULPHOCYANIDE
OF AMMONIUM (NH$_4$ Cy S$_2$) which possesses, in common with
all the other soluble sulphocyanides, the property of pro-
ducing, with persalts of iron, a *deep blood-red colour*. This test
may be applied in qualitative analysis in the following way.
When a solution has to be examined for free hydrocyanic acid, a
portion of the suspected liquid is placed in a watch-glass;
another watch-glass, which fits it accurately, is inverted over it;
a drop of sulphide of ammonium, containing sulphur in excess, is
placed in the centre of the inverted glass. After being allowed
to stand for about ten minutes, the drop of liquid in the inverted
glass is evaporated to dryness at a very *low temperature,* the
residue re-dissolved in a drop of water, and tested for the sulpho-
cyanide by means of perchloride of iron. When the cyanogen
is in combination with some metal, sulphuric acid must be placed
in the watch-glass, together with the substance suspected to con-
tain the cyanide.

HYDROBROMIC ACID (H Br).

This acid resembles very closely in its properties hydrochloric-acid gas. It is decomposed by chlorine, bromine being set free, and hydrochloric acid formed.

Bromates are decomposed by chlorine, nitric and concentrated sulphuric acid with the liberation of bromine, which communicates to the liquid a yellowish-red colour. Bromine is soluble in ether, and imparts an orange colour to starch paste.

To detect bromine in any compound, pass *chlorine gas* through the solution, or add an *aqueous* solution of that gas; the bromine being set free, will communicate a yellowish-red tint to the liquid, excepting the quantity be very minute. If the solution be now agitated with *ether*, it will remove all the bromine from the liquid, dissolving it, and forming a yellow-coloured solution. If the ethereal solution be agitated with potash, the colour will disappear, bromide of potassium and bromate of potash being formed. By evaporating this solution to dryness, and igniting the residue, the bromate of potash will be converted into bromide of potassium. On heating the bromide along with *peroxide of manganese* and *sulphuric acid* in a small retort, YELLOWISH-RED VAPOURS will be evolved, unless the quantity be very minute. These vapours, when brought in contact with *starch paste*, will communicate to it an ORANGE-YELLOW COLOUR, which disappears on exposure to the air.

HYDRIODIC ACID (H I).

This acid and its compounds resemble in their properties the corresponding compounds of chlorine and bromine. Many of the iodides of the heavy metals are more insoluble in water than the corresponding chlorides.

Protonitrate of mercury throws down from solutions of the iodides, a yellowish-green precipitate of IODIDE OF MERCURY (Hg I).

Perchloride of mercury throws down a red precipitate of PERIODIDE OF MERCURY (Hg I), which is soluble in an excess of the perchloride or of iodide of potassium.

Soluble salts of lead precipitate an orange-yellow precipitate of IODIDE OF LEAD (Pb I).

Iodine, in a free state, forms with *starch*, even in highly dilute solutions, a purple precipitate of IODIDE OF STARCH. If the iodine is in a state of combination with hydrogen, or any metal, it is necessary to liberate it before applying the starch test.

Nitric acid liberates iodine from its hydrogen and metallic compounds, nitric oxide being given off. The liberated iodine communicates a brownish-yellow tint to the solution, and if it is concentrated, a portion of the iodine separates as a black precipitate. When solid iodides are heated with nitric acid, the iodine sublimes in the form of violet-coloured vapours, which condense upon the colder parts of the vessel as a blackish sublimate.

Chlorine gas likewise liberates iodine from its combinations, but if added in excess they combine together, forming a colourless compound (chloride of iodine).

If iodides are heated with *sulphuric acid* and *peroxide of manganese*, the iodine sublimes in the form of violet-coloured vapours, which are easily recognised.

To detect iodine in a compound, add to the solution *nitric acid*, and subsequently thin *starch paste*. The fluid will acquire a BLUE or BLACKISH-BLUE tint, owing to the formation of iodide of starch.

The best method of separating iodine from its combinations in the dry state, and detecting it, is to introduce the compound into a flask, and add *concentrated sulphuric acid*, close the flask loosely with a stopper, attached to which is a piece of paper moistened with *starch paste*. After the lapse of some hours this will acquire a BLUE TINT.

When a solution, containing 1 part of *sulphate of copper* and 2½ parts of *sulphate of the protoxide of iron*, is added to a solution of an iodide, a white precipitate of SUBIODIDE OF COPPER (Cu_2 I) is formed. The sulphate of iron is added, to convert the sulphate of copper into a subsalt.

