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SALTS AND THEIR REACTIONS

A CLASS-BOOK OF PRACTICAL CHEMISTRY

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SIXTH EDITION

EDINBURGH
E. & S. LIVINGSTONE
16-17 TEVIOT PLACE
1936

Printed in Great Britain.

PREFACE TO SIXTH EDITION

THE genesis of *Salts and their Reactions* is related in the Preface to the fifth edition (see overleaf).

The rapid rate of progress in the extension of the science of Chemistry increases the difficulty of selecting suitable material for elementary laboratory instruction. For the student attending systematic lectures in which the preparation and properties of gases and the laws of combination of gases are experimentally demonstrated, it appears inadvisable to spend time repeating such experiments on a small scale in the laboratory. Moreover, many items of the apparatus employed in the lecture room for such demonstration purposes could not conveniently be supplied in sufficient numbers for laboratory classes. Again, various matters connected with modern theoretical conceptions that are now frequently dealt with in lectures do not provide suitable practical exercises for elementary classes.

On the other hand, the individual student may become practically acquainted with the properties of the metals, oxides, hydroxides, acidic and metallic radicals, upon which his general chemical knowledge is based, and be introduced to the laws of chemical combination by the performance of simple gravimetric and volumetric experiments.

The provision of such practical instruction is the purpose of this book, and, in addition to the sections on the Nature and Properties of Salts, Salt Formation and Decomposition, Simple Gravimetric Determinations, Reactions of Metallic and Acidic Radicals, Dry-way Reactions and Volumetric Analysis, there is an appendix giving Experiments with some Common Organic Substances. These Organic Substances are more or less familiar to the student in ordinary life, and some acquaintance with their chemical behaviour seems desirable.

In conjunction with a course of systematic experimental lectures, it is hoped that the course of practical work here outlined may prove useful to those preparing for First Examinations (*e.g.* First Science, Preliminary Scientific, First Professional, etc.) of the Universities and of the Royal Colleges of Physicians, of Surgeons, and of Veterinary Surgeons.

L. D.
J. E. M.

PREFACE TO FIFTH EDITION

A NEW edition of this book being called for, the first-named author (L. D.) has collaborated with the second-named (J. E. M.) in place of the late Professor Hugh Marshall, F.R.S., who died in 1913. Professor Marshall was a keen investigator of the properties of Salts, and he will be remembered as the discoverer of that interesting and important group of Salts, the Persulphates.

The teaching of Chemistry to students in laboratories as apart from that done in systematic experimental lectures has necessitated the preparation of notes of laboratory instruction. In 1889 Professor A. Crum Brown originated some notes of the reactions of a number of substances for use in his class of Practical Chemistry, each student being supplied with a leaflet detailing the work to be performed each day. Under the title *Notes on Reactions of Salts,* these notes were issued in several editions between 1889 and 1901. Later they were considerably extended by Dr. Dobbin and Dr. Marshall and, with the addition of an introduction, were published in 1904 under the title *Salts and their Reactions.* Subsequent editions (1908, 1912, and 1920) included sections dealing with volumetric analysis and with some common organic substances.

In the present edition the subject-matter of previous editions has been thoroughly revised and brought up to date, and some new sections have been added.

No attempt has been made to lay down a particular order in which the experimental work should be carried out. The individual teacher will arrange this to meet the special requirements of his mode of teaching the subject.

L. D.
J. E. M.

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THE NATURE AND PROPERTIES OF SALTS

Salts: Historical and General.—The name *salt* (*lat.* sal) was first given to the substance which is still known popularly by that name, with or without a qualifying prefix (common salt, sea salt, rock salt). Gradually it came to be employed as a generic or class name for various other substances which resembled common salt in some respect or other, though different writers apparently had widely different views as to the particular characters which should serve as the basis for the classification. The standard most generally adopted, for a time at any rate, appears to have been the property of dissolving in water, and crystallising from the solution on evaporation of the solvent; but such widely different characters as taste and fusibility or volatility also had prominence assigned to them by some. At one time the term salt was employed to designate not the substance itself, but a supposed elementary principle—that of fixedness and incombustibility. Those salts which were clearly recognised as distinct species were distinguished by special names which were often descriptive of the source, or of some striking property, of the salt, or were derived from the name of the discoverer. Thus we have such names as *sea salt, saltpetre, Epsom salt, sal volatile, Glauber's salt.*

By employing, as a basis of classification, such a general property as that of crystallising from aqueous solution, the substances to which the name salt was applied by the alchemists and early chemists formed rather a heterogeneous group as viewed from our present standpoint. Nevertheless, a large number of these substances (especially those of inorganic origin) still continue to rank as salts in the classification which is adopted at the present time. Among the crystallisable substances, and therefore " salts " in the then accepted sense of the term, which became known comparatively early, there were some of organic origin (vegetable, in most cases) which possessed peculiar properties distinguishing them markedly from other crystalline salts. Their solutions all possessed a sour taste, and also produced striking changes of colour when added to certain vegetable

extracts; for example, purple tincture of litmus (a colouring matter obtained from some lichens) was changed to bright red, as was also blue syrup of violets, on the addition of a small quantity of one of these sour solutions. These solutions were found also to have the property of dissolving many substances insoluble in water, as shown by their corrosive action on certain metals; in some cases (with the metals, and also chalk, for example) the process was accompanied by brisk effervescence. These substances were classed together as "*acid* salts," in reference to their sour taste in solution (*lat.* acidus, sour). It was found that the above-noted peculiarities of "acid salts" were shared also by some substances which did not possess the property of crystallising from aqueous solution. Although deficient in this respect, these were nevertheless classed as "acid salts," because they possessed the acid character so markedly that their kinship with the crystalline "acid salts" could not be overlooked. The most important of the substances thus included as "acid salts" were not of organic origin, and are even yet referred to as the "mineral" acids. The three best known were: "oil of vitriol," obtained by distilling the vitriols (a class of salts which were so named on account of the glassy appearance of their crystals); "spirit of salt," obtained by distilling common salt with alum, with one of the vitriols, or with oil of vitriol; and "aqua fortis," similarly obtained by distilling saltpetre with alum, with a vitriol, or with oil of vitriol.

In addition to the so-called "acid salts," a number of other substances were early recognised as possessing, in common, certain peculiar properties which marked them out as a special class of salts by themselves. Their aqueous solutions all had the same "mawkish" taste; they acted upon various vegetable colouring matters in a manner the reverse of that observed with acids, restoring the original colour to tincture of litmus or syrup of violets which had been reddened by acid solutions, and, if added in quantity more than sufficient to produce that change, imparting a distinct blue colour to the tincture of litmus and a green to the syrup of violets; yellow extract of turmeric root was turned brown by them, and this change could be reversed by acid solutions. Substances belonging to this class were called "*alkaline* salts." The word *alkali* is of Arabic origin, and is probably derived from the name of a plant yielding ashes from which an alkaline salt could be extracted in

considerable quantity. The alkaline salts clearly distinguished in comparatively early times were the *vegetable alkali*, later known as potash, obtained by the lixiviation of wood ashes and evaporation of the solution, or from the ashes of the tartar deposited in wine casks during fermentation; the *mineral alkali*, later known as soda, found in some rainless deserts and dissolved in the water of certain lakes; and the *volatile alkali* obtained by distillation from animal matters such as hair, horn, etc. Moreover, it was known at an early period that new substances, possessing the alkaline character in a much more marked degree, could be prepared from the first two of these alkaline salts by the action of slaked lime on their aqueous solutions, and evaporation of the clarified liquids to dryness. On account of their highly corrosive action on organic tissues, these new substances were called the *caustic* alkalies, and, in contradistinction to them, those from which they were prepared became known as the *mild* alkalies.

These two classes of salts, acid and alkaline, were found to be mutually destructive of each other's characteristic properties when their aqueous solutions were mixed, and, when the resulting solutions were evaporated, substances were obtained which, like common salt, yielded solutions that were neither acid nor alkaline, and otherwise more or less closely resembled common salt in general behaviour. Such substances were, therefore, called " mixed salts " or " compound salts." To take a particular example: when spirit of salt was " saturated " with mild mineral alkali (sodium carbonate), so that the solution no longer showed any acid character, and the resulting solution was evaporated, crystals of common salt were obtained. The same result was arrived at by using caustic mineral alkali (sodium hydroxide), the only difference being that whereas in the former case the process of saturation was attended with brisk effervescence, in the latter this was absent.

" Alkaline salts " were not the only substances which could saturate " acid salts " to produce new salts of the mixed type; this property was shared by many of the " earths," which were substances conspicuously fire-resisting and insoluble in water. These earths included chalk and quicklime (which were looked upon as merely varieties of the same substance, although the latter was known to be somewhat soluble in water while the former was not appreciably soluble), magnesia, and the " calces " or ashes obtained when metals were heated in

air. It was also known that certain metals, when dissolved by " acid salts," saturated these and gave the same " mixed salts " as were obtained from their calces.

Notwithstanding the knowledge of salts and their properties which was gradually accumulated, no reasonable theory as to their real nature was possible until the foundation of modern chemistry was securely laid, in the latter half of the eighteenth century, by the recognition of the true character of the chemical actions which take place during ordinary combustion and the calcination of metals. The metallic calces were then found to be compounds formed by the union of the metals—elements —with oxygen—likewise an element. It was also found that many substances which formed acids in an aqueous solution were compounds of oxygen with non-metallic elements, such as sulphur and phosphorus. After this the name salt became restricted to those substances which had been previously classed as " mixed salts," and the original " acid salts " were called simply **acids.** The oxides, etc., which saturated acids to form salts were classed together as **bases,** and those bases which dissolved in water to form alkaline solutions were specially designated as *alkalies* and *alkaline earths.* The substances previously known as the mild alkalies had now been recognised as really " mixed salts " derived from an acid which possessed the acid character to a very feeble extent. The exact nature of the alkalies and alkaline earths had not at that time been proved ; but from analogy it was assumed that they also must be oxidation products of metals, although the metals themselves were not obtainable by any means then available.

Towards the close of the eighteenth century it was supposed that all acids must be constituted similarly to those whose composition had been made out with certainty—*i.e.* that they also must be oxides (for at this time the name acid was applied to the substances which are now called *acid anhydrides*). Consequently the acid corresponding to common salt (then called muriatic acid or spirit of salt) was assumed to be the oxide of some unknown element which held the oxygen so firmly that it could not be withdrawn from it. The name oxygen (signifying the acid-producer) itself indicates the importance attached to the part which oxygen was supposed to play in the composition of all acids.

From the point of view indicated above, salts were regarded

as being composed of two oxides of opposite character—one basic and the other acidic—united together, and the presence of oxygen was assumed in every case, even although it was sometimes found impossible (as in the case of common salt itself) to prove its presence, despite the most exhaustive endeavours to do so.

The two-oxide, or *dualistic*, view of the constitution of salts was commonly accepted up till the beginning of the nineteenth century, when the experiments of Davy and others led to the conclusion that muriatic acid and its salts did not contain oxygen, but were compounds of an elementary substance—chlorine—with hydrogen and with the metals respectively. This conclusion was greatly strengthened later by the discovery of other substances which had all the characters of elementary substances, and resembled chlorine in that they were capable of forming typical acids by union with hydrogen, and salts by union with metals. On account of this latter property, these elements were all classed together as the *halogens* ("salt-producers").

For some time after the adoption of Davy's view as to the composition of muriatic acid (or hydrochloric acid, as it then came to be called), a distinction was drawn between those acids which contained oxygen (oxygen acids) and those which did not (hydracids); but in course of time this distinction was recognised as too artificial, and in order to bring the two groups into one general class, the name acid was no longer applied to acid anhydrides such as sulphuric anhydride (to give this substance its modern name), but was transferred to the compounds which they formed with water. These acids, which formerly had been designated "hydrated acids," resembled the hydracids, such as hydrochloric acid, in being hydrogen compounds in which the hydrogen was replaceable by metals to form salts. That part of an acid which was not hydrogen replaceable by metals was called the *salt radical* of the acid, because it was the essential or radical part of the series of salts derived from that acid. For example: all the hydrogen of sulphuric acid, H_2SO_4, being replaceable by metals, the salt radical or **acidic radical,** as it is now commonly called, was the group SO_4. This group is unstable by itself and unknown in the free state, but is an essential part of all sulphates. This view of the constitution of acids is the one generally accepted at present.

It is to be noted here that many acids contain hydrogen which is not replaceable by metals; such hydrogen forms part of the acidic radical. This is the case with acetic acid, the formula for which is generally written $HC_2H_3O_2$, because only one H atom is replaceable by metal, the acidic radical being $C_2H_3O_2$. Acids like sulphuric acid, which have two or more atoms of replaceable hydrogen in each molecule, may produce intermediate salts in which only part of the hydrogen is replaced, *e.g.* $KHSO_4$. Such salts are called **acid salts,** because they possess the character of acids, inasmuch as they still contain replaceable hydrogen. In contradistinction to these, salts which contain no replaceable hydrogen (all the active hydrogen of the acid having been replaced by metal) are called **normal salts.** There is another class, known as **basic salts,** which occupy a position intermediate between the normal salts and the bases, just as the acid salts stand between the normal salts and the acids. Substances which behave as bases include many metallic oxides and hydroxides, and a basic salt may still contain oxygen or hydroxyl of the base which is replaceable by acidic radical to form a normal salt. Examples of basic salts are antimonious oxychloride, SbOCl, and lead hydroxynitrate, $Pb(OH)NO_3$. The former of these is intermediate between antimonious oxide, Sb_2O_3, and antimonious chloride, $SbCl_3$, and the latter between lead hydroxide, $Pb(OH)_2$, and lead nitrate, $Pb(NO_3)_2$. By interaction with the appropriate acids, these basic salts can be converted into the respective normal salts.

Just as an acidic radical may be either elementary or compound, so also the other part of a salt may be either elementary or compound. Thus far, it has been assumed to consist of metal, and therefore to be simple. Certain substances, however, have long been known (*e.g. sal ammoniac,* ammonium chloride), and many others are known now, which possess the character of salts and yet have no metal entering into their composition. It is found that these compounds are strictly analogous to metallic salts as regards their composition, except that, in place of metal, they contain a complex group which, as a rule, is unstable by itself and cannot be isolated. The name **metallic radical** is applied to such a group, and also quite generally to anything which plays the part of metal in a salt, whether it be metal itself or a compound radical. The best-known examples of salts containing a compound metallic

radical are the ammonium salts, which are compounds of acidic radicals with the metallic radical ammonium, NH_4; in many respects the ammonium salts exhibit the closest resemblance to the potassium salts.

It is evident, from what has already been stated, that salts may possess the simplest composition possible for a compound, or may be of varying degrees of complexity, some being exceedingly complex indeed. The simplest salts are those typified by sodium chloride, NaCl, in which both metallic radical and acidic radical are elementary: as examples of a more complex type we may take ammonium chloride, NH_4Cl, and sodium nitrate, $NaNO_3$, in each of which one radical is compound; ammonium nitrate, NH_4NO_3, is a comparatively simple example of the most complex class, in which both radicals are compound.

The composition of compound radicals is exceedingly varied: in the majority of compound acidic radicals oxygen is an important constituent, in others it is entirely absent; nitrogen is one of the commonest constituents of compound metallic radicals, carbon and hydrogen being frequently associated with it. However, the fact that in such a salt as ammonium nitrate, nitrogen is a constituent of both radicals, indicates clearly enough that there is no hard-and-fast distinction to be drawn between the various elements as regards capacity for the formation of metallic radicals or of acidic radicals. Many metals themselves can form part of acidic radicals, as shown by the position of manganese in potassium permanganate, $KMnO_4$, where the metallic radical is K and the acidic radical MnO_4. In ammonium bichromate, $(NH_4)_2Cr_2O_7$, the metallic radical is ammonium and the acidic radical Cr_2O_7; in chromic nitrate, $Cr(NO_3)_3$, the positions of chromium and nitrogen are reversed, the latter being now a constituent of the acidic radical, and the former constituting the simple metallic radical. It is to be noted, however, that although a typical metal may enter into the composition both of metallic radicals and of acidic radicals, it always constitutes the metallic radical in the case of a salt formed by its union with one other element only; while a typical non-metallic element, if it forms a salt by union with one single element, always constitutes the acidic radical of such a salt.

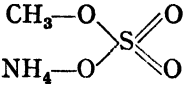
The necessity of clearly distinguishing between metal and metallic radical is further accentuated by the fact that many metals when combined with acidic radicals give rise to more

than one set of salts. Thus, there are two distinct sets of "iron salts"—ferrous and ferric. In each of these two sets of salts the metallic radical is simple, consisting of iron only, yet the one, as a metallic radical, is essentially distinct from the other; the salts which contain them united to the same acidic radical have quite different properties. Analogous cases are known among acidic radicals. The formula for potassium manganate is K_2MnO_4, and that for potassium permanganate is $KMnO_4$: the two acidic radicals have the same chemical composition, but are essentially distinct, and their salts are widely different in appearance and properties.

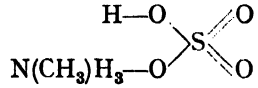
In view of the wide diversity in composition exhibited by salts, as indicated above, it might almost be supposed that any chemical compound whatever could be included in the term, the compound being looked upon as composed of two parts only, one of which might represent the metallic radical, and the other the acidic radical. Such, however, is not the case; for, in order that a compound may be classed as a salt, it is necessary that the properties of the compound, especially those exhibited in solution, should be divisible into two groups, those of one group being referable to the metallic radical, and those of the other to the acidic radical. In other words, all those salts which have a metallic radical in common behave similarly to one another under certain conditions, and those which have an acidic radical in common also behave similarly to one another under certain conditions. It is therefore possible to speak of the reactions of a particular metallic radical, or of a particular acidic radical; and the reactions of a salt are, in general, those of its metallic radical *plus* those of its acidic radical—not a special set of reactions peculiar to itself as a single substance.

The following case may serve to show that the division into metallic radical and acidic radical is not carried out in an arbitrary manner, merely on inspection of the formula of a substance. There is a well-crystallised saline substance possessing the composition represented by the empirical formula NCH_7SO_4. This substance, when dissolved in water, does not behave like a sulphate, but it shows all the properties of an ammonium salt, and its metallic radical is therefore ammonium, NH_4, and the remainder, CH_3SO_4, is its acidic radical. This is expressed by writing the formula in the form $NH_4CH_3SO_4$; the radical CH_3SO_4 is common to a large series of salts. There is another substance, differing markedly from the preceding one in

many respects, but agreeing in composition with the empirical formula given above. In solution this substance exhibits the properties of an acid salt (*i.e.* it still contains replaceable hydrogen) and of a sulphate; its formula may therefore be written NCH_6HSO_4, the acidic radical being SO_4, and the metallic radicals H (the acidic hydrogen) and the group NCH_6. The latter radical is called methyl-ammonium, and its formula is written $N(CH_3)H_3$, to indicate that it corresponds to ammonium with the methyl group (CH_3) in place of one atom of hydrogen. Extended formulæ for the two salts mentioned in this paragraph are :—



and



The property of dissolving in water and crystallising from the solution on evaporation of the solvent has been mentioned as a common character of salts (see p. 1), and it may be pointed out here that in some cases the crystals thus obtained are anhydrous (*e.g.* K_2SO_4; $NaNO_3$; NH_4Cl.); whereas in others, crystals of salt hydrates (*e.g.* Na_2SO_4, 10 H_2O; $BaCl_2$, 2 H_2O; $CaCl_2$, 6 H_2O) are formed in which the salt is combined with a definite proportion of " water of crystallisation." These salt hydrates frequently exhibit an instability on exposure to the atmosphere, dependent upon the relative vapour pressures of the hydrate and of the air respectively. Thus the vapour pressure of washing soda (Na_2CO_3, 10 H_2O) is generally greater than that of the water vapour in the atmosphere, and the crystals lose water and form a lower hydrate. This phenomenon is called **efflorescence,** the transparent crystals becoming coated with an opaque film. When the vapour pressure of the hydrate (*e.g.* $CaCl_2$, 6 H_2O) is distinctly less than that of the water vapour in the atmosphere, the hydrate takes up water from the atmosphere, forming a solution. Such a salt is said to **deliquesce.**

In addition to water, some salts dissolve in other solvents and occasionally crystallise from such solutions with " solvent of crystallisation " (*e.g.* from alcohol solution $CaCl_2$, 4 C_2H_5OH).

Solubility of salts in water (see Table of Solubilities on inside of front cover).—Salts vary very much in respect of solubility; some dissolve at ordinary temperatures in a fraction of their weight of water, others are so slightly soluble that they are generally spoken of as insoluble in water. It may,

however, be assumed that no salt is absolutely insoluble in water, though in some cases the solubility is so slight that it cannot easily be determined; what is meant, therefore, when it is stated that a salt is insoluble in water is, that the salt is soluble to such a minute extent that, with the quantity of solvent usually involved, the weight of substance dissolved is negligible.

As a rule, the solubility of a salt increases with rise of temperature, sometimes only to a small extent (*e.g.* sodium chloride), sometimes very greatly (*e.g.* potassium nitrate). There are, however, exceptional cases in which the solubility diminishes as the temperature rises; thus, a cold saturated solution of calcium citrate deposits a white precipitate of the salt when warmed (see p. 151).

In looking at the question of solubility it is important to remember the possibility of having supersaturated solutions. A solution is said to be *saturated* with a substance when its composition is such that it is in equilibrium with that substance, so that, on being shaken up with the solid, the concentration does not change; an *unsaturated* solution is less concentrated than this, and therefore dissolves some of the solid if shaken up with it; a *supersaturated* solution is more concentrated than a saturated one, and, if it is brought into contact with some of the solid, *solute*, *i.e.* the substance held in solution, separates out until the solution which remains (if any) is saturated. In some reactions by which salts are produced, supersaturated solutions frequently result, and crystals of the new salt may not be obtained for some time; in such cases crystallisation may be hastened by vigorously shaking or stirring the solution, and once the process has begun it proceeds until a state of equilibrium is established. The most certain method of starting crystallisation in such cases is to drop a particle of the solid salt into the supersaturated solution, or "seed" it. Where the new salt is less soluble in hot water than in cold, the formation of a precipitate may be accelerated by heating, as in the above-mentioned case of calcium citrate.

In the above paragraphs and throughout this book the solubility of salts in water is given in relation to "ordinary distilled water." The recently discovered "*heavy water*" behaves differently from "ordinary water" with regard to solution of salts and in many other ways. Thus the solubility of the chlorides of sodium and barium is about 15 per cent.

less in " heavy " than in " ordinary " water. The abundance and cheapness of " ordinary " as compared with " heavy " water make it improbable that its place in the laboratory will be taken by " heavy " water except in very special experiments.

Colours of salts.—The great majority of salts are practically colourless in the solid state, and yield colourless solutions ; but the salts of certain metallic radicals, as well as those of certain acidic radicals, exhibit well-marked colours. In *dilute* aqueous solution the different salts of any one metallic radical which has coloured salts, as a rule, show practically the same colour, independently of the acidic radical (assuming that the latter is not one which itself gives rise to coloured salts) ; the corresponding statement holds true for the different salts of any acidic radical which has coloured salts. Thus, dilute solutions of cupric salts are blue ; of cobaltous salts, pink ; of nickel salts, green ; of chromates, yellow ; of permanganates, purple-red. With concentrated solutions, or the crystallised salts themselves, the colours are often different ; a saturated solution of cupric chloride is green, while one of cupric sulphate is blue, and the solids exhibit similar differences. Although in cases such as these the salt hydrate (*i.e.* the salt with water of crystallisation) has a colour at least approximating to that of the aqueous solution, the anhydrous salt may have a different colour altogether ; *e.g.* anhydrous cobaltous chloride and iodide are respectively blue and green.

Chemical behaviour of salts : double decomposition.—The most striking character of salts in general is the great readiness with which they take part in the kind of chemical change known as double decomposition. This action consists in the mutual exchange of metallic radicals and of acidic radicals between two salts when they are brought together ; thus, if AX and BY be taken as general formulæ for any two salts (A and B representing metallic radicals and X and Y acidic radicals), double decomposition between these means the formation of the other two salts AY and BX, in accordance with the equation—

$$AX+BY=AY+BX.$$

If either AY or BX is practically insoluble in water, and the two original salts are soluble, this kind of action takes place on mixing solutions of the soluble salts ; the insoluble salt separates as a *precipitate*, and the action goes on until one or other of the original salts is used up. If the proper proportions are

employed, neither of the original salts will remain after the reaction. To take a few examples (see Table of Solubilities): When solutions of a silver salt (say silver nitrate) and of a chloride (say barium chloride) are mixed, a white precipitate of silver chloride is immediately produced and barium nitrate remains in solution—

$$2\,AgNO_3+BaCl_2=2\,AgCl+Ba(NO_3)_2.$$

When solutions of a barium salt (say barium chloride) and of a sulphate (say sodium sulphate) are mixed, a white precipitate of barium sulphate is produced, and sodium chloride remains in solution—

$$BaCl_2+Na_2SO_4=BaSO_4+2\,NaCl.$$

In certain instances both of the resulting salts are insoluble, and in these cases, if suitable proportions of the original salts are employed, the resulting liquid may be free from all but the merest traces of dissolved substance. Thus when solutions of silver sulphate and of barium chloride are mixed, silver chloride and barium sulphate are produced, both of which are all but completely precipitated as insoluble salts—

$$Ag_2SO_4+BaCl_2=2\,AgCl+BaSO_4.$$

Double decompositions such as these take place practically instantaneously, the precipitates appearing immediately the solutions are mixed, provided the latter are moderately concentrated. With exceedingly dilute solutions the precipitates appear more gradually, and in some cases, if the new salts are not very sparingly soluble, supersaturation may persist for some considerable time. Precipitates of even moderately soluble salts may often be obtained by double decomposition, by mixing together concentrated solutions which contain the appropriate radicals in the form of very soluble salts, although when only moderately concentrated solutions are employed, there may be no apparent action; in such cases, if precipitation does occur, the change may be far from complete. Thus, if concentrated solutions of potassium acetate and sodium sulphate are mixed, potassium sulphate crystallises out—

$$2\,KC_2H_3O_2+Na_2SO_4=K_2SO_4+2\,NaC_2H_3O_2;$$

but the residual solution still contains a proportion of all the four salts represented in the equation. As somewhat less

concentrated solutions of the original salts give rise to no formation of solid potassium sulphate, a question naturally arises, which may be put in the general form : Does any action take place when solutions of two salts are mixed without the formation of any precipitate ? It would appear that action does take place in all such cases. The solution obtained by mixing together solutions containing two salts AX and BY in equivalent proportions coincides exactly in all its physical and other properties with that obtained by mixing similar solutions of the two salts AY and BX ; it must therefore be assumed that in both these cases action takes place, and that the state of affairs in the mixture is an equilibrium expressed by the equation—

$$AX+BY \rightleftharpoons AY+BX,$$

so that four salts are present in the mixture, and it is immaterial which of the two pairs is employed originally.

This assumption is borne out by the fact that one and the same mixed solution may yield different salts on crystallisation, depending on the temperature at which this takes place. For example, a solution prepared by dissolving magnesium sulphate and sodium chloride in water yields crystals of the latter salt when it is evaporated at moderately high temperatures, but if the temperature is low, then sodium sulphate crystallises out. The state of affairs in the solution is represented by the equation—

$$MgSO_4+2\,NaCl \rightleftharpoons MgCl_2+Na_2SO_4.$$

At high temperatures sodium chloride is the least soluble of these four salts, but at low temperatures sodium sulphate is the least soluble, and the relative solubility determines which constituent will be first deposited. In the manufacture of potassium nitrate by the interaction of sodium nitrate and potassium chloride in hot aqueous solution, the success of the process depends upon the relatively sparing solubility of sodium chloride (see p. 31).

Closely related in some respects to double decomposition are those actions in which one metal displaces another in a salt. Thus, when a strip of iron or zinc is immersed in a solution of cupric sulphate, ferrous sulphate or zinc sulphate is formed in solution and metallic copper is deposited ; when metallic copper is immersed in a solution of silver nitrate, cupric nitrate is formed in solution and metallic silver is deposited. Similar

actions take place with some acidic radicals—those which are not compound ; thus, iodine displaces sulphur from a sulphide, bromine displaces iodine from an iodide, chlorine displaces bromine from a bromide.

Acids as hydrogen salts.—As regards their reactions in aqueous solution, and especially in the matter of double decompositions, acids behave just like the soluble salts which contain the same acidic radical, and therefore might be looked upon as a particular class of salts, the metallic radical being hydrogen. The liberation of hydrogen by the action of a metal, such as zinc, on dilute sulphuric acid, is analogous to the deposition of copper when iron or zinc is immersed in a solution of cupric sulphate. Hydrogen itself is not a metal as regards its physical characters, but it can play the part of a metallic radical in the formation of salts ; these salts have certain properties common to themselves and not shared by other salts, and it would be just as correct to speak of the reactions of hydrogen salts as to speak of the reactions of potassium salts or of ammonium salts.

As a matter of fact, acids are frequently employed in preference to the corresponding salts of a metallic radical for bringing about double decompositions, because the action takes place just as readily in the one case as in the other, and there are certain advantages (for example, great solubility and easy volatility) which the hydrogen salt may possess. Thus, if it is desired to prepare silver chloride from silver nitrate, the soluble chloride employed to effect the double decomposition is generally hydrogen chloride, *i.e.* hydrochloric acid—

$$AgNO_3 + HCl = AgCl + HNO_3.$$

In this case, if an excess of hydrochloric acid is employed, all the substances remaining at the end of the action, other than silver chloride, are easily volatile, and the silver chloride can be obtained pure more easily than would be the case were some metallic chloride employed in the interaction.

Bases as a particular class of salts.—The basic hydroxides may be looked upon as a special class of salts, in which the acidic radical is the hydroxyl group, OH. Thus the soluble hydroxides (the alkalies and alkaline earths) sometimes enter into double decompositions, similar to those into which salts enter, giving rise to precipitates consisting either (*a*) of an insoluble metallic hydroxide or (*b*) of an insoluble salt of the

metal, which was previously united to hydroxyl. For example, (*a*) when solutions of silver nitrate and sodium hydroxide are mixed, there is an immediate precipitation of silver hydroxide—

$$AgNO_3+NaOH=AgOH+NaNO_3;$$

and (*b*) when solutions of barium hydroxide and sodium sulphate are mixed, there is an immediate precipitation of barium sulphate—

$$Na_2SO_4+Ba(OH)_2=2\,NaOH+BaSO_4.$$

If the hydroxides be looked upon as a class of salts, then the hydrogen salt corresponding to them would be water itself, HOH. There are chemical actions, however, in which water behaves like a very feeble acid, and others in which it behaves like a very feeble base; these will be referred to later (pp. 18, 46). The neutralisation of acid and alkali becomes, then, from the present point of view, merely a particular kind of double decomposition—

$$NaOH+HCl=NaCl+HOH.$$

Relative strengths of acids and of bases.—In the preceding paragraph reference was made to the behaviour of water as a *feeble* base and as a *feeble* acid, and it is desirable to consider here the question of what is meant by the "strength" of an acid or of a base.

It was early recognised that acids did not all possess the acid characteristics to the same degree. Some acids produce only a slight change in the colouring matter of litmus, while others change it to a bright and decided red, even when added in very small quantity; the sour taste of some acids in solution is much more marked than that of others; substances which are insoluble in water, but soluble in acids, dissolve to a greater extent in some acids than they do in others. This is expressed by saying that some acids are stronger than others. It is to be observed that the relative strength of an acid is a matter quite distinct from its state of concentration or dilution; and to use the term **weak** sulphuric acid when **dilute** sulphuric acid is meant and **strong** sulphuric acid in place of **concentrated** is misleading. Dilute sulphuric acid possesses the typical acid characters in a very high degree, and is, though dilute, a strong acid.

Early attempts to arrange acids in a series, according to

their relative strengths, were based on a fallacious principle; one acid was said to be stronger than another if it could completely decompose a salt of that other and liberate the acid. For example, sulphuric acid was supposed to be a stronger acid than hydrochloric acid, because, when a solid chloride, such as sodium chloride, is heated with concentrated sulphuric acid, it is completely decomposed, with evolution of hydrochloric acid. As a matter of fact, the apparent relative weakness of hydrochloric acid is due to its greater volatility as compared with sulphuric acid. Since the typical characters of acids, as of other salts, are best exhibited only when these are in moderately dilute solution, comparisons of this kind should be made only when the substances are dissolved in a considerable proportion of water; in that case the results obtained are not influenced by such extraneous circumstances as difference of volatility, etc.

In order that the results obtained may be comparable among themselves, it is necessary that the conditions should correspond as closely as possible, especially as regards temperature and concentration. With respect to the latter condition, it is to be remembered that acids derive their peculiar properties from the replaceable hydrogen which they contain; and therefore when their solutions are to be compared as regards their acid character, it is necessary that they should coincide in respect to the concentration of this common constituent. Quantities of different acids which contain the same weight of replaceable hydrogen are said to be **equivalent** to one another; so that equivalent weights are proportional to the molecular weights in the case of monobasic acids (containing one atom of replaceable hydrogen in the molecule), to half the molecular weights in the case of dibasic acids (containing two such atoms), to one-third of the molecular weights in the case of tribasic acids (containing three such atoms), and so on.

Numerous methods of measuring the relative strengths of acids and of bases have been devised. Mention may be made of (1) measurement of the electric conductivities of equivalent solutions (see Electrolysis, p. 18); (2) the thermo-chemical method, based upon measurement of the heat of neutralisation (see p. 35); and (3) the accelerating influence of acids or bases upon certain reactions such as the hydrolysis of cane sugar, or of esters (see Hydrolysis, p. 18). The strongest acids are those generally referred to as the mineral acids; compared with these

the majority of organic acids are exceedingly weak. Further, the strongest acids of all are monobasic (hydrochloric acid, nitric acid, etc.), the strongest dibasic acid (sulphuric acid) being decidedly inferior to them; tribasic acids, such as phosphoric acid, are as a class still weaker than the dibasic acids. This is illustrated in the following table, which gives the relative strengths of a few typical acids as measured by the three methods mentioned above :—

	Electric Conductivity	Thermo-chemical	Sugar Hydrolysis
Hydrochloric . . .	100	100	100
Nitric.	99·6	100	100
Sulphuric	65·1	49	53
Oxalic	19·7	24	18·6
Phosphoric	7·3	13	6·2
Acetic	0·4	3	0·4

It will be observed that the order in which the acids follow each other is the same, though the numbers obtained in the different methods vary somewhat.

The relative strengths of bases can be determined by methods more or less resembling some of those applicable to acids, and the results are analogous to those obtained in the case of the acids. Thus by measurement of the rate at which bases hydrolyse methyl acetate the following numbers were obtained :—

Lithium hydroxide . . .	100	Triethylammonium hydroxide .	14
Sodium ,, . . .	98	Diethylammonium ,, .	16
Potassium ,, . . .	98	Ethylammonium ,, .	12
Tetraethylammonium hydroxide	75	Ammonium ,, .	2

The strongest bases are the hydroxides of the alkali metals, but those of the alkaline earth metals are very slightly inferior to them. Although ammonium hydroxide is a comparatively feeble base, it will be observed that the substituted hydroxides are much stronger and in some instances have a strength approaching that of the alkalies.

Many metallic hydroxides, which are almost insoluble in water, are very feeble bases and, in contact with very strong bases, they act as weak acids. Such hydroxides are termed *amphoteric* hydroxides. Reference may be made to the behaviour of lead hydroxide (p. 104), zinc hydroxide (p. 117), and aluminium

hydroxide (p. 125) respectively, when mixed with a solution of sodium hydroxide. In each case the hydroxide dissolves, yielding a solution of the corresponding sodium salt, *i.e.* sodium plumbate, sodium zincate, and sodium aluminate.

In certain cases, very weak bases and very weak acids do not interact to form salts, or at least not in aqueous solution; in some instances of this kind the salts can be formed under other conditions, and it is then found that the salts so produced are decomposed when brought into contact with water, with formation of the respective acid and base. Decomposition by water in this way is called **hydrolysis.**

While the solutions of the normal salts which can be formed by the interaction of a strong acid and a strong base are neutral in reaction, the salts which are derived from a strong acid and a weak base generally yield acid solutions, and those derived from a weak acid and a strong base generally yield alkaline solutions. Examples of the latter are presented by the soluble carbonates, sulphites, etc.; while several aluminium, ferric, and cupric salts exemplify the former state of affairs (see pp. 47, 69). These cases afford instances of compounds intermediate in their character between the salts which yield neutral solutions and those compounds referred to in the preceding paragraph; in contact with water partial hydrolysis takes place, with liberation of strong acid or strong base, as the case may be, and this exhibits its characteristic reaction when an appropriate test-paper is introduced into the solution. (This distinction between normal salts which yield acid, neutral, or alkaline solutions, must not be confused with the differentiation of salts, constitutionally, into acid, normal, and basic salts.) In the case of normal salts derived from polybasic acids, hydrolysis is sometimes found to take place to a considerable extent even although the acid itself is a moderately strong one, as, for example, in the case of phosphoric acid (see p. 46).

Electrolysis.—One of the most remarkable properties of aqueous solutions of typical salts is their power of conducting electricity. The conducting power of such solutions, however, differs markedly from that possessed by ordinary (metallic) conductors, for the passage of the current is invariably accompanied by chemical changes of a very definite kind. When two plates of suitable conducting material (called the **electrodes**), each of which is connected with a separate pole of an electric battery, are inserted, without touching each other, into a saline

solution contained in a suitable vessel (called the **electrolytic cell**), a current passes through the circuit, as may be shown by introducing a galvanometer also into the circuit. At the same time it is found that there is a separation of some substance at each of the electrodes, the particular substances depending on the salt dissolved in the solution. In all cases the substances first set free would appear to be the metallic radical and the acidic radical, the former at the electrode connected with the negative pole of the battery (called the **cathode**), and the latter at the electrode connected with the positive pole (called the **anode**). The separation of the two radicals of a salt in this way is called **electrolysis**, and the solution, in which it takes place, an **electrolyte.**

The final products of an electrolytic decomposition may, however, be the result of secondary actions, and be entirely different from the primary products. When solutions of cupric salts are electrolysed, metallic copper is deposited on the cathode ; but when solutions of potassium salts are electrolysed, although potassium may be momentarily liberated, it cannot exist in presence of the water, and there is immediate formation of potassium hydroxide in the solution surrounding the cathode, hydrogen being simultaneously evolved. When solutions of iodides are electrolysed, iodine is liberated at the anode ; but with solutions of sulphates there is evolution of oxygen, because the sulphate radical (SO_4) cannot exist in the free state, and as soon as it is liberated it interacts with water, forming sulphuric acid in the solution immediately surrounding the anode, and liberating oxygen.

The products of electrolysis make their appearance only at the electrodes, and, as the salt is at first dispersed equally throughout the solution, the metallic radical and acidic radical must gradually travel, the one towards the cathode and the other towards the anode. Faraday called these two parts, which travel, the **ions** ; the metallic radical, which travels towards the cathode, being distinguished as the **cation**, and the acidic radical, which travels towards the anode, as the **anion.**

Solutions of acids and alkalies likewise conduct the electric current and are decomposed by it—*i.e.* they are electrolytes—so that in this respect also these substances are to be looked upon merely as special classes of salts ; if they are so classed, then the general statement holds : Only salts can form electrolytes. The solid salts themselves are not electrolytes,

but fused salts, as well as their solutions in water (also in some other liquids) are.

In this connection the behaviour of hydrochloric acid may be shortly referred to, as it is interesting and typical. Pure liquefied (anhydrous) hydrochloric acid does not conduct electricity, or, at least, not to any noteworthy extent; in this respect it resembles pure water. Aqueous solutions of hydrochloric acid, however, are good conductors of electricity, and, on the passage of the current, are decomposed into hydrogen and chlorine. A mixture containing about 18 per cent. of hydrochloric acid conducts better than any other mixture of the two, the conductivity falling off as the composition recedes from that value. Similar behaviour is observed in the case of acids which are miscible with water in all proportions—they show a maximum of conductivity at some intermediate dilution.

Owing to their limited solubility in water, the majority of metallic salts do not behave like the acids in the above respect, for the saturated solution is generally the best conductor. With very soluble salts, however, the maximum conductivity may correspond to some intermediate concentration, as in the case of the acids.

When the conductivities of solutions of different concentrations are compared, not as regards their *absolute* values, but *in proportion to the quantity of solute* (see p. 10) *present*, it is found that, without exception, dilute solutions conduct better than more concentrated ones; so that a solution which is, say, twice as concentrated as another solution of the same substance, is not twice as good a conductor.

The conductivity of an electrolyte is affected by change of temperature, but in the reverse sense to that observed in the case of a metallic conductor; that is to say, the conductivity of the solution increases with rise of temperature.

As shown by Faraday, there is a very definite connection between the strength of current passing through an electrolyte and the amount of decomposition which takes place, and the regularities observed are known as Faraday's Laws of Electrolysis. The amount of salt decomposed in an electrolytic cell is in each case proportional to the *quantity* of electricity, irrespective of the rate at which the current is passed, or of the potential at the electrodes, so long as the potential is high enough to overcome the polarisation and keep the current passing. Further, the amount of salt decomposed by a given

quantity of current is exactly proportional to the chemical equivalent of that salt. For example, if a number of electrolytic cells, arranged in series, are filled with solutions of various chlorides, and a current of electricity is passed through them (so that the current is exactly the same in every cell), it is found that the quantity of chlorine liberated at the anode is in each case identical, quite irrespective of what the metallic radical may be, provided the conditions are such that secondary reactions do not take place. Thus, if the chlorides were hydrochloric acid, sodium chloride, calcium chloride, and ferric chloride, the quantities of salt decomposed would be in the proportion $HCl : NaCl : \frac{CaCl_2}{2} : \frac{FeCl_3}{3}$. Similarly, if a current is passed through solutions of a series of salts derived from the same metallic radical, the quantity of metal liberated is the same in all cases, irrespective of the acidic radical. For example, a series of acids would all yield the same volume of hydrogen at the cathode.

It is evident that salts in aqueous solution are characterised by the readiness with which they undergo chemical changes in which the metallic radical and the acidic radical become separated from one another. Double decompositions between salts can take place instantaneously in solution, and the feeblest current of electricity passing through an electrolyte brings about a certain amount of electrolysis. Non-saline substances do not, as a rule, exhibit any special tendency to take part in double decompositions, and if they do enter into such reactions the change is slow and gradual. When silver nitrate solution is shaken up with chloroform, $CHCl_3$ (which is appreciably, though sparingly, soluble in water), there is no precipitation of silver chloride ; chloroform is not a salt.

Analogy between the gaseous and dissolved states.—Substances dissolved in liquids are now looked upon as being in a condition which is in many respects comparable with the gaseous state ; the particles of a solute (see p. 10) move about in the solution in much the same way as the particles of a gas do in space, except that in the former case the motion is greatly interfered with by the presence of the solvent. There is a close analogy between the dissolution of a solid in a quantity of solvent and the vaporisation of a liquid into a limited space Each process goes on until equilibrium is reached at a definite concentration—the liquid is then saturated with the solute, and

the space is saturated with vapour—and in each case this concentration is constant for any given temperature. Gas or vapour in a closed vessel exerts a definite pressure, and this *gaseous pressure* depends on the concentration and the temperature. There is an analogous phenomenon, called *osmotic pressure*, due to the solute in a solution, though here the effect is not so obvious as in the preceding case. The " pressure of a gas " may be taken as that pressure which is necessary to prevent the gas expanding to fill a larger space. Similarly the (osmotic) pressure of a solute would be that pressure which must be exerted *upon the solute* to prevent it expanding to occupy a larger volume of solution. The volume of the solution, under constant conditions of temperature, etc., can only increase by taking up more solvent, and the effects of osmotic pressure are directly observable under conditions which allow of this taking place. Thus, if two dishes, one containing pure water and the other an aqueous solution, are placed under a bell-jar, and left for some time, the volume of the solution increases while the volume of the pure water correspondingly diminishes, the water passing to the solution, through the intervening space, in the form of vapour. If a quantity of solution is placed in a bladder (only partially filling it), and this, after the air has been expelled, is tied up and suspended in a quantity of pure water, the solution will increase in volume, owing to water passing through from the outside, so that the bladder will ultimately become distended and subject to considerable internal pressure.

The direct measurement of osmotic pressure is not an easy matter, but experimental results have been obtained which confirm the statements—(*a*) the osmotic pressure exerted by a given quantity of solute is inversely proportional to the volume of the solution which contains it, the temperature remaining constant; and (*b*) the osmotic pressure of a given solution is proportional to its absolute temperature, the volume remaining constant. The osmotic pressure therefore corresponds to gaseous pressure and, if " osmotic pressure " be substituted for " pressure " and " solute " for " gas," then statement (*a*) resembles that derived from Boyle's Law, *i.e.* the pressure of a given quantity of gas is inversely proportional to its volume, the temperature remaining constant; and statement (*b*) the Pressure-temperature Law, *i.e.* the pressure of a given quantity of any gas is proportional to its absolute temperature, the volume of the gas remaining constant. With reference to (*a*)

it may be pointed out that reduction of the volume of a solution involves the removal of the solvent, which is generally effected by evaporation, but the same result may usually be achieved by freezing it out from the solution, since it is only in exceptional cases that the frozen part contains solute. The osmotic pressure exerted by a solute must therefore offer a certain amount of resistance to the processes of evaporation and freezing; this is found to be actually the case, as is evidenced by the fact that the boiling points of solutions are higher, and the freezing points lower, than the corresponding points for the pure solvent. These facts may be expressed in another way, by saying that the presence of a solute lowers both the vapour pressure and the freezing point of a solvent. For a given solvent, the extent to which the boiling point or the freezing point is altered is proportional to the osmotic pressure, and this again is proportional to the molecular concentration of the solute, just as gaseous pressure is proportional to the molecular concentration of the gaseous substance (temperature in both cases being constant). It is thus possible to extend to solutes Avogadro's hypothesis concerning gases, remembering, however, that in the former case "pressure" means osmotic pressure.

When the pressure, temperature, and mass-concentration of a gas are known, the molecular weight can be obtained by a simple calculation; similarly, the molecular weight of a solute can be calculated if its (osmotic) pressure, temperature, and mass-concentration are known.* As has already been indicated, measurement of osmotic pressure cannot easily be carried out, but the two effects which, as already mentioned, are proportional to it—elevation of boiling point, and depression of freezing point—are capable of accurate measurement without much difficulty. By means of such determinations, therefore, it is possible to ascertain the relative molecular weights of dissolved substances.

Molecular weights of dissolved salts.—When the methods of determining molecular weights of solutes are applied in the case of salts (including acids and alkalies) in aqueous solution, results are obtained which do not fit in with other known facts,

* The expression **molar weight** is now used to represent the molecular weight of a substance measured in grams, or its gram molecular weight. For convenience the **mole** of oxygen is taken as 32 grams, this being the weight of oxygen which occupies 22·4 litres at 0° and 760 mm. This volume is known as the **molar volume**, and the weight of a substance in the gaseous state occupying this volume at 0° and 760 mm. is its molar weight.

unless it is assumed that these substances undergo some kind of decomposition in the process of solution. Thus, the smallest possible molecular weight of sodium chloride, as expressed in the formula NaCl, is 58·5 ;* as deduced from the freezing point of aqueous solutions, it is much lower, being little more than half that value in very dilute solutions, but increasing with increasing concentration. Similar results are observed with other salts, the numbers obtained in each case being always less than would be expected from the accepted formula of the salt. In many cases the discrepancies are slight, but in others they are very considerable. When the discrepancy is large, it is found that the aqueous solution of the salt concerned is a good conductor of electricity; but, in those cases where the determination of the molecular weight gives a result closely agreeing with the expected value, the aqueous solution is, as a rule, a very poor conductor.

Similar discrepancies have been observed in the determination of the molecular weights of some substances by the vapour density method. Thus the molecular weight of ammonium chloride determined by this method is little more than half that calculated from the formula NH_4Cl. As soon as it became known that ammonium chloride dissociates when vaporised by heating, a ready explanation of the discrepancy was forthcoming, namely, that the vapour density measured is not that of ammonium chloride itself, but that of a mixture of equal volumes of ammonia and hydrochloric acid, together with a small proportion of undissociated ammonium chloride.

The ionisation hypothesis.—When a salt dissolves in water, it may likewise be looked upon as undergoing dissociation, but the dissociation is of a very different character from that referred to above. It is sometimes named "electrolytic dissociation," because some of the effects of this dissociation first became apparent when an electric current was passed through the saline solution. On account of the products of this dissociation having been called "ions" by Faraday p. (19), the term "*ionisation*" will be used here. As has already been stated (p. 7), a salt may be looked upon as a combination of a metallic radical with an acidic radical. In the solid state a salt generally does not exhibit any electric charge, either positive or negative, and we may suppose either that it is

* **The mole**, or gram molecular weight of sodium chloride = 58·5 grams.

without any charge at all or that one part of it is positively charged and the other part of it is negatively charged, the two charges exactly neutralising each other. The second supposition seems the more probable, since a salt, when dissolved in water, or when fused, behaves as though it had dissociated partially at least into positively charged and negatively charged parts. So long as the solution or the fused salt is undisturbed, these charged parts move about freely, but if the electrodes from an electric battery are introduced, then the positively charged *cations* move towards the negative electrode or *cathode*, and the negatively charged *anions* towards the positively charged electrode or *anode*.

When an electric current is passed through a saline solution —even when the electrodes are far distant from each other— the cations instantly begin to be discharged on the cathode and the anions on the anode. It is therefore concluded that the already decomposed parts of the molecules or ions act as the carriers of the electric charges and thus enable the current to pass through the solution. Further evidence that electric energy is not expended in splitting up the dissolved salt molecules is that electrolytic solutions obey Ohm's Law exactly in the same manner as metallic conductors.

If, as is frequently the case, it is desirable to represent the ionisation of a salt by means of an equation, some special method of indicating the electrical charges is required. Such an equation as

$$NaCl=Na+Cl$$

does not represent the ionisation of sodium chloride, because the symbols on the right side stand for *free* atoms of sodium and chlorine, and these do not exist in the solution. One method of representing the ions consists in indicating the charges by means of small + or — signs (one for each charge), placed over the formulæ of the radicals. Another method, which is more convenient typographically, is the employment of a dot (˙) to represent a positive charge, and a dash (′) to represent a negative one, these signs being placed immediately after the formulæ of the radicals, as shown in the equations below. The ionisation process is reversible, and there is a balance in the solution between the ions and the non-ionised molecules of salt; it is sometimes important that this also should find expression in the equation. Omitting, as it is not really required, any symbol for the "molecule of neutral

electricity," the equilibrium in an aqueous solution of common salt may therefore be represented by the equation—

$$NaCl \rightleftharpoons Na^{\cdot} + Cl'.$$

The corresponding equation in the case of magnesium sulphate would be—

$$MgSO_4 \rightleftharpoons Mg^{\cdot\cdot} + SO_4''$$

because in this case the radicals are both bivalent, and assume double charges when they form ions. In the case of barium nitrate the equation would be—

$$Ba(NO_3)_2 \rightleftharpoons Ba^{\cdot\cdot} + 2\,NO_3'.$$

Some Applications of the Ionisation Hypothesis.

We may now look shortly at the application of the ionisation hypothesis to the explanation of the peculiarities of salts in solution.

Abnormal Molecular Weights

In the first place, it is evident that the theory furnishes a satisfactory explanation of the abnormal molecular weights of dissolved salts, as compared with non-saline solutes ; each ion is really an independent molecule, so that each salt molecule which becomes ionised gives rise to *at least* two new molecules, and the average molecular weight must be correspondingly diminished, as in the more or less analogous case of the dissociation of ammonium chloride. By a comparison of the molecular weight as found by experiment with that deduced from the formula of the salt, it is possible to calculate the proportion of salt which has undergone ionisation. In this way it is found that the ionisation increases with the dilution, and that the salts formed by the interaction of strong acids and strong bases are ionised to a very large extent even in solutions which are not highly dilute. There is a gradual transition from highly ionised salts to substances which are not appreciably ionised, so that the division between salts and non-saline substances is not a hard-and-fast one.

Reactions of Salts the Reactions of their Ions.

The ionisation theory further supplies an explanation of the fact that salts containing the same metallic radical, or

the same acidic radical, exhibit the same group of reactions, which are said to be the reactions of that particular metallic radical or acidic radical. The reactions referred to are not those of the salt itself, but those of one or other of its ions, and therefore all solutions which contain an ion in common will behave similarly towards the same reagent. Ferrous and ferric salts yield different ions ($Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$), and therefore different reactions. A solution of potassium ferrocyanide contains the ions $K^{\cdot}$ and $Fe(CN)_6^{\prime\prime\prime\prime}$, and does not give the reactions of either ferrous or ferric salts. Some metallic compounds are known which in their chemical constitution resemble salts, but which are scarcely appreciably ionised when dissolved in water; such substances are found to differ in many of their reactions from the ionised salts of the same metal. Mercuric cyanide is a good example of such a case (see pp. 38, 103).

Colours of Ions and of Salt Molecules.

The similarity in the colours of *dilute* solutions of salts is likewise explained. In most cases the colour of any such solution is due to one particular ion, and not to the salt molecule. The salt molecule may itself be coloured, however, in which case its colour is probably quite different from that of the ion, and from the colours of the molecules of the other salts derived from that ion. Therefore, in concentrated solutions (where non-ionised molecules may predominate) the colours may be distinctly different for different salts derived from the same metallic or acidic radical (see p. 11).

Relative Strengths of Acids and Bases.

The peculiar properties characteristic of acids on the one hand, and of alkalies on the other, are, from the ionisation point of view, to be attributed solely to the special ions of these two classes of salts—*i.e.* to hydrogen ions in the case of acids, and to hydroxyl ions in the case of alkalies. That being so, an acid should exhibit the characters peculiar to that class of substances, in a higher or lower degree according to the extent to which it is ionised in solution. The observed facts are found to bear this out with an agreement as close as could be expected when the various conditions of experiment are

taken into consideration. When parallel lists of various acids are drawn up, representing the relative strengths, the degrees of ionisation (as determined from the average molecular weight in solution), and the electric conductivities (see p. 17), there is a great similarity amongst all three—not only as regards the relative positions which the various acids take in the lists, but also as regards the numerical values expressing these different properties. A corresponding state of affairs holds for the alkalies. This close agreement, since it is required by the theory and actually exists, affords one of the strongest supports of the ionisation hypothesis.

When the strengths of acids are referred in this way to the concentrations of the hydrogen ions in their solutions, a simple explanation is afforded as to why the relative strength of weak acids should increase so much on dilution, in contrast to the behaviour of strong acids. Even in moderately concentrated solution the strong acids are already ionised as regards a very great proportion of their molecules, so that, on dilution, any considerable increase in the degree of ionisation is impossible. With weak acids, on the other hand, the proportion of molecules which have undergone ionisation in, say, normal solution is so small that a relatively great increase takes place as dilution proceeds. At infinite dilutions all acids would presumably be ionised completely, and therefore be equally strong.

