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A MANUAL OF PRACTICAL INORGANIC CHEMISTRY

A. M. KELLAS

OXFORD MEDICAL PUBLICATIONS

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A MANUAL OF
PRACTICAL INORGANIC CHEMISTRY

II.

OXFORD MEDICAL PUBLICATIONS

A MANUAL OF PRACTICAL INORGANIC CHEMISTRY

INCLUDING

PREPARATIONS AND QUALITATIVE AND QUANTITATIVE ANALYSIS WITH THE RUDIMENTS OF GAS ANALYSIS

SPECIALLY ADAPTED TO COVER PRELIMINARY AND
INTERMEDIATE UNIVERSITY COURSES AND THE
FIRST THREE STAGES OF THE SYLLABUS
OF THE BOARD OF EDUCATION

BY

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FORMERLY EXAMINER IN CHEMISTRY TO THE CONJOINT BOARD
OF THE ROYAL COLLEGES OF PHYSICIANS AND SURGEONS

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PREFACE

PART of what was mentioned in the author's *Introduction to Practical Chemistry* might be repeated here. The intention has been to correlate practical and theoretical work to the maximum extent, and so make students thoroughly understand the tests and experiments which they carry out.

The difference between the two books lies mainly in scope. In the elementary book the schemes of analysis were adapted so as not to confuse students making a limited study of the subject with mass of material. The present manual is much more complete and probably meets the requirements of most University courses, but should be more especially useful to Candidates preparing for Intermediate and Preliminary Scientific Examinations.

The book has been designed so as not only to aid the student, but also to lighten the work of the teacher as far as possible. Teachers often have to deal with students who may for any reason lag behind the others, and it is hoped that the present manual can be used by such students with the minimum amount of help and the maximum of benefit.

The scope of the book is probably different from that of any existing textbook, and the author trusts that it may be found particularly suitable for medical and pharmaceutical students. The methods of preparation of practically all the inorganic compounds in the British Pharmacopœia are clearly indicated, without however interfering with the general systematic arrangement of the book.

The Tables showing the relationships of the common compounds of the different metals which were a feature of the elementary work are given in this *Manual*, as they have been found of considerable value in teaching.

The author would be greatly obliged by any suggestions from teachers regarding arrangement or matter, which would receive careful consideration.

In conclusion it is a pleasure to thank Mr. Sydney A. Sewell for the care he has bestowed upon the figures in the text.

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INTRODUCTORY

PRELIMINARY NOTES ON CHEMICAL THEORY

DEFINITION. The Science of Chemistry deals with changes undergone by Matter where alteration of substance occurs (excluding ordinary change of state of aggregation).

The student will have already learned that all bodies may be referred to one of three classes, viz. :—**Elements**, **Compounds**, or **Mixtures**.

DEFINITION. An **Element** is a body which so far as we know cannot by ordinary means be split up into simpler bodies, e. g. oxygen, silver, arsenic.

DEFINITION. A **Compound** is formed by the union of two or more elements in fixed definite proportions by weight, e.g. water, sodium chloride (common salt).

DEFINITION. **Mixtures** may consist of mixtures of elements, mixtures of compounds, or mixtures of elements and compounds in any proportion by weight; e. g. ordinary black gunpowder is a mixture of carbon, sulphur, and potassium nitrate (nitre) in proportions which may vary within considerable limits, and mixtures of the constituents might be made in any proportion whatever.

One generally starts the study of Chemistry with a consideration of the elements known as the **'Non-metals'**, and the more important compounds of these elements with hydrogen and oxygen.

The elements are for convenience divided into two great groups, the **Non-metals** and the **Metals**, and there is a small sub-group—the **Metalloids**. The distinctions between these groups depend essentially upon chemical relationships, and cannot be profitably considered until later, when the more important types of compounds concerned in the distinctions will have been met with.

The following are the chief elements which, along with their compounds, are generally dealt with in an intermediate or preliminary science course, and will be considered here:—

I. NON-METALS.		II. METALLOIDS.		III. METALS.	
ELEMENT.	SYMBOL.	ELEMENT.	SYMBOL.	ELEMENT.	SYMBOL.
Hydrogen	H	**Antimony**	Sb	**Silver**	Ag
Oxygen	O	**Arsenic**	As	**Mercury**	Hg
Nitrogen	N	2		**Lead**	Pb
Phosphorus	P			**Copper**	Cu
Chlorine	Cl			**Bismuth**	Bi
Bromine	Br			**Cadmium**	Cd
Iodine	I			**Tin**	Sn
Carbon	C			**Aluminium**	Al
Sulphur	S			**Chromium**	Cr
Silicon	Si			**Iron**	Fe
Boron	B			**Nickel**	Ni
11				**Cobalt**	Co
				Zinc	Zn
				Manganese	Mn
				Barium	Ba
				Strontium	Sr
				Calcium	Ca
				Magnesium	Mg
				Sodium	Na
				Potassium	K
				20	

We are therefore concerned with only 33 out of the 81 known elements. [NOTE.—The total number of existing elements is probably greater than 81 as indicated by the periodic classification, for which students are referred to theoretical books.] A complete list of known elements with their atomic weights is given at the end of this book (p. 342).

The student should refer to his theoretical book for complete explanations regarding fundamental terms such as atom, molecule, valency, &c., but the following summary may prove useful:—

DEFINITION. An **Atom** is the smallest portion of an element which can enter into chemical combination. According to the Atomic Theory the Atom is indivisible under ordinary circumstances.

[NOTE.—According to a recent theory an atom consists of large numbers of particles termed corpuscles or electrons.]

Definition. The **Atomic weight** of an element is the weight of an atom of the element, relative to the weight of an atom of hydrogen, e.g. the atomic weight of oxygen is 16 because the smallest portion of oxygen which can enter into chemical combination is 16 times as great as that of the smallest portion of hydrogen met with in combination. The actual weights of atoms are of course quite unknown. They are ultra-microscopic.

Definition. A molecule is the smallest portion of an element or compound which can exist in the free state, e.g. H_2 stands for a molecule of hydrogen, there being 2 atoms in a molecule of that element.

Definition. The **Molecular weight** of an element or compound is the sum of the atomic weights of the atoms in the molecule, and therefore represents the weight of a molecule relative to the weight of an atom of hydrogen as unity, e.g. the molecular weight of nitrogen (N_2) is 28 and of carbon dioxide (CO_2) 44 (i.e. $12 + 2 \times 16$).

FORMULÆ. EQUATIONS. VALENCY.

To be able to understand and write chemical formulae and equations is of fundamental importance in both practical and theoretical chemistry. The student should therefore spare no trouble to acquire a knowledge of the principles upon which the writing of equations is based. If he does not comprehend the following explanations on a first perusal, he should return to them again and again until he does so.

Formulæ are used to represent molecules of substances, and indicate the relative number of atoms of each element present in a molecule; e.g. H_2O represents a molecule of water, and shows that the molecule consists of 2 atoms of hydrogen combined with one of oxygen, while H_2SO_4 represents a molecule of sulphuric acid, and indicates that two atoms of hydrogen, one of sulphur, and four of oxygen, are contained in a molecule of that body.

In **Chemical Equations** one generally indicates the decomposition of the molecules of a body, or the interaction of molecules of different substances. Before one can write equations one must therefore be able to write formulæ representing molecules, and before molecules can be correctly rendered, what is termed the **valency** of the different elements must be known.

Definition. The **Valency** of an element expresses the number of hydrogen atoms (or the equivalent of hydrogen) which one atom of the element can combine with or replace.

Elements are classed as **mono-valent, di-valent, tri-valent,** &c., the prefix indicating the number of hydrogen atoms which one atom of the element can combine with or replace, e.g. oxygen is divalent because it combines with 2 atoms of hydrogen in water H_2O. The valency of an element is frequently variable, especially in the case of the non-metals, and it is therefore inadvisable that the beginner should spend too much time upon attempts to fully understand all the equations in the following preparations of non-metallic elements and compounds, e.g. sulphur is divalent when combined with hydrogen in sulphuretted hydrogen, presumably tetravalent in sulphur dioxide SO_2, where it is combined with 2 atoms of oxygen, each of which are equivalent to 2 atoms of hydrogen, and hexavalent in sulphur trioxide SO_3. When he comes to the preparation of metallic salts, however, he should be able in most cases to balance up the equations from the following valency table, and should endeavour to acquire proficiency in writing such equations **as soon as possible.**

THE COMMON VALENCIES OF THE ELEMENTS.

Monovalent Elements		H, F, Cl, Br, I, Na, K, (NH_4) *, Ag, Cu^{ous} †, Hg^{ous} †.
Divalent	,,	O, S^{II}, Mg, Ca, Sr, Ba, Zn, Mn^{ous} †, Fe^{ous} †, Pb, Sn^{ous} †, Cu^{ic} †, Cd, Ni^{ous} †, Co^{ous} †.
Trivalent	,,	N, B, P, As, Sb, Bi, Fe^{ic} †, Al, Cr (Ni^{ic} †, Co^{ic} †).
Tetravalent	,,	C, Si, S^{IV}, Sn^{ic} †.
Pentavalent	,,	N, P, As, Sb, Bi.
Hexavalent	,,	S^{VI} (as in SO_3).
Heptavalent	,,	Cl (in $KClO_4$), Mn (in $KMnO_4$).

The full significance of the above table will not be appreciated

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* The Ammonium Group (NH_4) behaves like a monovalent metal.

† **Note regarding Nomenclature.** Many metals have two valencies, indicating the capacity for existing in two states of combination. In such a case the class of compounds formed when the metal has the lower valency is characterized by the suffix **-ous**, and the class formed when the metal has the higher valency is distinguished by the suffix **-ic**; e.g. **mercurous** chloride is written HgCl, and mercuric chloride $HgCl_2$. Since an atom of chlorine corresponds to an atom of hydrogen (both being monovalent), in the first compound mercury is monovalent and in the second divalent.

by the beginner until he comes to write the equations expressing the reactions which he carries out while testing for metals and acids. To enable the student to appreciate the general application of the table for the writing of formulæ and equations, one must anticipate the definitions for acids and salts which are more fully explained later on.

Acids are compounds containing hydrogen which can be replaced by a metal (e. g. hydrochloric acid HCl, nitric acid HNO_3, sulphuric acid, H_2SO_4), while **salts** are compounds formed from acids by replacement of part or all the replaceable hydrogen by metal.

We will consider as examples the salts derived from the three important acids mentioned above by replacing hydrogen by metal.

Consider first of all the salts termed **chlorides** which are **derived from hydrochloric acid, HCl.**

The formulæ for the **chlorides of the monovalent elements** would be derived from one molecule of acid by replacing the hydrogen atom by an atom of metal, and would therefore be:—NaCl, KCl, $(NH_4)Cl$, AgCl, HgCl (mercurous chloride), CuCl (cuprous chloride).

The formulæ for the **chlorides of the divalent elements** must be obtained by replacement of 2 atoms of hydrogen by 1 of metal. This obviously requires that the hydrogen of 2 molecules of hydrochloric acid be replaced, since one molecule of hydrochloric acid contains only 1 atom of hydrogen. One would obtain in this way the formulæ:—$MgCl_2$, $CaCl_2$, $BaCl_2$, $SrCl_2$, $ZnCl_2$, $FeCl_2$ (ferrous chloride), $PbCl_2$, $SnCl_2$ (stannous chloride), $CuCl_2$ (cupric chloride), $CdCl_2$, $NiCl_2$, $CoCl_2$.

In the case of the **trivalent elements** the formulæ would be obtained by replacing the hydrogen of three molecules of hydrochloric acid by one of metal:—$AsCl_3$, $SbCl_3$, $BiCl_3$, $FeCl_3$ (ferric chloride), $AlCl_3$, $CrCl_3$.

As regards **tetravalent elements** such as tin in the stannic condition, the formula would be derived from 4HCl by replacing 4 atoms of hydrogen by one atom of metal, the formula for stannic chloride being $SnCl_4$.

Consider next the salts of nitric acid, **H—NO$_3$**, known as the nitrates. In writing the formula for the nitrates one has merely to concentrate attention upon the valency of the elements because the radicle —NO_3 remains intact in the salts. The formulæ for the nitrates may therefore be similarly derived to those of the chlorides, and if one substitutes an $—NO_3$ group for each chlorine atom in the above list of chlorides, the correct formulæ for the nitrates will be obtained :—

Nitrates of monovalent metals. $NaNO_3$, KNO_3, NH_4NO_3, $AgNO_3$, $HgNO_3$. (Cuprous nitrate is not met with.)

Nitrates of divalent metals. $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Zn(NO_3)_2$, $Mn(NO_3)_2$, $Fe(NO_3)_2$, $Pb(NO_3)_2$, $Sn(NO_3)_2$, $Cu(NO_3)_2$.

Nitrates of trivalent metals. $Bi(NO_3)_3$, $Fe(NO_3)_3$, $Al(NO_3)_3$. Arsenic and antimony nitrates do not occur.

The formulæ of the **sulphates**, as the **salts of sulphuric acid** are called, are not similar to those of the chlorides and nitrates, because sulphuric acid (H_2SO_4) has two atoms of displaceable hydrogen in the molecule. In the case of sodium, potassium, and ammonium two sulphates are met with in each case, namely the acid salts or bisulphates where only one atom of hydrogen has been replaced, and the normal sulphates where both hydrogen atoms have been displaced by metal.

1. **Sulphates of monovalent metals.**
   (*a*) Bisulphates. $NaHSO_4$, $KHSO_4$, $(NH_4)HSO_4$.
   (*b*) Normal sulphates. Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, Ag_2SO_4, Hg_2SO_4. (Cuprous sulphate is not met with.)

2. **Sulphates of divalent metals.** $MgSO_4$, $CaSO_4$, $BaSO_4$, $ZnSO_4$, $MnSO_4$, $FeSO_4$, $PbSO_4$, $CuSO_4$. Here both atoms of hydrogen in H_2SO_4 are replaced by one atom of metal.

3. The formulæ for the **sulphates of trivalent metals** can be deduced in the following way : One molecule of sulphuric acid contains only 2 atoms of hydrogen, and therefore an insufficient number for replacement by one atom of a trivalent element. Two molecules of sulphuric acid ($2H_2SO_4$) contain 4 atoms of hydrogen, and 4 atoms of a monovalent element could not be replaced without remainder by atoms of a trivalent element. Three molecules of sulphuric acid, however ($3H_2SO_4$), contain 6 atoms of hydrogen, and 2 atoms of a trivalent element could exactly replace these 6 atoms. The formulæ would therefore be :—$Bi_2(SO_4)_3$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Cr_2(SO_4)_3$.

Other formulæ would be analogous. It is worth noting, for example, that the formulæ for the **oxides** and **sulphides**, which might be represented as if derived from H_2O and H_2S respectively, would in most cases be exactly similar to those of the sulphates: one has merely to put —O or —S for $-SO_4$ in above formulæ; e.g. zinc oxide has the formulæ ZnO, and zinc sulphide is ZnS, corresponding to zinc sulphate, $ZnSO_4$.

GENERAL MANIPULATIONS IN CONNEXION WITH THE SETTING UP OF APPARATUS. GENERAL EXPERIMENTAL PROCESSES.

Before going on to consider the preparation and important reactions of the non-metals and their compounds, the general manipulations required in the setting up of apparatus, and also a few general experimental processes, must be considered.

Apparatus required:—Flasks of various types, round-bottomed, flat-bottomed and conical, glass tubing of moderate bore—say 3 to 5 millimetres internal diameter, retorts, filter funnels, test-tubes, porcelain basins, corks (and cork-pressers), triangular and round files, wire gauze, retort stand, condenser, rubber tubing.

I. SETTING UP OF APPARATUS.

The cutting and bending of glass tubes and boring of corks are general operations which have to be performed in setting up apparatus.

The proper method of cutting a glass tube is as follows:—Place the tube horizontally on the bench and make a mark with a triangular file at the point where the glass is to be broken. Take the tube in both hands, but mainly gripped between the thumb and first fingers of each hand. The backs of the hands should be outwards, and the thumbs should be directed towards each other along the top of the tube. The file mark should be in the short space—say $\frac{1}{4}$ to $\frac{1}{2}$ inch—between the thumbs. On gripping firmly with the thumbs and pressing upwards and outwards with the fingers, the tube will usually break neatly at the file mark. The cut edges should always be rounded off by heating them in the Bunsen flame with constant rotation of the tube until the glass just fuses and forms a rounded surface.

Bending of glass tubes. The bending of tubes is generally carried out in the ordinary flat flame, and not with the Bunsen burner, the heat of which is too intense and localized for the purpose. Hold the tube along the top of the flat flame—which should be parallel to the operator's body—so that the point where the bend is to be made is at the middle of the heated area. Rotate the tube continually, and if the flame be small, move also slightly backwards and forwards so as to heat a fair length of tubing. When the glass has softened sufficiently withdraw from the flame and bend the tube as required while holding it at right angles to the face and on a level slightly below the eyes, so that one can look along the top of the tube during the bending process.

Cork-boring. As a preliminary to boring, the cork selected should either be squeezed in a cork press or covered with paper (to keep it clean) and then well rolled under the foot so as to make it resilient. The cork is then carefully bored with the number of holes required, starting from the small end. The cork-borer used should always be of slightly smaller diameter than the end of the tube to be introduced. Moisten the cork-borer with alcohol (or water) and rotate it while forcing it through the cork. Until proficiency is attained it is usually a good plan to bore half-way from each end of the cork. During boring the cork-borer is moved horizontally, the cork being held in the hand. If the beginner finds it more convenient to hold the cork against a vertical body (e. g. the wall) while boring, care must be taken to finish the boring in the hand, otherwise the end of the cork-borer may be blunted. Steel cork-borers (which are the most satisfactory) must be carefully dried before being put away. After boring, the holes made may be smoothed and slightly enlarged if necessary by means of a round file.

EXERCISE. **To fit up a wash bottle.**

A convenient wash bottle for students' use consists of a half litre flat-bottomed or conical flask of moderately stout glass fitted with a doubly bored cork. Through one opening of the cork passes a short tube bent up at an angle of about 45° to the horizontal from a point two or three inches above the cork, and projecting only a short distance into the flask. Through the other hole passes a tube which should reach down to near the bottom of the flask, and be bent round to make an angle of about 45°, so that by proper adjustment the bent part of the two tubes will be in one oblique line as indicated in Fig. 1.

A few inches below the bend the tube is either drawn out to form a jet, or is cut off and connected to a small jet by means of rubber tubing. The latter is the more convenient arrangement and is the one represented in the ordinary flask in Fig. 1.

To make a jet take a short length of tubing and heat the central portion in the Bunsen flame with constant rotation. When the glass is soft remove from the flame and push gently from the two ends towards the centre. If necessary repeat until the central portion of the tube is considerably thickened. Turn down the flame until only the thickened portion is heated, rotating as usual, and when quite soft remove from the flame and draw out steadily with constant rotation so as to increase the length of the tube two or three inches. On making a file mark near the centre and breaking in the manner described above, two jets would be obtained. Cautiously round the ends of one jet in the Bunsen flame, but do not overheat or the opening may close up.

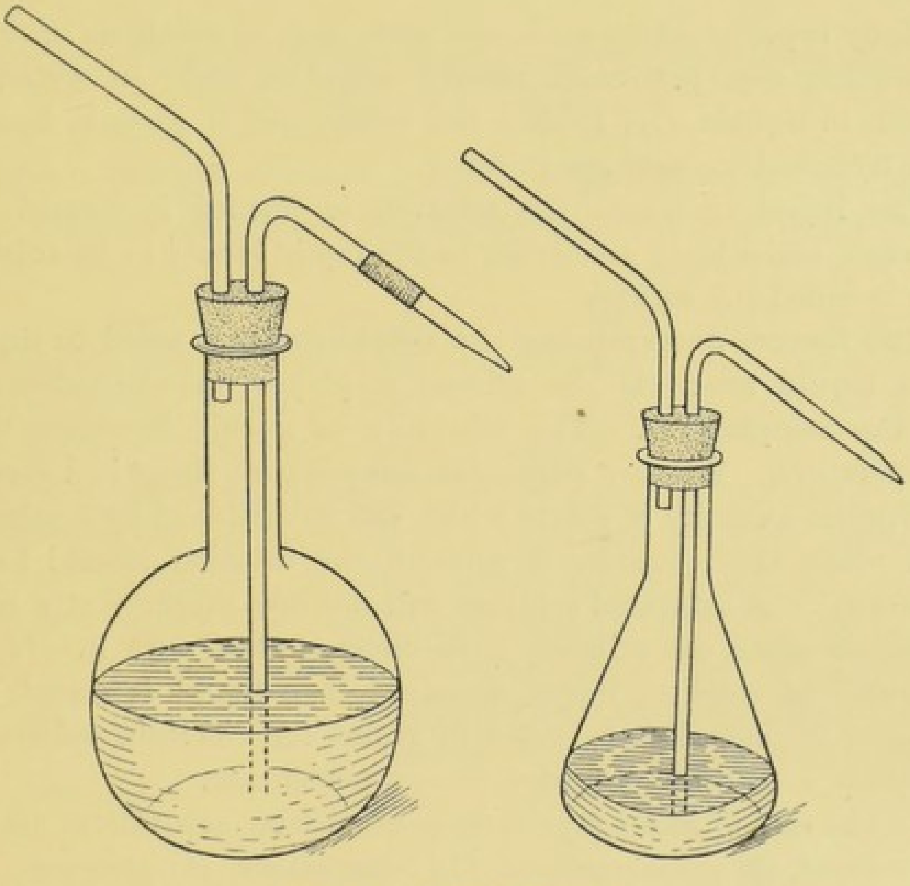

FIG. 1. WASH BOTTLES.

In putting glass tubes into cork or rubber stoppers it is well to moisten the tubes and insert them by a gentle turning motion. [**Caution.** Tubes may break and cut the hands seriously on attempting to force them carelessly through corks.]

II. GENERAL EXPERIMENTAL PROCESSES. Solution, Filtration, Evaporation, Crystallization, Distillation, Sublimation.

One of the commonest operations carried out in chemistry is the preparation of a solution.

Definition. A **solution** is a homogeneous mixture which cannot be split into its constituent parts by mechanical means. [Note.—Mechanical means excludes heat, electricity, or chemical action.]

Many types of solution are met with, such as solutions of solids in liquids, e. g. potassium nitrate (nitre) or sugar in water, of liquids in liquids, e. g. alcohol and water, and of gases in liquids, e. g. hydrochloric acid gas in water.

The liquid in which the solution is formed is termed the **solvent**, and a body dissolving in the liquid is said to be **soluble** and is called the **solute.**

The factors determining the solubility of a solid or liquid in a liquid are :—(1) the solvent employed, (2) the substance, (3) the temperature. The solubility as a rule increases with temperature. For any particular temperature there is a certain maximum quantity of solute which can be dissolved by a solvent, and when this quantity is present, the solution is said to be saturated. A saturated solution will not take up more of a solid or liquid when the solution is in direct contact with it. If the quantity of solid or liquid dissolved in a liquid is stated, the amount is generally expressed in grams for a certain volume of solution, e. g. grams per litre, or as a percentage.

In the case of **gases** four **factors condition solubility**, viz. :—(1) solvent, (2) gas considered, (3) temperature, (4) pressure. In the case of gases the solubility diminishes with rise of temperature, and as regards pressure a definite law can be given, generally called **Henry's Law.** The solubility of a gas varies directly as the pressure at which solution takes place, provided the volume of gas is always measured at standard temperature and pressure. The solubility is generally expressed as a coefficient.

Definition. The **coefficient of solubility** of a gas is the volume of gas soluble in one volume of solvent at normal temperature and pressure (i. e. at 0° C. and 760 mm.); e. g. the coefficient of solubility of ammonia is 1140, of hydrochloric acid 540, of sulphur dioxide 80, of sulphuretted hydrogen 4·5, of carbon dioxide 1·8, of nitrous oxide 1·3, of oxygen 0·04, of nitrogen 0·02, and of hydrogen 0·017. Coefficients of solubility may be stated for other temperatures, e. g. at 15° C. the coefficient for ammonia is 750 and for hydrochloric acid 450.

We are generally concerned in elementary analysis with solutions of solids in liquids, and a common operation which has to be effected is the separation of a soluble body from one insoluble in the particular solvent dealt with. An example of this type of operation is worth working out in detail.

EXERCISE INVOLVING FILTRATION, EVAPORATION, AND CRYSTALLIZATION.

Make a mixture of about 5 grams of potassium nitrate (nitre) and 5 grams of sand. Warm the mixture in a basin with 30–40 c.c. of water: the nitre will dissolve. Fold a round filter paper of say 3 to 5 inches diameter first along a diameter and then at right angles so as to form a quadrant of a circle. It

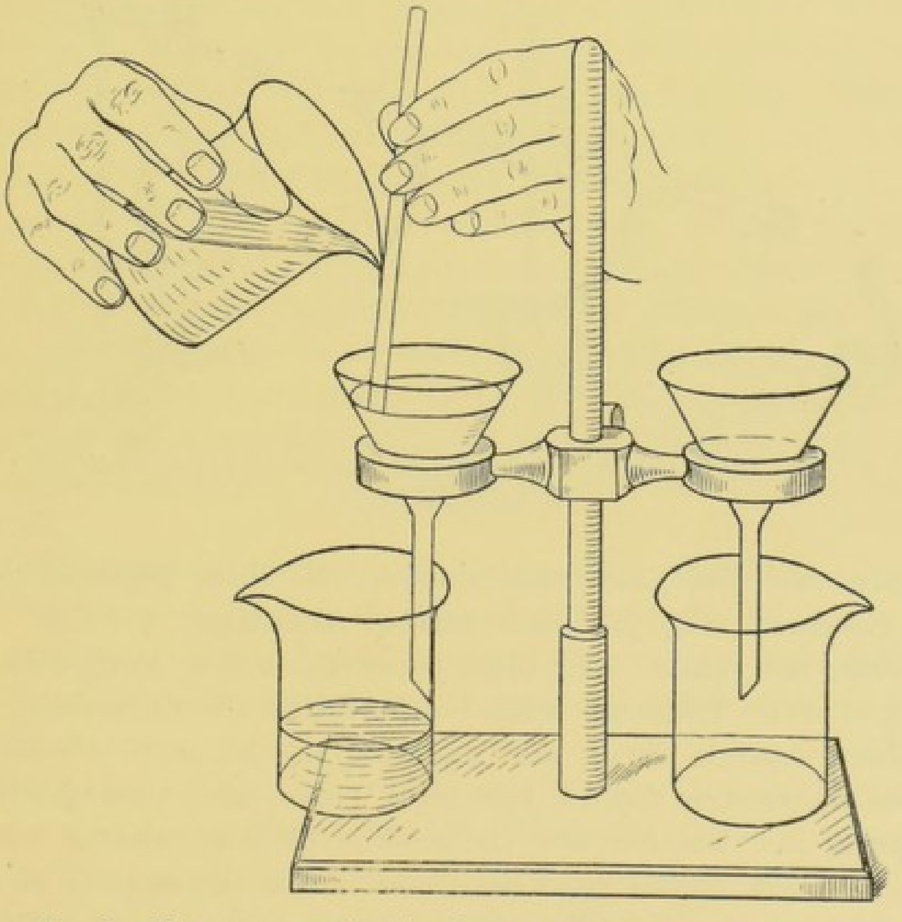

Fig. 2. Filtration. Showing how to avoid loss of material.

will be found that the paper can be opened from either side to form a hollow cone.

Open the paper in a cone, place in a filter funnel, moisten with water, press the paper against the sides of the funnel so as to make it fit tightly, put a porcelain dish under the funnel and separate the solution of nitre from the insoluble sand by slowly pouring the whole of the contents of the beaker into the funnel, taking care not to quite fill the cone at any moment. The solution should be poured from the vessel into the funnel along a glass rod as indicated in Fig. 2. The liquid which passes through the porous paper into the dish is called the filtrate, and the sand remaining on the filter paper is called the **residue**. The process is termed **filtration**.

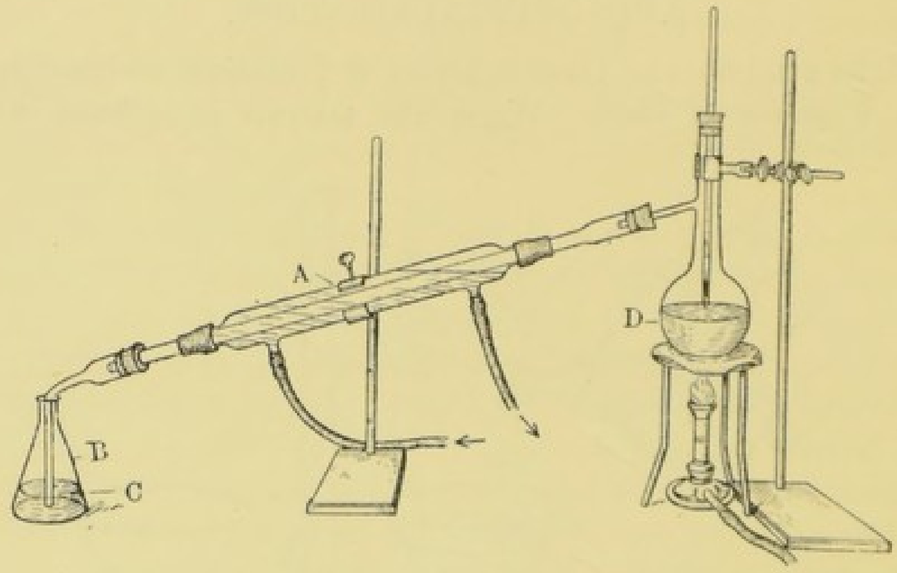

FIG. 3. DISTILLATION. A, Condenser; B, Receiver; C, Distillate; D, Distilling flask.

Wash the residue and filter paper quite free from nitre by a jet of water from the wash bottle, filling the filter paper two or three separate times, and directing the jet at first so as to strike above the top of the filter paper, and then gradually lowering it. In this way the residue of sand will be washed into the apex of the filter cone, and this is the general method of washing residues free from traces of adhering solution. The solution obtained in the dish may be evaporated down to crystallization. By evaporating down at a temperature near the boiling-point, the liquid can be brought into a state of saturation at that temperature, and crystals will begin to separate.

If the liquid be now allowed to cool to room temperature a large quantity of the solid will separate, because the quantity of nitre required to saturate water at room temperature (say 20° C.) is much less than that required to saturate water boiling about 100° C.

Sometimes the solvent may be required as well as the solute. In such a case the process of distillation must be effected.

Definition. **Distillation** means the conversion of a liquid into vapour and condensation into liquid in another vessel.

Place in a distilling flask of capacity 100 c.c. about 50 c.c. of tap water, add a few cubic centimetres of potassium permanganate solution, which will tint the water violet, connect with a condenser and receiver and carry out a distillation by heating the flask containing the liquid with a Bunsen flame. The flask should be placed over wire gauze as shown in Fig. 3.

Add a few small pieces of unglazed porcelain to the liquid before distilling to prevent the temperature rising above the true boiling-point (super-heating) and consequent irregular boiling. The condenser consists essentially of an inner tube which is connected to the side tube of the distilling flask, and an outer tube through which cold water is circulated. The water on heating vaporizes, and the vapour passing into the cooled condenser tube changes to the liquid state and runs into the receiver. Pure water distils over; this can readily be proved by evaporating a small quantity to dryness on a watch-glass, or by determining either of two important physical constants of the liquid, viz. the boiling-point or the freezing-point. Pure water boils at 100° C. and freezes at 0° C.

Sublimation is another general operation, worth mentioning here, by which separation of substances can be effected.

Definition. **Sublimation** means the conversion of a solid into vapour and recondensation of the vapour in another portion of the apparatus.

Exercise. As a practical instance of separation by sublimation make a mixture of about a gram of common salt and a gram of ammonium chloride (sal ammoniac), place in a dry test-tube, and heat cautiously with a Bunsen flame. The ammonium chloride sublimes and condenses on the cool upper portion of the tube. Ammonium, mercury, arsenic, and antimony compounds can sometimes be separated from non-volatile bodies in this way.

PART II

A. SIMPLE PREPARATIONS OF NON-METALLIC ELEMENTS AND COMPOUNDS

PREPARATION OF HYDROGEN. Symbol H.

Atomic weight 1. Density 1.

[**Caution.** Hydrogen forms an explosive mixture with air.]

From Zinc and dilute Sulphuric Acid.

(*a*) Place in a dry test-tube a few pieces of granulated zinc, and then add about 1 c.c. of concentrated sulphuric acid. Note that practically no action occurs. On heating, a gas is evolved which has a strong odour of burning sulphur. This gas is sulphur dioxide.

(*b*) Add slowly with constant shaking about 5 c.c. of concentrated sulphuric acid to about 30–40 c.c. of water. [**Caution.** Do not add the water to the acid.] Pour the solution on to a few grams of granulated zinc in a test-tube, small flask, or Woulff's bottle. Close the vessel by means of a cork (preferably of rubber) carrying a thistle funnel and delivery tube, the end of which should be placed under water in a trough as indicated in Fig. 4. After allowing time for the air to be displaced, collect some of the gas in small jars or test-tubes, and carry out the following tests:—

(1) If a jar is used, close it by means of a ground-glass plate the rim of which has been lightly smeared with vaseline; if a test-tube is used, close with the thumb, and, keeping the jar or tube inverted, apply a lighted match or taper to the mouth. The gas burns with an almost non-luminous flame. On putting the lighted match or taper up into the vessel, it will be extinguished. This experiment shows that hydrogen burns in air, but does not allow carbonaceous material such as wood or wax to burn in it. The gas is said to be combustible, but not to support combustion.

Definition. Combustion in chemistry generally means chemical action attended by the evolution of light and heat.

(2) Place a tube filled with gas with the mouth upwards,

remove the cover from the mouth, and after about a second apply a light. A sharp explosion is heard, and a flash of light passes down the tube.

(3) Remove the delivery tube from the trough and attach by means of a short piece of rubber tubing a small jet, preferably made of hard glass. Before attaching the jet place in the tube near the wide end a loose plug of cotton-wool, which will to a considerable extent obviate the risk of explosion if the hydrogen issuing from the jet is ignited before the air has been completely displaced from the vessel. Add more zinc and dilute sulphuric acid if necessary, and when the reaction has been proceeding vigorously for a few minutes apply a light to the jet. The hydrogen will take fire and burn with a nearly non-luminous flame. (Note.—If the jet is made of soft glass the flame will become yellow after a time because a trace of sodium will get into the flame from the glass.) Bring quickly over the burning jet a clean dry beaker, and hold it there for a few seconds. Note that the interior of the beaker becomes dimmed by the deposition of a film of moisture by condensation of the product of combustion of the hydrogen. Water is therefore formed when hydrogen burns in air.

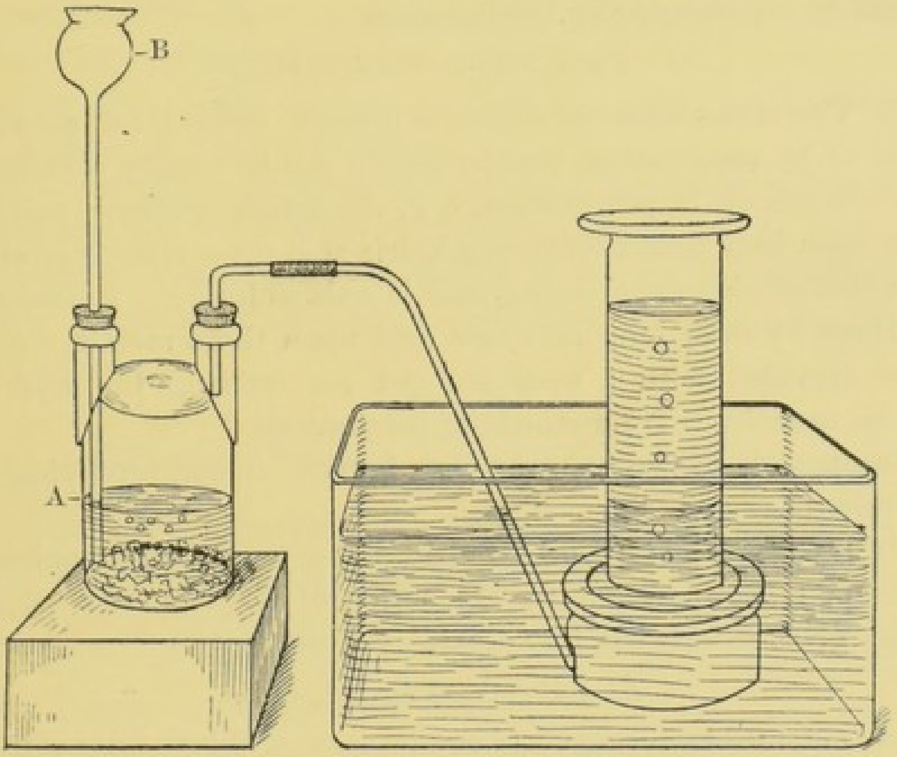

Fig. 4. Preparation of Hydrogen. a, Woulff's bottle; b, Thistle funnel.

(4) Pass hydrogen for a short time through a solution of ferric chloride to which sulphuric or hydrochloric acid has been added. No effect will be observed; the yellow colour of the solution remains unchanged. Now add a few pieces of granulated zinc to the liquid so as to set free hydrogen in the solution. In a few minutes the solution becomes practically colourless. The **nascent hydrogen**, as hydrogen just being liberated is termed, has reacted differently from ordinary hydrogen.* It is assumed that ordinary hydrogen consists of molecules formed by the union of 2 atoms, represented by H_2, whereas nascent hydrogen consists of free atoms. The above reaction, which is a reduction process, would be represented by the equation

$$FeCl_3 + H = FeCl_2 + HCl.$$

(5) The student should convince himself, either by direct experiment or by observation, that hydrogen can be readily obtained by other methods of preparation, e. g. the action of dilute sulphuric acid upon iron, action of hydrochloric acid upon zinc, iron or tin, or action of zinc upon strong caustic soda solution. It cannot be obtained by the action of nitric acid upon these metals. A test-tube provided with a cork and jet for igniting the hydrogen can be used for these methods of preparation.

Summary of what may be learnt from foregoing experiments.

(1) Hydrogen can be prepared by the action of dilute sulphuric acid upon zinc, but not by the action of the concentrated acid, which gives chiefly sulphur dioxide. The equation

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

must therefore be wrong. If one represents dilute sulphuric acid as H_2SO_4Aq, where Aq stands for an indefinite proportion of water (Latin *Aqua*), the correct equation would be as follows:—

$$Zn + H_2SO_4Aq = ZnSO_4Aq + H_2.$$

NOTE. **As a general rule it is always better to put Aq after substances which are dissolved in water, and this practice will usually be adhered to throughout this book, unless in the case of complicated equations and reagents mentioned separately.**

(2) Hydrogen can be obtained by the action of dilute sulphuric

---

* NOTE.—Another theory explains this type of reaction as being due to a catalytic action of the metal (cf. p. 18).

acid or of hydrochloric acid on other metals, but not by the action of nitric acid.

(3) Hydrogen burns in air to form water. The reaction depends upon the oxygen present in air and might be represented by an equation—

$$2H_2 + O_2 = 2H_2O.$$

(4) Hydrogen does not support combustion.

(5) A mixture of hydrogen with air explodes if heated.

[Note.—One might learn from this to be careful in applying a light to any mixture containing hydrogen and air; e. g. coal gas contains generally about 50 per cent. of hydrogen as well as other combustible gases, so that a light should not be brought near any large volume of coal gas admixed with air.]

Test for hydrogen. The gas burns with a nearly non-luminous flame. Water is the only product.

Note.—Similar summaries are not given in the further experiments described. The student should make them for himself. To learn how to summarize the results of a series of experiments in a few words is an important method of learning any experimental science.

OXYGEN. Symbol O. Atomic weight 16.

(Density, i. e. weight compared with hydrogen as unity = 16.)

Carry out the following experiments:—

(1) Take a few crystals of potassium chlorate ($KClO_3$) and heat in a test-tube of hard glass. The crystals fuse at about 360° C. and the liquid slowly gives off oxygen. Close the tube loosely with the thumb while heating, so as to allow for escape of displaced air, but prevent downward convection currents. When the tube may be supposed to be filled with the evolved gas, remove the thumb and insert into the tube a glowing splint of wood. (A cedar splint is best for this purpose.) The splint glows more brightly and then bursts into flame. This constitutes a test for oxygen, but it is not entirely reliable because nitrous oxide behaves similarly (cf. p. 31).

(2) Put into a 6 to 8 oz. round-bottomed flask of hard glass a mixture of about one ounce of powdered potassium chlorate and two ounces of manganese dioxide. Connect with a delivery tube as shown in Fig. 5, and fill 4 small wide jars (or 8-ounce conical flasks) with the gas over water. If flasks are used they must

be supported in position during the process of filling. [**Caution.** Be careful to heat very cautiously, otherwise the gas may come off so rapidly that the reaction flask will burst.] It will be noted during the experiment that the evolution of oxygen takes place at a much lower temperature in this second preparation although the manganese dioxide remains unaltered at the end. Substances behaving like the manganese dioxide are termed **'catalytic agents'**. The glass jars should be closed by ground-glass plates slightly greased round the edges: it will be sufficient to close the flasks with ordinary rolled corks. The following reactions should then be carried out:—

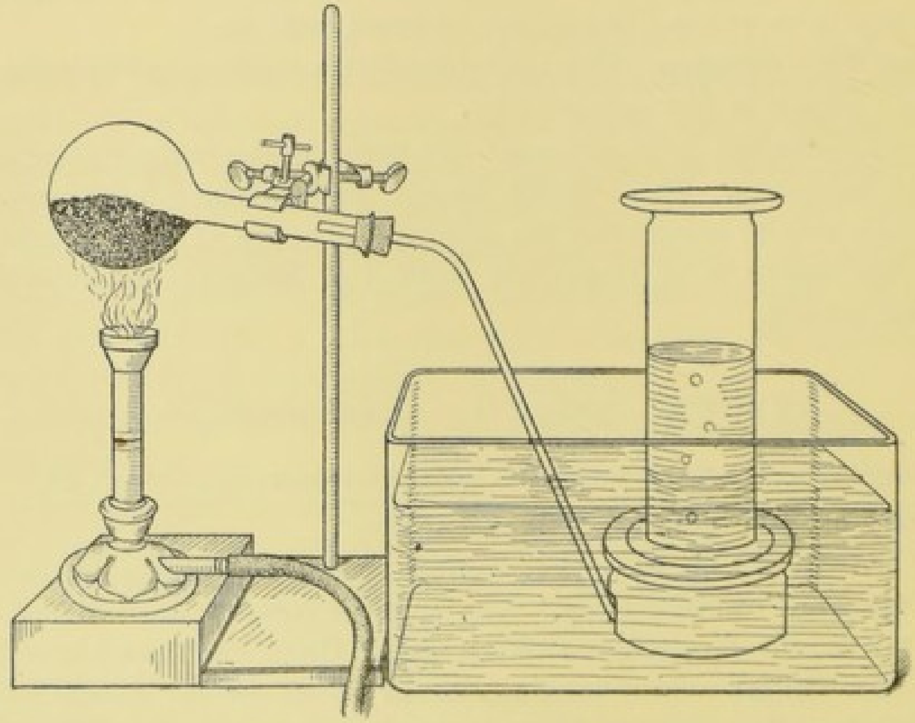

FIG. 5. PREPARATION OF OXYGEN.

(*a*) Heat in a deflagrating spoon in the Bunsen flame a small piece of carbon (e.g. wood charcoal) until it begins to glow at one point, and then rapidly place the spoon in one of the collection vessels. The ordinary deflagrating spoon consists of a shallow brass cup connected with a stout iron wire which passes through a cork in a brass disk. By pushing down or pulling up the wire one can adjust the position of the combustible body in the reaction vessel. [Note.—If a deflagrating spoon is not available, one can easily be improvised from a piece of stout brass or copper wire and a piece of asbestos sheet. Bend the end of the wire into a small circle, and then fix into the ring a small cup made from the asbestos sheet. The end of the wire is then passed through a disk cut from the sheet or a piece of cardboard, and can be raised or lowered as required. The best position for the cup is near the bottom of the flask.] The product of combustion is a colourless gas, carbon dioxide (see p. 40).

Equation expressing the reaction : $C + O_2 = CO_2$.

Add a small quantity of neutral litmus solution and shake the flask. The litmus turns red because of the formation of a solution of carbonic acid.

Equation : $CO_2 + H_2O + Aq = H_2CO_3Aq$.

(*b*) Carry out a similar experiment with sulphur. The sulphur burns with a blue flame much more vigorously than in air, and a white fume fills the flask. The white fumes are due to a small quantity of sulphur trioxide (SO_3), but the main product of the combustion is the colourless gas sulphur dioxide (SO_2).

Equation : $S + O_2 = SO_2$.

Add a few cubic centimetres of neutral litmus solution and shake the flask. The solution turns a bright red owing to the presence of sulphurous acid.

$$SO_2 + H_2O + Aq = H_2SO_3Aq.$$

(*c*) Heat the end of a few inches of magnesium ribbon (or wire) held vertically by means of tongs in the Bunsen flame. When it begins to burn plunge into one of the vessels containing oxygen. A far more vigorous combustion takes place. Place the white product in a small flask, add a few cubic centimetres of diluted red litmus solution—obtained by adding one drop of dilute hydrochloric acid to litmus solution—and warm gently on a wire gauze over a flame. The litmus turns blue, owing to the presence of a slightly soluble base, magnesium hydroxide. The magnesium burns to form magnesium oxide.

Equation : $2Mg + O_2 = 2MgO$.

The magnesium oxide takes up water to form magnesium hydroxide, which is slightly soluble in water.

$$MgO + H_2O = Mg(OH)_2.$$

Both magnesium oxide and magnesium hydroxide are 'bases' (see below).

(*d*) Heat a small quantity of metallic calcium (raspings) in a clean deflagrating spoon until it begins to glow and then at once plunge into a vessel containing oxygen. The calcium glows more brightly and finally a white powder remains. After allowing to cool, wash the product off the spoon with water and add a few cubic centimetres of reddened litmus solution. The litmus will be turned blue because of the presence of a soluble base, calcium hydroxide.

(*a*) $2Ca + O_2 = 2CaO$ (calcium oxide : quicklime).

(*b*) $CaO + H_2O = Ca(OH)_2$ (calcium hydroxide).

In order that above reactions may be thoroughly understood, a few explanations must be given. On glancing at the equations expressing above combustions it will be observed that in each case the oxygen has combined with the element to form an oxide.

DEFINITION. An **Oxide** is a compound formed by the union of oxygen with another element.

The **Oxides** form an important group of compounds, and there are several notable classes in the group. Two of the classes of oxides most commonly met with are the **Acid Anhydrides** and the **Basic Oxides.** The first and second products obtained in the above combustions (viz. CO_2 and SO_2) belong to the former group, and the third and fourth (MgO and CaO) to the latter, and it should be noted that the above acid anhydrides are oxides of non-metals, while the basic oxides are oxides of metals.

DEFINITION. An **Acid Anhydride** is an oxide which when added to water forms an acid, e. g. CO_2, SO_2, SO_3, P_2O_5, B_2O_3. They are generally oxides of non-metals, but CrO_3 (chromic anhydride) is a notable exception, being a metallic oxide which is an acid anhydride.

DEFINITION. A **Basic Oxide** is a compound of a metal with oxygen, which can react with acids to form a salt and water, e. g. MgO, CaO, BaO, CuO, Bi_2O_3, HgO, Ag_2O, Al_2O_3, Fe_2O_3, Cr_2O_3.

The basic oxides are invariably oxides of metals, and they belong to the group of substances called Bases.

Three fundamental groups of bodies have been mentioned in giving the above definitions, viz. **Acids**, **Bases**, and **Salts.** These may be defined as follows:—

DEFINITION. An **Acid** is a compound containing hydrogen which can be wholly or partially replaced by a metal by the action of the acid on a moist metallic oxide or hydroxide, e. g. HCl, HNO_3, H_2SO_4, H_3PO_4, $CH_3.COOH$ (Acetic acid. Only one of the 4 hydrogen atoms is replaceable by metal).

Definition. A **Base** is a metallic oxide or hydroxide, the metal in which can directly replace the hydrogen of an acid to form a salt and water, e. g. metallic oxides : MgO, CaO.

Metallic hydroxides (compounds of a metal with oxygen and hydrogen) : $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$, $Cu(OH)_2$, $Bi(OH)_3$, $Al(OH)_3$, $Fe(OH)_3$, $AgOH$, NH_4OH, $NaOH$, KOH. The last two substances, which are very soluble in water compared with most of the other metallic hydroxides, are called *caustic alkalies*.

Definition. A **Salt** is a compound derived from an acid by replacing part or all the replaceable hydrogen by metal. Most of the substances dealt with in qualitative analysis are salts, e. g. $NaCl$, KNO_3, $(NH_4)_2SO_4$, $CuCl_2$, $Ca(NO_3)_2$, $BaSO_4$.

Note.—Oxygen could be prepared by various other reactions ; e. g. a good method is to heat potassium permanganate.

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

CALCULATIONS OF WEIGHTS OF REACTING SUBSTANCES AND OF PRODUCTS OF REACTION FROM EQUATIONS. Estimation of the Volume of Gaseous Bodies.

In practical chemistry one has frequently to calculate the weights of bodies obtainable by reactions, and also weights of reacting substances ; e. g. one might calculate what weight of anhydrous zinc sulphate could be obtained from say 130 grams of zinc, and also the weight of sulphuric acid required for the reaction. The equation expressing the relationship between the weights of zinc, sulphuric acid, and zinc sulphate would be

$$\begin{array}{ccccccc} \underline{Zn} & + & \underline{H_2SO_4Aq} & = & \underline{ZnSO_4Aq} & + & \underline{H_2} \\ 65 & & \underline{2+32+64} & & \underline{65+32+64} & & 2 \\ & & 98 & & 161 & & \end{array}$$

It must be remembered in making calculations that the symbol for any element employed in an equation represents a number of parts by weight of the element corresponding to the atomic weight. Using the ‘unitary’ system of calculation one might proceed as follows :—

The equation shows that 65 parts by weight of zinc react with 98 parts by weight of sulphuric acid to yield 161 parts by weight of zinc sulphate. Parts by weight may be translated into any units we please,

∴ 65 grams of zinc react with 98 grams of H_2SO_4 to yield 161 grams of zinc sulphate,

1 gram of zinc reacts with $\frac{98}{65}$ grams of H_2SO_4 to yield $\frac{161}{65}$ grams of zinc sulphate,

and 130 grams of zinc react with $\left(\frac{98}{\underset{1}{\cancel{65}}} \times \overset{2}{\cancel{130}}\right)$ grams H_2SO_4 to

yield $\left(\frac{161}{\underset{1}{\cancel{65}}} \times \frac{\overset{2}{\cancel{130}}}{1}\right)$ grams of zinc sulphate.

Answer. 130 grams of zinc would react with 196 grams of sulphuric acid and yield 322 grams of anhydrous zinc sulphate.

In the case of gases one may have to find not only the weight, but also the volume at a given temperature and pressure. e.g. Find the weight and volume of hydrogen in above case, the temperature of collection being 25° C. and the pressure equivalent to 690 millimetres of mercury.

The equation shows that

65 grams of zinc would by interaction with H_2SO_4 yield 2 grams of hydrogen.

∴ 1 gram of zinc would by interaction with H_2SO_4 yield $\frac{2}{65}$ grams of hydrogen.

∴ 130 grams of zinc would by interaction with H_2SO_4 yield $\left(\frac{2}{\underset{1}{\cancel{65}}} \times \overset{2}{\cancel{130}}\right)$ grams of hydrogen.

= **4 grams. Answer.**

CALCULATION OF VOLUME FROM WEIGHT.

There are two starting-points for calculating the volume of a gas from its weight.

I. The molecular weight in grams of any gas occupies 22·4 litres at Normal Temperature and Pressure (termed N. T. P.); Normal temperature is 0° C.; Normal pressure is said to be 760 millimetres, because the pressure of the atmosphere at sea-level can on an average be balanced by a column of mercury 760 mm. high ; e. g. 2 grams of hydrogen (H_2), 32 grams of oxygen (O_2), 28 grams of nitrogen (N_2), 44 grams of carbon dioxide (CO_2) would each respectively occupy 22·4 litres at 0° C. and 760 mm. pressure.

II. The weight of one litre of Hydrogen (measured at N. T. P.) is 0·0899 gram. The weight of one litre of any other gas = 0·0899 × density, and the **density of a gas is half its molecular weight,**

∴ The weight of one litre of any other gas

$$= 0{\cdot}0899 \times \frac{\text{molecular wt.}}{2}.$$

The first starting-point is generally the more convenient. In this case 2 grams of hydrogen occupy 22·4 litres at 0° C. and 760 mm.

∴ 1 gram of hydrogen occupies $\frac{22{\cdot}4}{2}$ litres at 0° C. and 760 mm.

and 4 grams of hydrogen occupy $\left(\frac{22{\cdot}4}{2} \times 4\right) = 44{\cdot}8$ litres at N. T. P.

Corrections must next be applied for pressure and temperature, which can be done by taking into consideration the laws expressing the relationship of volume to pressure and temperature respectively.

A. Correct for Pressure.

Boyle's Law states that the volume of a gas varies inversely as the pressure (temperature remaining constant), so that if the pressure is increased the volume is diminished, and vice versa. The standard pressure is 760 mm., and the pressure at collection 690 mm. At 690 mm. the volume will be greater than at 760 mm. in the ratio $\frac{760}{690}$. The volume of hydrogen collected at 0° C. and 690 mm. would be $\left(44{\cdot}8 \times \frac{760}{690}\right)$ litres.

B. Correct for Temperature.

Charles' Law. The volume of a gas alters $\frac{1}{273}$ of its volume at 0° C. for each alteration of temperature of 1° C. (pressure remaining constant). If one considers a volume of 273 c.c., this volume at 1° C. would become $273 + \frac{1}{273} \times \frac{273}{1} = 274$ c.c., at 10° C. would be $273 + \frac{100}{273} \times \frac{273}{1} = 373$ c.c., and would double in volume at 273° C. If the temperature fell to − 1° C. the volume would become $273 - \frac{1}{\cancel{273}} \times \frac{\cancel{273}}{1} = 272$ c.c.

At − 100° C. the volume would be $273 - \frac{100}{\cancel{273}} \times \frac{\cancel{273}}{1} = 173$ c.c., and at − 273° C. the volume would theoretically become 0. Temperatures counted from − 273° C. (which is called the absolute zero) are called **absolute temperatures**, and Charles' Law might be stated as follows:—

The volume of a gas is directly proportional to its absolute temperature. **Absolute temperature = t° C. + 273.**

The absolute temperature corresponding to 0° C. and to 25° C. would be 273 and (273 + 25). The volume of gas at 298 absolute would be greater than the volume at 273 absolute, so that the volume of hydrogen at 690 mm. and 25° C. would be

$$44{\cdot}8 \times \frac{76\cancel{0}}{69\cancel{0}} \times \frac{298}{273} = 53{\cdot}87 \text{ litres.} \quad \textbf{Answer.}$$

From this detailed explanation and example the following general statement may be deduced: To convert volume at N. T. P. (i. e. 0° C. and 760 mm.) into volume at any other temperature and pressure multiply by two factors (**a**) by a factor expressing the ratio of the pressures, (**b**) by a factor expressing the ratio of the absolute temperatures.

The results might also be worked out by means of a formula, but it must be noted that it is not satisfactory to apply as a routine a formula which might not be understood.

The formula in question would be

$$\frac{VP}{T} = \frac{V'P'}{T'},$$

where V, P, and T are the initial volume, pressure, and absolute temperature (T and P being in above case 0° C. and 760 mm.), and V′, P′, and T′ the final volume, pressure, and absolute temperature V′ is required.

$$V' = V \times \frac{P}{P'} \times \frac{T'}{T}.$$

Applying this formula in above case $V' = 44{\cdot}8 \times \frac{760}{690} \times \frac{298}{273}$.

Exercise. Find the volume of oxygen collected at 20° C. and 1000 mm. pressure obtained on heating 24·5 grams of potassium chlorate. 5·48 litres. **Answer.**

Hydrogen and **Oxygen** unite to form two oxides of which the more important is **Hydrogen Oxide,** Water, H_2O: the other is **Hydrogen Peroxide,** H_2O_2.

HYDROGEN OXIDE, WATER, H_2O.

Preparation. If one wished to prepare a large quantity of pure water it could be done by distilling some form of natural water, e.g. rain, river, spring, or sea water. Distil over about 20 c.c. of tap water from a small flask, using the apparatus figured and described on p. 12. Carry out the following experiments:—

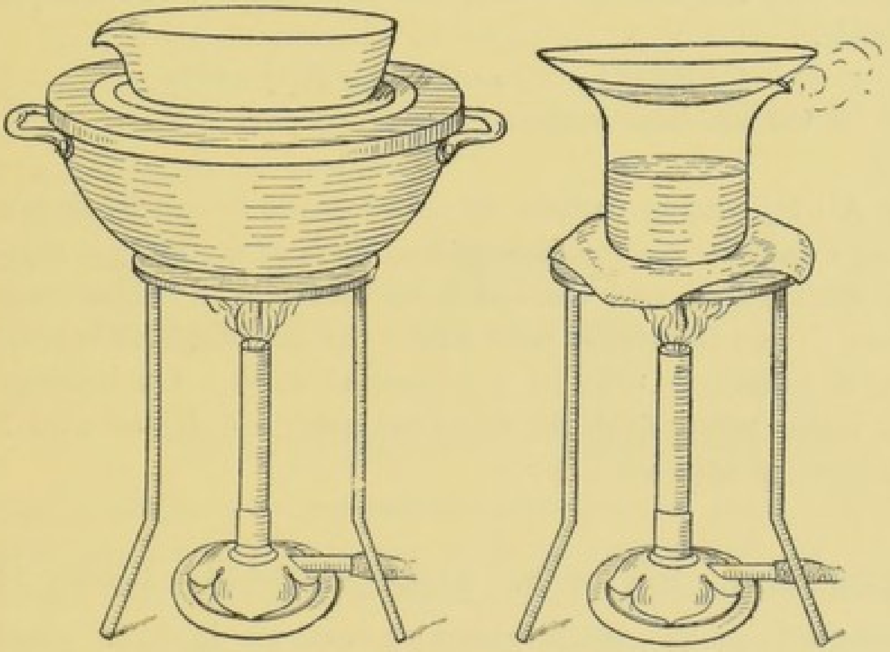

Fig. 6. Copper Water-bath and Beaker used as Water-bath.

(1) Evaporate about 3 c.c. of the distillate to dryness on a watch-glass placed on a water-bath. [**Note.**—A water-bath is an arrangement for heating by steam at ordinary pressure, and generally consists essentially of a copper vessel in which water is boiled. In this case a beaker containing water will do. Put a folded piece of paper between the watch-glass and the beaker

to allow for escape of steam, and then boil the water in the beaker.] Note that there is practically no residue. The different types of apparatus which might be used are represented in Fig. 6.

Now evaporate about the same volume of tap water. A distinct residue will be obtained.

(2) Add a few drops of a solution of silver nitrate to a few c.c. of distilled water and tap water in different test-tubes. No reaction is obtained with the distilled water, but a white opalescence or precipitate is obtained with tap water. Tap water always contains chlorides, hence the reaction (cf. p. 226).

Note. The above differences between distilled and tap water explain why distilled water is generally used in analytical work.

(3) If the tap water happens to be 'temporarily hard' it will usually give a precipitate on boiling down, say 100 c.c. to about half its bulk, owing to the decomposition of the bicarbonates of calcium and magnesium, which are the cause of the temporary hardness.

$$\underbrace{Ca(HCO_3)_2}_{\text{Calcium Bicarbonate.}} = \underbrace{CaCO_3}_{\text{Calcium Carbonate.}} + H_2O + CO_2$$

(4) All tap waters contain dissolved gases, as can be shown by boiling a sample in a round-bottomed flask of say 500 c.c. capacity filled with water, and connected by means of a rubber stopper with a delivery tube filled with water, the end of which is brought under a collecting tube in a trough of water. On boiling the water in the round flask the dissolved gases are driven over into the collecting tube (cf. p. 335).

NITROGEN. SYMBOL N. Atomic weight 14. Density 14.

Nitrogen can be readily prepared from air in large quantity by passage over heated metallic copper, which withdraws oxygen and leaves the nitrogen.

$$2Cu + O_2 = 2CuO.$$

Such nitrogen is impure, containing argon and other substances.

Preparation. A good method of preparing pure nitrogen in quantity would be to warm a solution containing sodium or potassium nitrite and ammonium chloride.

Nitrogen is evolved according to the equation

$$NH_4ClAq + KNO_2Aq = KClAq + 2H_2O + N_2.$$

Method of procedure. Dissolve 5 grams of sodium nitrite and 10 grams of ammonium chloride in 50 c.c. of water and warm gently in a small flask fitted with a delivery tube passing under water. Fill several jars or test-tubes with the gas, and note the following properties:—

(1) The gas is odourless, colourless, tasteless, nearly insoluble in water.

(2) A glowing splint is extinguished, and the gas does not burn. Positive tests are more satisfactory than negative tests. They are hardly suited for a beginner, but are worth summarizing:—

(*a*) Determination of density by weighing—14.

(*b*) Pass electric sparks through a mixture of oxygen and the gas over mercury. Brown fumes of nitrogen peroxide are obtained.

$$N_2 + 2O_2 = 2NO_2.$$

(*c*) Heat a small quantity of magnesium powder in the gas. Magnesium nitride is formed as a yellowish solid, which at once reacts on addition of a few drops of water to give ammonia, which can be recognized by its odour.

Equations:

$$(a)\ 3Mg + N_2 = \underset{\text{Magnesium Nitride.}}{\underline{Mg_3N_2}}$$

$$(b)\ Mg_3N_2 + 3H_2O = 3MgO + 2NH_3.$$

THE ATMOSPHERE. Density 14·43.

The atmosphere is a mechanical mixture of gases. There is usually approximately 21 per cent. of oxygen, 78 per cent. of nitrogen, and 1 per cent. of argon and allies present, measured by volume. Carbon dioxide is present to the extent of about 0·03 per cent. by volume, water vapour in variable quantity, and traces of ozone (O_3), ammonia (NH_3), nitrogen peroxide (NO_2), &c., may be present.

One can prove the presence of these gases in the following way:—

(1) Oxygen. On burning carbon, sulphur, magnesium, calcium, &c., identical products are obtained with those produced on burning in oxygen. The only difference apparent in the two sets of processes is that in the latter case the combustion is much more brilliant.

(2) Nitrogen. The nitrogen can be tested for by negative tests after removing the oxygen, or by passing electric sparks through a few c.c. of air over mercury. Brown fumes of nitrogen peroxide (NO_2) are formed.

[(3) Argon and allied gases can best be proved to be present by removing the other constituents, and then investigating the spectra.]

(4) Carbon dioxide can be detected by drawing a considerable volume of air through lime-water, or by exposing a few cubic centimetres of lime-water on a clock-glass for some time. In either case a white precipitate of calcium carbonate is formed.

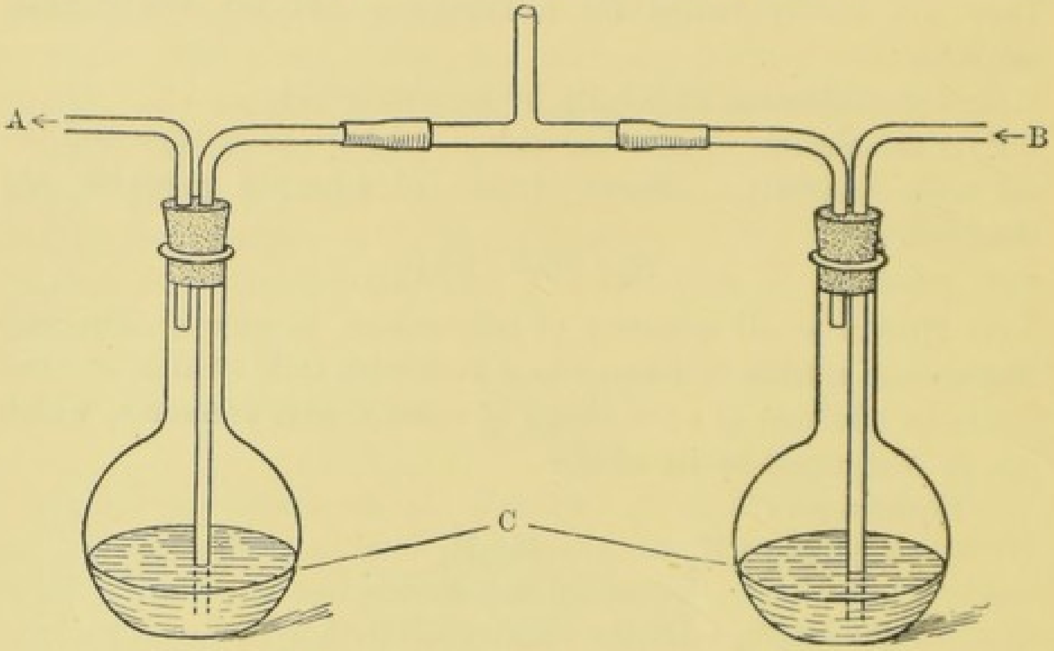

Fig. 7. Apparatus for proving that Respired Air contains far more Carbon Dioxide than Ordinary Air. A, Respired Air forced out; B, Ordinary Air drawn in; C, Lime-water.

$$Ca(OH)_2Aq + CO_2 = CaCO_3 + H_2O.$$

Note. There is far more carbon dioxide—over 100 times as much—in respired air than in atmospheric air, as can easily be proved by the following experiment. Fit up two test-tubes or small flasks closed by doubly-bored corks, through each of which pass two tubes in such a way that on connecting by a T-piece air can be drawn into the lungs through lime-water in one vessel and exhaled through lime-water in the other. In Fig. 7 the arrangement of the tubes is indicated.

In the solution through which the air passes into the lungs no precipitate is formed, but a copious precipitate is thrown down in the vessel through which the respired air passes.

(5) Water vapour can be tested for by exposing phosphorus pentoxide or calcium chloride for some time to air. Solutions are ultimately formed. The water vapour in the air will be deposited as dew if cold water is poured into a clean dry beaker.

(6) Ozone could be tested for by means of starch iodide paper (i. e. paper which has been moistened with potassium iodide and starch paste and then dried). Such papers turn blue because of liberation of iodine and formation of starch iodide (see p. 37).

$$O_3 + 2KI + H_2O = O_2 + 2KOH + I_2.$$

Nitrogen peroxide would also set free iodine.

Nitrogen forms several compounds with hydrogen. The most important is ammonia.

AMMONIA, NH_3. Molecular weight 17. Density 8·5.

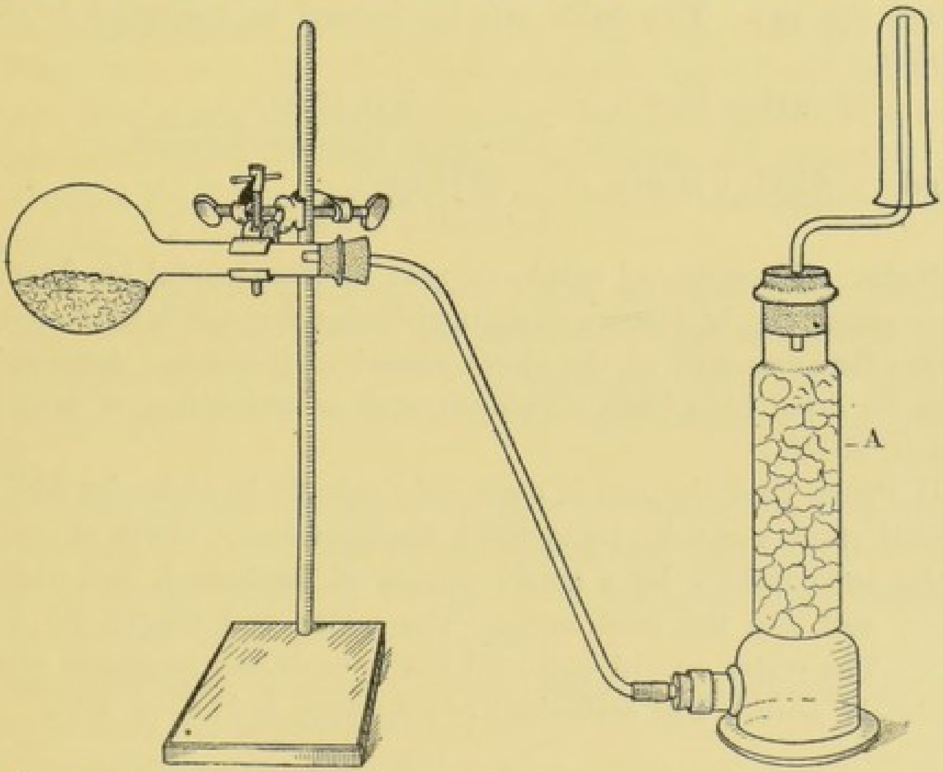

FIG. 8. PREPARATION OF AMMONIA. Collection by Upward Displacement (i. e. downward displacement of air). A, Drying Tower, containing lumps of Quicklime or Caustic Soda.

Preparation. Heat a mixture of slaked lime and ammonium chloride in a small flask of hard glass, and pass the gas evolved first over lumps of quicklime (CaO), or sticks of caustic potash or soda to dry it, and then up into a small flask or large test-tube as represented in Fig. 8. Note the following properties :—

(1) The pungent characteristic odour. Do not attempt to smell the pure gas, but by motion of the hand cause convection currents which will bring a small quantity of the gas to the nostrils.

(2) Note the alkaline reaction by putting a piece of moist red litmus paper in the stream of gas. It will be turned blue immediately.

(3) Note the formation of white fumes on bringing a drop of any strong volatile acid (e. g. HCl or HNO_3) into the flask containing the gas. The white fumes are due to the formation of ammonium salts, since ammonia reacts directly with acids, e. g.

$$NH_3 + HCl = \underset{\text{Ammonium Chloride,}}{\underline{NH_4Cl}}$$

$$NH_3 + HNO_3 = \underset{\text{Ammonium Nitrate.}}{\underline{NH_4NO_3}}$$

Ammonia is absorbed by sulphuric acid, which cannot be used to dry the gas. Two salts can be formed as indicated in the equations.

$$NH_3 + H_2SO_4 = \underset{\text{Ammonium Hydrogen Sulphate,}}{\underline{NH_4HSO_4}}$$

and $$2NH_3 + H_2SO_4 = \underset{\text{Ammonium Sulphate.}}{\underline{(NH_4)_2SO_4}}$$

[**Note.** Concentrated sulphuric acid is often useful for drying other gases, e.g. hydrogen, oxygen, chlorine, &c., but is worse than useless for ammonia, as the above equations indicate. Ammonia must be dried by a basic substance such as quicklime or caustic potash, KOH.]

(4) Prove that the gas is extremely soluble in water by filling a small stout test-tube by upward displacement. Cover the end of the tube tightly by a small square of cardboard, put under water, and slip the card aside. The water will nearly fill the tube. The water would quite fill the tube if the ammonia were absolutely pure. The coefficient of solubility is 1140 at 0° C.

OXIDES OF NITROGEN.

These are six in number and have the respective formulae N_2O, NO, N_2O_3, NO_2, N_2O_4, and N_2O_5. The oxides of nitrogen form an excellent example of the Law of Multiple Proportions.

I. Nitrous Oxide (N_2O). Molecular weight 44. Density 22.

Prepare a small quantity of nitrous oxide by cautiously heating a few grams of ammonium nitrate in a small round-bottomed flask carrying a cork and delivery tube (cf. Fig. 5). Collect the gas by downward displacement or over warm water as the gas is somewhat soluble in cold water (coeff. 1·3 at 0° C.). The tubes may be closed by well-pressed corks. The sweetish odour and the anæsthetic properties can hardly be used as tests, but the following reactions are noteworthy :—

(1) Note that the gas rekindles a glowing splint in a similar manner to oxygen. The heat splits up the gas into nitrogen and oxygen, the latter gas reacting with the hot carbon.

$$2N_2O = 2N_2 + O_2.$$

(2) Half fill a test-tube with the gas over water and then pass up into the tube a few c.c. of nitric oxide during preparation of that substance. No reaction takes place. Oxygen at once reacts with nitric oxide to give a deep brown gas, nitrogen peroxide (NO_2).

II. Nitric Oxide, NO. Molecular weight 28. Density 14.

Place in a flask provided with a thistle funnel and delivery tube a few grams of copper turnings and then about 50 c.c. of dilute nitric acid. Warm gently. A brown gas seems to be evolved at first, but after a time the gas in the flask becomes colourless.

(*a*) Fill a tube with the gas over water, and then open the tube in air. Deep brown fumes are produced owing to reaction with the oxygen of the air. $2NO + O_2 = 2NO_2$. The brown fumes have a pungent characteristic odour, reminding one of nitric acid.

(*b*) Pass the gas through a solution of ferrous sulphate made by shaking a few crystals of that substance with water. The solution changes to a deep brown colour, owing to the formation of an addition compound $NO \cdot 2FeSO_4$.

III. Nitrogen Trioxide, N_2O_3 **(Nitrous Anhydride),** is the anhydride of the unstable acid HNO_2.

This substance is unsuitable for laboratory preparation. Put a very small quantity of arsenious oxide in a test-tube, add a few drops of conc. nitric acid, and warm cautiously. A brown gas comes off which is a mixture of nitric oxide and nitrogen peroxide, and if condensed in a freezing mixture would give nitrogen trioxide as a blue liquid.

$$As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + NO + NO_2.$$
$$NO + NO_2 = N_2O_3.$$

IV. Nitrogen Peroxide (NO_2); and V. Nitrogen Tetroxide (N_2O_4).

(1) Heat a few crystals of lead nitrate in a test-tube until the brown gas evolved fills the tube. Equation $2Pb(NO_3)_2 = 4NO_2 + 2PbO + O_2$. Cautiously heat the tube along its length and note that the colour deepens. Loosely cork the tube and then put it into a Nessler glass (or into a wide test-tube) nearly filled with pounded ice and conc. hydrochloric acid. After allowing to stand for a few minutes note that the colour almost disappears. The reddish gas has condensed to form a modification called nitrogen tetroxide, which is colourless. Remove the tube from the freezing mixture, wipe dry, and heat: the colour reappears, the reaction being *reversible* as indicated by writing the equation $2NO_2 \leftrightarrows N_2O_4$.

The relationship between NO_2 and N_2O_4 is known as **polymerism**, the two gases being termed polymeric modifications.

Definition. **Polymerism** is a term applied to the existence of two or more bodies with the same elements in the molecule, and the same relationship between the relative numbers of atoms of these elements, but the molecular weight of the one is a multiple of that of the other, and one can be readily transformed into the other. A great many polymers are met with in Organic Chemistry.

(2) Test the solubility of the gas by filling a tube by downward displacement. Put the mouth of the tube under water and shake. The water rises and the brown colour disappears. Nitrogen peroxide reacts with water to give a mixture of nitrous and nitric acids.

$$2NO_2 + H_2O = \underbrace{HNO_2}_{\text{Nitrous Acid.}} + \underbrace{HNO_3}_{\text{Nitric Acid.}}$$

VI. Nitrogen Pentoxide, N_2O_5 (Nitric Anhydride).

This body is an unstable white solid which is unsuitable for laboratory preparation. It can be obtained by warming gently nearly pure nitric acid (prepared as described below) with a large quantity of phosphorus pentoxide in a retort, and condensing what comes off in a U-tube placed in a good freezing mixture.

$$P_2O_5 + 2HNO_3 = N_2O_5 + 2HPO_3.$$

NITRIC ACID, HNO_3. Liquid. Boiling pt. 86° C.

Prepare about 10 to 15 c.c. of nearly pure nitric acid by distilling slowly in a retort of 8 to 10 oz. capacity a mixture of 15 to 20 grams of potassium or sodium nitrate and excess of concentrated sulphuric acid—say 20 to 30 c.c. Cool the small flask used as a receiver by placing it in a basin of water and putting a moist cloth over the top as indicated in Fig. 9. Nearly pure nitric acid can also be prepared by distilling in a similar way the ordinary concentrated acid (about 70 per cent.) with excess of concentrated sulphuric acid.

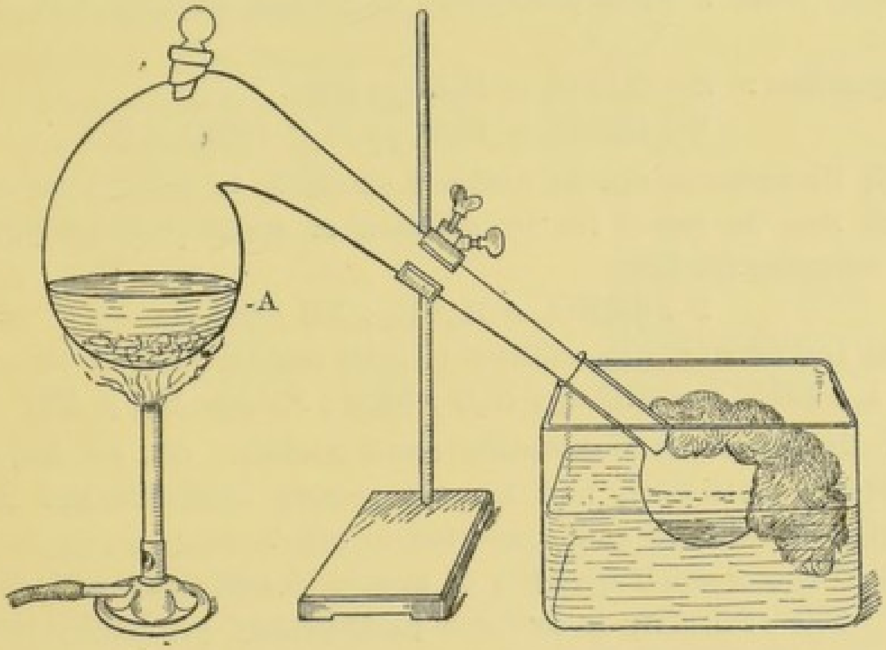

FIG. 9. PREPARATION OF NITRIC ACID. A, Retort.

The yellowish liquid collecting in the receiver is coloured by nitrogen peroxide produced by decomposition of nitric acid.

Equations: (*a*) $KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$.

(*b*) $4HNO_3 = 2H_2O + 4NO_2 + O_2$.

[**Caution.** **The strong acid collected is extremely corrosive. It stains the skin yellow and raises blisters.**]

Pure nitric acid is a colourless liquid, sp. gr. **1·5**. The concentrated acid used in the laboratory is an aqueous solution containing about 70 per cent. of acid, sp. gr. 1·42.

Nitric acid is a powerful oxidizing agent. Carry out a selection of the following experiments illustrating this fact.

A. Experiments with the non-metals. C, S, P, I.

(1) Warm a few grams of sawdust on a firebrick placed over a Bunsen burner until it begins to char. Then pour a few drops

of the acid prepared in above experiment upon it. The sawdust burns and brown fumes of nitrogen peroxide are produced.

$$C + 4HNO_3 = CO_2 + 2H_2O + 4NO_2.$$

(2) Boil up in a test-tube a small quantity of sulphur with the concentrated acid. The sulphur will be oxidized to sulphur trioxide (p. 49), which will form sulphuric acid with the water present. Test for sulphuric acid by adding barium chloride (p. 224), when a white precipitate of barium sulphate will come down.

Equations: $S + 2HNO_3 = H_2SO_4 + 2NO.$

$$S + 4HNO_3 = H_2SO_4 + H_2O + 3NO_2 + NO.$$

[(3) Phosphorus can be oxidized similarly to phosphoric acid, which may be tested for by addition of ammonium molybdate and warming (p. 231).

$$P + 3HNO_3 = H_3PO_4 + NO + NO_2.]$$

[(4) Iodine would be oxidized to iodic acid (HIO_3).

$I_2 + 4HNO_3 = 2HIO_3 + H_2O + 3NO + NO_2.$] See p. 233.

B. Reactions with metalloids and metals. Sb, As, Sn, Cu. Arsenic, antimony, and tin are merely oxidized, but most metals are oxidized and converted to salts.

(5) Warm a small quantity of powdered antimony with nitric acid. The antimony is oxidized to antimony pentoxide, which separates (hydrated) as a white powder.

Equation: $2Sb + 4HNO_3 = \underbrace{Sb_2O_5 \,.\, H_2O}_{2HSbO_3 \text{ (Metantimonic Acid)}} + 3NO + NO_2$

[(6) Warm a small quantity of powdered arsenic with the acid. It goes into solution as arsenic acid.

Equation: $As + 3HNO_3 = H_3AsO_4 + NO + 2NO_2.$]

(7) Warm a few small pieces of granulated tin with concentrated nitric acid. Dense brown fumes are evolved and the tin is oxidized to stannic oxide, SnO_2.

$$Sn + 4HNO_3 = SnO_2 \,.\, H_2O + H_2O + 4NO_2.$$

(8) Copper is at once dissolved. Ag, Bi, Hg, and Pb would behave similarly.

$$3Cu + 8HNO_3Aq = 3Cu(NO_3)_2Aq + 4H_2O + 2NO.$$

THE HALOGEN ELEMENTS. (F), Cl, Br, I.

Chlorine. Symbol Cl. Atomic weight 35·5. Density 35·5.

Preparation I. Prepare chlorine by warming in a flask a mixture of manganese dioxide (preferably granular) and concentrated hydrochloric acid.

Equation: $MnO_2 + 4HClAq = MnCl_2Aq + 2H_2O + Cl_2$.

The flask is closed by a cork carrying a thistle funnel and a tube for collection by downward displacement as indicated in Fig. 10. Fill a few test-tubes or small jars and also prepare a solution by saturating about 20 c.c. of water with the gas in a small flask. The preparation should preferably be carried out in a fume cupboard. Note the greenish-yellow colour and pungent odour, but (**Caution**) great care should be taken to avoid inhaling even a small quantity of the pure gas. Carry out the following experiments:—

(*a*) Shake into a vessel containing gas a small quantity of finely powdered antimony. A vigorous reaction takes place with evolution of light and heat, the antimony forming antimonious chloride ($SbCl_3$, solid) and the pentachloride ($SbCl_5$, liquid).

Equations:

$2Sb + 3Cl_2 = 2SbCl_3$: $2Sb + 5Cl_2 = 2SbCl_5$.

(*b*) Yellow phosphorus will react directly with chlorine to form similar compounds, viz. PCl_3 (liquid) and PCl_5 (solid).

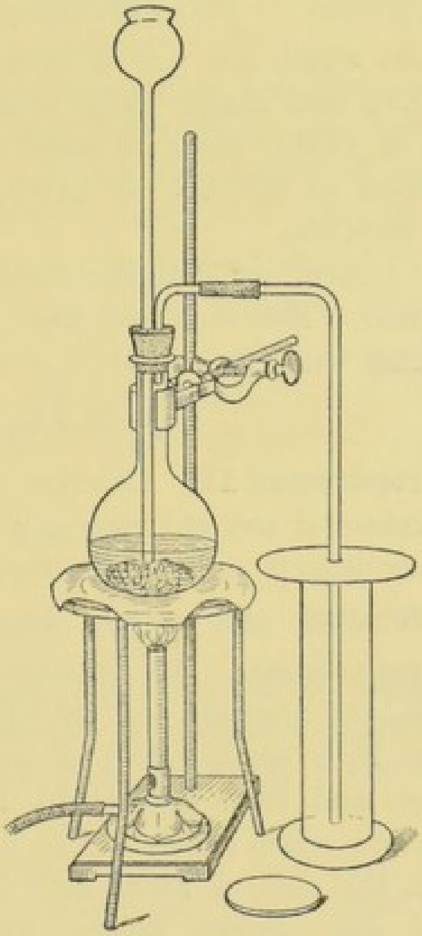

FIG. 10. PREPARATION OF CHLORINE. Collection by Downward Displacement (or upward displacement of air).

(*c*) Note the 'bleaching action'. Put a piece of moist blue litmus paper into the gas. It first turns red and then white. The bleaching effect is due to nascent oxygen set free by interaction of the chlorine and water in presence of an oxidizable body.

Equation: $Cl_2 + H_2O = 2HCl + \underbrace{O}_{\text{Nascent Oxygen.}}$

(*d*) Pass sulphuretted hydrogen through a solution of chlorine water. A precipitate of sulphur is thrown down.

Equation: $H_2S + Cl_2Aq = 2HClAq + S$.

(*e*) Add about one c.c. of chlorine water to a few c.c. of potassium bromide solution. Bromine is set free and the liquid turns brown.

Equation: $Cl_2 + 2KBrAq = 2KClAq + Br_2$.

Add about one c.c. of carbon disulphide (CS_2) or chloroform ($CHCl_3$) and shake. The bromine being much more soluble in CS_2 or $CHCl_3$ than in water dissolves to give a reddish orange solution in the CS_2 or $CHCl_3$, which settles at the bottom of the test-tube.

(*f*) Carry out a similar experiment to (*e*) with potassium iodide solution. Iodine is set free, giving a brown solution, but on shaking with CS_2 or $CHCl_3$ a violet solution will settle.

$$Cl_2 + 2KIAq = 2KClAq + I_2.$$

Preparation II. Chlorine can be readily prepared by warming a mixture of any chloride, e. g. NaCl or KCl, with powdered manganese dioxide and concentrated or slightly diluted sulphuric acid.

Bromine. At. wt. 80. Liquid. B. pt. 63° C. Sp. gr. 3·1.

Preparation. Mix intimately about 2 grams of powdered potassium bromide and an equal weight of manganese dioxide. Place in a small retort of about 8 oz. capacity, moisten with water, and then add about 10 c.c. of concentrated sulphuric acid and warm gently. Use a small flask as receiver, and cool as in the case of nitric acid (see Fig. 9). Bromine comes off as a deep brown vapour which condenses in the receiver, forming a dark brown liquid. Add water to the receiver and shake. A brown solution called bromine water is obtained. Experiments:—

(*a*) Add about one c.c. of bromine water to a few c.c. of a solution of potassium iodide. Iodine is liberated as indicated by the violet colour on shaking up with CS_2 or $CHCl_3$.

Equation: $Br_2 + 2KIAq = 2KBrAq + I_2$.

(*b*) Pass sulphuretted hydrogen through bromine water. The solution becomes colourless, and a precipitate of sulphur is formed.

Equation: $H_2S + Br_2 = 2HBr + S$.

Iodine. At. wt. 127. Grey solid. M. pt. 114°C. B. pt. 184°C. Prepare a small quantity of iodine by mixing a couple of grams of powdered potassium iodide with about 4 grams of manganese dioxide, moistening with water in a small porcelain dish, then adding a few c.c. of concentrated sulphuric acid, covering the dish with another, and warming gently. A sublimate of iodine is obtained as a grey solid on the upper dish.

NOTE.—(*a*) Colour of the vapour on heating—a beautiful violet.

(*b*) The very slight solubility in water.

(*c*) The ready solubility in potassium iodide solution.

(*d*) The deep blue colour obtained by adding one drop of the solution in potassium iodide to a small quantity of freshly prepared starch solution. Note.—To prepare this solution take a small granule of starch about the size of a pea, crush to a powder between the fingers, add a few c.c. of water, and boil for about a minute.

(*e*) Pass sulphuretted hydrogen through the solution of iodine in potassium iodide. A precipitate of sulphur is formed, and the solution becomes colourless.

$$I_2 + SH_2 = 2HI + S.$$

THE HALOGEN HYDRACIDS. (HF), HCl, HBr, HI.

All acids must contain hydrogen, but most contain oxygen as well; in fact, the replaceable hydrogen is generally hydrogen of **hydroxyl**, the name given to the group —O—H. The above halogen acids are therefore exceptional.

Hydrochloric Acid, HCl. Mol. wt. 36·5. Density 18·25. Put a few grams of rock-salt or common salt into a small flask, which can be closed by a cork carrying a thistle funnel and tube for collection by downward displacement (see Fig. 10). Add gradually strong sulphuric acid. Fill a test-tube with the gas. Note that it is colourless but fumes in air because of condensation of the moisture present. Note also the pungent odour and strongly acid reaction. Prove its great solubility by covering the mouth of the tube with a piece of cardboard, inverting, and immersing in water.

By a selection of experiments the student should convince himself of the truth of the following statements:—

(1) Hydrochloric acid does not react with Au, Pt, Hg, or Cu, and very slowly with silver, lead, arsenic, antimony, or bismuth. It should therefore not be used as a solvent for these metals.

(2) It reacts with other metals liberating hydrogen, but in cases where two salts of one metal can be obtained (e. g. iron) the '-ous' compound (that is, the compound with the smaller quantity of chlorine per atom of metal) is obtained, e. g.

$$\mathrm{Fe} + 2\mathrm{HClAq} = \underbrace{\mathrm{FeCl_2Aq}}_{\text{Ferrous Chloride.}} + \mathrm{H_2}.$$

If potassium ferricyanide is added to the solution obtained by dissolving iron in hydrochloric acid, a deep blue precipitate is obtained, proving the presence of a ferrous salt (p. 146).

Hydrobromic Acid, HBr. Mol. wt. 81. Density 40·5. Carry out the following experiment:—

Try a method analogous to that used for the preparation of hydrochloric acid, namely addition of sulphuric acid to potassium bromide (KBr). On warming about a gram of potassium bromide with concentrated sulphuric acid in a test-tube a gas is evolved which fumes in air like hydrochloric acid, but the tube soon fills with brown fumes of bromine and SO_2 is also present. Two reactions take place. (*a*) HBr is liberated.

$$KBr + H_2SO_4 = KHSO_4 + HBr.$$

(*b*) The hydrobromic acid reacts with the concentrated sulphuric acid.

$$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O.$$

The method is therefore not available for preparation of hydrobromic acid.

Either glacial phosphoric acid should be used or bromine be added to red phosphorus covered by a layer of water. (See Advanced Section, p. 45.)

Hydriodic Acid, HI. Mol. wt. 128. Density 64. Hydriodic acid is similar in preparation and properties to hydrobromic acid.

Add sulphuric acid to about one gram of potassium iodide in a test-tube. Hydriodic acid, sulphur dioxide, and iodine are set free. This method is therefore unsuitable for the preparation of hydriodic acid.

Equation: (*a*) $KI + H_2SO_4 = KHSO_4 + HI.$
(*b*) $2HI + H_2SO_4 = 2H_2O + SO_2 + I_2.$

For preparation see Advanced Section (p. 46).

CARBON. Atomic weight 12.

Preparation. Heat cautiously with a small flame about a gram of sugar or starch in a small closed crucible. The mass chars, froths up, and finally a residue of nearly pure carbon is left.

THE OXIDES OF CARBON.

I. Carbon Monoxide,* CO.

II. Carbon Dioxide or Carbonic Anhydride, CO_2.

Carbon Monoxide, CO. Mol. wt. 28. Density 14.

(1) Fill a test-tube with carbon monoxide by warming gently about a gram of sodium formate with one c.c. of concentrated sulphuric acid in a test-tube carrying a delivery tube for collection over water. Add about 2 c.c. of lime-water, and shake. No reaction occurs. Set fire to the gas. It burns with a blue flame, forming carbon dioxide. On shaking the lime-water is rendered turbid.

Equations:

$$HCOONa + H_2SO_4 = HCOOH + NaHSO_4$$
$$HCOOH + H_2SO_4 = H_2SO_4 . H_2O + CO$$
$$2CO + O_2 = 2CO_2$$
$$CO_2 + Ca(OH)_2Aq = CaCO_3 + H_2O.$$

Caution. Care should be taken not to inhale much of the gas, as it is very poisonous, combining with the hæmoglobin of the blood to form carboxy hæmoglobin.

(2) The gas could also be obtained from oxalic acid or potassium ferrocyanide by warming with concentrated sulphuric acid. (See Textbook.)

Equations:

$$H_2C_2O_4 + H_2SO_4 = H_2SO_4 . H_2O + CO + CO_2$$
$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 6CO + 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4.$$

Although water appears in the last equation it must not be added to the reaction mixture, as it is present in sufficient quantity in the sulphuric acid and as water of crystallization of the ferrocyanide. Dilute sulphuric acid would give hydrocyanic acid.

Test. The combustion with blue flame to form carbon dioxide is characteristic. $2CO + O_2 = 2CO_2$.

A more delicate test (e. g. for small quantities in air) could be carried out by shaking a considerable volume with a few c.c. of very dilute blood solution and then examining spectroscopically. A characteristic double-banded absorption spectrum is obtained, unaltered by warming with ammonium sulphide. A somewhat

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* The term carbonic oxide, formerly applied to this compound, should not be used.

similar spectrum given by the compound of oxygen and hæmoglobin (oxyhæmoglobin) is changed by ammonium sulphide.

Carbon Dioxide, CO_2. Mol. wt. 44. Density 22.

Prepare carbon dioxide by adding dilute hydrochloric acid to a few small pieces of marble in a flask provided with a thistle funnel and delivery tube (see Fig. 4). Collect over water or by downward displacement.

Note that the gas neither burns nor supports combustion, but gives a precipitate on shaking with lime-water.

Equation: $Ca(OH)_2Aq + CO_2 = CaCO_3 + H_2O$.

With excess of carbon dioxide the precipitate which first forms redissolves because of the formation of a soluble bicarbonate.

$$CaCO_3 + \overbrace{H_2O + CO_2 = Aq}^{H_2CO_3Aq} = \underbrace{Ca(HCO_3)_2Aq}_{\text{Calcium Bicarbonate.}}$$

Note.—The last reaction is important in nature. Limestone rocks are dissolved in this way by the carbonic acid dissolved in rain-water.

COMPOUNDS OF SULPHUR.

Sulphuretted Hydrogen. Mol. wt. 34. Density 17.

Prepare sulphuretted hydrogen by treating ferrous sulphide with dilute sulphuric acid in a flask fitted with a thistle funnel and delivery tube (see Fig. 4). Fill a few jars or test-tubes by downward displacement, as the gas is soluble in water. Then pass the gas into about 20 c.c. of water in a small flask, shaking from time to time until the liquid is saturated.

NOTE.—(1) Disagreeable odour.

(2) The gas burns with a blue flame, forming water and sulphur dioxide, the latter gas being recognized by its odour of burning sulphur. Equation: $2H_2S + 3O_2 = 2H_2O + 2SO_2$.

(3) The acid character. Moist blue litmus paper is slowly turned red. Sulphuretted hydrogen is a weak acid, both hydrogen atoms being replaceable by metal.

(4) Paper moistened with a soluble salt of Pb, Ag, Hg, Cu, or Bi is turned nearly black on immersion in the gas.

Test. The usual test for the gas besides the characteristic odour is the reaction with paper moistened with lead acetate.

Equation:

$$Pb(C_2H_3O_2)_2Aq + H_2S = \underset{\substack{\text{Lead}\\\text{Sulphide.}}}{\underline{PbS}} + 2H\,.\,C_2H_3O_2Aq$$

(5) The gas is a strong reducing agent, and reacts with many oxidizing agents, e. g. nitric acid, chlorine water, bromine water, iodine in potassium iodide solution, arsenates, ferric salts, concentrated sulphuric acid, potassium permanganate, and potassium chromate and dichromate. As sulphuretted hydrogen is an important reagent in detection of metals, the reactions are notable, since the presence of any of the above bodies in solution may interfere with the ordinary reactions. The reactions with nitric acid and ferric salts are especially important.

Add a few c.c. of the sulphuretted hydrogen solution to a few c.c. of each of the following bodies:—

(*a*) Dilute nitric acid, (*b*) ferric chloride solution, (*c*) chlorine water (p. 36), (*d*) bromine water (p. 36), (*e*) solution of iodine in potassium iodide solution (cf. p. 37), (*f*) sulphurous acid solution. Note that in each case a precipitate of sulphur is thrown down.

Equations:

$$2HNO_3 + 3H_2S = 4H_2O + S + 2NO$$

$$2FeCl_3Aq + H_2S = 2FeCl_2Aq + 2HCl + S$$

$$Cl_2Aq + H_2S = 2HClAq + S$$

$$\left.\begin{array}{r} Br_2Aq + H_2S = 2HBrAq + S \\ Aq + I_2 + H_2S = 2HIAq + S \end{array}\right\} \begin{array}{l}\text{These reactions could be}\\\text{utilized for preparation of}\\\text{solutions of hydrobromic}\\\text{and hydriodic acids.}\end{array}$$

$$H_2SO_3Aq + 2H_2S = 3H_2O + 3S.$$

Preparation of pure sulphuretted hydrogen.

The above method of preparation does not yield a pure product since ferrous sulphide is usually contaminated with iron. A pure sample could be obtained by warming antimonious sulphide (Sb_2S_3) with concentrated hydrochloric acid.

$$Sb_2S_3 + 6HClAq = 2SbCl_3Aq + 3H_2S.$$

OXIDES OF SULPHUR, SO_2, (SO_3).

I. Sulphur Dioxide (Sulphurous Anhydride), SO_2. Mol. wt. 64. Density 32.

Prepare sulphur dioxide by warming copper turnings with concentrated sulphuric acid in a flask fitted with a thistle funnel and delivery tube (see Fig. 10). Fill a test-tube with the gas by downward displacement, and then prepare a solution by passing the gas into a few c.c. of water in a flask.

Note. (1) The characteristic odour of burning sulphur.

(2) The gas is non-combustible and does not support combustion.

(3) Its aqueous solution is strongly acid in reaction.

(4) The body is a strong reducing agent. It converts arsenates to arsenites, chromates and dichromates to chromic salts, and solution of cupric chloride to cuprous chloride. Put a piece of filter paper moistened with potassium dichromate into the gas. The paper turns green because of reduction of the dichromate to chromic salt.

