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SYSTEMATIC QUALITATIVE ANALYSIS

FOR STUDENTS OF INORGANIC
CHEMISTRY

BY

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Late Professor of Inorganic and Analytical Chemistry in the
Royal Technical College, Glasgow

THIRD EDITION

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PREFACE

THE chief purpose of this book is so to present the reactions which lie at the foundation of inorganic chemical analysis, that the latter may contribute to a basis of general theoretical chemistry. Only as the operations of qualitative analysis can be utilized for the establishment of a broad system of scientific chemistry may they be considered a true adjunct of scientific education; and only then do they reach their highest value.

It will be fully recognized that the analysis of inorganic mixtures often becomes the performance of unintelligent routine; and it is a great gain to the student of chemistry when he realizes that whilst he is studying chemical reactions with a view to qualitative analysis, he is at the same time making his theoretical knowledge more sure by his personal investigation of some of the principles he has first heard of in the lecture room. The analytical chemist, too, will be best fitted to do his work, and solve the problems which are submitted to him, when his mind has thoroughly grasped the deep-seated principles of the science which must form the foundation of qualitative analysis.

The book is divided into three parts.

In Part I, of which indeed the rest of the book is a detailed development, the operations of analysis are reviewed, systematized, and generalized. Here is included the discussion of such subjects as the action of heat on substances, the general properties of substances in solution, hydrolysis, and precipitation. Here also the scheme of analysis for metallic radicles in solution is deduced

from the solubilities of metallic compounds, so that the student may know why the existing method of division of the metals into groups has been chosen. As a rule, this subject is dismissed briefly in analytical textbooks, but I believe it is wise to attach great importance to its elucidation.

Part II contains the reactions of the metallic radicles, and the tables of separation of the constituent metals of the various groups. For the study of the reactions of the metals of any particular group only those on which the table of separation directly depends are at first chosen, and these are arranged in the order in which they are to be employed; so that when the table is presented the student should discover that he understands, and is already familiar with, every part of it.

For the sake, however, of setting forth the chemistry of the metals in more detail, there follow the tables of separation those reactions which exemplify the more important properties of the metallic compounds not previously noticed, attention being drawn, from time to time, to general principles and analogies such as the periodic law makes prominent.

The order in which the acidic radicles are arranged is the same as that in which they are tested for in analysis; and the order of the principal tests for each acidic radicle is likewise the same as that in which these will be carried out in the analysis.

The actual instructions for analysis are brief, and form Part III of the book. They recapitulate methods that have already been studied, and therefore the student is referred back to earlier sections for details.

There are a few departures from the more customary methods of separation. The chief of these are: the adoption of substantially the method devised by Dr. James Walker for separating the metals of the tin group; the use of the ferricyanide reaction to identify but not separate cobalt in presence of nickel; the use of dilute nitric acid to oxidize and separate bromide from chloride.

I desire to mention that I am indebted to numerous textbooks, but perhaps chiefly to Treadwell's *Analytical Chemistry*. I also gladly acknowledge my obligation to Professors Clowes and Coleman, through whose valuable teaching I gained my first insight into the principles of Chemical Analysis; and I record my appreciation of the kindly interest they have shown in the publication of this book. My friend and colleague, Dr. H. J.*S. Sand, has also helped me with useful advice and criticism, and to him I tender my sincere thanks.

R. M. C.

May, 1909.

NOTE TO 1939 EDITION

For this Edition the text has been revised, and some adjustments have been made. An Appendix dealing with certain of the newer organic reagents has been added in the hope that it will serve to interest the student in these modern developments, and also to provide alternative tests where the older tests are not too satisfactory.

A. B. C.

ADVICE TO THE STUDENT

IN using this book the student should first read the Introduction regarding Manipulation, and then commence to work at the reactions of the metallic radicles beginning on p. 68, and confirm the knowledge he gains of each group by analysing mixed solutions of salts of metals in the group. At first he may mix his own solutions, and endeavour to identify the metals he knows to be present, afterwards he should analyse solutions of unknown composition. Then mixtures containing metals in two or more groups may be analysed by means of the general table in Part III. The supplementary reactions for the metals may be studied or omitted, either in part or entirely, at discretion.

The reactions of the acidic radicles should next be proceeded with, commencing with carbonate on p. 155.

This exercise may be somewhat shortened by omitting the matter in small type, and further curtailed by performing only those reactions in paragraphs with an asterisk, which alone are essential for purposes of identification.

While this practical work is in progress the student should direct his home studies to the mastery of the contents of Part I. This part contains the principles on which the processes of analysis are based, as well as information regarding a number of properties and reactions of substances to which reference is made during the course of analysis outlined in Part III. Sections 36 to 45 deserve specially thoughtful study. The student should perform the experiments in this part for which definite instructions are given, and any others

which may suggest themselves to him during the course of his reading.

The author hopes that the use of this book will enable the student to get a synthetic view of inorganic chemistry, so that the subject will no longer appear to be a mass of disconnected facts; and that ultimately the operations of qualitative analysis may become to him a conscious application of the broadest principles of theoretical chemistry.

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INTRODUCTION

REGARDING

MANIPULATION IN QUALITATIVE ANALYSIS

Exercises in Qualitative Analysis have interest and value. They have a sporting interest because of a trail to be followed, and a discovery to be made at the end of it; they have an educational value because of the many chemical reactions encountered, and the enlargement of chemical knowledge insured to the student. Nevertheless the facts need careful assimilation, and to the beginner are rather overwhelming in number. The interest and value, moreover, are in addition to the practical importance of the discovery of the composition of substances.

Yet these exercises are spoiled if not carried out in good style; indeed merely to find out what mixtures are made of by haphazard and inelegant procedure is very far from being a desirable accomplishment in chemical science.

Therefore the notes that follow are intended to help the student to do his work well, and to obtain his results in such a way as to give satisfaction to himself and his instructor.

Cleanliness and Tidiness.—This subject comes first, and what is to be said under this heading is not always superfluous. The student should receive his locker and set of apparatus in a clean condition, and should keep them so. Qualitative analysis should not be messy, but it easily becomes so in the hands of a careless student. Test-tubes, beakers, funnels, &c., should never be put away in a dirty condition, but should be cleaned at the end of the day's work ready for use on the next occasion. Let the same

rule apply to laboratory utensils as to plates and cups and dishes in the home. A test-tube brush is provided. The student who neglects this rule gives himself extra trouble, because dry dirt is more difficult to remove than wet dirt; and, of course, it is impossible to do good work with dirty apparatus.

Two cloths should be provided for cleaning purposes: a rough cloth to wipe up liquid spilt upon the bench, and a duster containing no dressing, for cleaning and drying glassware. Always wipe up quickly liquids that are spilt on the bench or on the filter stand when filtering, paying particular attention to strong acids. These should be neutralized with sodium carbonate solution before removal.

Reagent bottles should never be put down on the bench. Taken from their places on the shelf, they should be returned there immediately after use. Neither should their stoppers be laid down; with practice a stopper and a test-tube can easily be held in one hand while the liquid is poured from the bottle held in the other hand.

If a student finds a reagent bottle empty, and has no means of refilling it, and therefore goes to a neighbouring bench for what he requires, he must be careful to return the bottle he uses to the place he took it from. Reagent bottles must not be moved from bench to bench.

When a student has finished work for the day he should make sure that he puts away everything in his locker, and secures this with a good padlock. Apparatus is more likely to disappear if left on the bench than if locked up.

Disposal of Waste.—Drainage in a chemical laboratory is very important; neither strong acids, nor paper or any solid should be thrown into the sink. Acids should first be diluted; and solids should be put into the receptacles provided for them.

Risk of Fire.—There is always risk of fire in a chemical laboratory. A student should be on his guard to avoid every kind of fire risk. This remark applies more particularly to students of organic chemistry who handle inflammable liquids; but phosphorus and

sodium, employed in inorganic chemistry, are dangerous as possible sources of fire. Chlorates, nitrates, and permanganates may cause fire on account of their high oxygen content, whilst sodium peroxide may spontaneously ignite a moist filter paper.

Laboratory equipment should include some portable type of fire-extinguisher and buckets of sand and, in addition, a blanket for extinguishing burning clothing. The student should be familiar with the positions and use of these.

Accidents.—Every laboratory should have a first-aid equipment, in charge of a responsible person, to whom, or to a demonstrator, the student should immediately report all accidents. Acids or alkalis spilt on the clothing should be neutralized by dilute ammonia or dilute acetic acid solutions, respectively. Acid or alkali on the hands or face should at once be washed off by a copious stream of cold water, and the injury attended to, particularly if the eyes are affected, by a competent person.

Waste of Gas and Chemicals.—Gas must not be wasted. The Bunsen flame should be adjusted for the work in hand, and extinguished when no longer required, particularly when the student is leaving the laboratory. With a small Bunsen flame the air-holes should be adjusted to prevent striking-back. If striking-back occurs, the Bunsen tube may become hot enough to melt the rubber tube and the escaping gas may ignite, so that there is a risk of fire.

When a substance or mixture is received for qualitative analysis the amount of it should not be more than sufficient to lie conveniently in the middle of a watch glass, or half fill a specimen tube $\frac{3}{4}$ " $\times$ $\frac{5}{8}$ ". More can be obtained later if necessary. A quarter of this amount or less will be sufficient to be dissolved for the separation of the metals, or for the acidic radicle reactions.

Excess of Reagent.—When a reagent is directed to be added in excess, this means, not that an excessive amount of it should be used, but that enough should be added to complete the reaction which the reagent is to bring about. For instance, when an alkali is to be added to an acid solution only a little more than sufficient to neutralize the acid, as shown by litmus paper,

should be used. Obviously it is useless to add less than sufficient alkali if a reaction in alkaline solution is expected.

If a precipitant is being employed, e.g. hydrogen sulphide gas or a reagent in solution, it is necessary to know that the reagent has done its work. More precipitant is then wasteful and may be a hindrance.

The instructions that follow are set down in the order of procedure in qualitative analysis.

Ignition Tubes.—These may be made out of ordinary soft glass tubing which is drawn out and sealed in the Bunsen flame in 3-inch lengths. A small bulb may be made at the sealed end by heating this to redness in the flame, and then blowing down the tube. In some laboratories small test-tubes, $3'' \times \frac{3}{8}''$ or $\frac{1}{4}''$, are employed as ignition tubes. These are convenient, cheap, and better, because made of thinner glass. The larger test-tubes ($5'' \times \frac{5}{8}''$), commonly used for wet reactions, should not be used for ignition purposes.

Mounting and Use of Platinum Wire.—Platinum wire can be mounted in glass because the co-efficients of expansion of the two materials are almost exactly the same. The student should provide himself with 2 in. of platinum wire, and mount it in the following way. Choose a piece of glass tubing about 8 in. long; the tubing is called quill tubing because it is about the diameter of a quill. Heat the middle of the tube in the upper part of the Bunsen flame, while rotating it, until it is red hot and softens; then remove it from the flame and gently pull it out to the extent shown in the figure. Afterwards by means of



a scratch from a sharp triangular file divide it at the point shown by the vertical line. Then insert the platinum wire a quarter of an inch within the tube A, and by the use of a flame, preferably the tip of a blowpipe flame, heat the glass so as to fuse

it round the wire. Also round the other end of the glass tube by fusing it in the flame. Finally make a small loop at the end of the wire by twisting it round a thin glass rod or pencil point.

Another, but less satisfactory, way of mounting the wire is to use a piece of glass rod, and push the wire into the end of the rod when this has been made soft by heating it in a flame.

The uses of the mounted platinum wire are referred to in §§ 9 to 12 of this book. After use the wire should be thoroughly cleaned. Sometimes washing the wire in water and heating it in the flame are sufficient to clean it so that it imparts no perceptible colour to the flame; often, however, it is necessary to heat it in boiling hydrochloric acid in a test-tube. Contamination may also be removed by forming a borax bead (§ 10) on the wire, the bead being shaken off while hot. Alternate dipping into hydrochloric acid and heating will free the wire from any residual borate. If, however, the wire has been heated with tin or lead salts the end of it may be found corroded. For this there is no remedy but to break off the end. Fix the end of the glass mount in a cork, so that the wire when not in use may be kept immersed in hydrochloric acid in a test-tube.

The Blowpipe.—For operations with glass, and for borax bead and charcoal reactions, it is necessary to use the blowpipe. In most laboratories there is a lead-covered table supporting a standard blowpipe, which is blown by bellows or compressed air. Nevertheless the student must learn to use the portable mouth blowpipe. It is important to see that the nozzle of this blowpipe has a small hole, just large enough for a pin point to enter a little way.

It is first necessary to understand that, like the Bunsen flame, the blowpipe flame consists of inner and outer flames, with a zone of partially burnt gas between them. In the mouth blowpipe, however, the breath takes the place of the air which in the ordinary non-luminous flame enters at the base of the burner. Therefore a small luminous flame, about 2–3 in. long, obtained

by closing the holes at the base of the Bunsen burner, is employed for the blowpipe. It is a common error to blow into an already non-luminous flame. In use, the tip of the nozzle of the blowpipe should rest on the rim of the burner, the blowpipe being held in the right hand; it may even be supported by the teeth and lips so that both hands are free for manipulation. It will be found that gentle blowing is sufficient to convert the vertical luminous flame into a horizontal non-luminous flame, in which outer and inner flames are clearly distinguishable.

Beginners find difficulty in blowing for long enough without getting out of breath. The secret is to keep the cheeks distended so as to constitute the mouth a reservoir of air, supplied from the lungs, while breathing through the nose.

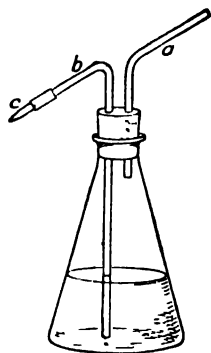
The Wash-bottle.—A wash-bottle is an essential part of the equipment for qualitative as well as quantitative analysis; and if the student is not provided with this article it should be one of his first operations to make one.

A 500 c.c. flask is required, preferably conical in shape, a cork or stopper which is to have two holes, a sufficiency of clean glass tubing, not too narrow, and a small piece of rubber tubing to fit over the glass tubing. The first operation is to cut the glass tubing into suitable lengths, and then bend it as required. The cutting is generally done with a triangular file. A deep scratch is made on one side of the tubing, which is then taken in the fingers of both hands, the thumbs being placed on each side behind the scratch. With gentle outward pressure the tube will then break cleanly where the scratch was made. An alternative way is to lay the file on the working bench, and the glass tube upon it with the scratch above the edge of the file; a sharp tap then causes the tube to break.

For bending the tubing a flat flame, not a Bunsen flame, must be used. It is a very common mistake for students to use a Bunsen flame. Obviously a bend cannot be wider than the part of the tube heated; therefore the bend made in the Bunsen

flame must necessarily be sharp, and the glass will be buckled and strained, and besides being ugly will be likely to break. A bend made in a flame 2 in. wide will, however, be gently curved, and will be elegant and strong. To make the required bend hold the tubing in the broad luminous flame with both hands, and rotate it whilst it becomes covered with soot. When it is soft enough, take it out of the flame and bend it to the required position, or, holding it just within the flame, allow it to drop by its own weight through the required angle.

Be careful that the obtuse and acute angles of the two bent tubes required for the wash-bottle are together equal to 180° , so that when fixed the mouthpiece (*a*) and delivery tube (*b*) will be in a straight line, as the figure shows. Cut the bent pieces to the required lengths and round the four ends by fusing them in the Bunsen flame. Then make a jet (*c*) by drawing out a piece of similar tubing after heating it in the Bunsen or blowpipe flame, and cut off the jet, and the tubing at the other end to a length of about 2 in. Round off the cut end and also the jet. It is better to have the jet too coarse rather than too fine at first, because in the former case it can be fused up in the flame. The bore should be of such a size as to deliver easily a fine jet of water.



The doubly bored stopper must now be provided. This is better of rubber, with two holes already bored. In that case the tubes may be slipped into place after being moistened with water. If, however, an ordinary cork is to be used great care must be taken in boring the holes. The cork chosen should be as free from blemishes as possible, and should be softened by using a cork press or rolling it under the foot. The cork-borer must be sharp, and slightly smaller than the tubes. It is used

wet with water, and with the help of the handle gradually worked half-way through the cork, whilst this is pressed against the bench. The hole is completed by boring from the other end of the cork. Holes can be enlarged, if necessary, by the use of a round (rat tail) file, until the tubes will fit them tightly. No attempt must be made, however, to force the tubes through the holes, or fracture will result, and perhaps a badly cut hand. A tube should be held near to where it enters the cork to avoid putting a length of it under strain.

Finally fix the jet in position by about 2 in. of good rubber tubing, and then the wash-bottle is complete. To test it put some water in the flask, fit in the stopper with the tubes and blow down the mouthpiece. The water should come out in a fine stream with considerable force if the bottle is air-tight. Whether any air escapes round the cork or where the tubes pass through it can be discovered by putting water on the cork and blowing into the bottle. If there is any considerable leak it will be better to bore another cork. Since the wash-bottle is generally to be used with hot water, coarse string should be wound round the neck for a length of 2 in., so that it can be handled comfortably when the bottle contains boiling water. Rubber tubing swells and perishes with heat, so that the little piece used as a junction may get loose and should be renewed from time to time; otherwise the jet may be blown off. This is troublesome, and may be fatal in quantitative analysis if it drops into the precipitate.

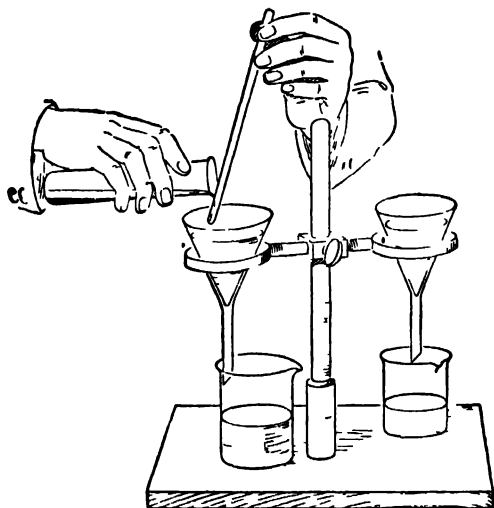
Filtering and Washing a Precipitate.—Precipitates differ greatly in the state of subdivision of the solid particles of which they consist, and consequently in the speed with which they can be filtered. Fine precipitates filter more slowly than coarse ones, not only because water runs away from between their particles less freely, but also because the pores of the filter paper become clogged or stopped up by particles of similar diameter. Besides this, a finely divided precipitate, such as precipitated sulphur, barium sulphate, or calcium oxalate, cannot be filtered

properly until the pores of the paper are partially stopped, because many of the particles are smaller than the pores. To wait during a lengthy filtration is a waste of time, so that any means by which the process may be hastened is desirable. The means are simple. Liquids containing precipitates should be heated before filtration. There are, however, one or two exceptions to this rule in qualitative analysis; e.g. the case of lead chloride which dissolves in hot water, and the alkaline liquid containing manganese hydroxide in suspension, since this may have zinc in solution which is precipitated by boiling. The effects of heating are various; it may cause coagulation of a colloidal precipitate, i.e. cause fine particles to coalesce to form bigger ones; or it may promote granulation, i.e. crystallization; also it hastens filtration owing to greater molecular activity of the liquid when hot. The effect is specially noticeable with the precipitates of the copper group. When a student tries to filter precipitated copper sulphide cold, and then is told to heat the liquid to boiling and try again, he greatly appreciates the difference boiling makes.

The filter papers used in qualitative analysis are generally 11 c.m. in diameter; 9 c.m. filters are sometimes used, but they are hardly large enough for all purposes. The circular filter paper is folded in half, and then again; then it is opened to form a cone which fits into a funnel, with three thicknesses of paper opposite one. If the paper is moistened and pressed with the finger against the sides of the funnel so as to extrude air from between paper and glass, and the filter is then filled with water, the water running through will fill the stem of the funnel, and by its weight exert a pull upon that in the funnel, and so hasten filtration. Also the oblique end of the funnel stem should touch the side of the beaker that receives the filtrate. This prevents splashing as well as hastening filtration.

Precipitation is generally carried out in a boiling tube, i.e. a large test-tube $6'' \times 1''$, or in a beaker. A flask, unless it

has a wide neck, is not so convenient for transferring the precipitate to the filter. If the precipitate is heavy, and settles quickly from the heated liquid, it may be washed by decantation, i.e. most of the supernatant liquid may be poured off through the filter, preferably down a glass rod as shown in the figure, leaving the precipitate to be transferred to the paper by a jet of hot water from the wash-bottle. In such case it is



undesirable to dilute the first filtrate with too much wash water. It is generally preferable, however, to transfer the precipitate to the filter as soon as possible, and wash it there after the filtrate has been collected and set aside. Two things are necessary for the efficient separation of a metal as an insoluble compound; first the precipitation must be complete, second, the washing of the precipitate must be adequate. Imperfect precipitation means that some metal that ought to have been removed remains to be reprecipitated in a later group and cause confusion; inadequate washing means that metallic salts belonging to subsequent groups contaminate the precipitate and cause error.

Lead and cadmium are liable to escape complete precipitation by hydrogen sulphide because of the solubility of their sulphides in dilute acid. Lead, for example, if left in solution will cause a white precipitate with ammonia or a black one with ammonium sulphide, and is a frequent cause of trouble with beginners. Imperfect washing of an arsenious sulphide precipitate will cause a blackening when alkali is used to dissolve it, if an iron salt was present in the original mixture, and its solution has not been completely removed from the sulphide precipitate by washing.

In washing a precipitate on the filter it is best to allow it to drain thoroughly, and then stir it up on the filter with a jet of hot water from the wash-bottle. It is generally sufficient in qualitative analysis to give two thorough washings of this kind; though to be quite sure the precipitate is clean it is necessary to test the final washings for a radicle, e.g. chloride known to have been present in solution.

Removal of the Precipitate from the Filter.—If the precipitate is bulky, and after washing forms a level surface in the filter, sufficient of it for examination can be removed on the tip of a spatula. The small horn spatulas that are sold as paper knives are convenient for this purpose. A clean knife blade is an obvious tool to use, but is likely to be tarnished by a sulphide precipitate; a nickel spatula is preferable to a steel knife blade. If there is not enough precipitate to remove in this way, the filter after thorough draining may be removed from the funnel, opened on a clockglass, and scraped, though this procedure is rather messy; or the precipitate may be removed from the filter by a jet of water from the wash-bottle. This may be done in one of two ways. First, the funnel may be held horizontally with its rim over a basin or beaker, and the jet of water applied so as to wash out the precipitate into the receptacle; second, a hole may be made in the base of the filter by a pointed glass rod, and the precipitate washed into the receptacle through the funnel stem. If this

method is used care must be taken not to stop up the stem with the fragment of filter paper broken away from the apex of the filter. To avoid such a contingency stemless funnels are sometimes employed.

When a precipitate is to be dissolved completely, and solution is easy, as in the case of the carbonates of the alkaline earth group, the solvent, preferably hot, may be poured on to the filter, and the process repeated if necessary until all the precipitate has disappeared.

Lastly, if only a small quantity of the precipitate is available, and this adheres firmly to the filter paper, the paper itself may be heated with the solvent until it is disintegrated, and the precipitate, generally coloured, is seen to have been dissolved. The liquid containing the filter paper pulp is then filtered, the pulp being pressed down in the filter by means of a spatula, so that as much as possible may pass through the filter; the pulp should afterwards be washed once, so as to lose as little as possible of the substance in solution. Small amounts of precipitate and liquid may conveniently be separated by a hand-driven centrifuge.

Entering Results in Notebook.—Students should try to make neat notes, preferably in ink, as they proceed with the analysis. Sometimes rough notes are permitted which are afterwards entered neatly in another book; but a good teacher will never accept a statement of results without seeing details. Students differ greatly in the elegance of their writing, and bad writing may not be blameworthy; but a student who knows himself to be a bad writer should on that account be the more careful with his record.

It is a very bad habit to carry out a number of experiments and leave the writing up till afterwards. In this way inaccuracies are sure to creep into the record.

To show a student how to enter notes, a "Model Analysis" appears at the end of this book.

SYSTEMATIC. QUALITATIVE ANALYSIS

PART I.—GENERAL

§ 1. The substances identified by inorganic chemical analysis, exclusive of gases, consist almost entirely of acids, bases, and salts, and elements and compounds which yield them when dissolved in water, acids, or alkalis. Substances insoluble in water and acids, but dissolved by other means, nevertheless yield acids, bases, or salts, when eventually obtained in solution.

Few pure liquids are met with in inorganic chemistry. The chief are water, bromine, mercury, the halides—*i.e.* fluorides, chlorides, bromides, and iodides—and oxyhalides of some non-metals and metalloids, and nitric and sulphuric acids. These acids, however, together with hydrochloric, phosphoric, and some others, occur more often in solution in a greater or less amount of water than in the anhydrous state.

METHODS OF ANALYSIS

§ 2. If a substance, or mixture of substances, in the solid state¹

¹ When the substance is in aqueous solution, it may generally be obtained in an anhydrous state by evaporation; if it cannot be so obtained, the analysis is limited to the examination of the solution. If the substance is a pure liquid, such of the "dry" reactions as are possible may still be applied to it.

is given for analysis, two general methods of treatment are available:

- I. Preliminary examination by dry reactions.
- II Systematic examination for basic and acidic radicles.

§ 3. I. PRELIMINARY EXAMINATION BY DRY REACTIONS

The substance is submitted to the action of heat, either alone or after admixture with another solid substance, and the physical and chemical changes which take place are observed.

This method of procedure—which is not chemical analysis in the narrower sense, since by its means no separation of substances according to any systematic scheme is possible—is of value because most of the metallic, and some of the acidic radicles which may be present in a given substance, are revealed by one or other of the empirical and disconnected tests applied under this heading; and thus guidance is given in view of the systematic examination to follow. It is sometimes possible to identify with certainty a given substance by dry tests alone, and some constituents of a substance, especially water of crystallization, will escape detection if these tests are omitted.

Nevertheless the examination in the dry way is of relatively small importance, since little will be detected by its means which is not found, and generally with greater certainty, by subsequent methods. Moreover, when mixtures are being dealt with, different products or effects occurring together may mask each other, and render identification difficult. Little time, therefore, need be spent on these tests in the actual process of analysis.

Apart, however, from their value for purposes of identification, the dry tests furnish many chemical reactions of great importance, and therefore well repay careful study.

The *preliminary dry reactions* may be classified as follows:—

- (A) Action of heat on substances.
- (B) Flame colorations.
- (C) Borax bead reactions.
- (D) Phosphate and sodium carbonate bead reactions.
- (E) Charcoal reactions.

§ 4. (A) Action of Heat on Substances

Single substances may be divided for analytical purposes into three general classes according to their behaviour when heated.

- (1) Substances which undergo change of state previous to, or without, decomposition.
- (2) Compounds, generally salts, which lose water of crystallization when heated.
- (3) Compounds which decompose when heated, evolving gases or vapours.¹

§ 5. (1) CHANGE OF STATE

Temporary Change of Colour.—A few solid compounds undergo temporary change of colour when heated, without, or previous to, other change.

They are:

	Cold.	Hot.
Zinc oxide, ZnO	White.	Yellow.
Mercuric oxide, HgO	Red.	Black.
Mercuric iodide, HgI_2	Crimson.	Yellow.
Mercuric sulphide, HgS	Scarlet.	Black.
Litharge, PbO	Light buff.	Brownish red.
Red lead, Pb_3O_4	Red.	Chocolate.
Stannic oxide, SnO_2	Straw colour.	Yellowish brown.
Bismuthous oxide, Bi_2O_3	Yellow.	Brown.

¹ Whether they contain water of crystallization or not. It is practically convenient to distinguish here between water of crystallization and the more intimate constituents of salts which may be lost on heating; but such a distinction has not necessarily any theoretical significance.

All chemical substances, when heated, can pass from the solid to the liquid, or from the liquid to the vaporous state, or sometimes directly from the solid to the vaporous state, unless they are previously decomposed by heat. Most inorganic substances, however, and especially the salts of the metals, are so decomposed.

Substances which readily change their state of solid, liquid, or vapour may be classified as follows:—

(a) Liquids at atmospheric temperature which distil unchanged.¹

Bromine, mercury.

Water, acetic acid, nitric acid, sulphuric acid.

Silicon tetrachloride, stannic chloride

Phosphorus trichloride, phosphorus oxychloride, antimony pentachloride.

Sulphur monochloride, sulphur dichloride, thionyl chloride, sulphuryl chloride, chlorosulphonic acid.

Chromyl chloride.

(b) Solids which may be melted in a glass tube and sometimes distilled.²

Elements—

Sodium, potassium, zinc, cadmium, tin, lead, phosphorus, bismuth, sulphur, iodine.

Oxides—

Litharge, antimonious oxide, bismuthous oxide, chromium trioxide.

Hydroxides—

Basic: Sodium, potassium, barium hydroxides.

Acidic: Boric, oxalic, phosphoric acids.

Halides—

Halides, especially iodides, of sodium and potassium.

Silver halides (AgCl, AgBr, AgI about equally fusible).

Alkaline earth halides (fusible with difficulty).

Zinc and cadmium halides.

Mercuric halides.

Aluminium bromide and iodide.

¹ Only those which are well known are mentioned.

² Sometimes a sublimate is formed, the vapour returning directly to the solid state. Sodium, potassium, and phosphorus will catch fire.

Stannous halides.

Stannic bromide and iodide.

Lead halides.

Antimonious and bismuthous halides.

Ferrous iodide, ferric chloride.

Nitrates—

Those of sodium, potassium, ammonium, silver, calcium, barium.

Other salts—

Alkali hydrogen sulphates, chromates, dichromates, chlorates, sulphocyanides, acetates, ammonium sulphate, lead chromate (fusible with difficulty).

With some of these substances, *e.g.* iodine and mercuric chloride, the melting- and boiling-points lie near together; consequently a certain amount of sublimation accompanies fusion.

(c) **Solids which sublime.**¹

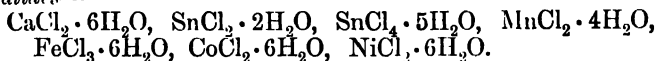
Ammonium halides, mercurous halides, aluminium chloride, phosphorus pentachloride, arsenic, arsenious oxide, chromic chloride.

§ 6. (2) LOSS OF WATER OF CRYSTALLIZATION²

(a) **With fusion.**

Various soluble salts containing much water of crystallization: chiefly chlorides, sulphates, nitrates.

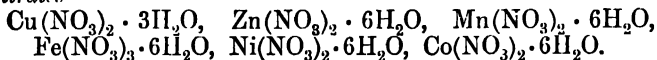
Halides—



Sulphates—



Nitrates—



(b) **Without fusion.**

Many hydrated salts.

¹ Under ordinary atmospheric pressure. Some, if not all, of these substances can be melted under increased pressure.

² If much water is combined with a salt as water of crystallization the salt may melt as a whole on slight elevation of temperature. Hydrated ferric chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, for instance, melts at 37°. The product is a concentrated solution of the salt, which loses water, and thus changes its properties, when further heated. This case is not therefore one of simple fusion.

The following salts change colour by loss of water of crystallization when heated:—

Hydrated Salt.	Colour	Colour after Heating
Cupric chloride	Greenish blue.	Brown.
Cupric sulphate	Blue.	White.
Chromic salts..	Violet.	Green.
Ferrous salts.....	Green or bluish green.	White.
Ferric chloride	Bright yellow.	Iron black.
Ferric alum.. ..	Pale violet	Yellowish white.
Nickelous salts ..	Bright green.	Yellow.
Cobaltous chloride..	Crimson.	Blue.
" bromide ..	Dark red.	Green.
" iodide	Dark red.	Violet.
" sulphate	Red.	Mauve hot, pink cold.
" nitrate....	Red.	{ Crimson to violet liquid before decomposition

Frequently loss of water of crystallization is accompanied or followed by the decomposition of the salt itself, by the action of heat, or this combined with hydrolysis—that is, decomposition of the salt by the water. When this decomposition takes place a basic salt or oxide remains, a volatile acid, acidic oxide, or other decomposition product being evolved together with the vapour of water, which on this account is likely to possess an acid reaction after condensation.

For example, hydrated magnesium chloride when heated yields hydrochloric acid and a basic chloride; and copper nitrate similarly gives an acid distillate, leaving a residue of oxide.

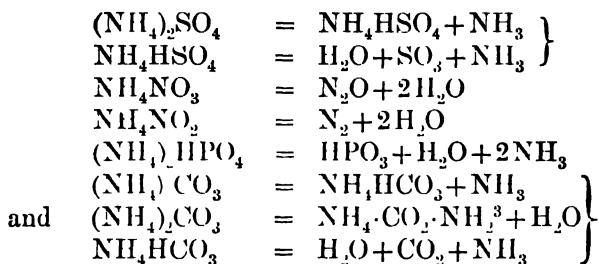
§ 7. (3) DECOMPOSITION WITH EVOLUTION OF GASES OR VAPOURS

(i) *Oxygen*.—Recognized by causing a glowing wood splint to inflame.

(a) Basic oxides— Ag_2O , Hg_2O , HgO .

(b) Acidic oxides— As_2O_5 , I_2O_5 , CrO_3 .

The chief ammonium salts decompose¹ when heated as follows:—



(b) amines, or metal-ammonia compounds, *e.g.* $2\text{AgCl} \cdot 3\text{NH}_3$, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$.

(viii) *Nitrous oxide*.—Behaving like oxygen towards glowing splint:—Ammonium nitrate

(ix) *Nitrogen peroxide*.—Reddish-brown gas:—Nitrates and nitrites of all metals except those of the alkalis and barium.

(x) *Nitric acid*.—Some nitrates containing water of crystallization.

(xi) *Phosphine*.—Easily inflammable and burning like phosphorus. Hypophosphites and phosphites.

(xii) *Sulphur*.—Giving yellow sublimate.

Thiosulphates and polysulphides.

(xin) *Sulphur dioxide*.—Recognized by smell and by turning potassium dichromate solution on filter paper green.

¹ The halides sublime, also the carbonate and sulphate yield sublimates but are partially decomposed by heat. It is thus a mistake to suppose that a sublimate will necessarily be obtained if an ammonium salt is present.

² With NH_4I the HI undergoes atmospheric oxidation, so that iodine is evolved with ammonia.

³ Ammonium carbamate, carbamic acid being $\text{CO} \begin{smallmatrix} \text{OH} \\ \text{NH}_2 \end{smallmatrix}$. Commercial "ammonium carbonate" or "sal volatile", prepared by subliming a mixture of ammonium chloride and calcium carbonate, is a mixture of NH_4HCO_2 and $\text{NH}_4\cdot\text{CO}_2\cdot\text{NH}_3$. When heated it sublimates with partial decomposition, the carbamate being more volatile than the bicarbonate.

Some normal and acid sulphites.

Some sulphates which yield higher oxides.¹

(xiv) *Sulphur trioxide*.—White fumes with acid reaction.

Sulphates such as H_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, $\text{Sb}_2(\text{SO}_4)_3$, $\text{Bi}_2(\text{SO}_4)_3$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$.

Persulphates—together with ozonized oxygen.

(xv) *Hydrogen sulphide*.—Smells like rotten eggs; turns lead acetate paper brown.

Hydrosulphides and hydrated sulphides.

(xvi) *Chlorine*.—Yellowish-green gas with irritating smell; bleaches litmus and turns starch potassium iodide paper bluish-black.

Some chlorides.

Chlorides of electronegative metals lose all their chlorine, *e.g.* PtCl_4 .

MnCl_2 , CuCl_2 lose some chlorine.

PCl_5 dissociates into PCl_3 and Cl_2 .

Other chlorides give chlorine in presence of an oxidizing agent.

Chlorine and oxygen.—Chlorates of heavy metals, *e.g.* $\text{Pb}(\text{ClO}_3)_2$.

(xvii) *Bromine*.—Reddish-brown gas with choking smell, and affecting the eyes.

Sources similar to those of chlorine.

Bromine and oxygen.—Bromates of heavy metals.

(xviii) *Iodine*.—Violet vapour condensing to black crystals.

Iodides, *e.g.* NIH_4I by atmospheric oxidation.

Iodine and oxygen.— I_2O_5 , and iodates of heavy metals.

(xix) *Hydrogen fluoride*.—Fuming acid gas.

Fluorides in presence of KHSO_4 , &c.

(xixa) *Silicon tetrafluoride*.—Fuming gas giving a precipitate with water on a glass rod.

Silicifluorides.

(xx) *Hydrogen chloride*.—Fuming acid gas turning silver nitrate milky on glass rod.

Some chlorides containing water of crystallization

¹ Stannous sulphate decomposes thus. $\text{SnSO}_4 = \text{SnO}_2 + \text{SO}_2$.

(xxi) *Hydrogen bromide or iodide*.—May be evolved together with bromine or iodine respectively from some bromides or iodides, in presence of combined water.

(xxii) *Mercury vapour*.—Condensing to a grey film of minute globules.¹

A compound of mercury.

(xxiii) *Arsenic vapour*.—Smelling of garlic, and condensing to a black mirror.

Reduction of an arsenious compound.

§ 8. Generalization.—The numerous facts regarding the decomposition of substances by heat, set forth above, are capable of generalization. The most usual mode of decomposition of a salt by heat is into its basic and acidic oxides.² Therefore halides, which are the principal salts incapable of such decomposition, are among the most stable inorganic compounds. This fact is strikingly shown by the large number of halides which can be melted without decomposition.

The readiness of decomposition of an oxysalt by heat depends, first, upon the volatility of the acidic anhydride or its decomposition products, and, second, upon the feebly basic character of the metallic oxide in the salt.

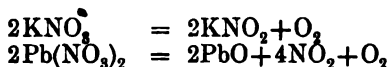
Thus carbonates are more easily decomposed than silicates or borates, owing to the volatility of carbon dioxide; silica and boric anhydride not being volatile except at high temperatures.

Similarly, nitrates are less stable than sulphates; for instance, copper nitrate readily yields the oxide by ignition, whilst copper sulphate only forms a basic salt even at a dull red heat.

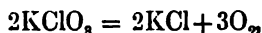
¹ If the film is rubbed with a glass rod or wood stick the mercury will cohere, forming larger globules.

² This recalls the dualistic theory of Berzelius that a salt consists essentially of a combination of basic and acidic oxides, whilst in accordance with the more modern view—the theory of electrolytic dissociation—a salt is regarded as composed of basic and acidic radicals, which yield ions in solution. The truth is, that oxysalts, more or less ionized in the solid state, break up differently under different circumstances, yielding decomposition products most stable under those circumstances. Basic and acidic oxides, being capable of independent existence, are the parts formed on heating the dry salt; whilst basic and acidic ions, being capable of existence in solution, are the parts obtained when a salt is dissolved.

The influence of the metal in determining the stability of its salts towards heat is shown in several ways. The alkali metals, being the most powerfully metallic or basigenic¹, form the most stable salts. It is only these and silver whose nitrates can be fused without decomposition. Other alkali salts, too, are more stable than the corresponding salts of other metals. Further, when oxysalts of the alkali metals, such as nitrates and chlorates, begin to decompose under the influence of heat, they do not break up into basic oxide, and acidic oxide or its decomposition products, as do similar salts of other metals; but they yield oxygen and another salt in which the nuclear atom of the original acidic radicle is retained. The following equations represent the manner of decomposition by heat of potassium and lead nitrates respectively:—



The chlorates show a similar difference of behaviour, for whilst potassium chlorate decomposes almost entirely thus:



some perchlorate being formed as an intermediate product, but not more than a trace of chlorine being evolved, lead chlorate gives off a considerable amount of chlorine, together with oxygen, according to the reaction



The influence of the nature of the metal is further seen with the sulphates and sulphites, but nowhere more clearly than in the case of the carbonates.

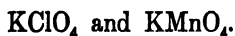
The alkali carbonates are relatively the most stable towards heat: *e.g.* with sodium carbonate, which melts at 850°C., the loss of carbon dioxide can just be detected at 400°C. The alkaline earth carbonates are less stable, though showing an increase in stability from calcium to barium. Apart, how-

¹ *i.e.* base producing.

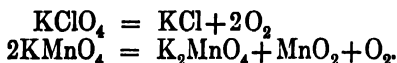
ever, from these salts, very few normal carbonates are known, basic carbonates appearing in their place; and metals at the other end of the scale, such as antimony and tin, do not form carbonates.

For the formation of a bicarbonate more powerfully basic properties are necessary than for the formation of a normal carbonate. Consequently, it is only the alkali metals which form solid bicarbonates, and these are easily decomposed by heat.

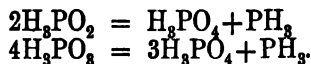
It is interesting to compare the manner of decomposition by heat of the isomorphous salts—



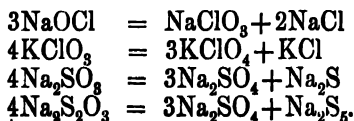
The following equations represent their decomposition:—



These reactions illustrate a general principle that a compound splits up on heating into a more volatile product, and a less volatile, and more stable, residue whose composition depends upon the nature of the elements present. The decomposition of hypophosphorous and phosphorous acids and their salts by heat is thus accounted for:



The behaviour of alkali hypochlorites, chlorates, sulphites, and thiosulphates when heated is analogous, although no volatile product need be formed; so that in these cases the principle of superior stability of the products alone applies:



§ 9.

(B) Flame Colorations

When some volatile substances are vaporized in the Bunsen flame their vapours become incandescent, and impart characteristic colours to the flame, by means of which the substances can be identified. It will be seen by reference to the information already given concerning the action of heat on substances, that chlorides are amongst the most volatile compounds. It is therefore advisable, before applying a flame test, to place a little of the substance in a watchglass and moisten it with concentrated hydrochloric acid, so that the chloride may be produced. A little of the moistened mass is then taken up on a loop of platinum wire—the wire being mounted in a piece of glass tube, which serves as a handle—and slowly introduced into the side of the Bunsen flame near the foot.

Chlorides, and some other compounds, of the following elements colour the Bunsen flame:—

Sodium		golden yellow.
Potassium		lilac.
Calcium		red.
Strontium		crimson.
Barium		light green.
Boron		bright green.
Copper		blue or bluish green.
Tin		greyish blue.
Lead		bluish grey.
Arsenic		grey.
Antimony		greyish green.
Zinc (sulphate)		flashes of green.
Manganese (chloride) ...		green.

If these flame colorations are examined by means of a spectroscope, those of the alkali metals will be found to give spectra consisting of fine lines. The sodium spectrum consists of two yellow lines so close together that they often appear as one line; that of potassium consists of three lines, two in the red and one in the violet part of the spectrum. Therefore the lilac flame colour observed with potassium salts is compounded of crimson and blue colours.

The spectra given by the alkaline earth chlorides are less simple than those given by alkali compounds; they consist of bands which are broader and more numerous. The flame spectrum of calcium contains several lines or bands in the red and orange, one in the green, and one in the violet; that of strontium contains numerous bands in the red and orange, and one in the blue; and that of barium one line with bands in the red and several bands in the green.

If several metals occur together their flame colorations may mask one another; sodium especially, owing to the brilliant yellow colour it imparts to the flame, masks the colour due to potassium and other metals. The spectroscope, by separating the colours, reveals the presence of each metal distinctly on account of its characteristic lines. A less perfect differentiation, useful for practical purposes, is effected by viewing the flame through a glass prism filled with indigo solution, or through deep blue glass. The yellow colour due to sodium cannot penetrate this medium, and other colours are modified, owing to constituents being removed by the blue absorbent, as is shown in the following statement:—

Metal.	Flame Coloration.	Flame Coloration seen through Blue Absorbent.
Sodium.....	Golden yellow.	<i>Nil.</i>
Potassium.....	Lilac.	Crimson.
Calcium	Red.	Light green.
Strontium	Crimson red.	Crimson.
Barium	Light green.	Green.

The bright green colour given by volatile boron compounds, that is, by boric acid and its derivatives, is resolved by the spectroscope into several broad bands in the green part of the spectrum.

If spectroscopic examination is made of the flame tints produced by compounds of copper, tin, lead, arsenic, and anti-

mony, no definite lines or bands are observed, but only ill-defined patches of colour. Therefore *spectrum-analysis* by means of these flame tints is not possible.

The reason for the difference between the metals of the alkalis and alkaline earths, and other metals whose compounds give flame colorations, is that these latter are not dissociated into simple molecules or atoms in the Bunsen flame. Their molecular vibrations are therefore complex, so that the individual properties of the atoms or ions of the metals do not become manifest.¹

Many other metallic compounds give no flame coloration at all, their molecular state in the flame approximating to that of liquids or solids, which give continuous spectra when rendered incandescent.

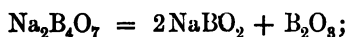
It may be added that when these latter compounds of the metals, or the metals themselves, are heated more strongly by means of the oxyhydrogen blowpipe, or by the electric arc or spark, spectra characteristic of the metals can be observed, because complete vaporization and dissociation of the metallic compounds takes place at the higher temperatures.

There is an important difference between the line spectra of the alkalis and the spectra, consisting of somewhat broader lines, of the alkaline earth metals. Those of the alkalis are the spectra of the metals themselves, probably of their ions; those of the alkaline earths, the spectra of the vaporized chlorides or other volatile salts. Consequently, non-volatile alkaline-earth compounds, such as oxides, carbonates, and phosphates, give no flame coloration. Indeed the flame coloration of calcium cannot be observed with calcium phosphate, even when the salt is previously moistened with concentrated hydrochloric acid, because the chloride is not formed in the flame.

¹ SbCl_3 is more volatile than KCl , but it must be heated in the electric arc in order to give a line spectrum. According to modern theory, KCl is an electrovalent compound whose constituent ions are easily separated; but SbCl_3 consists of molecules whose atoms are united by covalency, and are not easily separated.

§ 10. (C) Borax Bead Reactions

When a loop of platinum wire, made red-hot, is dipped into powdered borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, and the adhering mass is heated in the blowpipe flame, the salt swells up as it loses its water of crystallization, and then shrinks upon the loop, forming a colourless, transparent, glasslike bead. The anhydrous borax thus produced may be looked upon as a compound of sodium metaborate and boric anhydride:

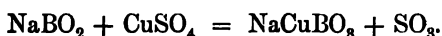


and this latter, being non-volatile in the blowpipe flame, displaces more volatile acidic oxides from oxysalts, forming metaborates with the remaining basic oxides. These compounds are fusible, and form transparent beads, which may possess characteristic colours, serving for the identification of certain metals.

The reaction with copper sulphate may be regarded as typical, and may be represented as follows:—

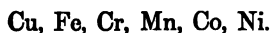


The following reaction also takes place:—



The bead may be heated in the outer oxidizing blowpipe flame, or in the tip of the inner reducing flame. These flames will easily be distinguished when the blowpipe is used. Before heating a bead in the inner flame it is well to form it on quite a small loop, or the whole of it will not enter the flame.

The following are the common metals which form coloured ions, and which may therefore be expected to give coloured borax beads:—



All of these, except nickel, form salts corresponding with more than one stage of oxidation; but since only basic oxides will enter into the composition of borates, the chromates, man-

ganates, and permanganates will not impart their characteristic colours to borax beads, but will lose oxygen, forming basic oxides which give coloured beads.

Copper.—The copper bead is light blue, or green if much copper salt is used, when formed in the outer blowpipe flame, the product being cupric borate. In the inner flame, where cuprous borate is formed by reduction, the bead becomes colourless; if, however, much copper is present, it may become reduced to the metallic state, and particles of metal, floating in the bead, will make it appear red or reddish brown and opaque. The reduction to the metallic state is promoted by the addition of a fragment of tin or zinc.

Iron.—Ferrous and ferric compounds, which are generally light green and yellow or brown respectively, are easily transformed the one into the other. Consequently, they are both formed in borax bead reactions—ferric compounds in the outer oxidizing flame, ferrous compounds in the inner reducing flame—and impart their characteristic colours to the bead.

Chromium.—Compounds of chromium give an emerald green borax bead of chromic borate, corresponding with the oxide, Cr_2O_3 . This colour is unaffected by heating the bead in the inner flame, since chromous compounds are not formed there.

Manganese.—Manganic salts are violet or amethyst coloured; manganous salts are pale pink, and appear colourless when diluted. Consequently a manganese bead appears amethyst when produced in the outer blowpipe flame, but becomes colourless in the inner flame.

Cobalt.—Compounds of this metal give a borate derived from CoO . Anhydrous cobaltous salts are blue; this is the colour of the bead, both in the inner and outer flame.

Nickel.—There is only one basic oxide of nickel, nickelous oxide, NiO . Anhydrous nickelous salts are generally yellow, but the borate produced in a bead heated in the outer blowpipe flame is brown. When this bead is heated in the inner flame it becomes grey, or black and opaque if much nickel is present, owing to the separation of the metal. Thus nickel

compounds, like those of copper, are easily reduced to the metallic state. That nickel compounds are more reducible than those of cobalt is also shown by these borax bead experiments.

Like those of certain metallic oxides, the colours of some of these beads vary with temperature. Noteworthy changes are recorded in the following table:—

§ 11.

BORAX BEAD COLOURS

Metal.	Colour of Bead in Outer Flame.	Colour or Appearance in Inner Flame.
Copper	Light blue or green	{ Colourless, or reddish brown and opaque.
Iron	{ Yellow or brown when hot, yellow when cold }	Bottle green.
Chromium ...	Emerald green	Emerald green.
Manganese...	Amethyst colour	Colourless.
Cobalt	Deep blue	Deep blue.
Nickel	{ Brown when hot, paler when cold }	Grey or black and opaque.

§ 12. (D) Phosphate and Sodium Carbonate Bead Reactions

PHOSPHATE BEADS

When microcosmic salt, $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, is heated in a loop of platinum wire it loses water and ammonia, forming first NaH_2PO_4 , and then sodium metaphosphate (NaPO_3) as a transparent bead.

This substance, like sodium metaborate, will combine with metallic oxides, *e.g.*:



Whilst, however, silica can displace boric anhydride from sodium metaborate, combining with the alkali to form a glass

in which particles of silica are not visible, it does not react with the phosphate bead; therefore particles of silica are seen floating in this bead after fusion.

This reaction is employed for the detection of silica.

§ 13. **Sodium Carbonate Beads.**—Sodium carbonate fuses in the blowpipe flame, but becomes opaque on cooling owing to crystallization. It is, however, a convenient *basic* matrix for beads.

Manganese compounds thus give with sodium carbonate, when heated in the oxidizing flame, a green bead of sodium manganate, the most stable salt in which manganese displays acidic properties; and, similarly, chromium compounds give yellow sodium chromate.

Silica forms a glass with sodium carbonate, thus making the bead transparent. This is a useful test for silica.

§ 14. (E) Charcoal Reactions

Reduction of Metallic Compounds on Charcoal.—The substance to be heated on charcoal before the blowpipe, is mixed with anhydrous sodium carbonate and placed in a cavity scooped in the block.¹ The sodium carbonate converts a metallic salt into carbonate or oxide on heating, thus promoting its reduction. It also acts as a flux, and, in the fused state, protects from oxidation the metallic globule which forms beneath it. Powdered potassium cyanide may be employed in addition in the more difficult cases of reduction, since it aids this process, being thereby oxidized to cyanate.

The reducibility of the oxide of a metal is directly connected with its electropositiveness. The following is the order of electropositiveness of the metals dealt with in this book, beginning with the most electropositive:—

K, Na, Ba, Sr, Ca, Mg, Al, Cr, Mn, Zn, Cd, Fe, Co, Ni, Sn,
Pb, Cu, As, Bi, Sb, Hg, Ag.

Oxides of manganese, and of the metals following, can be reduced when heated on charcoal before the blowpipe flame;

¹ Artificially prepared blocks are preferable to natural wood charcoal.

oxides of the preceding metals cannot be so reduced. The oxides of chromium, aluminium, and magnesium, for example, are not reducible on charcoal.

The following is the order of fusibility of the reducible metals:—

Hg, Sn, Bi, Cd, Pb, Zn, As, Sb, Ag, Cu, Co, Ni, Fe, Mn.

Mercury, cadmium, zinc, and arsenic volatilize at temperatures lower than that of the blowpipe flame, so that beads of these metals are not produced on charcoal. Cobalt, nickel, iron, and manganese cannot be fused before the blowpipe, so that at best they are obtained only as metallic powders; they are, however, magnetic, and especially so iron, and may be identified by this property.

Of the six remaining metals, while copper and silver are most easily reduced, tin, bismuth, lead, and antimony more easily give coherent globules, owing to their lower melting-points.

Volatile and combustible metals are oxidized by the outer flame of the blowpipe, and their oxides deposited as incrustations on the charcoal, the distance of the incrustation from the metallic globule depending upon the volatility of the metal. Even when no metallic globule is obtainable, as with zinc and cadmium, an incrustation of oxide forms on the charcoal. The white ash of wood charcoal must not be mistaken for an incrustation.

The colours and physical properties of the metals serve for their identification. The details observable in the charcoal reactions are given in the table opposite.

§ 15.

CHARCOAL REACTIONS

Metal	Appearance.	Incrustation.
Silver.....	{ Brilliant white metallic particles, hard but malleable }	None.
Antimony	White brittle globules	{ White incrustation, appearing at boundary of flame.
Bismuth	{ Pinkish - white globules, easily fusible and brittle }	Yellowish incrustation.
Copper.....	{ Metal appears as red fragments or tiny globules }	None.
Lead	{ Greyish-white globules, malleable or soft, marking paper }	Orange-red hot, pale yellow cold.
Tin	White malleable metal	None characteristic.
Nickel, cobalt, iron, manganese	{ Grey magnetic powders obtainable by levigation with water }	None.
Arsenic.....	{ No metallic residue, fumes of As_4O_6 , and smell of garlic }	White, appearing some distance from flame.
Zinc.....	No metal obtainable	{ Mass and incrustation, yellow hot, white cold.
Cadmium.....	No metal obtainable	{ Characteristic brown mass and incrustation }

§ 16. **Colour Reactions with Cobalt Nitrate.**—Certain other tests, which can be done on charcoal, may here be noted.

A compound of cobaltous and zinc oxide of a fine green colour, and known as Rinmann's green, is formed when cobalt nitrate and zinc oxide are heated together. A similar compound of a blue colour, known as Thénard's blue, is obtained from cobalt and aluminium compounds. Fusible phosphates, arsenates, borates, and silicates, also like aluminium, give a blue bead with cobalt nitrate. This reaction is therefore only of use as a test for aluminium in the known absence of those other substances. A delicate pink mass is formed when cobalt and magnesium compounds are heated together; this

colour is not due to the cobalt compound alone, since anhydrous cobalt salts are blue and cobalt oxide is black.

These reactions are best carried out by heating the substance on charcoal, moistening with cobaltous nitrate solution, and heating again.

They are here tabulated for reference:—

Substance heated on charcoal, moistened with $\text{Co}(\text{NO}_3)_2$ solution, and heated again.....	Green mass	Zinc compounds.
	Blue mass	Aluminium compounds and fusible phosphates, arsenates, borates, and silicates.
	Pink mass	Magnesium compounds.

§ 17. Numerous salts, such as some of those of the alkalis and alkaline earths, and others containing much water of crystallization, *fuse* when heated on charcoal and sink into the mass. Others, such as rock salt, *decrepitate*, that is crackle, split, and fly about. Compounds containing much oxygen, such as nitrates and chlorates, cause the charcoal to *deflagrate*, that is, to flare up and burn quickly.

Oxides of the alkaline earth metals, and of magnesium, zinc, and aluminium, *glow brightly* when heated; therefore compounds of these metals may leave a luminescent residue on charcoal.

§ 18. II. SYSTEMATIC EXAMINATION FOR BASIC AND ACIDIC RADICLES

This process is divisible into two parts:

- A. *Identification by volatile products obtained on treatment of the substance with acids and alkalis.*
- B. *Identification by reactions in solution.*

§ 19. (A) Identification by Volatile Products

Identification of a constituent part of a substance by causing the evolution of a volatile decomposition product depends

upon the action on the substance of a reagent analogous in chemical nature to, but less volatile than, the product of its action.

Thus volatile acids, or decomposition products of unstable acids, are obtained by decomposing the salts of these acids by less volatile or less unstable acids. The decompositions of sodium chloride and carbonate respectively by sulphuric acid serve to illustrate the principle. In one case a volatile acid, hydrogen chloride, in the other a volatile decomposition product, carbon dioxide, is evolved, and the recognition of these substances serves to identify the acidic radicles present in the original substance.

Similarly, the action of a non-volatile base serves to indicate the presence of a volatile base; if, therefore, ammonia is evolved by the action of sodium hydroxide upon a substance, the presence of an ammonium salt is inferred.

VOLATILE PRODUCTS OBTAINED ON TREATMENT OF A SUBSTANCE WITH ACIDS AND ALKALIS

§ 20. (1) Treatment with Acids.

(i) *Use of dilute sulphuric or hydrochloric acid.*¹—Dilute acid is poured upon the powdered substance in a test tube; little or no heat need be applied except in special cases, when directions are given.

The following gases and vapours may be evolved:—

Oxygen.—Recognized by causing a glowing splint to inflame.

- | | |
|---|---|
| (a) <i>Superoxides</i> —chiefly those of the alkali and alkaline earth metals, specially Na_2O_2 and BaO_2 . | |
| (b) <i>Persulphates</i> ² | } slow evolution on heating with dilute sulphuric acid. |
| (c) <i>Permanganates</i> | |

¹ If gases are evolved without heating, either acid may be employed, though in cases where insoluble sulphates or chlorides may be formed it is better to use hydrochloric or sulphuric acid respectively, and so facilitate the reaction by keeping the solution clear.

² Persulphates evolve ozonized oxygen when boiled with water.

Carbon dioxide.—Recognized by turning lime water milky.

Carbonates—in the case of the alkaline earth carbonates it is desirable to use hydrochloric acid.

Acetylene.—Burning with highly luminous flame.

Carbides—probably calcium carbide.¹

Nitrogen peroxide.—Brown gas turning starch potassium iodide paper bluish black.

Nitrites (in presence of atmospheric oxygen).

Phosphine.—Easily inflammable, burning like phosphorus.

*Phosphides.*¹

Sulphur dioxide.—Recognized by smell, and by turning potassium dichromate solution on filter paper green.

Sulphites.

Sulphur dioxide with gradual separation of yellow sulphur.

Thiosulphates.

Hydrogen sulphide.—Smells like rotten eggs; turns lead acetate paper brown or black.

Sulphides.

Hydrogen sulphide with precipitation of white sulphur.

Polysulphides.

Hydrogen cyanide (on gentle warming).—Poisonous gas smelling of bitter almonds.

Cyanides.

Chlorine—yellowish-green gas with irritating smell; bleaches litmus.

Hypochlorites.

(ii) *Use of concentrated sulphuric acid.*—The substance is heated gently with a few drops of the acid, the test-tube being inclined away from the person; small quantities should be used.²

Oxygen.

Peroxides, iodates, chromates, manganates, permanganates.

¹ Certain carbides and phosphides are decomposed by water.

² Especially if chlorate or permanganate is thought to be present.

Hydrogen fluoride.—Colourless, acid, fuming gas, corroding glass; when evolved in a test tube silicon tetrafluoride is also present, which gives milkiness with water on a glass rod.

Fluorides.

Hydrogen chloride.—Colourless, acid, fuming gas, turning silver nitrate solution milky.

Chlorides. After the addition of manganese dioxide, chlorine is evolved, and is recognized by its smell, and by bleaching litmus.

Hydrogen bromide—colourless fuming gas;
with bromine—deep-red vapour affecting the eyes;
and sulphur dioxide.¹

Bromides.

Hydrogen iodide—colourless fuming gas;
with iodine—violet vapour condensing to a black solid;
and sulphur dioxide.

Iodides.

Nitric acid vapour—often coloured brown by nitrogen peroxide. After the addition of copper turnings nitric oxide is evolved which turns brown in air.

Nitrates.

Chlorine dioxide.—Dark-yellow explosive gas.

Chlorates.

Boric acid vapour—crystallizing in tube, but not easily seen.

Borates. Whenever borate may be present, it should be tested for by the reactions in §§ 368 *et seq.*

Carbon monoxide.—Colourless gas burning with a blue flame.

Cyanides, ferrocyanides, ferricyanides.

Carbon monoxide and dioxide.

Oxalates.

¹ Derived from the sulphuric acid by reduction. Phosphites and hypophosphites also reduce sulphuric acid, causing sulphur dioxide to be evolved; in the case of hypophosphites sulphur may separate.

Carbon monoxide, and dioxide, with sulphur dioxide¹—with charring.

Tartrates.

Acetic acid vapour.—Smelling of vinegar; fruity smell after addition of alcohol.

Acetates.

Carbon oxysulphide.—Burning with a sulphurous flame.

Sulphocyanides (thiocyanates).

§ 21. (2) Treatment with Alkalis.

Use of sodium hydroxide solution.—**Ammonia** gas is evolved from ammonium salts, perceptibly at atmospheric temperature, extensively on heating.²

Sodium carbonate solution also decomposes ammonium salts on boiling.³

§ 22. (B) Identification by Reactions in Solution.

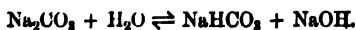
Identification by reactions in solution forms the major part of the process of qualitative analysis. This method consists in the production of: (i) insoluble compounds which form precipitates, (ii) colour changes in solution.