What has been stated above regarding acids generally, applies also to bases generally, except that in this case the relative strength is proportional to the concentration of the hydroxyl ions.

Mutual Effects of Salts having an Ion in Common.

Reasoning from the ionisation hypothesis, we should expect the solubility of a salt to be considerably affected by the presence in the solution of some other salt which has an ion in common with it. If to a solution of, say, sodium chloride there is added some other soluble chloride, say potassium chloride, the balance represented by the equation

$$NaCl \rightleftharpoons Na^{\cdot} + Cl'$$

is disturbed ; for, when the potassium chloride dissolves, it also gives rise to chloride ions

$$KCl \rightleftharpoons K^{\cdot} + Cl'.$$

Consequently, owing to this increase in the concentration of the chloride ions, an increased proportion of sodium ions and chloride ions will unite to form molecules of sodium chloride, and so restore equilibrium. A similar result will follow if the concentration of sodium ions is increased by the addition of some other sodium salt to the solution. In general, if two salts possessing an ion in common are present in the same solution, then each is ionised to a less extent than it would be were it present alone.

In a saturated solution of a salt which is in contact with some of the same salt in the solid condition we have a balance between solid salt and dissolved non-ionised salt on the one hand, and between the ions and the non-ionised salt in solution on the other. This, in the case of sodium chloride, might be represented as follows—

$$\underset{\text{(Solid)}}{NaCl} \rightleftharpoons \underset{\text{(Dissolved)}}{NaCl} \rightleftharpoons Na^{\cdot} + Cl'.$$

Anything which affects the balance between ionised and non-ionised salt must affect the balance between the dissolved salt and the solid, *i.e.* must affect the solubility. As stated above, the addition of a second salt having either $Na^{\cdot}$ or Cl' as one of its ions results in the formation of a larger proportion of non-ionised salt, and the excess so formed must crystallise out in order to restore the balance between solid and non-ionised salt. Direct experimental observations of the effects just referred to give quantitative results such as would be expected from theoretical considerations, in the case of sparingly soluble salts at least.

There are a number of important applications of the above fact to practical work, some of which may be shortly referred to. In soap-making it is the custom to precipitate the hard soap (sodium salts of certain organic acids) by adding a considerable quantity of common salt (sodium chloride) to the solution, the operation being known as " salting out " the soap (see p. 221). In the laboratory, chlorides and nitrates are often purified by adding hydrochloric or nitric acid respectively to their concentrated aqueous solutions. The result is to precipitate the salt, which, in many cases, is practically insoluble in the concentrated acid.

In some cases the results obtained are entirely different from what might at first be expected, and it can generally be

shown that this is due to the influence of chemical reactions giving rise to the formation of more complex substances. Thus, potassium sulphate is more soluble in dilute sulphuric acid than it is in water, but this is due to the fact that an acid sulphate is produced—$K_2SO_4+H_2SO_4=2\,KHSO_4$ and the SO_4'' ions are in great measure changed to HSO_4' ions—$KHSO_4 \rightleftharpoons K^{\cdot}+HSO_4'$. Similarly, silver cyanide is far more soluble in potassium cyanide solution than it is in pure water, because the salt $KAg(CN)_2$ is produced—$AgCN+KCN=KAg(CN)_2$, and instead of the concentration of the CN′ ions being increased by the addition of a small quantity of KCN, it is actually diminished, owing to the formation of the complex $Ag(CN)_2'$ ions—$KAg(CN)_2 \rightleftharpoons K^{\cdot}+Ag(CN)_2'$. Actions such as these will be dealt with more fully further on; it is only in cases where they are absent that the considerations dealt with in the preceding paragraphs of this section apply.

Double Decomposition.

The rapidity with which double decomposition between salts in solution occurs, in contrast with the slow rate at which apparently similar reactions between non-saline substances proceed, is easily explicable on the basis of the ionisation theory. In most cases a large proportion of the molecules of the dissolved salts have already undergone, at the time of dissolution, that separation of their radicals which is necessary before rearrangement to form the new salts can take place. The change which takes place when the two solutions are mixed, resulting in the precipitation of a new salt, requires therefore merely a process of direct chemical *combination*, and not decomposition at all, except in so far as the giving up of the electrical charges of the ions is concerned (and electrical discharge, it is well known, takes place with extreme rapidity).

In order to obtain a clearer insight into the mechanism of double decomposition, it will be best to consider first the case of the mixing of salt solutions in which there is no apparent change brought about. As a concrete example, we may take the pair of salts, potassium chloride and sodium nitrate. When these are mixed in equivalent proportions, the solution which is obtained is (as already stated generally) not recognisably different from that obtained by mixing together equivalent solutions of potassium nitrate and sodium chloride. If the

solutions dealt with are highly dilute, each of these four salts is ionised to a very large extent, so that, on mixing either of the above-mentioned pairs, there cannot be any very noteworthy change, since the great majority of the ions will still continue as ions in the mixed solution. There will be a certain amount of action, however, because the mixture contains the four ions $K^{\cdot}$ and $Na^{\cdot}$, Cl' and NO_3', and a state of general equilibrium will require the presence of a certain concentration of molecules of each salt that can be formed from them. Assuming that the salts originally taken were potassium chloride and sodium nitrate, then, on mixing them, there will be a small quantity of potassium nitrate and of sodium chloride formed by the union of the appropriate ions, and the general equilibrium might be represented by the following equation-diagram—

$$\begin{array}{ccccc} & & KNO_3 & & \\ & & \Updownarrow & & \\ & & K^{\cdot} & + Cl' \rightleftharpoons & KCl \\ & & + & + & \\ NaNO_3 & \rightleftharpoons & NO_3' & + Na^{\cdot} & \\ & & & \Updownarrow & \\ & & & NaCl. & \end{array}$$

It is easy to see from the diagram that the final result must be the same, irrespective of which pair of salts is taken to start with ; so long as the two anions and the two cations are present, equilibrium can only exist when non-ionised molecules of all four salts are present in appropriate concentration.

If the mixed solution obtained as above is concentrated by evaporation at a high temperature, the increasing concentration will bring about a correspondingly diminished ionisation—*i.e.* the balance represented in the above combined equations will shift outwards, in the case of each member. This will continue until the solution becomes saturated as regards the least soluble of the four salts (see Table of Solubilities)—sodium chloride, in the present instance. Further evaporation will therefore result in this least soluble salt beginning to crystallise out, and the process will continue steadily as the evaporation proceeds. The two kinds of ions which form this salt will therefore gradually be removed from the solution, and the other pair (in this case $K^{\cdot}$ and NO_3'), together with their salt in a non-ionised state (KNO_3), will accumulate in the solution that remains. In course of time the solution will become saturated as regards

the latter salt also, and it in its turn will begin to crystallise out if the evaporation be carried further. In cases where the second salt is very much more soluble than that which first crystallises, it is possible to separate a large proportion of the latter salt unmixed with the former.

The case of two salts yielding an immediate precipitate, when their solutions are mixed together, is merely a modification of that just considered, the least soluble salt being in this case soluble to such a slight extent that it may be spoken of as insoluble, or practically so. The final result is just the same as if the two solutions originally taken had been so dilute that no precipitate had occurred on mixing them, and the mixed solution had then been instantaneously concentrated to small volume.

Most salts which are precipitated immediately on mixing two solutions, separate in a non-crystalline form, owing to the great rapidity with which the solid has been produced. If precautions are taken to secure that the interacting salts mix very slowly, however, the resulting precipitate may be distinctly crystalline, since it is then formed in a much more gradual manner. Many of the salts which in every-day chemical work appear ordinarily as insoluble amorphous precipitates, are found in nature in the form of large crystals—*e.g.* barium sulphate. Such crystals are formed by the slow precipitation of the salt, brought about by double decomposition between dilute solutions of soluble salts mixing very slowly with one another. In laboratory work it is often highly desirable to obtain precipitates in a distinctly crystalline form, as they are then more easily filtered off and purified. In such cases the actual precipitation should be carried out with solutions as dilute as is otherwise permissible, and under conditions which retard the rate of separation. Many amorphous precipitates become finely crystalline when allowed to remain in contact with the liquids from which they have separated, owing to a process of gradual solution and simultaneous re-precipitation, the dissolution being always at the expense of the amorphous form, since the crystalline form is always distinctly less soluble. Advantage of this fact is frequently taken, in analytical operations, in order to bring precipitates into a more easily manipulated condition.

From what has been stated above, it is evident that in general a double decomposition is virtually complete, if either of the products is practically insoluble, and is therefore precipi-

tated from the solution. There are other cases in which double decomposition may become practically complete although all the products remain dissolved; and there are also cases in which an "insoluble" salt interacts with a soluble one to form soluble products. Such actions depend upon the formation of some product which is practically non-ionised, or has a complex ion formed by the combination of an ion of one of the interacting substances with the other substance, or with one of its ions. It may be stated generally that if solutions of two salts, AX and BY (see p. 11), are mixed together, then interaction will take place to a very considerable extent if either AY or BX (or both of them) is considerably less ionised than either of the original substances. On consideration of the general equation-diagram for two pairs of ions

$$\begin{array}{ccc} & & BX \\ & & \rightleftharpoons \\ AX & \rightleftharpoons & A'+X' \\ & & + \quad + \\ & & Y'+B' \rightleftharpoons BY \\ & & \Uparrow\Downarrow \\ & & AY \end{array}$$

it will therefore be possible to foretell what will happen on mixing two solutions, if it is known to what extent AX, BY, AY, and BX are ionised in solutions of the concentration dealt with. Since undissolved substances are not ionised, the case of precipitation resulting in complete double decomposition is, as already noted, only one particular example of the general phenomenon. Several other cases will be discussed later, as will also some in which ordinary double decomposition does not take place.

Equations to represent Ionic Reactions.

Seeing that the great majority of salt reactions by which precipitates are produced involve only one or other of the ions of each salt concerned, it is sometimes convenient to represent, in an equation expressing the change, only such ions as actually take part in the formation of the precipitate. For example, if it is desired to represent by an equation the action that occurs when a solution of any silver salt (*i.e.* a solution containing silver ions) is mixed with a solution of a chloride (*i.e.* a solution

containing chloride ions), it is not necessary to take a definite representative of each class of salt and write such an equation as

$$AgNO_3 + HCl = AgCl + HNO_3.$$

The more general equation

$$Ag^{\cdot} + Cl' = AgCl,$$

in which ionic symbols are used, is in some respects preferable, since the particular reaction under consideration is independent of the source of the silver ions or of the chloride ions. In balancing such equations, it is necessary to pay particular attention to the electrical charges indicated; if there is a like number of positive and of negative charges represented on one side, the same must be the case on the other, although the actual number on the two different sides need not be the same; if, on the other hand, there is an excess of one kind of charge on one side of the equation, there must be the *same excess* on the other. Thus

$$Ba^{\cdot\cdot} + SO_4'' = BaSO_4$$

(precipitation of barium sulphate from solutions of a barium salt and of a sulphate);

$$Mg^{\cdot\cdot} + 2\,OH' = Mg(OH)_2$$

(precipitation of magnesium hydroxide from solutions of a magnesium salt and of a hydroxide);

$$Cu^{\cdot\cdot} + Fe = Fe^{\cdot\cdot} + Cu$$

(precipitation of metallic copper from a cupric salt by means of metallic iron);

$$2\,Fe^{\cdot\cdot} + Cl_2 = 2\,Fe^{\cdot\cdot\cdot} + 2\,Cl'$$

(conversion of ferrous salt into ferric salt by means of chlorine).

Interaction of Acids and Bases.

The typical method of forming a salt by the interaction of an acid and a hydroxide is, as has already been observed, a particular kind of double decomposition. If the acid (a strong one) and the base (an alkali) are in dilute solution, then they will be to a large extent ionised to begin with, and the resulting salt, being also in dilute solution, will also be for the most part

ionised. Taking the case of hydrochloric acid and sodium hydroxide as an example, and representing it by the equation

$$(H^{\cdot}+Cl')+(Na^{\cdot}+OH')=(Na^{\cdot}+Cl')+H_2O,$$

it is evident that the anion of the acid and the cation of the alkali are practically unaffected by the action, as only a small proportion of these will unite to form molecules of the salt ; and we therefore have the result that the process of neutralisation consists merely in the mutual discharge of hydrogen ions and hydroxyl ions with formation of molecules of water. This explains why, in dilute solution, the heat of neutralisation is independent of the particular acid and base involved, provided they are both relatively strong—*i.e.* highly ionised.* The heat of neutralisation in such cases is merely the heat effect of the change represented by the equation

$$H^{\cdot}+OH'=H_2O.$$

In the case of comparatively weak acids and weak bases, however, where ionisation in moderately dilute solution is still very far from being complete, the heat effects due to the formation of the ions from their respective molecules also come into play, and the final results are different from the constant results obtained in the cases of strong acids and bases.

This particular kind of double decomposition is practically complete because one of the products—the water—is practically non-ionised. Perfectly pure water is an exceedingly poor conductor of electricity, but it is not absolutely non-conducting ; for this and other reasons, it is necessary to assume the existence of a certain very slight ionisation of water molecules, the ions being $H^{\cdot}$ and OH' (see p. 44).

Action of Acids on Substances insoluble in Water.

In the case of "insoluble" bases, the action of acids is analogous to that just described. As the substance is not absolutely insoluble in water, a small quantity of it dissolves, giving rise to a certain proportion of ions—the appropriate metallic ion or cation, and hydroxyl as anion (possibly some

* Thus the heat of neutralisation of one gram equivalent of hydrochloric, hydrobromic, hydriodic, or nitric acid by a strong base is very nearly 13,700 calories, and similarly the heat of neutralisation of one gram equivalent of sodium, potassium, calcium, or barium hydroxide is nearly the same number of calories.

oxides give the anion O″, but in most cases the small quantity of oxide dissolved will form hydroxide and yield OH′ as the anion). These hydroxyl anions unite with the hydrogen cations of the acid present to form water, and the balance between the dissolved base and the solid base is thereby destroyed; more of the solid dissolves, and the process continues. From this point of view, therefore, the solubility of the base in acid depends on its solubility in water, slight though that may be.

A similar explanation applies to the solubility of an insoluble salt of a weak acid in a solution of a strong acid, except that in this case the sparingly ionised product is not water, but the weak acid. With salts of exceedingly weak acids the double decomposition may be practically complete without excess of the strong acid being present, just as in the case of the neutralisation of a base by a strong acid. In those cases, however, where the acid liberated from the insoluble salt is not exceedingly weak, the double decomposition is more or less incomplete, and complete solution is only attained with a decided excess of the strong acid present. This is the state of affairs when calcium oxalate is dissolved by acids.

While the great majority of such cases are capable of quite simple explanation, there are some with which at first sight there appear to be difficulties. Of these latter cases, probably the most important are those involving the solubility or insolubility of metallic sulphides in acid solutions. Hydrogen sulphide is such an exceedingly weak acid that one might expect that all sulphides would dissolve easily in acids, even though these were not very strong. This, however, is very far from being the case. Some sulphides, insoluble in water, dissolve with great readiness in dilute acetic acid; manganous sulphide is a good example. Others, such as zinc sulphide, dissolve easily in strong acids, such as hydrochloric acid, but scarcely at all in acetic acid; others again, such as lead sulphide, are decomposed somewhat readily by strong acids, but yet can be completely precipitated by hydrogen sulphide in excess, even in presence of such acids, provided the solution is moderately dilute and the temperature low; a few, like arsenious sulphide, are scarcely attacked even by strong acids. The explanation of these differences is to be sought in the different degrees of solubility of the sulphides themselves *in water*. The balance existing between any solid sulphide and, say, hydrochloric acid may be represented thus:—

$$\begin{array}{ccccc} & & & & H_2S \\ & & & & \Updownarrow \\ MS \rightleftharpoons MS & \rightleftharpoons & M'' & + & S'' \\ \text{(Solid)} & & \text{(Dissolved)} & & \\ & & + & & + \\ & & 2\,Cl' & + & 2\,H' \rightleftharpoons 2\,HCl \\ & & \Updownarrow & & \\ & & MCl_2. & & \end{array}$$

Hydrochloric acid and metallic chlorides being all ionised to a much greater extent than hydrogen sulphide is, the factor which will decide whether or not the sulphide dissolves in the acid must be the relative extent to which the metallic sulphide and the hydrogen sulphide are ionised in the solution. If the metallic sulphide is so very sparingly soluble that its saturated aqueous solution contains a much lower concentration of S'' ions than a solution of hydrogen sulphide does, hydrogen sulphide will precipitate that sulphide from an acid solution of an appropriate salt. In such a case, however, the addition of a large quantity of free acid may, by greatly increasing the concentration of H' ions, so far diminish the ionisation of the hydrogen sulphide (see p. 29) that the latter becomes the least ionised product, whereupon the sulphide will begin to dissolve.

The diagram given above is not complete, because in many cases the balance

$$\underset{\text{(Dissolved)}}{H_2S} \rightleftharpoons \underset{\text{(Gas)}}{H_2S}$$

is of importance (especially at high temperatures), and in some cases also the balance

$$\underset{\text{(Solid)}}{MCl_2} \rightleftharpoons \underset{\text{(Dissolved)}}{MCl_2}$$

may come into play (in the case of lead sulphide, for example).

Other Cases of the Formation of Non-ionised Products.

That the solubility of "insoluble" salts is not due to a property peculiar to acids, but, as already mentioned (p. 33), depends upon the formation of some product which is either practically non-ionised or has a new complex ion, is shown by a number of very interesting cases, some of which may be considered here.

Silver cyanide is "insoluble," not only in water, but also in dilute nitric acid, in spite of the fact that hydrocyanic acid is a very weak acid. The quantity of silver cyanide dissolved by water is so very slight that the formation of hydrocyanic acid by double decomposition would not diminish the total concentration of CN′ ions. Nevertheless the ionic concentration in a saturated solution of silver cyanide is much greater than in a solution of mercuric cyanide, which, though easily soluble, is practically non-ionised, and consequently silver cyanide dissolves readily in a solution of mercuric nitrate, the practical completeness of the interaction being due to the formation of this almost entirely non-ionised mercuric cyanide—

$$2\,AgCN + Hg(NO_3)_2 = 2\,AgNO_3 + Hg(CN)_2.$$

The action here is quite analogous with that which takes place when silver oxide dissolves in dilute nitric acid, owing to the formation of non-ionised water—

$$Ag_2O + 2\,HNO_3 = 2\,AgNO_3 + H_2O.$$

The peculiar character of mercuric cyanide which has been referred to above, leads to some remarkable and exceptional reactions. Thus, notwithstanding that hydrochloric acid is so strong an acid and hydrocyanic acid so weak, mercuric chloride in solution is almost completely decomposed by hydrocyanic acid. Mercuric chloride solution is neutral, and hydrocyanic acid is very faintly acid; when they are mixed, however, a strongly acid solution is obtained, owing to the production of a considerable concentration of hydrogen ions derived from the liberated hydrochloric acid.

$$\underset{\text{(Neutral)}}{HgCl_2} + \underset{\text{(Very feebly acid)}}{2\,HCN} = \underset{\text{(Neutral)}}{Hg(CN)_2} + \underset{\text{(Strongly acid)}}{2\,HCl}.$$

Double Salts and Complex Salts.

While the above cases, resulting in the production of mercuric cyanide, illustrate the formation of a non-ionised product, the formation of a new complex ion is exemplified in the production of a complex salt by the union of two simpler ones, and the ionisation theory gives an explanation of the differences between such complex salts and double salts, which are also formed by the union of two salts. As an example of a double

salt we may take potassium magnesium sulphate, K_2SO_4, $MgSO_4$, $6\,H_2O$, which is obtained when solutions of potassium sulphate and magnesium sulphate are mixed and allowed to evaporate. When this double salt is dissolved in water the solution is found to behave simply as if it were a mixture of the two sulphates; it contains the ions $K^{\cdot}$, $Mg^{\cdot\cdot}$, and SO_4''. It might almost be said that the double salt existed only in the solid state. There are other cases, however, in which two salts unite together to form a definite compound which in solution does not behave like a mixture. Thus, ferrous cyanide (like most other cyanides practically insoluble in water) dissolves in solution of potassium cyanide (or other soluble cyanide, with the exception of mercuric cyanide), and forms a compound which might be represented by the formula $4\,KCN$, $Fe(CN)_2$. A solution of this substance does not, however, behave like a mixture of two cyanides. It contains $K^{\cdot}$ ions, but apparently practically no $Fe^{\cdot\cdot}$ ions or CN' ions; the metallic radical is potassium only, and the acidic radical all the remainder, *i.e.* $Fe(CN)_6$. Here we have to deal with a single salt, potassium ferrocyanide, and its formula is written $K_4Fe(CN)_6$. The solubility of the ferrous cyanide in solutions of other cyanides is therefore due to the action expressed by the equation—

$$Fe^{\cdot\cdot}+6\,CN'=Fe(CN)_6''''.$$

Complete solution is effected with practically no excess of the soluble cyanide, because the complex ion represented on the right of the equation yields practically none of the ions represented on the left. There are many similar cases known, some of which are mentioned later. Thus, practically all silver compounds (the only important exception is the sulphide) dissolve in solutions of thiosulphates and also of cyanides (*except mercuric cyanide*), giving rise to salts which do not exhibit the usual reactions of silver salts; in each case the silver forms part of the acidic radical, which yields its own complex ion Using ionic symbols, the actions may be represented thus—

$$Ag^{\cdot}+2\,CN'=Ag(CN)_2'.$$
$$Ag^{\cdot}+S_2O_3''=AgS_2O_3'.$$

The potassium salts corresponding to these would be represented by the formulæ $KAg(CN)_2$ and $KAgS_2O_3$ (see pp. 140, 138).

At first sight the double salts referred to above seem to be quite different from these complex salts; their formation

depends on the fact that they are less soluble than their component salts. Investigation shows, however, that there are intermediate stages between the two classes, and we may assume that a solution of potassium magnesium sulphate contains a certain proportion of $K_2Mg(SO_4)_2$ molecules in equilibrium with the $K^{\cdot}$ ions and with a small proportion of $Mg(SO_4)_2''$ ions; just as a solution of potassium argento-cyanide, $KAg(CN)_2$, contains a minute concentration of $Ag^{\cdot}$ and CN' ions, in equilibrium with the complex ion $Ag(CN)_2'$.

Electrolysis.

If the assumption that salts on dissolving in water undergo a process of ionisation is accepted, then the explanation of the process of electrolysis and of the regularities observed in connection with it becomes comparatively simple. On the basis of that assumption, the electrolyte consists of an immense number of minute independent particles of matter, highly charged with either positive or negative electricity, and moving freely about in all directions in a non-conducting medium—the solvent. The non-ionised portion of the solute may so far be ignored, but it must be remembered that though the quantity of it is constant under any given conditions, there is a continual resolution of molecules into ions and recombination of ions to form molecules; these two opposite reactions, however, take place at the same rate, so that there is equilibrium. When the electrodes from a sufficiently powerful battery are introduced into such a solution, the cathode (being negatively electrified) attracts towards it the positively charged cations, while the anode (being positively electrified) attracts towards it the negatively charged anions. On arriving at the respective electrodes the ions give up their charges, neutralising a similar quantity of electricity, of the opposite kind, on the electrode. This loss on the electrodes is made good from the battery, which maintains their potential at a constant level, and so the process continues. The discharged ions—*i.e.* the free radicals of the salt—behave differently in different cases according to their chemical character and the prevailing conditions. They may be deposited upon the electrode, as in the case of the electro-deposition of metals; or may unite with the substance of the electrode; or may interact with each other, with the solvent, or with the solute.

According to this view, the electricity from the battery does not itself *decompose* the salt; it merely separates the decomposition products and removes their electric charges. This explains satisfactorily the fact that the amount of electrolysis is proportional to the quantity of electricity supplied by the battery, and is independent of the electrode potential; a little consideration will also show that the explanation extends to the other regularities observed by Faraday. The fact that the minimum electrode potential necessary to maintain the process of electrolysis uninterruptedly varies with different salts, shows that different ions hold their charges with varying degrees of firmness.

It would appear from what has just been stated that the conducting power of an electrolyte is a property essentially different from that of metals, and that the current does not " pass through " the solution in the sense generally understood when the expression is used with reference to, say, a copper wire.

The conductivity of solutions depends on the rate at which the ions can be discharged, and this, again, depends on the *concentration* of the ions (only indirectly on that of the salt), and also on the *rate* at which they can travel through the solution; just as the carrying power of a tramway system depends both on the number of cars available and on the rate at which they travel. The conductivity of an electrolyte must depend on the rate at which both the anion and the cation travel, since the two kinds of ions must be discharged in equivalent proportions; the battery supplies positive and negative electricity only in equal quantities, and equivalent weights of different ions carry equal charges.

Owing to the connection between the conductivity of an electrolyte and its ionic concentration, it is possible to calculate the latter by means of the former, and electric conductivity methods are now largely used for determining the degree of ionisation of a salt in solution.

Indicators.

Among the properties of " acid salts " and " alkaline salts " reference has been made (see p. 2) to the changes of colour produced by addition of solutions of such salts to purple tincture of litmus or to blue syrup of violets. The purple tincture of

litmus becomes red on the addition of the " acid salt " and blue on the addition of the " alkaline salt," and the corresponding changes of the syrup of violets are from blue to red and from blue to green respectively. Substances whose solutions show distinct changes of colour on the addition of minute quantities of particular reagents or classes of reagents are called **indicators** (see p. 191), and they are useful in showing when enough of a reagent has been added to a quantity of a solution in order to complete a particular reaction. For example, a solution of sodium hydroxide is neutralised by the addition to it of a certain quantity of hydrochloric acid, but it is impossible by visual inspection to say when neutrality is attained, there being no colour or other change apparent. If, however, a few drops of litmus solution be added to the sodium hydroxide solution, it assumes a blue colour. When just the requisite amount and no more of hydrochloric acid is added to the blue solution it becomes purple, and when excess of hydrochloric acid is added the solution becomes red. In this instance, the litmus has acted as an indicator of the alkalinity, neutrality, and acidity respectively of the solution.

Indicators are not, however, confined to reactions of neutralisation. Thus in the reaction between iodine and sodium thiosulphate—

$$I_2+2\ Na_2S_2O_3=2\ NaI+Na_2S_4O_6$$

—it is difficult to decide when the last trace of the iodine has just passed from the free state into that of combination with sodium as shown by the disappearance of the brown, eventually only pale yellow, colour of the iodine solution, that is the change $2\ I \longrightarrow 2\ I'$. But if a little starch paste has been added to the iodine solution, the deep blue colour of the iodine-starch combination is easily visible so long as the merest trace of iodine remains uncombined with sodium. Starch in this instance is a useful indicator.

The so-called " adsorption indicators " are feebly acidic or basic dyestuffs, which are adsorbed by a precipitate and produce a strong colour on the surface of the coagulated particles at the moment of equilibrium between the initial and the final products of the reaction. Thus in the reaction

$$KCl+AgNO_3=AgCl+KNO_3$$

it is not easy to measure the point at which the addition of a

trace of either reagent to the other no longer produces a white precipitate of silver chloride. But if fluorescein, a feeble acid, is added to the solution of potassium chloride and then the silver nitrate is added, it is found that at the moment of equilibrium the white precipitate coagulates and becomes rose-pink in colour, owing to its adsorption of the dyestuff. According to Kolthoff the reaction may be expressed by the ionic equation—

$$\underset{\text{Surface}}{Ag^+Cl^-} + \underset{\text{Solution}}{Fln^-} \rightleftharpoons \underset{\text{Surface (reddish)}}{Ag^+Fln^-} + \underset{\text{Solution.}}{Cl^-}$$

Occasionally one of the reacting substances forms a strongly coloured solution and gives rise to a colourless or differently coloured product, thus acting as an indicator. Perhaps the best example of this type of reagent indicator is potassium permanganate ($KMnO_4$). Its aqueous solution is of a deep violet colour, due to the MnO_4' anion, whereas the manganous salt solution formed from it is colourless, the Mn'' cation being colourless. Thus if potassium permanganate be added to a solution of hydrogen peroxide containing excess of sulphuric acid, the permanganate solution is decolorised until the reaction according to the following equation has become complete—

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

The further addition of permanganate solution then produces a pink coloration.

An indicator may be defined as a substance, the presence of which in a titration mixture causes the end point to become apparent. The effect of an indicator is not confined to colour production, colour change, or disappearance of colour, as in the cases already referred to, but may be extended to the production of a precipitate in a clear solution ; the solution of a precipitate in a turbid solution ; the change in colour of a precipitate ; and other effects.

The substances used in laboratory practice as indicators in *acidimetry* (measurement of the quantity of acid) and *alkalimetry* (measurement of the quantity of alkali) are usually complex carbon compounds of feebly acidic or basic character ; sometimes derived from plants, *e.g.* litmus from lichens ; sometimes synthetic products, *e.g.* phenolphthalein and methyl red. Whatever be their origin, their solutions show changes of colour in passing from an acid to alkaline state and *vice versa*. These

changes of colour are probably due to changes of chemical constitution. Thus a solution of phenolphthalein is colourless and the phenolphthalein in it is only ionised to a very slight extent. If, however, sodium hydroxide be added to the solution, it immediately becomes pink owing to the ionisation of the sodium salt of phenolphthalein. The constitution of the sodium salt of phenolphthalein, in which one atom of hydrogen has been replaced by one atom of sodium, differs from that of phenolphthalein not merely in this replacement of hydrogen by sodium, but also in a rearrangement of certain of the carbon, hydrogen, and oxygen atoms whereby the " carboxyl " group (COOH), which is acidic in character, is formed. The acidic ions, thus produced, colour the solution pink; whereas the sodium ions do not colour it.

According to the character of the reaction to be carried out, special indicators are used. If a strong acid is being neutralised by a strong alkali, then each solution is highly ionised and it does not matter much what indicator is used. On the other hand, if a weak acid is being neutralised by a strong base, it is important to use an indicator which is highly ionised when converted into a salt. Phenolphthalein fulfils this condition. For the case of a strong acid being neutralised by a weak base, a suitable indicator is methyl red. In the above statement, the expression " neutralised " is an indefinite one and only applicable in each case to the particular indicator. For exact comparison, the neutrality of pure water is taken as the standard.

Hydrogen Ion (Hydrion) Concentration: p_H.

The measurement of the degree of ionisation of the most highly purified water has been found to give a hydrogen ion or **hydrion** concentration of 1×10^{-7} normal at 25°, or if both hydrion and hydroxidion be taken, the total ionisation is 1×10^{-14} normal. Some idea of how extremely small a proportion of pure water is thus ionised may be gained from the following two statements, derived from experimental evidence: (1) in one metric ton (1000 kilograms) of water only 1·8 milligram is ionised; and (2) out of every 555 million molecules of water only one molecule is ionised. The measurement of hydrion concentration of very pure water is extremely difficult and the use of certain indicators enables it to be dispensed with,

a comparison of the colours of these indicators in solutions of measured hydrion concentration having once been made.

The symbol "p_H" * is now frequently employed, more especially in biochemistry, and indicates the numerical value of the negative power to which 10 must be raised in order to express the hydrogen ion (hydrion) concentration, or normality of the solution with regard to hydrogen ion.

The following table gives the hydrion concentration for four frequently used indicators—

Indicator.	Methyl orange.	Methyl red.	Azolitmin (litmus).	Phenolphthalein.
Normality of $H^{\cdot}$ . .	10^{-4} to 10^{-5}	10^{-5} to 10^{-6}	10^{-6} to 10^{-8}	10^{-8} to 10^{-9}
p_H . .	4 to 5	5 to 6	6 to 8	8 to 9
	Acid.		Neutral.	Alkaline.

Thus a solution found to be neutral, using methyl orange as indicator, is said to have $p_H = 4$ to 5. It will be observed that litmus solution indicates a neutrality which extends on either side of the neutrality of water.

Ionisation of Polybasic Acids.

It has been pointed out that the strongest polybasic acids are decidedly weaker than the strongest monobasic acids, and the reason for this would appear to be that in the former case the ionisation takes place in stages, so that in moderately concentrated solution the greater proportion of the acid is ionised merely as if it were a monobasic acid—*i.e.* giving only one hydrogen ion from each molecule. Thus, sulphuric acid gives rise in the first place principally to the ions $H^{\cdot}$ and HSO_4'; the HSO_4' ions in their turn give rise to another $H^{\cdot}$ and the ion SO_4'', so that the state of affairs in the solution might be represented as follows—

$$H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4' \rightleftharpoons 2\,H^{\cdot} + SO_4''.$$

In the case of a tribasic acid like phosphoric acid three stages are possible, and the state of affairs in the solution might be represented in an analogous manner—

$$H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4' \rightleftharpoons 2\,H^{\cdot} + HPO_4'' \rightleftharpoons 3\,H^{\cdot} + PO_4'''.$$

In all such cases increased dilution results in the balance shifting towards the right, but the last stage may take place

* Sörensen introduced this expression, "p" standing for *Potenz* and "H" for hydrogen ion. (S. P. L. Sörensen, *Biochem. Zeitsch.*, xxi., 131 (1909).)

only to a very slight extent even in dilute solution. On this account phosphoric acid behaves in many respects practically as if it were a dibasic, and not a tribasic, acid.

Hydrolysis.

The fact that polybasic acids can give rise to several different anions, as described above, affords an explanation why the normal salts of some comparatively strong polybasic acids show a marked tendency to hydrolysis. Normal sodium phosphate undergoes hydrolysis to a very much greater extent than sodium acetate does, although determinations of the relative strength of phosphoric acid give results higher than those obtained for acetic acid. The action which takes place on the dissolution of sodium phosphate may be partially represented thus—

$$H_2O + Na_3PO_4 \rightleftharpoons 3\,Na^{\cdot} + HPO_4'' + OH'$$
$$\Downarrow$$
$$PO_4''' + H^{\cdot}.$$

As already pointed out, the further ionisation of the HPO_4'' ion into $H^{\cdot}$ and PO_4''' takes place to a very slight extent even in dilute solution of phosphoric acid itself, and in the present case the action represented by the main equation can take place to a very great extent before there is a sufficient accumulation of hydrogen ions to balance with the hydroxyl ions.

This process of hydrolysis is to be referred to the hydrogen and hydroxyl ions existing in water itself. Thus, we may assume that when sodium phosphate dissolves in water, it simply becomes ionised like any other salt, and gives the ions $3\,Na^{\cdot}$ and PO_4'''; there are also present the ions of water. These four ions must balance among themselves, and the state of affairs is in many respects similar to that already discussed for the mixture of two salt solutions, and might be represented thus—

$$\begin{array}{c} NaOH \\ \Downarrow \\ 2\,Na^{\cdot} + Na^{\cdot} + PO_4''' \rightleftharpoons Na_3PO_4 \\ + \quad + \\ H_2O \rightleftharpoons OH' + H^{\cdot} \\ \Downarrow \\ HPO_4''. \end{array}$$

Since HPO_4'' becomes so slightly ionised, even in very dilute solution, the action will result in the formation of a considerable proportion of such molecules, even although this requires the breaking up of a considerable proportion of water molecules. There will therefore be a decided accumulation of hydroxyl ions in the solution, and the latter must exhibit a marked alkaline reaction.

In the case of sodium acetate, hydrolysis involves the formation of free acetic acid, which, in solution, is ionised far more than water itself is. Hence, of the four compounds, represented in an equation-diagram indicating the state of affairs in solution of sodium acetate, water is by far the least ionised, and there is therefore very little tendency to form acetic acid. There is consequently only slight hydrolysis and a comparatively low concentration of hydroxyl ions in the solution, which is therefore not markedly alkaline. In order that a salt of a monobasic acid may yield a strongly alkaline solution by hydrolysis, it is necessary that the ionisation of the free acid should be so slight as to be almost comparable to that of water itself. A good example of such an acid is hydrocyanic acid.

The hydrolysis of salts derived from weak bases is explicable in a manner similar to that adopted in the case of salts of weak acids, only here it is the hydroxyl ions derived from the ionisation of the water which become used up to form a less ionised product, and there is therefore an accumulation of hydrogen ions in the solution, which consequently has an acid reaction. In some cases the free base is the product of the hydrolysis ; it is rare, however, that the base is distinctly soluble in water, except in the case of the organic bases corresponding to compound metallic radicals. When the base is insoluble in water, an additional factor is introduced, and the hydrolysis may be carried further than might otherwise have been expected. With salts derived from a poly-acid base hydrolysis very frequently gives rise, not to the base itself, but to a basic salt, which may either be precipitated or remain dissolved. In the latter case there will be a certain amount of ionisation, with formation of a cation containing hydroxyl united to the metal, just as in the corresponding case with a weak acid there is formation of an anion containing hydrogen.

GENERAL METHODS OF PREPARING SALTS.

(UNLESS otherwise stated, it is assumed that the normal salt is referred to.)

1. The typical and most general method of preparing salts is by the interaction of acids and bases, already referred to. It is important to remember that in these cases the only other product besides the salt is water. In order to write the equation for such an action it is only necessary to know the formulæ of the acid and the base respectively; these must be taken in such proportions that the acid hydrogen is sufficient to form water with the oxygen or hydroxyl of the base; the formula of the salt (or a multiple of it) is obtained by combining the remainders. Examples—

Hydroxides—

$$KOH+HCl=KCl+H_2O.$$
$$KOH+HC_2H_3O_2=KC_2H_3O_2+H_2O.$$
$$2\,KOH+H_2SO_4=K_2SO_4+2\,H_2O.$$
$$Ca(OH)_2+2\,HNO_3=Ca(NO_3)_2+2\,H_2O.$$
$$Ca(OH)_2+H_2SO_4=CaSO_4+2\,H_2O.$$
$$3\,Ca(OH)_2+2\,H_3PO_4=Ca_3(PO_4)_2+6\,H_2O.$$
$$2\,Al(OH)_3+3\,H_2SO_4=Al_2(SO_4)_3+6\,H_2O.$$

Oxides—

$$Ag_2O+2\,HNO_3=2\,AgNO_3+H_2O.$$
$$PbO+2\,HCl=PbCl_2+H_2O.$$
$$Fe_2O_3+3\,H_2SO_4=Fe_2(SO_4)_3+3\,H_2O.$$
$$Bi_2O_3+6\,HCl=2\,BiCl_3+3\,H_2O.$$

The corresponding method of producing salts of ammonium (and also of other similar compound radicals) from the base deserves special mention. In aqueous solution the case may be considered as exactly analogous to that of potassium hydroxide, since in ammonia solution partial production of ammonium hydroxide occurs—

$$NH_3+H_2O=NH_4OH.$$

But salts can also be produced from ammonia gas in the absence of water, or at least in the presence of very minute traces only, and it may be preferable to represent the action as taking place by the interaction of ammonia and the acid.

In such a case the proportions of acid and ammonia must be such that the hydrogen of the former is exactly sufficient to convert every NH_3 into NH_4, *i.e.* one H for each N—

$$NH_3+HCl=NH_4Cl.$$
$$2\,NH_3+H_2SO_4=(NH_4)_2SO_4.$$

2. Very similar to the action of acids upon basic oxides is their action upon the corresponding sulphides, hydrogen sulphide being produced instead of water. In such cases, however, there are possible complications, owing to the oxidisable character of hydrogen sulphide together with the fact that some acids act as oxidising agents. Thus, concentrated nitric acid may produce the sulphate of the metal instead of, or along with, the nitrate; while dilute nitric acid may produce the nitrate and free sulphur. Concentrated sulphuric acid may produce the sulphate, free sulphur, and sulphur dioxide. Such complications do not occur with hydrochloric acid.

$$FeS+H_2SO_4(\textit{dil.})=FeSO_4+H_2S.$$
$$PbS+2\,HCl(\textit{hot})=PbCl_2+H_2S.$$
$$3\,PbS+8\,HNO_3=3\,PbSO_4+8\,NO+4\,H_2O.$$
$$3\,PbS+8\,HNO_3(\textit{dil.})=3\,Pb(NO_3)_2+3\,S+2\,NO+4\,H_2O.$$

Although there is frequently a great similarity between the chemical actions of acids upon sulphides and those of acids upon basic oxides, there is generally a great difference in the readiness with which the actions take place. Many sulphides are hardly attacked, if at all, under conditions in which the corresponding oxides would be quickly acted upon. This is due partly to the slighter solubility of the sulphides, and also partly to the acid character of hydrogen sulphide. (See Section **6**.)

3. A considerable number of salts can be prepared from oxides other than the corresponding basic oxide. In most cases these oxides contain more oxygen than the basic oxide, and are known as peroxides, though some are acid anhydrides. The actions which take place may be of various types, depending on the particular peroxide or on the particular acid employed.

Some peroxides when treated with dilute acid produce a salt and hydrogen peroxide, an action closely resembling that

which takes place between the same acid and the basic oxide, with formation of the salt and water—

$$BaO_2+2\,HCl=BaCl_2+H_2O_2.$$

In other cases the salt and water are produced along with oxygen or an oxidation product of the acid—

$$2\,MnO_2+2\,H_2SO_4=2\,MnSO_4+2\,H_2O+O_2.$$
$$PbO_2+4\,HCl=PbCl_2+2\,H_2O+Cl_2.$$

Peroxides of this class are not as a rule attacked by nitric acid.

Towards some acids chromic anhydride behaves like a peroxide—

$$2\,CrO_3+12\,HCl=2\,CrCl_3+6\,H_2O+3\,Cl_2.$$

Some higher oxides form sulphates by the direct action of sulphur dioxide—

$$2\,CrO_3+3\,SO_2=Cr_2(SO_4)_3.$$
$$PbO_2+SO_2=PbSO_4.$$

At low temperatures manganese peroxide does not behave like lead peroxide towards sulphur dioxide. In this case dithionate is produced—

$$MnO_2+2\,SO_2=MnS_2O_6.$$

Cuprous oxide is interesting in its behaviour with acids. Towards halogen acids it acts as a basic oxide—

$$Cu_2O+2\,HCl=2\,CuCl+H_2O.$$

Towards other acids it acts as a suboxide, giving metallic copper and cupric salt—

$$Cu_2O+H_2SO_4=Cu+CuSO_4+H_2O.$$

4. A very common method of preparing salts is by the interaction of acids and metals. In some cases the chemical changes involved are exceedingly simple, but in those cases where the acid employed can act as an oxidising agent (nitric acid or concentrated sulphuric acid, for example) they are generally much more complex. Some metals are not directly attacked by certain acids. When interaction does take place, the typical change consists simply in the replacement of the

hydrogen of the acid by an equivalent quantity of metal, the hydrogen being liberated in the state of gas.

Hydrochloric acid.—When hydrochloric acid (either the gas or its aqueous solution) acts upon a metal, the interaction is always the typical one mentioned above—

$$Zn+2\,HCl=ZnCl_2+H_2.$$
$$Fe+2\,HCl=FeCl_2+H_2.$$
$$2\,Al+6\,HCl=2\,AlCl_3+3\,H_2.$$

If a metal forms two chlorides, as in the case of iron or tin, it is always the chloride containing the smaller proportion of chlorine (often called the " lower " chloride) which is produced by the interaction of hydrochloric acid and the metal.

Sulphuric acid.—Dilute sulphuric acid behaves towards a number of metals in a manner similar to that in which hydrochloric acid does, a sulphate being formed and hydrogen evolved—

$$Mg+H_2SO_4=MgSO_4+H_2.$$

When a metal which can form two sulphates dissolves in dilute sulphuric acid, the sulphate which contains the smaller proportion of the acidic radical SO_4 (the lower sulphate) is produced by the action.

Concentrated sulphuric acid by its interaction with metals does not yield free hydrogen, but reduction products of sulphuric acid, water and sulphates being produced at the same time. The hot concentrated acid attacks many metals upon which the dilute acid has no action.

$$Pb+2\,H_2SO_4=PbSO_4+SO_2+2\,H_2O.$$
$$2\,Hg+2\,H_2SO_4=Hg_2SO_4+SO_2+2\,H_2O.$$
$$Hg_2SO_4+2\,H_2SO_4=2\,HgSO_4+SO_2+2\,H_2O.$$

From these equations it will be observed that in the case of concentrated sulphuric acid the higher sulphate may be produced as well as the lower, while it is not so with the dilute acid.

In the case of many metals the reduction of part of the sulphuric acid may proceed further, with formation of free sulphur, hydrogen sulphide, or even a metallic sulphide. Several of these actions may take place simultaneously, and the general result in any particular case depends mainly on the temperature and on the concentration of the acid; it is to

be remembered, however, that the formation of sulphur dioxide is the predominant action.

$$3\,Zn+4\,H_2SO_4=3\,ZnSO_4+S+4\,H_2O.$$
$$4\,Zn+5\,H_2SO_4=4\,ZnSO_4+H_2S+4\,H_2O.$$
$$Cu+2\,H_2SO_4=CuSO_4+SO_2+2\,H_2O.$$
$$5\,Cu+4\,H_2SO_4=3\,CuSO_4+Cu_2S+4\,H_2O.$$

Nitric acid.—The reactions with nitric acid are invariably of a complex nature. In the majority of cases, with the concentration of nitric acid commonly employed (that is, diluted, if at all, to only a moderate extent), either hydrogen is not produced, or the quantity is negligible. Instead of it, reduction products of nitric acid are formed. The extent to which the acid is reduced depends on the metal as well as on the temperature and the concentration of the acid; as a rule, a mixture of reduction products is obtained, though one generally predominates largely.

With most metals, such as silver, copper, and bismuth, nitric oxide is the principal product—

$$6\,Ag+8\,HNO_3=6\,AgNO_3+2\,NO+4\,H_2O,$$
$$3\,Cu+8\,HNO_3=3\,Cu(NO_3)_2+2\,NO+4\,H_2O;$$

but a considerable quantity of nitrogen or of nitrogen peroxide may also be produced—

$$5\,Cu+12\,HNO_3=5\,Cu(NO_3)_2+N_2+6\,H_2O,$$
$$Cu+4\,HNO_3=Cu(NO_3)_2+2\,NO_2+2\,H_2O.$$

In the case of mercury either mercurous nitrate or mercuric nitrate may be produced. The former is obtained with dilute acid and moderate temperatures, the latter with concentrated acid in excess and a high temperature. In the first case the equation is similar to that for silver; in the second, to that for copper.

Some metals (zinc and tin, for example) dissolve in cold dilute nitric acid without the evolution of any gas. Here some of the nitric acid is reduced to ammonia, which at once forms ammonium nitrate—

$$4\,Sn+10\,HNO_3=4\,Sn(NO_3)_2+NH_4NO_3+3\,H_2O.$$

(With hot concentrated nitric acid tin forms metastannic acid, $H_{20}Sn_5O_{20}$, along with water and oxides of nitrogen.) With

certain concentrations of acid, zinc and some other metals dissolve with evolution of nitrous oxide—

$$4\,Zn+10\,HNO_3=4\,Zn(NO_3)_2+N_2O+5\,H_2O.$$

Other acids.—Most other acids, with the exception of those which are powerful oxidising agents, evolve hydrogen when they interact with metals—

$$Fe+2\,HC_2H_3O_2=Fe(C_2H_3O_2)_2+H_2.$$

It should be noted that some metals which are not readily attacked by acid in absence of air are attacked in presence of air. Thus copper, unless finely divided, does not dissolve readily in hydrochloric acid alone. If air is present, action takes place much more quickly, without liberation of hydrogen.

$$2\,Cu+4\,HCl+O_2=2\,CuCl_2+2\,H_2O.$$

The replacement of one metal by another, in a salt, is analogous to the replacement of the hydrogen of an acid by a metal. The metals, including hydrogen, may be arranged in an "*electrochemical*" or "*electromotive*" series, so that any metal in the series will replace those following it. For example, the metals—Mg, Al, Zn, Fe, Ni, Sn, Pb, H, Sb, Bi, Cu, Hg, Ag—form such a series, and reactions such as—

$$Fe+CuSO_4=Cu+FeSO_4$$
$$3\,Fe+Sb_2S_3=2\,Sb+3\,FeS$$

are carried out on a large scale principally as a means of obtaining the replaced metal, the new salt being only a by-product. In cases where such replacements are possible, the action may be used in preparing salts.

5. The metallic halides (*i.e.* chlorides, bromides, iodides) can in many cases be prepared by the direct union of the metal and the halogen. When the metal forms two sets of salts it is possible, as a rule, to obtain either the lower or the higher halide according as the metal or the halogen is in excess. Thus, when chlorine is passed over heated iron, ferrous chloride (non-volatile under the conditions of the experiment) is first

produced; by the further action of chlorine this is converted into ferric chloride, which can be sublimed—

$$Fe+Cl_2=FeCl_2.$$
$$2\,FeCl_2+Cl_2=2\,FeCl_3.$$

In the preparation of bromides the bromine may be employed along with water ("bromine water"), by itself in the liquid state, or it may be passed in the state of vapour over the heated metal. Perfectly dry liquid bromine, however, has little, if any, action on metals.

The readiness with which moist bromine unites with certain metals is well exemplified by the case of aluminium. If some bromine is placed in a porcelain basin and a piece of clean sheet aluminium, previously warmed in the Bunsen flame, is thrown upon it, chemical action takes place with considerable evolution of heat, so much so that the metal ultimately becomes red-hot and fuses to a globule. When all the bromine has been used up or vaporised, white crusts of aluminium bromide remain on the basin, though much of the salt has been lost in the form of dense white fumes.

$$2\,Al+3\,Br_2=2\,AlBr_3.$$

The preparation of iodides by this method may be effected by heating together, in the dry state, iodine and the finely divided metal, or by mixing them in presence of water—

$$Fe+I_2=FeI_2.$$

6. Many salts can be prepared by decomposing certain other salts of the same metal by means of the appropriate acid. The method is subject to considerable limitations. It is particularly applicable when the decomposed salt gives rise to an acid which is more volatile than the appropriate acid. For example, carbonates are decomposed by most acids with formation of carbonic acid and in most circumstances with evolution of its anhydride, carbon dioxide—

$$BaCO_3+2\,HCl=BaCl_2+H_2O+CO_2.$$
$$MgCO_3+H_2SO_4=MgSO_4+H_2O+CO_2.$$

Many crystallised carbonates which are insoluble in water, such as native barium carbonate, are not readily attacked in the cold, even by hydrochloric acid, and in order to effect this decomposition it is necessary to apply heat; but finely divided

amorphous carbonates, as obtained by precipitation, generally dissolve very easily.

As hydrogen sulphide is really a very weak acid, the preparation of salts from sulphides by means of acids, dealt with in Section **2**, might be included in this section.

Salts of strong but easily volatile acids, such as nitrates and chlorides, may serve as the starting-point in the preparation of sulphates and of salts of other acids which are volatile only at considerably higher temperatures; in such cases the mixtures require to be heated in absence of water. Immense quantities of sodium sulphate are manufactured in this way from common salt, and potassium sulphate is similarly prepared from the native chloride. In these cases the action takes place in two stages; the first results in the formation of the acid sulphate, and does not require a high temperature; the second stage, resulting in the formation of the normal sulphate, requires a much higher temperature.

$$NaCl+H_2SO_4=NaHSO_4+HCl.$$
$$NaCl+NaHSO_4=Na_2SO_4+HCl.$$

(It must not be supposed that the formation of acid sulphate is due to a smaller proportion of chloride being employed; even though a great excess of chloride be present the normal sulphate will be obtained only by the application of a high temperature.) This method is frequently employed in the manufacture of the acid, and the new salt is simply a by-product.

A case differing from any of the above is illustrated in the preparation of nitrates from chlorides, or *vice versa*, by means of the appropriate acid. Concentrated nitric and hydrochloric acids interact with the formation of easily volatile products—

$$HNO_3+3\,HCl=2\,H_2O+NOCl+Cl_2.$$

It is therefore possible to decompose completely salts of one of these acids by a sufficient excess of the other, provided much water is not present and the decomposition products of the acids are removed; the mixture is evaporated to dryness, and the whole process repeated, if necessary.

Another case is that in which the salt to be produced is sparingly soluble, and can be obtained by precipitation. In such cases, however, it is not generally necessary to employ the free acid, one of its soluble salts serving equally well, and such cases may be classed with those considered in the next Section.

7. The precipitation of insoluble or sparingly soluble salts by double decomposition between soluble ones has already been referred to (p. 12) in dealing with the general properties of salts. An important method of preparing salts is founded upon such actions, and will be shortly described in this section.

If the sparingly soluble salt which can be precipitated by such a reaction is itself required, the preparation is exceedingly simple. Thus, if it is desired to prepare lead chromate from lead nitrate, it is only necessary to add to a solution of the latter a solution of a convenient soluble chromate, say potassium chromate, then to collect the precipitate on a filter, wash, and dry it.

$$Pb(NO_3)_2 + K_2CrO_4 = 2\,KNO_3 + PbCrO_4.$$

It is not usually necessary to take the exact proportions of the ingredients, as indicated by the equation for the action, but it is of course more economical to do so. Care must be taken that only one of the products of the action is insoluble, otherwise a pure product cannot be obtained. Thus, barium chloride, or even calcium chloride, would not be employed for the preparation of silver chloride from silver sulphate, as the resulting sulphate is not an easily soluble one—

$$Ag_2SO_4 + BaCl_2 = BaSO_4 + 2\,AgCl.$$

In cases where the soluble salt produced by the double decomposition is desired, greater care is necessary. The interacting salts must be taken in as nearly as possible equivalent proportions, either by weighing them out exactly, or by cautiously adding the solution of the one to the solution of the other until a precipitate is no longer produced. It is impossible to avoid a slight excess of one or other of the ingredients, and this of course renders the resulting solution more or less impure; but, as a rule, such impurities may be got rid of by the process of crystallisation to which the filtered solution is subsequently subjected.

Silver salts and barium salts are frequently employed for the laboratory preparation of moderate quantities of soluble salts by this method: for this purpose they are made to interact with solutions of the appropriate chlorides and sulphates respectively. Suppose, for example, it is desired to prepare a small quantity of cupric chloride, and only cupric sulphate is available for the purpose. Both of these salts are easily soluble in water, and it

is impossible wholly to convert the latter into the former by the direct action of hydrochloric acid.* We can, however, weigh out 249·5 grams of crystallised cupric sulphate ($CuSO_4$, 5 H_2O), and 244·4 grams of crystallised barium chloride ($BaCl_2$, 2 H_2O), or other quantities in the same proportion, dissolve them in water, mix the solutions, filter, and evaporate the filtrate to small bulk so that it will crystallise on cooling.

$$CuSO_4+BaCl_2=CuCl_2+BaSO_4.$$

Even in cases where neither of the products of a double decomposition is very sparingly soluble, it may still be possible to effect an easy separation of them if there is a sufficiently great difference in their degrees of solubility. Thus potassium chlorate used to be prepared by adding potassium chloride to a mixture of calcium chloride and chlorate (obtained by treating bleaching powder with hot water) and allowing the mixed solution to crystallise.

$$5\,CaCl_2+Ca(ClO_3)_2+2\,KCl=6\,CaCl_2+2\,KClO_3.$$

Calcium chloride is exceedingly soluble in water, and potassium chlorate is the least soluble of all the salts represented in the above equation; the greater part of the latter therefore crystallises out before the former begins to separate from the solution (see Table of Solubilities).