When any compounds of the non-metallic elements—bromine, iodine, chlorine, and the compound body cyanogen—occur together in a mixture, it becomes a matter of some difficulty to detect them. The following is perhaps the easiest and most satisfactory plan. The precipitate insoluble in nitric acid is washed and treated with dilute ammonia, which dissolves the chloride and cyanide of silver if present, whilst the bromide and iodide of silver remain undissolved.

Nitric acid is added in excess to the ammoniacal solution, which may contain the cyanide and chloride of silver. If a precipitate is formed, it shows that one or both of them are present. A portion of the original solution is next examined, either by the prussian blue test, or the sulphide of ammonium one, for cyanogen. If it is absent, the precipitate produced by nitric acid in the ammoniacal solution is due solely to the presence of chlorine. But should cyanogen be present, that portion of the silver precipitate which was dissolved in ammonia and reprecipitated by nitric acid is collected, dried and ignited; by this means the cyanide of silver is decomposed, metallic silver being left, whilst the chloride of silver remains unaltered. On the addition of nitric acid to the residue, the metallic silver dissolves out, whilst if any portion is insoluble in the acid, chloride of silver is present. To procure further proof of the presence of cyanogen, add hydrochloric acid to the nitric-acid filtrate; this will precipitate the silver, originally in combination with the cyanogen, as chloride.

To detect the bromine and iodine, examine the original solution for the latter by means of nitric acid and starch. If iodine

is found to be present, then, in another portion of the original solution, remove it, by means of a subsalt of copper, and to the filtrate add chlorine, and proceed in the appropriate way for the examination of bromine.

NITRIC ACID (HO, NO_5).

The hydrate of nitric acid, when pure, is a colourless liquid, which fumes strongly in the air. It acts upon organic substances, destroying them quickly if concentrated; if they contain nitrogen, they are stained yellow by this acid. It oxidises all the metals, with the exception of gold, platinum, and some of the rarer ones, being itself reduced to the state of nitric oxide (NO_2), which, in contact with the air, is converted into red fumes of nitrous acid (NO_4). All the oxides treated of in this work dissolve in this acid, with the exception of binoxide of tin and oxide of antimony.

All the neutral nitrates are soluble in water, a few basic salts are insoluble in that liquid. All the salts of this acid are decomposed by ignition, the alkaline nitrates yielding oxygen and nitrogen, and the rest oxygen and nitrous acid.

When nitrates are ignited in the presence of substances capable of oxidation, a portion of the oxygen passes over to them, whilst an inferior oxide of nitrogen is evolved. In some cases the combination is attended with a violent detonation, in others vivid scintillations accompany the combustion.

To detect nitric acid in a solution : add to it one-fourth of its volume of concentrated *sulphuric* acid, and after the mixture has cooled, a *crystal* of *sulphate of iron*, the crystal or the liquid immediately surrounding it becomes of a DEEP BROWN COLOUR. This colour is due to the formation of a compound of nitric oxide with the salt of iron, which is destroyed by heat, nitric oxide being given off. When any base is present, which is precipitated by sulphuric acid, it ought to be thrown down by

dilute sulphuric acid, and the liquid filtered before the test is applied. The liquid ought not to be agitated after the iron salt has been added.

When nitrates are heated with *concentrated sulphuric acid*, in the presence of *copper turnings*, NITRIC OXIDE is evolved, which, in contact with the air, forms red fumes, owing to its conversion into nitrous acid. This experiment ought to be conducted in a narrow test-tube. The colour is best observed by looking into the test-tube in the direction of its length.

CHLORIC ACID (H O, Cl O₅).

This acid, in its concentrated state, appears in the form of a yellow oily liquid, the odour of which resembles that of nitric acid.

All the chlorates are soluble in water. They are decomposed upon ignition, oxygen gas being given off and a metallic chloride left. When heated along with organic substances they deflagrate with far greater violence than the nitrates.

To detect this acid, add to a small quantity of the solid substance under examination, a few drops of *concentrated sulphuric acid* in the cold. The chlorate will be decomposed, SULPHATE OF POTASH and PERCHLORATE OF POTASH (K O, Cl O₇) being formed along with a GREENISH-YELLOW COLOURED gas (chlorous acid Cl O₄), which escapes. The application of heat must be avoided, and the quantities operated upon should be small, to prevent any loud and violent explosion taking place.