It is applicable to all basic radicles except ammonium, and to numerous acidic radicles. Some acidic radicles, as will be seen later, may be identified both by Method A and Method B.

¹ Derived from the sulphuric acid by reduction.

² Amides of the type $R \cdot NH_2$ are decomposed less readily than ammonium salts, as follows: $R \cdot NH_2 + NaOH = R \cdot ONa + NH_3$. They are little met with in inorganic chemistry. Compounds of ammonia with metallic salts, the "ammines", e.g. $CuSO_4 \cdot 4NH_3 \cdot H_2O$, yield ammonia on treatment with alkali, and often, also when heated alone. Alkali cyanides, e.g. KCN, are hydrolyzed by hot alkali to formate and ammonia: $KCN + 2H_2O = HCOOK + NH_3$. A little $HgCl_2$ (which forms un-ionized $Hg(CN)_2$) prevents this.

³ On account of the alkali produced by the hydrolysis:



§ 23.

THE PROCESS OF SOLUTION

Water is the solvent almost invariably employed in inorganic analysis. If a substance dissolves directly in water, with or without chemical change, the process of solution is very simple; if this is not the case, the substance is acted on chemically by certain reagents in order to convert it into a compound or compounds soluble in water. The nature of the reagents to be used or avoided depends firstly on the solubilities of the compounds they will produce, and secondly upon the general nature of the substance or radicle to be identified.

An illustration will make this clear. If barium carbonate had to be dissolved, the use of sulphuric acid as a solvent would be avoided because of the insolubility of barium sulphate; or if a thiosulphate were to be identified by a reaction in solution, the use of all acids would be avoided because thiosulphates are decomposed by acids.¹

When the metals are to be tested for, it is best for the acids to be eliminated as far as possible; and, vice versa, before testing for acidic radicles in solution, all the metals except those of the alkalis are best got rid of.

Consequently the general method of treatment used in preparing a solution for the reactions of the metals differs from that employed when the acids are to be tested for in solution.

§ 24.

PREPARATION OF A SOLUTION FOR THE
METAL REACTIONS

The majority of salts and other inorganic substances dissolve in *water* or *dilute hydrochloric* or *nitric acid*.

The following list contains the most important inorganic substances soluble in water, together with those insoluble in dilute acids, so that compounds not mentioned dissolve in dilute acids though not in water —

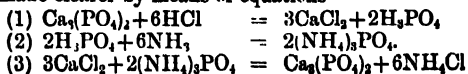
¹ It might not seem necessary to state that if a chloride is to be tested for, the substance must not be dissolved in hydrochloric acid; but this is commonly done by students.

	Soluble in Water.	Insoluble in dilute HCl or HNO ₃ .
Oxides and Hydroxides	Na, K, Ca, Sr, Ba, (Ca(OH) ₂ and Sr(OH) ₂ slightly soluble).	SnO ₂ , Sb ₂ O ₄ , Sb ₂ O ₅ , ignited Fe ₂ O ₃ , Al ₂ O ₃ , Cr ₂ O ₃ , SiO ₂ .
Carbonates	Na, K, NH ₄ .	
Nitrites	All. (AgNO ₂ sparingly soluble).	
Sulphides	Na, K, NH ₄ , (Ca, Sr, Ba hydrolyzed by water).	HgS, CoS, NiS.
Polysulphides ...	Na, K, NH ₄ .	White sulphur separates.
Sulphites	Na, K, NH ₄ .	
Thiosulphates ...	Na, K, NH ₄ , Ca, Sr, Ba (sparingly soluble), Ag (sparingly soluble and decomposed).	Yellow sulphur separates.
Hypochlorites ...	All.	
Fluorides	Na, K, NH ₄ , Ag, Sn ⁺⁺ .	Natural CaF ₂ .
Chlorides	All except Ag, Hg ⁺ , Cu ⁺ ; Pb (sparingly soluble). BiCl ₃ and SbCl ₃ decomposed forming insoluble basic chlorides.	AgCl, Hg ₂ Cl ₂ .
Bromides	Same as chlorides.	Anhydrous CrCl ₃ .
Iodides	All except Ag, Hg ⁺ , Cu ⁺ . PbI ₂ soluble hot water; SbI ₃ , BiI ₃ , SnI ₄ decomposed by water.	AgBr, Hg ₂ Br ₂ . AgI, Hg ₂ I ₂ , HgI ₂ (slightly soluble).
Cyanides	Na, K, NH ₄ , Mg, Ca, Sr, Ba, Hg ⁺⁺ .	AgCN (soluble in hot conc. HNO ₃).
Ferrocyanides ...	Na, K, NH ₄ , Mg, Ca, Sr, Ba.	Ag, Cu, Fe ⁺⁺ , Zn, &c.
Ferricyanides	Na, K, NH ₄ , Mg, Ca, Sr, Ba.	Ag, Cu, Fe ⁺⁺ , Zn, &c.
Sulphocyanides ..	All except Ag, Pb, Hg ⁺ , Hg ⁺⁺ , Cu ⁺ , Bi, Cd.	
Chlorates	All except Hg ⁺ .	
Perchlorates	All. KClO ₄ sparingly soluble.	
Bromates	Ag and Hg ⁺ sparingly soluble; others soluble.	
Iodates	Na, K, NH ₄ .	
Nitrates	All except Bi, Hg ⁺ and Hg ⁺⁺ which are decomposed forming basic salts. Other basic nitrates insoluble.	
Borates	Na, K, NH ₄ . Some others slightly soluble.	
Acetates	All. Ag and Hg ⁺ sparingly soluble. Some acetates, e.g. Fe ⁺⁺ acetate, are decomposed by boiling water, yielding insoluble basic salts.	

	Soluble in Water.	Insoluble in dilute HCl or HNO ₃ .
Oxalates	Na, K, NH ₄ .	Ignited PbCrO ₄ .
Tartrates . . .	Na, K, NH ₄ .	
Chromates	Na, K, NH ₄ , Ca, Sr (sparingly soluble), Mg.	
Manganates	K, Na.	
Permanganates ..	All. Ag slightly soluble.	
Arsenites	Na, K, NH ₄ .	
Arsenates	Na, K, NH ₄ .	
Phosphates	Na, K, NH ₄ .	
Phosphites	Na, K, NH ₄ .	
Hypophosphites.	All.	
Sulphates	All except (Ca), Sr, Ba, Pb, anhydrous Fe ⁺⁺ and Cr ⁺⁺⁺ . Hg ⁺⁺ and Ag sparingly soluble, Hg ⁺⁺ decomposed giving insoluble basic salt; also Cu, Fe ⁺⁺ , Fe ⁺⁺⁺ , Al, Cr ⁺⁺⁺ , Co slightly decomposed especially on heating.	SrSO ₄ , BaSO ₄ , PbSO ₄ , anhyd Cr ₂ (SO ₄) ₃ .
Persulphates....	All. K salt least soluble.	
Silicates	Na, K.	Nearly all.

§ 25. If the process of solution in dilute acid destroys the original acid whose salt was insoluble in water, such a solution is at once suitable for testing for the metals; but if the process of solution is simply one of *metathesis* or double decomposition, the acid of the original insoluble salt remaining in solution, then the addition of an alkali will precipitate this salt, and thus interfere with the process of analysis. For example, consider the two salts, calcium carbonate and calcium phosphate, both of which dissolve in dilute hydrochloric acid. In the former case, owing to the escape of carbon dioxide, only calcium chloride remains in solution; in the latter case, phosphoric acid is present, and on addition of excess of ammonia will cause the precipitation of the original salt.¹ In

¹ This will be made clearer by means of equations—



cases like this special methods of analysis have to be adopted which will be studied later.

In a few cases the use of dilute hydrochloric acid as a solvent will *produce* an insoluble substance. The chlorides of silver and mercurous mercury are insoluble in water and dilute acids, and lead chloride is but sparingly soluble in cold water. The production of these insoluble chlorides is not, however, necessarily a disadvantage, for a convenience is made of them to constitute an analytical group, as will be seen later. Their formation is avoided, however, by using dilute nitric instead of hydrochloric acid as the solvent. Sulphur will be precipitated from thiosulphates¹ and polysulphides² by dilute hydrochloric acid, or any other acid. Since it is a decomposition product of the acidic radicle, it must be eliminated before applying the tests for the metals.³

The readiness with which a substance dissolves in dilute acid depends upon the physical condition of the substance and the concentration of the acid. The more finely divided a substance is, the more easily will it dissolve; therefore a difficultly soluble substance should always be finely powdered, preferably in an agate mortar. Molecular complexity influences solubility; a substance is most soluble when freshly precipitated, and becomes less soluble when kept or heated in contact with the liquid from which it was precipitated,⁴ or when heated in the dry state.⁵ This is because crystallization or dehydration, accompanied by polymerization, that is the formation of complex molecules, has taken place.

§ 26. Concentrated hydrochloric acid has an advantage over the dilute acid as a solvent, in the case of sparingly soluble substances, including some metals, such as tin, many minerals,

¹ $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{O} + \text{S} + \text{SO}_2$.

² $\text{Na}_2\text{S}_x + 2\text{HCl} = 2\text{NaCl} + \text{S}_{x-1} + \text{H}_2\text{S}$.

³ By boiling the liquid to coagulate the sulphur, and filtering, through a double filter if necessary.

⁴ Precipitated alumina is an example; such precipitates are said to "age".

⁵ Silica, alumina, ferric oxide, &c., are rendered practically insoluble in acids by ignition.

and a few artificially prepared salts. It is also valuable in dissolving and reducing peroxides,¹ chromates, and permanganates.

§ 27. Concentrated nitric acid is useful for dissolving sulphur, red phosphorus, natural and artificial sulphides, metals, and alloys.²

§ 28. Aqua regia³ need seldom be used. It will dissolve mercuric sulphide and sublimed stannic sulphide (mosaic gold), and some minerals and alloys such as type metal.

All the nitric acid, together with most of the hydrochloric acid used to dissolve a substance, must be removed by evaporation⁴ before the solution is ready for testing for the metals.⁵

If a substance does not dissolve in aqua regia, the resources of solution by means of acids are well-nigh exhausted; silica dissolves in hydrofluoric acid, however, and the sulphates of lead and barium are soluble in concentrated sulphuric acid forming acid sulphates, but this latter fact is of no use for analytical purposes.

If several solvents have been used to effect the solution of successive portions of a mixture of substances, it is best, as a rule, to mix the solutions before proceeding to analysis. In case, however, a portion is insoluble in all acids, and is reserved for the special treatment about to be described, this part may well be examined separately.

¹ Such as MnO_2 , PbO_2 , Pb_3O_4 .

² If the action of concentrated nitric acid on an alloy leaves a white residue this may be metastannic acid, hydrated antimonie oxide, or silica; it must be examined separately after dilution and filtration. Metastannic acid, $\text{Sn}_2\text{O}_5(\text{OH})_{10}$, is converted by concentrated hydrochloric acid into the chloride, $\text{Sn}_2\text{O}_3\text{Cl}_2(\text{OH})_6$, which is soluble in water. Antimonie oxide may be dried and submitted to sulphur fusion. Silica may be tested for by fusion in a microcosmic salt or sodium carbonate bead. Phosphorus or sulphur may be present in the alloy, and these are converted by nitric acid into phosphoric or sulphuric acid.

³ "Aqua regia", a mixture of three volumes concentrated HCl with one volume concentrated HNO_3 , owes its action to the chlorine liberated according to the following reaction: $\text{HNO}_3 + 3\text{HCl} = \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O}$.

⁴ It is best to evaporate nearly to dryness, then add a little dilute hydrochloric acid, and again evaporate until the mass is pasty, afterwards diluting with water.

⁵ Otherwise hydrogen sulphide will be oxidized by the nitric acid, and the precipitation of the sulphides of the copper and tin groups retarded by the presence of too much acid.

A substance which cannot be dissolved by acids is described as "insoluble", and other means of solution have to be adopted, which will now be studied.

§ 29. TREATMENT OF INSOLUBLE SUBSTANCES

For the solution of a substance insoluble in hydrochloric acid, nitric acid, or aqua regia, one of several methods may be employed.

(1) **Displacement of Volatile Acid by Concentrated Sulphuric Acid.**—Pour a few drops of concentrated sulphuric acid on finely powdered¹ fluorspar in a small platinum capsule, and heat the mixture in a fume chamber, gently at first,² and then more strongly, until sulphuric acid fumes cease to be evolved. The white residue should completely dissolve on boiling with dilute hydrochloric acid.

Insoluble fluorides are best decomposed in this way. If the residual sulphate is insoluble in hydrochloric acid (SrSO_4 , BaSO_4) it may subsequently be treated according to Method 3b (ii).

1a. **Elimination of Silica by Heating with Hydrofluoric and Sulphuric Acids.**—Add a drop of sulphuric acid to some finely powdered felspar or glass in a platinum capsule, then add some hydrofluoric acid solution and gently heat,³ finally expelling the sulphuric acid. The residue will be free from silica, and will dissolve in water or hydrochloric acid.

(2) **Reduction by Nascent Hydrogen in Presence of Acid.**—Place some precipitated silver chloride in a small beaker with zinc and dilute sulphuric acid. The chloride is gradually reduced to metal, which may then be dissolved in dilute nitric acid.

¹ The mineral should be ground in an agate mortar till no gritty particles can be felt between the fingers.

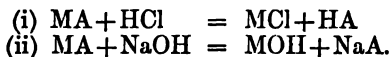
² HF is evolved thus: $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$.

³ $\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$. The sulphuric acid prevents the decomposition of the SiF_4 , thus: $3\text{SiF}_4 + 3\text{H}_2\text{O} = \text{H}_2\text{SiO}_3 + 2\text{H}_2\text{SiF}_6$, and converts the metals into sulphates.

Silver bromide and iodide as well as the chloride may be treated in this manner; which halide was present is discovered by examining the acid solution, after the removal of the silver and excess of zinc.

(3) **Decomposition by Alkalis.**

(a) *By alkali hydroxide solution.*—Suppose the salt MA to be decomposable (i) by dilute hydrochloric acid, (ii) by sodium hydroxide solution, according to the reactions:



The salt MCl and the base MOH may or may not be soluble in water, but provided they are soluble in acids, and no volatile product leaves the system in the above decompositions, it is immaterial which reaction is employed in preparing a solution for analysis. Certain salts, however, which are not decomposed by acids are readily hydrolyzed by alkalis; consequently the second of the above reactions is employed as an aid to solution. Three examples may be chosen to illustrate the method:

(i) Pour sodium hydroxide solution on Prussian blue¹ in a test tube; the salt is instantly decomposed. Dilute, warm, and filter. Ferric hydroxide remains on the filter, the filtrate containing sodium ferrocyanide. Other ferrocyanides behave similarly.

(ii) Boil finely divided strontium sulphate² with sodium hydroxide solution, add sodium carbonate to convert strontium hydroxide into the insoluble carbonate, warm, and filter. The residue of strontium carbonate after being washed can be completely dissolved in dilute hydrochloric acid, and the sulphate will be found in the filtrate after acidifying.

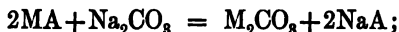
(iii) Boil lead sulphate with sodium hydroxide solution; it

¹ Ferric ferrocyanide.

² Either the thoroughly washed precipitated salt or finely powdered celestine. Barium sulphate, on account of its great insolubility, cannot be completely decomposed in this way.

completely dissolves.¹ Acidify the solution with hydrochloric acid; lead chloride crystallizes out, and the filtrate from these crystals may be tested for sulphate.

(b) *By fusion with alkali carbonate*.—Sodium carbonate solution decomposes a large number of salts in accordance with the reaction:



and, since most carbonates are insoluble in water, this is a convenient way of eliminating metals and obtaining their acidic radicles in solution as sodium salts suitable for testing.

(i) Prepare some precipitated and thoroughly washed barium sulphate; boil it with sodium carbonate solution and filter.² The filtrate, after acidifying with hydrochloric acid, will give a precipitate with barium chloride, showing the presence of sulphate; and the residue effervesces with hydrochloric acid, because some barium carbonate is present, which dissolves, so that the solution will give a precipitate with sulphuric acid.

Thus it is shown that barium sulphate is decomposed by sodium carbonate solution. Nevertheless the decomposition is very partial, and is valueless for analytical purposes.

Fused sodium carbonate³ is much more efficient than the aqueous solution, and will completely decompose barium sulphate and some other insoluble salts.

(ii) Mix a little barium sulphate with about six times its weight of fusion mixture, composed of equal parts of sodium and potassium carbonates.⁴ Place the mixture in a porcelain, iron, nickel, or platinum crucible or a boat made of platinum

¹ This is because hydrated lead oxide combines with NaOH:



² Ordinary qualitative filters may not efficiently retain $BaSO_4$, even when the salt has been precipitated from boiling solution. It may be better to employ a special quantitative filter paper for this experiment.

³ That is, a solution of infinite strength.

⁴ This mixture fuses at a lower temperature than either salt singly. A solvent containing a dissolved substance solidifies at a lower temperature than the pure solvent.

foil, and fuse it before the blowpipe flame. Maintain the mass in a liquid state for some minutes, then allow it to cool and solidify; digest it thoroughly with hot water, filter, and repeatedly wash the residue on the filter till all soluble matter has been removed. If the fusion has been properly carried out, the residue will now consist entirely of barium carbonate, which will dissolve completely in dilute hydrochloric acid, whilst all the sulphate will be found in the filtrate when tested for with barium chloride, after decomposing the excess of carbonate with hydrochloric acid.

In addition to barium sulphate, insoluble silicates, anhydrous alumina, and some minerals are fused in this manner.¹

(4) **Other Methods of Fusion.**—The method of fusion may be modified in three ways:

(a) Oxidizing fusion. (b) Sulphur fusion. (c) Reducing fusion.

(a) *Oxidizing fusion.*—Just as nitric acid, aqua regia, or hydrochloric acid and potassium chlorate dissolve some substances, such as insoluble sulphides, producing soluble oxidation products, so a mixture of sodium carbonate with potassium nitrate or chlorate, when fused with substances capable of forming stable oxy-salts, converts them into such alkali salts, soluble in water. Thus insoluble sulphur, chromium, and manganese compounds yield soluble sulphates, chromates, and manganates by this means.

Mix finely powdered chrome iron ore with sodium carbonate and a little potassium nitrate, and fuse the mixture in platinum or porcelain before the blowpipe. From the cooled mass hot water will extract yellow sodium chromate, a residue of ferric oxide remaining.²

(b) *Sulphur fusion.*—Mix a little finely powdered stannic oxide with five or six times its bulk of a mixture of about

¹ If the fusion is carried out in a porcelain crucible, silica and alumina may be dissolved from the crucible.

² $2\text{FeCr}_2\text{O}_4 + 4\text{Na}_2\text{CO}_3 + 7\text{O} = 4\text{Na}_2\text{CrO}_4 + \text{Fe}_2\text{O}_3 + 4\text{CO}_2$. It is possible for this reaction to take place by atmospheric oxidation alone.

equal parts of anhydrous sodium carbonate and flowers of sulphur, and fuse the mixture in an ignition tube or a porcelain crucible, until the excess of sulphur has been volatilized or burnt, and a dark-coloured mass remains. When this is cool add water; the whole will quickly dissolve, forming a yellow solution containing sodium thiostannate¹ and polysulphide. When this solution is acidified with hydrochloric acid, stannic sulphide is precipitated together with sulphur, and the former easily dissolves in excess of acid, forming a solution of stannic chloride.

All insoluble tin or antimony compounds may be treated in this way.²

(c) *Reducing fusion*.—Mix stannic oxide with sodium carbonate and potassium cyanide,³ and fuse the mixture in a porcelain crucible. A button of tin⁴ will be obtained, after dissolving the alkali salts in water, and this may be dissolved in hydrochloric acid.

All compounds of reducible metals, such as silver, antimony, and lead, may be reduced in this manner, but other methods of treatment are generally more convenient.

§ 30. ORDER OF PROCEDURE IN TREATMENT OF INSOLUBLE SUBSTANCES

The following are the principal substances met with in qualitative analysis which are insoluble in water and ordinary acids:—

Carbon, sulphur.

Calcium fluoride.

Strontium, barium, and lead sulphates.

Ferrocyanides: ferric (Prussian blue) copper, zinc.

Silver chloride, bromide, and iodide.

¹ $2\text{SnO}_2 + 2\text{Na}_2\text{CO}_3 + 9\text{S} = 2\text{Na}_2\text{SnS}_3 + 2\text{CO}_2 + 3\text{SO}_2$.

² Metals which do not form acidic sulphides leave a residue of sulphide after extraction with water. Ignited ferric oxide, otherwise difficult to dissolve, is thus converted into ferrous sulphide which dissolves in dilute hydrochloric acid.

³ Remember that potassium cyanide is exceedingly poisonous.

⁴ $\text{SnO}_2 + 2\text{KCN} = \text{Sn} + 2\text{KCNO}$ (cyanate).

Stannic oxide and sulphide (mosaic gold).

Antimony tetroxide and pentoxide.

Lead chromate (ignited), chrome ironstone (FeCr_2O_4), ignited ferric, aluminium, and chromic oxides.

Silica and various silicates.

Below is given the order of operations to which the unknown substance may be successively submitted until it has been dissolved.

§ 31. *Preliminary*.—Note colour and appearance. The following substances are coloured:—

Sulphur, carbon, ferric ferrocyanide (deep blue), copper ferrocyanide (dark brown), silver bromide (very pale yellow), silver iodide (light yellow). [Silver halides are violet after exposure to light, or they will appear as horny masses if they have been fused.] Mosaic gold, (SnS_2) (bronze), lead chromate (brown), chrome ironstone (dark grey), ferric oxide (dark red), chromic oxide (green).

The substance must be very finely powdered, preferably in an agate mortar.

A. Ignite a little of the substance on a porcelain crucible lid in the blowpipe flame; sulphur or carbon will burn away.

B. If fluoride has been found by heating with concentrated sulphuric acid (§ 20), examine by Method 1.

C. Heat a little of the substance on a loop of platinum wire in the inner blowpipe flame, then moisten it with hydrochloric acid. Evolution of hydrogen sulphide shows that sulphate was originally present. In this case examine flame coloration given by the moistened residue. If strontium is found, treat substance according to Method 3a (ii); if barium, according to Method 3b (ii).

D. Heat a little of the substance, mixed with sodium carbonate and potassium cyanide, on charcoal. The following metals may be found:—

Silver—Treat substance according to Method 2

Lead	"	"	"	3a (iii)
Tin	"	"	"	4b
Antimony	"	"	"	4b

E. Boil substance with sodium hydroxide solution. The following remaining compounds will be dissolved or decomposed:—

Ferric ferrocyanide gives sodium ferrocyanide and ferric hydroxide.

Copper ferrocyanide gives sodium ferrocyanide and copper oxide.

Zinc ferrocyanide dissolves: precipitate zinc by hydrogen sulphide, and test filtrate for ferrocyanide after acidifying and boiling off excess of hydrogen sulphide.

Lead chromate dissolves: add hydrochloric acid in excess and proceed with analysis.

Alumina: may dissolve; treat like lead chromate.

Silica: may dissolve.

F. If the substance has not yet been identified, it may be tested for silica by the microcosmic bead test (§ 12), and silica, if found, may be confirmed by elimination according to Method 1a. Or the substance may be fused according to Method 3b (ii).

G. Oxidizing fusion, 4a, is necessary for chromic oxide and chrome ironstone.

§ 32. GENERAL PROPERTIES AND REACTIONS OF SUBSTANCES IN SOLUTION

When a given inorganic substance, or mixture of substances, has been dissolved by any of the means described in detail above, an aqueous solution of one or more salts¹ is obtained. It might be said that water is really the only solvent, other reagents being used when necessary to produce salts soluble in water.

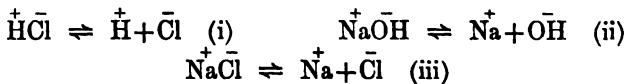
Such a solution behaves, however, towards reagents so as to justify the belief that salts do not chiefly exist as single individuals in solution, but that the metallic and acidic radicles are independent, and react apart from one another. Thus the solution of any sulphate is precipitated by a solution of any salt of barium, the nature of the other metallic and acidic

¹ For the time being acids and bases are considered as H and OH salts respectively.

radicles which are contained respectively in the two salts employed being a matter of indifference.

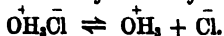
Or suppose the constituents of a mixture of phosphates insoluble in water are dissolved in hydrochloric acid and submitted to qualitative analysis. What is determined is, not that certain salts exist in solution, but that phosphate and chloride are present, and such and such metallic radicles.

§ 33. *Ionization*.—The independence of the metallic and acidic radicles in solution, which is the foundation fact upon which the operations of inorganic analysis are based, is expressed by means of the theory of ionization. This theory, in its modern form, states that acids, bases, and salts, *i.e.* electrolytes, consist of ions which are held together in the pure state by electrostatic attraction. These ions were produced when the compound was formed from its elements, by the transfer of one or more electrons from each metallic to each non-metallic atom concerned. The atoms of these elements, neutral before combination, have thus become ions which are positively and negatively charged respectively. The union between these oppositely charged ions is said to be due to electrovalency; and when the electrolyte is dissolved in a solvent the force of electrostatic attraction, through which electrovalency is manifested, is weakened, and the ions are dissociated and become reactive. Thus, taking HCl, NaOH, and NaCl as the simplest examples of an acid, a base, and a salt respectively, the effect of dissolution in water is expressed by the following reversible reactions:—

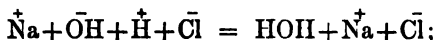


Since chloride ions are common to equations (i) and (iii), and sodium ions to equations (ii) and (iii), it follows that the acidity of a solution of hydrochloric acid, and therefore of any acid, is due to hydrogen ions ($\overset{+}{\text{H}}$),¹ and the alkalinity of sodium

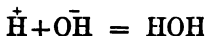
¹Hydrochloric acid really contains hydrated hydrogen chloride, the reaction of ionization being:



hydroxide or any alkaline solution to hydroxyl ions (OH^-); and so the process of neutralization is due to the combination of hydrogen and hydroxyl ions forming water. Thus:



or, subtracting what is common to both sides of the equation,



expresses the process of neutralization of an acid by an alkali.

A neutral solution thus contains excess of neither hydrogen nor hydroxyl ions, though there are always present a very small number of each, due to the ionization of pure water.

§ 34. Hydrolysis.—The aqueous solutions of many normal salts are acid or alkaline in reaction; it must not on that account be concluded that an acid or alkali was added originally to such a solution. In the process of analysis the moistened solid should always be tested with litmus paper, and its reaction recorded, ready to be interpreted in the light of later knowledge. If this test is omitted important conclusions may be missed. Suppose, for instance, a mixture of lime and chalk is given for analysis; calcium and carbonate will be found in the ordinary course, but the presence of the lime may be entirely overlooked if the behaviour towards water and the reaction with litmus of the moistened substance are not observed.

Soluble salts of the following metallic radicles with the common acids possess an acid reaction:—

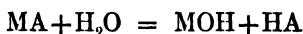
Mercurous, mercuric, cupric, aluminium, chromic, ferric, stannous, stannic, antimonious, bismuthous.

Soluble salts of the following acidic radicles have an alkaline reaction in solution:—

Borate, carbonate, chromate, hypochlorite, nitrite, phosphate, silicate, sulphide, sulphite.

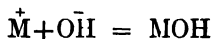
The departure from neutrality of solutions of these numer-

ous salts is due to *hydrolysis*, i.e. decomposition by water in the sense of the reaction—

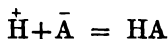


According to the ionic theory such reactions are brought about by means of the dissociated hydrogen and hydroxyl ions of water.

When the salt MA is dissolved in water it may be supposed that the ions $\overset{+}{\text{M}}$ and $\bar{\text{A}}$, together with $\overset{+}{\text{H}}$ and $\bar{\text{O}}\text{H}$ of the very slightly dissociated water, and molecules MA of undissociated¹ salt, are momentarily present in the liquid; and any chemical change that takes place is due to combination between them. If the combination—



takes place the solution becomes acid owing to the preponderance of the hydrogen ions remaining; if—



is the reaction which occurs, the solution becomes alkaline because hydroxyl ions remain over in excess.

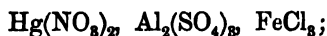
The strengths of acids and bases, however, are proportional to the degree to which their ions are dissociated in aqueous solution, weak acids and bases having few dissociated ions. Thus the metallic ions of weak bases, whose salts with strong acids, however, have their ions highly dissociated, will tend to combine with hydroxyl ions from the water, so that the solution becomes acid; and the acidic ions of weak acids, when their salts are dissolved in water, by combining with and removing hydrogen ions from the ionized water molecules, render the solution alkaline by reason of the remaining hydroxyl ions.

In this way the ionic theory accounts for the fact that the salts of strong acids with weak bases are acid, and the salts of strong bases with weak acids are alkaline in reaction.

Salts of weak bases with weak acids are generally insoluble in water.

¹ Nevertheless ionized according to the view already explained.

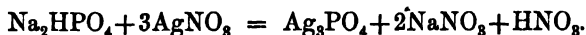
The student may show that solutions of the following salts of strong acids with weak bases have an acid reaction:—



and that solutions of the following salts of the strong base soda with weak acids are alkaline:—



The case of Na_2HPO_4 is specially striking, because otherwise it might be called an acid salt. Indeed the replaceable hydrogen the salt contains may be made to exhibit acidity by adding a solution to excess of silver nitrate solution, when, as the result of mixing an alkaline and a neutral liquid, an acid liquid is formed, in which yellow Ag_3PO_4 is suspended.



Hydrolysis of a salt appears only to occur if that salt is capable of ionic dissociation. Some mercuric, cadmium, and other salts, specially mercuric chloride and cyanide and cadmium iodide, are ionized but slightly in solution, and therefore provide little opportunity for the action of water upon them. They thus resemble organic compounds rather than salts, and like them are soluble in organic solvents. The contrast between the behaviour of mercuric chloride and sulphate towards water is sufficiently striking.¹

It will be instructive in this connection to compare together the compounds—



These are the chlorides of elements occupying five consecutive places in the periodic scheme, and which present a transition from strongly metallic properties in sodium to strongly non-metallic properties in phosphorus.

If the student can obtain specimens of each of these chlor-

¹ HgCl_2 forms a neutral solution in water; HgSO_4 is hydrolyzed according to the reaction $3\text{HgSO}_4 + 2\text{H}_2\text{O} = \text{HgSO}_4 \cdot 2\text{HgO} + 2\text{H}_2\text{SO}_4$.

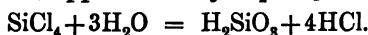
ides—and all except SiCl_4 are generally available—he will be able to confirm the following facts.

NaCl is not hydrolyzed by water, and therefore yields a neutral solution.

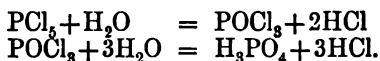
MgCl_2 gives a neutral solution with water, but when this solution is evaporated nearly to dryness, hydrochloric acid gas escapes with the steam, and the resulting pasty mass, containing the basic salt $\text{Mg}(\text{OH})\text{Cl}$, reacts alkaline. By ignition the oxide, MgO , is eventually formed.

AlCl_3 dissolves in water, reacting vigorously with it if anhydrous, and produces an acid solution by incipient hydrolysis; when this solution is evaporated to dryness and ignited, the oxide Al_2O_3 remains.

SiCl_4 is instantly decomposed by water with the separation of gelatinous silica, approximately H_2SiO_3 .

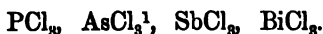


PCl_5 is similarly decomposed, liquid POCl_3 being first formed and then H_3PO_4 , thus:



These latter two are extreme cases of hydrolysis, and thus the property rises from zero to a maximum in the above series, at the same time that transition from metallic to non-metallic chloride takes place. The hydrolysis of non-metallic chlorides cannot, however, be attributed to previous ionic dissociation in water, as is the case with salts.

The following chlorides of the fifth group of the periodic system constitute an interesting series:—



All except the last are completely hydrolyzed by water, though AsCl_3 and SbCl_3 form intermediate basic chlorides; BiCl_3 forms BiOCl as a final product of aqueous hydrolysis.

¹ The student should not handle AsCl_3 ; the other chlorides, if obtainable, may be experimented with.

There is a diminution in volatility on passing from the non-metallic chloride, PCl_3 , to the chloride of a metalloid, BiCl_3 . PCl_3 and AsCl_3 , like most non-metallic chlorides are liquids; SbCl_3 and BiCl_3 are solids of comparatively low melting-point, so that even BiCl_3 can be melted and boiled in a test tube. All these chlorides are soluble in organic solvents, such as benzene, by which fact, as well as by their volatility, they are distinguished from metallic chlorides.

§ 35. **Precipitation.**—A solid which separates on mixing two liquids, or on passing a gas through a liquid, is called a precipitate.

Precipitates are often described, according to their physical condition, as *flocculent*, *granular*, or *gelatinous*.

Calcium carbonate, when first formed by precipitation from calcium chloride solution by ammonium carbonate, is *flocculent*, but on heating in contact with the liquid from which it has been precipitated it becomes *granular* because micro-crystalline. This is due to the fact that calcium carbonate is by no means insoluble in the solution of ammonium chloride formed in the above reaction, but that the smaller particles are more soluble than the larger ones; and that passing into solution, and out again in the crystalline form, the whole mass gradually becomes converted into crystals of appreciable size, and therefore appears granular.

A similar explanation applies to the change which precipitated barium sulphate undergoes when kept in contact with hot water.

Aluminium hydroxide, precipitated from alum solution by ammonia, is a good example of a *gelatinous* precipitate; "*gelatinous silica*" is another example. Substances which form these gelatinous precipitates are *colloidal* in nature, and may be obtained in a state of quasi-solution or "colloidal suspension" by the process of dialysis.

Occasionally the precipitation of a substance is partially or entirely prevented by its assumption of the *colloidal state*. For example, if hydrogen sulphide gas is passed through a

solution of arsenious acid—made by boiling arsenious oxide with water and filtering—a slightly opalescent yellow liquid is obtained, but no precipitate. If, however, a little hydrochloric acid, or ammonium or sodium chloride solution is added to this liquid, yellow arsenious sulphide is immediately precipitated.

This change is attributed to the catalytic interference of hydrogen or metallic ions with the unstable equilibrium of the colloidal state. Similarly the presence of ammonium chloride secures the complete precipitation of aluminium hydroxide by ammonia, by preventing it from remaining in "colloidal suspension".

The student may further study the nature of precipitation by performing the following experiments:—

(a) Add together solutions of potassium chloride and sodium nitrate, containing these salts in approximately equivalent proportions, and evaporate if necessary till solid separates. A crystalline precipitate of sodium chloride will thus be obtained.

(b) Add sodium phosphate solution to solutions of magnesium sulphate to which ammonium chloride and ammonia have been added, and let the solutions be (i) moderately concentrated so that a bulky precipitate appears at once, (ii) rather dilute so that a crystalline precipitate gradually separates, (iii) very dilute so that no precipitate appears for a little time, after which distinct crystals separate. In each case the solid separated consists of magnesium ammonium phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, whether at first it appears crystalline or not, and the size of the crystals depends upon the rate of separation of the solid from solution. In case (i) the precipitate will probably appear flocculent at first, but crystalline on standing.

(c) Add concentrated hydrochloric acid to concentrated solutions of sodium chloride and barium chloride. Crystalline precipitates of these salts will be obtained.

Experiment (a) illustrates a law of precipitation: that of

all possible combinations of metallic and acidic radicles in solution, that which produces the most insoluble compound will first take place. This combination is therefore determined not by affinity but by insolubility.

Experiment (b) is designed to show that precipitation and crystallization are connected phenomena; and that when a precipitate is amorphous, this is due to the suddenness of its separation. Thus the least soluble compounds, prominent among which are some metallic sulphides, are not obtained crystalline by precipitation.

It will readily be understood that when crystals of a substance separate from a solution the solution remains saturated with regard to that substance; the same is accordingly true of a precipitate and the supernatant solution, no precipitate being absolutely insoluble in water.

The student may now try to understand the explanation which the ionic theory gives of the phenomena of solubility and precipitation.

Suppose a saturated aqueous solution of an electrolyte, *e.g.* barium chloride, exists in contact with the solid substance. This solution contains dissociated ions together with more or less undissociated salt. The undissociated salt is in equilibrium on the one side with its ions, and on the other with the undissolved substance. Any disturbance of the equilibrium of the system will cause readjustment by solid entering or leaving the solution. Thus, suppose that by the addition of a reagent containing a common ion or, by evaporation, an increase in the concentration of one or other or both of the ions takes place; the amount of undissociated salt will tend to be increased; this increase will be prevented by the precipitation of some of the solid substance.

Further, in accordance with the law of mass action, the equilibrium between dissociated and undissociated, and thence between dissolved and undissolved salt, depends upon the product of the concentrations of the dissociated ions being kept at a certain value.

If the concentration of one ion becomes increased or diminished, that of the other must be proportionately diminished or increased, so that the product of these concentrations remains constant, or equilibrium will be disturbed, and salt will be precipitated or dissolved.

Precipitation of a salt thus results when by any means the concentration product of its ions is made to exceed a maximum which depends on the solubility of the salt in question. This maximum is called the *solubility product*.

The student should now understand why the addition of concentrated hydrochloric acid to a solution of barium chloride causes the precipitation of the solid salt. The concentration of the chloride ions is in this way greatly increased, whilst that of the barium ions is only diminished by the extent of the dilution of the solution by the liquid added. Thus the concentration product of the ions is increased until the solubility product is exceeded and the solid salt separates.

This principle is of wide application in the precipitation processes which are carried out in analysis. Thus it will at once be seen why an excess of precipitant is necessary to secure as complete precipitation as possible of a particular compound.

For precipitation to take place the solubility product of the compound must be exceeded by means of the ions in solution; and the larger the amount in which the precipitating ion is added, the less will be the remaining concentration in solution of the other ion which is entering into combination to form the precipitate, and therefore the more perfect will be the precipitation. Similarly, in the washing of a precipitated salt, the wash water will exert a solvent action until the solubility product of the ions of the salt is reached within it. If this wash water contains an ion which is present in the precipitate, the solubility product will be sooner reached, and therefore less of the precipitate will dissolve.

It may, however, occur to the student that there are some well-known phenomena which appear flatly to contradict

these conclusions. For instance, the complete precipitation of silver cyanide by means of potassium cyanide is not promoted by the addition of excess of the alkali cyanide; for the precipitate dissolves in this excess. Similarly, the precipitate formed by adding ammonia to copper sulphate solution dissolves in excess of ammonia; and many such examples might be quoted. These phenomena belong, however, to a different category from those considered above, for they depend upon the formation of complex ions of fresh substances in solution; therefore they do not invalidate the general principles of the ionic theory.

Other cases, in which this theory may be employed advantageously to throw light on the properties of precipitates, will be met with in the descriptive part that follows.

§ 36. CLASSIFICATION OF METALLIC RADICLES IN SOLUTION

The following metallic radicles will be included in the scheme:—

Aluminium, antimony, arsenic, barium, bismuth, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, silver, sodium, strontium, tin, zinc.

Copper may occur as the cuprous or cupric basic radicle.

Iron	"	"	ferrous or ferric	"
Mercury	"	"	mercurous or mercuric	"
Tin	"	"	stannous or stannic	"

Antimony, arsenic, bismuth (rarely), chromium, cobalt (rarely), lead (rarely), and manganese may exist in solution in a higher state of oxidation than corresponds to the basic radicle. These metals appear, however, as basic radicles after reduction in the course of analysis; and most of them are also subsequently identified in their original condition as acidic radicles when these are tested for.

§ 37.

PRINCIPLES OF SEPARATION

Analytical separation of these metals in mixed solutions of their salts depends on the difference in degree of solubility in water, or various reagents, of such compounds as may be produced in the course of analysis.

The metals are first divided into groups by successive precipitation of similar insoluble compounds by means of *group reagents*. Each group is then dealt with singly, and its individual members are separated by making use of existing differences in properties between their compounds. It might perhaps be supposed that the analytical groups would coincide with the groups of the periodic law. Such, however, is not by any means the case; and it could not be expected to be so for the following reasons:—

(i) The periodic grouping is according to a natural system; the analytical grouping is artificial, since it is conceivable that another arrangement than the existing one might be made by employing the relative solubilities of other sets of compounds.

(ii) The analytical separation is based on one property only of metallic compounds, viz. solubility; the periodic classification embraces all properties.

(iii) There is a considerable gradation of properties, including solubilities of hydroxides and salts, between the extreme or even the adjacent members of a group in the periodic scheme. On this account metals in the same natural group may belong to different analytical groups. An example of this is furnished by zinc and cadmium, whose sulphides differ in solubility in dilute acids; also by bismuth, arsenic, and antimony, the former metal being more metallic than the two latter, so that its sulphide is insoluble in alkali hydroxide or sulphide solutions, while the sulphides of arsenic and antimony are soluble in such solutions. Ferric iron differs from cobalt and nickel, although occurring in the same natural group, since its hydroxide is practically insoluble in ammonia solution in presence of ammonium chloride, whilst nickel salts,

like those of copper, form with ammonia soluble compounds called ammines, and cobaltous compounds form double salts with ammonium chloride, which prevent their precipitation by ammonia.

On the other hand, the resemblance between properties of analogous compounds of metals in the same natural group is sometimes very close, although gradation is even here perceptible. In such cases the metals will belong to the same analytical group; for example, the metals of the alkalis all belong to one group, and those of the alkaline earths to another.

In cases such as those just mentioned, where close resemblances exist between salts of the different metals in a group with the same acid, and these resemblances extend to several series of salts, analytical separation of the metals is difficult; and it is sometimes necessary to go somewhat far afield among the less common acids in order to find the necessary differences in the solubilities of the salts. Thus barium is separated from strontium and calcium by means of the insolubility of its chromate in acetic acid, potassium from sodium by means of the comparative insolubility of its hydrogen tartrate, platinum-chloride, or perchlorate, and sodium from potassium by reason of the very small solubility of the antimonate of sodium. When metals belonging to different natural groups are classed together in the same analytical group, this is on account of the similar degree of insolubility of one particular kind of compound. In these circumstances it is likely that in the case of other compounds there will be wide differences between the metals, and therefore that their analytical separation will be easy. This is so, for example, with silver, mercurous mercury, and lead, which constitute the first analytical group.

It will now be well to consider the facts upon which the division of the metals into analytical groups is based. Since this division depends upon successive precipitation from aqueous solution of such compounds as are insoluble in water, or in the reagents present under the conditions of the analysis,

the study of the solubilities of simple compounds of the metals will furnish a key to the problem of the classification of these metals in analytical groups.

The following table shows the solubilities in water, dilute acids, or alkalis of the necessary compounds:—

§ 38.

Compounds	Solubility.
Hydroxides	All nearly or quite insoluble in water except (Ca, Sr) Ba, Na, K, NH_4 .
Chlorides.....	All soluble in water except Ag, Hg ⁺ , Pb (sparingly soluble).
Sulphates.....	All soluble in water except Ca, Sr, Ba, Pb.
Nitrates	All soluble in water unless decomposed by it.
Carbonates (normal or basic).....	All that exist insoluble in water except Na, K, NH_4 .
Phosphates.....	All that exist insoluble in water except Na, K, NH_4 .
Sulphides	Fe ⁺⁺ , Al, Cr ⁺⁺⁺ insoluble or but slightly soluble in acetic acid.
	Ag, Hg ⁺ , Pb, Bi, Cd, Cu ⁺ , Sn ⁺ , Sn ⁺⁺⁺ , As, Sb nearly or quite insoluble in dilute hydrochloric acid.
	Sn ⁺ , Sn ⁺⁺⁺ , As, Sb, (Hg ⁺) soluble in alkali hydroxide and polysulphide solutions.
	Fe ⁺⁺ , Al, Cr ⁺⁺⁺ not formed in presence of water.
	Fe ⁺ , Zn, Mn soluble in dilute hydrochloric acid.
	Ni, Co insoluble in, but not precipitated in presence of, dilute hydrochloric acid.
	Ca, Sr, Ba, Na, K, NH_4 , Mg hydrosulphides formed in presence of water, but remaining in solution.

From the facts presented in the above table a method of dividing the elements into analytical groups may be devised. A small group of compounds insoluble in water must first be selected. Three such groups appear to be available: the chlorides, AgCl , Hg_2Cl_2 , PbCl_2 ; the sulphates, CaSO_4 , SrSO_4 , BaSO_4 , PbSO_4 ; and the phosphates, FePO_4 , AlPO_4 , CrPO_4 , insoluble in acetic acid.

The above sulphates, however, would be difficult to deal with, owing to the comparative or complete insolubility of

those of strontium, barium, and lead in dilute acids, and also because calcium sulphate is slightly, and strontium and lead sulphates very slightly, soluble in water. Grave objections exist, as will be seen later, to the introduction of phosphoric acid into a solution, owing to a difficulty which arises when the solution is subsequently made alkaline; hence separation by means of the above phosphates must be rejected. There remain, therefore, the three insoluble chlorides of silver, mercurous mercury, and lead; these three metals thus constitute the first analytical group—the *silver group*. The chlorides are precipitated from aqueous solution by dilute hydrochloric acid, and the filtrate is therefore acid in reaction.

The sulphides insoluble in water, although numerous, are differentiated into several groups; further, those precipitated by hydrogen sulphide¹ in presence of dilute hydrochloric acid are divisible into two classes according to whether or not they are soluble in alkali hydroxide or polysulphide solutions. Metals whose sulphides are precipitated in presence of dilute hydrochloric acid thus form the second analytical group; they are mercuric mercury, bismuth, cadmium, copper, stannous and stannic tin, arsenic, and antimony, to which must be added lead, whose chloride, being slightly soluble in cold water, is never completely precipitated in the silver group.

This group, being large, is conveniently divided into two sub-groups. The metals, mercuric mercury, lead, bismuth, cadmium, and copper, whose sulphides are insoluble in alkalis, form the *copper group*; whilst stannous and stannic tin, arsenic, and antimony, whose sulphides are soluble in alkali hydroxide or polysulphide solutions, constitute the *tin group*.

When the metals of the above two groups have been precipitated there remain the following metals:—

Ba, Ca, Cr, Co, Fe²⁺, Fe³⁺, Mg, Mn, Ni, K, Na, Sr, Zn,

¹ If certain oxidizing agents are present, especially ferric salts, chromates and permanganates (see later, § 466), these will be reduced by the hydrogen sulphide, with precipitation of sulphur, before metallic sulphides are precipitated by this reagent.

and separation of these into groups is effected in alkaline solution.

In view of making the solution alkaline by adding ammonia, the following points must be considered:—

(i) If hydrogen sulphide remains in solution after the separation of the copper and tin groups, the sulphides of cobalt, iron, manganese, nickel, and zinc will be precipitated on the addition of ammonia. In order to prevent this, all hydrogen sulphide must be removed by boiling the solution.

(ii) If the salt of a non-volatile or slightly volatile acid has been dissolved by means of hydrochloric acid, the neutralization of this acid may result in the precipitation of the original salt, which had been decomposed into chloride and the free acid of the salt by the hydrochloric acid. For instance, calcium phosphate¹ when dissolved in dilute hydrochloric acid is decomposed into calcium chloride and phosphoric acid. When this solution is made alkaline the original calcium phosphate will be precipitated.

The following acidic radicles may cause such precipitation on the addition of ammonia² after ammonium chloride,³ and means are taken to eliminate them so that the processes of analysis may take their normal course:

(1) Silicate, (2) fluoride (3) oxalate and tartrate, (4) phosphate.⁴

§ 39. 1. If **silicate** is present in hydrochloric acid solution, gelatinous silica will be precipitated when the solution is made alkaline with ammonia, because of the formation and hydrolysis of ammonium silicate.⁵ Silica is eliminated from

¹ A mixture of, say, calcium carbonate and sodium phosphate would behave similarly after being dissolved.

² If ammonia, added after ammonium chloride, causes no precipitation, those metallic radicles which form insoluble salts with the above acids are absent, and the acids, if present, need not be eliminated.

³ The reason for the addition of ammonium chloride will shortly be explained.

⁴ Arsenite, arsenate, and chromate would similarly cause precipitation with ammonia, but, together with permanganate, they have been got rid of by hydrogen sulphide; arsenite and arsenate by precipitation as As_2S_3 , the latter after reduction, chromate and permanganate by reduction to chromic and manganous salts. Borate likewise forms salts which would be precipitated by ammonia, but these are all soluble in ammonium chloride, which therefore prevents their precipitation.

⁵ See under silicic acid, § 446.

the acid solution by evaporation to dryness and ignition, it being thus rendered insoluble, so that when the residue is treated with acid the silica remains undissolved and may be filtered off.

§ 40. 2. When **fluoride** is present, it may be eliminated as hydrofluoric acid by repeated evaporation of the solution with hydrochloric acid, until on adding ammonia no fluoride is precipitated. In the absence of barium and strontium, sulphuric acid¹ may be advantageously substituted for hydrochloric acid, since, owing to its non-volatility, it will cause a more rapid volatilization of hydrofluoric acid.

§ 41. 3. **Oxalate** and **tartrate** are organic acidic radicles which are best destroyed by ignition after evaporation to dryness. Oxalate thus leaves a residue of carbonate, and tartrate the same mixed with carbon. On dissolving the ignited residue in hydrochloric acid and filtering, if necessary, a solution is obtained with which the analysis may be continued.

§ 42. 4. The elimination of **phosphate** is less simple than that of either of the foregoing acidic radicles, and the principles upon which it is based will best be elucidated by the performance of a few experiments.

(a) Add sodium phosphate to ammoniacal calcium chloride solution; calcium phosphate is precipitated. Add hydrochloric acid until the precipitate is just dissolved, and then ammonia till the liquid is alkaline; calcium phosphate is reprecipitated.

(b) Precipitate calcium phosphate as above from a little *concentrated* solution of the chloride and ammonia; then add to the turbid liquid a few drops of dilute acetic acid; the precipitate will dissolve; divide the solution into two parts:

(i) Boil the solution: a precipitate of CaHPO_4 forms.

(ii) Add a little concentrated solution of ammonium acetate: some calcium phosphate is reprecipitated.²

¹ As little sulphuric acid as possible should be used, because of the dense fumes evolved when it is evaporated; the operation must always be conducted in a fume chamber.

² It is an interesting fact that excess of ammonium acetate diminishes the solvent action of acetic acid. This is probably due to diminution in the ionic dissociation of the acid caused by the addition of acetate ions.

(c) Dissolve some precipitated calcium phosphate in a sufficiency of dilute hydrochloric acid; dilute the solution to about 30 c.cm., and add ammonium acetate as before; no precipitate will now be formed.¹

(d) Precipitate ferric phosphate by adding sodium phosphate to ferric chloride solution. Show that this precipitate is insoluble in dilute acetic acid; then dissolve a little of it in dilute hydrochloric acid, dilute the solution as in (c) and add ammonium acetate. Ferric phosphate is reprecipitated because of its insolubility in acetic acid.

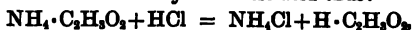
(e) Dissolve a little calcium phosphate in acetic acid, dilute, and add ammonium acetate as in (c); now add to the clear solution ferric chloride drop by drop. Ferric phosphate will be precipitated and the solution will thus eventually be freed from all its phosphate, whilst all the calcium remains in solution. Do not throw this away.

(f) Take about 30 c.cm. of water in a large test tube or a small beaker; add to it a little ammonium acetate and a few drops of ferric chloride; a red colour will be produced. Now boil the liquid for a minute; a precipitate of basic ferric acetate will be formed, and the solution when filtered will be free from iron.

Now continue experiment (e). When sufficient ferric chloride has been added to precipitate all the phosphate, red ferric acetate will be formed, and this will show itself by the apparent reddening of the precipitate. Boil the liquid containing this reddened precipitate for a minute as above, and filter; the filtrate should now be colourless and free from phosphate and iron.

Aluminium and chromium phosphates resemble ferric phos-

¹ Ammonium acetate reacts with hydrochloric acid thus:



so that no free acid but acetic acid is present; likewise there is excess of ammonium acetate, but on account of its diluted state it does not now sufficiently hinder the solvent action of the acetic acid to cause a precipitate. Thus it is shown that to prevent the reprecipitation of calcium phosphate by ammonium acetate the solution must be well diluted.

phate in being precipitated from dilute hydrochloric acid solution by ammonium acetate.¹

Except for one contingency, the method of treatment for phosphates is provided for in the facts established above.

(g) Add one or two drops of sodium phosphate to excess of ferric chloride solution. The precipitated ferric phosphate slowly dissolves on shaking the liquid. Now add ammonium acetate to this solution; there is the red colour of ferric acetate but no precipitate. This is because ferric phosphate is soluble both in ferric acetate and ferric chloride solution; and if this solution were boiled the precipitation would be partial and unsatisfactory. Dilute a little of the solution with water, and then add ammonium phosphate to it till the turbid liquid just remains red.²

When this solution is boiled the precipitate will separate satisfactorily, and the filtrate will be free from iron and phosphate as before.

If, therefore, iron is present in a solution originally, the amount of phosphate must be at least equivalent to it for a satisfactory separation to be effected. When this is not the case, ammonium phosphate must be added to supply the deficiency.

Since iron has been added in the process, it must be tested for separately in the original solution; but the residue should be examined for aluminium and chromium.³

¹ Aluminium and especially chromium phosphate are somewhat soluble in cold acetic acid, but are reprecipitated on boiling, also their acetates are hydrolyzed like ferric acetate, so that after addition of excess of ferric chloride, and boiling, all the aluminium and chromium is found with the iron and phosphate in the precipitate.

² If too much ammonium phosphate is added so that the precipitate appears cream coloured, ferric chloride may again be added until it begins to redden.

³ If ammonium acetate produces no precipitate when added to the diluted and slightly acid solution containing phosphate, aluminium and probably chromium are absent, so that the residue will contain only ferric phosphate and basic acetate, and may be discarded. As was shown above, unless the solution was well diluted, other phosphates, and especially calcium, may be precipitated by ammonium acetate; but they are decomposed by ferric chloride, so that the metals remain in solution and are detected in their proper place. It is, however, better to have the solution dilute in order to promote the hydrolysis of ferric acetate.

It is a useful coincidence that these two metals are also precipitated together with iron by ammonia in the ordinary course, and therefore the same table of separation serves for the examination of the phosphate and hydroxide precipitates.

Indeed the phosphate separation may be considered simply as an interpolation in the general scheme for the separation of the metals into groups.

The following directions for dealing with a solution containing phosphate may now be given:—

§ 43.

PHOSPHATE SEPARATION

If phosphate has been found in a solution prepared for the precipitation of the iron group, and ammonia, added after ammonium chloride, causes a precipitate, just redissolve this precipitate in dilute hydrochloric acid, dilute the solution to about 30 c.cm., add a few drops of dilute acetic acid and 1 to 2 c.cm. of saturated ammonium acetate solution, followed by ferric chloride drop by drop until the pale precipitate at first formed begins to turn red.¹ Boil the liquid for a minute and filter.

Residue.—Contains ferric phosphate and basic acetate, and, if ammonium acetate caused a precipitate, perhaps also Al and Cr.

In this case, wash thoroughly and examine for Al and Cr by table for iron group, § 134; then test the original solution for Fe^{++} and Fe^{+++} .

If ammonium acetate gave no precipitate this residue may be discarded.

Filtrate.—Should be free from Fe and PO_4 , and should give no precipitate with ammonia.

Examine for metals of subsequent groups.²

¹ If the liquid becomes red when ammonium acetate is added, and ferric chloride then gives no precipitate, add ammonium phosphate till a pale or reddish precipitate remains, and then a drop or two of ferric chloride, if necessary, till the precipitate just becomes red.

² A trace of iron may remain, and, if no precipitate is detected and removed after the addition of ammonia, will give a slight black precipitate of FeS with ammonium sulphide. This may cause the liquid to appear green, but, after filtering, a small black residue will remain on the filter paper, which will dissolve in cold dilute hydrochloric acid.

§ 44. Supposing that all hydrogen sulphide has been removed, and that acids requiring special treatment have also been got rid of, the effect of adding ammonia to the solution must now be considered. The addition of sodium or potassium hydroxide until the solution became alkaline would result in the precipitation of all hydroxides insoluble in water—or occasionally basic salts; though any hydroxides possessing acidic properties would dissolve in excess of the alkali hydroxide, forming unstable salts (*e.g.* $\text{Al}(\text{OH})_3$).

Ammonia solution, however, behaves somewhat differently, for two reasons: Firstly, because only about 58 per cent of the ammonia molecules in solution have reacted with water to form ammonium hydroxide, NH_4OH or its ions; the rest are present as NH_3 , and many metallic hydroxides and salts unite with ammonia molecules forming complex metal-ammonia compounds or ammines, which are generally soluble in water. The following are the metals whose compounds combine or react definitely with ammonia—in contradistinction to ammonium hydroxide:

Ag , Hg^+ , Hg^{++} , Cd , Cu^+ , Cu^{++} , Cr^{+++} , Zn^{++} , Ni^{++} , Co^{+++} , Ca , Sr .

The properties of some of the products thus formed will be examined in due course, but for the present it may be noted that with solutions containing zinc and nickel, as well as those containing copper or cadmium, the precipitate at first produced by ammonia solution is dissolved by excess of this reagent, apart from the agency of ammonium salt, since the ammines of these metals are soluble in water.

Secondly, some metallic hydroxides, *e.g.* those of ferrous iron, nickel, cobaltous cobalt, manganese, and magnesium, are not precipitated when ammonium chloride is present; and since ammonium chloride is formed when ammonia solution is added to a liquid containing hydrochloric acid, it follows that these hydroxides will be at most but partially precipitated by ammonia. The addition of sufficient ammonium chloride before ammonia

entirely prevents such precipitation, and the number of metals precipitated by ammonia is accordingly diminished.¹

The precipitation of magnesium, both as hydroxide and carbonate, is entirely prevented by a sufficiency of ammonium chloride. Ferrous iron, manganese, and cobalt, however, present more complicated phenomena owing to their tendency towards oxidation in solution.

Ferrous salts are not precipitated by ammonia in presence of sufficient ammonium chloride, if they are quite free from ferric salts; but since it is difficult to obtain them in this condition, owing to atmospheric oxidation, in practice ferrous salts are always oxidized by nitric acid to the ferric condition, in which state iron is completely precipitated as hydroxide by ammonia even in presence of ammonium chloride.

Manganous salts, like ferrous salts, are not precipitated from solution by ammonia in presence of ammonium chloride, but manganic hydroxide is slowly precipitated from ammoniacal solution by atmospheric oxidation.

Manganic salts, however, are unstable, and are not easily produced in solution; therefore manganic hydroxide cannot be completely precipitated in the course of analysis like ferric hydroxide. Consequently its partial precipitation by atmospheric oxidation of an ammoniacal solution containing manganese is prevented as far as possible by exclusion of air.

Traces of manganese are, nevertheless, precipitated together with the metals of the iron group, when these are present, and this metal might thus be missed subsequently. Small quantities of manganese may, however, be detected in the

¹The explanation of the fact that $Mg(OH)_2$ and some other hydroxides are not precipitated by ammonia in presence of NH_4Cl is stated, in terms of the ionic theory, as follows: an ammonium salt diminishes the concentration of OH ions derived from NH_4OH , so that the solubility product of Mg and OH ions is not exceeded. In the case of a more insoluble hydroxide, such as $Fe(OH)_3$, the addition of ammonium ions cannot reduce the concentration of OH sufficiently to prevent the solubility product of Fe and OH being exceeded; and therefore precipitation of $Fe(OH)_3$ takes place in presence of ammonium salts. The older explanation which ascribed the effect of NH_4Cl to the formation of double salts, e.g. $(NH_4)_2[MgCl_4]$, cannot adequately account for the reaction.

precipitate by ammonia by one of the tests to be described later (§ 133).

In the case of cobalt, the precipitate by ammonia, a basic cobaltous salt, is not soluble in excess in this reagent; it is, however, soluble in ammonium chloride, and therefore its precipitation is partial, and it appears to dissolve in excess of ammonia, or not to be formed when this reagent is added, if the solution originally contained much hydrochloric acid, so that ammonium chloride is produced in quantity on addition of ammonia.

In any case a sufficiency of ammonium chloride permanently retains the cobalt in solution. Cobaltous, like manganese compounds undergo atmospheric oxidation in solution in presence of ammonia, forming cobaltic amines; but, since these are soluble in water, no precipitate results from their formation. In thus remaining in solution after oxidation, cobalt compounds differ from those of manganese.

The addition of ammonia after ammonium chloride therefore results in the precipitation of three insoluble hydroxides only, those of ferric iron, chromium, and aluminium.

Chromium hydroxide, moreover, tends to combine with ammonia and pass into solution; but the compound thus formed, a chromic ammine, is decomposed, and the hydroxide reprecipitated, when the solution is boiled. These three metals thus constitute the *iron group*.

The metals remaining after the elimination of this group are—

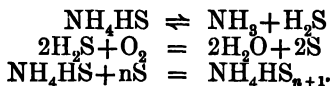
Mn, Zn, Ni, Co, Ca, Sr, Ba, Mg, Na, K;

and of these the first four form sulphides which are precipitated from alkaline solution, being insoluble in, and not decomposed by, water.