Equation:

$$\underbrace{K_2Cr_2O_7}_{\text{Potassium Dichromate.}} + 3H_2SO_3Aq + H_2SO_4Aq = K_2SO_4Aq + \underbrace{Cr_2(SO_4)_3Aq}_{\text{Chromic Sulphate.}} + 4H_2O.$$

(5) Carry out tests to prove that it is at once oxidized by certain bodies, e.g. NO_2, Cl_2Aq, Br_2Aq, which transform the dioxide into trioxide, and the latter, since water is present, immediately forms sulphuric acid.

(*a*) Add bromine water to some of the solution. Note that the brown colour at once disappears and that the liquid contains sulphuric acid, as can readily be proved by adding barium chloride solution, when a white precipitate of barium sulphate is formed, insoluble in acids.

$$SO_2 + H_2O + O\boxed{H_2 + Br_2}Aq = H_2SO_4Aq + 2HBr.$$

(*b*) Pass NO_2 into a solution of sulphur dioxide, and then test the liquid for sulphuric acid.

$$NO_2 + SO_2 + H_2O = H_2SO_4 + NO.$$

This is the chief reaction in the preparation of sulphuric acid on the large scale.

II. Sulphur Trioxide (Sulphuric Anhydride), SO_3.

This substance is not suited for preparation by one beginning the subject. It is a white fuming solid which reacts vigorously with water to form sulphuric acid ($SO_3 + H_2O = H_2SO_4$), and is obtained by passing a dry mixture of sulphur dioxide and oxygen over warmed platinized asbestos. $2SO_2 + O_2 = 2SO_3$. For apparatus and details of preparation see p. 49.

SULPHURIC ACID, H_2SO_4.*

Two methods of preparation have been indicated above. The pure acid is an oily liquid, sp. gr. 1·85, which reacts vigorously with water. **Caution.**—It must never be added to a hot solution.

Although rarely used as a solvent the following general properties of the acid are worth remembering, and the student should be able to devise experiments to verify the statements.

The dilute and concentrated acid respectively behave quite differently with metals, the dilute acting like hydrochloric acid (p. 37) and the concentrated acid like nitric acid (p. 34).

A. Dilute Sulphuric Acid.

The dilute acid does not act upon Au, Pt, Ag, Cu, Hg, and acts with difficulty upon Pb, As, Sb, Bi.

When it does act hydrogen is evolved, and if the metal forms two salts the -ous compound is obtained.

$$\text{e. g.}\quad Fe + H_2SO_4 = \underset{\text{Ferrous Sulphate.}}{\underline{FeSO_4Aq}} + H_2$$

B. Concentrated Sulphuric Acid.

(1) The concentrated acid does not act upon Au and Pt, but reacts with most other metals with evolution of sulphur dioxide.

$$\begin{aligned} \text{e. g.}\quad Cu + 2H_2SO_4 &= CuSO_4 + 2H_2O + SO_2 \\ Hg + 2H_2SO_4 &= HgSO_4 + 2H_2O + SO_2 \\ Zn + 2H_2SO_4 &= ZnSO_4 + 2H_2O + SO_2. \end{aligned}$$

In this last case sulphuretted hydrogen is also formed.

(2) Hot concentrated sulphuric acid is also a powerful oxidizing agent, e. g. it gives up oxygen to carbon and sulphur, which form dioxides.

$$\begin{aligned} C + 2H_2SO_4 &= CO_2 + 2SO_2 + 2H_2O \\ S + 2H_2SO_4 &= \underbrace{SO_2 + 2SO_2}_{3SO_2} + 2H_2O. \end{aligned}$$

COMPOUNDS OF PHOSPHORUS.

Phosphine: Phosphoretted Hydrogen, PH_3.

This gas is unsuitable for general laboratory preparation. It can be obtained by heating yellow phosphorus with caustic soda or potash.

$$4P + 3NaOHAq + 3H_2O = PH_3 + \underset{\substack{\text{Sodium}\\ \text{Hypophosphite.}}}{\underline{3NaH_2PO_2}}$$

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* The following acids mentioned in this section of the book are included in the British Pharmacopœia:—Sulphuric, Sulphurous, Nitric, Phosphoric, Hydrochloric, Hydrobromic, Boracic or Boric.

It is nearly insoluble in water, is poisonous, and has the odour of decaying fish. The compound is the chemical analogue of ammonia, and forms similar salts with acids, e. g.

$$HI + PH_3 = \underbrace{PH_4I}_{\text{Phosphonium Iodide.}}$$

The exact method of preparation of phosphine is indicated in the Advanced Section (p. 95).

Phosphorus Pentoxide, P_2O_5.

This substance is a white, very hygroscopic solid obtained by burning phosphorus in excess of air or oxygen.

$$4P + 5O_2 = 2P_2O_5.$$

It dissolves in cold water, forming metaphosphoric acid, and on boiling the solution orthophosphoric acid is obtained, as could be proved by tests (p. 231).

$$P_2O_5 + H_2O = 2HPO_3 \text{ (Metaphosphoric Acid).}$$
$$HPO_3 + H_2O = H_3PO_4 \text{ (Orthophosphoric Acid).}$$

Boron, B. At. wt. 11. **Silicon, Si.** At. wt. 28.

These two elements can be prepared by heating excess of the oxides with magnesium powder in a closed crucible to a high temperature.

$$B_2O_3 + 3Mg = 2B + 3MgO.$$
$$SiO_2 + 2Mg = Si + 2MgO.$$

After removal of the magnesium oxide by dilute hydrochloric acid, and filtering, the elements are obtained as nearly black powders, which glow in air when strongly heated, forming the oxides (B_2O_3 and SiO_2).

These oxides are anhydrides of boracic (H_3BO_3) and silicic acids (H_2SiO_3 and H_4SiO_4) respectively.

ADVANCED PREPARATIONS. COMPOUNDS OF NON-METALS

NOTE:—These advanced preparations are especially suitable for students who wish to become proficient in the subject, e. g. to Intermediate Science Candidates who intend to proceed to the Bachelor of Science Degree Examination. They should be read over by all Students however.

I. HALOGEN COMPOUNDS. (*a*) HALOGEN ACIDS.

HYDROBROMIC ACID, HBr (B.P.).

Method I. Place in a distilling flask about 7 grams of red phosphorus, cover with water, and add slowly from a dropping

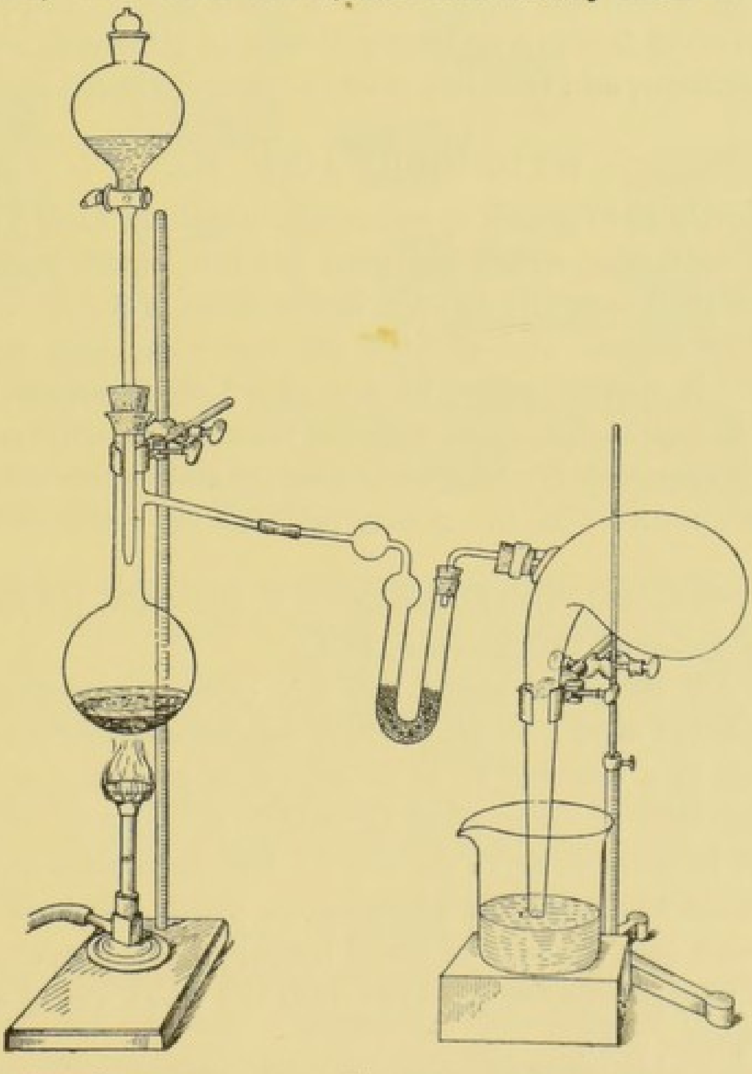

FIG. 11. PREPARATION OF A SOLUTION OF HYDROBROMIC ACID.

funnel 50 grams of bromine. The flask is connected as shown in the diagram with a U-tube, which is half filled with glass beads or broken pieces of glass which have been rubbed up with a paste of 4 grams of red phosphorus and 1 c.c. of water. The U-tube is connected to a retort, the end of which is placed just above the surface of water in a beaker. Warm gently with a rose burner * as long as hydrobromic acid passes over. Distil the product, and collect what comes over at 125°–126° C. separately. This part of the distillate will contain 48 per cent. of hydrobromic acid. If the gas is required, remove retort and collect by downward displacement from end of U-tube.

Equations: (*a*) $2P + 3I_2 = 2PI_3$.

(*b*) $PI_3 + 3HOH = 3HI + P(OH)_3$.

Method II. Add slowly 50 grams of bromine to 50 grams of benzene in which has been placed a gram of iron filings. Pass the gas evolved through an empty U-tube in a freezing mixture to remove benzene, and then into water as above. Distil the product.

HYDRIODIC ACID, HI.

Add slowly to 37 grams of iodine in a distilling flask 3 grams of yellow phosphorus, which has been cut into small pieces under water and then carefully dried. The reaction is at first a vigorous one. After cooling add about 5 c.c. water and heat cautiously. If the gas is wanted collect by downward displacement, but if a solution is required pass into water by the arrangement represented for hydrobromic acid. Distil the product and collect what comes over at about 125–128° C. A fifty per cent. acid is thus obtained.

(*b*) CHLORIDES FORMED BY DIRECT UNION.

(1) Phosphorus Trichloride, PCl_3.

Fill a dry retort of about 250 c.c. capacity one-third full of freshly ignited sand (i. e. sand which has been strongly heated for some time in a crucible so as to get rid of moisture and volatile matter and then cooled). Pass dry carbon dioxide† (p. 40) through the retort in order to drive out the air, and then place on the sand 15–20 grams of dry yellow phosphorus, which has been cut into small pieces (say the size of small beans) under water. The cut pieces of phosphorus are removed from the water one at a time by

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* Cf. footnote, p. 51.

† Dry by passage through a wash bottle containing concentrated Sulphuric Acid.

a forceps, and carefully dried on filter paper before placing in the retort. [**Caution.** Yellow phosphorus is extremely inflammable and should on no account be brought into direct contact with the skin.]

Pass chlorine through the apparatus, and connect the end of the retort with a small flask used as receiver, which should be placed in a mixture of ice and hydrochloric acid (conc.) or embedded in a mixture of pounded ice and salt. The diagram shows the arrangement of the apparatus.

The current of chlorine should be so regulated by raising or lowering the delivery tube above the phosphorus, that the phosphorus burns quietly, and phosphorus trichloride distils over steadily. If the current is too slow the pentachloride forms, and condenses on the retort as a yellow crust. Fractionate the product. Phosphorus trichloride is a colourless liquid boiling at 78° C.

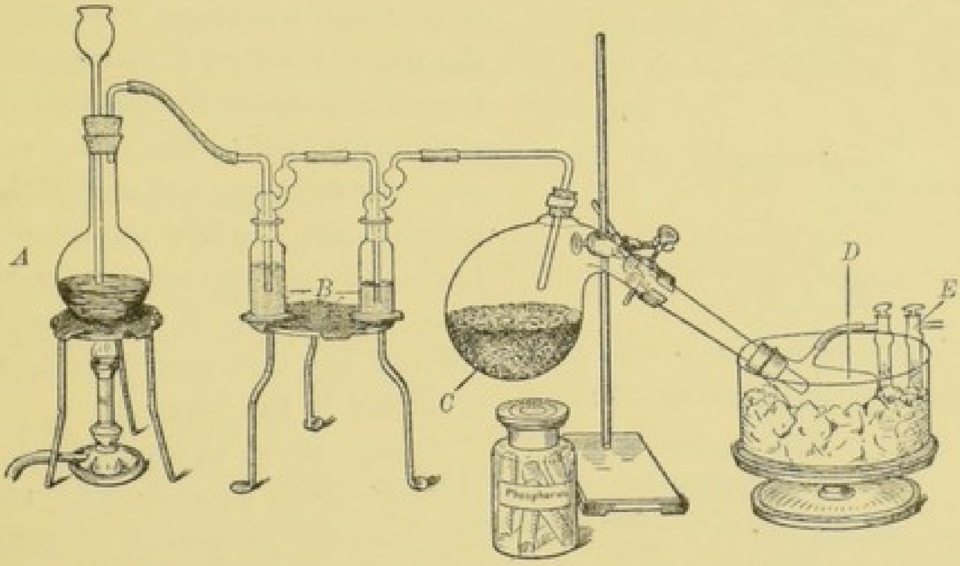

Fig. 12. Preparation of Phosphorus Trichloride (PCl_3). A, Chlorine Apparatus; B, Wash-bottles containing concentrated Sulphuric Acid; C, Retort; D, stout Filter Flask used as receiver; E, Tube containing Calcium Chloride to prevent access of moisture.

$$2P + 3Cl_2 = 2PCl_3.$$

Experiment. Add a small quantity of the product to water. It decomposes with formation of hydrochloric acid and phosphorus acid.

$$PCl_3 + 3HOH = P(OH)_3 + 3HCl.$$

[**Sulphur Chloride,** S_2Cl_2, could be prepared in a retort in a similar way, but no sand is required. The sulphur is placed in the dry retort, warmed gently, and chlorine passed over it. Sulphur chloride forms and can be distilled off into a receiver when the reaction has been completed. It is a liquid of a disagreeable odour which reacts with water and is used as a solvent for sulphur, b. pt. 138° C.

Sulphur Iodide, S_2I_2 (B. P.), is prepared by heating up in a flask 1 part of sulphur with 4 parts of iodine. It is a solid slightly soluble in glycerine.]

Phosphorus Pentachloride, PCl_5.

The pentachloride is readily obtained from the trichloride by the action of chlorine. Take a large bottle and fit it with a cork with three openings. Through one passes the stem of a separating funnel containing the phosphorus trichloride, while the other two serve for entrance and exit of dry chlorine gas. Allow phosphorus trichloride to flow from the funnel until the bottom of the vessel is covered, and then pass chlorine as indicated in the diagram.

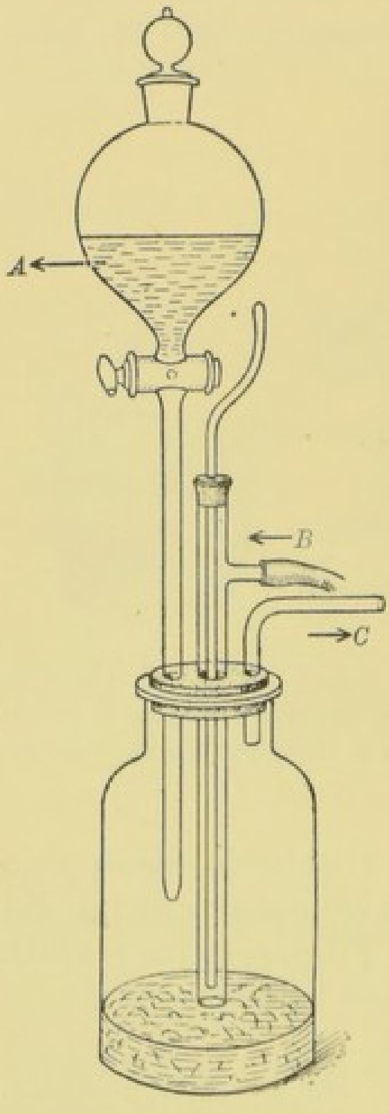

FIG. 13. PREPARATION OF PHOSPHORUS PENTACHLORIDE (PCl_5). A, PCl_3; B, Entrance for Dry Chlorine; C, Exit.

Admit more phosphorus trichloride from time to time and continue the passage of chlorine until the whole has become a solid mass. Allow to stand in an atmosphere of chlorine for a couple of days, stirring up from time to time with a glass rod. Finally, drive out the excess chlorine with carbon dioxide, and remove the product to a bottle. Cover the stopper of the bottle with melted paraffin wax, so as to prevent access of air to the substance. Phosphorus pentachloride is a faintly yellow solid which decomposes with water.

$$PCl_5 + 4HOH = H_3PO_4 + 5HCl.$$

[**Caution.** All operations with phosphorus chlorides should be carried out in fume cupboard. The fumes affect the respiratory organs.]

Phosphorus Oxychloride (Phosphoryl Chloride), $POCl_3$.*

The best method of preparation is to oxidize phosphorus trichloride by means of potassium chlorate. Put in a retort about 50 grams of phosphorus trichloride and then add slowly in small portions about 30 grams of potassium chlorate. Allow the reaction to complete itself before adding a fresh portion of chlorate, and if necessary warm gently with a rose burner.† Finally distil off the oxychloride into a thick-walled vessel such as a filter flask. Distil the product, which is a colourless liquid, and collect what comes over at about 110° C.

[Phosphorus oxychloride can also be prepared by heating up a mixture of phosphorus pentachloride with boric or oxalic acid. Heat in a retort and distil off the oxychloride.

$$3PCl_5 + 2H_3BO_3 = 3POCl_3 + 6HCl + B_2O_3.$$

It reacts with water.

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.]$$

Silicon Chloride, $SiCl_4$.

Silicon (p. 44) when heated in chlorine forms silicon chloride, a colourless volatile liquid which could be condensed in a receiver placed in a freezing mixture. Suitable apparatus is indicated in Fig. 14 if gasholder (A) and burner (F) be withdrawn.

The compound, like nearly all chlorides of non-metals, is decomposed by water.

$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl.$$

[**Boron Chloride, BCl_3.**

This compound could be prepared in a similar way to silicon chloride. Its properties are analogous, e. g. it decomposes with water.

$$BCl_3 + 3HOH = B(OH)_3 + 3HCl.]$$

II. COMPOUNDS CONTAINING OXYGEN.

Sulphur Trioxide, SO_3.

Pass sulphur dioxide and oxygen through strong sulphuric acid so as to thoroughly dry them, and then pass the mixed gases over heated platinized asbestos. (The platinized asbestos is easily prepared by soaking asbestos fibres in chloroplatinic acid and then decomposing the platinum compound on the fibres by heating cautiously.)

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* Conveniently described here because of its connexion with the Phosphorus Halides.

† Cf. Note on p. 51.

Equations: $$\underset{\text{2 vols.}}{\underline{2SO_2}} + \underset{\text{1 vol.}}{\underline{O_2}} = 2SO_3.$$

The apparatus is indicated in Fig. 14.

Condense the product in a well-cooled receiver placed in a freezing mixture. A white crystalline solid is obtained which fumes in air (m. p. 46° C.). On strongly heating it decomposes into sulphur dioxide and oxygen, so that the temperature of preparation must not be too high. The receiver might be sealed at E after the experiment.

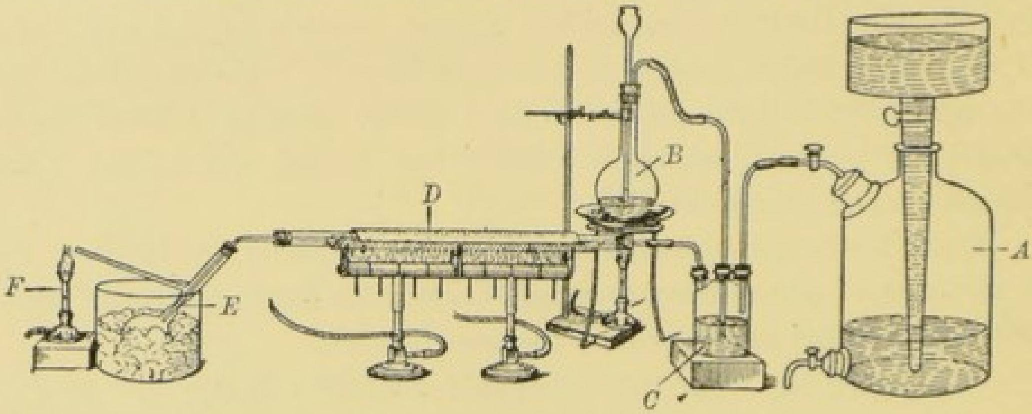

Fig. 14. Preparation of Sulphur Trioxide (SO_3). A, Gasholder containing Oxygen; B, Flask containing Copper and Sulphuric Acid for making Sulphur Dioxide; C, Wash-bottle containing concentrated Sulphuric Acid; D, Tube containing platinized Asbestos; E, Distilling Flask constricted at E to serve as receiver; F, Burner to decompose fumes of SO_3 which escape condensation.

Silica, SiO_2. Preparation from impure siliceous material (e. g. sand or flint).

Method I. Crush the material to powder in an iron mortar, mix with about twice the weight of anhydrous sodium carbonate and heat strongly in a porcelain or platinum crucible over a blowpipe until effervescence ceases. (See Fig. 36, p. 272.) Sodium silicate is formed.

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2.$$

Extract the product by boiling up for some time with a large quantity of water, filter, and add to the filtrate excess of hydrochloric acid. Evaporate to dryness and heat to about 200° C. The silica is rendered insoluble. Boil up with water and filter off the residual silica.

$$Na_2SiO_3 + 2HClAq = 2NaCl + H_2SiO_3$$
$$H_2SiO_3 = SiO_2 + H_2O.$$

Method II. Mix up the powdered silica with about 1½ times its weight of powdered calcium fluoride and add the mixture to concentrated sulphuric acid in a thick-walled glass flask. Warm gently on a sand bath. Silicon fluoride is evolved and could be collected by downward displacement in a dry jar: instead of doing so pass the gas through a dry wide tube into a layer of mercury about an inch deep at the bottom of a stout glass vessel containing water. As the gas escapes into water it is decomposed with precipitation of silicic acid and formation of a solution of hydrofluosilicic acid.

Equations: (*a*) $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$.
(*b*) $SiO_2 + 4HF = SiF_4 + 2H_2O$.
(*c*) $3SiF_4 + 4H_2O = 2H_2SiF_6Aq + H_4SiO_4$.

Filter off the silicic acid, wash, dry and heat.

$$H_4SiO_4 = SiO_2 + 2H_2O.$$

Iodic Acid, HIO_3, and Iodine Pentoxide, I_2O_5.

Place in a large retort of say one litre capacity (or in a litre flask) 10 grams of iodine and about 50 c.c. of fuming nitric acid (sp. gr. 1·5), and warm gently on a sand bath in fume cupboard until the iodine has been oxidized. Avoid loss of iodine by raising the vessel above the sand bath from time to time, and wash down any condensed iodine with a small quantity of nitric acid.

Pour the contents of the flask into an evaporating basin and evaporate nearly to dryness over a rose burner.* Drain off the crystals of iodic acid, and dry them by gently heating in the dish or in an air oven. The temperature should not exceed say 110° C., as at 170° C. the crystals lose water giving the pentoxide.

Equation: $I_2 + 4HNO_3 = 2HIO_3 + H_2O + 3NO + NO_2$.

Iodine Pentoxide, I_2O_5.

Prepare the pentoxide from a portion of the crystals by heating to about 200° C. in an air oven.

Equation: $2HIO_3 = H_2O + I_2O_5$.

The pentoxide is a white solid which decomposes at about 300° C. It is a powerful oxidizing agent, converting carbon monoxide quantitatively to the dioxide, and is used for this purpose in gas analysis.

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* The rose burner is a Bunsen burner with a short wide hollow cylinder having small holes at the sides fixed on its top. A set of small jets of gas arranged in a circle can be obtained, which are particularly suitable for evaporating substances to complete dryness.

Hydrogen Peroxide, H_2O_2.

Take about 8 grams of the hydrated peroxide of barium, dissolve in water in a thick-walled beaker, cool to about 0° C. by surrounding the beaker with ice, and then add slowly from a burette dilute sulphuric acid as long as a precipitate seems to form. The sulphuric acid should have been cooled before placing in the burette by means of a freezing mixture. Carry out the following reactions:—

(*a*) Add a small quantity to potassium iodide solution. Iodine is set free and can be readily recognized by adding a few c.c. of freshly prepared starch solution, when a deep blue colour is produced.

$$2KI + H_2O_2 = 2KOH + I_2.$$

(*b*) Shake up a few c.c. with the same volume of ether and then add a few drops of acidified potassium dichromate solution and shake. The ether is tinted a deep blue colour, constituting a very delicate test for hydrogen peroxide.

(*c*) Add a small quantity of dilute potassium permanganate acidified with sulphuric acid to a few c.c. of the hydrogen peroxide solution. The colour of the permanganate is discharged and oxygen is evolved.

Equation:

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

PART III

PREPARATION OF TYPICAL COMPOUNDS OF THE METALS

A. Preparation of Metallic Salts.

B. Preparation of Metallic Oxides and Hydroxides.

PREPARATION OF TYPICAL COMPOUNDS OF THE METALS

So far only **non-metals** and their compounds have been considered. Taking the usual scheme followed in theoretical work one would next come to the **metals** and their important compounds. As regards the metals themselves a few preparations in the dry way (e. g. Pb, Ag, Cu, Bi, Sb) and in the wet way (e. g. Hg, As, Sb) are of importance for purposes of identification, and are described under the tests for the metals.

One might merely indicate here that the experiments carried out already, especially those in connexion with oxygen, have indicated the **main chemical distinctions between Non-metals and Metals**, namely, that **Non-metals** (**a**) do not replace the hydrogen of acids to form salts, and (**b**) form oxides which are usually acid anhydrides, whereas **Metals** (**a**) do replace the hydrogen of acids to form salts, and (**b**) form as a rule basic oxides and hydroxides.

Various physical distinctions, such as the metallic lustre, and the greater malleability, ductility, tenacity, and conducting power for heat and electricity of the metals, as well as the general comparatively low specific gravity of the non-metals, will be found discussed in theoretical books.

A. PREPARATION OF METALLIC SALTS

Definition. Salts are compounds derived from acids by replacing part or all the replaceable hydrogen by metals.

There are four important types of salt met with in elementary chemistry, viz. :—

(1) **Normal** salts
(2) **Acid** „
(3) **Basic** „
(4) **Double** „

(1) Definition. **Normal Salts** are compounds derived from acids by replacing all the replaceable hydrogen by metal.

The reaction of these salts towards indicators is frequently neutral, but may be alkaline or acid ;

e. g. (*a*) Normal salts of neutral reaction :—

$$NaCl . KNO_3 . (NH_4)_2C_2O_4 . Ba(NO_3)_2 . Pb(NO_3)_2.$$

(*b*) Normal salts with alkaline reaction :—K_2CO_3 . Na_2CO_3 . KCN.

(*c*) Normal salts with acid reaction :—$CuSO_4$: $ZnSO_4$: $Al_2(SO_4)_3$.

(2) Definition. **Acid Salts** are compounds derived from acids by replacing part of the replaceable hydrogen by metals. The reaction of acid salts towards indicators is generally acid, but may be neutral or alkaline.

e. g. $KHSO_4$: $NaHSO_4$: NaH_2PO_4 and $KHC_4H_4O_6$ are acid in reaction, and Na_2HPO_4 (common sodium phosphate or disodium hydrogen phosphate) is nearly neutral—faintly alkaline.

(3) Definition. **Basic Salts** are compounds in which the metal functions partly as oxide or hydroxide (i. e. functions partly as base) and is partly combined with an acid radicle or radicles ;

e. g. $Bi(OH)_2 . NO_3$: BiOCl : SbOCl.

Basic salts are frequently insoluble, so that their reaction to indicators is not readily determined, but a few are soluble and generally alkaline in reaction ;

e. g. basic lead acetate, $Pb(OH) (C_2H_3O_2)$.

Definition. In **Double Salts** two salts are united together in some simple ratio of their molecular proportions, generally molecule to molecule ; e. g. common alum, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$.

Note. The preparation of double salts is not quite suitable for an elementary course.

Crystallization. In preparing salts one generally tries to obtain crystals. Most salts can be obtained in crystalline form under suitable conditions, and the following **factors influencing crystallization** must be taken into consideration :—

(a) The purity of the compound. As a rule the purer a compound is, the more readily will it crystallize.

(b) The solvent. Most metallic crystalline salts are soluble in water, and insoluble in alcohol and other organic solvents. Water is the general solvent employed for inorganic salts, and also for metallic salts of organic acids. Many compounds of carbon (i. e. organic compounds) are insoluble in water, but readily soluble in alcohol, ether, and other organic solvents from which they can be crystallized.

(c) Variation of solubility with temperature. If the increase of solubility with rise of temperature be small, as a rule it will be difficult to obtain large crystals in a short time and vice versa.

(d) Time allowed for crystallization. Crystals grow by accretion round nuclei, which generally form spontaneously when a liquid saturated at a temperature above that of the room, is allowed to cool. In order that large crystals may be obtained, the liquid should be saturated at its boiling-point, and the rate of cooling should be slow.

(e) Rapid convection currents will prevent regular crystallization, and therefore the solution should after saturation be placed upon a bad conductor, such as a filter pad, and should be covered so as to hinder surface cooling.

Methods of Preparation.

In selecting a method of preparation for any particular compound, the following general methods of obtaining salts should be kept in view.

I. Methods suitable for soluble salts.

(1) **Action of Acid upon a Base** (i. e. upon the metallic oxide or hydroxide).

(2) **Action of Acid upon a Carbonate.**

(3) **Direct replacement of the hydrogen in an acid by the metal.**

II. Method suitable for insoluble or sparingly soluble compounds.

(4) **Precipitation.**

I. Methods suitable for soluble salts.

1. Action of an Acid upon a Base, i. e. action of acid upon the metallic oxide or hydroxide.

e. g. (a) Preparation of potassium nitrate (nitre) from nitric acid and potassium hydroxide.

$$HNO_3Aq + KOHAq = KNO_3Aq + H_2O.$$

(b) Preparation of crystallized copper sulphate ($CuSO_4 . 5H_2O$) from copper oxide and dilute sulphuric acid;

$$CuO + H_2SO_4Aq = CuSO_4Aq + H_2O.$$

(c) Preparation of acid potassium tartrate (cream of tartar) from tartaric acid ($H_2 . C_4H_4O_6$) and potassium hydroxide;

$$H_2 . C_4H_4O_6Aq + KOHAq = KH . C_4H_4O_6 + N_2O.$$

These three reactions are typical and require further consideration. The first and second represent the preparation of normal salts, and the third of an acid salt.

Preparation of Normal Salts:

(a) **Preparation of Potassium Nitrate from Nitric Acid and Potassium Hydroxide.**

In this preparation the acid is said to be neutralized by the base, or conversely. This means that the acid reaction of the acid is destroyed by the addition of the proper proportion of base. If one adds more than the required quantity of base, the reaction mixture will have an alkaline reaction, and the salt will not crystallize so readily and will be impure. Many indicators could be used for testing neutrality, but litmus is generally the most convenient. As we have already seen, acids turn litmus red, and soluble bases turn litmus blue. A neutral salt has no action upon litmus. The conditions required in a successful experiment might be emphasized by writing the neutralization in the following way:—

$$\underset{\text{Turns litmus red.}}{\underline{HNO_3Aq}} \quad + \quad \underset{\text{Turns litmus blue.}}{\underline{KOHAq}} \quad = \quad \underset{\substack{\text{Has no action upon neutral}\\ \text{litmus, which has a violet}\\ \text{tint.}}}{\underline{KNO_3Aq + H_2O}}$$

The exact method of procedure is indicated below in describing the preparation of the body in detail (p. 63).

(b) **Preparation of Copper Sulphate from Copper Oxide and dilute Sulphuric Acid.**

Copper sulphate is, like potassium nitrate, a normal salt, but it is acid in reaction. We cannot therefore boil up copper oxide (the base) with sulphuric acid until a neutral reaction is obtained. We must in this case merely make certain that a sufficiency of base has been added by boiling dilute sulphuric acid with copper oxide until a small quantity of oxide remains unaltered after boiling for say ten minutes. The liquid is then filtered off and evaporated to crystallization.

Note. If an insufficiency of base is used when sulphuric acid is the solvent, it will in many cases be difficult to get crystals, especially if the salt contains water of crystallization. In this case, for example, if excess of sulphuric acid be used, a greenish white powder of nearly anhydrous copper sulphate will be obtained on evaporation instead of deep blue crystals of the composition $CuSO_4 . 5H_2O$.

(c) Preparation of Potassium Hydrogen Tartrate from Tartaric Acid and Potassium Hydroxide.

The preparation of potassium hydrogen tartrate is typical for acid salts. On inspection of the equation representing the reaction,

$$KOHAq + H_2.C_4H_4O_6Aq = KH.C_4H_4O_6Aq + H_2O,$$

we should understand that in the formula for tartaric acid ($H_2 . C_4H_4O_6$), which is a dibasic acid, the two hydrogen atoms taken to the left of the molecule are replaceable, and obviously only one of them is replaced in the salt ($KH . C_4H_4O_6$). The acid may be said, therefore, to be only half neutralized, and the product is strongly acid. We cannot proceed, therefore, as described above in experiment (*a*), but can, without weighing, use the proper quantity of acid by proceeding as follows. Take a certain volume of tartaric acid solution (say 50 c.c. of concentrated solution), and divide it into two equal parts. Take one half (25 c.c.), and neutralize with potassium hydroxide, using litmus as indicator, and then add to the neutral solution the other half (25 c.c.) of the acid solution, which will be exactly sufficient to form the acid salt required.

2. Action of the Acid upon the Carbonate of the Metal.

This is an excellent method for preparing many salts, e. g. KNO_3, $Ba(NO_3)_2$, $Pb(NO_3)_2$, NH_4Cl, &c.

One generally puts a solution of the acid in a dish or beaker, and gradually adds carbonate of the metal.

Carbonic acid (H_2CO_3) is set free and decomposes into water and carbon dioxide, the latter escaping as a gas with effervescence. This escape of gas affords a ready means of telling when we are just about to reach the end of the reaction. When about enough has been added, boil to get rid of carbon dioxide, and test for neutrality with litmus paper as described below under Potassium Nitrate (p. 63).

e. g. $K_2CO_3 + 2HNO_3Aq = 2\,KNO_3Aq + H_2O + CO_2$

$BaCO_3 + 2HNO_3Aq = Ba(NO_3)_2Aq + H_2O + CO_2$.

3. **Direct Replacement of Hydrogen in an Acid by Metal,** e. g. preparation of ferrous sulphate, $FeSO_4 . 7H_2O$.

One boils up the acid with excess of metal present until hydrogen ceases to be evolved, and then filters and evaporates to crystallization. In using this method one should know what metals are attacked by the different acids. To a certain extent this has been already indicated, but the following summary might prove useful:—

A. Metals insoluble in Hydrochloric Acid: Au, Pt, Cu, Hg.

Metals very slightly soluble in Hydrochloric Acid: Ag, As, Sb, Bi, Pb.

This general method of preparation would therefore not be available for the chlorides of these nine metals.

B. Metals insoluble in Nitric Acid: Au, Pt.

Note. Antimony and tin are oxidized by nitric acid (see p. 34).

C. In considering the **solubility of metals in Sulphuric Acid** one must note that dilute and concentrated acid may have different effects (cf. p. 43). The dilute acid reacts like hydrochloric acid, and the concentrated acid like nitric acid.

(a) **Metals insoluble in dilute Sulphuric Acid**: Au, Pt, Cu, Hg, Ag.

Metals slightly soluble in Sulphuric Acid: As, Sb, Bi, Pb.

(b) **Metals insoluble in concentrated Sulphuric Acid**: Au, Pt.

Although concentrated sulphuric acid acts upon most metals it is not a convenient solvent. The reaction takes place on heating and sulphur dioxide is generally evolved. It is difficult to get rid of excess of acid. The preparation of a sulphate from the metal as starting-point, in the case of a metal unacted upon by dilute sulphuric acid but dissolved by the concentrated acid, is generally better carried out by making a solution of the nitrate, preparing from this solution the oxide, hydroxide, or carbonate, and then reacting with dilute sulphuric acid (Method (b)).

II. Method of Preparation suitable for insoluble or sparingly soluble compounds.

4. Precipitation.

A very large number of salts can be prepared by this method. It is obvious that before one can properly apply the method the solubility of the more important classes of salts must be known. The matter is more fully treated later on (p. 122 et seq.), but a brief summary of **insoluble or sparingly soluble compounds** may for convenience be given here:—

(1) **Chlorides.** $PbCl_2$, $HgCl$, $AgCl$, $SbOCl$, $BiOCl$, (Cu_2Cl_2).

(2) **Bromides.** $PbBr_2$, $HgBr$, $AgBr$.

(3) **Iodides.** PbI_2, HgI, HgI_2, AgI, (Cu_2I_2).

(4) **Nitrates.** Only a few basic compounds, e. g. $Bi(OH)_2NO_3$.

(5) **Sulphates.** $CaSO_4$, $(SrSO_4)$, $BaSO_4$, $PbSO_4$.

(6) **Carbonates.** All insoluble except those of Na, K, and NH_4 and a few acid carbonates, e. g. $Ca(HCO_3)_2$.

(7) **Phosphates.** All insoluble except those of Na, K, NH_4 and a few acid phosphates, e. g. $Ca(H_2PO_4)_2$.

(8) **Sulphides.** All insoluble except those of Na, K, NH_4. A few react with water, e. g. Al_2S_3, Cr_2S_3, CaS, BaS, MgS.

General Note regarding quantities employed for Preparations. We should aim at getting a moderate quantity (say 4–10 grams) of the product. Such quantities can be conveniently prepared in a small beaker (250 c.c.), or in a porcelain dish of 4–5 inches diameter, and can be spread out on a four-inch clock-glass or filter paper.

The quantities of material required can be calculated from the equation representing the reaction in any particular case, but as one rarely gets the whole of the substance unless in the case of a precipitation, one should assume that we will only obtain 50–80 per cent. of the theoretical yield, and should therefore roughly weigh out quantities, which should theoretically yield 10–12 grams of the substance required; e. g. the equation representing the preparation of potassium nitrate is:—

$$\begin{array}{ccccccc}
\underline{KOH} & + & \underline{HNO_3} & = & \underline{KNO_3} & + & \underline{H_2O} \\
\underline{39+16+1} & & \underline{1+14+48} & & \underline{39+14+48} & & \underline{2+16} \\
56 & & 63 & & 101 & & 18
\end{array}$$

The equation shows that 56 grams of caustic potash would yield 101 grams of potassium nitrate when neutralized by nitric acid; therefore 5·6 grams of caustic potash would yield 10·1 grams of potassium nitrate (KNO_3). As nitre is fairly soluble in water 30–40 per cent. may remain in solution, and therefore in order to get about 7–8 grams of dry crystals one should take about 7 grams of caustic potash.

LIST OF IMPORTANT SALTS, THE PREPARATION OF WHICH IS INDICATED IN THE ELEMENTARY SECTION.

NOTE.—The substances included in the *British Pharmacopœia* are marked *B. P.* in the List, and in the detailed descriptions which follow, *Brit. Phar.* A complete List of the Inorganic Compounds in the *British Pharmacopœia* is given at the end of this part of the book arranged in alphabetical order, and with references to the pages on which the preparations are respectively described. A summary of possible impurities is given, and should be noted in connexion with analysis. The list should be useful for reference.

List of (A) Normal, (B) Acid, (C) Basic, and (D) Double Salts, the preparation of which is given in the following elementary section.

A. NORMAL SALTS.

Class of Salt.	Typical preparations.	Additional examples which could be prepared in a similar way.
Nitrates	Potassium nitrate, KNO_3 (*B.P.*) Barium nitrate, $Ba(NO_3)_2$ Lead nitrate, $Pb(NO_3)_2$	$NaNO_3$: NH_4NO_3 $Ca(NO_3)_2$: $Sr(NO_3)_2$ $AgNO_3$ (*B.P.*) : $Fe(NO_3)_3$ (*B.P.*) $Cu(NO_3)_2$: $Hg(NO_3)_2$ (*B.P.*) : $Zn(NO_3)_2$: $Mg(NO_3)_2$
Chlorides	Sodium chloride, $NaCl$	NH_4Cl (*B.P.*) : KCl (*B.P.*) : $CaCl_2$ (*B.P.*) : $SrCl_2$: $BaCl_2 . 2H_2O$
	Lead chloride, $PbCl_2$	
	Zinc chloride, $ZnCl_2$ (*B.P.*)	$MgCl_2$ (anhydrous)
	Cuprous chloride, Cu_2Cl_2 Mercuric chloride, $HgCl_2$ (*B.P.*) Mercurous chloride, $HgCl$ (*B.P.*)	
Bromides	Ammonium bromide, NH_4Br (*B.P.*)	
	Potassium bromide, KBr (*B.P.*)	$NaBr$ (*B.P.*)
	Lead bromide, $PbBr_2$	
Iodides	Potassium iodide, KI (*B.P.*)	NaI (*B.P.*)
	Lead iodide, PbI_2 (*B.P.*) Mercuric iodide, HgI_2 (*B.P.*)	
Sulphates	Sodium sulphate, $Na_2SO_4 . 10H_2O$ (*B.P.*)	K_2SO_4 (*B.P.*) : $(NH_4)_2SO_4$
	Copper sulphate, $CuSO_4 . 5H_2O$ (*B.P.*)	
	Ferrous sulphate, $FeSO_4 . 7H_2O$	$ZnSO_4 . 7H_2O$ (*B.P.*) : $MgSO_4 . 7H_2O$ (*B.P.*)
	Ferric sulphate, $Fe_2(SO_4)_3$ (*B.P.*)	
	Lead sulphate, $PbSO_4$	$BaSO_4$: $CaSO_4 . 2H_2O$
Sulphite	Sodium sulphite, $Na_2SO_3 . 7H_2O$ (*B.P.*)	
Borate	Sodium tetraborate (Borax), $Na_2B_4O_7 . 10H_2O$ (*B.P.*)	
Carbonates	Sodium carbonate (washing soda), $Na_2CO_3 . 10H_2O$ (*B.P.*)	K_2CO_3 (*B.P.*)
	Calcium carbonate, $CaCO_3$ (*B.P.*)	$BaCO_3$: $ZnCO_3$ (*B.P.*)
	Ammonium carbonate (*B.P.*)	
Phosphates	Sodium phosphate (tribasic sod. phosphate), Na_3PO_4	(See pp. 62, 79).
	Calcium phosphate, $Ca_3(PO_4)_2$ (*B.P.*)	$Mg_3(PO_4)_2$
	Ferrous phosphate, $Fe_3(PO_4)_2$ (*B.P.*)	$FePO_4$
Arsenate	Ferrous arsenate, $Fe_3(AsO_4)_2 . 6H_2O$ (*B.P.*)	
Notable Organic Salts.	Ammonium oxalate $(NH_4)_2C_2O_4 . \frac{1}{2}H_2O$ Lead acetate, $Pb(C_2H_3O_2)_2 . 3H_2O$ Tartar emetic, $K . SbO . C_4H_4O_6 . \frac{1}{2}H_2O$	

B. LIST OF ACID SALTS.

Class of Salt.	Typical preparations.	Additional examples which could be prepared in a similar way.
Sulphates	Potassium hydrogen sulphate or Potassium bisulphate, $KHSO_4$	$NaHSO_4$: NH_4HSO_4
Carbonates	Sodium bicarbonate, $NaHCO_3$ (*B.P.*) Magnesium bicarbonate Fluid Magnesia } $Mg(HCO_3)_2$ (*B.P.*) Potassium bicarbonate, $KHCO_3$ (*B.P.*)	
Phosphates	Sodium dihydrogen phosphate (monobasic sod. phosphate), NaH_2PO_4 Disodium hydrogen phosphate (common sodium phosphate), $Na_2HPO_4 . 12H\ O$ (*B.P.*)	$(NH_4)_2HPO_4$ (*B.P.*). NOTE.—For convenience the preparation of normal sodium phosphate is given here.
Arsenate	Disodium hydrogen arsenate, $Na_2HAsO_4 . 12H_4O$. (*B.P.*)	
Notable Organic Compds.	Potassium hydrogen tartrate, $KH . C_4H_4O_6$ (cream of tartar)	$KH . C_2O_4$

C. LIST OF BASIC SALTS.

Nitrates	Bismuth oxynitrate, $Bi(OH)_2NO_3$ (*B.P.*) or $BiO . NO_3 . H_2O$ Lead oxynitrate, $Pb(OH)(NO_3)$	
Chloride	Bismuth oxychloride, $BiOCl$	$SbOCl$
Carbonates	Bismuth oxycarbonate, $Bi_2O_2CO_3$ (*B.P.*) White Lead, $2PbCO_3 . Pb(OH)_2$ (*B.P.*) Magnesium oxycarbonate, $3MgCO_3 . Mg(OH)_2 . 4H_2O$	
Acetate	Basic lead acetate, $Pb(OH)(C_2H_3O_2)$.	

D. LIST OF DOUBLE SALTS.

Alums	Potash alum, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ (*B.P.*)	$(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ Iron alum, $K_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$ Chrome alum, $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$
Sulphate	Ferrous ammon. sulphate, $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$.	

A. DETAILED PREPARATIONS OF NORMAL SALTS.

POTASSIUM NITRATE, KNO_3 (cf. p. 56).

Chemicals required:—Nitric acid and either caustic potash or potassium carbonate.

(a) **Preparation from Potassium Hydroxide and Nitric Acid.** Dissolve in water 5–8 grams of potassium hydroxide in a small beaker or porcelain dish and neutralize carefully by addition of nitric acid in the following manner. Add nitric acid with frequent stirring until the reaction-mixture is nearly neutral to litmus paper. Do not put the litmus into the solution as it would tint the fluid and spoil the appearance of the crystals. Take out a drop of the solution from time to time by means of a glass-stirring rod and place on litmus paper. When nearly neutral raise the solution to boiling-point and boil for a minute to expel carbon dioxide which might be present. Test again with litmus paper. If the solution be acid add a few drops of potash solution until neutral, and if the solution be alkaline add a few drops of acid until neutral. [Note.—It would be preferable to have a drop of acid in excess rather than potash.]

When the solution is quite neutral filter so as to get rid of dust particles, and evaporate down to crystallization. The evaporation should not be too rapid towards the end. To know when to stop evaporating pour about one c.c. into a test-tube, and cool under the tap. From the quantity of solid which separates when the solution has reached room temperature, consider whether it would be worth while stopping the evaporation. The solution must not set quite solid on cooling, but an aqueous sludge would do quite well. If the liquid has been evaporated down too far, add a few c.c. of water, heat up until solution is effected, and then allow to cool. A crust of crystals generally begins to form round the edges of the liquid towards the end of the evaporation, but this is an unreliable guide, as also is the removal of a few drops of liquid on a rod. When sufficiently evaporated cover the dish or beaker with a filter pad and place on a bad conductor such as a filter pad or a few folds of paper, so as to ensure slow cooling. When quite cold pour off the supernatant liquid, allowing the liquid to drain away from the crystals as far as possible. Carefully push the crystals out of the dish on to a porous plate or filter pad by means of a spatula. Move the crystals about, but be careful not to break them, and when nearly dry remove to filter paper.

When quite dry remove to a dry clock-glass, and label them if they are to be shown up, otherwise they might be kept in a test-tube. The equation expressing the reaction would be :—

$$KOHAq + HNO_3Aq = KNO_3Aq + H_2O.$$

(b) Preparation from Potassium Carbonate and Nitric Acid. Put about 10–12 c.c. of concentrated nitric acid in a basin, add about thrice the bulk of water, warm gently, and slowly add potassium carbonate in small quantities as long as effervescence continues. Then heat to boiling, boil for a few minutes to expel carbon dioxide, which would in combination with water have an acid reaction, and then test by putting a drop on filter paper. If acid add more potassium carbonate, if alkaline more nitric acid. When neutral, filter if necessary, and evaporate to crystallization. Then proceed as in the preparation from potassium hydroxide and nitric acid.

Equation : $K_2CO_3 + 2HNO_3Aq = 2KNO_3Aq + H_2O + CO_2\nearrow.$

NOTE.—The directions given in this preparation regarding filtering before evaporation, and the general method of procedure in cooling slowly so as to obtain large crystals, apply to all the succeeding preparations. The directions regarding neutralization apply to all preparations where neutralization is required.

NOTE.—Sodium nitrate, $NaNO_3$, and ammonium nitrate, NH_4NO_3, could be obtained by similar reactions.

BARIUM NITRATE, $Ba(NO_3)_2$.

Chemicals required :—Nitric acid and barium hydroxide or carbonate.

Put in a beaker or dish 10–15 c.c. of concentrated nitric acid, and dilute with about 5 to 6 times the bulk of water.* Warm, and add slowly the barium hydroxide or carbonate until the solution is neutral. This would be indicated approximately in the case of the carbonate by the stoppage of effervescence on adding a fresh quantity, and also by the milkiness of the liquid, as barium carbonate is insoluble in water. Finish the neutralization in

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* NOTE.—A common mistake in preparing salts is to use too strong a solution of acid to start with. It is preferable to work with dilute rather than strong solutions. If a precipitate forms during neutralization in a case like this, while the solution is still acid **add more water** and not acid, because many salts, e. g. $Ba(NO_3)_2$, are far more soluble in water than in their own acid (cf. p. 67).

a similar way to that described under potassium nitrate (i. e. neutralize when boiling), filter if necessary, and evaporate to crystallization. The most suitable time for stopping the evaporation can be best tested by pouring about one c.c. of the boiling liquid into a test-tube, and cooling under the tap. The quantity in the test-tube can be returned to the main bulk of liquid.

Equations: $Ba(OH)_2 + 2HNO_3Aq = Ba(NO_3)_2Aq + 2H_2O$

$BaCO_3 + 2HNO_3Aq = Ba(NO_3)_2Aq + H_2O + CO_2\nearrow$.

NOTE. — Calcium nitrate, $Ca(NO_3)_2$, and strontium nitrate, $Sr(NO_3)_2$, can be prepared by similar methods.

LEAD NITRATE, $Pb(NO_3)_2$.

Chemicals required:—

(*a*) Nitric acid and lead oxide, hydroxide, or carbonate,
or (*b*) Nitric acid and metallic lead.

(*a*) The **preparation of lead nitrate from lead oxide, hydroxide, or carbonate** is exactly similar to that described above. Heat up to boiling-point in a basin or beaker about 40 c.c. of nitric acid of moderate concentration (one of strong acid to 5 or 6 of water).* Then add lead oxide (litharge), hydroxide, or carbonate as long as solution occurs. Boil well before adding more if any seems to remain undissolved. The solution may become alkaline if the liquid is boiled for some time with lead oxide or hydroxide, and this must be avoided, as alkaline solutions of lead nitrate do not crystallize properly. In such a case add a small quantity of acid so as to make the end reaction faintly acid rather than alkaline, filter and evaporate to crystallization. The proper time to stop evaporating should be gauged by cooling a small quantity in a test-tube.

Equations: $PbO + 2HNO_3Aq = Pb(NO_3)_2Aq + H_2O$.

$Pb(OH)_2 + 2HNO_3Aq = Pb(NO_3)_2Aq + 2H_2O$.

$PbCO_3 + 2HNO_3Aq = Pb(NO_3)_2Aq + H_2O + CO_2\nearrow$.

The crystals are nodular in form as a rule.

(*b*) Preparation from Nitric Acid and Metallic Lead.

The lead should be in such a form that as large a surface as possible is exposed to the action of the acid. Lead-foil would do fairly well. Cut the lead into small pieces and add to the boiling acid. Boil as long as solution continues, filter and evaporate to crystallization.

Equation: $3Pb + 8HNO_3Aq = 3Pb(NO_3)_2Aq + 4H_2O + 2NO$.

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* Cf. note, p. 64.

Note. — Silver nitrate, $AgNO_3$ (*Brit. Phar.*), ferric nitrate, $Fe(NO_3)_3$ (*Brit. Phar.*), copper nitrate, $Cu(NO_3)_2$, mercuric nitrate, $Hg(NO_3)_2$ (*Brit. Phar.*), zinc nitrate, $Zn(NO_3)_2$, magnesium nitrate, $Mg(NO_3)_2$, may be prepared by analogous methods. Oxide, hydroxide, carbonate, or metal can be used except in the case of mercury. Mercury hydroxide and carbonate are not met with.

SODIUM CHLORIDE, NaCl.

Chemicals required:—Sodium hydroxide (caustic soda) or carbonate and a solution of hydrochloric acid (cf. preparation of potassium nitrate).

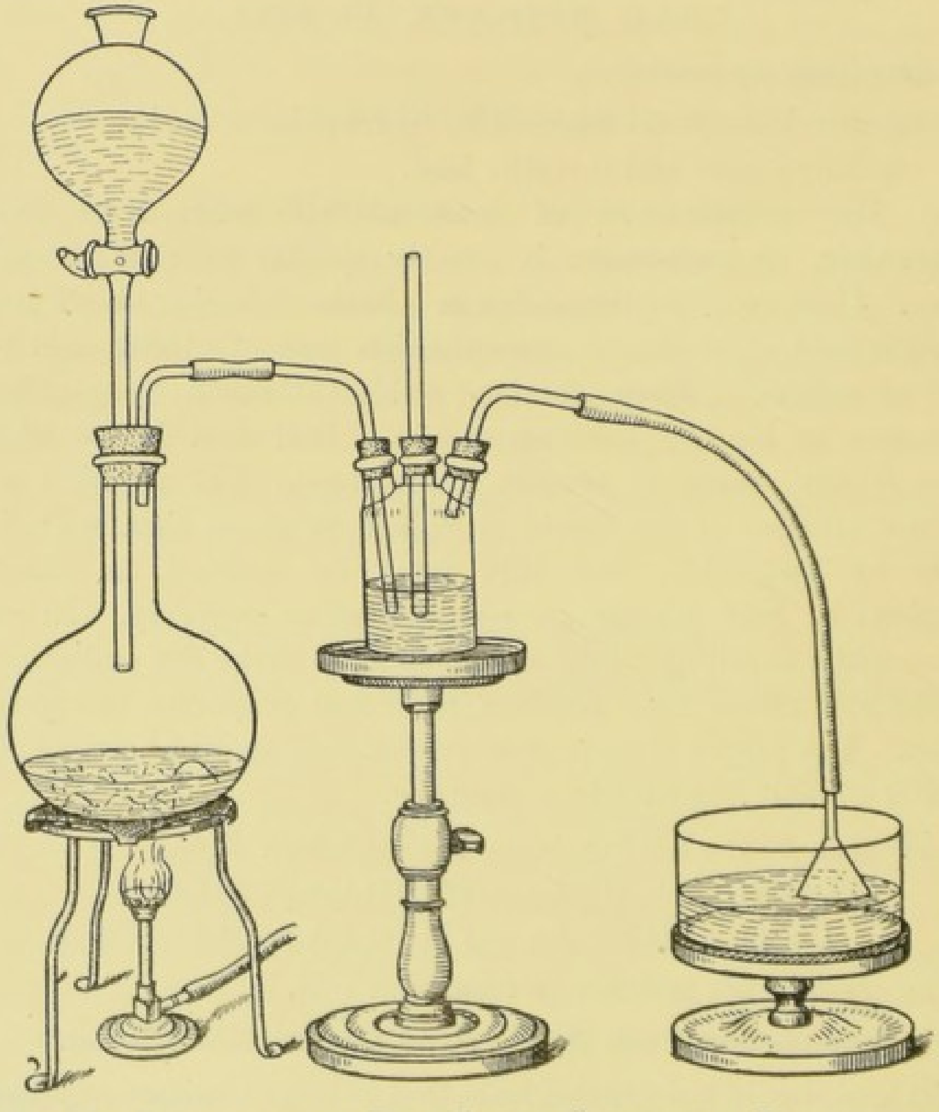

Fig. 15. Preparation of Pure Sodium Chloride by Precipitation from a Saturated Solution with Hydrochloric Acid Gas.

(*a*) Preparation from sodium hydroxide and hydrochloric acid. Neutralize about 50 c.c. of a twenty per cent. solution of caustic soda with hydrochloric acid, filter and evaporate to crystallization.

(*b*) Preparation from hydrochloric acid and sodium carbonate. Add an equal bulk of water to about 50 c.c. of concentrated hydrochloric acid in a porcelain basin, warm gently, and add solid sodium carbonate until the reaction is neutral. Filter, and evaporate to crystallization. NH_4Cl and $CaCl_2 . 6H_2O$ can be similarly obtained.

Preparation of chemically pure Sodium Chloride from crude material.

Most samples of commercial sodium chlorides contain large traces of impurities, e. g. $MgCl_2$, &c., but from them a pure compound can readily be obtained in the following way:—Dissolve about 100 grams of salt in 300 c.c. of water, place in a stout beaker of 500 c.c. capacity, and pass in a stream of hydrochloric acid gas through an inverted filter funnel, the end of which just dips into the liquid. Fig. 15 shows the arrangement of apparatus.

Sodium chloride, being nearly insoluble in concentrated hydrochloric acid, is slowly precipitated. When the liquid is saturated, filter off the salt, wash on the filter with concentrated hydrochloric acid, and dry by heating gently in a porcelain basin over a rose burner.

NOTE:—It is important to note in connexion with analysis that many salts are nearly insoluble in the acids from which they are derived, e. g. barium and lead nitrates are nearly insoluble in concentrated nitric acid.

LEAD CHLORIDE, $PbCl_2$.

The preparation of this compound, which is a white crystalline solid, is exactly similar to that of lead iodide described below, hydrochloric acid being added to the solution of lead salt instead of potassium iodide.

e. g. $$Pb(NO_3)_2Aq + 2HClAq = PbCl_2 + 2HNO_3Aq.$$

ZINC CHLORIDE, $ZnCl_2$ (*Brit. Phar.*).

A solution of this compound is readily obtained by dissolving metallic zinc, zinc oxide, or zinc carbonate in hydrochloric acid. If one evaporates a solution containing no excess of acid to dryness decomposition takes place, with formation of a basic compound, Zn_2OCl_2.

To get solid zinc chloride two methods can be employed:—

(*a*) Dissolve zinc, zinc oxide, or zinc carbonate in large excess of hydrochloric acid (i. e. make the solution strongly acid after solution has been effected), and evaporate to dryness in a fume cupboard. The resulting chloride can be fused and cast into sticks.

(*b*) Add more than a molecular proportion of ammonium chloride to a solution, evaporate to dryness, and heat to get rid of ammonium chloride. The latter compound forms a double compound with the zinc chloride which is not decomposed on evaporating to dryness in presence of water.

NOTE.—Anhydrous magnesium chloride, $MgCl_2$, could be prepared by an analogous method. A soluble double compound, $MgCl_2NH_4Cl6H_2O$, would separate on evaporation, and could be made to lose ammonium chloride and water without decomposition.

CUPROUS CHLORIDE, Cu_2Cl_2 or CuCl.

Method I. Put about 5 grams of copper oxide and 5 grams of copper turnings in a flask, add 104 c.c. of concentrated hydrochloric acid, and boil up gently for about half an hour in the fume cupboard. A funnel should be loosely placed in the neck of the flask so as to retard loss of hydrochloric acid. The copper oxide with hydrochloric acid will form cupric chloride ($CuCl_2$), which will be reduced by the copper present to form cuprous chloride, which is soluble in hydrochloric acid, but insoluble in water. When the solution is nearly colourless, pour into about 100 c.c. of water, and a white precipitate of cuprous chloride will at once form. Filter, dry, and keep in a sealed tube, or in a small bottle the stopper of which is afterwards covered with melted paraffin wax.

Equations: (*a*) $CuO + 2HClAq = CuCl_2Aq + H_2O.$

(*b*) $CuCl_2Aq + Cu = Cu_2Cl_2 + Aq.$

Method II. Cuprous chloride can also be prepared by passing sulphur dioxide into a solution of cupric chloride. The cuprous chloride comes down as a white crystalline precipitate.

Equations:

(*a*) $SO_2 + H_2O + Aq = H_2SO_3Aq.$

(*b*) $2CuCl_2Aq + H_2O + H_2SO_3Aq = Cu_2Cl_2 + 2HCl + H_2SO_4Aq.$

MERCURIC CHLORIDE (CORROSIVE SUBLIMATE), $HgCl_2$ (*Brit. Phar.*).

Method I. Triturate in a mortar half a gram of mercuric sulphate with about one gram of sodium chloride, and one gram of manganese dioxide. Put the mixture into a hard glass test-tube and heat cautiously. A sublimate of mercuric chloride is obtained. The sublimate can be dissolved in water after breaking the tube and the solution filtered and evaporated to crystallization, preferably in a small glass dish on a water bath. White crystals are formed.

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2.$$

NOTE:—The manganese dioxide prevents the sublimation of mercurous chloride by liberating chlorine, which will convert any mercurous chloride formed into the mercuric compound

$$2HgCl + Cl_2 = 2HgCl_2.$$

Method II. Dissolve a few grams of mercuric oxide in a sufficiency of hydrochloric acid, filter and evaporate to crystallization.

Equation: $HgO + 2HClAq = HgCl_2 + H_2O$.

MERCUROUS CHLORIDE (CALOMEL), HgCl. (*Brit. Phar.*).

Method I. Triturate thoroughly in a mortar about one gram of mercuric sulphate, $\frac{2}{3}$ gram mercury, and one gram of sodium chloride. Heat the mixture carefully in a hard glass test-tube. Calomel sublimes. Powder the product and wash it with boiling water to remove traces of the mercuric compound.

$$HgSO_4 + Hg + 2NaCl = 2HgCl + Na_2SO_4.$$

Method II. Mercurous chloride can be obtained by precipitation by adding hydrochloric acid to a solution of mercurous nitrate.

$$HgNO_3Aq + HClAq = HgCl + HNO_3Aq.$$

AMMONIUM BROMIDE, NH_4Br.

Neutralize (p. 63) about 50 c.c. of a moderately concentrated solution of hydrobromic acid with ammonium hydroxide or ammonium carbonate, filter and evaporate to crystallization.

$$HBrAq + NH_4OHAq = NH_4BrAq + H_2O.$$

POTASSIUM BROMIDE, KBr.

Dissolve about 6 grams of potassium hydroxide in 40–50 c.c. of water, and then add about 9 grams of bromine (3 c.c. approximately) with constant stirring until the liquid is tinted faintly yellow. [**Caution.** Be careful not to inhale bromine vapour, and note that bromine causes very painful burns.] Evaporate down to dryness, when a mixture of potassium bromide and potassium bromate will be obtained. Powder the residue in a mortar with about an equal weight of wood charcoal, remove to a crucible, and heat over a Bunsen burner for about fifteen minutes. The bromate is decomposed. Allow to cool, remove to a beaker containing about 50 c.c. of water, boil for a few minutes, filter off the excess of carbon, and evaporate to crystallization in a porcelain dish.

Equations:

(*a*) $6KOHAq + 3Br_2 = KBrO_3Aq + 5KBrAq + 3H_2O.$

(*b*) $KBrO_3 + 3C = KBr + 3CO\nearrow.$

Note:—Sodium bromide, NaBr (*Brit. Phar.*), potassium iodide, KI (see below), and sodium iodide, NaI, can be prepared by exactly similar methods.

LEAD BROMIDE, $PbBr_2$.

Lead bromide is obtained as a heavy white precipitate on adding a solution of potassium bromide to a solution of a lead salt, such as the nitrate or acetate. The precipitate should be washed by decantation and recrystallized as described under lead iodide (p. 71).

$$Pb(NO_3)_2Aq + 2KBrAq = PbBr_2 + 2KNO_3Aq.$$

POTASSIUM IODIDE, KI (*Brit. Phar.*).

Make a solution of caustic potash by dissolving about 5 grams in about 50 c.c. of water, and add about 10 grams of iodine slowly until the liquid is tinted yellow. Filter, evaporate to dryness, and complete the preparation as described above under potassium bromide.

(*a*) $6KOHAq + 3I_2 = KIO_3Aq + 5KIAq + 3H_2O.$

(*b*) $KIO_3 + 3C = KI + 3CO.$

Note:—Sodium iodide, NaI (*Brit. Phar.*), is prepared similarly, as noted above under potassium bromide.

LEAD IODIDE, PbI_2 (*Brit. Phar.*).

Chemicals required:—A soluble lead salt such as the nitrate or acetate; potassium iodide.

Method of procedure:—Make a moderately strong solution of the soluble lead salt, add a few drops of acetic acid, and then add a solution of potassium iodide as long as a precipitate forms.

Note.—The precipitate must be of a deep orange yellow colour. If it is light yellow a basic salt has been formed: a sufficiency of potassium iodide and a small quantity of acetic acid will usually alter the yellow colour to orange. Allow the precipitate to settle, pour off the supernatant liquid, and wash the yellow precipitate twice by decantation. To wash by this process add 50–100 c.c. of distilled water to the precipitate, stir up, allow the precipitate to settle, and then pour off the supernatant liquid. Recrystallize the product from boiling water. Add a quantity of water, boil, and while boiling continue slowly the addition of water until nearly the whole of the precipitate has dissolved. Then filter the boiling solution if necessary (i. e. if there seems to be a quantity of substance undissolved), and allow to crystallize. Characteristic golden yellow spangles should be obtained.

Equations:

$$Pb(NO_3)_2Aq + 2KIAq = PbI_2 + 2KNO_3Aq.$$

$$\underbrace{Pb(C_2H_3O_2)_2}_{\text{Lead Acetate}} + 2KIAq = PbI_2 + \underbrace{2K(C_2H_3O_2)Aq}_{\text{Potassium Acetate}}$$

NOTE.—If metallic lead, oxide of lead (litharge), or the carbonate be given as starting-point, prepare a solution of the nitrate, being careful to make the solution nearly neutral before adding the potassium iodide solution, otherwise iodine may be set free and the preparation spoiled.

Additional Preparation:—Lead chloride can be prepared in an exactly similar manner by adding hydrochloric acid to a solution of a lead salt.

e. g. $Pb(NO_3)_2Aq + 2HClAq = PbCl_2 + 2HNO_3Aq.$

MERCURIC IODIDE, HgI_2 (*Brit. Phar.*).

Take about 20 c.c. of a concentrated solution of mercuric chloride in water, and divide into two equal portions. To one half add a concentrated solution of potassium iodide until the precipitate which first forms nearly redissolves, and then add the other half of the mercuric chloride solution. A scarlet precipitate of mercuric iodide will be obtained. Allow to settle, pour off the supernatant liquid, wash once by decantation, and then recrystallize the residue from concentrated hot hydrochloric acid. Allow the crystals to settle, pour off the hydrochloric acid, and then dry the residue.

Equations: (*a*) $HgCl_2Aq + 2KIAq = HgI_2 + 2KClAq.$

(*b*) $HgI_2 + 2KIAq = HgI_2 . 2KIAq.$

(*c*) $HgI_2 . 2KIAq + HgCl_2Aq = 2HgI_2 + 2KClAq.$

Equation (*b*) indicates that the mercuric iodide first precipitated redissolves to form a double compound containing as much potassium iodide as was required for the precipitation.

SODIUM SULPHATE (Glauber's Salt), $Na_2SO_4 . 10H_2O$ (*Brit. Phar.*).

Method:—Neutralize about 50 c.c. of dilute sulphuric acid with sodium hydroxide or carbonate, filter if necessary, and evaporate to crystallization.

Equations:

$$H_2SO_4Aq + 2NaOHAq = Na_2SO_4Aq + 2H_2O.$$
$$H_2SO_4Aq + Na_2CO_3Aq = Na_2SO_4Aq + H_2O + CO_2 \nearrow.$$

Large efflorescent crystals are obtained.

Potassium sulphate, K_2SO_4 (*Brit. Phar.*), and ammonium sulphate, $(NH_4)_2SO_4$, may be prepared by analogous methods.

COPPER SULPHATE, $CuSO_4 . 5H_2O$ (Blue Vitriol) (*Brit. Phar.*).

Chemicals required:—Metallic copper, copper oxide, copper hydroxide, or copper carbonate and sulphuric acid.

(a) **Preparation from Oxide, Hydroxide, or Carbonate.** Heat about 50 c.c. of dilute sulphuric (one of conc. acid to about 8 of water) in a dish, and then slowly add small quantities of the copper compound until no more dissolves on boiling for say 10 minutes; filter and evaporate carefully to crystallization.

Equations:

$$CuO + H_2SO_4Aq = CuSO_4Aq + H_2O.$$
$$Cu(OH)_2 + H_2SO_4Aq = CuSO_4Aq + 2H_2O.$$
$$CuCO_3 + H_2SO_4Aq = CuSO_4Aq + H_2O + CO_2.$$

(The carbonate would probably be a basic salt, p. 54.)

(b) **Preparation from Metallic Copper.** If copper be given as the starting-point, the best plan is to first prepare copper oxide from it. This can be readily effected by dissolving the copper in a sufficiency of nitric acid, adding excess of caustic soda or potash, and boiling. A black precipitate of copper oxide is obtained. Allow to settle, decant off the supernatant liquid, and wash by decantation. Then dissolve in dilute sulphuric acid, filter, and evaporate to crystallization.

Equations:

$$3Cu + 8HNO_3Aq = 3Cu(NO_3)_2Aq + 4H_2O + 2NO.$$
$$Cu(NO_3)_2Aq + 2NaOHAq = Cu(OH)_2 + 2NaNO_3Aq.$$
$$Cu(OH)_2 = CuO + H_2O.$$

Alternative Methods of preparation from the metal.

(i) After solution in nitric acid, the solution may be evaporated to dryness and ignited, when copper oxide will be formed, and should be dissolved in dilute acid.

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

(ii) Dissolve the metal in a sufficiency of concentrated sulphuric acid with a few drops of concentrated nitric acid in a fume cupboard, dilute with water, boil, filter and evaporate to crystallization.

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2\nearrow.$$

NOTE.—This method is not a convenient one.

FERROUS SULPHATE, $FeSO_4 . 7H_2O$ (Green Vitriol).

Take 10–12 grams of iron filings in a flask or basin and boil up with dilute sulphuric acid (1 in 5 or 6 of water) as long as hydrogen is evolved, keeping the filings in slight excess. Filter and evaporate to crystallization.

When the crystals have separated, decant the supernatant fluid, and dry the crystals on a filter pad or plate.

$$Fe + H_2SO_4Aq = FeSO_4Aq + H_2.$$

The green crystals which separate have the composition

$$FeSO_4 . 7H_2O.$$

Additional Preparations:—Zinc sulphate, $ZnSO_4 . 7H_2O$ (White Vitriol) (*Brit. Phar.*), and magnesium sulphate, $MgSO_4 . 7H_2O$ (*Brit. Phar.*), may be prepared in the same way, or may be obtained by heating dilute sulphuric acid in a dish and adding the oxide or carbonate as long as solution takes place, then filtering and evaporating.

FERRIC SULPHATE, $Fe_2(SO_4)_3$ (*Brit. Phar.*).

Add about 1 c.c. of concentrated sulphuric acid to 50 c.c. of water and then dissolve in the solution about 4 grams of crystallized ferrous sulphate. A nearly colourless solution is obtained. Add about 1 c.c. of concentrated nitric acid and boil; the solution first becomes dark brown in colour and then changes to a yellow tint. On filtration and evaporation to dryness in a dish (placed on a water bath towards the end) a nearly white residue is obtained.

$$6FeSO_4Aq + 3H_2SO_4 + 2HNO_3Aq = 3Fe_2(SO_4)_3Aq + 4H_2O + 2NO.$$

The deep brown colour first produced depends on the formation of a compound of nitric oxide with ferrous sulphate. (Cf. brown ring test, p. 230).

LEAD SULPHATE, $PbSO_4$.

This substance is easily prepared as a white powder by precipitation. Add dilute sulphuric acid or a solution of a soluble sulphate (e. g. Na_2SO_4) to a solution of a soluble lead salt such as the nitrate or acetate. Filter, wash and dry.

$$Pb(NO_3)_2Aq + H_2SO_4Aq = PbSO_4 + 2HNO_3Aq.$$

NOTE:—Barium sulphate, $BaSO_4$, strontium sulphate, $SrSO_4$, and calcium sulphate, $CaSO_4 . 2H_2O$, can easily be prepared in a similar way.

SODIUM SULPHITE, $Na_2SO_3 . 7H_2O$ (*Brit. Phar.*).

Make a solution of sulphurous acid by passing sulphur dioxide gas into 100 c.c. of water. Add the solution to a warm solution containing about 10 grams of caustic soda or sodium carbonate until the reaction is slightly acid after raising to boiling-point, then filter and evaporate to crystallization. Drain and dry the crystals as previously described (p. 63).

$$2NaOHAq + H_2SO_3Aq = Na_2SO_3Aq + 2H_2O.$$
$$Na_2CO_3Aq + H_2SO_3Aq = Na_2SO_3Aq + H_2O + CO_2.$$

SODIUM PYROBORATE (Sodium Tetraborate), BORAX, $Na_2B_4O_7 . 10H_2O$.

Dissolve about 3 grams of boracic acid in boiling water, neutralize with sodium carbonate, filter, and evaporate to crystallization.

Equation: $4H_3BO_3Aq + Na_2CO_3 = Na_2B_4O_7Aq + 6H_2O + CO_2\nearrow$.

The orthoborates (salts of boracic or boric acid) are unstable. Borax is a salt of tetraboric or pyroboric acid, $H_2B_4O_7$.

SODIUM BICARBONATE (Baking Soda), $NaHCO_3$ (*Brit. Phar.*), and SODIUM CARBONATE: (*a*) anhydrous, Na_2CO_3; (*b*) hydrated (Washing Soda), $Na_2CO_3 . 10H_2O$ (*Brit. Phar.*).

On passing carbon dioxide through a solution of caustic soda, sodium carbonate is first obtained, and then, with excess of carbon dioxide, sodium bicarbonate is formed. It should be noted that this is a general type of reaction. The normal salt is first formed, and then, if more acid be added, the acid salt can be obtained (cf. preparation of $KH . C_4H_4O_6$, p. 57). In this case one adds an acid anhydride, which, with water, forms carbonic acid.

Method:—Dissolve about 6 grams of caustic soda in 20 c.c. of water and pass carbon dioxide (prepared from marble and hydrochloric acid, p. 40) into the solution until no further absorption seems to take place. A precipitate of sodium bicarbonate will probably be thrown down. Evaporate to dryness in a porcelain dish and then heat the residue. Sodium carbonate will be obtained. The anhydrous product may be dissolved in water and crystallized, when efflorescent crystals of the decahydrated salt will be formed.

Equations: $2NaOHAq + CO_2 = Na_2CO_3Aq + H_2O.$

$Na_2CO_3Aq + CO_2 + H_2O = 2NaHCO_3Aq.$

On heating $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$

NOTES:—(*a*) Potassium bicarbonate, $KHCO_3$ (*Brit. Phar.*), and potassium carbonate, K_2CO_3 (*Brit. Phar.*), can be similarly prepared.

(*b*) By using sulphur dioxide instead of carbon dioxide we can obtain sodium and potassium bisulphites and sulphites analogously:—$NaHSO_3$, $Na_2SO_3, 7H_2O$ (*Brit. Phar.*, see p. 74), $KHSO_3$, and K_2SO_3.

CALCIUM CARBONATE, $CaCO_3$ (*Brit. Phar.*).

This compound is readily prepared by precipitation. Add ammonium carbonate solution to a moderately concentrated solution of calcium chloride as long as a precipitate forms, filter, wash and dry.

$$CaCl_2Aq + (NH_4)_2CO_3Aq = CaCO_3 + 2NH_4ClAq.$$

Barium carbonate, $BaCO_3$, zinc carbonate, $ZnCO_3$ (*Brit. Phar.*), and magnesium carbonate, $3MgCO_3 . Mg(OH)_2 . 3H_2O$ could be prepared in a similar way.

AMMONIUM CARBONATE (*Brit. Phar.*).

Mix intimately by trituration in a mortar 1 gram of ammonium chloride and 1 gram of calcium carbonate. Heat the mixture in a hard glass test-tube. A white sublimate is obtained which is a mixture of ammonium hydrogen carbonate, $NH_4 \cdot HCO_3$, and ammonium carbamate, $NH_4(NH_2)CO_2$. This product, which is known as commercial ammonium carbonate, can be converted into the normal carbonate by digestion with a solution of ammonia.

SODIUM PHOSPHATE, Na_3PO_4. See p. 79.

CALCIUM PHOSPHATE, $Ca_3(PO_4)_2$.

Method I. Add sodium phosphate solution to calcium chloride. A white precipitate forms which can be filtered and washed.

$$3CaCl_2 + 3Na_2HPO_4 = Ca_3(PO_4)_2 + 6NaCl + H_3PO_4.$$

NOTE:—Magnesium phosphate, $Mg_3(PO_4)$, could be prepared similarly.

Method II. Dissolve bone ash in hydrochloric acid, and then add ammonium hydroxide as long as a precipitate forms. Filter and wash.

FERROUS PHOSPHATE, $Fe_3(PO_4)_2$ (*Brit. Phar.*).

To a warm solution of ferrous sulphate add a solution of sodium phosphate and then sodium bicarbonate solution. Filter, wash and dry at a low temperature. A slate blue product is obtained which contains an admixture of ferric phosphate.

$$3FeSO_4Aq + 2Na_2HPO_4Aq + 2NaHCO_3Aq = Fe_3(PO_4)_2 + 3Na_2SO_4Aq + 2H_2O + 2CO_2.$$

NOTE:—Ferric phosphate, $FePO_4$, is obtained as a faintly yellow powder from ferric chloride by similar treatment.

FERROUS ARSENATE, $Fe_3(AsO_4)_2$ (*Brit. Phar.*), is obtained from ferrous sulphate by the action of sodium arseniate and sodium bicarbonate. Filter, wash and dry at a low temperature.

$$3FeSO_4Aq + 2Na_2HAsO_4Aq + 2NaHCO_3Aq = Fe_3(AsO_4)_2 + 3Na_2SO_4Aq + 2H_2O + 2CO_2.$$

PREPARATION OF A FEW TYPICAL NORMAL ORGANIC SALTS.

(1) LEAD ACETATE (Sugar of Lead), $Pb(C_2H_3O_2)_2 . 3H_2O$, or $(CH_3 . COO)_2Pb . 3H_2O$.

Chemicals required:—Lead oxide or carbonate and acetic acid.

Method of procedure:—Dilute 10–15 c.c. of glacial acetic acid with about twice its bulk of water, heat to boiling in a porcelain dish, and then add the lead oxide or carbonate as long as it seems to dissolve, then filter, make distinctly acid with acetic acid and evaporate to crystallization. It must be noted that lead acetate is one of those compounds which tend to become supersaturated upon evaporation.

[NOTE:—A solution is said to be supersaturated when it retains in solution more than corresponds to the normal saturated state for the given temperature. On adding a crystal of the solute to a supersaturated solution the substance separates rapidly.]

If after evaporating to a small bulk no solid begins to separate, pour about one c.c. into a test-tube, cool well and stir thoroughly with a glass rod. If a crop of crystals separates, allow the rest of the solution to cool and then add the crystals. The solution generally crystallizes. If, as is sometimes the case, the whole sets to a solid mass, keep a few crystals of this mass, dissolve the rest in the minimum quantity of boiling water, and cool. If crystals do not separate, add those which were removed, and crystallization will generally ensue.

(2) AMMONIUM OXALATE, $(NH_4)_2C_2O_4$.

Chemicals required:—Ammonium hydroxide or carbonate and oxalic acid.

Dissolve about 5 grams of oxalic acid in water and add ammonia solution or ammonium carbonate until the reaction is neutral or faintly alkaline. Heat to boiling before finishing neutralization if ammonium carbonate is used. Filter the solution to free from dust particles, if necessary, and evaporate to crystallization. Large well-developed crystals should be obtained if the solution is allowed to cool slowly.

Equations:

$$H_2C_2O_4Aq + 2NH_4OHAq = (NH_4)_2C_2O_4Aq + 2H_2O.$$
$$H_2C_2O_4Aq + (NH_4)_2CO_3Aq = (NH_4)_2C_2O_4Aq + H_2O + CO_2.$$

(3) POTASSIUM ANTIMONYL TARTRATE (Tartar Emetic), $K . SbO . C_4H_4O_6\frac{1}{2}H_2O$ (Potassio-tartrate of Antimony).

Dissolve about 5 grams of potassium hydrogen tartrate in boiling water, and add gradually to the solution small quantities of antimonious oxide (Sb_2O_3). About 4 grams should be roughly weighed out and added slowly with constant boiling; filter and evaporate to crystallization. Determine when to stop evaporating by cooling a small quantity in a test-tube in the usual way.

$$2KH . C_4H_4O_6Aq + Sb_2O_3 = 2K . (SbO)C_4H_4O_6Aq + H_2O.$$

B. PREPARATION OF TYPICAL ACID SALTS.

POTASSIUM HYDROGEN SULPHATE (Potassium Bisulphate), **$KHSO_4$.**

Take 50 c.c. of dilute sulphuric acid, and divide into 2 equal parts. Neutralize one lot of 25 c.c. with caustic potash or potassium carbonate, and then add to the neutral solution of potassium sulphate which has been formed the other 25 c.c. of acid. Evaporate down the solution of potassium bisulphate thus obtained to crystallization.

Equations:

$$(a)\ H_2SO_4Aq + 2KOHAq = K_2SO_4Aq + 2H_2O$$
$$(b)\ H_2SO_4Aq + K_2SO_4Aq = 2KHSO_4Aq.$$

Note:—Sodium hydrogen sulphate, $NaHSO_4$, ammonium hydrogen sulphate, NH_4HSO_4, potassium hydrogen oxalate, $KH.C_2O_4$, and potassium hydrogen tartrate (cream of tartar) may all be similarly prepared.

The method of preparation of sodium bicarbonate, $NaHCO_3$ (*Brit. Phar.*), and of potassium bicarbonate, $KHCO_3$ (*Brit. Phar.*), has already been indicated (p. 75).

[Magnesium bicarbonate (fluid magnesia), $Mg(HCO_3)_2$. A solution of this substance is made from freshly precipitated magnesium carbonate (produced from magnesium sulphate and sodium carbonate) by saturating with carbon dioxide under 3 atmos. pressure.]

$$MgCO_3 + CO_2 + xH_2O = Mg(HCO_3)_2Aq.$$

PREPARATION OF THE TWO ACID PHOSPHATES OF SODIUM AND OF THE NORMAL SALT.

(*a*) **DISODIUM HYDROGEN PHOSPHATE** (Common Sodium Phosphate), **$Na_2HPO_4 . 12H_2O$.**

Method:—Neutralize 100 c.c. of a boiling solution of phosphoric acid with a measured volume of sodium hydroxide or sodium carbonate solution, filter, and evaporate carefully to crystallization.

Equations:

$$H_3PO_4Aq + 2NaOHAq = Na_2HPO_4Aq + 2H_2O.$$
$$H_3PO_4Aq + Na_2CO_3Aq = Na_2HPO_4Aq + H_2O + CO_2\nearrow.$$

As already mentioned (p. 54), common sodium phosphate is an acid salt, but is nearly neutral in reaction.

NOTE:—Sodium arsenate, $Na_2HAsO_412H_2O$, and ammonium phosphate can be prepared in a similar way from arsenic acid.

(*b*) SODIUM DIHYDROGEN PHOSPHATE, NaH_2PO_4.

The more acid phosphate can be prepared by adding to another 100 cc. of the same solution of phosphoric acid half the quantity of sodium hydroxide (or sodium carbonate) solution required for neutralization in the previous preparation. Filter and evaporate to crystallization. The solution is acid in reaction.

$$H_3PO_4Aq + NaOHAq = NaH_2PO_4Aq + H_2O.$$

(*c*) NORMAL SODIUM PHOSPHATE, Na_3PO_4.

Add to 100 c.c. of the solution of phosphoric acid used in above preparations three times as much caustic soda or sodium carbonate solution as was used in the immediately preceding preparation. Filter and evaporate to crystallization. The salt is strongly alkaline in reaction.

$$H_3PO_4Aq + 3NaOHAq = Na_3PO_4Aq + 3H_2O.$$

C. PREPARATION OF TYPICAL BASIC SALTS.

BISMUTH OXYNITRATE, $BiO.NO_3H_2O$ or $Bi(OH)_2.NO_3$.

Method:—Dissolve metallic bismuth or bismuth nitrate in dilute nitric acid and then pour the solution into a large volume of water. On filtering, washing, and drying, a white powder of fine crystalline scales is obtained.

$$Bi(NO_3)_3Aq + 2H_2O \rightleftarrows Bi(OH)_2NO_3 + 2HNO_3Aq.$$

LEAD OXYNITRATE, $Pb(OH)(NO_3)$.

This substance is best prepared by boiling up a dilute solution of lead nitrate with freshly precipitated lead hydroxide, filtering and evaporating to crystallization. White crystalline scales are obtained.

$$Pb(NO_3)_2 + Pb(OH)_2 = 2Pb(OH)(NO_3).$$

BISMUTH OXYCHLORIDE, BiOCl.

Dissolve bismuth hydroxide (which is readily obtained by adding ammonium hydroxide to a solution of the nitrate) in dilute hydrochloric acid, avoiding large excess of acid. Pour the solution into 500 c.c. of water. A white precipitate of the oxychloride comes down.

$$BiCl_3Aq + H_2O \rightleftarrows BiOCl + 2HClAq.$$

Antimony oxychloride, SbOCl, may be obtained similarly.

BISMUTH OXYCARBONATE, $Bi_2O_2CO_3$ (*Brit. Phar.*).

Add ammonium carbonate to a solution of bismuth nitrate, filter, wash and dry.

$$2Bi(NO_3)_3Aq + 3(NH_4)_2CO_3Aq = Bi_2O_2CO_3 + 2CO_2 + 6NH_4NO_3Aq.$$

LEAD OXYCARBONATE (White Lead), $(PbCO_3)_2 . Pb(OH_2)$ (*Brit. Phar.*).

This substance can be obtained by passing carbon dioxide into a solution of basic lead acetate. It is also prepared by the Dutch process, for a description of which see theoretical books.

$$Pb(OH)(C_2H_3O_2) + 2CO_2 = (PbCO_3)_2Pb(OH)_2 + 3Pb(C_2H_3O_2)_2 + 2H_2O.$$

MAGNESIUM OXYCARBONATE, $(MgCO_3)_3 . Mg(OH_2) . 4H_2O$ (*Brit. Phar.*).

Add to a boiling concentrated solution of magnesium sulphate a solution of sodium carbonate, evaporate for a few minutes, filter, wash and dry the resulting white powder.

$$4MgSO_4Aq + 4Na_2CO_3Aq + H_2O = Mg(CO_3)_3 . Mg(OH)_2 + 4Na_2SO_4Aq + CO_2.$$

LEAD OXYACETATE, BASIC LEAD ACETATE, $Pb(OH)(C_2H_3O_2)$.

Boil up a solution of lead acetate with excess of litharge or lead hydroxide, filter and evaporate. White crystals.

$$Pb(C_2H_3O_2)_2Aq + Pb(OH)_2 = 2Pb(OH)(C_2H_3O_2)Aq.$$

D. PREPARATION OF TYPICAL DOUBLE SALTS.

POTASH ALUM, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ (*Brit. Phar.*).

Mix concentrated solutions containing molecular proportions of potassium and aluminium sulphates (8·7 grams of potassium sulphate to 17·1 grams of anhydrous aluminium sulphate), filter and evaporate slowly at a low temperature. Cover and allow to stand for a considerable time. White crystalline solid.

Ammonia alum, $(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ (*Brit. Phar.*), white crystals; iron alum, $K_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$, a faintly amethyst tinted solid; and chrome alum, $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$, a deep violet solid, can be similarly prepared.

FERROUS AMMONIUM SULPHATE, $FeSO_4 . (NH_4)SO_4 . 6H_2O$.

Dissolve 13·9 grams of crystallized ferrous sulphate, $FeSO_4 . 7H_2O$, and 6·6 grams of ammonium sulphate separately in water at 40–45° C., making the solutions as concentrated as possible, mix at the same temperature, and allow to cool while stirring from time to time. Light green crystals separate. Cover and allow to stand. Drain the crystals and dry them carefully between filter paper.

PREPARATION OF TYPICAL OXIDES, HYDROXIDES AND SULPHIDES OF THE METALS.

I. OXIDES.

(*a*) Basic Oxides of Metals :—

Ferric Oxide, Fe_2O_3, Chromic Oxide or Chromium Sesquioxide, Cr_2O_3 : Mercuric Oxide (yellow and red) HgO (*B.P.*).
Silver Oxide, Ag_2O (*B.P.*) : Bismuth Oxide, Bi_2O_3 (*B.P.*).
Lead Oxide (Litharge), PbO (*B.P.*) : Calcium Oxide (Quicklime), CaO (*B.P.*).
Magnesium Oxide, MgO (*B.P.*) : Zinc Oxide, ZnO (*B.P.*).
Cupric Oxide, CuO : Cuprous Oxide (Copper Suboxide), Cu_2O.

(*b*) Acidic Metallic Oxide :—

Chromium Trioxide (Chromic Anhydride), CrO_3 (*B.P.*).

(*c*) Metalloidal Oxides :—

Arsenious Anhydride (White Arsenic), As_2O_3 (*B.P.*).
Antimonious Oxide, Sb_2O_3 (*B.P.*).

METALLIC DIOXIDES.

Lead Dioxide, PbO_2.
Manganese Dioxide, MnO_2.

II. METALLIC HYDROXIDES.

Sodium Hydroxide (Caustic Soda), $NaOH$.

Potassium Hydroxide (Caustic Potash), KOH.

Other Hydroxides :—

$Pb(OH_2)$: $Bi(OH)_3$: $Zn(OH)_2$: $Fe(OH)_3$: $Al(OH)_3$: $Ca(OH)_2$.

III. SULPHIDES.

(*a*) Preparation by precipitation.

Antimony Sulphide, Sb_2S_3 (*B. P.*).

Other Sulphides :—HgS: Ag_2S: CuS: Bi_2S_3: SnS: SnS_2: As_2S_3: FeS : ZnS: MnS : NaS : CoS.

(*b*) Preparation by direct union.

I a. BASIC METALLIC OXIDES.

FERRIC OXIDE, Fe_2O_3.

Add ammonium hydroxide to a warm solution of ferric chloride as long as a precipitate forms, filter off the brown precipitate of ferric hydroxide, dry in an air oven at about 100° C., remove from the filter paper or cloth, powder, and heat gently in a dish or crucible. The ferric oxide is obtained as a reddish powder.

Equations: $FeCl_3Aq + 3NH_4OHAq = Fe(OH)_3 + 3NH_4ClAq.$

$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$

NOTE :—Aluminium oxide, Al_2O_3, bismuth oxide, Bi_2O_3 (*Brit. Phar.*), chromium oxide, Cr_2O_3, lead oxide, PbO, zinc oxide, ZnO, and magnesium oxide, MgO, can be prepared by exactly similar processes.

MERCURIC OXIDE, HgO.

There are two varieties—(*a*) yellow, (*b*) red.

(*a*) **Preparation of yellow Mercuric Oxide.** Dissolve a few grams of mercuric chloride in water and then add sodium or potassium hydroxide solution as long as a precipitate forms. Filter the yellow precipitate, dry, and powder it.

Equation : $HgCl_2Aq + 2NaOHAq = HgO + H_2O + 2NaClAq.$

NOTE :—Mercurous oxide, Hg_2O, can be obtained as a black powder in a similar way from mercurous nitrate solution ($HgNO_3Aq$). Silver oxide, Ag_2O (*Brit. Phar.*), can be prepared in an analogous manner.

(*b*) **Preparation of red Mercuric Oxide.** Dissolve a few grams of mercury in moderately concentrated nitric acid, evaporate the solution of mercuric nitrate to dryness, and heat cautiously. A nearly black residue is left, which turns red on cooling.

Equations:

(*a*) $3Hg + 8HNO_3Aq = 3Hg(NO_3)_2Aq + 4H_2O + 2NO$.

(*b*) $2Hg(NO_3)_2 = 2HgO + 4NO_2 + O_2$.

NOTE:—Cupric oxide, CuO, can be prepared by an analogous process from metallic copper.

CUPRIC OXIDE, CuO.

Copper oxide can also be obtained by adding excess of caustic alkali (soda or potash) to a solution of a copper salt, boiling, filtering, washing, and finally drying and heating the black precipitate obtained. A blue precipitate of the hydroxide is first thrown down, but this decomposes on boiling to give oxide and water.

Equations:

$$CuSO_4Aq + 2NaOHAq = Cu(OH)_2 + Na_2SO_4Aq.$$

$$Cu(OH)_2 = CuO + H_2O.$$

CUPROUS OXIDE, Cu_2O.

Dissolve 3–5 grams of crystallized copper sulphate in about 100 c.c. of cold water. Add to the solution caustic soda or potash until the reaction just becomes alkaline. A blue precipitate of cupric hydroxide will form. Add 5–10 per cent. glucose solution with constant stirring until the precipitate just dissolves to give a deep blue solution. Boil for a few minutes. A deep red precipitate of cuprous oxide comes down. Filter and wash.

CALCIUM OXIDE (Quicklime, Calx), CaO (*Brit. Phar.*)

Heat about one gram of precipitated calcium carbonate over a blowpipe or burner until a small quantity added to a few drops of hydrochloric acid on a watch-glass causes no effervescence. After allowing to cool add a small quantity of cold water (2 or 3 c.c.). Note the great evolution of heat, and the alkaline character of the solution produced.

$$CaCO_3 = CaO + CO_2.$$

$$CaO + H_2O = Ca(OH)_2 \text{ (slaked lime).}$$

NOTE:—Magnesium oxide, MgO (*Brit. Phar.*), and zinc oxide, ZnO (*Brit. Phar.*), can also be obtained by heating the carbonate.

I b. ACIDIC METALLIC OXIDE.

CHROMIUM TRIOXIDE, CHROMIC ANHYDRIDE, CrO_3 (*Brit. Phar.*).

Add to 25 c.c. of saturated potassium dichromate solution about 40 c.c. of concentrated sulphuric acid. Stir and allow to cool. Pink crystals separate. Filter through a plug of glass wool placed in the apex of a filter funnel, and then wash repeatedly with small quantities of strong nitric acid until wash liquid gives no test for sulphuric acid. Dry on a piece of porous plate, and place in dry stoppered bottle.

NOTE:—Filter paper or other organic material cannot be used to dry chromic anhydride as oxidation takes place.

I c. METALLOIDAL OXIDES.

ARSENIOUS ANHYDRIDE (White arsenic), As_2O_3 (*Brit. Phar.*).

Powder in a mortar about half a gram of arsenic, place in bulb tube (preferably of hard glass), and after connecting one end of the tube to an aspirator and the other end to a small wash bottle containing sulphuric acid aspirate dry air through the apparatus while heating the arsenic cautiously. The arsenic gets oxidized, and a white crystalline sublimate of arsenious anhydride is obtained.

$$4As + 3O_2 = 2As_2O_3.$$

Carry out the following experiments:—

(*a*) Boil up a small quantity of the oxide with water. Very little seems to dissolve, but on adding sulphuretted hydrogen a yellow precipitate of arsenious sulphide is produced.

(*b*) Note the ready solubility in caustic soda or potash. An arsenite is formed.

(*c*) Note the garlic odour on heating a small quantity on charcoal.

NOTE:—Antimonious oxide, Sb_2O_3 (*Brit. Phar.*), could be similarly prepared or could be obtained by precipitation, e. g. by adding ammonium hydroxide to a solution of antimonious chloride in dilute hydrochloric acid.

$$2SbCl_3 + 6NH_4OHAq = Sb_2O_3 + 3H_2O + 6NH_4ClAq.$$

I d. METALLIC DIOXIDES.*

LEAD DIOXIDE, PbO_2.

The following experiments might be carried out in test-tubes :—

(*a*) Warm about a gram of red lead with dilute nitric acid for a few minutes. A portion dissolves, as could be proved by filtering and testing the filtrate for lead. The residue is lead peroxide, which could be filtered, washed, and dried.

$$Pb_3O_4 + 4HNO_3Aq = 2Pb(NO_3)_2Aq + 2H_2O + PbO_2.$$

(*b*) Add to a few c.c. of lead acetate solution excess of a freshly prepared solution of bleaching powder and a few drops of caustic soda and warm. The brown precipitate which forms should be filtered and washed with dilute nitric acid.

Equations :

(*a*) $(CH_3 . COO)_2PbAq + 2NaOHAq = Pb(OH)_2 + 2CH_3COONaAq.$

(*b*) $2Pb(OH)_2 + Ca(OCl)_2Aq = 2PbO_2 + 2H_2O + CaCl_2Aq.$

Test :—Warm a small quantity of the solid with a few c.c. of concentrated hydrochloric acid. Chlorine is evolved.

Note :—Manganese dioxide could be prepared from a manganous solution by Method (*b*).

II. METALLIC HYDROXIDES.

The hydroxides of Na, K, NH_4 are easily soluble in water and those of Ca, Sr, and Ba are moderately soluble. All the others are insoluble in water and can be obtained by precipitation.

(1) SODIUM HYDROXIDE, CAUSTIC SODA, NaOH.

Make a dilute solution of sodium carbonate by dissolving about 5 grams of the crystallized substance in 80-100 c.c. of water. Then add milk of lime gradually with constant stirring to the warm solution until, after allowing any precipitate to settle, it is found that a small test quantity of the solution does not effervesce with hydrochloric acid. Filter and evaporate nearly to dryness in an iron or silver dish : strong caustic soda solution attacks glass and porcelain.

$$Na_2CO_3Aq + Ca(OH)_2 = CaCO_3 + 2NaOHAq.$$

Note :—Potassium hydroxide (caustic potash), KOH, can be prepared in a similar manner.