ORGANIC ACIDS.

Organic acids cannot be detected with the same certainty and precision in qualitative analysis as the inorganic acids. The two which occur most commonly are the only ones which have been inserted.

TARTARIC ACID (2 HO, $C_8 H_4 O_{10}$ or 2 HO, $\overline{T}$).

Tartaric acid occurs in the form of large colourless prisms, which are soluble in water, and have an agreeable acid taste; if the solution is kept a short time it undergoes decomposition.

Tartaric acid and tartrates evolve, when heated, a peculiar odour.

Chloride of barium produces in solutions of the tartrates a white precipitate of TARTRATE OF BARYTA, which is soluble in solutions containing ammoniacal salts.

Chloride of calcium precipitates from solutions of the tartrates, a white precipitate of TARTRATE OF LIME, which is soluble in acetic acid and solutions containing ammoniacal salts. It is distinguished from phosphate of lime and borate of lime by dissolving in a cold solution of caustic potash, from which solution it is precipitated on boiling, and again redissolved as the liquid cools.

ACETIC ACID (HO, $C_4 H_3 O_3 = HO, \overline{A}$).

All the salts of acetic acid are soluble, the salts of mercury and silver are the least soluble.

The *persalts of iron* impart to solutions of the acetates a BLOOD-RED COLOUR.

When acetates are heated with *sulphuric acid* and *alcohol*, ACETIC ETHER is formed, which is readily distinguished by its characteristic odour.

CHAPTER VI.

EXAMINATION OF LIQUIDS AND SOLIDS.

PRELIMINARY EXAMINATION OF A LIQUID.

THE student, after he has passed through the different groups
of bases and acids in the manner previously described, commences
the analysis of liquids, in which he has to look for all the different
substances treated of in the work, with the exception of the
organic acids.[13]

Before commencing the actual analysis, it is necessary to
ascertain by preliminary experiments—1. Whether there is any
solid substance in solution. 2. Whether the solution is neutral,
acid, or alkaline.

1. *To ascertain whether there is any solid substance in solution.*
Evaporate by a gentle heat a portion of the liquid to dryness on
platinum foil. If no residue remain, it is probably pure water,
which will be further confirmed if it has no action upon test-

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[13] The student will find it conducive to his success in many respects,
if he does not engage in the detection of organic acids until he enters
upon the examination of solid substances. He will, of course, in *prac-
tice*, have always first to ascertain whether organic substances are
really present or absent in a solution, before he commences the actual
analysis, as the presence of fixed organic matter prevents the detection of
many inorganic substances : he will likewise in practice have frequently to
separate, by distillation, the liquid from the solid portion of a solution, in
order to be perfectly certain that the fluid is *water* and not any other
liquid. This he will ascertain by examining the distilled fluid, by the
smell, taste, boiling point, specific gravity, &c.

paper.   If a residue remain, which is completely volatilised when the temperature is increased, the only basic substances which can be present, are ammonia, mercury, arsenic and antimony. If the residue is not volatile, or at least not completely so, other substances besides these must be present.   In both cases it is requisite to perform the next experiment.

2. The solution is examined by well-prepared test-papers as to its neutrality, &c.   Each of the three cases which may occur, and the conclusions to which they lead are considered in the paragraphs *a*, *b*, and *c*.

a. The solution is *neutral*.   A large number of substances must therefore be absent, because the neutral salts of the greater proportion of the metals possess an acid reaction.   The only salts, which are neutral to test-papers, are the salts of silver and manganese, and some of the salts of the alkalies and alkaline earths.   The alkalies, alkaline earths, silver, and manganese are the only basic substances therefore which can be present; but to distinguish still further, add to a portion of the solution carbonate of soda.   If no precipitate ensue, the alkaline earths and the oxides of silver and manganese must be absent; but should a precipitate be formed, all these substances may be present.

b. The solution is *acid*.   The acidity may proceed from the presence of a free acid, an acid salt, or a neutral salt having an acid reaction.   To ascertain to which of these causes the acidity is due, place the end of a glass rod moistened with a solution of carbonate of soda, into a portion of the fluid in a watch-glass. If the solution becomes turbid and remains so, it is due to the presence of a neutral salt; if it becomes clear again, the reaction is due either to an acid salt or a free acid.   Carbonates and sulphides cannot be present in an acid solution.