The sulphides, ZnS, MnS, CoS, NiS, are therefore separated by passing hydrogen sulphide gas through the filtrate from the iron group, when they are completely precipitated, and may be removed by filtration. Their metals constitute the

zinc group. Instead of passing hydrogen sulphide gas into the alkaline liquid it is more customary to add ammonium sulphide solution to it.

Unless, however, this solution is made just before use, it contains polysulphide—indicated by its yellow colour—which has been produced as the result of the following changes, in which atmospheric oxygen plays a part:—



This yellow polysulphide in presence of ammonia dissolves traces of nickel sulphide, producing a deep-brown solution¹ which may, however, be decomposed by boiling for a few minutes. A brown filtrate from the ammonium sulphide precipitate thus serves to indicate the presence of nickel, but this metal is easily identified in other ways, especially by the red precipitate it gives with dimethylglyoxime (§ 481).

In the table in § 38 it was shown that of all the carbonates of the metals only those of the alkalis are soluble in water. Of the original list of metals there now remain to be accounted for, in addition to the alkali metals,

Ca, Sr, Ba, and Mg;

and, of these, Ca, Sr, Ba form by precipitation normal carbonates, and Mg a basic carbonate insoluble in water. Thus the original number of insoluble carbonates has been so far reduced by the removal of metals in other combinations, that a group may conveniently be made by precipitation of the remaining metals as carbonates. It will be remembered, however, that the precipitation of magnesium hydroxide by ammonia in the third group was prevented by ammonium chloride; the same reagent also prevents the precipitation of the basic carbonate on the addition of ammonium

¹The compound which dissolves in the ammonium polysulphide is probably nickel hexamine sulphide, $\text{Ni}(\text{NH}_3)_6\text{S}$. Colourless ammonium sulphide does not dissolve nickel sulphide if much ammonium chloride is present.

or sodium carbonate, whilst the normal carbonates of calcium, strontium, and barium are precipitated by this reagent. Precipitated calcium carbonate is, however, perceptibly soluble in ammonium chloride solution.

Ammonium carbonate is thus the group reagent for the *alkaline earth group*, the carbonates of calcium, strontium, and barium being precipitated by means of it. The remaining metals—magnesium, potassium, and sodium—form the *alkali group*. These are tested for singly, there being no group reagent for them, care, however, being taken to test and allow for a trace of calcium which may appear here.

The foregoing study has resulted in the division of the metals into groups as follows:—

§ 45.

Dilute hydrochloric acid added to the original solution precipitates:					
Chlorides of Ag, Hg, Pb. (Silver Group.)	From the filtrate hydrogen sulphide ¹ precipitates:				
	Sulphides of (Pb), Hg ⁺⁺ , Bi, Cu, Cd. (Insoluble in alkali hydroxide and polysulphide solutions) (Copper Group); and sulphides of Sn ⁺⁺ , Sn ⁺⁺⁺ , As, Sb. (Soluble in above solutions. (Tin Group.)	From the filtrate, after removal of H ₂ S, oxidation of ferrous compounds with HNO ₃ , and addition of ammonium chloride, ammonia precipitates: ²			
		Hydroxides of Fe ⁺⁺⁺ , Al, Cr. (Iron Group.)	From the filtrate ammonium sulphide precipitates:		
			Sulphides of Zn, Mn, Co, Ni. (Zinc Group.)	From the filtrate ammonium carbonate precipitates:	Filtrate contains:
				Carbonates of Ca, Sr, Ba. (Alkaline Earth Group.)	Mg, Na, K. (Alkali Group.)

¹ Hydrogen sulphide will be oxidized, with the precipitation of sulphur if, and as long as, any of the following acidic radicals are present: arsenate, dichromate, permanganate, chlorate, bromate, iodate, persulphate. Hypochlorous acid or free chlorine, free bromine and iodine, nitrous, and sulphurous acids, also oxidize hydrogen sulphide; traces of these may be present together with the hydrochloric acid, but will probably have been removed by boiling the solution. Nitric acid, which oxidizes hydrogen sulphide, should not be present in quantity.

² In the absence of silicate, fluoride, oxalate, tartrate, phosphate for which special provision is made.

§ 46. PREPARATION OF A SOLUTION FOR THE REACTIONS OF ACIDIC RADICLES

If a substance is soluble in water it may often be tested directly for acidic radicles by reactions in solution. For instance, if a solution of a cupric salt gives with barium chloride a precipitate insoluble in hydrochloric acid, it is rightly judged that sulphate is present, because the only other alternative, the formation of an insoluble chloride, cannot occur, since cupric chloride is soluble in water. But if a solution of a silver salt is to be tested for sulphate, the case is different; for on the addition of barium chloride silver chloride will be precipitated,¹ and it probably will not be possible to tell by inspection whether barium sulphate is formed as well.

Now, just as interfering, non-volatile acidic radicles, such as phosphate, have to be eliminated before certain metals are tested for, so interfering metallic radicles should similarly be got rid of. This is done by boiling the finely divided solid substance with sodium carbonate solution, whereby the metals form insoluble carbonates² or hydroxides, and the acidic radicles enter solution as sodium salts, together with the excess of sodium carbonate.³ All salts which are sufficiently reactive to be decomposed and dissolved by hydrochloric acid also yield to this treatment with sodium carbonate.

Substances which are insoluble in acids, and are not acted upon by boiling sodium carbonate solution, often yield their acidic radicles in solution, generally as sodium salts, when treated according to one or other of the methods described above for the treatment of such insoluble substances.

Before the solution obtained by the decomposition of a substance with sodium carbonate solution can be used for the acid

¹ $\text{Ag}_2\text{SO}_4 + \text{BaCl}_2 = 2\text{AgCl} + \text{BaSO}_4$.

² Occasionally soluble double carbonates are formed, e.g. a blue filtrate containing a double sodium cupric carbonate is sometimes obtained when copper is present.

³ E.g., $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{SO}_4$.

tests, the excess of carbonate must be removed by decomposition with a suitable acid.

The tests for the acidic radicles may be performed either in neutral or acid solution.

A neutral solution is obtained by boiling the substance with sodium carbonate solution and filtering, acidifying the filtrate with dilute nitric acid, warming to expel all carbon dioxide, and then carefully neutralizing with ammonia. Filter if necessary. This solution may then be used for testing for all acidic radicles except nitrate.

When tests are performed in acid solution the filtrate is acidified with an acid suitable to the test; *e.g.* before testing for sulphate with barium chloride, hydrochloric acid is used for acidifying; before testing for chloride, bromide, or iodide with silver nitrate, the liquid is acidified with dilute nitric acid; and before testing for nitrate by the "brown ring test" the solution is acidified with dilute sulphuric acid.

It is convenient, instead of performing two sets of tests, one in neutral and the other in acid solution, to acidify the solution first, and produce any precipitate that is formed in presence of acid. When the filtrate from this precipitate is neutralized by dilute alkali, salts insoluble in water, but soluble in acid, will be precipitated, if excess of the original precipitant is present.

§ 47. CLASSIFICATION OF ACIDIC RADICLES IN SOLUTION

In considering the analytical classification of the metals it was shown why the periodic system does not furnish a basis for such classification. Similarly, it is useless to attempt to classify acids according to the periodic law for practical purposes; for whilst the halogen hydracids, for example, closely resemble each other, acids in other groups show wide differences. Carbonic and silicic acids, and nitric and metaphosphoric acids, are pairs of acids the members of which show no

resemblance to each other, although their elements belong to the same groups in the periodic system.

The analytical classification of the acidic radicles is not so systematic as that of the metallic radicles. The formation of insoluble compounds as precipitates is the most characteristic way in which metallic radicles are separated and identified, and all are identified by this means except ammonium. A number of acidic radicles, however, are chiefly or only detected by means of the volatile products their compounds yield under the influence of heat and acids; for many of them cannot be obtained in solution at all if combined with metals forming insoluble salts. Any attempt to dissolve insoluble carbonates, sulphites, and some other salts results in the decomposition of the acid so that it does not enter into solution.

On account of the instability of their free acids, the following acidic radicles must always be identified by means of the volatile products evolved on heating their salts, or treating them with acids, unless suitable solutions of these salts can be prepared without the use of acids:—

Carbonate, nitrite, sulphide, polysulphide, sulphite, thiosulphate, hypochlorite.

Provision has been made for identifying all these acidic radicles in the scheme in § 20.

The following other acidic radicles can similarly be detected by means of volatile products, but may, as a rule, also be identified by reactions in solution:—

Fluoride, chloride, bromide, iodide, cyanide, sulphocyanide, chlorate, bromate, iodate, nitrate, borate, acetate, oxalate, tartrate, phosphite, hypophosphite, silicifluoride.¹

The following acidic radicles are identified during the course of the reactions for the metals:—

Chromate, dichromate, manganate, permanganate, arsenite, arsenate, phosphate, silicate.

¹ Solution of hydrofluosilicic acid decomposes on heating, and on treatment with alkalis.

The only acidic radicles, therefore, which remain to be identified entirely by reactions in solution are—

Sulphate, persulphate,¹ ferrocyanide, ferricyanide.²

Consequently, if the analyst has carried out perfectly the preliminary dry reactions, the processes for the identification of volatile products evolved by the use of acids, and the systematic separation of the metals, these latter are the only acidic radicles of whose presence he will not then be aware.

Nevertheless it is desirable to provide for the identification of as many acidic radicles as possible in solution; and all except those in the first list above may be so identified.

As in the case of basic radicles, identification in solution is by precipitation, and, occasionally, by colour change.

Division into groups cannot be elaborated as completely as with basic radicles. The solubilities and colours of the salts of *silver*, *barium*, and *iron* furnish the most characteristic tests. These tests will be given in detail at the end of the book. It is often possible and desirable to perform some special confirmatory test for an acidic radicle supposed to be present. These tests are found in the descriptive part.

§ 48.

SUMMARY

Before proceeding to the detailed examination of the reactions of metallic and acidic radicles, it will be well to summarize the chief methods of analysis which have been found applicable by reason of the facts studied in this part.

I. Reactions in the dry way (applicable to solids):

- (a) Heating in ignition tube.
- (b) Flame colorations.

¹ If persulphate is present ozonized oxygen will have been evolved on heating the original substance with dilute sulphuric acid, but this does not suffice to identify the acid.

² Ferro- and ferricyanides evolve CO when heated with concentrated sulphuric acid, but some other salts do the same. Salts of these two acidic radicles will almost certainly have been detected, however, by other properties.

- (c) Borax bead reactions (in case of coloured substances).
- (d) Charcoal reactions (optional).

II. Reactions with acids and alkali for indentification of volatile acids and their decomposition products, and of ammonia.

III. Processes of solution, and reactions for metallic radicles in solution by systematic separation into groups.

IV. Processes of solution, and reactions for acidic radicles in solution, depending chiefly on the properties of silver, barium, and iron salts.

PART II

REACTIONS OF THE METALLIC RADICLES SILVER GROUP

Silver, Mercurous Mercury, Lead

§ 49. **The Chlorides.**—Obtain precipitates of silver, mercurous and lead chlorides, by adding dilute hydrochloric acid to solutions of the nitrates of the respective metals. Filter and wash the precipitates; then remove portions from the filter papers and examine them in turn as follows:—

Action of boiling water on the chlorides.

Silver chloride, AgCl , is not dissolved, but becomes coagulated and begins to turn violet on exposure to light.

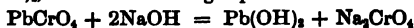
Mercurous chloride, Hg_2Cl_2 , is unaltered.

Lead chloride, PbCl_2 , dissolves if sufficient boiling water is used, and on cooling the solution the salt crystallizes in white needles.¹ Add potassium chromate² to the solution of lead chloride. A yellow precipitate of lead chromate, PbCrO_4 , is formed (chrome yellow), which is insoluble in acetic acid, but soluble in dilute nitric acid and sodium hydroxide solutions.³

¹ Since PbCl_2 is somewhat soluble in cold water, lead is never completely precipitated in the silver group, some remaining in solution and being brought down by H_2S in the next group. A trace of Pb will escape detection in the silver group altogether.

² This is a delicate test for Pb. Show this by experimenting with very dilute solutions.

³ The solubility of PbCrO_4 in alkalis depends on the feebly acidic properties possessed by $\text{Pb}(\text{OH})_2$, the reaction being represented as follows:—



If PbCrO_4 is heated with a little alkali it turns red owing to the formation of a basic chromate, Pb_2CrO_4 (chrome red).

Action of ammonia on the chlorides.

Silver chloride is dissolved by ammonia solution,¹ shaking and warming being necessary if the precipitate is coagulated; it is reprecipitated on acidifying with dilute nitric acid.

Mercurous chloride is blackened by ammonia, but not dissolved.²

Lead chloride is neither darkened nor dissolved by ammonia.

TABLE OF SEPARATION

From the above reactions the following table of separation of the metals of the silver group is directly derived. The student should carry out the separation of the three metals from a mixed solution.³

§ 50. SILVER GROUP

Wash the precipitate obtained by dilute hydrochloric acid with a little cold water; discard the washings; boil the precipitate with much water, and filter.		
Residue. —Wash thoroughly with hot water, ⁴ then mix with ammonia solution, warm, shake, and filter.		Filtrate. Add potassium chromate. Yellow precipitate shows Pb.
Residue. Black. Shows Hg.	Filtrate. Acidify with dilute nitric acid. White precipitate shows Ag.	

¹ The compound formed in solution is $\text{Ag}(\text{NH}_3)_2\text{Cl}$, from which the solid $2\text{AgCl} \cdot 3\text{NH}_3$ may be formed. Similarly, Ag_2O dissolves in ammonia forming the hydroxide $\text{Ag}(\text{NH}_3)_2\text{OH}$ or $\text{Ag}(\text{NH}_3)_3\text{OH}$. This is best shown by adding dilute ammonia to silver nitrate solution until the precipitate first formed dissolves. The solution then contains $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ or $\text{Ag}(\text{NH}_3)_3\text{NO}_3$. Ag_2O precipitated by NaOH is not soluble in excess of the reagent.

² The product is complex, consisting of a mixture of finely divided mercury with NH_2HgCl (see note on Hg^{++} salts). Hg_2O precipitated by NaOH is also black.

³ Some judgment must be used as to the quantities of material employed for analysis. If too little is taken some substances may be missed unless the student is on the lookout for traces; if too much, there is difficulty in thoroughly washing the bulky precipitate obtained, and time will be wasted, or error introduced. In this case, if a 9 cm. filter is half filled with the moist precipitate the amount will be found convenient.

⁴ Until the washings give no precipitate with potassium chromate. A little

SUPPLEMENTARY REACTIONS

SILVER

§ 51. Production of Metal.—Silver compounds are easily reduced to the metallic state, either in the dry way or in solution.

(i) Silver nitrate, when heated strongly, loses oxygen and nitrous fumes, leaving a residue of metal.

(ii) Silver chloride and other salts leave a button of metal when they are heated to a bright red heat¹ with sodium carbonate. Silver is recovered from "residues" by this means.

(iii) When a silver salt, mixed with sodium carbonate, is heated on charcoal before the blowpipe, a bead of the metal is easily produced by reduction.

(iv) Metallic silver is separated (a) in a crystalline form from a slightly acidified solution of a salt by metallic zinc or magnesium, (b) in a loose, finely divided state, by ferrous sulphate solution, and (c) in mirror form from ammoniacal solution by a neutral tartrate.²

thought will enable the student to understand the best way of removing a soluble substance from a precipitate by washing.

If the amount of substance in x c.cm. of solution wetting the precipitate is y gram, and ax c.cm. of wash water are used; the amount of substance remaining when the wash water has run through, leaving the same volume of solution wetting the precipitate as before will be $\frac{y}{a+1}$ gram. If this process is repeated

the amount will be $\frac{y}{(a+1)^2}$; and after n times $\frac{y}{(a+1)^n}$

In order that this quantity may be as small as possible, the value of a must be large. If the volume of wash water remains constant the most satisfactory result will be secured by allowing the precipitate to drain as thoroughly as possible after each washing. It is therefore of little use to add more water until all the liquid present on the filter has run through. The most efficient washing is secured when the precipitate can be drained by means of a filter pump.

In any case, however, the amount of wash water actually required will be greater than that indicated by the above theory, because phenomena of adsorption, that is retention of dissolved substance at the surface of the precipitate, occur.

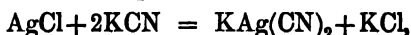
¹ In a muffle furnace.

² To carry out this experiment, add dilute ammonia to AgNO_3 solution in a perfectly clean test tube till the precipitated Ag_2O is nearly redissolved; then add a little sodium tartrate solution, and slowly raise the temperature.

§ 52. **Oxide.**—Sodium or barium hydroxide solution precipitates chocolate-coloured silver oxide, Ag_2O , from solutions of silver salts. When thoroughly washed this oxide still imparts a distinctly alkaline reaction to water, since AgOH goes into solution in small quantity. Silver oxide readily parts with its oxygen when gently heated.

§ 53. **Halides.**—Solution of a fluoride gives no precipitate with silver salts, since silver fluoride is soluble in water. Whilst the *chloride* is a white precipitate turned violet by exposure to light, the *bromide* is very pale yellow, and the *iodide* pale yellow. The bromide is less soluble in ammonia solution than the chloride, and the iodide practically insoluble in this reagent; a gradation of properties is thus shown.

Silver halides are readily soluble in potassium cyanide solution, forming soluble complex salts, *e.g.*—



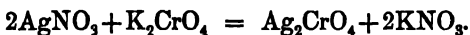
and also in sodium thiosulphate solution—



These reactions are employed in “fixing” photographic images.

§ 54. **Sulphate**, Ag_2SO_4 , being sparingly soluble in water, separates as a white crystalline precipitate on adding dilute sulphuric acid to a concentrated solution of a silver salt.

§ 55. **Chromate**, Ag_2CrO_4 , is a red precipitate soluble in dilute nitric acid.



Like many other silver salts the chromate dissolves in ammonia, forming an ammine.

§ 56. **Sulphide.**—Hydrogen sulphide precipitates black silver sulphide, Ag_2S , even in presence of dilute acid. The tarnishing of silver articles is due to the formation of this substance.

§ 57. **Carbonate**, Ag_2CO_3 , is formed as a white precipitate by adding sodium carbonate to silver nitrate solution. This precipitate turns yellow in boiling water, owing to the formation of a basic carbonate by partial hydrolysis, and finally yields the chocolate-coloured oxide.

MERCUROUS MERCURY

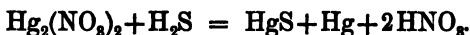
§ 58. **Production of Metal.**—Mercury resembles silver in the ease with which it is separated from its compounds. Many mercurous and mercuric salts, when mixed with Na_2CO_3 and heated in an ignition tube, yield the metal owing to the formation and subsequent decomposition of the corresponding oxide.¹

Reduction in Solution.—Stannous salts, *e.g.* stannous sulphate, reduce mercurous salts to the metallic state in cold solution; ferrous sulphate does so on boiling.

§ 59. **Decomposition of Mercurous Compounds.**—It was seen in § 49 that when ammonia is added to mercurous chloride a mercuric amine and metallic mercury are produced. Such decomposition into mercuric compound and metal is characteristic of mercurous compounds.

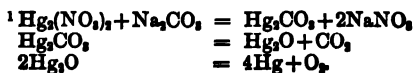
§ 60. **Mercurous oxide, Hg_2O ,** is obtained as a black precipitate by adding sodium hydroxide to a solution of mercurous nitrate. When this black oxide is boiled with water it begins to turn olive green owing to the formation of mercuric oxide and mercury. That the precipitate always contains some mercury is proved by adding dilute hydrochloric acid, when it turns grey instead of white. The same change, into mercuric oxide and mercury, takes place when this oxide is kept in the solid state.

§ 61. **Mercurous sulphide** is unstable, mercuric sulphide and mercury being produced instead:



§ 62. **Mercurous iodide, Hg_2I_2 ,** decomposes in a similar way into mercuric iodide and mercury. It is obtained as a bright-yellow precipitate when a little dilute potassium iodide solution is added to mercurous nitrate. Excess of potassium iodide promotes the decomposition, because mercuric iodide dissolves in this excess.² The dingy green precipitate ordinarily obtained, and often mistaken for mercurous iodide, is thus a mixture of this substance with metallic mercury. When much potassium iodide is added only finely divided mercury remains.

§ 63. **Hydrolysis** is a manner of decomposition to which mer-



curous salts are prone. If crystallized mercurous nitrate is boiled with water a basic salt is precipitated, and the solution becomes acid. The sulphate is similarly hydrolyzed. Thus soluble mercurous salts are acid in reaction.

LEAD

§ 64. **Production of Metal.**—(i) A solid lead compound, mixed with sodium carbonate and heated on charcoal before the blowpipe, gives a malleable bead of lead, and a yellow incrustation of PbO .

(ii) An oxide of lead fused with potassium cyanide in a porcelain crucible gives a button of metal, the cyanide, KCN , being oxidized to cyanate, KCNO .

(iii) Lead is displaced from its salt solutions by zinc, and is thus deposited in crystals forming the well-known lead tree.

§ 65. **Halides.**—It was seen in § 49 that *lead chloride* is formed as a white precipitate soluble in hot water. *Lead bromide* is similar to the chloride. *Lead iodide* is formed as a bright-yellow precipitate, and dissolves in hot water, forming a colourless solution,¹ from which it separates in golden spangles on cooling. When heated with concentrated potassium iodide solution it dissolves, and the solution on cooling forms pale yellow crystals of a double salt which are decomposed by water.

§ 66. **Hydroxide.**—Lead hydroxide, $\text{Pb}_2\text{O}(\text{OH})_2$, is precipitated on adding sodium hydroxide to a solution of a lead salt. It is dissolved by excess of alkali forming plumbite.²

When chlorine water is added to this solution, and the liquid warmed, a light-brown precipitate of the sesquioxide, Pb_2O_3 , is formed; this dissolves in excess of sodium hydroxide forming a colourless solution from which dilute nitric acid separates a brown precipitate of the hydrated dioxide. If the acid liquid, containing

¹ Lead and iodide ions are both colourless; it is only the undissociated salt that is yellow in the solid state.

² $\text{Pb}_2\text{O}(\text{OH})_2 + 2\text{NaOH} = 2\text{Na}[\text{HPbO}_2] + \text{H}_2\text{O}$.

the suspended dioxide, is boiled, chlorine is evolved again, and a colourless solution of lead nitrate remains.¹

§ 67. Carbonate.—Add sodium bicarbonate solution to lead acetate. A white precipitate is formed which is the normal carbonate, PbCO_3 . If normal sodium carbonate, Na_2CO_3 , is used as the precipitant a basic lead carbonate, $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$, is formed. This is the composition of **white lead** which may also be obtained by passing carbon dioxide gas through a dilute solution of lead acetate.²

§ 68. Red lead, Pb_3O_4 , formed by gently heating litharge, PbO , in air, again evolves its oxygen when more strongly heated.³ When dilute nitric acid is poured upon Pb_3O_4 , PbO goes into solution, forming lead nitrate, and a residue of the brown oxide, PbO_2 , remains.⁴

¹ The above reactions may be explained as follows:—

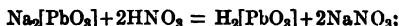
Pb_2O_3 may be regarded as the lead salt of metaplumbic acid, $\text{PbO}(\text{OH})_2$, being produced by the oxidizing action of chlorine, which is reduced to chloride:



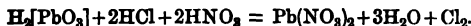
Sodium hydroxide then forms the soluble sodium salts thus:



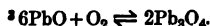
and dilute nitric acid liberates the acid $\text{H}_2[\text{PbO}_3]$ or $(\text{PbO}_2, \text{H}_2\text{O})$:



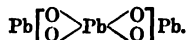
which on boiling oxidizes the hydrochloric acid derived from the sodium chloride above:



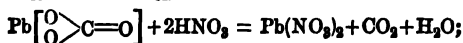
² Owing to incipient hydrolysis this solution contains some basic salt which reacts with carbonic acid; carbon dioxide has no power to precipitate a carbonate from a neutral salt solution. The Dutch process for the manufacture of white lead depends on this reaction; basic acetate is produced by the action of acetic acid vapour and air upon lead, and then decomposed by CO_2 evolved in the fermentation of tan.



Just as Pb_2O_3 is lead metaplumbate, $\text{Pb}\left[\overset{\text{O}}{\text{O}}\text{Pb}=\text{O}\right]$ so Pb_3O_4 is the orthoplumbate:



Compare $\text{Pb}[\text{PbO}_3]$ with $\text{Pb}[\text{CO}_3]$, thus:



Other reactions of lead, upon which its separation in the copper group depends, will be described under that group.

COPPER AND TIN GROUPS

Copper Group.—Mercuric mercury, lead, bismuth, copper, cadmium.

Tin Group.—Stannous and stannic tin, arsenic, antimony.

COPPER GROUP

Mercuric Mercury, Lead, Bismuth, Copper, Cadmium

§ 69. **Sulphides.**—Obtain precipitates of mercuric, lead, bismuth, copper, and cadmium sulphides by passing hydrogen sulphide gas (caution)¹ through small quantities of solutions of their salts containing a little dilute hydrochloric acid.² Note the following facts:—

In the case of *mercuric sulphide* the precipitate first appears white, then yellow, brown, and finally black.³

In the precipitation of *lead sulphide* a similar phenomenon is observed if hydrochloric acid is present, the precipitate being first red, then black.⁴

Bismuth sulphide is formed immediately as a dark-brown precipitate; *copper sulphide* is black, and *cadmium sulphide* yellow.⁵

and $\text{Pb}_2[\text{PbO}_4]$ with the analogous orthocarbonate:
$$\begin{array}{c} \text{C}_2\text{H}_5-\text{O} \\ \text{C}_2\text{H}_5-\text{O} \end{array} \text{C} \begin{array}{c} \text{O}-\text{C}_2\text{H}_5 \\ \text{O}-\text{C}_2\text{H}_5 \end{array}$$

¹ The student is warned that H_2S gas is very poisonous; serious and even fatal results have followed breathing too much of it.

² Solutions of HgCl_2 , $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{Bi}(\text{NO}_3)_3$, CuSO_4 , CdSO_4 may be employed, the sulphides formed being HgS , PbS , Bi_2S_3 , CuS , CdS . In the case of lead, acetic acid may be substituted for hydrochloric acid, but then no red precipitate will be at first produced.

³ This is due to the formation of the compound, $\text{Hg}_3\text{Cl}_2\text{S}_2$ (HgCl_2 , 2HgS), which is white, and which is gradually decomposed by excess of H_2S . $\text{Hg}(\text{NO}_3)_2$ forms a similar compound, which is produced by the prolonged action of concentrated HNO_3 on HgS .

⁴ The red compound is $\text{Pb}_2\text{Cl}_2\text{S}$.

⁵ In presence of HCl the precipitate is somewhat darker than in its absence, owing to formation of $\text{Cd}_2\text{Cl}_2\text{S}$, which is orange.

Filter these precipitates separately, and then wash them thoroughly with hot water; preserve them moist in test tubes for the subsequent tests. Atmospheric oxidation converts copper sulphide into soluble sulphate; this precipitate must therefore be kept from the air as much as possible.

§ 70. Action of Alkali Hydroxide Solution on the Sulphides.—If each of the above sulphides is warmed in turn with sodium hydroxide solution, in no case is the precipitate dissolved.¹

§ 71. Action of Dilute Nitric Acid on the Sulphides.—Each of the above sulphides except mercuric sulphide is soluble in hot dilute nitric acid. A little yellow sulphur is generally separated during solution, and a certain amount of sulphate precipitated in the case of lead, since sulphate is often formed as well as nitrate by the action of nitric acid on a sulphide, and lead sulphate is insoluble in water.² Mercuric sulphide is not dissolved even by concentrated nitric acid, though it is slowly converted into white $\text{Hg}_3(\text{NO}_3)_2\text{S}_2$ by this reagent.

Thus *bismuth*, *copper*, and *cadmium* may be separated from *mercury* on account of the solubility of their sulphides in dilute nitric acid. Lead is obtained partly in solution as nitrate, and partly precipitated as sulphate. By adding dilute sulphuric acid after boiling the mixed sulphides with dilute nitric acid, allowing to stand so that the lead sulphate may be completely precipitated, and filtering, practically all the lead³ is obtained in the residue with the mercury, while the bismuth, copper, and cadmium are in the filtrate.

§ 72. Solubility of Lead Sulphate and Identification of Lead.—Prepare some precipitated lead sulphate by adding dilute

¹This is because none of these sulphides is sufficiently acidic to combine with alkali hydroxide. This is noteworthy in the case of bismuth, because the sulphides of arsenic and antimony combine with alkalis, and these elements occur in the same natural group with bismuth, though in accordance with their lower atomic weights they are less metallic. Bi_2S_3 is, however, somewhat soluble in concentrated Na_2S solution. HgS dissolves slightly in alkali sulphide and polysulphide solutions, thus: $\text{HgS} + \text{Na}_2\text{S} = \text{Hg}(\text{SNa})_2$.

²The stronger the nitric acid, the more likely is lead sulphide to be converted into sulphate.

³ PbSO_4 is very slightly soluble in water, so that a trace still remains in solution. This may be precipitated by adding excess of alcohol.

sulphuric acid to lead acetate solution; filter and wash thoroughly. Then warm the precipitate with concentrated ammonium acetate solution; it dissolves,¹ and the presence of lead in solution can be proved by adding potassium chromate, when yellow lead chromate is precipitated.

§ 73. Identification of Mercury.—Pour a little concentrated hydrochloric acid on mercuric sulphide, add a few crystals of potassium chlorate, and heat. The sulphide dissolves. Boil the liquid until it ceases to smell of chlorine, dilute with water, and add a few drops of stannous chloride solution. A white silky precipitate² of mercurous chloride will be formed.

§ 74. Action of Ammonia on Solutions of Bismuth, Copper, and Cadmium Salts—Identification of Bismuth.—Ammonia solution gives with solutions of *bismuth* salts a white precipitate of the hydroxide, $\text{Bi}(\text{OH})_3$, containing some basic salt, insoluble in excess³ of ammonia. This precipitate may be dissolved in a sufficiency of dilute hydrochloric acid, and the solution dropped into much water, when a white precipitate⁴ or turbidity will be seen.

From solutions of *copper* and *cadmium* salts, ammonia, when added in small quantity, precipitates light blue basic salt and white $\text{Cd}(\text{OH})_2$ respectively. Each precipitate is soluble in excess of ammonia, a deep-blue liquid being formed with copper solutions, and a colourless solution with cadmium.⁵ By means of these reactions with ammonia, copper and cadmium in solution are separated from bismuth.

¹ $2\text{PbSO}_4 + 2\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 = (\text{NH}_4)_2\text{Pb}(\text{SO}_4)_2 + \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. The reaction is promoted by the solubility of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ in water.

² The precipitate is crystalline. The reaction is $2\text{HgCl}_2 + \text{SnCl}_2 = \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$. With excess SnCl_2 , particularly on heating, further reduction to grey metallic mercury occurs; $\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 = \text{SnCl}_4 + 2\text{Hg}$.

³ $\text{Bi}(\text{OH})_3$ is not sufficiently acidic to react with ammonia; neither do Bi compounds form amines with aqueous NH_3 .

⁴ This is due to hydrolysis of BiCl_3 : $\text{BiCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{BiOCl} + 2\text{HCl}$. This and similar reactions are highly characteristic of Bi and other feebly metallic elements, such as Sn and Sb.

⁵ These reactions are due, not to acidic properties of the hydroxides, but to the formation of amines, so that the basic radicles $[\text{Cu}(\text{NH}_3)_4]^{++}$ and $[\text{Cd}(\text{NH}_3)_6]^{++}$ exist in solution.

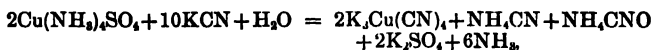
§ 75. Identification of Copper.—The deep-blue colour produced by excess of ammonia furnishes a delicate test for copper, though if very small quantities of the metal are present in solution the colour will be pale, and may be overlooked. Dilute a solution of copper sulphate, to which excess of ammonia has been added, until the blue colour is scarcely perceptible in a small quantity; acidify with acetic acid, so that the colour is quite discharged, then add a few drops of dilute potassium ferrocyanide ($K_4Fe(CN)_6$) solution. A brown colour due to copper ferrocyanide, $Cu_2Fe(CN)_6$, will be produced. Thus it is shown that potassium ferrocyanide is a more delicate reagent for copper than ammonia. In stronger solutions of copper this reagent produces a bulky chocolate-coloured precipitate.

§ 76. Identification of Cadmium in Presence of Copper.—(I) Add to a solution of copper sulphate excess of ammonia, followed by dilute potassium cyanide solution, until the blue colour is just discharged,¹ then pass hydrogen sulphide gas; no precipitate is formed.

Now repeat the experiment in presence of a cadmium salt. On passing hydrogen sulphide through the diluted mixed solution, cadmium sulphide is precipitated. This reaction therefore serves to identify cadmium in presence of copper.

(II) The mixed sulphides may be separated on account of the solubility of cadmium sulphide in a sufficiency of dilute hydrochloric or sulphuric acid, in which copper sulphide is

¹ The reaction is complex; it is represented as follows:—



stable potassium cuprocyanide being formed. A similar experiment may be made with a solution of a cadmium salt, omitting the ammonia. From a concentrated solution $Cd(CN)_2$ separates as a white precipitate which becomes crystalline on standing. This precipitate dissolves in excess of cyanide, forming $K_2Cd(CN)_6$, and if the solution is diluted, and H_2S gas passed, yellow CdS is precipitated, owing to the decomposition of the unstable double cyanide.

Note.—If impure KCN containing KOH is added to a Cd solution, a bulky white precipitate of hydroxide or basic cyanide is formed even in dilute solution; but this precipitate dissolves in excess of the cyanide solution.

insoluble. Obtain the mixed precipitates, wash thoroughly, boil with dilute hydrochloric acid, and filter, protecting the copper sulphide from atmospheric oxidation. Cool and dilute the filtrate, and pass hydrogen sulphide for some time. Cadmium sulphide will be reprecipitated.

It will now be understood that, owing to the solubility of the sulphides of this group in dilute nitric acid, and the additional solubility of cadmium sulphide in dilute hydrochloric acid, the presence of nitric acid must be avoided, and hydrochloric acid¹ must be present in small quantity only, when these sulphides are to be precipitated. In case cadmium is present, the filtrate from the group precipitate must always be well diluted and again saturated with hydrogen sulphide to complete the precipitation.

The foregoing reactions of the metals of the copper group are embodied in the following table of separation.

The student should perform the separation of these metals from a mixed solution of their salts, preferably chlorides.

¹ For satisfactory precipitation and separation from other metals, the solution should be 0.25N with respect to HCl. A lower value may allow ZnS to precipitate; higher values interfere with the precipitation of PbS, SnS and CdS. Acidity control is complicated by the production of acid when the sulphides are formed, and when ferric chloride (if present) is reduced. Permanganates and dichromates react with H₂S to diminish the acidity and form sulphur, and should therefore be previously reduced (§§ 402, 406).

A solution of suitable initial acidity may be prepared in two ways:—(a) Make the solution neutral to litmus by adding ammonia drop by drop. Then add 6.5 c.c. (or a little more to effect complete solution) of 2N HCl, and dilute to 50 c.c. (b) *By Indicators.* Add 2 drops of solution to 1 drop of brilliant cresyl blue indicator on a spotting plate. An orange-red colour indicates too much acid present; at the correct acidity the indicator just turns blue. Similarly, methyl violet gives a blue-green colour at a suitable value, being blue with weaker and yellow-green with stronger acidities.

The solution should be contained in a flask fitted with a double-bored cork, carrying a delivery tube reaching to the bottom and a short exit tube. The delivery tube should have a narrow tip to give small gas bubbles. An open beaker or test-tube is wasteful and inefficient.

Warm the solution, pass H₂S for a few minutes, and filter the liquid. Dilute a portion of the filtrate and test with more H₂S for completeness of precipitation, particularly if cadmium or arsenate (§ 104, note 2) are present. If necessary, dilute the whole of the filtrate and pass H₂S again.

PbSO₄ and BaSO₄ may be precipitated here if sulphate has been formed by oxidation of SO₂ used to reduce arsenate.

§ 77.

COPPER GROUP

The washed precipitate may contain the sulphides HgS , PbS , Bi_2S_3 , CuS ,¹ CdS ; also SnS , SnS_2 , As_2S_3 , Sb_2S_3 . Warm with NaOH solution to which a few drops of yellow ammonium sulphide solution are added,² filter, and wash residue.

Residue.—Warm with dilute HNO_3 , add dilute H_2SO_4 , let stand a few minutes, and filter.

Filtrate may contain Sn^{++} , Sn^{+++} , As , Sb compounds (tin group), see later.

Residue may contain HgS and PbSO_4 .³ Wash, boil with ammonium acetate solution and filter.

Filtrate may contain Bi , Cu , Cd as nitrates. Add ammonia in excess, warm and filter.

Residue (black) is HgS . Dissolve in concentrated HCl with KClO_4 —boil, dilute, and add SnCl_2 . White silky precipitate shows Hg^{++} .

Filtrate. Add K_2CrO_4 . Yellow precipitate in soluble in acetic acid shows Pb .

Residue.⁴ Wash and dissolve in a little hot dilute HCl ; then pour into much water. Turbidity shows Bi .

Filtrate if blue⁵ shows Cu . Examine by I or II.

I. To a part add KCN till colourless. Then pass H_2S —yellow precipitate shows Cd . Acidify the rest with acetic acid and add $\text{K}_4\text{Fe}(\text{CN})_6$ —brown colour or precipitate shows Cu .

¹Wash with H_2S water containing a few drops of HCl . Since CuS is slowly oxidized by the air to CuSO_4 , which goes into solution, precipitates containing this sulphide must be kept well moistened with the washing solution.

²That is, ammonium polysulphide, NH_4HS_x . The reason for the use of this solvent is explained under the tin group.

³Probably some sulphur will also be present.

⁴A little lead hydroxide may occur here unless alcohol is used to separate traces of PbSO_4 ; then the necessity of applying a confirmatory test for Bi . See also §§ 90 (iii) and 474.

⁵If this filtrate is quite colourless copper is absent, and only cadmium need be tested for.

II. Acidify with HCl . Saturate with H_2S , add more dilute HCl , boil, and filter.¹

Residue, CuS . To confirm dissolve in dilute HNO_3 , add ammonia in excess, then acetic acid in excess, and $\text{K}_4\text{Fe}(\text{CN})_6$, brown colour or precipitate shows Cu .

Filtrate. Dilute well and again pass H_2S . Yellow precipitate shows Cd .

SUPPLEMENTARY REACTIONS

MERCURIC MERCURY

§ 78. *Reduction of Compounds.*—Mercuric compounds, *e.g.* the chloride, are easily reduced to the mercurous and the metallic state. Stannous chloride precipitates first white mercurous chloride, and, when added in excess, grey mercury.¹

Metals more electropositive than mercury precipitate it from solution. Among these are copper, zinc, iron. Thus a copper coin may be coated with a film of mercury by immersing it in mercuric chloride solution, and this film when rubbed appears silvery.

Reference has previously been made (§ 58) to the production of mercury by heating its compounds with Na_2CO_3 .

§ 79. *Oxide.*—Dilute sodium hydroxide solution, added slowly to mercuric chloride, produces first a reddish-brown basic chloride, and then bright-yellow mercuric oxide, which is insoluble in excess of alkali. The hydroxide is unknown.

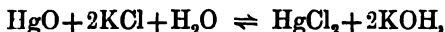
If dilute ammonia solution is poured upon this oxide the colour becomes paler, and the compound $\text{HO} \cdot \text{Hg} \cdot \text{O} \cdot \text{Hg} \cdot \text{NH}_2$ is formed.



This substance, known as Millon's base, gives rise to two important salts which will be noticed below.

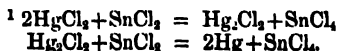
§ 80. Halides.

Chloride.—If to some mercuric oxide, precipitated and washed free from alkali, potassium chloride solution is added, the liquid becomes alkaline. This is due to the following change:—



rendered possible by the fact that mercuric chloride undergoes a comparatively small degree of ionic dissociation in solution, so that a certain quantity can exist unacted upon by the alkali hydroxide formed at the same time. Conversely it follows that mercuric oxide is never completely precipitated when alkali is added to mercuric chloride solution.

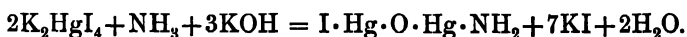
When ammonia is added to mercuric chloride solution there is



produced, not $\text{Hg}(\text{OH})_2$ or HgO , but a white substance having the composition NH_2HgCl . This amino-chloride may also be formed by a reaction between the chloride of Millon's base and ammonium chloride, thus: $\text{Cl} \cdot \text{Hg} \cdot \text{O} \cdot \text{Hg} \cdot \text{NH}_2 + \text{NH}_4\text{Cl} = 2\text{Cl} \cdot \text{Hg} \cdot \text{NH}_2 + \text{H}_2\text{O}$.

Iodide.—When potassium iodide is added to mercuric chloride solution a precipitate is formed which is first yellow and then scarlet, and finally dissolves in excess of the iodide, forming in solution the complex salt K_2HgI_4 , which may be obtained in yellow crystals. Mercuric iodide is known in two forms, yellow and red; the yellow being more stable at higher, and red at lower temperatures. Thus when the red variety is heated it becomes yellow, and the yellow variety kept at atmospheric temperature easily turns red. Mercuric iodide is somewhat soluble in hot alcohol, from which it separates on the addition of water in the less stable yellow form.

When K_2HgI_4 is dissolved in potassium hydroxide,¹ and ammonia is added to the solution, a reddish-brown precipitate having the empirical composition² NHg_2I , H_2O , is obtained. This is the iodide of Millon's base, and is formed in small quantity in solution in Nessler's test for ammonia.



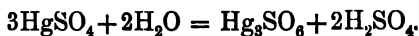
§ 81. Hydrolysis of Mercuric Salts.

Mercuric chloride is not visibly decomposed by water, undergoing but slight ionic dissociation³ in solution. Its solution possesses, however, an acid reaction.

$\text{Hg}(\text{CN})_2$ is also very stable in solution, being practically a non-electrolyte. It gives no precipitates with alkali carbonate, iodide, or hydroxide solutions, but is decomposed by hydrogen sulphide.

On account of these properties $\text{Hg}(\text{CN})_2$ often causes perplexity when given for identification.

Mercuric sulphate is a white salt, instantly decomposed by water, with the production of a bright-yellow basic salt as follows:—



¹ Or KOH is added to the solution obtained by adding KI in excess to HgCl_2 solution

² For a discussion of the constitution of ammoniacal mercuric compounds see Miss Holmes, *Chem. Soc. Trans.* (1918), 113, 74.

³ Hence HCl is not evolved when HgCl_2 is warmed with concentrated H_2SO_4 .

Mercuric nitrate, when acted on by water, gives the basic salt, $\text{Hg}(\text{NO}_3)\text{OH}$, and finally the oxide.

Carbonate.—No normal carbonate has been obtained, but reddish-brown basic carbonates are precipitated from mercuric nitrate solution by NaHCO_3 and Na_2CO_3 , and from mercuric chloride by Na_2CO_3 . These salts lose all their carbon dioxide when boiled with water, leaving the yellow oxide.

From a cold saturated solution of mercuric chloride NaHCO_3 causes the slow separation of a dark-red basic chloride, which turns brown on warming, no mercuric oxide being separated.

COPPER

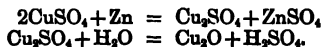
§ 82. **Production of Metal**.—Metallic copper may be obtained by reduction of its compounds in the dry way or in solution, though not quite so easily as silver.

(i) If a copper salt is mixed with sodium carbonate and heated on charcoal before the blowpipe, particles of copper are formed, and may be identified after removal and careful washing. The reduction is facilitated by the addition of potassium cyanide.

(ii) Copper is precipitated from a solution of copper sulphate by metallic zinc. If the CuSO_4 solution is dilute, some cuprous oxide¹ will be mixed with the copper unless its formation is prevented by adding a small quantity of sulphuric acid.

§ 83. **Borax Bead**.—A particle of a copper compound fused into a borax bead colours the bead green while hot, blue when cold, in the outer flame, and colourless or red in the inner.²

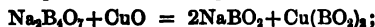
¹ This is on account of the formation and hydrolysis of cuprous sulphate:



Excess of sulphuric acid promotes the following decomposition of cuprous sulphate:—



² In the former case cupric metaborate is produced as follows:—



in the inner flame this is reduced to colourless cuprous salt, $\text{Cu}_2(\text{BO}_2)_2$, or red copper.

§ 84. **Flame Coloration.**—Copper salts colour the Bunsen flame green, or blue if chloride is present; thus if the compound is moistened with concentrated HCl it will impart a blue colour to the flame. These colours are complex, and their spectra contain no distinct lines.

CUPRIC COMPOUNDS

§ 85. **Hydroxide.**—Sodium hydroxide solution added to a solution of a cupric salt produces first a greenish-blue precipitate of a basic salt, and then the bright-blue hydroxide $\text{Cu}(\text{OH})_2$. This precipitate when heated loses water and turns dark brown or black, becoming nearly anhydrous at 100° . $\text{Cu}(\text{OH})_2$ is, however, much more stable than AgOH , which cannot be obtained, though it probably exists in solution in small quantity. Cupric hydroxide dissolves in excess of concentrated sodium hydroxide, forming a deep-blue solution which decomposes slowly when boiled, but rapidly if first diluted. This experiment probably shows that $\text{Cu}(\text{OH})_2$ possesses feebly acidic properties; in this it differs from AgOH .

§ 86. **Carbonate.**—Sodium carbonate precipitates a basic carbonate, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, which, when the liquid is boiled, loses carbon dioxide and water, leaving the oxide. This basic carbonate dissolves in excess of concentrated sodium carbonate solution forming an unstable double salt.

§ 87. **Halides.**—The difference in colour between cupric salts in the anhydrous and hydrated condition is well illustrated by means of *cupric chloride*. This salt is light brown when anhydrous and appears bluish green in the hydrated crystalline form, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

If the anhydrous chloride is dissolved in concentrated hydrochloric acid a yellowish-brown solution is obtained, the colour of which becomes more intense on warming. On dilution with water the solution becomes green and finally blue.¹

These halides show a tendency to decompose into the lower halide and free halogen. This tendency is greatest with the iodide, which on this account has never been obtained; for when potassium iodide is added to a solution of copper sulphate, cuprous iodide and iodine are formed instead of cupric iodide. All the copper is precipitated as fawn-coloured cuprous iodide in presence of sulphurous acid.²

¹ The green colour is a mixture of yellowish brown and blue. It is probable that cupric chloride forms a compound with hydrogen chloride, and that complex ions of this compound exist in the brown solution. The blue colour formed on dilution is attributable to hydrated ions of copper.

² $2\text{CuSO}_4 + 2\text{KI} + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} = 2\text{CuI} + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$.

Cupric cyanide, $\text{Cu}(\text{CN})_2$, decomposes similarly into CuCN and $(\text{CN})_2$, and this accounts for the formation of potassium cuprocyanide in the reaction in § 76.

§ 88. **Hydrolysis of Salts.**—Cupric salts show some tendency to be hydrolyzed in solution. Thus when a dilute solution of copper sulphate is boiled, a green precipitate of basic sulphate gradually separates, and the solution becomes acid. The precipitation of basic instead of normal carbonate by sodium carbonate, and its decomposition on boiling, illustrate the same tendency, and show that cupric oxide is a rather feebly basic oxide.

CUPROUS COMPOUNDS

§ 89. *Cuprous oxide*, Cu_2O , is obtained as a bright-red precipitate by reducing an alkaline cupric solution by grape sugar, arsenites, and other reducing agents.

Fehling's solution, prepared by adding a solution of an alkali tartrate, such as Rochelle salt, $\text{KNaC}_4\text{H}_4\text{O}_6$, together with sodium hydroxide, to copper sulphate solution, thus giving soluble alkali cupritartrate, is employed for this purpose.

If dilute hydrochloric acid is added to cuprous oxide suspended in a little water, the solid first turns white, and then dissolves, forming a colourless solution. When chlorine water is added to this solution a green liquid is obtained. Thus Cu_2O was converted into white CuCl , which is insoluble in water, but dissolves in dilute hydrochloric acid, probably combining with it. The CuCl in solution then readily combines with Cl_2 to form CuCl_2 , whose hydrochloric acid solution is green.

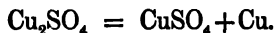
If a solution of *cuprous chloride*¹ in concentrated hydrochloric acid is poured into much water, a bulky white precipitate of CuCl is formed; and if this is allowed to settle, the supernatant liquid decanted, and the residue stirred with more water, it turns orange, owing to hydrolysis, with the formation of hydrated cuprous oxide.

The same orange precipitate is formed when sodium hydroxide is added to cuprous chloride solution free from cupric chloride. Hydrated cuprous oxide possesses no acidic properties, being insoluble in excess of sodium hydroxide. It loses water when warmed, forming red Cu_2O .

Cuprous chloride dissolves in ammonia, forming a colourless solution which rapidly turns blue owing to atmospheric oxidation. The compound formed is an ammine, $\text{Cu}(\text{NH}_3)\text{Cl}$.

¹ Cuprous chloride often appears green owing to the presence of basic cupric chloride, Cu_2OCl_2 , formed by oxidation. This compound dissolves first on treatment with dilute HCl , and CuCl may thus be purified.

When dilute nitric or sulphuric acid is added to cuprous oxide a blue solution of a cupric salt results, together with metallic copper. This is because the cuprous salts of these oxyacids are unstable, decomposing into cupric salt and copper:



Since no cuprous salts exist which are soluble in water, cuprous compounds are not precipitated from aqueous solution by dilute hydrochloric acid, although cuprous chloride is insoluble in water. Therefore cuprous copper does not appear in the silver group.

BISMUTH

§ 90. **Production of the Metal.**—(i) Brittle globules of metallic bismuth are obtained by heating a bismuth compound with sodium carbonate on charcoal before the blowpipe. At the same time a yellow incrustation of the oxide, Bi_2O_3 , is produced.

(ii) Spongy bismuth is precipitated from bismuth nitrate solution by metallic zinc.

(iii) A black precipitate is obtained when a solution of a bismuth salt is added to one of sodium stannite, made by adding sodium hydroxide to stannous chloride solution until the precipitated hydroxide is redissolved. This precipitate contains metallic bismuth, produced according to the reaction:



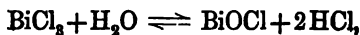
The precipitate is said also to contain the black suboxide Bi_2O_2 .

This reaction is known as the wet-reduction test, and sometimes as the magpie test, because a mixture of black and white precipitate is obtained by adding alkali stannite solution to precipitated $\text{Bi}(\text{OH})_3$.

Hydroxide.—Whilst the precipitate produced by adding ammonia to a bismuth solution contains more or less basic salt, that given by a sufficiency of sodium hydroxide is $\text{Bi}(\text{OH})_3$ only. When this precipitate is warmed with very concentrated sodium hydroxide solution it dissolves, but it is reprecipitated by cooling and on dilution. Thus $\text{Bi}(\text{OH})_3$ appears to possess very feebly acidic properties.

§ 91. Halides.

Chloride.—The hydrolysis of bismuth chloride according to the reaction—



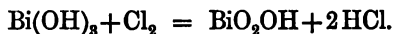
has already been made use of as a test for bismuth. Although bismuthyl chloride, as this basic chloride is called, is so easily formed, it is not further hydrolyzed by water, thus differing from SbOCl . It also differs from the latter compound by being insoluble in tartaric acid.

Bismuth chloride easily melts and volatilizes.

Iodide.—Potassium iodide precipitates dark chocolate-coloured BiI_3 . This dissolves in excess of the precipitant, forming KBiI_4 , and is hydrolyzed by boiling water, red BiOI being produced.

§ 92. *Hydrolysis of Salts.*—Hydrolysis, with the production of insoluble basic salts and free acid, is one of the most characteristic reactions of bismuth salts. The nitrate and sulphate, as well as the chloride, behave in this manner. A basic carbonate is formed by precipitation, and a stable phosphate, as well as the sulphide; these compounds, on account of their insolubility, not being acted on by water.

§ 93. *Bismuthic Acid.*—If chlorine water is added to precipitated Bi(OH)_3 , and the liquid is warmed, brown bismuthic acid, HBiO_3 , is formed:



This bismuth analogue of metantimonic and other acids of the fifth group of the periodic system is unstable, and therefore an oxidizing agent; it possesses only feebly acidic properties.

CADMIUM

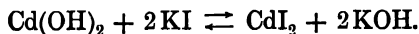
§ 94. *Production of Metal.*—Cadmium is not obtained by a blowpipe reaction, but is separated as a grey powder from the solution of its sulphate by magnesium and zinc.

§ 95. *Oxide.*—Cadmium oxide is the only brown basic oxide. It is formed by the gentle ignition of the hydroxide, and as an incrustation on charcoal in the blowpipe test, when the volatile metal burns in the flame.

§ 96. *Hydroxide.*—The precipitate of Cd(OH)_2 , obtained by adding sodium hydroxide to a solution of a cadmium salt, possesses no acidic properties, and is therefore insoluble in excess of alkali.

§ 97. *Halides.*—The halides of cadmium, and especially the iodide, resemble mercuric chloride in their small degree of ionic dissociation in solution. On this account, when precipitated cadmium hydroxide,

washed free from alkali, is suspended in potassium iodide solution, the solution becomes alkaline, thus:—



The solubility of cadmium iodide in alcohol is connected with the same property.

§ 98. Hydrolysis of Salts.—Cadmium sulphate dissolves in water, producing a neutral solution which turns only faintly acid when boiled. The chloride behaves similarly.

Thus cadmium salts suffer very slight hydrolysis; though a basic and not a normal carbonate is precipitated by sodium carbonate.

TIN GROUP

Stannous and Stannic Tin, Arsenic and Antimony

§ 99. Sulphides.—Obtain precipitates of the sulphides SnS (brown), SnS_2 (dull yellow), As_2S_3 (bright yellow), and Sb_2S_3 (orange red) by passing hydrogen sulphide through acidified solutions of stannous and stannic, arsenious, and antimonious chlorides respectively. Filter and wash the precipitates thoroughly with hot water, and then remove them with water to test-tubes. Note the appearance of the precipitates, and use a little of each for the following tests:—

§ 100. Action of Solvents on the Sulphides.—(1) *Alkali hydroxide.*—Show that stannic, arsenious, and antimonious sulphides are easily soluble in sodium or potassium hydroxide solution, but that stannous sulphide dissolves only with difficulty in these reagents, even on warming.¹ If, however, a little yellow ammonium sulphide is added to the hot alkaline liquid, stannous sulphide dissolves more easily.²

(2) *Concentrated hydrochloric acid.*—Show that stannous and stannic sulphides and antimonious sulphide are soluble,

¹ The student may sometimes find that SnS dissolves in hot NaOH or KOH solution; at other times it may be impossible to dissolve the precipitate. The solubility depends on the physical condition of the sulphide.

² It is to meet this case that yellow ammonium sulphide is employed with NaOH in the group separation (p. 80). The increase in solubility depends upon the formation of SnS_2 , which is more acidic than SnS .

and that arsenious sulphide is insoluble¹ in hot concentrated hydrochloric acid; arsenious sulphide may, however, be dissolved by the aid of a little potassium chlorate. Of the three former sulphides stannous sulphide is the most soluble in hydrochloric acid; therefore stannous salts are liable to escape complete precipitation by hydrogen sulphide if the solution is too acid. These differences in the solubilities of their sulphides in hydrochloric acid enable tin and antimony to be separated from arsenic.

(3) *Ammonium polysulphide* (yellow ammonium sulphide).—Stannic, arsenious, and antimonious sulphides are easily soluble in ammonium polysulphide; and stannous sulphide is moderately soluble.

(4) *Ammonia* dissolves arsenious sulphide easily, and antimonious sulphide less readily; stannous and stannic sulphides are not dissolved by ammonia.

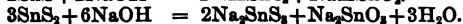
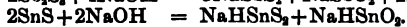
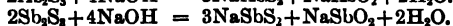
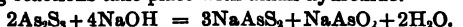
(5) *Ammonium carbonate* dissolves only arsenious sulphide. This is a characteristic reaction which serves for the identification of arsenic.

From all these alkaline solutions the sulphides are reprecipitated on adding acid. When a polysulphide has been used, the higher sulphides separate together with free sulphur. This is noticeable when dark-brown stannous sulphide has been dissolved in yellow ammonium sulphide, and the solution is acidified; pale-yellow stannic sulphide then separates.²

¹ The insolubility of As_2S_3 in concentrated HCl may be attributed to the feebly base-producing properties of As^{+++} .

² The solubility of these sulphides in alkalis reveals their acidic nature; they are thioanhydrides—or sulphanhydrides—and form thio- or sulpho-salts with bases. The degree of solubility is a measure of their acidic power; thus arsenious sulphide, which is shown to be the least basic of these sulphides by not reacting with hydrochloric acid, is the most acidic because it dissolves in the least basic solvent employed, viz. ammonium carbonate.

The following reactions take place with alkali hydroxide:—



Mixtures of thio- and oxy- arsenite, antimonite, stannite, and stannate, respectively, are thus formed in solution as meta-salts,

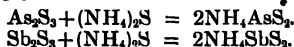
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§ 101. **Formation of Antimonate.**—Dissolve a little precipitated antimonious sulphide in a few c.c.'s of concentrated hydrochloric acid; boil the solution thoroughly to expel hydrogen sulphide, then add potassium hydroxide¹ solution. A white precipitate of antimonious hydroxide is formed, which dissolves in excess of alkali producing antimonite. Take parts of this solution for the following tests:—

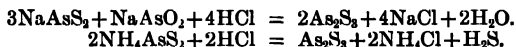
(a) Add solid ammonium chloride; antimonious hydroxide is reprecipitated.²

(b) Add bromine water, until the liquid remains yellow, then solid ammonium chloride; there is no precipitate³ even on heating, but nitrogen⁴ gas is evolved. Keep this solution.

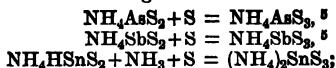
A hydrosulphide may be used as a solvent, and then only thiosalts are produced; e.g. As_2S_3 and Sb_2S_3 dissolve in colourless ammonium sulphide thus:—



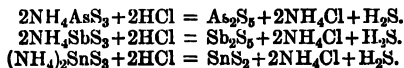
From all these solutions of thiosalts acids reprecipitate the sulphides; e.g. in the case of As:



If a polysulphide, such as is present in yellow ammonium sulphide, is used to dissolve the sulphides, additional sulphur is incorporated within the molecule by this means, in the three following cases:—



and from solutions of these thio-arsenates, antimonates, and stannates the higher sulphides are precipitated on acidifying:

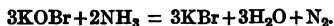


¹ KOH is preferable to NaOH, since the latter is likely to cause the precipitation of insoluble antimonate, $\text{NaH}_2\text{SbO}_4 \cdot 2.5\text{H}_2\text{O}$ (or possibly $\text{Na}[\text{Sb}(\text{OH})_6] \cdot 0.5\text{H}_2\text{O}$), on oxidation of the antimony.

² Owing to the hydrolysis of alkali antimonite. Cf. stannate and aluminate.

³ Antimonite has been oxidized to antimonate by the hypobromite formed on adding bromine to the alkaline solution; and alkali antimonate is stable.

⁴ The following reaction takes place between hypobromite and ammonia:—



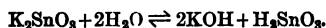
⁵ In solution these are probably ortho-salts $(\text{NH}_4)_3\text{AsS}_4$ and $(\text{NH}_4)_3\text{SbS}_4$, thus: $\text{NH}_4\text{AsS}_3 + (\text{NH}_4)_2\text{S} = (\text{NH}_4)_3\text{AsS}_4$.

§ 102. **Formation and Hydrolysis of Stannate.**—Dissolve precipitated stannous sulphide in concentrated hydrochloric acid, and boil as before to expel hydrogen sulphide. Then add potassium hydroxide in excess, bromine water until the liquid is yellow, and solid ammonium chloride. Stannic hydroxide will be precipitated on boiling.¹

§ 103. **Reduction of Stannic Hydroxide and Identification of Tin.**—Filter and thoroughly wash the precipitate obtained in the previous experiment. Then dissolve it in hot concentrated hydrochloric acid, dilute the solution a little, add pure iron in the form of borings, wire, or reduced iron, and heat. When the reaction has proceeded for a minute, dilute, cool, filter, and add mercuric chloride to the filtrate. A white precipitate of mercurous chloride shows the presence of tin.

§ 104. **Precipitation of Antimonic Sulphide from Antimonic Acid.**—Acidify the solution of potassium antimonate obtained above [§ 101 (b)] with dilute hydrochloric acid, and pass hydrogen sulphide through the cold solution. An orange-coloured precipitate of antimony pentasulphide is quickly obtained.²

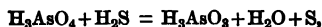
¹ Potassium stannate is formed, but is readily hydrolyzed:



Removal of alkali promotes hydrolysis, and ammonium chloride does so here exactly as with aluminates (§130). Precipitation is complete, for colloidal solution of the stannic acid (or stannic hydroxide) is prevented by excess ammonium salt. Potassium antimonate, the salt of a stronger acid, does not behave in this way.