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* The dioxides mentioned here are often termed peroxides, but it has been proposed to restrict this latter term to compounds like barium peroxide, BaO_2, which give hydrogen peroxide with dilute acid.

Prepare the following **Hydroxides** in a test-tube by adding NaOHAq, KOHAq, or NH_4OHAq to a soluble salt of the metal.

(2) **Lead Hydroxide, $Pb(OH)_2$.** White solid.

$$Pb(NO_3)_2Aq + 2NaOHAq = Pb(OH)_2 + 2NaNO_3Aq.$$

(3) **Copper Hydroxide, $Cu(OH)_2$.** Blue solid.

$$CuSO_4Aq + 2NaOHAq = Cu(OH)_2 + Na_2SO_4Aq.$$

Avoid adding excess of NaOHAq and do not heat.

(4) **Bismuth Hydroxide, $Bi(OH)_3$.** White solid.

$$Bi(NO_3)_3Aq + 3NaOHAq = Bi(OH)_3 + 3NaNO_3Aq.$$

(5) **Zinc Hydroxide, $Zn(OH)_2$.** White solid.

$$ZnSO_4Aq + 2NaOHAq = Zn(OH)_2 + Na_2SO_4Aq.$$

Do not add excess of NaOHAq, as the precipitate is soluble in excess.

(6) **Ferric Hydroxide, $Fe(OH)_3$.** Reddish brown solid.

$$FeCl_3Aq + 3NaOHAq = Fe(OH)_3 + 3NaClAq.$$

(7) **Aluminium Hydroxide, $Al(OH)_3$.** White gelatinous solid.

$$Al_2(SO_4)_3Aq + 6NaOHAq = 2Al(OH)_3 + 3Na_2SO_4Aq.$$

Do not add excess of NaOHAq, as the precipitate is soluble in excess.

(8) **Calcium Hydroxide, Slaked Lime, $Ca(OH)_2$.** White solid.

To a concentrated solution of calcium chloride add NaOHAq.

$$CaCl_2Aq + 2NaOHAq = Ca(OH)_2 + 2NaClAq.$$

Note:—All the above hydroxides can be filtered off and dried at 100° C. in air-bath without decomposition, with the exception of the hydroxides of iron and aluminium, which lose water and form oxides.

III. SULPHIDES.

(*a*) **Preparation by precipitation.** Antimonious sulphide, and the other sulphides indicated on p. 82, can readily be prepared by precipitation under suitable conditions, which are given under the tests for the respective metals.

(*b*) Mix about 6 grams of iron filings with half their weight of sulphur, and heat cautiously in a test tube (preferably of hard glass) until the bottom of the mass begins to glow. The reaction slowly spreads throughout the mixture. After cooling, break the tube and warm a small quantity of the product with hydrochloric or dilute sulphuric acid. Sulphuretted hydrogen is evolved.

ADVANCED PREPARATIONS.

METALLIC DERIVATIVES.

I. Chlorides :

$AlCl_3$: $FeCl_2 4H_2O$: $FeCl_2$. $FeCl_3 xH_2O$, *B.P.* : $FeCl_3$.
$SnCl_2 . 2H_2O$: $SnCl_2$: $SnCl_4$.

II. Oxidizing Agents:

(*a*) Chlorine compounds:—
$CaOCl_2$, *B.P.* : $NaOCl$, *B.P.* : ($KOCl$) : $KClO_3$, *B.P.* : $KClO_4$.
(*b*) Chromium compounds: CrO_2Cl_2 : K_2CrO_4 : $K_2Cr_2O_7$, *B.P.*
(*c*) Potassium permanganate : $KMnO_4$, *B.P.*

III. Nitrites: $NaNO_2$, *B.P.* : KNO_2.

IV. Hypophosphites : $Ca(H_2PO_2)_2$, *B.P.* : NaH_2PO_2, *B.P.*
$Ba(H_2PO_2)_2$.

V. Sodium Thiosulphate : $Na_2S_2O_3 . 5H_2O$.

I. METALLIC CHLORIDES.

ALUMINIUM CHLORIDE, $AlCl_3$.

Place in a dry combustion tube of convenient length 5–10 grams of aluminium in a moderately fine state of division, connect at

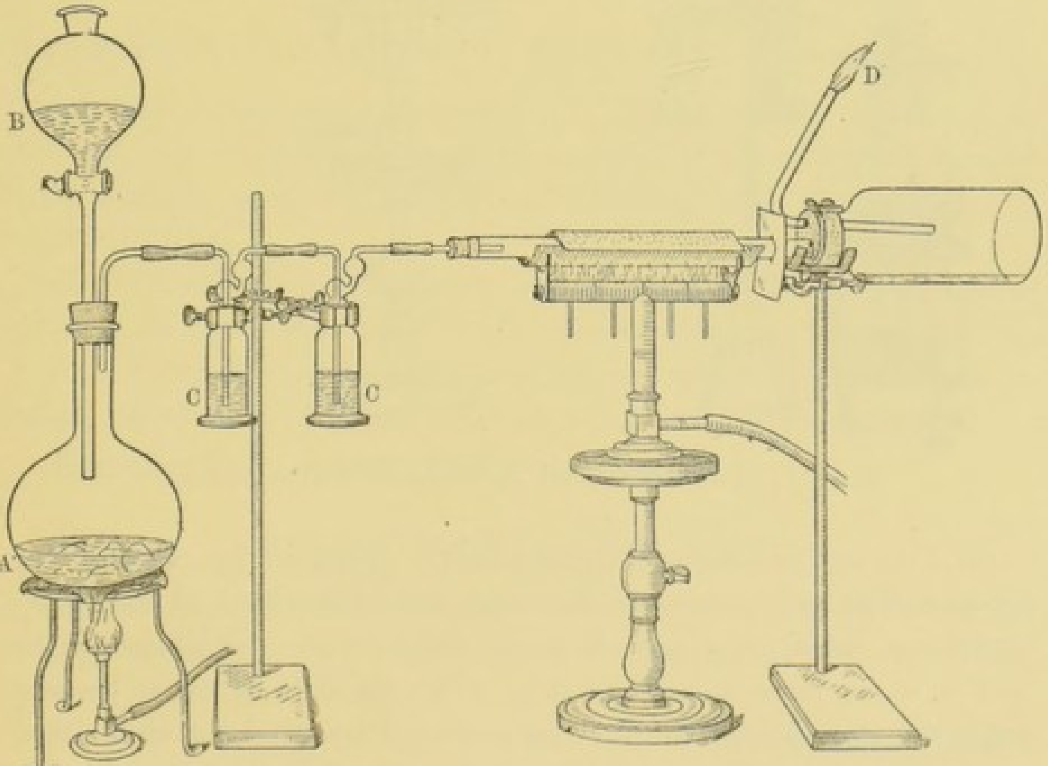

Fig. 16. Preparation of Aluminium Chloride. A, Flask containing saturated brine and Sodium Chloride; B, Dropping funnel containing concentrated Sulphuric Acid; C, Wash bottles containing concentrated Sulphuric Acid; D, Evolved hydrogen which has been ignited.

one end to an apparatus arranged for the supply of dry hydrochloric acid gas (see p. 37), and at the other with a large wide-mouthed bottle as receiver. The tube where it passes through the bung is not constricted in any way, and the bottle should be close to the small furnace in which the tube is heated. A small piece of asbestos card is put between furnace and cork to prevent the latter being burned, and a small exit tube should allow for escape of hydrogen. The diagram shows the method of arranging the apparatus.

$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

FERROUS CHLORIDE, (*a*) $FeCl_2 . 4H_2O$, (*b*) $FeCl_2$.

(*a*) The hydrated salt $FeCl_2 . 4H_2O$ can be obtained as a green crystalline solid by dissolving iron in hydrochloric acid, keeping the iron in excess, filtering and evaporating to crystallization.

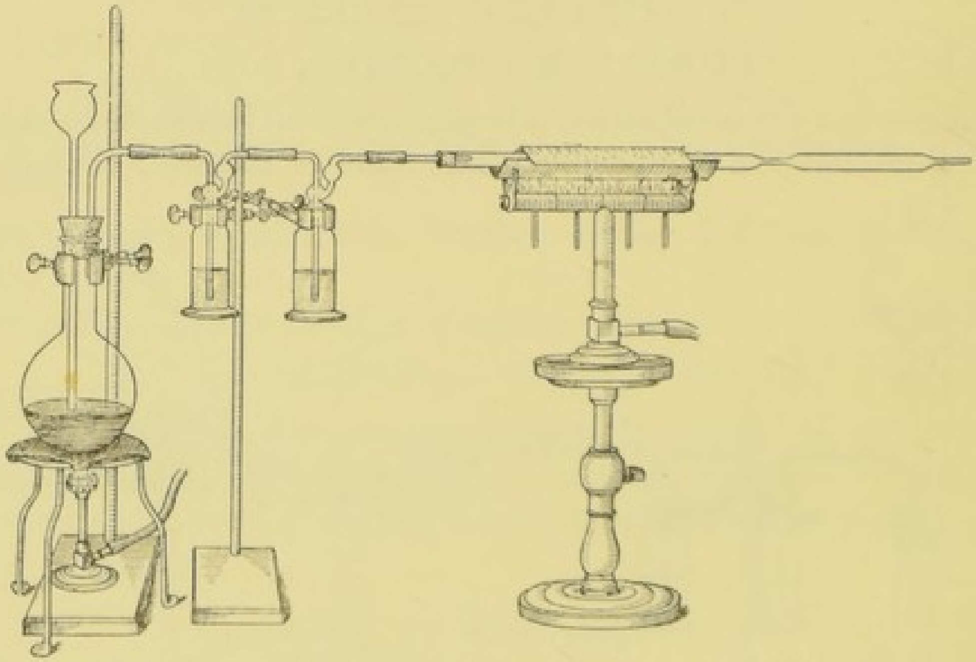

Fig. 17. Preparation of Ferrous Chloride ($FeCl_2$).

(*b*) The anhydrous substance can be prepared by passing dry hydrochloric acid gas over iron filings heated in a tube of hard glass which is constricted just beyond the furnace and again at the end so as to form a receiver (Fig. 17). (Note.—If oil is present with the iron filings it must be removed by washing with ether and then heating in a current of hydrogen or coal gas.)

The ferrous chloride usually crystallizes on the top of the tube above the iron at first, but by strongly heating in a rapid stream of gas may be driven over into the receiver portion of the tube and can be there sealed up. A blowpipe will be necessary for the latter portion of the experiment.

$$Fe + 2HCl = FeCl_2 + H_2.$$

FERRIC CHLORIDE, (*a*) $FeCl_3xH_2O$, *B.P.*, (*b*) $FeCl_3$ (anhyd.)

(*a*) Hydrated ferric chloride can readily be made from ferric oxide or hydroxide by solution in hydrochloric acid and evaporation to crystallization. A yellowish mass results containing different quantities of water of crystallization.

(*b*) Anhydrous ferric chloride can be made by passing dry chlorine over heated iron turnings (or iron powder made by strongly heating ferric oxide in hydrogen) in a tube similar to that used for the preparation of ferrous chloride. The ferric chloride is much more volatile than the ferrous chloride however, and readily passes into the receiver portion of the tube, condensing as jet black crystals. As it is extremely deliquescent it should be at once sealed up, or preferably removed to a clean dry bottle provided with a glass stopper. A small quantity of melted paraffin wax should be poured into the groove round the stopper.

STANNOUS CHLORIDE, (*a*) $SnCl_2 . 2H_2O$, (*b*) $SnCl_2$ (anhyd.).

(*a*) The hydrated substance $SnCl_2 . 2H_2O$, which is known as tin salt, can easily be obtained from metallic tin and concentrated hydrochloric acid by dissolving, filtering, and evaporating to crystallization.

(*b*) The anhydrous substance can be prepared by passing hydrochloric acid gas over melted tin, and condensing the product in a cooled receiver or by distilling the hydrated substance from a small retort of hard glass. A high temperature is required.

Equation: $Sn + 2HCl = SnCl_2 + H_2$.

STANNIC CHLORIDE, $SnCl_4$.

(*a*) To get a solution of stannic chloride in dilute hydrochloric acid pass chlorine into a solution of stannous chloride containing a small quantity of free acid.

(*b*) Pass dry chlorine over tin in a round-bottomed flask (which should not be heated) provided with a long tube as air condenser. The chlorine delivery tube passes at first to the bottom of the flask, and is gradually raised as liquid forms. The product is a colourless liquid boiling at 114° C. All parts of the apparatus should be thoroughly dry as stannic chloride is decomposed by moisture. Place in a dry bottle and run a small quantity of melted paraffin wax round the stopper.

II. OXIDIZING AGENTS.

(*a*) CHLORINE COMPOUNDS.

BLEACHING POWDER, $CaOCl_2$ (*Brit. Phar.*).

Put into a long tube bent up at each end about 10 grams of dry slaked lime. Pass chlorine slowly over the lime and shake from time to time. Finally allow to stand overnight with the tube full of chlorine. Draw air through the tube by means of an aspirator so as to expel the chlorine, and remove the compound to a bottle with glass stopper.

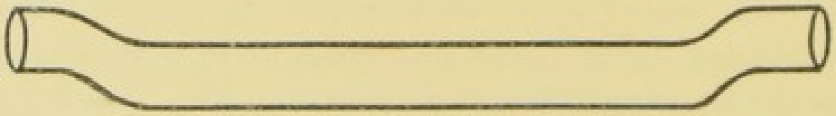

Fig. 18. Tube for preparation of Bleaching Powder.

$$Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O.$$

Carry out the following experiments :—

(*a*) Make a strong solution and soak a small piece of turkey red cloth in it. After a few minutes place the cloth in dilute sulphuric acid. The colour is rapidly discharged.

(*b*) Prepare dioxides of lead and manganese (p. 85).

(*c*) To a small quantity of solution add a few c.c. of potassium iodide, and then a few c.c. of acetic acid. Iodine is set free, and is proportional to the chlorine liberated (see p. 319).

SODIUM HYPOCHLORITE, NaOCl (*Brit. Phar.*).

Method I :—A solution is easily obtained by adding sodium carbonate to a solution of bleaching powder and filtering.

$$Ca(OCl)_2Aq + Na_2CO_3 = 2NaOClAq + CaCO_3.$$

Method II. Pass chlorine into dilute cold caustic soda solution.

$$2NaOHAq + Cl_2 = NaOClAq + NaClAq + H_2O.$$

In neither case can one evaporate to crystallization in the ordinary way, because chlorate would be produced.

$$3NaOClAq = NaClO_3Aq + 2NaClAq.$$

One must evaporate in a desiccator under reduced pressure at ordinary temperature if solid is required, as indicated in diagram. Impure crystals contaminated with chloride can be obtained.

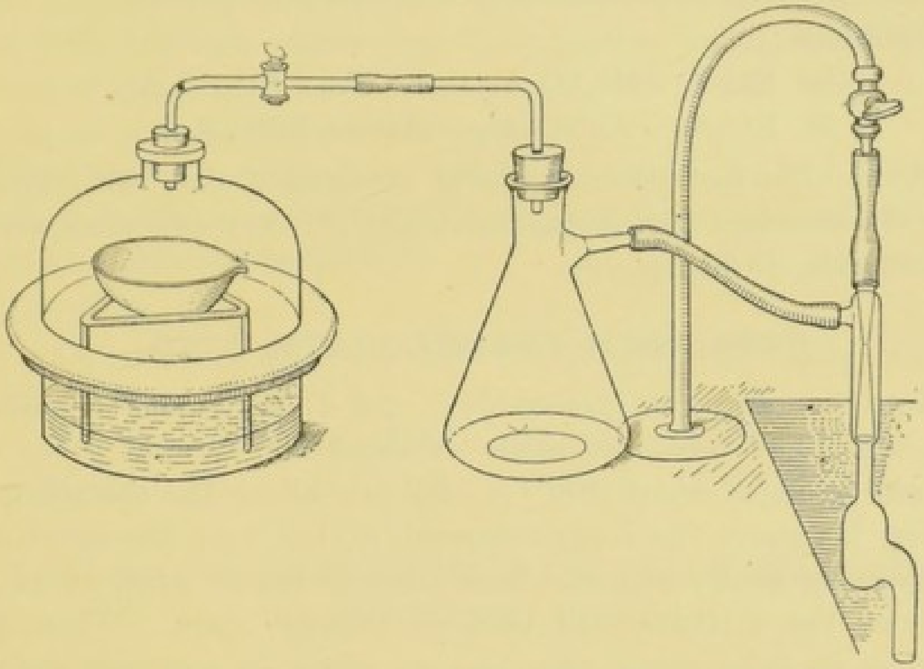

FIG. 19. EVAPORATION OF A SOLUTION UNDER DIMINISHED PRESSURE AT ORDINARY TEMPERATURE.

POTASSIUM CHLORATE, $KClO_3$.

Make a strong solution of caustic potash—say 40 to 50 grams of potash in 100 of water—heat the solution in a deep porcelain basin by means of a rose burner, and slowly pass chlorine into it until no more is absorbed. The chlorine should be passed into the liquid through an inverted filter funnel and need not be dried. The arrangement of apparatus would be similar to that represented on p. 66, for the preparation of pure sodium chloride. When the solution is saturated, boil the liquid, filter, evaporate slightly and then allow to cool. Potassium chlorate crystallizes out: filter, wash with a small quantity of cold water, and dry on a porcelain plate.

$$6KOHAq + 3Cl_2 = KClO_3 + 5KClAq + 3H_2O.$$

NOTE.—Compare preparations of potassium bromide and potassium iodide (p. 70).

Example of oxidizing power of substance:—

Dissolve a small quantity in warm water, and then add dilute nitric acid and silver nitrate. No precipitate is formed because all chlorates are soluble in water. Now add a few drops of sulphurous acid solution. An immediate precipitate of silver chloride is formed because the chlorate oxidizes the sulphurous acid to sulphuric with formation of potassium chloride.

Equations:

(*a*) $KClO_3 + 3H_2SO_3Aq = KClAq + 3H_2SO_4Aq.$

(*b*) $KClAq + AgNO_3Aq = AgCl + KNO_3Aq.$

Note:—For further examples of oxidizing action, see preparation of potassium permanganate, $KMnO_4$ (p. 94), and phosphorus oxychloride, $POCl_3$ (p. 49).

POTASSIUM PERCHLORATE, $KClO_4$.

Heat up in a crucible (preferably of nickel) 10 grams of potassium chlorate. The substance melts at about 360° C. and gives off oxygen freely at about 400° C. Do not allow the temperature to rise far above the latter temperature, but keep the substance effervescing gently and stir from time to time. After 10 to 20 minutes the mixture will tend to solidify again. When the mixture is quite pasty, stop heating, allow to cool, and extract with 150 c.c. of boiling water. When the substance has been dissolved, boil up the solution in a beaker with 5 c.c. of concentrated hydrochloric acid so as to decompose any chlorates present. On allowing to cool potassium perchlorate separates out. When quite cold, filter, wash with cold water, and recrystallize from boiling water. Potassium perchlorate is a white crystalline solid: it is one of the most insoluble potassium salts known.

Equations:

(*a*) $2KClO_3 = KClO_4 + KCl + O_2.$

(*b*) $4KClO_3 + 12HClAq = 4KClAq + 6H_2O + 3ClO_2 + 9Cl.$

II b. CHROMIUM COMPOUNDS.

CHROMYL CHLORIDE, CrO_2Cl_2.

Mix together powdered potassium dichromate and sodium chloride in the proportion of 29 grams of dichromate to 22 grams of chloride (21 and 17 grams respectively would be convenient quantities), dry in an air oven at 100° C. and then introduce into a glass-stoppered retort of 300 c.c. capacity, in which has been placed a few c.c. of concentrated sulphuric acid so as to prevent the dried mixture sticking to the sides of the retort and causing fracture on heating. Then add about 60 c.c. of concentrated sulphuric acid and warm gently. A red liquid distils over which should be collected in a dry flask cooled in ice. Redistil from a small retort, and collect what comes over at about 116° C. The cork through which the thermometer passes should have been immersed in melted paraffin wax, and should be protected as far as possible by asbestos paper.

The substance reacts vigorously with water and is a powerful oxidizer. Add a few drops to water and then add lead acetate. Lead chromate is precipitated.

Equations:

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = K_2SO_4 + 2Na_2SO_4 + 2CrO_2Cl_2 + 3H_2O.$$

With water:

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

$$(CH_3COO)_2PbAq + H_2CrO_4Aq = PbCrO_4 + 2CH_3COOHAq.$$

POTASSIUM CHROMATE, K_2CrO_4 and POTASSIUM DICHROMATE, $K_2Cr_2O_7$.

Mix together 10 grams of powdered chromite (chrome iron stone), 25 grams of potassium carbonate, and 15 grams of nitre, and heat up the mixture in an iron crucible of about 70 c.c. capacity over a blowpipe. Continue heating until the fused mass is deep orange. After cooling extract with hot water, filter from iron oxide, silica, &c., and divide the solution into 2 approximately equal parts.

(*a*) Evaporate half to crystallization. Light yellow crystals of potassium chromate will be obtained.

(*b*) Add to the other half about 10 c.c. of concentrated sulphuric acid and evaporate to crystallization. Orange crystals of potassium dichromate separate.

Equations:

$$4FeCr_2O_4 + 8K_2CO_3 + 7O_2 = 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2.$$

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + H_2O + K_2SO_4.$$

To prove the strong oxidizing nature of these substances, make a solution of potassium dichromate, add a few c.c. of sulphuric acid, and then add a few c.c. of solutions of following substances to different portions of the acidified solution, warming gently after mixing:—(*a*) Sulphurous acid solution; (*b*) Sulphuretted hydrogen; (*c*) Ferrous sulphate; (*d*) Alcohol. In each case the solution will turn green because of the transformation of the chromium to a chromic salt. The complex orange ion Cr_2O_7'' gives a green chromic ion $Cr^{\cdots}$ (p. 221). When potassium dichromate acts as an oxidizing agent, the compound itself gets reduced.

Equations :

(*a*) $K_2Cr_2O_7 + H_2SO_4 + 3H_2SO_3Aq = K_2SO_4Aq + Cr_2(SO_4)_3Aq + 4H_2O.$

(*b*) $K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S.$

(*c*) $K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O.$

(*d*) $K_2Cr_2O_7 + 4H_2SO_4 + 3CH_3 . CH_2OH = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3CH_3 . CHO.$

II c. POTASSIUM PERMANGANATE (*Brit. Phar.*).

Mix together 15 grams of caustic potash, 10 c.c. of water, and 5 grams of $KClO_3$ in an iron crucible. Heat and stir until fusion is effected, stop heating and then add slowly to the hot mixture 20 grams of manganese dioxide in powder with constant stirring. Heat until a dry mass remains, allow to cool, extract with water, and transfer solid and solution to a large flask ; make up to about half a litre and draw in carbon dioxide and air by means of an aspirator. A purple solution is formed, and a brownish-black precipitate appears. Filter and evaporate to crystallization : deep purple prisms separate. Make a solution, acidify strongly with dilute sulphuric acid, and carry out similar reactions to those detailed above under chromium. In each case the colour of the permanganate solution is discharged because of the reduction of the manganese to form a manganous salt which is almost colourless in solution. The deep purple permanganic ion MnO_4' has been decomposed, the manganese being transformed into the manganous ion $Mn^{\cdot\cdot}$ (p. 221).

Equations:

(*a*) $2KMnO_4 + 5H_2SO_3Aq = 2H_2SO_4 + K_2SO_4 + 2MnSO_4 + 3H_2O.$

(*b*) $2KMnO_4 + 3H_2SO_4 + 5H_2S = K_2SO_4 + 2MnSO_4 + 8H_2O + 5S.$

The sulphur may be further oxidized.

(*c*) $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$

(*d*) $2KMnO_4 + 3H_2SO_4 + 5C_2H_5 . OH = K_2SO_4 + 2MnSO_4 + \underbrace{5CH_3 . CHO}_{\text{Acetic Aldehyde.}} + 8H_2O.$

III. SODIUM NITRITE, $NaNO_2$ (*Brit. Phar.*).

Fuse up in a small porcelain crucible about 5 grams of sodium nitrate, $NaNO_3$. Do not allow the temperature to rise until oxygen is freely evolved. Add gradually about 10 grams of lead in small pieces and stir up in the molten mass for 15 to 20 minutes. The lead melts and slowly oxidizes.

$$NaNO_3 + Pb = PbO + NaNO_2.$$

When the reaction seems complete, cool, extract with water, filter and evaporate nearly to dryness. Sodium nitrite (mixed with nitrate) crystallizes out.

Tests:—(*a*) Add hydrochloric acid to a few of the crystals: oxides of nitrogen are evolved.

$$2NaNO_2 + 2HCl = 2NaCl + H_2O + NO + NO_2.$$

(*b*) Add a few crystals to a solution of ferrous sulphate. A brown colour appears (p. 219).

NOTE:—Potassium nitrite, KNO_2, can be similarly prepared.

PREPARATION OF CALCIUM HYPOPHOSPHITE, $Ca(H_2PO_2)_2$ (*Brit. Phar.*).

Place in a flask of about one litre capacity 20 grams of freshly slaked lime, or about 14 grams of quicklime, add half a litre of water and 6 grams of yellow phosphorus. Close the flask by

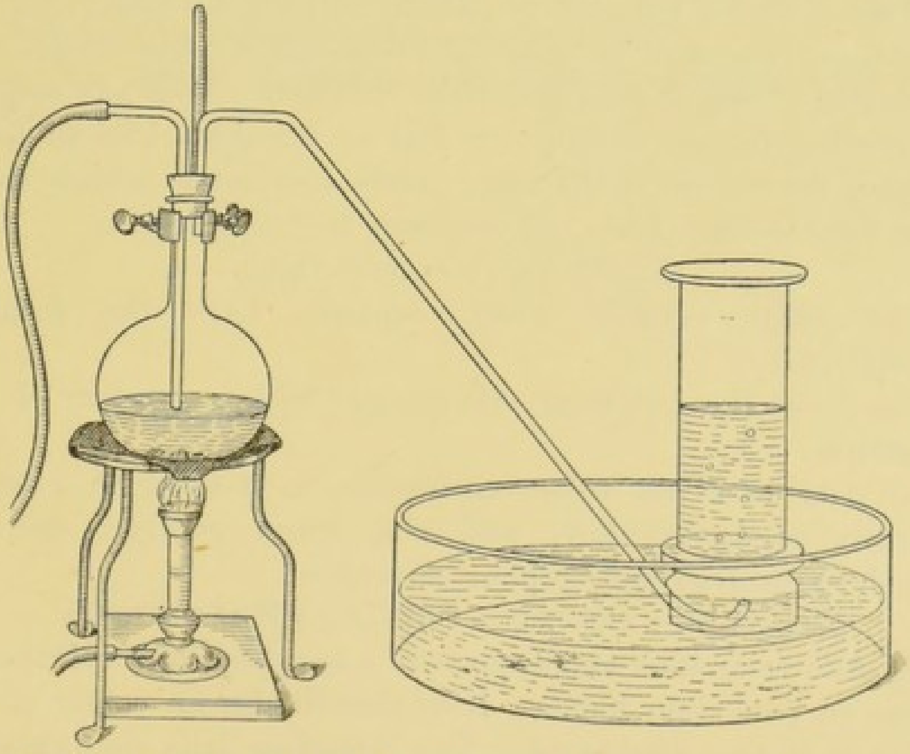

FIG. 20. PREPARATION OF PHOSPHORETTED HYDROGEN (PH_3) AND OF CALCIUM HYPOPHOSPHITE, $Ca(H_2PO_2)_2$.

a cork with 2 holes. Through one hole should pass a tube which dips into the liquid and is connected to the gas supply. Through the other passes a tube bent round and dipping under water as if to form a delivery tube for collection of gas as indicated in the diagram. Expel the air in the flask by coal gas and then boil up as long as phosphine is evolved. Pass coal gas so as to expel the phosphine and then pass carbon dioxide into the solution until completely saturated. Boil the liquid so as to decompose calcium bicarbonate, filter and evaporate slowly at low temperature on a water bath. Calcium hypophosphite crystallizes out.

Equations:

(*a*) $8P + 3Ca(OH)_2 + 6H_2O = 3Ca(H_2PO_2)_2Aq + 2PH_3$.

(*b*) $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$.

NOTE:—Sodium hypophosphite, NaH_2PO_2 (*Brit. Phar.*), can be obtained from the calcium salt by adding sodium carbonate to a solution, or can be prepared by boiling up phosphorus and caustic soda in a similar way to that described above.

Equations:

$$Ca(H_2PO_2)_2Aq + Na_2CO_3Aq = CaCO_3 + 2NaH_2PO_2Aq.$$

or $$4P + 3NaOHAq + 3H_2O = PH_3 + 3NaH_2PO_2Aq.$$

SODIUM THIOSULPHATE, $Na_2S_2O_3 . 5H_2O$.

Make a strong solution of sodium sulphite by dissolving the crystalline compound in water, or by passing sulphur dioxide into a solution of caustic soda or sodium carbonate. Then add sulphur in powder (flowers of sulphur), boil up for about half an hour, keeping the volume of the water nearly constant by adding water from time to time, filter and evaporate to crystallization.

$$Na_2SO_3Aq + S = Na_2S_2O_3Aq.$$

The white crystals which separate have the formula $Na_2S_2O_3 . 5H_2O$.

Carry out the following experiments with a solution of the substance:—

(*a*) Add to a few cubic centimetres in a test-tube a small quantity of hydrochloric acid and warm gently. Sulphur dioxide is evolved and sulphur separates.

$$Na_2S_2O_3Aq + 2HClAq = 2NaClAq + H_2O + SO_2 + S.$$

(*b*) Add to another small quantity a few drops of a solution of iodine in potassium iodide. Note that the brown colour of the iodine is at once discharged. Two colourless salts are formed as indicated in the equation:—

$$2Na_2S_2O_3Aq + I_2 = 2NaIAq + \underset{\text{Sodium Tetrathionate.}}{Na_2S_4O_6Aq}$$

SUMMARY OF COMPOUNDS (INORGANIC) IN THE BRITISH PHARMACOPŒIA, WITH IMPURITIES WHICH MAY BE PRESENT.

NOTES:—(1) The impurities which might be met with are stated as ions (see p. 103), but in the case of the metals the valency is not indicated by the usual dots. This method of representation should present no difficulty, as the table of impurities need not be considered until after the analysis of at least a set of simple substances, i. e. after Parts IV and V have been studied. The ions of the acids are as a rule the radicles left after subtracting replaceable hydrogen from the formula for the acid, e. g. SO_4'' is the ion of sulphuric acid, NO_3' the radicle of nitric acid, H_2PO_2' the radicle of hypophosphorous acid, &c. (p 107).

(2) One organic compound, viz. HCN, is mentioned for convenience.

Summary of Inorganic Compounds in British Pharmacopœia with impurities which may be present.

Name.	Latin Name in Pharmacopœia	Formula.	Impurities which may be present stated as Ions. See p. 103.	Page in book where preparation is described.
A.				
Arsenious Anhydride	Acidum Arseniosum	As_2O_3	Pb, Cd, Sb, Sn. Sulphides.	84
Acid, Boric	Acidum Boricum	$B(OH)_3$	Pb, Cu, Fe, Ca, Mg, K, Na, NH_4. Cl', SO_4''.	
(Acid, Chromic) Chromic Anhydride	Acidum Chromicum	CrO_3	SO_4'' (i. e. Sulphate).	84
Acid, Hydrobromic	Acidum Hydrobromicum	HBr	As, Ba. Cl', PO_4''', SO_4'', SO_3''.	45
Acid, Hydrochloric	Acidum Hydrochloricum	HCl	As, Pb, Cu, Fe, Al. Br', I', SO_4'', SO_3''.	37
Acid, Hydrocyanic	Acidum Hydrocyanicum	HCN	Cl', SO_4''.	
Acid, Nitric	Acidum Nitricum	HNO_3	Pb, Cu, As, Fe. Cl', BrO_3', IO_3', SO_4'.	32
Acid, Nitro-Hydrochloric (Aqua Regia)	Acidum Nitro-Hydrochloricum	(HCl and HNO_3)		
Acid, Phosphoric	Acidum Phosphoricum	H_3PO_4	Pb, Cu, As, Ca, K, Na, NH_4, Fe. Cl', NO_3', SO_4', PO_3''', PO_3', P_2O_7''''.	44
Acid, Sulphuric	Acidum Sulphuricum	H_2SO_4	Pb, Cu, As, Fe, NH_4. Cl', NO_2', NO_3', SO_3''.	42 and 43
Acid, Sulphurous	Acidum Sulphurosum	H_2SO_3	SO_4''.	42
Alum	Alumen	$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$	Cu, Pb, Zn, Ca, Na, Fe.	80
Ammonium Hydroxide (Ammonia solution)	Ammonia	NH_3	As, Pb, Fe, Al, Zn, Ca, Mg, K, Na. CO_3'', SO_4'', S'', Cl'.	30
Ammonium Bromide	Ammonii Bromidum	NH_4Br	Pb, Fe. BrO_3', I, NO_3', SO_4'', Cl'.	69
Ammonium Carbonate	Ammonii Carbonas	NH_4HCO_3 and $NH_4(NH_2)CO_2$	Cl', SO_4''.	75
Ammonium Chloride	Ammonii Chloridum	NH_4Cl	Pb, Cu, As, Ca, Fe. CO_3'', NO_3', SO_4'', CNS'.	67
Ammonium Phosphate	Ammonii Phosphas	$(NH_4)_2HPO_4$	Pb, Cu, As, Fe. Cl', SO_4''.	79
Antimonious Oxide	Antimonii Oxidum	Sb_2A_3	Pb, Cu, As, Ca, Na, K, Fe. Cl', SO_4''.	84
Antimonious Sulphide	Antimonium Nigrum (Purificatum)	Sb_2S_3	As.	86

Name.	Latin Name in Pharmacopœia	Formula.	Impurities which may be present stated as Ions. See p. 103.	Page in book where preparation is described.
Antimony, Sulphurated	Antimonium Sulphuratum	$Sb_2S_5Sb_2S_3$ $Sb_2O_5Sb_2O_3$	As.	
Arsenious Iodide	Arsenii Iodidum	AsI_3		
B.				
Bismuth Oxycarbonate	Bismuthi Carbonas	$(Bi_2O_2CO_3)_2H_2O$	Ag, Pb, Cu, As, Fe, Zn, Ca, Mg. Cl', SO_4'', NO_3'.	80
Bismuth Oxide	Bismuthi Oxidum	Bi_2O_3		82
Bismuth Oxynitrate	Bismuthi Subnitras	$Bi(OH)_2 . NO_3$ or $BiO . NO_3H_2O$	Ca. CO_3'', PO_4'''.	79
Borax	Borax	$Na_2B_4O_7 . 10H_2O$		74
C.				
Calcium Carbonate precipitated and Prepared chalk	Calcii Carbonas Precipitatus Creta preparata	$CaCO_3$	Fe, Al, Mg, Ba. PO_4''', SO_4'', Cl'.	75
Calcium Chloride	Calcii Chloridum	$CaCl_2 . 2H_2O$	Fe, Al, Mg. CO_3'', OCl'.	67
Calcium Hydroxide	Calcii Hydras	$Ca(OH)_2$	Fe, Al, Mg, Na, K. CO_3'', Cl', PO_4''', SO_4'', SiO_2.	83
Calcium Hypophosphite	Calcii Hypophosphis	$Ca(H_2PO_2)_2$	Pb, Cu, As, Fe, Al, Mg, Na, K. Cl', SO_4'', PO_4''', PO_3'''.	95
Calcium Phosphate	Calcii Phosphas	$Ca_3(PO_4)_2$	Pb, Cu, As, Fe, Al, Mg. CO_3'', Cl', SiO_2.	76
Calcium Oxide (Quicklime)	Calx	CaO	Fe, Al, Mg, Na, K. CO_3'', Cl', PO_4''', SO_4'', SiO_2.	83
Bleachingpowder (Chlorinated lime)	Calx Chlorinata	$CaOCl_2$		90
Sulphurated lime	Calx Sulphurata	$CaS . CaSO_4 . C$		
Carbon Disulphide	Carbonis Bisulphidum	CS_2	SO_4''.	
Copper Sulphate	Cupri Sulphas	$CuSO_4 . 5H_2O$	Pb, As, Zn, Al, Fe.	72
F.				
Ferric Chloride	Ferri Perchloridum	$FeCl_3$	Pb, Cu, As, Zn, Ca, Na, K, NH_4, $(Fe^{\cdot\cdot})$. NO_3'.	89
Ferric Nitrate	Ferri Pernitras	$Fe(NO_3)_3$	Pb, Cu, As, Zn, Ca, Na, K, NH_4, $(Fe^{\cdot\cdot})$. Cl', SO_4''.	65
Ferric Sulphate	Ferri Persulphas	$Fe_2(SO_4)_3$	$(Fe^{\cdot\cdot})$, i. e. Ferrous Salts.	73
Ferrous Arsenate	Ferri Arsenas	$Fe_3(AsO_4)_2 . 6H_2O$	SO_4''.	76

Name.	Latin Name in Pharmacopœia	Formula.	Impurities which may be present stated as Ions. See p. 103.	Page in book where preparation is described.
Ferrous Phosphate	Ferri Phosphas	$Fe_3(PO_4)_2 8H_2O$	As.	76
Ferrous Sulphate	Ferri Sulphas	$FeSO_4 . 7H_2O$	Cu. Zn, K, Na, NH_4, $(Fe^{\cdots})$.	73
Iron	Ferrum	Fe		
Reduced iron	Ferrum redactum	Fe	Fe_2O_3.	
H.				
Hydrogen Peroxide solution	Liquor Hydrogenii Peroxidi	H_2O_2	Ba.	52
I.				
Iodine	Iodum	I_2	(H_2O, Br_2).	37
Iron and its compounds. See **F**, ferrous and ferric.				
L.				
Lead Carbonate	Plumbi Carbonas	$(PbCO_3)_2 . Pb(OH)_2$	Zn, Ca, Mg.	80
Lead Iodide	Plumbi Iodidum	PbI_2	NO_3'. Acetates.	70
Lead Oxide	Plumbi Oxidum	PbO	Cu, Fe. CO_3''.	82
Lead Acetate	Plumbi Acetas	$Pb(C_2H_3O_2)_2 3H_2O$		76
Lithium Carbonate	Lithii Carbonas	Li_2CO_3	Pb, Cu, As, Fe, Al, Zn, Mg, Na, K, NH_4, Ca. Cl', SO_4''.	
M.				
Magnesia, light calcined	Magnesia levis	MgO	Fe, Al, Ca. CO_3'', Cl', SO_4''.	82
Magnesia, heavy calcined	Magnesia ponderosa	MgO		
Magnesium Carbonate, light	Magnesii Carbonas levis	$(MgCO_3)_3 . Mg(OH)_2 4H_2O$	Fe, Al, Ca. Cl', SO_4''.	75
Magnesium Carbonate, heavy	Magnesii Carbonas ponderosa	do		
Magnesium Bicarbonate (Fluid Magnesia)	Liquor Magnesii Carbonatis	$Mg(HCO_3)_2$		78
Magnesium Sulphate (Epsom Salt)	Magnesii Sulphas	$MgSO_4 . 7H_2O$	Fe, Al, Zn, Ca, Na, K, NH_4. NO_3', Cl'.	73
Mercury	Hydrargyrum	Hg		
Mercury, Ammoniated (White precipitate)	Hydrargyrum Ammoniatum	NH_2HgCl		
Mercuric Chloride	Hydrargyri Perchloridum	$HgCl_2$	(HgCl).	68
Mercurous Chloride	Hydrargyri Subchloridum	HgCl	$(HgCl_2)$.	69
Mercuric Iodide	Hydrargyri Iodidum rubrum	HgI_2		71

Name.	Latin Name in Pharmacopœi	Formula.	Impurities which may be present stated as Ions. See p. 103.	Page in book where preparation is described.
Mercuric Nitrate	Hydrargyri Nitras	$Hg(NO_3)_2$	$(Hg^{\cdot})$, i. e. Mercurous Compounds.	66
Mercuric Oxide (yellow)	Hydrargyri Oxidum flavum	HgO		82
Mercuric Oxide (red)	Hydrargyri Oxidum rubrum			83
P.				
Phosphorus	Phosphorus	P	As. SO_4''.	
Potassium Hydroxide (Caustic potash)	Potassa Caustica	KOH	Pb, Cu, As.	85
Potash, Sulphurated (Liver of Sulphur)	Potassa Sulphurata	$K_2S . K_2S_2$, &c.		
Potassium Bicarbonate	Potassii Bicarbonas	$KHCO_3$	Pb, Cu, As, Al, Ca, Mg, Na, Fe. NO_3', SO_4'', S'', Cl'.	75
Potassium Bichromate (better Dichromate)	Potassii Bichromas	$K_2Cr_2O_7$	SO_4'', Cl'.	93
Potassium Bromide	Potassii Bromidum	KBr	Pb, Cu, As, Fe, Al, Zn, Ca, Mg, Na, NH_4. BrO_3', IO_3', CN', Cl', I', SO_4'', CNS'.	69
Potassium Carbonate	Potassii Carbonas	K_2CO_3	Pb, Cu, Al, Ca, Mg, Na, Fe. CN', NO_3', SO_4'', S'', S_2O_3'', Cl'.	75
Potassium Chlorate	Potassii Chloras	$KClO_3$	Pb, Fe, Al, Ca, Mg, Na. NO_3', Cl', SO_4''.	91
Potassium Iodide	Potassii Iodidum	KI	Pb, Cu, As, Fe, Al, Ca, Mg, Na, NH_4. BrO_3', IO_3', CN', NO_3', Br', Cl', SO_4'', CO_3''.	70
Potassium Nitrate	Potassii Nitras	KNO_3	Pb, Cu, As, Fe, Al, Zn, Ca, Mg, Na, NH_4. Cl', I', SO_4''.	63 and 56
Potassium Permanganate	Potassii Permanganas	$KMnO_4$	Pb, As, Fe, Al, Ca, Mg, Na, NH_4. CO_3'', Cl', SO_4''.	94
Potassium Sulphate	Potassii Sulphas	K_2SO_4	Pb, Cu, As, Fe, Al, Zn, Ca, Mg, Na, NH_4. NO_3', Cl'.	72
S.				
Silver Nitrate (Lunar Caustic)	Argenti Nitras	$AgNO_3$	Pb, Cu, Fe, Na, K. SO_4''.	66
Silver Oxide	Argenti Oxidum	Ag_2O	Pb, Cu, Fe.	82
Sodium	Sodium	Na		

Name.	Latin Name in Pharmacopœia	Formula.	Impurities which may be present stated as Ions. See p. 103.	Page in book where preparation is described.
Sodium Arsenate	Sodii Arsenas	$Na_2HAsO_4 . 12H_2O$	Pb, Cu, Fe, Al, Ca, Mg, K, NH_4. CO_3'', Cl', NO_3', SO_4''.	79
Sodium Bicarbonate	Sodii Bicarbonas	$NaHCO_3$	Pb, Cu, Fe, Al, Ca, Mg, K, NH_4. SO_3'', SO_4'', Cl', S_2O_3'', CNS'.	74
Sodium Bromide	Sodii Bromidum	$NaBr$	Pb, Cu, As, Fe, Al, Zn, Ca, Mg, K, NH_4. CO_3'', CN', BrO_3', IO_3', Cl', I', SO_4'', CNS'.	70
Sodium Carbonate	Sodii Carbonas	Na_2CO_3		75
Sodium Chloride	Sodii Chloridum	$NaCl$	K, Ca, Mg. Br', I', SO_4''.	66
Sodium Hypophosphite	Sodii Hypophosphis	NaH_2PO_2	Pb, Cu, Fe, Al, Zn, Ca, Mg, K, NH_4. Cl', SO_4'', CO_3'', PO_4''', PO_3'''.	96
Sodium Iodide	Sodii Iodidum	NaI	Pb, Cu, As, Fe, Al, Ca, Mg, K, NH_4. BrO_3', CN', CO_3'', IO_3', Br', Cl', SO_4''.	70
Sodium Nitrite	Sodii Nitris	$NaNO_2$	Pb.	95
Sodium Phosphate	Sodii Phosphas	$Na_2HPO_4 . 12H_2O$	K, NH_4. CO_3'', SO_4'', Cl'.	78
Sodium Sulphate	Sodii Sulphas	$Na_2SO_4 . 10H_2O$	Pb, Fe, Al, Ca, Mg, K, NH_4. CO_3'', Cl'.	72
Sodium Sulphite	Sodii Sulphis	$Na_2SO_3 . 7H_2O$	S_2O_3''.	74
Sulphur	Sulphur Praecipitatum Sulphur Sublimatum	S	As_2S_3. SO_4''.	
Sulphur Iodide	Sulphuris Iodidum	S_2I_2		48
Z.				
Zinc Carbonate	Zinci Carbonas	$ZnCO_3$	Pb, Cu, Cd, As, Fe, Al, Ca, Mg, K, Na, NH_4. Cl', SO_4''.	75
Zinc Chloride	Zinci Chloridum	$ZnCl_2$	Pb, Cu, Cd, As, Fe, Al, Mg, Na, K, NH_4. SO_4''.	67
Zinc Oxide	Zinci Oxidum	ZnO	Pb, Cu, Cd, As. Fe. Al, Ca, Mg, Na, K, NH_4 CO_3'', Cl', SO_4''.	82
Zinc Sulphate	Zinci Sulphas	$ZnSO_4 . 7H_2O$	Pb, Cu, Cd, As, Al, Ca, Mg, Na, K, NH_4, Fe. Cl'. Acetates.	73

PART IV

TESTS FOR ELECTRO-POSITIVE RADICLES

A. Dry Tests for the Metals.

B. Wet Tests for the Metals.

C. Complete Summary of both Wet and Dry Tests for the Metals.

Detection of the Metals—the Electro-positive Radicles or Kations.

The metals are frequently termed **electro-positive radicles** or **kations**, and the **acid radicles** (e.g. NO_3, SO_4, Cl), **electro-negative radicles** or **anions**. These terms may be explained by the following considerations.

If one passes an electric current through solutions of (*a*) silver nitrate, (*b*) copper sulphate, using say a few cells to supply the current and strips of platinum as electrodes, **metal is set free** at the **kathode**—the electrode at which the current leaves the electrolytic cell—and **oxygen** at the **anode**—the electrode at which the current enters the cell. These facts are best explained by the **Ionization Hypothesis. This hypothesis assumes that all acids, bases, and metallic salts in solution in water are dissociated**[*] **more or less completely into small particles carrying electrical charges called ions.** These ions may be single atoms or groups of atoms; e.g. copper sulphate in dilute solution in water consists chiefly of ions of copper with positive charges of electricity, and sulphion ions (SO_4) with negative charges of electricity.

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[*] The distinction between dissociation and ordinary decomposition should be noted. Dissociation is a term applied to the splitting up of a body into radicles which recombine readily under ordinary conditions, whereas in true decomposition this recombination does not occur. Electrolytic and Thermal Dissociation are met with.

On placing such solutions in an electrical circuit using suitable electrodes, since **Like charges of electricity repel and Unlike charges attract**, the **negatively charged ions** will move over to the electrode connected with the positive pole of the battery (the **anode**), and the **positively charged ions** will move over to the electrode connected with the negative pole of the battery (the **kathode**). In the case of copper sulphate the sulphion ion being the negatively charged ion will be set free at the anode, and the positively charged copper ion moves to the kathode. The sulphion ion, on reaching the anode and giving up its charge, reacts with water, forming oxygen and sulphuric acid, while the copper ions stick to the kathode, forming a deposit of metallic copper. What takes place in each case might be represented by two equations:—

Anode **Kathode**

I. (*a*) $\overset{+}{Ag} + \overset{-}{NO_3} = \overset{-}{NO_3} \quad + \quad \overset{+}{Ag}.$

(*b*) $2NO_3 + H_2O = O \quad + 2HNO_3.$

The NO_3 ion (which is unknown in the free state) reacts with water to give oxygen, which comes off as gas and HNO_3, which remains in solution round the anode.

Anode **Kathode**

II. (*a*) $\overset{++}{Cu} + \overset{--}{SO_4} = \overset{--}{SO_4} \quad + \quad \overset{++}{Cu}$

(Note:—The divalent ions are represented as having double the electrical charges of the monovalent ions.)

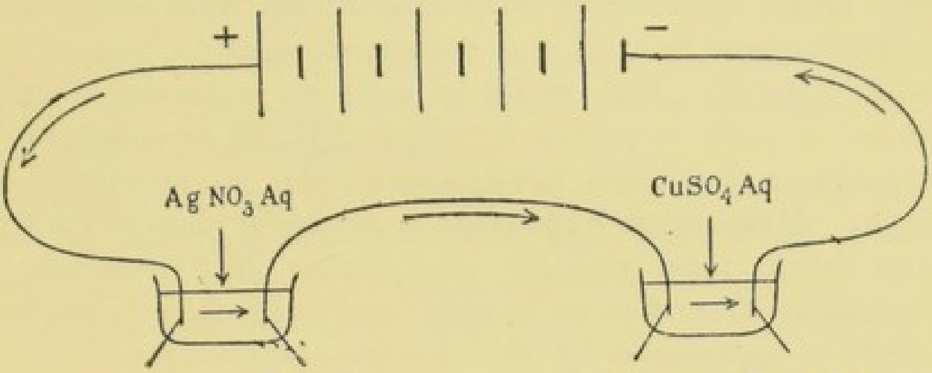
(*b*) $SO_4 + H_2O = O + H_2SO_4.$

The SO_4 ion is unknown in the free state. On giving up its electrical charge it reacts with water to give oxygen and sulphuric acid.

The metals in solutions of salts always move to the kathode and the acid radicles to the anode. In the case of acids, hydrogen moves to the kathode and acid radicles move to the anode, and in the case of soluble bases, metals to the kathode and hydroxyl ions to the anode. One might therefore say that **hydrogen and the metals are electro-positive radicles or kations**, and **oxygen, chlorine, acid radicles** (i.e. acid-less hydrogen), e.g. NO_3, SO_4,

$Fe(CN)_6$, **and hydroxyl OH are electro-negative radicles or anions.**

The following diagram summarizes what has been stated above.



	Anode	Kathode	Anode	Kathode
Subs. first set free.	$2NO_3$	2Ag	SO_4	Cu
Subs. ultimately set free.	O	2Ag	O	Cu

Fig. 21. Ions liberated on Electrolysis.

The above facts must be clearly grasped before the lists of tests given in the following pages are properly understood. The interactions are as a rule **ion reactions.** The precipitates formed are un-ionized bodies insoluble under the given conditions. A few examples may make the relationships clear.

1. If one adds **silver nitrate solution to potassium chloride,** a white precipitate of un-ionized silver chloride is formed, the reaction being most conveniently represented by the equation :

$$KClAq + AgNO_3Aq = \mathbf{AgCl} + KNO_3Aq.$$

Written from the ionic point of view :

$$\overset{+}{K} + \overset{-}{Cl} + \overset{+}{Ag} + \overset{-}{NO_3} = \mathbf{AgCl} + \overset{+}{K} + \overset{-}{NO_3}.$$

Other soluble chlorides, e.g. NaCl, $CaCl_2$, $BaCl_2$, would react in a similar manner, and one might suppose that any metallic compound containing chlorine would behave in the same way. This is not the case. **$AgNO_3Aq$ is a reagent for the ion chlorine,** and gives no reactions with bodies like potassium chlorate ($KClO_3$), where the chlorine forms part of a complex radicle. If one attempts to write an equation in this case the two sides would be identical.

$$(\overset{+}{K} + \overset{-}{ClO_3} + \overset{+}{Ag} + \overset{-}{NO_3} = \overset{+}{K} + \overset{-}{ClO_3} + \overset{+}{Ag} + \overset{-}{NO_3}).$$

Silver chlorate is soluble in water, and therefore ionized, and no precipitate forms.

2. **Ferrous and ferric salts give a precipitate of ferrous and ferric hydroxides with ammonium hydroxide,** and one might suppose that all iron compounds should give a precipitate with NH_4OH. This would be quite an erroneous assumption, as could easily be proved by adding NH_4OH to potassium ferrocyanide or potassium ferricyanide, when no precipitate would form. **Ammonium hydroxide is merely a reagent for ferrous and ferric ions,** and the precipitation of ferrous and ferric hydroxides from ferrous sulphate and ferric chloride respectively might be represented by the following equations:—

(a) Precipitation of Ferrous Salts.

Ordinary equation:

$$FeSO_4Aq + 2NH_4OHAq = \mathbf{Fe(OH)_2} + (NH_4)_2SO_4Aq.$$

Ionic equation:

$$\overset{++}{Fe} + \overset{--}{SO_4} + \overset{++}{2NH_4} + \overset{--}{2(OH)} = \mathbf{Fe(OH)_2} + \overset{++}{2NH_4} + \overset{--}{SO_4}.$$

(b) Precipitation of Ferric Salts.

Ordinary equation:

$$FeCl_3Aq + 3NH_4OHAq = \mathbf{Fe(OH)_3} + 3NH_4ClAq.$$

Ionic equation:

$$\overset{+++}{Fe} + \overset{---}{3Cl} + \overset{+++}{3NH_4} + \overset{---}{3(OH)} = \mathbf{Fe(OH)_3} + \overset{3+}{3NH_4} + \overset{3-}{3Cl}.$$

With NH_4OH and potassium ferrocyanide nothing occurs:

$$\overset{+}{NH_4} + \overset{-}{OH} + \overset{4+}{4K} + \overset{4-}{Fe(CN)_6} = \overset{+}{NH_4} + \overset{-}{OH} + \overset{4+}{4K} + \overset{4-}{Fe(CN)_6}.$$

[It might be pointed out that many peculiar phenomena difficult to understand otherwise are readily explained by the ionic theory. For example, potassium cyanide in solution is strongly alkaline in reaction. This follows because the body reacts with water to give un-ionized hydrocyanic acid and ionized potassium hydroxide.

$$\overset{+}{K} + \overset{-}{CN} + \overset{+}{H}{}^{*} + \overset{-}{OH}{}^{*} = HCN + \overset{+}{K} + \overset{-}{OH}$$

Free hydroxyl ions are present in quantity, and therefore the body is alkaline in reaction, as free hydroxyl ions cause alkalinity.

---

* Water is only very slightly ionized into H and OH.

Similarly, certain normal salts in solution (e.g. $CuSO_4$, $ZnSO_4$, $Al_2(SO_4)_3$) have an acid reaction, because of presence of free hydrogen ions which cause acidity.

Many other phenomena, e.g. abnormal depression of freezing-point and abnormal raising of boiling-point, can also be explained.]

Throughout this book ordinary equations are used, as ionic equations are unnecessarily complicated. The above explanations should, however, be kept in view.

In representing ions, the valency of metals is frequently represented by dots, and the valency of acid radicles by dashes:
e.g. (*a*) Metals :—$Ag^{\cdot}$; $Cu^{\cdot\cdot}$; $Fe^{\cdot\cdot\cdot}$;
(*b*) Acid radicles :—NO_3'; SO_4''; PO_4'''.

A. DRY TESTS FOR THE METALS.

The dry tests often afford a ready means for identification of a metal, and are particularly useful when the substance is soluble with difficulty.

The more **important dry tests** comprise :—

(1) Reduction of metals on charcoal.

(2) (*a*) Coloured residues obtained on ignition of filter paper saturated with the metallic salt and cobalt nitrate.

(*b*) Coloured masses on charcoal.

(3) Coloured incrustations around the heated area.

(4) Borax bead tests.

(5) Platinum wire tests—flame tests.

For all these tests a reducing or oxidizing flame is required. A reducing flame is one containing white-hot carbon, and is therefore generally luminous, while an oxidizing flame contains excess of oxygen, and is usually non-luminous.

The **Bunsen flame** is the most convenient for general use. When the holes for admitting air at the base of the tube are open the Bunsen flame has three zones:—

(*a*) A central zone of unburnt gas mixed with air reaching a short distance above the top of the tube.

[(*b*) A shallow zone of bluish colour round the inner zone, sometimes very thin except close to base of flame. Partial combustion of the carbon to carbon monoxide takes place here and hydrogen is present, so that the zone would have reducing action. From our point of view this zone need hardly be considered.]

(*c*) A zone of complete combustion surrounding the other zones and usually reaching to about double the height. To prove these statements as regards zones (*a*) and (*c*), after lighting the gas depress a piece of wire gauze until it is about an inch from the mouth of the tube. Note that the wire seems unaltered in the centre of the flame, but becomes red hot in the surrounding zone of complete combustion. The three zones are shown in the accompanying diagram, Fig. 22 (A).

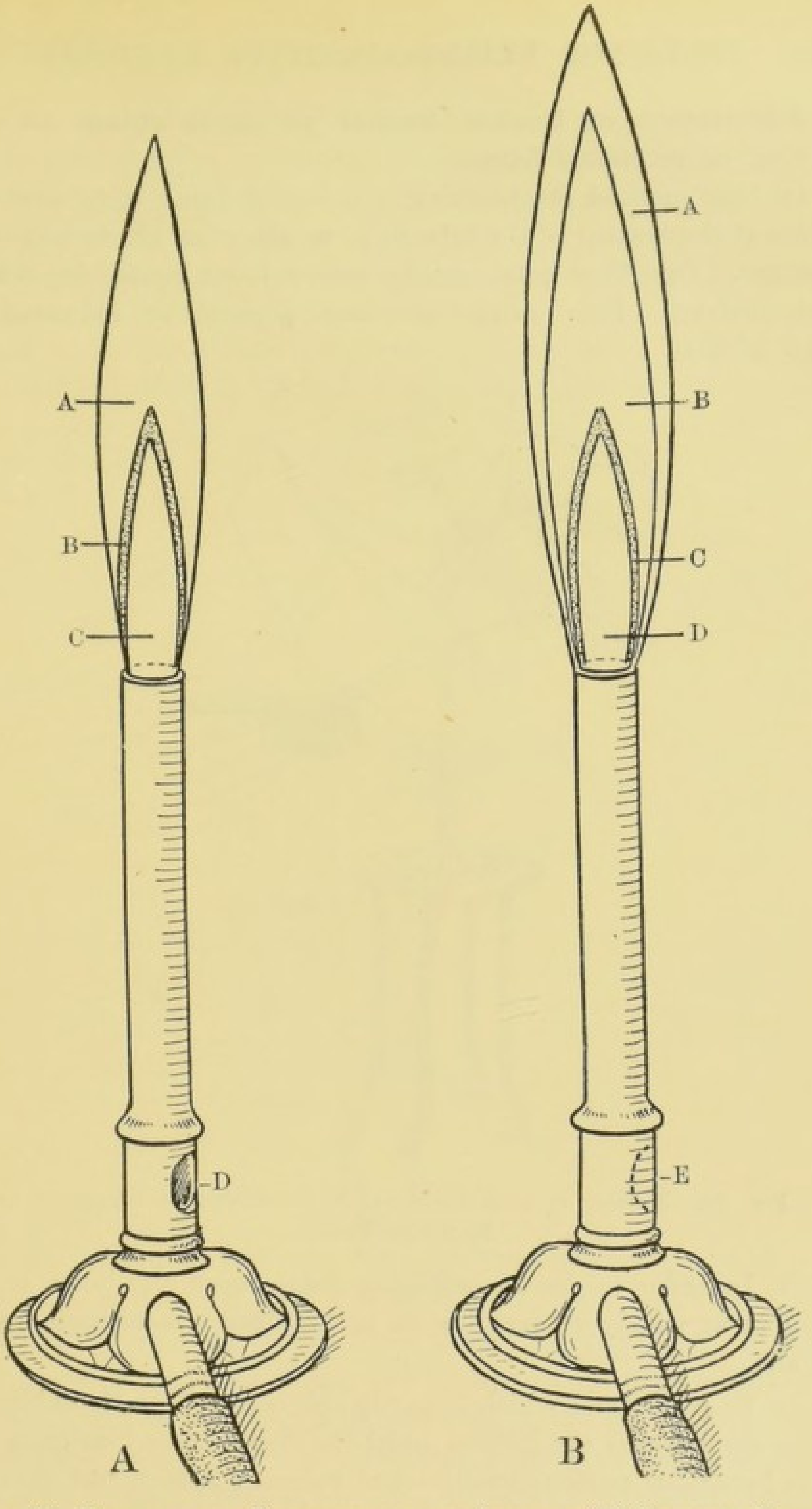


Fig. 22. Diagrammatic Representation of Zones of (A) Oxidizing Flame, (B) Reducing Flame. A, a, Zone of complete Combustion (Oxidizing); b, Bluish Zone; c, Inner Zone of unburnt Gas admixed with Air; d, Air Entrance. B, a, Zone of complete Combustion (Oxidizing); b, Yellowish Zone containing white-hot Carbon (reducing); c, Bluish Zone; d, Inner Zone of unburnt Gases; e, Opening closed.

Adjustment of Bunsen burner so as to obtain an oxidizing or reducing flame.

(*a*) One method of obtaining a reducing flame is to shut the holes at the bottom of the tube so as to allow no air to mix with the gas. One then gets a smoky yellow flame containing white-hot carbon. Four zones are here present as indicated in Fig. 22 (B).

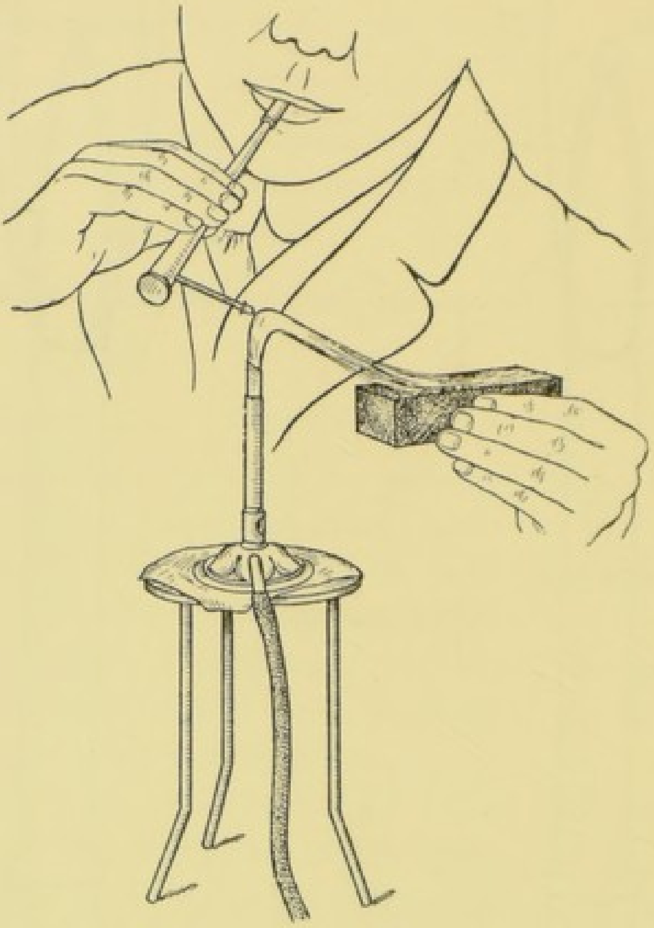


FIG. 23. METHOD OF HEATING METALLIC SUBSTANCE ON CHARCOAL IN REDUCING FLAME.

(*b*) In order to get an oxidizing flame, open the holes at the bottom as widely as possible so as to admit a maximum supply of air.

(*c*) To get a flame which is partly reducing and partly oxidizing, close the holes at the bottom until the flame has a luminous tip. The luminous portion would exert reducing action, but above it and at the sides of the flame there would be oxidizing zones.

(*d*) **Suitable flame for Reduction of Metals.**

Instead of using the Bunsen flame direct, it is more convenient to adapt the flame by means of a mouth blowpipe for the isolation of metals and for obtaining coloured masses and incrustations. The mouth blowpipe generally consists of a hollow conical tube open at the apex for blowing, and with a nozzle near the base. Close the holes at the bottom of the Bunsen burner so as to get a luminous flame, and then put a metal tube ending in a slit making an angle of about 50° with the horizontal, into the Bunsen tube so as to get a flame convenient to regulate. Adjust the flame until it is $2\frac{1}{2}$ to $3\frac{1}{2}$ inches high, and then put the tip of the mouth blowpipe about an inch above the upper end of the slit and just outside the flame and blow gently. The luminous reducing flame can be blown downwards in any given direction, as indicated in Fig. 23. The blowing should be done entirely from the cheeks, which should be kept inflated, breathing being carried on through the nostrils. With a little practice it will be found that one can blow steadily for 5 to 10 minutes without stopping.

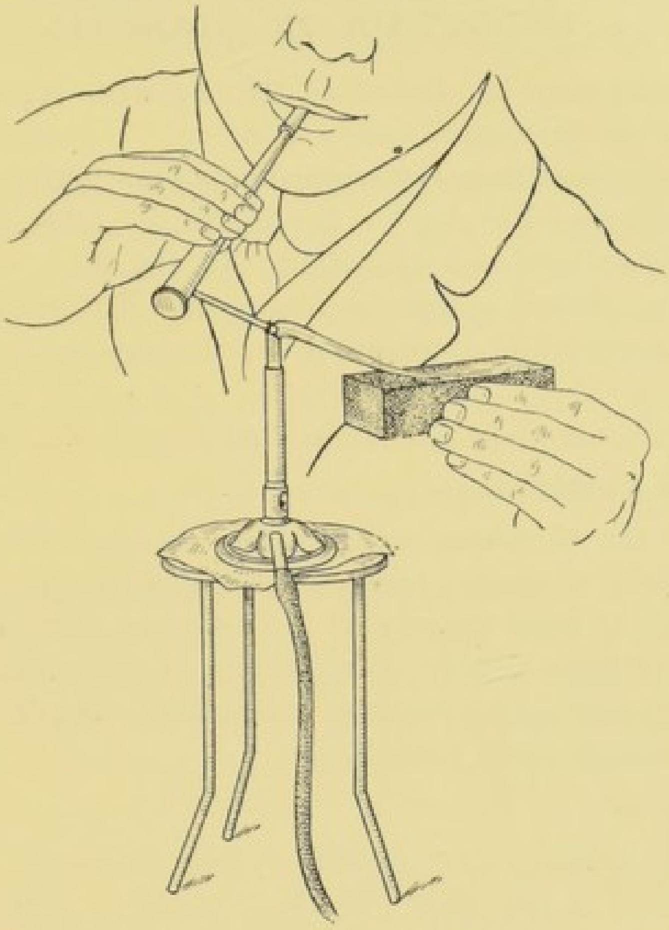


Fig. 24. Method of heating a Metallic Compound on Charcoal in Oxidizing Flame.

(*e*) If an oxidizing flame is wanted, such as gives best results when trying for coloured masses or incrustations, put the nozzle of the blowpipe into the flame, adapted as described above, and blow fairly strongly. A very hot non-luminous, strongly oxidizing flame is obtained. The proper method is indicated in Fig. 24. In Chemistry, 'Reduction' is a term applied to a general type of reaction, which here means removal of oxygen and other electronegative elements or groups, to set free the metal.

1. REDUCTION ON CHARCOAL.

The Metals may be classed as follows with regard to their reducibility on charcoal:—

(1) Metals reduced from their compounds, some giving beads under proper conditions: Pb, Ag, Cu, Bi, Sb, Sn, Fe, (Mn), (Cr), Ni, Co.

(2) Metals reduced and volatilized: As, Hg, (Sb).

Arsenic is oxidized to arsenious oxide on volatilization.

Note.—Ammonium compounds are decomposed or volatilized on heating.

(3) Metals not reduced on charcoal: Al, Zn, Cd, Mg, Ca, Ba, Na, K.

Mode of Procedure:—

Heat up the substance either alone or admixed with about twice its bulk of fusion mixture on a small hollow scraped in block carbon or wood charcoal in the reducing flame as indicated in Fig. 23. Fusion mixture is a mixture of anhydrous powdered sodium carbonate and potassium carbonate. If not obtainable, sodium carbonate alone will do.

Results:—

(1) **Lead Compounds readily yield Metallic Lead.** No fusion mixture is required. The bead tends to get covered with a yellowish film of oxide as it cools. When the cold bead is examined, it is found to be very malleable and to mark paper.

(2) **Silver** compounds give silver first as a film and then as a brilliant silvery bead. Fusion mixture assists the reaction, but is not absolutely necessary.

(3) **Copper.** In reducing copper compounds mix the powdered substance with fusion mixture and a small quantity of potassium cyanide. [Caution.—Potassium cyanide is a very poisonous compound.] Red scales are obtained after heating for some time.

(4) **Bismuth** compounds reduce fairly readily. A brittle bead is obtained.

(5) **Antimony** compounds generally give a brittle bead. On heating the reduced metal it volatilizes, and is oxidized by the oxygen of the air as it passes through the flame, giving a white fume of antimonious oxide which may partly condense on the charcoal outside the heated area.

(6) **Tin** compounds usually reduce with difficulty. Mix the powdered substance with fusion mixture (or borax) and potassium cyanide. A white silvery bead is obtained.

(7) **Iron** compounds usually yield a magnetic residue which can be tested by a magnetized knife-blade. Nickel and cobalt are feebly magnetic.

II. Reduction in Bulb Tube.

Take a small quantity of dry powdered substance, mix with powdered carbon and a small quantity of fusion mixture, and introduce into a small tube of hard glass, which should preferably be expanded into a small bulb at the closed end. Heat the mixture cautiously.

Arsenic compounds (with a few exceptions, e. g. As_2S_3) give a greyish mirror of arsenic.

NOTE.—If a small quantity of potassium cyanide is added to the above reaction mixture, *all* arsenic compounds will be reduced.

Antimony compounds give a similar mirror of antimony.

Mercury compounds give a metallic film of mercury. This test for mercury is unimportant as the wet tests for that element are so characteristic, but for arsenic and antimony it is valuable. The films of arsenic and antimony can be readily distinguished from each other by making a file mark at the base of the mirror, breaking off the tube, and heating up the mirror with bleaching powder solution in a test-tube. The arsenic film dissolves, while that of antimony remains nearly unaffected.

2. COLOURED MASSES.

The preparation of coloured masses affords convenient confirmatory tests for zinc, tin, magnesium, and aluminium.

a. **If the substance is a solution or soluble in water**, or is readily soluble in acid, proceed as follows:—

Pour about 1 c.c. of a concentrated solution of the substance on to say half a filter paper, so as to thoroughly wet a few square centimetres, then pour about the same quantity of cobalt nitrate solution on to the moistened portion of the paper. Incinerate by holding with tongs in the ordinary Bunsen flame (i. e. oxidizing flame). The following coloured residues are obtained :—

Zinc compounds give a light green residue.

Tin compounds (sometimes with difficulty) give a dark green residue.

Magnesium compounds give a light pink residue.

Aluminium compounds give a bright blue residue.

Precaution.—In connexion with this residue from aluminium compounds it must be observed that phosphates, arsenates, and borates may give a similar blue mass. The blue residue from a pure aluminium compound is infusible, while the others can be fused.

b. If the substance is not readily soluble, proceed as follows :—

Heat a small quantity of the substance in a shallow hollow on charcoal by the oxidizing blowpipe flame. If the residue is white, moisten with cobalt nitrate and reheat. Coloured masses similar to the residues obtained above will be formed.

3. COLOURED INCRUSTATIONS AROUND THE HEATED AREA.

Certain metals give characteristic incrustations around the heated area. These are not of primary importance, but they sometimes give a valuable hint, and are therefore worth mentioning.

(*a*) Yellow when hot, white when cold indicates **Zinc.**

(*b*) Orange when hot, light yellow when cold indicates **Bismuth.**

(*c*) Yellow, both hot and cold, indicates **Lead.**

(*d*) White fumes with garlic odour indicate **Arsenic.**

(*e*) Brown, both hot and cold, indicates **Cadmium.**

The compounds of **Antimony**, **Ammonium**, and **Mercury** may give fumes.

4. BORAX BEAD TESTS are often useful.

Preparation of a Borax bead. Make an oval loop, about 2 millimetres in length and 1 millimetre in breadth, at the end of a small piece of platinum wire, which should preferably be fused into the end of a glass rod about 4 inches long. Heat the loop and dip it into powdered borax ($Na_2B_4O_7 . 10H_2O$), some of which will adhere to the wire. Remove the wire and heat in the oxidizing flame. The mass at first froths up, owing to the disengagement of water of crystallization, and finally gives a clear glassy bead. Take a very minute trace of the powdered substance on to the bead by bringing the heated borax carefully into contact with the powder, and heat strongly in the oxidizing flame. It is not necessary to use a blowpipe, but it saves time to do so. In many cases the reducing flame would yield different products, but it is hardly necessary to use it.

Copper compounds give blue bead in oxidizing flame (and reddish in reducing flame).

Iron compounds give yellowish-brown bead in oxidizing flame (and bottle-green bead in reducing flame).

Chromium compounds give a green bead.

Manganese compounds give an amethyst coloured, i.e. light violet, bead.

Cobalt compounds give a deep blue bead, and Nickel compounds give a brownish bead.

To get rid of a bead, heat and dip into water; the bead will break into pieces and can be readily removed. If the bead is too dark it can be brought to a convenient tint by heating, taking up more borax, fusing, shaking off a portion and repeating the process if necessary.

5. PLATINUM WIRE TESTS.

These form admirable confirmatory tests, and are easily carried out. A trace of substance is taken on the tip of a platinum wire provided with a glass handle, and carefully introduced near the base of the edge of the flame. The colours depend upon the formation of vapour of metal in the flame zone, and therefore the substance must be volatile at the temperature of the flame. If non-volatile no colour results; e.g. pure copper oxide gives no colour to a Bunsen flame, but if moistened with hydrochloric acid and then introduced the flame is tinted a brilliant green to blue tint, because copper chloride is formed by interaction of the copper oxide and hydrochloric acid, and all chlorides are volatilized in the Bunsen flame.

Method. Moisten a small quantity of the solid substance on a watch-glass or in a small dish with concentrated hydrochloric acid. On dipping the tip of a platinum wire into the mixture a small quantity will adhere. Introduce at the base of the flame, and note the colour produced.

Bright green or blue flame indicates **Copper.**

Light green (apple-green) flame indicates **Barium.**

Brick-red flame indicates **Calcium.**

(Crimson flame indicates **Strontium** or **Lithium.**)

Violet flame indicates **Potassium.**

Intense yellow flame indicates **Sodium.**

Notes.—(1) **A Blue flame,** which must not be confused with the violet potassium flame, is given by **Lead, Bismuth, Arsenic,** and **Antimony.** These substances **corrode the platinum wire,** so that if they are suspected one is very careful in carrying out the platinum wire test, and should desist at once on noticing the blue flame, otherwise the end of the platinum wire is rendered brittle and breaks off.

(2) The wire should be cleaned between each test. To effect this, dip the wire repeatedly into concentrated hydrochloric acid, and then into the flame until no tint is given. Barium is particularly difficult to remove completely from a wire, especially if the heating with the barium salt has been prolonged.

(3) **In order to clean the wire thoroughly after each day's work** it is a good plan to have the free end of the glass rod fixed into a cork, which fits a test-tube containing a few c.c. of concentrated hydrochloric acid. The position of the wire should be so adjusted that on corking the test-tube, the end of the wire dips into the acid.

B. WET TESTS FOR THE METALS.

Preliminary Note.—The wet tests for the metals generally depend upon the precipitation of compounds, often of characteristic appearance, under definite conditions.

The student should understand at the outset that the reason for the formation of the numerous precipitates is simply that the bodies thrown down can be formed under the conditions of the experiment, and being insoluble under these circumstances are precipitated. He should recognize that if the conditions were altered, e. g. if in a particular case the solution was rendered strongly acid or alkaline before addition of the reagent, no precipitate might form.

It is very important also that he should grasp the fact that the List of Reactions given under each metal affords information regarding many of the chief compounds of the metal, and is therefore important from both practical and theoretical points of view. Indeed, **a thorough knowledge of the reactions detailed below and the reasons for precipitation in each case should help a student greatly with his theoretical work.**

In carrying out wet tests for identification of metals, they are conveniently divided into six groups, depending upon their behaviour towards certain compounds called **Group Reagents.**

Group I. Silver group: includes **Ag, Hg^{ous}, Pb.**

,, **II.** { **II** *a*. **Copper group:** includes **Cu, Bi, Hg^{ic}, (Pb), Cd.**
{ **II** *b*. **Arsenic Subgroup:** includes **As, Sb, Sn^{ous}, Sn^{ic}.**

,, **III. Aluminium Group:** includes **Al, Cr, Fe^{ous}, Fe^{ic}.**

,, **IV. Zinc group:** includes **Zn, Mn, Ni, Co.**

,, **V. Calcium group:** includes **Ba, Sr, Ca.**

,, **VI. This is a heterogeneous group: Mg, NH_4, K, Na.**

The reason for the above arrangement into groups will be fully considered on p. 173, after the reactions of the metals have been summarized. In carrying out the following reactions a student should take 1–2 c.c. of solution of the given metallic salt in a test-tube, and add a few drops of the reagent. If a precipitate occurs, he should try to write the equation expressing the reaction, so as to make certain that he comprehends exactly what has taken place.

If not sufficiently advanced to do so satisfactorily, he should study the equation given in the book. During analysis it is most important that equations should be written, and the valency table (p. 4) should be consulted for first attempts.

The following **general points** should be noted **in connexion with Precipitation Reactions**:—

(1) **Temperature** affects the result in most cases by accelerating the rate of interaction; therefore warming the reaction mixture may produce a precipitate, which might form so slowly in a cold dilute solution that it would be liable to escape observation.

(2) Reactions generally take place by **Double Decomposition** between two of the substances in solution. A chance is given for an insoluble compound to form, and it comes down: for example, if we add sulphuric acid to a solution of barium chloride a precipitate of barium sulphate forms, and if hydrochloric acid is added to a solution of silver nitrate a precipitate of silver chloride comes down.

Equations:

$$BaCl_2Aq + H_2SO_4Aq = \mathbf{BaSO_4} + 2HClAq.$$
$$AgNO_3Aq + HClAq = \mathbf{AgCl} + HNO_3Aq.$$

(3) Note that **what really conditions the formation of any particular precipitate is the presence of certain radicles or ions**, e. g. (*a*) In the precipitation of barium sulphate from a solution, the ions barium (Ba) and sulphion (SO_4) must be present. In using this reaction as a confirmatory test for the metal barium, dilute sulphuric acid is usually the reagent added which contains the sulphion ion. The student should note, however, that any salt in solution containing the sulphion radicle would cause a similar reaction; e. g. sodium sulphate (Na_2SO_4), sodium hydrogen sulphate ($NaHSO_4$), potassium sulphate (K_2SO_4), ammonium sulphate ($(NH_4)_2SO_4$), copper sulphate ($CuSO_4$), aluminium sulphate ($Al_2(SO_4)_3$), ferrous sulphate ($FeSO_4$), calcium sulphate ($CaSO_4$), and magnesium sulphate ($MgSO_4$) would all cause precipitation of barium sulphate if added to a solution of a barium salt; e. g.

Equations:

$$BaCl_2Aq + Na_2SO_4Aq = \mathbf{BaSO_4} + 2NaClAq.$$
$$BaCl_2Aq + K_2SO_4Aq = \mathbf{BaSO_4} + 2KClAq.$$
$$BaCl_2Aq + CaSO_4Aq = \mathbf{BaSO_4} + CaCl_2Aq.$$

(*b*) The precipitation of silver chloride is generally effected by adding dilute hydrochloric acid to a solution of a silver salt, the ions which must be present being silver (Ag) and chlorine (Cl). Silver ions are present in a solution of any silver salt, and chlorine ions in any solution of a chloride, so that any soluble silver salt added to any soluble chloride will cause the precipitation of silver chloride; e. g.

$$Ag_2SO_4Aq + 2NaClAq = \mathbf{2AgCl} + Na_2SO_4Aq.$$

$$\underset{\text{Silver Acetate.}}{\underline{Ag \,.\, C_2H_3O_2Aq}} + KClAq = \mathbf{AgCl} + \underset{\text{Potassium Acetate.}}{\underline{K \,.\, C_2H_3O_2Aq}}$$

(4) **Note the interchangeability of reagent and reacting body.** Take above cases for example.

(*a*) Any soluble sulphate produces a precipitate of barium sulphate ($BaSO_4$) with a solution of a barium salt, and therefore the addition of any soluble sulphate to a solution would constitute a test for barium, and, conversely, the addition of any soluble barium salt to a solution would constitute a test for a sulphate.

(*b*) Any soluble chloride causes the precipitation of silver chloride on addition to a soluble silver salt, and therefore the addition of a soluble chloride (e. g. hydrogen chloride, hydrochloric acid) constitutes a test for a silver salt, and, conversely, the addition of a silver salt constitutes a test for a soluble chloride.

(5) **Many substances may prevent precipitation** of a compound insoluble in water even if the required ions should be present in pure aqueous solution; **e. g. concentrated acids and alkalies will often entirely prevent reactions from taking place.** As the student must effect the solution of many substances in acids, he should therefore use a minimum of acid, otherwise many reactions may be prevented or modified.

Note carefully the necessary precautions in the following lists of reactions. In order to make the summary as convenient for reference as possible, the dry tests are added at the end of each list. Certain negative tests are given in some cases as facts which a student should know and as bearing on the general scheme of analysis.

In order to gain space, only the formulae for the reagents used are given, and in order to prevent chance of mistake the following is a complete list of the reagents generally employed. The arrangement followed is that used at the Examination Hall of the Royal Colleges of Physicians and Surgeons.

Lists of Compounds of the Metals.

The Summary of Important Compounds of each Metal which follows the List of Tests will, it is hoped, help a student to correlate his practical and theoretical work. After identification of a simple substance or of the constituents of a mixture, the candidate should consult the Lists and consider whether the properties agree with those indicated by experiment.

The numbers given in the last column of the Summary bear reference to the general methods of preparing salts previously detailed, viz.:—

1. **Action of Acid upon a Metallic Oxide or Hydroxide** (i. e. acid upon base) (p. 55).
2. **Action of Acid upon the Carbonate of a Metal** (p. 57).
3. **Action of Acid upon a Metal** (p. 58).
4. **Precipitation** (p. 59). This method can be used for preparation of many other compounds besides salts; e. g. many hydroxides can be obtained in this way.

LIST OF REAGENTS.

Name.	Formula.
Acetic Acid dil.	$CH_3.COOH$ or $H.C_2H_3O_2$
Hydrochloric Acid dil.	HCl
Nitric Acid dil.	HNO_3
Sulphuric Acid dil.	H_2SO_4
Tartaric Acid	$H_2.C_4H_4O_6$
Sulphuretted Hydrogen or Hydrogen Sulphide	SH_2
Ammonium Hydroxide	NH_4OH
Calcium Hydroxide or Lime-water	$Ca(OH)_2$
Potassium Hydroxide	KOH
Ammonium Carbonate	$(NH_4)_2CO_3$
Ammonium Chloride	NH_4Cl
Ammonium Oxalate	$(NH_4)_2C_2O_4$
Ammonium Sulphide	$(NH_4)_2S$
Barium Nitrate	$Ba(NO_3)_2$
Calcium Chloride	$CaCl_2$
Calcium Sulphate	$CaSO_4$
Chlorine Water	Cl_2Aq
Magnesium Sulphate	$MgSO_4$
Sodium Carbonate	Na_2CO_3
Sodium Phosphate	Na_2HPO_4
Hydrochloric Acid Conc.	HCl
Nitric Acid Conc.	HNO_3
Sulphuric Acid Conc.	H_2SO_4
Ammonium Sulphocyanide	NH_4SCN
Copper Sulphate	$CuSO_4$
Ferric Chloride	$FeCl_3$
Ferrous Sulphate	$FeSO_4$
Lead Acetate	$Pb(C_2H_3O_2)_2$ or $(CH_3.COO)_2Pb$
Mercuric Chloride	$HgCl_2$
Mercurous Nitrate	$HgNO_3$
Potassium Chromate	K_2CrO_4

Name.	Formula.
(Potassium Dichromate)	$K_2Cr_2O_7$
Potassium Ferricyanide	$K_3Fe(CN)_6$
Potassium Ferrocyanide	$K_4Fe(CN)_6$
Potassium Iodide	KI
Potassium Sulphate	K_2SO_4
Stannous Chloride	$SnCl_2$
Borax, solid	$Na_2B_4O_7.10H_2O$
Copper turnings and foil	Cu
Ferrous Sulphate, solid	$FeSO_4.7H_2O$
Manganese Dioxide, solid	MnO_2
Microcosmic Salt, solid	$H.Na.NH_4PO_4.4H_2O$
Potassium Nitrate, solid	KNO_3
Sodium Carbonate, solid anhydrous	Na_2CO_3
Starch, solid	$(C_6H_{10}O_5)x$
Test Papers:—Litmus red, Litmus blue, Turmeric	
Zinc, solid	Zn
Ethyl Alcohol	C_2H_5OH
Ammonium Molybdate (generally with Nitric Acid present)	$(NH_4)_2MoO_4$
Chloroform	$CHCl_3$
Barium Chloride	$BaCl_2$
Cobalt Nitrate	$Co(NO_3)_2$
(Indigo)	
Iodine in Potassium Iodide	I_2
Platinic Chloride Hydrochloroplatinic Acid	H_2PtCl_6
Silver Nitrate	$AgNO_3$
Starch Paste	$(C_6H_{10}O_5)x$
Sodium Hypobromite	$NaOBr$

Summary of Tests for the Metals.

GENERAL DIRECTIONS FOR WET TESTS:—**Add a few drops of reagent to about 2 c.c. of solution of substance and warm gently if necessary.**

Group I. Silver. Mercurous Salts. Lead.

Summary of Reactions. Silver. Ag. 108.

A solution of **Silver Nitrate** can be used in carrying out the wet tests.

Reagent.	Results observed.	Remarks.
*1. HCl	**White curdy precipitate** of **Silver Chloride,** insoluble in water and Nitric Acid, but readily soluble in NH_4OHAq. e.g. $\underset{\substack{\text{Silver}\\ \text{Nitrate}}}{\underline{\mathrm{AgNO_3Aq}}} + \mathrm{HClAq} = \underset{\substack{\text{Silver}\\ \text{Chloride}}}{\underline{\mathbf{AgCl}}} + \mathrm{HNO_3Aq}$	Acids may be present.
2. H_2S	**Black precipitate** of **Silver Sulphide,** soluble in boiling dil. HNO_3. $\underset{\substack{\text{Silver}\\ \text{Nitrate}}}{\underline{\mathrm{2AgNO_3Aq}}} + \mathrm{H_2S} = \underset{\substack{\text{Silver}\\ \text{Sulphide}}}{\underline{\mathbf{Ag_2S}}} + \mathrm{2HNO_3Aq}$	Free Nitric Acid should not be present in large quantity.
3. $(NH_4)_2S$	**Black precipitate** of **Silver Sulphide.** $\mathrm{2AgNO_3Aq} + \underset{\substack{\text{Ammon.}\\ \text{Sulphide}}}{\underline{\mathrm{(NH_4)_2SAq}}} = \mathbf{Ag_2S} + \underset{\substack{\text{Ammon.}\\ \text{Nitrate}}}{\underline{\mathrm{2NH_4NO_3Aq}}}$	
*4. K_2CrO_4	**Reddish precipitate** of **Silver Chromate,** soluble in acids. $\mathrm{2AgNO_3Aq} + \underset{\substack{\text{Potassium}\\ \text{Chromate}}}{\underline{\mathrm{K_2CrO_4Aq}}} = \underset{\substack{\text{Silver}\\ \text{Chromate}}}{\underline{\mathbf{Ag_2CrO_4}}} + \mathrm{2KNO_3Aq}$	Free acids should not be present.
5. KI	**Faintly yellow precipitate** of **Silver Iodide.** $\mathrm{AgNO_3Aq} + \underset{\substack{\text{Potassium}\\ \text{Iodide}}}{\underline{\mathrm{KIAq}}} = \underset{\substack{\text{Silver}\\ \text{Iodide}}}{\underline{\mathbf{AgI}}} + \mathrm{KNO_3Aq}$	
*6. KOH or NaOH	**Greyish precipitate of Silver Oxide.** $\mathrm{2AgNO_3Aq} + \mathrm{2KOHAq} = \underset{\substack{\text{Silver}\\ \text{Oxide}}}{\underline{\mathbf{Ag_2O}}} + \mathrm{2KNO_3Aq} + \mathrm{H_2O}$	Free acids should not be present.
7. NH_4OH	**Greyish precipitate** of **Silver Oxide,** readily soluble in excess. $\mathrm{AgNO_3Aq} + \mathrm{2NH_4OHAq} = \mathbf{Ag_2O} + \mathrm{2NH_4NO_3} + \mathrm{H_2O}$	*Very dilute* Ammonium Hydroxide solution should be used. Add a few drops of solution on bench to about 20 c.c. water.
8. Charcoal	Heated on Charcoal with fusion mixture a brilliant silvery bead is obtained. (The bead readily dissolves in Nitric Acid, and the solution would give above tests.)	

Note.—An asterisk * in connexion with any of the above or subsequent reactions denotes a test specially important from the analytical point of view.

Summary regarding Silver and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Ag	Metallic Silver	Brilliant lustre. Met with as foil, powder, &c.	Soluble in HNO_3. Insol. in HCl and dil. H_2SO_4.	Reduction processes.
$AgNO_3$	Silver Nitrate	White cryst. solid. Slowly affected by light.	Soluble in water.	1. 2. 3
($AgNO_2$	Silver Nitrite	Nearly white solid.	Slightly soluble in water.)	4
$AgCl$	Silver Chloride	White solid. Rapidly affected by light.	Insol. in water and acids. Readily soluble in NH_4OHAq.	4
$AgBr$	Silver Bromide	Very faint yellow compound.	Insol. in water and acids. Sol. in NH_4OHAq with difficulty.	4
AgI	Silver Iodide	Light yellow solid.	Insol. in water, acids, and NH_4OHAq.	4
Ag_2CO_3	Silver Carbonate	White solid.	Insol. in water. Soluble in many acids with decomposition.	4
Ag_2SO_4	Silver Sulphate	White cryst. solid.	Sparingly soluble in water.	1. 2. (3)
(Ag_2SO_3	Silver Sulphite	White solid.	Insol. in water. Soluble in acids with decomposition.)	4
Ag_3PO_4	Silver Phosphate	Light yellow solid.	Insol. in water. Soluble in HNO_3 and in NH_4OH.	4
Ag_3AsO_3	Silver Arsenite	do. do.	do. do.	4
Ag_3AsO_4	Silver Arsenate	Reddish brown solid.	do. do.	4
Ag_2CrO_4	Silver Chromate	Dark red solid.	Insol. in water. Soluble in HNO_3 to give a yellow solution.	4
$Ag_2Cr_2O_7$	Silver Dichromate	do. do.		
$AgCN$	Silver Cyanide	White solid.	Insol. in water, but sol. in NH_4OHAq, $KCNAq$, and (with difficulty) in conc. HNO_3.	4
Ag_2S	Silver Sulphide	Black solid.	Insol. in water. Sol. in boiling HNO_3.	4
Ag_2O	Silver Oxide	Grey or black solid.	Insol. in water. Sol. in HNO_3 and in NH_4OHAq.	4

Alloy :—British Coinage, 92·5 % Ag : 7·5 % Cu.

Summary of Reactions. Mercurous Mercury. Hg^{ous} or $Hg^{\cdot}$.

Use a solution of **Mercurous Nitrate.**

Reagent.	Results observed.	Remarks.
*1. HCl	**White precipitate** of **Mercurous Chloride.** $\underset{\text{Mercurous Nitrate}}{\underline{HgNO_3Aq}} + HClAq = \underset{\text{Mercurous Chloride}}{\underline{\mathbf{HgCl}}} + HNO_3Aq$ On pouring off the supernatant liquid and adding Ammonia Solution the precipitate turns black. $\underset{\text{Mercurous Chloride}}{\underline{2HgCl}} + 2NH_3Aq = \underset{\text{Dimercurous Ammonium Chloride}}{\underline{\mathbf{NH_2Hg_2Cl}}} + NH_4ClAq$	Distinction from Mercuric Compounds.
2. H_2S	A **black precipitate** which chiefly consists of **Mercuric Sulphide and Mercury** is obtained. e.g. $2HgNO_3Aq + H_2S = HgS + Hg + 2HNO_3Aq$	Mercuric Compounds give a similar precipitate of Mercuric Sulphide (HgS).
3 $(NH_4)_2S$	A **black precipitate** which may consist chiefly of **Mercurous Sulphide** comes down. $2HgNO_3Aq + (NH_4)_2SAq = \mathbf{Hg_2S} + 2NH_4NO_3$	do. do.
*4. KOH or NaOH	**Black precipitate** of **Mercurous Oxide** forms. $2HgNO_3Aq + \underset{\text{Potassium Hydroxide}}{\underline{2KOHAq}} = \mathbf{Hg_2O} + H_2O + \underset{\text{Potassium Nitrate}}{\underline{2KNO_3Aq}}$	Distinction from Mercuric Compounds (cf. p. 130).
*5. KI	**Finch green precipitate** of **Mercurous Iodide,** soluble in excess of Potassium Iodide. $HgNO_3Aq + KIAq = \underset{\text{Mercurous Iodide}}{\underline{\mathbf{HgI}}} + KNO_3Aq$	Distinction from Mercuric Compounds (cf. p. 130).
*6. $SnCl_2$	First a **white precipitate** of **Mercurous Chloride** comes down, and then with excess of reagent on warming a **grey precipitate** of **Metallic Mercury** appears. *a*) $2HgNO_3Aq + \underset{\text{Stannous Chloride}}{\underline{SnCl_2Aq}} = \underset{\text{Mercurous Chloride}}{\underline{\mathbf{2HgCl}}} + \underset{\text{Stannic Chloride}}{\underline{SnCl_4Aq}}$ *b*) $2HgCl + SnCl_2Aq = \mathbf{2Hg} + SnCl_4Aq$	The second part of this reaction is given by Mercuric Compounds.
*7. Cu and HCl	A strip of Metallic Copper warmed gently with a solution of a mercury salt acidified by HCl has a **coating of Mercury** deposited upon it. On removing the strip after warming for a few minutes, and rubbing between filter paper, the silvery appearance is very characteristic.	Mercuric Compounds react similarly.
8. K_2CrO_4	Light red precipitate of Mercurous Chromate. $2HgNO_3Aq + K_2CrO_4Aq = \mathbf{Hg_2CrO_4} + 2KNO_3Aq$	
9. Carbon and Na_2CO_3	On heating in a bulb tube dry substance mixed with C and Na_2CO_3, a **sublimate of Mercury** is obtained.	Mercuric Compounds behave in similar way.

Summary regarding Mercury and Mercurous Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Hg	**Metallic Mercury**	Silvery liquid.	Insoluble in water, soluble in Nitric Acid. Insol. in HCl and dil. Sulphuric Acid. (Sol. in conc. Sulphuric Acid.)	
$HgNO_3$	**Mercurous Nitrate**	Nearly white solid.	Soluble in water. Basic yellowish insoluble salts may be met with.	3
$HgCl$	**Mercurous Chloride** (Calomel)	White solid.	Insoluble in water. Blackened by NH_4OH. Dissolved by aqua regia (HCl and HNO_3).	4 or heat mixture of Hg_2SO_4 and NaCl.
$HgBr$	**Mercurous Bromide**	White solid.	Insoluble in water. Soluble in aqua regia.	4
HgI (or Hg_2I_2)	**Mercurous Iodide**	Finch green solid.	Insol. in water. Soluble in KIAq and in aqua regia.	4
Hg_2SO_4	**Mercurous Sulphate**	White solid.	Slightly soluble in water.	3
Hg_2O	**Mercurous Oxide**	Black solid.	Insol. in water. Soluble in Nitric Acid.	4
$Hg . C_2H_3O_2$	Mercurous Acetate	White solid.	Soluble in water.	1

Alloys of Metals with Mercury are termed Amalgams.

Summary of Reactions. Lead. At. wt. 207.

Use a solution of **Lead Acetate** or **Lead Nitrate** in carrying out the wet tests.