Double decomposition may also be employed for the preparation of easily volatile salts by sublimation from others which are less volatile. The reacting salts are mixed together in the dry state, and gradually heated. The best examples of this method are supplied by the ordinary preparations of ammonium chloride and of the chlorides of mercury from the corresponding sulphates.

$$(NH_4)_2SO_4+2\,NaCl=Na_2SO_4+2\,NH_4Cl.$$
$$HgSO_4+2\,NaCl=Na_2SO_4+HgCl_2.$$
$$Hg_2SO_4+2\,NaCl=Na_2SO_4+2\,HgCl.$$
$$(\text{or } Hg+HgSO_4+2\,NaCl=Na_2SO_4+2\,HgCl).$$

In each case the new chloride is the most volatile of the four salts involved in that particular action.

* The only cases of practical importance in which a chloride can be prepared directly from a sulphate by means of hydrochloric acid, are those in which the sulphate is easily soluble and the chloride sparingly soluble in water or in dilute hydrochloric acid.

8. When a metal forms two sets of salts, corresponding to two different basic oxides, methods of preparing the higher salts from the corresponding lower ones, and *vice versa*, are interesting and sometimes of importance. The former case involves the addition of more of the acidic radical, while the latter involves its removal.

Preparation of higher salts from lower ones.—In the case of halides the acidic radical can be supplied directly, in the form of the free halogen, and, as a rule, this is the most convenient method to adopt for effecting the change. The halogen may either be allowed to act upon a solution of the lower salt, or be passed in the form of gas or vapour over the dry salt heated to a suitable temperature (see p. 54)—

$$2\,FeBr_2+Br_2=2\,FeBr_3,$$
$$SnCl_2+Cl_2=SnCl_4.$$

In the cases of most salts other than the halides, the corresponding acidic radicals do not exist in the free state, and, as such a method is impossible with them, some other must be employed. The nearest approach to the above method which is applicable to these salts (and also to the halides) consists in using an acid solution of the salt as the electrolyte surrounding the anode in an electrolytic cell; the acidic radical is then liberated by the discharge of the anion, and unites with the lower salt present to form the higher one. In such cases the electrolytic cell should have the electrodes separated by a porous diaphragm to prevent the new salt from being carried to the cathode, where the reverse process would take place.

$$2\,CoSO_4+SO_4''=Co_2(SO_4)_3.$$

Such a method is not very frequently employed, though in some cases (as the above) it may be the only one possible. As a general rule the additional acidic radical required is obtained by oxidising the corresponding acid, in presence of the salt, by means of a suitable oxidising agent; the hydrogen of the acid forms water, and the acidic radical unites with the lower salt.

In some cases free oxygen (atmospheric air) may serve as oxidising agent, though its action is often slow—

$$4\,FeSO_4+2\,H_2SO_4+O_2=2\,Fe_2(SO_4)_3+2\,H_2O,$$
$$4\,CuCl+4\,HCl+O_2=4\,CuCl_2+2\,H_2O.$$

On the other hand, the oxidation of certain salts, *e.g.* the chromous salts (see p. 126), takes place so rapidly that in preparing them (the lower salts) every trace of free oxygen must be excluded from the solutions employed and from the atmosphere to which they are exposed.

When such salts are acted upon by oxygen in absence of free acid, basic salts are frequently produced—

$$4\,FeSO_4+O_2=2\,Fe_2O(SO_4)_2\,;$$

in some cases, however, a mixture of normal salt with oxide or hydroxide may be formed.

For preparations of this kind (on a small scale, at least) the commonest oxidising agent is concentrated nitric acid, which possesses the advantage of being itself volatile and yielding volatile decomposition products, so that, as a rule, a pure salt is easily obtainable by evaporation, even when nitric acid has been added in excess. The decomposition products, other than water, consist usually of a mixture of oxides of nitrogen in which nitric oxide preponderates—

$$3\,FeSO_4+4\,HNO_3=Fe_2(SO_4)_3+Fe(NO_3)_3+NO+2\,H_2O,$$
$$6\,FeSO_4+3\,H_2SO_4+2\,HNO_3=3\,Fe_2(SO_4)_3+2\,NO+4\,H_2O,$$
$$3\,HgNO_3+4\,HNO_3=3\,Hg(NO_3)_2+NO+2\,H_2O.$$

In the case of some sulphates, such as ferrous sulphate or mercurous sulphate, hot concentrated sulphuric acid will itself act as an oxidising agent, but it is not so convenient or certain as nitric acid—

$$2\,FeSO_4+2\,H_2SO_4=Fe_2(SO_4)_3+SO_2+2\,H_2O.$$

Other oxidising agents (see p. 90) are frequently available in special cases, but most of them are not of sufficiently general applicability to be considered here.

[The preparation of a higher salt from a lower one is analogous to the preparation of a salt from a metal which does not dissolve directly in the appropriate acid. In the majority of such cases the metal is attacked if a suitable oxidising agent is present along with the acid—

$$Cu+H_2SO_4(\textit{dil.})+O=CuSO_4+H_2O,$$
$$6\,Ag+3\,H_2SO_4(\textit{dil.})+2\,HNO_3=3\,Ag_2SO_4+2\,NO+4\,H_2O.]$$

Preparation of lower salts from higher ones.—The removal of the extra proportion of acidic radical in such cases is usually effected by means of a metal, hydrogen, or some reducing agent, so that a salt or the free acid is produced by the process. If the metal used is not that from which the original salt is derived, then it must be such that the salt produced from it is capable of separation from the one which is to be prepared. Thus, zinc would not be a suitable agent for the preparation of ferrous sulphate from ferric sulphate by the action represented by the equation—

$$Fe_2(SO_4)_3+Zn=2\ FeSO_4+ZnSO_4$$

owing to the difficulty of separating the two resulting salts. This restricts such a method very considerably, and, as a rule, the only metal which can be conveniently used is that from which the salt is itself derived—

$$CuCl_2+Cu=2\ CuCl.$$

This is a case in which such an action is employed as an actual means of preparation, since cuprous chloride is not very easily prepared directly from the metal and the acid. The preparation of cuprous chloride from a mixture of cupric oxide and metallic copper, by the action of hydrochloric acid, is really only a modification of the same process—

$$CuO+Cu+2\ HCl=2\ CuCl+H_2O.$$

In other cases the method is employed more as a means of freeing a solution of the lower salt from traces of the higher one, than as a method of preparation, the salt being more easily prepared by other methods—

$$Fe_2(SO_4)_3+Fe=3\ FeSO_4,$$
$$Hg(NO_3)_2+Hg=2\ HgNO_3.$$

If the metal itself is not easily available, the method might be employed in a modified form by using a solution of the salt as the electrolyte surrounding the cathode in a divided electrolytic cell such as that previously mentioned (p. 58).

The use of hydrogen is possible with many salts, especially the halides, the gas being passed over the dry salt heated to a suitable temperature—

$$2\ FeBr_3+H_2=2\ FeBr_2+2\ HBr,$$
$$2\ CrCl_3+H_2=2\ CrCl_2+2\ HCl.$$

It also acts upon some salts in solution, but the action is slow, partly owing to the slight solubility of the gas ; if the solubility is increased by greatly increasing the pressure, the action takes place more rapidly.

Sometimes heating the dry salt alone is sufficient without the presence of any other agent. In the case of halides, free halogen is evolved—

$$PtCl_4 = PtCl_2 + Cl_2,$$
$$2\,CuCl_2 = 2\,CuCl + Cl_2\,;$$

in other cases decomposition products of the acidic radical are formed.

If the salt is derived from a metal which does not form a sulphide insoluble in dilute acids, hydrogen sulphide may frequently be used, as in the case of ferric salts ; sulphur is precipitated, otherwise the products are the same as those yielded by hydrogen—

$$2\,FeCl_3 + H_2S = 2\,FeCl_2 + 2\,HCl + S.$$

In the case of some sulphates sulphurous acid may be used, although its action is often slow—

$$Fe_2(SO_4)_3 + H_2SO_3 + H_2O = 2\,FeSO_4 + 2\,H_2SO_4.$$

Similar actions may be brought about by many organic substances, and if these are easily volatile and yield volatile oxidation products, they are sometimes used in this way. As a rule these changes are accelerated by exposure to light. Advantage is taken of the latter fact in some processes for preparing photographic prints by means of iron salts.

In the great majority of the cases of salt preparation which have been discussed in the preceding sections, the salts are obtained in solution. The preparation is not complete, however, until the solid salt has been obtained. This is effected in most cases by (*a*) allowing the solution to evaporate slowly at a nearly constant temperature until the salt crystallises out, or (*b*) concentrating the solution by evaporation at a higher temperature and allowing the concentrated solution to crystallise by gradual cooling. Solutions should not be evaporated to dryness (unless they are quite pure), as most impurities tend to accumulate in the mother liquor, and by rejecting a sufficient

quantity of this, the great proportion of the impurities is got rid of. If a very pure salt is desired, the crystals first obtained should be dissolved in a fresh quantity of solvent and recrystallised.

It is necessary to distinguish clearly between *methods of preparation* and *methods of formation*. A method of preparation involves not merely the formation of the substance, but its production in a pure state unmixed with other substances. For example: magnesium chloride is formed when *dolomite*, $MgCa(CO_3)_2$, is dissolved in hydrochloric acid; but this is not by itself a method of preparation, for calcium chloride is simultaneously produced, and the two chlorides, being very soluble, are not easily separated from each other. On the other hand, magnesium sulphate can be easily prepared from dolomite by the action of dilute sulphuric acid, because it is much more soluble in water than the sparingly soluble calcium sulphate; it is therefore only necessary to filter off the solution of magnesium sulphate from the precipitate of calcium sulphate, crystallise out the former salt from the filtrate, and purify it by recrystallisation (see Table of Solubilities).

NOTES REGARDING MANIPULATION AND METHOD OF WORK.

In all chemical work cleanliness is absolutely necessary, and inattention to this requirement may lead to highly erroneous conclusions being arrived at. It is therefore of the greatest importance to attend carefully to the efficient cleansing of all apparatus, and to avoid contaminating in any way the reagents and materials employed.

As regards the cleansing of apparatus, it must be remembered that insoluble solid matter is usually the least objectionable form of impurity; it is substances in solution, generally less conspicuous and often quite invisible, which it is most necessary to remove completely. The test tube brush should only be employed when there is adherent solid matter to be dislodged, and after its use the test tube or other vessel is, from the chemical point of view, quite as dirty as before—perhaps more so. To clean a test tube, it must be thoroughly rinsed out at least three times with water: in order to effect this, half fill the test tube with clean water, close the mouth of the tube with the thumb, shake vigorously, and then pour away the water as completely as possible; repeat the operation the necessary number of times. In many cases it is advisable to rinse finally with distilled water. Other apparatus should be cleansed in a similar manner.

Some substances, when they are precipitated from solutions, adhere as films so firmly to the walls of the vessel, that they cannot be removed at all readily by means of the test tube brush. As a rule, however, they can be removed easily by chemical means, and a suitable method of doing so is noted below for several of the more commonly occurring cases.

Metals and metallic sulphides can be removed by heating nitric acid in the tube, which must then, of course, be thoroughly washed with water.

Peroxides are best removed by means of warm hydrochloric acid, or, still better, the acid solution of stannous chloride.

Prussian blue (*and other insoluble ferrocyanides*) should first be decomposed by sodium hydroxide or ammonia, the tube

rinsed with water, then treated with hydrochloric acid, and finally washed with water.

When it is desired to have test tubes, etc., dry internally, a towel or duster must on no account be employed, as this would almost certainly introduce objectionable matters. The vessels should simply be drained as thoroughly as possible, and should then be allowed to dry in the air. A test tube or flask may be dried rapidly by rotating it just above a Bunsen flame until the water adhering to the interior has become steam and then inserting a long tube and either sucking out the steam or blowing it out by means of an air blast.

Platinum wires, which have become contaminated with substances that are not easily volatilised, are best cleaned by fusing borax on them to form a bead and working this along the greater part of the wire. The bead can be made to travel in one direction or the other by tilting the wire at an appropriate angle and also by suitably applying the heat. Beads tend to travel away from the hotter part of the wire. After suitable treatment in this way the molten bead may be jerked off, and the operation repeated if necessary. The wire is finally heated until it no longer imparts a distinct coloration to the flame.

The working place should be kept tidy, and must not be encumbered with reagent bottles and unnecessary apparatus. Each reagent bottle should have its own proper place on the shelves, and should always be replaced there immediately after use. When bottles are left standing on the bench itself, loss of time results owing to the difficulty of seeing the labels, and mistakes are also more likely to occur.

In observing reactions which are carried out in test tubes, the tube should be held securely, but not too tightly, between the thumb and the first two fingers of the left hand, and in a sloping position, so that its mouth is directed towards the reagent bottle held in the right hand. The stopper of the bottle should then be removed by grasping it between the little finger and palm of the left hand, and be held in that way until the reagent has been added, when it is replaced. Stoppers should not be laid upon the bench, if this can possibly be avoided; if it is unavoidable, then they should be inverted, so that the part which goes inside the bottle does not come into contact with the bench, since it is impossible to keep the latter chemically clean. A stopper which has been dropped should be washed with water before being replaced.

When pouring from a bottle, the latter should be held with the label uppermost, so that if a drop of liquid is left adhering to the lip of the bottle, it will not, when the bottle is replaced, trickle down over the label (which would thus become destroyed), but over the back of the bottle.

The reagent should not be added in one large portion ; only a few drops at a time should be allowed to trickle down the inside of the sloping tube, which should then be gently oscillated so as to mix the two liquids. Any change must be carefully noted, and then more reagent may be added as before until there is no further action. The contents of the tube should be under close observation during the whole time that the reagent is being added.

The quantity of substance taken for examination should be as small as possible. In the case of most solutions about 1 c.c. is a sufficiency for all ordinary reactions ; frequently a single drop is all that is necessary. For the performance of the so-called " drop reactions," small watch-glasses, thin glass tubes drawn out to an internal diameter of a little more than 1 mm., and glass rods drawn out and having a spherical tip of about 2 mm. diameter, are required. Although no attempt is made here to pursue the specialised methods in text-books devoted to the subject, many of the reactions mentioned below (pp. 98-156), particularly those in which intensely coloured precipitates (*e.g.* silver chromate) or solutions (*e.g.* ferric thiocyanate) are produced, may be carried out by transferring drops of solution and of reagent by means of the pipettes (glass tubes above-mentioned) to a watch-glass resting on white paper and then mixing the drops with the help of a glass rod. If too great a quantity of material for the desired purpose has been taken from the stock, the excess should not be returned to the bottle or other vessel in which the stock is kept, but should either be thrown away or be transferred to another receptacle and used for subsequent work. It is much better to lose a small quantity of material than to run the risk of the stock being rendered impure, which would be the case, say, if the solution had originally been poured into a dirty test tube—a possibility which can never be absolutely excluded. For similar reasons test papers, etc., should not be dipped into the reagents in the bottles ; a small quantity should be poured from the bottle into a watch-glass or other convenient vessel.

When only small quantities of liquid have to be dealt with

in test tubes, it is possible to mix the contents thoroughly by gentle oscillation of the tube, but this is not possible when the volume of liquid is considerable ; in some cases it then becomes necessary to close the tube by means of the thumb and shake vigorously. When this is done, care must be taken that the thumb is as nearly as possible chemically clean, and immediately after the operation it should be again washed. Tubes containing hot liquids should not be treated in this way, especially tubes to which concentrated sulphuric acid has been added ; in these cases the volume of liquid should be kept to a minimum, and mixture effected as first described. It may be taken as a general rule that only in exceptional cases should the volume of liquid in a test tube be more than sufficient to half fill it.

When the contents of a tube have to be heated, especially if both solid and liquid are present, there is also a considerable advantage in restricting the quantity of material. The time necessary to attain the desired temperature is then shorter, and it is much easier to keep the solid matter in constant circulation throughout the liquid by gentle oscillation of the tube. By keeping the solid stirred up in this way it is possible to diminish considerably the risk of local over-heating, which might result in the fracture of the tube or in the sudden expulsion of its contents. As the latter event is possible even when considerable attention is paid to the work, the test tube should always be held, during heating operations, in a sloping position, with the mouth pointing towards the reagent shelves, so that the worker and his neighbours run no risk of accident from the hot liquid. Tubes should never be held quite stationary in the flame, and the flame should not be allowed to play, except momentarily, on any part of the tube above the level of the liquid.

The use of a special holder for test tubes, while being heated, is unnecessary if the heating is properly carried out. Glass is such a poor conductor of heat that the upper part of a test tube should never become too hot to hold comfortably, provided the tube is not too full of liquid, and the latter is not made to boil rapidly. Actual evaporations are not carried out in test tubes, and when mere heating to a high temperature is desired, there is no advantage in making the liquid boil briskly, seeing that it is then no hotter than when it is kept just at the boiling point

When a record of observations has to be kept, jottings should be made in the note-book as soon as possible; it is a great mistake to trust to memory alone more than is necessary. This applies more especially to cases where numerical results are involved; these should be recorded as they are observed, the actual readings being noted immediately, without any process of mental arithmetic intervening (see p. 195). Materials which are to be preserved for subsequent use, solutions set aside to crystallise, etc., should be labelled in all cases, otherwise mistakes are almost certain to occur.

The slight saving of time which may perhaps be gained occasionally by neglect of the above precautions is dearly bought when it may involve a considerable amount of work being rendered of no value whatever.

EXPERIMENTS ILLUSTRATING THE FORMATION AND DECOMPOSITION OF SALTS, TOGETHER WITH SOME SIMPLE QUANTITATIVE MEASUREMENTS.

1. Test papers as indicators of acidity or alkalinity.
2. Neutralisation of an acid by an alkali and *vice versa*.
3. Showing necessity of thorough mixing of solutions.
4. Preparation of sodium chloride.
5. Determination of the solubility of sodium chloride.
6. Recrystallisation of cupric sulphate.
7. Recrystallisation of ammonia alum.
8. Recrystallisation of a mixture of cupric sulphate and ammonia alum.
9. Recrystallisation of a mixture of cupric sulphate and ammonium sulphate.
10. Preparation of potassium sulphate.
11. Preparation of sodium sulphate.
12. Preparation of supersaturated solution of sodium acetate.
13. Experiments with calcium carbonate (marble).
14. Determination of the solubility of calcium sulphate.
15. Experiments with magnesium carbonate (magnesite).
16. Determination of the water of crystallisation of magnesium sulphate crystals.
17. Combustion of magnesium and determination of the ratio Mg : MgO.
18. Action of hydrochloric acid upon magnesium, and determination of the ratio Mg : H.
19. Action of acids upon zinc.
20. Determination of the zinc oxide derived from basic zinc carbonate.
21. Action of acids upon lead.
22. Action of heat and of hydrochloric acid upon lead carbonate (cerussite and white lead).
23. Preparation of lead nitrate.
24. Action of acids upon lead sulphide (galena).
25. Action of nitric acid upon red lead.
26. Action of heat and of acids upon lead peroxide.

27. Action of acids upon copper.
28. Determination of the ratio Cu : CuO.
29. Preparation of ferrous sulphide.
30. Action of acids upon iron.
31. Preparation of ammonium iron alum.
32. Determination of the iron in ammonium iron alum.
33. Determination of the sulphate radical in a soluble sulphate.
34. Action of acids upon aluminium.
35. Action of heat upon lead nitrate.
36. Action of heat upon ammonium nitrate.
37. Action of heat upon ammonium bichromate.
38. Action of heat upon potassium chlorate.
39. Determination of the ratio $KClO_3$: KCl.
40. Action of sulphuric acid upon sodium chloride.

1. In order to acquire some familiarity with the use of indicators (see p. 41) in the form of test papers, examine the behaviour of various reagents towards blue and red litmus papers and yellow turmeric paper, proceeding as follows :—

Divide a strip of each kind of paper into small pieces (about 1 cm. square) and spread them out on watch-glasses or on a clean sheet of paper. Clean a glass rod and pour on to it a drop of acetic acid. Touch a piece of each kind of paper with the wet end of the rod and note the effect of the acetic acid upon the indicator. Neither the rod nor the indicator test paper should be inserted into the reagent bottle. After washing the rod with distilled water, repeat the experiment with each of the following ordinary reagents : dilute hydrochloric acid, dilute nitric acid, dilute sulphuric acid ; sodium hydroxide, calcium hydroxide, ammonium hydroxide (ammonia) ; sodium hydrogen tartrate (sodium bitartrate) ; cupric sulphate, ferric chloride ; sodium carbonate ; potassium iodide, ammonium chloride, magnesium sulphate. In the case of ammonia an additional experiment should be tried as follows : moisten the end of a strip of red litmus paper with water and hold the strip over the mouth of the ammonia bottle after removing the stopper ; note the blue coloration produced rapidly on the wet portion, but much more slowly on the remainder of the paper.

The observations may be recorded in some such way as the following :—

Reagent.	Change of Colour.		
	Red Litmus.	Blue Litmus.	Yellow Turmeric.
Acetic acid . .	—	Red	—
Sodium carbonate .	Blue	—	Brown

2. Pour two or three cubic centimetres of, say, hydrochloric acid into a test tube, drop in a small piece of blue litmus paper (which, of course, will immediately become red), and then add, say, sodium hydroxide in small quantities, shaking the contents of the tube after each addition. For some time the paper will remain red, but at length it will become blue, indicating that excess of hydroxide is now present, the acid having all been changed into salt. Try a similar experiment in the reverse way by first putting the alkali into the tube and adding the acid until the paper becomes red. Instead of using a piece of litmus paper, the solution first placed in the tube may be coloured by the addition of a small quantity of litmus solution. (See p. 65.)

3. Pour about 5 c.c. of dilute hydrochloric acid (which is denser than water) into a test tube, and drop in a piece of litmus paper; then, holding the tube inclined at an angle of about 45°, pour in ammonia solution (which is lighter than water) until the tube is nearly full. The litmus paper remains red, but if the tube be now closed with the thumb and shaken so as to mix the contents, the colour changes to blue. This experiment demonstrates that when ammonia solution is added to another solution without shaking up, much more than is necessary may be added without the desired result being attained, owing to the ammonia resting as a distinct layer on the top of the other solution.

4. Pour about 10 c.c. of sodium hydroxide solution into a basin and add dilute hydrochloric acid until the liquid is slightly acid, as shown by taking out a drop of the liquid on a glass rod and testing it on blue litmus paper. Place the basin on a piece of gauze over the Bunsen flame and heat cautiously till the solution is evaporated to dryness, then heat

more strongly until all decrepitation ceases. The resulting white solid is common salt ; taste some of it ; dissolve some in water, and examine the solution by means of test papers.

5. *Determine the Solubility of Common Salt at Room Temperature.*—Prepare a saturated solution of common salt by adding small quantities of salt to water in a test tube and shaking frequently until no more will dissolve. The water may be boiled to assist in dissolving the salt, but the solution must be allowed to stand (best overnight) to acquire room temperature before the experiment is further proceeded with. Carefully weigh a clean porcelain basin and small glass rod, filter a portion of the solution (not more than 2-3 grm.) into this tared basin, using an unmoistened filter paper and a perfectly dry funnel, and weigh again. The solution must now be evaporated to dryness. Support the basin on wire gauze and heat very carefully, especially when approaching dryness, as spirting is liable to take place and some salt may be lost. Spirting can be avoided by stirring the solution with the glass rod and by using a small flame towards the end of the evaporation. When the evaporation is finished, allow the basin and its contents to cool and then weigh. Heat again and weigh after cooling. Repeat until the weight is constant.

Let b=weight of basin and glass rod, w=weight of basin, glass rod and solution, and w'=weight of basin, glass rod and dry salt ; then $w-b$=weight of solution, $w'-b$=weight of dry salt, and $(w-b)-(w'-b)=w-w'$=weight of water in which the salt was dissolved. The weight of salt dissolved by 100 grm. water is therefore $100(w'-b)/(w-w')$ grm.

6. *Recrystallise Cupric Sulphate to obtain well-formed Crystals.*—Dissolve 5-10 grm. cupric sulphate in hot water. If the resulting liquid is not quite clear, get rid of any suspended matter by filtering the hot solution. The cupric sulphate is apt to crystallise out during filtration, and clog the funnel ; to avoid this, the funnel should be previously warmed by running a tubeful of boiling water through the filter, collecting it in the crystallising dish, and rejecting it ; this should be followed immediately by the filtration of the solution.

Place a drop of the filtrate on a watch-glass to see if crystals separate on cooling. If not, evaporate somewhat and test again, repeating until this result is obtained. Then pour the hot solution into a crystallising dish and set aside to crystallise.

When crystals have formed, decant the "mother liquor," and dry the crystals by placing them between two pieces of filter paper and pressing them gently with the fingers.

7. *Recrystallise Alum.*—Dissolve 5-10 grm. alum in hot water, and then proceed as in Experiment 6.

8. *Recrystallise a Mixture of Cupric Sulphate and Alum.*—Dissolve about 6 grm. cupric sulphate and 4 grm. alum in about 15 c.c. of hot water, and then proceed as in Experiment 6. Record the result.

9. *Recrystallise a Mixture of Cupric Sulphate and Ammonium Sulphate.*—Dissolve about 5 grm. cupric sulphate and 5 grm. ammonium sulphate in about 15 c.c. of hot water, and then proceed as in Experiment 6. Record the result.

10. To about 10 c.c. of a 30 per cent. solution of potassium hydroxide, contained in a test tube, add very gradually and cautiously dilute (30 per cent.) sulphuric acid until the liquid is slightly acid; then add more of the potassium hydroxide until it is decidedly alkaline. Potassium sulphate separates as a white crystalline precipitate. Allow the liquid to cool gradually, when more of the salt will crystallise out. Pour away the alkaline mother liquor, draining as thoroughly as possible; add a very small quantity of cold water to the residue, shake up, allow to settle, and again drain off; repeat these operations. After washing in this way, add to the residue about twice its volume of water and heat gradually to boiling; if it does not all dissolve, add further small quantities of water, heating again, until it does dissolve; allow to cool slowly and crystallise. Pour away the mother liquor and wash the crystals by decantation (see below). Dissolve the remaining portion of the salt in water, and test the solution by means of test papers; it will be neutral if the deposit has been thoroughly washed (see p. 48).

If in this experiment a large excess of sulphuric acid is added to the potassium hydroxide, the white precipitate first formed dissolves, owing to the formation of potassium hydrogen sulphate, which is much more soluble than the normal salt.

The method of removing adhering mother liquor, etc., described in the foregoing, is known as *washing by decantation*; it can be adopted with crystalline substances which settle

quickly and well. In cases like the present, where the precipitate is soluble in water, it is necessary to employ very small portions of wash water, otherwise the loss due to dissolution of the substance in water will be very great. In all cases it is far more effective to wash frequently with small quantities than seldom with larger quantities, even though the total volume of liquid employed should be the same.

11. Place about 10 c.c. of dilute sulphuric acid in a porcelain basin. Add sodium hydroxide solution from a burette to the acid, stirring the mixture with a short glass rod, and testing from time to time as described in Experiment 1. When the solution has become alkaline, add a few drops of dilute sulphuric acid until the solution becomes distinctly acid and then neutralise it by adding the sodium hydroxide solution drop by drop. Concentrate the neutral solution by boiling it, until a drop transferred to a dry watch-glass deposits crystals on cooling and stirring. Then pour the hot solution into a crystallising dish, which has been warmed by pouring half a test tube full of boiling water into it and then emptying it. Cover the dish with a watch-glass and set it aside to cool. If crystals have not formed by the time the solution is cold, the solution must be *supersaturated* (see p. 10). In this case, the addition of the smallest particle of crystal from the watch-glass will cause the separation of the crystalline decahydrate, Na_2SO_4, 10 H_2O, called *Glauber's Salt* (see p. 1). A supersaturated solution requires the presence of a nucleus upon which and from which crystals may grow.

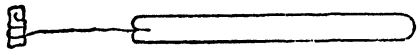
Drain the mother liquor from the crystals, transfer them to a filter paper and dry them as described in Experiment 6.

After exposure to air for several days, it will be observed that the crystals have *effloresced* (see p. 9).

12. The phenomenon of *supersaturation* may also be observed in a solution of sodium acetate. Place 5 grm. crystallised sodium acetate in a test tube (a layer about 1½ inch deep in a ⅝-inch tube). Add three drops of water from the tap. Heat cautiously until the whole of the solid matter has become liquid and raise just to the boiling-point. Set aside till quite cold (or cool rapidly by holding the tube in running water from the tap). The contents of the tube remain liquid when cold, but on introducing a minute fragment of crystallised sodium acetate, rapid crystallisation occurs with solidification of the whole or

almost the whole of the liquid. Note the rise of temperature which occurs on solidification.

13. Select a small elongated chip of marble (4 - 5 mm. long by 2-3 mm. thick is about the best size), and wrap round it the end of a platinum wire, as shown in the figure, taking

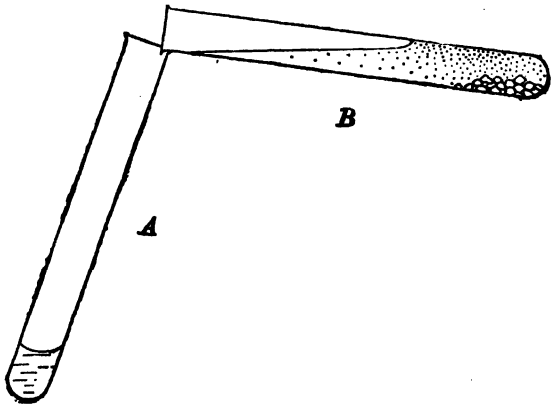


care to keep the chip at a considerable distance from the end of the glass holder. Now hold the chip in the flame of a Bunsen burner, keeping it in the hottest part for about two minutes. Decomposition takes place rapidly, and soon the chip will be seen to glow in a characteristic manner; it has now been converted into quicklime. Remove it from the flame, allow to cool, and examine it without touching it. Note that the original shape is retained, but that the crystalline appearance is gone. Holding the chip over the mouth of a clean dry test tube, press it between the finger and thumb; it will crumble and fall in powder to the bottom of the tube. Allow a single drop of water to trickle down the inside of the tube till it reaches the quicklime; combination occurs with considerable evolution of heat: note the hissing sound, the formation of a cloud due to the escape and condensation of steam, and, by placing the bottom of the tube against the back of the hand, the high temperature produced. Provided too much water has not been employed, the calcium hydroxide (" slaked lime ") will form a dry powder. Fill the tube about two-thirds with water and shake vigorously; some of the solid dissolves, but, as a good deal remains even after prolonged shaking, it is evident that calcium hydroxide is only sparingly soluble in water. Allow the undissolved portion to settle and pour off as much as possible of the clear solution (" lime water "), or, if necessary, filter it off. Note the taste and (by means of test paper) the alkaline reaction.

$$CaCO_3 = CaO + CO_2.$$
$$CaO + H_2O = Ca(OH)_2.$$

Pour some of the lime water into a shallow dish (a watch-glass will do), and leave it exposed to the air for some time; it slowly becomes covered with a pellicle of calcium carbonate formed by the absorption of carbon dioxide from the air.

Pour a fresh portion, diluted with its own volume of water, into a clean test tube. Through a long tube dipping into the liquid, gently blow so that the carbon dioxide of the breath (expired air contains 4 to 5 per cent. of carbon dioxide) acts upon the lime water, causing it to become turbid owing to the production of calcium carbonate. On continuing the experiment, the turbidity disappears and a solution of calcium bicarbonate is obtained (temporarily " hard " water).



In another clean tube place a fresh portion of lime water, diluted with its own volume of water, and pour into it carbon dioxide prepared in the following manner: put some roughly ground marble into a test tube *B*, and cover it with water, then add hydrochloric acid until brisk effervescence sets in. Place the lip of this test tube over that of the one containing the lime water, *A*, and tilt *B*, bringing it as nearly horizontal as possible (without permitting any of the liquid to run over), so as to pour the gas into *A*.* (If any of the acid liquid gets from *B* into *A* the experiment will not succeed, and a fresh portion of lime water must be taken in a clean tube.) Close *A* with the thumb and shake vigorously. A precipitate of calcium carbonate is formed. Repeat the operation several times, if necessary adding more hydrochloric acid to *B* so as to keep up a brisk evolution of carbon dioxide; the whole operation should be carried out as

* A more efficient but less simple method is to fit a cork provided with a bent glass tube into the tube *B*, and dip the free end of the bent tube, from which the gas escapes, under the surface of the liquid in *A*.

quickly as possible. The precipitate will be gradually dissolved, forming a clear solution of calcium bicarbonate. It will now be found that the alkaline reaction has disappeared.

This solution of calcium bicarbonate may be looked upon as a specimen of very " hard " water ; if to a portion of it a small quantity of clear soap solution is added, a curdy white precipitate will be formed. It may be " softened " in the following ways : to one portion of the bicarbonate solution add an equal volume of lime water : a white precipitate of the normal carbonate is produced. Boil another portion of the bicarbonate solution in a clean test tube for some time : calcium carbonate will be again precipitated—this time in a distinctly crystalline and more transparent condition ; the resulting liquid is practically pure water.

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2\,CaCO_3 + 2\,H_2O.$$
$$CaH_2(CO_3)_2 = CaCO_3 + H_2O + CO_2.$$

(*Any* calcium salt dissolved in water makes it " hard " in its behaviour towards soap, as may be observed both with lime water itself and with calcium chloride, referred to below. Hard waters in which calcium salts, other than the bicarbonate, are present cannot be softened by the above-mentioned means.)

The concentration of calcium hydroxide in the lime water prepared in the above way may be determined by the method described under alkalimetry (p. 197). The sample employed for the purpose must be quite free from sediment, or very erroneous results will be obtained.

The residue from the preparation of carbon dioxide by means of marble and hydrochloric acid consists of a solution of calcium chloride, along with any excess of hydrochloric acid or of marble, as the case may be. If the acid is in excess and no marble remains, add some of the latter and heat to boiling ; after some time test with blue litmus paper : there should be no acid reaction. Decant the solution from the undissolved marble, or, if the liquid is not quite clear, filter it. By evaporating the solution solid calcium chloride may be obtained, but owing to its great solubility (calcium chloride is very deliquescent) it is not advisable to try to crystallise the salt. Part of the solution may be evaporated to dryness in a basin, however, and the residue left exposed to the air for some time in order to observe its deliquescence (see p. 9).

Calcium sulphate is a sparingly soluble salt, and if dilute

sulphuric acid is added slowly to some of the solution of the chloride, a white crystalline precipitate having the composition represented by the formula $CaSO_4$, $2\,H_2O$ will be produced. This composition is the same as that of *gypsum*, the mineral from which plaster of Paris is prepared (see p. 233).

Part of the calcium chloride solution may be diluted and examined for the reactions of calcium salts as described on page 129; the flame test (page 170) may be best observed with the undiluted solution.

Since carbon dioxide is the only commonly occurring odourless gas which produces a white precipitate in lime water, this reagent is employed in testing for the gas. Instead of pouring the gas into a separate tube in the manner already described, the reaction may often be observed more satisfactorily by proceeding as follows: hold a glass rod, which has been dipped into a solution of calcium hydroxide, in the tube in which the gas to be tested is being liberated, taking care not to touch the wall of the tube. If carbon dioxide is present, the drop of solution adhering to the rod will become cloudy, owing to the formation of a pellicle of calcium carbonate. In those cases where the gas is being liberated by the action of an acid it is necessary to keep the drop at a considerable distance above the surface of the liquid, otherwise minute particles of acid solution will be spirted on to it and will nullify the test. The necessity for this precaution can be easily proved by holding a drop of water on the rod about an inch from the effervescing liquid, and thereafter touching with it a piece of blue litmus paper, whereupon an acid reaction will be observed. In all cases, therefore, in which a negative result is obtained when testing for carbon dioxide in this way, make sure that the drop, after withdrawal from the tube, still gives a distinct alkaline reaction.

14. *Determine the Solubility of Calcium Sulphate at Room Temperature.*—Prepare a saturated solution of calcium sulphate by adding 2-3 grm. calcium sulphate to 50 c.c. of water in a small flask and shaking at frequent intervals for a few hours. Note that, since calcium sulphate is more soluble in cold water than in hot, it is not desirable to apply heat in this case. Filter a portion of the solution (not less than about 20 grm.) into a tared basin and weigh again. Evaporate to dryness and complete the determination as described under Experiment 5.

15. Magnesium carbonate occurs nearly pure in nature as the mineral *magnesite*, forming white masses somewhat resembling chalk in appearance, but harder and more compact. It is practically insoluble in water.

Warm a small quantity of magnesite with hydrochloric acid; note the effervescence due to the escape of carbon dioxide; test for this gas as already described.

Heat a small fragment on a platinum wire; transfer the resulting piece of magnesium oxide, or "calcined magnesia" (which does not crumble like the quicklime prepared from marble), to a clean dry test tube, and allow a drop of water to fall upon it. The water will be absorbed by the porous mass, but, though the two substances slowly unite to form magnesium hydroxide, there will be none of the striking phenomena which are observed in the case of calcium oxide. Now add a considerable quantity of water and shake for some time; test the liquid with red litmus paper: magnesium hydroxide is practically insoluble in water, and no alkaline reaction should be observed. Pour off the water, lay the piece of hydroxide on a strip of red litmus paper and press them gently together; observe the blue stain indicating an alkaline reaction, which shows that magnesium hydroxide is not quite insoluble in water.* Replace the hydroxide in a test tube and add hydrochloric acid; on heating, solution will take place without effervescence, provided the magnesite has been completely decomposed.

Heat some powdered magnesite in a hard glass tube, and after a short time test for the presence of carbon dioxide in the tube. A very high temperature is not necessary; magnesium carbonate is much more easily decomposed by heating than calcium carbonate is.

Various magnesium salts can be formed by the action of acids on magnesite, but the only one suitable for crystallisation on a small scale is the sulphate. Instead of using magnesite itself, the artificially prepared carbonate or basic carbonate may be used, and is much more convenient, since it dissolves much more readily.†

* Many samples of magnesite, and of other native carbonates, contain admixed calcium carbonate, and the alkaline reaction might be referred to the presence of calcium hydroxide as an impurity in the magnesium hydroxide; but the purest specimens of magnesium hydroxide which can be prepared all show a similar behaviour, and the reaction is therefore not to be attributed to impurities.

† Dissolution of magnesite in acid can be effected more easily if it is first ignited (on a piece of wire gauze) so as to convert it into oxide.

To about 15 c.c. of hot dilute sulphuric acid add magnesium carbonate in successive small portions, waiting after each addition until effervescence stops before adding the next portion; continue until the liquid appears distinctly cloudy after the effervescence has stopped. Now heat the liquid gradually to boiling; filter it into a crystallising dish and allow it to cool; if crystals do not separate overnight, evaporate a little of the water and again allow to cool. The crystals of magnesium sulphate or " Epsom salt " thus obtained have the composition represented by the formula, $MgSO_4$, 7 H_2O. Drain off the mother liquor and press the crystals between filter paper. The crystals may be dissolved in water, and the solution examined for the reactions of magnesium salts as described on page 130.

16. *Determine the Water of Crystallisation in Magnesium Sulphate Crystals.*—Place a clean porcelain crucible and lid on a pipeclay triangle and heat them gently for two minutes; allow them to cool for at least ten minutes on a crucible carrier. Weigh the cold crucible and lid. Remove the crucible from the balance and place in it about 0·6 grm. magnesium sulphate crystals and weigh the crucible, lid, and crystals. Next gently heat them by supporting the crucible on a pipeclay triangle placed about six inches above a small flame. At intervals of a few minutes lower the crucible and increase the flame very gradually, until the bottom of the crucible is heated almost to dull redness. Allow the crucible, lid, and contents to cool for about twenty minutes, and then weigh. Repeat the heating, cooling, and weighing until constant weight is attained. From the loss of weight, calculate the percentage of water in the crystals.

17. Burn a piece of magnesium ribbon and collect the product of combustion, as follows: hold the ribbon by means of a pair of forceps and ignite the free end in the Bunsen flame; as soon as it is properly kindled withdraw it from the flame and hold it over a watch-glass to catch the magnesium oxide formed. Note the appearance and the friable character of the product. Press a small piece upon moist red litmus paper and observe the alkaline reaction. Transfer the remainder to a clean test tube and warm with a small quantity of hydrochloric acid; test the resulting solution for magnesium salt.

Determine the ratio Mg : MgO.—In the manner described in Experiment 16, heat, cool, and weigh a porcelain crucible and lid and place in it about 0·3 grm. magnesium wire or ribbon.

(The wire or ribbon must have a bright fresh surface. If dull, it should be rubbed with emery paper.) Then heat the crucible with the lid on until the magnesium begins to burn. By means of the crucible tongs lift the lid slightly to allow access of air so that the magnesium may continue to burn and be completely converted into oxide. Allow the crucible, lid, and contents to cool for about twenty minutes. Repeat the heating, cooling, and weighing until constant weight is attained. Calculate the ratio Mg : MgO.

18. Dissolve a small quantity of magnesium in hydrochloric acid ; note the evolution of hydrogen, which can be burned at the mouth of the tube if the evolution is sufficiently rapid. If the action is not very brisk a slight explosion may take place on the application of a light, owing to the presence of a mixture of air and hydrogen in the tube (see pp. 89, 184). When the metal has all dissolved, the solution thus obtained may also be tested for magnesium salt.

Determine the ratio Mg : H.—First find the volume of the burette * between the 30 c.c. mark and the stopcock by bringing 10 c.c. water from a pipette into the burette and subtracting 20 from the observed reading of the level of the water.

Weigh a piece of clean magnesium wire or ribbon (about 0·025 grm.). Pour about 10 c.c. concentrated hydrochloric acid into the empty burette, then carefully fill it up with water, avoiding undue mixing of the hydrochloric acid with the water. Fill a porcelain basin with water. Coil the magnesium wire so that it will just go into the burette, quickly insert it and, closing the end with the forefinger, invert the burette, removing the finger as soon as the end is under the surface of the water in the basin. The concentrated hydrochloric acid, being denser than water, flows down and mixes with the water and in contact with the magnesium liberates hydrogen gas. When the metal has all dissolved, transfer the burette and the basin to a bench sink or a cylinder filled with water and adjust the burette so that the level of the liquid is the same inside and outside the burette. Then measure the volume of the hydrogen,† the temperature of the water and the atmospheric pressure.

* The burette is assumed to be one graduated to deliver 30 c.c. If a 25 or a 50 c.c. burette is used, then the number to be subtracted from the observed reading will be 15 or 40.

† For precautions, consult the chapter on Volumetric Analysis, p. 194.

Let w = the weight of the metal employed (grm.)
„ v = „ observed volume of hydrogen (c.c.)
„ t = „ temperature of the water (° C.)
„ p = „ barometric pressure (mm.)
„ r = „ pressure of aqueous vapour at $t°$ (mm.)
„ v' = „ corrected volume of hydrogen at 0° C. and 760 mm. (c.c.)
„ w' = „ weight of the liberated hydrogen (grm.)
Then $v'=273\,v(p-r)/760\,(t+273)$.

Since 22,400 c.c. hydrogen at 0° and 760 mm. weigh 2 grm., $w'=2\,v'/22{,}400$, and the ratio Mg : H $=w : w'$.

Pressure of Aqueous Vapour.

t° C.	mm.	t° C.	mm.
8	8	24	22·2
10	9·2	26	25·0
12	10·5	28	28·1
14	11·9	30	31·5
16	13·6	32	35·4
18	15·4	34	39·6
20	17·4	36	44·2
22	19·7	38	49·3

The ratio Al : H may be determined in a similar manner.

19. Place 10-15 c.c. of dilute sulphuric acid in a test tube, and add to it from time to time small quantities of granulated zinc, so long as the metal dissolves. Hydrogen is evolved rapidly at first, but the action becomes much less brisk as the acid becomes used up ; the liquid should then be warmed while still in contact with excess of zinc, and afterwards filtered into a small beaker. To the clear solution add a small quantity of nitric acid, and boil for a minute or two ; then pour the liquid into a crystallising dish and set aside to cool slowly. The crystals of hydrated zinc sulphate or " white vitriol," $ZnSO_4$, 7 H_2O, which separate are similar to those of magnesium sulphate obtained in an earlier experiment ; the two salts are isomorphous. The crystals should be freed from the mother liquor and dried between filter paper. An aqueous solution prepared from them may be examined for the reactions of zinc salts (see p. 117). The reason for boiling with nitric acid is to oxidise any ferrous sulphate (formed from iron as an impurity

in the zinc) into ferric sulphate, which does not contaminate the crystals of zinc sulphate to the extent that ferrous sulphate would do.

Zinc dissolves in most of the common acids, but many of the salts so formed, such as the chloride and nitrate, are very deliquescent and not suitable for crystallising on a small scale. Observe, however, its interaction with hydrochloric acid and with acetic acid, giving rise to the evolution of hydrogen in each case, and notice also the reaction with nitric acid (see p. 53).

20. *Determine the percentage Weight of Zinc Oxide obtained by heating basic Zinc Carbonate.*—Proceed as in Experiment 16, with the following exceptions: weigh about 1 grm. zinc carbonate and raise the temperature of the crucible to full red heat instead of to dull redness. From the weight of the original basic zinc carbonate and that of the residual zinc oxide calculate the percentage weight of the latter derived from the former.

21. Warm together in a test tube several grams of finely granulated lead and 10-15 c.c. of nitric acid (30 per cent.). Note that the bubbles of escaping gas are colourless, but that the gas above the liquid is reddish-brown; the colourless gas is mostly nitric oxide, which forms coloured nitrogen peroxide by uniting with the oxygen of the air (see p. 52). Continue heating for some time until the solution becomes distinctly yellow, indicating that the nitric acid is all used up and that basic nitrite is being formed; then pour off the solution from the unattacked metal * into a clean test tube, add more nitric acid to it in order to destroy the nitrite and provide a decided excess; cool the acidified solution by running water from the tap over the outside of the tube. Small crystals of lead nitrate will quickly form and settle to the bottom. After thorough cooling, pour off the supernatant liquid into another tube; it is a solution of lead nitrate, containing the unattacked nitric acid. Wash the crystals of lead nitrate once by decantation, using a very small quantity of water, as the salt is very soluble in pure water though sparingly soluble in nitric acid. The purified salt thus obtained may be dissolved in water, and the solution examined for the reactions of lead salts, as described on page 103.

* If the metal, wet with solution, be left in the tube for any length of time, the whole will set to a hard mass, which cannot be easily cleaned out.

To the mother liquor decanted from the crystals (or to the original mother liquor) add hydrochloric acid; lead chloride, which is very sparingly soluble in cold water, will be obtained as a white precipitate. Allow the precipitate to settle somewhat and pour away the clear liquid; add water to the remainder, and warm in order to dissolve the precipitate. On cooling the solution, lead chloride will crystallise out; allow the crystals to settle, and wash with cold water by decantation. Dissolve the salt in moderately warm water, and add potassium iodide to the solution; a yellow precipitate of lead iodide will be produced. Heat the mixture to boiling; at least the greater part of the precipitate will dissolve. If all does not dissolve, add water and heat again until it does. The solution is colourless; allow it to cool, when crystals of lead iodide in the form of glistening yellow scales will gradually form. Dissolve the crystals again by warming the liquid and add dilute sulphuric acid to the solution; a white precipitate of lead sulphate will be produced, which will not dissolve on adding more water and warming, as it is one of the least soluble lead salts (see p. 105).

Heat a small quantity of granulated lead with dilute sulphuric acid; it does not dissolve. Pour off the acid, wash the metal thoroughly by decantation, add hydrochloric acid, and warm. In this case there is a very slow action, lead chloride being formed in solution, while hydrogen is evolved. If the heating is continued for some time, sufficient lead chloride may be produced to yield crystals on cooling the solution.

To another small quantity of lead in a dry test tube add concentrated sulphuric acid, and warm carefully; chemical action soon commences, lead sulphate is formed as a white powder, and there is a simultaneous evolution of steam and sulphur dioxide, the latter recognisable by its odour and its reducing action on ferric ferricyanide test paper (p. 238); the gases are accompanied by sulphuric acid fumes (p. 178).

NOTE.—Owing to the formation of fusible alloys of platinum with certain metals such as lead and copper, these metals and their compounds must on no account be strongly heated in platinum apparatus, otherwise the apparatus will be destroyed. (See also pp. 170, 173, 174.) In place of platinum wire, such substitutes as iron wire or thin porcelain rods as used for suspending gas mantles may be employed.

22. Lead carbonate occurs in nature as the mineral *cerussite*, frequently in clear lustrous crystals possessing a high density.

It is sometimes called " white lead ore," though its composition is different from that of commercial " white lead." Artificially prepared lead carbonate, having the same composition as cerussite, is also obtainable, and may be used in place of cerussite in the following experiments.

Warm a small quantity of cerussite with hydrochloric acid ; test the evolved gas for carbon dioxide. When the carbonate is completely decomposed, cool the solution, and observe the separation of crystals of lead chloride ; these may be further treated as described in the preceding experiment.

Heat some powdered cerussite in a hard glass tube. Decomposition soon commences ; test the escaping gas for carbon dioxide. The lead oxide (litharge *) which is produced has a very dark colour when hot, but when the tube is allowed to cool the colour gradually becomes lighter, and is finally yellow. Litharge fuses at a red heat, and then easily attacks glass ; care should therefore be taken not to overheat the substance in the above experiment. Litharge is insoluble in water and does not unite with it directly to any considerable extent ; it gives a distinct alkaline reaction, however, when pressed upon moist test paper. The litharge obtained may be converted into lead chloride by warming with hydrochloric acid ; the chloride may be recognised by its behaviour, as already indicated.

Heat a small quantity of litharge with hydrochloric acid : it dissolves with formation of lead chloride.

The " white lead " of commerce consists essentially of basic lead carbonate, $Pb_3(OH)_2(CO_3)_2$. When heated it is completely decomposed, leaving litharge.

Heat a quantity of dry " white lead " in a dry test tube : note the production of carbon dioxide as in the case of cerussite ; water vapour also escapes and will condense in the upper part of the tube to form either distinct drops or a slight cloud ; as may be calculated from the equation, however, the proportion of water is small. The residue of litharge is similar to that obtained in the previous experiment.

$$Pb_3(OH)_2(CO_3)_2 = 3\,PbO + 2\,CO_2 + H_2O.$$

* The name *litharge*, strictly speaking, applies only to oxide of lead which has been fused, the name *massicot* being given to that which has been prepared without fusion. For simplicity we shall use the former, as a convenient designation for the oxide, irrespective of its mode of formation. Commercial litharge is generally contaminated with carbonates formed by slow absorption of carbon dioxide from the air.

23. Prepare lead nitrate by heating together several grams of litharge and about 10 c.c. of dilute nitric acid. If the solution does not become quite clear, filter it as quickly as possible, collecting the filtrate in a crystallising dish. If small crystals have formed in any quantity, redissolve them by warming the solution, and set it aside to cool slowly. In this way large and distinct crystals of lead nitrate may be obtained, and should be preserved for subsequent use.

Try a similar experiment with dilute sulphuric acid; there is very little action, as the particles of litharge become coated with a thin layer of insoluble lead sulphate, which prevents the sulphuric acid penetrating further.

24. Warm together a small quantity of finely powdered *galena* (native lead sulphide) and dilute hydrochloric acid. The sulphide gradually dissolves with formation of lead chloride and evolution of hydrogen sulphide, which may be recognised by its disagreeable odour and its blackening effect upon lead acetate paper (p. 238). When a moderate quantity of galena has been decomposed, allow the remainder to settle, pour off the solution and allow it to cool; lead chloride will crystallise out, and may be recognised by its reactions, as described in previous paragraphs.

Perform a similar experiment with lead sulphide and dilute nitric acid. In this case there is no evolution of hydrogen sulphide, but free sulphur and oxides of nitrogen are produced, along with solution of lead nitrate. The sulphur forms a dark, sticky mass in the liquid, whilst the oxides of nitrogen mix with the air in the tube, giving rise to reddish "nitrous fumes," as observed when metallic lead was dissolved in nitric acid. The diluted nitric acid employed as a reagent does not give rise to lead sulphate by its direct action on the sulphide, but, by prolonged boiling with excess of nitric acid, the sulphur is gradually oxidised to sulphuric acid, which thereupon forms lead sulphate.

When lead sulphide is warmed with dilute sulphuric acid, there is only a very slight action; the particles of sulphide become coated with insoluble lead sulphate, and are so protected from further change.

25. "Red lead," obtained by heating litharge at a suitable temperature in a current of air, contains a higher proportion of oxygen than litharge does. It is generally assumed to have the composition represented by the formula Pb_3O_4, but it

often varies considerably from this. There is, however, a red oxide of lead having the above composition, and we shall assume that the " red lead " (or *minium*, which is a preferable name) employed for the following experiments is that substance.

Warm together several grams of minium and 5-10 c.c. of dilute nitric acid in a test tube. Chemical action proceeds rapidly, with formation of brown insoluble lead peroxide and solution of lead nitrate. Boil the solution, and then allow the peroxide to settle to the bottom, after which decant the hot solution from the deposit on to a filter, collecting the filtrate in a small crystallising dish ; set the solution aside to cool, when crystals of lead nitrate should separate similar to those previously obtained.

To the brown residue in the tube add more nitric acid, and again heat to boiling ; allow to settle, and pour off the liquid. Wash the residue by decantation ; in this case the substance to be washed is insoluble in water, so the latter may be used freely, and may be warmed with the residue. Add hydrochloric acid to the peroxide (or to part of it, if there is much), and warm ; the peroxide is rapidly attacked with formation of lead chloride and evolution of chlorine. The former will be at first dissolved, but will soon begin to crystallise out ; the latter may be recognised by its pale greenish-yellow colour, its characteristic odour (observe this with caution, as chlorine is a very irritating and harmful gas when inhaled in quantity), and its action on paper moistened with potassium iodide solution (p. 238).

$$Pb_3O_4 + 4\,HNO_3 = 2\,Pb(NO_3)_2 + PbO_2 + 2\,H_2O.$$
$$PbO_2 + 4\,HCl = PbCl_2 + Cl_2 + 2\,H_2O.$$

26. Heat some dry lead peroxide to redness in a hard glass tube, and after a short time test for oxygen by introducing a glowing splinter of wood into the tube. For this purpose cedar wood is more suitable than most of the commoner kinds ; the splinter employed should be long and narrow. Ignite it, allow it to burn for a few seconds, then blow out the flame, leaving the charred end glowing, but avoid having the wood charred, except for a very short distance from the end. Rapidly plunge the glowing end down into the tube till it is only a short distance above the decomposing peroxide, when it will be rekindled if there has been a sufficient quantity of oxygen liberated. If it is not rekindled immediately it should be

promptly withdrawn, and the heating of the peroxide continued for some time before making another attempt.