² The reaction is $2\text{H}_3\text{SbO}_4 + 5\text{H}_2\text{S} = \text{Sb}_2\text{S}_5 + 8\text{H}_2\text{O}$.

There is a noteworthy difference between the reactions of arsenic and antimonie acids with H_2S ; when little acid is present the former slowly oxidizes H_2S thus:



arsenious sulphide being subsequently precipitated; when the proportion of HCl in the solution lies between 7.9 and 14.3 per cent the precipitate consists of As_2S_3 only, the formation of which is probably preceded by that of H_3AsS_4 ; when the HCl is more concentrated As_2S_3 and sulphur again appear in the precipitate, which in presence of acid of 32 per cent strength consists of these two latter substances only; in this case the arsenic acid oxidizes the hydrochloric acid, and the liberated chlorine then oxidizes the H_2S . Arsenate thus presents some difficulty in the copper group separation, the precipitation of As_2S_3 at the recommended low acidity being slow. It should be reduced by SO_2 , excess SO_2 being boiled off, prior to passing H_2S .

TABLE OF SEPARATION

§ 105. The following table of separation for tin, arsenic, and antimony is based upon the reactions of these metals studied above.¹

§ 106.

TIN GROUP

To the filtrate³ from the copper group add dilute HCl in excess. [If any sulphides of the tin group were present in solution they will be reprecipitated, but if only white sulphur separates, the metals of this group are shown to be absent.] If a coloured precipitate forms, again pass H_2S to complete the precipitation. Filter and wash the precipitate; reject the filtrate. Boil the precipitate with a little concentrated HCl, dilute well, and filter.

Residue².—Heat gently for a minute or two with water and powdered ammonium carbonate. Filter.

Filtrate.—Boil thoroughly to expel H_2S ;⁴ then add KOH till any precipitate that forms is just redissolved,⁵ followed by bromine⁶ water until the liquid remains yellow. Then add solid NH_4Cl ,⁷ and boil in a beaker for a few minutes. Filter if necessary.

Residue,
if black,
confirms
presence of
 Hg^{++} .

Filtrate.—
Acidify with
dilute HCl.
Yellow pre-
cipitate
proves As .

Residue = $\text{Sn}(\text{OH})_4$.—Dissolve in hot concentrated HCl, dilute, add iron wire, and heat so that hydrogen is briskly evolved. After a minute filter, cool, and add a few drops of HgCl_2 .⁸ A white precipitate formed at once or on standing proves Sn .

Filtrate⁹.—
Acidify with
dilute HCl
and pass
 H_2S .
Orange pre-
cipitate proves
 Sb .

¹ It is a modification of the method recommended by James Walker, *Chem. Soc. Trans.* (1903), 83, 184.

² If a solution is given containing only the tin group metals, begin by adding dilute HCl in excess and passing H_2S .

³ An alternative method of identifying arsenic is to dissolve this residue in a mixture of concentrated hydrochloric acid and a little potassium chlorate, and then test for arsenate according to § 127.

⁴ An alternative and simpler method of identifying Sn and Sb is nearly to neutralize this solution and then reduce it with iron wire. SnCl_2 is formed in solution and black Sb precipitated. The Sn may be proved, after filtering, with HgCl_2 , and the Sb by dissolving it in dilute HNO_3 and passing H_2S .

⁵ Care must be taken not to add a large excess of KOH; very little more will be necessary after the liquid has reached the neutral point.

⁶ Bromine oxidizes alkali antimonite to antimonate; the former would give a precipitate of $\text{Sb}(\text{OH})_3$ on addition of NH_4Cl .

⁷ The hypobromite present will first oxidize ammonia, causing evolution of nitrogen; afterwards the tin will be precipitated.

⁸ If the liquid is not cooled, or if much tin is present, grey metallic mercury may be precipitated instead of white mercurous chloride.

⁹ The filtrate should be boiled again with more NH_4Cl , in case any tin still remains in solution.

SUPPLEMENTARY REACTIONS

TIN

§ 107. **Production of Metal.**—(i) Solid tin compounds, *e.g.* stannous chloride or stannic oxide, yield a bead of white malleable metal when mixed with sodium carbonate and potassium cyanide, and heated on charcoal before the blow-pipe. Since this bead can be dissolved in hydrochloric acid, difficultly soluble tin compounds will yield their tin in solution by this means.

(ii) Tin is precipitated from stannous chloride solution by metallic zinc, and, when separated slowly, the metal is obtained in well-defined crystals (the tin tree).

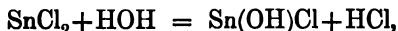
STANNOUS COMPOUNDS

§ 108. **Oxide.**—Stannous oxide is black, and is sometimes observed when dilute nitric acid is added to metallic tin. It separates as a grey powder when solid stannous chloride is added to concentrated potassium hydroxide solution.

§ 109. **Hydroxide.**— $\text{Sn}_2\text{O}(\text{OH})_2$ is formed as a white precipitate when alkali hydroxide is added to stannous chloride solution. It possesses acidic properties, since it dissolves in excess of alkali, forming stannite, $\text{M}[\text{HSnO}_2]$.

§ 110. **Chloride.**—Like the chlorides of the other metalloids, anhydrous stannous chloride is easily fusible.

The hydrated salt $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, though soluble in water, is readily hydrolyzed thus:—



and is easily oxidized by the air to stannic salt. If metallic tin is placed in an acidified solution of stannous chloride, the formation of stannic salt is prevented. Stannous chloride is a valuable *reducing agent*.

(i) Mercuric chloride is reduced by stannous chloride, as was previously seen; thus a white precipitate is obtained when stannous chloride is added to mercuric chloride solution, and this turns grey

when excess of stannous chloride is present, owing to reduction to metallic mercury.¹

(ii) Acidified ferric chloride solution, when hot, is rapidly reduced to the ferrous state, the yellow liquid becoming colourless.²

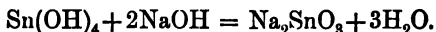
(iii) Gold chloride is reduced by stannous chloride solution, purple of Cassius, probably a compound of aurous and stannic oxides, being formed. A precipitate or colour, varying from purple to brown, is obtained, when the two solutions are mixed.

§ 111. **Hydrolysis of Stannous Salts.**—It has been seen above that stannous chloride undergoes hydrolysis with much water. Stannous sulphate and nitrate, formed by the action of the dilute acids on tin, are easily hydrolyzed, and stannous carbonate is not known.

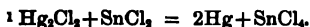
STANNIC COMPOUNDS

§ 112. **Hydrated stannic oxide** is formed as a cream-white powder by the action of moderately concentrated nitric acid on tin. Stannic nitrate is probably first produced, but at once decomposes into the hydrated oxide and oxides of nitrogen. The composition of this substance is represented by the formula $(\text{H}_2\text{SnO}_3)_5$, or $\text{Sn}_5\text{O}_5(\text{OH})_{10}$, and it is known as metastannic acid, or β -stannic acid. It is less soluble in hydrochloric acid and other reagents than α -stannic acid, H_2SnO_3 , obtained by drying $\text{Sn}(\text{OH})_4$ over sulphuric acid.³

§ 113. **Stannic hydroxide**, $\text{Sn}(\text{OH})_4$, is formed as a white gelatinous precipitate when alkali hydroxide is added to stannic chloride solution. It is readily soluble in dilute mineral acids, and is dissolved also by excess of alkali, forming α -stannate.



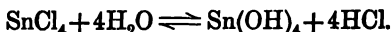
The hydrolysis of alkali stannate, a reaction closely related to the above, has already been studied in § 102.



² $2\text{FeCl}_3 + \text{SnCl}_2 = 2\text{FeCl}_2 + \text{SnCl}_4$. This method of reduction is used in volumetric analysis, previous to titration of iron originally in the ferric state, by $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Excess of SnCl_2 is removed by adding HgCl_2 to the cooled solution, since dichromate, as well as permanganate solution, oxidizes SnCl_2 but not Hg_2Cl_2 .

³ H_2SnO_3 or $\text{SnO}(\text{OH})_2$ is, properly speaking, metastannic acid, H_4SnO_4 or $\text{Sn}(\text{OH})_4$ being orthostannic acid. The polymer $\text{Sn}_5\text{O}_5(\text{OH})_{10}$ is best described for scientific purposes as β -metastannic acid, whilst $\text{SnO}(\text{OH})_2$ is α -metastannic acid.

§ 114. Stannic chloride, SnCl_4 , is a liquid, combining with a little water to form solid hydrates, *e.g.* $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$; but, on boiling with much water, complete hydrolysis takes place, with precipitation of gelatinous $\text{Sn}(\text{OH})_4$.

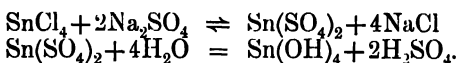


SnCl_4 combines with ammonium chloride to form ammonium stannic chloride $(\text{NH}_4)_2\text{SnCl}_6$. This compound separates in crystals when concentrated ammonium chloride solution is added to SnCl_4 dissolved in concentrated hydrochloric acid.

§ 115. **Hydrolysis of Stannic Salts.**—Stannic hydroxide possesses in a feeble degree both acidic and basic properties; therefore hydrolysis of salts in which it manifests either of these properties may be expected; and the decomposition of alkali stannate has already been observed as an example of the former. Stannic chloride may be regarded either as a stannic salt, or as the chloride of stannic acid; and consequently the stannic hydroxide produced by its hydrolysis, either as a base or an acid.

The following reaction furnishes an undoubted example of salt hydrolysis, since stannic sulphate is formed and hydrolyzed:—

Add sodium sulphate solution to a hot solution of ammonium stannichloride; stannic hydroxide is precipitated.



ARSENIC AND ANTIMONY

These elements and their compounds possess some properties and reactions in common, and the differences which occur between them are valuable for comparative purposes. The two elements will therefore be studied together.

§ 116. Production of the Elements—Arsenic.

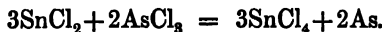
(a) *Formation in the dry way.*—(i) Heat in an ignition tube a mixture of arsenious oxide with potassium cyanide or powdered charcoal. A black mirror is formed on the sides of the tube, and an odour of garlic, due to arsenic vapour, observed. The same odour is noticed when a compound containing arsenic is heated on charcoal before the blowpipe.

(ii) Arsenic is deposited on a heated tube through which its gaseous hydride passes, owing to the decomposition of the

gas, and also when the flame of this gas impinges on cold porcelain (see later under Marsh's test).

(b) *Separation from solution.*—(i) By metallic copper in *Reinsch's test*. Heat arsenious oxide with hydrochloric acid and a clean copper strip. A grey deposit of Cu_3As_2 is formed on the copper. Dry the strip and heat it in a dry test tube. The arsenic volatilizes and is oxidized, so that crystals of arsenious oxide in the shape of regular octahedra or tetrahedra are formed on the sides of the tube. If the tube is warmed before the experiment, the crystals are larger. They may be examined with a microscope.

(ii) By stannous chloride in *Bettendorff's Test*.—Dissolve some stannous chloride in concentrated hydrochloric acid, and add this solution to one of arsenious oxide in the same acid. On warming, a black precipitate of arsenic is formed, the following reaction having taken place:—



§ 117. Antimony.

(a) *Formation in the dry way.*—Mix antimonious oxide with sodium carbonate and a little potassium cyanide, and heat the mixture on charcoal before the blowpipe. Globules of the brittle white metal are obtained, together with a white incrustation of oxide.

(b) *Separation from solution.*—(i) Antimony is precipitated by metallic zinc from acidified antimonious chloride solution; and if the zinc rests upon a piece of platinum foil, the antimony forms a black stain on the platinum. This deposit may be dissolved by warming with a little dilute nitric acid, and the solution after dilution gives with hydrogen sulphide an orange precipitate of antimonious sulphide. (Cf. note 4, p. 92.)

(ii) Metallic copper receives a deposit of antimony when placed in acidified antimonious chloride solution. This deposit is distinguished from that given by arsenic compounds (*Reinsch's test*) by its inferior volatility, and by giving a sublimate of oxide consisting of less well-defined crystals.

§ 118. Hydrides, AsH_3 , SbH_3 .—Arsenic and antimony both

form volatile hydrides when their compounds are present during the generation of hydrogen from dilute acids by zinc.¹ These important reactions constitute *Marsh's test*.

Fit up an apparatus for the generation of hydrogen, consisting of Woulfe's bottle, or flask with doubly bored cork, thistle funnel, and delivery tube bent once at right angles, and drawn out to form a jet. Place granulated zinc, free from arsenic and antimony, in the apparatus, cover it with water, and pour a little concentrated sulphuric acid through the thistle funnel.

When hydrogen is being evolved briskly, and it has been proved, by collecting a little gas and observing that it burns quietly, that all air has been displaced from the apparatus, ignite the hydrogen, and pour down the thistle funnel a solution containing arsenic. The flame immediately becomes grey, and white fumes of arsenious oxide rise from it. A porcelain dish held in the flame receives a black velvety deposit of arsenic, and if the horizontal part of the delivery tube is gently heated with a flame, a mirror of arsenic is formed within the tube owing to the decomposition of the hydride by heat. The deposit of arsenic on the dish or tube is dissolved by bleaching powder solution, arsenate being formed.

Repeat these experiments,² using a solution containing antimony instead of arsenic, and note that the deposit of metal obtained upon the porcelain is insoluble in bleaching powder solution, and that the film deposited in the tube is formed nearer to the flame than with arsenic, and even on both sides of it. This is because stibine³ is more unstable than arsine, and antimony is less volatile than arsenic.

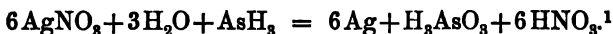
§ 119. *Hofmann's Test*.—Pass arsine, obtained as in Marsh's test, through dilute silver nitrate solution in a test tube. A

¹ These experiments, or at least that in which AsH_3 is generated, must be done in a fume chamber, because AsH_3 is very poisonous.

² The student is advised to perform Hofmann's test, given below, as far as regards arsenic, before preparing the apparatus for the tests with SbH_3 .

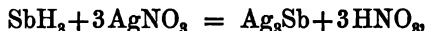
³ SbH_3 is called antimonetted hydrogen or stibine, AsH_3 being arsenetted hydrogen or arsine

black precipitate is obtained which is metallic silver, formed according to the reaction:



Filter the solution, and carefully neutralize the filtrate with dilute ammonia, when, if any silver remains in solution (silver nitrate may be added if necessary), a yellow precipitate of silver arsenite will be formed.

Now pass stibine through dilute silver nitrate solution. A black precipitate is again formed, but this is silver antimonide, produced by the reaction:



together with some metallic silver, formed by the reduction of the nitrate by hydrogen.²

Thus no antimony goes into solution, and therefore arsenic and antimony, if occurring together, may be separated by this test.

These reactions do not, however, fully elucidate the behaviour of the hydrides towards silver nitrate.

§ 120. For this *Gutzeit's test* must be performed.

Introduce a compound containing arsenic into a test tube with zinc and dilute sulphuric acid; push a little cotton wool loosely into the upper part of the tube in order to catch the spray carried up by the evolved gas, and on a piece of filter paper covering the top of the tube place a small crystal of silver nitrate. This will immediately turn yellow by reaction with the arsine, but when moistened with water will become black.

Repeat the experiment with antimony; similar effects will be observed.

The yellow product is a compound of silver arsenide or antimonide with silver nitrate, produced by the following reaction:—

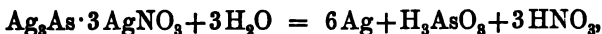


Thus in the absence of water AsH_3 and SbH_3 behave alike towards silver nitrate.

¹ Compare the oxidation of arsenic here with its solution by bleaching powder after deposition on porcelain in Marsh's test.

² The hydrides produced in these experiments are, of course, highly diluted with hydrogen.

The arsenic compound, however, is decomposed by water as follows:—

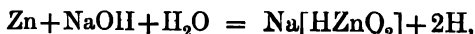


the final result being the same as in the Hofmann test.

Thus the oxidation of the arsenic was at first prevented by the formation of the double compound, $\text{Ag}_3\text{As} \cdot 3\text{AgNO}_3$.

When the analogous antimony compound is decomposed Ag_3Sb remains, as in Hofmann's test, antimony differing from arsenic in not being oxidized under these conditions.

§ 121. *Fleitmann's Test*.—Heat an arsenious compound in a test tube with zinc and sodium hydroxide solution. The hydrogen evolved in the reaction,



produces AsH_3 , as in Marsh's test. This gas is identified by holding a piece of filter paper moistened with silver nitrate solution at the mouth of the tube, when a grey stain of metallic silver is produced by the reaction previously studied.

Antimony compounds do not give this reaction, SbH_3 being too unstable to be formed in this way.

ARSENIOUS AND ANTIMONIOUS COMPOUNDS

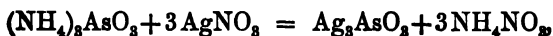
§ 122. Oxides, X_4O_6 .

Arsenious oxide, As_4O_6 .—Boil arsenious oxide with water, and filter the solution. **Arsenious acid, H_3AsO_3 ,** is formed in small quantity, so that the solution reacts acid.

Arsenious oxide dissolves in alkalis forming *arsenites*. Show that it is soluble in sodium carbonate solution, displacing carbonic acid.

Dissolve some arsenious oxide in a little dilute ammonia. Dilute the solution well, so that it smells but faintly of ammonia, and use it for the following reactions:—

(i) AgNO_3 gives a pale-yellow precipitate of silver arsenite:

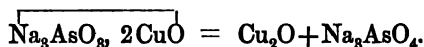


which, like so many silver salts, is soluble in ammonia as well as in dilute nitric acid.

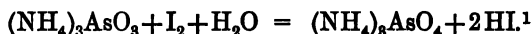
(ii) Copper sulphate gives a bright-green precipitate of copper hydrogen arsenite, Scheele's green:



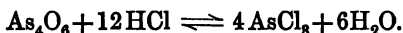
Add sodium hydroxide to the liquid containing this precipitate, until a clear blue solution is obtained. When this solution is boiled, cuprous oxide separates as a red powder. This is due to the self-oxidation and reduction of the alkali cupriarsenite in solution to arsenate and cuprous oxide:



(iii) Add a solution of iodine in potassium iodide to the arsenite solution: the iodine is decolorized, the arsenite being oxidized to arsenate:



§ 123. **Arsenious chloride, AsCl_3 .**—Arsenious oxide is easily dissolved by hot concentrated hydrochloric acid, arsenious chloride being produced in solution. When the solution cools, the oxide crystallizes in regular octahedra, the following reaction being reversible:



If, however, the solution is boiled, arsenious chloride, which is a volatile liquid, gradually escapes as vapour.²

The basic properties of arsenious oxide are of the feeblest description. Possibly the sulphate exists, but no other oxysalt.

§ 124. **Antimonious oxide, Sb_2O_3 , and Hydroxide, $\text{Sb}(\text{OH})_3$.**—Antimonious oxide dissolves in sodium hydroxide solution, but not in sodium carbonate.

Add sodium hydroxide to antimonious chloride solution until the white precipitate of $\text{Sb}(\text{OH})_3$ is just redissolved; then pass carbon dioxide gas through the solution; antimonious hy-

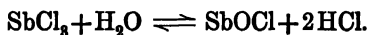
¹ If NaHCO_3 is added to neutralize the HI , the reaction is quantitative.

² This is very poisonous.

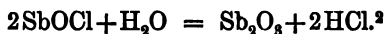
dioxide will be reprecipitated. As may be anticipated from this experiment, sodium carbonate precipitates the hydroxide from antimonious chloride solution, the precipitate being insoluble in excess of the reagent.¹ Ammonia gives the same precipitate.

§ 125. Antimonious Salts.

Antimonious chloride, SbCl_3 , is a colourless crystalline solid of low melting-point. It is soluble in hydrochloric acid, but is at once hydrolyzed by water, forming an insoluble basic chloride, antimonyl chloride, SbOCl .



When antimonyl chloride is heated with much water, complete hydrolysis takes place with separation of oxide:

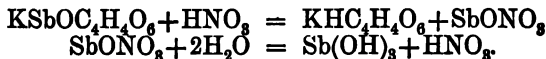


Heat antimonious oxide with potassium hydrogen tartrate and water, and filter. From the filtrate, crystals of potassium antimonyl tartrate—tartar emetic— $2[\text{K}, \text{SbO}, \text{C}_4\text{H}_4\text{O}_6] + \text{H}_2\text{O}$, separate on cooling.³ These dissolve in water without decomposition.

Show that antimonyl chloride, formed by adding a little water to antimonious chloride, is soluble in potassium hydrogen tartrate solution.⁴

Other antimonious salts are very unstable.

Add dilute nitric acid to a solution of tartar emetic: a white precipitate of antimonious hydroxide is formed, owing to the formation and hydrolysis of antimonyl nitrate.



¹ These reactions show that $\text{Sb}(\text{OH})_3$ is a weaker acid than $\text{As}(\text{OH})_3$.

² Thus Sb_2O_3 is shown to be less basic than Bi_2O_3 , for BiOCl is not affected by boiling water.

³ Antimonious oxide is also soluble in tartaric acid or Rochelle salt ($\text{KNaC}_4\text{H}_4\text{O}_6$) solution. The latter is added when antimonious compounds are titrated with iodine, to prevent precipitation of oxide by NaHCO_3 , which is used to neutralize HI formed in the reaction.

⁴ SbOCl is thus distinguished from BiOCl .

§ 126. Antimonious compounds in solution are easily *oxidized* to the antimonie state:

(i) *By iodine*.—Add a solution of iodine in potassium iodide to a solution of tartar emetic containing sodium bicarbonate; the iodine will be decolorized, alkali antimonate being formed. This reaction is reversed in acid solution, antimonie compounds in presence of acid liberating iodine from hydriodic acid.

(ii) *By silver oxide*.—Add sodium hydroxide to antimonious chloride solution until the precipitate first formed is redissolved; then add silver nitrate solution. Metallic silver is precipitated together with silver oxide, and the antimonite oxidized to antimonate.

ARSENIC AND ANTIMONIC COMPOUNDS

§ 127. It will suffice to study the reactions of arsenates and antimonates.

Silver nitrate gives with a nearly neutral solution of an arsenate, e.g. Na_2HAsO_4 , a chocolate-coloured precipitate of silver arsenate, Ag_3AsO_4 , soluble in ammonia and dilute nitric acid.¹

With a similar solution of an antimonate—potassium antimonate should be used—silver nitrate gives a white precipitate of Ag_3SbO_4 , also soluble in ammonia and nitric acid.

Magnesium sulphate added after ammonium chloride and ammonia gives with an arsenate a white crystalline precipitate of magnesium ammonium arsenate, $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$; with an antimonate no precipitate is formed.

IRON GROUP

Aluminium, Chromium, Ferrous and Ferric Iron

§ 128. Salts of aluminium are colourless or white; those of chromium deep purple or green; ferrous salts are generally

¹ Arsenite and arsenate, antimonite and antimonate, are distinguished by their reactions with silver nitrate.

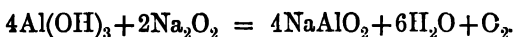
pale green, and white when anhydrous; ferric salts are yellow or brown.

These metals are separated from solution analytically as insoluble hydroxides, by precipitation with ammonia. Ferrous hydroxide, however, is imperfectly precipitated by ammonia in presence of ammonium chloride; ferrous iron is therefore always oxidized to the ferric state by nitric acid previous to precipitation.

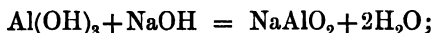
§ 129. **Hydroxides.**—Add ammonium chloride, and ammonia just in excess, to solutions of aluminium sulphate,¹ chromic sulphate,² and ferric chloride respectively. Heat to boiling, filter and wash the precipitates separately, and use them moist for the following tests.

ACTION OF SODIUM PEROXIDE ON THE HYDROXIDES IN PRESENCE OF WATER

§ 130. **Aluminium hydroxide** suspended in water is dissolved by sodium peroxide (Caution: add in portions) with evolution of oxygen, sodium aluminate being formed in solution:



Sodium hydroxide reacts similarly, thus:—



but is likely itself to contain traces of alumina.³

Add to the sodium aluminate solution hydrochloric acid little by little; the hydroxide is reprecipitated, dissolved again when more hydrochloric acid is added, and repre-

¹ Solution of alum, *i.e.* aluminium potassium (or ammonium) sulphate, may be used.

² Use chrome alum. The colour of the precipitate varies from dull green to bluish grey according to the amount of ammonia used, and a violet filtrate is sometimes obtained. The cause of this will be explained later (§ 139).

³ Sodium peroxide may not be perfectly free from alumina. A reagent certainly free from alumina may be obtained by acting on water with clean sodium in a nickel or silver dish, and then adding hydrogen peroxide to this solution.

cipitated by ammonia. Ammonium chloride causes permanent reprecipitation.¹ (For tests for $\text{Al}(\text{OH})_3$, see § 476.)

§ 131. **Chromic hydroxide** is readily converted into chromate by sodium peroxide and water, the reaction being,

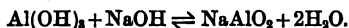


When the yellow solution thus obtained is acidified² with acetic acid, it gives with lead acetate a bright-yellow precipitate of lead chromate.

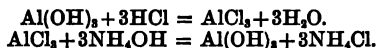
§ 132. **Ferric hydroxide** is unaffected when boiled with water and sodium peroxide. After being filtered and washed free from alkali, the precipitate may be dissolved in a little boiling dilute hydrochloric acid. The solution of ferric chloride thus obtained gives a deep-blue precipitate of Prussian blue with potassium ferrocyanide.³

It will be seen from the above reactions that the separate identification of aluminium, chromic and ferric compounds, when mixed in solution, may be very easily carried out. If, however, manganese is present in the original solution, some of it is likely to occur in the iron precipitate as hydrated manganese oxide. It may be detected in the following way.

¹ The aluminates, as salts of a weak acid, are readily hydrolyzed, but are stabilized by excess alkali (cf. stannates). The reaction is thus reversible.



Removal of alkali by adding acid helps hydrolysis, and the reaction proceeds to the left, first forming $\text{Al}(\text{OH})_3$, which dissolves in more acid, but is reprecipitated by ammonia,



Ammonium chloride removes hydroxyl ion by forming weakly dissociated ammonium hydroxide, which decomposes with evolution of ammonia; hence $\text{Al}(\text{OH})_3$ is again precipitated. These reactions show that $\text{Al}(\text{OH})_3$ is both a feeble base and a feeble acid; it is *amphoteric*. Aluminium hydroxide is soluble in a large excess of ammonia solution, probably because it assumes the colloidal state.

² Care must be taken that excess of peroxide is decomposed by boiling before the solution is acidified, or reduction to chromic salt may again take place by means of the liberated H_2O_2 .

³ This reaction will be studied later, § 161.

§ 133. **Detection of Manganese.**¹—A small amount of a manganese compound can be converted into permanganate, showing a crimson colour, in either of the following ways:—

- (a) Add to a little solution or precipitate lead peroxide and concentrated nitric acid, boil, and then dilute with water. Let stand to see colour.
- (b) Add sodium bismuthate and dilute nitric acid, shake without heating and let stand.
- (c) Add a very little copper sulphate solution, sodium hydroxide and bromine water, and boil. Thus permanganate is formed in alkaline solution by cupric catalysis.

The table of separation for the iron group now follows:—

§ 134. IRON GROUP

Wash the precipitate ² obtained by ammonia added after ammonium chloride, suspend it in water; add a little solid sodium peroxide, boil till oxygen ceases to be evolved, dilute and filter.			
Residue. ³ —Wash thoroughly, and examine by (i) and (ii).		Filtrate. —If yellow, shows the presence of Cr. In this case divide into two parts.	
(i) Test part by (a), (b), or (c) above. Crimson colour shows Mn .	(ii) dissolve rest of precipitate by boiling with dilute HCl, and add $K_4Fe(CN)_6$. Deep-blue precipitate proves Fe .	(i) Add to one half acetic acid in excess and lead acetate. Yellow precipitate proves Cr .	(ii) Add to the other half—or, if Cr is absent, to the whole—HCl in excess, then ammonia just in excess, and let stand. White gelatinous precipitate proves Al .
Test for Fe^{++} and Fe^{+++} in original solution by $K_4Fe(CN)_6$ and KONS respectively. See § 165.			

¹ It was pointed out in the general part, § 44, that if manganese is present, a little is liable to be precipitated with the iron.

² Small amounts of the other metals of the zinc group, besides manganese, are liable to occur in the iron group precipitate. They may be partially removed, if necessary, by dissolving this precipitate in dilute hydrochloric acid, and reprecipitating with ammonia, added after ammonium chloride. Their presence will not, however, interfere with the detection of Al, Cr, or Fe; nor will they on this account be missed in the next group, because their precipitation here is only partial. But Na_2O_2 will convert Co compounds into the insoluble black oxide, Co_3O_4 , which will darken the colour of any $Fe(OH)_3$ present.

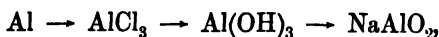
³ When this table of separation is being used for the phosphate precipitate (§ 43) this residue is rejected, and iron is tested for in the original solution.

SUPPLEMENTARY REACTIONS

ALUMINIUM

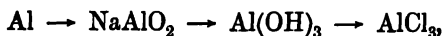
§ 135. The amphoteric property of aluminium hydroxide has already been illustrated by its solubility both in acids and alkalis, forming respectively aluminium salts and aluminates.¹ The metal itself dissolves both in acids and in alkalis, owing to the same cause.

Boil aluminium foil with hydrochloric acid, and then gradually add sodium hydroxide to the solution obtained; the following changes take place:—



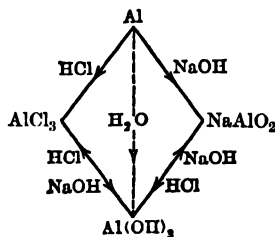
the precipitated hydroxide dissolving in excess of the alkali.

Now boil some of the foil with sodium hydroxide, and add dilute hydrochloric acid little by little to the solution; the following are the changes:—



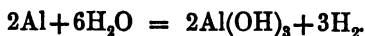
the alumina precipitated by the acid from sodium aluminate, dissolving in excess of acid.

The two sets of reactions may be represented diagrammatically as follows:—



The reaction intermediate between those of acids and of alkalis upon aluminium may be realized as follows:—

§ 136. Rub some mercuric chloride solution on a strip of aluminium foil, so as to form an amalgam, and then leave this in moist air. After a short time a crust of Al(OH)_3 will be formed by the action of water vapour on the finely divided aluminium.



¹ Lead, chromic, stannous, antimonious and perhaps zinc hydroxides are also amphoteric.

Precipitation of aluminium hydroxide by alkalis is prevented by the presence of tartrates and other hydroxy-acids in solution, as well as by polyhydric alcohols. This is due to the formation by aluminium of complex acidic ions with these compounds.

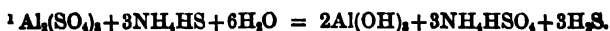
In this respect aluminium resembles ferric iron and copper.

§ 137. The feebly basic properties of alumina are shown by the *hydrolysis* of its salts, and are illustrated by the following experiments:—

- (a) Test a solution of alum with litmus, and by immersing a strip of magnesium ribbon in it. The litmus is reddened, and the magnesium causes the evolution of hydrogen. Therefore free acid is present, this being due to the incipient hydrolysis of aluminium sulphate.
- (b) Dissolve some aluminium chloride in water, and evaporate the solution to dryness. An insoluble residue of hydrated oxide will be obtained, the chloride being completely hydrolyzed.
- (c) Add ammonium acetate to alum solution, dilute well, and boil; insoluble basic aluminium acetate is precipitated.
- (d) Add ammonium sulphide to alum solution; the precipitate obtained is not aluminium sulphide but hydroxide, the former not being produced in presence of water.¹

Similarly, sodium carbonate precipitates the hydroxide, not the carbonate, because alumina does not form a salt with so weak an acid as carbonic acid.

§ 138. Aluminium phosphate, AlPO_4 , is formed as a white precipitate when sodium phosphate is added to alum solution; it is sparingly soluble in cold dilute acetic acid, and easily soluble in mineral acids. From the cold acetic acid solution, precipitation, probably of a mixture of phosphate and basic acetate, takes place on boiling.



CHROMIUM

§ 139. Hydroxide.—When chromic hydroxide, $\text{Cr}(\text{OH})_3$, is precipitated by adding sodium or potassium hydroxide to a chromic salt solution, the precipitate dissolves in excess of the reagent, producing a green solution of alkali chromite, MCrO_2 . This solution is decomposed by ammonium chloride, which hastens the hydrolysis of the alkali chromite.¹ On diluting and boiling the green solution, chromic hydroxide is reprecipitated, but in a partially dehydrated form.

Chromic hydroxide is slightly soluble in ammonia, like aluminium hydroxide, but from an entirely different cause.

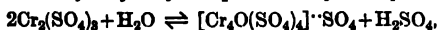
Add ammonia solution drop by drop, and with shaking, to a little dilute chromium sulphate solution. The precipitate, which is at first greyish green, gradually assumes a violet tinge, and eventually dissolves, forming a pale violet-coloured solution.² This solution contains, not ammonium chromite, but an ammoniacal chromium base or ammine of the composition $\text{Cr}(\text{NH}_3)_6(\text{OH})_3$. This compound is decomposed on boiling the solution, $\text{Cr}(\text{OH})_3$ being reprecipitated.

§ 140. Chromic Salts.—Chromic alum, $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, is the best known of these salts. It occurs in deep plum-coloured octahedra, which when heated to 100° turn green; it dissolves in cold water, forming a plum-coloured solution, which also becomes green when heated.³

¹ Cf. aluminate, § 130. Salts formed by combination between the oxide Cr_2O_3 and bases are called chromites, the name chromate being appropriated by derivatives of the oxide CrO_3 .

² Solution is promoted by gently warming the liquid. If the precipitate does not completely dissolve, the liquid may be filtered in order to render the violet colour more apparent.

³ The change in colour of the solid salt is due to the formation of potassium chromisulphate $\text{K}_2[\text{Cr}_2(\text{SO}_4)_4]$, in which the metal enters the acidic complex; that of the solution is caused by a hydrolysis represented by the equation:



the complex product being sulphochromyl sulphate. For a further account of these and other interesting chromic compounds the student should consult the theoretical textbooks.

§ 141. **Chromic phosphate**, CrPO_4 , is a dull-green precipitate, soluble in mineral acids and cold dilute acetic acid. Complete reprecipitation occurs on boiling the acetic acid solution.

§ 142. **Instability of Chromic Salts.**—Chromic oxide is not sufficiently basic to form stable salts with weak acids.

Add (a) ammonium sulphide, (b) sodium carbonate, to chromic sulphate solution. In each case the precipitate consists of chromic hydroxide, chromium sulphide not being formed in presence of water, and the carbonate being unknown.

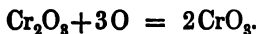
§ 143. **Oxidation of Chromic Compounds.**—Chromic compounds are oxidized to chromates (i) in the dry way, and (ii) in solution.

(i) *Dry way.*—Mix a little powdered chrome alum with sodium carbonate and a very little potassium nitrate,¹ and fuse the mixture before the blowpipe on platinum foil, or in a porcelain crucible. A yellow mass of sodium chromate is formed.²

(ii) *In solution.*—In addition to sodium peroxide, which has already been used (§ 131), oxidation may be effected in solution—

- (1) By chlorine or bromine water in presence of alkali.
- (2) By lead peroxide in presence of alkali.
- (3) By manganese dioxide in presence of alkali.
- (4) By potassium chlorate in presence of strong nitric acid.

In all these reactions the change is essentially that of derivatives of chromic oxide to those of the trioxide:



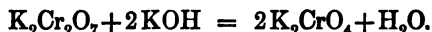
§ 144. **Action of Acids on Chromates.**—Chromates in solution are converted by acids into dichromates, the colour changing from yellow to orange-red, thus:—



¹ The addition of nitrate as oxidizing agent is not essential, since in presence of alkali atmospheric oxygen suffices, as in the commercial process.

² For analytical purposes this somewhat inconvenient process is now generally replaced by oxidation in solution by Na_2O_2 .

The change is reversed by alkalis:



§ 145. **Reduction of Dichromates.**—Dichromates are reduced in acid solution:¹

- (1) By hydrogen sulphide, which is oxidized to sulphur and water.
- (2) By sulphur dioxide or sulphurous acid, which is oxidized to sulphuric acid.
- (3) By hydrochloric, hydrobromic, and hydriodic acids, with liberation of halogen.
- (4) By ferrous sulphate, which is oxidized to ferric salt.
- (5) By alcohol, $\text{C}_2\text{H}_5\text{O}$, which is oxidized to aldehyde, $\text{C}_2\text{H}_4\text{O}^2$.

All the above reactions are easily carried out. The most convenient way, however, of reducing a chromate for analysis is by boiling it with concentrated hydrochloric acid until chlorine ceases to be evolved. The precipitation of sulphur when H_2S gas is passed through the solution is thus avoided, and also the formation of sulphuric acid, which takes place if SO_2 is used for reduction, and which, in presence of alkaline earth metals, would form insoluble precipitates.

§ 146. **Metallic Chromates.**

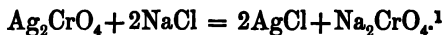
Silver chromate, Ag_2CrO_4 , is formed as a dark-red precipitate when potassium chromate is added to silver nitrate solution. It is soluble in dilute nitric acid, and is more soluble in water than silver chloride, so that it is decomposed in the following way when a solution of a chloride is added to it:—

¹ The reason why oxidation generally takes place in alkaline and reduction in acid solution is that acidic and basic oxides of chromium are produced respectively in the two cases, which the alkali or acid present can combine with and render stable.

² This reaction is represented by the following equation:—



The student should construct the remaining equations, the key to them all being: $2\text{CrO}_3 = \text{Cr}_2\text{O}_3 + 3\text{O}$.



Lead chromate, PbCrO_4 , is a yellow salt, very insoluble in water, so that it is precipitated from the most dilute solutions. Its formation, therefore, constitutes a delicate test for lead or chromate. This precipitate is soluble in mineral acids, but not in acetic acid (cf. § 49).

Barium chromate, BaCrO_4 , resembles lead chromate in being insoluble in acetic acid, though its colour is a paler yellow. Its formation enables barium compounds to be separated from those of strontium and calcium (§ 202).

§ 147. **Chromates and Hydrogen Peroxide.**—When hydrogen or sodium peroxide is added to acidified chromate solution an evanescent deep-blue colour is produced. The compound thus formed is soluble, and more stable, in ether, so that on adding ether and shaking the liquid a deep-blue ethereal layer separates.

The substance² in ethereal solution is a peroxide, CrO_5 . If the blue aqueous solution is heated it turns green owing to reduction to chromic salt.

IRON

§ 148. **Formation of Metal.**—Iron is too electropositive a metal to be easily separated from solutions of its salts, but it may be obtained in the dry way in the form of metallic particles, which are magnetic, by heating one of its compounds, mixed with sodium carbonate and potassium cyanide, on charcoal before the blowpipe.

§ 149. **Borax Bead Test.**—When a particle of an iron compound, *e.g.* ferrous sulphate, is fused into a borax bead, the bead is coloured yellow or brown when hot, and yellow when cold, in the outer blowpipe flame, and bottle green in the inner flame (see under Borax Bead Reactions, § 10).

¹ This reaction is used in volumetric analysis, K_2CrO_4 being employed as an indicator of the presence of excess of silver when a neutral chloride solution is titrated with silver nitrate.

² It was formerly thought that the blue colour was due to a perchromic acid having the composition HCrO_5 . Perchromates such as $\text{K}_2\text{Cr}_2\text{O}_{12}$, $2\text{H}_2\text{O}$ and $\text{K}_6\text{Cr}_2\text{O}_{16}$ are, however, known; the former is blue, the latter red. Chromium is hexavalent in these compounds, and in CrO_5 , as required by the periodic system.

FERROUS COMPOUNDS

§ 150. Hydroxide.—Ferrous hydroxide, $\text{Fe}(\text{OH})_2$, is white, but is only obtained pure when air is rigidly excluded during its precipitation. As ordinarily produced by adding alkali hydroxide to ferrous sulphate solution it is a dull-green¹ precipitate which turns rust colour superficially when oxidized by the air.

The precipitation of ferrous hydroxide by ammonia is prevented by ammonium chloride.

To show this, place a little fine iron wire in dilute hydrochloric acid, and before all the wire has dissolved add much ammonium chloride solution, and then ammonia just in excess. At most an opalescence will be produced, but no precipitate. If little or no ammonium chloride is present ammonia will give the dull-green precipitate of slightly oxidized ferrous hydroxide.

§ 151. Ferrous salts are generally green when hydrated, and white when anhydrous. They form pale-green solutions when soluble in water, and readily undergo oxidation to the ferric state by atmospheric oxygen and other oxidizing agents.

§ 152. Ferrous sulphate, or green vitriol, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, when dissolved in air-free water, forms a clear light-green solution with a neutral reaction. When this solution stands in the air it gradually becomes turbid, and at the same time develops acidity. This is due to oxidation, with formation of basic ferric sulphate,² which is then hydrolyzed so that free acid is produced. Ferrous salts, when dissolved in water, are often found to contain some ferric compound, if from no other cause than that of the air dissolved in the water. On this account their solutions generally show more or less of a red colour on the addition of potassium sulphocyanide, which is a delicate reagent for ferric salts (see later, § 164).

§ 153. Ferrous sulphide, FeS , is formed as a black precipitate when ammonium sulphide is added to a solution of a ferrous salt, or when hydrogen sulphide is passed through an alkaline liquid containing ferrous iron.

¹ This colour is due to the formation of a dark-coloured compound of ferrous and ferric hydroxides, i.e. hydrated Fe_3O_4 .

² $2\text{FeSO}_4 + \text{O} = \text{Fe}_2\text{O}(\text{SO}_4)_2$

It is also precipitated, together with sulphur, from a solution of a ferric salt, by an alkaline sulphide solution, when the ferric salt is in excess.¹ Ferrous sulphide is easily soluble in dilute mineral acids, and sparingly soluble in acetic acid. When it has been precipitated from a ferric salt, sulphur remains after its solution in acid.

§ 154. **Ferrous Carbonate, FeCO_3 .**—Add a solution of sodium bicarbonate—made by dissolving the salt in cold water—to one of ferrous sulphate. No precipitate is formed immediately because ferrous bicarbonate is soluble in water.²

A dingy-white precipitate of ferrous carbonate soon separates, however, and this turns dark green, and then rust coloured on the surface, with escape of carbon dioxide gas, when warmed or allowed to stand in the air, ferric hydroxide eventually being formed.

§ 155. **Ferrous potassium oxalate, $\text{K}_2\text{Fe}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$.**—Add potassium oxalate to ferrous sulphate solution. The liquid turns yellow, and a yellow crystalline precipitate, having the above composition, separates.³

§ 156. **Oxidation of Ferrous Salts.**—Ferrous salts can be easily and completely oxidized to the ferric state in acid solution.⁴ Nitric acid is a convenient oxidizing agent, because its reduction products leave the solution on boiling. Add a few drops of concentrated nitric acid to ferrous sulphate solution. The solution becomes dark brown,⁵ and, on boiling, brown nitrous fumes leave the liquid. A yellow solution remains which contains a mixture of ferric sulphate and nitrate.

¹ Whilst excess of iron causes Fe_2S_3 to decompose into $2\text{FeS} + \text{S}$, excess of alkali causes Fe_2S_3 to be stable.

² This compound is present in the water of chalybeate springs, which deposit ferric hydroxide on exposure to air.

³ Since the ferrous ion is pale green, the solution probably owes its characteristic yellow colour to the formation of the complex ion, $[\text{Fe}(\text{C}_2\text{O}_4)_2]$. The above salt is used in photography as the "oxalate developer".

⁴ *E.g.* by the halogens, peroxides, and potassium dichromate or permanganate, as in the well-known volumetric processes.

⁵ See under Nitric Acid, § 361.

FERRIC COMPOUNDS

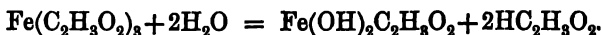
§ 157. **Ferric hydroxide**, $\text{Fe}(\text{OH})_3$, is formed as a reddish-brown precipitate, easily soluble in dilute acids, when ammonium or other alkali hydroxide is added to ferric chloride solution; its precipitation is independent of the presence of ammonium chloride. Ferric chloride solution added in excess dissolves a little ferric hydroxide, forming a brown solution of basic chloride.¹

The precipitation of ferric hydroxide by ammonia is prevented by the presence of tartrates, sugars, and other organic compounds containing hydroxyl groups.²

§ 158. **Ferric chloride**, FeCl_3 , is almost black when anhydrous and yellow when hydrated ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). The anhydrous salt is volatile, and is soluble in alcohol and ether as well as in water. Its aqueous solution is bright yellow, so that if hydrochloric acid is added in excess to a pale-coloured solution of another ferric salt, *e.g.* $\text{Fe}_2(\text{SO}_4)_3$, the solution turns yellow.

Ferric salts are readily hydrolyzed by water.³ If a crystal of ferric alum, $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, which is pale violet, is dissolved in water, a brown solution containing basic ferric salt, together with free sulphuric acid, is produced; and if this solution is poured into excess of boiling water complete hydrolysis takes place with precipitation of ferric hydroxide.

§ 159. **Ferric acetate** is formed in solution as a red substance when ammonium acetate is added to ferric chloride solution. On boiling, an insoluble basic acetate is formed by hydrolysis, and precipitated:



§ 160. **Ferric phosphate**, FePO_4 , is precipitated as a cream-coloured powder when sodium phosphate is added to ferric chloride solution. It is insoluble in acetic acid, but easily soluble in dilute mineral acids.

¹ If this solution is dialysed, soluble salts are removed, and colloidal ferric hydroxide or "dialysed iron" remains.

² Compare alumina.

³ More so than ferrous salts, because ferric oxide is less basic than ferrous oxide.

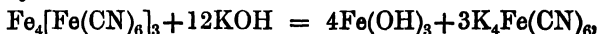
Ferric sulphide, as seen above, is precipitated from ferric solution by alkali sulphide when excess of alkali is present.

COMPLEX CYANIDES CONTAINING IRON

§ 161. **Formation and Reactions of Potassium Ferrocyanide**, $K_4Fe(CN)_6$.—Add potassium cyanide¹ to ferrous sulphate solution. A red precipitate is formed which probably contains ferrous cyanide, and which, on the addition of considerable excess of potassium cyanide and boiling, turns brown and dissolves almost completely. On filtering, a clear yellow solution of potassium ferrocyanide, $K_4Fe(CN)_6$, is obtained² which, after being acidified with dilute HCl, gives with ferric chloride a deep-blue precipitate of insoluble Prussian blue, ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, and with ferrous sulphate a white precipitate³ of ferrous ferrocyanide, $Fe_2[Fe(CN)_6]$.

If a drop of very dilute ferric chloride solution is added to excess of the acidified ferrocyanide solution a clear-blue solution of soluble Prussian blue, $FeK[Fe(CN)_6]$, is produced.

Prussian blue is insoluble in acids, but is at once decomposed by alkalis as follows:—



brown ferric hydroxide separating.

§ 162. **Formation of Potassium Ferricyanide**, $K_3Fe(CN)_6$.—Add to some of the ferrocyanide solution obtained above, chlorine or bromine water in excess; then boil off the excess of halogen, and add ferric chloride to some of the solution. No blue colour or precipitate is formed because the ferrocyanide has been oxidized to ferricyanide,⁴ and ferric ferricyanide is not a blue substance. Ferrous sulphate, however, gives a deep-blue precipitate with the ferricyanide solution.⁵

¹ The KCN solution employed must be made from the nearly pure salt, and not contain much KOH.

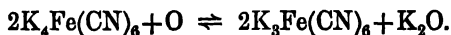
² If a little concentrated sulphuric acid is added to this solution, solid hydroferrocyanic acid, $H_4Fe(CN)_6$, separates.

³ Unless air is quite excluded, this precipitate is always pale blue, owing to admixture with Prussian blue formed by oxidation.

⁴ $K_4[Fe(CN)_6]''' + Cl = K_3[Fe(CN)_6]''' + KCl$.

⁵ This precipitate, which was originally called "Turnbull's blue", is found, after washing, to be identical with insoluble Prussian blue.

§ 163. **Reduction of Ferricyanide.**—Add to a little potassium ferricyanide solution, some sodium hydroxide and a few drops sulphurous acid or sodium sulphite solution and boil; the colour of the liquid becomes paler. Now acidify with hydrochloric acid and add ferric chloride; a deep-blue precipitate is formed showing the presence of ferrocyanide, formed from ferricyanide by reduction.¹ Thus a reversible reaction takes place between ferro and ferricyanide in the sense of the equation:



§ 164. **Sulphocyanides of Iron.**—Add solution of *potassium sulphocyanide* (thiocyanate) to *ferrous sulphate* solution. No precipitate or colour is produced if the solution is free from ferric salt, a trace of which causes a pink colour to be formed.

With *ferric chloride* sulphocyanide solution gives a deep blood-red colour. This is a delicate test for ferric salts; the colour is discharged by mercuric chloride,² alkali acetate, and some other substances.

Most of the above reactions with complex cyanides are employed in analysis for the identification of ferrous and ferric ions in solution. The tests are here tabulated.

§ 165.

	Ferrous.	Ferric.
Potassium ferrocyanide..	white or pale-blue precipitate.	deep-blue precipitate (Prussian blue).
Potassium ferricyanide...	deep-blue precipitate (Turnbull's blue).	no precipitate; solution becomes brown.
Potassium sulphocyanide	no colour in absence of ferric salts.	blood-red colour, discharged by $HgCl_2$.

¹ Potassium ferricyanide in alkaline solution is employed as a mild oxidizing agent.

² Owing to the formation of a double mercuric salt $Hg(CNS)_2 \cdot HgCl_2$ which is colourless.

ZINC GROUP

§ 166. Zinc, Manganese, Cobalt, and Nickel

Zinc salts are colourless or white, and form colourless solutions.

Manganous salts are pink in the solid, hydrated condition, and give pale-pink or practically colourless solutions.

Cobaltous salts are generally rose red or crimson in the solid state, and give pink solutions. When anhydrous they are commonly blue,¹ but may be green or brown.

Nickel salts are bright green in the hydrated solid state and in solution. When anhydrous they are yellow.

The colours of nickel and cobalt salts in solution are complementary, and it is possible to mix their solutions in such proportions that an almost colourless liquid results.

§ 167. Action of Ammonia.—Add dilute ammonia to solutions of zinc, manganese, cobalt, and nickel salts,² and observe the following facts.

From *zinc* solutions ammonia precipitates the white hydroxide, $\text{Zn}(\text{OH})_2$, easily soluble in excess of the reagent. This is due to the formation of an ammonia compound or "ammine"; *e.g.* with zinc sulphate the substance $\text{Zn}(\text{NH}_3)_4\text{SO}_4$ is produced in solution.³

From *manganous* solutions there is a precipitation of the white hydroxide, $\text{Mn}(\text{OH})_2$. This compound is insoluble in excess of ammonia, but soon darkens on exposure to air, being oxidized to manganic hydroxide, $\text{MnO}\cdot\text{OH}$.

¹ When cobaltous chloride is dissolved in alcohol or concentrated HCl, the deep-blue colour of the anhydrous salt appears, especially on heating; on addition of water the solutions turn pink on account of hydration. In HCl solution the colour change depends in part on the formation of the anions CoCl_3^- and CoCl_4^{--} , which are decomposed by water to give the hydrated cobaltous cation. Cupric chloride in HCl behaves similarly. An aqueous solution of cobalt chloride is employed as "sympathetic ink", because when dehydrated by heat the salt turns blue, and characters previously faint become plainly visible.

² ZnSO_4 , MnSO_4 , $\text{Co}(\text{NO}_3)_2$, and NiSO_4 are the most convenient salts to employ.

³ Compare reactions of Cu, Cr, Co⁺⁺⁺, and Ni salts with ammonia.

Cobaltous salts yield with ammonia a precipitate of a greenish-blue basic salt. This precipitate does not dissolve in excess of ammonia alone, but on standing gradually absorbs oxygen, and dissolves, forming a brown solution, which contains a cobaltic ammine (see later).

Nickelous salts give a green precipitate of basic salt, which dissolves in excess of ammonia, forming a blue nickelous "ammine", as, for instance, $\text{Ni}(\text{NH}_3)_4\text{SO}_4$.

Thus zinc and nickelous salts give precipitates easily dissolved by excess of ammonia; the precipitate with cobalt salts dissolves owing to atmospheric oxidation, and the manganese precipitate darkens, without dissolving, when exposed to the air.

§ 168. Influence of Ammonium Chloride.—Repeat the above experiments, adding some ammonium chloride solution before ammonia. No precipitate is formed in any case, though with manganese the solution gradually darkens and becomes turbid, eventually yielding a brown precipitate of $\text{MnO}\cdot\text{OH}$.

Thus it appears that with the exception of small quantities of manganese—which are provided for in the table of separation—none of the above four metals should be precipitated with the iron group, provided sufficient ammonium chloride is added before ammonia.¹ The reason ammonium chloride prevents the precipitation of the metals of this group by ammonia is that its presence so diminishes the hydroxyl ion content of the solution that the solubility product values for the hydroxides are not attained.²

§ 169. Properties of the Sulphides of Zinc, Manganese, Cobalt, and Nickel.—Add yellow ammonium polysulphide to solutions of salts of these four metals, to which ammonium chloride and ammonia have been added; or pass hydrogen sulphide through the same solutions. At once attempt to filter off the

¹ Assuming phosphates, &c., to be absent. Small amounts of these metals are, however, sometimes precipitated with the metals of the iron group.

In this case solution of the precipitate in hydrochloric acid, and reprecipitation by ammonia, added after ammonium chloride, are necessary.

² See § 35, and note 1, § 44 (p. 59).

precipitates from the cold liquids. The *white zinc sulphide* and *black cobalt sulphide* are readily separated by filtration; *manganese sulphide*, which on the filter is seen to be *flesh-coloured*, tends to run through the paper, because it is so finely divided,¹ and the *black nickel sulphide* gives a dark-brown filtrate, which contains some nickel in solution.

The dark-coloured filtrate obtained in the latter case, when nickel sulphide is precipitated by polysulphide in presence of ammonia, constitutes a delicate test for nickel, and probably contains the sulphide of a nickel "ammine" [see note (§44), p. 61]. Boil the liquid and precipitate thus obtained till no ammonia can be smelt, then filter. A clear colourless filtrate will result.

Boil the liquid containing the manganese sulphide precipitate for some time and filter; a clear colourless filtrate will be obtained.

When, therefore, yellow ammonium sulphide, used as the group reagent, produces a black precipitate, it should be added in portions, and a few drops of the filtrate should be tested after each addition for completeness of precipitation. If nickel is present, the necessary slight excess of reagent causes a brown filtrate. Boil the liquid and precipitate in an open dish till no more ammonia is evolved. On filtering, a clear colourless filtrate will be obtained.

It must be remembered that these precipitated sulphides will always contain free sulphur derived from the polysulphide used for precipitation.

§ 170. Solubilities of the Sulphides, ZnS, MnS, CoS, NiS.—Obtain precipitates of these four sulphides, and filter and thoroughly wash them. Digest a little of each separately with very dilute hydrochloric acid.² The sulphides of zinc and manganese will dissolve, leaving probably a little white sul-

¹ Filtration of fine precipitates is often aided by filter pulp, *i.e.* shredded filter paper boiled with concentrated HCl, filtered off, and washed; this is added to the liquid to be filtered.

² One volume of dilute acid mixed with about five volumes of water.

phur, which makes the solution turbid.¹ Cobalt and nickel sulphides will, however, appear to be quite insoluble in dilute hydrochloric acid.² Therefore a separation between zinc and manganese, on the one hand, and cobalt and nickel on the other, can be effected by means of this dilute acid.

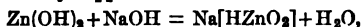
§ 171. Separation and Identification of Zinc and Manganese.—Add sodium hydroxide to solution of zinc sulphate; a white precipitate is produced which dissolves in excess of alkali.³ Pass H_2S through this solution; white zinc sulphide is precipitated. Filter off this precipitate, remove it from the filter by a spatula to a dish, and dissolve it in a very little concentrated HNO_3 . Add two or three drops of $Co(NO_3)_2$ solution; fold a filter paper several times, soak it in the solution, and burn it completely on a coil of platinum wire in the blowpipe flame. The ash will be tinted bright green by "Rinnmann's green", a compound of ZnO and CoO .

Add sodium hydroxide to a solution of manganese sulphate; a white precipitate is formed which is insoluble in excess of the precipitant, but soon begins to turn brown on

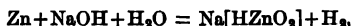
¹ The solutions may be made quite clear by adding a crystal of $KClO_3$ and boiling; by this means the sulphur is oxidized to sulphuric acid.

² Traces of these sulphides are generally, however, dissolved by the dilute acid. Since the sulphides are not precipitated in presence of dilute hydrochloric acid, and would therefore be expected to be dissolved by this reagent, the degree of their insolubility when precipitated depends upon the extent to which their molecules have undergone condensation into complex forms which are insoluble. The process of boiling which is recommended above increases the insolubility of these sulphides in dilute acid.

³ The reaction is generally supposed to be—



a solution of sodium zincate being formed. When this solution is boiled, much of the $Zn(OH)_2$ is reprecipitated, so that the salt existing in solution is unstable (cf. $Cr(OH)_3$). Owing to zinc being so electropositive, as shown by its rapid displacement of hydrogen from dilute acids, it is doubtful if $Zn(OH)_2$ possesses any acidic properties. If it does not, the reaction between Zn and $NaOH$ generally represented by the equation—



as well as the solubility of the hydroxide in $NaOH$ solution, may be attributed to $Zn(OH)_2$ passing into the colloidal state, the evolution of hydrogen in the former case being due to the action on water of the metal, unprotected by a film of oxide.

the surface. If thrown upon a filter, and thus exposed freely to the air, the whole of the precipitate soon becomes dark brown.

This brown mass may be further tested for manganese by either of the following methods:—

(i) Heat a little with concentrated HNO_3 and lead peroxide; dilute with water, and allow the undissolved peroxide to settle; or employ either of the alternative methods given in § 133. A crimson colour due to permanganic acid will be seen.

(ii) Fuse a little of the solid in a borax bead. The bead will be amethyst-coloured in the outer and colourless in the inner flame.

On account of the solubility of zinc hydroxide in excess of alkali, in which manganous hydroxide is not soluble, and by making use of the additional tests just described, it is easy to separate and identify zinc¹ and manganese.

§ 172. Solution of Cobalt and Nickel Sulphides.—Cobalt and nickel sulphides may be easily dissolved in concentrated hydrochloric acid, together with a very little potassium chlorate. The solutions of the respective chlorides should then be evaporated separately in porcelain dishes, after any necessary dilution, and filtering off undissolved sulphur.

The cobalt chloride solution, which is pink when dilute, leaves a fine blue-coloured solid ridge as it evaporates, and eventually a blue residue remains. Nickel chloride solution, which is green, leaves a yellow residue.

Now mix solutions of cobalt and nickel chloride in about equal proportions, and evaporate the mixed solution. The blue colour due to cobalt will still be seen, the nickel salt present scarcely affecting it.²

¹ Confirmatory tests for zinc will be found in § 479.

² The tinctorial effect of cobalt chloride is thus greater than that of nickel chloride. Cobalt can be detected by the formation of a greenish-blue ridge even if its proportion to nickel is not more than 1:20.

IDENTIFICATION OF COBALT AND NICKEL IN PRESENCE OF EACH OTHER

§ 173. Identification of Cobalt.—(i) To a solution of a cobalt salt add ammonium chloride and ammonia, and then some freshly prepared potassium ferricyanide solution. According to the concentration, a deep-red solution or a reddish-brown precipitate will form: heating aids precipitation.

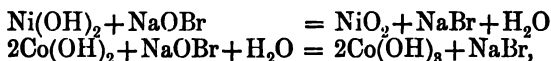
Repeat, using a nickel salt solution. A pale-yellow precipitate will probably appear on boiling.

By this test it is possible to identify cobalt (even as little as 0.001 grm.) in presence of much nickel. The test depends on the deep-red colour of cobaltous ferricyanide and its comparative insolubility in ammonia; nickelous ferricyanide is yellow and easily soluble in ammonia.

(ii) To 1 c.cm. of a cobalt salt solution add 1 grm. of solid ammonium thiocyanate, and either (a) add 1 c.cm. of acetone or alcohol, or (b) shake with 0.5 c.cm. of amyl alcohol.

In (a) a deep-blue solution of ammonium cobaltous thiocyanate forms, $(\text{NH}_4)_2[\text{Co}(\text{CNS})_4]$; in (b) this substance yields a blue amyl alcohol layer. Nickel does not interfere with the test. If ferric iron is present, either alkali fluoride or tartrate should be added to prevent the formation of red ferric thiocyanate.

§ 174. Identification of Nickel.—Add sodium hydroxide and excess of bromine water to solutions of nickel and cobalt salts; a black precipitate is obtained in each case. These precipitates of hydrated nickel dioxide, $\text{NiO}_2 \cdot x\text{H}_2\text{O}$, and cobaltic hydroxide, $\text{Co}(\text{OH})_3$, respectively, are produced by the oxidation of nickelous and cobaltous hydroxides by alkali hypobromite:



and it is noteworthy that nickel and cobalt compounds alike yield black precipitates in this oxidation.