Reagent.	Results observed.	Remarks.
*1. HCl	**White precipitate** of **Lead Chloride**, insoluble in NH_4OHAq. e. g. $Pb(NO_3)_2Aq + 2HClAq = \underset{\text{Lead Chloride}}{\underline{\mathbf{PbCl_2}}} + 2HNO_3Aq$ $\underset{\text{Lead Acetate}}{\underline{(CH_3COO)_2PbAq}} + 2HClAq = \mathbf{PbCl_2} + \underset{\text{Acetic Acid}}{\underline{2CH_3 . COOHAq}}$ The precipitate is soluble on boiling with a moderate quantity of water, and separates in characteristic white crystals on cooling.	The solution should not be very dilute, otherwise no precipitate may form, as Lead Chloride is *slightly* soluble in water. A large quantity of concentrated Hydrochloric Acid should not be present.
2. H_2S	**Black precipitate** of **Lead Sulphide** forms. e.g. $Pb(NO_3)_2Aq + H_2S = \mathbf{PbS} + 2HNO_3Aq$	Free acids should not be present in large quantity. With a fairly large amount of Hydrochloric Acid present a reddish precipitate of $PbS . PbCl_2$, is first precipitated.
3. $(NH_4)_2S$	**Black precipitate** of **Lead Sulphide.** $Pb(NO_3)_2Aq + (NH_4)_2SAq = \mathbf{PbS} + 2NH_4NO_3Aq$	Free acids should not be present.
*4. K_2CrO_4	**Yellow precipitate** of **Lead Chromate.** e. g. $\underset{\text{Lead Acetate}}{\underline{(CH_3 . COO)_2Pb}} + \underset{\text{Potassium Chromate}}{\underline{K_2CrO_4Aq}} = \underset{\text{Lead Chromate}}{\underline{\mathbf{PbCrO_4}}} + \underset{\text{Potassium Acetate}}{\underline{2CH_3COOKAq}}$	Free acids should not be present in large quantity.
*5. KI	**Yellow precipitate** of **Lead Iodide** ($\mathbf{PbI_2}$). On pouring off the supernatant liquid and boiling the precipitate with water, the Lead Iodide dissolves and crystallizes on cooling in characteristic golden spangles. e. g. $Pb(NO_3)_2Aq + 2KIAq = \mathbf{PbI_2} + 2KNO_3Aq$ $(CH_3 . COO_2)PbAq + \underset{\text{Pot. Iodide}}{\underline{2KIAq}} = \underset{\text{Lead Iodide}}{\underline{\mathbf{PbI_2}}} + 2CH_3COOKAq$	Certain free acids, e. g. Nitric Acid, should not be present.
*6. H_2SO_4	**Heavy white precipitate** of **Lead Sulphate.** e. g. $Pb(NO_3)_2Aq + H_2SO_4Aq = \mathbf{PbSO_4} + 2HNO_3Aq$	
7. **KOH, NaOH,** or **NH_4OH**	**White precipitate** of **Lead Hydroxide.** e. g. $Pb(NO_3)_2Aq + \underset{\text{Potassium Hydroxide}}{\underline{2KOHAq}} = \underset{\text{Lead Hydroxide}}{\underline{\mathbf{Pb(OH)_2}}} + 2KNO_3Aq$	
*8. C	Heated on Charcoal with or without fusion mixture, a characteristic **malleable bead which marks paper** is obtained. e.g. on heating Lead Nitrate it first splits up to give Lead Oxide, which readily reduces. *a*) $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$. *b*) $PbO + C = \mathbf{Pb} + CO \longrightarrow$	
9. **Flame test**	On Platinum Wire a blue flame is obtained.	The Platinum wire is so rapidly corroded that it is not advisable to use this test.

Summary regarding Lead and Lead Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Pb	Metallic Lead	Bluish white metal. Met with in many forms, e.g. sheet, granulated, foil, wire, &c.	Slightly affected by pure water with formation of Hydroxide. Dissolves in Nitric and Acetic Acids. HCl and dil. H_2SO_4 hardly attack it.	Reduction on Carbon, &c.
$Pb(NO_3)_2$	Lead Nitrate	White cryst. solid. Decomposes on heating, giving brown fumes of NO_2.	Soluble in water.	1. 2. 3
$PbCl_2$	Lead Chloride	White cryst. solid.	Slightly soluble in cold water; more soluble in hot water and in concentrated Hydrochloric Acid.	4
($PbBr_2$	Lead Bromide	White cryst. solid.	do. do.	4
PbI_2	Lead Iodide	Yellow cryst. solid. May be met with as characteristic golden spangles.	Slightly sol. in cold water; moderately soluble in boiling water, from which it can be recrystallized as golden spangles.	4
$PbCO_3$	Lead Carbonate	White solid (occurs native as Cerussite). White Lead is a basic Lead Carbonate.	Soluble in Nitric and Acetic Acids.	4
$PbSO_4$	Lead Sulphate	White solid.	Nearly insol. in water. Sol. in Potassium Hydroxide and Ammonium Acetate.	4
$Pb_3(PO_4)_2$	Lead Phosphate	White solid.	Insoluble in water. Soluble in Nitric Acid.	4
$PbCrO_4$	Lead Chromate	Yellow solid.	Insol. in water. Soluble in Nitric Acid unless after ignition, when it becomes very insoluble.	4
$Pb.(C_2H_3O_2)_2.3H_2O$ or $(CH_3.COO)_2Pb.3H_2O$	**Lead Acetate** (Sugar of Lead)	White crystalline solid, sweet taste.	Soluble in water.	1. 2. 3
PbC_2O_4	Lead Oxalate	White solid.	Insoluble in water. Soluble in Nitric Acid.	4
PbS	Lead Sulphide (ore is termed **Galena**)	Met with as a black powder or substance with metallic lustre (Galena).	Dissolves in moderately concentrated Nitric Acid, with partial conversion into $PbSO_4$. Insoluble in water.	4
$Pb(OH)_2$	Lead Hydroxide	White solid.	Soluble in Nitric Acid or Acetic Acid.	4
PbO	Lead Oxide	Met with in allotropic modifications: Orange compound — **Litharge**; Light yellow compound—Massicot.	Nearly insol. in water. Soluble with difficulty in boiling HCl, but readily soluble in Nitric or in Acetic Acid.	Heat metal in oxidizing blast.
Pb_3O_4	Red Lead (Triplumbic Tetroxide)	Bright red heavy solid. Turns yellow on heating strongly, oxygen being evolved.	Soluble in conc. HCl with evolution of Chlorine. $Pb_3O_4 + 8HCl = 3PbCl_2 + 4H_2O + Cl_2$ With Nitric Acid turns brown from separation of Lead Peroxide. $Pb_3O_4 + 4HNO_3Aq = PbO_2 + 2Pb(NO_3)_2Aq + 2H_2O$	Heat PbO to 400° C. in air.
PbO_2	Lead Peroxide	Deep brown powder.	Soluble in conc. HCl with separation of white crystals of Lead Chloride and evolution of Chlorine. $PbO_2 + 4HClAq = PbCl_2 + 2H_2O + Cl_2 \nearrow$	Action of HNO_3 on Pb_3O_4, &c.

Alloys:—Type Metal, 75 % Pb : 20 % Sb : 5 % Sn. Shot, Pb. As. Soft Solder, 50 % Pb : 50 % Sn. Pewter, 25 % Pb : 75 % Sn.

Group II $\left\{ \begin{array}{llllll} \text{II a.} & \text{(Pb).} & \text{Cu.} & \text{Hg}^{ic}. & \text{Bi.} & \text{Cd.} \\ \text{II b.} & \text{As.} & \text{Sb.} & \text{Sn}^{ous}. & \text{Sn}^{ic}. & \end{array} \right.$

Summary of Reactions. Copper. Cu. At. wt. 63.

Use a solution of **Copper Sulphate** or **Chloride** for wet tests.

Reagent.	Results observed.	Remarks.
Note. Solutions of Copper Compounds are generally blue or green.		
1. **HCl**	No reaction.	
*2. **H_2S**	**Black precipitate** of **Copper Sulphide.** e. g. $\underset{\text{Copper Sulphate}}{\underline{CuSO_4Aq}} + H_2S = \underset{\text{Copper Sulphide}}{\underline{\mathbf{CuS}}} + H_2SO_4Aq$	
3. **$(NH_4)_2S$**	**Black precipitate** of **Copper Sulphide.** $CuSO_4Aq + (NH_4)_2S = \mathbf{CuS} + \underset{\text{Ammon. Sulphate}}{\underline{(NH_4)_2SO_4Aq}}$	
*4. **KOH** or **NaOH**	**Blue precipitate** of **Cupric Hydroxide** forms from a cold solution. $CuSO_4Aq + 2NaOHAq = \underset{\text{Copper Hydroxide}}{\underline{\mathbf{Cu(OH)_2}}} + Na_2SO_4Aq$ On boiling with excess of alkaline Hydroxide the precipitate turns black, owing to partial dehydration to Cupric Oxide. $Cu(OH_2) + \mathbf{CuO} + H_2O$	
*5. **NH_4OH**	**Blue precipitate** of **Copper Hydroxide,** readily soluble in excess of reagent, giving a deep blue solution. e. g. $CuSO_4Aq + 2NH_4OHAq$ $= \mathbf{Cu(OH)_2} + (NH_4)_2SO_4Aq$	
*6. **$K_4Fe(CN)_6$**	**Brown precipitate** of **Copper Ferrocyanide.** $2CuSO_4Aq + K_4Fe(CN)_6Aq = Cu_2Fe(CN)_6 + 2K_2SO_4Aq$	Much free acid should not be present.
7. **KI**	**White precipitate** of **Cuprous Iodide with simultaneous liberation of Iodine,** which colours the solution brown. $2CuSO_4Aq + 4KIAq = \mathbf{Cu_2I_2} + \mathbf{I_2} + 2K_2SO_4Aq$	Note.—Most Copper Compounds are Cupric Compounds.
8. **Fe** or **Zn**	**Copper** is precipitated by replacement. $CuSO_4Aq + Fe = \mathbf{Cu} + FeSO_4Aq$ $CuSO_4Aq + Zn = \mathbf{Cu} + ZnSO_4Aq$	The metals Zn and Fe are more oxidizable than Copper, and as a rule a more oxidizable metal replaces a less oxidizable in solution.
*9. **Platinum wire test**	**Green** and **blue** flame.	Moisten the substance with concentrated Hydrochloric Acid before testing.
10. **Borax bead test**	**Blue** bead.	
11. **C**	Heated on Carbon with fusion mixture (and KCN) **reddish scales of metallic Copper** are obtained with difficulty.	

Summary regarding Copper and Copper Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Cu	Metallic Copper	Reddish metal. Met with as foil, wire, turnings, &c.	Insoluble in water, HCl, and dil. H_2SO_4. Readily soluble in Nitric Acid. Reacts with conc. H_2SO_4.	Reduction on Carbon, &c.
A. CUPRIC COMPOUNDS :—				
$Cu(NO_3)_2$	Copper Nitrate	Blue solid. Decomposes on heating, giving brown fumes of NO_2. $2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$	Soluble in water.	1. 2. 3
$CuCl_2$	Cupric Chloride	Hydrated Compound is generally green. (Anhydrous substance is brown.)	Soluble in water to give a green (or blue) solution.	1. 2
$CuBr_2$	Cupric Bromide		Soluble in water.	1. 2
(CuI_2	Cupric Iodide	Unknown.)		
$CuCO_3$	Copper Carbonate (Basic Compounds are generally met with).	Blue powder. A natural basic Carbonate, Malachite, $2CuCO_3.Cu(OH)_2$, is green. Azurite, another ore, is blue, $CuCO_3 . Cu(OH)_2$.	Insoluble in water. Soluble in acids.	4
$CuSO_4.5H_2O$	Copper Sulphate	Blue crystalline solid. On heating to 210° C. a white powder, $CuSO_4$, can be obtained.	Soluble in water.	1. 2. (3)
$Cu_3(PO_4)_2$	Copper Phosphate	Blue powder.	Insoluble in water. Soluble in acids.	4
$Cu(C_2H_3O_2)_2$	Copper Acetate	Blue cryst. solid.	Soluble in water.	1. 2
CuS	Copper Sulphide	Black powder.	Insol. in water. Soluble in boiling dilute Nitric Acid.	4
CuO	Cupric Oxide	Black solid. Met with as powder or in granular form.	Insoluble in water. Soluble in acids.	Heat nitrate or 4.
B. CUPROUS COMPOUNDS :—				
Cu_2Cl_2	Cuprous Chloride	White solid.	Insoluble in water. Soluble in conc. HCl and in NH_4OH.	
Cu_2I_2	Cuprous Iodide	do.	Insoluble in water.	4
Cu_2O	Cuprous Oxide	Red powder.	do.	4

Alloys:—Brass, 60–80 % Cu : 40–20 % Zn.
German Silver, Cu. Zn. Ni.
Bronze, Cu. Zn. Sn. Pb.
Gun and Bell Metal, Cu. Sn.

Summary of Reactions of Divalent Mercury } Mercury in Mercuric state. Hg^{ic} or $Hg^{\cdot\cdot}$

Use a solution of **Mercuric Chloride** ($HgCl_2$) for wet reactions.

Reagent.	Results observed.	Remarks.
1. HCl	No reaction.	Distinction from Hg^{ous} Compounds (p. 124).
*2. H_2S (in presence of HCl)	A **black precipitate** of **Mercuric Sulphide** is obtained, and there is generally a characteristic colour change, the precipitate being at first nearly white, and then changing to yellow, brown, and finally black. $HgCl_2Aq + H_2S = \mathbf{HgS} + 2HClAq$	The precipitate first formed is a double compound, e. g. $HgS . HgCl_2$ which is decomposed by H_2S.
3. $(NH_4)_2S$	**Black precipitate** of **Mercuric Sulphide.** $HgCl_2Aq + (NH_4)_2SAq = \mathbf{HgS} + 2NH_4ClAq$	
*4. KOH or NaOH	**Yellow precipitate** of **Mercuric Oxide.** $HgCl_2Aq + 2KOHAq = \mathbf{HgO} + H_2O + 2KClAq$	Distinction from Mercurous Compounds, which give a black precipitate.
5. NH_4OH	**White precipitate** of **Dimercur. Ammonium Chloride.** $2HgCl_2Aq + 2NH_4OHAq$ $= \mathbf{NH_2Hg_2Cl} + NH_4Cl + 2H_2O$	(Distinction from Hg^{ous} Compounds.)
*6. KI	**Scarlet precipitate** of **Mercuric Iodide,** soluble in excess of the reagent. $HgCl_2Aq + 2KIAq = \mathbf{HgI_2} + 2KClAq$ $HgI_2 + 2KIAq = HgI_2 + 2KIAq$	Distinction from Mercurous Compounds, which give a finch green precipitate.
*7. $SnCl_2$	A **white precipitate** of **Mercurous Chloride** is formed, which, if excess of reagent be added, reduces to **Metallic Mercury.** a) $2HgCl_2Aq + SnCl_2Aq = \mathbf{2HgCl} + SnCl_4Aq$ b) $2HgCl + \underbrace{SnCl_2Aq}_{\text{Stannous Chloride}} = \mathbf{2Hg} + \underbrace{SnCl_4Aq}_{\text{Stannic Chloride}}$	
8. K_2CrO_4	**Red precipitate** of **Mercuric Chromate.** $HgCl_2Aq + K_2CrO_4Aq = \mathbf{HgCrO_4} + 2KClAq$	
*9. Cu (and HCl)	A strip of Metallic Copper warmed gently with a solution of a Mercury salt acidified by Hydrochloric Acid has a **coating of Mercury** deposited upon it. On removing the strip after warming for a few minutes, and then rubbing between filter paper, the silvery appearance is very characteristic.	Mercurous Compounds react similarly.
10. C and Na_2CO_3	On heating the dry substance mixed with Carbon and Sodium Carbonate in a bulb tube, a **sublimate of Mercury** is obtained.	do. do.

Summary regarding Mercury and Mercuric Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Hg	**Metallic Mercury**	Silvery liquid.	(See p. 125, Hg^{ous}).	
$Hg(NO_3)_2$	**Mercuric Nitrate**	White crystalline solid. Decomposes on heating cautiously to give red Oxide of Mercury. $2Hg(NO_3)_2 = 2HgO + 4NO_2 + O$	Soluble in water.	1. 2. 3
$HgCl_2$	**Mercuric Chloride (Corrosive Sublimate)**	White solid.	Soluble in water.	1. 2. Heat $HgSO_4$ and NaCl
$HgBr_2$	**Mercuric Bromide**	White cryst. solid.	Soluble in water.	1. 2
HgI_2	**Mercuric Iodide**	Scarlet solid. Changes to allotropic yellow modification on heating.	Insoluble in water. Soluble in concentrated Hydrochloric Acid.	4
$HgSO_4$	**Mercuric Sulphate**	White solid.	Slightly soluble in water.	3
$HgCrO_4$	Mercuric Chromate	Red solid.	Insoluble in water. Soluble in acids.	4
$Hg(C_2H_3O_2)_2$ or $(CH_3COO)_2Hg$	Mercuric Acetate	White cryst. solid.	Soluble in water.	1. 2
HgO	**Mercuric Oxide**	Two allotropic modifications:— (*a*) HgO yellow, obtained by precipitation (p. 82). (*b*) HgO red solid, obtained by heating the nitrate. Decomposes to Mercury and Oxygen on strongly heating.	Insoluble in water. Soluble in dilute acids.	(*a*) Yellow 4 (*b*) Red. Heat nitrate.
HgS	**Mercuric Sulphide** (ore is called **Cinnabar**)	Allotropic varieties:— (*a*) Black powder. (*b*) Scarlet powder (vermilion). (*c*) Red solid (cinnabar).	Insoluble in water and dilute acids. Soluble in aqua regia.	(*a*) 4 (*b*) Sublimation of Hg and S.

Alloys:—Mercury Alloys are termed **Amalgams**.

	Sodium Amalgam	Silvery solid which becomes plastic on heating.	Reacts with water, giving off hydrogen.	Direct union.

Summary of Reactions. Bismuth. Bi.

Use a solution of **Bismuth Nitrate**, $Bi(NO_3)_3$, or **Bismuth Chloride**, $BiCl_3$.

Reagent.	Results observed.	Remarks.
*1. HCl	A precipitate of **Bismuth Oxychloride** (BiOCl) may form, not due to the HCl, but to the water in which the acid is dissolved. This precipitate dissolves on adding a little more Hydrochloric Acid and warming gently. *a*) $BiCl_3Aq + H_2O \rightleftarrows BiOCl + 2HClAq$ *b*) $BiOCl + 2HClAq \rightleftarrows BiCl_3Aq + H_2O$	It is to be noted that equation *b*) is the converse of equation *a*). Such a reaction is said to be reversible, because it proceeds in one direction or the other under different conditions. In this particular case the relative proportions of HCl and water are the factors which determine whether a precipitate will form or not.
*2. H_2S (in presence of **HCl**)	**Brownish black precipitate** of **Bismuth Sulphide** (Bi_2S_3), soluble in moderately concentrated boiling Nitric Acid. $2Bi(NO_3)_3Aq + 3H_2S = Bi_2S_3 + 6HNO_3Aq.$	
3. $(NH_4)_2S$	**Brownish black precipitate** of **Bismuth Sulphide** (Bi_2S_3). $2Bi(NO_3)_3Aq + 3(NH_4)_2SAq = Bi_2S_3 + 6NH_4NO_3Aq$	
4. KOH, NaOH, or NH_4OH	**White precipitate** of **Bismuth Hydroxide** $\{Bi(OH)_3\}$ e. g. $Bi(NO_3)_3Aq + 3KOHAq = Bi(OH)_3 + 3KNO_3Aq$	
*5. Water upon the Chloride	Filter off the precipitate of Bismuth Hydroxide obtained in Expt. 4, wash on the filter so as to get the precipitate into the apex, place the filter funnel in the mouth of a clean empty test-tube, and dissolve the white pp. by addition of a few drops of dilute Hydrochloric Acid dropped on to the Hydroxide. The solution will filter into the test-tube. Fill up the test-tube with water. A precipitate of Bismuth Oxychloride immediately forms. *a*) $Bi(OH)_3 + 3HClAq = BiCl_3Aq + 3H_2O$ *b*) $BiCl_3Aq + H_2O = BiOCl + 2HClAq$	Note.—This reaction may sometimes be obtained on adding water to the original solution, even when a nitrate, by adding Ammonium Chloride and then diluting with water.
6. KI	**Brown precipitate** of **Bismuth Iodide** (BiI_3) (soluble in excess to give a brown solution). $Bi(NO_3)_3Aq + 3KIAq = BiI_3 + 3KNO_3Aq$	
7. K_2CrO_4Aq	**Yellow precipitate** of **Bismuth Chromate** is formed. $2BiCl_3Aq + 3K_2CrO_4Aq = \underbrace{Bi_2(CrO_4)_3}_{\text{Bismuth Chromate}} + 6KClAq$	
8. C	Heated on Charcoal a **brittle bead** of **metallic Bismuth** is obtained.	
9. Flame test	Heated on Platinum wire gives a blue flame.	Bismuth rapidly corrodes Platinum, so that the test is better avoided.

Summary regarding Bismuth and notable Bismuth Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Bi	**Metallic Bismuth,** m. pt. 270° C.	Nearly white metal with peculiar lustre.	Insol. in HClAq and in H_2SO_4Aq, but soluble in HNO_3Aq. $Bi + 4HNO_3Aq = Bi(NO_3)_3Aq + 2H_2O + NO$	Reduction on Carbon.
$Bi(NO_3)_3$	**Bismuth Nitrate**	White crystalline solid; brown fumes on heating.	Reacts with water to give a white precipitate of Basic Nitrate, $Bi(OH)_2.NO_3$. Soluble in HNO_3Aq or HClAq.	1. 2. 3
$Bi(OH_2).NO_3$	**Basic Bismuth Nitrate** **Bismuth Oxynitrate**	White solid.	Insoluble in water. Soluble in Nitric Acid.	4
$BiCl_3$	**Bismuth Chloride**	White cryst. solid.	Reacts with water to give the Oxychloride. Soluble in HClAq or HNO_3Aq.	1. 2
BiOCl	**Bismuth Oxychloride**	White solid.	Insoluble in water. Soluble in Hydrochloric Acid.	4
$BiBr_3$	Bismuth Bromide	White solid.	Reacts with water.	1. 2
BiI_3	Bismuth Iodide	Brown solid.	Insoluble in water. Soluble in Potassium Iodide and in acids.	4
$Bi_2O_2CO_3$	**Bismuth Carbonate** (a basic salt)	White solid.	Insoluble in water. Soluble in acids with decomposition.	4
$Bi_2(SO_4)_3$	**Bismuth Sulphate**	White solid.	Slightly soluble in water. Soluble in acids.	1. 2
$BiPO_4$	**Bismuth Phosphate**	White solid.	Insoluble in water. Soluble in acids.	4
$Bi_2(CrO_4)_3$	Bismuth Chromate	Yellowish solid.	do. do.	4
Bi_2S_3	**Bismuth Sulphide**	Brownish black solid.	Insoluble in water. Soluble in moderately concentrated boiling Nitric Acid.	4
$Bi(OH)_3$	**Bismuth Hydroxide**	White solid.	Insoluble in water. Soluble in acids.	4
Bi_2O_3	**Bismuth Oxide**	Nearly white solid, turns brown on heating.	do. do.	Heat Hydroxide or Carbonate.

Alloy :—Fusible Metal, Bi. Pb. Sn.

Summary of Reactions. Cadmium. At. wt. 112.

Use a solution of **Cadmium Chloride** or **Sulphate.**

Reagent.	Result observed.	Remarks.
1. HCl.	No precipitate.	
*2. H_2S (in presence of small quantity of HCl).	Yellow precipitate of Cadmium Sulphide, which is moderately soluble in mineral acids, including HClAq, but is insoluble in Ammonium Sulphide. $CdCl_2Aq + H_2S = \mathbf{CdS} + 2HClAq.$	If the solution is made strongly acid with HCl no precipitate may form.
*3. **KOH** or **NaOH**	White precipitate of Cadmium Hydroxide insoluble in excess. $CdCl_2Aq + 2NaOHAq = \mathbf{Cd(OH)_2} + 2NaClAq.$	
4. NH_4OH	White precipitate of Cadmium Hydroxide soluble in excess. $CdCl_2Aq + 2NH_4OHAq = \mathbf{Cd(OH)_2} + 2NH_4ClAq.$	If Ammonium Salts (e. g. NH_4Cl) be present in quantity no precipitate forms.
5. KCN	White precipitate of Cadmium Cyanide soluble in excess. $CdCl_2Aq + 2KCNAq = \mathbf{Cd(CN)_2} + 2KClAq.$	
6. Ignition on Charcoal.	On heating on charcoal a brown incrustation of oxide is obtained.	

Summary regarding Cadmium and Cadmium Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Cd	**Metallic Cadmium**	Greyish metal—more malleable than Zinc, met with as sticks, granulated, sheet, &c.	Insoluble in water. Soluble in dilute acids.	Reduction by Carbon
$Cd(NO_3)_2$	**Cadmium Nitrate**	White cryst. solid.	Soluble in water.	1. 2. 3
(CdF_2)	Cadmium Fluoride	do.	do.	2. 3
$CdCl_2$	**Cadmium Chloride**	do.	do.	1. 2. 3
$CdBr_2$	Cadmium Bromide	do.	do.	1. 2. 3
CdI_2	Cadmium Iodide	do.	do.	1. 2. 3
$CdCO_3$	**Cadmium Carbonate**	White powder.	Insoluble in water. Soluble in acids, with evolution of CO_2.	4
$3CdSO_4 . 8H_2O$	**Cadmium Sulphate**	White cryst. solid.	Soluble in water.	1. 2. 3
$CdSO_3$	Cadmium Sulphite	do.	do.	
$Cd_3(PO_4)_2$	Cadmium Phosphate	White powder.	Insoluble in water. Soluble in acids.	4
$Cd(C_2H_3O_2)_2$	Cadmium Acetate	White cryst. solid.	Soluble in water.	2. 3
CdS	**Cadmium Sulphide**	Bright yellow solid.	Insoluble in water. Soluble in acids, including conc. HCl.	4
CdO	**Cadmium Oxide**	Brown powder.	Insoluble in water. Soluble in acids.	Heat Hydroxide Carbonate or Nitrate.
$Cd(OH)_2$	**Cadmium Hydroxide**	White powder.	do.	4
$Cd(CN)_2$	Cadmium Cyanide	White solid.	Insoluble in water. Soluble in acids.	4
$\left.\begin{array}{l}CdCrO_4\\Cd(OH)_2\end{array}\right\}$	Cadmium Chromate	Light yellow solid. Basic salt.	do.	4
$Cd(ClO_3)_2$	Cadmium Chlorate	White cryst. solid.	Soluble in water.	2. 3

Group II b. As. Sb. Sn^{ous}. Sn^{ic}. Summary of Reactions.

Arsenious and Arsenic Compounds.

For reactions of **Arsenious Compounds** use a solution of **Arsenious Oxide in Hydrochloric Acid,** or of **Sodium Arsenite.**

For **Arsenic Compounds** use a solution of **Sodium Arsenate.**

Reagent.	Arsenious Compounds.	Arsenic Compounds.
1. **HCl**	No reaction.	1) No reaction.
*2. **H_2S** in presence of **HCl**	**Yellow precipitate** of **Arsenious Sulphide.** $2AsCl_3Aq + 3H_2S = As_2S_3 + 6HClAq$ The **precipitate is soluble in :** *a*) $(NH_4)_2S$; *b*) **$(NH_4)_2CO_3$—Distinction from Antimony ;** *c*) KOHAq or NaOHAq. *d*) **Insoluble in conc. HCl—Distinction from Sb.** *a*) The solution in yellow $(NH_4)_2S$, which has Sulphur in solution, contains Ammonium Thioarsenate. $As_2S_3 + 3\underbrace{(NH_4)_2SAq + 2S}_{\text{Yellow Ammon. Sulphide}} = 2\underbrace{(NH_4)_3AsS_4Aq}_{\text{Ammon. Thioarsenate}}$ On addition of HClAq or K_2SO_4Aq to the solution Arsenic Pentasulphide is thrown down. $2(NH_4)_3AsS_4 + 6HClAq = 6NH_4ClAq + 3H_2S + As_2S_5$ *b*) The solution in Ammon. Carbonate contains Ammon. Arsenite and Ammon. Thioarsenite. $As_2S_3 + 3(NH_4)_2CO_3 = \underbrace{(NH_4)_3AsO_3Aq}_{\text{Ammon. Arsenite}} + \underbrace{(NH_4)_3AsS_3Aq}_{\text{Ammon. Thioarsenite}} + 3CO_2$ *c*) The solution in KOHAq or NaOHAq contains Sodium or Potassium Arsenite and Thioarsenite. $As_2S_3 + 6KOHAq = K_3AsO_3Aq + K_3AsS_3Aq + 3H_2O$	*2) Arsenic Compounds give **no precipitate with Sulphuretted Hydrogen until reduced** to the Arsenious condition. This is effected with considerable difficulty by the action of H_2S on the warm solution (e. g. $Na_2HAsO_4 + H_2S = Na_2HAsO_3 + H_2O + S$), but much more readily by Sulphurous Acid solution. $\underbrace{Na_2HAsO_4}_{\text{Sod. Hyd. Arsenate}} + H_2SO_3Aq = \underbrace{Na_2HAsO_3}_{\text{Sod. Hyd. Arsenite}} + H_2SO_4Aq$ N.B. To effect the reduction boil up with Sulphurous Acid solution and then pass Sulphuretted Hydrogen through it. $Na_2HAsO_3 + H_2SO_4Aq = Na_2SO_4Aq + H_3AsO_3$ $2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$
3. **$(NH_4)_2S$**	No precipitate.	3) No precipitate.
4. **KOH,** **NaOH,** or **NH_4OH**	**No precipitate — Distinction from Antimony.**	4) do.

Group II b. As. Sb. Sn^{ous}. Sn^{ic}. Summary of Reactions.
Arsenious and Arsenic Compounds *(continued)*.

For reactions of **Arsenious Compounds** use a solution of **Arsenious Oxide** in **Hydrochloric Acid**, or of **Sodium Arsenite**.

For **Arsenic Compounds** use a solution of **Sodium Arsenate**.

Reagent.	Arsenious Compounds.	Arsenic Compounds.
*5. Cu (and HCl)	**Reinsch's Test.** Acidify about 10 c.c. of solution with HClAq, add a strip of Copper, and boil for a few minutes. A greyish deposit of Arsenic comes down on the Copper. $3Cu + 2AsCl_3Aq = 3CuCl_2Aq + 2As$ Remove the strip, wash with distilled water, dry carefully between folds of filter paper, and heat in small **dry** tube of hard glass, closing the end with the thumb. Transparent glancing crystals of Arsenious Oxide deposit on glass above heated area. Examine with a lens.	*5) **Reinsch's Test.** This test only takes place after reduction of Arsenic Compounds to Arsenious condition. This is readily effected by boiling with Sulphurous Acid solution before adding the Copper and Hydrochloric Acid.
6. **$CuSO_4$**	Make solution neutral before adding reagent. Bright green precipitate of Scheele's green ($CuHAsO_3$). $CuSO_4Aq + Na_2HAsO_3Aq = CuHAsO_3 + Na_2SO_4Aq$	6)
*7. **$AgNO_3$**	With **neutral** solution a **yellow** precipitate of **Silver Arsenite**, Ag_3AsO_3, is obtained. $6AgNO_3Aq + 3Na_2HAsO_3Aq = \mathbf{2Ag_3AsO_3} + 6NaNO_3Aq + H_3AsO_3$	*7) Reddish brown precipitate of **Silver Arsenate** comes down from neutral solutions. $6AgNO_3Aq + 3Na_2HAsO_4Aq = \mathbf{2Ag_3AsO_4} + 6NaNO_3Aq + H_3AsO_4$
8. **Heated on Charcoal**	White fumes—garlic odour.	8) Same as Arsenious Compounds.
*9. **Reduction by C in tube**	Heat a small quantity of dry powdered substance mixed with powdered Carbon and Na_2CO_3 in hard glass tube. A grey **mirror of Arsenic** is generally obtained above heated area. The mirror is **soluble in bleaching powder :—Distinction from Antimony.**	9) do. do.
10. **Marsh's Test**	These are delicate reduction tests, by which traces of Arsenic can be detected. They are rarely necessary in Elementary Analysis (see p. 138).	10) do. do.
11. **Gutzeit's Test**		11) do. do.

The Marsh and Gutzeit Tests for Arsenic and Antimony.

Marsh's Test. Place in a Woulff's bottle about 10 grams of pure zinc, cover with water, and add a few c.c. of pure sulphuric acid. Hydrogen is evolved. The Woulff's bottle is connected with a tube containing granular calcium chloride to dry the gas, and then with a narrow tube of hard glass (say 3–4 mm. diameter) about 6 inches long, which is constricted in the middle, and drawn out and bent up to form a jet at the free end. When the air has presumably been expelled, light the jet and heat the hard glass tube just before the constriction. If after heating for 10 minutes no film of arsenic is deposited near the constriction, the chemicals may be assumed to be pure. Now add, say, 10–15 c.c. of solution which is to be tested to the reaction mixture, while continuing to heat near the constriction. If a deposit appears it may consist of arsenic or antimony. To distinguish between the two, cut off the tube at the constriction and put the portion with the deposit upon it into a small basin containing fresh bleaching powder solution. The arsenic deposit rapidly dissolves, while that due to antimony is only slightly affected.

Note.—Hydrogen is evolved very slowly from pure Zinc and Sulphuric Acid. To facilitate the action a few drops of Platinic Chloride or Copper Sulphate can be added.

Gutzeit's Test. Heat a small quantity of the substance with NaOHAq or KOHAq and pure Zinc. If Arsenic be present AsH_3 is evolved, which colours yellow a piece of filter paper moistened with $HgCl_2Aq$, and held in the mouth of the tube. Carry out a check experiment before adding the solution to be tested for Arsenic.

Summary regarding Arsenic and its notable Compounds.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
As	**Metallic Arsenic**	Greyish solid with metallic lustre.	Insoluble in water and HClAq. Oxidized and dissolved by HNO_3Aq. $As + 3HNO_3Aq = H_3AsO_4 + 2NO_2 + NO$	Reduction of As_2O_3 with C in tube.
A. ARSENIOUS COMPOUNDS.				
$(AsCl_3)$	Arsenious Chloride	Poisonous liquid.	Soluble in Hydrochloric Acid.	Direct union of elements.
As_2O_3	**Arsenious Oxide** (White Arsenic)	White solid.	Slightly soluble in water: more soluble in HClAq.	
As_2S_2	**Realgar** (native compound)	Reddish solid.	Soluble in HClAq and $KClO_3$ or in Nitric Acid.	do.
As_2S_3	**Arsenious Sulphide** (native subs. is called **Orpiment**)	Yellow solid.	Insoluble in water and HClAq (Note—Sb_2S_3 is readily soluble in conc. HCl). Dissolves in HCl and $KClO_3$ or in aqua regia. The minimum quantity of HNO_3 should be employed, when a small quantity of H_2S will come off, and H_2SO_4 will be found in solution.	
Na_2HAsO_3	**Sodium Arsenite**	White solid.	Soluble in water.	1
K_2HAsO_3	**Potassium Arsenite**	do.	do.	1
$CuHAsO_3$	**Copper Hydrogen Arsenite (Scheele's green)**	Bright green solid.	Insoluble in water. Soluble in acids.	4
Ag_3AsO_2	**Silver Arsenite**	Light yellow solid.	do. do.	4
B. ARSENIC COMPOUNDS.				
As_2O_5	**Arsenic Pentoxide**	White solid.	Sol. in water to give Arsenic Acid.	Heat H_3AsO_4.
H_3AsO_4	**Arsenic Acid**	do.	Sol. in water.	Oxidize As_2O_3 by HNO_3.
Na_2HAsO_4	**Sodium Hydrogen Arsenate**	do.	do.	1
K_2HAsO_4	**Potassium Hydrogen Arsenate**	do.	do.	1
Ag_3AsO_4	**Silver Arsenate**	Reddish brown solid.	Insol. in water. Soluble in acids.	4
As_2S_5	Arsenic Pentasulphide	Yellow solid.	Sol. in aqua regia.	4

Summary of Reactions. Antimony in Antimonious condition ($Sb^{\cdot\cdot\cdot}$) with a note on Antimonic Compounds.

Use a solution of **Antimonious Chloride** (**$SbCl_3$**) in dilute Hydrochloric Acid.

Reagent.	Antimonious Compounds.	Antimonic Compounds.
1. **HCl**	A white precipitate of **Antimony Oxychloride** (SbOCl) may be formed, which dissolves on adding a little more HClAq and warming. The reaction is reversible. $SbCl_3 + H_2O \rightleftarrows \mathbf{SbOCl} + 2HCl$	Note. Antimonic Compounds would rarely be met with in elementary analysis. On warming powdered Antimony with Nitric Acid, Metantimonic Acid is formed ($HSbO_3$), which dissolves in conc. HCl with addition of a crystal of Potassium Chlorate to form a solution which would give the tests summarized under Antimonious Compounds.
*2. **H_2S** (in presence of **HCl**)	**Orange precipitate** of **Antimonious Sulphide** (Sb_2S_3). $2SbCl_3 + 3H_2S = \mathbf{Sb_2S_3} + 6HClAq$ The precipitate is *a*) soluble in yellow Ammonium Sulphide; *b*) insoluble in Ammonium Carbonate (Distinction from Arsenic); *c*) soluble in KOH or NaOH; *d*) soluble in HClAq—Distinction from As. *a*) Ammonium Thioantimoniate is formed. $Sb_2S_3 + 3(NH_4)_2SAq + 2S = \underbrace{2(NH_4)_3SbS_4Aq}_{\text{Ammon. Thioantimoniate}}$ On addition of HClAq or H_2SO_4Aq, Antimony Pentasulphide is precipitated. $2(NH_4)_3SbS_4 + 6HClAq = 6NH_4ClAq + Sb_2S_5 + 3H_2S$ *c*) $Sb_2O_3 + 2NaOHAq = \underbrace{2SbO(ONa)}_{\text{Sodium Metantimoniate}} + H_2O$ *d*) $Sb_2S_3 + 6HClAq = 2SbCl_3Aq + 3H_2S\nearrow$	
3. **$(NH_4)_2S$**	No precipitate.	
*4. **KOH, NaOH,** or **NH_4OH**	**White precipitate** of **Antimonious Oxide** may be obtained—**Distinction from Arsenic.** $2SbCl_3 + 6NH_4OHAq = \mathbf{Sb_2O_3} + 3H_2O + 6NH_4ClAq$ As many metallic compounds give a white precipitate with KOH or NH_4OH it is **advisable to confirm further.** Filter, wash, dissolve the precipitate in a few drops of HClAq, and add the solution to about 50 c.c. of water. A white precipitate of Antimony Oxychloride (SbOCl) comes down, soluble in Tartaric Acid.	
*5. **Metallic Copper** (and HCl)	**Reinsch's Test.** Add a few drops of HClAq to 10 c.c. of solution, and heat for a few minutes with a strip of Copper. Remove the strip, dry, and heat in a small tube. Amorphous white sublimate.	
6. **Reduction in bulb tube**	Heat a small quantity of dry powdered substance mixed with Carbon and Sodium Carbonate in a hard glass tube. A brilliant sublimate forms. By means of a file break off the tube, and put portion with sublimate in H_2SAq—orange precipitate forms.	
7. **Carbon**	Antimony Compounds reduce to give brittle beads, which readily oxidize giving white fumes.	
8. **Marsh's Test**	Similar to test for Arsenic (p. 138).	

Summary regarding Antimony and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Sb	**Metallic Antimony**	Brilliant silvery lustre, brittle.	Nearly insoluble in Hydrochloric Acid. Dissolves in concentrated Hydrochloric Acid to which a few crystals of Potassium Chlorate have been added. On adding the solution to water, Antimony Oxychloride is precipitated, soluble in Tartaric Acid.	Reduction with Carbon.
$SbCl_3$	**Antimonious Chloride**	White soft solid.	Gives a white precipitate of Antimony Oxychloride with water, but is soluble in dilute Hydrochloric Acid.	Direct union.
$SbOCl$	**Antimony Oxychloride**	White powder.	Insoluble in water, soluble in Hydrochloric Acid.	4
$SbCl_5$	**Antimony Pentachloride** (Antimonic Chloride)	Yellowish liquid.	Decomposed by water.	Direct union.
Sb_2O_3	**Antimonious Oxide**	White solid.	Insoluble in water. Soluble in Hydrochloric Acid.	Direct union or 4.
(Sb_2O_4	Antimony Tetroxide	White solid.	Nearly insoluble.	
Sb_2O_5	**Antimony Pentoxide**	do.	Dissolves in conc. HCl with a few crystals of $HClO_3$ (or in aqua regia, using only a few drops of HNO_3).	Heat $HSbO_3$.
$HSbO_3$	Metantimonic Acid	do.	do. do.	Oxidize Sb by HNO_3.
$KSbO_3$	Potassium Metantimoniate	do.	Slightly soluble in water on boiling.	
$NaSbO_3$	Sodium Metantimoniate	do.	Nearly insoluble in water.	4
Sb_2S_3	**Antimonious Sulphide**	The naturally occurring substance (**Stibnite**) has either a grey metallic lustre, or is nearly black. The substance obtained by precipitation is orange.	Insoluble in water. Soluble in Ammonium Sulphide (p. 140). Soluble in concentrated HCl with evolution of H_2S. $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$	4
Sb_2S_5	Antimony Pentasulphide	Orange yellow solid.	Soluble in concentrated Hydrochloric Acid.	4
$K.SbO.C_4H_4O_6.\frac{1}{2}H_2O$ **Tartar Emetic**		White crystalline solid.	Soluble in water.	1

Summary of Reactions. Tin. Sn. { a) Stannous. $Sn^{\cdot\cdot}$. b) Stannic. $Sn^{\cdot\cdot\cdot\cdot}$.

Use a solution of **Stannous Chloride** ($SnCl_2$) for Stannous Compounds and a solution of **Stannic Chloride** ($SnCl_4$) for Stannic Compounds.

Reagent.	Stannous Compounds. Results.	Stannic Compounds. Results.
1. **HCl**	No precipitate.	1) No precipitate.
*2. **H_2S** (in presence of **HCl**)	**Brownish precipitate** of **Stannous Sulphide** (SnS)—Distinction from Stannic. $SnCl_2Aq + H_2S = \mathbf{SnS} + 2HClAq$ The precipitate is soluble in yellow Ammonium Sulphide, $(NH_4)_2S$. $SnS + (NH_4)_2SAq + S = \underset{\text{Ammon. Thiostannate}}{\underline{(NH_4)_2SnS_3Aq}}$ The Ammonium Thiostannate is easily decomposed by $HClAq$ or H_2SO_4Aq with precipitation of yellow Stannic Sulphide (SnS_2). $(NH_4)_2SnS_3 + 2HClAq = \mathbf{SnS_2} + H_2S + 2NH_4ClAq$	*2) **A yellow precipitate of Stannic Sulphide** (SnS_2) is obtained — Distinction from Stannous. $SnCl_4Aq + 2H_2S = \mathbf{SnS_2} + 4HClAq$ The precipitate is soluble in $(NH_4)_2SAq$, forming Ammonium Thiostannate. $SnS_2 + (NH_4)_2SAq = (NH_4)_2SnS_3Aq$ This solution is decomposed by acids as described under Stannous Compounds.
*3. **$HgCl_2$**	A white precipitate of **Mercurous Chloride** ($HgCl$) is formed, and if excess of Stannous Chloride be present a **greyish precipitate of Mercury** is ultimately obtained. *a*) $SnCl_2Aq + 2HgCl_2Aq = \mathbf{2HgCl} + SnCl_4Aq$ *b*) $SnCl_2Aq + 2HgCl = \mathbf{2Hg} + SnCl_4Aq$	*3) **No reaction. Important Distinction between Stannous and Stannic Compounds.**
4. **KOH, NaOH,** or **NH_4OH**	**White precipitate of Stannous Hydroxide,** $Sn(OH)_2$. $SnCl_2Aq + 2KOHAq = \mathbf{Sn(OH)_2} + 2KClAq$ The precipitate is soluble in excess of reagent, forming Stannite. $Sn(OH)_2 + 2KOHAq = \underset{\text{Potassium Stannite}}{\underline{K_2SnO_2Aq}} + 2H_2O$	4) **White precipitate of Stannic Hydroxide**, $Sn(OH)_4$, soluble in excess.
*5. **Zn** (and HCl)	**Metallic Tin** is deposited and can be separated and dissolved by boiling with Hydrochloric Acid. Then add Mercuric Chloride ($HgCl_2$).—Test 3 above. $SnCl_2Aq + Zn = \mathbf{Sn} + ZnCl_2Aq$	5) **Stannic Compounds are reduced** to Stannous by nascent hydrogen, and the Stannous reactions can then be obtained, e.g. reaction with Mercuric Chloride.
6. **Reduction on Carbon**	Mix the powdered substance with about double the quantity of a mixture of **Potassium Cyanide and Borax** and heat strongly in reducing flame. A bright bead of Tin will be obtained with some difficulty. To confirm Tin from this process boil up the residue with water, separate off globules of Tin, and dissolve by boiling with a small quantity of conc. HCl. Dilute somewhat and then add $HgCl_2$ and warm. (See Test 3 above for result.)	6) Similar to Stannous.
7. **$Co(NO_3)_2$ and ignition**	Moisten filter paper with a concentrated solution and then with $Co(NO_3)_2$ and burn the paper. A **bluish-green residue** is left.	7) Similar to Stannous.

Summary regarding Tin and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Sn	**Metallic Tin,** m. pt. 233° C.	Met with in different forms, e. g. sticks, granulated, foil, &c.	Soluble in Hydrochloric Acid (conc.). $Sn + 2HClAq = \underset{\text{Stannous Chloride.}}{\underline{SnCl_2Aq}} + H_2$	Reduction of Carbon
A. STANNOUS COMPOUNDS.				
$SnCl_2$	**Stannous Chloride**	Nearly white cryst. solid (faint yellowish tint usually noticeable).	Soluble in Hydrochloric Acid. A basic salt is precipitated with water, $Sn{<}^{OH}_{Cl}$. This basic salt may form after prolonged exposure of the dry salt to air.	3
$SnSO_4$	Stannous Sulphate	White solid.	Soluble in water.	1
(SnO	Stannous Oxide	Black solid.	Soluble in acids.	Heat Stannous Oxalate.)
$Sn(OH)_2$	Stannous Hydroxide	White solid.	Soluble in acids and also in alkaline hydroxides.	4
SnS	**Stannous Sulphide**	Brownish black or dark grey solid.	Soluble in concentrated Hydrochloric Acid with evolution of H_2S.	4
B. STANNIC COMPOUNDS.				
$SnCl_4$	**Stannic Chloride**	The pure substance is a fuming liquid decomposed by water.	Soluble in Hydrochloric Acid.	Direct union.
$Sn(SO_4)_2$	Stannic Sulphate	White solid.	Soluble in acids.	
SnS_2	**Stannic Sulphide** (Bronze powder, Mosaic Gold)	Golden yellow solid. May be met with in powder or crystalline scales similar to Lead Iodide.	Insoluble in water and in Hydrochloric Acid. Soluble in conc. HCl to which a few drops of HNO_3 have been added. With Zn and HClAq it gives off H_2S.	4
SnO_2	**Stannic Oxide (Tin-stone,** Putty powder, **Cassiterite)**	White solid.	Insoluble in water and acids. It can be reduced with KCN and Borax as described on p. 142.	Tin and HNO_3.
Na_2SnO_3	Sodium Stannate	White solid.	Substance met with is generally partially soluble in water.	Fuse SnO_2 and Na_2CO_3.

Group III. Al. Fe^{ous}. Fe^{ic}. (Cr.)

Summary of Reactions. Aluminium. $Al^{\cdots}$.

Use a solution of **Aluminium Sulphate** or of **Alum.**

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate	
2. H_2S (in presence of **HCl**)	No precipitate.	
*3. NH_4OH	**White gelatinous precipitate of Aluminium Hydroxide, $Al(OH)_3$.** $\underset{\text{Aluminium Sulphate}}{\underline{Al_2(SO_4)_3Aq}} + 6NH_4OHAq$ $= \underset{\text{Aluminium Hydroxide}}{\underline{\mathbf{2Al(OH)_3}}} + 3(NH_4)_2SO_4Aq$	
*4. KOH or NaOH	**White gelatinous precipitate** soluble in excess. $Al_2(SO_4)_3Aq + 6KOHAq = \mathbf{2Al(OH)_3} + 3K_2SO_4Aq$ With excess of reagent the precipitate dissolves to form Aluminate. $Al(OH)_3 + 3KOHAq = \underset{\text{Potassium Aluminate}}{\underline{Al(OK)_3Aq}} + 3H_2O$	
*5. $(NH_4)_2S$	White gelatinous precipitate of Aluminium Hydroxide, $Al(OH)_3$. One might expect to get Aluminium Sulphide, Al_2S_3, but that substance is at once decomposed by water, forming the Hydroxide and H_2S. The two part equations *a*) and *b*), or the single equation *c*), obtained from them by addition, may be used to explain this reaction. $\left\{\begin{array}{ll} a) & Al_2(SO_4)_3Aq + 3(NH_4)_2SAq \\ & \quad = Al_2S_3 + 3(NH_4)_2SO_4Aq \\ b) & Al_2S_3 + 6H_2O = 3H_2S + 2Al(OH)_3 \end{array}\right.$ $c)\ Al_2(SO_4)_3Aq + 3(NH_4)_2SAq + 6H_2O \quad \nearrow$ $= \mathbf{2Al(OH)_3} + 3(NH_4)_2SO_4Aq + 3H_2S$	Free acids should not be present.
*6. $Co(NO_3)_2$ and ignite	Heat original substance on Carbon in oxidizing flame and then moisten with Cobalt Nitrate and reheat for some time. **A bright blue mass** is obtained.	**Phosphates, borates,** and **arsenates** may give a similar sort of blue mass, but in these cases the masses can generally be fused. The masses obtained from Aluminium Compounds are infusible if Compounds of other elements are not present.

Summary regarding Aluminium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Al	**Metallic Aluminium,** m. pt. about 650° C.	Brilliant silvery metal. Met with as foil, sheet, wire, turnings, &c.	Soluble in Hydrochloric Acid or Sulphuric Acid; nearly insoluble in Nitric Acid.	Electrolysis.
$AlCl_3$	**Aluminium Chloride**	White deliquescent solid. Fumes in air.	Soluble in water with evolution of heat.	3
$AlBr_3$	Aluminium Bromide	do.	do.	3
$Al(NO_3)_3$	Aluminium Nitrate	White solid.	Soluble in water.	1
$Al_2(SO_4)_3$	**Aluminium Sulphate**	do.	do.	1
$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ or $KAl(SO_4)_2 . 12H_2O$	**Potash Alum**	White cryst. solid.	do.	
$(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ or $NH_4 . Al(SO_4)_2 . 12H_2O$	**Ammonia Alum**	do.	do.	
$AlPO_4$	**Aluminium Phosphate**	White powder.	Insoluble in water; soluble in acids.	4
Al_4C_3	**Aluminium Carbide**	Greyish powder.	Reacts with water to give Methane. $Al_4C_3 + 6H_2O = 3CH_4 + 2Al_2O_3$	
$Al(OH)_3$	**Aluminium Hydroxide**	White solid.	Insoluble in water. Easily soluble in acids (and also in KOH or NaOH).	4
$Al(ONa)_3$	Sodium Aluminate	White solid.	Soluble in water. Solution is strongly alkaline in reaction.	
Al_2O_3	**Aluminium Oxide (Alumina).** The hydrated Oxide occurring native is the important ore **Bauxite**	Met with in different forms — corundum, emery, &c.	Insoluble in water. May be easily soluble or almost insoluble in acids, depending upon the source and temperature to which it may have been exposed.	Heat $Al(OH)_3$.

Alloys:—Aluminium Bronze, Al (5–12 %) : Cu.
Magnalium, Al (70–94 %) : Mg.

Summary of Reactions for Iron Compounds { *a*) Ferrous. *b*) Ferric.

For reactions of **Ferrous Salts** use a solution of **Ferrous Sulphate** and for reactions of **Ferric Salts** use a solution of **Ferric Chloride.**

Reagents.	Ferrous Iron, Fe$^{\cdot\cdot}$.	Ferric Iron, Fe$^{\cdot\cdot\cdot}$.	Remarks.
1. HCl	No precipitate.	1) No precipitate.	
2. H_2S (in presence of HCl)	No action.	*2) **Ferric Salts are reduced to Ferrous Salts by Sulphuretted Hydrogen.** $2FeCl_3Aq + H_2S = 2FeCl_2Aq + 2HCl + S$	
3. $(NH_4)_2S$	**Black precipitate of Ferrous Sulphide** (FeS). $FeSO_4Aq + (NH_4)_2S = \mathbf{FeS} + (NH_4)_2SO_4Aq$	3) **Black precipitate** consisting chiefly of a mixture of **Ferrous Sulphide and Sulphur** $2FeCl_3Aq + 3(NH_4)_2SAq = \mathbf{2FeS} + \mathbf{S} + 6NH_4ClAq$	
*4. NH_4OH, KOH, or $NaOH$	**Greenish precipitate of Ferrous Hydroxide,** $Fe(OH)_2$, which slowly turns brown on the top because of the formation of Ferric Hydroxide on oxidation by the oxygen of the air. *a*) $FeSO_4Aq + 2NH_4OHAq = \underset{\text{Ferrous Hydroxide}}{\underline{\mathbf{Fe(OH)_2}}} + (NH_4)_2SO_4Aq$ The oxidation might be expressed by an equation. *b*) $2Fe(OH)_2 + O + H_2O = \underset{\text{Ferric Hydroxide}}{\underline{\mathbf{2Fe(OH)_3}}}$	*4) **Brown precipitate of Ferric Hydroxide,** $Fe(OH)_3$. $FeCl_3Aq + 3NH_4OHAq = \underset{\text{Ferric Hydroxide}}{\underline{\mathbf{Fe(OH)_3}}} + 3NH_4ClAq$	
*5. $K_4Fe(CN)_6$	**Light blue precipitate** consisting of slightly oxidized **Potassium Ferrous Ferrocyanide.** $FeSO_4Aq + K_4Fe(CN)_6Aq = \underset{\text{Potassium Ferrous Ferrocyanide}}{\underline{\mathbf{K_2Fe^{\cdot\cdot}[Fe(CN)_6]}}} + K_2SO_4Aq$	*5) **Deep blue precipitate** of **Ferric Ferrocyanide — Prussian blue.** $4FeCl_3Aq + 3K_4Fe(CN)_6Aq = \underset{\text{Ferric Ferrocyanide}}{\underline{\mathbf{Fe_4[Fe(CN)_6]_3}}} + 12KClAq$	Distinction between **Ferrous** and **Ferric** Compounds.
*6. $K_3Fe(CN)_6$	**Deep blue precipitate** of **Ferrous Ferricyanide — Turnbull's blue.** $3FeSO_4Aq + 2K_3Fe(CN)_6Aq = \underset{\text{Ferrous Ferricyanide}}{\underline{\mathbf{Fe_3[Fe(CN)_6]_2}}} + 3K_2SO_4Aq$	*6) Solution turns brown, but no precipitate is formed.	Distinction between **Ferrous** and **Ferric** Compounds.
7. **KCNS**	**No precipitate** and **if absolutely pure no coloration.** A trace of Ferric Salt is usually present, causing the solution to become tinted a **light pink.**	*7) **Deep red coloration** or **precipitate** of **Ferric Sulphocyanide.** $FeCl_3Aq + 3KSCNAq = \mathbf{Fe(SCN)_3} + 3KClAq$	
8. **Reduction on Charcoal**	**A metallic residue** is obtained, which is attracted by a magnet.		
9. **Borax bead**	Brownish bead in the oxidizing flame—bottle green in the reducing flame.		

Summary regarding Iron and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Fe	**Metallic Iron**, m. pt. about 1550° C.	Met with in different forms, e.g. filings, wire, sheet, &c.—grey metal.	Soluble in acids.	Reduction by C or CO.
A. FERROUS COMPOUNDS.				
$FeCl_2 . 4H_2O$	**Ferrous Chloride**	Light green crystalline solid.	Soluble in water.	3
$FeBr_2$	Ferrous Bromide	do.	do.	Direct union.
FeI_2	Ferrous Iodide		do.	do.
$FeSO_4 . 7H_2O$	**Ferrous Sulphate**	Green crystalline solid.	do.	3
$FeSO_4 . (NH_4)_2SO_4 6H_2O$	**Ferrous Ammonium Sulphate**	Light green crystalline solid.	do.	
$Fe_3(PO_4)_2$	**Ferrous Phosphate**	Bluish grey powder.	Insoluble in water; soluble in acids.	4
$FeCO_3$	**Ferrous Carbonate** (the ore is called **Spathic iron ore**)	Greyish white solid—the natural ore is grey.	Insoluble in water; soluble in acids with decomposition.	4
FeC_2O_4	Ferrous Oxalate	Yellow solid.	Insoluble in water; soluble in acids.	4
(FeO	Ferrous Oxide	Black powder.	Soluble in acids.	Heat FeC_2O_4.)
FeS	**Ferrous Sulphide**	*a*) Black solid or *b*) Sticks with grey metallic lustre.	Soluble in HClAq or H_2SO_4Aq, H_2S being given off.	4 or direct union.
B. FERRIC COMPOUNDS.				
$FeCl_3$	**Ferric Chloride**	Pure anhydrous compound is black, but the hydrated body is yellow.	Soluble in water to give a yellow solution.	Direct union or 1.
$Fe(NO_3)_3$	**Ferric Nitrate**	Yellow cryst. solid.	do.	1
$Fe_2(SO_4)_3$	**Ferric Sulphate**	Nearly white solid.	do.	1 or oxidation of $FeSO_4$.
$K_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$	**Iron Alum**	Light violet solid.	Soluble in water to give a yellow solution.	
$FePO_4$	**Ferric Phosphate**	Faintly yellow solid—nearly white.	Soluble in acids.	4
$Fe_2(CO_3)_3 . xFe_2O_3$	(Ferric Carbonate)	Brown powder consisting chiefly of Oxide of Iron.	Soluble in acids.	4
$Fe(OH)_3$	**Ferric Hydroxide**	Brown solid.	Easily soluble in acids.	4
Fe_2O_3	**Ferric Oxide**	Occurs in many forms, e.g. *a*) rust, *b*) hematite, *c*) specular iron ore.	Soluble in Hydrochloric Acid unless strongly ignited.	
Fe_3O_4	**Magnetic Oxide of iron** (Lodestone, Triferric Tetroxide)	Brown solid.	Soluble in acids with difficulty.	

Alloy :—Cast iron contains 93–94 % Fe, 3–4 % C; and also Si. P. S. (and Mn.).

Summary of Reactions for Chromium. $Cr^{\cdot\cdot\cdot}$. 52.

Use a solution of **Chromium Sulphate, $Cr_2(SO_4)_3$**, or **Chrome Alum, $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$.**

	Reagent.	Results observed.	Remarks.
1.	**HCl**	No precipitate.	
2.	**H_2S** (in presence of **HCl**)	No precipitate.	
3.	**$(NH_4)_2S$**	A **greyish green precipitate** of **Chromium Hydroxide**, $Cr(OH)_3$, is thrown down. $Cr_2(SO_4)_3Aq + 3(NH_4)_2SAq + 6H_2O$ $= 2Cr(OH)_3 + 3(NH_4)_2SO_4Aq + 3H_2S$	Cr_2S_3 is decomposed by water, which explains this reaction (cf. Al).
*4.	**NH_4OH, KOH,** or **NaOH**	**Greyish green precipitate** of **Chromium Hydroxide**, $Cr(OH)_3$. $Cr_2(SO_4)_3Aq + 6NH_4OHAq$ $= 2Cr(OH)_3 + 3(NH_4)_2SO_4Aq$	
*5.	**Bleaching powder** and then **$(CH_3COO)_2Pb$**	The solution turns yellow because the Chromic salt is oxidized to a Chromate. Add to the solution Lead Acetate. A yellow precipitate of Lead Chromate is thrown down. *a*) $Cr_2(SO_4)_3Aq + 6CaOCl_2Aq + 3H_2O$ $= 2H_2CrO_4Aq + 6CaCl_2 + 3H_2SO_4Aq$ *b*) $H_2CrO_4Aq + (CH_3COO)_2PbAq$ $= PbCrO_4 + 2CH_3COOHAq$	The Chromium is changed by oxidation from basic radicle to a portion of the acid radicle.
6.	Heat the dry powder with **Na_2O_2** or **KNO_3** in a **hard glass tube**	The mixture turns yellow because of the formation of a Chromate. Break the tube in a mortar, add water, filter, and add Lead Acetate to the solution. Lead Chromate is precipitated. *a*) $Cr_2(SO_4)_3 + 3Na_2O_2 = 3Na_2SO_4 + 2CrO_3$ *b*) $CrO_3 + H_2O = H_2CrO_4$ *c*) $H_2CrO_4Aq + (CH_3 . COO)_2PbAq$ $= PbCrO_4 + 2CH_3COOHAq$	
*7.	**Borax bead**	**Green.**	

Summary regarding Chromium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
(Cr	Metallic Chromium	Grey metal.	Soluble in HClAq.	Reduction by Al or C.)
A. CHROMIC COMPOUNDS.				
$CrCl_3$	Chromium Trichloride	The hydrated substance is green, and the anhydrous compound violet.	The hydrated substance is easily soluble in water.	1 and direct union
$Cr_2(SO_4)_3$	Chromium Sulphate	Green solid.	Soluble in water.	1
$K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$ or $KCr(SO_4)_2 . 12H_2O$	Chrome Alum	Purple solid.	do.	
$CrPO_4$	Chromium Phosphate	Green solid.	Insoluble in water; soluble in acids.	4
Cr_2O_3	Chromic Oxide	Bright green solid.	Soluble in concentrated Hydrochloric Acid unless the Oxide has been strongly ignited.	Heat the hydroxide.
$Cr(OH)_3$	Chromium Hydroxide	Greyish green solid.	Soluble in acids.	
B. CHROMIC ANHYDRIDE AND ITS DERIVATIVES.				
CrO_3	Chromium Trioxide Chromic Anhydride	Dark red solid.	Soluble in water to give a yellow solution of Chromic Acid. $CrO_3 + H_2O = H_2CrO_4$	$K_2Cr_2O_7$ and H_2SO_4.
K_2CrO_4	Potassium Chromate	Bright yellow solid. The solution is reduced by Sulphur Dioxide to give a green solution of Chromic Sulphate. SH_2 also reduces.	Soluble in water.	
$K_2Cr_2O_7$	Potassium Dichromate	Deep orange solid. The solution is reduced by SO_2 or H_2S.	Soluble in water.	
Ag_2CrO_4	Silver Chromate	Dark red solid.	Soluble in acids.	4
$BaCrO_4$	Barium Chromate	Light yellow solid.	Soluble in mineral acids (i.e. HCl, H_2SO_4, or HNO_3); insoluble in Acetic Acid.	4
$PbCrO_4$	Lead Chromate	Dark yellow solid.	Soluble in mineral acids unless strongly ignited.	4

Group IV. Ni. Co. Zn. Mn.

Summary of Reactions for Nickel. $Ni^{\cdot\cdot}$. At. wt. 58·7.

Use a solution of **Nickel Sulphate** or **Chloride.**

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	
2. H_2S (in presence of HCl)	No precipitate.	
*3. $\mathbf{(NH_4)_2S}$	Black precipitate of Nickel Sulphide. $NiSO_4Aq + (NH_4)_2SAq = \mathbf{NiS} + (NH_4)_2SO_4Aq.$ NOTE.—The supernatant liquid remains tinted brown because the precipitate is slightly soluble in Ammonia. On acidifying with Acetic Acid and warming, complete precipitation occurs and the solution clears.	NiS is nearly insoluble in Hydrochloric Acid, but dissolves easily in Hydrochloric Acid containing a few crystals of Potassium Chlorate.
*4. **NaOH** or **KOH**	Apple-green gelatinous precipitate of Nickel Hydroxide insoluble in excess. e. g. $NiSO_4Aq + 2NaOHAq = \mathbf{Ni(OH)_2} + Na_2SO_4Aq.$	
*5. $\mathbf{NH_4OH}$	Greenish precipitate of a basic compound forms which is soluble in excess to a blue solution.	No precipitate forms if Ammonium Salts (e. g. NH_4Cl) be present.
6. **KCN**	Green precipitate of Nickel Cyanide soluble in excess. *a*) $NiSO_4Aq + 2KCNAq = \mathbf{Ni(CN)_2} + K_2SO_4Aq.$ *b*) $Ni(CN)_2 + 2KCNAq = \underbrace{K_2Ni(CN)_4Aq.}_{\text{Potassium Nickelocyanide.}}$	
*7. **KCN**, NaOH, and $\mathbf{Br_2}$	Add KCN in barely sufficient quantity to form the Nickelocyanide, then add **slight** excess of NaOH and Bromine water in sufficient quantity to tint the liquid brown, and warm gently. A black precipitate of Nickelic Hydroxide is precipitated. Equations *a*) and *b*) as above (test 6). *c*) $K_2Ni(CN)_4Aq + 4Br_2 = NiBr_2Aq + 2KBrAq + CN{\cdot}Br$ *d*) $NiBr_2Aq + 2NaOHAq = \mathbf{Ni(OH)_2} + 2NaBr$ *e*) $Ni(OH)_2 + NaOBrAq + H_2O = \mathbf{Ni(OH)_3} + NaBrAq$	Avoid excess of both Potassium Cyanide and Caustic Soda. The test is important because Cobalt Compounds give no similar precipitate (p. 152).
8. Charcoal.	Reduction on Charcoal yields Nickel as a black powder which is slightly magnetic, i. e. is attracted by a magnet.	
9. Borax bead.	Yellowish brown bead in oxidizing flame.	

Summary regarding Nickel and Nickel Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Ni	**Metallic Nickel**	Silvery lustre with faint yellowish tint. Met with as cubes, powder, granular, gauze, &c.	Dissolves with difficulty in HClAq. Easily soluble in HNO_3Aq.	Reduction.
		Only Nickelous ($Ni^{\cdot\cdot}$) Salts are known.		
$Ni(NO_3)_2$	**Nickel Nitrate**	Green solid.	Soluble in water.	1. 2. 3
$NiCl_2.6H_2O$	**Nickel Chloride**	do.	do.	2. 3
$NiSO_4.6H_2O$	**Nickel Sulphate**	do.	do.	2. 3
$\left.\begin{matrix}(NH_4)_2SO_4.\\NiSO_4.6H_2O\end{matrix}\right\}$	**Ammonium Nickel Sulphate**	do.	do. Used in electro-plating.	
$NiCO_3$	Nickel Carbonate	do.	Insoluble in water. Soluble in acids with decomposition.	4
$Ni(C_2H_3O_2)_2$	Nickel Acetate	do.	Soluble in water.	
NiC_2O_4	Nickel Oxalate	Green powder.	Soluble in acids.	4
$Ni_3(PO_4)_2$	Nickel Phosphate	Bluish-green powder.	do.	4
NiS	**Nickel Sulphide**	Black powder.	Soluble in conc. acids and in HCl + crystal of $KClO_3$.	4
NiO	**Nickelous Oxide**	do.	Soluble in acids.	
Ni_3O_4	Nickelo-Nickelic Oxide	do.	do.	
Ni_2O_3	Nickelic Oxide	Black solid.	do.	Heat Nitrate cautiously.
$Ni(CO)_4$	Nickel Carbonyl	Colourless liquid, b.-p. 43° C. Vapour is poisonous.		Direct union.

Summary of Reactions of Cobalt. Co ˙˙. At. wt. 59.

Use a solution of **Cobalt Nitrate** or **Chloride.**

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	
2. H_2S (in presence of HCl)	No precipitate.	
*3. **$(NH_4)_2S$**	Black precipitate of Cobalt Sulphide. $Co(NO_3)_2Aq + (NH_4)_2SAq = CoS + 2NH_4NO_3Aq$	CoS is insoluble in HClAq, but dissolves in HClAq containing a few crystals of $KClO_3$.
*4. **NaOH** or **KOH**	A bluish precipitate of basic salt is first formed, which on boiling gives light red Cobaltous Hydroxide, and this substance takes up oxygen to form brown Cobaltic Hydroxide. *a*) $Co(NO_3)_2Aq + NaOHAq = Co\left\langle{}^{OH}_{NO_3}\right. + NaNO_3Aq$ *b*) $Co\left\langle{}^{OH}_{NO_3}\right. + NaOHAq = Co(OH)_2 + NaNO_3Aq$ *c*) $2Co(OH)_2 + O + H_2O = 2Co(OH)_3$	
5. NH_4OH	Bluish precipitate soluble in excess (cf. test 4).	
6. KCN	A brownish precipitate of Cobaltous Cyanide comes down soluble in excess to give first Potassium Cobaltocyanide, which by oxidation passes into Potassium Cobalticyanide. *a*) $Co(NO_3)_2Aq + 2KCNAq = Co(CN)_2 + 2KNO_3Aq$ *b*) $Co(CN)_2 + 4KCN = \underset{\text{Potassium Cobaltocyanide.}}{\underline{K_4Co(CN)_6}}$ *c*) $K_4Co(CN_6 + O + H_2O = \underset{\text{Potassium Cobalticyanide}}{\underline{2K_3Co(CN)_6}} + 2KOH$	Potassium Cobaltocyanide and Cobalticyanide are chemical analogues of Potassium Ferro- and Ferricyanide respectively.
*7. **KCN, NaOH,** and **Br**	No precipitate. This is an important distinction from Nickel.	Cf. Nickel (p. 150).
8. KNO_2 (and Acetic Acid).	Yellow crystalline precipitate of Potassium Cobaltinitrite. $Co(NO_3)_2Aq + 7KNO_2 + 2CH_3COOH = K_3Co(NO_2)_6 + 2CH_3COOK + 2KNO_3 + H_2O + NO$	Distinction from Ni.
9. NH_4SCN	If a conc. solution of Ammonium Thiocyanate is added to a conc. solution of a Cobaltous Salt, a blue coloration appears due to formation of Ammonium Cobaltous Thiocyanate. This subs, is soluble in a mixture of amyl, alcohol, and ether.	Distinction from Ni.
10. Charcoal.	Reduction on Charcoal yields Cobalt as a black powder which is slightly magnetic.	
*11. Borax bead.	A bright sapphire blue bead is obtained.	(Cf. Cu, p. 128).

Summary regarding Cobalt and Cobalt Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Co	Metallic Cobalt	Nearly silvery white, with faint pink tint.	Insoluble in water. Soluble in acids (esp. HNO_3Aq).	Reduction.

Note.—Only Cobaltous ($Co^{\cdot\cdot}$) Salts are usually met with, Cobaltic salts being completely decomposed by water.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
$Co(NO_3)_2 . 6H_2O$	**Cobalt(ous) Nitrate**	Hydrated substance is pink, but anhydrous subs. is blue.	Soluble in water, giving a pink solution.	2. 3
$CoCl_2 . 6H_2O$	**Cobalt(ous) Chloride**	do.	do.	2. 3
($CoBr_2$	Cobalt Bromide	do.	do.	2. 3)
CoI_2	Cobaltous Iodide	do.	do.	2. 3
$CoSO_4 . 7H_2O$	**Cobaltous Sulphate**	do.	do.	2. 3
$Co(C_2H_3O_2)_2$	Cobaltous Acetate	do.	do.	2. 3
$CoCO_3$	Cobalt Carbonate	Pink solid.	Soluble in acids with decomposition.	4
$Co(CN)_2$	Cobalt Cyanide	Brownish solid.	Soluble in acids.	4
CoC_2O_4	Cobalt Oxalate	Pink solid.	do.	4
$Co_3(PO_4)_2$	Cobalt Phosphate	Bluish solid.	do.	4
CoS	**Cobaltous Sulphide**	Black solid.	Soluble in conc. acids and in HCl + crystal of $KClO_3$.	4
CoO	Cobaltous Oxide	Black solid.	Soluble in acids.	Heat Cobaltous Hydroxide
Co_3O_4	Commercial Oxide of Cobalt	Black solid.	do.	Strongly ignite Nitrate.
Co_2O_3	Cobaltic Oxide	Black powder—acts as catalytic agent.	do.	Heat Nitrate cautiously or Cobaltic Hydoxide.

Summary of Reactions for Zinc. $Zn^{\cdot\cdot}$. 65.

Use a solution of **Zinc Sulphate** or **Zinc Chloride.**

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	
2. H_2S (in presence of HCl)	No precipitate.	
*3. $(NH_4)_2S$	**White precipitate** of **Zinc Sulphide**, ZnS. $ZnSO_4Aq + (NH_4)_2SAq = ZnS + (NH_4)_2SO_4Aq$	
4. NH_4OH	**White precipitate** of **Zinc Hydroxide**, $Zn(OH)_2$, soluble in Ammonium Chloride, NH_4Cl. $ZnSO_4Aq + 2NH_4OHAq = Zn(OH)_2 + (NH_4)_2SO_4Aq$	
*5. KOH or NaOH	**White precipitate** of **Zinc Hydroxide**, soluble in excess of reagent, forming a zincate. *a*) $ZnSO_4Aq + 2KOHAq = Zn(OH)_2 + K_2SO_4Aq$ *b*) $Zn(OH)_2 + 2KOHAq = Zn(OK)_2Aq + 2H_2O$	Cf. Al.
*6. $K_3Fe(CN)_6$	**Orange precipitate** of **Zinc Ferricyanide.** $3ZnSO_4Aq + \underbrace{2K_3Fe(CN)_6Aq}_{\text{Potassium Ferricyanide}} = \underbrace{Zn_3[Fe(CN)_6]_2}_{\text{Zinc Ferricyanide}} + 3K_2SO_4Aq$	
7. $K_4Fe(CN)_6$	**White precipitate** of **Zinc Ferrocyanide.** $2ZnSO_4Aq + K_4Fe(CN)_6Aq = Zn_2[Fe(Cn)_6] + 2K_2SO_4Aq$	
*8. $Co(NO_3)_2$	Moisten a few square centimetres of filter paper with a concentrated solution of the substance and then with a solution of Cobalt Nitrate. After ignition in Bunsen flame a **green residue** is left. *Or*, Heat on Charcoal, moisten with Cobalt Nitrate, and reheat.—Yellowish green mass is obtained.	
9. Ignition	The Oxide is white when cold, but turns yellow on heating, and white again on cooling.	

Summary regarding Zinc and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Zn	Metallic Zinc, m. pt. 430° C.	Silvery metal. Met with in many forms, e.g. stick, granulated, foil, and as a bluish grey powder.	Soluble in acids.	Reduction by Carbon.
$ZnCl_2$	Zinc Chloride	White solid—anhydrous compound is deliquescent and caustic.	Soluble in water.	1. 2. 3
$ZnBr_2$	Zinc Bromide	White solid.	do.	1. 2
ZnI_2	Zinc Iodide	White solid.	do.	1. 2
$Zn(NO_3)_2$	Zinc Nitrate	do.	do.	1. 2. 3
$ZnSO_4 . 7H_2O$	Zinc Sulphate	do.	do.	1. 2. 3
$ZnCO_3$	Zinc Carbonate (natural substance is called Calamine)	do.	Soluble in acids with decomposition.	4
$Zn_3(PO_4)_2$	Zinc Phosphate	do.	Soluble in acids.	4
ZnO	Zinc Oxide (Zinc white)	do. Turns yellow on heating, and white again on cooling.	do.	Heat metal or Carbonate.
ZnS	Zinc Sulphide (natural substance is called Blende)	White solid.	Soluble in HCl. H_2S is evolved.	4

Alloys:—Brass, 20-40 % Zn. Cu.
Bronze, Cu. Zn. Sn. Pb.
German Silver, Cu. Zn. Ni.

Summary of Reactions for Manganese. $Mn^{\cdot\cdot}$. 55.

Use a solution of **Manganous Sulphate** ($MnSO_4$) or **Chloride** ($MnCl_2$).

Reagent.	Results observed.	Remarks.
1. **HCl**	No precipitate.	
2. **H_2S** (in presence of **HCl**)	No precipitate.	
*3. **$(NH_4)_2S$**	**Salmon pink precipitate of Manganous Sulphide** (MnS). $MnSO_4Aq + (NH_4)_2SAq = MnS + (NH_4)_2SO_4Aq$	
*4. **NH_4OH, KOH,** or **NaOH**	**White precipitate** of **Manganous Hydroxide**, $Mn(OH)_2$, which rapidly turns brown on shaking with air, owing to formation of Manganic Hydroxide, $Mn(OH)_3$. *a*) $MnSO_4Aq + 2NH_4OHAq = \underset{\text{Manganous Hydroxide.}}{\overline{Mn(OH)_2}} + (NH_4)_2SO_4Aq$ *b*) $2Mn(OH)_2 + H_2O + \underset{\text{from air}}{\overline{O}} = \underset{\text{Manganic Hydroxide.}}{\overline{2Mn(OH)_3}}$	No precipitate is obtained on adding NH_4OH to a manganous salt if a sufficiency of Ammonium Chloride be present.
*5. **Bleaching powder**	A **brown precipitate** of the **hydrated Peroxide** of Manganese—$MnO_2 . xH_2O$—is obtained. $MnSO_4Aq + CaOCl_2{}^* + Ca(OH)_2{}^* = \mathbf{MnO_2} + CaCl_2Aq + CaSO_4Aq + H_2O$	* Bleaching powder is chiefly a mixture of $CaOCl_2$ and $Ca(OH)_2$. In solution it behaves as if it were a mixture of $Ca(OCl)_2$, $CaCl_2$, and $Ca(OH)_2$.
6. **Na_2O_2** or **KNO_3**	On heating the dry ignited powdered substance in a tube with Sodium Peroxide or Potassium Nitrate, the Manganese Compound is oxidized to greenish Manganate, K_2MnO_4, which dissolves in water, giving first a green tint, which changes to pink on dilution owing to conversion to Permanganate, $KMnO_4$.	
*7. **Borax bead**	**Amethyst**-coloured **bead** is obtained.	

Summary regarding Manganese and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Mn	Metallic Manganese	Greyish metal.	Soluble in acids.	Reduction by C or Al.
$MnCl_2,4H_2O$	**Manganous Chloride**	Light pink solid.	Soluble in water.	1. 2
$Mn(NO_3)_2$	Manganous Nitrate	do.	do.	1. 2
$MnSO_4 . 4H_2O$	**Manganous Sulphate**	do.	do.	1. 2
$MnCO_3$	**Manganous Carbonate**	Nearly white powder (slowly turns brown in air).	Soluble in acids with decomposition.	4
$Mn_3(PO_4)_2$	Manganous Phosphate	Nearly white solid.	Soluble in acids.	4
(MnO	Manganous Oxide	Greenish powder.	do.)	
Mn_2O_3	Occurs native **Braunite**	Brownish solid.	Soluble in acids.	
Mn_3O_4	Occurs native **Hausmannite**	Black solid.	do.	Decomposition of MnO_2 by heat.
MnO_2	**Manganese Peroxide** (Natural substance is called **Pyrolusite**).	Black powder, granules, or lumps.	Soluble in HClAq on warming to give $MnCl_2$ and Chlorine.	
Na_2MnO_4	Sodium Manganate	Green solid.	Soluble in water to give green solutions, which turn pink on dilution owing to conversion to Permanganate.	
K_2MnO_4	Potassium Manganate	do.		
$KMnO_4$	**Potassium Permanganate**	Dark purple solid.	Soluble in water to give a purple solution.	
$NaMnO_4$	Sodium Permanganate	do.	do.	

Group V. Ba. Sr. Ca.

Summary of Reactions for Barium. Ba$^{\cdot\cdot}$. 137.

Use a solution of **Barium Nitrate** or **Chloride.**

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	Conc. HClAq precipitates $BaCl_2$ from strong solutions.
2. H_2S (in presence of HCl)	No precipitate.	
3. NH_4OH, KOH, or NaOH	**White precipitate of Barium Hydroxide** may form in concentrated solution, but not if Ammonium Chloride be present. $BaCl_2Aq + 2NH_4OHAq = \mathbf{Ba(OH)_2} + 2NH_4ClAq$	
(4. $(NH_4)_2S$	White precipitate of Barium Hydroxide might be obtained from very conc. solutions, but not if Ammonium Chloride be present.	([illegible]it as a test.)
*5. $(NH_4)_2CO_3$	**White precipitate of Barium Carbonate** is formed. $BaCl_2Aq + (NH_4)_2CO_3Aq = \mathbf{BaCO_3} + 2NH_4ClAq$	
*6. K_2CrO_4	**Yellow precipitate of Barium Chromate** ($BaCrO_4$) is obtained, insoluble in Acetic Acid. $BaCl_2Aq + K_2CrO_4Aq = \mathbf{BaCrO_4} + 2KClAq$	Distinction from Strontium and Calcium.
*7. $CaSO_4$	**Immediate white precipitate of Barium Sulphate** ($BaSO_4$). $BaCl_2Aq + CaSO_4Aq = \mathbf{BaSO_4} + CaCl_2Aq$	Compare Strontium.
*8. H_2SO_4	**White precipitate of Barium Sulphate.** $Ba(NO_3)_2Aq + H_2SO_4Aq = \mathbf{BaSO_4} + 2HNO_3Aq$	
9. $(NH_4)_2C_2O_4$	**White precipitate of Barium Oxalate.** $BaCl_2Aq + (NH_4)_2C_2O_4Aq$ $= \mathbf{BaC_2O_4} + 2NH_4ClAq$	
*10. Platinum wire test	**Apple green flame.**	On heating a Barium Compound on Platinum wire use concentrated HCl, and note remark on p. 116.

Summary regarding Barium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
(Ba	Metallic Barium	Greyish white metal.	Reacts with water to form $Ba(OH)_2$ and Hydrogen.)	Electrolysis of fused Chloride.
$BaCl_2 . 2H_2O$	Barium Chloride	White crystalline solid.	Soluble in water.	1. 2
$BaBr_2$	Barium Bromide	do.	do.	1. 2
BaI_2	Barium Iodide	do.	do.	1. 2
$Ba(NO_3)_2$	Barium Nitrate	do.	do.	1. 2
$BaCO_3$	Barium Carbonate (native subs. is called Witherite)	White powder (or native subs. in lumps).	Soluble in acids.	4
$BaSO_4$	Barium Sulphate (native subs. is called Heavy spar or Barytes)	White powder or massive.	Insoluble in water and acids. To get into solution two methods can be used : *a*) Fuse up with Na_2CO_3. $BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$ *b*) Heat up with Carbon. $BaSO_4 + 4C = BaS + 4CO$	4
$BaSO_3$	Barium Sulphite	White solid.	Soluble in acids with decomposition.	4
$Ba_3(PO_4)_2$	Barium Phosphate	do.	Soluble in acids.	4
BaC_2O_4	Barium Oxalate	do.	do.	4
$BaCrO_4$	Barium Chromate	Yellow solid.	Soluble in HCl or HNO_3 but not in Acetic Acid.	4
BaO	Barium Oxide	Nearly white solid.	Reacts with water to form the hydroxide. $BaO + H_2O = Ba(OH)_2$	Heat the Nitrate.
$Ba(OH)_2$	Barium Hydroxide (Baryta)	White solid.	Soluble in water.	Oxide and water.
BaO_2	Barium Peroxide	do.	do.	Heat Oxide in air.
BaS	Barium Sulphide	do.	Nearly insol. in water, but slowly undergoes hydrolysis, forming $Ba(OH)_2$ and $Ba(SH)_2$—soluble in acids with decomposition.	$BaSO_4$ and C.

Summary of Reactions for Strontium. $Sr^{\cdot\cdot}$. 87.

Use a solution of **Strontium Chloride** or **Nitrate.**

Reagent.	Results observed.	Remarks.
1. **HCl**	No precipitate.	
2. **H_2S** (in presence of **HCl**)	No precipitate.	
3. **NH_4OH, KOH,** or **NaOH**	A **white precipitate** of **Strontium Hydroxide,** $Sr(OH)_2$, might form from a concentrated solution, but not in presence of excess of Ammonium Chloride. $SrCl_2Aq + 2NH_4OHAq = \mathbf{Sr(OH)_2} + 2NH_4Cl$	Of no value as a test.
4. **$(NH_4)_2S$**	No precipitate.	
*5. **$(NH_4)_2CO_3$**	**White precipitate** of **Strontium Carbonate,** $SrCO_3$. $SrCl_2Aq + (NH_4)_2CO_3Aq = \mathbf{SrCO_3} + 2NH_4ClAq$	
*6. **$CaSO_4$**	**White precipitate** of **Strontium Sulphate,** $SrSO_4$, forms slowly. $SrCl_2Aq + CaSO\ Aq = \mathbf{SrSO_4} + CaCl_2Aq$	Allow to stand ten minutes if necessary.
7. **H_2SO_4**	**White precipitate** of **Strontium Sulphate,** $SrSO_4$ (slowly from dilute solutions). $SrCl_2Aq + H_2SO_4Aq = \mathbf{SrSO_4} + 2HClAq$	
8. **K_2CrO_4**	As a rule no precipitate is obtained, but a yellow precipitate may form from very concentrated solutions, easily soluble in Acetic Acid. $SrCl_2Aq + K_2CrO_4Aq = \mathbf{SrCrO_4} + 2KClAq$	Distinction from Barium.
9. **$(NH_4)_2C_2O_4$**	**White precipitate** of **Strontium Oxalate,** SrC_2O_4. $SrCl_2Aq + (NH_4)_2C_2O_4Aq = \mathbf{SrC_2O_4} + 2NH_4ClAq$	
*10. **Platinum wire test**	**Crimson flame.**	Calcium gives a less brilliant, and Lithium a deeper red flame. Characteristic lines in spectra.

Summary regarding Strontium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
(Sr	Metallic Strontium	Not met with.)		
$SrCl_2$	**Strontium Chloride**	White solid.	Soluble in water.	1. 2
$SrBr_2$	Strontium Bromide	do.	do.	1. 2
SrI_2	Strontium Iodide	do.	do.	1. 2
$Sr(NO_3)_2$	**Strontium Nitrate**	do.	do.	1. 2
$SrCO_3$	**Strontium Carbonate** (native substance is called **Strontianite**)	do.	Soluble in acids with decomposition.	4
$SrSO_4$	**Strontium Sulphate** (native substance is called **Celestine**)	do.	Slightly soluble in water (1 part in 7,000).	4
$Sr_3(PO_4)_2$	Strontium Phosphate	do.	Soluble in acids.	4
($SrCrO_4$	Strontium Chromate	Yellow solid.	Sparingly soluble in water.	1. 4)
SrO	Strontium Oxide	White solid.	Reacts with water to form the hydroxide.	Heat the Carbonate.
$Sr(OH)_2$	**Strontium Hydroxide**	do.	Sparingly soluble in water—solution is strongly alkaline in reaction.	Heat the Carbonate in superheated steam.

Summary of Reactions for Calcium. Ca$^{\cdot\cdot}$. 40.

Use a solution of **Calcium Chloride** ($CaCl_2$) or **Nitrate** ($Ca(NO_3)_2$).

Reagent.	Results observed.	Remarks.
1. HCl	No precipitate.	
2. H_2S (in presence of HCl)	No precipitate.	
3. $(NH_4)_2S$	No precipitate.	
4. NH_4OH, KOH, or NaOH	A white precipitate of **Calcium Hydroxide**, $Ca(OH)_2$, may form from concentrated solutions, but not in presence of excess of Ammonium Chloride. $CaCl_2Aq + 2NH_4OHAq = \mathbf{Ca(OH)_2} + 2NH_4ClAq$	
*5. $(NH_4)_2CO_3$	**White precipitate** of **Calcium Carbonate**, $CaCO_3$. $CaCl_2Aq + (NH_4)_2CO_3Aq = \mathbf{CaCO_3} + 2NH_4ClAq$	
*6. $CaSO_4$	**No precipitate.**	**Distinction from Barium and Strontium.**
7. H_2SO_4	A white precipitate may form depending upon the concentration of the solution. $CaCl_2Aq + H_2SO_4Aq = \mathbf{CaSO_4} + 2HClAq$	
8. K_2CrO_4	A slight yellow precipitate may form from concentrated solutions which is easily soluble in Acetic Acid. Usually no pp. forms. $CaCl_2Aq + K_2CrO_4Aq = CaCrO_4 + 2KClAq$	**Distinction from Barium.**
*9. $(NH_4)_2C_2O_4$	White precipitate of Calcium Oxalate, CaC_2O_4, insoluble in Acetic Acid. $CaCl_2Aq + (NH_4)_2C_2O_4Aq = \mathbf{CaC_2O_4} + 2NH_4ClAq$	
*10. Platinum wire test	On moistening the substance with concentrated Hydrochloric Acid, and heating on Platinum wire in the oxidizing flame – **Brick red** flame.	The flame is less brilliant than that of Strontium or Lithium.

Summary regarding Calcium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Ca	**Metallic Calcium**	Grey solid.	Reacts with water to give Hydrogen and $Ca(OH)_2$. $Ca + 2HOH = Ca(OH)_2 + H_2$	Electrolysis of $CaCl_2$.
$CaCl_2$	**Calcium Chloride**	Met with generally as a granular solid, $CaCl_2 . 2H_2O$—also in lumps and in crystals.	Very soluble in water.	1. 2
$CaBr_2$	Calcium Bromide	White solid.	Soluble in water.	1. 2
CaI_2	Calcium Iodide	do.	do.	1. 2
$Ca(NO_3)_2$	**Calcium Nitrate**	do.	do.	1. 2
$CaCO_3$	**Calcium Carbonate (Marble, Limestone, Calc-spar)**	Met with in many forms — Limestone, Coral, Marble, Calc-spar, Chalk.	Soluble in acids with decomposition.	4
$CaSO_4$	**Calcium Sulphate (Gypsum, Selenite Anhydrite, Plaster of Paris)**	Occurs in various forms, generally as a white solid. Gypsum and Selenite have the composition $CaSO_4 . 2H_2O$.	Slightly soluble in water—about 1 part in 500.	4
$CaSO_3$	Calcium Sulphite	White solid.	Soluble in acids.	4
$Ca_3(PO_4)_2$	**Calcium Phosphate**	do.	do.	4
$Ca . C_2O_4$	**Calcium Oxalate**	do.	do.	4
$Ca(C_2H_3O_2)_2$ or $(CH_3.COO)_2Ca$	**Calcium Acetate**	do.	Soluble in water.	1. 2
$Ca . C_4H_4O_6$	**Calcium Tartrate**	do.	Soluble in acids.	4
$CaCrO_4$	Calcium Chromate	Light yellow solid.	Soluble in water.	1. 2
CaO	**Calcium Oxide (Quicklime)**	White solid if pure.	**Reacts vigorously with water to form slaked lime, Calcium Hydroxide.** $CaO + H_2O = Ca(OH)_2$.	Heat $CaCO_3$.
$Ca(OH)_2$	**Calcium Hydroxide (Slaked Lime)**	White solid if pure.	Soluble in water to give 'Lime-water'.	Water and CaO.
CaO_2	Calcium Peroxide	White solid.		
CaS	**Calcium Sulphide**	do.	Nearly insoluble in water, but undergoes hydrolysis to give $Ca(OH)_2$ and $Ca(SH)_2$. Soluble in acids, giving off H_2S.	$CaSO_4$ and C.
(CaF_2	Calcium Fluoride (Fluor-spar).	White solid, but natural subs. is often in transparent crystals tinted by metallic oxides.	Soluble in acids, often with difficulty.	4)

Group VI. Mg. NH$_4$. K. Na.

Summary of Reactions for Magnesium. Mg$^{\cdot\cdot}$. 24.

Use a solution of **Magnesium Sulphate** ($MgSO_4$) or **Magnesium Chloride** ($MgCl_2$).

Reagent.	Results observed.	Remarks.
1. **HCl**	No precipitate.	
2. **H_2S** (in presence of **HCl**)	No precipitate.	
*3. **NH_4OH, KOH,** or **NaOH**	White precipitate of Magnesium Hydroxide, $Mg(OH)_2$, which dissolves on addition of Ammonium Chloride, NH_4Cl. e. g. $MgSO_4Aq + 2NH_4OHAq = Mg(OH)_2 + (NH_4)_2SO_4Aq$	
4. **$(NH_4)_2S$**	No precipitate.	
5. **$(NH_4)_2CO_3$**	White precipitate of Magnesium Carbonate ($MgCO_3$) may form, which dissolves in Ammonium Chloride solution. e. g. $MgSO_4Aq + (NH_4)_2CO_3Aq = MgCO_3 + (NH_4)_2SO_4Aq$	
(6. **Na_2HPO_4**	White precipitate of Magnesium Phosphate ($MgHPO_4$ or $Mg_3(PO_4)_2$), the exact constitution of which depends upon the conditions of the experiment. $MgSO_4Aq + Na_2HPO_4Aq = MgHPO_4 + Na_2SO_4Aq$)	
*7. **Na_2HPO_4** and **NH_4OH**	**White precipitate** of **Magnesium, Ammonium Phosphate.** $MgSO_4Aq + NH_4OHAq + Na_2HPO_4Aq = \mathbf{MgNH_4PO_4} + Na_2SO_4Aq$	Group test for Magnesium (see pp. 198 and 200).
*8. **$Co(NO_3)_2$**	Moisten a few square centimetres of filter paper with the concentrated solution, pour over the same area a solution of Cobalt Nitrate, and then burn in oxidizing flame. **Pink residue.**	

Summary regarding Magnesium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Mg	**Metallic Magnesium**	Silvery white metal. Met with as foil, powder, ribbon, wire.	Soluble in acids.	Electrolysis of Chloride.
$MgCl_2$	**Magnesium Chloride**	White solid.	Soluble in water.	1. 2. 3
$MgBr_2$	**Magnesium Bromide**	do.	do.	1. 2
MgI_2	Magnesium Iodide	do.	do.	1. 2
$Mg(NO_3)_2$	**Magnesium Nitrate**	do.	do.	1. 2
$MgSO_4 . 7H_2O$	**Magnesium Sulphate**	do.	do.	1. 2. 3
$MgCO_3$	**Magnesium Carbonate** (Natural subs. is called **Magnesite.** The double compound, $MgCa(CO_3)_2$, is called **Dolomite**)	do.	Soluble in acids with decomposition, CO_2 being evolved.	4
$Mg_3(PO_4)_2$	**Magnesium Phosphate**	do.	Soluble in acids.	4
MgC_2O_4	Magnesium Oxalate	do.	do.	4
$Mg(C_2H_3O_2)_2$ or **$(CH_3COO)_2Mg$**	**Magnesium Acetate**	do.	Soluble in water.	1. 2
MgO	**Magnesium Oxide (Magnesia)**	do. Glows with white light on heating strongly.	Soluble in acids.	Heat the Carbonate.
$Mg(OH)_2$	**Magnesium Hydroxide**	White solid.	Very slightly soluble in water; soluble in acids.	4
$Mg(NH_4)PO_4$	Magnesium Ammonium Phosphate	do.	Very slightly soluble in water; less soluble in weak Ammonia.	4

Summary of Reactions for the Radicle $NH_4^{\cdot}$.

Use a solution of **Ammonium Chloride** (NH_4Cl), **Ammonium Sulphate** ($(NH_4)_2SO_4$), or **Ammonium Nitrate** (NH_4NO_3).

Reagent.	Results observed.	Remarks.
1. **HCl**	No precipitate.	
2. **H_2S** (in presence of **HCl**)	do.	
3. **NH_4OH**	do.	
4. **$(NH_4)_2CO_3$**	do.	
5. **Na_2HPO_4**	do.	
*6. **KOH** or NaOH or Na_2CO_3	On boiling an Ammonium Compound with Potassium or Sodium Hydroxide, Ammonia is evolved. $NH_4ClAq + KOHAq = \mathbf{NH_3} + KClAq + H_2O$	The odour of the evolved gas is characteristic, and the alkaline reaction towards moist red litmus paper.
7. **$NaHC_4H_4O_6$** or **$H_2C_4H_4O_6$**	With concentrated solutions of Ammonium Salts, Sodium Hydrogen Tartrate or Tartaric Acid gives a **white precipitate of Ammonium Hydrogen Tartrate**, $NH_4 . H . C_4H_4O_6$. $NH_4ClAq + H_2C_4H_4O_6Aq$ $= \mathbf{NH_4 . HC_4H_4O_6} + HClAq$	The test is rarely carried out, and is quite unnecessary, as Test 6 is conclusive. It must be kept in view to prevent mistake in the case of Potassium (p. 168).
8. **H_2PtCl_6**	**Yellow precipitate of Ammonium Chloroplatinate**, $(NH_4)_2PtCl_6$. $H_2PtCl_6Aq + 2NH_4ClAq$ $= \mathbf{(NH_4)_2PtCl_6} + 2HClAq$	Chloroplatinic Acid is too expensive for general use. Potassium Salts give a similar precipitate (p. 168).
*9. **Nessler's Reagent** (alkaline solution of HgI_2 in KIAq)	**Brown precipitate of Dimercuric Ammonium Iodide**, soluble in excess of Ammonium Salt. $NH_4ClAq + 2[HgI_2 . 2KI]Aq + 4KOHAq$ $= \mathbf{NHg_2I . H_2O} + 3H_2O + 7KIAq + KClAq$	This test is very delicate and will detect mere traces of Ammonium Salt (or Ammonia).

Summary regarding Ammonium ($NH_4^{\cdot}$) and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
NH_4	The group NH_4— is not met with : if set free it splits up into NH_3 and Hydrogen.			
NH_4Cl	Ammonium Chloride Sal Ammoniac	White solid.	Soluble in water.	
NH_4Br	Ammonium Bromide	do.	do.	1. 2
NH_4I	Ammonium Iodide	do.	do.	1. 2
NH_4NO_3	Ammonium Nitrate	do.	do.	1. 2
NH_4HSO_4	Ammonium Hydrogen Sulphate	do.	do.	1. 2
$(NH_4)_2SO_4$	Ammonium Sulphate	do.	do.	1. 2
$(NH_4)_2SO_3$	Ammonium Sulphite	do.	do.	
$(NH_4)_2CO_3$	Ammonium Carbonate	do.	do.	
$(NH_4)_2HPO_4$	Diammonium Hydrogen Phosphate	do.	do.	
$(NH_4)_2CrO_4$	Ammonium Chromate	Yellow solid.	do.	1. 2
$(NH_4)_2Cr_2O_7$	Ammonium Dichromate	Orange.	do.	1. 2
[$(NH_4)_2O$	Ammonium Oxide	Does not exist. Splits into NH_3 and H_2O at ordinary temp.]		
NH_4OH	Ammonium Hydroxide	Met with as a solution in water.	Solution in water smells of Ammonia.	NH_3 and H_2O.
$(NH_4)_2S$	Ammonium Sulphide	White solid.	Soluble in water. Colourless solution.	NH_3 and H_2S.
$(NH_4)_2S_x$	Ammonium Polysulphide	Yellow solid	Soluble in water. Yellow solution.	
$NH_4HC_2O_4$	Ammonium Hydrogen Oxalate	White solid.	Soluble in water.	1. 2
$(NH_4)_2C_2O_4$	Ammonium Oxalate	do.	do.	1. 2
$CH_3.COONH_4$	Ammonium Acetate	do.	do.	1. 2
$NH_4H.C_4H_4O_6$	Ammonium Hyd. Tartrate	do.	Sparingly soluble in water.	4
$(NH_4)_2C_4H_4O_6$	Ammonium Tartrate	do.	Soluble in water.	1. 2

Summary of Reactions for Potassium. $K^{\cdot}$. 39.