If the peroxide is heated sufficiently to cause complete decomposition, the residue will consist of litharge, and will become yellow or reddish on cooling.

$$2\,PbO_2 = 2\,PbO + O_2.$$

The general behaviour of red oxide of lead is similar to that of a mixture of litharge and peroxide of lead. When strongly heated, it evolves oxygen ; when it is warmed with hydrochloric acid, chlorine is evolved ; acetic acid attacks it but slowly, even when warmed, forming lead acetate in solution and leaving a residue of peroxide ; dilute sulphuric acid attacks it only slightly, owing to the insolubility of lead sulphate.

27. Warm a small quantity of copper turnings with nitric acid in a test tube ; cupric nitrate is formed in solution, and nitric oxide, mixed with small quantities of other reduction products of nitric acid, escapes as gas and unites with the oxygen of the air to form nitrogen peroxide. The cupric nitrate imparts a greenish-blue colour to the solution. It is not advisable to try to crystallise it on such a small scale, however, as it is very soluble and deliquescent (see p. 9).

Carry out a similar experiment with hydrochloric acid in place of nitric acid. There will be no appreciable action. If very finely divided copper and concentrated hydrochloric acid are warmed together, an action does take place, with formation of cuprous chloride in solution (see p. 105) and evolution of hydrogen.

Place some copper turnings on a piece of wire gauze and heat them for some time in the upper part of the Bunsen flame ; they become covered with a black coating which consists of cupric and cuprous oxides. Put some of these partially oxidised turnings into a tube, add a *small* quantity of hydrochloric acid, and warm. The coating of oxides dissolves, forming cupric and cuprous chlorides ; the solution of the former is greenish-yellow, but, in contact with the metallic copper, the colour disappears, owing to the reduction of the cupric chloride to cuprous chloride, which is colourless. The presence of copper in such a colourless solution may be shown by adding hydrogen sulphide to the latter, when a black precipitate of sulphide will be produced.

Warm a small quantity of copper turnings with dilute

sulphuric acid ; there is no appreciable action. Add a drop or two of dilute nitric acid to the sulphuric acid ; the metal now dissolves readily, forming cupric sulphate in solution, with evolution of nitric oxide (p. 59).

Warm the remainder of the partially oxidised copper turnings with a small quantity of dilute sulphuric acid ; the cupric oxide dissolves, forming a greenish-blue solution of cupric sulphate, and the core of metallic copper remains unchanged ; any cuprous oxide present produces cupric sulphate and finely divided copper (see p. 50).

Pour about 5 c.c. of concentrated sulphuric acid over 2-3 grm. copper turnings in a tube, and warm gently. Action soon begins, and sulphur dioxide is evolved, mixed with sulphuric acid fumes. Continue to warm cautiously for some time ; a dark granular deposit, consisting of white anhydrous cupric sulphate mixed with a small quantity of black cuprous sulphide, is gradually formed in the liquid (see p. 52). When a considerable quantity of this deposit has been formed, allow the contents of the tube to cool, then carefully decant and reject the supernatant liquid. Pour not more than 10 c.c. of water over the deposit left in the tube, and warm. The cupric sulphate dissolves, forming a blue solution ; filter this off from the insoluble sulphide and unattacked copper, collecting the filtrate in a small crystallising dish, and set the solution aside to cool slowly. In this way distinct crystals of hydrated cupric sulphate or "blue vitriol," $CuSO_4$, $5\,H_2O$, may be obtained. They should be freed from mother liquor and dried between filter paper, after which they may be dissolved in water and the solution examined for the reactions of cupric salts, as described on page 105.

28. *Determine the ratio Cu : CuO.*—Carefully weigh a clean porcelain crucible and lid. Place in the crucible about 0·5-1 grm. copper (thin wire or foil) and weigh again. Support the crucible on a pipeclay triangle and heat with the lid off, gently at first and afterwards strongly, for half an hour. Allow the crucible to cool, and when quite cold add 2 or 3 drops of concentrated nitric acid. Heat again, with the lid on, very gently at first to volatilise any liquid remaining and to decompose the cupric nitrate which has been formed, and then heat strongly for about ten minutes. Allow the crucible to cool, and, when cold, weigh. Repeat the treatment with nitric acid and the

subsequent heating, until the weight is constant. Calculate the ratio Cu : CuO.

29. Place some flowers of sulphur in a dry test tube—a depth of about 2 cm. will be sufficient ; then add as much fine iron filings as will occupy about half that bulk, and mix the two as thoroughly as possible by shaking. Heat the dry mixture ; the sulphur melts and darkens, and soon begins to unite with the iron to form ferrous sulphide. So much heat is given out in this process that the mass suddenly becomes red-hot. When the action is finished, break the tube and pick out the sintered mass of black ferrous sulphide. Place this in a clean tube, and add dilute sulphuric or hydrochloric acid ; bubbles of hydrogen sulphide are evolved rapidly (p. 49). This gas has a disagreeable and characteristic odour ; it is combustible and can be ignited at the mouth of the tube ; it has a reducing action, and also blackens lead acetate paper (p. 238).

30. For this experiment thin iron wire gauze may be used. It is usually coated with grease to prevent oxidation, and it should be heated until fumes cease to rise from it. Make a small roll of 2-3 grm. iron gauze and warm it with 10-15 c.c. of dilute sulphuric acid ; the metal dissolves with evolution of hydrogen. Continue to warm gently until the evolution of gas becomes feeble, when the solution should have a pale green colour. Filter (see p. 71, Expt. 6) the hot solution into a crystallising dish and set it aside to cool slowly, covering the dish with a watch-glass or glass plate to prevent free access of air ; well-formed crystals of hydrated ferrous sulphate or " green vitriol," $FeSO_4$, 7 H_2O, should be obtained. Decant the mother liquor and dry the crystals between filter paper in the usual manner. An aqueous solution of the salt may be employed for examining the reactions of ferrous salts (see p. 120) or for the preparation of ammonium iron alum (see below).

The acid mother liquor from the crystals of ferrous sulphate, when boiled with a small quantity of nitric acid, is converted into a solution of ferric sulphate, with evolution of nitric oxide ; the latter is immediately converted into nitrogen peroxide as soon as it mixes with the air (see p. 82, Expt. 21).

Iron dissolves easily in hydrochloric acid with evolution of hydrogen and formation of ferrous chloride. This salt is much more soluble in water than ferrous sulphate, and will not crystallise from the dilute solution on cooling ; in order to

obtain crystals, it is necessary to concentrate the solution very considerably, care being taken to prevent oxidation by the oxygen of the air.

Iron is readily attacked by warm nitric acid, provided the latter is somewhat diluted; ferric nitrate is formed in solution, with evolution of oxides of nitrogen. By applying cold dilute nitric acid, it is possible to obtain ferrous nitrate, along with ammonium nitrate (see p. 52). Neither ferrous nor ferric nitrate is suitable for preparation in the solid state on a small scale.

31. A saturated solution of ferrous sulphate may be employed for the preparation of ammonium iron alum—ammonium ferric sulphate, $(NH_4)_2Fe_2(SO_4)_4$, 24 H_2O—which, unlike most simple ferric salts, is obtainable in well-formed crystals. The ferrous solution may be oxidised to ferric by means of nitric and sulphuric acids, as above, and ammonium sulphate then added; but on a small scale the same result may be more simply obtained by using ammonium persulphate $(NH_4)_2S_2O_8$. This salt readily loses SO_4 to metals or radicals capable of uniting therewith, and itself becomes ammonium sulphate; with ferrous sulphate the action is represented by the equation—

$$2\,FeSO_4+(NH_4)_2S_2O_8=Fe_2(SO_4)_3+(NH_4)_2SO_4.$$

The two constituent salts of the alum are therefore produced in the appropriate proportions.

To about 12-15 c.c. of saturated ferrous sulphate solution add a few drops of dilute sulphuric acid, and warm to a moderately high temperature. Add solid ammonium persulphate in successive small portions as long as the colour of the solution continues to darken. Effervescence, due to the escape of oxygen, takes place and the liquid gradually becomes reddish-brown, but no solid should separate. Transfer to a crystallising dish, and set aside to cool and crystallise. The crystals thus obtained have a very pale purple colour, and are octahedral in shape. They may be dissolved in water, and the solution employed for examining the reactions of ferric salts (p. 121). The presence of the ammonium sulphate is, for this purpose, immaterial.

32. *Determine the percentage Weight of Iron in Ammonium Iron Alum.*—Weigh accurately on a tared watch-glass (see p. 71, Expt. 5) 0·5-0·6 grm. ammonium iron alum. Transfer

the alum to a 300 c.c. beaker, removing any particles adhering to the watch-glass by the aid of a stream of distilled water from the wash-bottle. Add a few drops of dilute sulphuric acid and then more distilled water until the volume of the solution has become about 100 c.c. Warm the solution and add ammonia solution in slight excess so that, when heated to boiling-point, ammonia is present in the escaping vapour. Remove the flame and allow the brown precipitate of ferric hydroxide to settle. Decant the clear solution through an "ashless" filter paper. Add to the residual precipitate about 50 c.c. of hot distilled water and again decant the clear solution. Repeat this process twice and then transfer all the precipitate from the beaker to the filter paper, using a glass rod, with about one inch length of rubber tubing covering the end, to detach any portions adhering to the beaker. The last traces of precipitate may be brought into the filter by directing a jet of water into the up-turned beaker, the glass rod being held against the edge of the beaker so that the water flows down the rod into the filter. Test the last portion of the filtrate by adding to it barium nitrate solution. If, after standing for a few minutes, no turbidity is apparent, the precipitate is free from sulphate. Should turbidity appear, the washing must be continued until a portion of the filtrate gives a negative result to this test.

While the precipitate is settling, weigh a porcelain crucible and lid as described in Experiment 16, p. 79. When the precipitate has been completely washed, transfer it in the paper to the crucible and gently heat the crucible and contents with the lid on until the water has been expelled. Then remove the lid, raise the flame and burn the filter paper and all the carbon formed from it. Heat the crucible and contents with a full flame for ten minutes, allow to cool, and then weigh the crucible, contents, and lid. Repeat the ignition and weighing until constant weight is obtained.

The results may be recorded as follows :—

Weight of	watch-glass	..... grm.
,,	watch-glass+ammonium iron alum	.....
,,	ammonium iron alum . . .	(say x)
Weight of	crucible and lid	..... grm.
,,	crucible and lid+ferric oxide . .	.....
,,	ferric oxide	(say y)

Calculation $Fe_2O_3 : Fe_2 = 159{\cdot}8 : 111{\cdot}8$.

$\therefore \quad 111{\cdot}8\,y/159{\cdot}8 =$ weight of iron $= z$.

and $100\,z/x =$ percentage weight of iron in the ammonium iron alum.

33. *Determine the percentage Weight of Sulphate Radical in a soluble Sulphate.*—Suitable sulphates for this determination are ammonium iron alum and magnesium sulphate. The procedure is as in Experiment 32, except as noted below.

About 0·4 grm. of either of the above sulphates is accurately weighed. The solution of the sulphate in about 100 c.c. water + 10 c.c. dilute hydrochloric acid + 10 c.c. ammonium chloride solution is heated to boiling-point. In another small beaker heat to boiling-point 25 c.c. of a 3 per cent. barium chloride solution + a few drops of dilute hydrochloric acid. Keeping both solutions at or near their boiling-points, add the barium chloride solution, a little at a time, to the sulphate solution, stirring the latter with a glass rod. After the addition of about 20 c.c. barium chloride solution, heat and stir the mixed solution for about five minutes. Then remove the flame, let the precipitate subside and test the clear supernatant liquid by the addition of a few drops of the barium chloride solution. If the liquid becomes turbid, add another c.c. of the barium chloride solution, stir and heat as before. When precipitation is complete, as shown by the supernatant liquid remaining clear after the addition of more barium chloride, cover the beaker and contents with a large watch-glass or a filter paper and allow the precipitate to subside for some hours—preferably overnight. The subsequent procedure is as in Experiment 32, except that the filtrate is tested for the presence of chloride by adding to it silver nitrate.

Calculation $BaSO_4 : SO_4 = 233{\cdot}4 : 96$.

$x =$ weight of ammonium iron alum or magnesium sulphate.

$y =$,, barium sulphate.

$\therefore \quad 96\,y/233{\cdot}4 = z$.

and $100\,z/x =$ percentage weight of sulphate radical (SO_4) in the salt employed.

34. Treat a fragment of sheet aluminium with dilute hydrochloric acid in a test tube; the metal dissolves readily, liberating hydrogen and forming aluminium chloride in solution.

The liquid becomes warm, and the action may then proceed with great briskness. Aluminium chloride is very deliquescent, and cannot be obtained readily by evaporation of its aqueous solution, as the very concentrated solution decomposes when heated, with formation of aluminium hydroxide and evolution of hydrochloric acid—

$$AlCl_3 + 3\,H_2O = Al(OH)_3 + 3\,HCl.$$

Warm about 1 grm. of sheet aluminium with dilute sulphuric acid; interaction may take place very slowly, with formation of aluminium sulphate in solution and evolution of hydrogen. As aluminium sulphate is very soluble in water, the small quantity which is produced in this way in a moderate time cannot conveniently be crystallised. To the acid liquid now add a few drops of hydrochloric acid, and warm slightly; action takes place quickly, with formation of aluminium sulphate in solution and brisk evolution of hydrogen. Should the addition of the hydrochloric acid not sufficiently accelerate the action, this result may be ensured by the further addition of a few drops of a solution of cupric sulphate. When the action slackens, heat the liquid and keep it nearly boiling for a minute or two so as to use up almost all the acid. Concentrate the solution and, if necessary, filter it. Crystals of aluminium sulphate should separate as the solution cools. The aluminium sulphate thus obtained may be employed for the preparation of ammonium alum, $(NH_4)_2Al_2(SO_4)_4$, $24\,H_2O$, a double salt which can be easily obtained in large octahedral crystals. For this purpose add 2-3 grm. ammonium sulphate to the solution and warm until it is all dissolved, then set the liquid aside in a crystallising dish to cool slowly. The crystals obtained should be removed from the mother liquor and dried as usual.

An aqueous solution of ammonium alum may be employed for the examination of the reactions of aluminium salts (see p. 125); the ammonium sulphate present in such a solution does not interfere with the reactions for aluminium.

Aluminium which has been coated with a layer of mercury so that the surface is converted into aluminium amalgam is much more easily attacked by many reagents than pure aluminium is. In that state it readily undergoes oxidation on exposure to ordinary air; it dissolves easily in dilute sulphuric acid, with evolution of hydrogen. Aluminium, plain or amalgamated, is frequently employed as a reducing agent, in

presence of water, alkalies, or acids. For example, nitrates may be reduced by it in presence of potassium hydroxide, yielding ammonia—

$$3\,KNO_3+5\,KOH+2\,H_2O+8\,Al=8\,KAlO_2+3\,NH_3.$$

To prepare amalgamated aluminium, the sheet metal is treated with dilute hydrochloric acid and mercuric chloride solution, and then washed with water. Mercury is deposited on the surface of the aluminium (see p. 53), while a corresponding quantity of aluminium is dissolved—

$$2\,Al+3\,HgCl_2=2\,AlCl_3+3\,Hg.$$

On account of this property, mercuric chloride (*corrosive sublimate*) solution may not be used as an antiseptic bath for surgical instruments made of aluminium.

The ready oxidability of amalgamated aluminium may be observed by drying a few small pieces on filter paper, and then exposing them for some time on a watch-glass; fine white moss-like growths of aluminium oxide sprout from the surface of the metal.

The ratio Al : H may be determined in a similar manner to that of Mg : H (see p. 80).

35. Heat a small quantity of dry lead nitrate in a hard glass tube (the crystals obtained in Experiment 23, page 85, may be employed for this purpose). At first the salt decrepitates strongly; thereafter chemical decomposition takes place and dense reddish-brown vapours of nitrogen peroxide are evolved, mixed with free oxygen, and ultimately only litharge is left behind.

$$2\,Pb(NO_3)_2=2\,PbO+4\,NO_2+O_2.$$

36. Heat a small quantity of ammonium nitrate in a hard glass tube; the salt fuses, and decomposes with evolution of nitrous oxide and water vapour. Owing to the large quantity of the latter substance, the escaping gas will not rekindle a glowing splinter, as pure nitrous oxide would do. This difficulty can be overcome by using a test tube instead of the smaller hard glass tube, placing a plug of loosely crumpled filter paper about the middle of the tube, and wrapping folds of wet filter paper outside the upper part of the tube, so as to condense a larger proportion of the water vapour. If the salt

is decomposed very rapidly, reddish fumes, due to the formation of higher oxides of nitrogen, may also be produced, and a slight explosion may take place. Unless a very small quantity of the salt is employed for the experiment, it is necessary that the heating should be performed very carefully, so as to avoid risk of explosion.

$$NH_4NO_3 = N_2O + 2\,H_2O.$$

37. Heat a small quantity of crystals of ammonium bichromate in a clean dry test tube. Decomposition commences at a moderate temperature and proceeds rapidly without the further application of heat, the action itself producing so much heat that the contents of the tube become red-hot. Steam and nitrogen are evolved so rapidly that considerable quantities of solid matter are projected from the tube. The bulky residue consists of dark green chromic oxide.

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4\,H_2O.$$

38. Heat a small quantity of potassium chlorate in a hard glass tube. The salt first fuses and soon thereafter begins to undergo decomposition, with evolution of oxygen; test for this gas by means of a glowing splinter. If a sufficiently high temperature is employed, the residue will consist entirely of potassium chloride. (Potassium perchlorate is also formed as an intermediate product.) When the tube has cooled, dissolve the residue in water and test the solution for chloride by adding silver nitrate, when a white precipitate will be obtained; a solution of the original substance gives no precipitate on the addition of silver nitrate.

$$2\,KClO_3 = 2\,KCl + 3\,O_2.$$

39. *Determine the ratio $KClO_3$: KCl.*—Weigh a clean, dry test tube. Place in it about 2·5 grm. potassium chlorate and weigh the tube and contents. Then add about 0·2 grm. manganese dioxide and again weigh the tube and contents. Gently heat the mixture in the tube until reaction begins, then remove the flame. When the reaction has subsided, heat strongly all parts of the tube, where any of the mixture is apparent, but not so strongly as to melt the glass. While the tube is cooling, heat distilled water in the wash-bottle. Select two filter papers and place one on each pan of the balance, and if their weights do not coincide, mark the lighter one with

a pencil (in order to distinguish it from the other) and add to it the weights necessary to obtain equilibrium. Weigh a clean, dry porcelain basin. Fold the two filter papers to make a double filter, place them in a funnel and pour hot water through the filter into the basin and empty the basin.

Add about 5 c.c. hot water to the residue in the tube and, after gentle shaking, decant the solution into the filter and collect the filtrate in the basin. Repeat this three times. Then direct a jet of hot water into the inverted test tube so that it sweeps the manganese dioxide out of the tube into the filter. If necessary, use a glass rod with rubber tip (see p. 91) to dislodge any particles adhering to the tube. Place the funnel with papers and manganese dioxide in a drying oven and when dry separate the inner from the outer filter paper and measure the difference in weight due to the manganese dioxide.

Evaporate the filtrate and washings in the basin to dryness, taking care that nothing is lost by spirting of the solid when nearly dry. Heat for two minutes and then allow the basin and contents to cool for about ten minutes before weighing. Repeat the heating, cooling, and weighing until constant weight is attained.

The results may be recorded thus—

	Grm.
Weight of test tube	....
,, test tube+Potassium chlorate . . .	....
,, Potassium chlorate	....
,, T.T.+Potassium chlorate+Manganese dioxide	....
,, Manganese dioxide	....
,, Manganese dioxide recovered . . .	....

(If the two filter papers were not equal in weight, then—

	Grm.
Filter paper 1=Filter paper 2+	....
Filter paper 1+Manganese dioxide=Filter paper 2+ .	....
Weight of Manganese dioxide recovered) . . .	....

	Grm.
Weight of basin	....
,, ,, +Potassium chloride . . .	....
,, ,, +Potassium chloride after reheating	....
,, Potassium chloride	....

This experiment not only gives a method of determining the ratio $KClO_3$: KCl, but also shows the catalytic effect of man-

ganese dioxide in accelerating the evolution of oxygen, though the manganese dioxide itself is recovered at the end of the experiment unchanged in weight and state.

40. Heat a small quantity of sodium chloride (common salt) with concentrated sulphuric acid in a test tube. The hydrochloric acid gas which is evolved fumes when it comes in contact with moist air, forming a cloud composed of minute drops of hydrochloric acid solution. Hold a piece of blue litmus paper in the escaping gas : it is immediately reddened. Hold a drop of water on the end of a glass rod just inside the mouth of the tube, taking care that none of the solid or liquid contents is spirted upon it. The water will dissolve a considerable quantity of the gas ; carefully remove the rod with the drop and dip it into a small quantity of water contained in a clean tube. The liquid will now be found to be strongly acid, and to give a white precipitate of silver chloride on the addition of solution of silver nitrate (see p. 153).

REACTIONS OF SALTS

PART I.—DEALING CHIEFLY WITH THE REACTIONS DUE TO THE METALLIC RADICALS *

SILVER.

Basic oxide, Ag_2O.

Examples of soluble silver salts :—Nitrate [**4**], chlorate, sulphate [**4**], acetate.

REACTIONS OF SOLUTIONS OF SILVER SALTS.

Hydrochloric acid produces a white curdy precipitate of silver chloride—

$$AgNO_3 + HCl = HNO_3 + AgCl.$$

Silver chloride is insoluble in dilute acids, and soluble in ammonia. From its solution in ammonia, it is reprecipitated on the addition of nitric acid in excess. It is very appreciably soluble in concentrated solutions of many chlorides, including hydrochloric acid. (Note that silver salts insoluble in water are, as a rule, soluble in dilute nitric acid and in ammonia. Principal exceptions :—Insoluble in dilute nitric acid—chloride, bromide, iodide, cyanide, ferrocyanide, ferricyanide, thiocyanate, sulphide ; insoluble in ammonia—iodide, ferrocyanide, sulphide. With the exception of the sulphide, insoluble silver salts generally dissolve in solutions of alkali cyanides, thiosulphates, and sulphites. For particulars, see under the reactions of these salts.)

Hydrogen sulphide produces a black precipitate of silver sulphide—

$$2\,AgNO_3 + H_2S = 2\,HNO_3 + Ag_2S.$$

(A similar action takes place with insoluble silver salts—

$$2\,AgCl + H_2S = 2\,HCl + Ag_2S.)$$

* The heavy-type numbers placed in square brackets after the examples of soluble salts in the succeeding pages refer to the general methods of preparing salts discussed on pages 48-62.

Silver sulphide is not soluble in dilute nitric acid or in ammonium hydrosulphide.

Concentrated nitric acid decomposes silver sulphide with formation of soluble silver salt; aqua regia decomposes silver sulphide with formation of insoluble silver chloride.

Sodium hydroxide produces a brown precipitate of silver hydroxide—

$$AgNO_3+NaOH=NaNO_3+AgOH.$$

This hydroxide decomposes very easily into silver oxide and water—

$$2\,AgOH=Ag_2O+H_2O.$$

The precipitate is insoluble in excess of sodium hydroxide.

Ammonia produces, with concentrated solutions, a brown precipitate of silver hydroxide, soluble in excess. Very dilute solutions of silver salts give no precipitate or only a very slight opalescence. Solutions containing ammonium salts give no precipitate; therefore solutions originally acid also give no precipitate.

Potassium iodide produces a pale yellow precipitate of silver iodide—

$$AgNO_3+KI=KNO_3+AgI.$$

Silver iodide is insoluble in dilute acids; it is changed by ammonia into a yellowish insoluble compound.

Potassium chromate produces a crimson precipitate of silver chromate—

$$2\,AgNO_3+K_2CrO_4=2\,KNO_3+Ag_2CrO_4.$$

Silver chromate is soluble in dilute nitric acid and in ammonia. It is easily decomposed by solutions of chlorides—

$$Ag_2CrO_4+2\,NaCl=2\,AgCl+Na_2CrO_4.$$

MERCURY.

Basic oxides:—Mercurous oxide, Hg_2O; mercuric oxide, HgO. The hydroxides are unknown.

Corresponding to the two basic oxides of mercury there are two series of salts, both of which are of importance. Mercurous salts resemble silver salts in many respects, whilst mercuric salts are more closely allied to the cupric salts. Most members of the one series of salts can be readily converted into those of

the other series by the methods which have already been described (pp. 58, 60). There are, however, some mercuric salts which have no analogues in the mercurous series, such as the sulphide and the cyanide.

Examples of soluble mercurous salts :—Nitrate [**4**], chlorate.

Examples of soluble mercuric salts :—Chloride (corrosive sublimate) [**5, 7**], bromide [**1, 5**], cyanide [**1**], acetate.

Many mercuric salts, as, for example, the nitrate and sulphate, are decomposed by water with formation of insoluble basic salts. These salts can be dissolved in water containing a sufficiency of the corresponding acid.

Mercuric cyanide when dissolved in water does not become ionised, and therefore it does not give the same reactions as the other mercuric salts, which are slightly ionised in solution. For the same reason its solution does not give the ordinary reactions of cyanides.

REACTIONS OF SOLUTIONS OF MERCUROUS SALTS.

Hydrochloric acid produces a white precipitate of mercurous chloride (calomel)—

$$HgNO_3+HCl=HNO_3+HgCl.$$

Calomel is insoluble in dilute acids. Ammonia changes it into a black substance—

$$2\,HgCl+2\,NH_3=NH_4Cl+NH_2Hg_2Cl.*$$

Hydrogen sulphide produces a black precipitate which is a mixture of mercuric sulphide and mercury—

$$2\,HgNO_3+H_2S=2\,HNO_3+HgS+Hg.$$

(A similar action takes place with insoluble mercurous salts—

$$2\,HgCl+H_2S=2\,HCl+HgS+Hg.)$$

Sodium hydroxide produces a black precipitate of mercurous oxide, insoluble in excess—

$$2\,HgNO_3+2\,NaOH=2\,NaNO_3+Hg_2O+H_2O.$$

Ammonia produces a black precipitate analogous to the substance formed by the action of the same reagent on calomel—

$$2\,HgNO_3+2\,NH_3=NH_4NO_3+NH_2Hg_2NO_3.*$$

* It is probable that these substances are really mixtures of the mercuric compounds (see p. 102) with metallic mercury.

Ammonia has a similar action upon most insoluble mercurous salts.

Potassium iodide in small quantity produces a yellow precipitate of mercurous iodide—

$$HgNO_3+KI=KNO_3+HgI.$$

Unless very dilute solution of potassium iodide is employed, it is difficult to obtain a pure yellow precipitate, a greenish mixture of mercurous iodide and mercury being generally formed owing to the decomposition of some of the former by excess of potassium iodide ; a considerable excess completely decomposes the mercurous iodide—

$$2\,HgI+KI=KHgI_3+Hg.$$

The potassium mercuric iodide is soluble in water, and forms a colourless solution, while the metallic mercury remains as a black precipitate. (See p. 102.)

Potassium chromate produces a red precipitate of mercurous chromate—

$$2\,HgNO_3+K_2CrO_4=2\,KNO_3+Hg_2CrO_4.$$

Stannous chloride, if the solution does not contain a very large excess of hydrochloric acid (see p. 236), produces a black precipitate of finely divided mercury—

$$2\,HgNO_3+2\,SnCl_2=2\,Hg+SnCl_4+Sn(NO_3)_2.$$

If the stannous chloride solution contains much hydrochloric acid a white precipitate of mercurous chloride is first formed, and this is then more slowly reduced to metallic mercury—

$$HgNO_3+HCl=HgCl+HNO_3.$$
$$2\,HgCl+SnCl_2=2\,Hg+SnCl_4.$$

Dilute sulphuric acid produces a white precipitate of mercurous sulphate—

$$2\,HgNO_3+H_2SO_4=2\,HNO_3+Hg_2SO_4.$$

Metallic copper becomes coated with metallic mercury, an equivalent quantity of copper dissolving—

$$2\,HgNO_3+Cu=Cu(NO_3)_2+2\,Hg.$$

Potassium cyanide produces a greyish precipitate of metallic mercury, whilst mercuric cyanide goes into solution—

$$2\,HgNO_3 + 2\,KCN = Hg + Hg(CN)_2 + 2\,KNO_3.$$

This reaction can be employed to detect the presence of a small quantity of a mercurous salt in a solution of mercuric salt.

REACTIONS OF SOLUTIONS OF MERCURIC SALTS.

Hydrogen sulphide produces a black precipitate of mercuric sulphide—

$$HgCl_2 + H_2S = 2\,HCl + HgS.$$

Mercuric sulphide does not dissolve in dilute acids, ammonium hydrosulphide, or sodium hydroxide, but does dissolve to some extent in a mixture of the hydrosulphide with sodium hydroxide (see p. 166). In the case of mercuric chloride (or of other mercuric salt to which hydrochloric acid has been previously added), hydrogen sulphide, when added in small quantity, produces a white precipitate. On the addition of more of the reagent, the colour of the precipitate changes through various shades of yellow, orange, and brown, to black. The same white substance may also be obtained by heating a small quantity of black mercuric sulphide with solution of mercuric chloride. Its composition is represented by the formula $HgCl_2$, 2 HgS. The yellow, orange, and brown substances are intermediate in composition between this and mercuric sulphide.

Sodium hydroxide produces a yellow precipitate of mercuric oxide insoluble in excess—

$$HgCl_2 + 2\,NaOH = 2\,NaCl + HgO + H_2O.$$

Ammonia produces a white precipitate of mercuri-ammonium salt—

$$Hg(NO_3)_2 + 2\,NH_3 = NH_4NO_3 + NH_2HgNO_3.$$

The precipitate is insoluble in excess of ammonia. Mercuri-ammonium chloride, NH_2HgCl, has long been known as "white precipitate."

Potassium iodide produces a precipitate of mercuric iodide, which is yellow at first, but rapidly becomes red—

$$HgCl_2 + 2\,KI = 2\,KCl + HgI_2.$$

The precipitate dissolves easily in excess of potassium iodide, giving a nearly colourless solution of potassium mercuric iodide, $KHgI_3$. This substance is not a mercuric salt in the strict sense, as it has potassium alone for metallic radical, and the

mercury forms part of the compound acidic radical HgI_3. Mercuric iodide also dissolves in excess of mercuric chloride, forming a colourless solution of a double salt.

Stannous chloride produces a white precipitate of calomel which darkens on adding more reagent owing to the formation of metallic mercury; the darkening is accelerated by warming—

$$2\,HgCl_2+SnCl_2=SnCl_4+2\,HgCl.$$
$$2\,HgCl+SnCl_2=SnCl_4+2\,Hg.$$

Metallic copper becomes coated with metallic mercury, an equivalent quantity of copper dissolving—

$$HgCl_2+Cu=CuCl_2+Hg.$$

When a solution of mercuric chloride is poured upon mercury, a film of mercurous chloride is formed upon the surface of the metal—

$$HgCl_2+Hg=2\,HgCl.$$

As a result the meniscus disappears, the surface becoming horizontal.

REACTIONS OF SOLUTION OF MERCURIC CYANIDE.

Hydrogen sulphide behaves as in the case of other mercuric salts.

Sodium hydroxide gives no reaction.

Ammonia gives no reaction.

Potassium iodide does not produce a precipitate in moderately dilute solution. Solution of mercuric cyanide, to which hydrochloric acid has been added, behaves towards potassium iodide exactly like one of mercuric chloride.

Stannous chloride gives reactions similar to those with other mercuric salts.

(See also Cyanides.)

LEAD.

Basic oxide, PbO.

Examples of soluble lead salts:—Nitrate [**1**, **4**], chlorate, acetate [**1**], chloride [**1**, **7**].

REACTIONS OF SOLUTIONS OF LEAD SALTS.

Hydrochloric acid produces no precipitate with dilute solutions, but with moderately concentrated solutions white lead chloride is partially precipitated. (See p. 83.)

$$Pb(NO_3)_2+2\,HCl=2\,HNO_3+PbCl_2.$$

The precipitate dissolves easily in boiling water, and some of it may separate again from the solution, on cooling, in needle-shaped crystals. Ammonia converts it into white insoluble basic salt.

Hydrogen sulphide produces a black precipitate of lead sulphide—

$$Pb(C_2H_3O_2)_2+H_2S=2\,HC_2H_3O_2+PbS.$$

(A similar action takes place with insoluble lead salts—

$$PbSO_4+H_2S=H_2SO_4+PbS.)$$

Lead sulphide is insoluble in ammonium hydrosulphide, but it dissolves in moderately concentrated hydrochloric acid, especially on warming.

When hydrogen sulphide is added to a dilute solution of lead chloride, or of another lead salt to which hydrochloric acid has been added, a reddish-brown precipitate may at first be produced. This precipitate is intermediate in composition between $PbCl_2$ and PbS. It is completely converted into black lead sulphide by adding a sufficiency of hydrogen sulphide.

Sodium hydroxide produces a white precipitate of lead hydroxide, soluble in excess—

$$Pb(NO_3)_2+2\,NaOH=2\,NaNO_3+Pb(OH)_2.*$$

Ammonia produces a white precipitate of lead hydroxide, or of basic salt, insoluble in excess.

Sodium carbonate produces a white precipitate of lead carbonate—

$$Pb(NO_3)_2+Na_2CO_3=2\,NaNO_3+PbCO_3.$$

Potassium iodide produces a yellow precipitate of lead iodide—

$$Pb(NO_3)_2+2\,KI=2\,KNO_3+PbI_2.$$

Lead iodide is nearly insoluble in cold water, but readily soluble in hot water; so that if the contents of the test tube are warmed the lead iodide dissolves, forming a colourless

* The precipitate probably corresponds to this formula. It readily loses water, however, and is converted into compounds intermediate in composition between lead hydroxide and lead oxide, such as $Pb_2O(OH)_2$.

solution from which it crystallises, on cooling, in thin yellow hexagonal plates.

Potassium chromate produces a yellow precipitate of lead chromate (chrome yellow)—

$$Pb(NO_3)_2 + K_2CrO_4 = 2\,KNO_3 + PbCrO_4.$$

The precipitate dissolves in hot dilute nitric acid, and also in sodium hydroxide. When lead chromate is boiled with calcium hydroxide, basic lead chromate (chrome orange) is formed—

$$2\,PbCrO_4 + Ca(OH)_2 = CaCrO_4 + H_2O + Pb_2OCrO_4.$$

Dilute sulphuric acid produces a white precipitate of lead sulphate—

$$Pb(NO_3)_2 + H_2SO_4 = 2\,HNO_3 + PbSO_4.$$

Lead sulphate is soluble in sodium hydroxide, and in concentrated solution of ammonium acetate, or of ammonium tartrate and ammonia.

COPPER.

Basic oxides :—Cuprous oxide, Cu_2O ; cupric oxide, CuO.

Corresponding to the two basic oxides of copper there are two series of salts. Cuprous salts derived from acids containing oxygen are few and comparatively unimportant. The most important cuprous salts are the halides and the cyanide, which are insoluble in water, but soluble in hydrochloric acid and also in ammonia. With the exception of the iodide and the cyanide, most cuprous salts readily undergo oxidation, especially in presence of the acid, forming the corresponding cupric salts.

Solution of cuprous chloride in hydrochloric acid or in ammonia absorbs carbon monoxide, and is employed for this purpose in gas analysis. It has likewise been employed for absorbing oxygen.

Cupric iodide has not been obtained in the solid state.

Examples of soluble cupric salts :—Sulphate [**4**], chloride [**1**], bromide, nitrate [**4**], acetate.

Solutions of cupric salts are blue or green.

REACTIONS OF SOLUTIONS OF CUPRIC SALTS.

Hydrogen sulphide produces a black precipitate of cupric sulphide, insoluble in dilute acids and in ammonium hydrosulphide—

$$CuSO_4 + H_2S = H_2SO_4 + CuS.$$

Cupric sulphide is soluble in solution of potassium cyanide.

Sodium hydroxide produces a blue precipitate of cupric hydroxide, insoluble in excess—

$$CuSO_4+2\,NaOH=Na_2SO_4+Cu(OH)_2.$$

On boiling the solution, to which sufficient sodium hydroxide has been added, the precipitate becomes black, decomposing into cupric oxide and water—

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

Ammonia produces a blue precipitate of basic salt, easily soluble in excess with formation of an intensely blue solution.

This is decolorised on addition of a sufficient quantity of potassium cyanide.

Sodium carbonate produces a blue precipitate of basic cupric carbonate.

Potassium iodide produces, somewhat slowly in dilute solutions, a white or brownish precipitate of cuprous iodide, with simultaneous liberation of iodine which imparts a brown colour to the solution—

$$2\,CuSO_4+4\,KI=2\,K_2SO_4+2\,CuI+I_2.$$

In order to avoid the presence of iodine in the solution, a suitable reducing agent, such as **sulphurous acid,** may be added—

$$I_2+H_2SO_3+H_2O=H_2SO_4+2\,HI.$$

Potassium ferrocyanide produces a brown precipitate of cupric ferrocyanide—

$$2\,CuSO_4+K_4Fe(CN)_6=2\,K_2SO_4+Cu_2Fe(CN)_6.$$

Metallic zinc or **iron** produces a precipitate of metallic copper—

$$CuSO_4+Fe=FeSO_4+Cu.$$

As a rule the copper is precipitated in the form of a dark brown spongy mass on the surface of the other metal; but in the case of iron, if only immersed for a short time, a bright, coherent deposit is obtained.

Stannous chloride, in presence of hydrochloric acid (see p. 236), reduces cupric salts, slowly in the cold and more rapidly on warming, with the formation of cuprous chloride—

$$2\,CuSO_4+SnCl_2+4\,HCl=2\,CuCl+SnCl_4+2\,H_2SO_4.$$

The cuprous chloride may either remain entirely dissolved, forming a colourless solution, or be partly precipitated as a white powder. By diluting sufficiently with water the greater part of the cuprous chloride is precipitated, unless a great excess of the acid reagent has been employed.

TIN.

Basic oxide :—Stannous oxide, SnO.

Examples of soluble stannous salts :—Chloride [4], bromide, sulphate. In consequence of the great tendency of stannous solutions to deposit basic salt, these solutions are generally prepared with dilute acid instead of pure water.

Stannic oxide, although there are compounds corresponding to it which are often called stannic salts, is not, strictly speaking, a basic oxide, but has much more the character of an acid anhydride. In some cases the so-called stannic salts, when treated with water, dissolve to form clear solutions. In reality almost complete hydrolysis takes place, and the solution contains stannic acid, H_4SnO_4, and the other acid produced by the action. Some characteristic reactions of such solutions are noted farther on (p. 108).

REACTIONS OF SOLUTIONS OF STANNOUS SALTS.

Hydrogen sulphide produces a dark brown precipitate of stannous sulphide, insoluble in dilute acids and in ammonium hydrosulphide, soluble in sodium hydroxide—

$$SnCl_2 + H_2S = 2\,HCl + SnS.$$

Stannous sulphide dissolves easily when warmed with solutions of polysulphides, and therefore with ammonium hydrosulphide which has become yellow, or to which sulphur has been added. This action is due to the formation of soluble thiostannate—

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

On acidification with hydrochloric acid the thiostannate solution gives a yellow precipitate of stannic sulphide, SnS_2, generally mixed with sulphur from the excess of polysulphide employed.

Sodium hydroxide produces a white precipitate of stannous hydroxide, soluble in excess—

$$SnCl_2 + 2\,NaOH = 2\,NaCl + Sn(OH)_2.$$

Ammonia produces a white precipitate of stannous hydroxide, insoluble in excess.

Mercuric chloride produces a white precipitate of mercurous chloride—

$$2\ HgCl_2+SnCl_2=SnCl_4+2\ HgCl.$$

If mercuric chloride is in excess the precipitate does not undergo further change, but in presence of excess of stannous chloride the white precipitate gradually darkens owing to the production of metallic mercury—

$$2\ HgCl+SnCl_2=SnCl_4+2\ Hg.$$

Metallic zinc produces a precipitate of metallic tin—

$$SnCl_2+Zn=ZnCl_2+Sn.$$

In the case of acid solutions hydrogen is simultaneously evolved.

Ammonium molybdate produces a bluish or greenish precipitate due to the reduction of the molybdate. In exceedingly dilute solutions a blue coloration is produced. This constitutes the most delicate known test for stannous salts.

REACTIONS OF STANNIC SOLUTIONS.

The solutions to be considered are those already referred to as being formed when the so-called stannic salts are dissolved in water, with or without the addition of acid. Stannic chloride, $SnCl_4$ [**5**], is the best example for the present purpose. It is a colourless volatile liquid which combines with water to form a white crystalline compound, $SnCl_4, 3\ H_2O$. This compound dissolves in water, forming what is generally called stannic chloride solution.

With this solution—

Hydrogen sulphide produces a yellow precipitate of stannic sulphide, SnS_2. The precipitate is produced slowly in the cold, more rapidly on warming. It is insoluble in dilute acids; easily soluble in ammonium hydrosulphide with formation of ammonium thiostannate—

$$SnS_2+2\ NH_4HS=(NH_4)_2SnS_3+H_2S.$$

Stannic sulphide also dissolves in sodium hydroxide or in ammonia, with formation of a mixture of the respective stannate and thiostannate. From all these solutions stannic sulphide is reprecipitated on acidification with hydrochloric acid—

$$3\ SnS_2+6\ NaOH=2\ Na_2SnS_3+Na_2SnO_3+3\ H_2O.$$
$$2\ Na_2SnS_3+Na_2SnO_3+6\ HCl=3\ SnS_2+6\ NaCl+3\ H_2O.$$

Sodium hydroxide produces a white precipitate of stannic acid, H_4SnO_4, soluble in excess with formation of sodium stannate—

$$H_4SnO_4+2\,NaOH=Na_2SnO_3+3\,H_2O.$$

Ammonia produces a white precipitate of stannic acid soluble with some difficulty in large excess.

CADMIUM.

Basic oxide, CdO.

Examples of soluble cadmium salts:—Chloride [**1**, **4**], bromide [**5**], iodide [**5**], nitrate [**1**, **4**], acetate, sulphate [**1**, **4**].

REACTIONS OF SOLUTIONS OF CADMIUM SALTS

Hydrogen sulphide produces a yellow precipitate of cadmium sulphide—

$$CdCl_2+H_2S=2\,HCl+CdS.$$

The precipitate dissolves easily in dilute hydrochloric acid, especially on warming, but can be reprecipitated completely by the addition of hydrogen sulphide solution in sufficient quantity. Cadmium sulphide is insoluble in ammonium hydrosulphide.

Sodium hydroxide produces a white precipitate of cadmium hydroxide insoluble in excess—

$$Cd(NO_3)_2+2\,NaOH=2\,NaNO_3+Cd(OH)_2.$$

Ammonia produces a white precipitate of basic salt, easily soluble in excess.

BISMUTH.

Basic oxide, Bi_2O_3.

Bismuth very readily forms insoluble basic salts, and when the normal nitrate, $Bi(NO_3)_3$ [**4**], or chloride, $BiCl_3$ [**1**, **5**], is treated with water, a basic salt is produced—

$$Bi(NO_3)_3+2\,H_2O=2\,HNO_3+Bi(OH)_2NO_3.$$
$$BiCl_3+H_2O=2\,HCl+BiOCl.$$

In order to prepare a solution of bismuth nitrate or chloride, a sufficiency of the corresponding acid (nitric or hydrochloric) must be present so as to prevent the formation of insoluble basic salt; in the case of the chloride more acid is required than in the case of the nitrate.

REACTIONS OF SOLUTIONS OF BISMUTH SALTS.

(In observing these reactions it is important to remember that the solution contains free acid.)

Hydrochloric acid, added in small quantity, may produce a white precipitate of bismuth oxychloride—

$$Bi(NO_3)_3+HCl+H_2O=BiOCl+3\ HNO_3.$$

The precipitation is not complete, and may not take place at all if the bismuth solution already contains enough free acid. The addition of a sufficient excess of hydrochloric acid redissolves any precipitate that may have been formed—

$$BiOCl+2\ HCl=H_2O+BiCl_3.$$

Hydrogen sulphide produces a black precipitate of bismuth sulphide, which is not soluble in cold dilute acids, or in ammonium hydrosulphide—

$$2\ BiCl_3+3\ H_2S=6\ HCl+Bi_2S_3.$$

Sodium hydroxide produces a white precipitate of bismuth hydroxide, insoluble in excess—

$$BiCl_3+3\ NaOH=3\ NaCl+Bi(OH)_3.$$

Ammonia produces a white precipitate of bismuth hydroxide, insoluble in excess.

Sodium carbonate produces a white precipitate of basic bismuth carbonate.

Potassium iodide produces ultimately a yellow solution. The formation of this yellow solution is preceded, in the case of some bismuth salts, by the production of a brownish-black precipitate of bismuth iodide—

$$Bi(NO_3)_3+3\ KI=3\ KNO_3+BiI_3.$$

This precipitate dissolves in considerable excess of potassium iodide, forming the yellow solution. It is also soluble in hydrochloric acid; hence no precipitate is formed from solutions containing this acid.

Water, added in sufficient quantity, along with a drop of **ammonium chloride**, produces a white precipitate of bismuth oxychloride—

$$Bi(NO_3)_3+NH_4Cl+H_2O=BiOCl+NH_4NO_3+2\ HNO_3.$$

In the case of a solution of bismuth chloride, the precipitate is formed without the addition of ammonium chloride (see above). As already stated, bismuth oxychloride is easily dissolved by adding enough hydrochloric acid.

Stannous chloride and then **sodium hydroxide** produce a black precipitate of finely divided bismuth.

ARSENIC.

Arsenic forms two well-defined oxides, arsenious oxide or anhydride, As_4O_6, and arsenic anhydride, As_2O_5. The former has very slight basic properties and, in a more marked degree, the characters of an acid anhydride; the latter is a typical acid anhydride.

Arsenious anhydride is somewhat sparingly soluble in water, and the solution has a feeble acid reaction. It is more soluble in water containing hydrochloric acid, in which case the greater part of it is converted into arsenious chloride—

$$As_4O_6 + 12\,HCl = 6\,H_2O + 4\,AsCl_3.$$

Similar actions take place with the other halogen acids. The arsenious halides are the only compounds of arsenic which can be regarded as arsenious salts.

When a solution of arsenious chloride is boiled some of the chloride passes off with the escaping vapours. By repeated distillation with hydrochloric acid it is possible, in most cases, to remove the whole of the arsenic from substances containing this element in combination.

Although arsenious anhydride dissolves in water to form what must be assumed to be arsenious acid, the latter itself has not been isolated. The known arsenites do not all correspond to one arsenious acid. Some of them must be looked upon as derived from the hypothetical metarsenious acid, $HAsO_2$, and others, again, from the hypothetical ortho-arsenious acid, H_3AsO_3. Most of the soluble arsenites belong to the former class (metarsenites), and many of the insoluble ones to the latter (ortho-arsenites).

While there are several acids derived from arsenic anhydride, the only important arsenates are the ortho-arsenates, corresponding to ortho-arsenic acid, H_3AsO_4.

Examples of soluble arsenious salts:—the halides [**1, 5**] mentioned above, which are best dissolved, however, in water containing the appropriate acid.

Examples of soluble arsenites :—Those of potassium, sodium, and ammonium.

Examples of soluble arsenates :—Those of potassium, sodium, and ammonium. Some acid arsenates of metals other than the alkali metals also dissolve in water.

The highly poisonous character of most derivatives of arsenic renders the detection of minute quantities of such substances very important. Methods devised by Marsh, Gutzeit, Reinsch and others enable the analyst to estimate quantities of arsenic weighing less than one-tenth of a milligram. These methods are described in more advanced text-books of chemical analysis.

REACTIONS OF SOLUTIONS OF ARSENIOUS SALTS.

The solutions are acid to **test paper.**

Hydrogen sulphide * produces a yellow precipitate of arsenious sulphide—

$$2\,AsCl_3+3\,H_2S=As_2S_3+6\,HCl.$$

Arsenious sulphide is not soluble in dilute hydrochloric acid, and it is scarcely appreciably soluble in the concentrated acid even on boiling. It dissolves easily in ammonium hydrosulphide, forming thiarsenite—

$$As_2S_3+2\,NH_4HS=2\,NH_4AsS_2+H_2S.$$

It is also soluble in sodium hydroxide, in ammonia, and in ammonium carbonate, forming mixtures of arsenite and thiarsenite—

$$2\,As_2S_3+4\,NaOH=NaAsO_2+3\,NaAsS_2+2\,H_2O.$$

From all these solutions arsenious sulphide is reprecipitated on acidification with hydrochloric acid.

Sodium hydroxide produces no precipitate, sodium chloride and arsenite being formed, both of which are soluble in water.

Ammonia produces no precipitate.

* With solution of arsenious acid, hydrogen sulphide produces colloidal arsenious sulphide, which imparts a yellow colour to the liquid. The addition of a small quantity of certain substances (*e.g.* hydrochloric acid and various salts) coagulates this sulphide, which then separates in the form of a yellow precipitate.

REACTIONS OF SOLUTIONS OF ARSENITES.

The solutions are alkaline to **test paper.**

Hydrogen sulphide * produces no precipitate, but it may produce a yellow coloration due to colloidal arsenious sulphide. On the addition of hydrochloric acid yellow arsenious sulphide is precipitated. The addition of hydrochloric acid to the solution of an arsenite gives rise to the formation of arsenious chloride and the chloride of the metallic radical, and in such a solution hydrogen sulphide produces a precipitate of arsenious sulphide as in the case of any other solution containing arsenious chloride.

In solutions which are not very dilute, **barium nitrate** and **ammonia** produce a white precipitate of barium ortho-arsenite, soluble in nitric acid—

$$2\,KAsO_2+3\,Ba(NO_3)_2+4\,NH_4OH=Ba_3(AsO_3)_2+2\,KNO_3+4\,NH_4NO_3+2\,H_2O.$$

Silver nitrate produces a yellow precipitate of silver ortho-arsenite, soluble in nitric acid and in ammonia—

$$3\,KAsO_2+3\,AgNO_3+H_2O=Ag_3AsO_3+3\,KNO_3+2\,HAsO_2.$$

Cupric sulphate produces a green precipitate of cupric hydrogen ortho-arsenite (Scheele's green), soluble in nitric acid and in ammonia—

$$2\,KAsO_2+CuSO_4+H_2O=CuHAsO_3+K_2SO_4+HAsO_2.$$

REACTIONS OF SOLUTIONS OF ARSENATES.

Arsenates on the addition of hydrochloric acid and a suitable reducing agent are decomposed with formation of arsenious chloride—

$$Na_2HAsO_4+3\,HCl+H_2SO_3=AsCl_3+Na_2SO_4+3\,H_2O.$$

Hydrochloric acid and **hydrogen sulphide** produce a yellow precipitate slowly in the cold, more rapidly when the liquid is warmed; the precipitate consists of a mixture of sulphur and arsenious sulphide—

$$2\,Na_2HAsO_4+4\,HCl+5\,H_2S=4\,NaCl+As_2S_3+2\,S+8\,H_2O.$$

In this reaction part of the hydrogen sulphide acts as a reducing agent with separation of sulphur; another part then precipi-

* See footnote on previous page.

tates arsenious sulphide from the arsenious compound produced. A precipitate of arsenious sulphide may be obtained immediately in the cold if a small quantity of **sodium thiosulphate** is added along with the other reagents.

Silver nitrate produces a brown precipitate of silver arsenate, soluble in nitric acid and in ammonia—

$$Na_2HAsO_4+3\,AgNO_3=Ag_3AsO_4+2\,NaNO_3+HNO_3.$$

Barium nitrate produces with common sodium arsenate (Na_2HAsO_4) a white precipitate of barium mono-hydrogen arsenate, soluble in nitric acid—

$$Na_2HAsO_4+Ba(NO_3)_2=BaHAsO_4+2\,NaNO_3.$$

In solutions of ordinary potassium or ammonium arsenate (KH_2AsO_4 or $NH_4H_2AsO_4$) no precipitate is produced, owing to the solubility of the corresponding barium salt ($BaH_4(AsO_4)_2$).

In the case of all these arsenates, if **ammonia** sufficient to produce a normal salt is added to the solution prior to the addition of **barium nitrate**, a white precipitate of normal barium arsenate is obtained, soluble in nitric acid—

$$2\,NH_4H_2AsO_4+4\,NH_3+3\,Ba(NO_3)_2=Ba_3(AsO_4)_2+6\,NH_4NO_3.$$

Magnesia mixture (see p. 235) produces a white precipitate of ammonium magnesium arsenate—

$$Na_2HAsO_4+MgCl_2+NH_3=2\,NaCl+NH_4MgAsO_4.$$

Ammonium molybdate in nitric acid solution produces, on boiling, a bright yellow precipitate of a complex salt (see p. 232).

ANTIMONY.

Basic oxide, Sb_2O_3. This oxide possesses more distinctly basic properties than arsenious oxide does, and forms antimonious salts, but nevertheless it is a very weak base. It also behaves as an acid anhydride, dissolving in solutions of alkali hydroxides to form antimonites. The oxide Sb_2O_5 is an acid anhydride (antimonic anhydride) and gives rise to the formation of antimonates, but the latter salts are not of sufficient importance to be discussed here. All antimonious salts are very readily decomposed by water with the formation of insoluble basic salt or of the oxide—

$$SbCl_3+H_2O=2\,HCl+SbOCl.$$

The only important antimonious salt is antimonious chloride [**2, 5**]. In order to prepare a solution of it, a sufficiency of hydrochloric acid must be present to prevent the formation of basic salt.

An important derivative of antimony, more especially from the medical point of view, is tartar emetic. It is potassium antimonyl tartrate, and its formula may be written $K(SbO)C_4H_4O_6$. Its reactions differ in some respects from those of antimonious salts and are given on page **116**. It is readily soluble in water.

REACTIONS OF A SOLUTION OF AN ANTIMONIOUS SALT (ANTIMONIOUS CHLORIDE).

The solution is strongly acid to **test paper** (see above).

Hydrogen sulphide produces an orange precipitate of antimonious sulphide—

$$2\,SbCl_3+3\,H_2S=Sb_2S_3+6\,HCl.$$

Antimonious sulphide is soluble in ammonium hydrosulphide, forming ammonium thiantimonite—

$$Sb_2S_3+2\,NH_4HS=2\,NH_4SbS_2+H_2S.$$

If yellow ammonium sulphide is used the solution will contain thiantimonate as well as thiantimonite—

$$NH_4SbS_2+(NH_4)_2S_2=(NH_4)_3SbS_4.$$

From a solution of thiantimonite, hydrochloric acid reprecipitates orange antimonious sulphide, Sb_2S_3; but from a solution of thiantimonate yellow antimonic sulphide, Sb_2S_5, is precipitated. Antimonious sulphide is insoluble in ammonia, but dissolves in sodium hydroxide, forming a mixture of thiantimonite and oxythiantimonite. It is dissolved by moderately concentrated hydrochloric acid on warming, but not by cold dilute hydrochloric acid.