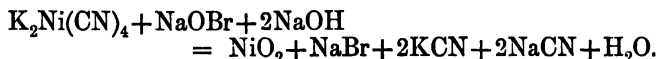
Now add dilute potassium cyanide solution drop by drop to nickel sulphate solution, till the light-green precipitate of

nickelous cyanide which is formed has just been redissolved by excess of cyanide.

Divide this solution into three parts, and perform the following experiments:—

- (i) Add dilute hydrochloric acid to the solution; pale-green nickelous cyanide is reprecipitated.
- (ii) Boil for a minute in an open dish and acidify; the same green precipitate is obtained.
- (iii) Add sodium hydroxide and bromine water in considerable quantity; a black precipitate of hydrated nickel dioxide is formed,¹ the cyanide present being ineffectual in preventing the normal action of the hypobromite.

The reason for this is that when $\text{Ni}(\text{CN})_2$ dissolves in excess of KCN it forms the unstable but complex salt, $\text{K}_2\text{Ni}(\text{CN})_4$, which is unaffected by boiling, but which is decomposed by acids or by alkali hypobromite, the nickel being oxidized by the latter reagent, thus:—



Next add potassium cyanide solution to cobalt nitrate till the buff-coloured cobaltous cyanide dissolves, forming a deep-yellow liquid. Acidify a little of this liquid; the cyanide is reprecipitated; boil the remainder of it in a dish for a minute, and observe that it becomes first brown and then lighter in colour; divide this liquid into two parts, and treat them as follows:—

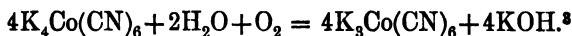
- (i) Acidify the solution; no precipitate now appears.
- (ii) Add sodium hydroxide and bromine water; no black precipitate is formed, even on heating and allowing to stand.²

¹ Warming promotes its formation. If the precipitate is filtered off and washed, it may be fused in a borax bead, when the characteristic brown nickel bead will be produced.

² Provided the cobalt solution is quite free from nickel. Most commercial samples of cobalt salts contain traces of nickel.

The reason for this different behaviour of cobalt salts is clearly seen when the reactions which take place are understood.

$\text{Co}(\text{CN})_2$ dissolves in excess of KCN , forming potassium cobaltocyanide $\text{K}_4\text{Co}(\text{CN})_6$.¹ This compound is, however, decomposed by acids, cobaltous cyanide, $\text{Co}(\text{CN})_2$ being reprecipitated. The change which takes place on boiling the solution in a dish is one of atmospheric oxidation, stable potassium cobalticyanide,² $\text{K}_3\text{Co}(\text{CN})_6$, which is not decomposed by acids or alkali hypobromite, being produced as follows:—



Thus through the agency of potassium cyanide cobalt is oxidized in solution by the air, to a stable condition, from which it is not precipitated like nickel by alkali hypobromite.⁴

The cobalt may, however, be identified by evaporating a few drops of potassium cobalticyanide solution nearly to dryness, and fusing the pasty residue in a borax bead. Even a trace of cobalt will show the fine blue colour.

By employing the reactions studied in the preceding paragraphs, the table of separation for the metals of the zinc group may be constructed as follows.

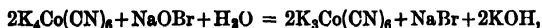
Additional reactions of zinc, cobalt and nickel, which may be used in the group separation, will be found in §§ 479, 480, 481.

¹ Analogous to the ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$.

² Analogous to potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$.

³ In the absence of air, oxidation may still take place at the expense of the water or HCN , hydrogen being evolved.

⁴ The oxidation of the cobaltocyanide may be effected by the hypobromite itself—



but it is better to employ atmospheric oxidation, so that the bromine added may at once be available to oxidize nickel if it is present.

§ 175.

ZINC GROUP

The precipitate may contain ZnS , MnS , CoS , and NiS ,¹ together with finely divided sulphur. Wash² thoroughly, digest with cold, very dilute³ HCl , and filter.

Filtrate.—Boil off H_2S , and if the liquid is turbid add a fragment of $KClO_3$ and boil till clear. Cool, add $NaOH$ in moderate excess and filter cold.

Filtrate.—

(i) Examine for **Zn** by methods in § 479. Or

(ii) Pass H_2S —white precipitate, which may be discoloured, shows **Zn**.

To confirm, filter and dissolve precipitate in a drop of concentrated HNO_3 ; add a drop of $Co(NO_3)_2$ solution, soak a folded filter paper in solution, and ignite in coil of platinum wire in blowpipe flame.

Green-tinted ash proves **Zn**.

Residue⁴—Turning brown on filter, shows **Mn**. Confirm by (i) or (ii).

(i) Boil a little of the precipitate with PbO_2 and concentrated HNO_3 ; dilute and let stand; or employ either of the alternative methods given in § 133.

Crimson colour proves **Mn**.

(ii) Fuse precipitate in borax bead. Amethyst bead proves **Mn**.

Residue.⁵—Heat with concentrated HCl and a fragment of $KClO_3$, and evaporate solution to dryness. Blue or bluish-green residue shows **Co**. Yellow residue shows **Ni** only present. Dissolve in water and divide into two parts.

(i) Add ammonium chloride, ammonia, and $K_3Fe(CN)_6$. Warm gently. Red colour or reddish-brown precipitate, insoluble in ammonia, shows **Co**.

Or, to 1 c.c. add potassium fluoride, 1 grm. solid NH_4CNS , and alcohol. Blue solution proves **Co**.

(ii) Add dilute KCN drop by drop till the precipitate which forms is just redissolved; boil in dish; then add $NaOH$ and bromine water and warm.

Black precipitate shows **Ni**.

Co and **Ni** may be confirmed, if necessary, as follows: add more bromine water to above, boil, and filter.

Filtrate.—Must give no more precipitate with bromine water. Evaporate a little just to dryness and fuse in borax bead. Blue bead proves **Co**.

Residue.—Wash thoroughly, and dissolve in HCl , boil, add dimethylglyoxime (§ 480) and excess ammonia. Red precipitate proves **Ni**.

¹ If CoS or NiS is present the precipitate will be black. FeS may also occur if a trace of Fe remains from a phosphate separation.

² Use 2 per cent NH_4Cl solution containing a little ammonium sulphide to diminish colloidal solubility of the sulphides.

³ 1 volume ordinary dilute HCl with 5 volumes of water.

⁴ A little $Co(OH)_2$ or $Ni(OH)_2$ may occur here.

⁵ The student may test this residue for **Co** and **Ni** by fusion in a borax bead. A trace of **Ni** in presence of much **Co** will have revealed itself by the dark-coloured filtrate originally obtained in separating this group, though not by the colour of the bead; a small amount of **Co** is sufficient to modify the colour of the **Ni** bead.

SUPPLEMENTARY REACTIONS

ZINC

Most of the reactions characteristic of zinc compounds have already been studied; the following remain.

§ 176. **Charcoal Test.**—Heat a mixture of zinc sulphate and sodium carbonate in a cavity on charcoal, before the blowpipe. The zinc oxide formed glows brightly in the flame, and appears yellow when hot and white when cold. If the mass is moistened with cobalt nitrate solution and again heated, there is formed the same green compound as was observed above (§ 171).

A white incrustation is formed on the charcoal during the heating of zinc compounds; this is due to the volatilization of zinc and the combustion of its vapour, with the deposition of oxide.

§ 177. **Zinc chloride**, ZnCl_2 , is a deliquescent salt, hydrolyzed with production of the basic salt, $\text{Zn}(\text{OH})\text{Cl}$, when its solution is evaporated. Therefore the solution reacts acid.

§ 178. **Zinc sulphate**, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, also reacts acid in solution owing to incipient hydrolysis.

§ 179 **Zinc carbonate** is formed as a white precipitate when sodium carbonate is added to zinc sulphate solution. It is probably normal, *i.e.* ZnCO_3 , when first precipitated, especially if sodium bicarbonate is used, but becomes basic on standing.

§ 180. **Zinc phosphate**, $\text{Zn}_3(\text{PO}_4)_2$, is a white precipitate easily soluble in acetic acid, and, like the hydroxide, soluble in ammonia, by which, therefore, it is not precipitated.

§ 181. **Zinc ferrocyanide**, $\text{Zn}_2\text{Fe}(\text{CN})_6$, is a pure-white precipitate, insoluble in dilute hydrochloric acid. Its production is sometimes used as a test for zinc, in the absence of iron.

§ 182. **Comparison of Zinc with Cadmium.**—Zinc and cadmium are associated together in nature, and classified together in the periodic system.

They occur in different analytical groups because of the difference in solubility of their sulphides. This difference, however, is not very great; cadmium sulphide is perceptibly soluble in dilute mineral acids, and zinc sulphide, whilst readily soluble in dilute mineral acids, is insoluble in acetic acid.

If a piece of zinc rod is placed in cadmium sulphate solution, the cadmium is precipitated as a grey powder. This shows that zinc is more electropositive than cadmium. On the other hand, metallic zinc and its hydroxide are soluble in sodium hydroxide solution,¹ in which neither cadmium nor its hydroxide dissolves; also zinc salts are more easily hydrolyzed than those of cadmium.

MANGANESE

There are six oxides of manganese, and some of these, together with the compounds to which they give rise, admit of brief practical study.

§ 183. **Manganous Oxide, Hydroxide, and Salts.**—The oxide, MnO , is unimportant, and the hydroxide, Mn(OH)_2 , has already been obtained, and its oxidation by air to brown $\text{MnO}\cdot\text{OH}$ observed.

§ 184. **Manganous salts** differ from the hydroxide, and from ferrous salts, in showing no tendency to oxidation; they give neutral solutions, and thus are not hydrolyzed.

§ 185. **Manganous phosphate** is a white precipitate, formed in presence of ammonium chloride, and easily soluble in acetic acid, but insoluble in ammonia.

§ 186. **Manganous carbonate** is also a white salt, insoluble in water and ammonium chloride solution.

§ 187. **Mangano-manganic oxide**, Mn_3O_4 , the most stable towards heat of all the oxides of manganese, is formed as a brownish-red powder when the dioxide loses oxygen by strong ignition. It may be regarded as a compound of MnO and Mn_2O_3 .

§ 188. **Manganic compounds**, derived from manganic oxide, Mn_2O_3 , are very unstable and difficult to obtain. The amethyst bead produced by heating a manganese compound with borax in the outer blowpipe flame is manganic borate.

§ 189. **Manganic sulphate**, $\text{Mn}_2(\text{SO}_4)_3$, may be obtained in small amount in solution, together with manganous sulphate, by digesting Mn_3O_4 with concentrated sulphuric acid; on standing an amethyst-coloured solution is observed.²

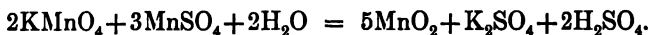
¹ Considerable excess alkali over that required to form $\text{Na}_2[\text{ZnO}_2]$ or $\text{Na}[\text{HZnO}_2]$ is needed to dissolve Zn(OH)_2 ; and even then most of the latter compound exists uncombined in a colloidal state. Thus the acidic properties of Zn(OH)_2 are very feeble. Nevertheless, both salts, in hydrated form, have been obtained.

² $\text{Mn}_3\text{O}_4 + 4\text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{Mn}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O}$. It may be necessary to allow the liquid to stand overnight; then the colour will be plainly visible.

§ 190. **Manganese dioxide, MnO_2 .**—This well-known substance is obtained artificially in a hydrated condition in several ways.

(i) Add alkali hypochlorite or hypobromite (NaOH and bromine water) to manganous sulphate solution. The brown precipitate is hydrated MnO_2 .

(ii) Add potassium permanganate solution to manganous sulphate; manganese dioxide is precipitated according to the following reaction:¹—



(iii) Add excess of lime water to a little manganese chloride solution; heat to about 55° , and aspirate air through the hot liquid. A dark-brown precipitate of MnO_2 , combined with more or less lime, separates.²

The compound $\text{CaMn}_5\text{O}_{11}$ ($= \text{CaO}, 5\text{MnO}_2$) is formed when manganous nitrate is poured into excess of bleaching-powder solution. This is calcium manganite, a salt of manganous acid, which in its simplest form may possess the composition H_2MnO_3 or H_4MnO_4 . MnO_2 is therefore manganous anhydride.

Manganous acid itself is formed in solution, having a rich brown colour, when potassium permanganate is reduced by being added to excess of warm oxalic acid solution.

When manganous hydroxide is oxidized alone, hydrated Mn_2O_3 is formed, but when oxidized in presence of a base the equivalent of MnO_2 results. In the former case, $\text{Mn}(\text{OH})_2$ itself serves as the base, the hydrated Mn_2O_3 produced being indeed manganous manganite, MnMnO_3 , which is not further oxidized. In the presence, however, of another base with which MnO_2 can combine, all the manganese is oxidized to the quadrivalent state.

§ 191. **Manganic anhydride, MnO_3 ,** corresponds with *manganic acid*, H_2MnO_4 , and the *manganates*.

Sodium manganate is the well-known green substance formed by heating a manganese compound with sodium carbonate in presence of an oxidizing agent such as potassium nitrate or chlorate, or even atmospheric air.

The experiment may be performed by heating a mixture of

¹ In both of these cases the MnO_2 is combined with more or less MnO and water.

² This experiment illustrates the method of the Weldon manganese recovery process.

a little manganous sulphate with sodium carbonate, and a very little potassium nitrate, on platinum foil; or by fusing some manganese compound into a sodium carbonate bead, on platinum wire held in the outer blowpipe flame.¹

The former method is often employed as a *confirmatory test for manganese*.

Manganic acid is unstable, and when liberated from its salts in solution undergoes spontaneous decomposition into the more stable permanganic acid and manganese dioxide, thus:—



so that if a manganate is dissolved in a little water, and the deep-green solution is acidified, or poured into excess of water, the crimson colour of permanganate is produced.

The reaction with water may be represented thus:—



If the water contains dissolved oxygen some direct oxidation to permanganate will take place.

§ 192. Permanganic anhydride, Mn_2O_7 , gives rise to permanganic acid, HMnO_4 , from which the important salts called *permanganates* are derived.

The acid itself decomposes on concentrating its solution, and potassium permanganate when heated to 240° breaks up as follows:—



The most important reactions of permanganates involve their reduction; and there are three stages in the completed

¹ It is instructive to note that whilst Mn gives an amethyst bead of manganic salt when fused borax, which constitutes an acidic matrix, is employed, with sodium carbonate, which is basic, manganese assumes an acidic function under the same external circumstances.

² This reaction takes place in dilute solution even when a little alkali is present, but is greatly promoted by the presence of acid, even of carbonic acid, which neutralizes the hydrolytic alkali.

³ Such a reaction might be anticipated from the fact that manganate and not permanganate is produced at high temperature by ignition.

process, which may be represented in terms of oxides by the following equations:—

- (i) $\text{Mn}_2\text{O}_7 = 2\text{MnO}_3 + \text{O}$ (manganate stage).
- (ii) $\text{Mn}_2\text{O}_7 = 2\text{MnO}_2 + 3\text{O}$ (manganite stage).
- (iii) $\text{Mn}_2\text{O}_7 = 2\text{MnO} + 5\text{O}$ (manganous salt stage).

The *first reaction* takes place only in alkaline solution and with a small amount of reducing agent, manganates being stable only in presence of free alkali and in the absence of reducing agents.

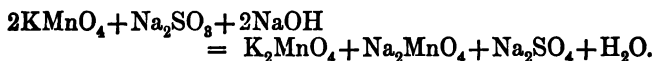
The *second reaction* is realized when the solution is alkaline, neutral, or only feebly acid, and an excess of reducing agent is present.

The *third reaction* takes place also when excess of reducing agent is present, and conditions exist under which manganous salts are stable. As a rule, the presence of free acid is necessary to this stability, but it may be attained in alkaline solution, as will appear below.

These reactions will now be studied in turn:

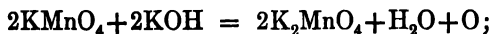
(i) **Reduction to Manganate.**

(a) Make a dilute solution of potassium permanganate alkaline with sodium hydroxide, and add to it a few drops of sodium sulphite solution; the green colour of manganate will appear:



(b) Add dilute permanganate solution to excess of caustic soda or potash; warm and allow to stand. A slow reduction of the permanganate will take place, the colour passing through intermediate shades of violet to green.¹

The change depends upon the reaction—



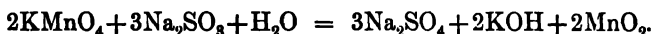
which takes place readily with impure alkali containing a trace of oxidizable matter. When, however, the reaction occurs in concentrated solution it is possible for oxygen gas to be expelled in the formation of the more stable manganate.

(ii) **Reduction to Manganite or Hydrated Manganese Dioxide.**

¹ This reaction has earned for permanganate the title "mineral chameleon".

(a) It has already been seen that when permanganate is added to warm oxalic acid solution a brown liquid containing manganous acid is obtained. The same colour is seen transitorily when warm oxalic solution containing sulphuric acid is titrated with permanganate,¹ and if the permanganate is added too rapidly a brown precipitate of hydrated dioxide is formed.

(b) Precipitation of hydrated manganese dioxide is the usual reaction in alkaline solution. Add dilute permanganate to sodium sulphite solution, made alkaline with sodium hydroxide, and boil the liquid. Green manganate may appear at first, but, on boiling, brown hydrated manganese dioxide will be precipitated according to the following reaction:—



Many organic substances are similarly oxidized, for instance, alcohol; not, however, alkaline oxalate.

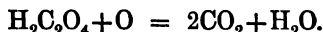
(iii) Reduction to Manganous Salt.

This reaction readily takes place in acid solution. The reducing agents mentioned below may be employed in presence of dilute sulphuric acid; the reaction of the permanganate is essentially—

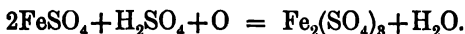


colourless manganous sulphate being produced, together with potassium sulphate, in solution.

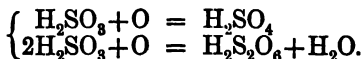
(a) Oxalic acid (warm solution):



(b) Ferrous sulphate (cold solution):

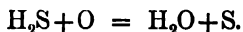


(c) Sulphurous acid, a mixture of sulphuric and dithionic acids, being produced:

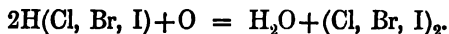


¹ It is often observed, when performing this titration, that the first drop of permanganate reacts slowly, but that subsequently, when manganous sulphate has accumulated in the liquid, oxidation is more rapid. This is because the latter salt reacts catalytically, being alternately oxidized to the MnO_2 stage by permanganate, and reduced by oxalic acid. The reaction between permanganate and manganous salt has already been studied.

(d) Hydrogen sulphide, sulphur being precipitated:

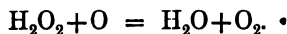


(e) Hydrochloric, hydrobromic, and hydriodic acids,¹ the halogen being liberated with increasing ease from chloride to iodide:



It will be observed that the colour of dilute permanganate added to hydrochloric acid fades only gradually when the solution is cold, but more rapidly on warming; hydrobromic and hydriodic acids readily reduce and decolorize permanganate.²

(f) Hydrogen peroxide, oxygen being evolved:



An equivalent reduction of permanganate may take place in alkaline solution, provided conditions of stability of manganous salt are realized.

(g) Add dilute permanganate solution to excess of ammonium polysulphide. Brown manganese dioxide at first appears, but is at once reduced to pale manganous sulphide.

(h) Add ammonium chloride to a little sulphurous acid and then excess of ammonia. Heat to boiling, and then add a few drops of dilute permanganate solution. The liquid, though perhaps brown at first, will become colourless on further heating, and will then contain ammonium manganous chloride $(\text{NH}_4)_2\text{MnCl}_4$.

COBALT AND NICKEL

§ 193. The remaining characteristics of these two closely related metals will best be seen by studying the formation and reactions of their compounds side by side.

§ 194. **Production of Metals.**—Cobalt and nickel resemble iron in degree of reducibility and fusibility. The metals are therefore obtained as grey powders by heating their salts with sodium car-

¹ Use sodium or potassium chloride, bromide, and iodide solutions.

² Hence a rough separation of chloride from bromide and iodide may be effected by means of this reaction.

bonate, with or without potassium cyanide, on charcoal before the blowpipe.

§ 195. **Precipitation of the Hydroxides.** Co(OH)_2 .—Add sodium hydroxide to hot dilute solution of cobaltous chloride. A deep-blue precipitate of the basic chloride, CoCl(OH) , is formed, which quickly changes to pink Co(OH)_2 . Ni(OH)_2 is at once formed as a pale-green precipitate when alkali hydroxide is added to a solution of a nickel salt.

§ 196. **Oxidation of the Hydroxides.**—Add sodium hydroxide in excess to cobalt chloride or nitrate solution; heat to boiling, and aspirate air through the liquid. The precipitate soon turns black, since Co(OH)_2 is oxidized by atmospheric oxygen to Co(OH)_3 .¹

Perform a similar experiment with nickel solution; the nickelous hydroxide remains green, not being oxidized.

The *superior oxidizability of cobaltous hydroxide* may be further illustrated by the following experiments:—

1. Mix together cobalt and nickel solutions; add chalk² and a little bromine water and boil. Black cobaltic hydroxide is at once precipitated, and, if the solution is filtered at the right juncture, the filtrate may be found to contain nickel only, which has escaped oxidation. On continued boiling, however, after addition of excess of bromine water, all the nickel, as well as the cobalt, is gradually precipitated.

2. Add a little sodium peroxide to a cobaltous solution, and heat; black cobaltic hydroxide is formed.

Repeat the experiment with a nickelous solution; there is no black precipitate, green nickelous hydroxide remaining unoxidized.

The oxidation of cobaltous compounds may be shown in yet another way.

Mix a cold solution of sodium or potassium bicarbonate with some hydrogen peroxide, and add a drop of cobaltous solution to the mixture. A bright-green liquid is formed which contains a highly oxidized cobalt compound.³

Nickelous compounds undergo no oxidation in these circumstances.

¹ Compare with this the atmospheric oxidation of Mn(OH)_2 , also the behaviour of cobaltous salts with ammonia in presence of air.

² CaCO_3 serves to keep the liquid very faintly alkaline, and so promotes the gradual precipitation of the hydroxides.

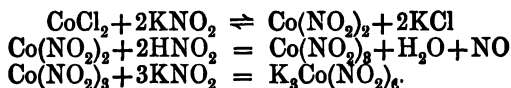
³ The nature of this compound is doubtful. It may be alkali cobaltite, a derivative of cobaltous acid, H_2CoO_3 ; or a complex alkali cobaltic carbonate. (*Vide* Durrant, *Chem. Soc. Trans.* (1905), 87, 1781.)

The oxidation of a cobaltous compound, when a nickelous compound remains unoxidized, has already been made use of in the separation of nickel and cobalt by the cyanide method, alkali cobaltocyanide being oxidized to stable cobalticyanide by air or bromine, whilst nickelocyanide is unaffected.

The formation of a stable acidic ion no doubt facilitates the oxidation of the cobalt; the same is true in the next experiment.

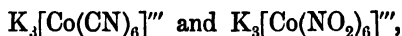
§ 197. **Potassium cobaltinitrite**, $K_3Co(NO_2)_6$, is produced as a yellow crystalline precipitate¹ when potassium nitrite is added to a cobaltous salt solution acidified with acetic acid.

The reaction involves oxidation from the cobaltous to the cobaltic state by free nitrous acid, and the combination of cobaltic nitrite with potassium nitrite, thus:—



As would be inferred from properties already studied, nickel forms no such complex salt; therefore this reaction serves, and is often employed, as a means of detecting cobalt in presence of nickel. It is indeed a delicate reaction for cobalt provided time is given for the crystalline precipitate to separate.

§ 198. **Theoretical.**—The compounds—

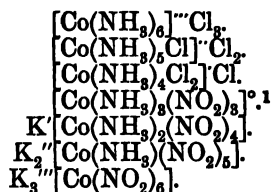


each containing a tribasic complex cobaltic ion, are evidently of the same type; they appear also to be related to the compound $Cl_3[Co(NH_4)_6]'''$ formed in solution by the oxidation of ammoniacal cobaltous chloride,² though the latter substance contains a tribasic instead of a triacidic cobaltic ion. That this is a true relationship is shown by the following series of compounds, in which chloride or other acidic radicle is shown successively entering the basic complex and displacing ammonia, until, after passing a neutral point, when a non-electrolyte is produced, the series ends with salts

¹ Fischer's yellow. If $NaNO_2$ is employed no precipitate is obtained, but only a yellow colour. The rubidium and caesium compounds, on the other hand, are less soluble than the potassium salt. This illustrates a general rule that the solubilities of complex salts diminish with increase in electropositivity of the basic metal in the alkali group. This will be further exemplified later.

² A reddish-brown solution containing this substance is formed when ammonia is added in moderate excess to $CoCl_2$ solution, and the liquid is aerated.

derived from acidic radicles containing cobalt, which eventually become trivalent.



§ 199. Phosphates of cobalt and nickel are formed as violet and light-green precipitates respectively, when sodium phosphate is added to their salt solutions. Both phosphates are easily soluble in acetic acid. If ammonia is added to acidified solutions of cobalt and nickel containing phosphate, cobalt phosphate will be found readily soluble, and nickel phosphate less easily soluble in excess of ammonia.

ALKALINE EARTH GROUP

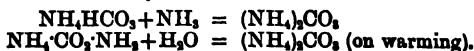
Calcium, Strontium, and Barium

§ 200. Precipitation of Carbonates.—Add ammonia, and then ammonium carbonate² solution to calcium, strontium, and barium salt solutions.³

Ammonia produces no precipitates, but the carbonates separate as bulky powders on the addition of ammonium carbonate. Heat to boiling the liquids containing these precipitates, and notice that the solids become granular and less bulky. They are then distinctly crystalline. Filter off the precipitates, and wash them thoroughly with hot water; reserve them for the flame tests below.

¹ This compound is a non-electrolyte.

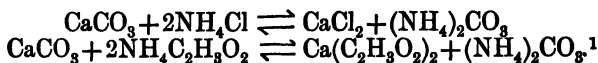
² Solid "ammonium carbonate" consists of the bicarbonate, NH_4HCO_3 , and carbamate, $\text{NH}_4\text{CO}_2\text{NH}_2$. When this substance is dissolved in water, ammonia added, and the solution heated to 60° , the solution contains, in addition to ammonia, normal carbonate only:



³ CaCl_2 , $\text{Sr}(\text{NO}_3)_2$, and BaCl_2 are generally used.

Calcium carbonate, and, to a less degree, strontium and barium carbonates are soluble in solutions of ammonium salts such as the chloride and acetate.

Show this by adding separately excess of ammonium chloride and of ammonium acetate solutions to very small amounts of freshly precipitated calcium carbonate; the calcium carbonate dissolves, the following reactions taking place:—



Now add ammonium carbonate to each solution; calcium carbonate is reprecipitated in each case, and on adding excess of ammonium carbonate² and boiling, nearly, if not quite, all the calcium is removed from the solutions, as may be shown by filtering and adding ammonium oxalate to the filtrates, when little or no precipitate will be obtained in either case.³

Ammonium chloride is always present in solutions from which the alkaline earth metals are precipitated by ammonium carbonate in the group separation; therefore for the separation to be as complete as possible it is necessary to add excess of ammonium carbonate and *just* boil the solution, when the carbonates will be precipitated in a granular form.

If this procedure is not carried out, traces of calcium may escape detection in the proper group, and, remaining in solution, will only be removed by ammonium oxalate, which is added for that purpose previous to testing for magnesium.

§ 201. Flame Colorations.—The alkaline earth chlorides give characteristic flame colorations. Place portions of the washed precipitates of the carbonates obtained in the previous experi-

¹ Partial reprecipitation of CaCO_3 occurs on warming these solutions, but boiling for a short time again dissolves the precipitate.

² Precipitated calcium carbonate is slightly soluble in excess of ammonium carbonate in the cold, probably with the formation of $\text{Ca}[\text{HCO}_3]_2$; this, however, is completely decomposed on heating, all the CaCO_3 being reprecipitated.

³ Ammonium oxalate is a delicate reagent for calcium. Strontium and barium oxalates are similarly precipitated from solutions containing these metals, but there is an increase in solubility in water of these salts from calcium to barium, and also in acetic acid in which calcium oxalate is insoluble.

ment in separate watchglasses, dissolve them in a few drops of dilute hydrochloric acid, and introduce the solutions on a loop of platinum wire into the Bunsen flame.

The following flame colorations will be observed:—

Calcium: red; green through blue glass or the indigo prism.

Strontium: crimson-red; crimson through blue glass or the indigo prism.

Barium: light green; green through blue glass or the indigo prism.

These colours are produced by the vapours of the chlorides, and the spectra differ from those given by the free metals. Non-volatile salts give no flame colorations, as may be seen by introducing such compounds as calcium fluoride and phosphate or barium sulphate into the flame. No colour will appear in these cases, even when the salts are moistened with hydrochloric acid. The presence of the alkaline earth metals may not therefore be revealed by trying the flame test with the original substance.

Barium sulphate may be reduced to sulphide by being heated on platinum wire in the inner blowpipe flame. The product will give a flame coloration after treatment with hydrochloric acid, because chloride is formed.

§ 202. **Properties of Chromates.**—Add potassium chromate to neutral solutions of calcium, strontium, and barium salts.

Calcium solutions give no precipitate.

Strontium solutions when concentrated give a yellow crystalline precipitate of SrCrO_4 , forming gradually.

Barium solutions, even when dilute, immediately give a pale-yellow precipitate of BaCrO_4 .

Show that strontium but not barium chromate is soluble in acetic acid, and that barium chromate is soluble in dilute hydrochloric acid.¹

Hence it follows that from a mixture of the three metals

¹ The solubilities of CaCrO_4 , SrCrO_4 , and BaCrO_4 thus show a gradation. Other examples of gradation in properties of alkaline earth compounds will be noticed later.

barium may be separated by precipitation, if potassium chromate is added to the solution obtained by dissolving the mixed precipitated carbonates in acetic acid.

§ 203. *Properties of Sulphates.*—Add dilute sulphuric acid to solutions of calcium, strontium, and barium salts. If the solutions are strong enough the sulphate will be precipitated in each case. Now repeat the experiment, using highly diluted solutions, and observe the following facts:—

Barium sulphate is precipitated from the most dilute solutions of barium salts in the cold.

Strontium sulphate is not precipitated in the cold from very dilute solutions, but when such solutions are boiled the sulphate is precipitated.

Calcium sulphate is not precipitated from sufficiently dilute solutions of calcium salts, even on boiling.

There is thus a gradation in the solubilities of these sulphates.

Now add boiling dilute sulphuric acid to boiling dilute solutions of calcium, strontium, and barium salts; continue to boil for a minute, and filter in each case. To the clear filtrates add ammonia in excess and ammonium oxalate. A white precipitate will be formed in the case of the calcium solution only, strontium and barium salts having been completely precipitated by boiling with dilute sulphuric acid.

Thence it is concluded that after the separation of strontium, and barium if necessary, from a mixed solution by boiling it with dilute sulphuric acid, sufficient calcium will remain in solution to be identified by adding ammonium oxalate after ammonia.

Calcium sulphate solution may itself be used to identify barium and strontium, since evidently it will give no precipitate with a calcium solution.

Add calcium sulphate solution to barium and strontium solutions. In the case of barium an immediate precipitate is formed; with strontium the precipitate forms slowly in the cold but quickly on heating.

By this test barium may be immediately identified, also strontium in the absence of barium.

The table of identification for the alkaline earth metals follows:

§ 204.

ALKALINE EARTH GROUP

Thoroughly wash on the filter the precipitate by $(\text{NH}_4)_2\text{CO}_3$. [Place a little of it in a watchglass; add a few drops of dilute HCl and examine flame coloration. ¹] Dissolve ² the precipitate in a little warm, dilute acetic acid poured on the filter—add K_2CrO_4 ³ to the solution obtained, boil and filter.		
Residue. —Pale yellow shows Ba.		Filtrate. —Divide into two parts.
¹ This test (see par. 201) should be omitted unless the precipitate is bulky. ² K_2CrO_4 may be added to a drop of this solution, and if no precipitate is formed, this reagent need not be added to the remainder.		(i) Boil with CaSO_4 solution. Small white precipitate ⁴ shows Sr. (ii) (a) Sr present. —Boil with dilute H_2SO_4 —filter and reject residue—add to filtrate ammonia in excess and ammonium oxalate. White precipitate shows Ca. (b) Sr absent. —Add ammonia in excess, and ammonium oxalate to remainder of filtrate from Ba. White precipitate shows Ca.

SUPPLEMENTARY REACTIONS

§ 205. The properties of the compounds of the alkaline earth metals furnish one of the most perfect examples of gradual change from member to member within a natural group. Gradation of solubility has already been seen in the case of the sulphates, chromates, and oxalates.

This will now be further illustrated; and the comparative study of these metals, which constitute at the same time a natural and an analytical group, yields results of much theoretical interest.

In most of the groups in the periodic system there is an increase in the electropositive properties of the elements, and in the basic properties of their hydroxides, with rise in atomic weight.⁵ This is the case here, calcium being the least electropositive of the three

³ Calcium may be identified in this solution by the ferrocyanide test, §482.

⁴ If Ba has been found, it is well to filter or centrifuge off this precipitate, wash, and confirm Sr by the flame test.

⁵ The exceptions to this rule are the metals of Groups VIII, IB, and IIB.

metals, and its hydroxide the least basic; and barium the most electropositive, and its hydroxide the most basic.

These facts must be kept in view in what follows.

§ 206. **Hydroxides.**—There is increase in solubility from calcium to barium.¹ Show that barium hydroxide may be crystallized from hot water; the crystals have the composition $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

Solutions of these hydroxides readily absorb carbon dioxide from the air, the carbonates being precipitated.

§ 207. **Peroxides**—better described as superoxides—increase in stability from CaO_2 to BaO_2 , and yield hydrogen peroxide when decomposed by dilute acids. Show this latter fact by adding dilute hydrochloric acid to barium peroxide suspended in potassium iodide solution. The solution will turn brown owing to liberation of iodine.²

Add hydrogen peroxide solution to baryta water. Crystallized barium peroxide, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$, will gradually separate.

§ 208. **Halides—Calcium Fluoride.**—Add solution of potassium fluoride or hydrofluoric acid to calcium chloride solution. A white precipitate of calcium fluoride is formed; strontium and barium fluorides are similarly precipitated, being insoluble in water.³ These facts illustrate the exceptional properties of fluorides as compared with other halides (cf. AgF and HgF_2).

§ 209. **Chlorides.**—Crystallized calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) is deliquescent, as may be shown by exposing some of the salt to the air on a watchglass. Strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) is also somewhat deliquescent, but barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) is not. Like most deliquescent salts, calcium chloride is soluble in absolute alcohol, in which strontium chloride is sparingly soluble and barium chloride insoluble. Barium chloride is also insoluble in concentrated hydrochloric acid, and is precipitated when this acid is added to its aqueous solution.⁴ This precipitate dissolves on adding water.

§ 210. **Nitrates.**—Calcium nitrate is deliquescent, and is

¹ There is thus an approach towards the solubilities of the alkali hydroxides.

² $\text{BaO}_2 + 2\text{HCl} = \text{BaCl}_2 + \text{H}_2\text{O}_2$

$\text{H}_2\text{O}_2 + 2\text{KI} = 2\text{KOH} + \text{I}_2$

³ Naturally occurring CaF_2 , fluor-spar, is insoluble in acids.

⁴ See § 35 (p. 47).

soluble in concentrated nitric acid, and in absolute alcohol. Strontium and barium nitrates are insoluble in both these reagents.

By making use of the solubility of calcium nitrate in alcohol, an alternative separation of the alkaline earth metals may be carried out, as is shown below. This method takes longer than that previously given, but has the advantage that each metal is precipitated separately and completely.

§ 211. ALTERNATIVE SEPARATION OF THE ALKALINE EARTH METALS

Dissolve the thoroughly washed precipitated carbonates in a little dilute nitric acid, and carefully evaporate until the residue is quite dry. Digest with a little warm absolute alcohol, ¹ and pour through a dry filter.		
Filtrate.—Evaporate to dryness, ² dissolve in water, and add ammonium oxalate. White precipitate proves Ca.	Residue.—Wash thoroughly with absolute alcohol to remove all $\text{Ca}(\text{NO}_3)_2$ and then dry. Dissolve in water, add acetic acid and potassium chromate in excess; boil and filter.	
	Residue.—Yel.-low = BaCrO_4 proves Ba.	Filtrate.—Add dilute sulphuric acid; white precipitate sometimes appearing only after a time, or on boiling, proves Sr.

§ 212. Sulphates.—The gradation in solubility of the sulphates has already been observed.

Calcium sulphate is readily soluble in concentrated hydrochloric acid, from which it crystallizes on cooling in needles having the composition $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

It also dissolves in hot concentrated ammonium sulphate solution, forming the complex salt $(\text{NH}_4)_2\text{Ca}(\text{SO}_4)_2$. Strontium and barium sulphates do not give this reaction.³

¹ Ninety-five per cent alcohol may dissolve a trace of strontium nitrate. The student should remember that alcohol vapour is inflammable.

² This residue may be tested by the flame coloration.

³ This reaction is sometimes employed to separate calcium from strontium and barium. The stability of a double or complex salt depends upon the difference of base-forming power between the metals of the two simple salts producing it, so that one salt appears to exercise a kind of basic, and the other a relatively acidic

Being more soluble in water than calcium carbonate, the sulphate is easily converted into this salt when boiled with sodium carbonate solution.

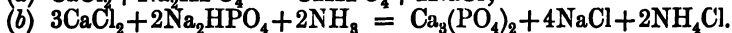
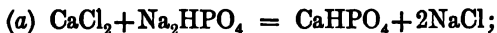
Strontium sulphate dissolves in hot concentrated hydrochloric acid, and is decomposed by boiling sodium carbonate solution.

Barium sulphate, owing to its extremely small solubility, is not decomposed by concentrated hydrochloric acid, and is acted on but slowly by boiling sodium carbonate solution. For rapid and complete decomposition it must be fused with solid alkali carbonate (cf. § 29, (3) (b), p. 34).

Hot concentrated H_2SO_4 dissolves barium sulphate, forming the acid sulphate $\text{Ba}(\text{HSO}_4)_2$, which is decomposed when the solution is poured into water.¹

§ 213. Phosphates.—Those of calcium are important.

Add solution of sodium hydrogen phosphate (a) to calcium chloride solution, (b) to calcium chloride and ammonia solution; boil in each case, and observe that precipitate (a) becomes granular and quickly subsides, while precipitate (b) remains flocculent. The final products are CaHPO_4 and $\text{Ca}_3(\text{PO}_4)_2$ respectively, and therefore the reactions may be represented thus:—



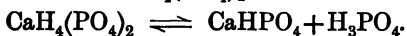
Dicalcium phosphate (CaHPO_4) is but sparingly soluble in dilute acetic acid, whilst tri-calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, when freshly precipitated, is easily soluble in this reagent.

Dissolve some freshly precipitated $\text{Ca}_3(\text{PO}_4)_2$ in a sufficiency of cold dilute acetic acid, and boil the solution: CaHPO_4 will

function. This is well seen in the alums such as $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$: the stability of these compounds of the alkali sulphates with aluminium sulphate increases from lithium to caesium with increase of base-forming power of the alkali metal. In the above case only calcium forms the double sulphate; strontium and barium approximate too nearly to the alkali metals in base-forming properties to do this.

¹ Cf. PbSO_4 .

be precipitated. This is probably due to the hydrolysis of the mono-calcium salt, $\text{CaH}_4(\text{PO}_4)_2$, which exists in solution:



Barium and strontium phosphates resemble calcium phosphate.

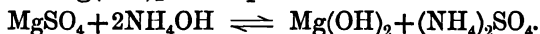
ALKALI GROUP

Magnesium, Sodium, Potassium, (Ammonium)

MAGNESIUM

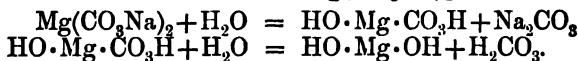
§ 214. **Preliminary Reactions.**—Add *sodium hydroxide* to magnesium sulphate solution; the hydroxide, $\text{Mg}(\text{OH})_2$, is precipitated.

Use *ammonia* instead of sodium hydroxide; a partial precipitation of $\text{Mg}(\text{OH})_2$ takes place:



Now add *ammonium chloride*; the precipitate dissolves, and would not be formed in presence of this reagent. Therefore when ammonium chloride is added before ammonia in the course of separation of the metals the precipitation of magnesium is prevented.¹

Add *sodium carbonate* to magnesium sulphate solution; the white precipitate is the hydroxycarbonate, $\text{HO} \cdot \text{Mg} \cdot \text{CO}_3\text{H} \cdot 2\text{H}_2\text{O}$, mixed with hydroxide, $\text{Mg}(\text{OH})_2$, and formed by the hydrolysis of the double carbonate, $\text{Mg}(\text{CO}_3\text{Na})_2$, thus:

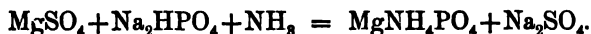


Now use *ammonium carbonate* instead of sodium carbonate solution; a precipitation of basic carbonate occurs on boiling, but the precipitate is dissolved by ammonium chloride, and its formation prevented by this reagent; thus magnesium is not precipitated with the alkaline earth metals in presence of ammonium chloride.²

¹ For a theoretical consideration of this reaction, see § 44.

² It has been seen that the solubility of the carbonate in ammonium chloride, which serves to keep magnesium in solution, also occurs to some extent with calcium, hindering its complete precipitation by ammonium carbonate.

§ 215. **Separation of Magnesium.**—Add sodium phosphate (Na_2HPO_4) to magnesium sulphate solution; no precipitate appears,¹ but if ammonia is now added a thick white precipitate of magnesium ammonium phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, is formed:



Vary the experiment by performing it as follows: To a little dilute magnesium sulphate solution add ammonium chloride and ammonia, and then to the clear solution a few drops of sodium phosphate. The same precipitate will be formed, but not instantaneously if the solution is dilute; if formed gradually the precipitate will appear distinctly crystalline.

Perform a third experiment by adding to a single drop of magnesium sulphate solution ammonium chloride and ammonia, followed by considerable excess of ammonium carbonate and a few drops of ammonium oxalate² solution; then add to the clear liquid a little sodium phosphate, shake well, and allow to stand. Unless the original magnesium solution was extremely dilute, a crystalline precipitate will appear after a time.³

§ 216. **Blowpipe Test for Magnesium.**—Mix magnesium sulphate with solid sodium carbonate, and heat the mixture on charcoal before the blowpipe. The product contains magnesium oxide, which glows brightly whilst hot. Moisten the mass with cobalt nitrate solution, and heat again; it will become pale pink owing to the formation of a compound of MgO and CoO .

§ 217. **Elimination of Magnesium.**—In order to judge of the

¹ If the solution is concentrated crystals of $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$ will gradually separate.

² These ammonium salts will be present after completely separating alkaline earth metals.

³ Thus it is unnecessary, as a rule, to get rid of ammonium salts before testing for magnesium. 0.5 mg. of Mg can be detected in presence of a large excess of ammonium salts.

amount of alkali salts present in a solution, or more certainly to detect their presence in traces, it is sometimes desirable to eliminate magnesium compounds. The following experiment shows the method by which this may be done.

To a solution of magnesium sulphate add excess of baryta water,¹ warm and filter off the magnesium hydroxide;² precipitate the excess of barium from the filtrate by ammonium carbonate, boil, and filter. The filtrate, being now free from magnesium and barium compounds, will leave no residue after evaporation to dryness and ignition; so that if sodium or potassium compounds had been present they alone would have remained after this treatment.

DETECTION OF AMMONIUM

§218. Ammonium salts may not be tested for in the course of analysis by methods of precipitation, because they have been added during the separation of the groups. Moreover, as will be seen later, the precipitation reactions of ammonium so closely resemble those of potassium that distinction is difficult. Only therefore when all other salts are absent from the original substance can ammonium salts be identified by precipitation tests; and, conversely, before potassium is tested for by precipitation methods, ammonium salts if present must be got rid of by ignition.

Ammonium salts are identified in the original substance: (a) by volatilization on ignition, (b) by evolving ammonia gas when the salts are warmed with solution of sodium hydroxide or carbonate.

(a) Heat ammonium chloride in an ignition tube, and observe that the substance is completely vaporized, a white crust of the sublimed salt forming on the cool parts of the tube.³

¹ Until the supernatant liquid is distinctly alkaline.

² Ammonium salts must be absent to secure the precipitation of magnesium as hydroxide.

³ Ammonium salts are not always vaporized without decomposition, that is, do not always sublime. For the behaviour of ammonium salts when heated, see § 7.

(b) Pour cold sodium carbonate solution on a little solid ammonium chloride in a test tube; on shaking the tube, and especially on warming, the smell of ammonia will be perceived, and this gas may be identified by its action on red litmus paper, which it turns blue, or on yellow turmeric paper, which it turns brown. The gas is evolved more rapidly on warming an ammonium salt with sodium hydroxide, solid or solution, or with slaked lime, milk of lime, or soda lime.¹

IDENTIFICATION OF SODIUM AND POTASSIUM

§ 219. I. Flame Colorations.

Sodium.—Dip a loop of platinum wire in moistened sodium chloride, and hold it in the Bunsen flame; the flame will be coloured **golden yellow**. This is a very delicate test for sodium, and is given by all sodium compounds. Owing to this fact, and the ubiquity of particles of common salt, a more or less yellow flame coloration is often seen when sodium compounds are not present in sufficient quantity to be recognizable in any other way. Care must be taken therefore in drawing conclusions from this test. The yellow colour is not visible through blue glass or the indigo prism.

Potassium.—Potassium chloride or other potassium salt imparts a **lavender** colour to the non-luminous Bunsen flame. This colour appears **crimson** through blue absorbent; and since the yellow light of sodium does not penetrate this medium, by its use potassium may be readily identified in presence of sodium.

Make a mixture of potassium and sodium chlorides in solution, and try the flame test with this mixture. The bright yellow coloration due to sodium will mask the lavender tint caused by potassium. Now interpose the blue glass or indigo

¹ A rough distinction is drawn between ammonium salts and amides, and other nitrogenous organic compounds, which latter evolve NH_3 with NaOH , but little or none with Na_2CO_3 solution.

prism; the crimson colour due to potassium will appear just as it would if sodium were absent.

§ 220. II. **Precipitation Tests.**—All sodium and potassium salts of common acids are easily soluble in water, but a few sparingly soluble salts can be precipitated.

Sodium.—1. Add cold aqueous **potassium antimonate** to sodium chloride solution; shake and allow to stand; crystalline **sodium dihydrogen antimonate**, $\text{NaH}_2\text{SbO}_4 \cdot 2.5\text{H}_2\text{O}$ will gradually separate. More dilute solutions of the sodium salt, on standing, yield the precipitate in distinct crystals. This is a delicate and distinctive test for sodium.¹

2. To sodium chloride solution add an equal volume of solution of **magnesium uranyl acetate** in dilute acetic acid. Then add one-tenth of the volume of alcohol. Small yellow crystals of $\text{NaMg}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 9\text{H}_2\text{O}$ will separate.

Potassium.—Comparatively insoluble salts² are—

1. Potassium perchlorate, KClO_4 .
2. „ hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$.
3. The complex cobaltinitrite, $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$, (§ 226).

1. Add a few drops of 20 per cent perchloric acid to some potassium chloride solution; crystalline potassium perchlorate will be formed. Very dilute solutions must first be evaporated somewhat. Potassium perchlorate, in contrast to the sodium salt, is almost completely insoluble in alcohol containing a little perchloric acid (caution).³ Thus potassium in presence of sodium may be detected and estimated.

2. Add a concentrated solution of **tartaric acid** $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, to potassium chloride solution and shake. A white crystalline precipitate of **potassium hydrogen tartrate**, $\text{KHC}_4\text{H}_4\text{O}_6$, will

¹ Ammonium salts give an amorphous precipitate on standing.

² Hexachloroplatinic acid, H_2PtCl_6 , commonly known as platinum chloride, gives a crystalline precipitate with potassium compounds, whose formation is promoted by stirring and the addition of alcohol. This test serves to distinguish and separate potassium from sodium, but the reagent is too expensive for general use.

³ The mixture of alcohol and perchloric acid must not be heated, for a dangerous explosion may occur. The cold mixture is quite safe.

be formed; this is soluble in potassium hydroxide solution, forming the normal tartrate, $K_2C_4H_4O_6$.

Use sodium hydrogen tartrate solution instead of tartaric acid; the same precipitate will be obtained.

Ammonium hydrogen tartrate is similarly precipitated.

The following table for the identification of magnesium and the alkali metals may now be submitted:—

§ 221. IDENTIFICATION OF MAGNESIUM AND THE ALKALI METALS

Add to the filtrate from the alkaline earth group a few drops of ammonium oxalate and ammonium sulphate solutions, ¹ boil and filter. Reject the precipitate and examine the solution as below.		
(1) Add to a portion ammonia and sodium phosphate, shake, and let stand. White precipitate appearing distinctly crystalline if formed slowly proves Mg. Confirm by tests in § 483.	(1) Evaporate the rest of the solution to dryness, and ignite gently in a porcelain dish or on platinum foil, till fumes of ammonium salts cease to be evolved. Dissolve the residue in a little water, filter if necessary, and examine solution for Na and K by flame tests and as follows:—	
	(a) Add to a portion a solution of (i) magnesium uranyl acetate or (ii) potassium antimonate. ² Shake and let stand five minutes. In (i) a yellow, in (ii) a white crystalline precipitate proves Na.	(b) Add ³ to the remainder (i) a concentrated solution of sodium hydrogen tartrate or tartaric acid, or (ii) perchloric acid solution; shake and allow to stand. ⁴ White crystalline precipitate proves K.

SUPPLEMENTARY REACTIONS OF THE ALKALI METALS

§ 222. The alkali metals—

Lithium, Sodium, Potassium, Rubidium, Cæsium, form an important group of related elements which, as regards the

¹ This is to remove traces of calcium group ions if present, which otherwise would give a precipitate with sodium phosphate.

² Care must be taken when performing this test that the solution is not acid and is kept cold, otherwise antimonie acid may be precipitated.

³ The cobaltinitrite test may be applied here (see § 226).

⁴ The solution may be concentrated by evaporation if necessary, provided no organic substance, *e.g.* alcohol, is present.

properties of the metals themselves, and the solubilities of their salts, strikingly exhibit *gradation*.¹

All these metals and their salts colour the Bunsen flame. Lithium and its compounds give a crimson colour, invisible through blue glass or the indigo prism; and the spectrum of the metal consists of a red and a faint orange line. The colours given to the flame by rubidium and caesium compounds resemble that shown by potassium salts, but the spectrum of rubidium contains characteristic dark-red lines, and that of caesium two bright-blue lines.²

There is an increase in electropositiveness in traversing the series from lithium to caesium; this is shown by the increasing reactivity of the metals towards water, as well as by the properties of their compounds.

§ 223. Hydroxides.—The properties of sodium and potassium hydroxides are well known, and those of rubidium and caesium hydroxides closely resemble them. Lithium hydroxide is not deliquescent, and is much less soluble in water than the others.

§ 224. Simple and Complex Chlorides.—The solubilities of the chlorides fall from lithium through sodium to potassium, but rise again through rubidium to caesium.

The solubilities of the complex halides, however, diminish with increase in electropositiveness of the alkali metal.

Platinichlorides, M_2PtCl_6 .—Add dilute H_2PtCl_6 solution to dilute solutions of the chlorides of these five metals. No precipitate will be obtained, even by concentration and stirring, in the case of lithium or sodium chloride; the rubidium and caesium platinichlorides will, however, be precipitated much more readily than the potassium salt.

Stannichlorides, M_2SnCl_6 .—Dissolve some solid hydrate of stannic chloride in concentrated hydrochloric acid, and add this reagent to solutions of potassium, rubidium, and caesium salts. Unless the solution is concentrated, no precipitate will be obtained with the potassium salt; but dilute rubidium chloride solution yields a crystalline precipitate, and a trace of caesium chloride is sufficient to be precipitated, since caesium stannichloride is almost insoluble in dilute hydrochloric acid.

§ 225. Simple and Complex Sulphates (Alums).—The order of

¹ Lithium salts can easily be obtained, but rubidium and caesium are rare metals, and their compounds are expensive. The advanced student should, however, experiment with small amounts of these if possible, since their reactions are very instructive; highly diluted solutions of the chlorides may be employed.

² Hence the names, derived from *rubidus*, dark red, and *caesius*, sky blue.

solubility of the sulphates of the alkali metals is the same as that of their chlorides, potassium sulphate being the least soluble.¹

The solubilities of the alums, however, like those of the complex halides, diminish throughout from sodium to caesium, lithium not forming an alum at all.

Formation of Alums.—Prepare a clear concentrated solution of aluminium sulphate, and add it in turn to solutions of (i) sodium, (ii) potassium, (iii) rubidium, and (iv) caesium chlorides; shake the liquids and allow them to stand. The following facts may be observed without performing quantitative experiments:—

(i) No precipitate appears with sodium chloride, even when the solution used is a concentrated one.

(ii) With potassium chloride a crystalline precipitate gradually separates; this is potassium alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, and its formation is promoted by adding excess of aluminium sulphate solution.

(iii) and (iv) With rubidium and caesium chlorides, crystals of the alum quickly separate even when only a few particles of the chloride are dissolved in 0.5 c.cm. of water, excess of aluminium sulphate is added, and the liquid shaken.

Other complex salts which exhibit the same gradation of solubility are the *cobaltinitrites* and the *phosphomolybdates*.

§ 226. **Cobaltinitrites.**—Mix together solutions of cobalt nitrate and sodium nitrite, and add to the mixture a little dilute acetic acid. The solution will gradually become deep yellow owing to the formation of sodium cobaltinitrite, $Na_3Co(NO_2)_6$. Let the solution stand for a few minutes, and, if it becomes turbid,² filter it.

Add this solution to solutions of lithium, potassium, rubidium, and caesium chlorides. No precipitate will be obtained with the lithium solution, but with potassium chloride a yellow precipitate will gradually separate even from dilute solutions;³ and in the case of rubidium and caesium salts, precipitates will at once be obtained with highly diluted solutions, owing to the very slight solubility of the cobaltinitrites. Ammonium salts also yield a precipitate.

§ 227. **Phosphomolybdates.**—Add solution of phosphomolybdic

¹ Thus there is a break in the solubility curves at potassium; this marks the transition from the "typical" to the long periods in the periodic system.

² Owing to the formation of potassium cobaltinitrite, due to KNO_3 present as an impurity in the $NaNO_2$.

³ This is a useful test for potassium salts, and may be substituted for the platinichloride or hydrogen tartrate test. The sodium cobaltinitrite solution is not stable, however, and should be prepared when required; the solid salt should be available as a laboratory reagent.

acid to solutions of lithium, sodium, potassium, rubidium, and cæsium chlorides, and observe that lithium and sodium phosphomolybdates are readily soluble in water, that the potassium salt is sparingly soluble, being precipitated from somewhat concentrated solutions, but that the rubidium and cæsium salts are almost insoluble, since they are precipitated when the solutions are dilute.

The above reactions suffice to establish the important generalization that *the solubilities of the complex salts of the alkali metals diminish with rise in atomic weight and electropositeness.*

To complete the present study of the alkali metals, two questions remain to be considered, viz.:—

- (i) The exceptional properties of lithium compounds; and
- (ii) the position of ammonium in the series.

§ 228. Exceptional Properties of Lithium Compounds.—Lithium, being the least electropositive of the alkali metals, approximates in the properties of the element and its compounds to the alkaline earth metals.

The following are some characteristics of alkaline earth compounds which distinguish them from compounds of the alkalis:—

- (i) Non-deliquescence of hydroxides.
- (ii) Comparative insolubility of sulphates in water.
- (iii) Insolubility of carbonates in water.
- (iv) Superior solubility of bicarbonates over carbonates (the opposite obtaining with the alkali metals).
- (v) Insolubility of normal phosphates and fluorides

It has already been observed that lithium hydroxide is not deliquescent; its sulphate being readily soluble in water differs from the alkaline earth sulphates. But the carbonate, phosphate and fluoride are only sparingly soluble, and the bicarbonate is more soluble than the carbonate; so that in these particulars lithium approaches the alkaline earth metals.

§ 229. Lithium Carbonate.—Add sodium carbonate to lithium chloride solution and warm the liquid. A white crystalline precipitate of Li_2CO_3 separates. Excess ammonium chloride prevents precipitation.

§ 230. Lithium Phosphate.—Add sodium hydrogen phosphate and sodium hydroxide to lithium chloride solution. Lithium phosphate, Li_3PO_4 , is formed as a crystalline precipitate. Its solubility in water is increased if ammonium chloride is present (distinction from magnesium).

§ 230a. **Separation and Identification of Lithium.**—The mixed chlorides of the alkalis are brought to dryness in presence of a little concentrated hydrochloric acid, and the lithium chloride is extracted by absolute alcohol, amyl alcohol, or dry dioxan (diethylene dioxide, $O:[CH_2 \cdot CH_2]_2:O$). The solvent is removed by evaporation, and the residue tested for lithium by the flame test, and, after solution in water, by precipitation of the phosphate. Excess ammonium fluoride, in presence of ammonia, precipitates gelatinous LiF . A solution of tartaric acid or of sodium cobaltinitrite gives no precipitate (distinction from potassium).

§ 231. **The Position of Ammonium in the Series of the Alkali Metals.**—It has been shown by Tutton¹ that, in regard to the properties of the sulphates, ammonium follows rubidium in the series. It is therefore interesting to enquire, with reference to the solubilities of the complex salts studied above, what position ammonium compounds occupy in the series of the alkali metals. Especially will it be useful to compare together analogous ammonium and potassium salts with regard to solubility.

The student may examine the relative solubilities of some potassium and ammonium complex salts by making equivalent solutions of the two chlorides, containing respectively 7.45 grm. KCl and 5.35 grm. NH_4Cl in 100 c.cm., and adding to equal volumes of these solutions, suitably diluted, solutions of phosphomolybdic acid and sodium cobaltinitrite. It will be seen that ammonium phosphomolybdate is less soluble than the potassium salt, but that the opposite relation holds with the cobaltinitrites, which are exceptional. It may be shown also that the phosphotungstate, stannichloride, and platinichloride of ammonium are less soluble than the corresponding potassium salts; in all these cases, however, the complex ammonium salts are more soluble than the corresponding rubidium compounds.

With sparingly soluble salts of simple acids, the ammonium compounds are more soluble than those of potassium.

By using the above equivalent solutions it may be shown that ammonium hydrogen tartrate is more soluble than the potassium salt; and the same relation holds with the perchlorates.

¹ *Chem. Soc. Trans.* (1903), 83, 1049.

REACTIONS OF THE ACIDIC RADICLES

Note.—Asterisks are prefixed to paragraphs containing reactions or principles of analysis. Other paragraphs, containing less important reactions, as well as the tests for the less common acidic radicles, may be omitted by the elementary student.

*§ 232. It was stated in the general part that the acidic radicles cannot be divided into groups in the same systematic way that the metals are divided. The process of examination for acidic radicles is, however, divided into the following two parts:—

- A. Identification by volatile products obtained on treatment with acids.
- B. Identification by reactions in solution.

Each of these processes may again be subdivided according to the following reactions:—

- A. (i) Gases evolved with dilute sulphuric acid.
(ii) Gases, or volatile acid vapours, evolved with concentrated sulphuric acid.
- B. (i) Oxidation or reduction in solution.
(ii) Precipitation.

This classification is not, however, rigid, because some of the acidic radicles belong to more than one of the above subdivisions. An iodide, for example, might be tested for by the evolution of hydriodic acid (A ii), by the liberation of iodine (A ii and B i), or by the precipitation of silver iodide (B ii); and a chromate, although first recognized probably by its reduction in solution (B i), may also be identified by the precipitation of its lead or silver salt (B ii).

This method of classification has, therefore, no theoretical significance; it is adopted here because it anticipates the order of procedure to be followed in the well-recognized method of testing for acidic radicles, and therefore prepares the way for the application of that method.

§ 233. CLASSIFICATION OF ACIDIC RADICLES

CLASS A

(i) *Gases evolved with dilute sulphuric acid:*

Carbonate (Bicarbonate).	Sulphite, thiosulphate.
Nitrite.	Hypochlorite.
Sulphide, polysulphide.	

(ii) *Gases or volatile acid vapours evolved with concentrated sulphuric acid:*

Fluoride, chloride, bromide, iodide.
Cyanide, complex cyanides,¹ sulphocyanide.
Chlorate, perchlorate.
Iodate.
Nitrate.
Borate.
Acetate, oxalate, tartrate.

CLASS B

(i) *Oxidation or reduction in solution:*

Chromate, dichromate.
Manganate, permanganate.

(ii) *Precipitation:*

Arsenite, arsenate.
Phosphate, phosphite, hypophosphite.
Sulphate, persulphate.²
Silicate.

Hydrogen peroxide may also be classed among the acids, its salts being the superoxides. Its reactions will be studied here, though strictly speaking it belongs to Class A i.