Use a solution of **Potassium Nitrate** (KNO_3), **Chloride** (KCl), or **Sulphate** (K_2SO_4).

Reagent.	Results observed.	Remarks.
1. **HCl**	No precipitate.	
2. **H_2S** (in presence of **HCl**)	do.	
3. **NH_4OH**	do.	
4. **$(NH_4)_2S$**	do.	
5. **$(NH_4)_2CO_3$**	do.	
6. **Na_2HPO_4**	do.	
*7. **$NaHC_4H_4O_6$** or **$H_2C_4H_4O_6$**	Sodium Hydrogen Tartrate or Tartaric Acid gives a **white precipitate of Potassium Hydrogen Tartrate** on addition to a concentrated solution of a Potassium Salt. $KClAq + NaHC_4H_4O_6Aq = \mathbf{KH \cdot C_4H_4O_6} + NaClAq$	If the precipitate does not form on shaking the tube, scratch the tube inside the liquid with a glass rod. The solution of Potassium Salt should be as concentrated as possible.
*8. **H_2PtCl_6**	Chloroplatinic Acid, H_2PtCl_6, gives a **yellow crystalline precipitate of Potassium Chloroplatinate**, K_2PtCl_6, on addition to a concentrated solution of a Potassium Salt. $2KNO_3 + H_2PtCl_6Aq = K_2PtCl_6 + 2HNO_3Aq$	(cf. NH_4).
*9. **Platinum wire test**	**Violet flame.**	Notes. *a*) **Pb, As, Sb, and Bi all give blue flames** which might be mistaken for the violet flame of Potassium. *b*) **Traces of Sodium are frequently present and may mask the Potassium flame.** Use a blue glass or a potassioscope.

Summary regarding Potassium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
K	Metallic Potassium, m. pt. 53° C.	Bluishwhite lustre —easily tarnished. Kept under petroleum oil.	Reacts with water. $2K + 2HOH = 2KOH + H_2$	Electrolysis of KCl, &c.
KCl	**Potassium Chloride**	White cryst. solid.	Soluble in water.	1. 2
KBr	**Potassium Bromide**	do.	do.	KOH and Br_2.
KI	**Potassium Iodide**	do.	do.	KOH and I_2.
KNO_3	**Potassium Nitrate**	do.	do.	1. 2
KNO_2	**Potassium Nitrite**	Nearly white solid. Generally faint yellow tint.	do.	KNO_3 and Pb.
$KHSO_4$	**Potassium Hyd. Sulphate**	White solid—acid reaction.	do.	1
K_2SO_4	**Potassium Sulphate**	White solid.	do.	1. 2
K_2SO_3	Potassium Sulphite	do.	do.	1
$KHCO_3$	**Potassium Hyd. Carbonate**	do.	do.	1
K_2CO_3	**Potassium Carbonate**	do.	do.	1, &c.
K_2HPO_4	**Dipotassium Hyd. Phosphate**	do.	do.	1
K_2CrO_4	**Potassium Chromate**	Bright yellow solid.	do.	1
$K_2Cr_2O_7$	**Potassium Dichromate**	Deep orange solid.	do.	1
(K_2O	**Potassium Oxide**)	Nearly white solid.	Reacts with water to give Caustic Potash, KOH.	KNO_3 and K.
KOH	**Potassium Hydroxide (Caustic Potash)**	White deliquescent solid—soapy feel, caustic.	Soluble in water—strongly alkaline reaction.	K_2CO_3 and $Ca(OH)_2$.
K_2S	Potassium Sulphide	White solid.	Soluble in water.	1
K_2S_4	Potassium Polysulphide	Yellow solid.	Sol. in water. Yellow solution.	K_2CO_3 and S.
KHC_2O_4	**Potassium Hyd. Oxalate**	White cryst. solid —acid reaction.	Soluble in water.	
$K_2C_2O_4$	**Potassium Oxalate**	White cryst. solid.	do.	1. 2
CH_3COOK	**Potassium Acetate**	do. deliquescent.	do.	1. 2
$KH.C_4H_4O_6$	**Potassium Hyd. Tartrate**	White cryst. solid —acid reaction.	Sparingly soluble in water.	1
$K_2C_4H_4O_6$	**Potassium Tartrate**	White cryst. solid.	Soluble in water.	1. 2
KCN	**Potassium Cyanide**	Whitesolid. Odour of bitter almonds, alkaline reaction.	do.	
$KMnO_4$	**Potassium Permanganate**	Deep violet solid.	Soluble in water. Reddish violet solution.	
$K_4Fe(CN)_6$	**Potassium Ferrocyanide**	Light yellow cryst. solid.	Soluble in water. Yellow solution.	
$K_3Fe(CN)_6$	**Potassium Ferricyanide**	Reddish orange solid.	Soluble in water. Brown solution.	
$KCNS$	**Potassium Sulphocyanide**	White cryst. solid.	Soluble in water.	
$KSbO_3$	**Potassium Metantimoniate**	White solid.	Sparingly soluble in water.	
K_2SiO_3	**Potassium Metasilicate**	White glassy solid.	do.	

Summary of Reactions for Sodium. $Na^{\cdot}$.

Use a solution of **Sodium Chloride** ($NaCl$), **Nitrate** ($NaNO_3$), or **Sulphate** (Na_2SO_4).

Reagent.	Results observed.	Remarks.
1. **HCl**	No precipitate.	
2. **H_2S** (in presence of **HCl**)	do.	
3. **NH_4OH**	do.	
4. **$(NH_4)_2S$**	do.	
5. **$(NH_4)_2CO_3$**	do.	
6. **Na_2HPO_4**	do.	
*7. **Flame test**	On heating a small quantity of substance on Platinum wire in oxidizing flame an **intense yellow flame** is obtained if Sodium is present.	**Note.** Sodium is present in traces in most compounds; traces are also present in the air, on bench, &c., so that a feeble Sodium flame is readily given by nearly all substances. The reaction indicating the presence of Sodium is nevertheless quite definite if properly carried out. The solid should always be used. If a solution is given, evaporate carefully to dryness before taking a trace upon Platinum wire.
[8. $KSbO_3$ Potassium Metantimoniate	White precipitate of Sodium Metantimoniate, $Na\ SbO_3$. $KSbO_3Aq + NaClAq = NaSbO_3 + KClAq$ This test is hardly satisfactory and is best omitted by a beginner.]	

Summary regarding Sodium and its notable Compounds,

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
Na	Metallic Sodium, m. pt. 96° C.	Brilliant yellowish lustre, but tarnishes by oxidation on exposure to air. Kept under petroleum oil.	Reacts vigorously with water, setting free Hydrogen.	Electrolysis, &c.
$NaCl$	Sodium Chloride	White cryst. solid.	Soluble in water.	1. 2
$NaBr$	Sodium Bromide	do.	do.	
NaI	Sodium Iodide	White cryst. (deliquescent).	do.	
$NaNO_3$	Sodium Nitrate	do.	do.	1. 2
$NaNO_2$	Sodium Nitrite	Nearly white solid—generally faint yellow tint.	do.	$NaNO_3$ and Pb.
$NaHSO_4$	Sodium Hydrogen Sulphate Sodium Bisulphate	White cryst. solid—strongly acid reaction.	do.	1. 2
$Na_2SO_4 . 10H_2O$	Sodium Sulphate (Glauber's salt)	White cryst. solid.	do.	1. 2
Na_2SO_3	Sodium Sulphite	do.	do.	1
$Na_2S_2O_3 . 5H_2O$	Sodium Thiosulphate (often erroneously termed 'Hyposulphite')	do.	do.	Na_2SO_3 and S.
$NaHCO_3$	Sodium Hydrogen Carbonate Sodium Bicarbonate 'Baking Soda'	White powder.	Sparingly soluble in water. The Ammonia-Soda process depends upon this fact.	1. Ammonia-Soda process.

Summary regarding Sodium and its notable Compounds

(*continued*),

most of which might be met with in elementary analysis.

Formula.	Name.	Appearance and special properties.	Solubility.	General methods of preparation (see p. 120).
$Na_2CO_3 . 10H_2O$	Sodium Carbonate Soda Crystals Washing Soda	White cryst. efflorescent solid. Anhydrous Na_2CO_3 is a white powder.	Soluble in water.	1. Leblanc and Ammonia-Soda.
$Na_2HPO_4 . 12H_2O$	Sodium Phosphate	White cryst. solid.	do.	1. 2
(Na_2O	Sodium Oxide	Nearly white solid.	Reacts with water to give Caustic Soda.	$NaNO_3$ or Na_2O_2 & Na)
Na_2O_2	Sodium Peroxide	Light yellow powder.	Reacts with water to give Caustic Soda and Oxygen.	Direct union.
$NaOH$	Sodium Hydroxide Caustic Soda	White solid—sticks, powder, or lumps.	Soluble in water—strongly alkaline reaction, soapy feel.	
Na_2S	Sodium Sulphide	White cryst. solid.	Soluble in water.	1
Na_2S_x	Sodium Polysulphide	Yellow solid.	Soluble in water—yellow to reddish solution.	
$NaHC_2O_4$	Sodium Hyd. Oxalate	White cryst. solid—acid reaction.	Soluble in water.	1. 2
$Na_2C_2O_4$	Sodium Oxalate	White cryst. solid.	do.	1. 2
$CH_3.COONa.3H_2O$	Sodium Acetate	do.	do.	1. 2
$NaH . C_4H_4O_6$	Sodium Hyd. Tartrate Sodium Bitartrate	do.	do.	1. 2
$Na_2C_4H_4O_6$	Sodium Tartrate	do.	do.	1. 2
$NaCN$	Sodium Cyanide	White solid.	do.	
$NaSbO_3$	Sodium Metantimoniate	do.	Nearly insoluble in water, and its formation can be used as a test for Na, but unless in experienced hands is apt to give erroneous results.	
Na_2SiO_3	Sodium Silicate (Water glass)	Glassy solid.	Slightly soluble in water.	Heat SiO_2 and Na_2CO_3.

NOTE.—The wet tests for **soluble metallic Hydroxides** (i. e. tests for the free hydroxyl ion in solutions of metallic salts) are best considered after the tests for the acids (p. 238).

ANALYTICAL TABLES BASED UPON THE FOREGOING LISTS OF TESTS.

A study of the first and second reactions given for each metal in the preceding summaries will indicate clearly the reasons which have caused the metals to be separated into the six analytical groups summarized on p. 117. Put as concisely as possible the results are as follows:—

Metal in solution as part of a salt.	Reagent.	
	Hydrochloric Acid.	Sulphuretted Hydrogen in presence of HCl.
Silver	White pp. of Silver Chloride ($AgCl$).	Black pp. of Silver Sulphide (Ag_2S).
Mercurous, $Hg^{\cdot}$	White pp. of Mercurous Chloride ($HgCl$).	Black pp. of Mercuric Sulphide (HgS) and Mercury.
Lead	White pp. of Lead Chloride ($PbCl_2$).	Black pp. of Lead Sulphide (PbS).
Copper	No precipitate.	Black pp. of Copper Sulphide (CuS).
Mercuric, $Hg^{\cdot\cdot}$	No precipitate.	Black pp. of Mercuric Sulphide (HgS).
Bismuth	A white pp. of $BiOCl$ may form, but dissolves on adding more HCl and warming.	Deep brown pp. of Bismuth Sulphide (Bi_2S_3).
Cadmium	No precipitate.	Yellow pp. of Cadmium Sulphide (CdS).
Arsenious, $As^{\cdot\cdot\cdot}$	do.	Yellow pp. of Arsenious Sulphide (As_2S_3).
Arsenic, $As^{\cdot\cdot\cdot\cdot\cdot}$	do.	No pp. with Arsenic Compounds until reduced to Arsenious condition.
Antimony	A white pp. of $SbOCl$ may form, but dissolves on adding more HCl and warming.	Orange pp. of Antimonious Sulphide (Sb_2S_3).
Stannous, $Sn^{\cdot\cdot}$	No precipitate.	Brown pp. of Stannous Sulphide (SnS).
Stannic, $Sn^{\cdot\cdot\cdot\cdot}$	do.	Yellow pp. of Stannic Sulphide (SnS_2).
Aluminium	do.	No precipitate.
Ferrous, $Fe^{\cdot\cdot}$	do.	do.
Ferric, $Fe^{\cdot\cdot\cdot}$	do.	do.
Chromic	do.	do.
Zinc	do.	do.
Manganese	do.	do.
Nickel	do.	do.
Cobalt	do.	do.
Barium	do.	do.
Strontium	do.	do.
Calcium	do.	do.
Magnesium	do.	do.
Ammonium	do.	do.
Potassium	do.	do.
Sodium	do.	do.

A consideration of these results indicates that if we add **Hydrochloric Acid** (HCl) to an unknown solution of a simple salt and obtain a white precipitate which does not dissolve on adding a few more drops of acid and gently warming, **Silver** (Ag), **Mercury in the mercurous condition** (i. e. Hg^{ous} or $Hg^{\cdot}$), or **Lead** (Pb) must be present. On the contrary, if we obtain no precipitate then these three metals must be absent. One must reiterate that **the reason for the precipitation depends upon the insolubility of the chlorides of Silver, Mercurous, and Lead in water.** The chlorides of all the other metals (with the exception of cuprous chloride (p. 68), which would hardly be met with in elementary analysis) are soluble in water, and are therefore not precipitated.

If we obtain no precipitate with hydrochloric acid and proceed to add **Sulphuretted Hydrogen** (H_2S) to the same solution we might get a precipitate of **Copper Sulphide** (CuS), **Mercuric Sulphide** (HgS), **Bismuth Sulphide** (Bi_2S_3), **Cadmium Sulphide** (CdS), **Arsenious Sulphide** (As_2S_3), **Antimonious Sulphide** (Sb_2S_3), **Stannous Sulphide** (SnS), or **Stannic Sulphide** (SnS_2). On the other hand, if no precipitate forms, the metals Cu, Hg^{ic}, Bi, Cd, As, Sb, and Sn are proved absent. **If no precipitate were obtained by these two simple tests, we would have proved the absence of nine of the metals.** By further gradual elimination we can test for the metals of Groups III to VI. **The tests must be carried out in an absolutely definite order,** and the reason for this is well exemplified by the summary of results for hydrochloric acid and sulphuretted hydrogen (in presence of hydrochloric acid) tabulated above. If we add sulphuretted hydrogen before adding hydrochloric acid we may get the metals of Group I—Ag, Hg^{ous}, Pb—precipitated as black sulphides. This would cause difficulty in testing, as the sulphides of bismuth (Bi), copper (Cu), mercuric ($Hg^{\cdot\cdot}$), and stannous ($Sn^{\cdot\cdot}$) are also nearly black.

The order of adding the group reagents, the division into groups, and the reasons for the precipitation of the metals in the respective groups are indicated in the following summary :—

THE ARRANGEMENT OF THE METALS INTO GROUPS.

Group.	Group Reagent.	Metals in group.	Substances precipitated.	Reasons for precipitation under given conditions: precautions.
I	Hydrochloric Acid (HClAq)	Ag, Hg^{ous}, Pb	AgCl HgCl $PbCl_2$	The Chlorides of Silver, Mercurous ($Hg^{\cdot}$), and Lead are insoluble in water.
II	Sulphuretted Hydrogen (H_2S) (in presence of HClAq)	(a) Cu, Hg^{ic}, Bi, Cd (b) As, Sb, Sn^{ous}, Sn^{ic}	(a) CuS, HgS, Bi_2S_3 (b) As_2S_3, Sb_2S_3, SnS, SnS_2	The Sulphides of Cu, Hg^{ic}, Bi, Cd, As, Sb, Sn^{ous}, Sn^{ic} are insoluble in dilute Hydrochloric Acid. Note.—HCl must be present for two reasons:— (1) If the solution be neutral or alkaline other sulphides, e. g. ZnS, might be precipitated. (2) If the solution is not acidified, As_2S_3 and Sb_2S_3 may not come down, as they are soluble in alkalies (pp. 136, 140).
III	Ammonium Hydroxide (NH_4OH) in presence of Ammonium Chloride (NH_4Cl)	Al, Fe^{ous}, Fe^{ic}, Cr	$Al(OH)_3$ $Fe(OH)_2$ $Fe(OH)_3$ $Cr(OH)_3$	The Hydroxides of Al, Fe^{ous}, Fe^{ic}, and Cr are insoluble in water and Ammonium Chloride solution. Note.—NH_4ClAq must be added in sufficient quantity, otherwise Hydroxides of Zn, Mn, and Mg might be precipitated. (See Lists of Tests for these metals.)
IV	Ammonium Sulphide ($(NH_4)_2S$) in presence of NH_4ClAq and NH_4OHAq	Zn, Mn, Ni, Co	ZnS, MnS, NiS, CoS	The Sulphides of Zn, Mn, Ni, and Co are insoluble in water and in NH_4ClAq and NH_4OHAq. Notes.—(1) NH_4ClAq must be present, otherwise Mg may be precipitated. (2) The solution must be made alkaline in reaction by addition of NH_4OHAq, because if $(NH_4)_2S$ be added to an acid solution, H_2S is evolved and Sulphur precipitated.
V	Ammonium Carbonate ($(NH_4)_2CO_3$) in presence of NH_4ClAq and NH_4OHAq	Ba, Sr, Ca	$BaCO_3$, $SrCO_3$, $CaCO_3$	The Carbonates of Ba, (Sr), and Ca are insoluble in water, NH_4ClAq, and NH_4OHAq. Notes.—(1) NH_4ClAq must be present, otherwise Mg may be precipitated. (2) $(NH_4)_2CO_3$ would be decomposed in an acid solution, therefore the solution is made alkaline with NH_4OHAq.
VI	No group reagent.			
	(a) Na_2HPO_4Aq in presence of NH_4ClAq and NH_4OHAq	Mg	$Mg.NH_4.PO_4$	Magnesium Ammonium Phosphate is insoluble in water, NH_4Cl, and NH_4OHAq.
	(b) Boil with NaOHAq	NH_4	NH_3 is evolved.	All Ammonium Compounds are decomposed on boiling with Sodium Hydroxide, giving off NH_3.
	(c) Flame test.	K Na	Violet flame. Brilliant yellow flame.	

The reader should now understand why the metals are divided into analytical groups, and should be ready to proceed to the analysis of simple salts and mixtures of compounds with a fair chance of understanding the reactions which he has to carry out.

We will consider the following cases which might be met with in order, as they form a series of gradually increasing difficulty.

A. ANALYSIS OF ANY GIVEN AQUEOUS SOLUTION OF A SIMPLE SUBSTANCE FOR A SINGLE METALLIC RADICLE.

B. ANALYSIS OF A SIMPLE SUBSTANCE GIVEN IN THE SOLID STATE WHICH IS—

(1) **SOLUBLE IN WATER.**

(2) **INSOLUBLE IN WATER.** **(a) The substance is not a phosphate or is a phosphate of a metal of Groups I or II. (b) The substance is a phosphate of a metal of Groups III, IV, V, or of Mg.**

General Notes.

(a) **Insoluble phosphates may seriously complicate analysis,** and when a body is insoluble in water and a precipitate is obtained in Group III phosphoric acid must be tested for. If present it must be removed before proceeding, as indicated on p. 193.

(b) **Insoluble oxalates and tartrates** of metals of Groups III, IV, V, or of magnesium **may complicate analysis** in a similar way to the corresponding phosphates. They must be decomposed by ignition (i. e. by heating the dry substance) before proceeding with Group III.

C. ANALYSIS OF A GIVEN AQUEOUS SOLUTION CONTAINING TWO OR MORE METALS BELONGING TO DIFFERENT ANALYTICAL GROUPS.

(Note.—Groups II*a* and II*b* are generally regarded as different groups, e. g. copper and arsenic might be present).

D. ANALYSIS OF A SOLID MIXTURE CONTAINING TWO OR MORE METALS BELONGING TO DIFFERENT ANALYTICAL GROUPS, and not more than one acid radicle.

(a) **Phosphates absent.**

(b) **Phosphates present.**

E. BRIEF SUMMARY OF ANALYSIS OF A MIXTURE, GIVEN IN SOLUTION OR IN SOLID STATE, CONTAINING TWO OR MORE METALS WHICH MAY BELONG TO THE SAME GROUP.

(NOTE.—This hardly belongs to an elementary course and can be omitted by most candidates for elementary examinations if time does not allow.)

(a) **Phosphates insoluble in water absent.**

(b) **Phosphates insoluble in water present.**

F. INSOLUBLE SUBSTANCES, i. e. **bodies insoluble in water and the common solvents.** The treatment of these will be better understood after considering the acids. See p. 205.

A. ANALYSIS OF ANY GIVEN AQUEOUS SOLUTION OF A SIMPLE SUBSTANCE FOR A SINGLE METALLIC RADICLE.

Carry out the following preliminary tests:—

(1) Test the solution with litmus paper.

If **neutral** this might indicate—

(*a*) Pure water.

(*b*) A salt of neutral reaction.

If **acid** one might suspect—

(*a*) A free acid, e. g. HCl, HNO_3, $CH_3 . COOH$.

(*b*) An acid salt, e. g. $NaHSO_4$, $KH . C_4H_4O_6$.

(*c*) A normal salt of acid reaction, e. g. $CuSO_4$, $ZnSO_4$, $Al_2(SO_4)_3$.

If **alkaline** the substance might be—

(*a*) A free base, e. g. KOH, $NaOH$, $Ca(OH)_2$.

(*b*) A normal salt of alkaline reaction, e. g. Na_2CO_3, K_2CO_3, KCN.

(*c*) A basic salt, e. g. basic lead acetate.

NOTE.—Very few basic salts are soluble in water.

(2) **If the solution is acid** add a pinch of **solid sodium carbonate**, and if effervescence takes place suspect a free acid. Evaporate 20–30 c.c. of solution to dryness, finishing the evaporation either with a very small flame, or preferably on a water-bath, so as to avoid loss and decomposition of any solid residue. A beaker containing boiling water will serve for a water-bath, the basin containing the substance being placed over the beaker. If the beaker has no lip, put two small pieces of folded paper between basin and beaker to allow for escape of steam. While the evaporation is proceeding, test through the general analytical scheme and group tests detailed below (pp. 180 and 181). Any residue obtained can be used for dry tests for both bases and acids.

(3) Test a few c.c. of the original solution with sodium carbonate solution.—If no precipitate forms, one need only look for sodium, potassium, or ammonium.

(NOTE.—If the solution is acid, and causes effervescence on addition of the carbonate, continue adding carbonate solution until after effervescence ceases, and the reaction mixture is alkaline.)

ANALYTICAL TABLES FOR DETECTION OF METALS.

Method of procedure in using the tables :—

(1) Carry out the tests given in order until a positive result is obtained.

(2) Try to identify the metal (or metals)—

- (*a*) By its group reaction (column 3, p. 180);
- (*b*) By application of confirmatory tests summarized in Tables I to VI, but more completely given under the summaries for the respective metals.

(3) Having found the metal, the student may write equations for the positive reactions he has carried out, letting X stand for the radicle of a monobasic acid, X^2 for the radicle of a dibasic acid, &c. ; e. g. if copper were detected, the precipitate as sulphide might be represented by the equation

$$CuX_2 + H_2S = CuS + 2HX.$$

The valency table and remarks given on p. 4 should be consulted if necessary. When a student can carry out analyses for both bases and acids, it is better as a rule to wait until the acid has been detected before writing the equations expressing the positive reactions carried out.

Scheme of General Group Tests to be carried out in order.

Tests to be carried out in regular order.	Result observed.	Inference as to composition of precipitate.	Distinctions between substances which might be precipitated.
1. To about 2 c.c. of original solution in a test-tube add **dilute Hydrochloric Acid** (**HClAq**). If a precipitate is obtained add a little more acid and warm gently. (Note.—Do not heat to boiling-point, as $PbCl_2$ might go into solution.)	(*a*) White precipitate.	(*a*) The substance precipitated may be AgCl, HgCl, or $PbCl_2$. (BiOCl and SbOCl might be precipitated on first adding acid, but would redissolve on adding more acid and warming.)	See Table I (p. 182).
	(*b*) No precipitate.	(*b*) Ag, Hg^{ous}, and Pb are absent.	
2. If no precipitate, to the same portion of original solution (i.e. the portion to which HCl has been added) add **Sulphuretted Hydrogen** (H_2S), either as gas or in solution. (Note.—If gas be used be sure that the delivery tube is clean.)	(*a*) Black or brownish precipitate.	(*a*) Substance precipitated might be (PbS) : CuS : HgS (characteristic changes of colour generally occur during precipitation) : Bi_2S_3.	See Tables II A and II B.
	(*b*) Yellow precipitate.	(*b*) As_2S_3 : SnS_2 : CdS.	
	(*c*) Orange precipitate.	(*c*) Sb_2S_3.	
	(*d*) No precipitate.	(*d*) Absence of (Pb), Cu, Hg^{ic}, Bi, Cd, As, Sb, Sn^{ous}, Sn^{ic}.	
3. If no precipitate, to fresh portion (about 2 c.c.) of original solution add **Ammonium Chloride** and **Ammonium Hydroxide.** (Note.—Add at least twice the volume of Ammonium Chloride to that of solution taken.)	(*a*) White gelatinous precipitate.	(*a*) The substance precipitated may be $Al(OH)_3$. (Note.—From very strong solutions of Zinc and Magnesium Salts, white precipitates of the Hydroxides, $Zn(OH)_2$ and $Mg(OH)_2$, might be obtained. They would dissolve on adding more Ammonium Chloride and warming.)	See Table III.
	(*b*) Greenish precipitate turning brown on the top of the solution where in contact with air.	(*b*) $Fe(OH)_2$, indicating a Ferrous Compound.	
	(*c*) Flocculent brown precipitate.	(*c*) $Fe(OH)_3$, indicating a Ferric Compound.	
	(*d*) Greyish green precipitate.	(*d*) $Cr(OH)_3$.	
	(*e*) No precipitate.	(*e*) Absence of Al, Fe^{ous}, Fe^{ic}, Cr.	

Scheme of General Group Tests to be carried out in order (*continued*).

Tests to be carried out in regular order.	Result observed.	Inference as to composition of precipitate.	Distinctions between substances which might be precipitated.
4. If no precipitate, to same solution (i. e. solution to which **NH_4ClAq** and **NH_4OHAq** have been added) add **Ammonium Sulphide,** $(NH_4)_2S$.	(*a*) Black precipitate. (*b*) White precipitate. (*c*) Salmon - pink precipitate. (*d*) No precipitate.	(*a*) The substance precipitated may be Nickel Sulphide, NiS, or Cobalt Sulphide, CoS. (*b*) The substance precipitated may be Zinc Sulphide, ZnS. (*c*) The precipitate may be Manganous Sulphide, MnS. (*d*) Nickel, Cobalt, Zinc, and Manganese are absent.	See Table IV (p. 188).
5. If no precipitate, to fresh portion of original solution add **NH_4ClAq, NH_4OHAq,** and **$(NH_4)_2CO_3Aq$** and warm gently.	(*a*) White precipitate. (*b*) No precipitate.	(*a*) The substance precipitated may be Barium Carbonate, $BaCO_3$, Strontium Carbonate, $SrCO_3$, or Calcium Carbonate, $CaCO_3$. (*b*) Ba, Sr, and Ca are absent.	See Table V (p. 189).
6. If no precipitate, to original solution add **NH_4ClAq, NH_4OHAq,** and **Na_2HPO_4Aq.** (Note.—One could add Na_2HPO_4 to solution used in Test 5 instead.)	(*a*) White precipitate. Formation hastened by stirring. (*b*) No precipitate.	(*a*) The substance precipitated may be Magnesium Ammonium Phosphate, $MgNH_4PO_4$. (*b*) Magnesium is absent.	See Table VI.
7. If no precipitate, boil **a few c.c. of original solution with $NaOHAq$.**	(*a*) Evolution of Ammonia gas, recognized by its odour and effect on moist red litmus paper. (*b*) No Ammonia evolved.	(*a*) Ammonium (NH_4) Salt is present. (*b*) Ammonium Salt is absent.	See Table VI.
8. Evaporate a few c.c of original solution cautiously to dryness in porcelain basin. Moisten the residue by concentrated HNO_3 (or HCl), take a small quantity on tip of **Platinum wire** and heat in **Bunsen flame.**	(*a*) Flame test is violet. (*b*) Flame is coloured an intense yellow.	(*a*) Potassium is present. (*b*) Sodium is present.	See Table VI.

TABLE I.

Distinction between Silver, Mercurous, and Lead.

The **white precipitate** may be **silver chloride** (AgCl), **mercurous chloride** (HgCl), or **lead chloride** ($PbCl_2$).

To determine which metal is present proceed as follows:—Allow the precipitate to settle, pour off the supernatant liquid, and then **warm gently a small quantity of the precipitate with ammonia solution.** If the precipitate is silver chloride it will dissolve, while mercurous chloride will be turned black, and lead chloride will remain white. It follows therefore that

if the precipitate dissolves, silver is indicated:
if it turns black, mercury is present;
and if it remains white, lead is the metallic radicle in the original solution.

To make certain, carry out at least a couple of confirmatory tests. Each test is carried out with about 2 c.c. of original solution.

Confirmatory Tests.

Reagent.	Silver.	Reagent.	Mercurous.	Reagent.	Lead.
(1) K_2CrO_4	Deep red precipitate of Silver Chromate, Ag_2CrO_4.	(1) KOH or NaOH	Black precipitate of Mercurous Oxide, Hg_2O	(1) K_2CrO_4	Yellow precipitate of Lead Chromate, $PbCrO_4$.
(2) KOH or NaOH	Grey precipitate of Silver Hydroxide, Ag_2O	(2) KI	Finch-green precipitate of Mercurous Iodide, HgI.	(2) KI	Yellow precipitate of Lead Iodide, PbI_2, which can be recrystallized in golden spangles from boiling water (p. 70).
(3) KI	Faintly yellow precipitate of Silver Iodide, AgI.	(3) K_2CrO_4	Reddish precipitate of Mercurous Chromate, Hg_2CrO_4.	(3) H_2SO_4Aq	White precipitate of Lead Sulphate, $PbSO_4$.
	For complete explanations and equations see p. 122.		See p. 124.		See p. 126.

DISTINCTION BETWEEN THE METALS OF GROUPS II A AND II B.

The precipitate might be PbS, CuS, HgS, Bi_2S_3, CdS, As_2S_3, Sb_2S_3, SnS, or SnS_2.

Proceed as follows:—

Decant off the supernatant liquid and some of the precipitate (say about three-fourths) into another test-tube, and warm the remaining precipitate with **yellow ammonium sulphide** $(NH_4)_2S_x$.

If the precipitate dissolves, proceed to **Table II** B.

If the precipitate does not dissolve, As, Sb, Sn^{ous}, and Sn^{ic} are absent. (Pb), Cu, Hg^{ic}, Bi, or Cd might be present. To distinguish between the five latter elements two methods can be used.

Group II A.

Method I.—If the original solution were blue or green, **copper** is indicated, and if during precipitation a change of colour from white through yellow, brown, and black took place, **mercuric mercury** is probably present, and one might at once proceed to carry out the confirmatory tests for copper or mercury. **Lead** should have been indicated in Group I, unless the solution was extremely dilute. The addition of a few drops of sulphuric acid (dilute) to the original solution, which would give a characteristic white precipitate of lead sulphate if lead were present, could be used for confirmation. Cadmium is sufficiently characterized by the yellow precipitate insoluble in ammonium sulphide. This would leave **bismuth**, which can be confirmed by the bismuth oxychloride test in the following manner: Add NH_4OH to a few c.c. of original solution. If bismuth be present a white precipitate of bismuth hydroxide, $Bi(OH)_3$, would be obtained. Filter off this white precipitate, wash it into the apex of the filter paper, and then dissolve it in as small a quantity of hydrochloric acid as possible—say 6 to 10 drops—catching the filtrate in a test-tube. Fill up the test-tube with distilled water, when a milky precipitate of bismuth oxychloride (BiOCl) is at once formed if bismuth is present.

Equation: $BiCl_3Aq + H_2O = BiOCl + 2HClAq.$

Method II.—If the precipitate is yellow cadmium is indicated. If black, filter off the precipitate, wash it with water on the filter, boil 2 c.c. of nitric acid (one volume of concentrated acid to two volumes of water) in a test-tube, and pour the boiling acid on the precipitate, using another test-tube to catch what comes through. Repeat, if necessary, with the same quantity of acid (which should always be freshly boiled before pouring on to the precipitate). PbS, CuS, Bi_2S_3, and CdS would dissolve to give solutions of nitrates. Mercuric sulphide (HgS) would remain insoluble. [NOTE.—If the precipitate were not properly washed before adding the boiling dilute acid, even HgS might dissolve, because there might be sufficient HCl adhering to it to form aqua regia.] To the nitrate solution add excess of ammonium hydroxide, NH_4OH. Copper will give a blue coloration ; bismuth and lead would give white precipitates of $Bi(OH)_3$ and $Pb(OH)_2$ respectively. If lead be suspected, test for it by the chromate and sulphuric acid tests. Test for bismuth by filtering off the white precipitate of hydroxide, dissolving it in a few drops of HClAq, and adding water to form the precipitate of oxychloride as detailed in Method I. Confirm mercury by means of KIAq and NaOHAq.

TABLE II A. (Summary from above.)

Method I.

(a) If solution is green or blue, test for **copper.**

(b) If during precipitation with SH_2 change of colour took place, test for **mercury.**

(c) If there is any reason to suspect **lead,** test for it by H_2SO_4.

(d) Test for **bismuth** by the oxychloride reaction.

(e) Yellow precipitate insoluble in ammon. sulphide indicates cadmium.

Method II.

(a) If the precipitate is yellow cadmium is indicated.

(b) Filter the black precipitate, wash it, and then try to dissolve in boiling dilute nitric acid. If insoluble, test original solution for mercury by KIAq.

(c) If soluble, add to the solution in nitric acid NH_4OHAq until reaction is alkaline. A blue coloration may indicate copper; a white precipitate, lead or bismuth.

(d) Test the original solution for bismuth by oxychloride test, and before or after doing so test for lead by K_2CrO_4Aq and H_2SO_4Aq.

Summary of Confirmatory Tests.

(Carried out on original solution.)

(Pb).	Cu.	Hg^{ic}.	Bi.	Cd.
(1) K_2CrO_4. (2) H_2SO_4Aq. (3) KI. (4) Reduction on Charcoal. For complete explanation and equations, see p. 126.	(1) Flame test. Platinum wire. (2) $K_4Fe(CN)_6$. (3) NH_4OHAq. See p. 128.	(1) *Copper test,* i. e. acidify original solution with HCl and boil with Cu. Silvery deposit. (2) NaOH. (3) KI. See p. 130.	(1) Oxychloride test. (2) KI. (3) K_2CrO_4—Do not confuse the pp. obtained with Lead Chromate. See p. 132.	(1) KOH. (2) KCN. (3) Brown incrustation on Charcoal. See p. 134.

TABLE II B.

Distinction between As, Sb, Sn^{ous}, and Sn^{ic}.

If the precipitate given by SH_2 in presence of HCl dissolves in yellow ammonium sulphide, $(NH_4)_2S_x$, then As, Sb, Sn^{ous}, or Sn^{ic} may be present.

If the precipitate is brown, stannous tin is indicated; if orange, antimony; and if yellow, arsenic or stannic tin. Stannous tin is therefore readily distinguished by colour, and, after a little practice, the orange colour of antimonious sulphide is recognized. To distinguish between the two yellow precipitates, As and Sn^{ic}, warm a small quantity of the precipitate with $(NH_4)_2CO_3Aq$. As_2S_3 dissolves, SnS_2 (and Sb_2S_3) do not. Use the following confirmatory tests :—

As.	Sb.	Stannous Tin.	Stannic Tin.
(1) Reinsch's test.	(1) NH_4OHAq.	(1) $HgCl_2Aq$. Grey pp. of Mercury.	(1) Reduce to Stannous by nascent Hydrogen Zn and HClAq—then add $HgCl_2Aq$
(2) Dry test Na_2CO_3 and powdered substance in hard glass tube.	(2) Precipitation of Oxychloride (SbOCl), soluble in Tartaric Acid.	(2) KOHAq.	[Note.—The Zinc should preferably be pure.]
(3) Fumes on charcoal—garlic odour.	(3) Reinsch.		
	(4) Dry test.		
For complete explanations and equations, see p. 136	See p. 140.	See p. 142.	See p. 142.

TABLE III.

Distinction between Al, Fe^{ous}, Fe^{ic}, Cr.

The colours of the different precipitates are sufficient guides in this group, and one could at once proceed to the confirmatory tests.

The greyish green precipitate of chromium hydroxide, $Cr(OH)_3$, is readily distinguished from the greenish precipitate of ferric hydroxide, because the latter becomes brown on the top on shaking with air, owing to oxidation to ferric hydroxide, $Fe(OH)_3$.

NOTE.—From concentrated solutions of Zn, Mn, or Mg compounds, white precipitates may be obtained in this group, because of the difficulty of adding a sufficiency of ammonium chloride (NH_4Cl) to prevent precipitation of the hydroxides of the metals. These white precipitates are flocculent, and not gelatinous like the precipitate of aluminium hydroxide, $Al(OH)_3$. On decanting off the supernatant liquids, and warming the residue with ammonium chloride, solution will be effected. Aluminium hydroxide is insoluble in ammonium chloride.

Carry out the following **confirmatory tests**:—

Al.	Fe^{ous}.	Fe^{ic}.	Cr.
(1) **KOH** or **NaOH**. White precipitate soluble in excess.	(1) **$K_3Fe(CN)_6$**. Dark blue precipitate.—Turnbull's blue.	(1) **$K_3Fe(CN)_6$**. No precipitate.	(1) **KOH** or **NaOH**. Greyish green precipitate of Chromium Hydroxide.
(2) Moisten filter paper first with a concentrated solution of substance and then with **$Co(NO_3)_2$** and ignite.—**Blue residue.**	(2) **$K_4Fe(CN)_6$**. Gives a light blue precipitate of potassium ferrous ferrocyanide, $K_2Fe^{\cdot\cdot}[Fe(CN)_6]$	(2) **$K_4Fe(CN)_6$**. Gives a deep blue precipitate of Prussian blue.	(2) Fuse up in a hard glass tube or iron spoon with **KNO_3** or **Na_2O_2**—mass turns yellow — extract with water, acidify with Acetic Acid and add Lead Acetate,—yellow pp. of Lead Chromate is formed.
For complete explanations and equations, see p. 144.	See p. 146.	See p. 146.	See p. 148.

TABLE IV.

Distinction between Ni, Co, Zn, and Mn.

The colour of the precipitate is a useful guide If the precipitate is black Ni or Co is indicated, if salmon-pink Mn, and if white zinc. The precipitate of zinc sulphide may look yellow because of the yellow colour of the ammonium sulphide, $(NH_4)_2S$, but if filtered off and washed its real colour will be apparent.

Confirmatory Tests:

Zn. Indicated by white precipitate of ZnS.	Mn. Indicated by salmon-pink precipitate of MnS.
(1) **KOH** or **NaOH.** White precipitate of Zinc Hydroxide, $Zn(OH)_2$, soluble in excess to give a solution of Aluminate.	(1) **KOH** or **NaOH.** White precipitate of Manganous Hydroxide, $Mn(OH)_2$, which rapidly turns brown.
(2) Moisten a few square centimetres of filter paper first with a concentrated solution of the substance and then with $Co(NO_3)_2$ and ignite. Yellowish green mass is obtained.	(2) Heat on charcoal with Na_2CC_3 and KNO_3 or Na_2O_2. A green mass is obtained which gives a green solution of Sodium Manganate. On dilution the solution turns pink.
For complete explanations and equations, see p. 154.	See p. 156.

If the precipitate is black it may consist of CoS or NiS.

Filter and wash, take up a trace of the black residue on a borax bead and heat with mouth-blowpipe in oxidizing flame.

Deep blue bead indicates Cobalt.
Brownish bead „ Nickel.

Confirmation:—If the original solution were pink cobalt is indicated, and if green nickel. For further tests see pp. 150 and 152.

TABLE V.

Distinction between Ba, Sr, and Ca.

Two cases might be met with: (1) **Sr presumably absent.**
(2) **Sr perhaps present.**

1. Sr presumably absent.

Ca and Ba are readily distinguished by adding $CaSO_4Aq$ to the original solution. If a precipitate forms, Ba is present; if not, Ca. Confirm as below.

2. Sr may be present.

(a) Filter off the white precipitate of carbonate, and wash the precipitate into the apex of the filter paper. Test by platinum wire moistened with HCl.

Ba gives a light green flame.
Sr gives a pink flame.
Ca gives a brick-red flame.

(b) Dissolve the precipitate in a few drops of acetic acid, and add to half of the solution obtained K_2CrO_4Aq.—Yellow precipitate of barium chromate insoluble in acetic acid indicates Ba.

(c) If there is no precipitate, in order to distinguish between Sr and Ca add to the other half of the solution $CaSO_4Aq$. Warm gently and allow to stand five minutes. White precipitate indicates strontium.

Confirmatory Tests:

	Ba	Sr.	Ca.
(1) Platinum wire test	Green flame	Crimson flame	Brick-red flame
(2) $(NH_4)_2C_2O_4Aq$	White pp.	White pp.	White pp.

TABLE VI.

The tests already given are sufficiently distinctive, but the following tests applied to the original solution might be used for confirmation :—

Mg.	NH_4.	K.	Na.
(1) **NaOHAq.** White precipitate soluble in Ammonium Chloride. (2) **A pink residue** is obtained after moistening filter paper first with a concentrated solution of the substance and then with $Co(NO_3)_2$ and igniting. For list of tests with equations, see p. 164.	No further test is necessary. The odour and alkaline reaction of Ammonia are characteristic. See p. 166.	Confirm by evaporating a portion of original solution to dryness, dissolving in a few drops of water, placing in a test-tube, and adding an equal quantity of Tartaric Acid or Sodium Hydrogen Tartrate solution. Shake the tube violently, closing the top with the thumb ; if no precipitate forms, scratch the side of the tube inside the liquid by rubbing with a glass rod. (Note.—The addition of a few drops of alcohol may aid precipitation, but should be employed with caution.) See p. 168.	No further test beyond that of the flame is advisable. This should if possible be invariably carried out with the solid substance as already indicated. See p. 170.

B. ANALYSIS OF A SIMPLE SUBSTANCE GIVEN IN THE SOLID STATE.

Preliminary Note regarding solution. In the case of a substance given in the solid state, the method of procedure followed would vary with the analyst's knowledge of chemistry. It is not always advisable to carry out dry tests if time be limited, but it should be noted that the appearance of the body taken in conjunction with a few dry tests may often give a clue as to the most suitable solvent; e.g. if the substance were a heavy orange powder insoluble in water, which gave a malleable bead which marked paper by heating on charcoal, the substance would presumably be lead oxide, and the best solvent in the circumstances would be dilute nitric acid. A decision of this sort, however, means considerable acquaintance with the subject, and it is advisable that the beginner should have a definite scheme to fall back upon. **A convenient method is as follows:—**

(1) Take in a test-tube as much solid as would occupy the volume of a small drop of water (say about 0·05 c.c.) and boil with 4–5 c.c. of distilled water. If the substance dissolves, proceed with the general analytical scheme detailed above (A, p. 180).

(2) If the substance does not seem to dissolve, pour off the water, and add about 4–5 c.c. of dilute HCl (or add about 1 c.c. of concentrated HCl to the water), warm carefully, and finally boil. If the substance dissolves, note whether any effervescence takes place, indicating carbonate, &c., as detailed under Acids (p. 217), and then proceed with tests as in A, omitting the addition of HCl to test for Group I.

(3) If the substance does not dissolve in dilute HCl, pour off the dilute acid and add about 2 c.c. of concentrated acid and boil. If solution is effected, add more solid gradually and continue boiling until solid remains undissolved. Then dilute with water and filter.

NOTES.—(*a*) If chlorine is evolved, a peroxide or oxidizing agent is indicated, e.g. $PbO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O$.

(*b*) If a heavy white crystalline precipitate separates on dilution with water or on cooling, lead is probably present, as precipitate will probably be $PbCl_2$.

(4) If the substance does not dissolve in conc. HCl, wash out the test-tube, put in a fresh quantity of the solid, and boil with

dilute nitric acid. If solution is effected, proceed as with concentrated HCl, i. e. add more solid, and boil until no more solid is taken up. Dilute with water, and carry out the general tests detailed under A (p. 180).

(5) If substance does not dissolve, try concentrated nitric acid. Proceed as with concentrated HCl and dilute HNO_3.

(NOTE.—Many nitrates, e.g. $Ba(NO_3)_2$, $Pb(NO_3)_2$, are nearly insoluble in concentrated nitric acid, but easily soluble in water. They may separate during boiling with the strong acid, but will dissolve on diluting with water.)

(6) **Aqua regia**, a mixture of hydrochloric and nitric acids, might be next tried. A minimum quantity of the mixture and a minimum quantity of nitric acid in the mixture should be employed. Proceed as follows: Add about 1 c.c. of concentrated HCl to the solid, and then add three or four drops of concentrated HNO_3, boil, and if solution seems to be effected, add if necessary a few more drops of nitric acid. **Aqua regia owes its powerful solvent properties chiefly** to the presence of **nascent chlorine** produced by the following decomposition:—

$$3HCl + HNO_3 = Cl_2 + \underset{\text{Nitrosyl Chloride}}{\overline{NOCl}} + 2H_2O.$$

(7) In a few cases, e.g. if substance be yellow and As_2S_3 is suspected, it is much better to dissolve in concentrated hydrochloric acid with addition of a crystal of potassium chlorate, rather than in nitric acid. Using HCl and $KClO_3$ a solution is obtained which reacts readily with H_2S, whereas dissolving in HNO_3 no reaction will take place with H_2S until the arsenic in solution is reduced to the arsenious state.

General Notes regarding solution:

(1) If anything stronger than dil. HCl has been used, and if the solution is strongly acid, evaporate nearly to dryness in the fume cupboard before going on to test for metals.

(2) In getting a substance into solution a student should aim at using the least possible quantity of acid. Excess of acid, especially HNO_3, tends to prevent sulphides coming down in Group II, e.g. H_2S is at once destroyed by HNO_3.

$$H_2S + 2HNO_3 = 2H_2O + S + 2NO.$$

It is no uncommon thing to find a beginner effecting solution with about 10 c.c. of aqua regia. Such a solution is almost valueless for analytical work. It must be evaporated nearly to dryness in the fume cupboard to get rid of excess of acid, and then diluted with water before proceeding.

Having effected solution, it is sufficient as a rule to proceed through the Scheme of General Tests as detailed under A, p. 180.

Under certain conditions, however, e. g. (*a*) **when insoluble Phosphates are present**, and (*b*) when insoluble Oxalates or Tartrates are present, a modification of the General Scheme must be employed as follows :—

(*a*) **Insoluble Phosphates present.**

If phosphates insoluble in water are present they may cause trouble during analysis. Phosphates insoluble in water, i. e. phosphates of metals other than Na, K, or NH_4, are all soluble in HClAq and in HNO_3Aq. On adding NH_4OHAq to their solutions, however, they are precipitated, as the ammonium hydroxide neutralizes the acid which keeps them in solution; e. g. $Zn_3(PO_4)_2$, $Ca_3(PO_4)_2$, and $Mg_3(PO_4)_2$ are insoluble in water, but easily soluble in HClAq, indicating absence of metals of Group I. If one tests the solution systematically for metals, no reaction is obtained with H_2S, indicating absence of metals of Group II, but **on adding NH_4ClAq and NH_4OHAq to test for Group III, the original substances are precipitated** because the NH_4OHAq neutralizes the acid used for dissolving them.

$$HClAq + NH_4OHAq = NH_4ClAq + H_2O.$$

As the above phosphates are white they might easily be mistaken for $Al(OH)_3$. In such a case it is impossible to get the group tests for Zn, Ca, and Mg until the phosphoric acid has been removed. This is generally effected by adding $FeCl_3Aq$ under suitable conditions, and eliminating the acid from solution as ferric phosphate, $FePO_4$.

Method of Procedure:—

Boil the filtrate from Group II until all the SH_2 has been removed and then test about 1 c.c. of solution for iron with $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$. If ferrous iron be in solution (and if it has been necessary to add H_2S in presence of iron it will be present), boil the solution with 1–2 c.c. of conc. HNO_3Aq for ten minutes to oxidize any ferrous to ferric. Neutralize the solution by cautious addition of NH_4OH to the solution placed in a porcelain basin, with constant stirring until the reaction is nearly neutral to litmus.

A precipitate may form. Add 10–15 c.c. of ammonium acetate (prepared by adding acetic acid to NH_4OHAq until the reaction is just acid). **Then add $FeCl_3Aq$ drop by drop until the supernatant liquid has a reddish tint.** Boil, filter, and wash. The ferric chloride added precipitates all the phosphoric acid, because ferric phosphate is insoluble in acetic acid. The filtrate is tinted reddish.

On boiling the solution after excess of iron has been added, the excess of iron, and aluminium if present, are precipitated as basic acetate. Chromium too may be precipitated as hydroxide, so that after boiling until the liquid is seen to be colourless, all the iron, and probably all the Al and Cr, are removed from the solution.

Test (*A*) **the Filtrate** and (*B*) **the Residue** separately.

A. **Filtrate.** Proceed to test through the groups as usual. Test for Groups III, IV, V, and VI. Fe and probably Al will be absent. Cr may be present.

B. **Residue.** The residue should be tested for Al and Cr by one of the following two methods:—

Method I.

Put the washed residue in a dish with a little water, add about a gram of solid sodium peroxide, boil and filter. The residue will be $Fe(OH)_3$. The solution may contain Al as sodium aluminate, $Al(ONa)_3$, and chromium as chromate.

(*a*) Test for Al by acidifying one half with HClAq and then adding excess of NH_4OH and boiling. White gelatinous pp. of $Al(OH)_3$ indicates aluminium.

(*b*) Test the other half for chromium by acidifying with acetic acid and adding lead acetate. A yellow pp. of $PbCrO_4$ indicates chromium.

Method II.

If Na_2O_2 is not available, proceed as follows:—

(*a*) Boil up the residue with caustic soda. Filter. Acidify with HCl and then add NH_4OHAq and boil. White pp. of $Al(OH)_3$ indicates aluminium.

(*b*) Fuse up the residue with Na_2CO_3 and KNO_3 on platinum foil or in a small iron spoon. Extract with water and filter. The solution will be yellowish if chromium be present. Acidify with acetic acid and add lead acetate. Yellow precipitate of $PbCrO_4$ indicates chromium.

(*b*) **Oxalates or Tartrates insoluble in water present.** If oxalate or tartrate insoluble in water be indicated on heating a small quantity of dry substance, heat strongly about a gram of the substance until the organic compounds are completely decomposed; dissolve the residue in dil. HCl or dil. HNO_3; filter if necessary and proceed as usual through the groups.

NOTES:—(1) Other organic compounds should be treated similarly to oxalates and tartrates.

(2) Silicates should be ignited, and silver filtered off after extracting residue with dilute acid before proceeding to Group III.

(3) Fluorides and Borates of Ca, Ba, and Mg might be precipitated with metals of Group III. This rarely causes trouble, however, as both metals and acids are detected by usual tests.

C. ANALYSIS OF A SOLUTION CONTAINING TWO OR MORE METALS BELONGING TO DIFFERENT ANALYTICAL GROUPS.

Preliminary Note.—In testing a solution containing two or more metals, the general scheme of analysis detailed under A (p. 180) is followed, but a few precautions are necessary to avoid mistakes.

(1) One must test for all metals (except the Ammonium group) with the same portion of the solution.

(2) A metal of an earlier group must be completely eliminated from the solution before a metal of a later group is tested for.

To indicate how important this statement is, suppose we consider what might happen if one started to test a concentrated solution of lead nitrate for more than one metal, and did not take care to eliminate the lead in Groups I and II. One could obtain the following results:—

Test for Group I. Add a few drops of HClAq.—A white pp. of $PbCl_2$ forms.

Test for Group II. Filter, and to filtrate add H_2S in small quantity.—A black pp. of PbS comes down.

Test for Group III. Filter, boil off the H_2S, and to same solution add NH_4ClAq and a few drops of NH_4OHAq.—A white pp. of $Pb(OH)_2$ is obtained.

Test for Group IV. Filter, and to same solution add $(NH_4)_2S$ in small quantity.—A black pp. of PbS appears.

Test for Group V. Filter, and to same solution add a small quantity of $(NH_4)_2CO_3Aq$.—A white pp. of $PbCO_3$ is thrown down.

Test for Mg in Group VI. Filter, and to same solution add a few drops of Na_2HPO_4Aq.—A white pp. of $Pb_3(PO_4)_2$ forms.

Lead might thus be made to appear in all the groups, and as many other metals, e.g. Ag, Hg^{ous}, Hg^{ic}, Bi, Cu, would behave similarly, the student will appreciate how important it is to get rid of one metal before going on to test for the next.

(3) Always carry out preliminary tests before going on to any particular group, and if no metal of that group be present, do not add the reagent for its precipitation to the bulk of the solution, but pass on, discarding the small quantity of solution used in the preliminary test.

The exact method of procedure would be as follows :—

(1) To solution add a few drops of HCl, until solution is distinctly acid. If a precipitate comes down, continue adding HClAq as long as a pp. forms, filter, and as soon as a few drops have run through, test the filtrate by addition of another couple of drops of HCl. If no pp. forms, one can go on to test the filtrate for Group II. If, however, a precipitate does form, one must mix the different portions of the liquid, add more HCl until precipitation is complete, and then pass the liquid through a fresh filter paper.

Note.—If in carrying out this test one warms the solution to aid precipitation, the reaction mixture should be thoroughly cooled before filtration by holding under the tap, to ensure precipitation of as much lead chloride as possible should it chance to be present.

(2) **Preliminary Test.** About 1 c.c. of the filtrate can be tested for Group II by adding excess of SH_2, and one should keep in view the fact that if lead be present as indicated by the precipitation of the characteristic heavy crystalline precipitate (soluble in boiling water) with HClAq, a slight black precipitate of PbS is certain to come down in Group II, since $PbCl_2$ is slightly soluble in water, while PbS is almost insoluble. Lead is the only metal which can come down in two groups if the scheme of testing indicated is correctly carried out. If lead is present, and the black precipitate in Group II is small in amount, one can filter it off and reserve it for further examination after testing through the remaining groups. If a precipitate is obtained in the preliminary test, add excess of H_2S to the bulk of the solution, warm and filter. Test the first few drops of filtrate by addition of H_2S so as to make sure of complete precipitation.

Note.—If the preliminary test indicates that no metal of Group II is present, it is better to proceed at once to Group III, without adding H_2S, because H_2S reduces ferric salts to ferrous, as indicated below.

(3) Expel the SH_2 from the filtrate by boiling for a few minutes, and then add NH_4ClAq and NH_4OHAq to about 2 c.c. If a greenish pp. forms which seems to be ferrous hydroxide, $Fe(OH)_2$, test another small quantity with $K_3Fe(CN)_6$. If a deep blue

pp. (Turnbull's blue) comes down, indicating that a ferrous compound is present, it is necessary to oxidize the ferrous salt to ferric before proceeding further if one intends to test for metals in succeeding groups. To do this, add about 1 c.c. of concentrated HNO_3 to the solution, and boil for a few minutes. Then add NH_4Cl and excess of NH_4OH, when the iron will be precipitated completely as $Fe(OH)_3$. This conversion of ferrous iron to ferric is necessary, because ferrous iron is not completely precipitated by NH_4OH, and trouble would be caused in the next group by a trace of iron passing through into the filtrate. Make certain that precipitation is complete, as in previous groups.

NOTE.—The presence of a ferrous salt as indicated by above tests does not indicate that the iron was present in the ferrous state. All ferric salts are reduced to ferrous by SH_2, e.g.

$$2FeCl_3Aq + H_2S = 2FeCl_2Aq + 2HClAq + S.$$

If iron be present, the original solution must be tested with $K_3Fe(CN)_6$.

(4) To a few drops of the filtrate from Group III add $(NH_4)_2SAq$. If a pp. forms, add excess of $(NH_4)_2SAq$ and filter.

(5) Filter and test a small quantity with $(NH_4)_2CO_3$, and warm gently. If a pp. forms, warm the solution and then add excess of $(NH_4)_2CO_3Aq$; filter.

(6) To a few c.c. of the filtrate add Na_2HPO_4Aq, and warm. If a pp. forms, divide the residual liquid into two parts.

(*a*) Add slight excess of Na_2HPO_4Aq to one half, filter and evaporate to dryness. Ignite, to get rid of ammonium salts, and reserve the residue for carrying out confirmatory tests for potassium if detected.

(*b*) Evaporate the other half of the solution to dryness, ignite, to get rid of ammonium salts, and then moisten with a few drops of HNO_3 and test for potassium and sodium by platinum wire. Use blue glass or potassioscope if necessary.

(7) Boil the original solution with excess of NaOHAq to test for ammonium salts.

Precautionary Note.—It is obvious that one cannot test the filtrate from Group V for ammonium compounds, because NH_4ClAq, NH_4OHAq, or $(NH_4)_2CO_3Aq$ may have been added previously, and one would therefore be certain to obtain a positive result. This is a fundamental mistake of the beginner in analysis.

He uses reagents, and then tests the solution for a metallic or acid radicle which he has added. Another common mistake, for example, is to dissolve a substance in HClAq, and then test for a chloride. See remarks under Acids.

Confirmatory Tests. Although after detection of a metal by the group tests one can frequently use the original solution for confirmatory tests, even when two or more metals are present, this is not invariably the case. Suppose, for example, that one thought one had identified lead in a solution which really contained a barium salt and not a lead salt. One might select as two confirmatory tests the precipitation of chromate on addition of K_2CrO_4Aq, and the precipitation of sulphate on adding dil. H_2SO_4. The Ba present would give a yellow pp. of $BaCrO_4$ and a white pp. of $BaSO_4$ respectively, which a beginner might mistake for $PbCrO_4$ and $PbSO_4$ respectively.

Rule. If in doubt, one can generally proceed as follows:—

Wash the precipitate obtained in carrying out the group reaction for the metal. One obtains in this way a pure compound of the metal, which can usually be dissolved in an appropriate solvent and tested by the usual confirmatory tests. It may be necessary that the solution obtained should be made nearly neutral before carrying out certain confirmatory tests; e.g. K_2CrO_4Aq added to a strongly acid solution of a silver salt gives no pp. of silver chromate, because that body is soluble in acids.

The conditions for precipitation in the different cases are fully indicated under the **Lists of Tests** for the respective metals. To neutralize a solution, place it in a porcelain dish, add a drop of litmus, and then add NH_4OHAq or dil. HNO_3Aq with constant stirring until the reaction is approximately neutral. The following summary indicates concisely the method of procedure:—

Test. Note:—Filtration is unnecessary unless a pp. forms.	Result.	Confirmatory Tests.
1. Add to solution **HClAq** as long as a pp. forms. Filter.	Pp. may be $AgCl$ $HgCl$ $PbCl_2$	Add NH_4OHAq to pp.; AgCl dissolves; HgCl blackens; $PbCl_2$ does not dissolve. Confirm further with original solution. Use tests on p. 182.
2. To filtrate add excess of SH_2. Filter.	Pp. may be (PbS)	(1) K_2CrO_4. (2) H_2SO_4.
	CuS	(1) NH_4OH. (2) Flame test. (3) $K_4Fe(CN)_6$.
	HgS	(1) Cu and HCl. (2) $SnCl_2$.
	Bi_2S_3	(1) Oxychloride test. (2) KI.
	CdS	(1) NaOH. (2) NH_4OH.
	As_2S_3	(1) Reinsch's test.
	Sb_2S_3	(1) NH_4OH. (2) Reinsch.
	SnS	$HgCl_2$.
	SnS_2	$HgCl_2$ after appropriate treatment.
3. **Boil off H_2S** and then add NH_4ClAq and NH_4OHAq in excess. Filter. **N.B. Ferrous Salts must be oxidized to ferric before adding NH_4ClAq and NH_4OHAq.**	Pp. may be $Fe(OH)_3$ $Al(OH)_3$ ($Cr(OH)_3$)	Dissolve the pp. in minimum of dilute hot HClAq, and carry out confirmatory tests given on p. 187.
4. To filtrate add $(NH_4)_2S$ in excess. Filter.	Pp. may be CoS NiS	(1) Confirm by borax bead test. (2) Dissolve in conc. HCl + a crystal of $KClO_3$. Evaporate to dryness; dissolve residue in water, add KCNAq, then NaOH and Br_2Aq. Black pp. indicates Ni.
	ZnS MnS	Dissolve in minimum of dil. HCl, and confirm as described on p. 188.
5. To filtrate add $(NH_4)_2CO_3$ in excess. Filter.	Pp. may be $BaCO_3$ ($SrCO_3$) $CaCO_3$	Dissolve in minimum of acetic or HClAq, and confirm as described on p. 189.
6. To half the filtrate add Na_2HPO_4Aq. Filter.	Pp. may be $Mg.NH_4.PO_4$.	This pp. is of little value for carrying out confirmatory tests. If necessary, the original solution after removal of metals in first five groups and evaporation to dryness and ignition should be used.
7. Evaporate half the filtrate from (5) to dryness, and ignite to get rid of Ammonium Salts. Moisten with HNO_3 and test with Platinum wire.	**K** or **Na** may be indicated.	Confirm Potassium by precipitation of Potassium Hydrogen Tartrate by dissolving residue in a few drops of water and adding Tartaric Acid or Sodium Hydrogen Tartrate (see p. 190).
8. Test the **original solution** for Ammonium Compounds by boiling up with NaOHAq or KOHAq.	Evolution of NH_3.	No further test necessary.

D. ANALYSIS OF A SOLID MIXTURE CONTAINING TWO OR MORE METALS BELONGING TO DIFFERENT ANALYTICAL GROUPS.

(Groups II A and II B might be regarded as different groups.)

The substance must be obtained in solution before going on to the wet tests, and the remarks made under B would, generally speaking, apply in this case; e. g. one generally tries **(a) water**, **(b) dil. HCl**, **(c) conc. HCl**, **(d) dil. HNO_3**, **(e) conc. HNO_3**, and **(f) aqua regia**, in order, unless the appearance of the body or any preliminary dry tests which one may have carried out has indicated what would probably be the best solvent. Attention should be given to the following points:—

(1) If anything stronger than dilute HCl is required for solution, the student should be particularly careful to use a minimum of acid. Boil up with excess of solid for some time (e. g. 5 minutes), dilute with water, filter, and use solution for testing through the groups in the usual way. If the solution seems to be strongly acid after filtering, evaporate nearly to dryness, and add water before proceeding to Group II.

(2) A mixture often consists of one substance soluble in water, and of one substance insoluble in water, but soluble in acids. In such a case by far the best method of procedure may be to boil up with water, filter, and use the filtrate for testing for one metal, and the carefully washed residue on the filter for testing for the other. If one dissolves both substances in acid, the mixture may become more difficult to analyse. e.g. Suppose the two substances are lead oxide and magnesium sulphate. The magnesium sulphate is easily soluble in water, and might be dissolved and analysed without difficulty: the residue of litharge would from appearance and reactions be quite easy to identify. Suppose, however, that the two substances are dissolved in HClAq or HNO_3Aq. If HClAq is used a mixed precipitate of lead chloride, $PbCl_2$, and lead sulphate, $PbSO_4$, will form during the experiment, and if HNO_3Aq be used, $PbSO_4$ will come down. The identification of $PbSO_4$ might present difficulties to a beginner.

(3) If more than one acid be present in the mixture, the difficulties are considerably increased, because there is greater chance of two soluble bodies interacting to give insoluble products; e.g. barium chloride and potassium sulphate given in a mixed

solid would interact immediately on solution in water, with precipitation of barium sulphate, $BaSO_4$, which a beginner would probably find very difficult.

$$K_2SO_4Aq + BaCl_2Aq = BaSO_4 + 2KClAq.$$

Having dissolved the substance in an appropriate solvent, carry out the analysis as follows:—

(*a*) If Phosphates insoluble in water are absent, proceed as described under C, p. 196.

(*b*) If Phosphates insoluble in water are present, the Phosphoric Acid must as a rule be eliminated by the method described under B, p. 193.

E. SUMMARY OF ANALYSIS OF A MIXTURE, GIVEN IN SOLUTION OR IN SOLID STATE, CONTAINING TWO OR MORE METALS WHICH MAY BELONG TO THE SAME GROUP.

In analysing a mixture which may contain two or more metals in one group, the methods of solution already given would apply, and it is important to note that **separate analysis of extracts** with (a) **Water**, and (b) **Hydrochloric Acid**, might give suggestive results. Any residue insoluble in water and hydrochloric acid should be examined separately, and if a portion is found to be quite insoluble in the ordinary solvents, Section F should be consulted (p. 205). **Dry tests** are often of great value. A larger quantity of substance should be taken for solution than in previous cases.

Having effected solution and got rid of as much acid as possible proceed to the systematic analysis outlined in following table :—

GENERAL TABLE. EXAMINATION FOR METALLIC RADICLES.

Experiment.	Result.	Distinction and Confirmation.
1. To the solution add **HClAq** as long as a precipitate forms. Filter.	Precipitate may be **AgCl** **HgCl** **$PbCl_2$**	Examine by **General Table I.**
2. Test a small quantity of filtrate with H_2SAq, and if a pp. forms pass **gaseous SH_2** into the rest of filtrate in a small flask. (Note proper method of saturating as explained on **p. 180.**) Filter and wash with H_2SAq. Reserve filtrate for Expt. 4.	Precipitate may be :—(**PbS**), **HgS**, **Bi_2S_3**, **CuS**, **CdS**. **As_2S_3**, **Sb_2S_3**, **SnS**, or **SnS_2**.	Group II.
3. Pierce the filter, wash the residue in a flask or test-tube, and digest at moderate temperature with **$(NH_4)_2S$**. Filter.	(a) **Residue insoluble in $(NH_4)_2S$** might be :—(**PbS**), **HgS**, **Bi_2S_3**, **CuS**, **CdS**.	Examine by **General Table II A.**
	(b) The following sulphides might go into solution in the **$(NH_4)_2S$**. **As_2S_3**, **Sb_2S_3**, **SnS**, **SnS_2**.	Examine the solution by **General Table II B.**
4. Boil up filtrate until free from H_2S, and then test a few c.c. for Group III by adding NH_4ClAq and NH_4OHAq and warming. If a positive result be obtained, test solution for Iron by $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, and also for Phosphoric Acid by warming a few c.c. with excess of Ammonium Nitromolybdate. If ferrous Iron be present, oxidize it to ferric state by boiling up with about one c.c. of conc. **HNO_3**, and if H_3PO_4 be present, remove it as described on p. 193. Then add NH_4ClAq and NH_4OH; warm, filter.	Precipitate may be :— **$Al(OH)_3$**, **$Fe(OH)_3$**, **$Cr(OH)_3$**.	Examine by **General Table III.**
5. Test a small quantity of filtrate with $(NH_4)_2S$. If a pp. forms, add $(NH_4)_2S$ in slight excess, warm and filter.	Precipitate might be **NiS**, **CoS**, **ZnS**, or **MnS**.	Examine by **General Table IV.**
6. To a few c.c. of filtrate add $(NH_4)_2CO_3Aq$, and warm gently. If a precipitate forms, add **$(NH_4)_2CO_3Aq$** to the bulk of the solution, warm and filter.	Precipitate may be **$BaCO_3$** (**$SrCO_3$**) **$CaCo_3$**	Examine by **General Table V.**
7. Test a small portion of filtrate with Na_2HPO_4Aq. If a pp. forms, add this reagent to half the filtrate, warm and set aside for a few minutes.	Precipitate may be **$Mg.NH_4.PO_4$**	Resummarized in **General Table VI.**
8. Examine the other half of the filtrate from Expt. 6 for Potassium and Sodium by evaporation to dryness and ignition to get rid of Ammonium Salts, and then employing flame test.—Platinum wire.	Flame test may indicate **K** or **Na**.	
9. While above evaporation is proceeding, boil a few c.c. of original solution with NaOHAq or KOHAq.	Evolution of **NH_3** indicates (NH_4) compound.	

F. NOTEWORTHY SUBSTANCES, MANY OF WHICH ARE OF CHARACTERISTIC APPEARANCE, AND SOME OF WHICH ARE DIFFICULTLY SOLUBLE OR INSOLUBLE.

A few of the more insoluble substances commonly met with are worth special comment. Many have characteristic appearance and properties.

(1) **Metallic lustre.** The metals, e. g. Pb, Bi, Ag (these three are soluble in HNO_3). Arsenic has greyish lustre (soluble in HNO_3). Powdered zinc is generally bluish grey and dissolves in HClAq or H_2SO_4Aq, giving off hydrogen which can be burnt. Certain sulphides (mostly of natural occurrence) may have metallic lustre, e. g. FeS_2 (pyrites), Sb_2S_3 (stibnite), PbS (galena), $Cu_2S . Fe_2S_3$ (copper pyrites), FeS (ferrous sulphide, formed by direct union of Fe and S).

(2) **Black or brown.** Many sulphides and a few oxides, e. g. FeS (pp^d), Bi_2S_3, PbS (pp^d), CuS, SnS, HgS (pp^d), Sb_2S_3 (black variety), CuO, PbO_2 (very dark brown), MnO_2.

(3) **Yellow.** HgO (yellow variety), PbI_2, As_2S_3, (As_2S_5), SnS_2 (sometimes in crystals similar to PbI_2), $PbCrO_4$, $BaCrO_4$, Ag_3PO_4, Ag_3AsO_3, (PbO massicot).

Faint yellow. AgBr, AgI, $FePO_4$.

(4) **Orange or Brownish.** Sb_2S_3 (deep orange), PbO (light brown, litharge), Ag_3AsO_4 (chocolate brown).

(5) **Red.** HgO (red variety), HgI_2, Pb_3O_4 (red lead), HgS cinnabar (red) and vermilion (scarlet).

(6) **White substances particularly insoluble.** Sb_2O_5, SnO_2, $BaSO_4$, $PbSO_4$, $CaSO_4$ (is slightly soluble), AgCl, HgCl (calomel).

Many substances are met with in a **variety of forms**, e. g. mercuric oxide HgO (red and yellow), mercuric sulphide HgS (black, red, and scarlet), antimony sulphide Sb_2S_3 (greyish metallic lustre, black or orange). The solubility of above substances has in most cases been previously mentioned, but a few notes might be found useful:—

(1) Many oxides with more oxygen than corresponds to the ordinary valency of the metal, e. g. PbO_2, Pb_3O_4, MnO_2, yield chlorine on heating with conc. HCl.

(2) **Manganese Dioxide and conc. H_2SO_4** are convenient reagents for testing halides insoluble in cold water, e. g.

AgCl, AgBr, AgI, SbOCl, BiOCl, HgI_2, HgI, PbI_2.

[NOTE.—Halogen can be detected in such substances as dimercurous ammonium chloride (black precipitate), $NH_2 . Hg_2Cl$, and in mercuric ammonium chloride (white precipitate), NH_2HgCl, by the same reagents.]

(3) As already noted, **certain sulphides** (e.g. FeS_2, As_2S_3, HgS) give off H_2S only in small quantity on treatment with conc. HCl or aqua regia, the bulk of the sulphur being transformed to H_2SO_4. The sulphuric acid can be tested for as usual with $Ba(NO_3)_2Aq$ and HNO_3Aq (or $BaCl_2Aq$ and HClAq), and, being found, conclusively proves the presence of sulphide, taking into consideration appearance and properties.

(4) **Slightly soluble bodies**, e.g. $CaSO_4$, $PbCl_2$, should be kept in view while preparing solutions.

(5) Many substances behave in a characteristic manner with certain reagents; e.g. (*a*) Red lead turns brown on addition of HNO_3Aq, owing to separation of lead peroxide, while lead nitrate will be found in solution.

(*b*) Metallic Sb and Sn react with HNO_3, giving brown fumes of NO_2 with separation of white insoluble powders, Sb_2O_5 and SnO_2. If the latter substances be given for analysis they can be reduced on charcoal, the metals dissolved in conc. HCl (with crystal of chlorate in the case of antimony), and the solutions tested.

(6) Certain organic compounds in solution, e.g.

$$CaC_2O_4,\ CaC_4H_4O_6,\ K.SbO.C_4H_4O_6, \text{ and } Hg(CN)_2,$$

do not give all the tests for the respective metals until the organic material is got rid of. This is easily effected in the case of tartrate and oxalate by heating strongly, when oxide or carbonate of metal is left, and in the case of mercury cyanide by heating with HClAq.

(7) Many substances, quite insoluble in the ordinary reagents, e.g. $BaSO_4$ and AgCl, may be obtained in soluble form by mixing the dry powdered substance with solid Na_2CO_3 or K_2CO_3 and heating for some time in a crucible by means of a blowpipe or special burner.

The metal is generally transformed into carbonate by such treatment—silver compounds, however, yield metal—and the acid radicle combines with sodium to give a salt soluble in water, e.g. $BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$.

On powdering up the residue and extracting with water, the sodium salt dissolves and the solution can be tested for the acid radicle after acidifying. The portion insoluble in water can be dissolved in HClAq or HNO_3Aq and tested for metal in the usual way, e.g. $BaCO_3 + 2HClAq = BaCl_2Aq + H_2O + CO_2$.

This procedure is rarely necessary in Elementary Analysis.

IDENTIFICATION AND SEPARATION OF METALS OF GROUP I.

GENERAL TABLE I.

The precipitate obtained on addition of **$HClAq$** to original solution may contain **$AgCl$**, **$HgCl$**, and **$PbCl_2$**. After filtering, wash the precipitate on the filter paper with boiling water until free from **$PbCl_2$** if present.

(Note.—When the liquid coming through gives no reaction with SH_2Aq, the washing is sufficient.)

<table>
<tr>
<td rowspan="2">Filtrate may contain **$PbCl_2Aq$.**
Confirm by addition of *a*) **K_2CrO_4Aq.**
b) **$KIAq$.**
Yellow pp. in each case confirms **Pb.**</td>
<td colspan="2">White residue may be **$AgCl, HgCl$.** Warm Ammonia slightly in a test-tube and pour on to this white residue.
AgCl dissolves and passes through.
HgCl blackens.</td>
</tr>
<tr>
<td>The solution may contain **AgCl.**
Make acid with HNO_3Aq.—If white curdy pp. of AgCl forms,
Ag
is present.</td>
<td>The residue on the filter would be black Dimercurous Ammonium Chloride, **$NH_2 . Hg_2Cl$.**
Dissolve in a few drops of aqua regia, nearly neutralize, add Cu, strip and warm. Grey deposit on the copper, which becomes silvery on rubbing, confirms
Hg^{ous}.</td>
</tr>
</table>

IDENTIFICATION AND SEPARATION OF METALS OF GROUP II.

(1) GENERAL TABLE II A.

Identification and Separation of the Metals of Group II A.

After digesting the precipitate obtained on adding sulphuretted hydrogen with $(NH_4)_2S$, and filtering, the residue may contain **PbS, CuS, HgS, CdS,** and Bi_2S_3. Wash the precipitate free from HClAq if necessary. Boil up a mixture of about 1 c.c. of conc. HNO_3 and 2 c.c. water in a test-tube, and pour on to the precipitate. Collect the filtrate in a test-tube and repeat. The residue may be HgS, or, if white, $PbSO_4$. The solution might contain nitrates of Pb, Cu, and Bi.

<table>
<tr><th colspan="3">Treatment of Solution.</th><th>Treatment of Residue (HgS).</th></tr>
<tr><td colspan="3">Test a small quantity of solution with H_2SO_4Aq. If a pp. is obtained, add a sufficiency of H_2SO_4Aq and equal bulk of alcohol to main portion of solution. Filter. The precipitate may be $PbSO_4$. Filtrate may contain Copper and Bismuth Nitrates.</td><td rowspan="3">Dissolve in a few drops of aqua regia, boil off the Chlorine, nearly neutralize with NaOHAq, but still keep distinctly acid, add a strip of Copper and boil.
The Copper strip becomes grey, and if dried and then rubbed between filter paper, silvery. This confirms Hg^{ic}.</td></tr>
<tr><td rowspan="2">Confirmation of Lead.
Dissolve $PbSO_4$ in Ammonium Acetate by boiling. Cool and add K_2CrO_4. Yellow pp. of $PbCrO_4$ forms, confirming Pb.
Note.—Ammonium Acetate solution for this test can be made by adding Acetic Acid to about 2 c.c. of conc. NH_4OHAq until the reaction is acid.</td><td colspan="2">Examination of solution which may contain Bismuth, Cadmium, and Copper Nitrates.
Add NH_4OHAq in excess. If solution turns blue, Copper is indicated; Cadmium gives a white precipitate soluble in excess and therefore remains in solution. A white precipitate is probably $Bi(OH)_3$. Filter.</td></tr>
<tr><td>Confirm Bi.
Dissolve the pp. in a few drops of dil. HCl. Fill up the test-tube used as receiver with water. A white pp. of BiOCl confirms Bi.</td><td>Confirm Cu.
(a) If solution is blue divide into two parts.
(b) Add KCN until blue colour disappears and pass H_2S.
Yellow precipitate indicates Cadmium.
Note.—If the solution is not blue KCN need not be added before passing H_2S through the solution.
Add Acetic Acid until solution is acid, and then add $K_4Fe(CN)_6$. Brown coloration or precipitate of $Cu_2Fe(CN)_6$ confirms Cu.</td></tr>
</table>

(2) GENERAL TABLE II (B).

Identification and Separation of the Metals of Group II B.

The solution of ammonium polysulphide may contain **arsenic, antimony,** and **tin** as **thiosalts.** Add **HClAq** to the solution until the reaction is acid. **As_2S_5, Sb_2S_5,** and **SnS_2** are precipitated, and also **sulphur,** from the excess of ammonium polysulphide. Filter and wash. Pierce the filter paper, wash the residue into a small flask, add about 10 c.c. **ammonium carbonate** solution and one or two small pieces of **solid ammonium carbonate.** Digest for five to ten minutes at moderate temperature. Arsenic sulphide will dissolve, antimony and tin sulphides are almost insoluble. Filter and wash.

Treatment of filtrate.	**Treatment of Residue.**	
Acidify with HClAq when **As_2S_3** may be precipitated. Filter, wash; dissolve the pp. in a few drops of conc. HCl with a crystal of Potassium Chlorate. Boil down until all Chlorine has been got rid of, dilute and divide into two parts: *a*) Add **H_2SAq** or pass SH_2. Yellow pp. of As_2S_3 forms. *b*) Add a strip of **Copper,** boil, and carry out the Reinsch test.	Dissolve the residue in **conc. HCl** (with addition of a crystal of $KClO_3$ if necessary). Evaporate down, dilute with water, and place in a dish with a small piece of pure stick Zinc rolled in a piece of Platinum foil. Antimony, if present, will deposit on the Platinum as a black stain, and Tin on the Zinc.	
	Confirmation of **Antimony.**	Confirmation of **Tin.**
	Wash the Platinum with water, and put in a shallow dish with a few c.c. of water and a few drops of $(NH_4)_2S$. Evaporate to dryness on a water-bath. The stain on the Platinum is coloured orange, owing to formation of Sb_2S_3, which confirms **Sb.**	Scrape off any deposit from the Zinc, and boil it up with conc. HCl (preferably in presence of a piece of Platinum). Stannous Chloride is obtained. Dilute and add one or two drops of Mercuric Chloride ($HgCl_2Aq$). A white precipitate changing to a grey deposit of Mercury confirms **Tin.**

GENERAL TABLE III.

The precipitate may consist of **$Al(OH)_3$**, **$Fe(OH)_3$**, and **$Cr(OH)_3$**. Dissolve in HClAq, and then boil for some time with **NaOHAq.** (NOTE.—The caustic alkali used should be free from alumina. If uncertain regarding this point a check experiment is necessary.)

The aluminium hydroxide dissolves to form sodium aluminate, **$Al(ONa)_3$**. The iron and chromium hydroxides remain unaltered. Filter.

Treatment of Filtrate.	Treatment of Residue.	
Acidify the solution of Sodium Aluminate with HCl, and then add NH_4OH and warm. If **Al** be present, a white gelatinous pp. of **$Al(OH)_3$** will come down. **Aluminium.**	Dissolve by warming with HCl, and divide into two parts.	
	Part I.	Part II.
	Test for Iron by **$K_4Fe(CN)_6$**. Deep blue pp. (Prussian blue) indicates **Iron.**	Nearly neutralize with NaOHAq, add **fresh bleaching powder** solution, and warm. Solution turns yellow. Acidify with Acetic Acid and add **Lead Acetate.** Yellow pp. of **$PbCrO_4$** indicates **Chromium.**

GENERAL TABLE IV

(for cases where two metals in the same Group may be present).

The precipitate formed on adding ammonium sulphide may consist of **ZnS, MnS, NiS,** and **CoS.** Pierce the filter, and wash the precipitate into a small flask with a few c.c. of dilute HCl (made by diluting the concentrated acid to about five times its volume with water), allow to stand for about five minutes with frequent shaking and then filter. A black insoluble residue may consist of **NiS** and **CoS**: the solution in hydrochloric acid may contain the zinc and manganese as chlorides.

<table>
<tr><th>Treatment of Residue.</th><th colspan="2">Treatment of Filtrate.</th></tr>
<tr><td rowspan="3">Test black residue (after washing) with borax bead.
a) If the bead is brownish Nickel is indicated. Confirm by dissolving the black pp. in a small quantity (say ½ c.c.) of concentrated HCl to which a few crystals of $KClO_3$ have been added, evaporate nearly to dryness, add NaOH and bromine water and warm. Black pp. confirms Ni.
b) If the bead were bluish Cobalt and Nickel might both be present, as the brownish coloration due to Nickel would be masked by the deep blue Cobalt reaction. Dissolve in HCl and $KClO_3$ as above, evaporate to dryness, add water and KCN till the pp. which first forms barely redissolves. [Caution.—No excess of KCN should be present.] Boil, make slightly alkaline with NaOH (avoiding excess), and then add bromine water and warm. Black precipitate indicates Nickel. Filter.
c) Evaporate filtrate to dryness and test with borax bead. A clear sapphire blue bead should now be obtained, confirming Cobalt.</td><td colspan="2">Add NaOHAq in excess and boil. The manganese is precipitated as Manganous Hydroxide, $Mn(OH)_2$, while the zinc is precipitated as Zinc Hydroxide, but this dissolves in excess to form Sodium Zincate, $\mathbf{Zn(ONa)_2}$.</td></tr>
<tr><th>Treatment of Filtrate.</th><th>Treatment of Residue.</th></tr>
<tr><td>To the filtrate add $(NH_4)_2SAq$. White pp. of Zinc Sulphide, ZnS, indicates Zinc.
Confirm by dissolving the Zinc Sulphide in a few drops of HCl, pouring on to filter paper, moistening with Cobalt Nitrate and igniting.
Green residue confirms Zinc.</td><td>Dissolve the residue in HCl and add $(NH_4)_2SAq$.
Salmon-pink pp. of MnS indicates Manganese.
Confirm by dissolving in HClAq, avoiding excess, and then warming with bleaching powder solution. Brownish black pp. of $\mathbf{MnO_2 . xH_2O}$ confirms Manganese.</td></tr>
</table>

GENERAL TABLE V.

The precipitate obtained with $(NH_4)_2CO_3$ may consist of **$BaCO_3$**, **$SrCO_3$**, **$CaCO_3$**. Boil acetic acid in a test-tube and pour on to the filter, and repeat if necessary, using what has come through the filter paper. A solution containing acetates is obtained. Add **K_2CrO_4Aq** in slight excess, and filter if a pp. forms.

Precipitate.	**Filtrate.**	
Yellow precipitate indicates **Barium.** Confirm by flame test. **Barium.**	To half the filtrate, which may contain solutions of Strontium and Calcium Acetates, add **$CaSO_4Aq$**, warm gently, and allow to stand ten minutes. White precipitate may be **Strontium Sulphate, $SrSO_4$.**	
	Filter pp. of **$SrSO_4$** and confirm Strontium by Platinum wire test. **Strontium.**	If a pp. was obtained with $CaSO_4Aq$, add to the other half of the filtrate a concentrated solution of Ammonium Sulphate, boil and then cool, and allow to stand ten minutes. The Strontium should be entirely precipitated as Strontium Sulphate, while the Calcium will partly remain in solution as Calcium Sulphate. Filter, and add **$(NH_4)_2C_2O_4$**. A white pp. of Calcium Oxalate indicates **Calcium.** Filter and confirm by Platinum wire test.

GENERAL TABLE VI.

The solution on filtration, after adding $(NH_4)_2CO_3$, might contain **magnesium, potassium,** and **sodium.** Divide into two parts.

(*a*) **Small portion.**	(*b*) **Major portion.**
Add **Na_2HPO_4Aq** to about a fourth of solution, stir, and allow to stand. If Magnesium Ammonium Phosphate, $Mg.NH_4.PO_4$, comes down, the presence of **Magnesium** is indicated.	Evaporate to dryness in a porcelain dish, and ignite until all Ammonium Compounds are volatilized. Test the residue for **Sodium** and **Potassium** by the flame test (using a blue glass or potassioscope if necessary). If **Potassium** is indicated, confirm by the Potassium Hydrogen Tartrate test.

Note. In testing for **Ammonium Salts** by heating with caustic soda or potash the **original solution must be employed.**

PART V

A. IDENTIFICATION OF ACID RADICLES

B. IDENTIFICATION OF METALLIC OXIDES AND HYDROXIDES

A. IDENTIFICATION OF ACID RADICLES.

The Acids cannot be tested for so systematically as the Bases, but the student should have a general scheme to fall back upon for any particular type of analysis.

A few general points must be noted:—

(1) **Solubility.** The solubility of the different salts of the metals found should be carefully kept in view throughout the analysis; e. g. if the substance was soluble in water, and barium has been found, it is useless to look for sulphuric acid, because barium sulphate is practically insoluble in water, and similarly, if silver has been found in a simple solution, it is useless to look for chloride.

(2) In dealing with solids, the appearance of the substance given should agree with the properties of the substances detected by analysis, and the student should find the **lists of common compounds** of the metals given on the **pages adjoining the tests for the respective metals** helpful in coming to a decision as to what substances could possibly be present.

(3) The substance should be analysed for metals before going on to the acids. Metals may have to be removed before testing for acids as indicated on p. 241.

The following List of Acids includes all those met with in General Inorganic Analysis.

List of Acids.

The acids of small importance from the analytical point of view are enclosed in brackets.

Acid.	Formula.	Name of Salts.	Remarks.
1. **Carbonic Acid**	H_2CO_3	Carbonates	Pure Carbonic Acid, H_2CO_3, is unknown. The acid is only known in solution H_2CO_3Aq.
2. **Hydrogen Sulphide (Sulphuretted Hydrogen)**	H_2S	Sulphides	The acid is a gas soluble in water; the solution is feebly acid in reaction.
3. **Sulphurous Acid**	H_2SO_3	Sulphites	The pure acid is unknown. A solution H_2SO_3Aq smells strongly of SO_2.
4. **Thiosulphuric Acid**	$H_2S_2O_3$	Thiosulphates	The acid is unstable, and is not met with.
5. **Nitrous Acid**	HNO_2	Nitrites.	The pure free acid has not been obtained.
6. **Hypochlorous Acid**	$HOCl$	Hypochlorites.	The free acid is unstable.
7. **Chloric Acid**	$HClO_3$	Chlorates	do. do.
8. Bromic Acid	$HBrO_3$	Bromates	do. do.
9. **Chromic Acid**	H_2CrO_4	Chromates	The anhydride of both acids (CrO_3) is met with.
10. **Dichromic Acid**	$H_2Cr_2O_7$	Dichromates	
11. **Permanganic Acid**	$HMnO_4$	Permanganates	The acid is not met with.
[12. Manganic Acid	H_2MnO_4	Manganates	do. do.]
13. **Hydrocyanic Acid**	HCN	Cyanides	A solution of the acid might be met with.
14. **Sulphuric Acid**	H_2SO_4	Sulphates	One of the more important acids.
15. **Hydrofluoric Acid**	HF	Fluorides	The free pure acid occurs.
[16. Hydrofluosilicic Acid	H_2SiF_6	Silicofluorides	Solution of free acid might very rarely be met with.]
17. **Hydrochloric Acid**	HCl	Chlorides	One of the most important group of acids.
18. **Hydrobromic Acid**	HBr	Bromides	The free acid would rarely be met with.
19. **Hydriodic Acid**	HI	Iodides	do. do.

Acid.	Formula.	Name of Salts.	Remarks.
20. Thiocyanic Acid (Sulphocyanic Acid)	$HCNS$	Thiocyanates (Sulphocyanides)	The free acid would not be met with.
21. Hydroferrocyanic Acid	$H_4Fe(CN)_6$	Ferrocyanides	Free acid would not occur.
22. Hydroferricyanic Acid	$H_3Fe(CN)_6$	Ferricyanides	do. do.
23. **Nitric Acid**	HNO_3	Nitrates	The free compound is one of the most important acids.
24. **Phosphoric Acid**	H_3PO_4	Phosphates	do. do.
25. **Boracic Acid** (or Boric Acid)	H_3BO_3	Borates	The acid is a white crystalline substance.
26. **Silicic Acid** (Metasilicic Acid)	H_2SiO_3	Silicates	The free acid would very rarely occur, but the anhydride (SiO_2) is common.
27. **Iodic Acid**	HIO_3	Iodates	Acid is a white cryst. solid, but would rarely be met with.
28. **Arsenious Acid**	H_3AsO_3	Arsenites	Arsenious Anhydride, As_2O_3, which gives a very dilute solution of the acid on boiling with water, is a common substance.
29. **Arsenic Acid**	H_3AsO_4	Arsenates	The acid and its anhydride (As_2O_5) occur but rarely.
30. Hypophosphorous Acid	H_3PO_2	Hypophosphites	Free acid does not occur.
[31. Pyrophosphoric Acid	$H_4P_2O_7$	Pyrophosphates	The acid and its salts are rarely met with.]
[32. Metaphosphoric Acid	HPO_3	Metaphosphates	Acid occurs as a cryst. solid. Its salts rarely occur.]
[33. Persulphuric Acid	$H_2S_2O_8$	Persulphates	The acid is not met with.]

A few organic acids are introduced for convenience.

Note.—HCN and HCNS are organic acids, but for convenience it is better to put them with the inorganic acids in a book like this.

REACTIONS OF SALTS OF THE ACIDS, WITH TESTS FOR THE FREE ACIDS, WHERE MET WITH.

CARBONATES.

Reagent.	Result observed.	Remarks.
*1. HClAq or H_2SO_4 Gas evolved is tested by lime-water.	All Carbonates are decomposed by addition of acids to the solution and gentle warming. e.g. $BaCO_3 + 2HClAq = BaCl_2Aq + H_2O + \mathbf{CO_2}$ If the Carbon Dioxide is passed into lime-water a white precipitate of Calcium Carbonate will be thrown down. $CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$	A Carbonate would probably be attacked on testing for Group I of the metals, or on trying to dissolve the substance in acid.
2. $CaCl_2$ or $AgNO_3$	If the Carbonate is soluble in water the precipitation of insoluble Carbonates could be used as a test, e.g. precipitation of $CaCO_3$ and Ag_2CO_3. e.g. $(NH_4)_2CO_3Aq + CaCl_2Aq = \mathbf{CaCO_3} + 2NH_4ClAq$ $Na_2CO_3Aq + 2AgNO_3Aq = \mathbf{Ag_2CO_3} + 2NaNO_3Aq$	This test is only applicable to Carbonates of Na, K, or NH_4. (The **free acid** could only be met with in dilute solution, e.g. in soda water.)

SULPHIDES (AND SULPHURETTED HYDROGEN).

Reagent.	Result observed.	Remarks.
*1. HCl	H_2S is evolved,[1] and can be recognized by its odour, and by the blackening of a piece of filter paper moistened with a solution of a Lead salt, e.g. Lead Acetate. $FeS + 2HClAq = FeCl_2Aq + \mathbf{H_2S}\uparrow$ $(CH_3 . COO)_2Pb + H_2S = \mathbf{PbS} + 2CH_3 . COOH$	
2. $AgNO_3$ $(CH_3 . COO)_2Pb$ or $CuSO_4$ for soluble Sulphides.	Soluble Sulphides cause the formation of characteristic precipitates with salts of metals which form insoluble Sulphides. e.g. $(NH_4)_2SAq + 2AgNO_3Aq = \mathbf{Ag_2S} + 2NH_4NO_3$	This test would only apply to the Sulphides of Na, K, NH_4, or to the free acid in solution H_2SAq.

[1] Special Notes on Sulphides.

(1) With **polysulphides,** HClAq sets free SH_2 and precipitates Sulphur as a nearly white precipitate, e.g.

$$(NH_4)_2S_x + 2HClAq = 2NH_4ClAq + \mathbf{H_2S} + \mathbf{S_{x-1}}.$$

(2) A few Sulphides are practically insoluble unless in HNO_3Aq or Aqua regia, e.g. $\mathbf{As_2S_3}$, **HgS**, and $\mathbf{FeS_2}$. **Aqua regia, using minimum quantity of Nitric Acid,** may cause evolution of enough H_2S to blacken Lead Acetate paper. The Sulphur present is, however, chiefly converted into $\mathbf{H_2SO_4}$, which, if tested for with $BaCl_2Aq$ and found, would, taking into account the physical properties of the body, be regarded as confirming Sulphide.

(Free Acid.

(3) The free acid, Hydrogen Sulphide, would be readily detected by its odour and reactions with the metals of Groups I and II. No residue would be left on evaporation of Sulphuretted Hydrogen solution to dryness.)

SULPHITES AND SULPHUROUS ACID.

Reagent.	Result observed.	Remarks.
*1. HCl or H_2SO_4	Sulphurous Acid is liberated, which splits up to form SO_2 and water. The Sulphur Dioxide is readily detected by its odour on warming the solution. e. g. $Na_2SO_3Aq + 2HClAq = 2NaClAq + H_2O + \mathbf{SO_2}$	The pure acid is unknown, but a solution which smells strongly of SO_2 is readily obtained by passing $\mathbf{SO_2}$ into water. No residue is left on evaporation to dryness.
2. **$BaCl_2$**	A white precipitate of Barium Sulphite, $BaSO_3$, is obtained, soluble in $HClAq$. e. g. $Na_2SO_3Aq + BaCl_2Aq = \mathbf{BaSO_3} + 2NaClAq$	The solubility of the precipitate in HCl is rarely complete because Sulphites are generally contaminated with Sulphates produced by the action of the oxygen of the air.
*3. **$AgNO_3$**	A white precipitate of Silver Sulphite is obtained, soluble in hot dil. HNO_3. e. g. $Na_2SO_3Aq + 2AgNO_3Aq = \mathbf{Ag_2SO_3} + 2NaNO_3Aq$ Silver Sulphite is decomposed on boiling, turning grey owing to the deposition of Silver, Silver Sulphate being also formed. $2Ag_2SO_3 = 2Ag + Ag_2SO_4 + SO_2$	
*4. **Decolorization of $KMnO_4Aq$**	An acidified solution of a Sulphite readily decolorizes Potassium Permanganate because of the transformation of Sulphur Dioxide to Sulphur Trioxide. $2KMnO_4 + 5H_2SO_3Aq = K_2SO_4 + 2MnSO_4 + 3H_2O + 2H_2SO_4$	
*5. $K_2Cr_2O_7$	Solutions of Chromates and Dichromates are **turned green** if added to an acidified solution of a Sulphite. $K_2Cr_2O_7 + H_2SO_4 + 3H_2SO_3 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O$	
6. **Carbon and Na_2CO_3**	On heating a Sulphite with Na_2CO_3 on charcoal Sodium Sulphide is formed, which can be detected by placing a little of the fused mass on a **silver coin** and moistening with water. A black stain is formed.	

SALTS OF THIOSULPHURIC ACID, $H_2S_2O_3$.

The free acid is unknown. Use a solution of Sodium Thiosulphate.

*1. **HCl.** Thiosulphates are decomposed with liberation of SO_2 and precipitation of Sulphur.

$$Na_2S_2O_3Aq + 2HClAq = 2NaClAq + H_2O + SO_2 + S.$$

*2. **$AgNO_3$.** A white precipitate of Silver Thiosulphate comes down, which on boiling turns first yellowish, then brown, and finally black, because of transformation to Sulphide.

$$a)\ Na_2S_2O_3Aq + 2AgNO_3Aq = Ag_2S_2O_3 + 2NaNO_3Aq$$
$$b)\ Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4Aq.$$

3. $BaCl_2$. White precipitate of Barium Thiosulphate, unless the solution is very dilute, when no precipitate forms.

$$Na_2S_2O_3Aq + BaCl_2Aq = BaS_2O_3 + 2NaClAq.$$

4. $FeCl_3$. Thiosulphates of the alkalies give a violet coloration which disappears on warming or standing.

$$3Na_2S_2O_3Aq + 2FeCl_3Aq = Fe_2(S_2O_3)_3 + 6NaClAq.$$

*5. **I_2 in KI.** The iodine solution is decolorized.

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6 \text{ (Sod. Tetrathionate).}$$

6. Dry Test. Charcoal and Na_2CO_3. Heated on charcoal with Sodium Carbonate Sodium Sulphide is formed, which, when placed on a moist silver coin, blackens it.

NITRITES.

*1. **HCl** or **H_2SO_4.** Nitrites are decomposed, giving Nitric Oxide, NO, and Nitric Peroxide, NO_2.

e.g.
$$a)\ NaNO_2 + HClAq = NaClAq + HNO_2$$
$$b)\ 3HNO_2 = HNO_3 + H_2O + 2NO$$
$$c)\ 2NO + \underset{\text{from air}}{\underline{O_2}} = 2NO_2$$

The free acid is not met with. Even a dilute solution splits up at ordinary temp. as indicated in equation *b*.