Water in sufficient quantity produces a white precipitate of basic salt (antimonious oxychloride), soluble in hydrochloric acid—

$$SbOCl+2\,HCl=H_2O+SbCl_3.$$

Sodium hydroxide produces a white precipitate of antimonious hydroxide—

$$SbCl_3+3\,NaOH=3\,NaCl+Sb(OH)_3.$$

Antimonious hydroxide dissolves in excess of sodium hydroxide, forming sodium antimonite.

Ammonia produces a white precipitate of basic salt or of antimonious hydroxide, insoluble in excess.

Silver nitrate added to an alkaline solution of sodium antimonite produces a black precipitate due to the reduction of the silver nitrate. This reaction may be applied in the following manner to detect the presence of an antimonious salt, such as antimonious chloride :—

Add **silver nitrate** until no more silver chloride is produced and excess of silver nitrate remains in solution ; then add **sodium hydroxide** until the liquid is alkaline ; if sufficient silver nitrate has been added, the precipitate will darken. Next add enough **ammonia** to dissolve the silver chloride and silver hydroxide that have been formed, when a black precipitate of silver and antimony will remain undissolved.

REACTIONS OF SOLUTION OF TARTAR EMETIC.

The pure solution is neutral to **test paper.**

Hydrochloric acid produces a white precipitate of antimonious oxychloride, soluble in excess—

$$K(SbO)C_4H_4O_6+HCl=SbOCl+KHC_4H_4O_6.$$

This reaction cannot be obtained by means of metallic chlorides ; free hydrochloric acid is necessary.

Hydrogen sulphide produces an orange coloration but no precipitate. On the addition of hydrochloric acid, antimonious sulphide separates as an orange-coloured precipitate—

$$2\,K(SbO)C_4H_4O_6+3\,H_2S=Sb_2S_3+2\,KHC_4H_4O_6+2\,H_2O.$$

The orange coloration first produced is due to colloidal antimonious sulphide. The latter is coagulated and precipitated on the addition not only of hydrochloric acid, but of many other acids and salts.

Sodium hydroxide produces, after some time, a white precipitate of antimonious hydroxide. As this precipitate is soluble in excess of the reagent and its formation only takes place slowly, it is necessary, in order to obtain it at all in the cold, to add only a very small quantity of sodium hydroxide and to allow the liquid to stand. The formation of the precipitate is greatly accelerated by warming.

Ammonia produces no immediate precipitate, but on allowing the liquid to stand, a white precipitate of antimonious hydroxide is formed. The precipitate is insoluble in excess of ammonia.

Silver nitrate and **sodium hydroxide** produce the black precipitate mentioned under the reactions of antimonious chloride. The reaction can be much more easily observed in this case, as there is no precipitation of silver chloride.

ZINC.

Basic oxide, ZnO.

Examples of soluble zinc salts [**1**, **4**] :—Nitrate, chlorate, sulphate, chloride, bromide, iodide, acetate.

REACTIONS OF SOLUTIONS OF ZINC SALTS.

Hydrogen sulphide produces a white precipitate of zinc sulphide—

$$ZnCl_2 + H_2S = 2\,HCl + ZnS.$$

A strong acid such as hydrochloric acid, even when moderately dilute, prevents the precipitation of zinc sulphide by hydrogen sulphide, therefore the zinc salts of strong acids are only partially decomposed by hydrogen sulphide owing to the formation of acid by the action. Zinc salts of weak acids, such as acetic acid, can, on the other hand, be completely decomposed by hydrogen sulphide. If a sufficient quantity of hydrochloric acid is added to the solution of any zinc salt before adding hydrogen sulphide, no precipitation takes place.

Any solution of a zinc salt to which a sufficiency of a soluble acetate, such as sodium acetate, has been added, is completely precipitated by hydrogen sulphide.

Ammonium hydrosulphide produces a white precipitate of zinc sulphide, which dissolves easily in dilute hydrochloric acid, but not in acetic acid—

$$ZnSO_4 + 2\,NH_4HS = (NH_4)_2SO_4 + H_2S + ZnS.$$

Sodium hydroxide produces a white precipitate of zinc hydroxide, soluble in excess—

$$ZnCl_2 + 2\,NaOH = 2\,NaCl + Zn(OH)_2.$$

The solution formed by dissolving zinc hydroxide in sodium hydroxide gives an immediate precipitate of zinc sulphide when hydrogen sulphide is added to it, even in small quantity. It gives no precipitate with ammonium chloride, even when added in considerable quantity. (Compare the Reactions of Aluminium Salts, p. 125.)

Ammonia produces a white precipitate, soluble in excess. The precipitation is prevented by the presence of a sufficient quantity of ammonium chloride.

Potassium ferrocyanide produces a white precipitate of potassium zinc ferrocyanide, insoluble in hydrochloric acid—

$$K_4Fe(CN)_6+Zn(NO_3)_2=2\ KNO_3+K_2ZnFe(CN)_6.$$

Unless the ferrocyanide solution has been freshly prepared, the precipitate, instead of being white, generally has a greenish-yellow colour.

Sodium carbonate produces a white precipitate of basic zinc carbonate.

MANGANESE.

Basic oxides :—Manganous oxide, MnO ; manganic oxide, Mn_2O_3.

The manganic salts are exceedingly unstable, and of no practical importance.

Manganese also forms higher oxides which do not exhibit basic properties but are acid anhydrides. Two of these, manganic anhydride, MnO_3, and permanganic anhydride, Mn_2O_7, form well-defined and crystallisable salts. Of these salts, the only important ones are those of the alkali metals. The oxide MnO_2 is generally called a peroxide, but it is nevertheless a feeble acid anhydride. The manganites derived from it are insoluble substances of somewhat indefinite composition.

Examples of soluble manganous salts :—Chloride [**3**], nitrate [**6**], sulphate [**3**], acetate [**6**].

REACTIONS OF SOLUTIONS OF MANGANOUS SALTS.

Hydrogen sulphide does not produce any precipitate, except with salts derived from weak acids such as acetic acid, in which cases partial precipitation of manganous sulphide may take place

Ammonium hydrosulphide produces a buff precipitate of manganous sulphide, easily soluble in dilute acids, including acetic acid—

$$MnSO_4 + 2\,NH_4HS = (NH_4)_2SO_4 + H_2S + MnS.$$

Sodium hydroxide produces a white precipitate * of manganous hydroxide, insoluble in excess—

$$MnSO_4 + 2\,NaOH = Na_2SO_4 + Mn(OH)_2.$$

Manganous hydroxide darkens on exposure to air, absorbing atmospheric oxygen and becoming converted into a more highly oxidised hydroxide or a manganite.

Ammonia produces a white precipitate * of manganous hydroxide, insoluble in excess. The precipitation is retarded by the presence of a sufficiency of ammonium chloride.

Sodium carbonate produces a white precipitate of manganous carbonate—

$$MnCl_2 + Na_2CO_3 = 2\,NaCl + MnCO_3.$$

Bleaching solution produces, either at once or on warming, a brown precipitate of a manganite.

The most delicate test for small quantities of manganous salts in solution consists in the production, by means of powerful oxidising agents, of permanganic acid, which is easily recognised in minute quantity by the pink colour which it imparts to the liquid. The oxidation may be effected in either of the following ways, but the experiments should only be made with very small quantities of the solutions under examination :—

(*a*) A small quantity of **lead peroxide** is warmed with **dilute nitric acid** and a few drops of the solution to be tested are then added. After shaking the mixture the lead peroxide is allowed to settle, so that the colour of the liquid may be observed.

(*b*) The solution is warmed with **ammonium persulphate** (solid), **dilute nitric acid,** and a drop of dilute solution of **silver nitrate.**

MANGANATES AND PERMANGANATES.

A manganate, such as potassium manganate, is decomposed by water, with formation of the corresponding permanganate together with manganite and hydroxide. The general nature of the change may be represented by the following equation—

$$3\,K_2MnO_4 + 2\,H_2O = 4\,KOH + 2\,KMnO_4 + MnO_2;$$

* When ordinary solutions are employed the precipitate is not white, even at first, owing to the action of the oxygen dissolved in them. A nearly white precipitate can be obtained if the manganous solution and the solution of sodium hydroxide are boiled for some time, to expel this dissolved oxygen, before they are mixed.

but it is to be borne in mind that some of the potassium hydroxide represented in the equation is really neutralised with formation of insoluble manganite. The decomposition of a manganate by water is prevented by the presence, in sufficient quantity, of free hydroxide, and in such a case the manganate dissolves to form a green solution. This green solution becomes red on the addition of dilute sulphuric acid, owing to the formation of permanganate—

$$5\ K_2MnO_4 + 4\ H_2SO_4 = MnSO_4 + 3\ K_2SO_4 + 4\ KMnO_4 + 4\ H_2O.$$

Permanganates are easily recognised by the colour of their solutions and the readiness with which this colour is destroyed by reducing agents in presence of acid (see pp. 148, 205).

IRON.

Basic oxides :—Ferrous oxide, FeO ; ferric oxide, Fe_2O_3.

Corresponding to the two basic oxides of iron there are two series of salts, both of which are of importance. Most ferrous salts can be easily oxidised into the corresponding ferric salts, and the ferric salts reduced to the corresponding ferrous salts. Solutions of ferrous salts slowly absorb atmospheric oxygen and become converted, partly at least, into ferric salts—often with simultaneous formation of insoluble basic ferric salt—and hence the ordinary ferrous solutions of the laboratory do not behave as perfectly pure ferrous solutions would.

Examples of soluble ferrous salts :—Sulphate and ammonium ferrous sulphate [**2**, **4**], chloride [**2**, **4**, **5**], bromide [**5**], iodide [**5**], acetate [**4**].

Solutions of ferrous salts are pale green or nearly colourless.

Examples of soluble ferric salts :—Chloride [**5**], bromide [**5**], sulphate [**4**], nitrate [**4**], iron alum.

Solutions of ferric salts generally have a yellow or brownish colour.

REACTIONS OF SOLUTIONS OF FERROUS SALTS.

Hydrogen sulphide does not produce any precipitate.

Ammonium hydrosulphide produces a black precipitate of ferrous sulphide, easily soluble in dilute acids, including acetic acid—

$$FeCl_2 + 2\ NH_4HS = 2\ NH_4Cl + H_2S + FeS.$$

Sodium hydroxide, when added to a **purely ferrous** solution, produces a white precipitate of ferrous hydroxide, insoluble in excess—

$$FeCl_2 + 2\ NaOH = 2\ NaCl + Fe(OH)_2.$$

Ferrous hydroxide rapidly undergoes oxidation on exposure to the air, becoming dirty green, then nearly black, and finally, when it has become completely converted into ferric hydroxide, reddish-brown. As noted above, ordinary solutions of ferrous salts always contain at least a small proportion of ferric salt, and unless special precautions have been taken to avoid this, and also to avoid the presence of dissolved oxygen, the precipitate obtained will not be white. (Compare note on p. 119.)

Ammonia produces a white precipitate of ferrous hydroxide, insoluble in excess (see preceding paragraph).

Sodium carbonate (see sodium hydroxide above) produces a white precipitate of ferrous carbonate—

$$FeSO_4+Na_2CO_3=Na_2SO_4+FeCO_3.$$

On exposure to the air ferrous carbonate becomes slowly oxidised into ferric hydroxide, carbon dioxide being evolved. The oxidation takes place more slowly than in the case of ferrous hydroxide, but the colour changes observed are similar.

Potassium ferrocyanide (see sodium hydroxide above) produces a white precipitate of ferrous ferrocyanide—

$$2\,FeSO_4+K_4Fe(CN)_6=2\,K_2SO_4+Fe_2Fe(CN)_6.$$

The precipitate rapidly undergoes oxidation on exposure to the air, and is eventually converted into Prussian blue (see under Reactions of Ferric Salts). With ordinary ferrous solutions, the precipitate will, of course, be more or less blue from the beginning.

Potassium ferricyanide produces a dark blue precipitate of ferrous ferricyanide (Turnbull's blue).

REACTIONS OF SOLUTIONS OF FERRIC SALTS.

Hydrogen sulphide produces a transient black precipitate, probably consisting of ferric sulphide. The black precipitate almost immediately disappears and a white precipitate of sulphur remains, ferrous salt being formed in solution—

$$2\,FeCl_3+H_2S=2\,HCl+2\,FeCl_2+S.$$

If the original solution of ferric salt contains free acid, the formation of a black precipitate is not observed, and the reduction to ferrous salt, with precipitation of sulphur, takes place slowly.

Ammonium hydrosulphide produces a black precipitate which consists, according to circumstances, of ferric sulphide or of ferrous sulphide and sulphur, or of a mixture of all three—

$$2\,FeCl_3+6\,NH_4HS=6\,NH_4Cl+3\,H_2S+Fe_2S_3.$$
$$2\,FeCl_3+6\,NH_4HS=6\,NH_4Cl+3\,H_2S+2\,FeS+S.$$

The black precipitate, whatever its composition, dissolves in hydrochloric acid yielding a solution of ferrous salt and a white residue of sulphur—

$$Fe_2S_3+4\,HCl=2\,H_2S+2\,FeCl_2+S.$$
$$2\,FeS(+S)+4\,HCl=2\,H_2S+2\,FeCl_2(+S).$$

Sodium hydroxide produces a reddish-brown precipitate of ferric hydroxide, insoluble in excess—

$$FeCl_3+3\,NaOH=3\,NaCl+Fe(OH)_3.$$

Ammonia produces a reddish-brown precipitate of ferric hydroxide, insoluble in excess.

Potassium ferrocyanide produces a dark blue precipitate of ferric ferrocyanide (Prussian blue).

Potassium ferricyanide produces a brown solution, due to the formation of ferric ferricyanide, which is soluble in water. This brown solution yields a dark blue precipitate when treated with reducing agents such as hydrogen sulphide, sulphurous acid, and stannous chloride (see p. 238).

Potassium thiocyanate produces a deep red solution (see p. 141). The colour is due to the formation of ferric thiocyanate, and is destroyed by mercuric chloride.

COBALT.

Basic oxides:—Cobaltous oxide, CoO; cobaltic oxide, Co_2O_3.

The cobaltic salts are difficult to prepare and are very unstable, decomposing spontaneously with formation of cobaltous salts. They cannot be obtained by the action of acids on cobaltic oxide or hydroxide. Their reactions need not be considered here.

Examples of soluble cobaltous salts:—Nitrate [**4**], sulphate [**4**, **6**], chloride [**4**, **5**], acetate.

Solutions of cobaltous salts have a characteristic red or pink colour (see p. 11).

REACTIONS OF SOLUTIONS OF COBALTOUS SALTS.

With salts derived from weak acids such as acetic acid ($HC_2H_3O_2$ being represented as $H\bar{A}$), **hydrogen sulphide** produces a black precipitate of cobaltous sulphide, insoluble in dilute acids—

$$Co\bar{A}_2 + H_2S = 2\,H\bar{A} + CoS.$$

In such cases the precipitation is complete. With salts derived from strong acids no precipitate is formed immediately in the cold, but partial precipitation as sulphide takes place gradually, especially on warming, and in the latter case some of the sulphide may form a metallic-looking deposit on the wall of the tube. The presence of a small quantity of a strong acid, such as hydrochloric acid, entirely prevents the formation of sulphide, although when it is once formed dilute hydrochloric acid will not dissolve it.

Ammonium hydrosulphide produces a black precipitate of cobaltous sulphide, insoluble in dilute acids—

$$Co(NO_3)_2 + 2\,NH_4HS = 2\,NH_4NO_3 + H_2S + CoS.$$

Sodium hydroxide produces a blue precipitate of basic salt, insoluble in excess, but becoming reddish on boiling, owing to its conversion into hydroxide—

$$Co(NO_3)_2 + 2\,NaOH = 2\,NaNO_3 + Co(OH)_2.$$

Ammonia produces a blue precipitate of basic salt, soluble in excess with formation of a nearly colourless solution ; this solution is rapidly oxidised by the oxygen of the air and becomes brown. The presence of a sufficiency of ammonium chloride prevents the precipitation.

Sodium carbonate produces a pink precipitate of basic cobaltous carbonate.

Bleaching solution produces, somewhat slowly, a black precipitate of cobaltic hydroxide $Co(OH)_3$. When excess of bleaching solution is added and the mixture warmed, oxygen is evolved, due to the decomposition of the hypochlorite present in the bleaching solution.

Potassium cyanide produces a reddish-brown precipitate of cobaltous cyanide, which is soluble in excess, forming ultimately a reddish solution of potassium cobaltocyanide—

$$Co(NO_3)_2 + 2\,KCN = 2\,KNO_3 + Co(CN)_2.$$
$$Co(CN)_2 + 4\,KCN = K_4Co(CN)_6.$$

When **sodium hydroxide** and an oxidising agent such as **bromine** (or free oxygen) are added to the solution of potassium cobaltocyanide obtained as above, the cobalt is completely converted into soluble cobalticyanide. (Compare Nickel.) (The conversion of potassium cobaltocyanide into potassium cobalticyanide takes place with great readiness; so much so that when the solution of potassium cobaltocyanide is warmed in absence of air, water is decomposed and hydrogen is evolved—

$$2\ K_4Co(CN)_6 + 2\ H_2O = 2\ K_3Co(CN)_6 + 2\ KOH + H_2.)$$

When a solution of a cobaltous salt is added to a solution of **potassium nitrite** in dilute **acetic acid** the cobalt is completely precipitated as yellow potassium cobaltinitrite, $K_3Co(NO_2)_6$. (Note that this is a cobaltic compound, the oxidation taking place at the expense of part of the nitrous acid.)

NICKEL.

Basic oxide, NiO. (The oxide Ni_2O_3 is not a basic oxide, salts corresponding to it being unknown.)

Examples of soluble nickel salts:—Sulphate [**4**, **6**], nitrate [**4**], chloride [**4**, **5**], acetate.

Solutions of nickel salts have a bright green colour.

REACTIONS OF SOLUTIONS OF NICKEL SALTS.

The reactions of solutions of nickel salts with **hydrogen sulphide** and with **ammonium hydrosulphide** are exactly similar to those of cobaltous salts (see above).

Sodium hydroxide produces a pale green precipitate of nickel hydroxide insoluble in excess—

$$NiSO_4 + 2\ NaOH = Na_2SO_4 + Ni(OH)_2.$$

Ammonia produces a pale green precipitate of basic salt, which dissolves in excess forming a blue solution. The presence of a sufficiency of ammonium chloride prevents the precipitation.

Sodium carbonate produces a pale green precipitate of basic nickel carbonate.

Bleaching solution produces exactly similar effects to those obtained with cobaltous salts.

Potassium cyanide produces a greenish precipitate of nickel cyanide which is soluble in excess, forming a yellow or brownish solution of potassium nickel cyanide—

$$NiSO_4 + 2\ KCN = K_2SO_4 + Ni(CN)_2.$$
$$Ni(CN)_2 + 2\ KCN = K_2Ni(CN)_4.$$

When **sodium hydroxide** and a suitable oxidising agent, such as bromine, are added to the solution of potassium nickel cyanide obtained as above,

and the mixture is warmed, the nickel is completely precipitated as nickelic hydroxide. (Compare Cobalt.)

ALUMINIUM.

Basic oxide, Al_2O_3.

Examples of soluble aluminium salts:—Sulphate [**1**, **6**], ammonia alum, nitrate, chloride [**5**, **6**], bromide [**5**], acetate.

REACTIONS OF SOLUTIONS OF ALUMINIUM SALTS.

Sodium hydroxide produces a white gelatinous precipitate of aluminium hydroxide, soluble in excess—

$$Al_2(SO_4)_3 + 6\,NaOH = 3\,Na_2SO_4 + 2\,Al(OH)_3.$$

From the solution obtained by dissolving the precipitate in excess of sodium hydroxide, ammonium chloride, if added in sufficient quantity, reprecipitates aluminium hydroxide. The reason of this is that ammonium chloride interacts with sodium hydroxide, forming water, sodium chloride, and ammonia, in which mixture aluminium hydroxide is almost insoluble. The solution of aluminium hydroxide in sodium hydroxide gives no precipitate on the addition of a small quantity of hydrogen sulphide; but if the latter reagent is added until all the sodium hydroxide is converted into sodium hydrosulphide the whole of the aluminium hydroxide is reprecipitated, because it is insoluble in sodium hydrosulphide (compare the Reactions of Zinc Salts, p. 117).

Ammonia produces a white precipitate of aluminium hydroxide, slightly soluble in excess, but reprecipitated on boiling off the excess.

Ammonium hydrosulphide produces a white precipitate of aluminium hydroxide—

$$Al_2(SO_4)_3 + 6\,NH_4HS + 6\,H_2O = 3\,(NH_4)_2SO_4 + 6\,H_2S + 2Al(OH)_3.$$

Sodium carbonate produces a white precipitate of aluminium hydroxide or of basic aluminium carbonate, with evolution of carbon dioxide.

After acidifying with **hydrochloric acid, potassium ferrocyanide** produces no precipitate (compare the Reactions of Zinc Salts, p. 118).

CHROMIUM.

Basic oxides :—Chromous oxide, CrO ; chromic oxide, Cr_2O_3.

The chromous salts are of little practical importance. They are very easily oxidised into chromic compounds, and in consequence it is difficult to obtain them pure. They will not be further considered here.

Chromium also forms a well-defined acid anhydride, chromic anhydride, CrO_3. The chromates, corresponding to this anhydride, are an important set of salts, but chromic acid itself (H_2CrO_4) is not known.

Examples of soluble chromic salts :—Sulphate [**3**], chrome alum, chloride [**3**, **6**], bromide, nitrate, acetate.

Solutions of chromic salts have a characteristic bluish-purple colour ; in some cases the colour changes to green when the solution is boiled, owing to the formation of a complex salt.

Examples of soluble chromates : — Potassium, sodium, ammonium, calcium, and magnesium chromates.

Solutions of chromates are yellow.

REACTIONS OF SOLUTIONS OF CHROMIC SALTS.

Sodium hydroxide produces a bluish or greenish-grey precipitate of chromic hydroxide, which dissolves in excess, forming a green solution—

$$CrCl_3 + 3\,NaOH = 3\,NaCl + Cr(OH)_3.$$

The green solution obtained by dissolving chromic hydroxide in excess of sodium hydroxide gives a green precipitate of chromic hydroxide on boiling, provided only a slight excess of sodium hydroxide has been employed.

Ammonia produces a bluish-grey precipitate of chromic hydroxide, which is only very slightly soluble in excess.

Ammonium hydrosulphide produces a bluish-grey precipitate of chromic hydroxide—

$$CrCl_3 + 3\,NH_4HS + 3\,H_2O = 3\,NH_4Cl + 3\,H_2S + Cr(OH)_3.$$

Sodium carbonate produces a bluish-grey precipitate of chromic hydroxide or of basic chromic carbonate.

Bleaching solution oxidises solutions of chromic salts to chromates, a yellow solution being ultimately produced. The reaction takes place much more rapidly on warming.

Ammonium persulphate oxidises chromic solutions, either acid or alkaline, to chromate. The reaction takes place only very slowly in the cold.

REACTIONS OF SOLUTIONS OF CHROMATES.

The addition of a small quantity of **acid** changes the colour from yellow to orange, bichromate * being formed—

$$2\,K_2CrO_4 + 2\,HCl = 2\,KCl + H_2O + K_2Cr_2O_7.$$

A **reducing agent** added to the above acid solution causes the colour of the solution to change from orange to bluish-purple or green, a chromic salt being formed and, in some instances, sulphur being precipitated. Hydrogen sulphide, sulphurous acid, alcohol, and stannous chloride may be taken as examples of reducing agents. In some cases it is necessary to heat the mixture.

$$K_2Cr_2O_7 + 4\,H_2SO_4 + 3\,H_2S = Cr_2(SO_4)_3 + K_2SO_4 + 7\,H_2O + 3\,S.$$

$$K_2Cr_2O_7 + H_2SO_4 + 3\,H_2SO_3 = Cr_2(SO_4)_3 + K_2SO_4 + 4\,H_2O.$$

$$K_2Cr_2O_7 + 4\,H_2SO_4 + 3\,\underset{\text{Ethyl Alcohol.}}{C_2H_6O} = Cr_2(SO_4)_3 + K_2SO_4 + 7\,H_2O + 3\,\underset{\text{Acetaldehyde.}}{C_2H_4O}.$$

$$K_2Cr_2O_7 + 14\,HCl + 3\,SnCl_2 = 2\,CrCl_3 + 2\,KCl + 3\,SnCl_4 + 7\,H_2O.$$

Silver nitrate produces a red precipitate of silver chromate, soluble in nitric acid and in ammonia—

$$K_2CrO_4 + 2\,AgNO_3 = 2\,KNO_3 + Ag_2CrO_4.$$

Barium nitrate produces a yellow precipitate of barium chromate, soluble in nitric acid—

$$K_2CrO_4 + Ba(NO_3)_2 = 2\,KNO_3 + BaCrO_4.$$

Lead acetate produces a yellow precipitate of lead chromate—

$$K_2CrO_4 + Pb\bar{A}_2 = PbCrO_4 + 2\,K\bar{A}.$$

BARIUM.

Basic oxide, BaO.

Examples of soluble barium salts [**1**, **6**] :—Nitrate, chlorate, acetate, chloride, bromide, iodide.

* The bichromates are really an independent set of salts, derived from the acid $H_2Cr_2O_7$; this acid is not known by itself, but probably it is formed when chromic anhydride is dissolved in water—

$$2\,CrO_3 + H_2O = H_2Cr_2O_7.$$

Bichromates are easily converted into chromates by the action of alkalies—

$$K_2Cr_2O_7 + 2\,KOH = H_2O + 2\,K_2CrO_4.$$

The reactions of the bichromates resemble generally those of the chromates, so far at least as the appearance of the precipitates is concerned.

REACTIONS OF SOLUTIONS OF BARIUM SALTS.

Ammonium carbonate produces a white precipitate of barium carbonate, soluble in dilute acids with evolution of carbon dioxide—

$$Ba(NO_3)_2+(NH_4)_2CO_3=2\ NH_4NO_3+BaCO_3.$$

Sodium hydroxide, even if quite free from carbonate, produces in concentrated solutions a white precipitate of barium hydroxide—

$$BaCl_2+2\ NaOH=Ba(OH)_2+2\ NaCl.$$

Commercial sodium hydroxide, or sodium hydroxide solution which has been exposed to the air, always contains carbonate, and this interacts even with dilute solutions of barium salts, producing a white precipitate of barium carbonate—

$$Ba(NO_3)_2+Na_2CO_3=2\ NaNO_3+BaCO_3.$$

Ammonia, if quite free from ammonium carbonate, does not produce any precipitate.

Dilute sulphuric acid produces a white precipitate of barium sulphate, insoluble in dilute acids—

$$BaCl_2+H_2SO_4=2\ HCl+BaSO_4.$$

Calcium sulphate produces a white precipitate of barium sulphate—

$$Ba(NO_3)_2+CaSO_4=Ca(NO_3)_2+BaSO_4.$$

Potassium chromate produces a yellow precipitate of barium chromate, insoluble in acetic acid—

$$Ba(NO_3)_2+K_2CrO_4=2\ KNO_3+BaCrO_4.$$

Ammonium oxalate produces a white precipitate of barium oxalate, soluble in hydrochloric acid—

$$Ba(NO_3)_2+(NH_4)_2C_2O_4=2\ NH_4NO_3+BaC_2O_4.$$

STRONTIUM.

Basic oxide, SrO.

Examples of soluble strontium salts [**1**, **6**] :—Nitrate, chlorate, acetate, chloride, bromide, iodide.

REACTIONS OF SOLUTIONS OF STRONTIUM SALTS.

The reactions of solutions of strontium salts with **ammonium carbonate, sodium hydroxide** and with **ammonia** are similar to those of barium salts (see above).

Dilute sulphuric acid produces a white precipitate of strontium sulphate, insoluble in dilute acids—

$$SrCl_2 + H_2SO_4 = 2\,HCl + SrSO_4.$$

The precipitate does not form quite so rapidly as in the case of barium salts.

Calcium sulphate produces, on standing for some time or more rapidly on boiling, a white precipitate of strontium sulphate—

$$SrCl_2 + CaSO_4 = CaCl_2 + SrSO_4.$$

Potassium chromate produces, on standing for some time or more rapidly on boiling, a yellow precipitate of strontium chromate, soluble in acetic acid—

$$SrCl_2 + K_2CrO_4 = 2\,KCl + SrCrO_4.$$

Ammonium oxalate produces a white precipitate of strontium oxalate, soluble in hydrochloric acid—

$$SrCl_2 + (NH_4)_2C_2O_4 = 2\,NH_4Cl + SrC_2O_4.$$

CALCIUM.

Basic oxide, CaO.

Examples of soluble calcium salts [**6**] :—Nitrate, chlorate, acetate, chloride, bromide, iodide, sulphate.

REACTIONS OF SOLUTIONS OF CALCIUM SALTS.

The reactions of solutions of calcium salts with **ammonium carbonate** and with **sodium hydroxide** are similar to those of barium salts (see above).

With moderately concentrated solutions **dilute sulphuric acid** produces a white precipitate of calcium sulphate, which is sparingly soluble in water. The precipitation of the calcium as sulphate is never complete.

$$CaCl_2 + H_2SO_4 = 2\,HCl + CaSO_4.$$

Calcium sulphate does not produce any precipitate, even on standing or boiling (compare Reactions of Barium and Strontium Salts).

Potassium chromate does not produce any precipitate in moderately dilute solutions, even on standing or boiling. In concentrated solutions partial precipitation takes place on boiling (see under Reactions of Barium and Strontium Salts).

Ammonium oxalate produces a white precipitate of calcium oxalate, insoluble in acetic acid but soluble in hydrochloric acid—

$$CaCl_2+(NH_4)_2C_2O_4=2\,NH_4Cl+CaC_2O_4.$$

MAGNESIUM.

Basic oxide, MgO.

Examples of soluble magnesium salts [**1**, **6**] :—Nitrate, sulphate, chloride, bromide, iodide, acetate, nitrite.

REACTIONS OF SOLUTIONS OF MAGNESIUM SALTS.

Ammonium carbonate produces no precipitate unless the solutions are very concentrated.

Sodium carbonate produces, on warming, a white precipitate of basic magnesium carbonate.

Sodium hydroxide produces a white precipitate of magnesium hydroxide, insoluble in excess—

$$MgSO_4+2\,NaOH=Na_2SO_4+Mg(OH)_2.$$

The precipitate is soluble in ammonium chloride.

Ammonia produces a white precipitate of magnesium hydroxide, insoluble in excess—

$$MgSO_4+2\,NH_4OH=(NH_4)_2SO_4+Mg(OH)_2.$$

The precipitation is not complete, however, owing to the formation of ammonium salt, which dissolves magnesium hydroxide. If free acid is present in the original solution, sufficient ammonium salt may be formed to prevent the precipitation of any magnesium hydroxide.

Ammonium chloride, ammonia, and **ammonium phosphate** produce a white precipitate of ammonium magnesium phosphate—

$$MgSO_4+(NH_4)_2HPO_4+NH_3=(NH_4)_2SO_4+MgNH_4PO_4.$$

The ammonium chloride is added to prevent the precipitation of magnesium hydroxide by the ammonia alone.

Iodine and then **sodium hydroxide** (the latter in very small quantity) produce a dark brown precipitate which consists of magnesium hydroxide coloured by free iodine. Excess of sodium hydroxide decolorises the precipitate, removing the free iodine and leaving the white magnesium hydroxide undissolved.

AMMONIUM.

Ammonium salts are, with few exceptions, readily soluble in water.

REACTIONS OF SOLUTIONS OF AMMONIUM SALTS.

When boiled with **sodium hydroxide** ammonia gas is evolved—

$$(NH_4)_2SO_4+2\,NaOH=Na_2SO_4+2\,NH_3+2\,H_2O.$$

The ammonia can be recognised by its odour and by its action on moist turmeric or red litmus paper. (See note on p. 141.)

With very concentrated solutions **sodium hydrogen tartrate** may produce a white precipitate of ammonium hydrogen tartrate (the tartaric acid radical $C_4H_4O_6$, being represented as $\overline{T}$)—

$$NH_4Cl+NaH\overline{T}=NaCl+NH_4H\overline{T}.$$

With very dilute solutions **Nessler's reagent** (see p. 235) produces a yellow coloration or brownish precipitate due to the formation of a substance the composition of which is represented by the formula NH_2Hg_2OI. This substance is easily dissolved by ammonium salts (but not by ammonia), and therefore only a very small quantity of solution should be employed in trying the reaction. The precipitate is also dissolved by potassium iodide.

$$NH_4Cl+2\,KHgI_3+4\,KOH=NH_2Hg_2OI+5\,KI+KCl+3\,H_2O.$$

POTASSIUM.

Basic oxide, K_2O.

The majority of the potassium salts are readily soluble in water, potassium hydrogen tartrate and potassium perchlorate being two of the most sparingly soluble.

REACTIONS OF SOLUTIONS OF POTASSIUM SALTS.

When, to a moderately concentrated neutral solution, an equal volume of **sodium hydrogen tartrate** solution is added, a white crystalline precipitate of potassium hydrogen tartrate is produced—

$$KNO_3+NaH\overline{T}=NaNO_3+KH\overline{T}.$$

The precipitate forms slowly in dilute solutions, and its formation is promoted by vigorous shaking, but hindered by heating. Potassium hydrogen tartrate dissolves in hydrochloric acid and in sodium hydroxide or potassium hydroxide. In the case of the latter solvent normal potassium tartrate is formed—

$$KH\overline{T}+KOH=K_2\overline{T}+H_2O.$$

The formation of the precipitate is entirely prevented by the presence, in sufficient quantity, of hydrochloric or nitric acid, but not of acetic or tartaric acid. The latter acid may be used instead of sodium hydrogen tartrate to produce the precipitate, but the precipitation is always to some extent interfered with (and it may even be entirely prevented) by the free acid which is formed simultaneously—

$$KNO_3+H_2\overline{T}\rightleftharpoons HNO_3+KH\overline{T}.$$

In the case of potassium salts which yield alkaline solutions, such as the carbonate or cyanide, the sodium hydrogen tartrate or the tartaric acid must be added until the mixture is distinctly acid before the precipitate can be produced. When sodium hydrogen tartrate is added to such a solution, the first action is to form an easily soluble normal salt—

$$K_2CO_3+2\,NaH\overline{T}=2\,KNa\overline{T}+H_2O+CO_2,$$

but this interacts with a further quantity of the reagent, forming potassium hydrogen tartrate—

$$KNa\overline{T}+NaH\overline{T}=KH\overline{T}+Na_2\overline{T}.$$

Ammonium perchlorate, when added to a moderately concentrated solution of potassium chloride, produces a white crystalline precipitate of potassium perchlorate—

$$KCl+NH_4ClO_4=KClO_4+NH_4Cl.$$

When two or three drops of a solution of a potassium salt are added to a mixture of one drop of **sodium thiosulphate** solution and one drop of **bismuth nitrate** solution with about 10 c.c. of **alcohol**, a yellow precipitate of potassium bismuth thiosulphate is produced, easily soluble on the addition of water (Carnot's reaction).

SODIUM.

Basic oxide, Na_2O.

The sodium salts of all the usually occurring acidic radicals are readily soluble in water, hence solutions of sodium salts give no precipitate with any of the ordinary reagents. The only well-defined reaction for sodium compounds is the flame coloration, for which see page 170.

Classification of the commoner Metallic Radicals from the point of view of the Reactions of their Salts (see pp. 158-169).

A. Metallic radicals, the salts of which give sulphides (insoluble in water and dilute mineral acid) when treated with hydrogen sulphide, even in the presence of moderately dilute hydrochloric acid: $As^{'''}$, $Sb^{'''}$, $Sn^{''''}$, $Ag^{'}$, $Hg^{'}$, $Hg^{''}$, $Pb^{''}$, $Cu^{''}$, $Bi^{'''}$, $Cd^{''}$, $Sn^{''}$.

B. Metallic radicals, the salts of which do not give sulphides when treated with hydrogen sulphide in the presence of moderately dilute hydrochloric acid, but do give sulphides (insoluble in water) when treated with ammonium hydrosulphide: $Fe^{'''}$, $Fe^{''}$, $Zn^{''}$, $Co^{''}$, $Ni^{''}$, $Mn^{''}$.

C. Metallic radicals, the sulphides of which are soluble in water or cannot be prepared from the salts in the wet way: $Cr^{'''}$, $Al^{'''}$, $Ba^{''}$, $Sr^{''}$, $Ca^{''}$, $Mg^{''}$, $K^{'}$, $Na^{'}$, $(NH_4)^{'}$.

A may be divided into the following three groups:—

I. The sulphides are thio-anhydrides, and dissolve in ammonium hydrosulphide: $As^{'''}$, $Sb^{'''}$, $Sn^{''''}$.

II. The chlorides are insoluble in water and dilute acids, and therefore solutions of the soluble salts give a precipitate of chloride on the addition of a soluble chloride: $Ag^{'}$, $Hg^{'}$. (Note the sparing solubility of $PbCl_2$ in cold water, and the insolubility of SbOCl and BiOCl.)

III. The sulphides are not thio-anhydrides, and the chlorides are soluble in dilute hydrochloric acid: $Hg^{''}$, $Pb^{''}$, $Cu^{''}$, $Bi^{'''}$, $Cd^{''}$, $Sn^{''}$.

B need not be further divided.

C may be divided into the following four groups:—

I. Ammonium hydrosulphide precipitates the hydroxide: $Cr^{'''}$, $Al^{'''}$. These hydroxides are soluble in sodium hydroxide; while the sulphides of class **B** are insoluble in sodium hydroxide.

II. The carbonates are insoluble in water, and very sparingly soluble in ammonium chloride: $Ba^{''}$, $Sr^{''}$, $Ca^{''}$.

III. The carbonate is insoluble in water, but easily soluble in ammonium chloride: $Mg^{''}$.

IV. The carbonates and phosphates are soluble in water: $(NH_4)^{'}$, $K^{'}$, $Na^{'}$.

PART II.—THE REACTIONS DUE TO THE ACIDIC RADICALS.

CARBONATES.

Carbonic acid, H_2CO_3; dibasic.

Examples of soluble carbonates :—Carbonates of potassium, sodium, and ammonium.

REACTIONS OF SOLUTIONS OF CARBONATES.

The solutions are alkaline to **test paper**.

Hydrochloric acid decomposes carbonates, with production of carbonic acid—

$$K_2CO_3+2\,HCl=2\,KCl+H_2CO_3.$$

In very dilute solutions the whole of the carbonic acid remains dissolved, but with moderately concentrated solutions most of it decomposes, and carbon dioxide escapes with effervescence; the latter may be detected by means of **calcium hydroxide**, as described on page 77.

$$CO_2+Ca(OH)_2=CaCO_3+H_2O.$$

Barium nitrate produces a white precipitate of barium carbonate, soluble in dilute hydrochloric acid—

$$K_2CO_3+Ba(NO_3)_2=BaCO_3+2\,KNO_3.$$

Silver nitrate produces a nearly white precipitate of silver carbonate, soluble in nitric acid and in ammonia—

$$K_2CO_3+2\,AgNO_3=Ag_2CO_3+2\,KNO_3.$$

SULPHITES.

Sulphurous acid, H_2SO_3; dibasic.

Examples of soluble sulphites :—Sulphites of potassium, sodium, ammonium, and magnesium.

On exposure to air sulphites become gradually oxidised, forming sulphates.

REACTIONS OF SOLUTIONS OF SULPHITES.

The solutions are alkaline to **test paper.**

Hydrochloric acid decomposes sulphites, with production of sulphurous acid—

$$K_2SO_3+2\,HCl=2\,KCl+H_2SO_3.$$

With concentrated solutions a considerable proportion of the sulphurous acid decomposes into water and sulphur dioxide, and the latter may escape with effervescence—

$$H_2SO_3=H_2O+SO_2.$$

In cases where there is no effervescence, a quantity of sulphur dioxide will be given off on heating the solution, sufficient to permit of its being recognised by its odour and by its reducing action on **ferric ferricyanide** or **chromic acid** test paper (see p. 238).

Hydrochloric acid and **hydrogen sulphide** produce a pale yellow precipitate of sulphur—

$$H_2SO_3+2\,H_2S=3\,S+3\,H_2O.$$

Barium nitrate produces a white precipitate of barium sulphite, soluble in hydrochloric acid—

$$Na_2SO_3+Ba(NO_3)_2=2\,NaNO_3+BaSO_3.$$

As barium sulphate is insoluble, the precipitate obtained with a partially oxidised sulphite solution consists of a mixture of barium sulphite and barium sulphate; on the addition of hydrochloric acid the barium sulphite alone dissolves, while the barium sulphate remains unchanged.

Silver nitrate, when added in small quantity, produces locally a white precipitate which dissolves on shaking up the liquid. The precipitate consists of silver sulphite, which unites with the unchanged soluble sulphite, producing a soluble complex salt in which silver forms part of the acidic radical—

$$Na_2SO_3+2\,AgNO_3=2\,NaNO_3+Ag_2SO_3.$$
$$Ag_2SO_3+Na_2SO_3=2\,NaAgSO_3.$$

On adding sufficient silver nitrate a permanent precipitate of silver sulphite is produced—

$$NaAgSO_3+AgNO_3=NaNO_3+Ag_2SO_3.$$

When silver sulphite is warmed with water, silver is deposited as a dark powder, or as a mirror on the wall of the tube ; silver sulphate and sulphur dioxide are also produced—

$$2\,Ag_2SO_3 = 2\,Ag + Ag_2SO_4 + SO_2.$$

Most silver salts, insoluble in water, dissolve in solutions of sulphites, with formation of the complex salts referred to above—

$$AgCl + Na_2SO_3 = NaCl + NaAgSO_3.$$

Iodine is converted into iodide, and the brown colour of the reagent disappears—

$$Na_2SO_3 + I_2 + H_2O = NaI + HI + NaHSO_4.$$

Ferric chloride, in small quantity, produces a red coloration due to the formation of ferric sulphite in solution. The coloration disappears on the addition of hydrochloric acid.

THIOSULPHATES.

Thiosulphuric acid, $H_2S_2O_3$; dibasic.

Examples of soluble thiosulphates :—Thiosulphates of potassium, sodium, ammonium, calcium, strontium, and magnesium ; barium thiosulphate is sparingly soluble.

REACTIONS OF SOLUTIONS OF THIOSULPHATES.

Hydrochloric acid liberates thiosulphuric acid, which decomposes into sulphurous acid and sulphur—

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + H_2S_2O_3.$$
$$H_2S_2O_3 = H_2SO_3 + S.$$

With dilute solutions this decomposition takes place slowly in the cold, but much more rapidly on warming ; with concentrated solutions precipitation of sulphur takes place almost immediately. The presence of sulphurous acid can be recognised by observing the evolution of sulphur dioxide as described under the reactions of sulphites.

With moderately concentrated solutions **barium nitrate** produces a white precipitate of barium thiosulphate, but with dilute solutions no precipitate is formed.

Silver nitrate, when added in small quantity, produces locally a white precipitate which dissolves on shaking up the

liquid. The precipitate consists of silver thiosulphate, which unites with the unchanged soluble thiosulphate producing a soluble complex salt (see p. 39) in which silver forms part of the acidic radical—

$$K_2S_2O_3+2\,AgNO_3=2\,KNO_3+Ag_2S_2O_3.$$
$$Ag_2S_2O_3+K_2S_2O_3=2\,KAgS_2O_3.$$

On adding sufficient silver nitrate, a permanent precipitate is produced—

$$KAgS_2O_3+AgNO_3=KNO_3+Ag_2S_2O_3.$$

Silver thiosulphate rapidly decomposes in presence of water with formation of silver sulphide and sulphuric acid, the colour of the precipitate changing from white to yellow, orange, brown, and finally black—

$$Ag_2S_2O_3+H_2O=Ag_2S+H_2SO_4.$$

Most silver salts, insoluble in water, dissolve in solutions of thiosulphates with formation of the complex salts referred to above—

$$AgI+Na_2S_2O_3=NaI+NaAgS_2O_3.$$

Iodine is converted into soluble iodide and the brown colour of the reagent disappears; tetrathionate is produced simultaneously—

$$2\,Na_2S_2O_3+I_2=2\,NaI+Na_2S_4O_6.$$

Ferric chloride, in small quantity, produces a purple coloration, which gradually disappears on standing.

SULPHIDES AND HYDROSULPHIDES.

Hydrosulphuric acid, H_2S; dibasic.

Examples of soluble sulphides and hydrosulphides:— Sulphides and hydrosulphides of potassium, sodium, and ammonium; hydrosulphides of barium, strontium, calcium, and magnesium.

REACTIONS OF SOLUTIONS OF SULPHIDES AND HYDROSULPHIDES.

The solutions are alkaline to **test paper.**

Hydrochloric acid produces hydrogen sulphide and a chloride—

$$K_2S+2\,HCl=2\,KCl+H_2S.$$
$$KHS+HCl=KCl+H_2S.$$

Some of the hydrogen sulphide escapes as gas, especially if the liquid is warmed; it may be recognised by its odour, by the dark stain it produces on **lead acetate** test paper, and by its reducing action on **ferric ferricyanide** test paper (see p. 238).

Solutions of sulphides or hydrosulphides which have undergone oxidation by exposure to the air and have become yellow from the formation of disulphide, give a precipitate of sulphur (besides yielding hydrogen sulphide) on the addition of **hydrochloric acid**—

$$(NH_4)_2S_2+2\,HCl=2\,NH_4Cl+H_2S+S.$$

Silver nitrate produces a black precipitate of silver sulphide, insoluble in nitric acid and in ammonia—

$$(NH_4)_2S+2\,AgNO_3=2\,NH_4NO_3+Ag_2S.$$

Sodium nitroprusside [$Na_2Fe(NO)(CN)_5$] produces a violet coloration. This coloration is only produced in an alkaline solution.

CYANIDES.

Hydrocyanic acid, HCN; monobasic.

Examples of soluble cyanides:—Cyanides of potassium, sodium, and ammonium; mercuric cyanide.

As has already been stated, mercuric cyanide, not being ionised in solution, does not give all the ordinary reactions of mercuric salts or of cyanides. Its special reactions are given at page 103. Unless the contrary is specially stated, the reactions described below do not apply to solution of mercuric cyanide.

Solutions of alkali cyanides, unless specially prepared and preserved out of contact with air, always contain some carbonate, since cyanides are decomposed even by such a weak acid as carbonic acid—

$$2\,KCN+H_2CO_3=K_2CO_3+2\,HCN.$$

REACTIONS OF SOLUTIONS OF CYANIDES.

The solutions are alkaline to **test paper**.

Hydrochloric acid produces hydrocyanic acid and a chloride—

$$KCN+HCl=KCl+HCN.$$

When mercuric cyanide is warmed with hydrochloric acid an action similar to the above takes place, but very much more slowly. The hydrocyanic acid may be recognised by its odour. Hydrocyanic acid and its soluble salts are extremely poisonous. Great care must be exercised in working with them.

With pure solutions, **barium nitrate** produces no precipitate, but with ordinary solutions containing carbonate (see above) a white precipitate of barium carbonate is produced.

Silver nitrate, when added in small quantity, produces locally a white precipitate which dissolves on shaking up the liquid. The precipitate consists of silver cyanide, which unites with the unchanged soluble cyanide producing a soluble complex salt (see p. 39) in which silver forms part of the acidic radical—

$$KCN+AgNO_3=KNO_3+AgCN.$$
$$AgCN+KCN=KAg(CN)_2.$$

On adding sufficient silver nitrate a permanent precipitate of silver cyanide is produced, insoluble in nitric acid, soluble in ammonia—

$$KAg(CN)_2+AgNO_3=KNO_3+2\,AgCN.$$

Most silver salts insoluble in water dissolve in solutions of cyanides, with formation of the complex salts referred to above—

$$AgCl+2\,KCN=KCl+KAg(CN)_2.$$

Ferrous sulphate and **sodium hydroxide** produce a soluble ferrocyanide, the action taking place more rapidly on warming. The ferrocyanide is formed by the interaction of the precipitated ferrous hydroxide with the dissolved cyanide—

$$6\,KCN+Fe(OH)_2=K_4Fe(CN)_6+2\,KOH.$$

Simultaneously, part of the ferrous hydroxide which has not been attacked by the cyanide becomes oxidised to ferric hydroxide. On acidifying the mixture with **hydrochloric acid**, Prussian blue is produced, this being formed by the interaction of the ferrocyanide with the ferric chloride which

results from the action of the hydrochloric acid on the ferric hydroxide. For the sake of brevity this reaction is often referred to as the " Prussian blue test " for cyanides.

NOTE.—When solutions of cyanides are boiled, especially with sodium hydroxide or potassium hydroxide, formate and ammonia are very slowly produced—

$$KCN + 2\,H_2O = KCHO_2 + NH_3.$$

This reaction is unimportant as a test for cyanide, but must not be overlooked in testing for ammonium salts.

The presence of free hydrocyanic acid may be detected by the production from it of ammonium thiocyanate, and the recognition of the thiocyanate by means of ferric chloride solution. To carry out the reaction, suspend for some time in the loosely covered vessel in which the hydrocyanic acid is being liberated, a strip of filter paper moistened with a drop of **yellow ammonium sulphide**. Withdraw the strip, acidify with **hydrochloric acid** to destroy the excess of ammonium sulphide, and add a drop of **ferric chloride**. The presence of thiocyanate is indicated by the formation of red ferric thiocyanate (see p. 122).

$$HCN + (NH_4)_2S_2 = NH_4HS + NH_4CNS.$$

HYPOCHLORITES AND "BLEACHING SALTS."

Hypochlorous acid, HClO ; monobasic.

The substances known as " bleaching salts," which are obtained by the action of chlorine on the hydroxides of some metals (such as potassium, sodium, and calcium), consist largely of chloride and hypochlorite, or at least yield solutions containing these substances. The most of the reactions to be considered here in the case of such solutions are due to the hypochlorite alone.

REACTIONS OF BLEACHING SOLUTIONS.

The solutions are alkaline to **test papers**, but the colour becomes bleached almost instantaneously.

Bleaching solutions which are exposed to air smell of hypochlorous acid, because the carbonic acid, formed by the absorption of carbon dioxide from the air, decomposes the hypochlorite, forming carbonate and hypochlorous acid—

$$2\,KClO + H_2CO_3 = K_2CO_3 + 2\,HClO.$$

Hydrochloric acid produces hypochlorous acid and a chloride. The hypochlorous acid interacts with more hydrochloric acid, producing chlorine and water—

$$HCl+HClO=H_2O+Cl_2.$$

Some of the chlorine produced by this reaction escapes as gas, especially on warming, and can be recognised by its odour and by its action on **potassium iodide** test paper (see pp. 154, 238).

Chlorine may also be produced by means of any strong acid, for example, **dilute sulphuric acid**, owing to the liberation both of hypochlorous acid from the hypochlorite and of hydrochloric acid from the chloride—

$$2\,KClO+H_2SO_4=K_2SO_4+2\,HClO.$$
$$2\,KCl+H_2SO_4=K_2SO_4+2\,HCl.$$

Cobaltous nitrate produces a black precipitate of cobaltic hydroxide (see p. 123).

Hydrogen sulphide, with or without the previous addition of hydrochloric acid, produces a precipitate of sulphur—

$$Cl_2+H_2S=2\,HCl+S.$$
$$KClO+H_2S=KCl+H_2O+S.$$

Barium nitrate produces no precipitate.

Silver nitrate produces a white precipitate of silver chloride. Even in solutions of hypochlorites which do not contain any chloride, silver nitrate produces a precipitate of silver chloride—

$$3\,KClO+3\,AgNO_3=3\,KNO_3+2\,AgCl+AgClO_3.$$

CHLORATES.

Chloric acid, $HClO_3$; monobasic.

Some chlorates are decomposed by water with formation of insoluble basic salts; these can be dissolved in water containing chloric acid. The other chlorates, such as those of potassium, sodium, calcium, and barium, are soluble in water.

REACTIONS OF SOLUTIONS OF CHLORATES.

Hydrochloric acid produces, on warming, a mixture of chlorine peroxide and chlorine, which is sometimes called "euchlorine." It may be recognised by its characteristic odour and by its action on **potassium iodide** test paper.

Hydrogen sulphide, added to a solution which has been warmed with **hydrochloric acid**, produces a slight precipitate of sulphur.

Barium nitrate produces no precipitate.

Silver nitrate produces no precipitate.

NOTE.—The following reaction should only be tried with small quantities of solutions, or with very minute quantities of solids, as the production of chlorine peroxide, even in comparatively small quantity, may give rise to violent and dangerous explosions :—

Concentrated sulphuric acid produces a yellow coloration in the liquid, due to dissolved chlorine peroxide. Some of the latter escapes and can be recognised by its characteristic odour—

$$3\,KClO_3+2\,H_2SO_4=2\,KHSO_4+KClO_4+2\,ClO_2+H_2O.$$

When **sulphurous acid** in small quantity is added to a solution of a chlorate to which **silver nitrate** and **dilute nitric acid** have been added, a precipitate (of silver chloride) slowly forms, and does not dissolve on the addition of more nitric acid.

When solid chlorates are sufficiently strongly heated, they decompose with formation of chlorides and evolution of oxygen (see p. 95). The residue (if any) when dissolved in water gives with **silver nitrate** a white precipitate of silver chloride.

NITRITES.

Nitrous acid, HNO_2 ; monobasic.

Nitrites are, as a rule, soluble in water ; silver nitrite is sparingly soluble in cold water.

REACTIONS OF SOLUTIONS OF NITRITES.

Hydrochloric acid produces chloride and nitrous acid—

$$KNO_2+HCl=KCl+HNO_2.$$

Unless the solution is very dilute, much of the nitrous acid decomposes, especially on warming, into nitric acid and nitric oxide—

$$3\,HNO_2=HNO_3+H_2O+2\,NO.$$

The nitric oxide which escapes, meeting atmospheric oxygen, combines with it to form nitrogen peroxide. This can be

recognised by its colour and odour, by its action on **potassium iodide** test paper, liberating iodine, and by its reducing action on **ferric ferricyanide.**

In moderately concentrated solutions, **silver nitrate** produces a white precipitate of silver nitrite, soluble in nitric acid and in ammonia—

$$KNO_2+AgNO_3=KNO_3+AgNO_2.$$

With dilute solutions no precipitate is produced.

Barium nitrate produces no precipitate, unless, as is sometimes the case, the nitrite contains carbonate as impurity.

Ferrous sulphate produces, in the cold, a brown solution; when this is heated a brownish precipitate of basic ferric sulphate is formed, and nitric oxide escapes—

$$2\,KNO_2+2\,FeSO_4=K_2SO_4+Fe_2O_2SO_4+2\,NO.$$

Potassium iodide and **acetic acid** produce a yellow or brownish coloration, due to the liberation of iodine by the interaction of nitrous acid and hydriodic acid—

$$2\,KNO_2+2\,KI+4\,H\overline{A}=4\,K\overline{A}+2\,H_2O+2\,NO+I_2.$$

Hydrochloric acid and **hydrogen sulphide** produce a yellow precipitate of sulphur—

$$2\,HNO_2+H_2S=2\,H_2O+2\,NO+S.$$

ACETATES.