In addition to the above two classes of reaction, another, the decomposition of the solid substance by heat, sometimes serves to indicate what acidic radicle is present. For instance,

¹ Complex cyanides are mainly identified by reactions in solution, but it is more convenient to consider them with cyanides.

² Persulphates belong strictly speaking to class B i, but are best studied together with sulphates.

chlorates, iodates, some nitrates, as well as other oxy-salts, yield oxygen. Many carbonates give off carbon dioxide, phosphites and hypophosphites evolve phosphine; and numerous other salts give gaseous decomposition products when heated in an ignition tube. This subject has been dealt with systematically in § 7, and will be referred to in detail under the reactions of each acidic radicle.

CLASS A i

Carbonate, CO₃"

***§ 234. Action of Heat on Carbonates.**—The carbonates of the alkali metals are but slightly decomposed when heated in the blowpipe flame; those of strontium and calcium are so decomposed, whilst barium carbonate is stable. All other existing carbonates, normal and basic, as well as the alkali bicarbonates, decompose when heated in the Bunsen flame.

Heat (a) copper carbonate, (b) anhydrous sodium carbonate, in ignition tubes. Copper carbonate is easily decomposed, evolving carbon dioxide¹ and leaving a residue of the black oxide, CuO; sodium carbonate is much more stable, and no carbon dioxide will be detected by the simple test used.

***§ 235. Reaction of Carbonates with Acids.**—Add dilute hydrochloric acid to (a) sodium carbonate, (b) calcium carbonate, (c) solution of sodium carbonate in water. In each case effervescence, with escape of carbon dioxide, takes place;² and

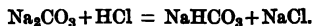
¹ This gas may be tested for by the first method given below.

² This is due to the liberation and spontaneous decomposition of carbonic acid, H₂CO₃:



Some H₂CO₃ can remain in solution in cold water; but all is decomposed on boiling. Hence to expel all the CO₂ originally present in the carbonate the solution must be boiled.

If the acid solution is very dilute it will cause no effervescence with sodium carbonate solution (c), bicarbonate being formed instead:



Such comparatively weak acids as acetic and tartaric acids will decompose car-

clear solutions result, because the chlorides are soluble in water.

Now add dilute sulphuric acid to precipitated calcium carbonate. The effervescence will be less vigorous than with hydrochloric acid; and if lumps of marble are used instead of the precipitated carbonate the reaction will gradually subside and cease. The different behaviour with sulphuric acid is due to the slight solubility in water of calcium sulphate, this salt forming a protective coating on the surface of the marble lumps.

Identification of Carbon Dioxide.—Carbon dioxide is identified by its action on lime water,¹ which is turned milky by the gas owing to the precipitation of calcium carbonate. The test may be applied in one of three ways:

- (1) By means of a dropping tube, or a glass rod, hold one drop of lime water in the gas as it is evolved in a test-tube. The drop will turn milky.
- (2) Allow the carbon dioxide to accumulate in the tube, then pour the heavy gas into another tube containing lime water; on shaking a milkiness appears.
- (3) By means of a cork, fit to the generating tube a bent glass tube so that the gas, passing into lime water in another test-tube, turns it milky.

***§ 236. Solubilities of Carbonates.**—All carbonates, except those of the alkali metals, are insoluble in water.

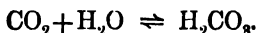
§ 237. Study of Carbonic Acid and its Salts.—(1) Add one drop of very dilute sodium hydroxide solution to about 10 c.cm. of distilled water and a few drops of litmus solution in a small beaker, and pass carbon dioxide gas through the

bonates, but hydrocyanic and hypochlorous acids, being weaker than carbonic acid, will not do so. Bleaching powder, and potassium cyanide, evolve hypochlorous and hydrocyanic acids respectively, by the action upon them of atmospheric carbon dioxide.

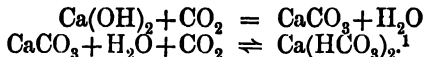
¹ Ba(OH)_2 solution is sometimes used instead of lime water, when BaCO_3 is formed. If SO_2 is also present, e.g. from a sulphite or a thiosulphate, it will vitiate the test for CO_2 by forming insoluble BaSO_3 . In such a case, first add potassium dichromate solution to the substance or solution under test; then add the acid. Sulphur dioxide is then oxidized to sulphate, and carbon dioxide alone will be liberated.

liquid. This is conveniently done by blowing down a glass tube, since exhaled air contains sufficient of the gas.

The blue colour of the litmus will soon change to bluish red, but on boiling for a minute the original colour will return. The acid present in the solution was carbonic acid, H_2CO_3 ; and this compound, being unstable, is decomposed on boiling the liquid, carbon dioxide escaping:



(2) Dilute a little lime water in a test tube with an equal volume of water, and blow through the liquid. The precipitate of calcium carbonate first formed will dissolve in excess of carbonic acid, as the blowing is continued, forming a solution of calcium bicarbonate. This will be decomposed on boiling, like carbonic acid itself, with reprecipitation of the insoluble carbonate. The following reactions have therefore taken place:—



Calcium bicarbonate is not known in the solid state, owing to its instability. It is only the alkali metals, sodium, potassium, rubidium, and caesium, together with ammonium, which form solid bicarbonates, and even these are easily decomposed by heat.

*(3) *Reactions of Bicarbonates.*—(a) Heat a little sodium bicarbonate, NaHCO_3 , in an ignition tube. Water collects in the upper part of the tube, and the presence of carbon dioxide can be detected by lime water.²

*(b) Drop sodium bicarbonate into boiling water, or make a solution in cold water, and then boil it. Carbon dioxide is rapidly evolved. The chief bicarbonates known in solution, in addition to those of the alkali metals, are those of barium,

¹ This reaction accounts for the temporary hardness of water, which is destroyed by boiling.

² $2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$.

strontium, calcium, magnesium, and ferrous iron. They are all decomposed by boiling their solutions, hence the following:—

*** Test for Bicarbonate.**—Make a solution of sodium bicarbonate in cold water, and add it to magnesium sulphate solution. No precipitate is formed, because magnesium bicarbonate remains in solution. Now boil the liquid: magnesium carbonate—probably basic—is precipitated.

(4) *Stability of Carbonates.*—Add sodium carbonate solution to (a) calcium chloride, (b) magnesium sulphate, (c) mercurous nitrate, (d) stannous chloride, (e) arsenious chloride solution. The following results are obtained:—

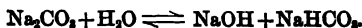
- (a) A white precipitate of normal calcium carbonate, CaCO_3 .
- (b) A white precipitate of basic magnesium carbonate, having approximately the composition $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2$ together with combined water.
- (c) An almost white precipitate of mercurous carbonate, which rapidly darkens, yielding, when washed with water, a greenish-black residue of mercurous oxide.
- (d) A white precipitate of stannous hydroxide.
- (e) No precipitate, but a clear solution containing sodium arsenite. Now add sodium bicarbonate solution to mercurous nitrate. A yellowish-white precipitate is obtained which remains permanent in contact with the bicarbonate solution, but when washed with hot water, passes into the oxide.

The explanation of these facts is as follows:—

Carbonic acid is a feeble acid, and its salts are unstable, being easily hydrolyzed by water, often with the formation of a basic salt (b). Hydrolysis occurs, more or less, with all carbonates, even the alkali carbonates showing an alkaline reaction from this cause.¹ Moreover, the feebler the basic oxide in combination, the more unstable the carbonate (c), and the more complete its hydrolysis; so that, indeed, beyond a certain point in a series of bases of diminishing strength, no carbonate can exist (d). Oxides which form no carbonate often show acidic properties, and if these are sufficiently powerful, the hydroxide is not precipitated by sodium carbonate, but combines with it, displacing carbon dioxide and forming a salt (e).

Hydrolysis is hindered by substituting bicarbonate for carbonate

¹ *E.g.* Na_2CO_3 dissolved in water shows a distinctly alkaline reaction owing to the change—



in precipitating. Thus normal mercurous carbonate is formed when sodium bicarbonate is added to mercurous nitrate solution.¹

From the above study the following generalization is derived. Traversing the metals from the most to the least electropositive or basigenic, the following stages of stability of carbonates can be roughly traced:—

- I. Solid bicarbonates and normal carbonates. *
- II. Bicarbonates in solution and normal carbonates.
- III. Normal carbonates easily becoming basic.
- IV. Basic carbonates only.
- V. No carbonates.

What is true of carbonates is also true of other salts, with modifications depending on the strengths of the acids, and the solubilities of their salts. Indeed the principle underlying these phenomena, that of the properties of oxides, is a foundation principle of chemical classification.

§ 238. **Double or Complex Carbonates.**—Add a saturated solution of sodium carbonate to a few drops of dilute copper sulphate solution; a clear blue liquid results, copper carbonate being combined with sodium carbonate to form a soluble complex carbonate. Other complex carbonates of this kind exist.

Nitrite, NO_2'

*§ 239. **Action of Heat on Nitrites.**—Sodium and potassium nitrites are stable unless heated to a very high temperature, being produced from the nitrates by ignition. Ammonium nitrite decomposes, when heated, into nitrogen and water; other nitrites evolve nitrous fumes, and leave a residue of basic oxide or metal.

*§ 240. **Reaction of Nitrites with Acids.**—Pour dilute sulphuric acid on a little solid sodium or potassium nitrite in a test tube. Observe that a pale-blue liquid is produced, and that a brown gas fills the tube at first. As this brown gas is displaced, it will be noticed that the gas leaving the liquid is colourless, only becoming brown on contact with air. The blue liquid contains nitrous acid or its anhydride, and the colourless gas,

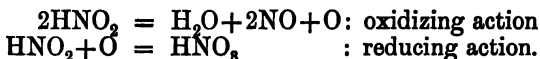
¹ This difference may be used as a test to distinguish between carbonate and bicarbonate in solution.

turning brown in the air, is nitric oxide¹ formed by the decomposition of nitrous acid as follows:—



Similar results will be obtained by the use of nitrite solution; acetic acid decomposes nitrites, though less rapidly than mineral acids.

§ 241. **Nitrous acid**, which is very unstable, only existing in solution, behaves under different circumstances either as an oxidizing or a reducing agent. This is shown by the following equations:—



§ 242. **Oxidizing Action.**—Add to an acidified solution of potassium iodide a little starch solution, and a drop of dilute solution of sodium nitrite. The blue colour of iodide of starch will be produced, owing to the liberation of iodine from hydriodic acid by nitrous acid.² Apply this test to the potassium nitrite obtained by igniting a little nitrate on platinum foil in the blowpipe flame.

§ 243. **Reducing Action.**—Add dilute nitrite solution, drop by drop, to dilute acidified permanganate solution. The colour of the permanganate will gradually be discharged³ without the evolution of gas, the nitrite being oxidized to nitrate.

* § 244. **Solubilities of Nitrites.**—All the simple nitrites⁴ are soluble in water, the silver salt being the least soluble.

§ 245. **Silver Nitrite.**—Mix together concentrated solutions of silver nitrate and sodium nitrite; a white precipitate results. Now

¹ That no brown gas is liberated in any quantity by the action of dilute acid on a nitrite may be shown by pouring dilute hydrochloric acid on marble in a test tube, and, when carbon dioxide is being evolved briskly, carefully introducing dilute nitrite solution below the level of the liquid by means of a pipette. Little or no brown colour will be seen, except at the top of the tube, where NO gas comes in contact with the air.

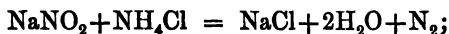
² $2\text{HNO}_2 + 2\text{HI} = 2\text{H}_2\text{O} + 2\text{NO} + \text{I}_2.$

³ See under manganese for the reactions of permanganate.

⁴ It has been seen previously that potassium cobaltinitrite, a complex nitrite, is very slightly soluble in water.

heat to boiling and filter if necessary.¹ From the clear filtrate silver nitrite crystallizes in shining needles.

***§ 246.—Reaction of Nitrite with Ammonium Chloride.**—Add some solid ammonium chloride to a solution of sodium nitrite, and boil the liquid till frothing ceases; nitrogen is evolved by the reaction:



the nitrite being completely destroyed if ammonium chloride was present in excess, so that no brown gas will be seen on adding dilute sulphuric acid.

This reaction is used to destroy nitrite when nitrate has to be tested for; it is not sufficient to decompose the nitrite by dilute acid, since nitric acid is formed in the process.

§ 247. Reaction of Nitrous Acid with Ferrous Sulphate.—Mix together cold neutral solutions of ferrous sulphate and sodium nitrite, and add one drop of dilute acetic acid. The solution turns deep brown owing to the reduction of free nitrous acid by ferrous sulphate, and the formation of the compound FeSO_4NO . Nitrate gives a corresponding reaction only when concentrated sulphuric acid is added. (Cf. nitrate, § 361.)

Sulphide, S''

***§ 248. Action of Heat on Sulphides.**—Sulphides, except those of the noble metals—as distinct from polysulphides—do not decompose when heated; but those of the volatile metals, arsenic and mercury, sublime. When heated in a current of air, sulphides are oxidized with evolution of sulphur dioxide.

***§ 249. Reaction of Sulphides with Dilute Acid.**—Pour dilute sulphuric acid on some small pieces of ferrous sulphide in a test tube. Hydrogen sulphide gas is evolved, and may be identified—

- (i) By its offensive smell.
- (ii) By burning with a pale-blue flame, and depositing sulphur on the sides of the tube.²

¹ AgCl may be present owing to the nitrite containing NaCl.

² The gas must be evolved vigorously before it will burn.

- (iii) By darkening paper moistened with lead acetate solution, or by tarnishing a silver coin, owing to the formation of lead and silver sulphides respectively.
- (iv) By giving a purple colour to paper moistened with solution of sodium nitroprusside containing sodium hydroxide.¹

It must be borne in mind that only sulphides which are soluble in water or dilute acid will give hydrogen sulphide in these circumstances.

***§ 250. Solubilities of Sulphides.**—The alkali sulphides are soluble in water, and those of the alkaline earths, magnesium, zinc, cadmium, iron, and manganese in dilute hydrochloric acid. Antimonious, stannous, and stannic sulphides dissolve in concentrated hydrochloric acid. Silver, lead, copper, bismuth, arsenious, nickel, and cobalt sulphides dissolve in nitric acid, dilute or concentrated; mercuric sulphide in aqua regia. When nitric acid is used as solvent, oxidation occurs, with separation of sulphur, or its conversion into sulphuric acid.

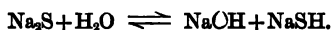
§ 251. Study of Hydrogen Sulphide and the Metallic Sulphides.—The student will probably be familiar with the chief properties of hydrogen sulphide; but he should prepare a solution of the gas in water, after previously washing it with water, and demonstrate the following facts:—

(a) *Hydrogen sulphide is a feeble acid.*—Show that its solution perceptibly reddens litmus paper.²

(b) *Oxidation in acid solution* takes place in accordance with the reaction, $\text{H}_2\text{S} + \text{O} = \text{H}_2\text{O} + \text{S}$, and may be brought

¹ Sodium nitroprusside, $\text{Na}_2\text{Fe}(\text{NO})(\text{CN})_5$, is a very delicate reagent for alkali sulphides, though not for hydrogen sulphide itself, because this substance, being a feeble acid, is but slightly ionized in solution. Add a drop of yellow ammonium sulphide to some water in a test tube, and then a few drops of dilute nitroprusside solution; a beautiful purple colour will gradually develop.

² Since this acid is weak, its soluble salts are much hydrolyzed by water. If some crystallized sodium sulphide is dissolved in water its solution will be found to be strongly alkaline owing to the reaction—



about in various ways.¹ Acidify the hydrogen sulphide solution with dilute sulphuric acid, and add to some of it:

- (i) Dilute potassium permanganate solution; the colour of the permanganate is discharged, and white sulphur separates.
- (ii) Dilute potassium dichromate solution; sulphur gradually separates, the solution becoming green. The reaction is hastened by warming.
- (iii) Hydrogen peroxide solution; sulphur separates on warming, owing to oxidation.
- (iv) Nitric acid, dilute and concentrated; hydrogen sulphide is oxidized with precipitation of sulphur, and brown nitrous fumes are evolved.²
- (v) Chlorine, bromine, and iodine solutions; sulphur separates, halogen hydracid being produced.

(c) *Oxidation in alkaline solution, i.e.* of an alkali sulphide, produces sulphate. Add sodium hydroxide to some hydrogen sulphide solution, and then perform the following tests:—

- (i) Add potassium permanganate in excess, boil and filter. On acidifying the filtrate with hydrochloric acid, and adding barium chloride, the presence of sulphate will be proved by the formation of a white precipitate of barium sulphate.
- (ii) Add bromine water in excess and boil; then acidify and add barium chloride; barium sulphate will again be precipitated.
- (iii) Add hydrogen peroxide and boil; there will be no precipitation of sulphur, but the presence of sulphate may be proved by barium chloride.

Oxidation of a sulphide by fusion.—Since a soluble sulphide can be oxidized to sulphate in alkaline solution, an insoluble sulphide may similarly be oxidized by alkaline fusion.

Powder a little ferrous sulphide, mix a little of it with sodium carbonate and a little potassium nitrate, and heat the mixture to incipient fusion in an ignition tube, or on platinum foil. Boil the mass with water and filter. Dark-red ferric oxide will be found on

¹ The student should write the equations for the reactions that follow.

² Nitric acid acts similarly on metallic sulphides. This may be shown by heating a little ferrous sulphide with concentrated nitric acid.

the filter paper, and the filtrate, when acidified with hydrochloric acid, will give a white precipitate with barium chloride, showing the presence of sulphate.¹

Polysulphide, S_x''

*** § 252.** From polysulphides, containing a larger proportion of sulphur combined with a metallic radicle than normal sulphides, this extra sulphur is liberated by the action of heat or acids:

- (i) Heat "liver of sulphur"² in an ignition tube; it fuses and yields a yellow sublimate of sulphur:



- (ii) Add dilute hydrochloric acid to yellow ammonium sulphide, which is a polysulphide, NH_4HS_x ; hydrogen sulphide is evolved, and sulphur immediately precipitated as a white amorphous powder:



- (iii) Boil sodium hydroxide solution with a few particles of sulphur; the sulphur gradually dissolves, forming a yellow liquid containing sodium polysulphide, from which amorphous sulphur is precipitated by dilute acid.³

Sulphite, SO_3''

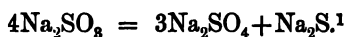
*** § 253. Action of Heat on Sulphites.**—Heat a little sodium sulphite in an ignition tube; it will give off its water of crys-

¹ It has thus been shown that whilst the reaction $MS + O = MO + S$ generally takes place in acid solution, the reaction $MS + 4O = MSO_4$ occurs in an alkaline medium. In either case the more stable product results: in presence of acid the formation of a metallic salt first occurs, and sulphur is separated, only to be dissolved subsequently by the slow action of an oxidizing agent; in the presence of alkali the sulphur is at once dissolved and therefore easily converted into alkali sulphate.

² This substance, obtained by heating together potassium carbonate and sulphur, contains potassium polysulphide, thiosulphate, and sulphate.

³ Compare this sulphur with that precipitated from a thiosulphate by dilute acid.

tallization, and eventually fuse. When the fused mass is cold, break the tube, and pour dilute hydrochloric acid upon the product in a test tube. Hydrogen sulphide will be evolved, and a precipitate of sulphur will appear, probably owing to the interaction between hydrogen sulphide and sulphurous acid. When the sulphur has been filtered off, the filtrate will give a precipitate with barium chloride, showing the presence of sulphate. The following reaction therefore takes place on heating sodium sulphite:—



Sulphites of metals less electropositive than sodium lose sulphur dioxide without fusion, leaving the oxide of the metal,² or, in the case of silver, the metal itself.

***§ 254. Reaction of Sulphites with Dilute Acid.**—Place a little coarsely powdered sodium sulphite in a test tube, and pour dilute sulphuric acid upon it. Sulphur dioxide gas is evolved,³ the rate of evolution being increased by warming. This gas may be identified—

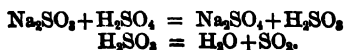
- (i) By its smell, which is that of burning sulphur.
- (ii) By turning potassium dichromate green. To show this a piece of filter paper should be moistened with the dichromate solution, and held over the mouth of the test tube from which the gas is escaping.

Sulphur dioxide gas gives no precipitate with lime water, calcium sulphite being about as soluble in water as the hydroxide. When, however, the gas is passed through baryta water, which may be made more concentrated than lime water,

¹ This process of self-oxidation and reduction is further exemplified by the behaviour when heated of alkali chlorates, hypophosphites, phosphites, and thio-sulphates, as well as of hypochlorites, and nitrous and manganic acids in solution. The student should search out these reactions.

² Thus $\text{CaSO}_3 = \text{CaO} + \text{SO}_2$; cf. $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$.

³ This is due to the liberation and spontaneous decomposition of sulphurous acid:



owing to the greater solubility of barium hydroxide, a precipitate of barium sulphite is formed.

§ 255. **Sulphurous Acid, H_2SO_3 .**—Prepare a solution of sulphurous acid by passing sulphur dioxide gas—obtained by heating copper with sulphuric acid, or direct from a siphon of the liquid—into water. The solution smells strongly of the gas.¹

Sulphurous acid may be oxidized to sulphuric acid, or reduced to hyposulphurous acid, hydrogen sulphide, or sulphur.

§ 256. **Oxidation of Sulphurous Acid.**

(i) *By halogen.*—Add sulphurous acid, drop by drop, to a solution of iodine in potassium iodide till the colour is just discharged; the solution now contains hydriodic and sulphuric acids,² and the presence of the latter should be proved by adding barium chloride.

(ii) *By dichromic and permanganic acids.*—Add dilute solutions of potassium dichromate and permanganate to separate quantities of sulphurous acid. The dichromate is reduced to green chromic salt, and the permanganate to colourless manganous salt, sulphuric acid being formed in each case.³

(iii) *By nitric acid.*—Add a few drops of concentrated nitric acid to some sulphurous acid solution. Brown fumes of nitrogen peroxide are evolved, owing to the reduction of the nitric acid, and sulphuric acid is found in solution.

(iv) *By atmospheric oxygen.*—Sulphurous acid which has been kept for some time in contact with the air always contains more or less sulphuric acid, formed by atmospheric oxidation. Prove this by testing for sulphate (see § 432).

§ 257. **Reduction of Sulphurous Acid.**

(1) *To hyposulphurous acid.*—Allow some granulated zinc to remain

¹ Sulphur dioxide is much more soluble in water than carbon dioxide, and sulphurous acid is more stable in solution than carbonic acid. Consequently the evolution of SO_2 from sulphites on addition of acid is not so vigorous as that of CO_2 from carbonates.

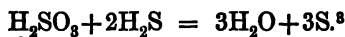
² $\text{H}_2\text{SO}_3 + \text{OH}_2 + \text{I}_2 = \text{H}_2\text{SO}_4 + 2\text{HI}$.

³ These reactions have already been studied under chromium (§ 145) and manganese (§ 192) respectively. The student should write the equations.

in contact with sulphurous acid solution for a short time; then pour off some of the clear, pale-brown solution, and add some silver nitrate solution to it. A black precipitate of metallic silver is obtained. The solution contained the zinc salt of hyposulphurous acid, $\text{H}_2\text{S}_2\text{O}_4$, which is a powerful reducing agent.¹

(2) *To hydrogen sulphide*.—Pour dilute sulphuric acid on some zinc in a test tube, and then add a few drops of sulphurous acid; hydrogen sulphide will be evolved, owing to reduction of the sulphurous acid by nascent hydrogen,² and may be detected by means of lead acetate paper.

(3) *To sulphur*.—The precipitation of sulphur will probably have been observed in the previous experiment; it is due to the interaction of H_2SO_3 and H_2S in the following way:—



If hydrogen sulphide gas is passed through sulphurous acid solution much sulphur is precipitated. It should be observed that two-thirds of the sulphur comes from the hydrogen sulphide.

§ 258. *The Sulphites*.—Sulphurous acid, H_2SO_3 , is dibasic, and acid or normal salts are produced by displacing one or both hydrogen atoms respectively by metals.

*§ 259. *Solubilities of Sulphites*.—The sulphites resemble the carbonates in their solubilities; only those of the alkali metals are readily soluble in water; calcium and magnesium sulphites are slightly soluble, all others practically insoluble in water. Like the carbonates, again, all sulphites dissolve in dilute acid. Some also dissolve in sulphurous acid, forming acid sulphites.

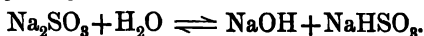
§ 260. *Sodium Sulphite*.—Dissolve some crystallized sodium sulphite, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, in water, and test the reaction of the solution towards litmus. It will be found to be alkaline.

¹ On this account it is used in the arts for the reduction of indigo.

² $\text{H}_2\text{SO}_3 + 6\text{H} = \text{H}_2\text{S} + 3\text{H}_2\text{O}$.

³ This represents the final stage in a series of reactions in which polythionic acids are produced. These are present in Wackenroder's solution, formed by passing hydrogen sulphide into concentrated sulphurous acid solution at 0°.

This is owing to the weakness of sulphurous acid, and the consequent hydrolysis of the salt:



Acid sodium sulphite is a crystalline powder whose aqueous solution reacts feebly acid.¹

§ 261. **Silver Sulphite.**—Add sodium sulphite solution to silver nitrate. A white precipitate is obtained, resembling silver chloride in appearance, but soluble in dilute nitric acid, and also in excess of sulphite solution, forming NaAgSO_3 ; this latter solution when boiled deposits metallic silver, the solution then containing sulphate.²

§ 262. **Barium Sulphite.**—Add sodium sulphite solution to barium chloride; a white precipitate is obtained even when the solutions are dilute, owing to the very slight solubility of barium sulphite³ (cf. thiosulphate). The precipitate dissolves completely in dilute hydrochloric acid, provided the original sulphite was free from sulphate.

Pass sulphur dioxide into the liquid in which barium sulphite is suspended; the precipitate dissolves, forming the acid sulphite $\text{Ba}(\text{HSO}_3)_2$, but on boiling, BaSO_3 is reprecipitated with escape of sulphur dioxide gas.

In the formation of soluble acid salts of the alkaline earth metals, sulphurous strongly resembles carbonic acid.

§ 263. **Ferric Sulphite.**—Add sodium sulphite solution to ferric chloride. Dark-red ferric sulphite is produced in solution, and on boiling hydrolysis takes place with separation of a reddish-brown basic salt. This reaction is similar to that given by acetates and formates, but differs from that of thiosulphates.

Thiosulphate, $\text{S}_2\text{O}_3^{2-}$

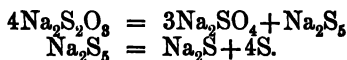
* § 264. **Action of Heat on Thiosulphates.**—Heat crystallized sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, in an ignition tube. The salt first melts in its water of crystallization, and, when

¹ This salt may be NaHSO_3 or $\text{Na}_2\text{S}_2\text{O}_5$; the latter substance is sodium pyrosulphite or "metabisulphite", which is used as an antiseptic and reducing agent, and in preparing wood pulp.

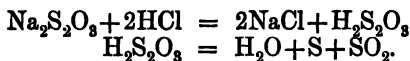
² $\text{Ag}_2\text{SO}_3 + \text{H}_2\text{O} = 2\text{Ag} + \text{H}_2\text{SO}_4.$

³ BaSO_3 , as well as SrSO_3 , is much less soluble in water than CaSO_3 .

all the water has been driven off and the mass is again solid, it melts on further heating, becoming dark-coloured, and giving a yellow sublimate of sulphur. When the product is cold it is yellow, and consists of a mixture of sodium sulphate, sulphide, and polysulphide. Add dilute hydrochloric acid, and observe the evolution of hydrogen sulphide; then filter off the sulphur, and add barium chloride to the clear filtrate; a white precipitate will show the presence of sulphate. The following reactions¹ have taken place:—

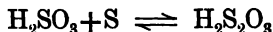


* § 265. **Reaction of Thiosulphates with Dilute Acid.**—Add dilute hydrochloric acid to a solution of sodium thiosulphate; a gradual² separation of sulphur takes place, which eventually appears pale yellow; also a smell of sulphur dioxide is observed. Thiosulphuric acid, liberated from its salt by hydrochloric acid, has undergone gradual decomposition in the following manner:—



§ 266. **Formation of Thiosulphate.**—Boil some solution of sodium sulphite with a little flowers of sulphur for a short time and filter. When dilute hydrochloric acid is added to the filtrate, yellow sulphur will gradually separate, showing that some thiosulphate has been formed.

Regarding the reaction—



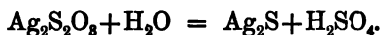
¹ These reactions differ from that which sodium sulphite undergoes, only to the extent of the extra sulphur which the thiosulphate contains, some of which is evolved as vapour.

² If the solution is dilute and cold, it may remain clear for a few seconds after the addition of the acid; warming greatly promotes the decomposition. The appearance of the sulphur differs from that of the same substance precipitated from a polysulphide by acid; in the latter case the sulphur is white because, on account of its rapid precipitation, it is very finely divided.

as a reversible one, the presence of alkali promotes the reaction from left to right, and acid that from right to left.¹

§ 267. **Solubilities of Thiosulphates.**—Thiosulphates of the alkali metals, and of calcium, strontium, magnesium, ferrous and ferric iron, zinc, manganese, cobalt, nickel, and cadmium are soluble in water; barium thiosulphate is sparingly soluble, others are insoluble. Insoluble thiosulphates dissolve in sodium thiosulphate solution, forming double or complex salts.

§ 268. **Silver Thiosulphate.**—Add sodium thiosulphate to silver nitrate solution. The white precipitate of silver thiosulphate first produced quickly becomes yellow, and then orange, brown, and black, being converted into sulphide² according to the reaction:



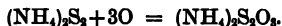
Silver thiosulphate is soluble in excess of sodium thiosulphate,³ forming the complex salt, $\text{Na}_4[\text{Ag}_2(\text{S}_2\text{O}_3)_3]$.

§ 269. **Barium Thiosulphate.**—Add sodium thiosulphate to barium chloride solution. Only if the solutions are concentrated is a white crystalline precipitate of barium thiosulphate, $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$, at once obtained, though the salt crystallizes in time from more dilute solutions. The comparative solubility of this salt enables a separation to be made between sulphite and thiosulphate, since barium sulphite is a very insoluble salt.

SEPARATION OF SULPHITE AND THIOSULPHATE

To a mixed solution of the two salts add barium chloride in excess, filter, and wash the residue thoroughly. Then show that the residue dissolves completely⁴ in dilute hydrochloric acid,

¹ Alkali thiosulphate is also produced by oxidation of polysulphide. On this account "yellow ammonium sulphide," contains thiosulphate formed by atmospheric oxidation:



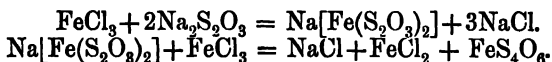
² Compare this reaction with the behaviour of sodium thiosulphate when heated.

³ Compare with this the solubility of silver halides in sodium thiosulphate, reactions made use of in photography.

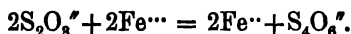
⁴ If sulphate was present, insoluble BaSO_4 will remain.

because it consists of barium sulphite only, and that the filtrate, when acidified, evolves sulphur dioxide with the gradual separation of sulphur, showing the presence of thiosulphate.

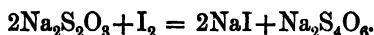
§ 270. **Ferric Thiosulphate.**—Add a little ferric chloride to sodium thiosulphate solution. A purple colour, due to a complex ferric thiosulphate, is produced, which quickly fades as ferrous salts and tetrathionate are formed. The reactions are:



The condensation of two molecules of thiosulphate to one of a tetrathionate is fundamentally the oxidation of thiosulphate ions to tetrathionate ions by ferric ions, which are reduced to ferrous ions, thus:



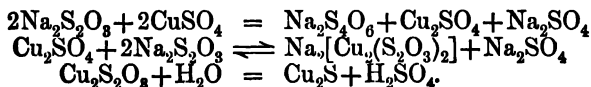
§ 271. **Reaction of Thiosulphate with Iodine.**—Add sodium thiosulphate to a solution of iodine in potassium iodide. The colour is discharged owing to the reaction:



Here the condensation is effected by the oxidizing action of iodine atoms (from KI_3) which are reduced to iodide ions.

§ 272. **Cuprous Thiosulphate.**—The two characteristic reactions of thiosulphates illustrated above, viz.: (i) condensation to tetrathionate; (ii) decomposition to sulphide and sulphuric acid, occur successively in the action of copper sulphate on sodium thiosulphate. In this case the cupric salt is the oxidizing agent.

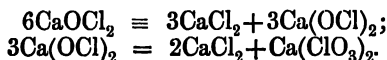
Add copper sulphate solution drop by drop to sodium thiosulphate as long as the colour of the former is discharged; then boil the colourless solution, which contains sodium cuprous thiosulphate; black cuprous sulphide gradually separates:



Hypochlorite, OCl'

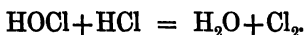
* § 273. **Action of Heat on Hypochlorites.**—Heat some bleaching powder in an ignition tube. The substance gives off water

and a little chlorine and then fuses. Allow the mass to cool, and add dilute hydrochloric acid to it. Little or no chlorine will be evolved, most of the hypochlorite having been changed into chloride and chlorate by the heating:



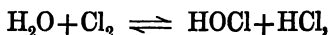
***§ 274. Reaction of Hypochlorites with Dilute Acid.**—Shake up some bleaching powder with water; decant some of the turbid liquid into a test tube, and add dilute hydrochloric acid. There is effervescence due to the evolution of a greenish-yellow gas; this may be identified as chlorine by its suffocating smell, and its action on starch-potassium iodide paper, which it turns bluish black.

Bleaching powder is calcium chlorohypochlorite, $\text{CaCl} \cdot \text{OCl}$, together with calcium hydroxide; and the former substance decomposes in water into a mixture of chloride and hypochlorite. When mineral acid is added to bleaching powder hypochlorous and hydrochloric acids are liberated,¹ and these react on one another, producing chlorine, thus:—



***§ 275. Solubilities of Hypochlorites.**—All existing hypochlorites are soluble in water.

§ 276. Preparation of Hypochlorous Acid and Properties of its Salts.—The above reaction is a reversible one,



but the production of hypochlorous acid by the action of chlorine on water can only be recognized when a suitable basic substance is present to form salts with one or both of the acids.² Now hypochlorous acid is very weak, weaker even than carbonic acid; it is therefore possible, by the use of a feebly basic substance, to fix

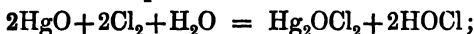
¹ Therefore the same result would have been obtained if sulphuric acid had been used for the experiment instead of hydrochloric acid.

² Chloride and hypochlorite are freely produced by the action of chlorine on sodium hydroxide:



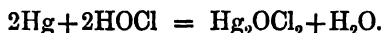
the hydrochloric acid, and leave the hypochlorous acid uncombined. A suitable basic substance is yellow mercuric oxide.

Suspend some yellow mercuric oxide¹ in chlorine water,² and shake occasionally, until after a few minutes the smell of chlorine has given place to the faint odour of hypochlorous acid. The following reaction takes place:—



filter off the mixture of basic mercuric chloride and unchanged oxide. On distilling the filtrate, a colourless, faintly-smelling solution of pure hypochlorous acid is obtained which may be used for the following experiments:—

- (i) Test the solution with litmus paper; the litmus is bleached.
- (ii) Add dilute hydrochloric acid; the solution turns yellow and chlorine is evolved: $\text{HOCl} + \text{HCl} = \text{H}_2\text{O} + \text{Cl}_2$.
- (iii) Pour a little of the solution on a drop of mercury; dark-brown basic chloride is gradually produced.

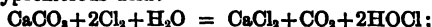


- (iv) Place a little powdered chalk in the liquid; there is no effervescence, since carbonates are not decomposed by hypochlorous acid.
- (v) Add silver nitrate to the solution; there is no immediate precipitate, silver hypochlorite, and indeed all hypochlorites, being soluble in water. A white precipitate of silver chloride slowly separates, however, and its formation is promoted by heating. Silver hypochlorite has undergone the following change:—

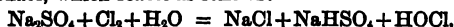


- (vi) Add lead acetate solution to hypochlorous acid; there is no precipitate, but, on boiling, brown lead dioxide separates, owing to oxidation.³

¹ Calcium carbonate may be employed for the same purpose, since it is not decomposed by hypochlorous acid:



also sodium sulphate, which reacts as follows:—



² The easiest way to prepare chlorine water is to drop concentrated hydrochloric acid from a tap funnel on to bleaching powder contained in a flask, and pass the evolved chlorine into water. No heating is required.

³ If bleaching powder solution or other alkaline hypochlorite is added to a lead salt, a white precipitate of lead hydroxide is first produced, and this turns orange (Pb_2O_3) and brown (PbO_2) when heated.

- (vii) Pass chlorine into a solution of potassium hydroxide until the liquid remains yellowish, and smells of hypochlorous acid. Now evaporate this solution to small bulk and allow it to cool; from the liquid, now colourless, crystals of potassium chlorate will separate, the following reactions having taken place:—

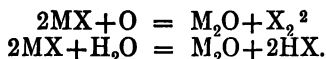


CLASS A ii

Halides—Fluoride, Chloride, Bromide, and Iodide

§ 277. **Action of Heat on Halides.**—When heated sufficiently in absence of air most halides melt or volatilize unchanged. A few acid fluorides, *e.g.* KHF_2 , evolve hydrofluoric acid. Some polyhalides yield a lower halide and free halogen when heated. (PCl_5 , CuCl_2 .)

In presence of air, or water of crystallization, oxidation or hydrolysis may occur on heating, with evolution of halogen or halogen hydracid, thus:—



Magnesium chloride, for example, undergoes both these changes. Liability to oxidation in presence of a trace of water, which does not exist in fluoride, increases from chloride through bromide to iodide, because of the increasing ease of dissociation of hydracid; therefore the evolution of bromine, and especially of iodine, frequently occurs with the less basigenic metals, an oxide of the metal remaining. Hydrated calcium chloride undergoes hydrolysis when heated, and the iodide is oxidized with the loss of halogen; but the halides of the alkali metals and of barium do not change.

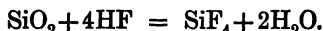
ACTION OF SULPHURIC ACID ON HALIDES

*§ 278. **Fluoride.**—Add to some calcium or potassium fluoride in a test tube concentrated sulphuric acid, and warm. A colourless, corrosive gas is evolved, which fumes in the air and reddens litmus; at the same time the test tube assumes a

¹ Compare with this the reaction of hypochlorous acid with silver nitrate. Attention has previously been drawn to reactions of self-oxidation and reduction.

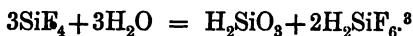
² M = equivalent of metal; X = atom of halogen.

greasy appearance, seen by the behaviour of the liquid at the surface of the glass. The gas is hydrogen fluoride,¹ and its corrosive action on glass, accounting for the greasy appearance,² is due to the fact that it dissolves silica, according to the reaction:



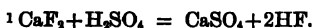
Thus silicon tetrafluoride, which is a gas, accompanies the hydrogen fluoride, and its presence serves for the identification of a fluoride by reason of its reaction with water, shown as follows.

Hold a moistened glass rod in the fumes evolved; it becomes coated with a gelatinous pellicle of silicic acid, which is approximately H_2SiO_3 , on account of the following reaction:—



The *etching of glass* by hydrogen fluoride gas may be shown by taking a watchglass whose convex surface has been coated with wax, on which a design has been traced so as to leave some of the glass bare, and placing it with the coated surface downwards upon a small leaden capsule containing powdered fluorspar (CaF_2) and concentrated sulphuric acid. Water may be placed in the watchglass to prevent the wax from melting; then, when hydrogen fluoride has been evolved by heating, its action on the glass will be shown, after removing the wax, by the design which will be found etched upon the surface.

***§ 279. Chloride.**—Pour concentrated sulphuric acid on sodium or ammonium chloride. Even without heat,⁴ a fuming⁵ acid gas is evolved.



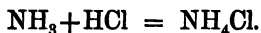
² If the tube is washed and dried after the experiment, the surface of the glass will appear corroded.

³ Hydrofluosilicic acid.

⁴ Especially in the case of ammonium chloride.

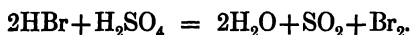
⁵ Hydrogen chloride is quite invisible in absence of moisture, but with the moisture of the air it forms a cloud consisting of minute droplets of hydrochloric acid solution. The same is true of the other halogen hydracids.

- (i) Hold a rod moistened with strong ammonia solution in the gas; dense white fumes of solid ammonium chloride appear:



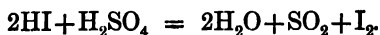
- (ii) Hold a rod moistened with silver nitrate solution in the gas; the liquid on the rod becomes opalescent, owing to the formation of insoluble silver chloride.

***§ 280. Bromide.**—When concentrated sulphuric acid is poured on potassium bromide the solution formed gradually turns reddish brown, and a brown vapour accompanies the fuming hydrobromic acid gas which is at first evolved. The brown vapour is bromine,¹ and its production becomes more marked on heating; its presence is due to the oxidation of hydrobromic acid by sulphuric acid as follows:—



Now repeat the experiment, substituting syrupy phosphoric acid for sulphuric acid. On heating, pure hydrogen bromide, unmixed with bromine, will be evolved, since phosphoric acid, being difficultly reducible, does not oxidize hydrogen bromide.²

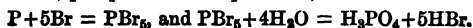
***§ 281. Iodide.**—Add concentrated sulphuric acid to potassium iodide crystals. At once the mass becomes black, owing to the separation of iodine; this on warming is seen as a violet vapour in the tube, which forms a dark deposit appearing crystalline in parts. Colourless, fuming hydrogen iodide is present in relatively small amount, most of it being oxidized to water and iodine by the sulphuric acid:



§ 282. Action of Manganese Dioxide and Sulphuric Acid on Halides.—Repeat the above experiments with fluoride, chloride, bromide, and iodide, adding a little manganese dioxide with

¹ A useful test for bromine is given by fluorescein; see § 484.

² In the usual way of preparing hydrobromic acid by dropping bromine on red phosphorus and water, phosphoric acid is produced, thus:—



the sulphuric acid. This oxidizing agent will have no effect on the hydrofluoric acid liberated from the fluoride, but will oxidize hydrochloric acid to water and chlorine,¹ and more easily complete the oxidation of hydrobromic and hydriodic acids, otherwise partially oxidized by the sulphuric acid.²

DISTINCTIVE PROPERTIES OF FLUORIDES³

§ 283. **Hydrogen fluoride** has already been distinguished from the other halogen hydracids by its action on silica, as well as by its stability towards oxidizing agents. It is further distinguished by the solubilities and other properties of many of its salts.

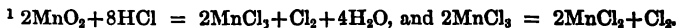
*§ 284. **Solubilities of Fluorides.**—The solubilities of fluorides in water are, in the case of silver and the alkaline earth metals, reciprocal to those of the other halides.

Alkali, silver, aluminium, and stannous fluorides are soluble in water; both mercury fluorides are hydrolyzed by water; other fluorides are insoluble in water.

Most fluorides insoluble in water dissolve in hydrochloric acid, except minerals such as fluorspar. Hydrofluoric acid readily dissolves many fluorides, forming acid salts.

§ 285 **Silver Fluoride.**—Add hydrofluoric acid, or a solution of potassium fluoride, to silver nitrate; there is no precipitate,⁴ since silver fluoride is soluble in water.

*§ 286. **Calcium Fluoride.**—Add together potassium fluoride and calcium chloride solutions; a white precipitate of calcium fluoride is formed. Warm this precipitate with dilute hydrochloric acid; it gradually dissolves,⁵ but is reprecipitated by ammonia.



² Thus the reaction $2\text{HX} + \text{O} = \text{H}_2\text{O} + \text{X}_2$ advances from zero with HF to a maximum with HI; and the reverse action, $\text{H}_2\text{O} + \text{X}_2 = 2\text{HX} + \text{O}$, which is at a maximum with fluorine, becomes almost inappreciable with iodine.

³ See also § 477.

⁴ A little chloride may, however, be present.

⁵ Fluorspar, i.e. naturally occurring calcium fluoride, is insoluble in hydrochloric acid, and must be decomposed by special methods.

Now add concentrated hydrochloric acid,¹ and evaporate nearly to dryness; again add more hydrochloric acid and evaporate. On dissolving the residue in water and adding ammonia little or no precipitate will be obtained, most or all of the hydrofluoric acid having been volatilized,² calcium chloride remaining in solution. Repeated evaporation with hydrochloric acid will completely eliminate fluoride.

COMPARISON BETWEEN CHLORIDES, BROMIDES, AND IODIDES

***§ 287. Solubilities of Chlorides, Bromides, and Iodides.**—All chlorides, bromides, and iodides are soluble in water, except the silver, mercurous, and cuprous salts and a few iodides; the lead salts are sparingly soluble in cold but readily dissolve in hot water. Antimony, bismuth, and tin salts are hydrolyzed by water.

All the above halides dissolve in dilute or concentrated hydrochloric or nitric acid, except the silver salts.

***§ 288. Silver Salts.**—Add silver nitrate solution to solutions of sodium chloride, potassium bromide, and potassium iodide, and observe that—

Silver chloride is a white precipitate, coagulated by shaking and heat, and turned violet by sunlight.

Silver bromide is pale yellow and *silver iodide* rather deeper yellow; otherwise these salts resemble the chloride in physical properties.

Allow the three precipitates to settle, after adding a little dilute nitric acid, in which none of them dissolves; wash them in the tubes with hot water by decantation, and show that:³

¹ HF is more easily eliminated by heating with sulphuric acid, and this method may be employed in analysis provided barium is absent. It was seen in § 38 that fluoride, if present, must be got rid of, if a precipitate forms on adding ammonia.

² This is not because hydrofluoric acid is more volatile than hydrochloric, for such is not the case; the change depends upon "mass action", hydrogen chloride molecules, by force of numbers, displacing those of hydrogen fluoride.

³ These halides also show progressive insolubility in water. If dilute silver nitrate solution is added little by little to a mixed solution of chloride, bromide, and iodide, silver iodide is precipitated first, then bromide, and finally chloride,

Silver chloride is readily soluble in ammonia solution.

Silver bromide is sparingly " " "

Silver iodide is nearly insoluble " "

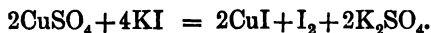
It may also be shown that each of these precipitates dissolves in sodium thiosulphate and potassium cyanide solutions.¹

§ 289. Lead Salts.—Show that lead chloride and bromide are white salts, which are sparingly soluble in cold and readily soluble in hot water, from which they crystallize in needles; and that lead iodide is a bright-yellow precipitate forming a colourless solution in hot water, from which it crystallizes in golden spangles (vide Lead, § 65).

§ 290. Mercuric Salts.—Mercuric chloride and bromide are colourless salts, the chloride fairly easily, the bromide sparingly soluble in cold water. Mercuric iodide, precipitated by adding potassium iodide to mercuric chloride solution, first appears yellow, but quickly turns scarlet.² It dissolves in excess of potassium iodide solution (vide Mercury, § 80).

§ 291. Cupric Salts.—Cupric chloride and bromide when heated in absence of air decompose into cuprous salt and free halogen, but cupric iodide is unstable and unknown, cuprous iodide and free iodine appearing in its place.

Add potassium iodide to copper sulphate solution; the light grey precipitate of cuprous iodide formed is coloured brown by free iodine,³ the following reaction having taken place:—



so that a rough separation of the halides can thus be effected; likewise silver chloride is converted into bromide or iodide when shaken with solutions of the respective alkali salts.

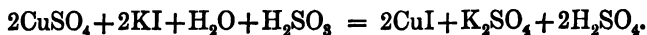
¹ The reactions are respectively:



² In the three cases studied above the iodides are deeper in colour and less soluble in water than the chlorides or bromides. The colours of some iodides of non-metals and weak metals are very striking. Thus PI_3 , SbI_3 , and SnI_4 are red, whilst BiI_3 is nearly black. This colour, however, appertains to the undissociated and solid compound, and not to its dissociated ions. Thus PbI_2 forms a colourless aqueous solution.

³ PtI_4 undergoes a similar change into $\text{PtI}_2 + \text{I}_2$.

Now add sulphurous acid¹, or repeat the experiment, previously adding sulphurous acid² to the copper sulphate solution. The whole of the iodide will be precipitated as insoluble cuprous iodide:



By this reaction iodide can be completely separated from chloride and bromide in solution.

§ 292. **Displacement of Halogens.**—Each of the halogen elements except fluorine may be displaced from its compounds with hydrogen or metals either by (i) a suitable halogen, or by (ii) oxygen in the process of oxidation.

§ 293. (i) **Displacement by Halogen.**

Fluorine will displace chlorine, bromine, and iodine.

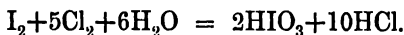
Chlorine „ „ bromine and iodine.

Bromine „ „ iodine only.³

Perform the following experiments:—

(a) Add a little carbon disulphide to some dilute potassium bromide solution, and then chlorine water little by little. The aqueous layer becomes yellow, owing to the liberation of bromine, and when this is shaken with the carbon disulphide that liquid dissolves the bromine and becomes reddish brown. Add chlorine water in excess to the brown carbon disulphide layer and shake; the colour fades and ultimately disappears, owing to the formation of bromic acid.

(b) Repeat the experiment, using potassium iodide instead of bromide solution. The liberated iodine is dark brown or black, and imparts to the carbon disulphide a beautiful violet colour. When this solution of iodine is shaken with excess of chlorine water the colour disappears altogether, colourless iodic acid being formed by the oxidation of the iodine,⁴ thus:—



¹ To reduce the free iodine to iodide.

² To reduce cupric ions to cuprous.

³ Agreeing with the progressive instability of the halides from fluoride to iodide.

⁴ Chloride of iodine is probably formed as an intermediate product.

(c) Mix together bromide and iodide solutions; add carbon disulphide, and then chlorine water, with constant shaking. Iodine is displaced first by the chlorine, and, dissolving in the carbon disulphide, colours it violet. Then, as the violet colour disappears on the addition of more chlorine, as in experiment (b), it gives place to brown, when the bromine in turn is displaced by chlorine. Thus the appearance of violet and brown colours successively shows the presence of both iodide and bromide in a solution.¹

(d) Add bromine water to potassium iodide solution; iodine is liberated, and may be dissolved in carbon disulphide, giving a violet solution.

§ 294. (ii) Displacement by Oxidation.—It has already been shown (§ 278–282) by the action of sulphuric acid, with or without manganese dioxide, upon the halides, that the oxidizability of the halogen hydracids increases from fluoride, which cannot be oxidized, to iodide.

This fact is further illustrated with different oxidizing agents in the experiments that follow:—

§ 295. (i) Chromic Acid.

(a) Intimately mix together potassium dichromate and a little potassium iodide, and pour concentrated sulphuric acid on the mixture. Iodine is at once liberated, and on heating little or no hydriodic acid escapes, the following reaction taking place:—

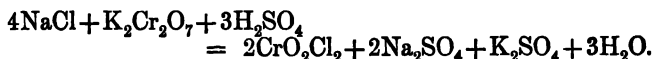


(b) Perform a similar experiment with potassium bromide. An analogous reaction takes place, and if the liquid is distilled, bromine passes over, together with, possibly, a trace of hydrobromic acid; but no volatile chromium compound is formed either with bromide or iodide.

(c) Distil a mixture of potassium dichromate and sodium chloride with concentrated sulphuric acid, and pass the dis-

¹ Obviously chloride cannot be tested for in this solution, since it is produced from the chlorine water added.

tillate into water.¹ The deep-red volatile oil obtained is chromyl chloride, CrO_2Cl_2 , produced as follows:—



It is the chloride of chromic acid, and is decomposed by water, thus:—



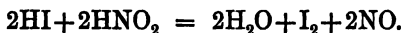
Show that the yellow solution, formed when the red oil reacts with water, contains chloride; also add to some of it ammonia in excess, then acetic acid in excess, and lead acetate. A yellow precipitate shows the presence of chromate.

Since only chloride can give rise to a volatile chromium compound, the presence of chromic acid in the distillate, although bromine and iodine may also be present, serves to identify chloride when mixed originally with bromide and iodide.

Chromyl fluoride also exists, but is not easily formed by the above process. The non-existence of chromyl bromide and iodide is accounted for by the oxidizability of hydrobromic and hydriodic acids, which therefore reduce chromic acid instead of condensing with it.

*** § 296. (ii) Nitrous Acid.**

(a) Acidify a solution of potassium iodide with dilute sulphuric acid, and then add solution of sodium nitrite; iodine is at once liberated according to the reaction:



(b) Perform the same experiment with potassium bromide; no bromine is liberated, the solution remaining colourless, though brown nitrous fumes are evolved from the nitrite.

¹ Use either a test tube with cork and bent tube, the end of which dips beneath the surface of water in a small beaker; or else the special Clarke's retort, designed for the purpose, water being placed in the bend of the receiver.

² Chromic acid, H_2CrO_4 , does not exist in solution, dichromic acid being formed instead.

These experiments show that hydriodic acid is more easily oxidized than hydrobromic acid.

§ 297. (iii) **Permanganic Acid.**

(a) Drop dilute potassium permanganate solution into acidified potassium bromide; the permanganate is at once decolorized, and the solution turns yellow by the liberation of bromine. Iodine is liberated from hydriodic acid still more easily.

(b) Repeat the experiment, using chloride instead of bromide solution, and adding very little permanganate. The colour of the permanganate fades very slowly when the liquid is cold, but more quickly on heating.

Thus it is shown that hydrobromic is more readily oxidized than hydrochloric acid.

* § 298. (iv) **Nitric Acid.**

(a) Mix together small quantities of bromide and iodide solutions, evaporate just to dryness, and add about 5 c.cm. of dilute nitric acid (1 vol. 1.42 acid to 3 vol. water). Iodine is liberated, colouring the solution brown; and if the liquid is boiled, first iodine and then bromine is displaced until the liquid becomes colourless, and, if originally free from chloride, will give no precipitate with silver nitrate.

(b) Repeat the experiment, adding a trace of chloride solution before evaporating. When the reaction with dilute nitric acid is completed the chloride will remain, and will give a white precipitate with silver nitrate.

Thus chloride can be identified, although originally mixed with bromide and iodide.

* § 299. **Identification of Chloride, Bromide, and Iodide occurring together in Solution.**¹ — This identification depends upon—

(i) The oxidation of iodide by nitrous acid.

(ii) The oxidation of bromide by dilute nitric acid (or iodic acid).

¹ *Vide J. Soc. Chem. Ind.* (1909), 28, 505.

Just acidify the dilute neutral or alkaline solution of the mixed halides with dilute sulphuric acid; then add sodium nitrite solution, and boil till the liquid is colourless, and coloured fumes have disappeared.

A brown solution or black precipitate on addition of nitrite shows presence of iodide.

Confirm (i) by holding in the escaping vapour a moistened rod dipped in powdered starch. A purple colour proves Iodide; or

(ii) by shaking a little of the dark solution with carbon disulphide. A violet colour proves Iodide.

Add a little more nitrite and again boil to expel the last traces of iodide. Neutralize with sodium carbonate and evaporate just to dryness in a dish. Add 5 c.cm. of dilute nitric acid, and heat just to boiling.¹

A brown colour shows the presence of bromide.

Confirm by exposing to the vapours a drop of dichloro-fluorescein solution on filter paper (§ 484). A red colour proves Bromide.

Boil the rest of the solution till it is colourless,² adding more dilute nitric acid if necessary to keep volume of solution up to about 3 c.cm. Then add silver nitrate.

White precipitate proves Chloride.³

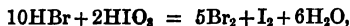
Cyanide, CN'

* § 300. **Action of Heat on Cyanides.**—Heat a little solid potassium cyanide,⁴ KCN, in an ignition tube. The salt will fuse and probably give off a little water, but will show no sign of decomposition. In the fused state it absorbs oxygen, forming cyanate, KCNO, either from the air or from oxidizing agents such as metallic oxides. It is therefore a convenient reducing agent, and its use for this purpose has already been observed (§ 14).

Mercuric cyanide, Hg(CN)₂, when heated, gives the metal and cyanogen, (CN)₂, which burns with a pink flame.

Silver cyanide, AgCN, behaves similarly.

¹ If a trace of bromide needs to be looked for, this method is unsuitable, since by heating all the bromine may be vaporized as soon as it is liberated. In this case, instead of heating, solid potassium iodate may be added to some of the cold, dilute nitric acid solution, when the bromine, together with iodine, will gradually be liberated:



Iodide must be absent or eliminated before this test is applied.

² The last traces of bromine appear brown within the bubbles arising from the liquid as it boils in a white dish.

³ A trace of chloride appearing here may be due to sodium chloride present in the nitrate employed. If this is the case the use of nitrite may be avoided by evaporating a fresh portion of the original solution, and heating the residue with dilute nitric acid until iodine and bromine are both expelled. If chloride is now found in the residual solution it was originally present.

⁴ Potassium cyanide is exceedingly poisonous and must not be handled.

Some other cyanides, such as those of lead and iron, yield, when heated, nitrogen gas, and the carbide of the metal, or the metal and free carbon. (Compare the decomposition of ferro- and ferricyanides by heat.)

Hydrocyanic acid, HCN, of which cyanides are the salts, is a very weak acid; consequently—

- (i) It is easily and completely displaced from its soluble salts by most other acids.
- (ii) Its soluble salts react alkaline in solution by reason of hydrolysis.

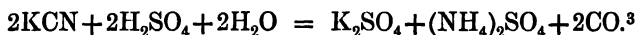
§ 301. **Potassium Cyanide, KCN**.—This salt, which occurs in crystalline masses, serves to illustrate the above facts.

(i) The salt has a smell of bitter almonds,¹ due to the constant evolution of hydrocyanic acid by the action upon it of atmospheric carbonic acid.²

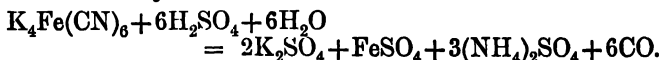
Dilute sulphuric acid displaces HCN from dilute solution of potassium cyanide, and the vapour may be smelt on warming the liquid.

(ii) Solution of potassium cyanide has a strongly alkaline reaction.

§ 302. **Action of Concentrated Sulphuric Acid on Cyanide**.—Pour concentrated sulphuric acid on a little solid potassium cyanide. On heating a gas is rapidly evolved which may be ignited; it is carbon monoxide, formed by the following reaction:—



All cyanides, simple and complex, give this reaction, *e.g.* potassium ferrocyanide:



*§ 303. **Solubilities of Cyanides**.—All metallic cyanides are

¹ Hydrocyanic or prussic acid is very poisonous, and should be inhaled as little as possible.

² Compare HOCl.

³ Liberated HCN yields formic acid, HCOOH, of which it is the nitrile, and ammonia; the former gives CO by dehydration. This decomposition of nitrile into carboxylic acid and ammonia is common in organic chemistry.

insoluble in water except those of the alkalis and alkaline earths, and mercury.

*** § 304. Silver Cyanide.**—Add dilute potassium cyanide to silver nitrate solution. A white precipitate of silver cyanide is formed, resembling silver chloride; but it is soluble in excess of cyanide solution, forming the complex cyanide $\text{KAg}(\text{CN})_2$. This is decomposed by dilute nitric acid, with reprecipitation of silver cyanide.

Prepare and wash some silver cyanide, and show that, like silver chloride, it is soluble in ammonia and sodium thiosulphate solutions; but that, unlike the chloride, it also dissolves slowly in boiling dilute nitric acid, and more readily in the concentrated acid. By this latter test cyanide is distinguished from chloride.¹

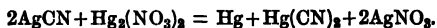
Identification of Cyanide.—Cyanide in solution is best identified by one or other of the following tests:—

*** § 305. Formation of Prussian Blue.**—Add to some cyanide solution sodium hydroxide and a little dilute ferrous sulphate solution, and boil. Ferrocyanide is thus produced in solution, and on acidifying with hydrochloric acid and adding a little ferric chloride, Prussian blue, ferric ferrocyanide is formed.²

*** § 306. Formation of Ferric Sulphocyanide.**—Alkali cyanide combines directly with sulphur, forming sulphocyanide or thiocyanate, *e.g.* KCNS . The sulphur is best derived from an alkali polysulphide.

Add a little yellow ammonium sulphide to potassium cyanide solution and evaporate to dryness in a porcelain dish; dissolve the residue in water, and acidify with hydrochloric acid to destroy the sulphide.³ On adding a drop of ferric chloride

¹ AgCN in presence of silver halides may also be identified by adding $\text{Hg}_2(\text{NO}_3)_2$ solution to the mixed precipitate. Grey metallic mercury is first produced, but this dissolves in excess of the reagent (which contains nitric acid), leaving the halides unchanged.



² Probably a blue colour is already present, due to ferric salt in the solution.

³ Sulphur will be precipitated here, if any polysulphide remained.

to the resulting solution the blood-red colour of ferric sulphocyanide, $\text{Fe}(\text{CNS})_3$, will appear.

§ 307. **Complex Cyanides.**—It has been observed above that the solution of silver cyanide in excess of potassium cyanide contains the complex salt $\text{KAg}(\text{CN})_2$.