c. The solution is *alkaline*.   The alkalinity may proceed from an alkaline carbonate, silicate, borate, or phosphate; or it may

arise from the presence of a free alkali or alkaline earth, or from the cyanogen and sulphur compounds of these metals. If the alkalinity proceeds from ammonia or its carbonate, a large number of substances (those which are insoluble in these reagents) must be absent. If it is due to the presence of the fixed alkalies or their carbonates, a still larger number of substances are excluded. If it is occasioned by the sulphides of the metals of the alkalies or alkaline earths, all the metals whose sulphides are insoluble in water and alkaline sulphides must be absent.

After the preliminary experiments have been completed, the actual analysis must be commenced, by dividing first of all the substances into groups, and these finally into individuals, as described in the former part of this work. The basic substances are first determined in analysis. When these have been discovered, correct conclusions may be drawn as to the acids which must be absent. If, for instance, baryta was found to be present in an aqueous solution, then the acids, which form with it salts insoluble in water, must be absent.

The student should never employ the whole of the solution at his disposal, but should always reserve a portion in the event of any unforeseen accident occurring, and for confirmatory experiments.

If the liquid under examination contains inorganic matter in suspension,[14] the latter after being separated by filtration must be brought into solution according to the methods described under the head of solid substances. The solid and liquid portions ought in most cases to be examined separately.

[14] The method of preparing for analysis a solution which is thick or turbid from the presence of organic matter, is described under the head of " Solid Substances containing Organic Matter."

EXAMINATION OF SOLIDS.

PRELIMINARY EXAMINATION OF SOLID SUBSTANCES.

The substance is first examined as to its lustre, colour, odour, and whether it is crystalline or amorphous, since these will frequently afford a means of classifying the substance. Thus, a metallic lustre will indicate probably a pure metal or an alloy. A blue colour will indicate the probable presence of some salt of copper, a crystalline structure the probable presence of a salt.

The substance is next submitted to the different blowpipe operations described in the Table. In these experiments only small quantities of the substance in a state of powder must be employed, for if too much is operated upon, uncertain results are the consequence.

TABLE VIII.

(1)—COURSE OF BLOWPIPE OPERATIONS TO WHICH SUB-
STANCES MUST BE SUBMITTED BEFORE COMMENCING
THEIR ANALYSIS IN THE HUMID WAY.

Heat the substance in a glass tube, sealed at one end, by means
of a spirit-lamp.

Condenses on the cold sides of the tube   } WATER . . . . { Examine whether it has an *alkaline* or *acid* reaction; if the former, probably due to *ammonia*.

A *yellow* sublimate . . } SULPHUR . . . . { Due either to its presence in the free state, or the partial reduction of a sulphide.

The substance *blackens* . . } ORGANIC MATTER . . . Charcoal being left.

Volatile Oxides
- OXIDE OF ANTIMONY . . Sublimes without fusing.
- ARSENIOUS ACID . . . { Condenses in white crystals.
- ARSENIC ACID . . . . { Converted into arsenious acid and oxygen.

Volatile Salts
- AMMONIACAL SALTS . . { Volatilised unaltered, except when the alkali is in combination with the fixed acids.
- Most SALTS OF MERCURY { Yellow sublimate: iodide of mercury.

If the substance is completely volatile, ammonia, mercury, arsenic, and
antimony, need only be looked for.

(2)—COURSE OF BLOWPIPE OPERATIONS—*continued.*

Heat the substance in a glass tube, open at both ends, held
obliquely.

White
Sublimates . .
- AMMONIACAL SALTS.
- OXIDE OF ANTIMONY.
- ARSENIOUS ACID.
- OXIDE OF BISMUTH . . . . { Melts into brownish yellow drops when heated.
- MERCURIAL COMPOUNDS.
- CHLORIDE OF LEAD . . . . { Melts readily when heated.
- SULPHATE OF LEAD . . . . { Formed from the oxidation of the sulphide.

The substance
blackens . .
- OXIDE OF COBALT . . . . . } Acid vapours
- OXIDE OF COPPER . . . . . } evolved.
- ORGANIC MATTER . . . . . { Empyreumatic vapours.

Acid Vapours .
- FLUORIDES . . . . Etching the glass.
- SULPHIDES . . . . { Yielding an odour of sulphurous acid.