Acetic acid, $HC_2H_3O_2$ or $H\overline{A}$; monobasic.

All the acetates are soluble in water except some basic acetates; the latter dissolve in dilute acetic acid.

REACTIONS OF SOLUTIONS OF ACETATES.

Hydrochloric acid or **dilute sulphuric acid** liberates acetic acid, part of which is evolved on warming the liquid, and may be recognised by its odour—

$$K\overline{A}+HCl=KCl+H\overline{A}.$$

A few drops of **alcohol** and then **concentrated sulphuric acid** produce acetic ester (ethyl acetate), part of which is

evolved on cautiously warming the liquid, and may be recognised by its odour—

$$H\overline{A}+C_2H_5OH=H_2O+C_2H_5\overline{A}.$$

Ferric chloride, which should be added only in small quantity, produces a red coloration, due to the formation of ferric acetate. The coloration disappears on the addition of hydrochloric acid, the ferric acetate being decomposed. On heating the red solution, a brown precipitate of basic ferric acetate is formed—

$$3\,Na\overline{A}+FeCl_3=Fe\overline{A}_3+3\,NaCl.$$
$$Fe\overline{A}_3+2\,H_2O=Fe(OH)_2\overline{A}+2\,H\overline{A}.$$

Barium nitrate produces no precipitate.
Silver nitrate produces no precipitate.

FORMATES.

Formic acid, $HCHO_2$ or $H\overline{F}$; monobasic.

All the formates are soluble in water except some basic formates.

REACTIONS OF SOLUTIONS OF FORMATES.

Dilute sulphuric acid liberates formic acid which is partially evolved when the liquid is heated and passes off on boiling, along with the water vapour to which it contributes a distinct pungency.

Silver nitrate does not yield any precipitate in dilute solutions in the cold, but, on warming, a black precipitate of finely divided metallic silver is obtained, due to the reducing action of the formate.

Mercuric chloride produces, on warming, a white precipitate of mercurous chloride.

A few drops of **alcohol** and then **concentrated sulphuric acid** produce formic ester (ethyl formate), which has an odour resembling that of ethyl acetate. (See Acetates.)

Ferric chloride, added in small quantity, produces a red coloration, due to the formation of ferric formate. On boiling the mixture a brown precipitate of basic ferric formate is obtained. The red colour of ferric formate disappears on the addition of hydrochloric acid.

Barium nitrate produces no precipitate.

When solid formates, or formic acid, are gently heated with **concentrated sulphuric acid** they are decomposed with the liberation of carbon monoxide—

$$NaCHO_2+H_2SO_4=NaHSO_4+H_2O+CO.$$

SULPHATES.

Sulphuric acid, H_2SO_4; dibasic.

Most of the sulphates are soluble in water, the principal exceptions being lead sulphate, mercurous sulphate, barium sulphate, and strontium sulphate. A few sulphates are decomposed by water with formation of insoluble basic salts; the latter may be dissolved in water containing sulphuric acid. Silver sulphate and calcium sulphate are sparingly soluble.

REACTIONS OF SOLUTIONS OF SULPHATES.

Barium nitrate produces a white precipitate of barium sulphate, insoluble in dilute acids—

$$K_2SO_4+Ba(NO_3)_2=2\ KNO_3+BaSO_4.$$

With concentrated solutions **silver nitrate** produces a white precipitate of silver sulphate—

$$K_2SO_4+2\ AgNO_3=2\ KNO_3+Ag_2SO_4.$$

Lead acetate produces a white precipitate of lead sulphate—

$$K_2SO_4+Pb\overline{A}_2=2\ K\overline{A}+PbSO_4.$$

Solid sulphates (and the salts of sulphur acids generally), when fused with **carbon** and **sodium carbonate,** yield sulphide, recognisable by the dark stain produced when the mass is placed upon a silver coin and moistened with water (" Hepar " test).

PHOSPHATES.

Orthophosphoric acid, H_3PO_4; tribasic.

Of the several acids derived from phosphoric anhydride, by far the most important is orthophosphoric acid, H_3PO_4; and

the reactions of its salts, the orthophosphates (usually called simply the phosphates), will alone be considered in this place.

Examples of soluble phosphates :—Phosphates of potassium, sodium, and ammonium. (Some acid phosphates of metals other than the alkali metals also dissolve in water.)

REACTIONS OF SOLUTIONS OF PHOSPHATES.

Silver nitrate produces a yellow precipitate of silver phosphate, soluble in nitric acid, and in ammonia—

$$Na_2HPO_4 + 3\,AgNO_3 = 2\,NaNO_3 + HNO_3 + Ag_3PO_4.$$

With solutions of the common phosphates, such as sodium mono-hydrogen phosphate, Na_2HPO_4, or potassium dihydrogen phosphate, KH_2PO_4, **barium nitrate** produces a white precipitate of a barium hydrogen phosphate.

Ammonia added in quantity sufficient for the production of a normal salt, and then **barium nitrate**, produce a white precipitate of normal barium phosphate, soluble in nitric acid—

$$2\,Na_2HPO_4 + 2\,NH_3 + 3\,Ba(NO_3)_2 = 4\,NaNO_3 + 2\,NH_4NO_3 + Ba_3(PO_4)_2.$$

Magnesia mixture (see p. 235) produces a white precipitate of ammonium magnesium phosphate—

$$Na_2HPO_4 + MgCl_2 + NH_3 = 2\,NaCl + NH_4MgPO_4.$$

Ammonium molybdate in nitric acid solution produces, on warming, a bright yellow precipitate of a complex salt.

OXALIC ACID AND OXALATES.

Oxalic acid, $H_2C_2O_4$; dibasic.

Oxalic acid is a white crystalline solid, easily soluble in water, yielding a strongly acid solution. Oxalic acid and its soluble salts are extremely poisonous.

Examples of soluble oxalates :—Oxalates of potassium, sodium, and ammonium.

REACTIONS OF OXALIC ACID.

Heat a small portion in a silica spoon. The acid fuses and gives off water of crystallisation ; acid fumes (poisonous) are then given off which contain formic acid and some undecomposed

oxalic acid, along with carbon monoxide and water vapour. There is no charring.

Heat another small portion of the acid or of a solid oxalate in a dry test tube with **concentrated sulphuric acid**. Carbon dioxide and carbon monoxide are evolved without charring. Test for the former by means of **calcium hydroxide**, and for the latter by trying to kindle the evolved gas.

To a solution of oxalic acid add a solution of **calcium hydroxide**. A white precipitate of calcium oxalate is formed at once, irrespective of whether calcium hydroxide has been added in excess or not. (Compare the behaviour of tartaric and citric acids.) Calcium oxalate is insoluble in acetic acid.

Heat a mixture of equal volumes of a saturated solution of **oxalic acid** and of dilute **sulphuric acid** to about 60° C. Divide into two portions :—

(*a*) To one portion add solution of **potassium permanganate** (see p. 205).

(*b*) To the other portion add **manganese dioxide**.

Note the effervescence in each case, and test the evolved gas for carbon dioxide by means of **calcium hydroxide.**

REACTIONS OF SOLUTIONS OF OXALATES.

Barium nitrate produces a white precipitate of barium oxalate, soluble in nitric acid—

$$K_2C_2O_4+Ba(NO_3)_2=2\ KNO_3+BaC_2O_4.$$

Silver nitrate produces a white precipitate of silver oxalate, soluble in a considerable quantity of nitric acid, and in ammonia—

$$K_2C_2O_4+2\ AgNO_3=2\ KNO_3+Ag_2C_2O_4.$$

Calcium chloride produces a white precipitate of calcium oxalate, soluble in hydrochloric acid but insoluble in acetic acid—

$$K_2C_2O_4+CaCl_2=2\ KCl+CaC_2O_4.$$

TARTARIC ACID AND TARTRATES.

Tartaric acid, $H_2C_4H_4O_6$, or $H_2\overline{T}$; dibasic.

Tartaric acid is a white crystalline solid, easily soluble in water, yielding an acid solution.

Examples of soluble tartrates:—Tartrates of potassium, sodium, and ammonium; rochelle salt (sodium potassium tartrate). Potassium hydrogen tartrate and ammonium hydrogen tartrate (the former in particular) are sparingly soluble in water.

REACTIONS OF TARTARIC ACID.

Heat a small portion in a silica spoon.* The acid fuses, darkens, and chars, giving off volatile products with "burnt sugar" odour. Solid tartrates, when heated alone, also char and give off similar fumes.

Heat another small portion of tartaric acid or of a solid tartrate in a dry test tube with **concentrated sulphuric acid**. The mixture rapidly darkens (more rapidly than is the case with a citrate) with evolution of carbon monoxide, carbon dioxide, and sulphur dioxide.

When a very small quantity of a solid tartrate is mixed with twice its bulk of **resorcinol** and about 2 c.c. of **concentrated sulphuric acid**, and the mixture is very gently heated, a bright red coloration is gradually produced.

To a small quantity of a solution of tartaric acid add a solution of **calcium hydroxide** until the acid is neutralised. As soon as this stage has been reached, a white precipitate of calcium tartrate is formed in the cold. (Compare the behaviour of citric and oxalic acids.) Calcium tartrate is soluble in acetic acid.

To a solution of tartaric acid (or of a tartrate) add **sodium hydroxide** till the mixture is strongly alkaline, then add a few drops of a solution of **potassium permanganate** and boil. The purple colour rapidly changes to green, and this is soon succeeded by the formation of a brown solution or a brown precipitate. (Distinction from citric acid and citrates.)

REACTIONS OF SOLUTIONS OF TARTRATES.

(A solution of rochelle salt is a convenient one to employ.)

Silver nitrate produces in neutral solutions a white precipitate of silver tartrate, easily soluble in dilute nitric acid and in ammonia. When this precipitate (best after separation by filtration from the liquid in which it was precipitated and

* A fragment of a broken porcelain basin may be used instead of a silica spoon.

thorough washing with water on the filter paper) is dissolved in the smallest possible quantity of very dilute ammonia and the solution is heated by immersion of the test tube containing it in hot water, a shining mirror of metallic silver is deposited in the tube. This is a delicate and characteristic test.

Barium nitrate does not produce any precipitate.

Calcium chloride produces, in moderately concentrated solutions, a white precipitate of calcium tartrate, which may be flocculent at first but soon assumes a crystalline character. The formation of the precipitate may be hastened by rubbing with a glass rod the part of the test tube which is wet with the mixed solutions. The precipitate is soluble in dilute acids (including acetic acid, in which the crystalline precipitate dissolves slowly on boiling).

Potassium chloride and **acetic acid** give, with solutions of normal tartrates, a white crystalline precipitate of potassium hydrogen tartrate. Solutions of acid tartrates give this precipitate with potassium chloride alone. (Compare the reaction of potassium salts with sodium hydrogen tartrate, page 132.)

$$Na_2\overline{T}+KCl+H\overline{A}=KH\overline{T}+NaCl+Na\overline{A}.$$

CITRIC ACID AND CITRATES.

Citric acid, $H_3C_6H_5O_7$, or $H_3\overline{Ci}$; tribasic.

Citric acid is a white crystalline solid, easily soluble in water, yielding an acid solution.

Examples of soluble citrates :—Citrates of potassium, sodium, and ammonium.

REACTIONS OF CITRIC ACID.

Heat a small portion in a silica spoon. The acid fuses, darkens, and eventually chars (but less rapidly than tartaric acid) giving off volatile products with " burnt sugar " odour. Solid citrates also char upon heating and give off similar fumes.

Heat another small portion of the acid or of a solid citrate in a dry test tube with **concentrated sulphuric acid.** The mixture darkens (less rapidly than in the case of tartaric acid) with evolution of carbon monoxide, carbon dioxide, and sulphur dioxide.

To a small quantity of a solution of citric acid add a solution

of **calcium hydroxide** until the liquid, after shaking, has an alkaline reaction. No precipitate is produced in the cold, but a white precipitate of calcium citrate is formed on boiling, which redissolves on cooling. (Compare the behaviour of tartaric and oxalic acids.) Calcium citrate is soluble in acetic acid.

To a solution of citric acid (or of a citrate) add **sodium hydroxide** till the mixture is strongly alkaline; then add a few drops of solution of **potassium permanganate** and boil. The purple colour gradually changes to green, but no further change takes place unless the boiling be long continued. (Distinction from tartaric acid and tartrates.)

REACTIONS OF SOLUTIONS OF CITRATES.

Silver nitrate produces in neutral solutions a white precipitate of silver citrate, easily soluble in dilute nitric acid and in ammonia. When this precipitate (after filtration and washing) is dissolved in the smallest possible quantity of very dilute ammonia, and the solution is digested for a considerable time at a moderate temperature (60° to 70° C.), no mirror of metallic silver is deposited. When the solution is boiled, however, silver is slowly precipitated in the form of a black powder. (Compare silver tartrate, p. 149.)

Barium nitrate produces in neutral solutions a white precipitate, which dissolves, however, when shaken up with excess of the citrate solution. When a sufficient quantity of barium nitrate has been added, a permanent precipitate of barium citrate is obtained. This precipitate dissolves on the addition of a large excess of barium nitrate.

Calcium chloride does not produce any precipitate in neutral solutions in the cold, even on rubbing the tube with a glass rod (compare tartrates). When, however, calcium chloride is added in excess to a neutral solution of a citrate and the mixture is boiled, a white precipitate of calcium citrate is usually formed slowly. (Calcium citrate is less soluble in hot water than in cold.)

Calcium hydroxide does not produce any precipitate in a neutral solution in the cold, but when such a solution is mixed with excess of calcium hydroxide and the mixture is boiled, a precipitate of calcium citrate is formed, which redissolves completely, or nearly so, on standing till cold.

When 5 c.c. of a solution of a citrate is mixed with 1 c.c.

of a solution of **mercuric sulphate** in **sulphuric acid** * and the mixture is boiled, and a 2 per cent. solution of **potassium permanganate** is then carefully added, drop by drop, to the nearly boiling liquid, the permanganate is at once decolorised and carbon dioxide is evolved, with the production, at first, of a clear solution; then, somewhat suddenly, a white precipitate separates, which is produced by the interaction of the mercuric sulphate with the acetone-dicarboxylic acid resulting from the oxidation of the citric acid radical.

BORATES.

Although only one boric acid, H_3BO_3, is known, there are many salts corresponding to other (hypothetical) acids derived from boric anhydride. The only important soluble borate is borax, $Na_2B_4O_7$, $10\,H_2O$, but there are also soluble potassium and ammonium borates. All of these give the reactions described below, but the composition of the precipitates is variable.

REACTIONS OF SOLUTIONS OF BORATES.

The solutions are alkaline to **test paper**.

Unless the solution is very dilute, **silver nitrate** produces a white precipitate of silver borate, soluble in nitric acid and in ammonia. When silver borate is heated with water it is decomposed with formation of brown silver oxide, and of boric acid, which dissolves.

Except in dilute solutions, **barium nitrate** produces a white precipitate of barium borate, soluble in nitric acid.

Calcium chloride produces a white precipitate of calcium borate, soluble in nitric acid and in acetic acid.

Turmeric paper, when dipped into a moderately concentrated solution of a borate to which **hydrochloric acid** has been added, assumes a reddish colour. In the case of a dilute solution the colour is not produced at once, but appears if the paper is dried.† On the addition of **sodium hydroxide** the colour is changed to dark green.

If a solid borate is moistened with **concentrated sulphuric**

* A suitable solution can be prepared by adding 20 c.c. of concentrated sulphuric acid to 100 c.c. of water, and dissolving 5 grams of mercuric oxide in the hot liquid resulting.

† The drying can be easily effected by wrapping the paper round the outside of test tube containing hot water.

acid and held on a platinum wire in the outer margin of a Bunsen flame, a green colour is imparted to the latter, due to the easily volatile boric acid liberated by the sulphuric acid.

CHLORIDES.

Hydrochloric acid, HCl; monobasic.

Most chlorides are soluble in water; the important exceptions are the following:—Silver chloride, mercurous chloride, cuprous chloride. Some chlorides are decomposed by water with formation of insoluble basic salts. The latter dissolve in water containing hydrochloric acid. Lead chloride is sparingly soluble in cold water (see p. 83).

REACTIONS OF SOLUTIONS OF CHLORIDES.

Silver nitrate produces a white curdy precipitate of silver chloride, insoluble in nitric acid, but readily soluble in ammonia—

$$KCl + AgNO_3 = KNO_3 + AgCl.$$

Barium nitrate produces no precipitate.

Manganese dioxide and **concentrated sulphuric acid** liberate chlorine, which can be recognised by its odour and colour, and by its action on **potassium iodide** test paper (see p. 238).

$$2\,KCl + MnO_2 + 2\,H_2SO_4 = K_2SO_4 + MnSO_4 + 2\,H_2O + Cl_2.$$

NOTE.—The above reaction does not apply in the case of mercuric chloride; mercuric chloride is not attacked by concentrated sulphuric acid.

BROMIDES.

Hydrobromic acid, HBr; monobasic.

Most bromides are soluble in water. The insoluble or sparingly soluble bromides correspond generally to the chlorides mentioned above.

REACTIONS OF SOLUTIONS OF BROMIDES.

Silver nitrate produces a very pale yellow curdy precipitate of silver bromide, insoluble in nitric acid, but sparingly soluble in ammonia—

$$KBr + AgNO_3 = AgBr + KNO_3.$$

Barium nitrate produces no precipitate.

Chlorine, which may be employed as gas or in solution, liberates bromine, which can be recognised by its odour and colour—

$$2\,KBr+Cl_2=2\,KCl+Br_2.$$

Manganese dioxide and **concentrated sulphuric acid** liberate bromine, which can be recognised by its odour and colour, and by its action on **potassium iodide** test paper—

$$2\,KBr+MnO_2+2\,H_2SO_4=K_2SO_4+MnSO_4+2\,H_2O+Br_2.$$

IODIDES.

Hydriodic acid, HI ; monobasic.

Most iodides are soluble in water ; the important exceptions are :—Silver iodide, mercurous iodide, mercuric iodide, bismuth iodide. Lead iodide is very slightly soluble in cold water, but moderately soluble in hot water.

REACTIONS OF SOLUTIONS OF IODIDES.

Silver nitrate produces a yellow precipitate of silver iodide, insoluble in dilute nitric acid—

$$KI+AgNO_3=KNO_3+AgI.$$

The silver iodide at first formed frequently has a colloidal character, but is coagulated on the addition of nitric acid. Ammonia unites with silver iodide, forming an insoluble compound, very slightly different in appearance from the original precipitate.

Barium nitrate produces no precipitate.

Chlorine, which may be employed as gas or in solution, liberates iodine, forming either a brown solution or a black precipitate—

$$Cl_2+2\,KI=2\,KCl+I_2.$$

On heating the mixture containing free iodine, part of the latter is driven off as vapour, which can be recognised by its characteristic violet colour. If excess of chlorine is added to the mixture, the iodine is oxidised to iodic acid, and a nearly colourless solution is produced—

$$5\,Cl_2+I_2+6\,H_2O=2\,HIO_3+10\,HCl.$$

Free iodine can also be recognised by its action on starch, with which it unites, forming an intensely blue coloured compound.

Manganese dioxide and **concentrated sulphuric acid** liberate iodine recognisable as above—

$$2\,KI+MnO_2+2\,H_2SO_4=K_2SO_4+MnSO_4+2\,H_2O+I_2.$$

Concentrated sulphuric acid liberates iodine with simultaneous evolution of sulphur dioxide—

$$2\,H_2SO_4+2\,KI=K_2SO_4+2\,H_2O+SO_2+I_2.$$

Lead acetate produces a yellow precipitate of lead iodide (see p. 104).

Mercuric chloride produces a red precipitate of mercuric iodide, as described under the reactions of mercuric salts (see p. 102).

NITRATES.

Nitric acid, HNO_3; monobasic.

Some nitrates, such as bismuth and mercuric nitrates, are decomposed by water, with formation of insoluble basic salts; these can be dissolved in water containing nitric acid. The other nitrates are soluble in water.

REACTIONS OF SOLUTIONS OF NITRATES.

When a solution of a nitrate is mixed with excess of **ferrous sulphate**, and **concentrated sulphuric acid** is carefully added to the mixture so as to form a separate layer of liquid at the bottom of the test tube, a brown coloration is produced slightly above the interface, due to a compound formed by the action of nitric oxide on ferrous sulphate. At the interface the nitrate is decomposed by sulphuric acid, forming sulphate and nitric acid—

$$KNO_3+H_2SO_4=KHSO_4+HNO_3.$$

This nitric acid is reduced to nitric oxide by the ferrous sulphate—

$$6\,FeSO_4+3\,H_2SO_4+2\,HNO_3=3\,Fe_2(SO_4)_3+2\,NO+4\,H_2O.$$

Care must be taken that a sufficient quantity of ferrous sulphate is added, so that some may remain unoxidised to dissolve the nitric oxide and form the brown compound mentioned above.

The formation of an insoluble sulphate, *e.g.* $BaSO_4$, does not interfere with this reaction.

The reactions of solutions of **Arsenites, Arsenates,** and **Chromates** have been described on pages 113, 114, and 127.

Classification of the commoner Acidic Radicals, from the point of view of the Reactions of their Salts.

A. Acidic radicals, of which the salts give off a gas or a recognisable vapour when warmed with dilute hydrochloric acid : CO_3'', SO_3'', S_2O_3'', S'', CN', ClO', ClO_3', NO_2', $C_2H_3O_2'$, CHO_2'.

B. Acidic radical, of which the barium salt is insoluble in water and in dilute acids : SO_4''.

C. Acidic radicals (not belonging to **A**), of which the silver salts are insoluble, or nearly so, in water, but soluble in nitric acid and in ammonia ; and of which the barium salts are insoluble, or nearly so, in water, but soluble in dilute acids : PO_4''', AsO_4''', C_2O_4'', $C_4H_4O_6''$, $C_6H_5O_7'''$ BO_2', AsO_3''', CrO_4''.

D. Acidic radicals, of which the silver salts are insoluble in water and in dilute nitric acid : Cl', Br', I', CN', S''.

E. Acidic radicals, of which all the normal salts are soluble in water : NO_3', ClO_3', $C_2H_3O_2'$, CHO_2'.

CHARACTERS AND REACTIONS OF CERTAIN GASES.

GAS	NH_3	CO_2	SO_2	H_2S	NO_2	ClO_2	Cl_2	Br_2
Has characteristic colour	—	—	—	—	Reddish	Pale yellow	Pale greenish-yellow	Reddish-brown
Has characteristic odour	X	—	X	X	X	X	X	X
Acts as a reducing agent	—	—	X	X	X	—	—	—
Liberates iodine from KI.	—	—	—	—	X	X	X	X
Renders $Ca(OH)_2$ solution turbid	—	X	[X] *	—	—	—	—	—
Blackens lead acetate paper	—	—	—	X	—	—	—	—
Has alkaline reaction	X	—	—	—	—	—	—	—

To test for reducing action use plain paper dipped in a mixture of ferric chloride and potassium ferricyanide solutions ; reducing agents produce a Prussian blue stain (see p. 122).

To test for liberation of iodine use either plain paper dipped in potassium iodide solution (brown stain produced), or " starch and potassium iodide paper " moistened with water (dark blue stain produced) (see p. 238).

* It is difficult to get a precipitate by the action of sulphur dioxide when the experiment is carried out in the manner described on p. 75.

SCHEME

FOR THE

SYSTEMATIC APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE DETECTION OF A SINGLE SALT IN SOLUTION.

BEFORE commencing the systematic examination, as described in what follows, ascertain by means of **test paper** whether the solution is acid, or alkaline, or neutral. Knowledge with respect to this point is often essential to the proper application of the subsequent tests.

The examination for the metallic radical does not necessarily precede that for the acidic radical, and in many cases a knowledge of what acidic radical is present facilitates the procedure. The tests should first be performed with ½ c.c. of the solution and, if a reaction takes place, about 2 c.c. may then be used.

1. To a portion of the original solution add **hydrochloric acid**; if no immediate precipitate is produced, and no recognisable gas is evolved in the cold, warm gently.

(*a*) A WHITE PRECIPITATE, which does not dissolve on adding more hydrochloric acid, may be silver chloride, mercurous chloride, or lead chloride.

To the precipitate add **ammonia** in excess:

Silver chloride dissolves; confirm * **SILVER** by means of **potassium iodide** [p. 99].

Mercurous chloride is blackened; confirm **MERCUROUS** by means of **stannous chloride** [p. 101].

Lead chloride is changed into white basic salt which remains undissolved; confirm **LEAD** by means of **potassium iodide** [p. 104].

(*b*) A WHITE or PALE YELLOW PRECIPITATE of sulphur produced immediately and accompanied by the liberation of hydrogen sulphide indicates a **POLYSULPHIDE**; confirm sulphide by means of **silver nitrate** [p. 139].

* All confirmatory tests are to be applied to fresh portions of the original solution.

If the precipitate is produced somewhat slowly in the cold, but more rapidly on warming, and sulphur dioxide is simultaneously evolved, the presence of thiosulphate is indicated. Confirm **THIOSULPHATE** by means of **silver nitrate** [p. 137]. (If thiosulphate is proved to be present, resume testing for the metallic radical at **4**, p. 163.)

(*c*) A RECOGNISABLE GAS is evolved in the cold, or on gentle warming [see p. 157]. The gases and the acidic radicals which they indicate are as follows :—

CARBON DIOXIDE indicates carbonate [see p. 165, Note] ; confirm **CARBONATE** by means of **barium nitrate** and **silver nitrate** [p. 135]. (Resume at **6**, p. 163.)

SULPHUR DIOXIDE, if evolved without simultaneous precipitation of sulphur, indicates a sulphite ; confirm **SULPHITE** by means of **silver nitrate** [p. 136]. (Resume at **4**, p. 163.)

SULPHUR DIOXIDE with simultaneous PRECIPITATION OF SULPHUR indicates thiosulphate. [See **1** (*b*) above.]

HYDROGEN SULPHIDE indicates sulphide or hydrosulphide ; confirm **SULPHIDE** or **HYDROSULPHIDE** by means of **silver nitrate** [p. 139]. [See **1** (*b*) above.] (Resume at **4**, p. 163.)

HYDROCYANIC ACID indicates cyanide ; confirm **CYANIDE** by means of **silver nitrate** and the **Prussian blue test** [p. 140]. [See also **8** (*a*) below.] (Resume at **4**, p. 163.)

NOTE that MERCURIC CYANIDE is exceptional in its reactions.

HYPOCHLOROUS ACID or CHLORINE indicates hypochlorite ; confirm **HYPOCHLORITE** by means of **cobaltous nitrate** [p. 142]. (Resume at **4**, p. 163.)

" EUCHLORINE " indicates chlorate ; confirm **CHLORATE** by means of **concentrated sulphuric acid** [p. 143]. [See also **9**.] (Resume at **2** below.)

NITROGEN PEROXIDE indicates a nitrite ; confirm **NITRITE** by means of **potassium iodide** and **acetic acid**, and of **ferrous sulphate** [p. 144]. (Resume at **3**, p. 161.)

ACETIC ACID indicates an acetate ; confirm **ACETATE** by means of **ferric chloride**, and distinguish acetate from formate [p. 145]. [See also **9**.] (Resume at **2** below.)

FORMIC ACID indicates a formate ; confirm **FORMATE** by means of mercuric chloride [p. 145].

2. If a precipitate is not produced (or if a precipitate is produced, which dissolves in excess of hydrochloric acid) and a recognisable gas is not evolved, even on warming, to the same

solution (containing **hydrochloric acid**) add **hydrogen sulphide** until the mixture, after shaking, smells of the reagent.

(*a*) A YELLOW PRECIPITATE, consisting of a sulphide, indicates the presence of a cadmium salt, an arsenious halide, or an arsenite.

To the precipitate add **hydrochloric acid**, and warm if necessary :

Cadmium sulphide dissolves ; confirm **CADMIUM** by means of **sodium hydroxide** and of **ammonia** [p. 109].

Arsenious sulphide does not dissolve in hydrochloric acid, but dissolves in **ammonia**. If the original solution is acid to **test paper**, arsenious halide is indicated ; confirm **ARSENIOUS** by observing the absence of a precipitate on the addition of **sodium hydroxide** or of **ammonia** [p. 112]. If the original solution is alkaline to **test paper**, an arsenite is indicated ; confirm **ARSENITE** by means of **silver nitrate** and of **cupric sulphate** [p. 113]. (If arsenite is proved to be present, resume testing for the metallic radical at **6**, p. 163.)

(*b*) A YELLOW PRECIPITATE is produced slowly on warming. The precipitate, consisting of sulphur and arsenious sulphide, indicates the presence of an arsenate ; confirm **ARSENATE** by means of **silver nitrate** [p. 114]. (Resume at **6**, p. 163.)

(*c*) A WHITE or PALE YELLOW PRECIPITATE, consisting of sulphur only, is produced by the oxidation of hydrogen sulphide. Such oxidation occurs in presence of salts which in virtue of their acidic radicals yield an oxidising mixture when treated with hydrochloric acid. Of these, the following should have been already detected [1 (*c*) above] if present :—sulphite, thiosulphate, hypochlorite, chlorate, nitrite ; and only chromate and ferric salt remain to be considered.

CHROMATE [p. 127]. In the case of chromate the original yellow solution becomes orange-red on the addition of hydrochloric acid, and changes to green when reduced by hydrogen sulphide : confirm **CHROMATE** by means of **silver nitrate** and of **lead acetate** [p. 127]. (Resume at **3**, p. 161.)

FERRIC SALT [p. 121]. The ferric salt is reduced to ferrous, and the yellow solution becomes practically colourless [see **3**, p. 161].

(*d*) An ORANGE PRECIPITATE, consisting of antimonious sulphide, insoluble in **ammonia**, indicates the presence of an antimonious salt or of tartar emetic.

If the original solution is strongly acid to **test paper**, anti-

monious salt is indicated, but if neutral then tartar emetic is indicated; confirm **ANTIMONIOUS** or **TARTAR EMETIC**, as the case may be, by means of **sodium hydroxide**, of **ammonia**, and of **hydrogen sulphide** alone [pp. 115, 116].

(*e*) A DARK BROWN or BLACK PRECIPITATE, consisting of a sulphide, indicates the presence of a stannous, a mercuric, a cupric, a bismuth, or a lead salt.

NOTE that, on the addition of hydrogen sulphide to solutions of mercuric or lead salts previously acidified with hydrochloric acid, the precipitates produced are not black until the reagent has been added in sufficient quantity. In the case of mercuric salts the precipitate is at first white, or nearly so, and passes through yellow, orange, and brown, to black, as more and more hydrogen sulphide is added [p. 102]. In the case of lead salts the precipitate is often reddish-brown at first, and becomes black on further addition of the reagent [p. 104].

To the original solution add a small quantity of **potassium iodide**:

NO PRECIPITATE or COLORATION indicates mercuric cyanide or stannous salt. To the same solution (containing **potassium iodide**) add **hydrochloric acid**:

A BRIGHT RED PRECIPITATE, soluble in excess of potassium iodide, indicates **MERCURIC CYANIDE** [p. 103].

NO PRECIPITATE indicates stannous; confirm **STANNOUS** by means of **mercuric chloride** [p. 108].

A YELLOW PRECIPITATE, soluble in boiling water, indicates lead; confirm **LEAD** by means of **potassium chromate** [p. 105].

A YELLOW PRECIPITATE RAPIDLY CHANGING TO PINK, and soluble in excess of potassium iodide, indicates mercuric; confirm **MERCURIC** by means of **stannous chloride** [p. 103].

A YELLOW SOLUTION, or

A BROWN PRECIPITATE, soluble in considerable excess of potassium iodide to form a yellow solution, indicates **BISMUTH** [p. 110].

A WHITE PRECIPITATE IN A BROWN SOLUTION, appearing somewhat slowly in dilute solutions (the original solution being blue) indicates cupric; confirm **CUPRIC** by means of **potassium ferrocyanide** [p. 106].

3. If no precipitate is produced by the addition of **hydrochloric acid** and **hydrogen sulphide** to the original solution, even on warming, add **ammonia** to the mixed solution until, after shaking, it smells of ammonia. If, however, precipitation

of sulphur [**2** (*c*)] has taken place, then to a fresh portion of the original solution add **ammonium chloride, ammonia** until the mixture, after shaking, smells of it, and **ammonium hydrosulphide**.

(*a*) A WHITE PRECIPITATE, consisting of sulphide or of hydroxide, indicates the presence of a zinc or an aluminium salt.

To the original solution add **hydrochloric acid** and **potassium ferrocyanide** :

Zinc solution gives a white gelatinous precipitate ; confirm **ZINC** by addition of a *small* quantity of **hydrogen sulphide** to the solution obtained by adding excess of **sodium hydroxide** to the original solution [p. 118].

Aluminium solution gives no precipitate ; confirm **ALUMINIUM** by addition of a small quantity of **hydrogen sulphide** to the solution obtained by adding excess of **sodium hydroxide** to the original solution [p. 125].

NOTE.—A solution of a thiosulphate to which hydrochloric acid and hydrogen sulphide have been added, without warming, generally gives a white precipitate of sulphur on adding ammonia, and may therefore be mistaken for a solution of an aluminium salt, as it gives no precipitate with potassium ferrocyanide. This difficulty is entirely avoided if the instructions previously given are properly carried out (see **1**, p. 158).

(*b*) A BUFF PRECIPITATE, consisting of the sulphide, indicates the presence of a manganous salt ; confirm **MANGANOUS** by means of **bleaching solution** [p. 119].

(*c*) A BLACK PRECIPITATE, consisting of a sulphide, indicates the presence of a ferrous, a ferric, a cobaltous, or a nickel salt.

To the precipitate add **hydrochloric acid** :

Ferrous sulphide (which is formed both from ferrous and from ferric salts, in the latter case along with sulphur) dissolves, with or without leaving a residue of sulphur ; confirm **FERROUS** or **FERRIC** by means of **potassium ferrocyanide** and of **potassium ferricyanide** [pp. 121, 122].

Cobaltous sulphide or nickel sulphide does not dissolve ; in the case of cobaltous salts the original solution is pink, and in the case of nickel salts it is bright green ; confirm **COBALTOUS** or **NICKEL** by means of **sodium hydroxide** and of **ammonia** [pp. 123, 124].

(*d*) A BLUISH-GREY or GREEN PRECIPITATE, consisting of chromic hydroxide, indicates the presence of a chromic salt ; confirm **CHROMIC** by means of **bleaching solution** [p. 126].

4. If no precipitate is produced in **3**, to a fresh portion of the original solution add **ammonium chloride, ammonia** until the mixture, after shaking, smells of it, and **ammonium carbonate.**

A WHITE PRECIPITATE, consisting of carbonate, indicates the presence of a barium, a strontium, or a calcium salt.

To the original solution add **calcium sulphate** :

Barium solution gives an immediate white precipitate; confirm **BARIUM** by means of **potassium chromate** [p. 128], and the **flame test** [p. 170].

Strontium solution gives a white precipitate on standing some time or on boiling; confirm **STRONTIUM** by means of **potassium chromate** [p. 129], and the **flame test** [p. 170].

Calcium solution does not give any precipitate, even on boiling; confirm **CALCIUM** by means of **potassium chromate** [p. 130], and the **flame test** [p. 170].

5. If no precipitate is produced in **4**, to the same solution (containing **ammonium chloride, ammonia**, and **ammonium carbonate**) add **ammonium phosphate.**

A WHITE PRECIPITATE, consisting of ammonium magnesium phosphate, indicates the presence of a magnesium salt; confirm **MAGNESIUM** by means of **iodine** and **sodium hydroxide**, adding the latter drop by drop [p. 131].

6. If no precipitate is produced in **5**, the original solution may contain a salt of ammonium, potassium, or sodium.

(*a*) Add sodium hydroxide to a fresh portion of the original solution and heat the mixture [p. 131, but see Note on p. 141]; confirm **AMMONIUM**, by means of *Nessler's reagent* added to a single drop of the solution highly diluted with water. (See p. 131.)

(*b*) If ammonium is proved to be absent, to another portion of the original solution add sodium hydrogen tartrate till decidedly acid and shake up the mixture [p. 132]; a white crystalline precipitate indicates potassium; confirm **POTASSIUM** by means of **ammonium perchlorate** [p. 132], and by the **flame test**, using the cobalt-blue glass [p. 170].

(*c*) If ammonium and potassium are both proved to be absent, evaporate 2 or 3 c.c. of the original solution to dryness and test the residue for **SODIUM** by means of the **flame test** [p. 170].

A SCHEME for the examination for those **acidic radicals**, of which no indications are observable (or which, like carbonates in dilute solutions, may not be detected easily) in the course of the operations hitherto described, is given below.

7. To a portion of the original solution add **barium nitrate**. A white precipitate, which is insoluble in nitric acid, indicates the presence of a sulphate; confirm **SULPHATE** by means of **lead acetate** [p. 146].

8. To a portion of the original solution add **silver nitrate**.

(*a*) A WHITE or YELLOW PRECIPITATE, which is insoluble in nitric acid, indicates the presence of a cyanide (white), a chloride (white), a bromide (very pale yellow), or an iodide (pale yellow).

If the locally formed precipitate produced by the addition of a few drops of silver nitrate to the original solution dissolved on shaking the liquid, a cyanide is indicated; confirm **CYANIDE** by means of the **Prussian blue test** [p. 140].

A persistent white precipitate indicates chloride; confirm **CHLORIDE** by means of **manganese dioxide** and **concentrated sulphuric acid** [p. 153].

To the original solution add **chlorine water**:—

The liberation of bromine indicates bromide; if necessary, confirm **BROMIDE** by means of **manganese dioxide** and **concentrated sulphuric acid** [p. 154].

The liberation of iodine indicates iodide; confirm **IODIDE** by means of **mercuric chloride** [p. 155].

A negative reaction indicates cyanide or chloride. In this case test the original solution by means of **silver nitrate** in small quantity (see above).

NOTE.—Mercuric chloride is not decomposed by concentrated sulphuric acid, even on warming, and there is no evolution of chlorine when it is heated with manganese dioxide and sulphuric acid. If the metallic radical of a salt proves to be mercuric, and the solution gives a white precipitate, insoluble in nitric acid, on the addition of silver nitrate, the only two salts which can be present are chloride and bromide, since mercuric iodide is insoluble and mercuric cyanide solution gives no precipitate with silver nitrate. To distinguish between the chloride and bromide, the reaction with chlorine water is the only convenient test.

(*b*) A WHITE PRECIPITATE, which is soluble in nitric acid, indicates the presence of a borate, an oxalate [see p. 148], a tartrate, or a citrate (or a carbonate; see Note, p. 165).

To the original solution add hydrochloric acid and test the mixture for borate by means of **turmeric paper**; confirm **BORATE** by means of **calcium chloride** and **acetic acid** [p. 152]. Turmeric is not affected by oxalic, tartaric, or citric acid.

To the original solution (neutralised, if necessary, by addition of ammonia or of nitric acid) add **calcium chloride**:—

(1) A white precipitate, insoluble in acetic acid, indicates an oxalate; confirm **OXALATE** by means of **calcium hydroxide** [p. 148].

(2) A white precipitate on standing (or, more rapidly, on shaking the solution), the precipitate being soluble in acetic acid, indicates a tartrate; confirm **TARTRATE** by means of the silver mirror test [p. 149].

(3) A white precipitate on boiling indicates a citrate; confirm **CITRATE** by means of **potassium permanganate** [p. 151].

NOTE that if a carbonate is not detected by means of hydrochloric acid in the early part of the examination it falls into this section, as it gives a white precipitate with silver nitrate, soluble in nitric acid. A solution of a carbonate would not give the turmeric reaction, and the precipitate produced by calcium chloride would dissolve in acetic acid.

(*c*) A YELLOW PRECIPITATE, which is soluble in nitric acid, indicates a phosphate or an arsenite. The latter should have been already detected [see **2** (*a*)]. Confirm **PHOSPHATE** by means of **magnesia mixture** [p. 147].

(*d*) A BROWN PRECIPITATE, which is soluble in nitric acid, indicates an **ARSENATE** [see **2** (*b*)].

(*e*) A CRIMSON PRECIPITATE indicates a **CHROMATE** [see **2** (*c*)].

(*f*) A BLACK PRECIPITATE, which is insoluble in nitric acid, indicates sulphide or hydrosulphide; confirm **SULPHIDE** or **HYDROSULPHIDE** by means of **hydrochloric acid** and **lead acetate** test paper [p. 139].

9. Taking a fresh portion of the original solution for each experiment, test for

NITRATE, by means of **ferrous sulphate** and **concentrated sulphuric acid** [p. 155].

CHLORATE, by means of **concentrated sulphuric acid** [p. 143].

ACETATE and **FORMATE**, by means of **ferric chloride** [p. 145] and **mercuric chloride** [p. 145].

METALLIC RADICALS: Separation into Groups.

To the cold original solution (if HCl has not been employed in its preparation) add dilute HCl, drop by drop, as long as any precipitate is produced, and, in any case, until the mixture has an acid reaction. Filter. Wash the precipitate.

Precipitate.
AgCl
HgCl
$PbCl_2$
(Silver Group).

To the **Filtrate** add saturated H_2S water in excess, and shake well. Filter. Wash the precipitate.

Precipitate.
HgS, CuS, PbS, Bi_2S_3, CdS, SnS, SnS_2, Sb_2S_3, As_2S_3 (Copper and Arsenic Groups).

Transfer to a porcelain dish, and digest with NaOH solution, to which a few drops of yellow ammonium sulphide have been added. Dilute. Filter. Wash the residue.

Residue.
HgS
CuS
PbS
Bi_2S_3
CdS
(Copper Group).

Filtrate.
Add HCl in excess. Filter. Reject the filtrate. Wash the precipitate.
SnS_2, Sb_2S_3, As_2S_3 (Arsenic Group).
[HgS may find its way partly or completely into this precipitate.]

Expel H_2S by boiling down the **Filtrate** to a small volume. Add a few drops of concentrated HNO_3, and boil. Add NH_4Cl and slight excess of NH_4OH. Mix thoroughly, and confirm excess of NH_4OH by litmus paper [p. 70, 3.] Warm gently. Filter. Wash the precipitate.

Precipitate.
$Fe(OH)_3$
$Cr(OH)_3$
$Al(OH)_3$
(Iron Group).

To the **Filtrate** add NH_4HS in slight excess. Filter. Wash the precipitate.

Precipitate.
ZnS
MnS
NiS
CoS
(Zinc Group).

To the **Filtrate** add $(NH_4)_2CO_3$ in excess and warm gently. Filter. Wash the precipitate.

Precipitate.
$BaCO_3$
$SrCO_3$
$CaCO_3$
(Barium Group).

To the **Filtrate** add $(NH_4)_2HPO_4$ in excess and set aside for a few minutes. Filter.

Precipitate.
NH_4MgPO_4
(Magnesium).

Filtrate.
Evaporate to dryness and drive off ammonium salts by gentle ignition. Test for K and Na in the residue.

Test for NH_4 in the original substance by boiling with NaOH solution.

SCHEME FOR THE SEPARATION OF METALLIC RADICALS INTO EIGHT GROUPS.

IN the scheme given on pages 158 *et seq.*, provision is made for the detection of a single salt only. It is obvious that by suitable application of the analytical reactions of metallic radicals, schemes for the detection of not only one, but for the detection of many or all of the metallic radicals can be devised. This is the province of treatises on qualitative chemical analysis. There may, however, be given here, as introductory to such work, a scheme in which the metallic radicals so far dealt with are divided up into eight groups. The following scheme allows of the detection of any one metallic radical in each of the eight groups :—

The **Recognition of Individual Metals** of the groups separated by the methods described in the table on the preceding page.

1. **Silver Group.**—Pour boiling water over the precipitate on the filter paper; collect in a test tube the liquid which passes through, cool it, and test it for lead by means of potassium iodide [p. 104]. If no positive result is obtained for lead, pour ammonia over the precipitate. If it consists of silver chloride it will dissolve [p. 98], yielding a solution from which silver chloride will be reprecipitated on acidifying with dilute nitric acid. If it consists of mercurous chloride, it will turn black [p. 100] but will not dissolve.

2. **Copper** and **Arsenic Groups.**—The first precipitate mentioned in the second column of the table may contain a sulphide of each of these groups. After the treatment described in that column for the separation of the groups, there may be (*a*) a copper group residue or (*b*) an arsenic group precipitate (or both), to be further treated as follows :—

(*a*) **Copper Group Residue.**—Heat in a porcelain basin with dilute hydrochloric acid. If it does not dissolve, add some concentrated hydrochloric acid and continue heating. If it still does not dissolve, add a few drops of concentrated

nitric acid and heat till dissolved. Boil down the solution almost to dryness to expel the greater part of the acid, dilute with water [Note 1], and test the resulting solution for metals of the copper group [Note 2].

Note 1. Should a white precipitate appear on adding water, this is most likely to consist of bismuth oxychloride. It can be dissolved by the careful addition of hydrochloric acid.

Note 2. If lead was detected in the silver group, some lead sulphide is certain to be present in the copper group residue.

(*b*) **Arsenic Group Precipitate.**—Mix with concentrated hydrochloric acid in a test tube and heat momentarily to the boiling-point. A yellow residue consists of arsenious sulphide [Notes 3 and 4]. If the precipitate dissolves, cool the solution, dilute it with water, and add hydrogen sulphide. An orange precipitate indicates antimony [p. 115]; a pale yellow precipitate indicates tin [p. 108].

Note 3. A white or very slightly yellow residue of sulphur, sometimes met with at this stage, must not be mistaken for arsenious sulphide.

Note 4. Arsenic can be confirmed by dissolving the residue of arsenious sulphide in hydrochloric acid, with the addition of a very small quantity of nitric acid, diluting the solution with water, adding ammonia in slight excess and then magnesia mixture, when a precipitate of ammonium magnesium arsenate will appear on standing, if not at once.

3. **Iron Group.**—Dissolve the precipitate [Note 5] in dilute hydrochloric acid. Test a portion of the solution for iron by means of potassium ferrocyanide [p. 122]. If no positive result is obtained for iron, to the remainder of the solution add ammonia in slight excess and boil till the odour of ammonia is no longer recognisable. A bluish-grey or green precipitate indicates chromium [p. 126]; a white precipitate indicates aluminium [p. 125].

Note 5. The iron group precipitate frequently contains some manganese, and a small portion of the precipitate should be examined for manganese by means of the test with lead peroxide and dilute nitric acid [p. 119], or of the sodium carbonate bead test [p. 175], before proceeding to dissolve it.

4. **Zinc Group.**—If the sulphide precipitate is light-coloured, zinc or manganese may be suspected; if black, cobalt or nickel. Zinc sulphide is insoluble in acetic acid [p. 117], while manganous sulphide is soluble [p.119]. [See also Note 5.] Cobalt and

nickel sulphides are insoluble in cold dilute hydrochloric acid, but they may be decomposed and the metals obtained in solution by heating with hydrochloric acid and a little nitric acid, cobalt sulphide yielding a red or pink solution and nickel sulphide a green solution. Sodium hydroxide added in excess gives with the cobalt solution a blue precipitate [p. 123] and with the nickel solution a pale green precipitate [p. 124], both precipitates insoluble in excess. The insoluble cobalt and nickel sulphides may also be distinguished by means of the borax bead test [p. 173].

5. **Barium Group.**—Dissolve the precipitate in acetic acid. To one portion of the solution add potassium chromate. An immediate yellow precipitate indicates barium [p. 128]. If no positive result is obtained for barium, to another portion of the solution add calcium sulphate and boil. A white precipitate indicates strontium [p. 129]. No precipitate will appear if the metal present is calcium [p. 130]. Apply also the flame coloration and spectroscope tests [p. 170] for barium, strontium, and calcium.

DRY-WAY REACTIONS.

Flame Coloration Tests.

THE compounds of certain metals when introduced, on the end of a fine platinum wire (see p. 83), into the non-luminous flame of a Bunsen burner, impart special colours to the flame. A small quantity of the substance is either tested alone, or it is mixed with concentrated hydrochloric acid on a watch-glass, and some of the mixture is then taken up on the platinum wire and heated, first in the lower part of the flame where the temperature is comparatively low, and afterwards in the hottest part of the flame. Colorations of the flame may be observed as follows :—

Orange yellow *	Sodium.
Pale violet *	Potassium.
Red or yellowish-red	Calcium.
Crimson	Strontium, Lithium.
Pale green	Barium, Manganese chloride.
Bright green	Copper, Thallium, Boric acid.
Livid blue	Lead, Arsenic, Antimony.
Bright blue	Cupric chloride.

Spectra.

The identification of metals by means of the spectra they produce is a comparatively simple matter in the case of such metals as lithium, sodium, potassium, calcium, strontium, barium, and thallium—even in presence of each other. A direct vision spectroscope is handiest for use, and the substance is introduced into the flame as described under flame coloration tests. The element sodium being always present, the yellow D line is useful as a reference point in looking for the lines in the spectra of other elements.

* The yellow flame coloration due to sodium is entirely cut off when the flame is viewed through a piece of cobalt-blue glass of sufficiently intense colour, but the cobalt glass does not cut off the coloration due to potassium. A suitable blue glass may be used in testing for potassium salts in presence of sodium salts, but it is not applicable in testing for potassium salts in presence of strontium salts, lithium salts, etc.

Film Tests.

An asbestos thread, about four inches long, is first wetted with water and then suspended in the Bunsen flame, by which treatment it loses its flexibility. A small quantity of the solid substance to be tested is taken up on the stiffened asbestos thread, by moistening the end of the thread with water and dipping it into the powder, and is then held in the *reducing* (slightly luminous) tip of the Bunsen flame. To collect the films, a glazed porcelain basin, containing water to keep it cool, is held in one of the positions indicated below for the two classes of films obtainable. Care must be taken that the outside of the basin is dry.

Metallic Films.—To collect the black or grey metallic film, hold the basin close above the asbestos. Treat the film with a drop of cold 20 per cent. nitric acid, when behaviour may be observed as follows :—

Antimony, Arsenic .	. Not appreciably attacked.
Bismuth, Mercury *	. Slowly dissolved.
Cadmium, Lead, Zinc	. Instantly dissolved.

Films of arsenic and antimony may be distinguished from each other by their behaviour when treated with a drop of a solution of a hypochlorite (bleaching solution) :—

Arsenic . .	. Instantly dissolved.
Antimony . .	. Very slowly attacked.

Notes respecting Metallic Films:—

1. Care must be taken that the flame employed in testing for the production of metallic films is not sufficiently luminous to yield a soot film.
2. Soot films may sometimes be obtained when the substance under examination is an organic compound. Thus, tartar emetic may yield a film consisting of antimony mixed with soot.
3. Molybdic acid and some molybdates yield a characteristic blue film of a lower oxide of molybdenum instead of a metallic film.
4. Some ammonium salts, such as ammonium chloride, and some metallic chlorides, such as lead chloride, yield colourless films, which consist simply of the original substances.

Oxide Films.—To collect the oxide film, hold the porcelain basin just above the tip of the flame. The film, after its colour has been noted, may be further submitted to the action of reagents for the observation of characteristic changes, as tabulated on page 172.

* The film of mercury is grey and scattered.

The iodide films referred to are obtained by exposing the oxide films to the fumes of hydriodic acid (see p. 230). The object of breathing upon the iodide films so produced is to ascertain whether the iodides dissolve or not in the moisture deposited from the breath. The iodide films are treated with ammonia by exposing them to the gas given off from concentrated ammonia solution.

The white oxide films obtained from antimony and arsenic compounds may be distinguished from each other by moistening

	Oxide Film.	Iodide Film.	Iodide Film when Breathed Upon.	Iodide Film with Ammonia.
Antimony	White	Orange-red	Disappears temporarily	Disappears permanently
Arsenic .	White	Yellow	Disappears temporarily	Disappears permanently
Bismuth	Yellowish-white	Bluish-brown to pink at edges	Disappears temporarily with difficulty	Red to yellowish-brown
Lead .	Pale yellow	Yellow	Unchanged	Disappears temporarily
Cadmium	Brown	White	No visible change	No visible change
Zinc .	White	White	No visible change	No visible change

them with a drop of silver nitrate solution, and then exposing to ammonia gas :—

Antimony . Black precipitate of metallic silver.
Arsenic . . Yellow precipitate of silver arsenite.

Notes respecting Oxide Films:—

1. Mercury compounds do not yield an oxide film. When operating to obtain oxide films, a film of metallic mercury is often obtained from these compounds. Hydriodic acid has very little effect upon such a film of metallic mercury, but occasionally a slight reddish film of mercuric iodide is formed.

2. As the film of zinc oxide is white, and is therefore not easily observed when deposited on a white surface, it may with advantage be collected on the bottom of a test tube, half filled with cold water and held above the tip of the flame. A deposit of an ammonium salt must not be mistaken, however, for a zinc oxide film.

3. The production of oxide films in certain cases (such, for example, as that of zinc in presence of compounds of iron, manganese, or chromium) is only attained, if at all, by prolonged heating.

General Note respecting Metallic and Oxide Films.—Metallic sulphides, as a class, seldom yield satisfactory film reactions. Substances

known to contain sulphides may be oxidised by treatment with concentrated nitric acid prior to the application of the film tests.

Borax Bead Tests.

On the end of a fine platinum wire, which should not be looped, fuse a small quantity of borax so as to form a colourless, transparent bead not exceeding 1·5 millimetre in diameter (about the size of this mark ●). Moisten the bead, and bring it into contact with a very small quantity of the solid substance to be examined, so that the latter may adhere to it. Then, in order to note the effect produced by oxidation at a high temperature, hold bead and substance for some time in the outer (oxidising) mantle of the Bunsen flame. Withdraw the bead from the flame, allow it to cool, and observe its colour. Next, in order to note the effects of reduction, hold the oxidised bead for some time in the centre of the luminous tip of the Bunsen flame. Withdraw it again, allow it to cool, and observe its colour, etc. The following table shows the chief colour, etc., effects that may be observed :—

Metal.	Oxidising Flame.	Reducing Flame.
Manganese	Amethyst	Colourless
Copper	Blue	Brown-red, usually opaque; later, shows scales of metallic copper; finally, colourless and transparent, the copper becoming alloyed with the platinum of the wire
Iron	Hot, yellow; cold, colourless or pale yellow	Pale green
Nickel	Reddish-brown	Grey, opaque from separation of metallic nickel; finally, colourless and transparent, the nickel becoming alloyed with the platinum of the wire
Cobalt	Blue	Blue
Chromium	Green *	Green
Molybdenum	Hot, yellow; cold, almost colourless	Dark brown, or brown flakes
Tungsten	Colourless	Yellow
Uranium	Yellow	Green
Titanium	Colourless	Yellow, becoming dark blue on prolonged heating
Vanadium	Hot, yellow; cold, greenish-yellow	Hot, brown; cold, clear green

* Chromates and bichromates (themselves yellow or red) do not give a green bead in the oxidising flame unless they are first reduced to chromic salt (reducing flame).