*2. **$FeSO_4Aq$** and acid. A solution of Ferrous Sulphate with a few drops of Acetic Acid gives a deep brown solution of $NO\,.\,2FeSO_4Aq$ (brown ring).

$$a)\ NaNO_2 + CH_3COOHAq = CH_3COONa + HNO_2$$
$$b)\ 3HNO_2 = HNO_3 + H_2O + 2NO$$
$$c)\ NO + 2FeSO_4Aq = NO\,.\,2FeSO_4.$$

3. **$AgNO_3$.** With a concentrated solution of a nitrite, a white precipitate of **Silver Nitrite** is thrown down.

e.g. $$NaNO_2Aq + AgNO_3Aq = \mathbf{AgNO_2} + NaNO_3Aq.$$

*4. **KI, H_2SO_4** and starch. On adding KIAq, starch solution, and dilute Sulphuric Acid to a solution of a Nitrite, a deep blue coloration is obtained, due to the formation of Starch Iodide.

e.g.
$$a)\ NaNO_2Aq + H_2SO_4Aq = NaHSO_4Aq + HNO_2Aq$$
$$b)\ KIAq + H_2SO_4Aq = KHSO_4Aq + HIAq$$
$$c)\ 2HIAq + 2HNO_2Aq = 2H_2O + I_2 + 2NO.$$

The Iodine and Starch form Starch Iodide.

HYPOCHLOROUS ACID, $HOCl$.

Use bleaching powder for following tests. Reagents are indicated in thick type.

*1. **Odour.** Hypochlorous Acid and its salts have a pleasant odour like seaweed.

*2. **HCl** (or H_2SO_4). Chlorine is evolved.

e.g. $CaOCl_2 + 2HClAq = CaCl_2Aq + H_2O + Cl_2$.

*3. **$Pb(C_2H_3O_2)_2$** and NaOH. A white pp. of Lead Hydroxide forms which turns brown on heating because of conversion to Lead Peroxide.

e.g. *a*) $Pb(C_2H_3O_2)_2Aq + 2NaOHAq = Pb(OH)_2 + 2Na.C_2H_3O_2Aq$
b) $Pb(OH)_2 + CaOCl_2 = PbO_2 + CaCl_2 + H_2O$.

*4. **Manganese Sulphate** and NaOH reacts similarly. A black pp. of Hydrated Manganese Dioxide comes down.

5. **$AgNO_3$**. A white pp. of Silver Chloride forms because of decomposition of soluble Silver Hypochlorite.

e.g. *a*) $NaOClAq + AgNO_3Aq = AgOClAq + NaNO_3Aq$
b) $3AgOCl = 2AgCl + AgClO_3$.

CHLORIC ACID, $HClO_3$.

Ions $H^{\cdot}$ and ClO_3'. All Chlorates are soluble in water. Use **Potassium Chlorate** for following tests.

*1. **$AgNO_3$ and H_2SO_3Aq.** $AgNO_3Aq$ gives no pp., but on addition of a few drops of H_2SO_3Aq the Chlorate is reduced to Chloride and a white pp. of Silver Chloride comes down.

a) $KClO_3Aq + 3H_2SO_3Aq = KClAq + 3H_2SO_4Aq$
b) $KClAq + AgNO_3Aq = AgCl + KNO_3Aq$.

*2. **HCl Conc.** The mixture turns yellow on warming and a mixture of Chlorine and Chlorine Peroxide is evolved.

$4KClO_3 + 12HClAq = 4KClAq + 3ClO_2 + 6H_2O + 9Cl$.

3. **H_2SO_4 Conc.** Add the reagent to a very small quantity of solid (2 or 3 crystals) in a dry test-tube. Chlorine Peroxide is evolved as a greenish gas which explodes on warming. [**Caution.**—The contents of the test-tube are liable to be projected.]

$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + 2ClO_2 + H_2O$.

*4. Dry Test. On heating Oxygen is evolved. $2KClO_3 = 2KCl + 3O_2$.

BROMIC ACID, $HBrO_3$.

1. $AgNO_3$. A white pp. of Silver Bromate ($AgBrO_3$) forms.

*2. **HCl.** On warming with mineral acids Bromine is set free.

*3. **H_2SO_3Aq.** Bromide is formed and can be tested for (cf. Chlorate).

4. Dry Test. Alkali Bromates give Oxygen, other Bromates give Bromine and Oxygen.

CHROMIC ACID (H_2CrO_4), CHROMATES AND DICHROMATES.

Chromic Anhydride, CrO_3, is met with as a crimson solid. Potassium Chromate, K_2CrO_4, and Potassium Dichromate, $K_2Cr_2O_7$, are common bodies. Carry out the following tests with Potassium Chromate. The reactions of a soluble Dichromate are similar.

*1. **$AgNO_3$.** A dark red precipitate of Silver Chromate, Ag_2CrO_4, soluble in HNO_3Aq and in NH_4OH, but insoluble in Acetic Acid, is obtained.

$$K_2CrO_4Aq + 2AgNO_3Aq = Ag_2CrO_4 + 2KNO_3Aq.$$

*2. **$BaCl_2$.** A light yellow precipitate of Barium Chromate, insoluble in Acetic Acid, but soluble in mineral acids, comes down.

$$K_2CrO_4 + BaCl_2Aq = BaCrO_4 + 2KClAq.$$

*3. **$Pb(C_2H_3O_2)_2$.** A yellow precipitate of Lead Chromate forms.

$$(CH_3COO)_2PbAq + K_2CrO_4Aq = PbCrO \ + 2CH_3COOK.$$

Reducing agents generally react with Chromates and Dichromates, which are powerful oxidizing agents.

*4. **H_2SO_3Aq.** A solution of Sulphurous Acid changes Chromates and Dichromates from yellow and orange to green, owing to reduction :—

$$2K_2CrO_4 + 3H_2SO_3Aq + 2H_2SO_4 = 2K_2SO_4 + Cr_2(SO_4)_3 + 5H_2O$$
$$K_2Cr_2O_7 + 3H_2SO_3Aq + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O.$$

5. H_2S. Reduction to green Chromic Salt takes place if acid be present, otherwise green Chromium Hydroxide is precipitated.

$$2K_2CrO_4 + 3H_2S + 10HCl = 4KCl + 2CrCl_3 + 8H_2O + 3S$$
$$K_2Cr_2O_7 + 8HCl + 3H_2S = 2KCl + 2CrCl_3 + 7H_2O + 3S.$$

Note :—The change of colour during these reduction processes is due to the alteration of condition of the Chromium. In Chromates and Dichromates Chromium is present as the yellow and orange Chromate and Dichromate anions CrO_4'' and Cr_2O_7'', while in the Chromium Salts produced the Chromium is present as the green kation $Cr^{\cdot\cdot\cdot}$.

PERMANGANIC ACID, $HMnO_4$.

Ions $H^{\cdot}$ and MnO_4'.

Carry out the following tests with Potassium Permanganate.

*1. Colour of solution. Both the acid (which is only known in solution and would not be met with) and its salts are soluble in water, forming characteristic purple solutions.

*2. $FeSO_4$. Ferrous Salts (e. g. $FeSO_4$) immediately reduce and decolorize Permanganates if added to a solution rendered strongly acid by Sulphuric Acid. The alteration of colour depends upon the change of the purple Permanganate ion MnO_4' to give a Manganese Salt where the Manganese is present as the nearly colourless ion $Mn^{\cdot\cdot}$

e. g. $2KMnO_4 + 10FeSO_4 + 8H_2SO_4Aq = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$

*3. Sulphurous Acid solution, H_2SO_3Aq. Sulphur Dioxide or a solution of Sulphurous Acid decolorizes Permanganate.

$$2KMnO_4 + 5H_2SO_3Aq = K_2SO_4 + 2MnSO_4 + 5H_2O + 2H_2SO_4.$$

4. SH_2. Sulphuretted Hydrogen reduces Permanganate with precipitation of Sulphur.

   (*a*) Without addition of acid.

   $$2KMnO_4 + 3H_2S = 2MnO_2 + 3S + 2KOH + 2H_2O.$$

   (*b*) With Sulphuric Acid present.

   $$2KMnO_4 + 3H_2SO_4 + 5H_2S = K_2SO_4 + 2MnSO_4 + 8H_2O + 3S.$$

5. Oxalic Acid, $H_2C_2O_4$. Oxalic Acid decolorizes Permanganate on warming to about 60° C. in presence of Sulphuric Acid. If acid is not added MnO_2 precipitates.

   $$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2.$$

*6. HCl Conc. Chlorine is evolved. This usually takes place with oxidizing agents (cf. $K_2Cr_2O_7$).

$$2KMnO_4 + 16HClAq = 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O.$$

7. H_2O_2. Hydrogen Peroxide causes evolution of Oxygen.

   $$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = 5Cl_2 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

8. Dry Test. Heat solid. Oxygen is evolved.

   $$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

MANGANIC ACID, H_2MnO_4.

Only the Sodium and Potassium Salts might be met with. They are dark green solids which give a green solution, but on dilution (or on passing Carbon Dioxide or Chlorine) change to pink solution of Permanganate with precipitation of Manganese Dioxide.

$$3K_2MnO_4 + 2CO_2 = 2KMnO_4 + 2K_2CO_3 + MnO_2.$$

CYANIDES AND HYDROCYANIC ACID.

Reagent.	Result observed.	Remarks.
*1. $\mathbf{HCl}$ or $\mathbf{H_2SO_4}$	HCN is evolved on warming gently. The odour is characteristic. e. g. $KCNAq + HClAq = KClAq + \overset{\nearrow}{\mathbf{HCN}}$	The acid itself and the Alkali Cyanides NaCN and KCN have the characteristic odour of bitter almonds. Some have difficulty in detecting this odour. A student should find out whether he can recognize it both because the acid is poisonous and for analytical reasons.
*2. **Prussian Blue Test.** $\mathbf{FeSO_4 . NaOH}$ $\mathbf{FeCl_3 . HCl}$	Add $FeSO_4Aq$ and NaOHAq and warm gently, then add two or three drops of $FeCl_3Aq$ and enough HClAq to dissolve any hydroxides which may have precipitated. A deep blue precipitate—Prussian blue—is thrown down. The following equations explain the different stages of the reaction: a) $FeSO_4Aq + 2NaOHAq = Fe(OH)_2 + Na_2SO_4Aq$ b) $6KCNAq + Fe(OH)_2 = K_4Fe(CN)_6Aq + 2KOHAq$ c) $3K_4Fe(CN)_6Aq + 4FeCl_3Aq$ $= \mathbf{Fe_4[Fe(CN)_6]_3} + 12KClAq$	
3. **Sulphocyanide Test.**	Evaporate a few c.c. of the Cyanide solution with two or three drops of yellow Ammonium Sulphide in a porcelain basin on a water-bath to dryness; then add a drop of dil. HCl and a couple of drops of $FeCl_3Aq$. An intense red coloration will be obtained. On warming a Cyanide with Ammonium Sulphide, Ammonium Sulphocyanide is formed, and this substance with $FeCl_3Aq$ gives Ferric Sulphocyanide (thiocyanate) which is red. $FeCl_3Aq + 3NH_4SCNAq = \mathbf{Fe(SCN)_3} + 3NH_4ClAq$	

Tests for free Acid.

The free acid HCNAq (*a*) would have odour of bitter almonds, (*b*) would give above tests, and (*c*) would yield **no residue** on evaporation to dryness.

SULPHATES AND SULPHURIC ACID.

Reagent.	Result observed.	Remarks.
*1. $BaCl_2$	A white precipitate of Barium Sulphate, $BaSO_4$, is obtained, insoluble in acids. e. g. $CuSO_4Aq + BaCl_2Aq = \mathbf{BaSO_4} + CuCl_2Aq$	
*2. $(CH_3COO)_2Pb$	A white precipitate of Lead Sulphate, $PbSO_4$, is thrown down. The precipitate is soluble with difficulty in Ammonium Acetate and in Potash. $Na_2SO_4Aq + (CH_3COO)_2PbAq = \mathbf{PbSO_4} + 2CH_3 . COONa$	
*3. Dry Test. Carbon and Na_2CO_3	Heated on charcoal with Na_2CO_3 all Sulphates give Sulphide. e. g. $BaSO_4 + 2C + Na_2CO_3 = \mathbf{Na_2S} + BaCO_3 + 2CO_2$ On putting a little of the fused mass (after cooling) on a silver coin and moistening with water, a black stain is produced, due to formation of Ag_2S.	Sulphites give a similar reaction (p. 218).

Special Tests for free Sulphuric Acid in Solution.

(The pure free acid is an oily liquid, sp. gr. 1·85.)

(1) The reaction would be strongly acid. (**Note.**—$NaHSO_4$ and $KHSO_4$ would also be strongly acid.)

(2) On evaporating a solution of Sulphuric Acid a few drops of an oily liquid would be obtained which would dissociate into $\mathbf{SO_3}$ and H_2O, dense white choking fumes being evolved.

(3) The hot concentrated solution would immediately **char organic substances** e. g. filter paper, starch, &c.

(4) The solution would give above tests with $BaCl_2$ and $\mathbf{(CH_3 . COO)_2Pb}$.

HYDROFLUORIC ACID, HF.

Use a solution of Sodium, Potassium, or Ammonium Fluoride.

1. $AgNO_3$. No precipitate. HF is the chemical analogue of HCl, HBr and HI, but AgF is soluble in water.

*2. **$BaCl_2$.** White precipitate of Barium Fluoride soluble in Hydrochloric Acid.

$$2KFAq + BaCl_2Aq = BaF_2 + 2KClAq.$$

*3. **$CaCl_2$.** White gelatinous precipitate of Calcium Fluoride.

$$2KFAq + CaCl_2Aq = CaF_2 + 2KClAq.$$

*4. **H_2SO_4 conc.** Solid Fluorides, on heating with concentrated Sulphuric Acid in a platinum or lead dish, give off Hydrofluoric Acid. If the gas evolved is caused to act on a piece of waxed glass from which the wax has been partly removed by writing with the end of a file, etching takes place, and can be detected after immersing the glass in hot water to remove the wax and subsequent drying.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

*5. **H_2SO_4 and SiO_2.** Mix a solid Fluoride with a small quantity of pure sand or silica, and warm with conc. H_2SO_4 in a test-tube. Silicon Fluoride is evolved, and can be recognized by holding a glass tube with a drop of water at the end in the mouth of the test-tube. A white gelatinous precipitate is formed in the water.

$$a)\ CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

$$b)\ SiO_2 + 4HF = SiF_4 + 2H_2O$$

$$c)\ 3SiF_4 + 4H_2O = 2H_2SiF_6Aq + H_4SiO_4.$$

FREE HYDROFLUORIC ACID.

The free acid is a colourless liquid which fumes in air: the fumes attack glass. It is best kept in a bottle of paraffin wax or caoutchouc.

Caution.—The acid is very corrosive.

HYDROFLUOSILICIC ACID, H_2SiF_6.

The acid is obtained by passing SiF_4 into water.

$$3SiF_4 + 4H_2O = 2H_2SiF_6Aq + H_4SiO_4.$$

*1. **$BaCl_2$.** A white precipitate of Barium Silicofluoride comes down.

$$Na_2SiF_6Aq + BaCl_2Aq = BaSiF_6 + 2NaClAq.$$

2. KCl. From concentrated solutions Potassium Silicofluoride comes down as a gelatinous pp.

$$Na_2SiF_6Aq + 2KClAq = K_2SiF_6 + 2NaClAq.$$

3. H_2SO_4 conc. Hydrofluoric Acid is evolved.

*4. **Dry Test.** On heating Silicofluorides, Silicon Fluoride comes off, and a Fluoride is left.

$$K_2SiF_6 = 2KF + SiF_4.$$

CHLORIDES AND HYDROCHLORIC ACID.

Reagent.	Result observed.	Remarks.
*1. $AgNO_3$	A white curdy precipitate of Silver Chloride, AgCl, is obtained, easily soluble in NH_4OHAq, insoluble in Nitric Acid. e. g. $CaCl_2Aq + 2AgNO_3Aq = 2\mathbf{AgCl} + Ca(NO_3)_2Aq$	
*2. Cl_2Aq, Chlorine water	No action (cf. Bromides and Iodides).	
*3. MnO_2 and H_2SO_4 (concentrated)	On addition of MnO_2 and conc. H_2SO_4 to solid subs. or concentrated solution, Chlorine gas is evolved and recognized by colour, odour, and bleaching action on moist litmus paper. Warm gently if necessary. e. g. $CaCl_2 + MnO_2 + 2H_2SO_4 = ZnSO_4 + MnSO_4 + 2H_2O + \overset{\nearrow}{\mathbf{Cl_2}}$ The bleaching action depends upon the formation of nascent oxygen. $Cl_2 + H_2O = 2HCl + O.$	**Caution.** Do not add conc. H_2SO_4 to a hot solution.
*4. H_2SO_4 (concentrated)	With conc. solution or solid, HCl is evolved as a fuming gas with pungent odour. It gives dense white fumes when a rod moistened with Ammonia solution is brought over the test-tube. e. g. $NaCl + H_2SO_4 = NaHSO_4 + \overset{\nearrow}{\mathbf{HCl}}$ $HCl + NH_3 = NH_4Cl.$	
5. $(CH_3COO)_2Pb$	White precipitate of Lead Chloride ($PbCl_2$), which can be recrystallized from boiling water in characteristic crystals. e. g. $CaCl_2Aq + (CH_3 . COO)_2PbAq = \mathbf{PbCl_2} + \underbrace{(CH_3 . COO)_2CaAq}_{\text{Calcium Acetate}}$	

Special Tests for free HCl in Solution.

Free Hydrochloric Acid solution would give above tests and also the following :—

(1) It would be strongly acid in reaction.

(2) No residue would be left on evaporation if the free acid alone were present. During evaporation pungent acid fumes would be evolved, which would give dense white fumes with a drop of Ammonia solution held over the evaporating basin on a glass rod.

BROMIDES AND HYDROBROMIC ACID.

Reagent.	Result observed.	Remarks.
*1. **$AgNO_3$**	A faintly yellow precipitate of Silver Bromide comes down, insoluble in HNO_3Aq, but **soluble with difficulty in NH_4OHAq.** $KBrAq + AgNO_3Aq = \mathbf{AgBr} + KNO_3Aq$	Cf. HCl and HI.
*2. **Cl_2Aq, Chlorine water**	Bromine is liberated, which colours the liquid brown. $2KBrAq + Cl_2Aq = 2KClAq + \mathbf{Br_2Aq}$ On shaking with Carbon Disulphide, CS_2, or Chloroform, $CHCl_3$, the Bromine dissolves to give a brown solution of Bromine in CS_2 or $CHCl_3$ at the bottom of the test-tube.	Large excess of Chlorine water will discharge the colour, oxidizing the Bromine to Bromic Acid.
*3. **MnO_2 and H_2SO_4 (concentrated)**	On addition of MnO_2 and conc. H_2SO_4 to solid substance or concentrated solution, Bromine, readily recognized by its colour and pungent odour, is set free. e. g. $2KBr + MnO_2 + H_2SO_4$ $= \mathbf{Br_2} + K_2SO_4 + MnSO_4 + 2H_2O$	**Caution.** Do not add conc. H_2SO_4 to a hot solution.
4. **H_2SO_4 (concentrated)**	On addition of conc. H_2SO_4 to solid or concentrated solution, Hydrobromic Acid is evolved as a fuming gas with pungent odour, but Bromine is always given off at the same time, because of the oxidizing action of the Sulphuric Acid on the HBr. *a*) $KBr + H_2SO_4 = KHSO_4 + \mathbf{HBr}$ *b*) $2HBr + H_2SO_4 = 2H_2O + \mathbf{Br_2} + \mathbf{SO_2}$	
5. **$(CH_3COO)_2Pb$**	Lead Acetate gives a white precipitate of Lead Bromide, which can be recrystallized from boiling water. $2NaBrAq + (CH_3COO)_2PbAq$ $= \mathbf{PbBr_2} + 2CH_3COONaAq$	

Note.—Free Hydrobromic Acid Solution would not readily be met with. It is similar in properties to Hydrochloric Acid, HCl.

IODIDES AND HYDRIODIC ACID.

Reagent.	Result observed.	Remarks.
*1. $AgNO_3$	A light yellow precipitate of Silver Iodide, AgI, comes down, **insoluble in** HNO_3Aq and in NH_4OHAq. $KIAq + AgNO_3Aq = \mathbf{AgI} + KNO_3Aq$	Cf. HCl and HBr.
*2. Cl_2Aq, Chlorine water	Iodine is liberated, forming a brown solution. On shaking with CS_2 or $CHCl_3$ the Iodine dissolves to give a violet solution of Iodine in CS_2 or $CHCl_3$ at the bottom of the tube. $2KIAq + Cl_2Aq = 2KClAq + I_2$	Large excess of Chlorine water will discharge the colour, oxidizing the Iodine to Iodic Acid. $I_2 + 5Cl_2 + 6H_2O = \underbrace{2HIO_3}_{\text{Iodic Acid}} + 10HCl$
*3. MnO_2 and H_2SO_4 (concentrated)	With solid substance or concentrated solution, Iodine vapour of characteristic violet colour is set free. The Iodine may condense on the upper portion of the tube in glistening grey crystals. $2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2$	Cf. HBr.
4. H_2SO_4 (concentrated)	With concentrated solution or solid, HI is evolved as fuming gas with pungent odour, but Iodine is always given off at the same time. *a*) $2KI + H_2SO_4 = 2HI + K_2SO_4$ *b*) $2HI + H_2SO_4 = I_2 + 2H_2O + SO_2$	
5. $HgCl_2$	A scarlet precipitate of Mercuric Iodide, HgI_2, is obtained. $2KIAq + HgCl_2Aq = \mathbf{HgI_2} + 2KClAq$	
6. $(CH_3COO)_2Pb$	A yellow precipitate of Lead Iodide, PbI_2, forms. $2KIAq + (CH_3COO)_2PbAq = \mathbf{PbI_2} + 2CH_3 . COOKAq$	

Note.—Free Hydriodic Acid solution is rarely met with in Analysis. It is similar in properties to HClAq and HBrAq, but is generally coloured brown from presence of free Iodine.

SALTS OF THIOCYANIC ACID (SULPHOCYANIC ACID), HCNS.

The Thiocyanates of Ag, Pb, Cu, and Hg are insoluble in water. Most others are soluble. Use a solution of Potassium or Ammonium Thiocyanate for following tests:—

*1. **$FeCl_3$.** Ferric Chloride gives a bright dark red coloration (or pp.) due to the formation of Ferric Thiocyanate.

$$FeCl_3Aq + 3NH_4SCNAq = Fe(SCN)_3 + 3NH_4ClAq.$$

*2. **$AgNO_3$.** A white curdy precipitate of Silver Thiocyanate, soluble in large excess of Ammonium Hydroxide, forms.

$$KCNSAq + AgNO_3Aq = AgSCN + KNO_3Aq.$$

3. $HgCl_2$. A white precipitate of Mercuric Thiocyanate forms.

$$2KCNSAq + HgCl_2Aq = Hg(CNS)_2 + 2KClAq.$$

HYDROFERROCYANIC ACID AND FERROCYANIDES.

Ions of acid: $4H^{\cdot}$ and $Fe(CN)_6''''$.

Use Potassium Ferrocyanide for the following tests.

*1. **$FeCl_3$.** Ferric Salts (e.g. $FeCl_3Aq$) give a dark blue precipitate of Ferric Ferrocyanide (Prussian blue) insoluble in dilute acids.

$$3K_4Fe(CN)_6 + 4FeCl_3Aq = Fe_4\{Fe(CN)_6\}_3 + 12KClAq.$$

*2. **$FeSO_4$.** Ferrous Salts give a light blue precipitate as a rule. The substance precipitated, Potassium Ferrous Ferrocyanide, is white when quite pure, but under the conditions of the experiment a trace of Ferric Salt is present, causing the precipitate to be blue.

$$K_4Fe(CN)_6Aq + FeSO_4Aq = K_2Fe\{Fe(CN)_6\} + K_2SO_4Aq.$$

*3. **$CuSO_4$.** A brown precipitate of Cupric Ferrocyanide forms.

$$2CuSO_4Aq + K_4Fe(CN)_6Aq = Cu_2Fe(CN)_6 + 2K_2SO_4Aq.$$

*4. **$AgNO_3$.** A white precipitate of Silver Ferrocyanide insoluble in dilute acids is formed.

$$K_4Fe(CN)_6Aq + 4AgNO_3Aq = Ag_4Fe(CN)_6 + 4KNO_3Aq.$$

5. $ZnSO_4$. A white precipitate of Zinc Ferrocyanide comes down.

$$K_4Fe(CN)_6Aq + 2ZnSO_4Aq = Zn_2Fe(CN)_6 + 2K_2SO_4Aq.$$

HYDROFERRICYANIC ACID AND FERRICYANIDES.

Ions of acid: $3H^{\cdot}$ and $Fe(CN)_6'''$.

Use a solution of Potassium Ferricyanide.

*1. **$FeSO_4$.** Ferrous Salts give a dark blue precipitate of Ferrous Ferricyanide—Turnbull's blue.

$$2K_3Fe(CN)_6 + 3FeSO_4Aq = Fe_3\{Fe(CN)_6\}_2 + 3K_2SO_4Aq.$$

*2. **$FeCl_3$.** Ferric Salts give no precipitate, but the solution changes to a brownish green tint.

*3. **$ZnSO_4$.** Zinc Salts give an orange precipitate of Zinc Ferricyanide.

$$2K_3Fe(CN)_6Aq + 3ZnSO_4Aq = Zn_3\{Fe(CN)_6\}_2 + 3K_2SO_4Aq.$$

4. $AgNO_3$. A reddish brown precipitate of Silver Ferricyanide forms.

$$K_3Fe(CN)_6Aq + 3AgNO_3Aq = Ag_3Fe(CN)_6 + 3KNO_3Aq.$$

NITRATES AND NITRIC ACID.

Reagent.	Result observed.	Remarks.
*1. **H_2SO_4 (concentrated)** and **Cu turnings**	Add to concentrated solution an equal bulk of conc. H_2SO_4, and then a few pieces of Cu turnings: brown fumes of NO_2 are evolved, and a blue solution is formed. HNO_3 is first liberated, which reacts with the Copper to give Copper Nitrate with evolution of NO. The oxygen of the air in the tube causes formation of brown fumes of NO_2. e.g. $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$ $3Cu + 8HNO_3Aq = 3Cu(NO_3)_2Aq + 4H_2O + 2NO$ $2NO + O_2 = 2NO_2$	Warm if necessary.
*2. **Brown Ring Test.** H_2SO_4 and **$FeSO_4$**	There are various methods of carrying out this test. The following is probably the most delicate: Add to conc. solution rather less than equal bulk of conc. H_2SO_4, **cool well**, and then pour carefully down the side of the tube so as to form an upper layer a freshly prepared **cold** solution of Ferrous Sulphate, $FeSO_4$. A brown ring or band is produced at the junction of the liquids by the formation of an unstable double compound of Nitric Oxide and $FeSO_4$, which has the composition $NO . 2FeSO_4$ at ordinary temperatures (p. 31). The Sulphuric Acid in the first instance sets free Nitric Acid, which oxidizes part of the Ferrous Sulphate to Ferric Sulphate with separation of NO, which combines with unaltered $FeSO_4$ to give the brown ring. e.g. *a*) $KNO_3Aq + H_2SO_4 = KHSO_4Aq + HNO_3Aq$ *b*) $6FeSO_4Aq + 3H_2SO_4 + 2HNO_3Aq = 3Fe_2(SO_4)_3Aq + 4H_2O + 2NO$ *c*) $2FeSO_4 + NO = NO . 2FeSO_4$ Note.—A quicker but less reliable method of carrying out this test is to add a crystal of Ferrous Sulphate to the original conc. solution and then conc. Sulphuric Acid. A brownish black coloration appears round the crystal.	The brown ring test must be used with great caution if Bromide or Iodide be present, as, under the conditions of the experiment, rings of Bromine or Iodine may be produced which simulate the brown ring. In the presence of Nitrites the test is valueless.
3. **Charcoal.**	On heating Nitrates on charcoal they generally deflagrate.	
*4. **Heat solid in dry tube.**	On heating in dry tube of hard glass Nitrates decompose, giving off brown fumes.	Nitrates of Na . K and NH_4 may give no fumes.

Special Tests for Free Nitric Acid.

Free HNO_3Aq would be strongly acid in reaction, would give above reactions easily, and leave no residue on evaporation. Towards the end of the evaporation acid fumes would be evolved with pungent odour, and at this stage a few pieces of Copper foil added would cause immediate evolution of brown fumes.

PHOSPHORIC ACID AND PHOSPHATES.

Reagent.	Result observed.	Remarks.
*1. $(NH_4)_2MoO_4$ and HNO_3	**Ammonium Nitromolybdate Test.** Add to 2-3 c.c. of solution of subs.—dissolved in water or in HNO_3Aq—about double the volume of Ammonium Nitromolybdate (i.e. Ammon. Molybdate and HNO_3) and warm gently. A yellow coloration and finally a canary yellow precipitate of Ammonium Phosphomolybdate indicate Phosphoric Acid. The precipitate is of complicated constitution, $\mathbf{11MoO_3 . (NH_4)_3PO_4 . 6H_2O}$, and no satisfactory simple equation can be given.	Arsenates may give a similar precipitate on boiling.
*2. $AgNO_3$	In neutral solutions Phosphates give a yellow precipitate of Silver Phosphate, Ag_3PO_4. $3Na_2HPO_4Aq + 6AgNO_3Aq$ $= \mathbf{2Ag_3PO_4} + 6NaNO_3Aq + H_3PO_4Aq$	The precipitate is exactly similar in appearance to Silver Arsenite.
3. Magnesia mixture, $MgSO_4$, NH_4Cl, and NH_4OH	On addition of NH_4ClAq, NH_4OHAq, and $MgSO_4Aq$ to solution of a Phosphate a white precipitate of Magnesium Ammonium Phosphate may be obtained. e.g. $Na_2HPO_4Aq + NH_4OHAq + MgSO_4Aq$ $= \mathbf{Mg . NH_4PO_4} + Na_2SO_4Aq$	The NH_4Cl is added to prevent precipitation of Magnesium Hydroxide by NH_4OHAq.
4. $CaCl_2$ or $BaCl_2$	White precipitates of Calcium and Barium Phosphates soluble in Acetic and in Mineral Acids are obtained. e.g. $Na_2HPO_4Aq + CaCl_2Aq$ $= \mathbf{CaHPO_4} + 2NaClAq$	$Ca_3(PO_4)_2$ would also be precipitated.
*5. $FeCl_3$	A yellowish white precipitate of Ferric Phosphate is obtained which is soluble in Mineral Acids, but not in Acetic Acid. [This reaction is of special importance because it is used in quantitatively separating Phosphoric Acid from solution. In order to make the reaction quantitative Ammonium or Sodium Acetate should be added to the solution to prevent free HCl being formed during the reaction (see p. 194).] $Na_2HPO_4Aq + FeCl_3Aq$ $= \mathbf{FePO_4} + 2NaClAq + HClAq$ $HCl + CH_3 . COONaAq$ $= NaClAq + CH_3 . COOH$	

BORACIC ACID (H_3BO_3) AND BORATES.

Boracic Acid is used as an antiseptic and food preservative. Borax or Sodium Pyroborate, $Na_2B_4O_7 . 10H_2O$, is a common substance.

Use Borax for the following tests.

*1. **H_2SO_4 and Ethyl Alcohol,** C_2H_5OH. Mix the Borate with conc. H_2SO_4, add more than an equal bulk of Alcohol, stir and set fire to the Alcohol. The flame is tinted light green, especially at the edges, because of combustion of Ethyl Borate formed from the Alcohol and Boracic Acid.

a) $Na_2B_4O_7 + H_2SO_4 + 5H_2O = 4H_3BO_3 + Na_2SO_4$

b) $H_3BO_3 + \underbrace{3C_2H_5OH}_{\text{Ethyl Alcohol}} = \underbrace{(C_2H_5)_3BO_3}_{\text{Ethyl Borate}} + 3H_2O.$

*2. **Turmeric.** Acidify the Borate solution slightly with HCl, dip turmeric paper in the solution and dry. The paper is tinted reddish brown: moisten this brown paper by means of a rod dipped in NaOHAq: the colour changes to a greenish black tint.

3. Platinum wire and $KHSO_4$. Mix the dry substance thoroughly with about an equal quantity of powdered Potassium Hydrogen Sulphate, and heat a little of the mixture on platinum wire. A green flame is obtained.

NOTE.—In a complex mixture which may contain metals of Groups III, IV, or V, Boric Acid must be got rid of before going on to Group III, by evaporating repeatedly to dryness with concentrated HCl in a porcelain dish. [A more rapid method of removal is to evaporate with HF in a platinum dish.]

SILICIC ACID, H_2SiO_3.

This is Metasilicic Acid. Orthosilicic Acid, H_4SiO_4, would rarely be met with. Metasilicic Acid is very slightly ionized. Ions $2H^{\cdot}$ and SiO_3''.

Use a solution of Sodium or Potassium Silicate.

*1. **HCl.** Acidify with HCl and evaporate down the solution over a small flame. A gelatinous precipitate of H_2SiO_3 forms.

$$Na_2SiO_3Aq + 2HClAq = H_2SiO_3 + 2NaClAq.$$

Evaporate to dryness, and heat the dry residue. A white insoluble powder is left after extracting the cold residue with water which consists of Silica, SiO_2. Reserve for Test 6.

*2. **$AgNO_3$.** An orange precipitate of Silver Silicate soluble in NH_4OHAq and HClAq is obtained.

$$Na_2SiO_3Aq + 2AgNO_3Aq = Ag_2SiO_3 + 2NaNO_3Aq.$$

3. $CaCl_2$. A white precipitate of Calcium Silicate soluble in acids forms.

$$Na_2SiO_3Aq + CaCl_2Aq = CaSiO_3 + 2NaClAq.$$

4. $BaCl_2$. A white precipitate of Barium Silicate comes down.

$$Na_2SiO_3Aq + BaCl_2Aq = BaSiO_3 + 2NaClAq.$$

Dry Tests:—

*5. **NaF** and **H_2SO_4.** Mix powdered substance with a pure powdered Fluoride (free from Silicate) and warm gently with conc. H_2SO_4 in a platinum crucible or lead dish. Silicon Fluoride is evolved, and can be detected by holding a rod with a drop of water on it over the dish.

a) $KF + H_2SO_4 = KHSO_4 + HF$

b) $Na_2SiO_3 + H_2SO_4 = Na_2SO_4 + H_2SiO_3$

c) $H_2SiO_3 + 4HF = SiF_4 + 3H_2O.$

6. Borax bead. Take up a small quantity of the Silica obtained in Test 1 in a borax bead. It does not dissolve but floats in molten bead as a Silica skeleton of characteristic appearance.

7. Ash and $Co(NO_3)_2$. Moisten filter paper first with solution and then with Cobalt Nitrate. The ash is tinted blue. Compare Aluminium, Borates and Phosphates.

IODIC ACID, HIO_3.

Ions $H^{\cdot}$ and IO_3'.

Use Potassium Iodate for the following tests.

*1. **$AgNO_3$.** A white curdy precipitate of Silver Iodate soluble in Ammonia and in acids is obtained.

$$KIO_3Aq + AgNO_3Aq = AgIO_3 + KNO_3Aq.$$

2. $BaCl_2$. A white precipitate of Barium Iodate forms, soluble in acids.

$$2KIO_3Aq + BaCl_2Aq = Ba(IO_3)_2 + 2KClAq.$$

*3. **HCl** and **KI.** On warming Iodates with mineral acids and Potassium Iodide, Iodine is set free. Shake up with CS_2 or $CHCl_3$.

a) $KIO_3Aq + HClAq = KClAq + HIO_3Aq$

b) $KIAq + HClAq = KClAq + HIAq$

c) $HIO_3 + 5HI = 3I_2 + 3H_2O.$

*4. **H_2SO_3Aq.** Sulphurous Acid solution reduces Iodates with formation of Iodides.

$$KIO_3Aq + 3H_2SO_3Aq = KI + 3H_2SO_4Aq.$$

Iodine is at once set free because of reaction previously mentioned (Test 3).

5. SH_2. Sulphuretted Hydrogen reduces Iodates to Iodides.

$$KIO_3 + 3H_2S = KI + 3H_2O + 3S.$$

6. Dry Test. The Iodates of Sodium and Potassium are those most generally met with. They decompose into Iodide and Oxygen on heating.

$$2KIO_3 = 2KI + 3O_2.$$

ARSENITES AND ARSENIOUS ACID.

*1. **SH_2 (in presence of HCl).** A yellow precipitate of Arsenious Sulphide, As_2S_3, is thrown down. The solution must be acid as the precipitate is soluble in NaOHAq or KOHAq. (See p. 136.)

$$2H_3AsO_3Aq + 3H_2S = \mathbf{As_2S_3} + 6H_2O.$$

*2. **$AgNO_3$.** With neutral solutions a yellow precipitate of Silver Arsenite, Ag_3AsO_3, comes down. The precipitate is soluble in acids and in NH_4OHAq.

$$Na_3AsO_3Aq + 3AgNO_3Aq = \mathbf{Ag_3AsO_3} + 3NaNO_3Aq.$$

Cf. Ag_3PO_4 above (p. 231).

*3. **Iodine in KIAq.** The solution is decolorized owing to oxidation of the Arsenite to Arsenate.

$$H_3AsO_3Aq + I_2 + H_2O = H_3AsO_4Aq + 2HIAq.$$

ARSENATES AND ARSENIC ACID.

*1. **SH_2.** On passing gaseous SH_2 through a solution of an Arsenate, reduction to Arsenite **slowly** takes place, and afterwards a precipitate of Arsenious Sulphide forms.

$$a)\ H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S$$
$$b)\ 2H_3AsO_3 + 3H_2S = \mathbf{As_2S_3} + 6H_2O.$$

*2. **H_2SO_3Aq.** Rapid reduction of Arsenate to Arsenite takes place, and after boiling off any excess of Sulphur Dioxide, the solution will give a precipitate with SH_2.

$$\underbrace{H_3AsO_4Aq}_{\text{Arsenic Acid}} + H_2SO_3Aq = \underbrace{H_3AsO_3Aq}_{\text{Arsenious Acid}} + H_2SO_4Aq$$

*3. **$AgNO_3$.** With neutral solutions a reddish brown precipitate of Silver Arsenate forms, soluble in acids and in NH_4OHAq.

$$3Na_2HAsO_4Aq + 6AgNO_3Aq = \mathbf{2Ag_3AsO_4} + 6NaNO_3Aq + H_3AsO_4Aq.$$

4. **Magnesia mixture, $MgSO_4$, NH_4Cl, and NH_4OH.** From neutral or alkaline solutions of Arsenates a white precipitate of Magnesium Ammon. Arsenate is obtained.

$$Na_2HAsO_4Aq + MgSO_4Aq + NH_4OHAq = \mathbf{MgNH_4AsO_4} + Na_2SO_4Aq + H_2O.$$

HYPOPHOSPHOROUS ACID, H_3PO_2.

Ions $H^{\cdot}$ and $H_2PO_2{}'$.

Use Sodium Hypophosphite for following reactions:—

*1. **$HgCl_2$.** Mercury salts give Metallic Mercury as a greyish precipitate, but Mercuric Chloride gives first a precipitate of Mercurous Chloride, which then becomes further reduced. NOTE.—The wet tests generally depend on reduction, as Hypophosphites are powerful reducing agents.

$$NaH_2PO_2Aq + 2HgCl_2 + 2H_2O = 2Hg + 3HCl + NaCl + PH_3.$$

*2. **$CuSO_4$.** A solution of a Copper salt added to a faintly acid solution of a Hypophosphite gives a precipitate of Cuprous Hydride, yellow at first, but changing rapidly to brown.

$$2CuSO_4Aq + 2NaH_2PO_2 + 3H_2O = Cu_2H_2 + 2H_3PO_4 + Na_2SO_4 + H_2SO_4Aq.$$

3. HCl and Zn. Acidify with HCl, add Zn and warm gently. Nascent Hydrogen is generated, and reduces the Hypophosphite to Phosphoretted Hydrogen.

$$a)\ NaH_2PO_2 + HClAq = H_3PO_2 + NaClAq$$
$$b)\ H_3PO_2 + 4H = PH_3 + 2H_2O.$$

4. **$AgNO_3$.** In neutral solution a white precipitate of Silver Hypophosphite is formed, which is reduced on boiling.

$$NaH_2PO_2Aq + AgNO_3Aq = AgH_2PO_2 + NaNO_3Aq.$$

*5. **Dry Test.** On heating Phosphine is evolved and Phosphate or Pyrophosphate formed.

$$2NaH_2PO_2 = PH_3 + Na_2HPO_4$$
$$(2Na_2HPO_4 = Na_4P_2O_7 + H_2O).$$

PYROPHOSPHORIC ACID, $H_4P_2O_7$.

*1. **$AgNO_3$.** Silver Nitrate gives a white precipitate of Silver Pyrophosphate. Orthophosphoric Acid gives a yellow pp.

$$Na_4P_2O_7Aq + 4AgNO_3Aq = Ag_4P_2O_7 + 4NaNO_3Aq.$$

*2. **$MgSO_4$ in presence of NH_4Cl.** A white precipitate of Magnesium Pyrophosphate comes down.

$$Na_4P_2O_7Aq + 2MgSO_4Aq = Mg_2P_2O_7 + 2Na_2SO_4Aq.$$

3. Albumen. Albumen solution (e. g. white of egg in water) is not coagulated. Metaphosphoric Acid coagulates albumen.

METAPHOSPHORIC ACID, HPO_3

*1. **$AgNO_3$.** A white precipitate of Silver Metaphosphate is formed. Distinction from Orthophosphoric Acid.

$$NaPO_3Aq + AgNO_3Aq = AgPO_3 + NaNO_3Aq.$$

*2. **Albumen.** Albumen (e. g. white of egg dissolved in water) is coagulated. Distinction from Ortho- and Pyrophosphoric Acids.

PERSULPHURIC ACID, $H_2S_2O_8$.

Ions $2H^{\cdot}$ and S_2O_8''. Only the Sodium, Potassium, and Ammonium Salts might be met with.

*1. **$AgNO_3$.** Silver Nitrate gives a black precipitate of Silver Peroxide, Ag_2O_2.

$$2AgNO_3Aq + K_2S_2O_8 + 2H_2O = 2KHSO_4 + 2HNO_3 + Ag_2O_2.$$

2. $BaCl_2$. Barium Chloride gives no precipitate at first, but on warming Barium Sulphate comes down.

$$a)\ BaCl_2Aq + K_2S_2O_8Aq = BaS_2O_8 + 2KClAq$$
$$b)\ BaS_2O_8 + H_2O = BaSO_4 + H_2SO_4 + O.$$

*3. **KI.** Potassium Iodide is slowly decomposed in the cold, rapidly on heating, Iodine being set free.

$$K_2S_2O_8 + 2KIAq = 2K_2SO_4 + I_2.$$

4. HCl conc. Conc. Hydrochloric Acid causes an evolution of Chlorine.

$$K_2S_2O_8 + 2HCl = 2KHSO_4 + Cl_2.$$

5. Dry reaction. On heating solid Persulphates, Sulphur Trioxide and Oxygen are evolved.

$$Na_2S_2O_8 = Na_2SO_4 + SO_3 + O.$$

B. IDENTIFICATION OF METALLIC OXIDES AND HYDROXIDES.

I. Metallic Oxides.

The Oxides of the Metals might be divided into two classes with regard to their behaviour towards water.

(1) The oxides of Na, K, Ca, Sr, and Ba react with water to give hydroxides which are soluble ; e. g.

$$Aq + \underbrace{CaO}_{\text{Quicklime}} + H_2O = \underbrace{Ca(OH)_2Aq}_{\text{Slaked lime}}$$

These hydroxides are strongly alkaline in reaction, and give the tests for soluble hydroxides mentioned below.

(2) The other oxides either react very slightly with water to give slightly soluble hydroxides (e.g. MgO), or are practically insoluble. Most of them, however, dissolve readily in acids and many have characteristic appearance and properties ; e.g. HgO is red or yellow ; CuO is black ; Bi_2O_3 is yellowish and turns brown on heating ; ZnO turns yellow on heating ; MgO glows on heating strongly ; PbO is light brown or yellow ; Fe_2O_3 is brown ; SnO_2 and Sb_2O_5 are white and very insoluble. Many of these oxides take up carbon dioxide from the air, so that on solution in an acid slight effervescence frequently occurs.

There are **no simple direct tests for Oxides**, and the analyst must therefore arrive at a conclusion from the **appearance, general properties**, and **behaviour.** A couple of examples might make the method of reasoning clear.

I. Analysis of Litharge, PbO.

Suppose a light brown substance is being analysed which is insoluble in water, but soluble with difficulty in boiling HCl, and easily soluble in HNO_3. All the tests for lead are obtained, e. g. reduction on charcoal, precipitation of $PbCl_2$ on adding HCl to solution in nitric acid, yellow pp. of $PbCrO_4$ with K_2CrO_4Aq, and deep yellow precipitate of PbI_2 with KIAq. The substance is therefore a compound of lead.

Any one with a slight acquaintance with Chemistry should know that nitrate, chloride, bromide, carbonate, phosphate, and sulphate of lead are white solids, the first of which is easily soluble in water, the second and third moderately soluble in hot water, while the others are insoluble, but dissolve in HNO_3.

The only common yellow and brown compounds of lead are the monoxide (PbO), the iodide (PbI_2), (and the chromate, $PbCrO_4$). The chromate dissolves in acid to give a yellow solution; the iodide dissolves in boiling water and can be recrystallized in golden spangles. Iodine could readily be detected in the latter compound by means of H_2SO_4 and MnO_2, and chromium in the former. Litharge would give no tests for iodide or chromate. By a process of exclusion one would therefore be driven to the conclusion that the substance from appearance, general properties, and behaviour must be an oxide of lead—presumably litharge.

NOTE.—The composition of the substance could easily be quantitatively proved by passing dry hydrogen over a weighed quantity of the heated oxide and weighing the water produced after absorption in tubes containing calcium chloride; e. g.

$$PbO + H_2 = Pb + H_2O.$$

Such an investigation lies outside elementary analysis.

II. Analysis of ZnO.

Zinc oxide is a white solid, which turns yellow on heating and white again on cooling. It is insoluble in water, but easily dissolves in dilute HCl, HNO_3, or H_2SO_4. The tests for zinc would readily be obtained, and the analyst should then reason as follows:—

(1) As the body is insoluble in water it cannot be zinc chloride, bromide, iodide, nitrate, or sulphate, which are easily soluble.

(2) From solubility it might be oxide, hydroxide, carbonate, sulphide, or phosphate. It might also possibly be oxalate.

(3) The substance could not be carbonate or sulphide, because neither CO_2 nor H_2S is evolved on solution in HCl.

(4) On dissolving in HNO_3 and testing with ammonium nitromolybdate no coloration or precipitate is obtained; therefore it is not a phosphate.

(5) By exclusion the subject must therefore be oxide or hydroxide.

[NOTE.—Zinc oxalate would give zinc carbonate on heating with slight charring and would give a mixture of CO and CO_2 with conc. H_2SO_4.]

The student would not as a rule be expected to discriminate between oxide and hydroxide, but one might point out that the hydroxide on cautious heating in a long dry tube would give off a considerable proportion of water, forming the oxide

$$(Zn(OH)_2 = ZnO + H_2O),$$

while the oxide would give off no water and would turn yellow on heating.

From above examples one might therefore conclude that **a decision as to whether a body is an Oxide or Hydroxide depends upon the application of general chemical knowledge in an intelligent manner.** The **Tables of Common Compounds of the respective Metals given opposite the Lists of Tests** should be of great help to a beginner in getting a general idea as to the relationships of the compounds of the metals. When a student requires more complete information he should consult a theoretical handbook.

II. Hydroxides of the Metals.

The hydroxides might, like the oxides, be divided into two classes with regard to their behaviour towards water.

(1) The hydroxides soluble in water: $NaOH$, KOH, NH_4OH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$.

(2) The other hydroxides are either insoluble or very slightly soluble. A few of these insoluble hydroxides are of characteristic appearance, e. g. copper hydroxide, $Cu(OH)_2$, is blue, and ferric hydroxide, $Fe(OH)_3$, brown.

Reactions of Soluble Hydroxides.

Reagent.	Observation.
1) **Litmus**	**Strongly alkaline** in reaction. The caustic alkalies have a soapy feel, and Ammonium Hydroxide a characteristic odour, owing to loss of NH_3.
2) **NH_4ClAq** and boil	On boiling an Ammonium Salt with a soluble Hydroxide, Ammonia is evolved. ↗ e. g. $NH_4ClAq + NaOHAq = NaClAq + H_2O + NH_3$ ↗ $2NH_4ClAq + Ca(OH)_2Aq = CaCl_2Aq + 2H_2O + 2NH_3$
3) **$AgNO_3Aq$**	**A greyish precipitate**, consisting chiefly of **Silver Oxide,** Ag_2O, is obtained. (Note.—In the case of NH_4OH the precipitate is so easily soluble in excess of reagent, that without special precautions it would hardly be seen.) e. g. $2AgNO_3Aq + 2NaOHAq = \mathbf{Ag_2O} + H_2O + 2NaNO_3Aq$ $2AgNO_3Aq + Ca(OH)_2Aq = \mathbf{Ag_2O} + H_2O + Ca(NO_3)_2Aq$
4) **$CuSO_4Aq$**	**Blue precipitate** of Copper Hydroxide, $Cu(OH)_2$. $CuSO_4Aq + 2NaOHAq = \mathbf{Cu(OH)_2} + Na_2SO_4Aq$
5) **$FeCl_3Aq$**	**Brown precipitate** of **Ferric Hydroxide.** $FeCl_3Aq + 3NaOHAq = \mathbf{Fe(OH)_3} + 3NaClAq$

SUMMARY OF TESTS FOR ACID RADICLES.

The acids can be grouped in various ways, but for simplicity perhaps the following will be found most convenient:—

Class I. Acids recognized on adding HClAq or H_2SO_4Aq to solid or concentrated solution (but preferably to solid) and warming gently.

(1) H_2CO_3. (2) H_2S. (3) H_2SO_3. (4) $H_2S_2O_3$.
(5) HNO_2. (6) HOCl. (7) $HClO_3$. (8) $HBrO_3$.
(9) H_2CrO_4. (10) $H_2Cr_2O_7$. (11) $HMnO_4$.
(12) [H_2MnO_4]. (13) HCN.

Class II. Acids recognized in strongly acid solution by addition of $Ba(NO_3)_2$ or $BaCl_2$.

(1) H_2SO_4. (2) HF. (3) [H_2SiF_6].

Class III. Acids recognized in strongly acid solution by addition of $AgNO_3$.

(1) HCl. (2) HBr. (3) HI.
(4) HCNS. (5) $H_4Fe(CN)_6$. (6) $H_3Fe(CN)_6$.

Class IV. Acids detected by special tests in strongly acid solution.

(1) HNO_3. (2) H_3PO_4. (3) H_3BO_3.
(4) H_2SiO_3. (5) HIO_3.

Class V. Acids precipitated from neutral solution by $AgNO_3$ (after proving absence of previous Groups).

(1) H_3AsO_3. (2) H_3AsO_4. (3) H_3PO_2. (4) [$H_4P_2O_7$.]
(5) [HPO_3]. (6) [$H_2S_2O_8$].

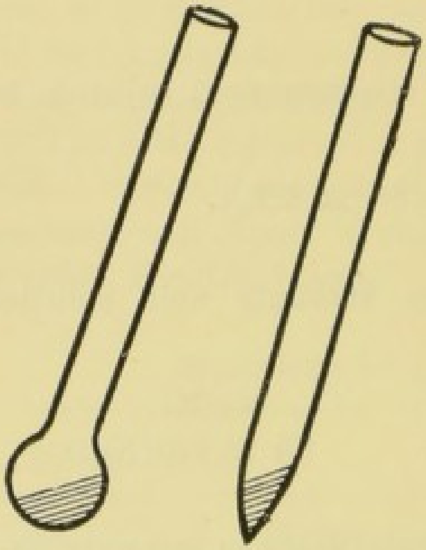
Complete Summary of Method of Procedure in carrying out tests for Acid Radicles and for soluble metallic Hydroxides.

I. Dry Tests.

II. Wet Tests.

The tests should preferably be carried out in the given order.

I. Dry Tests.

Experiment.	Result and Deduction.
1. Heat a small quantity of powdered solid in a narrow tube of hard glass.  Fig. 25. Hard Glass Tubes for Heating Solids.	*a*) Charring indicates an organic compound. *b*) Brown fumes with odour of NO_2 indicate Nitrites or Nitrates. *c*) Brown fumes of Bromine might indicate Bromates (or Bromides and oxidizing agent). *d*) Oxygen evolved might indicate: (i) Chlorate; (ii) Perchlorate; (iii) Hypochlorite; (iv) Oxide (e. g. PbO_2, MnO_2, HgO). Test with cedar splint. *e*) Ammonium, Mercury, Tin, Arsenic, and Antimony Compounds might sublime, e. g. NH_4Cl, $HgCl_2$, $SbCl_3$. *f*) Sulphur might come off from Persulphides; e. g. $FeS_2 = FeS+S$. *g*) The characteristic changes of colour of the metallic Oxides would be observed in this test (cp. p. 114); e. g. Zinc Oxide turns yellow on heating, white on cooling, &c.
2. Heat a small quantity of the substance with concentrated H_2SO_4 in a test-tube.	*a*) Fuming colourless or brown gas—Nitric Peroxide odour—indicates Nitrate or Nitrite. *b*) Fuming colourless gas with pungent odour of HCl indicates Chloride. *c*) Fuming brown gas with odour of Bromine indicates mixture of Br_2 and HBr from a Bromide. *d*) Fuming gas and violet vapour indicate HI and I_2 from Iodide. *e*) Chlorine may come off from Hypochlorite or Chloride with oxidizing agent. *f*) Chlorine and Chlorine Peroxide indicate Chlorate. [**Caution.**—A very small quantity of solid should be used.] *g*) CO_2 evolved with effervescence indicates Carbonate. *h*) SH_2 evolved indicates Sulphide. *i*) SO_2 evolved indicates Sulphite, Thiosulphate, or metal (e. g. Cu).

WET TESTS FOR ACIDS AND SOLUBLE METALLIC HYDROXIDES.

A. Preparation of a solution.

B. Working Scheme of Analysis.

A. Preparation of a Solution.

(1) **If the substance is soluble in water**, use an aqueous solution for following tests, keeping in view that metals which have been found may affect the tests.

(2) **If insoluble in water** the substance may be dissolved in HClAq or HNO_3Aq and the solution tested for all acids **except that used as solvent.** It is usually possible to test for the acid used as solvent if one considers it advisable, e. g. if hydrochloric acid has been used as solvent, heat up original solid with MnO_2 and H_2SO_4 conc. Chlorine evolved would probably indicate chloride. [Note.—Hypochlorite and Chlorate might also give off chlorine, but with important distinctions. Hypochlorites always smell of hypochlorous acid, and chlorine is evolved on adding dilute acids—e. g. H_2SO_4Aq or HClAq—without MnO_2. Chlorates give chlorine peroxide as well as chlorine.] Again, if one dissolves in nitric acid, and suspects that the substance may be a basic nitrate (the only type of nitrate insoluble in water), one can test the original solid for nitric acid by mixing with conc. H_2SO_4 and adding copper turnings.

A consideration of the appearance, solubility, and metal or metals found might give one an important hint as to the actual composition of the substance on consultation of the list of common compounds of the different metals given opposite the Lists of Tests for respective metals; e. g. if the substance was a simple body, contained barium, and was found to be insoluble in water, but easily soluble in HClAq, it would be useless to look for chloride, nitrate, or sulphate, barium chloride and nitrate being easily soluble in water and barium sulphate insoluble in acids.

(3) Although rarely necessary in testing a simple substance, the following method is excellent when more than one metal has been detected, and it is feared that the **reactions of these metals may interfere** with tests for the acids. In such a case if metals other than Na, K, and NH_4 have been found, boil up say

about 2 grams of substance with a slight excess of a strong solution of Na_2CO_3 for 10 to 20 minutes in a porcelain basin, adding water from time to time so as to keep the volume constant. In this way the metals will be precipitated as carbonates, and on filtering a solution of the sodium salts of acids admixed with Na_2CO_3 will be obtained for analysis. After appropriate treatment the solution can be used for testing for Classes II, III, IV and V of acids :—

(*a*) **In testing for Class II** (H_2SO_4, HF, H_2SiF_6) the solution should be made acid by boiling with excess of HCl to get rid of excess Na_2CO_3 and then $BaCl_2$ added.

(*b*) **In testing for Class III** (HCl, HBr, HI, HCNS, &c.) make acid by boiling with excess of HNO_3 before adding $AgNO_3Aq$.

(*c*) The solution containing carbonate can be tested direct for acids of **Class IV** (HNO_3, H_3PO_4, &c.), but the acid solution must be added gradually to avoid trouble owing to rapid evolution of CO_2.

(*d*) Boil with **slight excess of acetic acid** and then carefully neutralize with very dilute ammonia before going on to test for **Class V.**

(4) In the case of substances insoluble in acids, e. g. $BaSO_4$, AgCl, which usually react rather slowly on boiling up with a solution of sodium carbonate, one can fuse them up for 10 to 15 minutes with solid Na_2CO_3 (or fusion mixture, which is a mixture of Na_2CO_3 and K_2CO_3) in a crucible before the blowpipe, as shown in Fig. 36, p. 272.

The metal is transformed to carbonate and the acid to sodium salt.

$$\text{e. g. } BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4.$$

On extracting with water and filtering, the solution could be tested for acids after appropriate treatment, as indicated above, to remove excess of carbonate. The residue could be employed to test for metals as already mentioned (p. 206.)

Working Summary of Wet Tests to be carried out in order

Experiment.	Result observed.	Acid or Salt indicated.	Confirmatory Tests to be carried out with original solution. (Consult Lists of Reactions under respective acids at pages indicated.)
I. Add to concentrated solution or solid moderately conc. HCl and warm gently.	1) **CO_2 evolved.** Pass into lime-water as described on p. 217.	1) **Carbonate**	If Carbonate is soluble in water one can confirm by addition of a) $AgNO_3$. b) $CaCl_2$. See p. 217.
	2) **SH_2 evolved,** as proved by odour and reaction with lead acetate paper.	2) **Sulphide**	If Sulphide is soluble in water, one could confirm by a) $AgNO_3$. b) $CuSO_4$. See p. 217.
	3) **SO_2 evolved.** Odour of burning sulphur.	3) **Sulphite**	
	4) **SO_2 evolved and S precipitated.**	4) **Thiosulphate**	Confirm by 1) Solution of Iodine in KI. 2) $AgNO_3$. See p. 219.
	5) **Brown fumes—Oxides of Nitrogen** evolved.	5) **Nitrite**	a) Acetic Acid and $FeSO_4$. b) H_2SO_4, KI, and starch. See p. 219.
	6) **Chlorine evolved**—original solution has a sweet characteristic odour of HOCl.	6) **Hypochlorite**	a) Lead Acetate and NaOH. b) $MnSO_4$ and NaOH. See p. 220.
	7) **Chlorine and ClO_2 evolved**—solution turns yellow.	7) **Chlorate**	a) Conc. H_2SO_4 to crystal [Caution]. b) Heat dry subs. Chloride is formed. See p. 220.
	8) **Bromine evolved.** Recognized by odour or solution in CS_2 or $CHCl_3$.	8) **Bromate**	
	9) and 10) **Chlorine evolved while solution changes from orange to green.**	9) and 10) **Chromate and Dichromate**	a) $AgNO_3$—red pp. b) $BaCl_2$—yellow pp.
	11) **Chlorine evolved from purple solution.**	11) **Permanganate**	a) Reduce to colourless solution by H_2SO_3Aq. Solution will then give reactions for Manganous Salt. b) Reduce by $FeSO_4$. See p. 221.

Working Summary of Wet Tests to be carried out in order (*continued*).

Experiment.	Result observed.	Acid or Salt indicated.	Confirmatory Tests to be carried out with original solution. (Consult Lists of Reactions under respective acids at pages indicated.)
	[12) Chlorine evolved from deep green solution which on dilution turns pink.	12) Manganate	*a*) Reduce to colourless solution by H_2SO_3Aq. Solution will then give reactions for Manganous Salt. *b*) Reduce by $FeSO_4$. See p. 222.]
	13) HCN evolved, as indicated by odour of bitter almonds.	13) Cyanide	*a*) Prussian blue test. *b*) $AgNO_3Aq$ gives white pp. of AgCN. See p. 223.
II. To original solution add HNO_3 and $Ba(NO_3)_2$ (or if Group I of metals be absent, HCl and $BaCl_2$).	1) White powdery pp. of $BaSO_4$.	1) Sulphuric Acid or Sulphate	*a*) Lead Acetate—white pp. *b*) Na_2CO_3 and solid. Heat on charcoal. Na_2S is formed. Place on moist silver coin. See p. 224.
	2) White gelatinous precipitate of BaF_2.	2) Fluoride	Mix with sand and heat with H_2SO_4. SiF_4 is evolved. Decompose with water. A white pp. forms. See p. 225.
	[3) White gelatinous precipitate of $BaSiF_6$	3) Silicofluoride	Heat dry substance. SiF_4 comes off.]
III. To original solution add HNO_3 and $AgNO_3$. NOTES :— 1) The three sets of salts which might give white precipitates in this group, viz. Chlorides, Thiocyanates, and Ferrocyanides, are readily distinguished on adding $FeCl_3$ as indicated. 2) Cyanides would give a similar precipitate, but should have been detected previously.	1) Chlorides give a white precipitate of AgCl soluble in NH_4OH. [NOTE.—HCNS, $H_4Fe(CN)_6$, and HCN give a similar pp. See under (p. 245).	1) Chloride	*a*) MnO_2 and H_2SO_4 conc. to solid—Cl_2 evolved — bleaching action and odour. *b*) H_2SO_4 to solid—HCl evolved. See p. 226.
	2) Bromides give a faintly yellow pp. of AgBr soluble with difficulty in NH_4OHAq.	2) Bromide	*a*) Chlorine water and CS_2 or $CHCl_3$. *b*) MnO_2 and H_2SO_4 conc.—Bromine evolved. See p. 227.
	3) Light yellow pp. insoluble in NH_4OH may be AgI.	3) Iodide	*a*) Chlorine water and CS_2 or $CHCl_3$. *b*) MnO_2 and H_2SO_4 conc.—Iodine set free. See p. 228.

Working Summary of Wet Tests to be carried out in order *(continued)*.

Experiment.	Result observed.	Acid or Salt indicated.	Confirmatory Tests to be carried out with original solution. (Consult Lists of Reactions under respective acids at pages indicated.)
	4) White pp. might be AgCNS.	4) Thiocyanate	$FeCl_3$—blood-red coloration. See p. 229.
	5) White pp. might be $Ag_4Fe(CN)_6$.	5) Ferrocyanide	*a*) $FeCl_3$—deep blue pp. *b*) $CuSO_4$. Brown pp. of $Cu_2Fe(CN)_6$. See p. 229.
	6) Orange pp. might be Ag_3FeCN_6.	6) Ferricyanide	*a*) $FeCl_3$—light blue pp. *b*) $ZnSO_4$—brownish pp. See p. 229.
IV. **Test for HNO_3** by adding H_2SO_4 and Cu to solid or concentrated solution.	1) Brown fumes of characteristic odour.	1) Nitrate or Nitric Acid	Brown ring test. See p. 230.
V. **Test for H_3PO_4** by adding excess of Ammon. Nitro-molybdate and warming gently.	2) Canary yellow precipitate.	2) Phosphate or Phosphoric Acid	*a*) $AgNO_3$ to neutral solution—yellow pp. of Ag_3PO_4. *b*) NH_4Cl, NH_4OH, and $MgSO_4$—white pp. of $Mg.NH_4.PO_4$. See p. 231.
VI. **Test for Borate** by mixing solid with H_2SO_4 conc. and alcohol, and then setting fire to the alcohol.	3) Green tinted flame.	3) Borate or Boracic Acid	Turmeric test. See p. 232.
VII. **Test for Silicate** by mixing solid with pure Fluoride and conc. H_2SO_4 in platinum or lead crucible and warming gently.	4) SiF_4 is evolved, as indicated by gelatinous precipitate on moist rod. See p. 233.	4) Silicate	*a*) HCl and evaporate. *b*) Borax bead. See p. 232
VIII. **Test for Iodic Acid** by adding H_2SO_3Aq to solution of substance.	5) Iodine set free. Shake with CS_2 or $CHCl_3$.	5) Iodic Acid	Add KI and HCl—Iodine is set free. See p. 233.

Working Summary of Wet Tests to be carried out in order (*continued*).

Experiment.	Result observed.	Acid or Salt indicated.	Confirmatory Tests to be carried out with original solution. (Consult Lists of Reactions under respective acids at pages indicated.)
*IX. To neutral solution add $AgNO_3$.	1) Yellow pp.	1) Arsenite (or Phosphate)	As should be detected when testing for metals with HClAq and H_2S. See p. 233.
	2) Chocolate brown precipitate.	2) Arsenate	*a*) Ammon. Nitromolybdate—yellow coloration, pp. on boiling. *b*) Magnesia mixture. See p. 234.
	3) White pp. turning dark on heating.	3) Hypophosphite	Copper sulphate test. See p. 234.
	[4) and 5) White precipitate might be $Ag_4P_2O_7$ or $AgPO_3$.	4) Pyrophosphate and 5) Metaphosphate	*a*) Both are changed to Orthophosphate on boiling with acids, but *b*) Metaphosphoric Acid coagulates albumen while Pyrophosphoric does not.
	6) Black pp. of Ag_2O_2.	5) Persulphate	Reaction with KI. See p. 235.]
*X. If original aqueous solution is alkaline add $AgNO_3$.	Grey precipitate of Ag_2O.	Soluble metallic Hydroxide	Boil original solution with an Ammonium Salt and carry out other tests on p. 238.

Alternative Method of Classifying Acids.

The classification of the acids already given is most convenient for general practical work, but another method is worth noting which depends upon the behaviour of the acid radicles towards Silver Nitrate and Barium Nitrate under definite conditions. The colour of the precipitate is indicated in each case.

Group I. Silver Nitrate gives a precipitate insoluble in Nitric Acid, while Barium Nitrate gives no precipitate :—

HCl (white), HBr (faintly yellow), HI (light yellow), HOCl (white), HCN (white), HCNS (white), $H_4Fe(CN)_6$ (white), $H_3Fe(CN)_6$ (orange).

Group II. Silver Nitrate gives a precipitate in neutral solution soluble in Nitric Acid: Barium Nitrate gives no precipitate.

Note.—It is obvious that the acids of Group I would also give a precipitate.

HNO_2 (white), H_2S (black), H_3PO_2 (white but turning black on warming).

Group III. Both (*a*) Silver Nitrate and (*b*) Barium Nitrate give precipitates in neutral solution :—

H_2CO_3 (white); H_2SO_3 (white); $H_2S_2O_3$ ((*a*) white but turns brown or black on heating, (*b*) white); H_3PO_4 ((*a*) yellow, (*b*) white); H_3AsO_3 ((*a*) yellow, (*b*) white); H_3AsO_4 ((*a*) chocolate brown, (*b*) white); H_3BO_3 (white); H_2CrO_4 ((*a*) deep brown, (*b*) yellow); $H_2Cr_2O_7$ ((*a*) deep brown, (*b*) yellow); HIO_3 (white); $HBrO_3$ (white); H_2SiO_3 ((*a*) orange, (*b*) white).

Group IV. Barium Nitrate gives a white precipitate insoluble in acid, while Silver Nitrate gives no precipitate :—

H_2SO_4 (white), HF (white), H_2SiF_6 (white).

Group V. Neither Silver nor Barium Nitrate produces any precipitate :—

HNO_3, $HClO_3$, $HMnO_4$, (H_2MnO_4).

PART VI

QUANTITATIVE ANALYSIS

In the chemical investigation of a body qualitative analysis, where one merely determines what elements or groups of elements are present, plays a preliminary part. If the substance seems to be a compound or mixture of compounds and we wished to ascertain the exact composition, we would next proceed to make a **quantitative analysis**, in which we determine the actual weights of the elements or groups of elements present in a given weight of substance. So far we have considered only qualitative analysis, and we now naturally come to **quantitative estimations.**

Quantitative Analysis might be divided into two different types of determinations:

A. Gravimetric Analysis.

B. Volumetric Analysis.

In **Gravimetric Analysis** we determine the percentages of elements and groups of elements (e. g. SO_4) in a substance by processes involving weighing the products of reactions.

In **Volumetric Analysis** we estimate the percentages of substances in solution by finding the volumes of reagents of known strength required to complete definite reactions.

A. Gravimetric Analysis.

The principles of gravimetric analysis are generally more readily grasped than those of volumetric analysis, so that a few typical determinations of the former type will first be considered.

Before going on to discuss gravimetric determinations however, it might be well to say a little about the balance generally employed in quantitative chemical work, as accurate weighing is indispensable in gravimetric estimations.

The Balance.

The ordinary chemical balance consists essentially of a straight lever balanced at the centre on a knife edge and having a pan at each end. The pans are supported on knife edges, which like the central one should preferably be of agate, although the balance is rarely kept in the laboratory, where steel knife edges would tend to rust.

The diagram (Fig. 26) shows one of the modern short-beam balances by means of which it is possible to weigh rapidly and accurately to the third or fourth place of decimals, grams being the unit. A pointer is attached to the centre of the beam, and with the balance at rest, its point is arranged to be at the centre of a graduated scale over which it can swing. The balance is generally enclosed in a glass case with doors at the front and sides. The case is kept dry by means of a small glass dish containing calcium chloride.

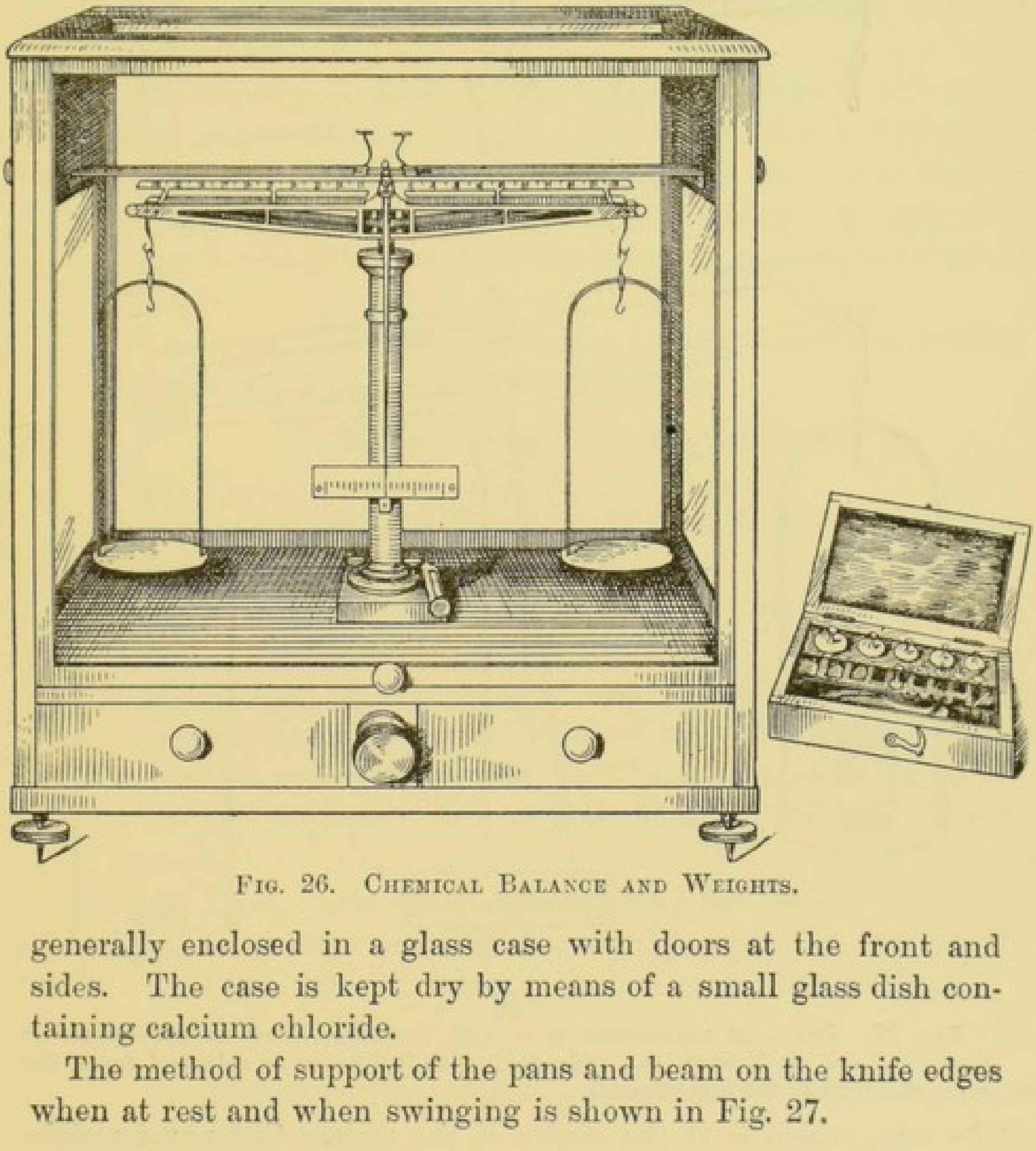


Fig. 26. Chemical Balance and Weights.

The method of support of the pans and beam on the knife edges when at rest and when swinging is shown in Fig. 27.

Method of Procedure when weighing.

(1) Find the working zero of the Balance.

On starting work by turning the milled head in front, release the beam and set the pans swinging. It may be necessary to open the front of the balance case, and by moving one's hand backwards and forwards a short distance from the pans cause currents of air to start movement. The balance case should then be closed. Observe whether the pointer moves over equal distances on each side of the zero. If it does, then in subsequent weighings arrange that the pointer swings equal distances on each side of the zero, which is at the centre of the scale. One never weighs 'dead', i. e. with the pointer at zero and the pans steady. Preferably arrange that in all weighings the pointer swings two to seven scale divisions on each side of the scale zero.

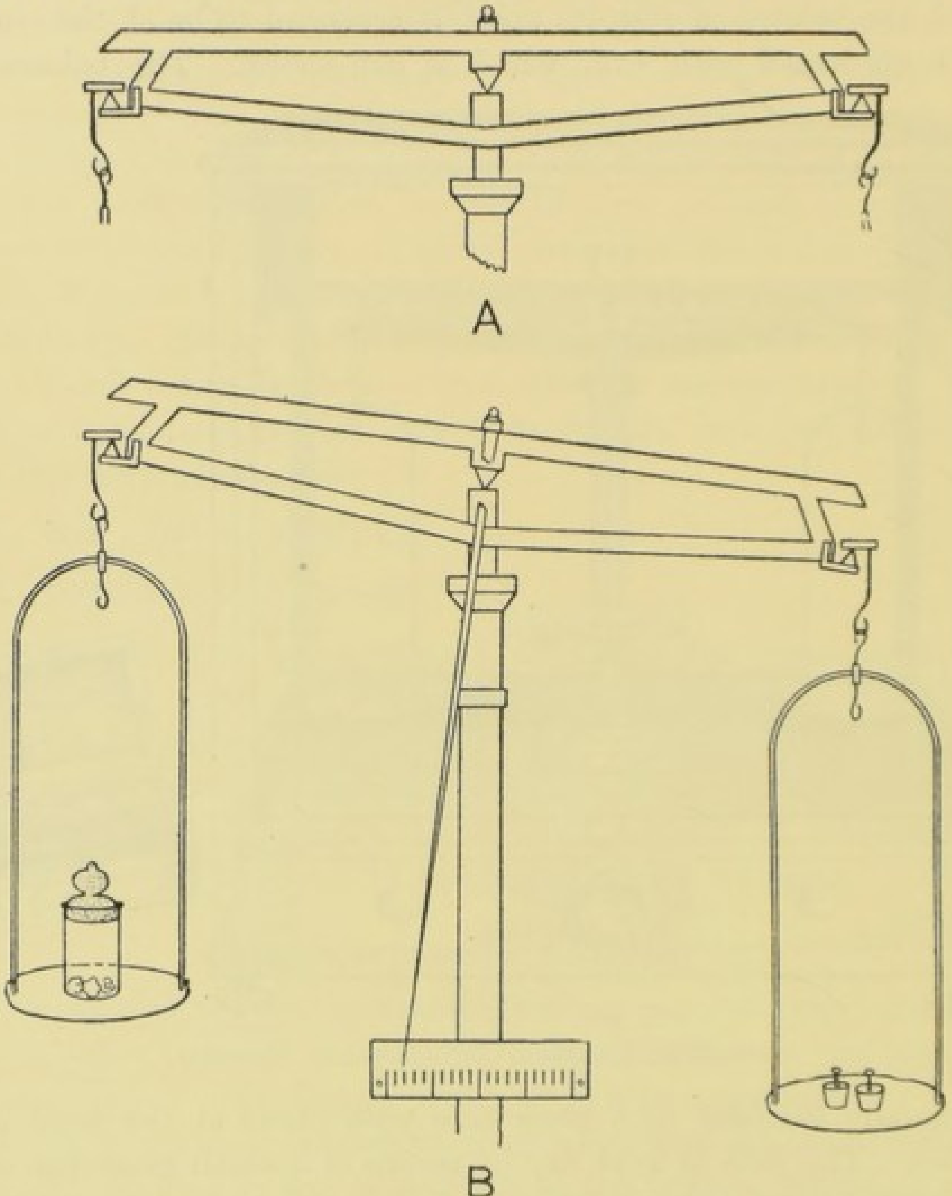


Fig. 27. Diagram indicating how the Balance Beam is supported at Rest (a), and in Motion (b). (In each case the beam is released from the supports, which are not shown.)

If the pointer swings over an unequal number of divisions on each side of the scale zero, then calculate a **working zero** for weighing purposes; e.g. if the balance swings over four divisions to the left and six divisions to the right, then the **working zero** is obviously midway between the two numbers, namely one division to the right of the scale zero, and this should be used in subsequent weighings.

As a rule the junior student should not attempt to adjust the balance so as to make the actual scale zero the working zero, which would rarely be the case in a laboratory balance. Exact coincidence is unnecessary. All fine adjustments should be made by the teacher.

(2) Having obtained a '**working zero**' proceed to weigh, and work systematically, using the heavier weights first, and **invariably support beam and pans** by turning the milled head before putting anything on to the pans or taking anything off. As a rule the body is placed on the left-hand pan and weights on the right.

The rules which should be kept in view in manipulating the balance might be summarized as follows:—

Rules for Balance Manipulation.

(1) Find the working zero of the balance.

(2) Do not put chemicals directly on the pan. Watch-glasses or weighing bottles should generally be used.

(3) If weighing bodies which give off corrosive fumes closed vessels must be employed.

(4) Proceed systematically while weighing and **invariably support beam and pans by turning the milled head** before putting anything on to the pans or taking anything off.

(5) Do not touch the weights with the fingers, always use forceps.

(6) Towards the end of the weighing the balance case should be kept closed to prevent disturbance of the pans by currents of air.

(7) Leave the balance as found with the beam and pans supported.

I. Determination of the percentage of Oxygen in Potassium Chlorate.

Method.—Weigh into a small crucible 0·5 to 1·0 gram of potassium chlorate and heat on pipeclay triangle over a Bunsen flame for 15–20 minutes, as indicated in Fig. 28. Oxygen will be driven off. Equation: $2KClO_3 = 2KCl + 3O_2$. Weigh. Heat again for 5–10 minutes and weigh again. If the weight is the same as before, calculate the percentage of oxygen present. If not, reheat and reweigh until weight is constant. The cooling before weighing should be carried out in a desiccator. A desiccator is a stout glass vessel, containing some hygroscopic material such as calcium chloride or conc. sulphuric acid, and bodies which have been heated should invariably be allowed to cool in a desiccator before weighing, as this gets over difficulties in connexion with condensation of moisture from the atmosphere. Enter the results as follows:—

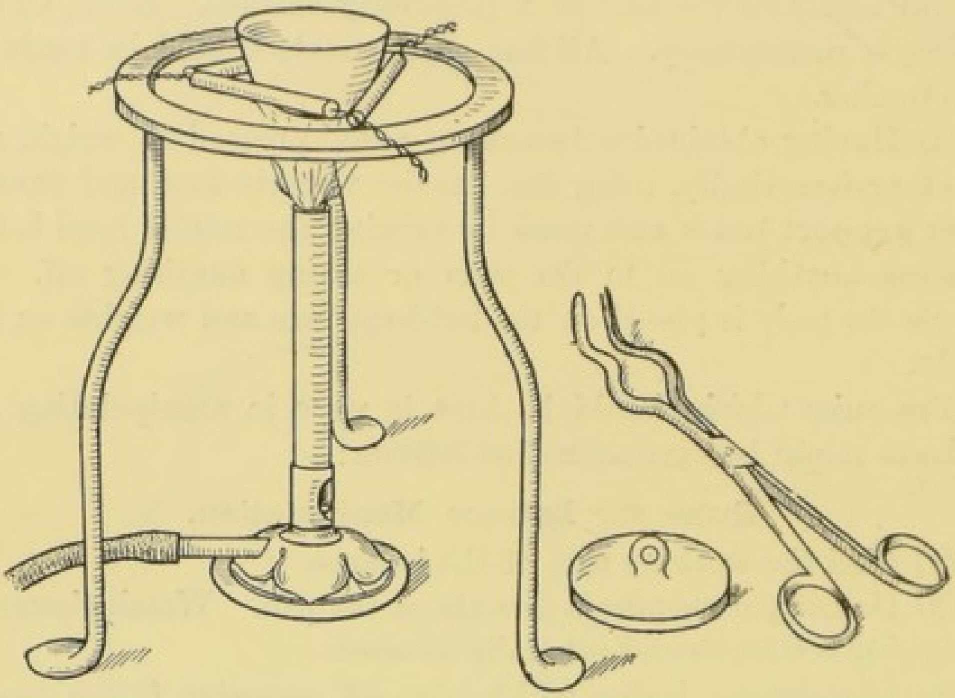


Fig. 28. Method of heating a Crucible on Pipeclay Triangle.

Grams.
Weight of crucible + potassium chlorate = 17·320
Weight of empty crucible = 16·320
Weight of potassium chlorate taken = 1·00 Gram.
After heating 20 min. weight of crucible + residue = 16·928
Heated for 5 min. and reweighed, wt. = 16·928

The weight of oxygen in 1 gram of potassium chlorate is therefore 17·32 − 16·928 = 0·392 gram.

The **chlorine** in the residue can be easily estimated by a volumetric determination, by dissolving in water, making up to a known volume, say 100 c.c., taking a fractional part of this and titrating against standard silver nitrate, using potassium chromate as indicator as described on p. 295.

The quantity of oxygen and chlorine in a certain weight of chlorate having been determined, the potassium can be calcuculated by difference, and from the results a formula could be found.

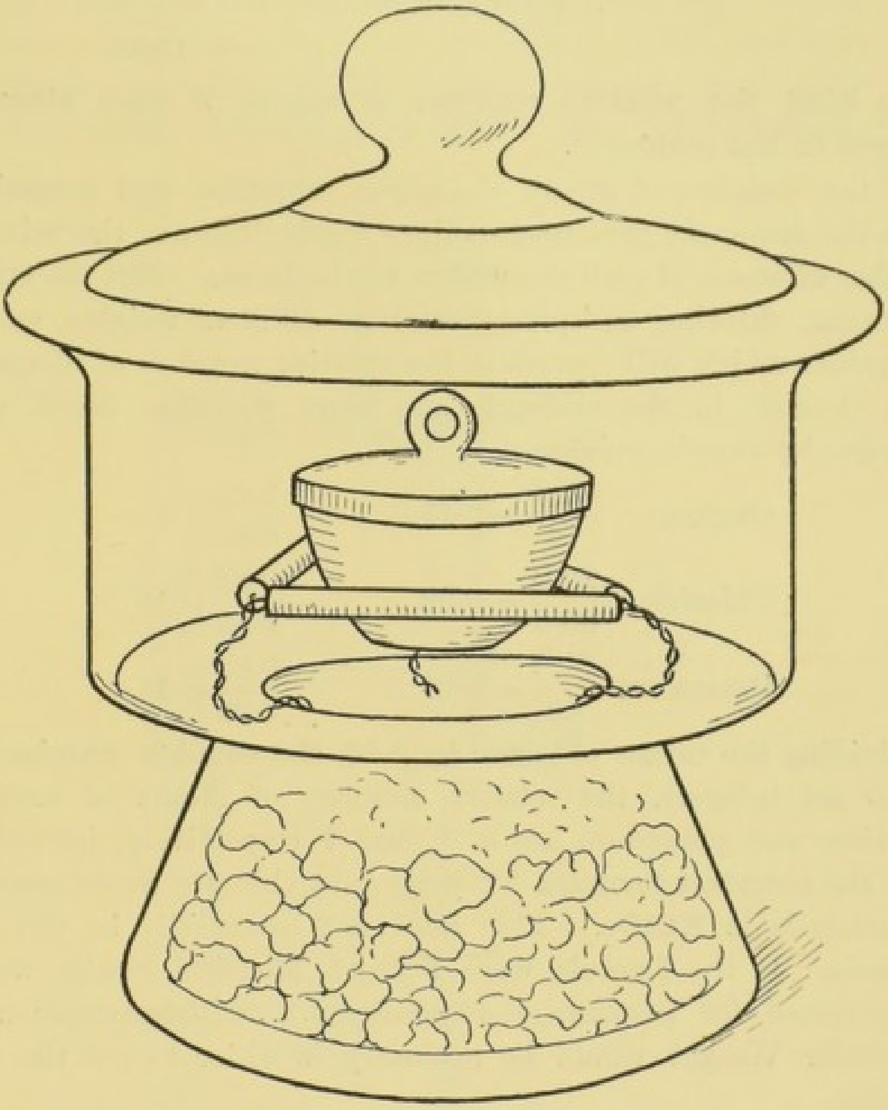


Fig. 29. Desiccator containing Calcium Chloride as Drying Agent.

	Gram.
e. g. Wt. of oxygen in 1 gram of $KClO_3$	= 0·392
Wt. of chlorine in 1 ,, ,, ,,	= 0·290
Wt. of potassium by difference	= 0·318
	1·000

From above values one could determine the formula of the body (supposing it to be unknown) in the following way:-

(1) Find percentage of Oxygen, Chlorine, and Potassium present.

The percentages or weights in 100 grams (or parts by weight) could easily be found by multiplying by 100.

$$\begin{array}{llr} \text{Percentage of oxygen} & 0{\cdot}392 \times 100 = & 39{\cdot}2 \\ \text{,, \quad ,, chlorine} & 0{\cdot}29 \ \ \times 100 = & 29{\cdot}0 \\ \text{,, \quad ,, potassium} & 0{\cdot}318 \times 100 = & \underline{31{\cdot}8} \\ & & 100{\cdot}0 \end{array}$$

(2) Find the relative number of atoms of each element present in the molecule.

If the weights of atoms of oxygen, chlorine, and potassium were the same, the percentage values would indicate the relative number of atoms of each element in the molecule. But the atoms of oxygen, chlorine, and potassium have different weights, and to get values which will represent the relative number of atoms of each element in the molecule one must therefore divide percentages by atomic weights.

$$\begin{array}{lll} \text{Oxygen} & \frac{39{\cdot}2}{16} = 2{\cdot}45 & \frac{2{\cdot}45}{0{\cdot}82} = 3 \\ \text{Chlorine} & \frac{29{\cdot}0}{35{\cdot}5} = 0{\cdot}82 & \frac{0{\cdot}82}{0{\cdot}82} = 1 \\ \text{Potassium} & \frac{31{\cdot}8}{39} = 0{\cdot}82 & \frac{0{\cdot}82}{0{\cdot}82} = 1 \end{array}$$

Dividing the values obtained by 0·82, the smallest number, so as to get integers, the relative number of atoms of oxygen, chlorine, and potassium are 3, 1, and 1 respectively, indicating that the **simplest formula** for potassium chlorate as determined by analysis is **$KClO_3$**. This need not necessarily be the real formula. If the formula were $K_2Cl_2O_6$ identical results would be obtained for percentage composition. A determination of Molecular Weight would be necessary in order to get the real formula.

II. Investigation of Crystallized Barium Chloride.

Qualitative Analysis. Barium chloride is a white crystalline solid easily soluble in water, and on testing for metals and acids in ordinary way barium and chloride could readily be detected. Water of crystallization would be indicated by heating a small quantity of substance in a dry tube. Water would be deposited on sides of tube, and crystals would fall to pieces.

Quantitative Analysis. The qualitative results would indicate that barium, chlorine, and water of crystallization should be determined.

(1) Water of Crystallization.

Preliminary. A moderate quantity of the crystals should preferably be dissolved in water, **recrystallized**, and dried on filter paper at ordinary temperature. They might then be powdered and placed in a small weighing bottle (Fig. 30). Weigh into a porcelain crucible 0·25 to 1 gram of the powder, and heat carefully either in an air oven (Fig. 30) to a temperature of about 200° C. or in a crucible directly over a small flame. Heat for about thirty minutes, weigh, reheat for ten minutes, and weigh again. Repeat until weight is constant. The cooling should take place in a desiccator.

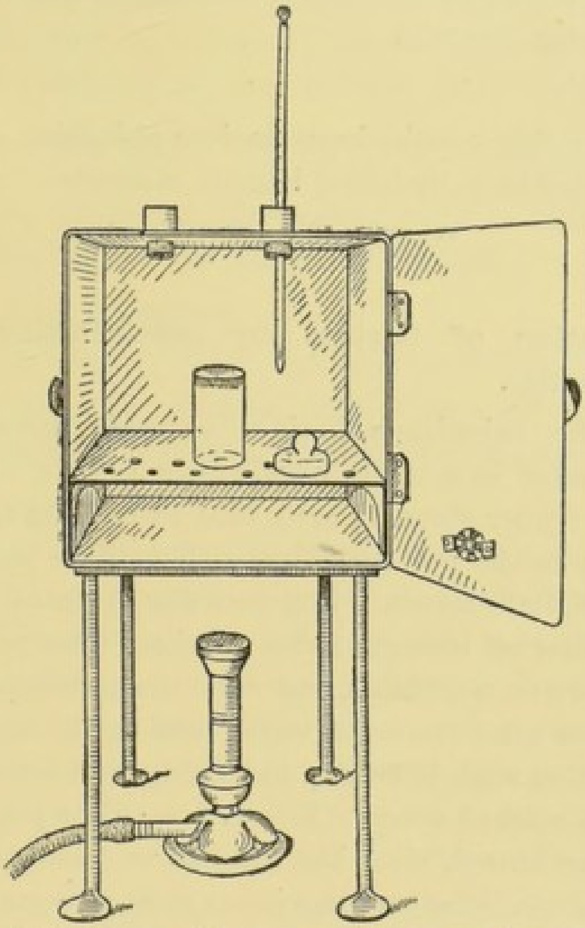


FIG. 30. DRYING OVEN WITH WEIGHING BOTTLE.

NOTES.—(a) If a compound containing water of crystallization decomposes on heating strongly, the air oven must be employed for similar determinations to that described above; e.g. the water of crystallization of copper sulphate ($CuSO_4 . 5H_2O$) should be determined in an air oven by heating to 210° C.

(b) It will generally be found that 0·3 to 0·5 gram of a substance is quite sufficient for any quantitative estimation, provided the weighing can be made to one milligram. One gram is indicated as taken here merely to simplify calculations.

Grams.
e. g. Weight of empty crucible = 16·320
Weight of crucible and barium chloride = 17·320

Weight of crystallized barium chloride taken = 1·0 gram
After heating for thirty minutes in air oven weight = 17·180
Reheated for ten minutes ,, = 17·172
Do. ,, = 17·172

Weight of crucible + anhydrous barium chloride = 17·172
Weight of crucible + hydrated barium chloride = 17·320

Weight of water driven of = 0·148 gram

(2) Estimation of Barium by precipitation as Barium Sulphate, $BaSO_4$.

Dissolve the anhydrous barium chloride remaining in the crucible in water in a small beaker, add 1–2 c.c. of concentrated HCl so as to render strongly acid, heat to boiling, and add slowly, with stirring, to the boiling solution hot dilute sulphuric acid as long as a precipitate forms. Boil for a few minutes, and then allow to settle. Filter off through a close-grained filter paper,[1] the ash of which is known or negligible, and wash the precipitate on the filter with hot water until the wash water passing through gives practically no reaction with $BaCl_2Aq$, indicating that excess of sulphuric acid has been washed away. Remove the filter paper and its contents from the funnel, close the cone so as to form a quadrant of a circle, and press between filter paper so as to remove large excess of moisture. Make into a roll, starting with the apex of the cone, and then throw into a red-hot platinum or porcelain crucible. Heat strongly over Bunsen flame until a nearly white residue remains,[2] breaking up any lumps with a piece of wire, preferably of plati-

---

[1] In removing precipitates to the filter paper a glass rod rounded at the end and tipped with about half an inch of rubber tube will be found to be a great convenience.

[2] On heating as described, some of the Barium Sulphate gets reduced to Barium Sulphide, but after all the Carbon has burnt off the Sulphide takes up Oxygen from the air, forming Sulphate with evolution of light and heat. The re-oxidation is promoted by stirring with a wire.

num. Weigh, and from the weight of barium sulphate found calculate the weight of barium in barium chloride taken.

Results :—		Grams.
Weight of crucible + barium sulphate ($BaSO_4$)	=	17·275
Weight of empty crucible	=	16·320
Weight of barium sulphate	=	0·955 gram

The molecular weight of barium sulphate ($BaSO_4$) is $137 + 32 + 64 = 233$, and it follows that 137 parts by weight of barium must be present in 233 parts by weight of barium sulphate.

Therefore the weight of barium in 0·955 gram barium sulphate $= \frac{137}{233} \times 0{\cdot}955 = 0{\cdot}562$ gram. This must be the weight of barium in one gram, the weight of crystallized barium chloride taken, and would give 56·2 as the percentage of barium.

(3) **Estimation of Chlorine.**

Summary of Process. The chlorine can be estimated by adding silver nitrate to a solution containing a certain weight of substance and weighing the silver chloride precipitated.

Method of Procedure.

Weigh out about half a gram of the crystallized chloride into a beaker of 250–400 c.c. capacity, dissolve in about 100 c.c. of distilled water, acidify with nitric acid, and then add silver nitrate solution slowly as long as a precipitate forms. In order not to waste silver nitrate it is advisable to weigh out a small quantity of the solid substance, say about a fourth more than is theoretically necessary for precipitation. e.g. Suppose 0·5 gram $BaCl_2 . 2H_2O$ taken: from the equation expressing the reaction, viz. :—

$$\left\{\underset{244}{\underline{BaCl_2 . 2H_2O}} + \underset{2 \times 170}{\underline{2AgNO_3}} = 2AgCl + Ba(NO_3)_2 + 2H_2O\right\}$$

the weight of silver nitrate required to precipitate the chlorine in 0·5 gram $BaCl_2 . 2H_2O$ would be $\frac{340}{244} \times \frac{0{\cdot}5}{1} = 0{\cdot}7$ gram (approx.). Weigh out about 0·9 gram $AgNO_3$, dissolve in water, and add gradually to the barium chloride solution until precipitation is complete. Heat to boiling, allow to cool in the dark, and filter rapidly. It is somewhat difficult to remove the last particles of silver chloride from the beaker to the filter paper by pouring along a rod, but a jet of water projected up into the beaker as shown in Fig. 31 will rapidly clean the beaker thoroughly.