Arsenious acid and the oxides of bismuth and antimony may have
existed as such in the original substance, or they may have been formed in
the operation from the oxidation of their metals or sulphides.

(3)—COURSE OF BLOWPIPE OPERATIONS—*continued.*

Expose the substance to the inner blowpipe flame on
CHARCOAL.

If deflagration ensue, the presence of a *chlorate* or *nitrate*
is indicated.

Substances which volatilise or pass off in vapour.	*Substances which are not volatilised.*		
MERCURY, ARSENIC, CADMIUM, ANTIMONY, ZINC, AMMONIA, SULPHUR, and LEAD partly.	SILVER, COPPER, BISMUTH, LEAD, TIN, GOLD, PLATINUM, COBALT, NICKEL, MANGANESE, IRON, ALUMINUM, CHROMIUM, BARIUM, STRONTIUM, CALCIUM, MAGNESIUM, SODIUM, POTASSIUM, SILICA, &c.		

Colour of the different Sublimates.	Substances which yield *coloured incrustations.*	Substances which are *infusible, but become luminous.*	Substances which *fuse, or run into the charcoal.*
MERCURY, ZINC, AMMONIA, } White. ANTIMONY, white, imparting a greenish-blue colour to the flame. CADMIUM, red brown.	LEAD, BISMUTH, } Yellow.	ALUMINA, BARYTA, STRONTIA, LIME, and MAGNESIA, *and their salts.*	SALTS OF THE FIXED ALKALIES.

The following substances impart to the flame
a *characteristic colour :*

COPPER	.	.	.	*deep* green.
BARYTA and BORACIC ACID, *light* green.
STRONTIA	.	.	.	deep crimson.
LIME	.	.	.	.	crimson red.
POTASH	.	.	.	violet.
SODA	.	.	.	.	yellow.

(4)—COURSE OF BLOWPIPE OPERATIONS—*continued*.

Mix the substance with *Carbonate of Soda*, and expose the mixed mass to the inner blowpipe flame on CHARCOAL.[15]	Heat the substance before the blowpipe on PLATINUM WIRE, with a bead of BORAX.	Heat the substance on CHARCOAL, with the blowpipe flame, then moisten it with a solution of PROTONITRATE OF COBALT: again strongly heat it in the *outer flame*.

Column 1: Oxides and Combinations of, Oxides which can be reduced to the *metallic state*.

Oxide of	Character of the Metal.
BISMUTH	Brittle.
ANTIMONY	Brittle; volatilises in white fumes, yielding an incrustation.
SILVER	Malleable; very white.
TIN	Malleable.
LEAD	Malleable, very.
COPPER GOLD	Well known colours of the metals.
NICKEL, COBALT, IRON,	These three are rendered magnetic, and can therefore be at once distinguished from the rest.

To discover the reduced metal, remove the fused mass from the charcoal, and

Column 2: Substances which give *coloured beads*.

In the outer flame.

COPPER, COBALT,	} .. blue.
NICKEL	. reddish.
IRON	. yellow.
MANGANESE,	} Amethyst.
CHROMIUM	. green.

In the inner flame.

COPPER	. red.
COBALT	. blue.
NICKEL	. grey.
IRON	. green.
MANGANESE,	} colourless.
CHROMIUM	. green.

Column 3: Substances which yield *coloured masses* when thus treated.

OXIDE OF ZINC	} green.
ALUMINA, SILICIC ACID, PHOSPHATES,	} blue.
MAGNESIA	. pink.
BINOXIDE OF TIN	{ a bluish-green colour.

grind it up in a small mortar with water; allow it to stand a minute, and then pour off the water and the suspended matter in it, and continue to repeat the process until the metal remains at the bottom of the mortar, perfectly free from charcoal, &c. If it is brittle, it will be in the state of very small spangles; if malleable, it will have adhered to the mortar or pestle, or a portion of it, whilst the rest may be in large spangles.

15. If the colour of the substance is not altered in the least by *sulphide of ammonium*, this experiment need not be performed, as all the different compounds of the metals enumerated must be absent.

When the student has completed the different preliminary experiments, he will be able to arrange the substance under one of the three following divisions.

a. The solid substance under examination is neither a pure metal nor an alloy, and is destitute of organic matter.

b. The solid substance under examination is neither a pure metal nor an alloy, but contains organic matter.

c. The solid substance under examination is either a pure metal or an alloy.