Notes respecting Borax Beads:—

1. Fused borax interacts with the basic oxides of certain metals to form coloured metaborates, and the colours of these are imparted to the bead, the latter remaining transparent unless too much of the original oxide has been employed—

$$Na_2B_4O_7 + CuO = Cu(BO_2)_2 + 2\ NaBO_2.$$

Other compounds of these metals, and also the metals themselves, eventually produce a similar result. When a metal forms two sets of salts, differently coloured beads are often obtainable, according as the bead is held in the oxidising or in the reducing part of the flame. In some cases (copper and nickel) the metal itself may be obtained when the bead is held in the reducing flame.

2. Reduced beads may, with advantage, be allowed to cool in the hollow part of the flame immediately above the burner tube, so as to avoid re-oxidation.

Microcosmic Bead Tests.

When microcosmic salt is heated on a platinum wire in the Bunsen flame, water and ammonia are evolved and a bead of sodium metaphosphate remains—

$$NaNH_4HPO_4,\ 4\ H_2O = 5\ H_2O + NH_3 + NaPO_3.$$

Fused sodium metaphosphate dissolves metallic oxides, forming orthophosphates—

$$NaPO_3 + CuO = NaCuPO_4.$$

In the case of compounds of manganese, copper, nickel, cobalt, chromium, and uranium, the colour effects produced are similar to those obtained with borax. The following table gives details for some of those metallic compounds in which different effects are produced :—

Metal.	Oxidising Flame.	Reducing Flame.
Iron . .	Hot, yellowish-red ; cold, colourless	Hot, conc., red ; cold, conc., red. Small quantities produce no colour
Molybdenum	Hot, green ; cold, almost colourless	Hot, dark green ; cold, less intense pure green
Tungsten .	Colourless	Blue. In presence of iron, blood-red
Titanium .	Hot, yellow ; cold, colourless	Hot, yellow ; cold, violet. In presence of iron, blood-red
Vanadium .	Hot, dark yellow ; cold, pale yellow	Hot, brownish ; cold, fine green

When heated in the microcosmic bead, silicates undergo decomposition, leaving an easily recognised " skeleton " of undissolved silica. Silica itself is not attacked and remains in the clear bead in opaque form, which is easily visible in both the hot and the cold bead.

Sodium Carbonate Bead Tests.

On the end of a fine platinum wire, which should be looped, fuse a small quantity of sodium carbonate so as to form a bead. The bead should be opaque and quite white when cold. Moisten the bead (as in the case of the borax beads), take up a small quantity of the solid substance to be examined, and also some potassium nitrate, and heat in the oxidising portion of the Bunsen flame. Compounds of **chromium** yield a *yellow* bead and those of **manganese** a *green* bead. The former colour is due to the formation of a chromate and the latter to the formation of a manganate.

The oxidation takes place when the substance is heated with sodium carbonate alone in the oxidising portion of the flame, but it is greatly accelerated when potassium nitrate is employed also to act as an oxidising agent.

Should the original solid substance contain sulphur, free or combined, sodium sulphate will be formed in the bead. To recognise the presence of this sulphate, dissolve the bead in water, filter if necessary, acidify the clear solution with dilute nitric acid, and test with barium nitrate. [See also the sulphide test (so-called " hepar " test), under Sulphates, p. 146.]

Match Tests.

Having removed the head from a common wooden match, hold a lump of crystallised sodium carbonate in the Bunsen flame until part of it is liquefied, and coat one-half of the match with the liquid. Heat the coated part till the wood under the sodium carbonate has been converted into charcoal. Place a small quantity of the powdered solid to be examined on a watch-glass and beside it a drop of the liquefied " soda." Moisten the tip of the charred match with the liquid and pick up a little of the powder and hold it for some time in the centre of the reducing flame, so as to heat it to the highest temperature there obtainable. Then break up the fused mass and the charred remains of the match, by slight pressure in an agate

mortar or in a porcelain basin, using the round end of a test tube as a pestle, and, either by frequent additions of water and pouring off again, or by means of a steady gentle flow of water from the tap, carefully wash away all the contents of the mortar except the reduced metallic beads and powder.

The following results may be obtained :—

Malleable bead : Red—Copper.
White, produces a grey mark on paper—lead.
White, does not mark paper—silver, tin.
Brittle bead (white) : Antimony, bismuth.
Grey or black magnetic powder : Iron, cobalt, nickel.

Notes respecting Match Tests:—

1. When reduction is taking place during the heating in the reducing flame, a distinct effervescence, due to the escape of carbon monoxide and carbon dioxide, is observed to go on in the fused mass. The occurrence of this effervescence serves as an indication of the progress of the reduction.

2. The reduced beads obtained from tin compounds are extremely small, and hence tin may be overlooked unless the wet powder which results from breaking up the fused mass under water is somewhat heavily rubbed in the agate mortar so as to produce characteristic white metallic streaks.

3. Particles of iron, cobalt, or nickel can be easily removed from the deposit in the mortar, while the latter is nearly full of water, by introducing into it the point of a magnetised knife-blade, and withdrawing it carefully, so as to avoid detaching the adhering particles.

Sublimation Tube Tests.

Place a small quantity of the solid under examination in a hard-glass sublimation tube, and, holding it at an angle of about 60 degrees from the perpendicular, heat it in the Bunsen flame, gently at first, afterwards more strongly. The following are some of the more important observations that may be made :—

1. **The substance does not appear to undergo any change.** (Note that there are few solid substances which are free from sensible quantities of hygroscopic moisture, the expulsion of which may be the only noticeable change produced on heating. A part of such moisture usually condenses in drops in the cool upper portion of the sublimation tube.)

2. **The colour of the substance changes**, but little or no further effect is observable. Some colourless metallic oxides

become coloured, and some coloured metallic oxides have their colour intensified. Thus, zinc oxide (white) becomes yellow when heated; stannic oxide (white or yellowish-white) becomes yellowish-brown; bismuth oxide (greenish-yellow) becomes orange or reddish-brown; lead oxide (pale brown) becomes dark brown. Mercuric oxide (red) and red oxide of lead become nearly black, and if the temperature be sufficiently high, decomposition takes place, with evolution of oxygen (see 4 (*b*) below). Potassium chromate (yellow) becomes dark red. The original colour, or an approximation to it, is usually assumed by the substance on cooling.

3. **The solid substance becomes liquid**, but this change is not accompanied or succeeded by any indication of decomposition, and the substance resolidifies on cooling. A number of inorganic salts, which are free from "water of crystallisation," also some other substances, behave in this way. (Note that liquefaction is often accompanied or succeeded by decomposition, sublimation, etc., whereby recognisable gaseous or liquid products, sublimates, etc., may be produced. See 4 and 5 below.)

4. **Volatile products are given off.** If these products are gaseous or liquid at ordinary temperatures, they are practically always products of decomposition. If they are solid, they may be of the same composition as the original substances, or they also may be products of decomposition. Volatile solid substances give rise to *sublimates*. (See 5, below.)

As water is nearly always given off in greater or less quantity when solid substances are heated (see 1, above), it may be most conveniently discussed here—

(*a*) *Water vapour*, which is often given off at a relatively low temperature, and of which a part usually condenses in drops in the cool upper portion of the tube, may be due to hygroscopic moisture, to the decomposition of substances containing water of crystallisation, to the decomposition of oxygen acids, of hydroxides, of acid salts, of basic salts, of some ammonium salts, etc. The water so condensed often contains dissolved substances, and its reaction to test papers should be observed. *Alkaline* reaction is usually due to the presence of ammonia, derived from ammonium salts, from cyanogen compounds, etc. *Acid* reaction is due to the presence of a volatile acid, such as

one of the halogen acids, sulphurous acid, sulphuric acid, nitric acid, acetic acid, etc. After testing the liquid with litmus paper, it is advisable, before proceeding to heat the dry residue further, to dry the sides of the sublimation tube as completely as possible by means of filter paper, otherwise drops may run back into the hot part of the tube and crack it. The evolution of water, when a substance is being tested as here described, should never be disregarded.

Volatile decomposition-products may further include—

(*b*) *Oxygen*: From certain metallic oxides and peroxides, as HgO, BaO_2, etc.; also from chlorates, bromates, iodates, perchlorates, permanganates, persulphates, bichromates, some nitrates, etc.

(*c*) *Chlorine*: From platinic, auric, and some other chlorides.

(*d*) *Nitrogen peroxide* (mixed with oxygen): From nitrates of heavy metals, as lead nitrate, bismuth nitrate, etc.

(*e*) *Ammonia*: From some ammonium salts, *e.g.*, sulphate, phosphate, borate, etc.

(*f*) *Carbon dioxide*: From cyanates, oxalates, certain carbonates, etc.; is sometimes mixed with carbon monoxide.

(*g*) *Carbon monoxide* (burns with a blue flame): From oxalates and formates; is often mixed with carbon dioxide, and sometimes with hydrogen.

(*h*) *Cyanogen* (burns with a peach-blossom-coloured flame): From cyanides of some heavy metals; also from cyanates and thiocyanates.

(*i*) *Sulphur dioxide*: From acid sulphites, and some sulphates and thiosulphates; from the oxidation of sulphides, thiocyanates, etc.; may be mixed with oxygen.

(*j*) *Hydrogen sulphide*: From hydrosulphides; also from sulphites and thiosulphates in presence of water.

5. **The volatile product forms a sublimate** in the cool upper part of the tube. The chief substances which form sublimates are noted below, together with the nature of the sublimate, and the effect of heating the substance with dry sodium carbonate in a sublimation tube.

Substance.	Nature of Sublimate.	Substance heated with dry Sodium Carbonate.
Mercuric chloride	White (substance melts)	Metallic sublimate, which gives globules of mercury on rubbing
Mercurous chloride	White (substance does not melt)	
Mercuric iodide	Yellow, red on rubbing	
Mercuric sulphide	Black; also some metallic globules	
Arsenious oxide	White; part, at least, crystalline	Black shining sublimate
Arsenious sulphide	Reddish-yellow	
Ammonium chloride and some other ammonium salts	White	Odour of ammonia; no sublimate
Sulphur	Pale yellow; yellowish-brown drops	
Iodine	Black shining crystals; violet vapour	
Oxalic acid	White; white fumes	

Blowpipe and Charcoal-Block Tests.

Make a small cavity near one end of a piece of wood charcoal, or of one of the compressed charcoal blocks prepared for blowpipe purposes. Place in the cavity a small quantity of the powdered solid substance to be examined, hold the charcoal in a slightly inclined position, and heat the powder by directing the blowpipe flame upon it.

To obtain the oxidising blowpipe flame, first adjust the Bunsen burner to give a small luminous flame, then introduce the blowpipe jet a short distance into the flame, and blow with sufficient force to obtain a non-luminous flame. This flame has an inner blue cone, and the hottest part of the flame is situated immediately in front of this inner cone. The most powerfully oxidising effect is obtained, however, when the substance under examination is heated near the tip of the outer mantle of the flame, where, besides a very high temperature, there is ready access of air.

To obtain the reducing blowpipe flame, hold the blowpipe jet just outside the flame and blow gently, so that the flame which is deflected along the charcoal is still to some extent luminous. The most powerfully reducing effect is obtained when the substance is heated a short distance back from the tip of the flame.

Examine the effects both of the oxidising and of the reducing flame, and note the following points :—

(*a*) Flame coloration [compare page 170].

(*b*) Odour of the vapour given off, if any. A garlic-like odour is characteristic of arsenic.

(*c*) Formation of an incrustation. The following are the most common :—

Metal.	Incrustation.
Lead . .	Lemon-yellow hot, paler yellow cold. Consists of lead oxide. Often shows a bluish-white margin of lead carbonate.
Bismuth .	Orange-yellow hot, lemon-yellow cold. Consists of bismuth oxide. Often shows a yellowish-white margin of bismuth oxide mixed with bismuth carbonate.
Antimony .	White ; in thin deposits, bluish-white. Consists of antimonious oxide. Is easily volatilised by the oxidising flame, but is less volatile than arsenious oxide. Disappears in the reducing flame.
Silver . .	After prolonged heating, a slight reddish-brown deposit of silver oxide.
Cadmium .	Reddish-brown. Consists of cadmium oxide. The outer portions sometimes show a great variety of colours.
Arsenic .	White. Consists of arsenious oxide. Is very easily volatilised.
Zinc . .	Pale yellow hot, white cold. Consists of zinc oxide.

(*d*) Reduction to the metallic state.

Compounds of certain metals yield metallic beads. [Compare the character of the beads obtained in the match tests, page 175.] In some cases, such as that of copper, it is difficult to obtain the metallic bead, but the admixture of a small quantity of dry powdered sodium carbonate aids the reduction.

If a white residue remains after a substance has been heated on charcoal, a drop of cobalt nitrate solution may be added and

the whole reheated in the oxidising flame, when one or other of the following colorations may result :—

Green . . .	Zinc.
Pale pink. . .	Magnesium.
Blue . . .	Aluminium (also phosphates, silicates, and borates).

EXAMINATION OF SOLID SUBSTANCES.

THE solid may be examined in the first place by means of the dry-way reactions described on pages 170 *et seq.* For examination by wet-way reactions, the solid must first be dissolved in water, or in acid if insoluble in water. Acid should be employed only when really necessary, and it is therefore important to test the solubility in water with great care. In many cases the solid is so readily soluble that there is no difficulty in recognising the fact; but in cases of doubt, where the substance is, at most, sparingly soluble, one or other of the following precautions should be observed before concluding that it is insoluble: 1. A minute but distinctly visible quantity of the solid is shaken up, and, if need be, warmed, with a considerable quantity of water in a test tube; unless the solubility is practically negligible the solid will entirely disappear. 2. A moderate quantity of the solid is shaken and warmed with water in a test tube, so as to get a nearly saturated solution; this is filtered off from the undissolved portion, and some of the clear solution is evaporated to dryness in a watch-glass or other glass dish. If there is a distinct residue, the solid is appreciably soluble in water, otherwise it is not. If it is found to be insoluble a small portion should be treated with dilute hydrochloric acid, and, if this does not yield a clear solution, then with dilute nitric acid. Substances which are insoluble in all of these liquids may be treated with concentrated nitric acid (see p. 186).

I. SUBSTANCES SOLUBLE IN WATER.

When a solid is found to be soluble in water, a solution should be prepared by placing a moderate quantity of it (say about 0·5-1 grm.) in a clean test tube, adding 10-20 c.c. of water, and shaking them together; if the substance does not dissolve completely within a reasonable time the liquid may be warmed, and if some remains, even on warming, then the solution should be cooled and filtered into another tube. The solution obtained is examined exactly like any other solution of

an unknown salt, in accordance with the scheme given on pages 158 *et seq.*

II. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN DILUTE ACIDS.

When substances are said to dissolve in dilute acids it is meant, as a rule, that the acids act upon them to produce new compounds which are soluble in water; thus, when it is stated that zinc dissolves in dilute sulphuric acid, what is really meant is that the sulphuric acid acts upon the zinc with formation of a substance—*i.e.* zinc sulphate—which is soluble in water, and is therefore dissolved by the water present in the dilute acid.

As a rule, hydrochloric acid is employed in preparing a solution from substances insoluble in water, and there are several advantages attending its use. For example, it does not yield products which might introduce possible complications, as nitric acid does (see Sulphides and Sulphites below); and further, any excess can be removed by evaporation (if necessary) much more easily than in the case of sulphuric acid. With some substances, however, hydrochloric acid cannot be employed, the most important of these being compounds of metallic radicals whose chlorides are insoluble (*e.g.* silver carbonate), and certain metals. In such cases nitric acid is used.

Many compounds, insoluble in water but soluble in dilute acid, are excluded from consideration here, even although they are salts of metallic and acidic radicals included in the general scheme. The reason for this is that, when they are dissolved in acid, the resulting solution contains *two* acidic radicals, and such mixtures do not lie within the scope of simple qualitative analysis. For example, if calcium phosphate is dissolved in dilute hydrochloric acid the resulting solution contains both chloride and phosphate; when ammonia is added to such a solution, a white precipitate of calcium phosphate is formed, the addition of ammonia in this case being equivalent to the addition of a mixture of ammonium phosphate and ammonia to a solution of calcium chloride.

The only insoluble salts which are dealt with here are therefore such as dissolve in dilute acids to give a solution containing a single acidic radical—that of the acid employed for solution. Such substances are—(1) metals, (2) oxides, (3) carbonates, (4) sulphides, (5) sulphites.

1. **Metals** which dissolve in dilute hydrochloric acid do so with evolution of hydrogen ; this is often recognisable on applying a light, when the gas may ignite and burn at the mouth of the tube, or, with a smaller proportion of hydrogen, the gaseous mixture in the tube may explode. If the temperature of the liquid is high, the evolved gas is sometimes mixed with so much steam that neither of these phenomena is observed. Often in such cases the desired result may be attained by holding a second tube for some time inverted over the mouth of the first, so as to collect the gas escaping from it ; a large proportion of the water vapour will be condensed on the cold walls of the upper tube. After some time, the mouth of the latter is closed by means of the thumb, and brought close to a flame ; the thumb is then withdrawn so as to allow the contents to escape into the flame.

Many metals contain, as impurities, small quantities of carbides and other similar compounds ; these compounds are, in some cases at least, decomposed by acids with formation of hydrides (hydrocarbons, etc.). The hydrogen liberated, when such impure metals are dissolved in acid, is therefore contaminated with small quantities of these hydrides, which impart to it a characteristic odour, though pure hydrogen is odourless.

Metals which are insoluble in dilute hydrochloric acid, but dissolve in dilute nitric acid, cause the evolution, not of hydrogen, but of reduction products of the nitric acid, which are recognisable by their reddish-brown colour in the upper part of the tube. The resulting solution generally contains nitrous acid, which should be got rid of as far as possible by boiling or evaporating.

2. **Basic oxides** (and **hydroxides**), when they dissolve in acids, do so without any evolution of gas, and, among the substances now under consideration, are recognisable thereby ; frequently they possess a characteristic appearance. Many basic oxides slowly absorb carbon dioxide from the atmosphere, forming carbonates. In such cases there is often a more or less marked effervescence on treatment with acid, although the quantity of carbonate present may be small.

Some **peroxides** (*e.g.* PbO_2, MnO_2), when warmed with not too dilute hydrochloric acid, yield chlorine ; other peroxides (*e.g.* Na_2O_2, BaO_2) yield oxygen. The former gas is easily recognisable by the usual tests ; the latter can generally be

recognised by its rekindling a glowing splinter, provided there is not too much water vapour present. The presence of a peroxide can be confirmed by adding potassium iodide and hydrochloric acid to a small portion of the original insoluble solid, when iodine will be liberated in the cold or on warming; it is to be noted, however, that this reaction is also given by cupric oxide and by ferric oxide.

3. **Carbonates** dissolve in dilute acids with evolution of carbon dioxide, recognisable by means of lime water; after effervescence ceases the solution should be boiled to expel all carbon dioxide, which otherwise might interfere with some of the reactions.

4. **Sulphides**, when dissolved in hydrochloric acid, yield hydrogen sulphide, which is easily recognisable. The solution should be boiled until there is no longer any smell of the gas.

When nitric acid is used, hydrogen sulphide is not evolved, the oxidising action of nitric acid resulting in the formation of water and sulphur; the latter may undergo further oxidation to sulphuric acid.

5. **Sulphites**, when treated with hydrochloric acid, yield a chloride and sulphurous acid. On warming, the latter is nearly all decomposed with evolution of sulphur dioxide, which is easily recognisable; the gas should be expelled as completely as possible by boiling.

Nitric acid, in the cold, liberates sulphurous acid from sulphites; on standing, and much more rapidly on warming, oxidation to sulphuric acid takes place.

To prepare a solution from any of the above substances, a moderate quantity should be placed in a test tube, and the appropriate acid, as determined by the preliminary experiment, added *in small quantity*; if any gas escapes, this should be investigated immediately, and recognised by its smell, chemical behaviour, etc. The liquid should then be warmed to hasten the dissolution, further small quantities of acid being added from time to time, if necessary, till the whole of the substance is dissolved; or, if so preferred, when a sufficiency has been dissolved, the liquid may be filtered into a clean tube. It is important to avoid a great excess of acid, as such excess sometimes causes complications in the subsequent examination. After the clear solution has been boiled to expel dissolved gas,

it is diluted with water to a suitable volume. This solution is then examined for the metallic radical in the usual way; the salt in solution will, of course, be either a chloride or a nitrate, according to the acid employed. If the original substance was itself one of the salts included in the above list, its acidic radical should have been detected by recognising the gas evolved on dissolving in acid.

III. ALLOYS.

Many alloys can be dissolved or disintegrated by treatment with a mixture of concentrated nitric acid and water in equal volumes, heat being applied if required. No more acid should be used than is absolutely necessary. Should the alloy be unattacked or very slowly attacked by the diluted acid, undiluted nitric acid may be used. After moderate dilution of the resulting solution with water, any white residue (which may contain tin or antimony as oxide) can be separated by filtration, washed, and examined by dry-way tests (p 170) or by treatment with a concentrated solution of **tartaric acid**, in which tin oxide is insoluble, but antimony oxide is soluble, and the solution thus obtained gives on addition of sulphuretted hydrogen an orange precipitate. The solution (or filtrate) should be evaporated almost to dryness to expel the excess of nitric acid, diluted with water, and examined for metallic radicals.

VOLUMETRIC ANALYSIS.

THE measurement of the quantities or masses of the component parts of a substance or mixture of substances is known as *quantitative analysis*. Before proceeding to make a quantitative analysis, it is necessary to make a *qualitative analysis*—in other words, to find out what different component parts are present in the substance or mixture. The subject of qualitative analysis has been dealt with in a simple manner and to a limited extent in the preceding pages (pp. 98 to 186), and larger text-books must be consulted for a fuller treatment.

Quantitative analysis may be carried out in various ways. Simple instances in which a component part or a definite compound of a component part is weighed have been given on pages 68 to 97. These illustrate some of the methods of *gravimetric* analysis. It is, however, often much more convenient to measure the volume of a solution of previously ascertained concentration, which reacts with a definite weight of a component part or compound, than to measure the definite weight directly. As an illustration of this process of **volumetric** analysis, the measurement of a quantity of sodium hydroxide may be taken.

The neutralisation of sodium hydroxide by hydrochloric acid takes place according to the equation—

$$\underset{23+16+1=40}{NaOH} + \underset{1+35{\cdot}5=36{\cdot}5}{HCl} = \underset{23+35{\cdot}5=58{\cdot}5}{NaCl} + \underset{2+16=18}{H_2O}$$

that is, 36·5 grm. of hydrochloric acid neutralises 40 grm. of sodium hydroxide. If a solution of hydrochloric acid of known concentration be added to a solution of sodium hydroxide until neutrality is reached, as shown by an indicator, and, if the volume of the acid added be measured, then the weight of the sodium hydroxide may be calculated. Suppose 50 c.c. of acid solution of a concentration of 36·5 grm. per litre is required to neutralise the sodium hydroxide, then the weight of hydrochloric acid taken is $\frac{36{\cdot}5}{1000} \times 50 = 0{\cdot}0365 \times 50 = 1{\cdot}825$ grm., and as

36·5 grm. hydrochloric acid is neutralised by 40 grm. sodium hydroxide, the weight of the latter will be

$$\frac{40}{36{\cdot}5} \times 1{\cdot}825 = 2{\cdot}0 \text{ grm.}$$

It will often be found in laboratory practice that several volumetric determinations can be carried out in the same time that is required for a single gravimetric one.

In volumetric analysis solutions * of accurately determined concentration are known as **standard** solutions, and for convenience of calculation such standard solutions are defined by their relationship to a **normal** solution. One may say of the latter that one litre (1000 ml. or 1000·027 c.c., see p. 193) of a normal solution contains one gram equivalent of the reactive substance. For example, one litre of normal hydrochloric acid contains 36·5 grm. hydrochloric acid; one litre of normal sulphuric acid contains 49 grm. sulphuric acid

$$\frac{H_2SO_4}{2} = \frac{2+32+64}{2} = \frac{98}{2} = 49.$$

For the sake of brevity such solutions would be described as N . HCl and N . H_2SO_4 respectively. In the case of alkalies the gram equivalent is the weight which contains 16+1=17 grm. basic hydroxyl (OH). Hence a litre of normal sodium hydroxide solution contains 23+16+1=40 grm. sodium hydroxide; a litre of normal barium hydroxide contains 85·7 grm. barium hydroxide

$$\frac{Ba(OH)_2}{2} = \frac{137{\cdot}4+32+2}{2} = \frac{171{\cdot}4}{2} = 85{\cdot}7.$$

A normal solution of silver nitrate contains 169·9 grm. silver nitrate

$$\frac{AgNO_3}{1} = 107{\cdot}9+14+48 = 169{\cdot}9.$$

in one litre of solution. In the case of an oxidising agent, one litre of the normal solution liberates 8 grm. of oxygen or an equivalent weight of some other oxidising element or group. Thus potassium permanganate in presence of sulphuric acid reacts with a reducing substance according to the equation—

* These solutions are usually aqueous ones, though in some instances alcohol or other solvent is used in place of water. In the following descriptions of volumetric exercises, *distilled water* is to be understood in every case where "water" is mentioned.

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,[O]$$
$$2[39{\cdot}1+55+64] = 316{\cdot}2 \qquad\qquad 80$$

hence one litre N . $KMnO_4$ contains $\frac{316{\cdot}2}{10}$ or 31·62 grm. potassium permanganate, which, under the condition noted, liberates $\frac{80}{10}$ or 8 grm. oxygen. Again, iodine acts as an oxidising agent in the reaction expressed by the equation—

$$I_2 + 2\,Na_2S_2O_3 = Na_2S_4O_6 + 2\,NaI,$$

hence one litre N . I contains 126·9 grm. iodine.

It frequently happens that it is convenient to use solutions which are not exactly normal. For example, it may be desirable to use a much more dilute solution than a normal one—say of a concentration one-tenth or one-hundredth that of the normal solution. The tenth normal solution is called *decinormal* and is represented as $\frac{N}{10}$ or 0·1 N. For example, one litre $\frac{N}{10}$ HCl or 0·1 N . HCl contains 3·65 grm. hydrochloric acid. The hundredth normal or *centinormal* solution is represented as $\frac{N}{100}$ or 0·01 N and one litre 0·01 N . HCl contains 0·365 grm. hydrochloric acid.

When a solution does not happen to be exactly normal or decinormal, etc., it is generally more convenient to use it as it is, rather than to alter it so that its concentration becomes exactly normal or decinormal. This involves using a fraction or factor in all calculations. For example, a litre of hydrochloric acid solution contains 4·380 grm. hydrochloric acid. Its normality is therefore $\frac{4{\cdot}380}{36{\cdot}5} = 0{\cdot}12$ N. The factor 0·12 will then be used in all calculations regarding this particular hydrochloric acid solution.

A litre of a normal solution of an acid is required to neutralise a litre of a normal solution of an alkali, and it follows that if the number of c.c. of a normal solution of an acid required to neutralise a definite number of c.c. of an alkali of unknown concentration is measured, then the normality and the concentration of the latter may be calculated. Thus assuming that in the example given on p. 187, 50 c.c. N . HCl is required

to neutralise 25 c.c. sodium hydroxide solution, then 50 c.c. N . HCl neutralises 25 c.c. $\times x$ N NaOH and $x=\frac{50}{25}=2$, hence 50 c.c. N . HCl $\equiv$ 25 c.c. 2 N . NaOH.

The sign $\equiv$ is used to express " is equivalent to " or in this instance " is neutralised by." The normality of the sodium hydroxide is twice normal or 2 N., and its concentration is 2×40 or 80 grm. sodium hydroxide per litre.

In general one may say :

A c.c. $\times y$ N. acid $\equiv$ B c.c. $\times x$ N. alkali where " A " is the number of c.c. of acid of normality " y " and " B " the number of c.c. of alkali of normality " x." It is necessary to know both " A " and " B " and either " y " or " x," before " x " or " y " can be calculated. In the example given, " y " is known.

Suppose 10 c.c. of hydrochloric acid of unknown concentration requires 22 c.c. $\frac{N}{10}$ or 0·1 N . NaOH for neutralisation, then :

$$\text{A c.c.}\times y \text{ N acid} \equiv \text{B c.c.}\times x \text{ N alkali}$$
$$10 \text{ c.c.}\times y \text{ N acid} \equiv 22 \text{ c.c.}\times 0{\cdot}1 \text{ N alkali}$$
$$y \text{ N} \equiv \frac{22}{10}\times 0{\cdot}1 \text{ N}$$
$$y \text{ N} \equiv 0{\cdot}22 \text{ N},$$

hence the acid is 0·22 N and one litre contains $36{\cdot}5\times0{\cdot}22=8{\cdot}03$ grm. hydrochloric acid. In general, the statement holds good that the concentration in grams per litre = normality $\times$ gram-equivalent weight.

In all volumetric calculations it must be remembered that the more concentrated a solution is, the less will be the volume of it required to interact with a solution of another substance. It will be obvious then that if 50 c.c. of an acid of unknown concentration neutralises 10 c.c. of N . NaOH, the normality of the acid will be $\frac{10}{50}$ or $\frac{1}{5}$ N or 0·2 N. On the other hand, suppose 15 c.c. N . HCl neutralises 10 c.c. sodium hydroxide of unknown concentration, then the normality of the sodium hydroxide will be $\frac{15}{10}$ or 1·5 N. If the beginner remembers this point, he will not make blunders in the calculations of normality. The process involved in the comparison of an unknown solution with a standard one is called *titration* (French *titrer*).

Indicators.

One of the requirements of volumetric analysis is a means of knowing when the interaction of two reacting substances is completed. Frequently not only the reacting substances but also the products of the interaction are colourless. For example, the interaction of hydrochloric acid and sodium hydroxide produces sodium chloride and water—all of which substances are colourless. Consequently one cannot tell by mere inspection when the interaction is completed. If, however, some substance which loses colour, becomes coloured, or changes colour, by the action of traces of either the acid or the alkali, be added to the solution, then the end-point can be recognised. Such a substance is called an **indicator** (see pp. 41-44). Coloured extracts of plants, *e.g.* violets, red cabbage, litmus, were used in this way at an early date. Some of these are still used, but the indicators now most largely used in acidimetry and alkalimetry are synthetic products of feebly basic or acidic character or potentially so (see p. 43). When a *strong* acid is to be titrated by a *strong* base, it does not matter very much what indicator is used, so long as it is sufficiently sensitive. The sensitiveness of indicators varies, some requiring much larger quantities of reagent to produce a visible change than others. Litmus solution requires a larger quantity of an acid or an alkali to change its colour than methyl red. Hence in the case of such a neutralisation reaction as that of hydrochloric acid by sodium hydroxide, it is preferable to use methyl red instead of litmus.

When a *weak* acid is to be titrated by a *strong* alkali * it is important to choose an indicator which will be readily affected by the alkali. Such an indicator is phenolphthalein.

When a *weak* alkali is to be titrated against a *strong* acid, the converse holds good. A suitable indicator is methyl red.

Most organic acids, *e.g.* acetic, tartaric, and carbonic acids are typical weak acids. The mineral acids, *e.g.* hydrochloric, sulphuric, nitric, are typical strong acids. Ammonia is a typical weak base, and the alkalies, sodium and potassium hydroxides, are typical strong bases.

Besides indicators for acidimetry and alkalimetry, there are many other substances which are used as indicators in

* Again note should be made of the point that "strong" and "weak" have nothing to do with the concentration, but only with the degree of ionisation of the acid or alkali (see pp. 15, 27), the weak acid or alkali being less ionised in solution than the strong acid or alkali.

volumetric analysis. In oxidations by means of potassium permanganate in sulphuric acid solution, the permanganate itself behaves as an indicator, the MnO_4' anion being violet in colour and the $Mn^{\cdot\cdot}$ cation, which is produced, being colourless. Another example is ferric sulphate, which is used in determining the end-point in the interaction of silver nitrate and ammonium thiocyanate. Only after all the silver in the solution has been precipitated as silver thiocyanate and a slight excess of ammonium thiocyanate has been added does the solution become coloured red owing to the formation of feebly ionised ferric thiocyanate.

" Adsorption indicators " are referred to on page 42, and the use of fluorescein as such in the standardisation of silver nitrate is described on page 211.

Apparatus.

The apparatus employed for accurate volumetric analysis is usually the following :—

1. Graduated flasks (fig. 1 *a*) and cylinders (fig. 1 *b*), used in making up solutions to definite volumes. The flasks most often required are those to contain 100 c.c., 250 c.c., 500 c.c., and 1000 c.c. They should have ground-in glass stoppers, so that the solutions may be shaken up without loss.

2. Pipettes (fig. 1 *c*), employed to deliver predetermined volumes of liquid, such as 10, 20, 25, or 50 c.c.

In the following exercises a 10 c.c. pipette is made use of, but any other size might be used, making due allowance for the change.

3. Burettes (fig. 1 *d* and *e*), long, graduated tubes, provided with a tap at the lower end, so that sufficient liquid to produce a certain change can be run out, and the volume employed measured by observing the levels before the experiment is begun and after it is completed. In this section, the burette is supposed to be of a capacity of either 25 or 30 c.c. Frequently a 50 c.c. burette is used in more advanced work and in analytical laboratories.

4. Conical flasks (fig. 1 *f*) of about 100 and 150 c.c. capacity.

5. Porcelain basins of about 100 and 150 c.c. capacity.

6. Glass rods with smooth ends.

In 1924, a Joint Committee for the Standardisation of Scientific Glassware recommended "that the recognised international metric units—the 'litre' (l.) and 'millilitre' or thousandth part of the litre (ml.)—shall be used as the standard units of volume, and that standard volumetric glassware shall be graduated in terms of these units and marked 'ml.' instead

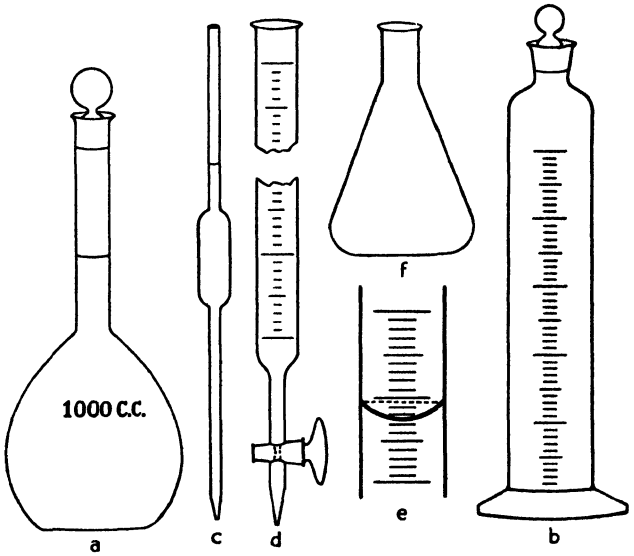


FIG. 1.

of 'c.c.'" When apparatus is marked "ml." it may be used in place of that marked "c.c.," the relationship between the "c.c." and the "ml." being— 1000 ml.=1000·027 c.c.

Much of the apparatus now in use being marked "c.c.," it has not yet been considered advisable to substitute "ml." for "c.c." in this book.

Exercises in Manipulation.

Practise manipulating and reading the burette, which is here assumed to be of 30 c.c.* capacity and graduated in

* As noted above, the apparatus may be graduated in millilitres (ml.). Where this is the case, "ml." should be substituted for "c.c." in these and other volumetric exercises.

cubic centimetres and tenths, *i.e.* the space between any two neighbouring marks corresponds to 0·1 c.c., with each fifth mark longer than the intermediate ones, so that the space between two successive long marks corresponds to 0·5 c.c.

After cleaning the burette, pour water into it until the level stands considerably above the zero (top) graduation. Open the stopcock and allow some water to run out into a flask or basin placed to receive it. It is highly important that no air should remain in the stopcock or jet, and, if these are clean, this is easily ensured by opening the stopcock suddenly, so that the water comes out with a rush, driving the air before it. If, after this operation, the level of the liquid is still above the zero mark, the stopcock should again be opened, this time gradually, until the level sinks slightly below the zero ; it is a waste of time to try to adjust the level exactly to the zero mark, and generally leads to somewhat less accurate results.

Read, to the nearest twentieth (0·05) of a cubic centimetre, the level at which the liquid stands, and note it down. As the burette is graduated only to tenths, it is necessary to *estimate* twentieths ; with a little practice it will soon become easy to judge whether the level is nearer to the upper or lower of two neighbouring graduations (between which it lies) or to an imaginary line midway between them. In taking readings of this kind, there are several precautions to be observed. Owing to capillary action, the surface of the liquid in the tube is not flat, but forms a *meniscus*, which is concave downwards in the case of liquids which wet the walls of the tube, such as water, and convex upwards in the case of liquids which do not wet the walls of the tube, such as mercury. In the former case, the lowest point of the meniscus is taken to indicate the level of the liquid ; in the latter, the top of the meniscus. If the solution be intensely coloured (see p. 205) it may not be possible to see the bottom of the meniscus and a reading of the top edge must be taken. The lateral distance of the bottom of the meniscus from the graduations on the outside of the tube leads to the possibility of considerable errors due to parallax. These are avoided by holding the burette, when a reading is to be made, in a vertical position, and at such a height that the surface of the liquid and the eye of the observer are in the same horizontal plane. The vertical position of the burette is secured by holding it lightly but securely by the top between the thumb and forefinger of one hand, when it will of itself

hang in a position sufficiently near the vertical. The necessity for these precautions can be easily proved by taking a reading in the correct manner and then changing the position of the burette.

In making the reading, first note the value of the nearest long division *above* the surface of the liquid. (Sometimes only alternate cubic centimetre marks are numbered on burettes, the odd numbers being omitted.) Then count the number of small divisions which intervene between this and the surface of the liquid, and allow 0·1 c.c. for each of them. In fig 1 *e*, where the topmost long mark represents 9·0 c.c., the middle one 10·0 c.c., and the lowest one 11·0 c.c., the level is about half-way between 10·2 and 10·3, and the reading would be 10·25. With practice it is possible to estimate smaller fractions than half divisions ; this is unnecessary for the present work, but students may practise reading to fiftieths (0·02), or even to hundredths (0·01) of a cubic centimetre, especially if a narrow burette is used.

Run out from the burette successive small portions of the contents, and each time note the level of the liquid. The differences between the successive readings give, of course, the volumes of liquid withdrawn on the various occasions. It is advisable to practise manipulating the stopcock with one hand so as to be able to withdraw liquid slowly, drop by drop, as frequently this is necessary in actual work.

In work of this kind it should be made an invariable rule to *record each observation immediately in a note-book*, setting down the numbers actually read off, without performing any operation of mental arithmetic, even of the simplest kind. This diminishes, so far as practicable, the possibility of introducing errors incapable of subsequent rectification.

As a rule, in working with a burette, the liquid is allowed to run out very slowly towards the end of the operation, giving time for the liquid to drain away from the walls, so that only a very thin layer is left adhering. If at any time a large quantity of liquid is run out quickly from a burette, it is necessary to wait a minute or two before taking a reading, in order to allow of proper drainage, otherwise an incorrect result will be obtained. This can easily be observed by running out the contents of the burette as quickly as possible until the bottom mark is nearly reached, taking one reading immediately and another after two or three minutes. Of course, if the jet of the

burette has a very fine opening, it is impossible to empty the burette quickly, and error due to the above cause is prevented. For accurate work it is further necessary that burettes (and all other graduated vessels) should be free from all traces of greasy matter ; otherwise, proper drainage does not take place, and drops adhere to the walls.

Practise also the manipulation of the pipette, in the following way: Holding it in the right hand, near the wide end, insert the narrow end into a flask containing water, and suck water into it until the level is well above the mark on the upper stem ; quickly close the upper opening with the forefinger of the right hand, and then, by slightly releasing the pressure of the finger, allow liquid to trickle out until the bottom of the meniscus reaches the mark, when the further escape should be prevented by tightly closing the upper end again.

The drop adhering to the tip is removed by bringing the surface of some water into contact with the tip and then removing it without jerking. The pipette is then allowed (by raising the forefinger) to deliver the water into the vessel into which the liquid is to be transferred, the vessel being slightly inclined so that the tip of the pipette is in contact with the side of the vessel. The small quantity of liquid which remains inside the tip of the pipette should not be blown out. The tip of the pipette should be made with a gradual taper, and for a 10 c.c. pipette the time of delivery should be between 15 and 30 seconds, and to this should be added another 15 seconds for draining the pipette before removing it from the vessel.

When the manipulation has been mastered, the pipette and burette may be checked against each other by pouring water into the burette up to a point slightly above the bottom graduation, noting the exact level, and then running in 10 c.c. of water from the pipette. On again reading the burette, the difference should amount to exactly 10·0 c.c. A further quantity of 10 c.c. should be again added and the level again read.

In this manner, by running in volumes of 10 c.c. to the burette already having water up to the 30 c.c., 25 c.c., 20 c.c., 15 c.c., and 10 c.c. marks, a rough " calibration " of the burette is obtained. If a discrepancy exceeding 0·2 c.c. be found, the apparatus should be shown to the instructor, who will decide whether it should be discarded or used after making the necessary corrections.

Graduated flasks and measuring cylinders should also be

calibrated against each other and against suitable burettes or pipettes.

Alkalimetry.

Using a standard acid solution (conveniently, normal or decinormal) determine in the following manner the concentration of a dilute solution of **sodium hydroxide** :—

After cleaning the burette, and allowing the water to drain away as completely as possible, rinse it twice with 2 or 3 c.c. of the standard acid solution, allowing this in its turn to drain away. The object of these preliminary rinsings is to remove the water adhering to the walls of the burette, which otherwise would dilute the standard acid solution.

Fill the burette with the acid, taking care that the air is completely removed from the jet, and adjust the level of the liquid until it is at or below the zero mark.

Clean the pipette, and, after draining, rinse it twice with a very small quantity of the alkaline solution which is to be tested; then by means of it measure 10 c.c. of the solution into a clean basin or flask. Add to this solution a small quantity of neutral solution of litmus, just sufficient to colour it faintly but distinctly.

Read the level of the liquid in the burette, and note it. After replacing the burette in its stand, place the vessel containing the 10 c.c. of alkaline solution below it and run in the standard acid from the burette in small quantities at a time. After each addition of acid, the whole should be thoroughly mixed, by stirring with a glass rod if a basin is employed, or, in the other case, by gently shaking the flask itself. (The flask should have a piece of white paper placed beneath it during the titration, in order that the colour changes may be easily observed.) As the acid drops into the blue liquid, the colour becomes locally changed to red, but this disappears again on agitation of the liquid. In course of time each succeeding drop has a more and more marked effect, the red coloration disappearing less and less quickly, and the acid must now be added more and more carefully in order that the end-point may be observed as exactly as possible. When at last, after the addition of a drop of acid, the colour remains red throughout the liquid even after thorough agitation, the alkali has been neutralised and a slight excess of acid is present in the solution. With careful work this excess ought not to

exceed a drop of the standard solution, and in very exact work a fraction of a drop can be withdrawn from the jet by means of the rod, and stirred into the solution. The greater the excess added, the less accurate is the numerical result obtained. When the operation has been completed, a fresh reading of the burette must be taken and recorded.

Repeat the determination with another 10 c.c. of solution. (When the same pipette is used, it is not necessary to clean it afresh, provided care is taken to keep the lower stem clean in the interval.) If the quantity of standard acid remaining in the burette is not sufficient for a new determination, a fresh quantity should be poured in beforehand; this is much better than having to replenish the burette in the middle of a titration. As the first determination has shown more or less accurately what quantity of acid is required for neutralisation, it is possible in the second experiment to run in somewhat less (say, 0·5 c.c. less) than this quantity, and thereafter proceed carefully, adding only a drop at a time. If the two results agree sufficiently closely, the average is taken; if there is more than a slight discrepancy, another determination should be made. (As the first determination is likely to be less accurate than the succeeding ones, which are carried out with a fairly accurate knowledge of the amount of standard solution required, the first is sometimes neglected in the final calculation, the average of a second and a third determination being taken.)

The results should be noted somewhat as follows :—

	Volume of alkali solution taken.	Burette readings.	Volume of standard acid required.
(1)	10 c.c.	0·30	
		11·65	11·35 c.c.
(2)	10 c.c.	11·65	
		22·95	11·30 c.c.
		Average,	11·325

Assuming that the standard acid employed in the above case is decinormal, the normality of the solution of sodium hydroxide is $\frac{11{\cdot}325 \times 0{\cdot}1}{10} = 0{\cdot}11325$, and its concentration in grams per litre is $0{\cdot}11325 \times 40 = 4{\cdot}53$ (40 being the equivalent weight of sodium hydroxide).

This determination should be repeated, using methyl red as indicator instead of litmus, and the results compared with those obtained when using litmus (see p. 191).

Instead of measuring the sodium hydroxide solution by means of the pipette, the latter might have been employed to measure 10 c.c. of standard acid and the sodium hydroxide solution then run into the latter from the burette. Sometimes two burettes are employed, one for the standard solution and the other for the solution under examination.

By a similar procedure, using a suitable indicator (see p. 191), determine the concentration of other alkaline reagents, such as potassium hydroxide or calcium hydroxide, employing the appropriate equivalent weight in the calculation.

One litre of normal acid will neutralise the equivalent weight in grams of any of the various basic hydroxides. Some of the commoner of these equivalent weights are—

NaOH	. 40	NH_4OH	. 35
KOH	. 56·1	$Ca(OH)_2$	. 37·05 (*i.e.* 74·1÷2).

The **alkali carbonates** may also be titrated in a similar manner, bearing in mind that carbon dioxide affects litmus indicator, and to a less extent methyl red. To avoid error the solution must be boiled to expel the carbon dioxide which is liberated when the strong acid (HCl, H_2SO_4, or HNO_3) is run from the burette into the measured volume of alkali carbonate solution (see p. 201). The equivalent weights for sodium and potassium normal carbonates are—

Na_2CO_3 53=106÷2 K_2CO_3 69·1=138·2÷2.

Temporary Hardness of Water.

Temporary hardness may be due to the presence in solution of calcium bicarbonate, or of magnesium bicarbonate, or of both. Water, temporarily hard from this cause, shows an alkaline reaction towards methyl red indicator owing to the hydrolysis of these salts—*e.g.* in the case of the calcium salt—

$$Ca(HCO_3)_2+2\ H_2O \rightleftharpoons Ca(OH)_2+2\ H_2CO_3.$$

If a strong acid (HCl) is added, reaction takes place thus—

$$Ca(OH)_2+2\ HCl=CaCl_2+2\ H_2O—$$

and the amount of hydrochloric acid used is therefore a measure of the amount of calcium bicarbonate in the hard water.

Procedure.—Transfer 100 c.c. of the temporarily hard water to a conical flask, add 5 drops of methyl red indicator and then 0·02 N . HCl from the burette until the liquid acquires a reddish tint. Then boil the water for about a minute to expel the carbon dioxide. The yellow colour of the indicator should reappear. Now add more acid, drop by drop, until a permanent red coloration is obtained. Suppose 100 c.c. of the water requires 4·0 c.c., 0·02 N . HCl, then, since the equivalent weight of $CaCO_3$ is 50·05, $4{\cdot}0 \times \frac{0{\cdot}02 \times 50{\cdot}05}{1000} = 0{\cdot}004$ grm. $CaCO_3$ is contained in 100 c.c. [as $Ca(HCO_3)_2$] or 4 grm. in 100,000 c.c., which is approximately 4 grm. in 100,000 grm. water.

Acidimetry.

By means of normal or decinormal alkali solution, determine the concentration of the various dilute acids, using a suitable indicator (see p. 191).

One litre of normal alkali will neutralise the equivalent weight in grams of any of the various acids. Some of the commoner of these equivalent weights are—

HCl . . .	36·5	H_2SO_4 . .	49 (*i.e.* 98÷2)
HNO_3 . . .	63	$H_2C_2O_4$ (oxalic acid)	45 (*i.e.* 90÷2)
$HC_2H_3O_2$ (acetic acid)	60		

Instead of employing normal or decinormal alkali to determine the concentration of the acids, as indicated above, the solution of, say, potassium hydroxide, the normality of which has already been determined, may be used.

NOTE.—In very accurate work the equivalent weights should be based upon exact atomic weights ; in the above tabulation they have been rounded off.

Standardisation of a Solution of an Acid (HCl or H_2SO_4) **by means of pure, anhydrous Sodium Carbonate,** Na_2CO_3, **or pure "soda crystal,"** Na_2CO_3, 10 H_2O.

Weigh a watch-glass accurately. Remove it from the balance-case and place upon it from 0·4 to 0·6 grm. anhydrous sodium carbonate (about as much as will lie on a halfpenny)

or from 1·4 to 1·8 grm. of the crystals. Weigh the watch-glass and contents. Transfer the sodium carbonate to a 300 c.c. beaker, washing the last traces from the watch-glass by means of a jet of water from the wash-bottle. Add about 25 c.c. water and then gently heat the contents of the beaker until all the carbonate has dissolved. After the addition of 5 drops of methyl red indicator, run in the acid from the burette—having first noted the level—until a distinct reddish tint is observed. Boil the solution for about a minute in order to expel carbon dioxide. Then add more acid, drop by drop, to the hot solution until it acquires a permanent red tint.

The following example shows how the experimental data and calculations may be recorded :—

Weight of watch-glass . . .	7·372 grm.
,, watch-glass+Na_2CO_3 . .	7·824 ,,
,, Na_2CO_3 taken . . .	0·452 ,,
Burette reading, initial . . .	0·35 c.c.
,, final	22·80 ,,
Volume of acid required . .	22·45 ,,

Calculation—

$$Na_2CO_3+2\,HCl=2\,NaCl+CO_2+H_2O$$
$$106+2\times36{\cdot}5.$$

The equivalent weight of Na_2CO_3 is therefore $106\div2=53$. Hence 53 grm. Na_2CO_3 is contained in 1000 c.c. of normal solution and 0·452 grm. is contained in

$$\frac{1000\times0{\cdot}452}{53}=8{\cdot}53 \text{ c.c. of normal solution.}$$

Therefore,

$$22{\cdot}45 \text{ c.c. } y \text{ N . HCl} \equiv 8{\cdot}53 \text{ c.c. N . } Na_2CO_3$$
$$y=8{\cdot}53\div22{\cdot}45=0{\cdot}380.$$

The hydrochloric acid solution has a normality 0·380 and one litre of solution contains $0{\cdot}380\times36{\cdot}5=13{\cdot}870$ grm. hydrochloric acid.

Standardisation of a Solution of Sodium Hydroxide by means of pure crystallised Oxalic Acid, $H_2C_2O_4$, 2 H_2O.

The procedure is similar to that described above except that between 0·25 and 0·3 grm. oxalic acid is weighed instead

of soda crystal, that the sodium hydroxide solution is placed in the burette instead of the acid, and that phenolphthalein indicator is used instead of methyl red. The end-point is marked by a faint pink coloration, which must persist throughout the solution for at least half a minute.

Calculation—

$$H_2C_2O_4,\ 2\ H_2O + 2\ NaOH = Na_2C_2O_4 + 4\ H_2O.$$
$$90 + (2 \times 18) = 126 \qquad 2 \times 40.$$

The equivalent weight of oxalic acid crystals is therefore $126 \div 2 = 63$.* Hence 63 grm. $H_2C_2O_4,\ 2\ H_2O$ is required to produce 1000 c.c. of normal solution, and assuming the weight of the oxalic acid crystals used in the experiment to be 0·28 grm. and the volume of sodium hydroxide solution required for neutralisation to be 13·35 c.c., then the volume of normal solution corresponding to this weight of crystals is—

$$\frac{1000 \times 0{\cdot}28}{63} = 4{\cdot}45 \text{ c.c.}$$

Therefore,

$$13{\cdot}35 \text{ c.c. } x \text{ N . NaOH} \equiv 4{\cdot}45 \text{ c.c. N . } H_2C_2O_4,\ 2\ H_2O$$
$$x \text{ N} \equiv \frac{4{\cdot}45}{13{\cdot}35} \text{N} \equiv 0{\cdot}333 \text{ N.}$$

The sodium hydroxide solution has a normality 0·333, and one litre contains $0{\cdot}333 \times 40 = 13{\cdot}32$ grm. sodium hydroxide.

Analysis of Ammonium Salts.

Weigh accurately about 0·5 to 1 grm. of, say, ammonium chloride in a beaker or other suitable vessel, dissolve it in 10 to 20 c.c. of water, run in exactly 20 c.c. (or other suitable excess) of normal sodium hydroxide solution, and heat the beaker on wire gauze until the liquid boils. Keep the liquid boiling for some time, taking care that no loss by spirting occurs, and that no solid is deposited on the wall of the beaker; periodically test the escaping steam for ammonia by holding in it a strip of moistened red litmus paper. When the liberated ammonia has been completely expelled, remove the beaker, cool somewhat, add a small quantity of water, and titrate the

* Note should be made that the equivalent weight of *anhydrous* oxalic acid is $90 \div 2 = 45$.

contents with standard acid solution. From the amount of residual alkali thus determined, the quantity of alkali used up in decomposing the ammonium salt can be easily found, and the proportion of NH_4 radical in the salt calculated—

$$NH_4Cl+NaOH=NaCl+NH_3+H_2O.$$

The method of calculation may be seen from the following example :—

Weight of crude ammonium chloride .	0·802 grm.
Volume of N . NaOH added . . .	20·0 c.c.
Volume of 0·75 N . HCl required for neutralisation of residual solution .	7·3 c.c.

7·3 c.c. 0·75 N . HCl $=7·3\times0·75=5·4$ c.c. N . HCl.

Hence $20·0-5·4=14·6$ c.c. N . NaOH has been used in decomposing the ammonium chloride.

Now 1000 c.c. N . NaOH liberates 17 grm. NH_3, corresponding to 18 grm. NH_4.

$\therefore$ 14·6 c.c. liberates NH_3 corresponding to—

$$\frac{18\times14·6}{1000}=0·2628 \text{ grm. } NH_4.$$

The percentage of ammonium in the crude ammonium chloride is, therefore,

$$\frac{0·2628\times100}{0·802}=32·77 \text{ per cent.}$$

(The percentage of ammonium in pure ammonium chloride is 33·66.)

This method can be used to determine the concentration of solutions of many ammonium salts. If the solution also contains free acid, the amount of this must be first determined by a preliminary titration, and allowed for in the calculation.

Determination of the Equivalent Weight and the Formula Weight of an Acid or an Alkali.

In the exercises in acidimetry and alkalimetry the normality and the concentration have been measured, making use of the relation : Concentration (grams per litre)=Normality $\times$ Gram Equivalent Weight. If the concentration and the normality are

known, then the gram equivalent weight can be calculated from the equation—

$$\text{Gram Equivalent Weight} = \frac{\text{Concentration (grams per litre)}}{\text{Normality}}$$

and if the basicity or acidity, as the case may be, of the acid or alkali is known, then the gram formula weight can be calculated.

Exercises.—(1) Determine the gram equivalent weight of the " weak " acid contained in the given solution of which one litre contains 6 grm. of acid, using phenolphthalein as indicator.

(2) Determine the gram formula weight of the " weak " crystalline acid, which is dibasic, using phenolphthalein as indicator. About 0·25 grm. crystals is a suitable quantity to use.