Other complex cyanides have been met with in the course of the metal reactions; and they possess different degrees of stability.

They are:

Potassium cadmium cyanide, $\text{K}_2\text{Cd}(\text{CN})_4$, decomposed by hydrogen sulphide, with precipitation of cadmium sulphide. (§ 76.)

Potassium cuprocyanide, $\text{K}_3\text{Cu}(\text{CN})_4$, not affected by hydrogen sulphide. (§ 76.)

Potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, soluble in water and fairly stable. (§§ 161 and 162.)
Potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, stable. (§§ 161 and 162.)
Insoluble ferrocyanides of copper, ferrous and ferric iron, and zinc. (§ 31.)

Insoluble ferricyanides of ferrous iron (§ 165), and cobalt (§ 173).

Potassium nickelocyanide, $\text{K}_2\text{Ni}(\text{CN})_4$, unstable, decomposed by dilute acid. (§ 174.)

Potassium cobaltocyanide, $\text{K}_4\text{Co}(\text{CN})_6$, unstable, decomposed by dilute acid. (§ 174.)

Potassium cobalticyanide, $\text{K}_3\text{Co}(\text{CN})_6$, stable towards dilute acid. (§ 174.)

Other important complex cyanides are—

Manganocyanides, *e.g.* $\text{K}_4\text{Mn}(\text{CN})_6$.

Manganicyanides, „ $\text{K}_3\text{Mn}(\text{CN})_6$.

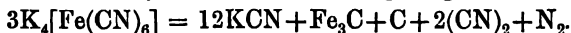
Platinocyanides,¹ „ $\text{BaPt}(\text{CN})_4$.

Aurocyanides,² „ $\text{KAu}(\text{CN})_2$.

Ferro- and ferri-cyanides are the most important of the above complex cyanides, and only those will be dealt with here.

Ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$

* § 308. **Action of Heat on Ferrocyanides.**—Ferrocyanides break up, when strongly ignited, into the simple cyanides from which they are derived, ferrous cyanide further decomposing:



¹ These are fluorescent substances showing a fine play of colour. The barium salt fluoresces under the influence of Röntgen rays.

² Produced in the cyanide gold industry.

§ 309. **Hydroferrocyanic acid**, $\text{H}_4\text{Fe}(\text{CN})_6$, separates as a white solid when concentrated sulphuric acid is added to potassium ferrocyanide solution. As before observed, when solid potassium ferrocyanide is heated with concentrated sulphuric acid, decomposition results with evolution of carbon monoxide.

* § 310. **Solubilities of Ferrocyanides.**—The ferrocyanides of the alkalis and alkaline earths are soluble in water. Most of the other salts are insoluble in water and dilute acids, but are easily decomposed by alkalis.

The formation of ferrocyanides has already been studied under iron. A few insoluble salts with characteristic properties must be noticed here.

§ 311. **Ferrous ferrocyanide**, $\text{Fe}_2[\text{Fe}(\text{CN})_6]$, precipitated by adding potassium ferrocyanide to ferrous sulphate solution, is white when pure, but rapidly turns blue by oxidation.

§ 312. **Ferric ferrocyanide**, Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, is formed from potassium ferrocyanide and ferric chloride solutions. It is decomposed by alkali hydroxide, with separation of ferric hydroxide.

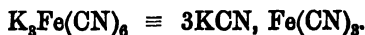
§ 313. **Copper ferrocyanide**, $\text{Cu}_2\text{Fe}(\text{CN})_6$, is a brown precipitate, whose formation constitutes a delicate test for copper. It is decomposed by alkalis.

§ 314. **Silver ferrocyanide**, $\text{Ag}_4\text{Fe}(\text{CN})_6$, is a white precipitate insoluble in ammonia (difference from ferricyanide). It is oxidized by concentrated nitric acid to the orange ferricyanide.

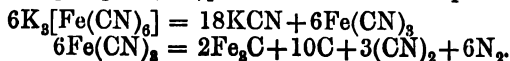
§ 315. **Zinc ferrocyanide**, $\text{Zn}_2\text{Fe}(\text{CN})_6$, a white precipitate, is soluble in alkali hydroxide solution. From this solution the zinc can be precipitated as sulphide by hydrogen sulphide, or as carbonate, by saturating the liquid with carbon dioxide and boiling.

Ferricyanide, $[\text{Fe}(\text{CN})_6]'''$

Ferricyanide is derived from ferrocyanide by oxidation, and contains ferric iron, thus:—

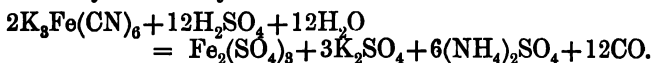


§ 316. **Action of Heat on Ferricyanides.**—Heat a little powdered potassium ferricyanide in an ignition tube. The substance decomposes to form carbide and cyanide, and gives off, in addition to nitrogen, cyanogen gas, $(CN)_2$, which burns with a pink flame.



§ 317. **Hydroferricyanic acid**, $H_3Fe(CN)_6$, separates as a brown powder when concentrated sulphuric acid is added to potassium ferricyanide solution.

The solid ferricyanide is decomposed by concentrated sulphuric acid similarly to ferrocyanide:



§ 318. **Solubilities of Ferricyanides.**—The solubilities of the ferricyanides resemble those of the ferrocyanides, except that of ferric ferricyanide, which is soluble in water.

§ 319. **Ferrous ferricyanide**, $Fe_3[Fe(CN)_6]_2$, is a dark-blue precipitate known as Turnbull's blue. After washing in presence of air, this compound is found to be identical with Prussian blue.

§ 320. **Ferric ferricyanide**, $Fe[Fe(CN)_6]$, is not precipitated, but exists in solution, giving a brown colour when ferricyanide is added to ferric chloride solution (cf. Ferrocyanide).

§ 321. **Silver ferricyanide**, $Ag_3Fe(CN)_6$, formed as an orange precipitate when potassium ferricyanide is added to silver nitrate solution, differs from the corresponding ferrocyanide by being soluble in ammonia.

§ 322. **Separation of Ferro- and Ferri-cyanide.**—This is effected by making use of the different solubilities of the silver salts in ammonia (see above).

Mix together potassium ferro- and ferri-cyanide in dilute solution, and add excess of silver nitrate; a deep orange precipitate will appear. Now add ammonia, shake, and filter cold. Silver ferrocyanide will remain on the filter, and, after washing, will appear white; and from the yellow filtrate orange-coloured silver ferricyanide will be reprecipitated by dilute nitric acid.

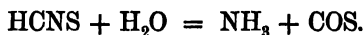
Sulphocyanide or Thiocyanate,¹ CNS'

§ 323. **Action of Heat on Sulphocyanides.**—Heat a little potassium sulphocyanide in an ignition tube. The salt easily fuses, and turns first pink, then green, and finally deep blue, but becomes white again on cooling.²

Mercuric sulphocyanide, formed by precipitation from mercuric nitrate and potassium sulphocyanide, swells up enormously when heated, forming "Pharaoh's serpents".

Sulphocyanides of the heavy metals when ignited evolve cyanogen, carbon disulphide, and nitrogen, leaving a residue of sulphide.

§ 324. **Action of Sulphuric Acid on Sulphocyanides.**—When dilute sulphuric acid is added to a solution of a sulphocyanide there is no visible action, HCNS remaining in solution. With moderately concentrated acid, however, the following change takes place:—



Place some potassium sulphocyanide in a test tube with a few drops of water, and add a little concentrated sulphuric acid. Carbonyl sulphide, or carbon oxysulphide, is evolved,³ and will burn with a flame similar to that of hydrogen sulphide.

§ 325. **Solubilities of Sulphocyanides.**—Silver, mercury, and copper sulphocyanides are insoluble in water; the lead salt is sparingly soluble; other salts are soluble.

§ 326. **Ferric Sulphocyanide.**—Add together dilute solutions of ferric chloride and potassium sulphocyanide. Blood-red ferric sulphocyanide, $\text{Fe}(\text{CNS})_3$, is produced. Divide the solution into two parts:

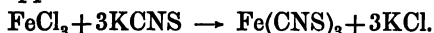
- (i) Shake with ether; the compound dissolves in the ether, imparting to it a rich crimson colour.

¹ M·CNO is cyanate, therefore M·CNS is thiocyanate.

² These curious changes are probably due to the separation of sulphur in the colloidal form.

³ Compare the analogous reaction with cyanides: $\text{HCN} + \text{H}_2\text{O} = \text{NH}_3 + \text{CO}$.

- (ii) Add mercuric chloride; the colour is discharged, owing to the formation of the double salt, $\text{Hg}(\text{CNS})_2 \cdot \text{HgCl}_2$.
 (iii) Pour the deep-red solution into much water; the colour disappears because of the reversal of the reaction:

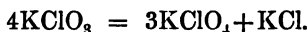


§ 327. **Silver sulphocyanide**, AgCNS , is formed as a white precipitate insoluble in dilute nitric acid¹ by adding sulphocyanide to silver nitrate solution.

§ 328. **Cuprous sulphocyanide**, CuCNS . Add sulphurous acid to copper sulphate solution and then potassium sulphocyanide; white cuprous sulphocyanide is precipitated.² When this compound is ignited it decomposes, leaving a residue of cuprous sulphide.³

. Chlorate, ClO_3'

*§ 329. **Action of Heat on Chlorates**.—All chlorates are decomposed by heat; those of strong metals, such as potassium, yield ultimately the chloride and oxygen; those of feebler metals, such as lead, whose salts do not tenaciously retain their acidic constituents, give more or less metallic oxide, free chlorine, and oxygen.⁴ Chlorate, however, is capable of self-oxidation and reduction; when, for example, potassium chlorate is first heated the following change accompanies the direct decomposition of the chlorate into chloride and oxygen:



The perchlorate formed gives up its oxygen on further heating.

*§ 330. Heat some potassium chlorate⁵ in an ignition tube,

¹ Silver may be estimated by titrating a nitric acid solution containing it with standard sulphocyanide solution, a drop of ferric sulphate solution being used to indicate when excess of sulphocyanide has been added.

² This reaction furnishes a method for the gravimetric estimation of copper.

³ $8\text{CuCNS} = 4\text{Cu}_2\text{S} + 2\text{CS}_2 + 3(\text{CN})_2 + \text{N}_2$.

⁴ The two reactions are:



(*Vide* Sodeau, *Chem. Soc. Trans.* (1901), 79, 252.)

⁵ It is well known that a little manganese dioxide mixed with potassium chlorate causes the evolution of oxygen at a much lower temperature than that at which the pure salt decomposes. This catalytic action is due to the formation and subsequent decomposition of a higher oxide of manganese. Since this reaction takes

and keep the salt fused during the evolution of oxygen, until the mass becomes pasty; then allow it to cool, and dissolve it in boiling water. The solution contains potassium perchlorate and chloride; cool it and filter off the crystals of perchlorate which form.

Show that the filtrate contains chloride by adding silver nitrate to it; recrystallize the perchlorate from hot water, filter off and dry the crystals on a porous plate, and preserve them for a subsequent test.

***§ 331. Action of Sulphuric Acid on Chlorates.**—Pour a very little concentrated sulphuric acid on a few fragments of potassium chlorate¹ in a test tube. The liquid at once turns deep orange, owing to the liberation of chlorine dioxide, which possesses this colour; and on warming explosive crackling takes place owing to the decomposition of this compound into its elements. Perchlorate and sulphate remain in solution in the concentrated acid, the reaction being:²—



***§ 332. Action of Hydrochloric Acid.**—Pour dilute hydrochloric acid on potassium chlorate and warm; then repeat the experiment, using concentrated acid. The liquid turns yellow in both cases, and a yellow gas smelling of chlorine is evolved; it is a mixture of chlorine with more or less chlorine dioxide, and has been called “euchlorine”. The reaction consists essentially in the oxidation of hydrochloric acid by chloric acid, and if this reaction were completed the change would be represented by the equation:



place at a lower temperature than that required for the self-oxidation and reduction of the chlorate, no perchlorate is formed. (*Vide* Sodeau, *Chem. Soc. Trans.* (1902), 81, 1076.) Lead dioxide, ferric oxide, and cupric oxide also aid the decomposition of potassium chlorate by heat.

¹ Great care must be taken to use very little chlorate or a violent explosion will occur. Direct the mouth of the test-tube away from yourself.

² Owing to the self-oxidation and reduction of perchloric acid, thus:—



but more or less of the product of partial reduction, chlorine dioxide, appears, together with a correspondingly less proportion of chlorine.¹

***§ 333. Solubilities of Chlorates.**—All the chlorates are soluble in water, potassium chlorate being among the least soluble of these salts. There are therefore no direct precipitation tests for chlorates.

***§ 334. Reduction of Chlorates.**—*In the dry way.*—Chlorates are reduced when heated on charcoal, the charcoal deflagrating and burning at the expense of the oxygen of the chlorate.

Chlorates also aid in oxidizing fusions; e.g. potassium chlorate facilitates the conversion of chromic compounds into chromates and manganese compounds into manganates, when they are fused with alkali carbonate.

In solution.—Chlorates are reduced in solution, not only by hydrogen chloride,² but by sulphurous acid and by nascent hydrogen.

Pour dilute sulphuric acid on zinc, and add a few crystals of potassium chlorate. After a short time decant some of the solution and add silver nitrate to it. Chloride will be found owing to the reduction of the chlorate.

§ 335. Detection of Chloride and Chlorate when Mixed.—This depends upon the foregoing reaction.

Add a few drops of dilute hydrochloric acid to some water in a test tube, and dissolve in the liquid a small amount of potassium chlorate. Add silver nitrate in excess, boil, and filter. Add to the clear filtrate more silver nitrate, in order to show that all the chloride has been precipitated; then add to the clear liquid zinc and dilute sulphuric acid. A precipitate of silver chloride will gradually appear as the chlorate is reduced.

¹ The equation, $4\text{KClO}_3 + 12\text{HCl} = 4\text{KCl} + 6\text{H}_2\text{O} + 3\text{ClO}_2 + 9\text{Cl}$, is sometimes given, or the simpler one, $2\text{KClO}_3 + 4\text{HCl} = 2\text{KCl} + 2\text{H}_2\text{O} + 2\text{ClO}_2 + \text{Cl}_2$, might serve; but neither possesses any permanent value, because the reaction varies with the conditions of the experiment.

² Potassium chlorate, with hydrochloric acid, serves as an oxidizing agent, like *aqua regia*, on account of the chlorine set free on warming. It is employed for dissolving sulphides, free sulphur, &c.

By this means chloride and chlorate are detected when occurring together.

Perchlorate, ClO_4'

[The specimen of potassium perchlorate, prepared from the chlorate, should suffice for the following tests.]

§ 336. **Action of Heat on Perchlorates.**—Heat a little potassium perchlorate in an ignition tube, and observe that it fuses and evolves oxygen, leaving a residue of chloride.

§ 337. **Action of Acids.**—Neither hydrochloric nor sulphuric acid, dilute or concentrated, has any action on a perchlorate beyond setting free perchloric acid.

Heat a little potassium perchlorate with concentrated sulphuric acid. The salt will dissolve, and the solution will boil quietly, emitting perchloric acid vapour, which in moist air forms dense white fumes of the hydrate, $\text{HClO}_4 \cdot \text{H}_2\text{O}$. Too strong heating may decompose some of the perchloric acid.

§ 338. **Solubilities of Perchlorates.**—Like the chlorates, all the perchlorates are soluble in water, potassium perchlorate being the least soluble, and much less soluble than the chlorate. There are, therefore, no precipitation tests for perchlorates apart from the formation of the potassium salt (q.v.).

§ 339. **Stability of Perchlorates.**—The formation of perchlorate and chloride, by the self-oxidation and reduction of chlorate, shows that perchlorate is more stable towards heat than chlorate. The fact that sulphuric acid does not decompose perchloric acid, again illustrates the great stability of this acid in solution. Anhydrous perchloric acid is, however, an unstable explosive liquid. It is therefore perchlorate ions,¹ and not the undissociated acid, which possess such stability. In accordance with this stability a solution of perchloric acid is not reduced by nascent hydrogen, nor sulphurous acid. Perchlorates part with their oxygen only when fused, either alone, or with charcoal or other reducing agent.

§ 340. **Separation of Chlorate and Perchlorate when Mixed.**—Separation of chlorate from perchlorate may be effected by taking advantage of the difference of solubility between the potassium

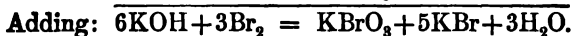
¹ HClO_4 is a powerful acid, itself and its ions being highly dissociated in solution.

salts of the two acids.¹ If a mixture of these salts is dissolved in a suitable quantity of boiling water, potassium perchlorate crystallizes on cooling, and, after separation and one recrystallization, is obtained very nearly pure, as may be shown by its reaction with concentrated sulphuric acid.

Chlorate is rapidly reduced to chloride by boiling with sulphurous acid; therefore if a mixed solution of potassium chlorate and perchlorate is evaporated with this reagent in a dish, perchlorate will crystallize almost pure at once, and the presence of chloride in the filtrate will show the original presence of chlorate.

Bromate, BrO_3'

§ 341. A specimen of potassium bromate, sufficient for the tests that follow, may be prepared by dissolving half a stick of caustic potash in water and adding bromine² to the solution until the liquid remains red. On evaporation, the excess of bromine will leave the liquid, and potassium bromate will crystallize when the concentrated solution is cooled. After one recrystallization it will be pure. The following reactions have taken place:—

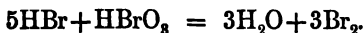


§ 342. **Action of Heat on Bromates.**—Heat a little potassium bromate in an ignition tube. It fuses, and evolves oxygen, leaving a residue of bromide. No perbromate is formed.

§ 343. **Action of Sulphuric Acid.**—Drop concentrated sulphuric acid on a little potassium bromate; bromine is immediately evolved without heating, together with oxygen, owing to the decomposition of the liberated bromic acid:



§ 344. **Interaction of Bromic and Hydrobromic Acids.**—Mix together potassium bromate and bromide in dilute aqueous solution, and add a little dilute sulphuric acid to the mixture; bromine is liberated owing to the following action of bromic upon hydrobromic acid:



¹ 1 part KClO_4 dissolves in about 17 parts water at atmospheric temperature.

1 " KClO_4 " " 65 " " " "

² This operation should be done in a fume chamber, and great care taken that bromine vapour does not come near the eyes.

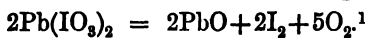
§ 345. **Solubilities of Bromates.**—Most bromates are readily soluble in water, and none are insoluble; the silver and mercury salts are the least soluble.

§ 346. **Silver Bromate.**—Mix together silver nitrate and potassium bromate solutions. A crystalline precipitate of silver bromate forms unless the solutions are very dilute. This salt is soluble in hot water, and easily soluble in ammonia, but not in dilute nitric acid.

Iodate, IO_3'

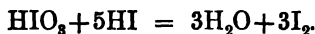
[Some potassium iodate may be prepared in a way exactly similar to that employed for bromate.]

§ 347. **Action of Heat on Iodates.**—Heat some potassium iodate in an ignition tube; oxygen is evolved, and iodide remains. Iodides of less basigenic metals evolve iodine and oxygen, leaving a residue of oxide. Lead iodate, for instance, thus decomposes:—

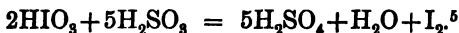


§ 348. **Action of Sulphuric Acid.**—Add concentrated sulphuric acid to potassium iodate, and heat the mixture; no change will be observed, because iodic acid, unlike bromic acid, is stable in the absence of reducing agents.

§ 349. **Reduction of Iodic Acid.**—(1) *By Hydriodic Acid.*—Mix together potassium iodate and iodide in dilute solution, and add a few drops of acetic acid; iodine is liberated² according to the reaction:³



(2) *By Sulphurous Acid.*—Add to potassium iodate solution a few drops of dilute sulphurous acid;⁴ iodine is liberated according to the reaction:



¹ Compare the similar decomposition of lead chlorate, § 330.

² Just as bromine is liberated by the interaction of bromic and hydrobromic acids, and chlorine by the interaction of chloric and hydrochloric acids; though in the latter case, owing to the relatively greater stability of hydrochloric acid, a strong solution must be employed and must be heated with chlorate.

³ Since the amount of iodine liberated depends directly upon the number of equivalents of acid added, and organic acids can effect the change, the equivalent of such an acid is sometimes estimated by titrating the iodine liberated when a known weight of it reacts with excess of iodate and iodide.

⁴ Too much sulphurous acid must not be added or the iodine will be changed to hydriodic acid by the reaction: $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} + \text{I}_2 = \text{H}_2\text{SO}_4 + 2\text{HI}$.

⁵ Five-sixths of the iodic acid is reduced to hydriodic acid by the sulphurous acid; and the remaining one-sixth reacts with the hydriodic acid formed to give iodine and water. This reaction is employed commercially to precipitate iodine from the sodium iodate occurring in Chili saltpetre.

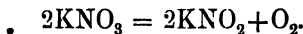
§ 350. **Solubilities of Iodates.**—As a class iodates are less soluble in water than bromates; those of the alkalis are soluble, all others more or less insoluble in water.

Silver iodate is a curdy, white precipitate, dissolved by ammonia, but not by dilute nitric acid.

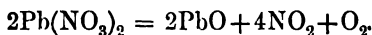
*Barium, mercuric and lead iodates*¹ form as white precipitates.

Nitrate, NO₃'

*§ 351. **Action of Heat on Nitrates.**—Heat some potassium nitrate in an ignition tube; the salt fuses and slowly gives off gas, which is oxygen. After a minute or two cool the mass and drop dilute sulphuric acid upon it; the evolution of brown fumes shows the presence of nitrite. The reaction is:—



Heat lead nitrate in the same way. It decrepitates, and gives off brown fumes, finally leaving a residue of oxide:—



The above difference in behaviour between these two nitrates is instructive. Potassium nitrate, which when gently ignited gives nitrite, when very powerfully heated evolves nitrous fumes, leaving the oxide; but whilst two stages in the decomposition are thus clearly marked in the case of alkali nitrates, this is not so with other nitrates which, being salts of less basigenic metals, lose their nitrogen atom together with oxygen when heated moderately.

Thus silver nitrate, which melts at 217°, at a higher temperature yields oxygen and oxides of nitrogen, leaving a residue of metal; calcium and barium nitrates² melt—the latter salt at high temperature—and, on further heating, evolve similar gases, leaving a residue of oxide. Strontium nitrate melts,³ at the same time decomposing. Ammonium nitrate easily melts and then decomposes into nitrous oxide and water.

Other nitrates melt in their water of crystallization; but, when anhydrous, decompose without melting, leaving a residue of oxide.

¹ Barium iodate is soluble in dilute HCl. From the well-washed precipitate a few drops of sulphurous acid liberate iodine, which colours CCl₄, confirming iodate. The insoluble mercuric salt distinguishes iodate from bromate.

² Also lithium nitrate.

³ All these statements refer to the anhydrous salts.

***§ 352. Action of Sulphuric Acid on Nitrates.**—Heat a little potassium nitrate with concentrated sulphuric acid. Nitric acid vapour is evolved, which fumes in the air, and may be condensed. On continuing the heating, orange vapours are seen; these are due to the decomposition of nitric acid by heat, thus:



All nitrates are decomposed in this manner by sulphuric acid.

***§ 353. Solubilities of Nitrates.**—All normal nitrates are soluble in water, except that a few by hydrolysis yield insoluble basic salts, which, however, dissolve in dilute nitric acid.

Add water to crystallized bismuth nitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$; a white powder separates, which is the basic nitrate, $\text{Bi}(\text{NO}_3)(\text{OH})_2$. Add dilute nitric acid to the powder; it dissolves.¹

Mercuric nitrate behaves similarly.

Owing to the solubility of normal nitrates, there are no precipitation tests for nitrate.

Nitrates are therefore generally identified by liberating nitric acid from them, and studying the behaviour of this acid towards reducing agents.

§ 354. Experiment with Nitric Acid.—Boil some dilute nitric acid in a porcelain dish, heated with a small flame.² Acid fumes will escape with the steam, but all the liquid will evaporate without evolving any of the brown fumes which are produced when a nitrate is heated with concentrated sulphuric acid. Now evaporate a little ordinary concentrated nitric acid (sp. gr. 1.42, containing 69 to 70 per cent HNO_3); still no brown fumes will appear, for it is only acid of about 96 per cent³ and upwards which decomposes on boiling. This concentration was not reached in the above experiments for the following reason:—

When a liquid containing 68 per cent of pure nitric acid with

¹ Thus the following reaction is reversible:—



² Conduct this experiment in a fume chamber.

³ A weaker acid than this may be decomposed by light, so that the ordinary concentrated acid often turns yellow from this cause. On heating the yellow acid, however, or drawing air through it, nitrous fumes are evolved, and the acid becomes colourless.

32 per cent of water is boiled, acid and water evaporate at the same rate, so that the liquid distils unchanged in composition. A solution containing a less proportion of acid than this loses water more rapidly than acid, and one containing a larger proportion loses acid more rapidly than water, until in either case a liquid of the same constant strength eventually distils.

§ 355. **Reduction of Nitric Acid.**—The following reduction products of nitric acid may be observed:¹—

Nitrogen peroxide	...	...	...	NO ₂
Nitrous acid	...	...	...	HNO ₂
Nitric oxide	...	...	...	NO
Nitrous oxide	...	...	...	N ₂ O
Hydroxylamine...	...	...	...	NH ₂ OH
Ammonia	...	...	...	NH ₃ .

§ 356. **Nitrogen Peroxide.**—Heat a little red phosphorus or arsenious oxide with concentrated nitric acid. Deep-brown nitrogen peroxide gas is evolved, mixed with nitric oxide and a small proportion of nitrous anhydride, N₂O₃, the phosphorus or arsenious oxide being oxidized to phosphoric or arsenic acid.

§ 357. **Nitrous Acid.**—Nitric acid is reduced by nascent hydrogen to nitrous acid, whose presence may be shown by the liberation of iodine from hydriodic acid.

Mix together a little nitrate solution, dilute sulphuric acid, starch solution, and potassium iodide; and drop a piece of zinc into the mixture. The starch will be turned blue by the liberated iodine.

§ 358. **Nitric Oxide.**—(a) *By copper.*—Pour dilute nitric acid on copper. A colourless gas is evolved which turns brown in the air; this is nitric oxide, and the reaction furnishes a test for nitrate when performed as follows:—

*§ 359. **Copper Test for Nitrate.**—Pour concentrated sulphuric acid on a little potassium nitrate in a test tube, add a few copper turnings and apply heat: a brown gas will appear in the tube.

§ 360. (b) *By ferrous sulphate.*—Ferrous sulphate reduces

¹ For a discussion of the mechanism of reduction, and details of the preparation and properties of the oxides of nitrogen, a textbook of theoretical chemistry should be consulted.

nitric acid to nitric oxide, and combines with the latter forming in solution a dark-brown compound, $\text{FeSO}_4 \cdot \text{N}(\text{O})$, which is decomposed by heat; this delicate test for nitrate is carried out in either of two ways.¹

***§ 361. Brown Ring Test for Nitrate.**—(1) Mix a little nitrate solution with ferrous sulphate solution, and pour concentrated sulphuric acid slowly in a thin stream through the mixture, so that the acid forms a layer beneath it. A brown ring will form where the two liquids meet.²

(2) Add to a little nitrate solution twice its volume of concentrated sulphuric acid, and thoroughly cool the mixture; then pour ferrous sulphate solution upon the top of the denser liquid. The brown ring will form below the ferrous sulphate.

When the liquid is heated the brown compound is destroyed and nitric oxide liberated.

§ 362. Nitrous Oxide.—Cover a little granulated zinc in a test tube with water, and then add a little dilute nitric acid.³ The colourless gas at first evolved is nitrous oxide, probably mixed with nitrogen, but soon brown fumes appear owing to the formation of nitric oxide, as the reaction becomes more vigorous.

§ 363. Hydroxylamine.—Pour dilute sulphuric acid on zinc, and when hydrogen is being rapidly evolved, add a few drops of dilute nitric acid; the evolution of gas will subside somewhat, owing to the reduction of the nitric acid by nascent hydrogen. After a minute, decant a little of the solution, and add to it excess of sodium hydroxide so as to dissolve the zinc hydroxide first precipitated by the alkali; then add a drop of copper sulphate solution. A yellow precipitate of cuprous hydroxide, forming gradually by the reducing

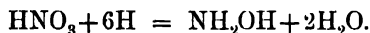
¹ The nitrate solution must be free from heavy metals and barium, and from salts which evolve gas when acidified. If prepared by boiling the original substance with sodium carbonate, the solution should be just acidified with dilute sulphuric acid before being used for this test.

There is little to choose between the two methods, provided that in using the first method, care is taken in adding sulphuric acid, lest the heat generated by mixture might be sufficient to dissociate the brown compound.

² If bromide is present, bromine will be liberated by sulphuric acid and show a brown colour. If necessary, bromide may be eliminated by chlorine water before nitrate is tested for.

³ The more dilute the acid, the slower the action and the more perfect the reduction.

action of hydroxylamine, proves the presence of this substance formed by the reduction of nitric acid, thus:



§ 364. **Ammonia.**—Zinc copper couple reduces nitric acid to ammonia.¹ Let copper sulphate solution remain in contact with granulated zinc until the metal is coated with copper; then decant the solution and wash the metal. Pour very dilute nitric acid on the couple, and after a few minutes add excess of sodium hydroxide solution and boil. Ammonia will be detected by its smell and its action on red litmus paper.

§ 365. **Detection of Nitrate when Nitrite is present.**—It was shown under nitrite that the decomposition of this substance by dilute acid produces some nitrate. Whilst, therefore, the behaviour with dilute acid distinguishes nitrite from nitrate, this reaction cannot be employed to eliminate nitrite before testing for nitrate.

Ammonium chloride is used for this purpose, as was shown under nitrite (§ 246).

Add ammonium chloride solution to a little sodium nitrite,² and boil till effervescence ceases. The solution should now show no reaction for nitrate by means of the brown ring test.

Repeat the experiment, first adding a little nitrate. This will then be found by the brown ring test, after nitrite has been destroyed.

§ 366. **Detection of Nitrate and Chlorate when mixed.**—Zinc dust and boiling sodium hydroxide solution gradually reduce nitrate to ammonia, which may be detected by its smell and its action on red litmus paper. Chlorate in presence of alkali does not interfere with this reaction.

Chlorate can be reduced to chloride by zinc and dilute sulphuric acid, and then identified, if chloride was originally absent, by the silver nitrate test.

Show that nitrate and chlorate can thus be detected independently in presence of each other.

¹ This reaction is employed in the estimation of nitrate in drinking water.

² If sodium carbonate is present in the solution it will react first with the ammonium chloride; and when ammonia ceases to be evolved, nitrogen will come off.

§ 367. **Detection of Nitrate when Bromide is present.**—Add chlorine water or solution of bleaching powder and dilute sulphuric acid to the mixed solution, and boil till all bromine fumes have disappeared; cool, and test for nitrate by the brown ring test.

Borate, $\text{BO}_3'''(\text{BO}_2', \text{B}_4\text{O}_7'')$

Boric Acid is one of the few common inorganic acids easily obtained in a solid crystalline state.

Add a little concentrated sulphuric acid to a strong solution of borax. A crystalline precipitate of boric acid will be obtained.

*§ 368. **Action of Heat on Boric Acid.**—Carefully heat a little boric acid in an ignition tube; it easily melts and begins to give off water, also partially subliming, so that a crust forms on the tube consisting of small colourless plates of the acid. As the heating is continued, the fused substance becomes nearly solid and swells up, passing through the stages of meta- (HBO_2) and pyro-acid ($\text{H}_2\text{B}_4\text{O}_7$); finally there is left a fused, glass-like residue of the anhydride, B_2O_3 .

Tests for Boric Acid.—Most of the tests by which borates are identified are those for boric acid itself.

*§ 369. **Flame Coloration.**—Boric acid and its volatile compounds impart a green colour to a non-luminous flame. This may be illustrated in three ways:—

(i) Introduce some boric acid on a loop of platinum wire into a Bunsen flame; the flame will be coloured bright green.¹

(ii) Intimately mix a borate, *e.g.* borax, with powdered calcium fluoride, and a little concentrated sulphuric acid; and bring a little of the paste thus formed, on a loop of platinum wire, within an eighth of an inch of the base of a Bunsen flame. Volatile boron fluoride,² BF_3 , is formed under these conditions, and, entering the flame, colours it green.

¹ Metallic borates do not thus directly colour the flame.

² This test identifies borate in presence of copper and barium compounds.

(iii) Mix a little borax with sulphuric acid and alcohol in a porcelain dish; heat the mixture and set fire to the alcohol. The flame will be tinged with green owing to the presence of ethyl borate.¹

*§ 370. *Turmeric Coloration.*—Dip turmeric paper in a solution of boric acid, or of a borate in dilute hydrochloric acid, and carefully dry the paper; it will turn brown, and will become bluish-grey or black when moistened with sodium hydroxide or ammonia solution.

*§ 371. *Action of Heat on Borates.*²—Heat powdered borax—sodium pyro- or tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ —in an ignition tube. The salt loses its water of crystallization, swelling up, and then subsiding, and leaves a vitreous residue of the anhydrous salt. It is this substance which dissolves metallic oxides producing borax beads of metaborates having characteristic colours.³

Precipitated borates undergo no change when heated to a moderate temperature.

*§ 372. *Action of Sulphuric Acid on Borates.*—Heat powdered borax with concentrated sulphuric acid. The salt dissolves without effervescence, but white fumes of boric acid are evolved, and a crystalline sublimate, not easily seen, is formed in the upper part of the tube on cooling. Other borates behave similarly.

*§ 373. *Solubilities of Borates.*—The alkali borates, both pyro- and meta-salts, are readily soluble in water. Other borates, which are generally meta-salts, are sparingly soluble, or almost insoluble in water.

§ 374. *Properties of Borax Solution.*—An aqueous solution of

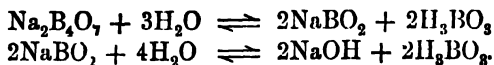
$13\text{C}_2\text{H}_5\text{OH} + \text{B}(\text{OH})_3 = (\text{C}_2\text{H}_5\text{O})_3\text{B} + 3\text{H}_2\text{O}$. Methyl is sometimes preferred to ethyl alcohol for this test owing to its greater volatility. The test may be modified by heating the mixture in a small flask provided with a cork through which passes a short wide piece of glass tubing open at both ends, and igniting the alcohol vapour at the end of the tube. Some minerals containing boron, such as borosilicates, do not give this reaction. With such substances test (ii) will be successful.

² The only known orthoborates are those of magnesium and alkyl radicles. Precipitated borates are meta-salts.

³ *E.g.* with $\text{CuO} : \text{Na}_2\text{B}_4\text{O}_7 + \text{CuO} = \text{Cu}(\text{BO}_2)_2 + 2\text{NaBO}_2$.

borax is alkaline in reaction to litmus and methyl orange.¹ This is owing to hydrolysis, boric acid being a very weak acid.

This hydrolysis takes place in two stages, viz.:—



From a concentrated solution of borax, therefore, a metaborate is likely to be precipitated, and from a highly diluted solution, a hydroxide. This is the case with silver.

§ 375. **Silver Metaborate.**—(a) Mix together concentrated solutions of borax and silver nitrate; a white precipitate of silver metaborate, AgBO_2 , is formed. Heat the precipitate with water; it turns dark brown, being completely hydrolyzed with separation of silver oxide.

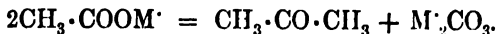
(b) Add dilute silver nitrate solution to a highly diluted solution of borax. It is possible, by suitable dilution, to produce an immediate precipitation of brown silver oxide.

§ 376. **Barium Metaborate, $\text{Ba}(\text{BO}_2)_2$.**—Add barium chloride to borax solution; barium metaborate is precipitated. Dissolve this precipitate in a little dilute hydrochloric acid and add ammonia; the borate is reprecipitated, but may be dissolved by adding sufficient ammonium chloride.

Repeat the experiment, adding ammonium chloride after dissolving the precipitated borate in hydrochloric acid. No precipitation now takes place on adding ammonia, this being prevented by ammonium chloride.²

Acetate, $(\text{C}_2\text{H}_3\text{O}_2)'$

*§ 377. **Action of Heat on Acetates.**—Acetates, when heated sufficiently, evolve acetone, leaving a residue of carbonate or oxide, or, in the case of silver, the metal itself. The reaction is essentially:



¹ Boric acid does not react acid to methyl orange. Therefore a solution of borax can be titrated as an alkali by means of standard mineral acid, methyl orange being used as indicator.

² The same is true of other insoluble borates; therefore the presence of boric acid introduces no irregularity in the course of separation of the metals.

Heat lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, in an ignition tube. The salt melts in its water of crystallization, and when all the water has been driven off, an inflammable, condensible vapour, burning with a somewhat luminous flame, is evolved; this is acetone, and the dark residue, which effervesces with dilute nitric acid, contains lead carbonate.

Barium and calcium acetates behave similarly; sodium acetate requires a high temperature for its decomposition.

*§ 378. **Action of Sulphuric Acid on Acetates.**—Heat sodium acetate with concentrated sulphuric acid. Acetic acid¹ is evolved, and is recognized by its pungent smell, somewhat similar to, but stronger than that of vinegar.

*§ 379. **Formation of Ethyl Acetate.**—An acetate is identified by the formation of ethyl acetate, a volatile liquid, having a fruity smell like that of apples.

Pour a little ethyl alcohol on some sodium acetate, add a few drops of concentrated sulphuric acid, and gently warm the mixture. Ethyl acetate is evolved,² and is recognized by its smell.

*§ 380. **Solubilities of Acetates.**—All acetates, except the silver salt, are readily soluble in water. Owing, however, to the feeble nature of the acid, some of its salts are easily hydrolyzed, with the formation of insoluble basic salts.

*§ 381. **Ferric Acetate.**—Add sodium acetate to ferric chloride solution. A deep-red colour appears, ferric acetate, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$, being formed in solution.

Now dilute and boil the liquid. A dark-red precipitate of basic ferric acetate, $\text{Fe}(\text{OH})_2\text{C}_2\text{H}_3\text{O}_2$, is formed.³

§ 382. **Silver Acetate.**—Mix together concentrated solutions of sodium or ammonium acetate and silver nitrate. A white

¹ $\text{CH}_3\text{COONa} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{CH}_3\text{COOH}$. Pure acetic acid solidifies at 16° and boils at 118° . It dissolves in water, alcohol, and ether; and is itself a valuable solvent.

² $\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COOH} = \text{C}_2\text{H}_5\text{OOCCH}_3 + \text{H}_2\text{O}$. Sulphuric acid acts as a dehydrating agent.

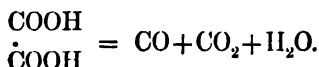
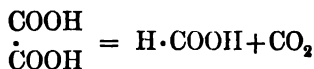
³ $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3 + 2\text{HOH} \rightleftharpoons \text{Fe}(\text{OH})_2(\text{C}_2\text{H}_3\text{O}_2) + 2\text{HC}_2\text{H}_3\text{O}_2$. This reaction is employed in the phosphate separation.

crystalline precipitate of silver acetate is produced. If this precipitate is filtered off, dried and ignited, it decomposes, leaving a residue of metallic silver.¹

Oxalate, (C₂O₄)''

§ 383. **Oxalic Acid**, crystallizing with two molecules of water, H₂C₂O₄ · 2H₂O,² is obtained by oxidizing sugar or starch with concentrated nitric acid, and crystallizing the product from water.

*§ 384. **Action of Heat on Oxalic Acid and Oxalates.**—Heat *crystallized oxalic acid* in an ignition tube. The acid melts in its water of crystallization, and when further heated loses this water and sublimes, a crust of the anhydrous acid being deposited on the sides of the tube. At the same time the anhydrous acid partially decomposes into formic acid and carbon dioxide, and at a higher temperature into carbon monoxide, carbon dioxide, and water:



Heat *calcium oxalate* in an ignition tube; carbon monoxide gas is evolved, and carbonate³ remains, which at a higher temperature loses carbon dioxide, and leaves a residue of oxide.

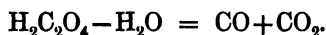
The oxalates of the alkali metals decompose similarly at high temperature; those of easily reducible metals, such as silver and copper, evolve carbon dioxide and leave a residue of metal.

¹ From the loss of weight incurred when a known quantity of a silver salt of an organic acid is ignited, so that a residue of metallic silver remains, the equivalent of the acid can be calculated.

² Being dibasic, oxalic acid forms normal and acid salts, *e.g.* K₂C₂O₄ and KHC₂O₄; also quadroxalates, *e.g.* (KHC₂O₄)₂ · H₂C₂O₄.

³ This is the same inorganic residue which acetate yields. Carbon dioxide, whether combined or not with a base, is the most stable product of decomposition of many "organic" compounds.

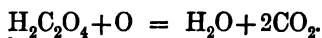
***§ 385. Action of Sulphuric Acid on Oxalic Acid.**—Heat oxalic acid with concentrated sulphuric acid. The elements of water are removed by the sulphuric acid, and carbon monoxide and carbon dioxide are evolved in equal volumes:



The carbon monoxide may be made to burn, though feebly, owing to the presence of carbon dioxide; this latter gas is identified by the lime-water test.

All oxalates are similarly decomposed by sulphuric acid, oxalic acid being first liberated from the salt.

§ 386. Oxidation of Oxalic Acid.—Some oxidizing agents oxidize oxalic acid thus:—



(1) Add dilute potassium permanganate solution to a warm solution of oxalic acid or a soluble oxalate, acidified with sulphuric acid. The permanganate is decolorized¹ and carbon dioxide is evolved.

(2) Add a little manganese dioxide to a solution of oxalic acid containing sulphuric acid, and heat the turbid liquid. The manganese dioxide is dissolved and carbon dioxide is evolved.²

Chlorine and nitric acid have no action on oxalic acid.

***§ 387. Solubilities of Oxalates.**—The oxalates of the alkali metals and magnesium are soluble in water, other oxalates are nearly or quite insoluble in water, but dissolve in dilute hydrochloric acid.

***§ 388. Calcium Oxalate.**—Add ammonium oxalate to calcium chloride solution; a white precipitate of calcium oxalate is formed.

This precipitate is insoluble in acetic acid but soluble in dilute hydrochloric acid.

¹ Upon this reaction depends a volumetric process for the estimation of permanganate, or oxalic acid, one or other solution being of standard strength.

² $\text{H}_2\text{C}_2\text{O}_4 + \text{MnO}_2 + \text{H}_2\text{SO}_4 = \text{MnSO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2$. Manganese dioxide may thus be estimated by the amount of oxalic acid oxidized.

From the latter solution it is reprecipitated by ammonia even in presence of ammonium chloride.¹

***§ 389. Ferrous Potassium Oxalate.**—Add potassium oxalate to ferrous sulphate solution; the solution turns yellow, and if sufficiently concentrated gives a yellow crystalline precipitate of potassium ferrous oxalate,² $K_2Fe(C_2O_4)_2 \cdot H_2O$.

This characteristic yellow colour makes the reaction valuable as a test for oxalate.

§ 390. Silver Oxalate is a white curdy precipitate, slightly soluble in water, and easily soluble in ammonia, but not in dilute nitric acid. When ignited it leaves a residue of metallic silver.

Tartrate, $(C_4H_4O_6)''$

Tartaric Acid, $H_2C_4H_4O_6$, obtained from its acid potassium salt, which occurs in grapes and other fruits, is a dibasic acid, which crystallizes anhydrous.

***§ 391 Action of Heat on Tartaric Acid and Tartrates.**—Heat *tartaric acid* in an ignition tube. It melts, turns brown and chars, giving off inflammable vapours smelling of burnt sugar, and leaves a residue of carbon.

Heat *potassium* or *sodium tartrate*, or *Rochelle salt*.³ These salts behave in the same way, leaving a residue of carbon and alkali carbonate.⁴

Other tartrates are decomposed similarly by heat, leaving a residue of carbon mixed with carbonate, oxide, or metal.⁵

¹ Therefore if an oxalate is present an irregularity is introduced into the scheme of analysis. The oxalate should have been previously destroyed by ignition, the probability of its presence having been indicated by the behaviour of the original substance with sulphuric acid.

² This salt, being a powerful reducing agent, is used as a "developer" in photography. It is not strictly a ferrous salt, but potassium ferro-oxalate.

³ $KNaC_4H_4O_6 \cdot 4H_2O$.

⁴ Again carbonate is the stable, inorganic residue, though the decomposition is too complex to be represented by an equation. The mixture of carbonate and carbon when distilled at high temperature yields the alkali metal (Brunner's process).

⁵ Cf oxalates.

***§ 392. Action of Sulphuric Acid on Tartaric Acid.**—Heat tartaric acid with concentrated sulphuric acid. The mass blackens and evolves carbon monoxide and dioxide, together with sulphur dioxide, due to reduction of the sulphuric acid. The reaction is complex.

***§ 393. Solubilities of Tartrates.**—Normal tartrates, of the alkalis, and sodium hydrogen tartrate, are easily soluble in water; acid tartrates of potassium and ammonium are sparingly soluble; other simple tartrates are but slightly soluble in water; but complex tartrates exist which are soluble.

***§ 394. Potassium Hydrogen Tartrate—Cream of Tartar,** $\text{KHC}_4\text{H}_4\text{O}_6$. Shake together solutions of potassium chloride and tartaric acid; unless the solutions are very dilute, a crystalline precipitate of potassium hydrogen tartrate will be formed.

Repeat the experiment, using sodium hydrogen tartrate solution instead of tartaric acid. The same precipitate is obtained. Add a little potassium or sodium hydroxide to the precipitate; it dissolves owing to the formation of readily soluble normal tartrate, $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ or $\text{KNaC}_4\text{H}_4\text{O}_6$.

***§ 395. Calcium Tartrate.**—Add sodium tartrate, or Rochelle salt solution, to calcium chloride. A granular precipitate of calcium tartrate is produced, which dissolves in excess of alkali tartrate with formation of a soluble complex salt; the precipitate is also soluble in sodium hydroxide solution for the same reason.

Calcium tartrate is soluble in hydrochloric acid, and also in acetic acid on boiling (difference from calcium oxalate). Dissolve a little precipitated calcium tartrate in dilute hydrochloric acid, and add ammonium chloride to the solution and ammonia in excess. On shaking or allowing to stand, calcium tartrate is reprecipitated.¹

§ 396. Potassium Antimonyl Tartrate, tartar emetic $[\text{K}, \text{SbO}, \text{C}_4\text{H}_4\text{O}_6]_2\text{H}_2\text{O}$. Boil together cream of tartar, and antimonious oxide

¹ Therefore tartrate interferes with the course of analysis, and, if present, must be destroyed by ignition.

with water, and filter the solution. On cooling, crystals of tartar emetic separate, which readily dissolve again in pure water without decomposition. This is not a characteristic of antimonious salts, which are hydrolyzed by water, nor of antimonyl compounds, which are insoluble. No doubt a complex ion is present; and this compound is therefore best regarded as the potassium salt of antimonyl tartaric acid, $K[SbOC_4H_4O_6]$.¹

§ 397. **Complex Tartrates.**—Other metallic oxides form complex ions with tartaric acid, notably those of copper and ferric iron.

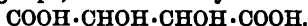
Add to solution of copper sulphate, Rochelle salt and sodium hydroxide; the alkali causes no precipitation, but there is formed instead a deep-blue solution containing alkali cupri-tartrate.²

Perform a similar experiment with ferric chloride; no precipitate is formed on adding alkali.³

*§ 398. **Silver Reduction Test.**—A neutral tartrate solution reduces ammoniacal silver nitrate with separation of silver. Carefully clean a test tube, boiling in it a little caustic soda solution to remove all grease from the inner surface; then rinse the tube with water, and place in it a little silver nitrate solution. Add to this solution very dilute ammonia, made by diluting a few drops of the bench reagent with half a testtubeful of water, until the precipitated silver oxide is nearly, but not quite redissolved. Next add a little solution of a neutral tartrate, such as Rochelle salt, and gradually warm the solution by placing the test tube containing it in a beaker of cold water, which is then heated nearly to the

¹ Rochelle salt, $KNaC_4H_4O_6$, is used to retain antimonious and stannous compounds in solution, by the formation of complex ions, in their estimation by iodine titration in presence of sodium bicarbonate.

² This is Fehling's solution; and it is employed for the estimation of glucose and other sugars, because it is reduced by them with the precipitation of cuprous oxide. The formation of complex anions by combination with cupric and ferric hydroxide is due to the presence in tartaric acid of hydroxyl (OH), as distinct from carboxyl (COOH) groups; this is shown by the constitution:



³ Therefore if tartrate is present in a mixture it must be destroyed by ignition, or iron will not be precipitated by ammonia.

boiling point. A bright silver mirror will be deposited on the inner surface of the test tube.

CLASS B(i)

Chromate and Dichromate, $(\text{CrO}_4)''$, $(\text{Cr}_2\text{O}_7)''$.

[See also under Chromium, § 143 *et seq.*]

* § 399. **Action of Heat on Chromates.**—Potassium chromate melts at a high temperature without decomposition; the dichromate melts below a red heat, and decomposes at a white heat into oxygen, chromic oxide, and the normal chromate.

Ammonium chromate and dichromate give nitrogen, water, and chromic oxide when ignited. Chromates of mercury give oxygen, chromic oxide, and metal on ignition; other chromates are stable when moderately heated. Chromic anhydride, CrO_3 , yields Cr_2O_3 and oxygen when heated.

* § 400. **Action of Sulphuric Acid.**—Heat a little powdered potassium dichromate with concentrated sulphuric acid. Oxygen is evolved, and the liquid turns dark green, chromic sulphate being formed.¹

* § 401. **Solubilities of Chromates.**—The chromates of the alkalis, and of calcium and magnesium, are readily soluble in water; strontium chromate is sparingly soluble; other chromates are insoluble in water, but soluble in dilute mineral acids unless they have been ignited. Barium and lead chromates are insoluble in acetic acid.

* § 402. **Behaviour of Chromates in Analysis.**—Since chromic acid oxidizes hydrogen sulphide, precipitating sulphur and changing from orange to green, this reaction will take place during analysis unless chromate when present has been previously reduced. Sulphurous acid may be used for this purpose, but an objection to its use is that the sulphuric acid formed

¹ $2\text{K}_2\text{Cr}_2\text{O}_7 + 10\text{H}_2\text{SO}_4 = 4\text{KHSO}_4 + 2\text{Cr}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} + 3\text{O}_2$. The above experiments show that in absence of free alkali, CrO_3 and its derivatives under suitable conditions pass by loss of oxygen into the more stable Cr_2O_3 or its salts, even when no reducing agent is present.

will precipitate lead and barium if these metals are present. Hot concentrated hydrochloric acid also effects reduction; and it is generally best to reduce a chromate by heating the solid substance with this reagent, evaporating off most of the acid, and diluting well with water. Thus a solution is obtained suitable for the metal reactions.

Manganate and Permanganate, $(\text{MnO}_4)''$, $(\text{MnO}_4)'$

These acidic radicles have been studied under Manganese (§§ 191–2).

*§ 403. *Action of Heat on Permanganates.*—Heat powdered potassium permanganate in an ignition tube. Oxygen is evolved, and a mixture of potassium manganate, which is stable towards heat, and manganese dioxide remains.

*§ 404. *Action of Sulphuric Acid.*—*Dilute.*—Add dilute sulphuric acid to crystals of potassium permanganate, and boil; oxygen is evolved, and manganese dioxide separates.¹

**Concentrated.*—Add a few drops of strong sulphuric acid to a single crystal of potassium permanganate; the salt dissolves, forming a dark-green solution.² Carefully heat the solution; an explosion takes place with flashes of light; oxygen is evolved, and brown manganese dioxide separates; eventually the acid becomes nearly colourless, and contains in solution potassium hydrogen sulphate and manganous sulphate.³ Potassium manganate is decomposed similarly.

*§ 405. *Solubilities of Manganates and Permanganates.*—The alkali manganates are soluble in water, but are decomposed by excess of water (see under Manganese). Other manganates



² Containing permanganic sulphate:



Probably oily drops will also be seen; these are permanganic anhydride, Mn_2O_7 .

³ $4\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 = 4\text{KHSO}_4 + 4\text{MnSO}_4 + 6\text{H}_2\text{O} + 5\text{O}_2$. Thus a salt of MnO is the final product. Compare the action of sulphuric acid on potassium chromate, when the sulphate of Cr_2O_3 is formed.

are insoluble in water. All permanganates are soluble in water, silver permanganate but slightly.

* § 406. **Behaviour of Permanganates in Analysis.**—Permanganates, like dichromates, oxidize hydrogen sulphide, and should be reduced first. Reduction may be effected by sulphurous acid, or, better, by boiling with hydrochloric acid.

CLASS B(ii)

Arsenite and Arsenate, $(\text{AsO}_2)'$ or $(\text{AsO}_3)'''$, $(\text{AsO}_4)'''$

[See also under Arsenic, § 122 *et seq.*]

The following tests are distinctive:—

(1) Precipitation of Silver Salts

* § 407. *Arsenite.*—Dissolve some arsenious oxide in a little dilute ammonia, and dilute the solution well. With this arsenite solution silver nitrate gives a pale-yellow precipitate, which is soluble in ammonia as well as in dilute nitric acid.

Arsenate.—Show that a solution of sodium arsenate gives with silver nitrate a chocolate-coloured precipitate soluble in both ammonia and dilute nitric acid.

(2) Reduction of Alkaline Cupric Solution

Arsenite.—Add to some alkali arsenite solution a few drops of copper sulphate solution; a grass-green precipitate—Scheele's green, CuHAsO_3 —is formed. Add to this precipitate sodium hydroxide in excess, and heat to boiling; a deep-blue solution is formed, which becomes paler on heating, and deposits red cuprous oxide.

Arsenate.—Repeat the same operations with arsenate solution. There is a pale-blue precipitate of cupric arsenate, and a blue solution on adding alkali; but on boiling, if the solution was quite clear, no precipitate is formed.¹

Therefore arsenite can be detected in presence of arsenate by the reduction of an alkaline cupric solution.

¹ Arsenate here performs a similar function to tartrate in "Fehling's solution"; whilst arsenite is comparable with glucose in its power of reducing alkaline cupric solutions.

(3) Precipitation of Magnesium Ammonium Arsenate

Arsenate gives with magnesium sulphate in presence of ammonium chloride and ammonia a white precipitate of magnesium ammonium arsenate, $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$. *Arsenite* gives no precipitate.

*** § 408. Separation of Arsenite and Arsenate.**—These two acidic radicles may be separated and identified by precipitating the arsenate as above, filtering, acidifying the filtrate with hydrochloric acid, and passing hydrogen sulphide through it. If arsenite is present there will be an immediate precipitation of yellow arsenious sulphide. If phosphate might also be present the precipitate with magnesium sulphate must be examined according to § 421.

Phosphate, $(\text{PO}_4)''$

§ 409. Phosphoric Acid, H_3PO_4 , is tribasic, forming three classes of salts, $\text{M} \cdot \text{H}_2\text{PO}_4$, $\text{M}'_2\text{HPO}_4$, $\text{M}''_3\text{PO}_4$.

*** § 410. Action of Heat on Phosphoric Acid and the Phosphates.**—Heat crystallized phosphoric acid, or its concentrated solution, in a porcelain dish, or preferably in platinum. The acid melts,¹ and loses water, forming first pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$,² and then metaphosphoric acid, HPO_3 , which at a red heat volatilizes without yielding the anhydride. After this heating a sticky hygroscopic mass of metaphosphoric acid remains. This will crystallize if kept away from moisture, yielding "glacial phosphoric acid".

The alkali phosphates yield similar dehydration products when heated.

Heat ordinary sodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, in an ignition tube or on platinum foil. The salt fuses in its water of crystallization, and when the water has been volatilized,

¹ The M.P. of H_3PO_4 is 39° . The acid is generally sold in concentrated solution as syrupy phosphoric acid.

² $2\text{H}_3\text{PO}_4 = \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$; $\text{H}_4\text{P}_2\text{O}_7 = 2\text{HPO}_3 + \text{H}_2\text{O}$.

and the residue ignited until the tube begins to fuse, sodium pyrophosphate¹ remains. Keep this residue.

Heat microcosmic salt, $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, similarly. This salt fuses, loses water and ammonia, and finally leaves a glassy residue² of sodium trimetaphosphate³ (NaPO_3)₃. Also keep this residue.

Normal phosphates, *e.g.* Na_3PO_4 , undergo no chemical change when ignited, but those of the alkalis fuse.

§ 411. **Blue Cobalt Phosphate formed in the Dry Way.**—Just as cobaltous oxide combines with sodium metaborate and boric anhydride in the borax bead to form a blue borate (§ 10), so it combines with sodium metaphosphate to form a blue glassy phosphate, NaCoPO_4 . Moreover, when phosphates are heated on charcoal with cobalt nitrate, they often yield a blue mass for the same reason. This must not be mistaken for the blue compound which cobalt oxide forms with alumina.

§ 412. **Reduction of Phosphates.**—Phosphates are so stable that they cannot be reduced in solution. Fusion with magnesium powder reduces them to phosphide.

Heat in an ignition tube an intimate mixture of sodium phosphate and magnesium powder, until the magnesium burns at the expense of the oxygen of the phosphate. When the dark mass is cold, drop water upon it; phosphine,⁴ PH_3 , is evolved, and is recognized by its smell and its inflammability.

§ 413. **Action of Acids on Phosphates.**—Since phosphoric acid is neither volatile, nor easily yields volatile decomposition products, sulphuric or other acid, dilute or concentrated, has no action on phosphates beyond liberating phosphoric acid in solution.

¹ $2\text{Na}_2\text{HPO}_4 = \text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$.

² This is used as a basis for "phosphate beads", see § 12.

³ $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O} = \text{NaPO}_3 + \text{NH}_3 + 5\text{H}_2\text{O}$. NaH_2PO_4 similarly forms NaPO_3 . It will be observed that a molecule of sodium salt containing two atoms of sodium gives on ignition a product containing four such atoms, whilst a molecule containing a single atom of sodium gives a product still containing that one atom. Ammonium phosphates yield metaphosphoric acid on ignition.

⁴ $\text{Na}_3\text{PO}_4 + 4\text{Mg} = \text{Na}_3\text{P} + 4\text{MgO}$; $\text{Na}_3\text{P} + 3\text{H}_2\text{O} = 3\text{NaOH} + \text{PH}_3$.

***§ 414. Solubilities of Phosphates.**—Phosphates of the alkali metals, and the acid phosphates of the alkaline earths, are soluble in water; other phosphates are insoluble. All these insoluble phosphates are soluble in dilute hydrochloric acid; ferric phosphate is insoluble, and aluminium and chromium phosphates are sparingly soluble in dilute acetic acid, in which other phosphates are soluble.

***§ 415. Behaviour of Phosphates in Analysis.**—Owing to the non-volatility of phosphoric acid, a phosphate which is insoluble in water, and has been dissolved in dilute acid, is reprecipitated on neutralizing the acid by ammonia. This fact causes a complication in the course of analysis, which has been dealt with in § 42-3.

§ 416. Hydrolysis of Phosphates.—Phosphoric acid is not one of the strongest acids, and its salts are somewhat hydrolyzed by water.

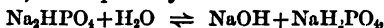
Dissolve a little crystallized sodium phosphate, $\text{Na}_3\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, in water, and examine its reaction towards litmus paper; it reacts alkaline¹ owing to hydrolysis.

Some phosphates, practically insoluble in water, such as ferric phosphate, FePO_4 , and normal calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, are hydrolyzed by prolonged action of water, producing a basic salt, and free acid in solution.

***§ 417. Silver Phosphate.**—Add sodium phosphate solution to silver nitrate; a yellow precipitate of silver phosphate is produced² (compare silver arsenate). This precipitate is soluble

¹ The ionic theory gives the following explanation of the phenomenon:—Phosphoric acid being a polybasic acid, and of only moderate strength, does not produce in solution the free ions 3H^+ and PO_4^- , but 2H^+ and HPO_4^- . The above salt would therefore give the ions 2Na^+ and HPO_4^- ; and, there being no free H^+ or OH^- ions, the solution would be neutral if ionization alone took place.

Hydrolysis, however, occurs probably thus:—



and the ionic dissociation of NaH_2PO_4 into $(\text{Na}^+, \text{H}^+)$ and HPO_4^- is less complete than that of NaOH into Na^+ and OH^- at equivalent dilution; therefore OH^- ions predominate, and the solution reacts alkaline.

² $\text{Na}_2\text{HPO}_4 + 3\text{AgNO}_3 = \text{Ag}_3\text{PO}_4 + 2\text{NaNO}_3 + \text{HNO}_3$. Thus by mixing an alkaline and a neutral solution, an acid liquid is produced. This may be proved by testing with litmus paper.

in dilute nitric acid, and also, like so many other silver salts, in ammonia.

*§ 418. **Magnesium Ammonium Phosphate.**—Add to sodium phosphate ammonium chloride, ammonia, and magnesium sulphate; a white crystalline precipitate of magnesium ammonium phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, is produced.¹ (Compare the corresponding arsenate.)