Each of the three cases just named are separately considered under their respective heads.

THE SOLID SUBSTANCE UNDER EXAMINATION IS NEITHER A PURE METAL NOR AN ALLOY, AND IS DESTITUTE OF ORGANIC MATTER.

Before a solid can be acted upon by reagents it must be brought into a state of solution. For this purpose it is submitted to the action of different fluids; and the one in which it dissolves is termed its solvent. The solvents employed in qualitative analysis are water, hydrochloric, nitric and nitro-hydrochloric acids. Water, when it can be employed, is always to be preferred.

The student must particularly guard against adding too much of the solvent, especially if it be an acid. To avoid this he must add it in small quantities at a time, and apply heat after each addition. The substance should, before being submitted to the action of solvents, be reduced to the state of a very fine powder, and fifteen or twenty grains employed for the analysis. The whole of the substance must however never be employed, but always a portion kept in case of any unforeseen accident, or for confirmatory experiments.

I. The powdered substance is boiled in ten times its amount of water. *It all dissolves;* make the preliminary experiments described under the head of Liquids, and then proceed with the actual analysis. *A portion remains undissolved;* filter a few drops of the liquid, and evaporate them to dryness on platinum foil. If a large residue remains on evaporation, the whole of the solution must be filtered, and submitted to analysis. The insoluble residue, after being well washed with boiling water, must be examined according to II. If no residue remains on evaporating the aqueous solution, or at all events a very slight one, the remainder of the water may be poured off and disregarded, and the insoluble substance treated according to II.

II. The substance, which was partly or entirely insoluble in water, is boiled in concentrated hydrochloric acid.[16] *It all dissolves;* dilute the solution with a small quantity of water, and then proceed with the analysis. *A portion remains undissolved;* ascertain if anything has dissolved, by evaporating a portion of the fluid to dryness on platinum foil. Should this be the case, place the tube, with its contents, on one side, and proceed with the next experiment.

III. A fresh portion of the original substance is boiled in concentrated nitric acid. *The substance dissolves;*[17] remove as

[16] If hydrochloric acid causes any effervescence, the evolved gas must be examined for carbonic, hydrosulphuric, and hydrocyanic acids, as directed under the " General Properties of the Acids."

[17] If the substance dissolves with the separation of a light-yellow coloured mass of sulphur, it points out the presence of a sulphide. When nitric acid is employed as the solvent, as much of the free acid as possible ought to be removed by evaporation, before passing hydrosulphuric-acid gas through the solution, as both acids suffer mutual decomposition in the presence of each other, the decomposition being attended with the separation of a large amount of sulphur.

much of the free acid as possible by evaporation; dilute the concentrated solution with water, and then proceed with the analysis. *It does not dissolve;* allow it to settle; pour off one half the acid, add a like quantity of concentrated hydro-chloric acid, and again boil. If a portion still remains undis-solved, return to the strong hydrochloric-acid mixture; filter, and examine the filtrate, if anything has passed into solution. The residue insoluble in acids, after being well washed, must be treated according to IV.   . .

IV. The usually occurring substances, which are insoluble in water and acids, are the sulphates of baryta, strontia, lime and lead, alumina, peroxide of iron and their phosphates, the chlorides of silver and lead, fluoride of calcium, silicates, silica, and sulphur.

A small portion of the residue insoluble in water and acids is heated on a slip of platinum foil. If sulphurous acid is evolved along with the volatilisation of the whole of the substance, sulphur only can be present. When other substances are pre-sent, add to another small portion a drop of sulphide of ammo-nium. If the colour remains white, silver, lead, and probably iron, are absent.

A small quantity of the dry residue, in the state of a very fine powder, is mixed with four times its weight of carbonate of soda and potash. The mixed mass is placed in a platinum crucible,[18] and heated over a Berzelius' spirit-lamp for about half an hour; or, what is still better, the platinum vessel is placed within a Hessian crucible, containing a little carbonate of

[18] The compounds of the easily reduced metals, such as silver, lead, &c., must not be fused in platinum vessels, as they form alloys with that metal, which greatly injures or altogether destroys the platinum vessel : porcelain crucibles must therefore be employed in such cases.

·magnesia, which is placed there to prevent the platinum from coming in contact with the Hessian crucible, and exposed to a full red heat, for the same length of time, in a furnace.