Wash the precipitate repeatedly with water from a wash-bottle until no reaction is given, when hydrochloric acid is added to a few drops of filtrate, indicating that excess of silver nitrate has been removed. Cover the filter funnel with a piece of paper and stand in the air oven at 100° C. until quite dry. Then open the filter paper, detach the silver chloride as completely as possible by gently rubbing so that the precipitate falls on to a piece of coloured glazed paper (or on to a watch-glass), sweep into a heap with a camel-hair brush, and cover with the dry funnel. Make a roll of the filter paper so that the apex of the cone is in the centre (Fig. 32), or cut the filter paper into quarters, and then cut each quarter into two or more triangles by cutting from what was the circumference to the portion which was at the apex of the cone. In the former case burn the roll in a coil of platinum wire (Fig. 32), and in the

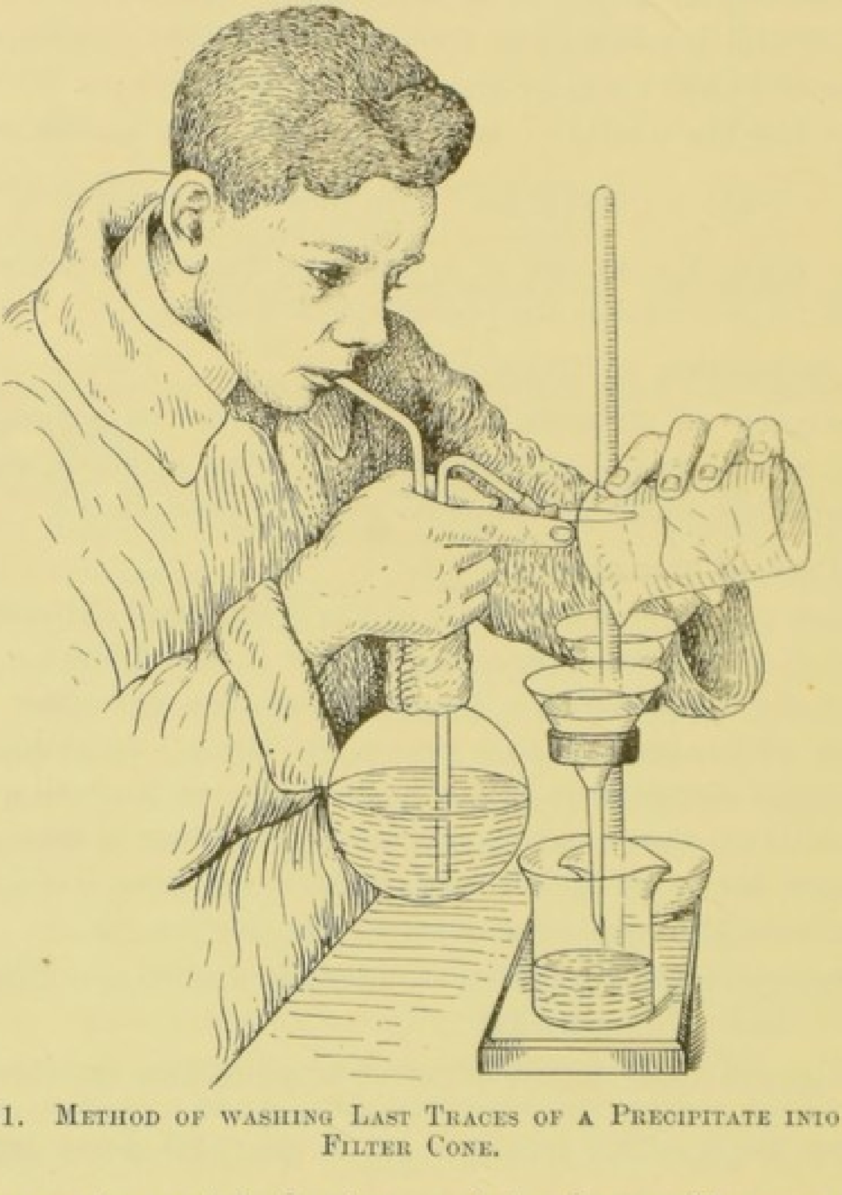


FIG. 31. METHOD OF WASHING LAST TRACES OF A PRECIPITATE INTO THE FILTER CONE.

latter burn each piece separately, holding it with a portion of the circumference in the tongs so that no silver chloride touches the tongs, as in Fig. 33. Drop the residue into the crucible in each case and heat strongly until all the carbon has burnt off. The oxidation of the carbon can be facilitated by adding a couple of drops of concentrated nitric acid to the cold residue, heating strongly and repeating the process if necessary. The silver will have been reduced to the metallic state by treating as described. Add a few drops of nitric acid and warm until all the silver is in solution, then add a couple of drops of HCl and warm over a rose burner or small flame until the residue of silver chloride is quite dry. Add the bulk of the silver chloride, sweeping any small particles into the crucible with a camel-hair brush. Heat carefully over a rose burner until the silver chloride begins to fuse at the edges, cool in a desiccator, and weigh.

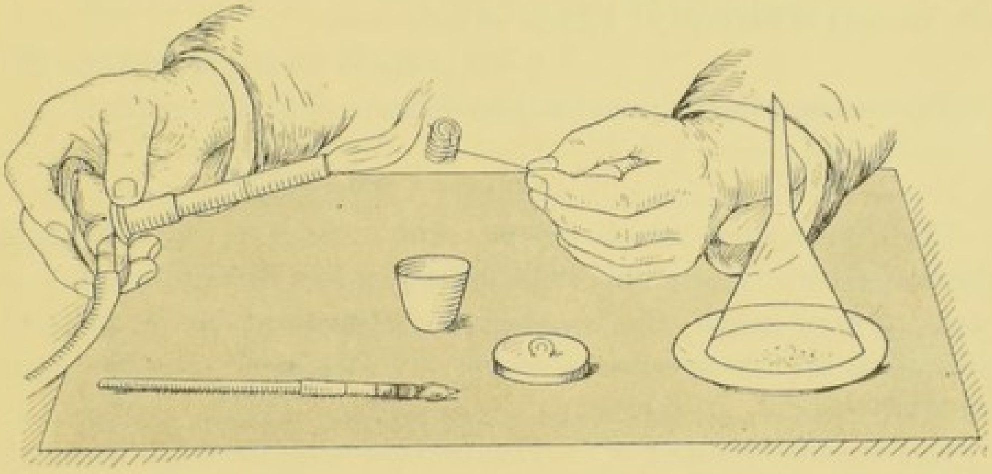


FIG. 32. METHOD OF BURNING FILTER PAPER IN A ROLL IN PLATINUM WIRE COIL.

Calculation of percentage of chlorine from results of analysis.

Gram
Weight of weighing bottle + $BaCl_2 . 2H_2O$ = 10·7260
Weight of bottle alone = 10·3160

Weight of $BaCl_2 . 2H_2O$ taken = 0·410 gram

Weight of crucible + AgCl = 16·802
Weight of crucible = 16·320

Weight of silver chloride = 0·482 gram

The molecular weight of silver chloride is $108 + 35{\cdot}5 = 143{\cdot}5$, and indicates that 35·5 parts out of 143·5 parts by weight consist of chlorine.

The weight of chlorine in 0·482 gram of AgCl must therefore be $\left(\frac{35\cdot5}{143\cdot5} \times 0\cdot482\right)$ gram. This represents the quantity of chlorine in 0·410 gram of $BaCl_2 . 2H_2O$, which was the weight taken.

The percentage of chlorine in crystallized barium chloride is therefore $$\frac{100}{0\cdot41} \times \left(\frac{35\cdot5}{143\cdot5} \times 0\cdot482\right) = 29\cdot08.$$

Determination of Formula from Results of Analysis.

(1) Weight of water in 1 gram of substance
= 0·148 gram = 14·80 per cent. (p. 256).

(2) Weight of barium in 1 gram of substance
= 0·562 gram = 56·20 per cent. (p. 257).

(3) Percentage of chlorine as calculated above = 29·08 per cent.

Total 100·08

The discrepancy here is ·08 per cent., which is well within the limit of error. If a single determination is within 0·2 to 0·3 per cent. it may usually be considered satisfactory, but some determinations are much easier to carry out with great exactitude than others.

The relative number of barium and chlorine atoms to molecules of water in a molecule of the compound is found in a similar manner to that given for the determination of formula of potassium chlorate (p. 254), namely, by dividing the percentages by numbers representing atomic weights (or formula weights for a substance like water).

			Relative number of radicles.			Divide by smallest number.
Barium	$\frac{56\cdot2}{137}$	=	0·41	$\frac{0\cdot41}{0\cdot41}$	=	1
Chlorine	$\frac{29\cdot08}{35\cdot5}$	=	0·82	$\frac{0\cdot82}{0\cdot41}$	=	2
Water	$\frac{14\cdot8}{16+2}$	=	0·82	$\frac{0\cdot82}{0\cdot41}$	=	2

The simplest formula would therefore be $BaCl_2 . 2H_2O$.

III. Analysis of crystallized Copper Sulphate, $CuSO_4.5H_2O$.

Preparation of substance for analysis.

To make certain that the water of crystallization has the correct value it is advisable to recrystallize. Dissolve 15 to 20 grams of the commercial crystals in water in a beaker, acidify with nitric acid, filter into a porcelain basin, and evaporate over a small flame until a few c.c. taken in a test-tube and cooled under the tap yield a good crop of crystals. Allow to crystallize, drain off the mother liquor, and dry the crystals on filter paper. Powder in a mortar, press between filter paper, and place in a weighing bottle.

(1) Determination of the water of crystallization.

Water is lost in two stages.

(*a*) Heat a weighed quantity of the blue powder (say one gram) to 110° C. in an air oven for an hour. Water is lost and a faintly bluish substance remains. Reheat and weigh until the result is constant.

(*b*) Heat the residue to 210° C. in an air oven until the weight is constant. A further loss of weight takes place and a nearly white powder remains.

Example :—(*a*) On heating one gram of substance to 110° C. the following results were obtained :—

(i) Weight after heating for one hour	0·7125 gram
(ii) After repeating for 10 minutes	0·7120 „

The loss of weight at 110° C. is therefore

$$1 - 0{\cdot}7120 = {\cdot}0288 \text{ gram} = 28{\cdot}80 \text{ per cent.}$$

[Note.—To avoid complication, the weight of the weighing bottle is not stated.]

(*b*) On heating the residue from (*a*) to 210° C. until the weight was constant, the final weight of the substance was 0·640 gram.

∴ the loss of weight was

$$0{\cdot}712 - 0{\cdot}640 = {\cdot}072 \text{ gram} = 7{\cdot}20 \text{ per cent.}$$

(2) Determination of the Copper.

The copper in copper salts may be conveniently estimated gravimetrically by either of the following two methods.

Method I. Determination as Oxide after precipitation as Hydrated Oxide. Weigh out about half a gram of the crystallized substance (or the dehydrated substance can be used if preferred), dissolve in water in a porcelain basin,* add enough of a clear solution of caustic soda to make the solution strongly alkaline, boil for a few minutes, allow to settle, filter and wash with boiling water† until a few c.c. of the filtrate give no precipitate with barium chloride, indicating absence of sulphuric acid.

Cover the funnel with paper and dry in the air oven. Remove as much as possible of the copper oxide to a watch-glass and cover with a funnel as shown in Fig. 32, and then burn the filter paper after cutting into pieces as indicated in Fig. 33, or make up into a small compact roll with the apex of the cone in the centre and burn in a coil of platinum wire as represented in Fig. 32. Allow the residue to drop into a porcelain (or platinum) crucible, add a few drops of concentrated nitric acid, allow to stand a minute, and then warm cautiously with lid on until the residue seems to be pure copper oxide. Add the bulk of the copper oxide, ignite, and weigh.

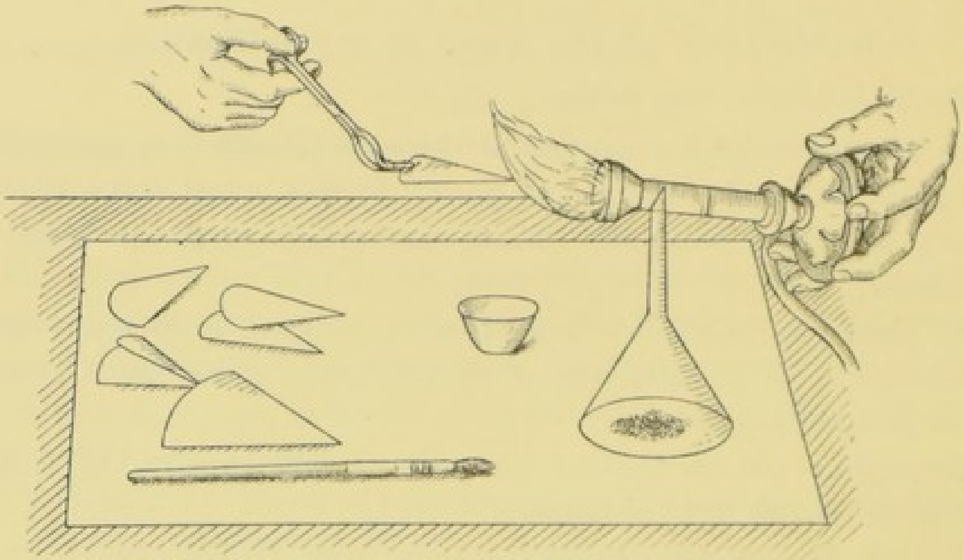


FIG. 33. METHOD USED WHEN BURNING FILTER PAPER CUT INTO PIECES.

Equations:

$$(a)\ CuSO_4Ag + 2NaOHAg = Cu(OH)_2 + Na_2SO_4Ag.$$

$$(b)\ Cu(OH)_2 = CuO + H_2O.$$

---

* Always use porcelain in preference to glass if caustic alkalies or alkaline carbonates are to be added and the solution subsequently boiled. These bodies attack glass, forming a small quantity of silicate, which tends to vitiate the results of analysis.

† In gravimetric analysis one washes with hot water unless the precipitate happens to be slightly soluble. It is advisable to fix a short length of stout wide rubber tubing, or to sew a piece of baize round the neck of the wash-bottle to allow of convenient handling. A wash-bottle with baize round it is shown in Fig. 31.

Example:—Weight of crystallized copper sulphate
($CuSO_4.5H_2O$) taken = 0·498 gram
Weight of copper oxide found = 0·160 ,,

The molecular weight of copper oxide is $63 + 16 = 79$, so that $\frac{63}{79}$ths of copper oxide represent copper. The weight of copper in this case $= \left(\frac{63}{79} \times 0{\cdot}160\right)$ gram, and this must be the weight of copper in 0·498 gram of crystallized copper sulphate. The percentage of copper

$$= \frac{100}{0{\cdot}498} \times \frac{63}{79} \times 0{\cdot}160 = 25{\cdot}63.$$

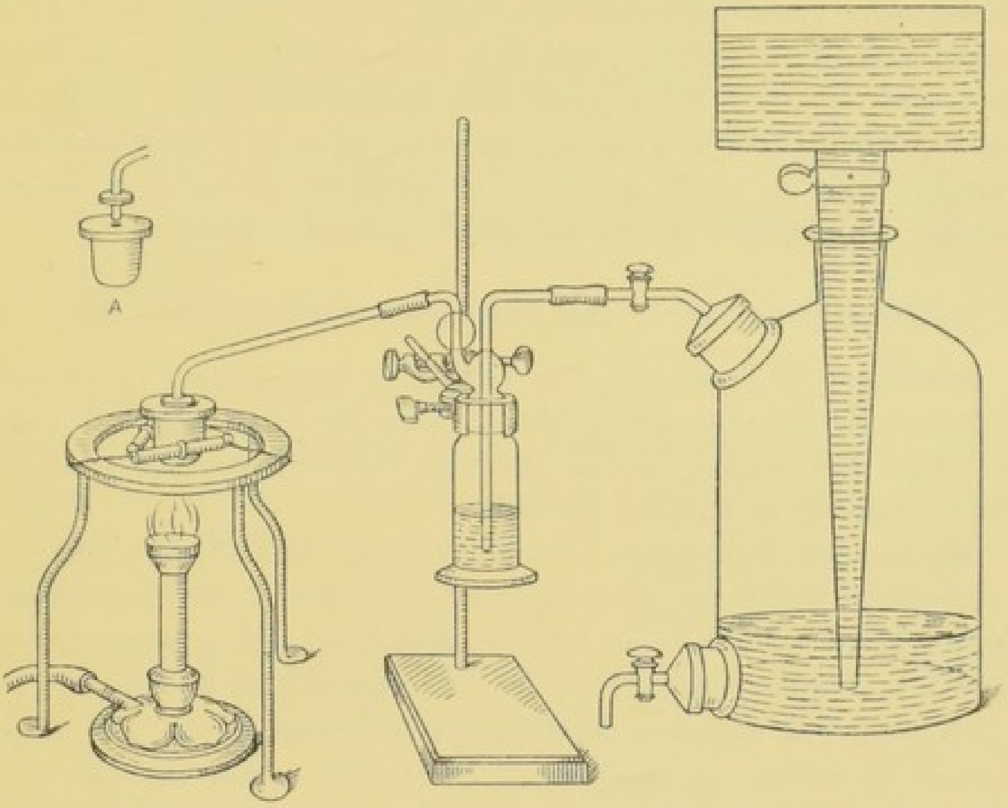


FIG. 34. ROSE'S CRUCIBLE (A). DIAGRAM SHOWING HOW DRY HYDROGEN CAN BE PASSED THROUGH THE APPARATUS.

Method II. The copper can be estimated as cuprous sulphide, Cu_2S, after precipitation as cupric sulphide, CuS, filtering and heating with sulphur in a reducing atmosphere.

Method of Procedure. Weigh out about half a gram of substance, dissolve in water, warm, and then pass sulphuretted hydrogen as long as a precipitate forms. Filter at once, so as to prevent oxidation of sulphide to sulphate, wash with water containing sulphuretted hydrogen, dry in the air oven, and then transfer the sulphide to a Rose crucible, which is of porcelain, and is provided with a lid with a small hole in the centre, through which hydrogen or coal gas can be passed by means of a small porcelain tube, as shown in Fig. 34A. Separate the precipitate and burn the filter as above described.* After burning the filter, and before introducing the bulk of the copper sulphide, add a small quantity of pure sulphur and heat until excess is burnt off. Then introduce the bulk of the precipitate, add a small quantity of sulphur, and heat cautiously in a stream of dry† hydrogen for 10 to 15 minutes after excess of sulphur has burnt off. Allow to cool in hydrogen and then place in a desiccator and weigh. Add a small quantity of sulphur, repeat and weigh again. The weight should not alter. Repeat if necessary.

(3) Determination of the Sulphuric Acid Radicle SO_4''.

Summary of Process. The radicle is transformed to barium sulphate ($BaSO_4$) by adding barium chloride to an acid solution, so that the process is the converse of that described under determination of barium (p. 256).

Method of Procedure. Dissolve from half to one gram of crystallized substance in water, add 2 or 3 c.c. of concentrated hydrochloric acid, heat to boiling, and then add a concentrated solution of barium chloride as long as a precipitate forms.

[NOTE.—The solution must be made strongly acid, and large excess of barium chloride must be avoided, otherwise the precipitate is very difficult to filter.] Filter, wash free from chloride with boiling water, fold the filter paper and roughly dry it by pressing between dry filter paper, then make into a roll and pitch into an inclined red-hot platinum crucible. After burning to a white residue and making certain that no sulphide is present (see p. 256), allow to cool in a desiccator and weigh. The method of calculating the percentage of SO_4 from the results of analysis is indicated in the following example :—

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* If a Rose crucible is not available, use an ordinary crucible with a lid, and pass hydrogen into the crucible through a piece of clay pipe-stem.

† The hydrogen should be dried by passage through sulphuric acid, and it is advisable to start the passage of the gas before bringing the porcelain tube into the crucible. The crucible should be cold when the hydrogen is introduced, and should then be gradually heated. A gas-holder containing hydrogen should be used, so as to make it easy to regulate the stream of gas.

0·5 gram of copper sulphate, $CuSO_4 . 5H_2O$, was taken.

Weight of barium sulphate found = 0·467 gram. Molecular weight of $BaSO_4 = 137 + 32 + 64 = 233$.

∴ weight of SO_4 in 0·5 gram copper sulphate

$$= \frac{SO_4}{BaSO_4} \times 0{\cdot}467 = \left(\frac{96}{233} \times 0{\cdot}467\right) \text{gram},$$

and the percentage of SO_4 in the compound

$$= \frac{100}{0{\cdot}5} \times \frac{96}{233} \times 0{\cdot}467 = 38{\cdot}48.$$

Summary of Results of Analysis.

Percentages :—

(*a*) Water driven off at 110° C.	= 28·80
(*b*) Water driven off between 110° C. and 210° C.	= 7·20
(*c*) Copper	= 25·63
(*d*) Sulphion (SO_4)	= 38·48
Total	100·11

Calculation of Formula :—

Divide the percentages by numbers representing the relative weights of atoms or radicles and then divide the values obtained so as to get integers :—

$$\left.\begin{array}{ll} (a)\ \text{Water driven off at } 110^\circ \text{ C.} & = \dfrac{28{\cdot}80}{16+2} = 1{\cdot}60 = 4 \\ (b)\ \text{Water driven off between} & \\ \quad 110^\circ \text{ C. and } 210^\circ \text{ C.} & = \dfrac{7{\cdot}20}{18} = 0{\cdot}40 = 1 \end{array}\right\} 5H_2O.$$

$$(c)\ \text{Copper} \qquad \frac{25{\cdot}63}{63} = 0{\cdot}42 = 1Cu.$$

$$(d)\ \text{Sulphion } (SO_4) \qquad \frac{38{\cdot}48}{96} = 0{\cdot}40 = 1SO_4.$$

The simplest formula would therefore be **$CuSO_4 . 5H_2O$.**

Gravimetric Estimation of the Metals.

Arranged in the order of the Analytical Groups in Qualitative Analysis.

Group I. (1) **Silver,** (2) **Mercury in Mercurous State,** (3) **Lead.**

Note.—Atomic weights are given on p. 342.

(1) **Silver** is estimated gravimetrically by precipitation as chloride. Use dilute HCl, and after precipitation proceed as described on p. 257. Use recrystallized silver nitrate, $AgNO_3$.

(2) **Mercurous Mercury** can be determined as chloride by precipitation with HCl, and filtering through a tared filter, drying at 100° C. and weighing as chloride.

Note.—A **tared filter** is a weighed filter which has been dried at a definite temperature—generally 100° C.—until the weight is constant. Dry in a weighing bottle in air oven.

(3) **Lead** can be estimated as sulphate or as oxide after precipitation as basic carbonate.

Estimation as Sulphate. Dissolve about half a gram of substance {e.g. lead acetate, $Pb(C_2H_3O_2)_2 . 3H_2O$} in water with the addition of a few drops of acetic acid if necessary, and then add dilute sulphuric acid as long as a precipitate forms. Allow to settle, and add a few more drops of sulphuric acid to make certain that precipitation is complete: then add double the volume of alcohol and stir. After settling filter, wash with methylated spirit until free from sulphuric acid, dry in an air oven at 100° C., detach the precipitate as completely as possible from the filter, and burn the filter paper in pieces as described under Chlorine (p. 257). After complete oxidation of the filter paper, the adherent lead sulphate will have been reduced to metallic lead. Add a few drops of nitric acid, and after standing and warming two drops of dilute sulphuric acid, heat cautiously until dry and then add the bulk of the precipitate. Heat to dull redness: dry and weigh.

Group II. (1) **Mercury in Mercuric State,** (2) **Copper,** (3) **Bismuth,** (4) **Cadmium,** (5) **Arsenic,** (6) **Antimony,** (7) **Tin.**

Note.—All can be precipitated as sulphide, which might be expected from the analytical relationships.

(1) **Mercuric Mercury.** Precipitate as mercuric sulphide (HgS) by passing sulphuretted hydrogen through a warm solution. Filter through a tared filter, dry at 100° C., and weigh. Use mercuric chloride, $HgCl_2$, or mercuric oxide.

(2) **Copper** is estimated as oxide or sulphide (Cu_2S). See pp. 261 and 263.

(3) **Bismuth** can be determined as sulphide (Bi_2S_3) similarly to mercury, or as oxide after precipitation as basic carbonate.

Estimation as Oxide. Make a solution of the bismuth compound in dilute acid, add **slight** excess of ammonium carbonate to the solution, heat nearly to boiling for 10 minutes, filter, dry, and ignite. The filter paper should be burnt separately after removing the bulk of the precipitate. The metal is formed by reduction during this ignition. Add a few drops of conc. nitric acid, and heat until all carbon is burnt off. Add the bulk of the precipitate, heat, and weigh. Repeat heating and weighing until result is constant.

(4) **Cadmium** can be estimated as oxide or sulphide (CdS). The estimation as oxide (CdO) is similar to that described under Zinc (p. 270).

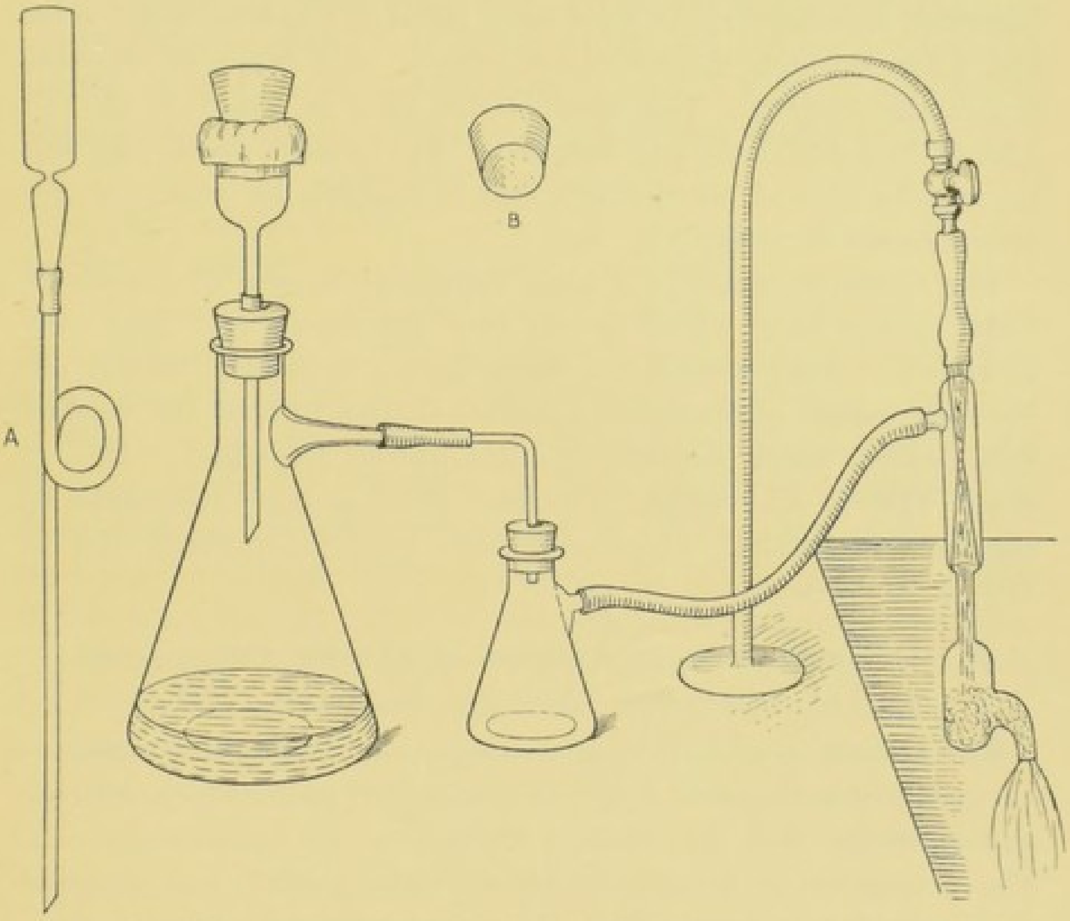

Fig. 35. Filtration through a Gooch Crucible (B). A. Alternative Apparatus consisting of Constricted Tube and quick Filtering Attachment.

(5) **Arsenic. A. Determination of Arsenic in Arsenious state.**

Summary of Process. The arsenic is precipitated from an acid solution by sulphuretted hydrogen as arsenious sulphide (As_2S_3), filtered and weighed as such.

Method of Procedure. Dissolve 0·3 to 0·5 gram of substance (e. g. As_2O_3) in dilute HCl by warming gently on a water-bath in a conical flask. The liquid must not be boiled or arsenic may be volatilized as arsenious chloride.

Dilute with water, warm to about 50° C., and pass sulphuretted hydrogen through the solution as long as a precipitate forms. Drive out the sulphuretted hydrogen from the solution by passing carbon dioxide. Filter through a tared filter, or, as a tared filter is troublesome to prepare, the following alternative is recommended. Take a Gooch porcelain or platinum crucible, the bottom of which is perforated with a few very small holes. Rub up purified long-fibre asbestos (purified by digestion with concentrated hydrochloric acid for some time) in a mortar with water and filter through the Gooch so that a thin layer of asbestos covers the bottom. The crucible can then be dried at 110° to 120° C. in a desiccator and weighed. The arsenic precipitate can be rapidly filtered off through such a crucible by means of the arrangement shown in Fig. 35.

The Gooch is fixed in a glass funnel by means of a piece of wide rubber tube which is put into the funnel and bent over as shown. After fixing, the water pump is gently turned on. The precipitate of arsenious sulphide is then filtered and washed with warm water containing sulphuretted hydrogen. Dry at about 110° C. and weigh. Extract with carbon disulphide to remove any sulphur which may have been precipitated, dry at 110° C., and reweigh.

B. Determination of Arsenic in Arsenic Compounds.

e. g. Common Sodium Arsenate, $Na_2HAsO_4 . 12H_2O$.

The arsenic is precipitated as ammonium magnesium arsenate by means of a magnesium salt in presence of ammonium chloride and ammonia (i. e. by what is known as 'magnesia mixture'). The precipitate is filtered, dried, strongly ignited, and weighed as magnesium pyroarsenate, $Mg_2As_2O_7$ (cf. estimation of magnesium, p. 273).

(6) **Antimony.** Use tartar emetic $(K . SbO . C_4H_4O_6)_2 . H_2O$. Precipitate the antimony in a flask as sulphide (Sb_2S_3) from an acidified solution, allow to stand an hour, filter off through a tared filter, or preferably use a Gooch crucible and asbestos. Dry, weigh, remove sulphur by carbon disulphide, heat to 210° C., and weigh. If a tared filter is used a weighed portion of the product dried at 100° C. is heated at 210° C. in a boat in a stream of CO_2 and weighed.

(7) **Tin,** either in the stannous or stennic state, in the case of substances which can be dissolved in water or dilute acid can be estimated by precipitation as sulphide and conversion to stannic oxide by heating.

Group III. (1) Fe, (2) Al, (3) Cr.

The metals of this group can be estimated gravimetrically by precipitation as hydroxide and weighing as oxide, as might be expected from their behaviour in quantitative analysis.

(1) Iron, Fe. At. wt. 56.

Summary of Process. Iron is generally estimated gravimetrically by precipitation as ferric hydroxide, which is converted into oxide by heating and weighed as such. Ferrous compounds must be converted into the ferric state before precipitation.

Ferric Compounds.

If the substance is a ferric salt, e. g. iron alum, $K_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$, dissolve enough substance in water to yield 0·1 to 0·25 gram of ferric oxide. Solution should be effected in a porcelain dish. Add ammonium hydroxide to the boiling solution as long as a precipitate forms, boil until excess of ammonia is driven off, filter, wash and dry thoroughly in the air oven at 100° C. Remove the precipitate as completely as possible from the filter paper, and by rubbing the sides of the cone gently together above a watch-glass remove small particles which are adherent. Cut up and burn the filter paper (p. 262), or roll up and burn in a coil of platinum wire held over a crucible (p. 259). When the filter paper has been got rid of, and it may be assumed that any reduced particles of iron have been oxidized, add the bulk of the precipitate and heat over a Bunsen with the lid on, so as to obviate reduction by reducing gases of the flame. Allow to cool in the desiccator and weigh.

(2) **Aluminium** is estimated in a similar manner to iron, but a strong solution of ammonium chloride equal in bulk to half the volume of aluminium solution must be added before the ammonium hydroxide used as precipitant.

Use well crystallized potash alum, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$.

(3) **Chromium** in the case of chromic compounds like chrome alum ($K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$); the chromium is precipitated by ammonium hydroxide as chromium hydroxide, which after drying is transformed to oxide by heating as described above under Iron (p. 269).

Chromates and dichromates must first be reduced by freshly prepared sulphurous acid solution.

Group IV. (1) **Zinc**, (2) **Manganese**, (3) **Nickel**, (4) **Cobalt.**

It might be expected that the metals of this group could be estimated as sulphides. Although precipitation as sulphide can be used as a stage in the process, only in the case of zinc is direct estimation as sulphide a good method.

(1) **Zinc**, Zn. At. wt. 65·4.

Zinc can be determined as oxide or sulphide.

Method I. **Determination as Oxide.**

Summary of Process. The metal is precipitated as basic carbonate by adding potassium or sodium carbonate solution. The carbonate is transformed into the oxide by ignition and weighed as such; e. g.*

$$(a)\quad ZnSO_4 . 7H_2O + Na_2CO_3 = \mathbf{ZnCO_3} + Na_2SO_4 + 7H_2O$$

$$(b)\quad ZnCO_3 = \mathbf{ZnO} + CO_2.$$

Method of Procedure. Use about half a gram of recrystallized zinc sulphate, $ZnSO_4 . 7H_2O$. Dissolve in water in a deep porcelain basin, and add slowly sodium carbonate until the reaction is strongly alkaline. Cover the dish with a clock-glass and boil for a few minutes. Allow the precipitate to settle, filter, and wash until sulphate is proved absent (on testing a few drops of the filtrate with barium chloride), and then dry in an air oven at 100° C. Remove the precipitate as completely as possible from the filter on to a watch-glass, and by rubbing the sides of the cone gently against each other detach adhering particles: cover the bulk of the precipitate with a funnel. Moisten the filter paper with a concentrated solution of ammonium nitrate and heat in air oven until dry. Make into a roll and burn cautiously either in the crucible or in a platinum wire coil above porcelain crucible. The danger here lies in the volatilization of reduced metal. When the residue in the crucible is white add the bulk of the precipitate and heat strongly in a closed crucible over a Bunsen flame. Cool in the desiccator and weigh. Repeat until constant.

(2) **Manganese** can be estimated by precipitation as hydrated peroxide (or basic carbonate), which is converted on ignition to Mn_3O_4.

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* When a substance contains water of crystallization, this must be noted in calculating from equations.

Dissolve about half a gram of the substance in water in a porcelain dish. If potassium permanganate is used add sulphurous acid solution slowly with constant stirring until the solution becomes colourless. Add caustic soda solution and then bromine water until the liquid remains tinted brown, boil off the excess of bromine, filter off the black precipitate, dry, and ignite in a crucible with a foot-blowpipe to constant weight. The filter paper should be cut in pieces and burned apart from the bulk of the precipitate.

(3) **Nickel** may conveniently be estimated as nickelous oxide (NiO) after precipitation as hydroxide.

Dissolve about half a gram of substance (e.g. $NiSO_4 . (NH_4)_2SO_4 . 6H_2O$) in water in a porcelain dish, and add caustic soda in slight excess to the hot solution, boil, allow to settle, filter, wash, dry and treat as in the case of copper oxide (p. 261).

(4) **Cobalt** can be determined as metallic cobalt after precipitation as cobaltous hydroxide and subsequent reduction to metal.

Precipitate the hydroxide as described under Nickel: filter and dry. Burn the filter paper and allow the residue to fall into a Rose crucible (p. 263). After burning off the filter paper, add the bulk of the precipitate and ignite in a stream of hydrogen. The oxide is reduced to metallic cobalt.

Group V. (1) Calcium, (2) Strontium, (3) Barium.

The metals of this group can all be precipitated and estimated as carbonates, as might be anticipated from the analytical relationships. Calcium is, however, generally precipitated as oxalate and barium as sulphate.

(1) **Calcium** is most conveniently precipitated as oxalate, which is converted into oxide by heating.

Method of Procedure. Use calc-spar or precipitated calcium carbonate.

Dissolve 0·3 to 0·5 gram of substance in dilute hydrochloric acid in a beaker. The substance is weighed into the beaker, water added, and the beaker is covered by a clock-glass. Dilute hydrochloric acid is then added—the clock-glass being slipped aside for a moment—and the beaker allowed to stand until solution is effected. Make alkaline with ammonium hydroxide, heat the liquid to boiling-point, and then add hot ammonium oxalate solution. Calcium oxalate is precipitated.

Allow to settle. Pour off the supernatant liquid through a filter paper, wash twice by decantation, filter off the precipitate through the filter, and wash until free from chloride as indicated by the absence of a precipitate with silver nitrate. Dry at 100° C., remove the precipitate as far as possible on to a watch-glass, and burn the filter paper in a platinum coil or in pieces as described under Chlorine (p. 259). When the filter paper has been completely burnt off and a white residue remains, add the bulk of the precipitate and heat over a Bunsen flame for about 15 minutes. Finally, ignite over a blowpipe until the weight is constant.

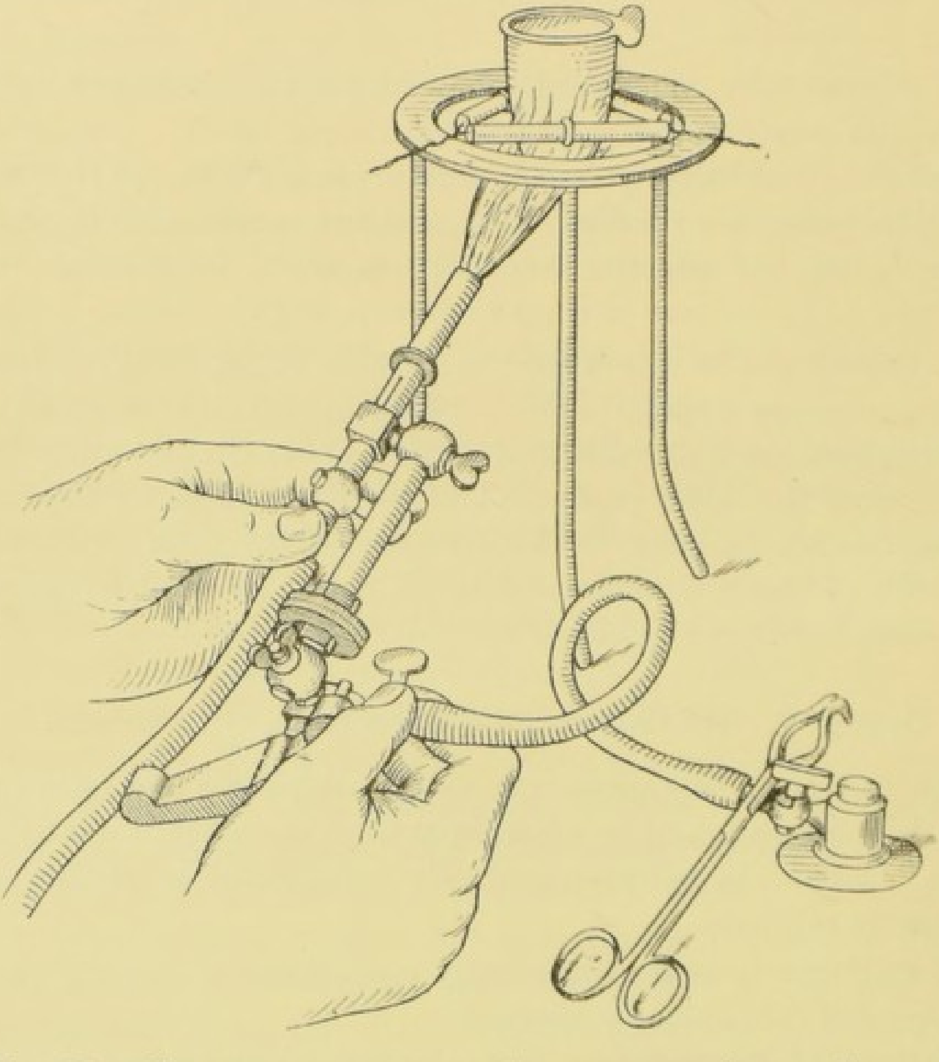

FIG. 36. METHOD OF HEATING UP SUBSTANCES IN CLOSED CRUCIBLE BY FOOT-BLOWPIPE. Note the position of the tongs. The tips should never be placed on the table.

(2) **Strontium** can be precipitated as carbonate with ammonium carbonate and weighed as such. On ignition of the substance adherent to the filter paper, which should be as small as possible, oxide (SrO) is obtained,

which is recarbonated by heating with solid ammonium carbonate before adding the bulk of the precipitate.

(3) **Barium** is estimated as sulphate as already described (p. 256).

Group VI. (1) Magnesium, (2) Ammonium, (3) Potassium, (4) Sodium.

(1) **Magnesium** is precipitated as magnesium ammonium phosphate, which is converted into magnesium pyrophosphate by heating.

Method of Procedure. Weigh out about half a gram of substance (e.g. $MgSO_4 . 7H_2O$) into a wide-mouthed conical flask which can be closed by a rubber stopper, and dissolve in about 50 c.c. of water. Add first about an equal bulk of ammonium chloride and next ammonium hydroxide until the liquid smells strongly. Then add to the mixture excess of sodium phosphate solution. A white crystalline precipitate of magnesium ammonium phosphate comes down. In order to get the whole of the substance precipitated with maximum rapidity proceed as follows:—Stir with a glass rod tipped with rubber, close the flask with a rubber stopper, shake at intervals of a few minutes for 15 to 20 minutes. Remove and wash the stopper so that wash water passes through a filter paper. Cover the top of the flask with a watch-glass and allow to stand for an hour. Then filter through the paper used for the washings from the stopper, wash with moderately concentrated ammonia (1 to 4 or 5 of water) until all chloride is removed, and dry in an air oven. Detach the precipitate as far as possible, cut the filter paper into pieces, and burn as described on p. 262. Moisten the residue in the crucible with saturated ammonium nitrate, dry and heat cautiously. When a white residue remains, add the bulk of the precipitate and heat at first with a small flame, which is afterwards turned up. Finish the ignition with a blowpipe. Ignite until the weight is constant.

(2) The **radicle ammonium**, NH_4, which behaves like a monovalent metal, can be estimated gravimetrically by precipitation as **ammonium chloroplatinate, $(NH_4)_2PtCl_6$**.

Weigh out about half a gram of substance (e.g. NH_4Cl or $(NH_4)_2SO_4$) and dissolve in a small quantity of water in a porcelain basin. Add chloroplatinic acid (H_2PtCl_6), preferably of known strength so as to avoid large excess, and evaporate down on a water-bath until a paste is left. Add alcohol and stir, and note whether the supernatant liquid is yellow, showing excess of platinic chloride. If not, add platinic chloride a few drops at a time until after stirring the liquid is tinted yellow. Filter through a tared Gooch crucible or filter paper, wash with alcohol, and dry at 110° C. until the weight is constant. Alternative treatment of the precipitate would be to filter through an untared filter paper, wash as before, ignite, and from weight of platinum determine the weight of ammonium.

(3) **Potassium** can be estimated (*a*) as chloroplatinate, K_2PtCl_6, as described for ammonium; (*b*) as sulphate.

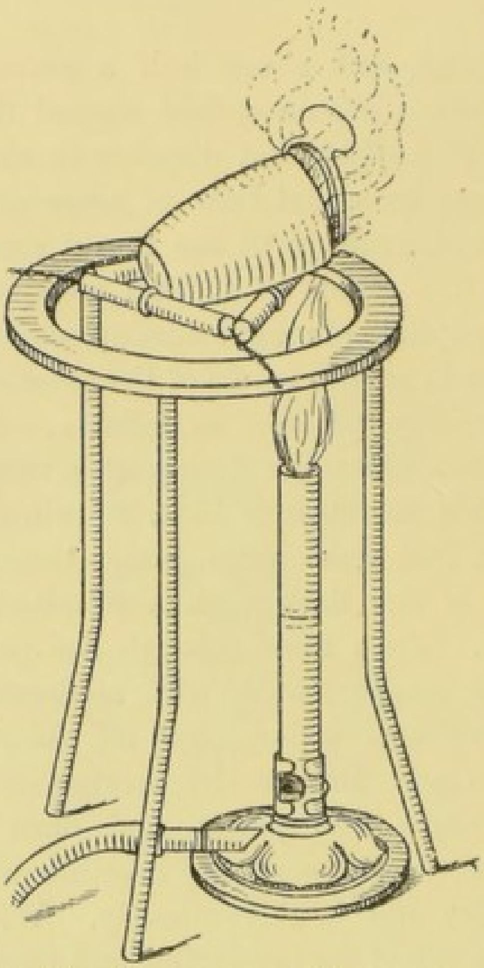

Fig. 37. Estimation of Potassium as Sulphate.

Estimation as Sulphate.

This method can only be used if the acid radicle is capable of being readily volatilized on heating with sulphuric acid.

Weigh out about half a gram of substance (e. g. KCl or KNO_3) into a platinum or deep porcelain crucible. Drop on to the solid about 0·3 c.c. (say 7 or 8 drops) of concentrated sulphuric acid and at once cover the crucible with a lid so placed that a small opening remains for escape of fumes. Support the crucible in an inclined position on a pipeclay triangle as shown, and place a burner so that the upper part of the crucible is heated. The flame must be turned very low at first and gradually raised as the reaction proceeds. First the volatile acid escapes and then excess of sulphuric acid. Potassium bisulphate is left. This substance requires a high temperature to convert it into the normal sulphate, and as an atmosphere of ammonia promotes the decomposition it is advisable, after the bulk of the white fumes seems to have gone, to allow to cool and add a few small pieces of commercial ammonium carbonate. Heat and repeat if necessary. Heat finally with a strong flame with the crucible in the upright position until the weight is constant.

Note.—The reason for heating at the top as described is to prevent the acid salt from creeping over the edge and vitiating the analysis.

(4) **Sodium,** when combined with a volatile acid radicle, can be estimated as sulphate by heating with sulphuric acid as described above under Potassium.

Gravimetric Determination of Acid Radicles.

(1) **Chlorine in Chlorides** can be estimated by precipitation as silver chloride (see p. 257).

(2) **Bromide in Bromides** and (3) **Iodine in Iodides** can be similarly estimated as silver bromide and iodide respectively.

(4) The **Sulphate Radicle** (SO_4'') is estimated as barium sulphate as described on p. 256.

(5) The **Sulphite Radicle** (SO_3'') is first converted into sulphate by adding bromine water until the liquid remains tinted brown; after boiling off the excess of bromine the sulphate is estimated (p. 256).

(6) The **Nitrate Radicle** usually expressed as N_2O_5 is estimated by heating up a weighed quantity of the salt with a weighed quantity of freshly ignited powdered silica, which combines with the metallic oxide, eliminating N_2O_5 as oxides of nitrogen and oxygen. The loss is calculated as N_2O_5.

(7) **Estimation of the Carbonic Acid Radicle.**

I. Difference Method. The carbon dioxide is driven off from a weighed quantity of substance by decomposition with an acid and subsequent heating.

A great number of types of apparatus have been devised for this estimation. One of the best is Schrotter's, which is represented in Fig. 38. Tube A is nearly filled with hydrochloric or sulphuric acid of moderate strength. (**Note.**—If calcium, barium, strontium, or lead carbonate is to be estimated, do not use sulphuric acid.) Tube B is half filled with concentrated sulphuric acid which is intended to dry the escaping gas. Weigh the prepared apparatus; introduce from 1 to 2 grams of substance through C and weigh again. The difference in weight gives the quantity of substance taken. Allow the acid to escape from A drop by drop; stopper D will have to be raised from time to time. The rapidity of evolution of the carbon dioxide should not be too great (say 2 bubbles per sec.) or it will be imperfectly dried by the sulphuric acid, causing a loss of water as well as carbon dioxide. After the evolution of carbon dioxide has stopped, open F and D, and using a small flame raise the temperature of the liquid in G to the boiling-point. Attach a short length of rubber tubing to E and suck or aspirate air slowly through the apparatus to remove carbon dioxide. Then close E by a small piece of rubber tubing and glass plug and allow to cool. When cold remove the rubber from E and weigh. The loss represents carbon dioxide.

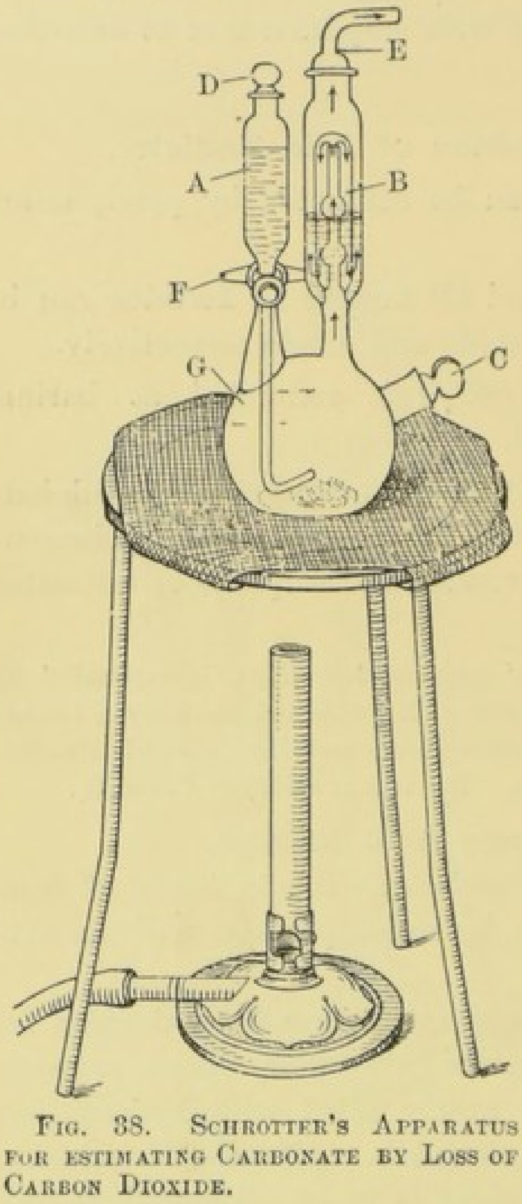

Fig. 38. Schrotter's Apparatus for estimating Carbonate by Loss of Carbon Dioxide.

If apparatus with glass stoppers is not available the student can fit up a small flask with small tap funnel containing HCl and test-tube containing sulphuric acid. A rubber stopper should be used.

Method II. Absorption method.

Decompose a weighed quantity of the carbonate and pass the carbon dioxide evolved through weighed soda-lime tubes. The increase in weight of these tubes gives the weight of carbon dioxide liberated.

(8) Determination of the Phosphoric Acid Radicle (PO_4''').

The process is similar to that described under Magnesium. The phosphoric acid radicle is precipitated by a mixture of ammonium chloride, ammonium hydroxide, and magnesium sulphate as magnesium ammonium phosphate, which by ignition is converted to pyrophosphate (see p. 273).

(9) Determination of the Radicle SiO_2 in Silicates.

If the silicate can be decomposed by boiling with HCl heat up a weighed quantity of substance **in the finest possible state of division** with the acid. The silicic acid separates on evaporation. Continue evaporation to dryness, finally on a water-bath, and heat to about 160° C. in an air-oven to render the silica insoluble. Boil up with HCl, filter, and wash until free from chloride. Ignite and weigh as silica, SiO_2.

If the silicate is not decomposed by boiling with HCl it must first be fused up, after reducing to finest state of subdivision possible, with 3 to 4 times its weight of sodium carbonate or fusion mixture in a platinum crucible, and then treated as above described.

B. VOLUMETRIC ANALYSIS.

Volumetric determinations of the weights of elements or radicles present in given weights of bodies can only be effected under certain definite conditions.

(1) **The end point of the reaction must be sharply defined.** If one is determining quantities by adding a measured volume of a reagent, one must know when the reaction which is being carried out is completed. This is often effected by the addition of an indicator which becomes coloured or alters in colour when the reaction is complete, e. g. litmus, in alkalimetry and acidimetry; but sometimes one of the reacting bodies acts as indicator, e. g. in case of oxidation of substances by potassium permanganate as detailed below.

(2) **The change which takes place on adding the reagent must be known, so that an equation can be written expressing the reaction.** From the equation one can calculate the relative weights of reagent and reacting body.

In Volumetric Analysis one uses solutions of reagents of known strength, so that one can calculate the weight of reagent in any volume which may be used.

One could employ solutions of any strength one pleased; e. g. one could use reagents containing 100 grams to the litre. If one used 25 c.c. of such a solution for a certain determination then obviously the weight of reagent present is

$$\frac{25}{1000} \times \frac{100}{1} = 2{\cdot}5 \text{ grams.}$$

From the equation expressing the reaction one could then readily determine the weight of reacting substance which had been acted upon by that weight of reagent.

It is more convenient, however, to deal with what are termed **Normal Solutions**, or solutions bearing a simple relationship to such solutions.

Definition.—**A Normal Solution** is defined as one which—

(*a*) contains one gram of replaceable hydrogen or its equivalent per litre, or

(*b*) **in the case of oxidizing agents** (e. g. $KMnO_4$) contains in one litre such a weight of substance as will oxidize one gram of hydrogen, or give up 8 grams of oxygen to an oxidizable body.

Normal Solutions are generally designated by the symbol **N.**

Such solutions, and submultiples, are in common use. **Half** or **semi-normal** solutions are represented as $\frac{N}{2}$, tenth or **deci-normal** solutions as $\frac{N}{10}$, and so on. Multiples of Normal, e. g. **2N, 3N,** are sometimes employed.

It follows from above Definition that the **strengths of normal solutions** of a few common acids and bases would be as follows:—

(1) **HCl.** A normal solution of HCl would contain the molecular weight in grams, viz. **36·5 grams per litre,** because 36·5 grams contain 1 gram of replaceable hydrogen.

(2) **HNO_3.** A normal solution of HNO_3 would contain molecular weight in grams, viz. **63 grams per litre,** because 63 grams of HNO_3 contain 1 gram of replaceable hydrogen.

(3) **H_2SO_4.** A normal solution of H_2SO_4 would contain half the molecular weight in grams, viz. $\frac{98}{2}$ = **49 grams per litre,** because 98 grams of sulphuric acid contain 2 grams of displaceable hydrogen.

(4) **$H_2C_2O_4 . 2H_2O$.** A normal solution of oxalic acid would contain half the molecular weight in grams, viz. $\frac{126}{2}$ = **63 grams per litre,** because 126 grams contain 2 grams of replaceable hydrogen.

In the case of **alkaline solutions** one has to consider how many hydrogen atoms the metal present represents. The hydroxides might be regarded as derived from water by replacement of one of the two hydrogen atoms in each molecule by metal; e. g. **NaOH.** Normal solution of NaOH would contain the molecular weight in grams = **40 grams in one litre,** because 1 atom of sodium is equivalent to 1 atom of hydrogen.

Similarly a **Normal Solution of KOH** contains **56 grams per litre.** In the case of a body like sodium carbonate, Na_2CO_3, a normal solution would contain half the molecular weight in grams, viz. $\frac{106}{2}$ = 53 in one litre.

Apparatus required in Volumetric Determinations.

In volumetric analysis one requires (*a*) **burettes,** (*b*) **measuring flasks,** (*c*) **pipettes,** and (*d*) **graduated cylinders.** These are indicated in Figs. 39 and 40.

(*a*) **Burettes** are narrow graduated tubes usually capable of delivering any quantity up to 50, 25, or 10 c.c., depending upon capacity, and graduated to tenths of a c.c. For ordinary laboratory work a burette graduated to give 50 c.c., closed at the bottom by a glass tap, is preferable. The two common types are represented in Fig. 39.

(*b*) **Measuring flasks.** These are flasks with moderately narrow necks, which contain definite volumes at a certain temperature when filled up to a mark on the neck. The volumes are generally one litre or some simple fraction thereof, e. g. 500, 250, 200, or 100 c.c., and the temperature is generally 15° C., which as a rule is approximately room temperature, so that temperature corrections are as a rule negligible. See Fig. 40.

(*c*) **Pipettes** are generally cylindrical glass tubes connected to narrow pieces of tubing at each end as indicated in the figure. The tip of the pipette is drawn out to form a capillary. A mark is etched on the upper piece of narrow tubing to indicate the height to which a liquid must be taken to enable one to deliver the volume indicated on the pipette. The pipettes most generally used are those for 100, 50, 25, or 10 c.c. capacity respectively. See Fig. 40.

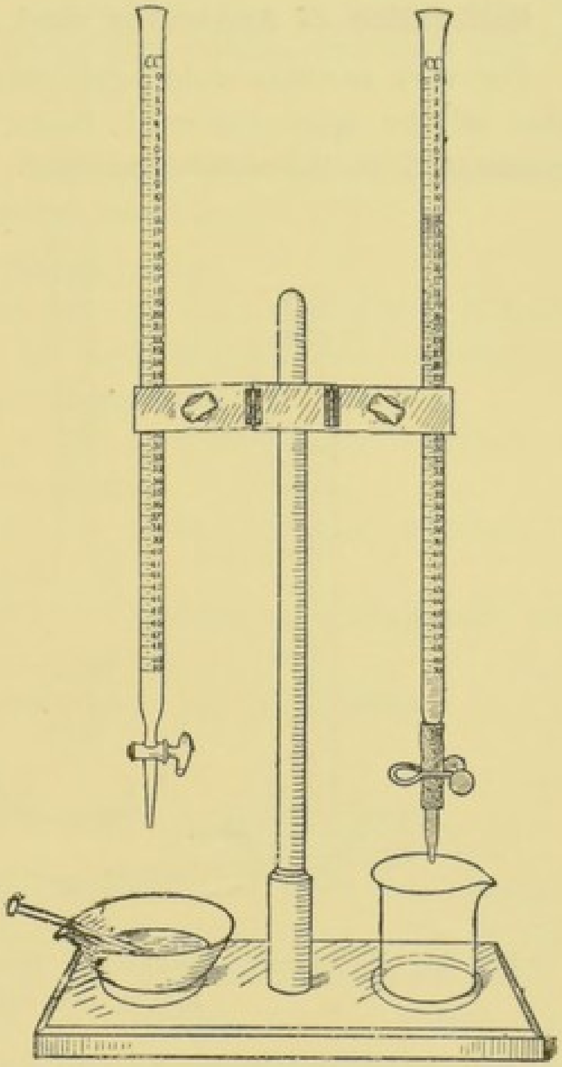

FIG. 39. VOLUMETRIC APPARATUS. Burettes with Glass Stopper and Pinchclip respectively.

(*d*) **Graduated cylinders** are merely used for measuring out approximate quantities. Their width is such that any slight error in reading volume may mean a considerable error in calculation. A 100 c.c. measure is indicated in Fig. 40.

Calibration of Apparatus used in Volumetric Analysis.

For very accurate volumetric work it is necessary to secure that all the apparatus used, flasks, burettes, pipettes, &c., are **graduated to the same standard.**

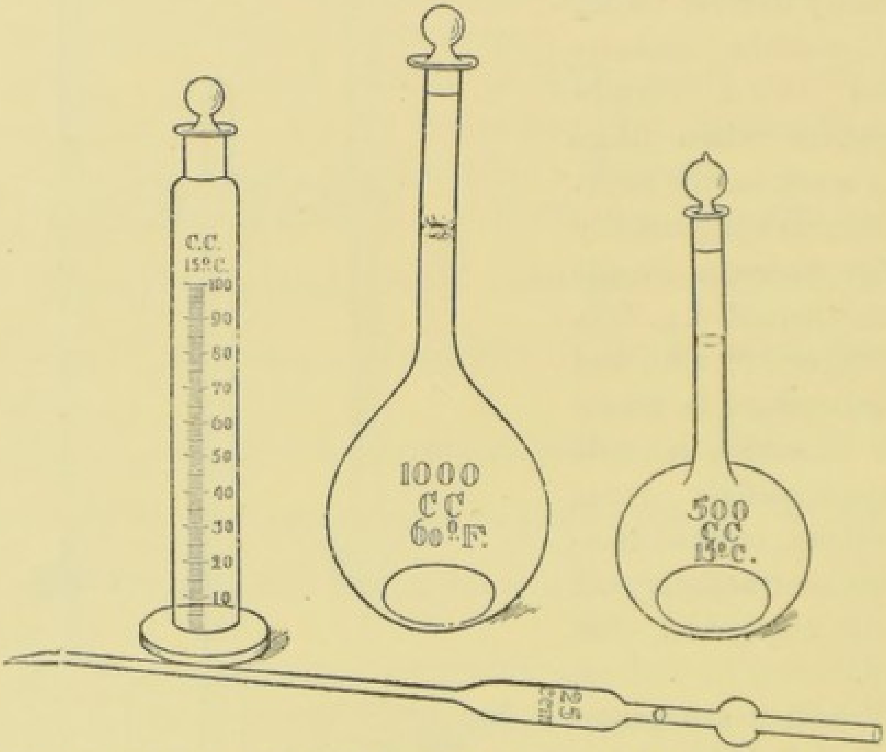

FIG. 40. VOLUMETRIC APPARATUS. Measuring Cylinder, Measuring Flasks, and Pipette.

For flasks and measures use a balance. Weigh the empty vessel, then fill to the graduation mark and weigh again.

Burettes. Cleanse thoroughly, fill with water, and deliver slowly into a counterpoised weighing bottle with ground glass stopper. Weigh after addition of each 1 or 2 c.c. [NOTE.—If great accuracy is required, mercury can be used instead of water.]

Pipettes are sometimes calibrated for 'delivery' by merely draining for about half a minute with the point against the side of the vessel into which the liquid has been delivered, and sometimes by draining for a short time and then blowing once. It is easy to ascertain which method has been used by weighing the quantities delivered under different conditions, employing a small weighing bottle for the experiment.

As it is of special importance that the pipettes and burettes used should agree among themselves, it is advisable to find out whether there is any noteworthy difference by filling the burette to the 50 c.c. mark and then delivering into the burette with the pipette, noting the volume after each delivery until the burette is full.

The more important Volumetric Determinations will be summarized in the following order:—

I. Acidimetry and Alkalimetry.
II. Estimation of Chlorine by standard Silver Nitrate.
III. Standardization of and Estimations effected by Potassium Permanganate.
IV. Standardization of and Estimations effected by Potassium Dichromate.
V. Standardization of and Estimations effected by means of Iodine.
VI. Estimations effected by Iodine in conjunction with standard Thiosulphate.
VII. Volumetric Determination of Phosphates.

I. ACIDIMETRY AND ALKALIMETRY.

The determination of the quantities of acids and alkalis in solution is termed acidimetry and alkalimetry. **Three indicators** are in common use for indicating the end point in measurements of this kind, viz. **Litmus, Methyl Orange,** and **Phenol Phthalein.** The action of these indicators depends upon the formation of coloured ions when free acid or alkali is in excess.

Litmus in neutral solution is violet. It turns red with acids and blue in alkaline solution, as already noted.

Methyl Orange is orange in neutral solution, red in acid solution, and yellow in alkaline solution.

Phenol Phthalein is colourless in neutral or acid solutions, but scarlet in alkaline solution.

Indicators should not be used indiscriminately. Each has its own merits under proper conditions.

Litmus if properly made and preserved is one of the best indicators. In using it one must keep in view that its colour changes to red with even weak (i. e. slightly ionized) acids, such as carbonic, so that in estimating carbonates one must boil off the carbon dioxide set free before finishing the reaction when using litmus as indicator.

Methyl Orange is acid in character. It is unaffected by **carbonic** acid, so that it can be used to estimate carbonates without boiling. It obviously follows that methyl orange is of little value for estimating weak acids, but being a fairly strong acid it easily forms ionized salts with even weak bases, and is therefore **admirable for estimating alkalies including Ammonium Hydroxide.** The acid radicle (i. e. the acid less hydrogen) is of a yellow colour, and the free acid itself is red, hence the colours observed with alkalies and acids respectively.

Phenol Phthalein, a very weak acid, is almost unionized in its solutions, which are colourless. On neutralization with a strong base, e.g. NaOH, the deep red colour of its acid radicle is seen. **Phenol Phthalein is sensitive to even weak acids and can therefore be used for estimating slightly ionized acids like acetic if a strong base is employed. It should not be used for Ammonium Hydroxide.**

Preparation of Standard Solutions.

The preparation of standard solutions is of primary importance in volumetric analysis. As a rule, a student is given standard solutions, but he should clearly understand how they can be prepared.

In **acidimetry** and **alkalimetry**, if one solution is prepared of absolutely correct strength, it is easy to prepare others. The **initial standard solution** chosen is generally one of **pure sodium carbonate**. As already noted, a standard solution of sodium carbonate would contain $\frac{106}{2} = 53$ grams per litre. There is no necessity to prepare a litre of solution. For all practical purposes 100 c.c. is enough, and one can proceed as follows: Weigh roughly into a platinum (or porcelain) dish enough pure sodium bicarbonate to give rather more than $\frac{53}{10}$ grams of sodium carbonate on heating—the quantity required to give a normal solution when dissolved in water and made up to 100 c.c. The equation expressing the decomposition of $NaHCO_3$ to give Na_2CO_3 would be :—

$$\frac{2NaHCO_3}{168} = \frac{Na_2CO_3 + H_2O + CO_2}{106.}$$

This equation shows that—

106 grams of Na_2CO_3 are obtained from 168 gm. $NaHCO_3$.

$\therefore \frac{106}{20} = \frac{53}{10}$,, ,, ,, $\frac{168}{20} = 8{\cdot}4$ grams of bicarbonate.

Method of procedure:

Weigh out into a dish about 9 grams of $NaHCO_3$, place on a fireclay triangle, and heat gently over a clear Bunsen flame until, on cooling in a desiccator and weighing, the weight is constant.

When the weight is constant, keep the dish on the balance pan, and, by removing small quantities with a spatula on to a watch-glass, adjust the weight in the dish exactly to 8·4 grams. Dissolve this quantity in distilled water, and make up to 100 c.c. in a 100 c.c. measuring flask. NOTE :—Thoroughly shake after making up to the required volume by stoppering the flask and then inverting it a few times, so as to make the solution homogeneous.

Instead of preparing a normal solution one might somewhat more conveniently prepare a semi-normal $\left(\frac{N}{2}\right)$ or deci-normal solution $\left(\frac{N}{10}\right)$. From this single normal solution one could readily prepare standard solutions of acids and alkalis of any required strength.

e.g. **Preparation of Normal Hydrochloric Acid.**

Take the specific gravity of the concentrated hydrochloric acid on the bench by means of a hydrometer. It will be found to be approx. 1·16 at 15° C. Looking up a table giving the weights of HCl in solution corresponding to different specific gravities one finds the percentage of acid present to be 32·2 per cent. (approx.). Now N. HCl contains 36·5 grams per litre. The volume of conc. hydrochloric acid containing 36·5 grams would be

$100 \times \frac{36{\cdot}5}{32{\cdot}2} = 113{\cdot}4$ c.c. Take say 115-120 c.c. and dilute up to a litre with water in a measuring flask. Shake thoroughly, and then find the exact strength by titration against the normal carbonate. Remove say 50 c.c. for this purpose, leaving 950 c.c. in the flask. Suppose that one found that 19·8 c.c. HCl were required to neutralize 20 c.c. of normal sodium carbonate. The HClAq is obviously the stronger since less of it is required. Every 19·8 c.c. should be diluted to 20 c.c. to make it normal. The residual volume of HCl, viz. 950 c.c., should therefore be diluted until it occupies $950 \times \frac{20}{19{\cdot}8} = 959{\cdot}6$ c.c.

Add 9·6 c.c. to the 950 c.c. in the flask, shake, and titrate again against the carbonate solution. 20 c.c. HCl should now be found, equivalent to 20 c.c. Na_2CO_3. Remove to a bottle, and label as N. HCl.

Standard Sulphuric and **Standard Nitric Acid** could be prepared by exactly similar methods. In the case of the sulphuric acid one could readily prove its normal character by a gravimetric estimation of the quantity present in a certain volume. The gravimetric estimation would be exactly similar to the estimation of barium already described. One would acidify strongly, boil, add $BaCl_2Aq$ as long as a precipitate formed, filter, and weigh the $BaSO_4$ thrown down.

Semi-normal or **deci-normal** solutions could, of course, be prepared from the normal solutions; e. g. to make a $\frac{N}{10}$ solution of HCl after preparation of the N solution, one has merely to take 100 c.c. N solution and dilute to a litre.

Standard Oxalic Acid could be made direct by weighing out 63 grams of freshly crystallized oxalic acid, $H_2C_2O_4 . 2H_2O$, dissolving in water, and making up to a litre.

Standard Caustic Soda and **Standard Caustic Potash** could be prepared by weighing out rather more of the solids than would be necessary to give a normal solution, making solutions of approximately the strength required, and then titrating against one of the standard acids prepared from the standard carbonate, or the solution might be titrated directly against the oxalic acid.

METHOD OF DETERMINING THE STRENGTH OF A SOLUTION OF ACID OR ALKALI, GIVEN A SOLUTION OF KNOWN STRENGTH.

Example I. Given standard Normal HCl to find the strength of a solution of Caustic Soda.

The fundamental fact which one should always keep in view in determinations of this type could be stated as follows:—Normal solutions of acids and alkalies are always equivalent to each other, e.g. any given volume of N, $\frac{N}{2}$, or $\frac{N}{10}$ acid is neutralized by the same volume of N, $\frac{N}{2}$, or $\frac{N}{10}$ NaOH or KOH respectively.

This statement could readly be proved from the equations expressing the reaction:—

$$\underset{36{\cdot}5}{\underline{\mathrm{HClAq}}} + \underset{40}{\underline{\mathrm{NaOHAq}}} = \mathrm{NaClAq} + \mathrm{H_2O}.$$

$$\underset{36{\cdot}5}{\underline{\mathrm{HClAq}}} + \underset{56}{\underline{\mathrm{KOHAq}}} = \mathrm{KClAq} + \mathrm{H_2O}.$$

From these equations it is obvious that 36·5 grams of HCl are neutralized by 40 grams of NaOH and 56 grams of KOH. But the three quantities mentioned are those present in 1 litre of N solution. ∴ 1000 c.c. of N. HCl is neutralized by 1000 c.c. N. NaOH or N. KOH.

METHOD OF PROCEDURE IN ABOVE CASE.

Place in a porcelain dish or conical flask 10–25 c.c. of the caustic soda solution, add a few drops of litmus or methyl orange to act as indicator, and then slowly run in from the burette the standard hydrochloric acid until the neutralization point is reached as indicated by change of tint to reddish violet or orange. Note the volume used. Carry out a check experiment, and if the volume required in the second case is identical or within 0·1 c.c. of the previous one, take a mean of the two results. If there be a greater difference than 0·1 c.c., repeat.

Special Notes regarding Manipulative Details.

(1) In taking 10–25 c.c. of the caustic soda solution preferably use a pipette which has been tested regarding the proper method which must be followed to ensure delivery of the volume recorded upon it (cf. p. 280).

(2) **Use only a small quantity of indicator,** so that the tint is not darker than that of the bench solution of potassium ferrocyanide. e. g. Do not use more than **one or two drops** of a moderately strong solution of **methyl orange,** which should be transferred by dropping from a rod or pipette and not by pouring.

(3) **In filling the burette with acid proceed as follows:—** After washing the burette with water (if necessary), add a few c.c. of the acid solution to be used, close the top with the thumb, invert a few times, and run off completely. Then fill up the burette a few c.c. beyond the top mark. On allowing the liquid to run out until the bottom of the meniscus just reaches the graduation mark, the space beyond the stopcock becomes filled with acid, which is essential, as one is measuring volume by difference as indicated by the position of the meniscus. Record the result to $\frac{1}{100}$ of a c.c. By putting a piece of paper or card behind the meniscus, as indicated in the diagram, a better reading may be obtained. It is rather better, however, to hold a card at an angle of about 35° to the vertical near the surface of the liquid.

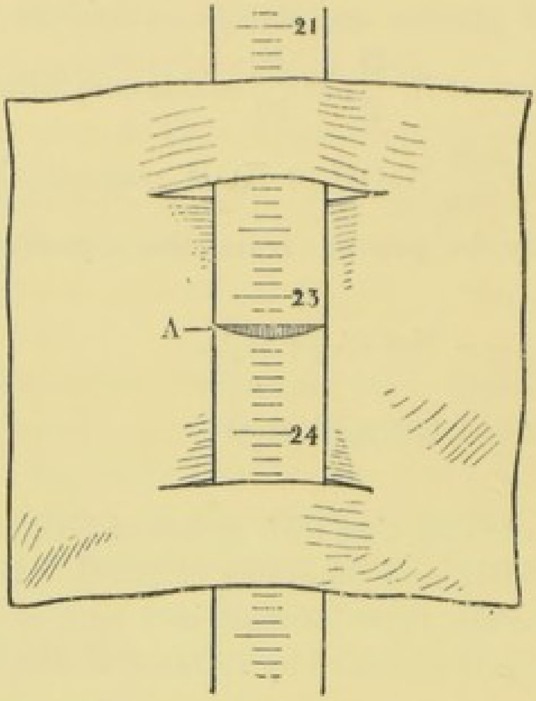

Fig. 41. Method of reading Position of Liquid in a Burette. The reading here would be 23·30. A, Meniscus.

An excellent method of avoiding the difficulty in connexion with the meniscus is to use some form of float. There are many types, two of the best of which are shown in Fig. 42. A float has a circular line on it, and one reads the positions of this line with reference to the scale graduations instead of the relative positions of the surface of the liquid. In float A the line is in the liquid, but in float B the line is on the upper bulb outside the liquid, and this type of float is convenient for use with deeply coloured liquids like potassium permanganate.

The float employed should always occupy the same relative position to the surface of the liquid, in which case the line upon it remains parallel to the graduations on the burette.

Another device which is worth mentioning is shown in Fig. 42 c. Along the back of the burette is a broad band of white enamel with a brightly coloured strip along its centre. On looking at the remains of the liquid, the coloured strip seems to be contracted there to a point, the position of which is easy to read.

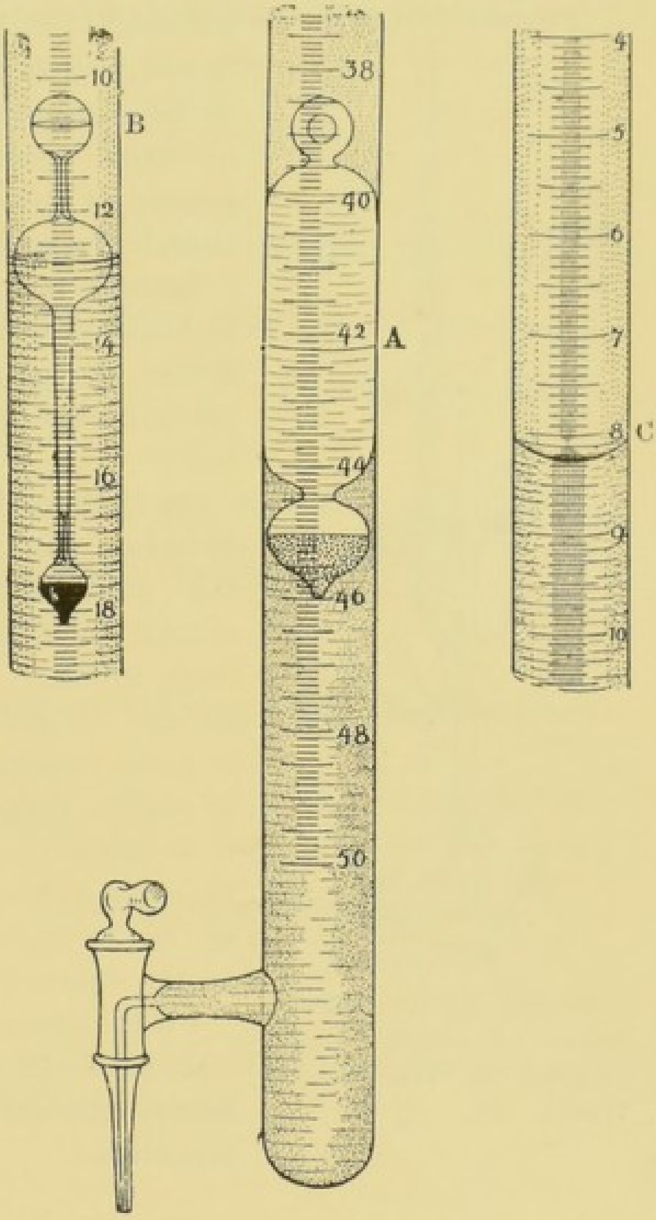

Fig. 42. Additional Aids to Exact Measurement of Position of a Liquid in a Burette.

(4) **Avoid error of parallax** by having the eye horizontally opposite the graduation which is being read. In some of the better types of burette the graduation lines are continued right round the burette. When reading this type it is easy to tell if the eye is at the proper level by noting whether the nearest graduation appears as a line or a circle.

(5) In running the liquid from the burette, the tap should be controlled by the thumb and first two fingers of the left hand, which is passed round behind the burette as indicated in Fig. 43. The tap (which should be carefully smeared when dry with a very small quantity of vaseline) is gently pressed inwards, and by proper manipulation one can run in the liquid at moderate speed, and yet stop exactly as required. The right hand is used either for stirring the liquid, if placed in a beaker or

porcelain basin, or for shaking the vessel if a conical flask (Erlenmeyer) is employed. The exact method of procedure is indicated in Fig. 43.

General Notes:

(*a*) With regard to the **most suitable indicator** to employ, one might reiterate that **methyl orange is the best if any carbonate is likely to be present** (cf. p. 282). Carbonate in small quantity is nearly always present in solutions of sodium or potassium hydroxide.

Litmus can be used if the solution is boiled towards the end of the reaction, so as to decompose dissolved carbonic acid, which colours the litmus red.

(*b*) **If there is a great discrepancy between the respective volumes of the acid and alkali** required for mutual neutralization, e. g. if more than 100 c.c. of acid is required for 10 c.c. of caustic soda, or (and this is more important) if less than 2 c.c. of acid is required for 10 c.c. of soda, it is advisable to dilute one or other to (say) a tenth its former strength, so as to make the solutions more nearly equivalent to each other.

(*c*) It often saves time to **carry out first an approximate experiment,** and then **two accurate determinations.**

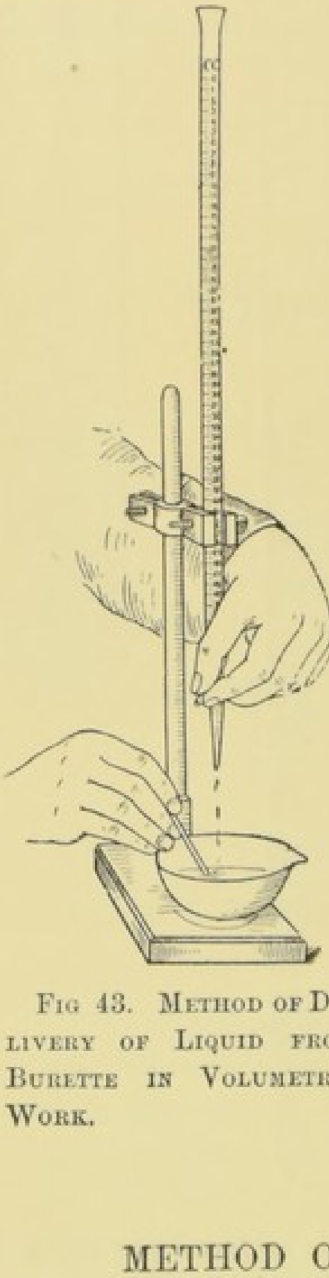

FIG 43. METHOD OF DELIVERY OF LIQUID FROM BURETTE IN VOLUMETRIC WORK.

METHOD OF CALCULATING RESULTS OF EXPERIMENTS.

The student should be able to record his results in three ways:

(1) **As a fraction of normal.**

(2) **In grams per litre.**

(3) **As a percentage, which generally means grams per 100 c.c.**

A few concrete examples will make the methods of calculation clear.

Case 1. 20 c.c. NaOH were neutralized by 10 c.c. N. HCl.

As the strength of a solution must be inversely as the volume required for a reaction, the caustic soda solution is the weaker;

$$20 \text{ c.c. NaOH} \equiv 10 \text{ c.c. N. HCl.}$$

$$1 \text{ c.c. NaOH} \equiv \frac{10}{20} \text{ c.c. N. HCl.}$$

i.e. the caustic soda solution is half as strong as the acid, or $\frac{N}{2}$.

But normal caustic soda contains 40 grams per litre (p. 231).

$\therefore$ the strength of the solution $= \frac{40}{2} =$ **20 grams per litre.**

Rule.

Let x = vol. of N. HCl used, and 20 c.c. = vol. of NaOH taken. Then the strength of NaOH solution $= \frac{x}{20}$ N.

More generally—

Let x = vol. of N solution used, and y = vol. of solution to be estimated taken.

Then the strength required $= \frac{x}{y}$N.

If $\frac{N}{2}$ or $\frac{N}{10}$ acid be used, the strength required becomes $\frac{x}{y}\frac{N}{2}$ or $\frac{x}{y}\frac{N}{10}$ respectively.

It is advisable not to use formulæ like these, but to work from first principles as indicated below.

Case 2.

Given N. NaOH, to find the strength of the solution of HCl supplied.

Results:—

(1) 20 c.c. N. NaOH $\equiv$ 18·2 c.c. HCl.

(2) 20 c.c. N. NaOH $\equiv$ 18·3 c.c. HCl.

Mean result 20 c.c. N. NaOH $\equiv \frac{18{\cdot}2 + 18{\cdot}3}{2} = 18{\cdot}25$ c.c. HCl.

Method I.

The acid is evidently the stronger in the proportion of 20 to 18·25,

$$\therefore \text{ its strength must be } \frac{20}{18{\cdot}25}\text{ N.}$$

But a normal solution of HCl contains 36·5 grams,

$$\therefore \text{ the strength of the acid} = \underset{1}{\frac{20}{\cancel{18{\cdot}25}}} \times \frac{\overset{2}{\cancel{36{\cdot}5}}}{1} = \mathbf{40 \text{ grams per litre.}}$$

Method II.

It is always advisable for the beginner to check his results determined as above by another calculation from the fundamental equation expressing the reaction carried out.

$$\text{Equation} \qquad \underset{40}{\underline{\text{NaOHAq}}} + \underset{36{\cdot}5}{\underline{\text{HClAq}}} = \text{NaClAq} + H_2O.$$

Here 20 c.c. N. NaOH were taken.

$$1000 \text{ c.c. N. NaOH contain } 40 \text{ grams.}$$

$$\therefore \quad 1 \text{ c.c. N.} \quad ,, \quad \text{contains } \frac{40}{1000} \text{ gram.}$$

$$\text{and} \quad 20 \text{ c.c. N.} \quad ,, \quad \text{contain } \frac{40 \times 20}{1000} = \frac{8}{10} \text{ gram.}$$

The equation shows that

$$40 \text{ grams NaOH} \equiv 36{\cdot}5 \text{ grams HCl.}$$

$$\therefore \quad 1 \text{ gram NaOH} \equiv \frac{36{\cdot}5}{40} \quad ,, \quad ,,$$

$$\text{and } \frac{8}{10} \;,, \quad \text{NaOH} \equiv \left(\frac{36{\cdot}5}{40} \times \frac{8}{10}\right) \text{ grams HCl,}$$

which must be the weight of HCl in the volume neutralized by the 20 c.c. N. NaOH, viz. in 18·25 c.c.

If 18·25 c.c. contain $\left(\frac{36{\cdot}5}{40} \times \frac{8}{10}\right)$ grams HCl, the weight in 1000 c.c. would be

$$\underset{1}{\frac{100\cancel{0}}{\cancel{18{\cdot}25}}} \times \left(\underset{1}{\frac{\overset{2}{\cancel{36{\cdot}5}}}{\cancel{40}}} \times \frac{\overset{2}{\cancel{8}}}{1\cancel{0}}\right) = \mathbf{40 \text{ grams.}} \quad \text{(Cf. Method I.)}$$

Case 3.

Given $\frac{N}{10}$ H_2SO_4, to find the strength of a solution of KOHAq.

Results :—

(1) 20 c.c. KOH were neutralized by 14·05 c.c. $\frac{N}{10}$ H_2SO_4.

(2) 20 c.c. KOH „ „ „ 13·95 c.c. $\frac{N}{10}$ H_2SO_4.

Mean result :

20 c.c. KOH were neutralized by $\frac{14{\cdot}05 + 13{\cdot}95}{2} = 14$ c.c. $\frac{N}{10}$ H_2SO_4.

Method I.

The KOH is evidently weaker than the acid in the proportion of 14 to 20,

$$\therefore \quad \text{strength of KOH} = \frac{14}{20} \times \frac{N}{10}.$$

But N. KOH contains 56 grams per litre (p. 278),

∴ strength of potash

$$= \frac{\overset{7}{\cancel{14}}}{\underset{10}{\cancel{20}}} \times \frac{56}{10} = \frac{392}{100} = \textbf{3·92 grams per litre.}$$

Method II.

$$\text{Equation: } \underset{\underset{112}{\underline{2 \times 56}}}{\underline{2KOHAq}} + \underset{\underset{98}{\underline{2+32+64}}}{\underline{H_2SO_4Aq}} = K_2SO_4Aq + 2H_2O.$$

(a) Find weight of substance in volume of standard solution taken.

1000 c.c. $\frac{N}{10}$ H_2SO_4 contains $\frac{49}{10} = 4{\cdot}9$ grams.

1 c.c. $\frac{N}{10}$ „ „ $\frac{4{\cdot}9}{1000}$ grams.

14 c.c. $\frac{N}{10}$ „ „ $\left(\frac{4{\cdot}9}{1000} \times \frac{14}{1}\right)$ grams.

(b) Find the weight of substance in the volume of solution neutralized by standard.

From equation

$$98 \text{ grams } H_2SO_4 \equiv 112 \text{ grams KOH.}$$

$$\therefore \quad 1 \text{ gram } H_2SO_4 \equiv \frac{112}{98} \quad „ \quad „$$

And $\frac{4 \cdot 9 \times 14}{1000}$ grams $H_2SO_4 \equiv \left(\frac{112}{98} \times \frac{4 \cdot 9 \times 14}{1000}\right)$ grams KOH,

which must be the weight of potash in the volume neutralized, viz. in 20 c.c.

(c) **Find the strength in grams per litre.**

$$20 \text{ c.c. contain } \left(\frac{112}{98} \times \frac{4 \cdot 9 \times 14}{1000}\right) \text{ grams KOH.}$$

$$\therefore \; 1000 \text{ c.c.} \quad " \quad \frac{1000}{20} \times \frac{112}{98} \times \frac{4 \cdot 9 \times 14}{1000} = \mathbf{3 \cdot 92 \text{ grams KOH.}}$$

(Cf. Method I.)

Case 4.

The strength of standard acid or alkali is not given as a fraction of normal, but in grams per litre.

E.g. Find the strength of a solution of KOH, 20 c.c. of which are neutralized by 15 c.c. of HNO_3, containing 30 grams of the acid per litre.

Method I.

Transform the strength of acid into fraction of normal. In this case N. HNO_3 contains 63 grams per litre,

$$\therefore \quad 30 \text{ grams per litre} = \frac{30}{63}\text{N.}$$

$$\text{If} \quad 20 \text{ c.c. KOH} \equiv 15 \text{ c.c. } \frac{30}{63}\text{N. } HNO_3$$

$$\text{the strength of the KOH} = \frac{15}{20} \times \frac{30}{63}\text{N.}$$

But N. KOH contains 56 grams per litre,

$$\therefore \text{ strength} = \frac{15}{20} \times \frac{30}{63} \times \frac{56}{1} = 20 \text{ grams per litre.}$$

Method II.

Calculate direct from equation as before—

$$\underset{56}{\underline{KOHAq}} + \underset{63}{\underline{HNO\ Aq}} + KNO_3Aq + H_2O.$$

$$1000 \text{ c.c. } HNO_3 \text{ contain } \quad 30 \text{ grams per litre,}$$

$$\therefore \quad 1 \text{ c.c.} \quad " \quad \text{contains } \frac{30}{1000} \text{ grams}$$

$$\therefore \quad 15 \text{ c.c.} \quad " \quad \text{contain } \left(\frac{30 \times 15}{1000}\right) \text{ grams.}$$

Equation shows that

$$63 \text{ grams } HNO_3 \text{ will neutralize } 56 \text{ grams KOH,}$$

$$\therefore \quad 1 \text{ gram } HNO_3 \quad ,, \qquad ,, \quad \frac{56}{63} \quad ,, \quad ,,$$

$$\text{and } \frac{30 \times 15}{1000} \text{ gm. } HNO_3 \quad ,, \qquad ,, \quad \frac{56}{63} \times \frac{30 \times 15}{1000} \text{ gm. KOH.}$$

$$= \text{weight of KOH in 20 c.c.}$$

$\therefore$ strength of KOH in grams per litre

$$= \frac{1000}{1000} \times \frac{56}{63} \times \frac{30 \times 15}{1000} = 20 \text{ grams.}$$

Note. 20 grams per litre would be a 2 per cent. solution.

Indirect Determinations.

A great many indirect determinations can be made by using standard acid and alkali. The following are interesting types :—

I. Determination of strength of a given solution of an Ammonium Salt (e. g. ammonium chloride), given standard caustic soda and standard acid.

Method. Boil up a certain volume of the solution of ammonium salt in a porcelain basin with a measured volume of NaOHAq in excess until ammonia ceases to be evolved. Calculate how much NaOH is still present by adding litmus or methyl orange, and titrating against standard acid until neutral. Knowing the weight of NaOH taken, the quantity used up can be found by difference.

$$\text{Equation:} \quad \underset{53\cdot5}{\underline{NH_4ClAq}} + \underset{40}{\underline{NaOHAq}} = \mathbf{NH_3}\nearrow + NaCl + H_2O.$$

From the equation it is obvious that 40 grams of NaOH are required to decompose 53·5 grams of NH_4Cl.

II. Determination of strength of a given solution of Barium Chloride ($BaCl_2 . 2H_2O$) **by precipitation of the metal as Carbonate with standard Sodium Carbonate solution.** Standard acid is also supplied.

Method. To a measured volume of the given solution add a certain volume of the standard Na_2CO_3, more than enough to completely precipitate the metal as indicated in the equation:

$$\underset{244}{\underline{BaCl_2 . 2H_2O}} + \underset{106}{\underline{Na_2CO_3Aq}} = \mathbf{BaCO_3} + 2NaClAq.$$

Filter and wash thoroughly, collecting the filtrate and wash water in a beaker or porcelain basin. Add methyl orange and titrate the excess of carbonate (which will of course be in the filtrate) against standard acid.

From the equation,

$$106 \text{ grams } Na_2CO_3 \equiv 244 \text{ grams } BaCl_2 . 2H_2O.$$

III. Determination of strength of a given solution of Copper Sulphate ($CuSO_4 . 5H_2O$) by two methods:

(a) **By precipitation of the Copper as Hydroxide** with standard NaOH. Add a known volume of standard NaOH in excess to a measured volume of the solution of copper sulphate. Boil. Filter, wash and titrate filtrate and washings against standard acid, so as to estimate how much NaOH has been required for precipitation.

Equation: $\underbrace{CuSO_4 . 5H_2O}_{249} + \underbrace{2NaOHAq}_{80} = Na_2SO_4Aq + Cu(OH)_2.$

From equation, $80 \text{ grams } NaOH \equiv 249 \text{ grams } CuSO_4 . 5H_2O.$

(b) **By precipitation of Copper as Sulphide.**

Pass washed H_2S gas through a measured volume of the copper sulphate until precipitation is complete. Filter, wash, boil off the dissolved SH_2, and titrate the sulphuric acid formed during the reaction against standard caustic soda, using a suitable indicator (e. g. litmus).

Equation: $\underbrace{CuSO_4 . 5H_2O}_{249} + H_2S = CuS + \underbrace{H_2SO_4Aq}_{98}.$

Equation shows that

$$98 \text{ grams } H_2SO_4 \equiv 249 \text{ grams } CuSO_4 . 5H_2O.$$

In either case (*a* or *b*) the filtration and washing can be avoided by precipitating in a graduated flask, say 200 cc. Cool, dilute with water to the mark, shake well, and allow to settle. Then pipette out 100 cc. of the clear liquid and titrate, and multiply the result by 2.

II. Estimation of Chlorine by standard Silver Nitrate.

Two methods may be employed.

1. Estimation by standard Silver Nitrate using Potassium Chromate as indicator.

2. Estimation by standard Silver Nitrate and standard Thiocyanate using a ferric salt as indicator.

Method I. In the case of solutions which have no free mineral acid present, the quantity of chlorine is easily estimated by means of standard silver nitrate using potassium chromate as indicator. If the solution is acid it should be neutralized carefully with sodium carbonate.

Principle of the Process :—On adding silver nitrate to a mixture of chloride and chromate, silver chloride is first precipitated. If, while chloride is present, chromate is formed at any place by local excess of nitrate, as would be indicated by a red coloration, on stirring the red colour disappears because the silver chromate reacts with the chloride to give silver chloride. When all the chlorine has been precipitated, the next drop of silver nitrate causes a permanent reddish coloration.

Required :—Standard silver nitrate, $\frac{N}{10}$ or $\frac{N}{20}$: pure potassium chromate; neutral solution of chloride.

Method of Procedure :—Place a certain volume of the solution (say 10 c.c.) in a porcelain basin, and add a few drops of a concentrated solution of potassium chromate (free from chloride). Add the standard silver nitrate $\left(\frac{N}{10} \text{ or } \frac{N}{20}\right)$ from a burette with constant stirring until a faint reddish tint is perceptible.

Note.—In the case of a substance like barium chloride one must add potassium chromate until all the barium is precipitated as chromate, and the solution remains tinted yellow.

Example :—

10 c.c. of barium chloride solution required 7·3 c.c. of $\frac{N}{10}$ $AgNO_3$.

The barium chloride solution is therefore the weaker in the proportion of 7·3 to 10 (cf. p. 290).

Its strength must therefore be $\frac{7{\cdot}3}{10} \times \frac{N}{10}$.

But normal barium chloride ($BaCl_2 . 2H_2O$) would contain

$$\frac{244}{2} = 122 \text{ grams per litre,}$$

∴ the strength of the crystallized barium chloride, $BaCl_2 . 2H_2O$, in grams per litre

$$= \frac{7 \cdot 3}{10} \times \frac{122}{10} = 8 \cdot 906 \text{ grams.}$$

Method 2. Estimation of Chlorine by standard solutions of Silver Nitrate and Thiocyanate, using ferric alum as indicator.

Principle of the Process:—Excess of standard silver nitrate is added to a certain volume of the substance. The excess of silver solution used is then found by means of a standard solution of thiocyanate using a ferric salt as indicator.

Required:—(*a*) Standard $AgNO_3$ $\left(\frac{N}{10} \text{ or } \frac{N}{20}\right)$: (*b*) by standard thiocyanate solution, KCNS or NH_4CNS $\left(\frac{N}{10} \text{ or } \frac{N}{20}\right)$: (*c*) strong solution of iron alum: (*d*) nitric acid.

Method of Procedure:—Acidify a certain volume of solution (say 20 c.c.) with nitric acid, and then add from a burette excess of standard silver nitrate. Filter off the silver chloride, wash,* and add to filtrate and washings 5 c.c. of nitric acid (1 of strong acid to 1 of water) and 5 c.c. of saturated ferric alum solution. Then add from a burette standard thiocyanate solution until a reddish coloration is produced. The filtrate from the silver chloride contains the excess of silver nitrate. This excess is found by adding thiocyanate solution, preferably of such a strength that 1 c.c. $AgNO_3 \equiv 1$ c.c. thiocyanate. When enough thiocyanate has been used to precipitate all the excess silver as silver thiocyanate, the next drop will give a reddish coloration of ferric thiocyanate by interaction with the ferric alum indicator, e. g.

$$\begin{aligned} \text{Equations:}\quad KCl + AgNO_3 &= KNO_3 + AgCl \\ AgNO_3 + KCNS &= AgCNS + KNO_3 \\ Fe_2(SO_4)_3 + 6KCNS &= 2Fe(CNS)_3 + 3K_2SO_4 \end{aligned}$$

The nitric acid must be present so as to keep the solution strongly acid and to destroy the colour of the ferric alum, which is brown in slightly acid solution.

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* The filtering and washing are sometimes dispensed with, but the results are not reliable unless the experiment is carried out as described, because of solubility of the silver chloride in the thiocyanate.

Example :—To 20 c.c. of potassium chloride, 15 c.c. of $\frac{N}{20}$ $AgNO_3$ were added. After filtering and washing the filtrate required 4·2 c.c. of standard $\frac{N}{20}$ NH_4CNS. This indicated that 4·2 c.c. excess silver nitrate had been used, since 1 c.c. $\frac{N}{20}$ thiocyanate $\equiv$ 1 c.c. $\frac{N}{20}$ $AgNO_3$. Therefore the actual quantity of silver nitrate required for the precipitation $= 15 - 4{\cdot}2 = 10{\cdot}8$ c.c.

$$20 \text{ c.c. } KCl \equiv 10{\cdot}8 \text{ c.c. } \frac{N}{20} AgNO_3 .$$

$\therefore$ the KCl is weaker in the proportion of 10·8 to 20 (p 290).

It follows that its strength must be $\frac{10{\cdot}8}{20} \times \frac{N}{20}$.

But N.KCl contains $39 + 35{\cdot}5 = 74{\cdot}5$ grams per litre,

$\therefore$ the strength of the KCl in grams per litre

$$= \frac{10{\cdot}8}{20} \times \frac{74{\cdot}5}{20} = \mathbf{2{\cdot}011 \text{ grams.}}$$

III. Standardization of and Estimations effected by means of Potassium Permanganate.

Notes :—(1) **A Normal Solution of an oxidizing agent is, it must be remembered (cf. p. 277), of such a strength as will give up 8 grams of Oxygen per litre.**

The general oxidizing equation which shows how much oxygen potassium permanganate can give up to an oxidizable body in acid solution is as follows :—

$$\underset{316}{\underline{\underset{2(39+55+64)}{\underline{2KMnO_4}}}} + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2 + O\,\underset{80}{\underline{\underset{5 \times 16}{\underline{5Cl}}}}.$$

This equation shows that 316 grams of $KMnO_4$ can give up 80 grams of oxygen to an oxidizable body,

$\therefore$ **a normal solution of $KMnO_4$ should contain**

$$316 \div \frac{80}{8} = \mathbf{31{\cdot}6 \text{ grams per litre.}}$$

(2) The burette used for permanganate must be closed by a glass stopper, as organic bodies like rubber are attacked.

A large number of direct and indirect estimations can be made by means of potassium permanganate, so that its standardization is important. Any of the following methods can be used, but only one need be employed if the student is proficient.

(1) Standardization by pure iron.

(2) Standardization by ferrous ammonium sulphate,

$$FeSO_4 . (NH_4)_2SO_4 . 6H_2O.$$

(3) Standardization by ferrous sulphate, $FeSO_4 . 7H_2O$.

(4) Standardization by oxalic acid, sodium oxalate, or ammonium oxalate.

1) Standardization of Potassium Permanganate by Iron.