*§ 419. **Ammonium Phosphomolybdate.**—It was shown under the alkali metals that ammonium phosphomolybdate is practically insoluble in water. Since it is easily produced from a nitric acid solution of ammonium molybdate and a phosphate, and is thus formed in acid solution, it constitutes a valuable and universal test for phosphate.

Add to a few c.cm. of ammonium molybdate solution² two or three drops³ of sodium phosphate solution, and gently warm the mixture. The liquid turns yellow, and a yellow precipitate of ammonium phosphomolybdate separates (compare the corresponding arsenate precipitate).⁴

Allow the precipitate to settle, and pour ammonia upon it after decanting the supernatant liquid; the precipitate dissolves.⁵ If ammonium chloride and magnesium sulphate are now added to the solution, magnesium ammonium phosphate will be precipitated.⁶

¹ The conditions of formation of this precipitate have been studied under magnesium, § 215.

² If the molybdate solution has been made without the addition of concentrated nitric acid, this acid must be added to the quantity taken until the precipitate of molybdic acid first formed is redissolved.

³ The molybdate solution must be in large excess over the phosphate; if the opposite obtains the precipitate will not form. The precipitate is complex; it contains 12 molecules of MoO_3 combined with $(\text{NH}_4)_2\text{PO}_4$; hence the necessity for excess of molybdate.

⁴ Ammonium nitrate assists precipitation of both salts. Ammonium arsenomolybdate does not form if tartaric acid is present (distinction between phosphate and arsenate). For the benzidine test, see § 478.

⁵ Alkalis decompose the complex acid, yielding in solution a mixture of phosphate and molybdate.

⁶ These two successive reactions are employed in the gravimetric estimation of phosphates insoluble in water.

***§ 420. DISTINCTION BETWEEN PHOSPHATE AND ARSENATE**

Reagent.	Phosphate.	Arsenate.
Silver nitrate to neutral solution.....	yellow precipitate.	brown precipitate.
Ammonium molybdate solution.....	yellow precipitate on gently warming.	yellow precipitate on boiling.

§ 421. Detection of Phosphate and Arsenate when occurring together.—Arsenic acid can be reduced by sulphurous acid, and the resulting arsenious acid will at once give a yellow precipitate of arsenious sulphide with hydrogen sulphide; phosphate remains unchanged, and can be detected in the filtrate from this precipitate.

Add to the mixed solution of phosphate and arsenate ammonium chloride and ammonia in excess,¹ and then magnesium sulphate. Filter and wash the precipitate, and dissolve it in dilute hydrochloric acid. Pass sulphur dioxide through this solution for a few minutes,² and boil until the gas is no longer smelt. Then pass hydrogen sulphide into the solution till no more precipitate forms, and filter.

Precipitate of yellow arsenious sulphide proves **arsenate**.

Filtrate.—Boil off excess of hydrogen sulphide, and add ammonia in excess. White crystalline precipitate proves **phosphate**.³

§ 422. Reactions of Pyrophosphate and Metaphosphate.—The sodium salts of these acidic radicles have been obtained above by the ignition of sodium hydrogen phosphate and micro-

¹ If ammonia causes a precipitate, the phosphate and arsenate must be precipitated together by boiling with excess of ammonium molybdate; this precipitate is then filtered, washed, and dissolved in ammonia.

² Or boil with sulphurous acid solution, though this is not so efficient as the gas. If, however, hydrogen sulphide is passed through the hot solution, it will complete the reduction, and eventually precipitate all the arsenic, though the process is rather tedious.

³ This may be confirmed by filtering, washing the residue on the filter, and pouring silver nitrate solution upon it; yellow silver phosphate will be formed.

cosmic salt respectively. Dissolve the products in cold water,¹ and employ the solutions for the following tests. The reactions of orthophosphate are set forth side by side with those of pyro- and metaphosphate for comparison; the three acids are readily distinguished by means of these tests.

§ 423. REACTIONS OF PHOSPHATES

Reagent.	Ortho-	Pyro-	Meta-
Silver nitrate...	yellow precipitate, soluble in ammonia and dilute nitric acid	white precipitate, soluble in ammonia and dilute nitric acid.	white, curdy precipitate in strong solution; soluble in excess of metaphosphate.
Barium chloride	white precipitate, soluble in dilute acetic acid.	white precipitate, insoluble in dilute acetic acid.	white precipitate, insoluble in dilute acetic acid.
Albumen and dilute acetic acid	no coagulation.	no coagulation.	coagulation. ²

Phosphite and Hypophosphite, $(\text{HPO}_3)''$, $(\text{H}_2\text{PO}_2)'$

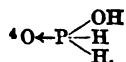
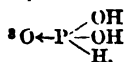
The two lower oxyacids of phosphorus, phosphorous acid, H_3PO_3 ,³ and hypophosphorous acid, H_3PO_2 ,⁴ together with their salts, display certain similarities and differences.

§ 424. Similarities between Phosphite and Hypophosphite.—

1. The acids and their salts yield phosphine and phosphate on ignition.⁵

¹ The pyro- and meta-salts revert to the ortho-form in solution, slowly in the cold, but rapidly on boiling. Hence they are precipitated by ammonium molybdate.

² That is to say, albumen forms an insoluble compound with free metaphosphoric acid liberated from its salt by acetic acid. If the solution was previously acid, the addition of acetic acid will not be necessary.



⁵ $4\text{H}_3\text{PO}_3 = 3\text{H}_3\text{PO}_4 + \text{PH}_3$, and $2\text{H}_3\text{PO}_2 = \text{H}_3\text{PO}_4 + \text{PH}_3$. Owing to ignition the salts yield pyro- or metaphosphate.

Heat in ignition tubes (a) sodium phosphite, (b) sodium hypophosphite. In each case an inflammable gas is evolved which burns like phosphorus, and red phosphorus is deposited in the tube. Hypophosphite gives the gas more readily than phosphite.

On boiling the residues with water, filtering, and adding to the filtrate ammonium chloride, ammonia, and magnesium sulphate, phosphate will be found in each case.

2. Both acids and their salts, although without action on dilute sulphuric acid, reduce the concentrated acid, when heated with it, causing evolution of sulphur dioxide. Hypophosphite when present in large quantity separates sulphur as well.

3. Neutral salt solutions of the two acids reduce silver and mercuric salts similarly.

Silver nitrate solution gives white precipitates both with phosphite and hypophosphite solutions, which begin to turn brown on standing, and are quickly reduced to metallic silver on warming.

Mercuric chloride gives in each case a white precipitate of mercurous chloride, which is reduced to grey mercury on heating with excess of the reducing solution.

In all these cases phosphite and hypophosphite are oxidized to phosphate.

4. Both acids are similarly reduced by nascent hydrogen to phosphine.

Add solution of sodium phosphite to zinc and hydrochloric acid in a test tube, and place a small crystal of silver nitrate on filter paper covering the top of the tube.

The crystal turns first yellow and then black.¹ A similar result is obtained with hypophosphite.

§ 425. Differences between Phosphite and Hypophosphite.

1. *Solubilities of Barium Salts.*—Add neutral phosphite solution to barium chloride; white barium phosphite² is precipitated; it is soluble in acetic acid.

Add neutral hypophosphite solution to barium chloride. There is no precipitate, since barium hypophosphite³ is soluble in water.

2. *Behaviour towards Copper Sulphate.*—The superior reducing power of hypophosphite is shown by its action on copper sulphate solution. Add neutral phosphite solution to copper sulphate; light-

¹ $\text{H}_3\text{PO}_3 + 6\text{H} = 3\text{H}_2\text{O} + \text{PH}_3$. Phosphine reacts with silver nitrate exactly like arsine in Gutzeit's test, *q.v.* § 120.

² Only the alkali phosphites are readily soluble in water, other phosphites are slightly soluble or insoluble, though soluble in dilute acids.

³ All hypophosphites are soluble in water.

blue copper phosphite is precipitated. Add acetic acid and boil; the precipitate dissolves, but no reduction takes place.

Add neutral hypophosphite to copper sulphate; there is no precipitate, but, on heating, brown cuprous hydride is precipitated.¹

The same reaction takes place in presence of acetic acid, but if hydrochloric acid is present, a colourless solution of cuprous chloride is formed.

Sulphate, (SO₄)"

*§ 426. Sulphuric Acid.—Sulphates are derived from sulphuric acid, H₂SO₄, an oily liquid of specific gravity 1·84. When this acid is heated white fumes of sulphur trioxide, SO₃, are evolved, a 98-per-cent acid distilling at 338°. The concentrated acid dissolves lead, barium,² and other sulphates, forming acid sulphates,³ and on this account the commercial acid generally contains a little lead sulphate as an impurity, which is precipitated on dilution with water.⁴

The concentrated acid is very hygroscopic⁵ and corrosive. This may be shown by the following experiments:—

- (1) Drop a crystal of copper sulphate into sulphuric acid; the crystal gradually becomes nearly white, and falls to powder, owing to the removal of its water of crystallization.
- (2) Pour sulphuric acid with stirring into strong sugar solution. A mass of carbon⁶ is liberated, which

¹ $3\text{H}_2\text{PO}_3 + 4\text{CuSO}_4 + 6\text{H}_2\text{O} = 3\text{H}_2\text{PO}_4 + 4\text{H}_2\text{SO}_4 + 4\text{CuH}$. Cuprous hydride dissolves in concentrated hydrochloric acid thus: $\text{CuH} + \text{HCl} = \text{CuCl} + \text{H}_2$, and is by this means distinguished from metallic copper.

² This may be shown by adding sulphuric acid little by little to a drop of solution of lead nitrate or barium chloride; the white precipitate first formed will redissolve, and appear again when the acid solution is poured into water.

³ *E.g.* Pb[HSO₄]₂ and Ba[HSO₄]₂.

⁴ Sulphuric acid combines with water to form a hydrate with evolution of much heat. If water is poured into the concentrated acid this may cause the acid to spurt; in diluting, therefore, the acid should always be poured into water that the heat may be diffused through it, and the temperature thus kept down.

⁵ On this account it is a valuable drying agent.

⁶ Sugar is a carbohydrate, and the elements of water are removed from it by the acid: $\text{C}_{12}\text{H}_{22}\text{O}_{11} = 12\text{C} + 11\text{H}_2\text{O}$.

swells up, the heat of the reaction causing some of the water to be turned into steam.

- (3) Place a drop of dilute sulphuric acid in the centre of a piece of filter paper, and dry the paper in the steam oven or by waving it over a flame. The paper¹ will be charred where it was wetted by the dilute acid.

Sulphuric acid, H_2SO_4 , is dibasic, forming two classes of salts: acid and normal sulphates, $\text{M}\cdot\text{HSO}_4$ and $\text{M}_2\cdot\text{SO}_4$.

*§ 427. *Action of Heat on the Sulphates.*—Acid sulphates, e.g. NaHSO_4 , evolve water and sulphuric anhydride when heated. Pyrosulphate, $\text{Na}_2\text{S}_2\text{O}_7$, is an intermediate product formed by gentle ignition.²

The normal sulphates of the alkali metals melt without decomposition; those of the alkaline earth metals do not melt, but are stable on ignition; sulphates of less basigenic metals lose sulphuric anhydride when heated, leaving a residue of basic sulphate or oxide.³

Occasionally sulphur dioxide is evolved, owing to self-oxidation and reduction.⁴

*§ 428. *Reduction of Sulphates.*—Sulphates are not reducible in solution, but when heated with sodium carbonate on charcoal give a mixture of sodium sulphide and the carbonate or oxide of the metal.

§ 429. *On Charcoal.*—Mix a little calcium sulphate with anhydrous sodium carbonate, and thoroughly heat the mixture in a cavity on charcoal.⁵ When the mass is cool remove it, place it on a bright silver coin, and moisten it with water.

¹ Paper is cellulose, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, also a carbohydrate.

² $2\text{NaHSO}_4 = \text{Na}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$.
 $\text{Na}_2\text{S}_2\text{O}_7 = \text{Na}_2\text{SO}_4 + \text{SO}_3$. }

³ The behaviour of alum when heated is instructive. Potassium alum loses water of crystallization and SO_3 , leaving a mixture of K_2SO_4 and Al_2O_3 ; ammonium alum leaves a residue of Al_2O_3 only.

⁴ E.g. $\text{SnSO}_4 = \text{SnO}_2 + \text{SO}_2$.

⁵ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 + 4\text{C} = \text{CaCO}_3 + \text{Na}_2\text{S} + 4\text{CO}$.

A black stain will be formed on the silver,¹ and if a drop of dilute hydrochloric acid is added to the mass, hydrogen sulphide will be smelt.

§ 430. *In the Reducing Flame.*—Moisten a little powdered barium sulphate with water, and heat some of it upon a loop of platinum wire in the inner blowpipe flame;² add a drop of dilute hydrochloric acid to a drop of lead acetate in a watch-glass, and dip the loop into the mixture; the white lead chloride will be turned brown, showing the presence of sulphide.

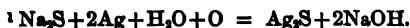
*§ 431. *Solubilities of Sulphates.*—Sulphates of lead and barium are practically insoluble in water, and strontium sulphate is very slightly soluble. Mercurous, silver, and calcium sulphates are sparingly soluble in water; all other normal sulphates,³ which are not hydrolyzed⁴ by water, are soluble in it, as well as all acid sulphates. There are a number of basic sulphates, insoluble in water, which dissolve in dilute acid.

*§ 432. *Barium Sulphate.*—Add dilute sulphuric acid to barium chloride solution; a finely divided⁵ white precipitate is formed which is insoluble in acids.

Since barium sulphate is an “insoluble” substance, if it is given for analysis, it must be decomposed by fusion with a mixture of potassium and sodium carbonates (see § 29).

§ 433. *Lead Sulphate.*—Precipitate lead acetate solution with dilute sulphuric acid; filter, and wash the precipitate with hot water.

Show that the precipitated lead sulphate is soluble (1) in



² Pure barium sulphate will give no flame coloration, but when the sulphide formed by this treatment has been converted into chloride by hydrochloric acid the coloration will be obtained.

³ Anhydrous chromic sulphate, however, like the chloride, is anomalous, being insoluble in water and acids.

⁴ Mercuric sulphate (*q.v.*) is a good example of a sulphate hydrolyzed by water

⁵ This precipitate, formed in the cold, is difficult to filter; if both solutions are boiling when precipitation takes place the salt is more granular, and filters better.

boiling dilute nitric acid; (2) in sodium hydroxide solution; and that if this solution is acidified with hydrochloric acid, the lead crystallizes as chloride;¹ (3) in ammonium acetate solution.

Persulphate, (S₂O₈)''

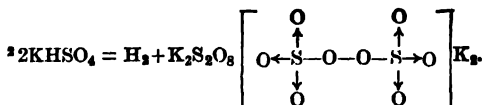
§ 434. Potassium persulphate, K₂S₂O₈, separated at the anode during the electrolysis of potassium hydrogen sulphate² solution, is a white crystalline salt, sparingly soluble in water. The only other persulphates likely to be met with are those of ammonium and barium.

§ 435. Action of Heat on Persulphate.—Heat potassium persulphate in an ignition tube; it fuses, giving off sulphur trioxide and ozonized oxygen, and leaving a residue of sulphate.³

§ 436. Action of Sulphuric Acid on Persulphate.—The dilute acid has no specific action on potassium persulphate, but concentrated sulphuric acid at 0° C. dissolves this salt, producing Caro's acid.⁴

§ 437. Action of Water on Persulphate.—Drop a little potassium persulphate into cold water in a test tube; add a piece of blue litmus paper and a few drops of barium chloride solution. The litmus shows that the solution is neutral, and the barium chloride causes no precipitate if the salt was pure,⁵ because barium persulphate is soluble in water. Now boil the liquid; it becomes acid, barium sulphate is precipitated, and ozonized oxygen escapes, as may be shown by starch potassium

¹ This is the best way to treat lead sulphate given for analysis.



³ K₂S₂O₈ = K₂SO₄ + SO₃ + O. That the oxygen contains ozone may be proved by the purple colour produced on starch potassium iodide paper held at the mouth of the tube.

⁴ This is H₂SO₅ [HO·O·SO₃·OH], for an account of which the theoretical textbooks should be consulted.

⁵ A trace of sulphate is generally found.

iodide paper, or the ozone may actually be smelt at the mouth of the tube.¹

§ 438. **Oxidation by Persulphate.**—The oxygen which is liberated on heating persulphate alone or with water may be caused to oxidize various substances in solution.²

(a) Heat potassium persulphate with dilute hydrochloric acid; chlorine is evolved; iodine is similarly liberated from potassium iodide.

(b) Heat potassium persulphate with a little ferrous sulphate solution; the iron is oxidized to the ferric state.

(c) Add a little manganous sulphate solution to potassium persulphate and then sodium hydroxide; dark-brown hydrated manganese dioxide is at once precipitated.

From cobalt, nickel, copper, and silver salts the higher oxides are similarly precipitated.

Potassium permanganate is not decolorized by persulphate;³ this reaction serves to distinguish persulphate from hydrogen peroxide, which in other respects it resembles as regards oxidizing action.

Silicate, $(\text{SiO}_4)^{4-}$, $(\text{SiO}_3)^{2-}$

*§ 439. **Orthosilicic Acid**, H_4SiO_4 or $\text{Si}(\text{OH})_4$, is an exceedingly weak acid, known only in aqueous solution; "gelatinous silica" corresponds nearly to **metasilicic acid**, H_2SiO_3 .

Dissolve some soluble glass⁴ in water:

(1) Add dilute acetic acid to a dilute solution; no

¹The following is the reaction: $\text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} = \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{O}$. Persulphate may be estimated by the acid, or by the total sulphate produced on boiling; or, as will be illustrated in the next section, by the oxidation of ferrous solution.

²For the reaction of persulphate with benzidine, see § 486.

³This is because the available oxygen in persulphate is internal (see structure, note 2, previous page), and permanganic acid cannot attack it. Indeed, persulphate, in presence of sulphuric acid and silver nitrate as a catalyst, will oxidize manganous ion to permanganate.

⁴Obtained by fusing silica with sodium carbonate; soda and silica are usually present in the ratio $\text{Na}_2\text{O} : (2 \text{ to } 3) \text{ SiO}_2$.

precipitate is formed, but orthosilicic acid remains in solution.¹ Warm this solution; if it is of suitable strength gelatinous silica will separate.

- (2) Add acetic acid to a more concentrated solution; gelatinous silica separates at once.²
- (3) Acidify with hydrochloric acid a very dilute solution of soluble glass, and evaporate it. A point is reached sooner or later, according to the strength of the solution, at which gelatinous silica³ separates; and, on continuing the heating, anhydrous silica remains, together with sodium chloride, as a fine white powder, insoluble in hydrochloric acid,⁴ somewhat soluble on lengthened boiling in sodium carbonate solution, and readily soluble in boiling caustic alkali.

§ 440. **Silica**, whether occurring as a powder or in a crystalline form, is insoluble in all acids except hydrofluoric acid. Pour a little hydrofluoric acid solution on silica in a test tube; the silica easily dissolves, forming hydrofluosilicic acid in solution.⁵

Heat a little silica with hydrofluoric acid, and a drop of sulphuric acid, in a platinum capsule. No residue will be left after evaporation and ignition, provided the silica was pure.⁶

* § 441. **Detection of Silica by Microcosmic Salt Bead.**⁷—Fuse some microcosmic salt in a loop of platinum wire heated in

¹ And may be obtained in a concentrated state by "dialysis".

² The reactions in the two cases are:—

(1) $\text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} + 2\text{HCl} = 2\text{NaCl} + \text{H}_4\text{SiO}_4$;

(2) $\text{Na}_2\text{SiO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{SiO}_2$.

³ Gelatinous silica, when freshly precipitated, is soluble in dilute acids and alkalis; when air-dried it is slightly soluble in acids, and easily soluble in alkalis. The higher the temperature at which it is dried, the less soluble it becomes.

⁴ Thus the silica is rendered insoluble by a process of polymerization by which a complex structure is formed. In this respect silica is utterly different from carbon dioxide, its analogue according to the periodic system.

⁵ $\text{SiO}_2 + 6\text{HF} = 2\text{H}_2\text{O} + \text{H}_2\text{SiF}_6$.

⁶ $\text{H}_2\text{SiF}_6 = 2\text{HF} + \text{SiF}_4$. Both of the products of decomposition of H_2SiF_6 are gaseous. Sulphuric acid is added to prevent the hydrolysis of silicon tetrafluoride by water, by which silicic acid would be regenerated:

$3\text{SiF}_4 + 3\text{H}_2\text{O} = \text{H}_2\text{SiO}_3 + 2\text{H}_2\text{SiF}_6$.

⁷ See § 12 for the sodium carbonate bead test for silica.

the blowpipe flame; introduce into the transparent bead a little powdered silica or silicate, and again fuse. The silica will not dissolve in the bead, though a metallic oxide with which it may be combined will do so; consequently particles of silica will be seen floating in the bead, or will make it opaque, and may thus be identified.

§ 442. **Action of Heat on Silicates.**—Beyond promoting fusion in some cases, heat has no specific action on silicates.

§ 443. **Action of Sulphuric Acid.**—Dilute sulphuric acid separates gelatinous silica from soluble silicates, and from some hydrated silicates insoluble in water.

Concentrated sulphuric acid has a similar action. Many silicates, otherwise insoluble, are slowly decomposed when heated with concentrated sulphuric acid.

* § 444. **Solubilities of Silicates.**—Those of the alkalis are the only silicates soluble in water. Many hydrated natural and artificial silicates are decomposed by dilute hydrochloric acid.

There are therefore three classes of silicates:

- (1) Alkali silicates soluble in water.
- (2) Hydrated silicates decomposed by dilute hydrochloric acid, with separation of gelatinous silica.
- (3) Insoluble silicates.

* § 445. **Treatment of Insoluble Silicates.**

(1) *Fusion with Alkali Carbonate.*—The finely-powdered silicate¹ is mixed with about six times its weight of fusion mixture,² and fused over the blowpipe flame—preferably in platinum—being kept liquid for five or ten minutes. It is then quickly cooled,³ the mass broken up with water, dilute hydrochloric⁴ acid added in excess, and the liquid evaporated to dryness and ignited in a porcelain dish. On warming the residue with acid, insoluble silica will remain, while the metals

¹ The silicate must be reduced to an impalpable powder by rubbing in an agate mortar, in order that fusion may be effective.

² A mixture of sodium and potassium carbonates. See also § 29.

³ If the red-hot platinum crucible or boat is plunged into cold water, the mass will contract, so as to be readily removable.

⁴ If silver salts are present dilute nitric acid must be used. If lead occurs, the silica must be thoroughly washed from lead chloride with hot water.

will go into solution as chlorides, together with the alkali chlorides. The silica is filtered off, and the analysis proceeded with.

(2) *Evaporation with Hydrofluoric and Sulphuric Acids.*—The method of fusion cannot be applied if the alkali metals are to be tested for; in this case the silica is eliminated by heating the finely-powdered silicate with hydrofluoric acid, and a drop of sulphuric acid, in a platinum capsule, until most of the latter acid, remaining after the reaction with hydrofluoric acid is finished, has been expelled. Sulphates of the metals¹ now remain, together with free sulphuric acid, and their solution in water² is suitable for analysis.

* § 446. *Behaviour of Silicates in Analysis.*—Make a solution of sodium silicate in water, and add to it ammonium chloride solution; gelatinous silica is precipitated.³

Modify the experiment by adding to dilute sodium silicate solution a little dilute hydrochloric acid, followed by excess of ammonia; the same precipitate is obtained.

Therefore since silicic acid, present in acid solution, is precipitated by ammonia, its presence interferes with the course of analysis. Consequently all silica must be rendered insoluble by the evaporation of the solution to dryness with hydrochloric acid, before ammonium chloride and ammonia are added to precipitate the metals of the iron group.

Silicifluoride (Fluosilicate), $(\text{SiF}_6)''$

Hydrofluosilicic acid, H_2SiF_6 , of which the silicifluorides are salts, is one of the products of the action of water on silicon tetrafluoride,⁴ and is formed also when silica is dissolved in a solution of hydrofluoric acid.⁵

¹ If barium sulphate is present it will require the special treatment for insoluble substances.

² A little hydrochloric acid may be necessary to effect complete solution. This method of treatment of insoluble silicates will be found more expeditious than the method of fusion.

³ Due to hydrolysis, cf. stannate and aluminate (§§ 102, 130).

$2\text{H}_2\text{O} + \text{Na}_2\text{SiO}_3 \rightleftharpoons 2\text{NaOH} + \text{H}_2\text{SiO}_3$ and $\text{NaOH} + \text{NH}_4\text{Cl} = \text{NH}_4\text{OH} + \text{NaCl}$.
For the benzidine test for soluble silicates, see § 478.

⁴ $3\text{SiF}_4 + 3\text{H}_2\text{O} = \text{H}_2\text{SiO}_3 + 2\text{H}_2\text{SiF}_6$.

⁵ $\text{SiO}_2 + 6\text{HF} = \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$.

§ 447. **Action of Heat on Silicifluorides.**—When a solution of hydrofluosilicic acid is evaporated in platinum it leaves no residue, the acid being decomposed by heat into volatile hydrogen and silicon fluorides.¹ The salts are similarly decomposed by heat, leaving a residue of fluoride. Heat potassium silicifluoride in an ignition tube. A fuming gas is evolved, which is silicon tetrafluoride, and gives a precipitate of gelatinous silica with water; the residue is potassium fluoride.

§ 448. **Action of Sulphuric Acid.**—Concentrated sulphuric acid liberates hydrofluosilicic acid, which decomposes so that hydrofluoric acid gas and silicon tetrafluoride are evolved on heating.

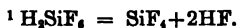
§ 449. **Preparation of Hydrofluosilicic Acid.**—Drop concentrated sulphuric acid from a tap funnel on to a mixture of fine sand and powdered calcium fluoride contained in a flask. Heat the mixture, and pass the evolved gas into water, letting the end of the delivery tube dip just beneath a little mercury placed in a cylinder with the water.²

When a considerable amount of gelatinous silica has separated, it may be filtered off; the filtrate contains the hydrofluosilicic acid.³ A simpler way of obtaining a solution of this acid, mixed with hydrofluoric acid, is by dissolving silica in cold aqueous hydrofluoric acid, and then diluting and filtering the solution if necessary.

§ 450. **Solubilities of Silicifluorides.**—Potassium silicifluoride is sparingly soluble, and the barium salt very slightly soluble in water. Other silicifluorides are soluble.

§ 451. **Barium Silicifluoride.**—Add solution of hydrofluosilicic acid⁴ to barium chloride. A white, crystalline precipitate gradually forms, its separation being promoted by warming the liquid. This precipitate is insoluble in dilute hydrochloric acid, but is distinguished from sulphate by yielding hydrofluoric acid when it is heated in a tube with concentrated sulphuric acid, so that the tube is etched.

§ 452. **Decomposition of Silicifluorides by Alkalis.**—Add excess of ammonia to solution of hydrofluosilicic acid; gelatinous silica gradually separates, ammonium fluoride remaining in solution.⁵



² This prevents the tube becoming clogged with gelatinous silica.

³ This solution also contains HF which has passed over with the SiF₄, and will therefore give a precipitate with lead acetate solution, although lead silicifluoride is soluble in water. In order to free the solution from HF, a lead salt is added in excess, the lead fluoride filtered off without heating, and the excess of lead precipitated by H₂S.

⁴ The presence of hydrofluoric acid does not signify, since the free acid gives no precipitate with barium chloride.

⁵ Silicifluorides in solution tend to decompose into fluoride and silicon tetrafluoride, which is easily hydrolyzed. This decomposition is promoted by alkali, thus: $(\text{NH}_4)_2\text{SiF}_6 = 2\text{NH}_4\text{F} + \text{SiF}_4$; $\text{SiF}_4 + 4\text{NH}_4\text{OH} = 4\text{NH}_4\text{F} + \text{H}_2\text{SiO}_3 + \text{H}_2\text{O}$

Add sodium carbonate solution to hydrofluosilicic acid; gelatinous silica separates; and if carbonate is added in excess and the liquid boiled and filtered, the filtrate will be found to contain no silicifluoride.¹

§ 453. Examination of a Solution which may contain Sulphate, Fluoride, and Silicifluoride.

The solubilities of the precipitated lead salts of these acidic radicles are as follows:—

Lead sulphate is insoluble in water and boiling dilute acetic acid.
 Lead fluoride " " " but soluble in " "
 Lead silicifluoride is soluble in water.

Consequently the following method of separation is employed:—

Add to the solution of the free acids or their alkali salts² lead acetate solution in excess, and filter cold.³

Residue.

Wash thoroughly with cold water.

(1) Add to a little of the moist precipitate dilute acetic acid in excess, and boil.⁴ A precipitate remaining shows **Sulphate**.

(2) Heat some of the well-drained moist precipitate with concentrated sulphuric acid in a test tube. Etching of the tube, or milkiness with water on a glass rod held in the vapour, shows **Fluoride**.

Filtrate.

Add barium nitrate⁵ solution and warm gently.

A crystalline precipitate gradually separating shows **Silicifluoride**.

¹ Therefore this acid radicle is not likely to be found in the course of analysis, after boiling the original substance with Na_2CO_3 before testing for acids in solution. It is best looked for in the solution of the substance in cold water or dilute HCl.

² Ammonium salts must not be present, since lead sulphate and fluoride dissolve in ammonium acetate. A solution which is actually alkaline cannot contain silicifluoride.

³ The liquid must not be heated, or the silicifluoride will be decomposed, and lead fluoride precipitated.

⁴ It is well to shake up a little of the precipitate with dilute acetic acid, throw away most of the turbid liquid, add more acetic acid to the remainder, and boil. Lead fluoride will then dissolve completely.

⁵ Barium chloride must not be used, or lead chloride will be precipitated.

Hydrogen Peroxide, H_2O_2 (syn. *Hydrogen dioxide*)

Pure hydrogen peroxide, H_2O_2 , is a syrupy liquid (sp. gr. 1.46) having feebly acidic properties. It is therefore to be regarded as an acid of which the superoxides¹ are salts.

***§ 454. Action of Heat on Hydrogen Peroxide Solution and the Superoxides.**—An aqueous solution of hydrogen peroxide² decomposes when boiled, evolving oxygen. Such a solution decomposes slowly at atmospheric temperature; the presence of free alkali, certain metallic salts, and suspended matter hastens decomposition.

Superoxides evolve oxygen when heated. Show this by heating barium peroxide, and testing for oxygen with a glowing wood splint.

***§ 455. Action of Water and Acids on the Superoxides.**

Sodium peroxide is partially decomposed by water into sodium hydroxide and hydrogen peroxide, the latter evolving oxygen by decomposition, especially on heating.³

Acids produce a similar change, yielding a sodium salt in solution.

Barium peroxide is not decomposed by cold water; dilute acids liberate hydrogen peroxide; cold concentrated hydrochloric acid causes oxygen to be evolved, but chlorine is produced on heating.

***§ 456. Solubilities of Superoxides.**—Only the alkali superoxides dissolve readily in water; other superoxides show the same solubilities in acids as the corresponding basic oxides.

§ 457. Formation of a Salt of Hydrogen Peroxide.—Add hy-

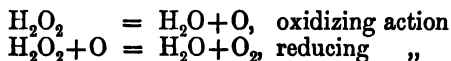
¹ H_2O_2 is generally supposed to have the constitution $\text{HO}\cdot\text{OH}$; thence follow the formulæ $\text{Na}[\text{O}\cdot\text{O}]\text{Na}$ and $\text{Ba}[\text{O}\cdot\text{O}]$. Superoxides, of which these are examples, thus contain a chain of two oxygen atoms. They are distinguished from polyoxides, such as $\text{O}=\text{Pb}=\text{O}$, by readily yielding hydrogen peroxide and free oxygen with dilute acids.

² Solution of H_2O_2 can now be purchased containing 30 per cent H_2O_2 by weight.

³ $\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2\text{O}_2$; $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$.

drogen peroxide solution to clear baryta water. A white crystalline precipitate of hydrated barium peroxide, $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$, separates.

§ 458. **Oxidizing and Reducing Action of Hydrogen Peroxide.**—Hydrogen peroxide may behave, in different circumstances,¹ either as an oxidizing or a reducing agent, according to one or other of the two following reactions:—



§ 459. **Oxidizing Action.**—The following examples of oxidation by hydrogen peroxide have already been noticed:—

(1) **Chromic hydroxide to chromate** (§ 131) in presence of alkali.

(2) **Chromic to perchromic oxide** (§ 147) in presence of acid;

and to these may be added the following:—

(3) **Lead sulphide to sulphate.**—Precipitate and thoroughly wash a little lead sulphide; then pour upon it dilute hydrogen peroxide solution. The black sulphide gradually changes into white sulphate.²

* (4) **Liberation of iodine from a solution of iodide.**—Add hydrogen peroxide solution to potassium iodide; iodine is liberated. This reaction is promoted catalytically by ferrous sulphate.

(5) **Oxidation of manganous hydroxide.**—Add sodium hydroxide to manganous sulphate solution, and then hydrogen peroxide. The white manganous hydroxide immediately turns dark brown, owing to the formation of hydrated dioxide.

A similar reaction occurs with ferrous and cobaltous hydroxides, but not with nickelous hydroxide.

¹ Conditions of stability of the product determine which kind of reaction takes place. The presence of alkali generally promotes the formation of highly oxygenated compounds, and acid their decomposition. Consequently oxidation is more usual, though not invariable, in alkaline solution, and reduction in the presence of acid.

² The restoration of paintings which have darkened with age depends upon this reaction of hydrogen peroxide.

§ 460. Reducing Action.

1. The reduction of acidified permanganate solution by hydrogen peroxide has already been observed (§ 192).

2. *Manganese dioxide*.—Precipitate manganous hydroxide and oxidize it with hydrogen peroxide as above; then add excess of dilute sulphuric acid, and more hydrogen peroxide if necessary. The manganese dioxide dissolves with evolution of oxygen,¹ forming a solution of manganous sulphate.

3. *Silver oxide*.—Precipitate silver oxide by sodium hydroxide, and then add hydrogen peroxide solution; the oxide is reduced to metal with consequent evolution of oxygen.²

§ 461. Catalytic Decomposition of Hydrogen Peroxide.—Add more hydrogen peroxide solution to the metallic silver formed in the last experiment; evolution of oxygen again takes place, and will continue as long as hydrogen peroxide is present. The finely-divided silver decomposes hydrogen peroxide catalytically; other finely-divided metals, finely-powdered glass, and other solids also possess this power.³

¹ $\text{MnO}_2 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 = \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{O}_2$. This is a good example of the influence upon the stability of compound of the change from an alkaline to an acid medium.

² Thus reduction takes place in presence of alkali, because the stability of silver oxide is not enhanced by alkali. Similarly, precipitated mercuric oxide is reduced to metal when warmed with H_2O_2 solution.

³ Therefore a solution of hydrogen peroxide is best preserved in a vessel having no rough surface. For this reason the glass bottles used are sometimes coated inside with paraffin wax, and fitted with a paraffin stopper.

§ 462. A Model Analysis

The student should cultivate the habit of writing out his notes, preferably in ink, during the course of his work. Only thus can a faithful record of all observations be made. Clearness and brevity should be aimed at, and these can best be secured by tabulation, somewhat on the following lines:—

Description: MIXTURE FOR ANALYSIS

Pale green powder; colour seems due to bright green crystals.

I. Preliminary Dry Tests:

- (a) Heated in ignition tube:
 Water evolved; mass turns yellow, then darker; brown gas; grey residue ...
- (b) Flame coloration:
 Pale lavender with yellowish tinge; crimson through indigo prism ...
- (c) Borax bead:
 Brown, outer flame; opaque, inner ...
- (d) Charcoal: omitted.
- { **Water** (of crystallization).
NO₂ from nitrite or nitrate.

K.

Ni.

II. Examination for Acidic Radicles by Volatile Products and for NH₃:

- (a) Warmed with dilute H₂SO₄; no gas.
- (b) Heated with concentrated H₂SO₄; acid fumes followed by brown gas; Cu increases brown gas ...
- (c) Warmed with NaOH aq. No NH₃.
- { **Nitrate.**

Moistened with water was faintly acid to litmus.

III. Wet Tests for Metals:

Mixture dissolved in dilute HCl; solution diluted.				
Ag group absent.	Passed H ₂ S. Nearly black precipitate; warmed and filtered.			
	Residue. Cu-Sn group. (A)	Filtrate.—No further precipitate with H ₂ S; boiled off H ₂ S, and boiled with concentrated HNO ₃ . Tested for PO ₄ ; found. Nearly neutralized with ammonia; added a little dilute HA; diluted well; added NH ₄ A; no precipitate.		
		Fe group absent.	Added FeCl ₃ aq. till reddening appeared, boiled, filtered, and rejected residue. To filtrate added ammonia and ammonium sulphide; black precipitate, and at first a dark filtrate (Ni); boiled well and filtered.	
			Residue. Zn group. (B)	Filtrate. — Added (NH ₄) ₂ CO ₃ in good quantity; boiled and filtered.
			Residue. Alkaline earth group. (C)	Filtrate. Examined for Mg, Na, K. (D)

A

Washed precipitate; boiled it with NaOH aq. and a little yellow ammonium sulphide, filtered.		
Residue. —Washed and dissolved in dilute HNO ₃ ; added dilute H ₂ SO ₄ ; no precipitate.		Filtrate. —Acidified with dilute HCl, and again passed H ₂ S. Precipitate is white S only.
No Hg or Pb.	Added ammonia; white precipitate, filtered. Residue. —Washed, dissolved in hot dilute HCl, and let solution drop into much water; turbidity shows Bi.	
	Filtrate. —Colourless; passed H ₂ S; no precipitate. No Cu or Cd.	

B

Washed precipitate, and digested it with very dilute HCl, filtered.	
Residue. —Black (Ni or Co). Dissolve in concentrated HCl + KClO ₃ , and evaporated solution; yellow ridge. ∴ Co absent. Borax bead has already shown Ni. Confirmed by adding KCN aq. just to redissolve precipitate, then NaOH aq. and Br aq.; black precipitate, Ni.	Filtrate. —Boiled off H ₂ S, and gradually added NaOH aq. till alkaline; no precipitate. No Zn or Mn.

C

Washed precipitate; dissolved some in dilute HCl; flame test shows Ca. Dissolved rest in HA aq. and added K ₂ CrO ₄ aq.; no precipitate.	
No Ba.	I. Tested for Sr by boiling with CaSO ₄ aq.; no precipitate; no Sr. II. Added ammonia in excess and ammonium oxalate; white precipitate shows Ca.

D

Filtrate from alkaline earth group gave no precipitate with (NH ₄) ₂ C ₂ O ₄ aq. To part added Na ₂ HPO ₄ aq.; no precipitate on shaking and standing.	
No Mg.	Remainder evaporated to dryness and ignited. Residue dissolved in little water and filtered. Flame coloration and precipitate with NaHC ₄ H ₄ O ₆ aq. show K.

IV. Acidic Radicles in Solution:

Nitrate and phosphate have already been indicated.

Boiled original mixture with Na₂CO₃ aq., filtered, rejected residue, and used successive parts of filtrate.

- | | | |
|--|---|-------------------|
| (i) Acidified part with dilute HNO_3 and added AgNO_3 aq.; no precipitate. Added NH_3 aq.; yellow precipitate soluble in excess shows | } | Phosphate. |
| (ii) Acidified part with dilute HCl and added BaCl_2 aq.; white precipitate shows ... | | |
| (iii) Acidified part with dilute HA and added FeCl_3 aq.; yellowish-white precipitate shows | } | Phosphate. |
| (iv) Acidified part with dilute H_2SO_4 and did brown ring test; found | | |
| | | Nitrate. |

Found:

Basic radicles	...	...	$\text{Bi}^{\cdots}$	$\text{Ni}^{\cdots}$	$\text{Ca}^{\cdots}$	$\text{K}^{\cdot}$
Acidic „	...	...	NO_3'	SO_4''	PO_4'''	
			Water of crystallization.			

NOTE.—The process of qualitative analysis of an inorganic substance or mixture of substances is summarized in §§ 463–471 on the separate sheets at the end of the book.

APPENDIX I

SOME NEWER ANALYTICAL REAGENTS

§ 472. In this section some newer tests for metallic and acidic radicles are introduced for use where the older tests are rather uncertain. These tests are generally so sensitive that blank tests on the reagents are required. They may be performed as "drop" reactions if a recognized technique¹ is followed, using porcelain spotting plates or good quality filter paper. It should be noted that very few reactions are "specific" for a given ion in the sense that the production of purple permanganic acid is specific for manganese: some preliminary separations are therefore required, as, for example, the group separations.

§ 473. **Detection of Copper.**—(i) Reagent: dissolve 1 grm. of *α*-benzoinoxime ("cupron"), $C_6H_5 \cdot CHOH \cdot C(:NOH) \cdot C_6H_5$, in 100 c.cm. of alcohol.

To an almost neutral solution of a cupric salt add some tartaric acid solution, then 1 c.cm. of the reagent, followed by a slight excess of ammonia solution. A green precipitate of the complex $(C_{14}H_{11}O_2N)Cu$ is specific for copper.

(ii) Reagent: *salicylaldoxime*, $C_6H_4(OH) \cdot CH : NOH$. Dissolve 1 grm. in 5 c.cm. of alcohol, and add dropwise to 95 c.cm. of warm water, with shaking. Cool, and filter if necessary.

To a solution of a cupric salt containing excess acetic acid add

¹See Fritz Feigl, *Qualitative Analysis by Spot Tests*, English translation by Janet W. Matthews (Nordemann Publishing Co., Inc., New York (1937)).

0.5 c.cm. of the reagent. A yellowish precipitate of the complex $[\text{C}_6\text{H}_4(\text{OH})\cdot\text{CH}:\text{NO}]_2\text{Cu}$ is obtained.

Under these conditions iron, silver, mercury and zinc do not interfere. If nickel is present with copper (cobalt being absent), it will be found in the filtrate, from which the analogous green nickel complex is precipitated on adding ammonia until the solution is just faintly acid. For this separation excess of the reagent must be used.

(iii) Reagent: *ammonium mercuric thiocyanate* (see § 479).

§ 474. Detection of Bismuth.—(i) Reagent: 10 grm. of *thiourea*, $\text{SC}:(\text{NH}_2)_2$, dissolved in 100 c.cm. of water.

To a cold, acidified solution of bismuth chloride add 1 c.cm. of the reagent. A deep yellow colour is produced.

Bismuth may thus be confirmed in the group separation. Lead and small amounts of antimony do not interfere; ferric iron must first be reduced by SO_2 or SnCl_2 , or rendered innocuous by adding potassium fluoride solution to form the stable ferri-fluoride ion $[\text{FeF}_6]'''$.

(ii) Reagent: *dimethylglyoxime* solution (see § 481).

Add 1 c.cm. of reagent to an acidified bismuth chloride solution and make strongly alkaline with ammonia. A yellow colour or precipitate indicates bismuth. Lead, arsenic and cadmium do not interfere; ferrous iron forms a deep red colour.

§ 475. Precipitates in the Iron Group.—During analysis for the commoner metallic ions, ammonium chloride and ammonia, besides precipitating hydroxides of the iron group, may also reprecipitate acid-soluble phosphates and fluorides. In addition, gelatinous silicic acid may be formed, being derived from the reagents or the apparatus used, or from failure to eliminate SiO_2 completely at the start (§ 39). It is convenient to have distinguishing tests for these, and, in particular, a confirmatory test for aluminium hydroxide.

§ 476. Aluminium may be identified by the red lakes which it forms with “aluminon” (ammonium aurine-tricarboxylate),

or with alizarin-S (sodium alizarin sulphonate). Iron must be removed: the ordinary sodium peroxide method suffices. Silicic acid does not interfere; fluoride should be absent.

(i) Reagent: *aluminon*. Dissolve the precipitate of aluminium hydroxide (or phosphate) in 5 c.cm. of N hydrochloric acid; add an equal volume of sodium acetate solution, followed by 5 c.cm. of a 1 per cent aqueous solution of aluminon. Allow to stand, then add slight excess of ammonia; a red solution or gelatinous precipitate will form.

Beryllium and chromium give similar lakes; that due to chromium is destroyed by ammonium carbonate solution, which, however, lessens the intensity of the aluminium lake.

(ii) Reagent: *alizarin-S*. Dissolve the precipitate of aluminium hydroxide (or phosphate) in 2 c.cm. of N hydrochloric acid, add 5 c.cm. of a 1 per cent solution of the reagent in alcohol, followed by ammonia solution to slight alkalinity. Set aside for 5 minutes, then add dilute acetic acid. A red colour or gelatinous precipitate will form.

Moderate amounts of zinc, calcium and magnesium, and small amounts of iron and chromium do not interfere.

§ 477. **Fluorides** will hinder formation of these lakes, since the stable $[\text{AlF}_6]'''$ ion formed will prevent aluminium from reacting. The following sensitive test for fluorides which are sufficiently soluble in dilute hydrochloric acid makes use of this property of the fluoride ion.

Mix 3 volumes of alizarin-S solution with 2 volumes of a 0.4 per cent aqueous solution of zirconium nitrate, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, and acidify with dilute hydrochloric acid. Add a few drops of the resulting violet-red solution to a fluoride solution (or to the solid fluoride); the deep colour of the zirconium lake will be discharged, owing to the formation of the stable zirconifluoride ion $[\text{ZrF}_6]'''$.

§ 478. **Soluble Silicates and Soluble Colloidal Silicic Acid.**—The analogous ammonium salts of phospho-, arseno- and silicomolybdic acids have an oxidizing power superior to that of the

simple molybdic acid. In almost neutral solution they will oxidize benzidine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, to a blue oxidation product, being themselves reduced to blue molybdenum compounds. Ammonium silicomolybdate is much more soluble than the other two salts, and can be prepared when oxalic acid, but not tartaric acid, is present (distinction between silicate and phosphate). Ammonium arsenomolybdate is not formed in presence of tartaric acid. It should not, however, occur here, since arsenate should be removed in the copper group. The formulæ of the anhydrous salts are:



To detect **silicate** in presence of phosphate proceed thus: to 1 c.cm. of aqueous ammonium molybdate add dilute nitric acid until the white precipitate of molybdic acid first formed just redissolves. To this add a few drops of the test solution, heat almost to boiling, and filter to remove ammonium phosphomolybdate. Add oxalic acid solution to the filtrate, then 2 drops of *benzidine* solution (0.05 grm. in 100 c.cm. of 10 per cent acetic acid), followed by excess of sodium acetate solution. A deep-blue colour shows the presence of silicate.

In the absence of phosphate no filtration is required, and the oxalic acid is omitted. **Phosphate** may be detected in presence of arsenate and silicate by using tartaric acid instead of oxalic acid.

§ 479. Detection of Zinc.—(i) Reagent: a solution of *ammonium mercuric thiocyanate*, $(\text{NH}_4)_2[\text{Hg}(\text{CNS})_4]$, prepared by dissolving 8 grm. of mercuric chloride and 9 grm. of ammonium thiocyanate in 100 c.cm. of water.

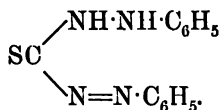
This reagent forms crystalline precipitates of the type $\text{M}[\text{Hg}(\text{CNS})_4]$ from solutions containing cations (M) such as zinc (white), cadmium (white), copper (green), cobalt (blue), and nickel (green). If certain pairs of these ions are present together in solution, the colour of the precipitate, or its rate of formation, may be so modified as to form a useful test.

To a solution of a zinc salt add, in the order given, a few drops of dilute copper sulphate solution, a little dilute sulphuric acid, and 1-2 c.cm. of the reagent. A purple zinc-copper complex forms, $\text{CuZn}[\text{Hg}(\text{CNS})_4]_2$. Heat if necessary; shaking with a little amyl alcohol or acetate will "float" the precipitate.

Zinc may thus be identified in the group separation (the solution must be free from H_2S), or, alternatively, small amounts of copper may be identified. Copper with cadmium gives a similar precipitate. If iron is present, first add ammonium phosphate or potassium fluoride solution. Manganous and chromic ions do not interfere.

Very dilute solutions of cobalt salts react but slowly with the reagent. If a few drops of a zinc salt solution are first added, followed by the reagent, the precipitation of the blue cobalt complex is much hastened.

(ii) Reagent: *diphenylthiocarbazon*e ("dithizone"),



Dissolve 1 mgm. in 100 c.cm. of carbon tetrachloride or chloroform. The solution does not keep well.

Prepare a dilute solution of sodium zincate by adding excess caustic soda to a zinc salt solution, and to this add a little of the reagent. The green colour of the reagent turns red, a soluble zinc complex being formed. The reaction is characteristic for zinc when isolated by NaOH in the group separation. Aluminium does not interfere.

Many heavy metals give coloured complexes insoluble in water, but soluble in the organic solvent.

§ 480. Detection of Cobalt. — Reagent: *α -nitroso- β -naphthol*, $\text{C}_{10}\text{H}_6(\text{NO})\text{OH}$. Dissolve 1 gram. of the substance in 50 c.cm. of glacial acetic acid, then add water to 100 c.cm.

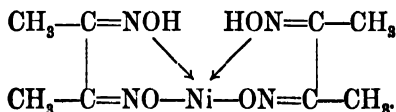
Acidify the cobalt solution with dilute acetic acid or hydro-

chloric acid, and add a few drops of the reagent. A brown precipitate forms, $[\text{C}_{10}\text{H}_6(\text{NO})\text{O}]_3\text{Co}$, which may be extracted by carbon tetrachloride to give a claret-coloured solution.

Since other metallic ions may interfere, the test is best applied in the group separation; nevertheless, the deep colour of the tetrachloride extract permits cobalt to be recognized in the presence of considerable amounts of other metals. Potassium fluoride or phosphate render iron innocuous, and hydrochloric acid prevents interference by nickel.

§ 481. **Detection of Nickel.** — Reagent: *dimethylglyoxime*, $\text{CH}_3\text{-C}(\text{:NOH})\text{-C}(\text{:NOH})\text{-CH}_3$. Dissolve 1 grm. of the substance in 100 c.cm. of alcohol.

To a nickel solution add a few drops of the reagent, followed by ammonia solution to neutralize the free acid produced when the hydrogen atoms of the oxime groups are replaced by nickel. Heat if necessary, and allow to cool. Nickel dimethylglyoxime forms as a brilliant red precipitate, soluble in potassium cyanide solution. Its structure is



Oxidizing agents may prevent precipitation, giving instead a red or orange solution. Ferrous iron forms a red soluble complex which is stable to potassium cyanide; ferric iron does not interfere in presence of alkali tartrate. If cobalt is also present in quantity, the soluble brown cobaltous complex retards the precipitation of nickel. In this case first add a little hydrogen peroxide to the ammoniacal solution to form the stable cobaltic ion $[\text{Co}(\text{NH}_3)_6]^{3+}$. Boil to destroy excess peroxide, then add the reagent. Should the nickel precipitate be masked by coloured solutions or by other precipitates, shaking with ether (or amyl alcohol) will, in most cases, concentrate the nickel complex at the ether-water interface.

§ 482. **Detection of Calcium.**—Reagent: *potassium ferrocyanide*.

To a solution of a calcium salt containing ammonium chloride add potassium ferrocyanide solution. A white crystalline precipitate of calcium potassium ammonium ferrocyanide of variable composition is obtained.

The test should be applied in the calcium group; barium in moderate dilution does not interfere. Magnesium behaves similarly. Chromate must be absent.

§ 483. **Detection of Magnesium.**—The tests given below for magnesium depend on the precipitation of magnesium hydroxide in presence of a dyestuff, whereby a coloured adsorption complex is produced. Metals forming insoluble hydroxides should therefore be absent, and the tests are best applied to the alkali group solution. A great concentration of ammonium salts should be avoided, either by igniting in the usual manner, or by boiling the test solution with caustic soda solution.

(i) Reagent: *p-nitrobenzene-azo-resorcinol* ("magneson"), $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})_2$. Dissolve 0.1 grm. in 100 c.cm. of 1 per cent sodium hydroxide solution.

Slightly acidify 2 c.cm. of the magnesium solution, add 1 drop of the reagent, then 2–3 c.cm. of sodium hydroxide solution. A blue colour or precipitate will form.

The test may be applied to the group precipitate of magnesium ammonium phosphate. The alkaline earth ions do not interfere. Manganese forms a deep purple lake.

(ii) Reagent: *Titan Yellow*. Dissolve 0.1 grm. in 100 c.cm. of water or alcohol.

To the slightly acid magnesium solution add 2 drops of the reagent, followed by caustic soda solution to distinct alkalinity. A rose-red precipitate will form.

§ 484. **Detection of Bromine.**—Reagent: *dichlorofluorescein* (or *fluorescein*). Dissolve 0.1 grm. in 100 c.cm. of aqueous alcohol.

Expose a drop of the reagent solution on filter paper to bromine

vapour; the drop turns red owing to the formation of a red bromo-derivative.

Chlorine bleaches the reagent; iodine forms the red iodo-derivative and must first be removed (§ 299). Nitrogen dioxide and sulphur dioxide do not interfere.

Bromine in presence of chlorine may often be detected by holding a dropping tube containing a drop of the reagent in the vapours. The bleaching action of the chlorine is minimized, and the bromine partially turns the drop red.

§ 485. Detection of Nitrite.—Reagent: mix solutions (a) and (b) in equal volumes as required. (a) Dissolve, with aid of heat, 1 grm. of *sulphanilic acid*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, in 100 c.cm. of dilute acetic acid. (b) Boil 0.2 grm. of *α -naphthylamine*, $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, with 50 c.cm. of water, decant the clear liquid, and add to it 20 c.cm. of glacial acetic acid, followed by 30 c.cm. of water.

To a solution of a nitrite, either neutral or containing acetic acid, add a little of the reagent: a red colour is produced. This very sensitive and specific test for nitrite depends on the formation of the red azo dyestuff



Nitrate may be detected by first reducing it to nitrite by means of zinc and acetic acid. Nitrites must first be removed (§ 365).

§ 486. Detection of Persulphate.—Reagent: *benzidine* (see § 478 for the preparation of the solution).

To a neutral solution (or one weakly acid with acetic acid) of alkali persulphate, add a few drops of the reagent. A blue colour will develop.

Benzidine yields a blue oxidation product with most oxidizing agents, but under the above conditions (Feigl, *loc. cit.*), perborate, hydrogen peroxide, chlorate, perchlorate, bromate, iodate and nitrate do not react.

§ 487. Detection of Chromate.—Reagent: *diphenylcarbazide*,

$\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$. Dissolve 0.2 grm. in 100 c.cm. of alcohol.

To an alkali chromate solution, slightly acid with acetic acid, add a little of the reagent: a violet colour will develop. Chromic salts may be identified by oxidizing to chromate with alkaline hydrogen peroxide, boiling to destroy the excess of peroxide, and thereafter acidifying with acetic acid.

The reagent gives coloured complexes with many heavy metals, and is used to detect mercury and cadmium.

APPENDIX II

REAGENTS IN SOLUTION

It is desirable to employ, as far as possible, aqueous solutions of equivalent strengths in qualitative analysis, so that the volumes required for the specific reactions may be approximately known. By this means separations are more satisfactorily carried out, and waste of material is avoided.

This principle is adopted in the directions for making solutions here given.

I. CONCENTRATED ACIDS

Concentrated hydrochloric acid, HCl.....	Sp. gr. 1.16
„ nitric „ HNO ₃	„ 1.42
„ sulphuric „ H ₂ SO ₄	„ 1.82

II. DILUTE ACIDS, 2N¹

Dilute acetic acid, HC ₂ H ₃ O ₂	120	gram. per litre = about 240
		gram. 50 per cent "glacial" acid
„ hydrochloric acid, HCl....	73	gram. per litre = about 220 gram.
		ordinary concentrated acid
„ nitric „ HNO ₃ ..	126	gram. per litre = about 180 gram,
		ordinary concentrated acid
„ sulphuric „ H ₂ SO ₄ ..	98	gram. per litre = about 102 gram.
		ordinary concentrated acid

¹ 2N = twice normal, i.e. containing two gram-equivalents of the reagent per litre of the solution.

III. DILUTE ALKALIS, 2N

Sodium hydroxide, NaOH.....	80 grm. per litre = about 90 grm. ordinary pure sticks
Potassium „ KOH.....	112 grm. per litre = about 130 grm. ordinary pure sticks
Ammonia „ NH ₃ → NH ₄ OH...	34 grm. per litre = about 90 grm. concentrated solution (0.880 sp. gr.)

IV. SALTS, 2N

Ammonium chloride, NH ₄ Cl.....	107 grm. per litre
„ carbonate (sal volatile, N ₃ H ₁₁ C ₂ O ₄)...	70.5 grm. per litre
Add 200 c.cm. strongest ammonia before diluting to 1 litre with water	
Sodium carbonate, Na ₂ CO ₃ ·10H ₂ O...	286 grm. per litre

V. SALTS, $\frac{N}{5}$

Mercurous nitrate, Hg ₂ (NO ₃) ₂ ·2H ₂ O	. . .52.5 grm. per litre
Mercuric chloride, HgCl ₂	27.1 „
Lead acetate, Pb(C ₂ H ₃ O ₂) ₂ ·3H ₂ O	 37.9 „
Copper sulphate, CuSO ₄ ·5H ₂ O ..	 24.9 „
Bismuth nitrate, Bi(NO ₃) ₃ ·5H ₂ O ¹	32.3 „
Cadmium sulphate, 3CdSO ₄ ·8H ₂ O...	25.6 „
Stannous chloride, SnCl ₂ ·2H ₂ O ¹	22.6 „
Stannic chloride, SnCl ₄ ·5H ₂ O ¹	17.5 „
Arsenious oxide, As ₂ O ₃ , in dilute ammonia...	6.6 „
Antimonious chloride, SbCl ₃ ¹	15.1 „
Aluminium potassium sulphate, Al ₂ (SO ₄) ₃ ·K ₂ SO ₄ ·24H ₂ O.....	31.6 „
Chromic potassium sulphate, Cr ₂ (SO ₄) ₃ ·K ₂ SO ₄ ·24H ₂ O.....	33.3 „

¹ These salts are hydrolyzed by water with separation of insoluble basic salts. some dilute acid is therefore necessary to dissolve them.

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Ferric chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	18·0	gram. per litre
Zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	28·7	„
Manganous sulphate, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	22·3	„
Cobalt nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	29·1	„
Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	28·1	„
Calcium chloride, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	21·9	„
Strontium nitrate, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	28·4	„
Barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	24·4	„
Magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	24·6	„
Sodium chloride, NaCl	11·7	„
„ nitrite, NaNO_2	13·8	„
„ sulphite, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	25·2	„
„ thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	24·8	„
„ sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	22·2	„
„ phosphate, $\text{Na}_3\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	23·9	„
„ arsenate, $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$	26·8	„
Potassium chloride, KCl	14·9	„
„ bromide, KBr	23·8	„
„ iodide, KI	33·2	„
„ cyanide, KCN	13·0	„
„ ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	20·8	„
„ sulphonycyanide, KCNS	19·4	„
„ nitrate, KNO_3	20·2	„
„ chromate, K_2CrO_4	19·4	„
„ dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$	9·8 ¹	„
„ permanganate, KMnO_4	6·3 ¹	„
Ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	14·2	„

¹ This solution is $\frac{\text{N}}{5}$ as regards available oxygen, not potassium.

VI. SOLUTIONS OF SPECIAL STRENGTH

Silver nitrate, $\text{AgNO}_3\left(\frac{\text{N}}{20}\right)$	8.5 gm. per litre
Potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$	dilute solution made when required
Ammonium polysulphide, NH_4HS_x	1 vol. concentrated solution to 1 vol. water
(Yellow ammonium sulphide)	
Ammonium acetate, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	saturated solution
molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ¹	

Dilute 200 c.cm. of concentrated ammonia with an equal volume of water, and dissolve in the liquid 140 gm. of crystallized ammonium molybdate. Add this solution slowly to 1440 c.cm. of nitric acid 1.2 sp. gr., kept cool, and allow the whole to stand. Before use decant the clear solution from any molybdic acid which has separated, and dilute it with an equal volume of water.

Calcium hydroxide, lime water, $\text{Ca}(\text{OH})_2$...	saturated solution
„ sulphate, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	„ „
Sulphurous acid, H_2SO_3	„ „
Bromine water, Br_2	„ „
Iodine in potassium iodide, $\text{KI}_3\left(\frac{\text{N}}{10}\right)$	12.7 gm. I_2 , and 30 gm. KI per litre
Ferrous sulphate, $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$	dilute solution made when required

Magnesium uranyl acetate. Add 100 gm. of uranyl acetate $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 2\text{H}_2\text{O}$ to 100 gm. glacial acetic acid and 400 c.cm. of water. To another 200 c.cm. of water add 300 gm. of magnesium acetate $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 4\text{H}_2\text{O}$. Heat both solutions almost to boiling, then mix them when almost clear. Dilute to 1 litre and filter after 24 hours.

¹ An alternative is to dissolve 150 gm. of ammonium molybdate in water, with a little dilute nitric acid, and dilute the solution to 1 litre. Concentrated nitric acid is then added to a few c.cm. of this solution in a test-tube just before use. In this way the crystallization and waste of hydrated molybdic acid, $\text{MoO}_3\cdot 2\text{H}_2\text{O}$, is avoided (cf. § 419).

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