On cooling, the fused mass is boiled with water, and filtered. The filtrate is to be examined for the *acids* and *alumina*, the residue for the *bases*.

Examination of the filtrate. To one portion of the filtrate add hydrochloric acid until the solution is distinctly acid, evaporate to dryness, and ignite until acid fumes are no longer evolved. To the dried mass add dilute hydrochloric acid, and boil ; if a residue remains, silicic acid is present. To the filtrate from the silica add ammonia in excess, and then warm the solution ; if a precipitate is formed, it must be due either to alumina or its phosphate. After having filtered and washed the precipitate, examine whether it is soluble in acetic acid. In the filtrate from the alumina precipitate, or in the solution which has failed to give a precipitate, test for phosphoric acid, by adding chloride of ammonium, and then sulphate of magnesia. Acidulate another portion of the original filtrate with hydrochloric acid, and examine for sulphuric acid, by adding chloride of barium. Another portion must be acidulated with nitric acid, and tested for chlorine, by nitrate of silver. To detect fluorine, a portion of the original substance must be treated with concentrated sulphuric acid, in the manner described under the head of hydrofluoric acid.

Examination of the residue. After having removed all the substances soluble in water, by repeated washings, dissolve the residue, if lead and silver are absent, in hydrochloric acid, and proceed with the analysis in the usual way. If the residue does not completely dissolve in the acid, and the two metals just named are absent, it shows that a portion of the substance has

not been decomposed. When this is the case, filter off, and examine the filtrate.

When the fixed alkalies are to be looked for in the insoluble residue, another portion, in fine powder, must be mixed with about four times its weight of carbonate of baryta, and fused in a platinum crucible, in the manner already described. On cooling, the fused mass is digested with dilute hydrochloric acid, and filtered. The filtrate is evaporated to dryness, and ignited; the dry residue must be treated with water, and again filtered. The filtrate, after being freed from iron, alumina, baryta, lime, and magnesia, must be evaporated to dryness, to expel the ammoniacal salts which have been employed in their precipitation; if a residue remains it must be examined for potash and soda.

THE SOLID SUBSTANCE UNDER EXAMINATION IS NEITHER A PURE METAL, NOR AN ALLOY, BUT CONTAINS ORGANIC MATTER.

The presence of fixed organic matter [19] interferes with the detection of many substances. Thus, in the presence of tartaric acid, which is a fixed organic acid, the oxides of aluminum, chromium, and iron, and many other metallic oxides, are not precipitated by the alkalies. When an inorganic analysis has therefore to be performed upon a substance containing organic matter, this last must generally be destroyed before the examination is attempted. In most cases, this may be accomplished by simply igniting the substance in a porcelain or platinum crucible, until all the organic matter has been destroyed, and afterwards dissolving the residue in water or acids. The solution must then be examined in the regular way. A separate examination must always be made in an undecom-

[19] Organic substances are termed *fixed* when they cannot be distilled or volatilised without decomposition.

posed portion, for the salts of ammonia, mercury, arsenic, and antimony, as these substances might be entirely volatilised by the heat employed to destroy the organic matter.

Sometimes we are obliged to have recourse to the following method for destroying the organic matter, especially in the case of solutions which have to be examined for *poisons*. The solid substance or solution is boiled with concentrated hydrochloric acid, to which chlorate of potash, in powder, is added gradually until the mixture becomes perfectly fluid; the solution is then heated until all free chlorine is evolved; after which it is diluted with water and filtered. The filtrate must be examined in the regular way. The residue must be examined for chloride of silver.

THE SUBSTANCE UNDER EXAMINATION IS A PURE METAL OR AN ALLOY.

Nitric acid behaves with metals in the following manner. Gold and platinum are neither dissolved nor altered in the least degree by it. Tin and antimony are converted by nitric acid into oxides, which do not dissolve in, or combine with, an excess of the acid. The other metals are oxidised and converted by it into soluble nitrates. On account of the different behaviour therefore which nitric acid exhibits with the metals, it is usual to employ it as the solvent of alloys, &c.

To the metal or alloy under examination, which is placed in a small flask, is added concentrated nitric acid and heat applied. One of the three following cases will then occur—1. Complete solution takes place. 2. A white insoluble substance separates. 3. A metallic residue remains. Each of the three cases are considered separately in detail.