Method of Procedure :– Weigh out accurately about one gram of the best iron wire and multiply the weight taken by $\frac{99{\cdot}6}{100}$ to get the weight of pure iron taken, as the best iron is only about 99·6 per cent. pure. Place in a round-bottomed flask, add dilute sulphuric acid, close the flask by means of a rubber cork carrying a small piece of glass tubing on which is fixed a small piece of rubber tube closed at the top by a piece of glass rod. The rubber has a small slit cut in it as shown to allow for escape of hydrogen and steam. The following diagram (Fig. 44) shows the simplest arrangement which can be used, and an alternative arrangement by which sodium carbonate solution can be added to the contents of the flask at the end of the operation is shown in Fig. 45.

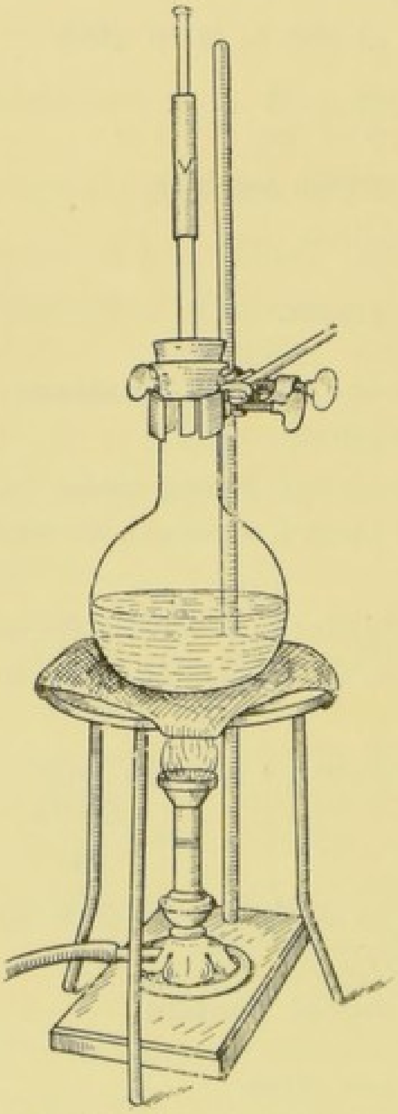

Fig. 44. Preparation of a Solution of pure Ferrous Sulphate from Iron using Bunsen Valve.

Boil gently on gauge over a Bunsen burner until all the iron is dissolved and the solution is practically clear. Allow to cool somewhat, and then cool quickly to room temperature by immersion in cold water. Pour the solution into a measuring flask, and make up to a definite volume with freshly boiled and cooled water, so as to obviate any chance of oxidation of the iron to the ferric state: the heating of the iron and dilute acid is carried out as described for the same reason.

Directions for titration:—Take a certain volume of the iron solution, add about an equal bulk of dilute sulphuric acid, and then run in from the burette potassium permanganate until a faint pink tint remains, the permanganate itself thus serving as indicator. Carry out a duplicate experiment. Any brown turbidity appearing during the titration is due to the precipitation of hydrated oxides of manganese through insufficiency of sulphuric acid.

Method of finding the strength of the Permanganate from the results of analysis.

The equation expressing the oxidation of ferrous sulphate to ferric sulphate by potassium permanganate in presence of sulphuric acid would be as follows:—

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

As a mean of two experiments 25 c.c. of a solution of ferrous sulphate containing 0·1 gram of pure iron in 100 c.c. required 3·75 c.c. of potassium permanganate for oxidation.

∴ 100 c.c. of the iron solution would require $4 \times 3{\cdot}75 = 15$ c.c. $KMnO_4$, i.e. 0·1 gram of iron requires 15 c.c. $KMnO_4$ to oxidize it. But from the equation

560 grams of ferrous iron are oxidized by 316 grams of $KMnO_4$,

∴ 1 gram of ferrous iron is oxidized by $\frac{316}{560}$ grams of $KMnO_4$,

∴ 0·1 gram of ferrous iron is oxidized by $\left(\frac{316}{560} \times 0{\cdot}1\right)$ grams of $KMnO_4$,

which must be the weight of $KMnO_4$ in 15 c.c.

∴ The strength of the permanganate in grams per litre

$$= \left(\frac{316}{560} \times \frac{1}{10}\right) \times \frac{1000}{15} = 3{\cdot}76 \text{ grams.}$$

(2) Standardization of Potassium Permanganate by Ferrous Ammonium Sulphate, $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$.

Dissolve ferrous ammonium sulphate in **freshly boiled and cooled dilute sulphuric acid**, and make up to a certain volume with **freshly boiled and cooled water.**

To a certain volume of the solution in a porcelain basin, add about an equal bulk of dilute sulphuric acid and then run in permanganate from a burette with constant stirring until the solution is tinted faintly pink. Calculate the strength of the permanganate from the equation representing oxidation of the ferrous salt to ferric condition.

Equation :—

$$\underbrace{2KMnO_4}_{316} + 8H_2SO_4 + \underbrace{10\{FeSO_4 . (NH_4)_2SO_4 . 6H_2O\}}_{10 \times 392}$$
$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 10(NH_4)_2SO_4 + \underbrace{60H_2O + 8H_2O}.$$

The mean of two experiments indicated that 50 c.c. of a solution of ferrous ammonium sulphate containing 5 grams in 250 c.c. required 21·4 c.c. $KMnO_4$ to oxidize it.

50 c.c. of ferrous ammonium sulphate solution contain $\frac{50}{250} \times 5$ = 1 gram of the compound.

The equation shows that 3920 grams of ferrous ammonium sulphate would be oxidized by 316 grams of $KMnO_4$.

∴ 1 gram $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$ would be oxidized by $\frac{316}{3920}$ grams $KMnO_4$ = weight of $KMnO_4$ in 21·4 c.c. (volume used).

∴ The strength of the permanganate in grams per litre

$$= \frac{1000}{21{\cdot}4} \times \frac{316}{3920} = 3{\cdot}77 \text{ grams.}$$

[**Note.**—The weight of iron in ferrous ammonium sulphate $= \frac{56}{392} = \frac{1}{7}$th by weight of the compound.]

(3) Standardization of $KMnO_4$ by Ferrous Sulphate, $FeSO_4 . 7H_2O$.

Prepare a solution as described above for ferrous ammonium sulphate, and carry out a similar determination.

Equation :—

$$\underbrace{2KMnO_4}_{316} + 8H_2SO_4 + \underbrace{10\{FeSO_4 . 7H_2O\}}_{10 \times 278}$$
$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + \underbrace{8H_2O + 70H_2O}.$$

In the first experiment 30·1 c.c. and in the second 30 c.c. of $KMnO_4$ were required to oxidize 50 c.c. of a solution of ferrous sulphate containing 5 grams of the salt in 250 c.c.

The mean is therefore 30·05 c.c. $KMnO_4$ required to oxidize $\frac{50}{250} \times \frac{5}{1} = 1$ gram of ferrous sulphate.

The equation shows that 2780 grams of ferrous sulphate would be oxidized by 316 grams $KMnO_4$,

∴ 1 gram of ferrous sulphate would be oxidized by $\frac{316}{2780}$ grams $KMnO_4$ = weight of $KMnO_4$ in 30·05 c.c. (volume used).

∴ The strength of the permanganate in grams per litre

$$= \frac{1000}{30{\cdot}05} \times \frac{316}{2780} = 3{\cdot}78 \text{ grams.}$$

(4) **Standardization of Permanganate by Oxalic Acid, $H_2C_2O_4{\cdot}2H_2O$.**

Use oxalic acid freshly crystallized and dried between filter paper, so as to make certain that the water of crystallization has the correct value.

Method of Procedure :—Weigh out about 2·5 grams of the freshly crystallized acid and make up to say 250 c.c. Take 50 c.c. of the solution in a porcelain basin, add about an equal bulk of dilute sulphuric acid, **heat up to about 60° C.** and then add permanganate from a burette until a faint pink tint remains.

Mean of two experiments.

50 c.c. oxalic acid solution $\equiv$ 66·70 c.c. $KMnO_4$.

Equation:

$$\underset{316}{\underline{2KMnO_4}} + 3H_2SO_4 + \underset{630}{\underline{5H_2C_2O_4 . 2H_2O}}$$
$$= K_2SO_4 + 2MnSO_4 + 10CO_2 + 18H_2O.$$

50 c.c. of the oxalic acid solution contain $\frac{50}{250} \times \frac{5}{2} = 0{\cdot}5$ gram.

The equation shows that 630 grams of oxalic acid are oxidized by 316 grams $KMnO_4$.

∴ 1 gram of oxalic acid is oxidized by $\frac{316}{630}$ grams $KMnO_4$,

and $\frac{1}{2}$ gram of oxalic acid is oxidized by $\frac{316}{630} \times \frac{1}{2}$ grams $KMnO_4$

= weight of $KMnO_4$ in 66·7 c.c.

∴ strength of $KMnO_4$ in grams per litre

$$= \left(\frac{316}{630} \times \frac{1}{2}\right) \times \frac{1000}{66{\cdot}7} = 3{\cdot}76 \text{ grams.}$$

Note.—It might be convenient to employ recrystallized ammonium oxalate, $\{(NH_4)_2C_2O_4\}_2H_2O$, or sodium oxalate, $Na_2C_2O_4$, instead of the acid. The latter salt is especially convenient as it is anhydrous.

Summary of the results:—

(1) Strength of $KMnO_4$ as estimated by Iron = 3·76 grams per litre.
(2) Strength as estimated by Ferrous Ammonium Sulphate = 3·77 „ „ „
(3) Strength as estimated by Ferrous Sulphate = 3·78 „ „ „
(4) Strength as estimated by Oxalic Acid = 3·76 „ „ „
Mean strength 3·768 „ „ „

Estimations by means of standard Permanganate:—

(1) Ferrous Iron; (2) Ferric Iron; (3) Mixture of Ferrous and Ferric Iron; (4) Hydrogen Peroxide; (5) Sulphur Dioxide solution; (6) Oxalic Acid or soluble Oxalate; (7) Indirect Estimation of Calcium; (8) Tin as Stannous Chloride.

(1) **Estimation of Ferrous Iron.**

To a certain volume of the ferrous solution (10 to 50 c.c.) add an equal bulk of dilute sulphuric acid, and then run in $KMnO_4$ from a burette until the solution is tinted a faint pink.

Equation:
$$\underset{316}{\underline{2KMnO_4}} + 8H_2SO_4 + \underset{10 \times 56}{\underline{10FeSO_4}}$$
$$= K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

The equation shows that 316 grams of $KMnO_4$ can oxidize 560 grams of ferrous iron. The result may be stated in grams of ferrous iron per litre, or, in the case of salts of known composition, e. g. $FeSO_47H_2O$ or $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$, the weight of salt in a litre might be calculated. For equations and mode of calculation of results see p. 299.

(2) **Estimation of Ferric Iron**, e. g. Estimation of strength of a solution of Iron Alum.

The ferric iron must first be reduced to the ferrous state. To a convenient volume of the solution add dilute sulphuric acid and a few small pieces of metallic zinc in the apparatus shown in Fig. 44 or Fig. 45, and warm for a short time until the zinc is dissolved. Part of the nascent hydrogen produced reduces the ferric iron to the ferrous state according to the equation, and part escapes at the valve.

$$K_2SO_4 . Fe_2(SO_4)_3 . 24H_2O + 2H = K_2SO_4 + 2FeSO_4 + H_2SO_4 + 24H_2O.$$

If the apparatus in Fig. 45 is used allow to cool partly and then run in from the funnel a freshly boiled solution containing about 3 grams of sodium carbonate in 20 or 30 c.c. of water. An atmosphere of carbon dioxide fills the flask, and one can allow the solution to stand for some time before use.

After the solution is quite cold (one can cool under the tap) decant the solution into a measuring flask (say 250 c.c.). While pouring, the carbon dioxide will pass into the measuring flask, so that the liquid will not come in contact with air. Make up to the graduation mark with freshly boiled distilled water. Remove 10 to 50 c.c. to a basin, add dilute sulphuric acid, and titrate with permanganate until the liquid is tinted pink. From the weight of ferrous iron present, the weight of ferric salt per litre can readily be determined.

(3) Estimation of Ferrous and Ferric Iron when together.

First estimate the ferrous iron in a certain volume as described in (1), and then reduce an equal volume as described in (2), and estimate the total iron. The difference between the result and that previously obtained gives ferrous iron corresponding to the ferric iron originally present. The method of calculation is obvious.

Example:—Mix definite weights of ferrous sulphate and iron alum and dissolve in cold dilute freshly boiled sulphuric acid.

NOTE.—The total quantity of iron, and recognition of the relative quantities present in the ferrous and ferric state in iron ores, can be found by above methods. The ore should be in the **finest possible state of division.** If hydrochloric acid is used to dissolve iron or its compounds, the concentration of that acid in the solution titrated must be small, otherwise error may arise from liberation of chlorine.

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

(4) Estimation of Hydrogen Peroxide.

Method of Procedure.—Place in a porcelain basin 250 c.c. of water and 5 c.c. of dilute sulphuric acid, and add $KMnO_4$ from a burette until a faint pink tint remains. Then add 5 c.c. of hydrogen peroxide solution and standard permanganate until a faint pink tint is permanent.

Equation:

$$\underset{316}{\underline{2KMnO_4}} + 3H_2SO_4 + \underset{5 \times 34}{\underline{5H_2O_2}} = K_2SO_4 + 2MnSO_4 + 8H_2O + 5Cl_2.$$

From the equation 316 grams $KMnO_4 \equiv 170$ grams H_2O_2.

Notes.—(1) If any organic preservative such as glycerine or salicylic acid be present with the peroxide this method cannot be employed, because, as already noted, permanganate attacks most organic compounds. In such a case potassium iodide and thiosulphate should be employed.

(2) Hydrogen peroxide is sold in different strengths, generally described as 5, 10, or 20 volumes. Ten volume strength means that 1 c.c. of the peroxide should yield 10 c.c. of oxygen, or 20 c.c. of oxygen if treated with permanganate, for it is obvious that only half the oxygen evolved in above equation comes from the hydrogen peroxide, the remainder coming from the permanganate.

If standard $KMnO_4$ containing 2·625 gram per litre is used in the above experiment, and 5 c.c. of hydrogen peroxide be taken, then one tenth of the volume of $KMnO_4$ employed represents the volume of oxygen liberated by 1 c.c. of peroxide.

(5) **Estimation of Sulphur Dioxide solution** (Sulphurous Acid).

Take a certain volume of the sulphur dioxide solution, add dilute sulphuric acid, and then standard permanganate from a burette until liquid remains tinted pink.

Equation:

$$2KMnO_4 + \underbrace{5SO_2 + 5H_2O} = 2H_2SO_4 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

The result might be calculated as sulphur dioxide or as sulphurous acid. This method gives only approximate values, because other products are formed. A better method for the estimation of sulphur dioxide is given on p. 317.

(6) **Estimation of Tin as Stannous Chloride.**

A solution of stannous chloride can be estimated by adding a certain volume to a solution of ferric chloride and titrating the resulting ferrous chloride with permanganate. The concentration of the chlorine ion should be small (cf. p. 303).

Equation: $$2FeCl_3 + \underset{119}{\underline{SnCl_2}} = \underset{2 \times 56}{\underline{2FeCl_2}} + SnCl_4.$$

The equation shows that 119 parts by weight of tin correspond to 112 parts by weight of ferrous iron.

(7) **Estimation of Oxalic Acid**, or soluble oxalate (cf. p. 301).

Method of Procedure. Take a convenient volume of the oxalic acid (or oxalate) solution in a porcelain dish, add an equal bulk of dilute sulphuric acid, **heat to about 60° C.**, and then run in permanganate from a burette until solution is tinted a faint pink.

$$\text{Equation: } \underset{316}{\underline{2KMnO_4}} + 3H_2SO_4 + \underset{630}{\underline{5\{H_2C_2O_4 . 2H_2O\}}}$$
$$= K_2SO_4 + 2MnSO_4 + 10CO_2 + 18H_2O.$$

The equation shows that 316 grams of permanganate can completely oxidize 630 grams of oxalic acid, and $\therefore$ 31·6 grams of $KMnO_4 \equiv$ 63 grams of oxalic acid, which is the weight of oxalic acid in a normal solution.

N. $KMnO_4$ is therefore equivalent to N. oxalic acid, so that calculations of strength can be effected as in alkalimetry and acidimetry.

The calculations are worth giving in detail:—

Case 1. The standard permanganate given is $\frac{N}{10}$, i. e. it contains 3·16 grams per litre.

25 c.c. oxalic acid are oxidized by 37·5 c.c. $\frac{N}{10}$ $KMnO_4$.

Method I. The oxalic acid is the stronger in the proportion of 37·5 to 25, since strength is inversely proportional to volume required as already noted.

$$\therefore \text{ strength of oxalic acid} = \frac{37{\cdot}5}{25} \times \frac{N}{10}.$$

But N. oxalic acid contains 63 grams per litre.

$$\therefore \text{ strength of oxalic acid} = \frac{37{\cdot}5}{25} \times \frac{63}{10} = \mathbf{9{\cdot}45 \text{ grams per litre.}}$$

Method II. Check this result by an analogous method to that used in acidimetry and alkalimetry.

$$1000 \text{ c.c. } \frac{N}{10} \; KMnO_4 \text{ contain } 3{\cdot}16 \text{ grams.}$$

$$\therefore \; 1 \text{ c.c. } \frac{N}{10} \quad \text{,,} \quad \text{contains } \frac{3{\cdot}16}{1000} \quad \text{,,}$$

$$\therefore \; 37{\cdot}5 \text{ c.c. } \frac{N}{10} \quad \text{,,} \quad \text{contain } \left(\frac{3{\cdot}16 \times 37{\cdot}5}{1000}\right) \text{ grams.}$$

From equations:

$$316\text{ grams }KMnO_4 \equiv 630\text{ grams oxalic acid.}$$

$$\therefore\quad 1\text{ gram}\quad ,,\quad \equiv \frac{630}{316}\quad ,,\quad ,,\quad ,,$$

$$\therefore\quad \frac{3{\cdot}16 \times 37{\cdot}5}{1000}\quad ,,\quad \equiv \frac{630}{316} \times \frac{3{\cdot}16 \times 37{\cdot}5}{1000}$$

= weight of oxalic acid in 25 c.c.

∴ strength of oxalic acid in grams per litre

$$= \frac{1000}{25} \times \frac{630}{316} \times \frac{3{\cdot}16 \times 37{\cdot}5}{1000} = \mathbf{9{\cdot}45\ grams.}$$

Case 2. The strength of the permanganate is not given as fraction of normal, but as 5 grams per litre.

Result:—20 c.c. $KMnO_4 \equiv$ 30 c.c. oxalic acid.

Method I. Calculation from fraction of normal.

N. $KMnO_4$ contains 31·6 grams per litre.

$$\therefore\quad \text{strength in this case} = \frac{5}{31{\cdot}6}\text{ N.}$$

Hence the strength of the oxalic acid $= \frac{20}{30} \times \frac{5}{31{\cdot}6}$ N,

and N. oxalic acid contains 63 grams per litre.

$$\therefore\quad \text{strength} = \frac{20}{30} \times \frac{5}{31{\cdot}6} \times \frac{63}{1} = 6{\cdot}64\text{ grams per litre (approx.).}$$

Method II. Calculation from equations.

$$1000\text{ c.c. }KMnO_4\text{ contain 5 grams.}$$

$$1\text{ c.c.}\quad ,,\quad \text{contains } \frac{5}{1000}\text{ grams.}$$

$$20\text{ c.c.}\quad ,,\quad \text{contain } \frac{5 \times 20}{1000}\text{ grams} = \frac{1}{10}\text{ gram.}$$

From equations

$$316\text{ grams }KMnO_4 \equiv 630\text{ grams oxalic acid.}$$

$$1\text{ gram}\quad ,,\quad \equiv \frac{630}{316}\quad ,,\quad ,,\quad ,,$$

$$\frac{1}{10}\quad ,,\quad ,,\quad \equiv \frac{630}{316} \times \frac{1}{10}\text{ grams oxalic acid}$$

= weight of oxalic acid in 30 c.c.

∴ strength of the oxalic acid in grams per litre

$$= \frac{1000}{30} \times \frac{630}{316} \times \frac{1}{10} = 6{\cdot}64\text{ grams.}$$

IV. Standardization of and Estimations effected by means of Potassium Dichromate.

The general oxidizing equation which indicates how much oxygen can be given up to an oxidizable body by potassium dichromate in acid solution is as follows :—

$$\underbrace{K_2Cr_2O_7}_{294} + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + \underbrace{3O.}_{48}$$

This equation indicates that 294 grams of potassium dichromate could give up 48 grams of oxygen, and since a litre of a **normal solution of an oxidizing agent** can give up 8 grams, therefore a **normal solution of potassium dichromate** should contain $\frac{294}{6} = 49$ grams per litre. As a rule a **decinormal solution** is employed, which should contain 4·91 grams per litre.

Standardization of Potassium Dichromate.

To standardize potassium dichromate any ferrous solution of known strength could be employed, so that one might conveniently use (1) metallic iron, (2) ferrous ammonium sulphate, or (3) ferrous sulphate.

(1) Standardization by means of metallic Iron.

Prepare a pure ferrous solution from metallic iron as described in connexion with potassium permanganate. A modified apparatus from Fig. 44 is shown in Fig. 45, which has the advantage that a freshly boiled solution of sodium carbonate containing about 3 grams of solid can be added from the tap funnel at the end of the experiment after partial cooling so as to fill the flask with carbon dioxide. If the flask is to stand for some time this is an advantage.

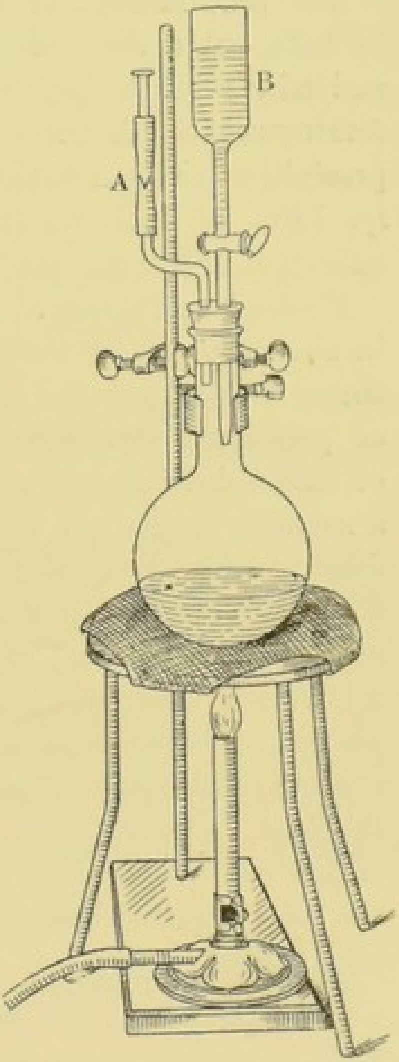

FIG. 45. PREPARATION OF PURE FERROUS SOLUTION. Bunsen valve (A) and tap funnel containing sodium carbonate (B).

Having made the ferrous solution up to a convenient volume with freshly boiled and cooled water, place from 10 to 50 c.c. in a porcelain basin, add an equal bulk of dilute sulphuric acid, and run in potassium dichromate from a burette. The end point of the reaction is not so readily found as in the case of potassium permanganate because, although there is a colour change from orange to green as the dichromate gets reduced, it is impossible to say when the change has been completed from the appearance of the solution.

The best method of determining the end of the reaction is to take out a drop of the reaction mixture from time to time and add it to a drop of **dilute freshly prepared potassium ferricyanide.** A ferrous salt and ferricyanide give a deep blue precipitate, while a ferric salt gives merely a brownish coloration (p. 146), so that when no blue precipitate is obtained, the oxidation of ferrous salt to ferric may be regarded as complete.

Proceed as follows:—Dissolve a small crystal of ferricyanide in about 20 c.c. of water in a test-tube so as to give a solution tinted yellow, say the same depth of tint as the bench solution of potassium **ferrocyanide.** By means of a pipette put drops of this solution over a white tile. The best form of tile has a number of shallow circular depressions on it. A drop of the dilute ferricyanide solution is put into each cup. When adding the dichromate, stop from time to time, take out a drop of the reaction mixture and place on one of the spots of ferricyanide. At first a blue precipitate will probably form. Continue the addition of dichromate until no precipitate is obtained.

Having roughly determined the volume of the dichromate required, carry out a couple of accurate experiments, in performing which one can rapidly add the dichromate to within one c.c. of the total required before testing.

Example. 0·1006 gram of pianoforte wire containing 99·6 per cent. of iron was weighed out. The weight of pure iron taken was therefore $\frac{99.6}{100} \times .1006 = 0.1$ gram, which was dissolved in dilute sulphuric acid and made up to 100 c.c. 25 c.c. of this solution—which would contain $\frac{25}{100} \times 0.1 = 0.025$ gram of pure iron—were found to be oxidized by 7·5 c.c. of $K_2Cr_2O_7$. The equation expressing the reaction,

viz. $\underbrace{K_2Cr_2O_7}_{294} + 7H_2SO_4 + \underbrace{6Fe}_{6 \times 56}SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$, shows that 294 grams of $K_2Cr_2O_7 \equiv 336$ grams ferrous iron.

$$\therefore \quad 1 \text{ gram of ferrous iron} \equiv \frac{294}{336} \text{ grams } K_2Cr_2O_7,$$

$$\text{and } \cdot 025 \text{ gram ferrous iron} \equiv \left(\frac{294}{336} \times \cdot 025\right) \text{ gram } K_2Cr_2O_7,$$

which must be the weight of $K_2Cr_2O_7$ in 7·5 c.c.

$\therefore$ the strength of $K_2Cr_2O_7$ in grams per litre

$$= \frac{294}{336} \times \cdot 025 \times \frac{1000}{7 \cdot 5} = 2 \cdot 917.$$

(2) Standardization of Potassium Dichromate by Ferrous Ammonium Sulphate, $FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$.

Make up a standard solution of ferrous ammonium sulphate as detailed under Potassium Permanganate. Take say 25 c.c. in a basin, add an equal bulk of dilute sulphuric acid, and then dichromate from a burette. Use potassium ferricyanide as **outside indicator** as described in Method I.

Equation:

$$\underbrace{K_2Cr_2O_7 + 7H_2}_{294}SO_4 + 6\underbrace{\{FeSO_4 . (NH_4)_2SO_4 . 6H_2O\}}_{6 \times 392}$$
$$= K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6(NH_4)_2SO_4 + 43H_2O.$$

The equation shows that 294 grams $K_2Cr_2O_7 \equiv 2352$ grams of $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$.

(3) Standardization by Ferrous Sulphate, $FeSO_4 . 7H_2O$.

This process is not quite so satisfactory as Methods I and II as a rule owing to the difficulty of getting absolutely pure crystallized ferrous sulphate. The method of procedure is similar to that described above.

$$\text{Equation : } \underbrace{K_2Cr_2O_7}_{294} + 7H_2SO_4 + \underbrace{6\{FeSO_4 7H_2O\}}_{6 \times 278}$$
$$= K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 49H_2O.$$

The equation shows that 294 grams $K_2Cr_2O_7 \equiv 1668$ grams of $FeSO_4 . 7H_2O$.

Estimations which can be effected by means of Standard Potassium Dichromate.

(1) Estimation of the strength of a Ferrous Iron solution.

The method of procedure has been fully described on p. 308. Take a certain volume of the ferrous solution, add an equal bulk of dilute sulphuric acid, and then run in potassium dichromate from a burette until a drop of the reaction mixture gives no blue precipitate with a drop of dilute and freshly prepared potassium ferricyanide.

$$\text{Equation: } \underset{294}{\underline{K_2Cr_2O_7}} + 7H_2SO_4 + \underset{6 \times 56}{\underline{6FeSO_4}}$$
$$= K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O.$$

The equation shows that 294 grams $K_2Cr_2O_7$ will oxidize 336 grams of ferrous iron.

(2) Estimation of the strength of a Ferric solution, e. g. strength of Iron Alum, $K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$.

Reduce a certain volume by means of zinc and dilute sulphuric acid in the apparatus represented in Fig. 45, add dilute sulphuric acid, and titrate against the standard potassium dichromate solution. The equation expressing the reduction process is as follows:—

$$K_2SO_4.Fe_2(SO_4)_3.24H_2O + 2H = K_2SO_4 + 2FeSO_4 + H_2SO_4 + 24H_2O.$$

This equation indicates that

$$K_2Cr_2O_7 \equiv 3\{K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O\},$$

i.e. 294 grams $K_2Cr_2O_7 \equiv 3018$ grams of ferric alum.

(3) Estimation of the amount of Ferrous and Ferric Iron in a mixture containing Iron in both states of oxidation.

(*a*) Determine in one quantity (e.g. 25 c.c.) the amount of ferrous iron present as described above. (*b*) Reduce the ferric iron in another measured volume—preferably the same as previously used—and then titrate. Use the apparatus in Fig. 44 or Fig. 45. Subtracting the amount of ferrous iron found in the first experiment from the amount of ferrous and ferric iron in the second, the quantity of iron present in the ferric state is indicated.

(4) Estimation of Sulphur Dioxide (SO_2) or of Sulphurous Acid (H_2SO_3) by means of Potassium Dichromate.

To a certain volume of the sulphur dioxide solution (sulphurous acid) add first an equal bulk of dilute sulphuric acid and then potassium dichromate from a burette, until a drop of the reaction mixture gives no precipitate with dilute potassium ferricyanide as outside indicator.

$$\text{Equation: } \underset{294}{\underline{K_2Cr_2O_7}} + H_2SO_4 + \underbrace{3SO_2 + 3H_2O}_{3 \times 64 + 3 \times 18} = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O.$$

The equation shows that 294 grams of $K_2Cr_2O_7$ will oxidize 192 grams of SO_2 (or 246 grams of sulphurous acid) to sulphuric acid.

V. Standardization of and Estimations which can be effected by means of Iodine dissolved in Potassium Iodide.

Iodine may be regarded as an oxidizing agent in many of its reactions; e. g. it oxidizes SO_2 to SO_3 in presence of water according to the equation

$$SO_2 + \underset{16}{\underline{OH_2}} + \underset{254}{\underline{I_2}} = SO_3 + 2HI.$$

A litre of a normal solution of an oxidizing agent can react so as to give up, or cause the giving up of, 8 grams of oxygen. The equation shows that 254 grams of iodine would react so as to cause 16 grams of oxygen to be given up, and therefore **a normal solution of iodine would contain 127 grams per litre.** One prepares as a rule a **decinormal solution** containing 12·7 grams per litre, or an $\frac{N}{20}$ solution (6·35 grams per litre).

Preparation of a Decinormal Solution.

Weigh out in a weighing bottle with ground glass stopper exactly 12·7 grams of pure resublimed and crushed iodine.* Tip the contents of the bottle into a litre flask, preferably through a cut-off funnel with wide tube, and wash the bottle and funnel thoroughly with a solution of potassium iodide prepared by dissolving 20 to 25 grams of potassium iodide in 150 to 250 c.c. of water. Then pour the rest of the iodide solution into the flask, and shake from time to time until solution of the iodine is effected. Make up to the graduated mark with water.

Many substances can be estimated directly by standard iodine, and a larger number by iodine and thiosulphate. The following substances can be estimated by iodine alone :—

(1) Arsenious compounds, e. g. arsenious oxide, As_2O_3.

(2) Antimonious oxide, Sb_2O_3.

(3) Sulphuretted hydrogen.

(1) **Estimation of Arsenious Oxide,** As_2O_3, by means of stan-

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* Note.—If only commercial iodine is procurable, powder about double the quantity of iodine required in a mortar along with a few grams of potassium iodide. Place on a dry shallow porcelain dish (or on a clock-glass) and cover with a glass funnel. After thoroughly drying the sand on a sand bath, place the basin and funnel on the sand and heat gently. The iodine sublimes and condenses on the inside of the funnel.

dard iodine. Iodine oxidizes arsenious oxide to arsenic oxide according to the equation

$$\underset{198}{As_2O_3} + \underset{508}{2I_2} + 2H_2O = As_2O_5 + 4HI.$$

Method of Procedure. Weigh into a small flask about 2·5 grams of powdered arsenious oxide, add about 200 c.c. of water and approximately 15 grams of sodium bicarbonate, $NaHCO_3$. Warm on a water-bath to a temperature of 60° to 70° C. until solution is effected. Cool under the tap, pour into a half-litre flask, wash out the small flask into the measuring vessel, and then make up to the standard volume.

Experiment. Take say 20 to 25 c.c. of the solution in a small conical flask, add a few drops of freshly prepared starch solution, and then run in the $\frac{N}{10}$ iodine from a burette until the blue colour due to the formation of starch iodide is permanent. From the values obtained it is easy to calculate the percentage of pure arsenious oxide in the sample taken.

Example. A mean of three experiments indicated that 25 c.c. As_2O_3 solution were oxidized by 24·5 c.c. $\frac{N}{10}$ iodine. The strength of the arsenious oxide is therefore less than that of the iodine in the proportion $\frac{24·5}{25}$.

The equation given above shows that 12·7 grams iodine, the weight in a litre of $\frac{N}{10}$ solution, $\equiv$ 4·95 grams of As_2O_3.

$\therefore$ one might say that an $\frac{N}{10}$ As_2O_3 solution contained 4·95 grams per litre.

$\therefore$ the strength of the arsenious oxide $= \frac{24·5}{25} \times \frac{4·95}{1} =$ **4·852 grams per litre.**

The weight of substance taken, 2·5 grams in 500 c.c., is equivalent to 5 grams per litre.

$\therefore$ the percentage of arsenious oxide $= \frac{4·852}{5} \times 100 =$ **99·43 per cent.** Antimonious oxide can be estimated in a similar manner.

$$Sb_2O_3 + 2H_2O + 2I_2 = Sb_2O_5 + 4HI.$$

Notes:—

(1) If pure **resublimed arsenious oxide** is used, which would be prepared by heating As_2O_3 in a porcelain basin covered with another basin or a funnel on a dry sand bath, then the **iodine** can be **standardized.**

An $\frac{N}{10}$ solution of As_2O_3 contains 4·95 grams per litre as already indicated. If 25 c.c. of such a solution exactly balance 25 c.c. of iodine solution, then the latter must be exactly $\frac{N}{10}$ = 12·7 grams per litre.

(2) The sodium bicarbonate is added to take up the hydriodic acid formed during the reaction.

$$NaHCO_3 + HI = NaI + H_2O + CO_2.$$

Normal sodium carbonate and caustic soda react with the iodine of starch iodide so that they cannot be employed.

$$6Na_2CO_3 + 3I_2 + 3H_2O = 5NaI + NaIO_3 + 6NaHCO_3.$$
$$6NaOH + 3I = 5NaI + NaIO_3 + 3H_2O.$$

(4) Estimation of Sulphuretted Hydrogen in solution, (SH_2Aq).

Two methods might be employed:—

(*a*) Direct estimation by means of standard iodine solution.

(*b*) Estimation by means of standard solutions of arsenious acid and iodine.

Method I. Direct titration by means of standard iodine solution.

Method of Procedure. Run into a conical flask from a burette a convenient quantity of $\frac{N}{100}$ iodine solution (prepared by diluting 25 c.c. of $\frac{N}{10}$ iodine to 250 c.c.). Add the sulphuretted hydrogen solution from another burette until the colour due to the iodine is discharged. Then add 5 c.c. of a freshly prepared starch solution (p. 37), and run in iodine solution until the blue colour reappears. Add together the two quantities of iodine and subtract the quantity of iodine required to produce a similar blue colour. This latter quantity is easily found by taking distilled water equal to total volume previously used, adding starch solution and then standard iodine.

The strength of the sulphuretted hydrogen is readily calculated from the equation

$$\underset{34}{\underline{H_2S}} + \underset{2\times127}{\underline{I_2}} = 2HI + S.$$

$$127 \text{ grams iodine} \equiv 17 \text{ grams } H_2S.$$

∴ a normal solution of SH_2 would contain 17 grams per litre.

A preferable method of estimation is to employ standard solutions of arsenious acid and iodine.

Method II. Estimation of Sulphuretted Hydrogen by standard arsenious acid solution and iodine.

Summary of Process. This method depends upon the fact that arsenious acid solution gives a precipitate of arsenious sulphide with sulphuretted hydrogen. More than enough arsenious acid is employed, and the excess found by means of a standard iodine solution.

$$\begin{aligned} As_2O_3 + 3H_2S &= As_2S_3 + 3H_2O \\ As_2O_3 + 2I_2 + 2H_2O &= As_2O_5 + 4HI. \end{aligned}$$

VI. Estimations effected by means of Standard Solutions of Iodine and Sodium Thiosulphate.

Standard solutions of iodine and thiosulphate are convenient for a great many estimations, of which the examples given below may be taken as typical.

(1) Estimation of chlorine and bromine in aqueous solution.
(2) ,, ,, sulphur dioxide and sulphites.
(3) ,, ,, available chlorine in bleaching-powder.
(4) ,, ,, oxidizing agents (e. g. MnO_2, PbO_2, $KMnO_4$) by heating with concentrated hydrochloric acid and passing the chlorine into potassium iodide solution.

The reaction on which the above-mentioned estimations are based is one between iodine and thiosulphate, which may be represented by the equation

$$2Na_2S_2O_3 \cdot 5H_2O + I_2 = 2NaI + \underbrace{Na_2S_4O_6}_{\text{Sodium Tetrathionate}} + 10H_2O.$$

The sodium iodide and sodium tetrathionate formed give colourless solutions, so that when enough thiosulphate has been used to react with all the iodine present, the solution becomes colourless. The delicacy of the reaction is increased by adding starch towards the end, the dark blue starch iodide formed being readily decomposed by the thiosulphate.

Principles of reactions employed.

Two types of reaction are met with :—

(*a*) Standard iodine is added in excess, and the excess found by standard thiosulphate.

(*b*) Iodine is liberated by reaction of the substance (or a body set free by the substance) with potassium iodide, and the quantity of iodine so set free is titrated against standard thiosulphate.

Standardization of Sodium Thiosulphate.

The equation expressing the reaction between thiosulphate and iodine,

$$\text{viz. } \underbrace{2\{Na_2S_2O_3 \cdot 5H_2O\}}_{2 \times 248} + \underbrace{I_2}_{2 \times 127} = 2NaI + Na_2S_4O_6 + 10H_2O,$$

indicates that 248 grams of crystallized thiosulphate react with 127 grams of iodine, so that a solution of thiosulphate corresponding to an $\frac{N}{10}$ iodine solution should contain 24·8 grams per litre, and such a solution is termed $\frac{N}{10}$.

Dissolve 24·8 grams of sodium thiosulphate (preferably recrystallized) in water in a litre flask and make up to a litre. The salt can be powdered, if desired, as the crystals dissolve rather slowly in cold water, but there is more liability to loss of water of crystallization from the powder than from the crystals.

The solution should be standardized against the standard iodine prepared as previously described.

Example:—If 25·2 c.c. thiosulphate solution are required to decolorize 25 c.c. of $\frac{N}{10}$ iodine, using starch as indicator, the strength of the thiosulphate would be $\frac{25}{25{\cdot}2} \times \frac{N}{10} = \left(\frac{25}{25{\cdot}2} \times 24{\cdot}8\right) = 24{\cdot}6$ grams per litre.

It might be convenient in such a case to add a weighed quantity of thiosulphate so as to make the solution up to $\frac{N}{10}$. Sodium thiosulphate solution deteriorates slowly on keeping, but it has been found that if 2 grams (approx.) of potassium bicarbonate be added to a litre, and the solution kept in the dark, it keeps much better.

Sodium thiosulphate solution could also be standardized against standard potassium permanganate or standard dichromate.

(1) Standardization by Permanganate.

Make up a solution of $\frac{N}{30}$ $KMnO_4$ by appropriate dilution of a solution which has been carefully standardized.

Take 20 c.c., add an equal bulk of dilute H_2SO_4, dilute with water, and then add a few crystals of pure KI and shake. The solution turns brown, and, depending upon the quantity of KI present, a precipitate of iodine may form. Titrate at once against the thiosulphate. Add the latter from a burette until the colour changes to yellow, then add starch and complete the titration. The equations expressing the reactions taking place would be :—

$$(a)\quad 2KMnO_4 + 8H_2SO_4 + 10KI = 5I_2 + 6K_2SO_4 + 2MnSO_4 + 8H_2O.$$

$$(b)\quad 2Na_2S_2O_3 . 5H_2O + I_2 = 2NaI + Na_2S_4O_6 + 10H_2O.$$

$$\therefore \quad \underset{316}{\underline{2KMnO_4}} \equiv \underset{10 \times 248}{\underline{10Na_2S_2O_3 . 5H_2O.}}$$

(2) Standardization by Dichromate.

Standard $K_2Cr_2O_7$ can be used. On warming with HCl and KI, iodine is liberated proportional to the dichromate present, according to the equation

$$K_2Cr_2O_7 + 14HCl + 6KI = 3I_2 + 2CrCl_3 + 8KCl + 7H_2O.$$

This reaction can be carried out either in a stoppered bottle, which is placed in warm water for some time, or by distilling off the chlorine set free by the interaction of $K_2Cr_2O_7$ and concentrated HCl into a solution of KI in a Bunsen's Apparatus (Fig. 46).

The potassium iodide solution is contained in the inverted retort and the $K_2Cr_2O_7$ and HCl (preferably along with a lump of magnesite) is warmed in the small flask with the ground glass stopper until the whole of the evolved chlorine has been driven into the iodide solution. Titrate the iodine set free by thiosulphate as before.

Equations: $K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$.

$3Cl_2 + 6KI = 3I_2 + 6KCl$.

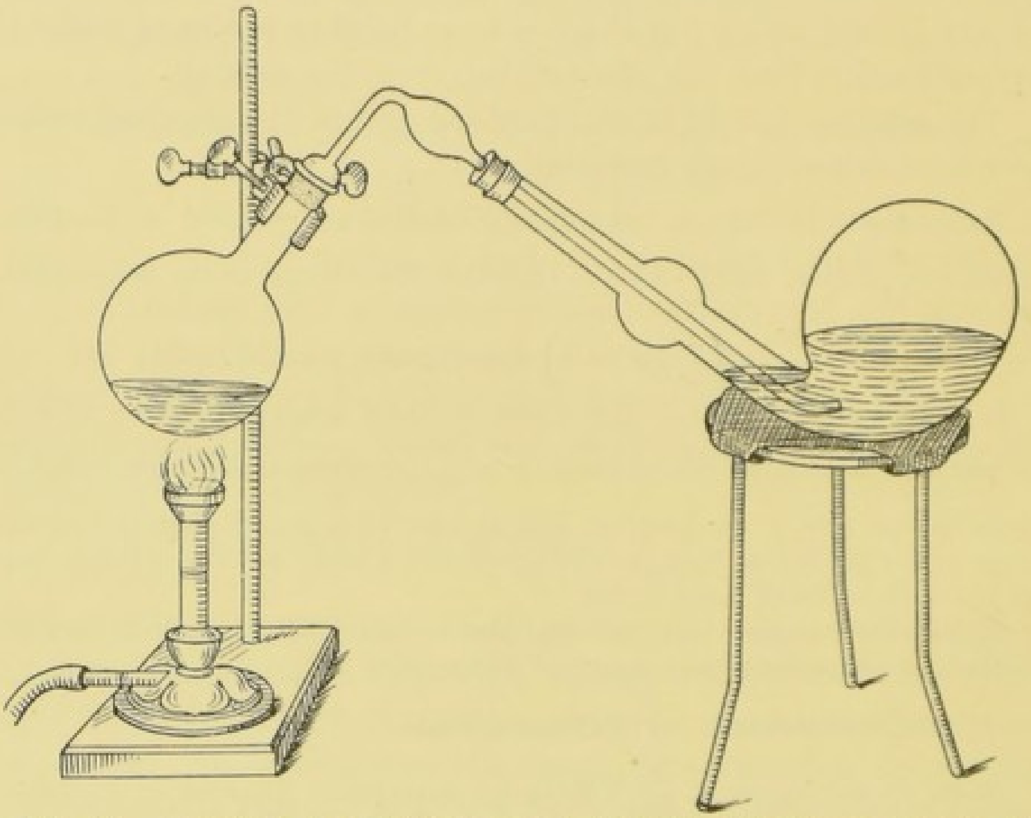

FIG. 46. BUNSEN'S APPARATUS FOR ESTIMATING SUBSTANCES WHICH ON HEATING WITH ACID GIVE OFF CHLORINE AND CAUSE LIBERATION OF IODINE FROM POTASSIUM IODIDE.

Estimations by means of Standard Solutions of Iodine and Thiosulphate.

(1) Estimation of Chlorine in Aqueous Solution—Chlorine Water.

To a measured volume of the solution in a conical flask add excess of pure potassium iodide solution. Iodine is liberated according to the equation $Cl_2 + 2KIAq = 2KClAq + I_2$. Standard thiosulphate is then added from a burette until the colour becomes light yellow, when a few c.c. of freshly prepared starch solution are added. The thiosulphate is then added very slowly, and with constant shaking of the flask until the blue colour is discharged.

Example:—20 c.c. of chlorine water liberated iodine which reacted with 12·5 c.c. of $\frac{N}{10}$ thiosulphate.

Equation :

$$\underset{2\times35\cdot5}{Cl_2}+2KI = 2KCl+\underset{2\times127}{I_2}.$$

The chlorine solution is the weaker in the proportion of 12·5 to 20.

$\therefore$ strength of chlorine solution $= \frac{12\cdot5}{20}\ \frac{N}{10}$.

And the equation shows that 35·5 Cl $\equiv$ 127 I, so that 35·5 grams of chlorine per litre would represent a normal solution.

$\therefore$ strength of the chlorine $= \left(\frac{12\cdot5}{20}\times\frac{35\cdot5}{10}\right) =$ **grams per litre.**

Note. The strength of **bromine water** could be estimated in an exactly similar manner.

(2) Estimation of (a) Sulphurous Acid, (b) Sulphites.

The estimation of sulphurous acid solution (SO_2 solution) and of sulphites depends upon the following reactions:—

$$I_2+SO_2+OH_2=2HI+SO_3 \text{ or } I_2+H_2SO_3+OH_2=2HI+H_2SO_4$$

$$I_2+Na_2SO_3+OH_2 = Na_2SO_4+2HI.$$

(*a*) Estimation of Sulphurous Acid Solution.

Place in a conical flask a measured volume of standard iodine, which from a rough preliminary experiment is known to be excess of what is required, and then add a definite volume of SO_2 solution. The solution remains tinted brown. Titrate with thiosulphate, and when the colour changes to a light yellow add starch and complete the titration.

Note. If the sulphur dioxide solution is very concentrated, it must be diluted, or, after cooling in ice, sealed up in thin bulbs which are broken under the iodine solution.

The result can be calculated in terms of SO_2 or H_2SO_3.

Example. 20 c.c. $\frac{N}{10}$ I_2 were taken and 50 c.c. of SO_2 solution added. 10 c.c. $\frac{N}{10}$ thiosulphate were required in titrating back.

$\therefore$ 20 − 10 = 10 c.c. $\frac{N}{10}$ iodine were used in oxidizing the SO_2.

$$10 \text{ c.c. } \frac{N}{10} I_2 \equiv 50 \text{ c.c. } SO_2 \text{ solution.}$$

$\therefore$ the SO_2 solution is the weaker in the proportion of 10 to 50.

$$\therefore \text{strength of } SO_2 = \frac{10}{50}\times\frac{N}{10}.$$

And from the equation N . SO_2 solution contains $\frac{64}{2} = 32$ grams per litre.

$\therefore$ strength of $SO_2 = \frac{10}{50} \times \frac{32}{10} = 0{\cdot}64$ gram per litre.

Calculation as H_2SO_3. N . H_2SO_3 contains $\frac{H_2SO_3}{2} = 41$ grams per litre.

Strength of $H_2SO_3 + \frac{10}{50} \times \frac{41}{10} = \frac{82}{100} = 0{\cdot}82$ grams per litre.

(*b*) **Estimation of Sulphites.** Weigh out into a conical flask 0·5 to 1 gram of sulphite. Add excess of iodine and shake. Titrate back with standard thiosulphate.

(3) **Estimation of Available Chlorine in Bleaching-powder.**

Bleaching-powder is not a simple substance, but consists of a variable mixture of calcium chlor. hypochlorite, $Ca\begin{matrix}\diagup Cl\\ \diagdown O{-}Cl\end{matrix}$, Calcium Chloride, $CaCl_2$, Calcium Hydroxide, $Ca(OH)_2$, and Calcium Chlorate, $Ca(ClO_3)_2$.

The calcium chlor. hypochlorite is the most important, and the available chlorine is practically entirely furnished from it. Acetic acid should be employed for the decomposition if it is intended to avoid chance of decomposing chlorate, which would be attacked by hydrochloric or sulphuric acid. Dilute acids decompose the chlor. hypochlorite as indicated in the following equations:—

$$Ca\begin{matrix}\diagup Cl\\ \diagdown OCl\end{matrix} + 2CH_3 . COOH = (CH_3 . COO)_2Ca + H_2O + Cl_2$$

$$CaCl(OCl) + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

The value of any sample of bleaching-powder depends upon the quantity of available chlorine it can produce, i. e. the quantity of chlorine present as chlor. hypochlorite, and is generally expressed in this country as percentage of available chlorine. If the compound consisted of pure CaCl(OCl), the percentage should be

$$\frac{2 \times 35{\cdot}5}{40 + 16 + 71} = \frac{71}{127} = 55{\cdot}9.$$

The percentage usually varies considerably, but good samples contain 30 to 35 per cent. Two methods of estimation might be employed:—

Estimation of Available Chlorine. Method I.

Summary of Process. Dissolve a weighed average sample of the bleaching-powder in water as far as possible, add first excess of potassium iodide and then acetic acid. Chlorine is liberated and sets free iodine: the liberated iodine is titrated against standard thiosulphate.

Method of Procedure. Weigh out 7·1 grams into a mortar, rub up by means of a pestle with water to form a cream, allow to settle, and pour through a funnel into a litre flask, rub up the residue with water, allow to settle, pour off and repeat several times until finally the whole has been removed to the flask and the mortar washed. Make up to a litre, shake thoroughly, remove 50 c.c. to a conical flask, add an equal bulk of water and then excess of potassium iodide. The weight of potassium iodide required might be calculated [$CaCl(OCl) \equiv 2KI$], but a few crystals dissolved in several c.c. of water are generally sufficient. To the mixture acetic acid is next added, which liberates chlorine, which in turn sets free iodine. The liberated iodine is then titrated against standard thiosulphate, using starch as indicator.

If 50 c.c. of the bleaching-powder solution be taken, and $\frac{N}{10}$ thiosulphate be employed for the titration, the volume of the latter solution used gives directly the percentage of available chlorine.

This could readily be proved by calculation. e.g. 50 c.c. of the bleaching-powder solution were taken, and after iodine had been liberated as described above, 30·5 c.c. of $\frac{N}{10}$ thiosulphate were required. The bleaching-powder contains 30·5 per cent. of available chlorine.

Calculation. 50 c.c. bleaching-powder $\equiv$ 30·5 c.c. $\frac{N}{10}$ thiosulphate. And 30·5 c.c. $\frac{N}{10}$ thiosulphate $\equiv$ 30·5 c.c. $\frac{N}{10}$ iodine, which $\equiv$ 30·5 c.c. $\frac{N}{10}$ chlorine. It follows that 30·5 c.c. $\frac{N}{10}$ chlorine must be the quantity of available chlorine given up from 50 c.c. One litre of bleaching-powder solution should therefore be able to furnish $\left(\frac{1000}{50} \times 30{\cdot}5\right)$ c.c. $\frac{N}{10}$ chlorine $=$ 610 c.c. But one litre of $\frac{N}{10}$ chlorine contains 3·55 grams of chlorine and 610 c.c. would thus contain $\left(\frac{610}{1000} \times 3{\cdot}55\right)$ grams, which must be the quantity of chlorine in 7·1 grams of substance. The percentage of chlorine would be

$$\frac{100}{7{\cdot}1} \quad \frac{610}{1000} \times \frac{3{\cdot}55}{1} = 30{\cdot}5.$$

Method II. The available chlorine in bleaching-powder can be found by a second method which depends upon its oxidizing effect upon arsenious oxide.

(4) **Estimation of Dioxides, e. g. MnO_2 or PbO_2 and other substances which give up Chlorine on heating with concentrated Hydrochloric Acid. e. g. $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, $KClO_3$.**

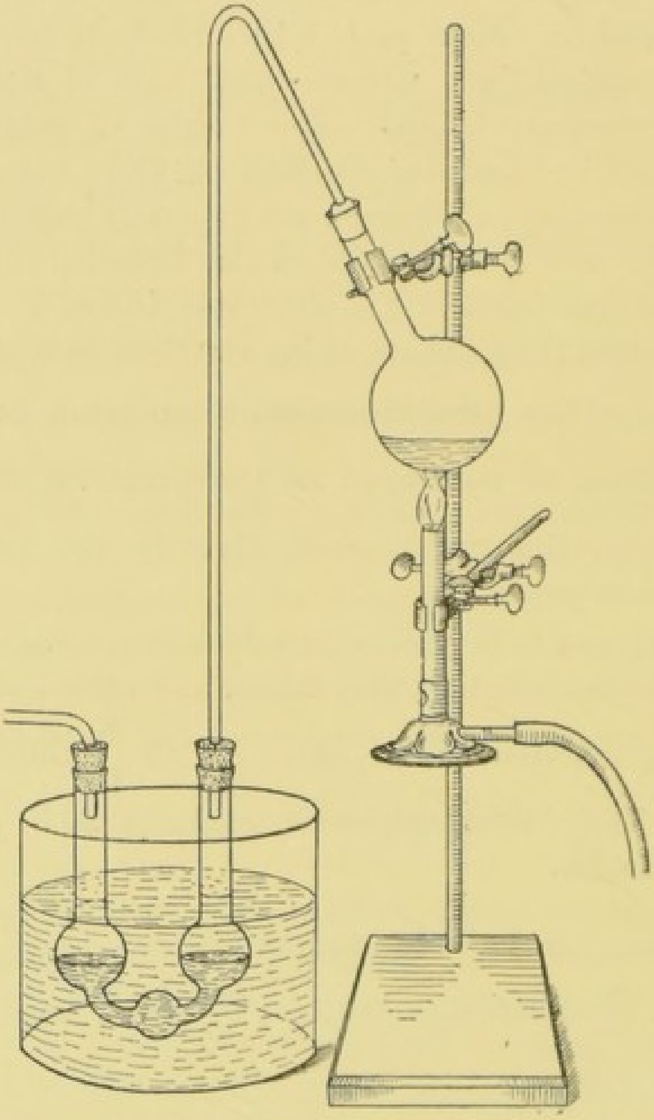

FIG. 47. METHOD OF DRIVING EVOLVED CHLORINE INTO POTASSIUM IODIDE SOLUTION. For alternative apparatus see Fig. 46.

EXAMPLE. **Estimation of Manganese Dioxide (MnO_2) in Pyrolusite.**

Summary of Process. A weighed quantity of substance is heated up with concentrated hydrochloric acid, and the chlorine evolved is passed into excess of potassium iodide solution, so as to set free an equivalent quantity of iodine. The liberated iodine is then estimated by means of standard thiosulphate, using starch as indicator.

Method of Procedure. e. g. **Analysis of Pyrolusite.**

Use Bunsen's apparatus, a diagram of which is given in Fig. 46, or the apparatus shown in Fig. 47.

Place in the flask about a c.c. of water and run the water over the bottom so as to prevent caking of the substance, and add a small piece of magnesite. Then weigh out into the flask about 0·3 to 0·6 gram of ore, and add about 30 c.c. of concentrated hydrochloric acid. The flask should be connected with a delivery tube which is expanded to make a ground glass connexion fitting the flask as indicated in Fig. 47. The ground glass connexion should have a trace of grease on it. If a ground glass connexion is not available use a rubber stopper which has been boiled with caustic soda solution to remove sulphur, or a paraffined cork.

The flask is connected with the inverted retort (Fig. 46) or with a U-tube (Fig. 47) containing potassium iodide. The U-tube, if employed, is conveniently placed in a beaker containing water.

Heat carefully until all the chlorine is evolved. The lump of magnesite which gives off CO_2 tends to prevent the liquid from being sucked back, but the quantity of liquid in the retort or bulbs should be such that a suck back of liquid is practically impossible.

At the end of the distillation wash the contents of the receiver into a measuring flask and make up to the graduated mark. Take an aliquot part in a conical flask and titrate against standard thiosulphate, using starch as indicator.

Example:—0·4 gram of pyrolusite was taken and distilled with concentrated HCl. The potassium iodide and iodine solution in the receiver was made up to 250 c.c. and 50 c.c. taken. 18 c.c. $\frac{N}{10}$ thiosulphate were required to decolorize the solution. This quantity of thiosulphate corresponds to 18 c.c. $\frac{N}{10}$ iodine, so that the total quantity of iodine liberated

$$= \frac{250}{50} \times 18 = 90 \text{ c.c. } \frac{N}{10} \text{ iodine} = (90 \times 0{\cdot}0127) \text{ gram } I_2.$$

The equation expressing the reaction (viz. $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$) shows that 127 grams iodine ≡ 43·5 grams MnO_2.

$$\therefore \quad 1 \text{ gram iodine} \equiv \frac{43{\cdot}5}{127} \quad \text{,,} \quad \text{,,}$$

and $(90 \times 0{\cdot}0127)$ gram iodine $\equiv \left(\frac{43{\cdot}5}{127} \times 90 \times 0{\cdot}0127\right)$ gram MnO_2 = weight of pure MnO_2 in 0·4 gram substance.

∴ The percentage of MnO_2 in the sample of pyrolusite

$$= \frac{43{\cdot}5 \times 9}{1000} \times \frac{100}{0{\cdot}4} = \mathbf{97{\cdot}88} \text{ per cent.}$$

VII. Volumetric Estimation of Phosphates.

The phosphoric acid radicle can be estimated in solution by means of a standard solution of a uranium salt. The results are usually stated not in terms of the radicle PO_4''', but in terms of phosphoric anhydride P_2O_5.

Required:—(1) Standard solution of uranium acetate or uranium nitrate.

(2) Standard solution of phosphate to standardize the uranium solution.

Summary of Process:—

If a standard uranium solution is added to a boiling solution of phosphate in such a way that no free mineral acid can be formed, a brown precipitate of uranyl phosphate comes down as long as phosphate is in solution. The end of the reaction is determined by using freshly prepared potassium ferrocyanide solution as **outside indicator.** When the uranium solution has been added in excess a drop of the reaction mixture gives a brown precipitate of uranyl ferrocyanide with a drop of the ferrocyanide solution.

Equations required in calculations:—

$$\underbrace{(UO_2)''(C_2H_3O_2)_2 \,.\, 2H_2O}_{426} + Na_2H\underbrace{PO_4}_{95} = 2Na\,.\,C_2H_3O_2 + (UO_2)''HPO_4 + 2H_2O.$$

$$\underbrace{(UO_2)''(NO_3)_2 6H_2O}_{503} + Na_2H\underbrace{PO_4}_{95} = 2NaNO_3 + (UO_2)''HPO_4 + 6H_2O.$$

Standardization of the Uranium Solution.

The uranium solution must be standardized under similar conditions to those which will obtain during its use in analysis.

(*a*) For determinations where sodium, potassium, or ammonium salts will be present use microcosmic salt, $HNa\,.\,NH_4PO_4\,.\,4H_2O$, common sodium phosphate, $Na_2HPO_4\,.\,12H_2O$, or potassium dihydrogen phosphate, KH_2PO_4, for standardization purposes.

(*b*) For use in determinations where calcium and magnesium salts are present in quantity, e.g. in estimation of superphosphates, the uranium solution should be standardized against a standard solution of calcium phosphate dissolved in the minimum quantity of hydrochloric acid.

Preparation of a standard solution.

Dissolve about 32 grams of acetate or 37 of nitrate in water, add 40 to 50 c.c. of glacial acetic acid and make up to a litre. The quantity of uranium salt indicated is arrived at from the following considerations:—

Above equations show that 426 grams of acetate or 503 grams of the nitrate are equivalent to 95 parts of PO_4 or 71 parts of P_2O_5. The standard solution should be made up so that 1 c.c. $\equiv$ 0·005 gram of P_2O_5. The weight of acetate equivalent to this would be $\frac{5}{71} \times 426 = 29{\cdot}98$ grams. It is better to make up a stronger solution and to dilute after titration against the standard phosphate. The latter solution is made of such a strength that 50 c.c. contain 0·1 gram of P_2O_5. e.g. 10·08 grams of $Na_2HPO_4 \cdot 12H_2O$ or 5·886 grams of microcosmic salt,

$$H . NaNH_4PO_4 . 4H_2O.$$

50 c.c. of such a solution would be equivalent to 20 c.c. of a solution of uranium, one c.c. of which would be $\equiv$ 0·005 gram of P_2O_5.

Method of procedure in titration. Take 50 c.c. of standard phosphate solution in a beaker, heat to boiling, and if uranium nitrate is employed as standard solution add 5 c.c. of a 10 per cent. sodium acetate solution containing acetic acid. From the burette add the standard uranium solution with constant stirring until a drop of the reaction mixture gives a brownish tint when added to a drop of ferrocyanide. If 19·1 c.c. of uranium solution $\equiv$ 50 c.c. of standard phosphate then each 19·1 c.c. must be diluted to 20 c.c. e.g. 950 c.c. should be diluted to occupy

$$\left(\frac{20}{19{\cdot}1} \times 950\right) \text{c.c.} = 994{\cdot}8 \text{ c.c.}$$

Estimation of Phosphate. Prepare a solution and make up to a convenient volume, and then carry out estimations at a temperature of about 95° C., using potassium ferrocyanide as outside indicator, as above described.

e.g. 20 c.c. of a solution required 8·3 c.c. of standard uranium solution, one c.c. of which was equivalent to 0·005 gram of P_2O_5.

∴ one litre of the phosphate solution contained

$$\left(\frac{1000}{20} \times 8{\cdot}3 \times 0{\cdot}005\right) = \mathbf{2{\cdot}075 \text{ grams of } P_2O_5}.$$

PART VII

INTRODUCTION TO QUANTITATIVE GAS ANALYSIS

This division of Practical Chemistry has recently been brought to a high degree of refinement, so that very small quantities of gases can be accurately analysed. We will only consider here, however, the more important methods of manipulation by which considerable volumes of gases can be approximately estimated.

One invariably deals with measured volumes of gases. As a rule the volume employed in analysis does not exceed 100 c.c., but if the percentage of a certain gas which it is required to determine be small it may become advisable to work with considerable volumes, and to cause the gas in question to react in such a way with a definite volume of solution of a standard reagent that one can by volumetric analysis determine the volume of gas which has acted. As this type of gas analysis is practically a part of Volumetric Analysis it will be first considered.

I. Estimation of gases present in small quantity in gas mixtures by reaction with definite volumes of standard reagents which are afterwards titrated, e. g. estimation of carbon dioxide in air.

Other typical methods suitable when the gas is present in moderate quantity would be:—

II. Estimation by difference after direct absorption.

This method depends upon absorption of the gas in a definite volume by a suitable reagent, and measurement of the difference in volume.

III. Determination by combustion and subsequent absorption.

I. Estimation of a gas by reaction of a certain volume of the gas mixture with a definite quantity of reagent, which is subsequently titrated (or weighed).

Examples: (A) Estimation of CO_2 in air.

(B) Estimation of the sulphur dioxide in flue gases.

A. Estimation of Carbon Dioxide in Air.—Pettenkofer's Method.

Summary of Process. A sample of air is collected in a large bottle of known capacity, 50 c.c. of lime-water (or baryta) are added, and the closed bottle is then shaken until absorption is supposed to be complete. The carbon dioxide is taken up by the lime-water according to the equation

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O.$$

An aliquot portion of the lime-water which has been acted upon is then titrated against standard oxalic acid. An equal volume of pure unused lime-water is also titrated direct against the oxalic acid. The lime-water which has been acted on by carbon dioxide requires less oxalic acid, and from the difference in the results of titration it is easy to calculate the volume of CO_2 in the volume of air taken.

$$Ca(OH)_2 + H_2C_2O_4 . 2H_2O = CaC_2O_4 + 4H_2O.$$

Solutions required. (*a*) **A standard solution of oxalic acid.** This should conveniently contain 2·813 grams per litre, as one c.c. of such a solution is $\equiv$ 0·5 c.c. of CO_2 at normal temperature and pressure. The weight of oxalic follows from the equations given above, from which it is seen that 44 grams of CO_2 or ·22400 c.c. of $CO_2 \equiv 126$ grams oxalic acid, or $\frac{1}{2}$ c.c. CO_2 $= \frac{126}{22400 \times 2}$ = weight of oxalic in 1 c.c. of a solution containing 2·813 grams per litre.

(*b*) A solution of lime-water. The ordinary saturated solution on the bench will do quite well. [Note:—A half-saturated solution of baryta is often used, but it is more troublesome to prepare and keep than lime-water.]

(*c*) A solution of phenol phthalein in alcohol to act as indicator.

Method of Procedure. Fill a large bottle of say 5 litres capacity with water by means of a graduated measure so as to determine its volume up to the stopper. Various methods can be employed for filling the bottle with air. The simplest way is to empty out the water from the bottle at the place from which the sample is to be taken, and immediataly close the bottle. The breath should be held during this operation for obvious reasons (cf. p. 28). The sample of air collected in this way is wet. If a dry sample is required, the bottle must be dried either by wiping with a cloth if the neck is wide enough to admit the hand, or by rinsing the bottle with alcohol, inverting and draining for some time, and then heating the bottle carefully in the smoky blowpipe flame while a rapid current of air is blown through a tube inserted in the bottle. After cooling, the sample of air may be collected at the place required by blowing air through a tube passing to the bottom of the bottle and connected with a bellows. The time required for this process will depend upon the relative volumes of bellows and bottle. An ordinary kitchen bellows is suitable. The bottle is closed by a two-holed rubber stopper. Insert through the openings small pieces of solid glass as plugs. Fill a pipette of capacity 50 c.c. with lime-water, remove the glass plugs, and, inserting the tip of the pipette through one opening of the stopper, allow the pipette to empty itself. **Do not blow through it** when it has been emptied, but closing the upper end of the pipette with the thumb of one hand, grasp the bulb with the other hand. The expansion of the air inside due to the warmth of the hand will expel the last few drops. The 50 c.c. of air displaced will escape at the other opening in the stopper, so that the actual volume of air analysed will be the volume of the bottle less 50 c.c. Remove the pipette, insert the plugs, and by shaking and moving the lime-water round the sides of the bottle at intervals during 40 to 50 minutes promote complete absorption of the carbon dioxide.

After tilting the bottle and allowing any precipitate to settle, insert the tip of a 25 c.c. pipette into the liquid (or if the tip does not reach far enough, attach a piece of glass tube to the pipette by means of rubber) and fill the pipette. Run the 25 c.c. into a conical flask, add a drop of the phenol-phthalein solution, and then add the standard oxalic acid from the burette until the pink colour is just discharged. Carry out a titration of 25 c.c. of lime-water which has not been acted upon, and from the difference one can calculate the percentage of carbon dioxide in the sample of air examined.

Example. The capacity of the bottle was 5350 c.c. Temp. 15° C., pressure 770 millimetres.

25 c.c. of the lime-water removed from the bottle at the end of the experiment required 9·1 c.c., so that 50 c.c. would require 18·2 c.c. standard oxalic acid for neutralization.

25 c.c. of lime-water titrated direct required 11·8 c.c.
∴ 50 c.c. of ,, ,, ,, ,, ,, 23·6 c.c.

The oxalic acid equivalent to CO_2 in bottle $= 23·6 - 18·2 = 5·4$ c.c. and 1 c.c. oxalic $\equiv 0·5$ c.c. CO_2 at N. T. P.

∴ 5·4 c.c. oxalic $\equiv 2·7$ c.c. CO_2 at N. T. P.

Volume of air taken measured at 20° C. and 770 mm.

$$= 5350 - 50 = 5300 \text{ c.c.}$$

Correct this volume to N. T. P.

Case 1. Suppose the air to be dry.

$$\text{Volume at N. T. P.} = 5300 \times \frac{770}{760} \times \frac{273}{293} = 5003 \text{ c.c.}$$

$$\text{The percentage of } CO_2 = \frac{2·7 \times 100}{5003} = 0·054.$$

NOTE:—The air would not as a rule be dry, but a correction for its hygrometric state, obtained by determination of the dew-point and reference to tables, would make little difference to the calculation as the following case shows. A good general rule in this latitude is to assume the air to be half saturated.

Case 2. Suppose the air to have been collected in a wet bottle and to be therefore saturated with moisture. The vapour pressure of water vapour at 20° C. is 17·4 mm. The actual pressure of the air in the bottle was therefore $770 - 17·4 = 752·6$ mm.

The volume of the air at N. T. P.

$$= 5300 \times \frac{752·6}{760} \times \frac{273}{293} = 4890 \text{ c.c.}$$

$$\text{The percentage of } CO_2 = \frac{2·7 \times 100}{4890} = 0·055.$$

II. Estimation of a gas by direct absorption with a convenient absorbent.

Examples:—

(*a*) CO_2, SO_2, HCl, HBr, HI, and other acidic gases are absorbed by caustic potash, KOH.

(*b*) Oxygen is absorbed by alkaline pyrogallol.

(*c*) Carbon monoxide is absorbed by cuprous chloride.

(*d*) Ethylene, C_2H_4, acetylene, C_2H_2, and other unsaturated hydrocarbons can be absorbed by bromine water, or by fuming sulphuric acid (i. e. H_2SO_4 containing SO_3).

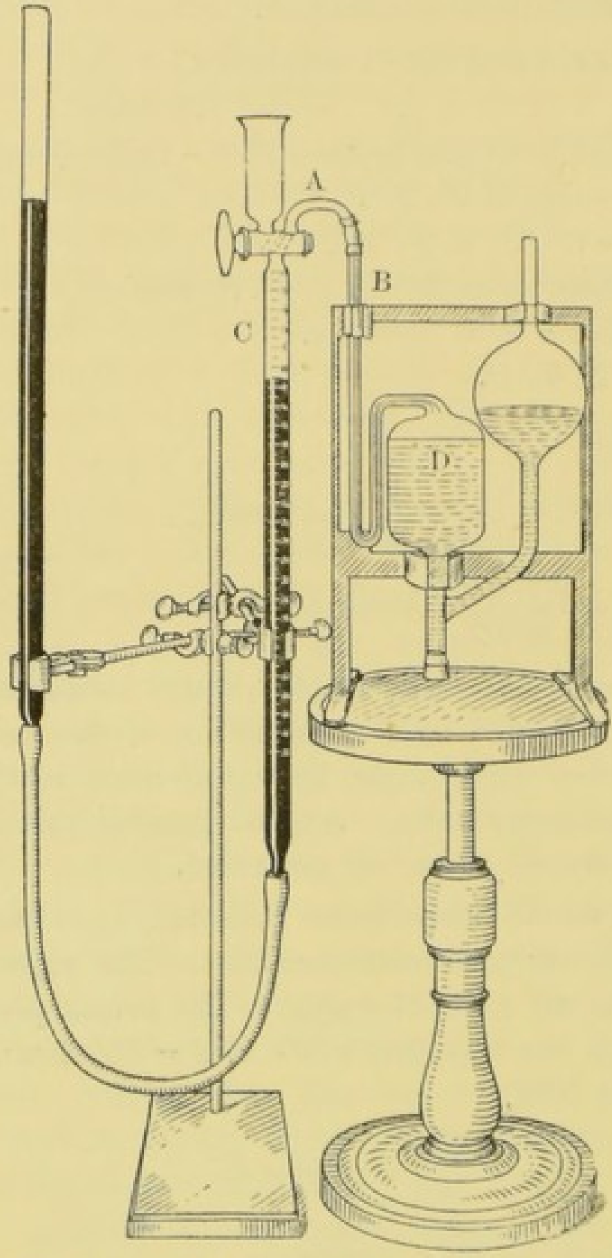

Fig. 48. Estimation of a Gas by Direct Absorption. Lunge's gas burette (c), and simple Hempel pipette (d).

The first two cases mentioned might be taken as typical and completely described.

Estimation of carbon dioxide in a gas mixture containing no other acidic gases, e. g. in respired air.

Method 1. Apparatus required:—Lunge's gas burette containing mercury and Hempel's gas pipette containing caustic potash.

Various forms of gas burette and pipette are in use. One of the more convenient gas burettes is Lunge's, which is shown in Fig. 48, along with a single Hempel gas pipette.

The **gas burette** consists essentially of a graduated tube connected with a reservoir. The burette can be filled with mercury or water. The graduations may be tested by the method given on p. 280. The **gas pipette** consists of a bulb containing the absorbent connected with a bulb into which displaced liquid can move when gas is passed into the pipette.

Method of Procedure. If mercury is to be employed fill the burette and small side tube A, which can be connected with it by means of the 3-way tap, completely with mercury by raising the reservoir, then connect with a vessel containing a sample of the gas, and by lowering the reservoir draw in a convenient quantity, say 20 to 100 c. c., depending upon the quantity of carbon dioxide expected to be present. Close the tap and measure the volume at atmospheric pressure, by reading off the volume when the mercury in the reservoir is supported on a level with the mercury in the burette.

Then connect the end of the side tube with the absorption pipette, the potash in which has by suction been drawn up to the top of the capillary tube B. The connexion is made by means of a small piece of stout rubber tubing, which should be wired on as shown. The diagram shows the position of matters during passage of gas into the pipette. After shaking at intervals during a few minutes lower the reservoir, open the tap, and draw the gas back into the burette. From the diminution in volume the percentage of carbon dioxide can be directly calculated. e. g. 50 c.c. of gas after absorption of CO_2 diminished in volume to 47·5 c.c.

$\therefore$ percentage of carbon dioxide $= 2(50 - 47{\cdot}5) = 5$.

Estimation of Carbon Dioxide. Method 2. A direct measurement of the carbon dioxide could be rapidly made without employing a pipette. After drawing a sample of the gas mixture into a Lunge burette over mercury, measure its volume at atmospheric pressure. Then introduce a suitable quantity, e. g. 10 to 20 c.c. of the potash solution from the cup at the top, which can be made to connect with the burette through one opening of the 3-way tap. Read the volume after shaking the burette backwards and forwards and allowing to stand for a short time. The calculation is a direct one, exactly similar to that given above under Method 1.

If an accurate determination is required then **the degree of humidity** must be attended to. After introducing the gas suck in a drop of water from the cup so as to saturate the gas with moisture. Measure the volume of the wet gas, introduce caustic potash solution and absorb the carbon dioxide, and after the reaction is complete remeasure the wet gas. The calculation is direct as given above.

Estimation of Carbon Dioxide. Method 3. Carbon dioxide can be estimated gravimetrically. A known volume of gas, say 5 to 100 litres, is first dried by passage through tubes containing calcium chloride, and is then aspirated through a weighed soda-lime tube properly protected by having the last quarter filled with calcium chloride. From the increase in weight of the soda-lime tube (or tubes) the percentage of carbon dioxide can be calculated.

The main types of apparatus in use having now been mentioned, a few general rules might be given.

General Rules to be observed in Analysing Gases.

(1) **Invariably note temperature and pressure** and measure the volume at atmospheric pressure unless under special conditions. The gas burette should not be handled when occupied by the gas, otherwise temperature errors may result.

(2) **If the volumes are all observed at the same temperature and pressure** the percentage of gas absorbed can obviously be calculated without correcting for temperature and pressure. e. g. if 100 c.c. of gas containing carbon dioxide as the only acidic gas diminishes in volume to 63 c.c. after absorption with caustic potash solution, all measurements being made say at 20° C. and 740 millimetres pressure, the percentage of carbon dioxide would be $100-63=37$ per cent.

(3) **If the volumes measured before and after absorption are at different temperatures and pressures,** then all volumes should be reduced to the same temperature and pressure, which preferably (but not necessarily) is normal temperature and pressure, i. e. 0° C. and 760 mm. of mercury, before calculating percentage (cf. p. 23).

(4) The gas should as a rule be measured **in the same condition as regards humidity** throughout, and generally by introducing a few drops of water **one arranges to measure the gas when saturated with moisture.** If one does not do so, then an error may be introduced due to the varying pressures of water vapour admixed with the gas.

(5) If mercury is used to confine the gas, then no difficulties as regards **solubility** arise, but if the gas is confined over water then the water should be saturated with the gas by shaking with another portion of sample before commencing the analysis.

(6) **The order in which the different constituents of a gas mixture are eliminated is of great importance.** e. g. if both oxygen and carbon monoxide are present the oxygen must be

absorbed before the carbon monoxide because oxygen acts upon cuprous chloride.

(7) In analysing gas mixtures containing methane, ethylene, or other hydrocarbons only small quantities of these bodies should be exploded with oxygen, and the pressure should be considerably reduced during the explosion to avoid fracturing the apparatus.

II. Estimation of Oxygen in a Gas Mixture. e. g. air.

Various methods might be employed.

Method 1. Estimation by absorption with alkaline pyrogallol in the Lunge gas burette.

Collect a sample of air in the Lunge gas burette and measure the volume after admitting a drop of water from the cup. Then draw in about 5 to 10 c.c. of a solution of caustic potash containing 250 grams per litre, and afterwards an equal volume of a solution of pyrogallol containing 10 grams per hundred c.c. On shaking the tube backwards and forwards and inclining and then shaking, the absorption takes place, and after allowing to stand for a few minutes one can measure the volume and calculate the percentage of oxygen.

e.g. 50 c.c. of air saturated with moisture were taken. After absorption with the alkaline pyrogallol the volume left occupied 39·7 c.c. The volume of oxygen in 50 c.c. $= 50 - 39{\cdot}7 = 10{\cdot}3$ c.c., and the percentage $=$ **20·6**.

Method 2. Carry out the absorption of oxygen with the alkaline pyrogallol in a gas pipette. Convenient apparatus is indicated in Fig. 49 or Fig. 48.

If more than one determination is required a ‘double Hempel pipette’ would be suitable. This consists essentially of an ordinary simple pipette containing the reagent and a couple of bulbs containing water to act as a ‘seal’ and prevent the air from reacting with the reagent (Fig. 49).

[Note :—Such double pipettes should be employed for other absorbents which are acted upon by air. e. g. cuprous chloride in hydrochloric acid, or in ammoniacal solution.]

A Lunge burette might be used as shown in Fig. 48, or a Hempel pipette as shown in Fig. 49.

Method of procedure. Draw in a sample of gas by lowering the reservoir in the usual way. If water is used in the burette it should previously be shaken up with air. Pass into the absorption pipette, which contains alkaline pyrogallol, shake and draw back into the burette as previously described. Measure the residual volume, and if there is any doubt as to whether the absorption is complete repeat the operation. The volume should not alter.

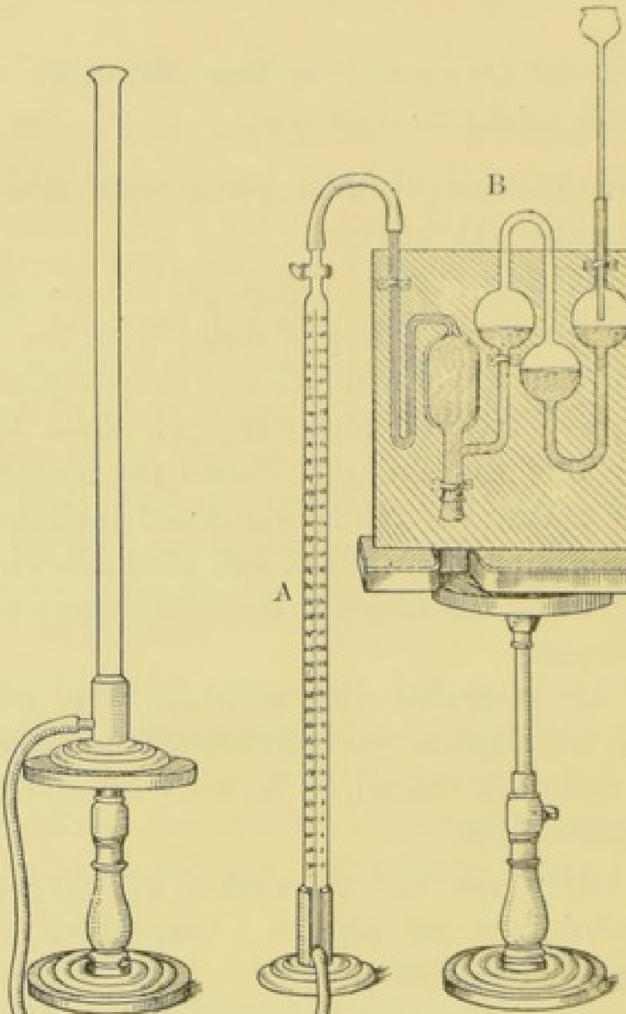

Fig. 49. Apparatus employed for the Estimation of Oxygen in Air by absorption with Alkaline Pyrogallate. a, Hempel's burette; b, Absorption pipette for use when employing absorbents acted upon by air.

In the diagram a small piece of pressure rubber tubing is bent round and one end is wired on to the tip of the burette and the other end on to the capillary of the pipette as shown. Another method of junction less liable to strain the capillary tube of the pipette would be a shallow inverted ∪ of capillary glass tubing joined by rubber and wired to burette and pipette.

Method 3. The quantity of Oxygen in air might be estimated by explosion with Hydrogen under diminished pressure in an explosion burette.

Take into the explosion gas burette (Fig. 50) 20 to 30 c.c. of air, measure the volume when moist, then add excess of hydrogen, say 15 to 20 c.c., and remeasure.

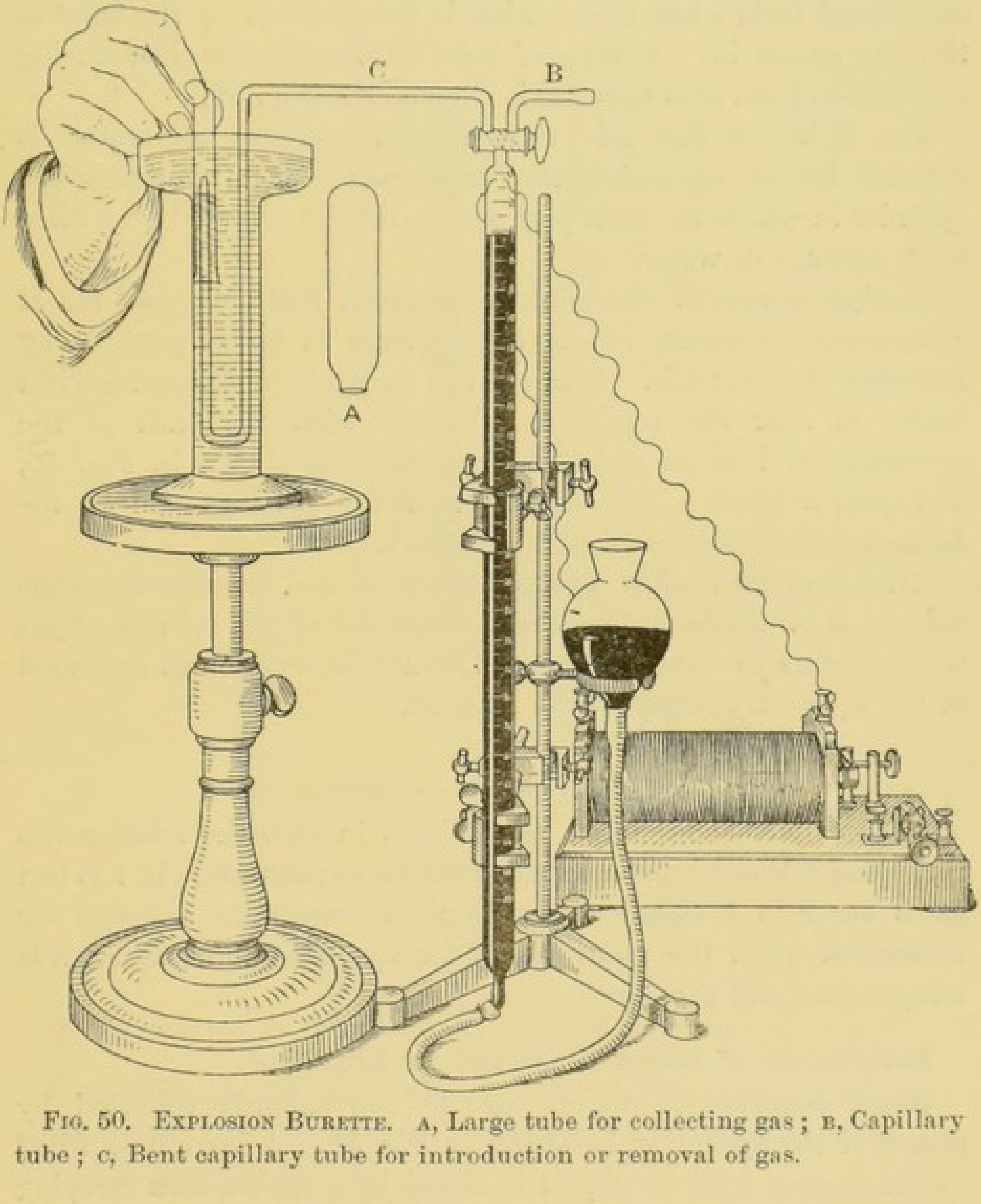

FIG. 50. EXPLOSION BURETTE. A, Large tube for collecting gas ; B, Capillary tube ; C, Bent capillary tube for introduction or removal of gas.

The air can be introduced through the capillary tube (B) which passes from the right-hand opening of the tap. Having turned the tap so that this capillary tube is connected with the burette, raise the reservoir so that the mercury passes through the opening in the tap and fills the capillary tube. A few drops which might escape are collected in a test-tube and put back into the reservoir. Draw in the air, moisten and measure it.

The hydrogen could be introduced by the same capillary, but should preferably be drawn in through the tube communicating with the left side of the tap (c). This tube is shown in the diagram with the bent part immersed in water, and gas is being introduced from a test-tube, which is forced down by the hand as the gas passes in. A type of tube convenient for introducing quantities of gas into burettes is shown at A (Fig. 50).

The filling of the side tube C with mercury (or water) is effected before beginning the experiment, the wide-mouthed cylinder in which the bent part of the tube is shown being filled with mercury or water.

Having measured the mixture of moist hydrogen and air at atmospheric pressure, reduce the pressure as far as possible by lowering the reservoir. Connect the ends of the platinum wires sealed in near the top of the burette with the ends of the secondary coil of an induction apparatus as shown in Fig. 50, and pass a spark. The terminals of the primary coil of the Ruhmkorff are connected with a battery.

After explosion allow to stand a minute and then measure the volume at atmospheric pressure. One-third of the volume of gas which seems to have disappeared would be oxygen, as indicated in the equation expressing the reaction.

$$\underbrace{2H_2}_{\text{2 vols}} + \underbrace{O_2}_{\text{1 vol}} = \underbrace{2H_2O}_{\text{(liquid water—negligible volume)}}.$$

In gas analysis one often has to keep in view the relationship regarding volumes known as **Avogadro's hypothesis**, viz.: When gases occur in a chemical equation one can write volumes for molecules, when the gases are under like conditions as regards temperature and pressure.

Estimation of Gases dissolved in Liquids.

Gases dissolved in liquids can be conveniently collected by means of the apparatus indicated in Fig. 51. A large flask filled to the stopper with the liquid is closed by a rubber cork carrying a tube filled with water, which is connected as shown to the capillary of a Lunge gas burette. The latter is jacketed by a wide tube through which hot vapour can be passed. The reservoir is placed so as to reduce pressure, and on boiling the whole of the gas with some liquid can be driven into the burette. After closing the tap, disconnect the flask, connect the capillary with another burette filled with mercury, pass steam (or other vapour) through the outer tube so as to boil the liquid, and draw the gas over into the burette by raising the reservoir. The gas collected can then be analysed.

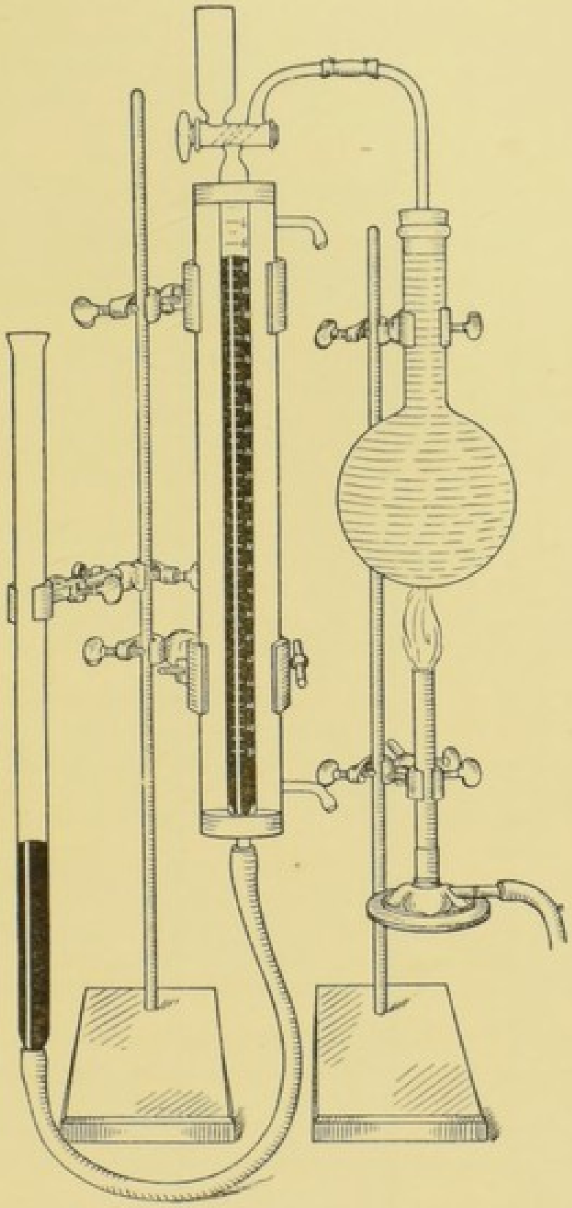

FIG. 51. APPARATUS FOR COLLECTION OF GASES DISSOLVED IN A SOLVENT.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	4	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	4	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3556	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	3200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	30
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	4	7	9	11	14	16	18	20

WEIGHTS AND MEASURES. IMPERIAL (OR BRITISH) AND METRIC SYSTEMS.

I. IMPERIAL (OR BRITISH) SYSTEM.

Length.

Smallest unit :—inch. 12 in. = 1 foot. 3 ft. = 1 yard. 1760 yards = 1 mile.

(Note.—A halfpenny is 1 inch in diameter.)

Avoirdupois Weight.

Smallest unit :— drachm.	16 dr. = 1 ounce.	16 oz. = 1 pound (lb.).	112 lb. = 1 cwt.	20 cwt. = 1 ton.
Grains 27.3	437.5	7000		

Troy Weight (for Gold, Silver, and Platinum).

Smallest unit :—grain.	24 gr. = 1 pennyweight (dwt.).	20 dwt. = 1 ounce.	12 oz. = 1 lb.
Grains 1	24	480	5760

Diamond and Pearl Weight.

Smallest unit :—grain.	4 gr. = 1 carat.	150 carats = 1 ounce Troy.
Grains (Troy) 0.8	3.2	480

Apothecaries' Weight (for Prescriptions).

Smallest unit :—grain.	20 gr. = 1 scruple.	3 scr. = 1 drachm.	8 dr. = 1 ounce.	12 oz. = 1 lb.
Grains (Apoth. or Troy) 1	20	60	480	5760

Apothecaries' Fluid Measure.

Smallest unit :—	Minim.	60 min. = 1 dr.	8 dr. = 1 oz.	20 oz. = 1 pint.	8 pints = 1 gall.
Vol. at 62°F. occupied by	0.91 grain of water.	54.7 gr. water.	437.5 gr. water.	8750 gr. water.	70000 gr. water.

II. METRIC SYSTEM.

Mass 1 gramme = weight of 1 cubic centimetre (c. c.) of dist. water at 4° C. (usually written gram).

1 kilogram = 1000 grammes
1 decigram = $\frac{1}{10}$ gramme
1 centigram = $\frac{1}{100}$ gramme
1 milligram = $\frac{1}{1000}$ gramme

Note.—Greek prefixes multiply. Latin prefixes divide.

Capacity 1 cubic centimetre (c. c.) = Vol. occupied by 1 gram of water at 4° C.
1 litre = 1000 c. c.

Length
1 metre
1000 metres = 1 kilometre.
1 decimetre = $\frac{1}{10}$ metre.
1 centimetre = $\frac{1}{100}$ metre.
1 millimetre = $\frac{1}{1000}$ metre.

III. RELATION OF IMPERIAL STANDARDS TO METRIC.

a) **Mass** 1 ounce = 28.35 grams. 1 lb. = 453.6 grams (approx.).

b) **Capacity** 1 minim = 0.059 c. c. [practically 1 drop (approx.)].
1 fluid drachm = 3.552 c. c.
1 fluid ounce = 28.42 c. c.
1 pint = 568.34 c. c. (rather more than ½ litre).
1 gallon = 4.546 litres.

c) **Length** 1 inch = 2.54 centimetres (cm.).
1 foot = 30.48 centimetres.
1 yard = 0.9144 metre (approx.).

IV. RELATION OF METRIC STANDARDS TO IMPERIAL.

Length 1 metre = 39.37 inches.
Capacity 1 litre = 1.76 pints. 1 c. c. = 16.9 minims.
Mass 1 gramme = 15.432 grains. 1 kilogramme = 2 lb. 3 oz. 119.86 grains (approx.).

Scale divided in inches (above) and centimetres (below).

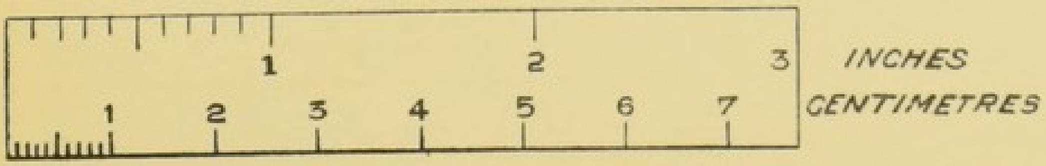

TABLE OF ATOMIC WEIGHTS (1909).

The values are given to the second decimal place where known. O = 16.

Element.	Symbol.	Atomic Weight. O = 16.		Element.	Symbol.	Atomic Weight. O = 16.	
		Accurate Values.	Useful Approximations.			Accurate Values.	Useful Approximations.
Aluminium	**Al**	**27·1**	27	**Molybdenum**	**Mo**	**96·0**	
Antimony	**Sb**	**120·2**	120	Neodymium	Nd	144·3	
Argon	**A**	**39·9**		Neon	Ne	20·0	
Arsenic	**As**	**75·0**	75	**Nickel**	**Ni**	**58·68**	
Barium	**Ba**	**137·37**	137	**Nitrogen**	**N**	**14·01**	14
Bismuth	**Bi**	**208·0**	208	Osmium	Os	190·9	
Boron	**B**	**11·0**	11	**Oxygen**	**O**	**16·0**	16
Bromine	**Br**	**79·92**	80	Palladium	Pd	106·7	
Cadmium	**Cd**	**112·40**		**Phosphorus**	**P**	**31·0**	31
Cæsium	Cs	132·81		**Platinum**	**Pt**	**195·0**	
Calcium	**Ca**	**40·09**	40	**Potassium**	**K**	**39·10**	39
Carbon	**C**	**12·0**	12	Praseodymium	Pr	140·6	
Cerium	Ce	140·25		**Radium**	**Ra**	**226·4**	
Chlorine	**Cl**	**35·46**	35·5	Rhodium	Rh	102·9	
Chromium	**Cr**	**52·1**	52	Rubidium	Rb	85·45	
Cobalt	**Co**	**58·97**		Ruthenium	Ru	101·7	
Columbium	Cb	93·5		Samarium	Sa	150·4	
Copper	**Cu**	**63·57**	63·6	Scandium	Sc	44·1	
Dysprosium	Dy	162·5		**Selenium**	**Se**	**79·2**	
Erbium	Er	167·4		**Silicon**	**Si**	**28·3**	28
Europium	Eu	152·0		**Silver**	**Ag**	**107·88**	108
Fluorine	**F**	**19·0**	19	**Sodium**	**Na**	**23·0**	23
Gadolinium	Gd	157·3		**Strontium**	**Sr**	**87·62**	
Gallium	Ga	69·9		**Sulphur**	**S**	**32·07**	32
Germanium	Ge	72·5		**Tantalum**	**Ta**	**181·0**	
Glucinum or Beryllium	Gl	9·1		**Tellurium**	**Te**	**127·5**	
				Terbium	Tb	159·2	
Gold	**Au**	**197·2**		**Thallium**	**Tl**	**204·0**	
Helium	**He**	**4·0**		Thorium	Th	232·42	
Hydrogen	**H**	**1·008**	1	Thulium	Tm	168·5	
Indium	In	114·8		**Tin**	**Sn**	**119·0**	119
Iodine	**I**	**126·92**	127	Titanium	Ti	48·1	
Iridium	Ir	193·1		Tungsten	W	184·0	
Iron	**Fe**	**55·85**	56	**Uranium**	**U**	**238·5**	
Krypton	Kr	81·8		Vanadium	V	51·2	
Lanthanum	La	139·0		Xenon	Xe	128·0	
Lead	**Pb**	**207·10**	207	Ytterbium (Neoytterbium)	Yb	172·0	
Lithium	**Li**	**7·0**					
Lutecium	Lu	174·0		Yttrium	Y	89·0	
Magnesium	**Mg**	**24·32**	24	**Zinc**	**Zn**	**65·37**	65
Manganese	**Mn**	**54·93**	55	Zirconium	Zr	90·6	
Mercury	**Hg**	**200·0**	200				

Note.—The elements in thick type are important for practical or theoretical reasons, or both.

INDEX

NOTE.—This Index is supplementary to that given on pp. 98 to 102.

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