1. *If complete solution ensues,* GOLD, PLATINUM, TIN, and

ANTIMONY must be absent. After removing the greater part of the free acid by evaporation dilute the solution with water,[20] and proceed with the analysis in the regular way. Mercury if present will be found in the state of peroxide.

2. *If a white insoluble substance separates*, TIN and ANTIMONY are indicated. After removing the greater part of the free acid by evaporation, dilute the solution with water, filter, and proceed with the filtrate in the ordinary way. The precipitate after being well washed with water, is treated with a hot concentrated solution of tartaric acid. If it all dissolves, TIN is absent. The presence of ANTIMONY is confirmed by hydrosulphuric acid producing in the tartaric-acid solution, to which hydrochloric acid has been added, an orange-red precipitate. If the whole of the *insoluble substance* does not dissolve in tartaric acid, the solution is filtered. The filtrate is examined for antimony by the method just stated. The residue after being well washed is mixed with carbonate of soda and cyanide of potassium, and exposed on a charcoal support to the inner blowpipe flame. If tin is present, ductile metallic grains will be obtained.

3. *If a metallic residue remains*, GOLD and PLATINUM are indicated. After removing the greater part of the free acid by evaporation, dilute the solution with water, filter, and examine the filtrate in the usual way. The metallic residue is dissolved in aqua regia. One portion of the solution is tested for GOLD by means of protosulphate of iron. The other portion is tested for PLATINUM by means of chloride of potassium.

[20] If the solution becomes turbid, on the addition of water, it indicates the presence of bismuth.

ARRANGEMENT OF THE RESULTS OF THE ANALYSIS.

The student, during the course of his analytical studies, ought invariably to record the results of each analysis, in his note-book, in a systematic and tabular form. An illustration is given to show the method to be pursued.

PRELIMINARY EXAMINATION OF A SOLID SUBSTANCE.

1. It is a colourless crystalline substance; probably a salt.

2. Heated alone, on charcoal, it deflagrates, a white infusible substance remaining behind, which becomes luminous, and imparts a crimson colour to the flame, probably strontia.

3. Soluble in water; the solution is neutral to test-paper.

The preliminary experiments indicate therefore the presence of nitrate of strontia.

ACTUAL EXAMINATION.

On the addition of hydrochloric acid no effervescence; absence of CO_2 and HS.

H Cl. No precipitate.	H S. No precipitate.	Boiled to expel H S; added a few drops of H O, N O₅; again boiled; added, lastly, N H₄ Cl, and N H₄ O. No precipitate.	N H₄ S. No Precipitate.	N H₄ O, C O₂. A white precipitate formed.	Divided the filtrate into two portions.
Absent: Ag O, Hg₂ O, and probably Pb O.	Absent: Hg O, Pb O, Bi O₃. Absent: Cd O, Cu O, and As O₃ As O₅ Sn O Sn O₂ Sb O₃ Pt O₂ Au O₃	Absent: Fe₂O₃, Al₂O₃, and Cr₂O₃. The substance being soluble in water, the phosphates and oxalates of the alkaline earths could not be present.	Absent: Mn O. Zn O. Ni O. Co O.	May be present. Ba O, CO₂, Sr O, CO₂, CaO, CO₂; dissolved in H O, Ā; divided into two portions. — To one portion added CaO, SO₃. A precipitate, after lapse of sometime, presence of Sr O, absence of Ba O. No precipitate. Absent: Ba O. — Precipitated the Sr O from the other portion, by H O, S O₃. Added to the filtered liquid N H₄ O, and H O, Ō. No precipitate. Absent: Ca O.	To one portion added 3 N H₄ O, As O₅. No precipitate. Absent: Mg O. — Evaporated the other portion to dryness, to expel ammoniacal salts. No residue. — Absent: NaO, K O. — Boiled a portion of the original solution with NaO, H O. No ammonia evolved; absence of ammoniacal salts.

EXAMINATION FOR ACIDS.

The following acids, viz., CO_2, HS, AsO_3, AsO_5, and CrO_3, were proved to be absent on the examination for the bases.

The remainder of the acids, which give precipitates with a salt of baryta, could not be present; as they likewise form, with strontia, insoluble salts.

Added to a portion of the original solution AgO, NO_5, no precipitate; absent Cl, Cy, Br, and I.

Added to another portion HO, SO_3, and copper turnings, nitrous fumes were evolved, showing the presence of nitric acid.

The examination for chloric acid yielded a negative result.