Similar exercises may be devised involving alkalimetry.

Oxidation by Potassium Permanganate.

In presence of an excess of sulphuric acid, potassium permanganate solution oxidises many substances and in doing so its dark violet colour disappears. Hence the completion of the oxidation process occurring when, *e.g.* potassium permanganate solution is gradually added to a solution of ferrous sulphate in dilute sulphuric acid, is easily observable owing to the permanganate being decolorised so long as any oxidisable ferrous salt is present, but immediately all the ferrous salt has been oxidised the addition of a drop of permanganate solution produces a permanent pink coloration. The reaction is represented by the following equations :—

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,[O].$$
$$2\,FeSO_4 + H_2SO_4 + [O] = Fe_2(SO_4)_3 + H_2O.$$

Care must be taken that a large excess of dilute sulphuric acid is added to the solution, otherwise the separation of a brown precipitate ($MnO(OH)_2$) may take place.

It is also to be noted that neither hydrochloric acid nor nitric acid may be used in place of sulphuric acid, the former acting to some extent as a reducing agent towards the permanganate and the latter as an oxidising agent towards the ferrous salt.

A normal solution of potassium permanganate contains 31·62 grm. of permanganate in one litre. For most purposes it is more convenient to use a decinormal solution, and this may be

got by weighing exactly 3·162 grm. pure crystals of potassium permanganate, dissolving the crystals in water and making the solution up to one litre by the addition of water. The dark violet prismatic crystals are not always pure, and it is advisable to standardise the solution by means of oxalic acid or ammonium ferrous sulphate (see p. 206).

Standardisation of Potassium Permanganate Solution by means of crystallised Oxalic Acid.

Oxalic acid and dilute sulphuric acid, at a temperature of about 60° C., form a mixture which reduces potassium permanganate. The oxidation of the oxalic acid may be represented thus—

$$\underset{126}{H_2C_2O_4}, 2\,H_2O + \underset{16}{[O]} = 2\,CO_2 + 3\,H_2O,$$

hence the oxalic acid present in 126÷2=63 grm. oxalic acid crystals is oxidised by 16÷2=8 grm. oxygen or 31·62 grm. potassium permanganate.

Procedure (see p. 200).—Weigh from 0·1 to 0·12 grm. oxalic acid crystals. Transfer the crystals to a conical flask through a funnel placed in the neck of the flask and wash down any traces adhering to the watch-glass or funnel by a jet of water. Add about 25 c.c. dilute sulphuric acid and heat the mixture to about 60° (the flask feels hot to the hand but not painfully so) and slowly run in the potassium permanganate solution from the burette. Owing to the intense colour of the permanganate solution, it is difficult to read the bottom of the meniscus, so the burette reading of the top edge is taken. The solution is heated so as to keep the temperature about 60°, and at first the local pink coloration due to the permanganate should completely disappear. If insufficient sulphuric acid is present, the solution becomes brown or a brown precipitate forms in it. In such case the experiment should be repeated, using a larger proportion of sulphuric acid. When the oxidation is nearly complete, the disappearance of the colour of each drop of permanganate added becomes slower and the reaction is complete when the pink coloration endures for more than two minutes.

Calculation.—Suppose the weight of oxalic acid crystals dissolved was 0·126 grm. and the solution of oxalic acid was oxidised by 25·0 c.c. potassium permanganate solution.

The volume of N. oxalic acid produced from 0·126 grm. oxalic acid crystals is

$$\frac{1000 \times 0{\cdot}126}{63} = 2{\cdot}0 \text{ c.c.}$$

hence $25{\cdot}0$ c.c. x N . $KMnO_4 \equiv 2$ c.c. N . $H_2C_2O_4$.

$$x = 2 \div 25 = 0{\cdot}08.$$

The solution is therefore 0·08 N . $KMnO_4$, and one litre of it contains $31{\cdot}62 \times 0{\cdot}08 = 2{\cdot}529$ grm. potassium permanganate.

The standardisation may also be effected by means of **ammonium ferrous sulphate,** $(NH_4)_2SO_4$, $FeSO_4$, 6 H_2O (formula weight 391·9), a salt which is easily obtainable in a pure state. The procedure is similar to that adopted for oxalic acid except that heating of the solution is unnecessary. Only the ferrous sulphate is oxidised according to the equation—

$$\underset{2 \times 151{\cdot}9}{2\,FeSO_4} + H_2SO_4 + \underset{16}{[O]} = Fe_2(SO_4)_3 + H_2O.$$

Now 391·9 grm. ammonium ferrous sulphate contains 151·9 grm. ferrous sulphate or 55·9 grm. iron, and this is oxidised by 8 grm. oxygen. Hence a normal solution of ammonium ferrous sulphate will be obtained by dissolving 391·9 grm. of the salt in water and making the solution up to one litre. To standardise an approximately 0·1 N . $KMnO_4$, it is advisable to use from 0·5 to 0·8 grm. ammonium ferrous sulphate.

Titration of Hydrogen Peroxide Solution.

Transfer 10 c.c. of the peroxide solution to a conical flask, add to it about 25 c.c. dilute sulphuric acid, and then slowly run in the standardised permanganate until a permanent pink coloration is obtained. If the hydrogen peroxide solution is a concentrated one it may be diluted to one-tenth or one-hundredth concentration by transferring 10 c.c. of it to a 100 c.c. or a 1000 c.c. flask, adding water until the solution reaches the graduation mark, and mixing thoroughly.

The reaction is represented thus—

$$\underset{34}{H_2O_2} + \underset{16}{[O]} = H_2O + O_2.$$

Thus $34 \div 2 = 17$ grm. hydrogen peroxide requires $16 \div 2 = 8$ grm. oxygen, hence one litre of N . H_2O_2 solution contains 17 grm. hydrogen peroxide.

Determinations involving the use of Sodium Thiosulphate and Iodine.

The equation representing the interaction of these two substances is

$$\underset{2\times158}{2\,Na_2S_2O_3} + \underset{2\times126{\cdot}9}{I_2} = 2\,NaI + \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6}.$$

A solution of iodine containing 126·9 grm. per litre is called a normal solution and, by convention, a solution containing 158 grm. sodium thiosulphate (corresponding to 248 grm. crystallised salt, $Na_2S_2O_3, 5\,H_2O$) is also called a normal solution. A decinormal solution of iodine is prepared by shaking up 12·69 grm. pure iodine with the solution obtained by dissolving about 22 grm. potassium iodide in about 25 c.c. of water, and, when the iodine has dissolved completely, making up the volume with water to a litre. An approximately decinormal solution of sodium thiosulphate can be prepared by dissolving 25 grm. of the crystals in water and making up the volume with water to a litre.

The thiosulphate is usually run from the burette into the iodine solution and the change from a dark brown to pale yellow and finally to a colourless solution is observable. The final change may be made much more obvious by the addition of a few drops of starch paste. Even traces of iodine colour starch intensely blue, and the colour disappears immediately the iodine has reacted with the thiosulphate. It is advisable not to add the starch paste until the iodine has nearly disappeared. The starch paste is most conveniently prepared by rubbing about a gram of starch with 10 c.c. of cold water and pouring the mixture into about 90 c.c. of boiling water. After allowing it to cool, the clear upper liquid is decanted off for use. A freshly prepared paste is much more sensitive than an old one.

Standardisation of Sodium Thiosulphate Solution.

Procedure.—Weigh accurately about 0·7 grm. pure copper foil and transfer it to a porcelain basin containing a mixture of 5 c.c. concentrated nitric acid and 5 c.c. water. On gently warming the acid, the copper will dissolve rapidly in it. Evaporate the solution almost to dryness, taking care to avoid

spirting. Dissolve the residue in hot water, adding, if necessary, two drops of concentrated hydrochloric acid to complete the solution. Add ammonia solution until a permanent precipitate is just obtained and redissolve the precipitate in the minimum quantity of acetic acid. Transfer the solution to a graduated 100 c.c. flask and, after rinsing the basin two or three times with water, make up the volume of the solution to the graduation mark by the addition of water. Invert the stoppered flask two or three times to ensure complete uniformity of the solution and then transfer 20 c.c. by the pipette into a flask, add 30 c.c. potassium iodide solution (concentration 15 grm. per litre). Titrate the solution with the thiosulphate solution. Repeat with a second 20 c.c. of solution and, if results are not concordant, with a third 20 c.c.

The reactions are :—

$$3\,Cu+8\,HNO_3=3\,Cu(NO_3)_2+2\,NO+4\,H_2O.$$
$$Cu(NO_3)_2+2\,NH_4OH=Cu(OH)_2+2\,NH_4NO_3.$$
$$Cu(OH)_2+2\,HC_2H_3O_2=Cu(C_2H_3O_2)_2+2\,H_2O.$$
$$2\,Cu(C_2H_3O_2)_2+4\,KI=4\,KC_2H_3O_2+2\,CuI+I_2.$$
$$I_2+2\,Na_2S_2O_3=2\,NaI+Na_2S_4O_6.$$

Thus 63·5 grm. copper (as cupric acetate) is equivalent to 126·9 grm. iodine.

Calculation.—Suppose 0·72 grm. copper to be taken and the titrations for the first and second 20 c.c. to be 22·2 and 22·3 c.c. thiosulphate solution respectively. If the solution containing 0·72 grm. copper were normal it would occupy

$$\frac{1000\times0{\cdot}72}{63{\cdot}5}=11{\cdot}34\text{ c.c.}$$

Now 20 c.c. copper solution (one-fifth of the whole copper) is found to be equivalent to 22·25 c.c. thiosulphate solution, therefore the whole copper solution, which if normal would occupy 11·34 c.c., is equivalent to $5\times22{\cdot}25$ c.c. $=111{\cdot}25$ c.c., and hence 11·34 c.c. N . $Cu(C_2H_3O_2)_2\equiv111{\cdot}25$ c.c. x N . $Na_2S_2O_3$

$$x=\frac{11{\cdot}34}{111{\cdot}25}=0{\cdot}1019.$$

The sodium thiosulphate solution is 0·1019 N. and one litre of it contains $158\times0{\cdot}1019=16{\cdot}10$ grm. anhydrous sodium thiosulphate corresponding to 25·27 grm. crystals.

Determination of the Copper in a Solution of Cupric Sulphate.

The solution may be slightly acid with sulphuric acid or acetic acid, but must be free from hydrochloric and nitric acids. Transfer 10 c.c. of the solution to a flask and add to it considerable excess of potassium iodide solution, so that complete precipitation of the copper as cuprous iodide takes place according to the equation—

$$2\,CuSO_4 + 4\,KI = 2\,K_2SO_4 + 2\,CuI + I_2.$$

Then run in 0·1 N . $Na_2S_2O_3$ from the burette until the colour of the liquid has almost disappeared, and after the addition of a few drops of starch paste continue to run in the thiosulphate solution drop by drop until the blue colour disappears.

Calculation. — Suppose 10 c.c. cupric sulphate solution requires 22 c.c. 0·1028 N . $Na_2S_2O_3$,

then 10 c.c. x N . $CuSO_4$ = 22 c.c. 0·1028 N . $Na_2S_2O_3$

$$x = \frac{22}{10} \times 0{\cdot}1028 = 0{\cdot}2262.$$

The cupric sulphate solution is therefore 0·2262 N. and one litre of it contains $0{\cdot}2262 \times 63{\cdot}5 = 14{\cdot}36$ grm. copper.

Determination of the Percentage Weight of Copper in Brass.

Procedure. — The procedure is exactly similar to that described for the standardisation of sodium thiosulphate solution (see p. 207).

Calculation.—Suppose the following data—

Weight of brass taken = 0·550 grm.

20 c.c. of the solution requires 11·0 c.c. 0·1028 N . $Na_2S_2O_3$.

5×20 c.c. requires $5 \times 11 = 55$ c.c.

55 c.c. contains $55 \times 0{\cdot}1028 \times 0{\cdot}0635 = 0{\cdot}3590$ grm. copper

$$\frac{0{\cdot}3590 \times 100}{0{\cdot}55} = 65{\cdot}27 \text{ per cent. of copper in the brass.}$$

Standard Silver Nitrate Solution.

Various titrations may be carried out with silver nitrate solution. Neutral solutions of chlorides, bromides, and iodides

may be titrated directly using potassium chromate as indicator, the reactions being represented by the equations, *e.g.*—

$$NaCl + AgNO_3 = AgCl + NaNO_3.$$
$$K_2CrO_4 + 2\,AgNO_3 = Ag_2CrO_4 + 2\,KNO_3.$$

The precipitation of the silver chloride, bromide, or iodide is complete before the silver chromate begins to show itself permanently as a red precipitate.

Fluorescein (see p. 43) may also be used as an indicator in neutral solutions.

Acid solutions (nitric acid) of the chloride, bromide, or iodide may likewise be titrated by adding an excess of silver nitrate solution to, *e.g.* the chloride solution and then titrating the excess by potassium thiocyanate, using ferric indicator.* The equations representing the reactions are—

$$NaCl + AgNO_3 = AgCl + NaNO_3.$$
$$KCNS + AgNO_3 = AgCNS + KNO_3.$$
$$Fe_2(SO_4)_3 + 6\,KCNS = 2\,Fe(CNS)_3 + 3\,K_2SO_4.$$

The ferric thiocyanate colours the solution red when concentrated, but the appearance of a permanent pale brown coloration shows the beginning of the ferric thiocyanate formation.

Standardisation of Silver Nitrate Solution.

Three processes are described, of which the first and second are only applicable to neutral solutions, while the third requires the presence of free nitric acid.

I. (Gay-Lussac; Mohr). *Procedure.*—Weigh accurately from 0·10 to 0·12 grm. pure dry sodium chloride. Transfer it to a porcelain basin and dissolve it in about 50 c.c. of water. Add 1 c.c. of a 2 per cent. solution of potassium chromate and then run in the silver nitrate solution from the burette, constantly stirring the mixture. When the locally formed red precipitate disappears only slowly, add the silver solution drop by drop until a faint reddish tinge persists after brisk stirring.

Repeat the process until at least two concordant results are obtained.

* The ferric indicator may be prepared by dissolving 5 grm. ammonium iron alum in 50 c.c. water.

Calculation. — Suppose 0·117 grm. sodium chloride corresponds to 18·0 c.c. of silver nitrate solution. Seeing 58·5 grm. sodium chloride is contained in 1000 c.c. N . NaCl, then 0·117 grm. will be contained in $\frac{0{\cdot}117 \times 1000}{58{\cdot}5} = 2{\cdot}0$ c.c. N . NaCl, but 18·0 c.c. x N . $AgNO_3$ was required, therefore the normality of the silver nitrate solution is $2{\cdot}0 \div 18{\cdot}0 = 0{\cdot}111$ N. and one litre of the solution contains $0{\cdot}111 \times 169{\cdot}9 = 18{\cdot}859$ grm. silver nitrate.

II. (Fajans). *Procedure.*—Weigh accurately between 0·6 and 0·8 grm. pure dry sodium chloride. Transfer the salt to a graduated 100 c.c. flask through a funnel placed in the neck of the flask, and wash down any traces adhering to the watch-glass or funnel by a jet of water. Add water until the flask is three-quarters full, and shake the contents until all the solid has dissolved. Then add more water until the 100 c.c. mark is reached, and finally invert the flask several times to secure uniform concentration of the salt solution.

Transfer 10 c.c. of the chloride solution to a PORCELAIN BASIN, add about 15 c.c. water and 10 drops of fluorescein solution (0·03 grm. fluorescein in 100 c.c. alcohol). Run in the silver nitrate solution from a burette, stirring vigorously all the time. The silver chloride does not coagulate until equilibrium is nearly reached, and then, at equilibrium, the clotted precipitate becomes rose-pink in colour. The titration should be done quickly in diffuse light, silver chloride being darkened rapidly in sunlight. Repeat the titration until concordant results are obtained. Calculate the normality and concentration of the silver nitrate solution as before.

III. (Volhard). *Procedure.* — Weigh accurately 0·09 to 0·11 grm. pure dry sodium chloride and dissolve it in about 20 c.c. of water in a conical flask. Add 1 c.c. of dilute nitric acid and 20 c.c. of silver nitrate solution. Shake the mixture until the precipitate settles in curdy form, leaving the supernatant liquid clear. Add 1 c.c. more of the silver nitrate solution. If excess of silver nitrate is already present, no further precipitation takes place. If the solution becomes turbid, repeat the shaking and add still another cubic centimetre of silver nitrate solution. Decant the clear solution through a filter into a porcelain basin and wash the precipitate with cold distilled water until all the silver nitrate is removed. To the filtrate and washings add 5 c.c. of ferric indicator and titrate the unused silver nitrate with thiocyanate solution.

Calculation.—Suppose 20·0 c.c. silver nitrate solution required 22·1 c.c. thiocyanate solution for titration. Suppose, further, that to 0·11 grm. sodium chloride 21·0 c.c. silver nitrate solution was added and the filtrate required 1·6 c.c. thiocyanate for titration of the excess of silver nitrate. Then 1·6 c.c. thiocyanate $\equiv 1{\cdot}6 \times \frac{20}{22{\cdot}1} = 1{\cdot}45$ c.c. silver nitrate solution.

Hence 0·11 grm. NaCl $\equiv 21{\cdot}0 - 1{\cdot}45 = 19{\cdot}55$ c.c. x N . $AgNO_3$.

Now 0·11 grm. NaCl $\equiv \frac{0{\cdot}11 \times 1000}{58{\cdot}5} = 1{\cdot}88$ c.c. N . $AgNO_3$,

and the normality of the silver nitrate solution is therefore $\frac{1{\cdot}88}{19{\cdot}55} = 0{\cdot}0962$ N. and one litre of the solution contains $169{\cdot}9 \times 0{\cdot}0962 = 16{\cdot}34$ grm. silver nitrate.

Titration of Silver Nitrate with Potassium (or Ammonium) Thiocyanate.

Transfer 20 c.c. of the silver nitrate solution to a porcelain basin, add 5 c.c. ferric indicator, and then run in the thiocyanate solution from the burette, constantly stirring the mixture. When the red colour locally produced begins to disappear slowly, add the thiocyanate drop by drop until a permanent reddish-brown coloration is obtained. As it is easier to observe the end-point by comparison of an uncompleted and a completed reaction, it is advisable after completing the first titration to add 1 c.c. silver nitrate solution, thus destroying the brown coloration, and keep this mixture for comparison with the product obtained in the second titration.

The normality of the thiocyanate solution may be calculated after the silver nitrate solution has been standardised by method III. above.

APPENDIX I.

EXPERIMENTS WITH SOME COMMON ORGANIC SUBSTANCES.

SUGARS.

APPLY the following treatment to each of the sugars supplied, viz. :—**Sucrose** (cane sugar) ; **Lactose** (milk sugar) ; **Maltose** (malt sugar) ; and **Glucose** (dextrose or grape sugar). Tabulate the results obtained.

1. **Taste** each of the sugars and indicate the order in which they stand as regards sweetness.

2. **Heat** each carefully in a silica spoon and record the observed phenomena.

3. Heat a small quantity of each with **concentrated sulphuric acid.**

4. Boil a small quantity of each for a short time with solution of **sodium hydroxide.**

5. Dissolve a small quantity of each in water, add **Fehling's solution** (see p. 234), and boil.

6. In the case of cane sugar, dissolve a small quantity in water, add a few drops of dilute **sulphuric acid**, and boil for 5-10 minutes. Make slightly alkaline with **sodium hydroxide**, add **Fehling's solution**, and boil.

ALCOHOLIC FERMENTATION.

Into a flask of about 200 c.c. capacity introduce 20 c.c. of glucose solution (100 grm. glucose, traces of calcium sulphate and ammonium phosphate, and one litre of water) and 1-2 c.c. of brewers' yeast. Plug the mouth of the flask with cotton-wool to prevent the access of dust and organisms which might interfere with the alcoholic fermentation. Set the flask aside for four or five days. Then (1) test the gas in the flask for carbon dioxide by means of lime water ; (2) fit a cork and bent-glass tube to the neck of the flask and let the longer limb of the tube pass down a test tube to act as a receiver. Gently heat the contents of the flask until the alcohol has all distilled

over into the receiver test tube, which should be immersed in cold water. Test the distillate by producing iodoform from it (see p. 218).

STARCH.

Insoluble in cold water. Partially soluble in boiling water. **Heat** in a silica spoon.

Prepare a solution (or, rather, a dilute mucilage) of starch : crush a gram of starch with a little cold water to form a paste ; pour the paste into 100 c.c. boiling water ; cool.

Experiments with Starch Mucilage :—

1. To 5 c.c. add one drop of **iodine** solution ; note the colour produced ; divide the mixture into three parts and treat as follows, recording the results :—

(*a*) **Heat** one part ; cool again.

(*b*) To another part add **sodium hydroxide** till strongly alkaline ; then add **hydrochloric acid** in excess.

(*c*) To the third part add **sodium thiosulphate**, drop by drop, until no further visible change takes place.

2. To 5 c.c. add **Fehling's solution**, and boil.

3. To 5 c.c. add a few drops of dilute **sulphuric acid** and boil for 5-10 minutes to effect hydrolysis ; make alkaline with **sodium hydroxide** ; then add **Fehling's solution**, and boil.

4. Take about 5 c.c. of the liquid into the mouth ; retain it for thirty seconds, allowing it to mix with the **saliva** ; then return it to an empty test tube, add **Fehling's solution**, and boil. (Note that healthy saliva is faintly alkaline. The action of the saliva on starch mucilage is inhibited by the addition to the latter of a few drops of dilute acetic acid.)

5. **Conversion of Starch into Dextrin and Glucose.**—To 50 c.c. of the mucilage add 5 c.c. of dilute **sulphuric acid** and keep boiling gently. Pour out into separate test tubes, at intervals of five minutes, samples each consisting of about 1 c.c. of the boiling liquid. Cool each of these 1 c.c. samples and add to each one drop of **iodine** solution. Compare the colours of the resulting liquids.

Conversion of Starch into Dextrin.—Heat dry starch powder over a small flame, in a porcelain dish, very carefully and with continuous stirring, until the colour of the whole is pale yellow. (Charring, with evolution of visible fumes, must be avoided.)

Allow the whole to cool ; shake up the powder with cold water and filter. Add one drop of **iodine** solution to the filtrate.

DEXTRIN.

Easily soluble in cold water, yielding a mucilaginous solution (British gum), which, if prepared from the commercial article, has a characteristic odour.

Heat a small quantity of dextrin in a silica spoon : it melts, darkens, and eventually chars, giving off acid fumes which have an odour resembling, to some extent, that of " burnt sugar."

Taste dextrin and note its slightly sweet taste.

To a solution of dextrin add a few drops of **iodine** solution. A reddish-brown colour is produced which, like the blue colour produced by iodine with starch, disappears when the liquid is heated and reappears when it is cooled again. Solutions containing both dextrin and starch yield with iodine more or less purple coloured liquids.

MALT.

Taste unmalted and malted barley.

Grind 25-30 pickles of malt to a coarse powder in a mortar, or take about a teaspoonful of ground malt. Place the powder in a small flask, add 20 c.c. of cold water and set aside for 24 hours. Then filter and

(*a*) Boil a small quantity of the filtrate with **Fehling's solution.**

(*b*) Reserve the remainder of the filtrate for Experiment 3 in the examination of Flour (see below).

WHEATEN FLOUR.

1. Heat a small quantity in a silica spoon.

2. **Test for Starch.**—Grind a small quantity of flour with enough cold water to produce a thin cream. Add one drop of this cream to half a test-tubeful of boiling water and boil again for a short time. After cooling the opalescent liquid add a drop of **iodine** solution and observe the formation of the dark blue coloration which this reagent imparts to starch.

3. To the aqueous extract of malt previously prepared (*b* in

the examination of Malt, see above) add about 2 grm. of flour and 100 c.c. of water, and set aside for 24 hours. Filter, then

(*a*) Test both residue and filtrate for starch by means of **iodine** solution.

(*b*) Boil a few drops of the filtrate with **Fehling's solution.**

4. **Test for Nitrogen.**—Grind a small quantity of flour with its own bulk of **soda-lime.** Heat the mixture in a sublimation tube and examine the escaping vapours for ammonia by means of moistened **turmeric paper** or **red litmus paper.**

5. **Preparation of Gluten from Flour.**—Mix about 5 grm. of flour with 2-3 c.c. of water to produce a stiff dough. Knead the dough with the fingers for a short time and allow it to stand for 20-30 minutes. Then tie it up in a piece of muslin and knead beneath the surface of some water in a porcelain basin until the greater part of the starch is washed through the muslin. A yellowish sticky mass of gluten remains.

If desired, a part of the washed-out starch may be obtained from the washing water in the basin by allowing the latter to stand until most of the granules settle out. The water can then be poured off and some of the residue tested with **iodine** solution, after boiling with water and cooling (see 2, above).

6. Flour contains compounds (*a*) of **Phosphorus** and (*b*) of **Potassium**: Heat in a small porcelain basin as much flour as will lie on a shilling, until charring takes place and the greater part of the carbonaceous matter of the charred mass has burned away. Crush the black mass with a glass rod from time to time during the heating, to aid the burning of the carbonaceous matter. When the residue is cold, powder it and transfer it to a test tube; boil it with dilute **nitric acid** and filter; then

(*a*) Test a small portion of the filtrate for phosphates by means of **ammonium molybdate** (see p. 147).

(*b*) Evaporate the remainder of the filtrate to dryness at a gentle heat. Dissolve the residue in two or three drops of water and test for potassium by means of alcoholic solution of **sodium bismuth thiosulphate** (see p. 133).

BREAD.

Heat a small quantity of bread crumb in a silica spoon: Observe charring, and escape of inflammable vapours.

Test bread crumb for starch and for sugar: Boil some

fragments of bread crumb with water; filter, and divide the filtrate into two parts—

(*a*) To one part add **iodine** solution.

(*b*) To the other part add **Fehling's solution,** and boil.

Heat some fragments of bread in a porcelain crucible until inflammable vapours are no longer evolved, and the greater part of the carbon of the charred mass has burned away. Powder the black residue; boil it with dilute **nitric acid** and filter; divide the filtrate into two parts—

(*a*) Test one part for phosphates by means of **ammonium molybdate.**

(*b*) Test the other part for chlorides by means of **silver nitrate.**

Test for Nitrogen.—Grind a small quantity of dried and powdered bread with its own bulk of **soda-lime** and heat the mixture in a sublimation tube. Examine the escaping vapours for ammonia by means of moistened **turmeric paper** or **red litmus paper.**

Test bread **crust** for dextrin: Shake up powdered bread crust for a few minutes with cold water and filter. Test a small quantity of the filtrate for dextrin by adding, drop by drop, a very dilute solution of **iodine.** Observe the coloration produced and compare it with that yielded by flour (see paragraph 2 in the examination of Flour, p. 215).

Carefully evaporate the remainder of the filtrate in a porcelain basin over a small flame; a sticky residue is left which consists mainly of dextrin.

ALCOHOL.

Common or ethyl alcohol, when free from impurities, is a colourless and nearly odourless liquid. It mixes with water in all proportions, diminution in volume taking place on mixing. If not too highly diluted with water, it burns with an almost non-luminous flame.

1. To a mixture of a solution of **potassium bichromate** and dilute **sulphuric acid,** in a test tube, add a few drops of alcohol and heat gently. The orange colour of the mixture changes to brown and afterwards (if sufficient alcohol has been employed) to green, and the characteristic odour of common aldehyde (acetaldehyde) can be recognised at the mouth of the tube—

$$CH_3 . CH_2OH + [O] = CH_3 . CHO + H_2O.$$

2. Mix 1 c.c. of a solution of **sodium hydroxide** with 1 c.c. of alcohol, then add a moderately concentrated solution of **iodine** in solution of potassium iodide until the mixture remains distinctly yellow when shaken up in the cold. On heating gently, the characteristic odour of iodoform can be recognised at the mouth of the tube and a pale yellow crystalline deposit of iodoform separates when the liquid cools.

3. Put 1 c.c. of alcohol into a dry test tube and add about a gram of solid **sodium acetate.** Then pour in carefully about 2 c.c. of concentrated **sulphuric acid** and heat gently. The pleasant and characteristic fruity odour of ethyl acetate can be recognised at the mouth of the tube (see p. 144).

4. To 5 c.c. of a cold saturated solution of **calcium sulphate** add 5 c.c. of alcohol. An immediate separation of calcium sulphate, as a white flocculent precipitate, takes place, the salt being much less soluble in dilute alcohol than in water.

5. To 2 c.c. of a cold saturated solution of **potassium hydrogen tartrate** add 5 c.c. of alcohol, mix thoroughly, and set aside for 5-10 minutes. A finely crystalline precipitate of potassium hydrogen tartrate slowly separates, the salt being more sparingly soluble in dilute alcohol than in water.

6. Place a small fragment of shellac or of sealing-wax in each of two test tubes. To one add 2 c.c. of water and to the other 2 c.c. of alcohol. Heat both gently and note what takes place in each case.

GLYCEROL.

Glycerol (or glycerine) is a colourless liquid of syrupy consistence. It mixes with water in all proportions.

To about 2-3 c.c. of glycerol in a test tube add twice its volume of water. The glycerol, being denser than water, remains for the most part as a separate layer at the bottom of the tube. Now shake vigorously, when the two liquids intermix completely to form a colourless solution. Use this solution for the following purposes :—

1. Taste the solution (or a drop of the original glycerol) and note that it is sweet.

2. In each of two test tubes place a small quantity of a solution of **cupric sulphate**, and to one add an equal volume of the solution of glycerol. Then to each add a solution of **sodium hydroxide.** A blue precipitate of cupric hydroxide

is produced in the tube which does not contain glycerol, but precipitation is prevented in the other by the glycerol.

3. To a solution of **borax** add **phenolphthalein**, when a red colour is produced. Then add some solution of glycerol. The red colour disappears, but it reappears on boiling provided too much glycerol has not been added.

Heat 1-2 c.c. of pure glycerol with some powdered **potassium hydrogen sulphate.** The elements of water are removed from the glycerol, with the formation of acrolein. Note the extremely pungent odour of the latter.

OLIVE OIL.

Olive oil is a non-drying oil—*i.e.* when smeared on a glass or metal surface and exposed to the air it does not dry (see Linseed Oil), but it tends to become rancid owing to decomposition. It is composed chiefly of olein (glyceryl oleate), with some palmitin and a small proportion of linolein.

1. Place a drop of olive oil on a piece of white paper and note the production of a translucent (oily) stain.

2. Add 2 c.c. of olive oil to 10-15 c.c. of water in a test tube, close the tube with the thumb, and shake vigorously. A turbid mixture results, but the oil does not dissolve in the water, and, being lighter than the latter, it gradually rises and floats as a separate layer on the surface. (See Experiment 3, under Soap, p. 221.)

3. Place 2 drops of olive oil in a dry test tube, add 2 c.c. of ether and shake. The oil dissolves in the ether. Pour the solution upon a watch-glass and leave it exposed to the air. The ether soon evaporates and oil-drops are left behind.*

4. **Saponification of Olive Oil.**—By heating to the boiling point a mixture of an aqueous solution of sodium hydroxide and olive oil, soap is slowly formed. The slow rate of the saponification is partly due to the oil not dissolving in the aqueous solution. In a small vessel not provided with a stirrer, the boiling is apt to be of an explosive character—" bumping " —causing the contents of the vessel to be ejected. In view of these facts it is preferable to carry out a small-scale experi-

* A semi-solid or a solid fat—say cocoa-nut oil or beef suet—might be used for this experiment instead of olive oil. On the evaporation of the ether, the fat left behind would resemble in consistence that originally dissolved in the solvent.

ment in the following manner, using alcohol and ether as solvents :—

Place 1 c.c. of olive oil in a 25 c.c. measuring-tube, add 2 c.c. of ether and shake gently till a homogeneous solution is obtained. Then add 10 c.c. of a 2 per cent. alcoholic solution of sodium hydroxide, cork the tube securely, mix the whole thoroughly, and set aside for a few hours, when the contents will set to a semi-solid mass of soap. Break up the latter with a glass rod and add 10 c.c. of water, when complete solution takes place and there is no separation of unsaponified oil. Shake the solution vigorously and observe the production of an abundant lather. Pour the solution into a solution of common salt and observe the precipitation of soap. (See Experiment 2, under Soap, p. 221.)

LINSEED OIL.

Linseed oil is a drying oil—*i.e.* when smeared on a glass or metal surface and exposed to the air it gradually becomes dry, owing to the formation of a solid resin-like product of oxidation which constitutes a continuous waterproof coating. On this account it is used for mixing with pigments, etc., in preparing oil-paint. It is composed mainly of the glyceryl esters of isolinolenic, linolenic, and linoleic acids, the first of these predominating largely. These esters are all unsaturated substances.

1. Crush two or three flax seeds on a piece of clean white paper and observe the production of oily stains.

2. To about 1 c.c. of linseed oil, in a test tube, add 2 c.c. of ether, and shake gently till a homogeneous solution is obtained ; then add 1 or 2 c.c. of **bromine water** and shake up. The bromine is rapidly removed from solution, forming addition compounds with the unsaturated constituents of the linseed oil. Similar additions of bromine water can be repeated several times before a permanent coloration, due to excess of bromine, is imparted to the mixture. This behaviour is not peculiar to linseed oil, but is common to unsaturated oils. Linseed oil takes up a larger proportion of bromine in this way, however, than almost any other oil.

In contrast with the behaviour of linseed oil towards bromine, that of cocoa-nut oil may be examined in an experiment similar to the foregoing. Cocoa-nut oil contains

unsaturated constituents to a small extent only, and takes up very little bromine.

3. **Saponification of Linseed Oil.**—Repeat Experiment 4 under Olive Oil, but substituting Linseed Oil for the latter. Note that the resulting soap is much more translucent than that obtained from Olive Oil.

SOAP.

Ordinary household hard soap consists mainly of sodium palmitate, stearate, and oleate.

1. Dissolve half a gram of shredded hard soap in 100 c.c. of hot distilled water. Cool the solution and filter it. Then to separate small portions add—

(*a*) Solution of **calcium chloride.** A white precipitate of calcium soap is formed which is insoluble in water.

(*b*) Solution of **magnesium sulphate.** A white precipitate of magnesium soap is formed which is insoluble in water.

(*c*) Dilute **sulphuric acid.** A white precipitate of fatty acids (palmitic, stearic, oleic) is formed which is insoluble in water and on heating separates as an oil.

(*d*) Solution of **phenolphthalein.** The mixture assumes a pink colour, indicating that the solution is alkaline.

2. Pour a small quantity of the solution of soap into about 15 c.c. of a solution of **common salt.** A white precipitate of soap separates because it is insoluble in the salt solution.

3. **Emulsifying power of Soap.**—Add 2 c.c. of **olive oil** to 10-15 c.c. of the solution of soap in a test tube, close the tube with the thumb and shake vigorously. A fine emulsion results, and the oil remains in suspension for many hours (see Experiment 2 under Olive Oil, p. 219).

4. Dissolve a fragment of soap in **alcohol** and add a drop of a solution of **phenolphthalein.** In the case of a good soap (which should not contain free alkali) this does not produce any coloration. Next, dilute largely with **water**: a coloration appears, which is due to the hydrolysis of the soap with the formation of free alkali (sodium hydroxide).

5. Boil half a gram of shredded soap for a short time with 10 c.c. of dilute **sulphuric acid.** The soap is decomposed with the formation of sodium sulphate and a mixture of free fatty acids. The latter forms a separate layer which floats on the aqueous solution and solidifies, on cooling, into a nearly colourless cake.

UREA.

Easily soluble in water.

Heat a few crystals of urea in a silica spoon, very gently, until they fuse and bubbles of ammonia are slowly evolved, but be careful to discontinue the heating before solidification takes place. Test for the ammonia by means of **red litmus paper**. By the loss of ammonia the urea is partly converted into biuret. Test for the latter as follows :—

Dissolve the residue in a small quantity of water; add **sodium hydroxide** and one or two drops of a dilute solution of **cupric sulphate.** The liquid assumes a violet-pink colour.

Heat another portion of urea more strongly in the silica spoon. Ammonia is given off and a solid infusible residue is left which consists of cyanuric acid and biuret.

Prepare a concentrated solution of urea by dissolving the crystals in a very small quantity of water. Test as follows :—

1. To a few drops of the solution, on a watch-glass, add the same quantity of a saturated solution of **oxalic acid**. Crystals of urea oxalate, $2\,CO(NH_2)_2$, $H_2C_2O_4$, slowly separate.

2. To a few drops of the solution, on a watch-glass, add the same quantity of **concentrated nitric acid.** Crystals of urea nitrate, $CO(NH_2)_2$, HNO_3, slowly separate.

3. To a portion of the solution add **sodium hydroxide** and boil. Ammonia is evolved.

4. To another portion add a dilute solution of **mercuric nitrate**. A white basic precipitate, $2\,CO(NH_2)_2$, $Hg(NO_3)_2$, $3\,HgO$, is formed.

5. To another portion add **bleaching solution** (or alkaline solution of **sodium hypochlorite** or **hypobromite**) and warm gently. Nitrogen is evolved.

6. To another portion add **potassium nitrite** and dilute **hydrochloric acid.** A brisk evolution of a mixture of nitrogen and carbon dioxide takes place in the cold.

BONE.

Bone contains about 33 per cent. of organic matter, of which a large proportion is nitrogenous and some is fatty; and it yields about 67 per cent. of ash. The ash consists mainly of

calcium phosphate, with smaller quantities of calcium carbonate and of magnesium phosphate and carbonate.

Heat a small fragment of bone on a platinum wire in the Bunsen flame. Observe that it blackens, that it gives off combustible vapours which have an unpleasant odour, and that on sufficiently prolonged heating the black matter (carbon) burns away and a white residue (bone ash) is left.

Test bone—

(*a*) For nitrogen, by heating some bone meal with **soda-lime** and examining the escaping vapours for ammonia by means of **red litmus paper.**

(*b*) For phosphates, by boiling some bone meal with dilute **nitric acid**, filtering and testing a few drops of the filtrate by means of **ammonium molybdate.** The portion of the bone meal which remains undissolved by dilute nitric acid consists mainly of nitrogenous organic matter (ossein).

Examination of Bone Ash :—

Dissolve half a gram of bone ash (as much as will lie on a sixpence) in hot dilute **hydrochloric acid**. Observe the evolution of gas bubbles (carbon dioxide) when the acid is first poured upon the ash. If the solution is not quite clear on boiling, filter it. To the filtrate add **ammonia** in excess ; filter ; wash the precipitate on the filter paper three or four times with hot distilled water, rejecting the washings :—

Precipitate	**Filtrate**
Consists of $Ca_3(PO_4)_2$. Dissolve a small portion in acetic acid and add $(NH_4)_2C_2O_4$ until no further precipitate is formed. Boil, cool, and filter :—	Contains $CaCl_2$ and $MgCl_2$. Add $(NH_4)_2C_2O_4$ until no further precipitate is formed. Boil, cool, and filter :—
Precipitate	**Filtrate**	**Precipitate**	**Filtrate**
Consists of CaC_2O_4. Dissolve in HCl and apply flame test.	Contains PO_4. Add NH_4Cl, NH_4OH in excess, and $MgSO_4$. Precipitate of NH_4MgPO_4.	Consists of CaC_2O_4 (from Ca present as carbonate in the bone ash). Dissolve in HCl and apply flame test.	Contains Mg. Evaporate to dryness and ignite. Heat residue with a few drops of dilute HCl and filter. To filtrate add NH_4OH in excess and $(NH_4)_2HPO_4$. Precipitate of NH_4MgPO_4 on standing.

WOOL ; SILK ; HAIR ; FEATHERS (Nitrogenous animal substances). COTTON ; LINEN (Non-nitrogenous vegetable fibres).

Hold a small fragment of each of the above in a flame. In the case of the animal substances the part heated burns with intumescence, forming rounded black carbonaceous masses ; the burning usually ceases on withdrawal from the flame, and the volatile products evolved have a characteristic disagreeable odour. The vegetable fibres burn without intumescence or the production of disagreeably smelling volatile products, and the burning usually continues after withdrawal from the flame.

Examine each of the above for nitrogen by heating in a sublimation tube with **soda-lime** and testing for the evolution of ammonia.

Boil a fragment of wool with solution of **sodium hydroxide** for two or three minutes. Cool the liquid, divide it into two parts, and test for the presence of a sulphide by adding—

1. **Lead acetate** : a brown coloration or a black precipitate appears.
2. **Sodium nitroprusside** : a violet coloration is produced.

Boil a fragment of cotton with solution of **sodium hydroxide**, and compare the result with the above.

Place a woollen thread and a cotton thread in a test tube, add a small quantity of **concentrated nitric acid** and heat carefully till just boiling. Then dilute largely with cold water, wash thoroughly, and compare the effects produced upon the two materials.

Place a woollen thread, a cotton thread, a silk thread, a linen thread, and a small white feather in a test tube, add a solution of " **Crystal Scarlet** " * and a few drops of **acetic acid**, and boil for one minute. Wash thoroughly with water and compare the effects produced upon the various materials.

MILK.

Cow's milk usually contains about 87·5 per cent. of water and about 12·5 per cent. of other substances (proteins, fat, sugar, mineral matter) partly in solution and partly in suspension. Approximately, the proteins and the fat amount to 3·5 per cent.

* Many other colouring matters may be employed for this test—*e.g.* picric acid (yellow) or indigo-carmine (blue).

each, the sugar to 4·7 per cent., and the mineral matter to 0·75 per cent. The mineral matter (ash) consists mainly of combined potassium, sodium, calcium, phosphorus, and chlorine, with iron, magnesium, and sulphur in smaller proportions.

Examine the reaction of milk by means of **red** and **blue litmus papers.**

In a cubic centimetre measuring tube measure 15 c.c. of fresh milk, add five or six drops of dilute **sulphuric acid** and mix thoroughly. Observe the result. Allow the mixture to stand for a few minutes; then shake the tube and its contents vigorously to break up the curd and pour upon a filter paper, previously moistened with water.

<table>
<tr>
<td>Residue (Curd).
Consists mainly of casein and fat. Wash with water and then dry the filter paper with its contents on a water bath—i.e. place it in a porcelain basin and heat over water boiling in a beaker. As the whole becomes dry, grease marks will appear on the paper due to the fat (butter). Casein remains.
Mix part of the casein with soda-lime and heat in a sublimation tube: test the escaping vapours for ammonia by means of red litmus paper.</td>
<td colspan="3">Filtrate.
Contains milk sugar (lactose) and inorganic salts. Divide into three parts :—
<table>
<tr>
<td>(1)
Make alkaline with NaOH. Divide into two parts :—
<table>
<tr>
<td>(1)
Add Fehling's solution and boil.</td>
<td>(2)
Acidify with acetic acid and test for Ca by means of $(NH_4)_2C_2O_4$.</td>
</tr>
</table>
</td>
<td>(2)
Test a few drops for PO_4 by means of ammonium molybdate.</td>
<td>(3)
Test for Cl by means of $AgNO_3$.</td>
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ALBUMEN.

A solution of egg albumen is prepared by separating the white of raw eggs from the yolks, shaking up the former thoroughly with cold water and then filtering (or allowing to settle and pouring off the clear liquid).

Evaporate a few drops of this solution to dryness in a silica spoon and heat the residue more strongly. Observe the charring, and notice the odour of the escaping fumes.

Evaporate about 5 c.c. to dryness in a porcelain basin, carefully avoiding charring. Mix the dry residue with **soda-lime**, heat in a sublimation tube, and test for the evolution of ammonia.

To successive small portions of the solution add—

1. **Nitric acid.** A white precipitate is formed, which turns yellow on boiling. On adding **ammonia**, the yellow precipitate turns orange.

2. Solution of **sodium hydroxide** and a drop of **cupric sulphate** solution. A violet colour is produced which becomes deeper on warming.

3. Solution of **mercuric chloride.** The albumen separates as a white precipitate.

4. Solution of **salicylsulphonic acid** (see p. 231). Pour the albumen solution into a test tube containing a half c.c. reagent, so as to form a layer on the top of the reagent. A white film or a precipitate is formed above the interface of the solution and reagent.

5. Solution of **lead acetate**, then **sodium hydroxide** until the precipitate at first formed redissolves. On boiling, a black precipitate of lead sulphide is produced, proving the presence of sulphur in albumen.

DRIED BLOOD.

Dried blood contains about 80 per cent. of nitrogenous organic matter and it yields about 8 per cent. of ash. The ash contains combined potassium, sodium, phosphorus, and chlorine in considerable proportions, and smaller quantities of iron and calcium.

Heat a very small quantity in a silica spoon : observe the charring, and notice the odour of the escaping fumes.

Test for nitrogen : Mix a small quantity with twice its bulk of **soda-lime** and heat the mixture in a sublimation tube. Examine the escaping vapours for ammonia by means of moistened **turmeric paper** or **red litmus paper.**

Heat as much dried blood as will lie on a shilling, in a small porcelain basin, until the escape of a large quantity of inflammable volatile matter has ceased and a voluminous charred mass remains. When the residue is cold, powder it and transfer it to a test tube ; boil it with 6-8 c.c. of dilute **nitric acid** and filter ; then make the following tests :—

1. Test a small portion of the filtrate for phosphates by means of **ammonium molybdate.**

2. Test another small portion for chlorides by means of **silver nitrate.**

3. Test another small portion for iron by means of **potassium ferrocyanide** or **potassium thiocyanate.**

4. Test one-half of the remainder for calcium by adding **ammonia** in slight excess, dissolving the resulting precipitate (which consists mainly of phosphates) in dilute **acetic acid**, and then adding **ammonium oxalate.**

5. Test the other half of the remainder for potassium and sodium by evaporating it to dryness at a gentle heat, dissolving the residue in two or three drops of water, and then

(*a*) Adding one drop of the resulting solution to an alcoholic solution of **sodium bismuth thiosulphate** (see p. 133).

(*b*) Applying the flame test for sodium and potassium to the rest of the liquid.

WOOD.

When quite dry, wood contains about 99 per cent. of organic matter and yields about 1 per cent. of ash. The greater part of the organic matter consists of non-nitrogenous substances (chiefly cellulose and lignin). The total nitrogen in wood amounts to about 1 per cent. The ash consists mainly of calcium, magnesium, and potassium carbonates, phosphates, and sulphates.

Heat some sawdust, or other wood fragments, in a dry test tube. Observe that the volatile matters evolved are combustible and that they redden blue litmus paper. (They contain vapour of free acetic acid.) Wood charcoal remains in the test tube.

Grind up some fine sawdust with **soda-lime**; then heat the mixture in a sublimation tube, and test by means of **red litmus paper** for the evolution of ammonia.

The ash of wood may be examined for the potassium and the phosphates which it contains, but this need not be repeated here if it has already been done with the ash of flour (see p. 216).

PLANT ASH.

Burn some dried plant parts (such as hay, straw, leaves, twigs, seeds, etc.) in a porcelain basin and heat the charred residue until most of the carbon has burned away and a white, or nearly white, ash remains. Boil the ash for a minute or two

with dilute **nitric acid** and filter the solution. Test successive small portions of the filtrate—

(*a*) and (*b*) For phosphates and for potassium as directed under (*a*) and (*b*), paragraph 6, in the examination of Flour (see p. 216).

(*c*) For sulphates by adding **barium nitrate** and allowing to stand, if necessary, for 5-10 minutes.

(*d*) For iron by means of **potassium thiocyanate.**

(*e*) For calcium by adding **ammonium chloride** and slight excess of **ammonia**, filtering if not perfectly clear, adding **ammonium oxalate** to the filtrate, and boiling. After the removal of the precipitated calcium oxalate, magnesium may be tested for in the filtrate, as in the examination of bone ash.

The quantities of ash obtained from different plant parts vary considerably, as do also the relative proportions of the several ash constituents. Sometimes, therefore, only faint indications are obtained on examining the ash derived from the small quantity of plant material employed.

APPENDIX II.

NOTES ON THE COMMONER REAGENTS.

THE following is a list of the commoner reagents which it is convenient to have on the shelves of the working benches. It is not unusual for some of these reagents to be employed in a much more concentrated state than that here indicated. It is advisable, however, to study chemical reactions with somewhat dilute solutions, both of reagent and of the substance under examination, and the concentrations here given are amply sufficient for all ordinary work. In order to give some idea of the equivalent concentrations, the approximate normality (p. 188) of the solution has been indicated within brackets, N standing for normal. In the case of the various salts, the formula given shows the amount of water of crystallisation (if any) of the solid which is commonly procurable.

ACIDS.

Hydrochloric acid, HCl.—Two solutions are generally employed, one concentrated and the other dilute; for the operations described in this book, however, one solution of moderate concentration (2 N) is all that is necessary. Such a solution may be prepared by diluting one part of the concentrated solution to five times its volume. Hydrochloric acid is employed both for its acid properties (solvent, etc.) and as a soluble chloride (precipitation of insoluble chlorides).

Nitric acid, HNO_3.—Except where otherwise specified under some of the preparations, the dilute acid obtained by diluting one part of ordinary concentrated nitric acid to ten times its volume (2 N) is sufficient for all purposes. Nitric acid is employed chiefly for its acid properties; also as an oxidising agent.

Sulphuric acid, H_2SO_4.—For some purposes pure concentrated sulphuric acid has to be employed. Great care is necessary in using this reagent. If it has to be mixed with water or an aqueous solution, the acid should invariably be added last; the test tube containing the other liquid should be held

in a slanting position and the sulphuric acid allowed to run to the bottom in a steady stream along the wall of the tube; when enough has been introduced, the two layers are to be mixed by gently oscillating the tube. On no account should the tube be closed by the thumb and shaken in the usual way, as the acid liquid is almost certain to be forced out, owing to the expansion of the air in the tube, caused by the heat evolved when sulphuric acid and water are mixed. Concentrated sulphuric acid should never be added to a hot liquid. Special care is also necessary when sulphuric acid is warmed, as it is difficult to prevent it being ejected by "bumping"; in such cases the liquid should be kept in gentle motion by agitation of the tube. As a reagent, concentrated sulphuric acid is employed (along with manganese dioxide) in testing for the halogens; also for nitrates, chlorates, etc. It is a powerful dehydrating agent, and should be kept closely stoppered (not corked, as it chars organic matter) to prevent it absorbing moisture from the air.

Dilute sulphuric acid.—A solution obtained by diluting one part of the acid to ten times its volume (4 N) is of convenient concentration. It is used for its acid properties, especially in cases where hydrochloric or nitric acid is inadmissible, and also as a soluble sulphate.

Acetic acid, $HC_2H_3O_2$ or HA.—A solution containing about 100 grm. of the acid in the litre (2 N) will serve. It is used in cases where a comparatively weak acid is required. Acetic acid can dissolve the insoluble salts of weak acids (*e.g.* carbonates, borates), but those of moderately strong acids are attacked only to a much slighter extent (*e.g.* oxalates).

Hydriodic acid, HI.—The gas is obtained by placing in a 4-oz. wide-mouthed stoppered bottle small quantities of red phosphorus and of iodine and moistening the mixture with a very little water. The bottle should be kept stoppered and the stopper removed only when an oxide film is to be exposed to the hydriodic acid.

Hydrogen sulphide, H_2S.—A saturated aqueous solution of the gas (water dissolves about three times its volume at ordinary temperatures). The bottle containing the solution must be kept closely corked when not in use; otherwise the sulphide either escapes as gas, or is oxidised by oxygen dissolved from the air, sulphur being liberated and giving the solution a milky appearance. Unless the solution smells strongly of the gas, it is of no use as a reagent. (Note that if small quantities of

hydrogen sulphide are inhaled for even a moderate length of time, the sense of smell for that particular gas is temporarily lost.) Hydrogen sulphide is used chiefly for the precipitation of sulphides, especially from acid solution; it also acts as a reducing agent, generally with deposition of sulphur.

Salicylsulphonic acid, $C_6H_3 . SO_3H . OH . COOH$.—A solution obtained by dissolving 25 grm. in 100 c.c. water. Used in testing for albumen.

ALKALIES.

Sodium hydroxide, NaOH.—Solution containing about 80 grm. per litre (2 N). Employed chiefly for precipitation of metallic hydroxides, some of which dissolve in excess of the reagent; used generally as a strong alkali for neutralisation of acids, decomposition of ammonium salts, etc. The ordinary reagent always contains carbonate formed by absorption of carbon dioxide from the air.

Potassium hydroxide, KOH, is sometimes employed in place of sodium hydroxide, though there are a few differences between them in some comparatively unimportant reactions. The normal solution contains 56 grm. per litre.

Calcium hydroxide, $Ca(OH)_2$.—A saturated, but nevertheless very dilute, solution (lime water, 0·04 N). Used chiefly to test for carbon dioxide; also as an alkali. The reagent rapidly deteriorates on exposure to the air, owing to the formation of calcium carbonate, which is deposited.

Ammonia, NH_3.—A suitable solution may be obtained by diluting one part of the saturated solution to ten times its volume (2 N); ammonia solution contains both ammonium hydroxide, NH_4OH, and free ammonia, NH_3. In some of its reactions it behaves like a hydroxide, and gives the same precipitates as sodium hydroxide; in other cases its action is entirely different, giving rise to the formation of complex replaced ammonium salts, some of which are soluble, while others are insoluble. Also used as an alkali for the neutralisation of free acid; since the solution is less dense than water and most aqueous solutions, it is necessary, in using it as a reagent, to shake up the contents of the test tube (see p. 70) When ammonia solution is exposed to the air it becomes weaker owing to the gradual escape of ammonia; in course of time only water would remain.

SALTS, ETC.

Alcohol, C_2H_5OH.—A mixture of rectified (not methylated) spirit and water in about equal portions may be employed. Used as a reducing agent and also in testing for acetates.

Ammonium carbonate $(NH_4)_2CO_3$.—Commercial "ammonium carbonate" is largely ammonium hydrogen carbonate mixed with ammonium carbamate. A suitable reagent (2 N) may be prepared from this by dissolving 80 grm. in a litre of water, and adding about 20 c.c. of saturated ammonia solution. Used for precipitating carbonates, and especially as a constituent of the group reagent for the calcium group of metals. Ammonium carbonate solution gradually loses ammonia on exposure to air, and becomes bicarbonate.

Ammonium chloride, NH_4Cl.—A solution obtained by dissolving 100 grm. in the litre (2 N). Used sometimes as a soluble chloride; for distinguishing between zinc and aluminium; also as a constituent of the group reagents for the metals of the iron and calcium groups, since it prevents magnesium salts from being precipitated by ammonia, ammonium hydrosulphide, or ammonium carbonate (but not by a phosphate in presence of ammonia).

Ammonium hydrosulphide, NH_4HS.—A solution obtained by the action of hydrogen sulphide on moderately concentrated (4 N) ammonia solution. Used as a soluble sulphide for precipitation of sulphides insoluble in water and alkalies, and also as a soluble thio-base to dissolve certain sulphides insoluble in dilute acid. The reagent undergoes oxidation on exposure to the air, and becomes yellow owing to the formation of disulphide. On prolonged exposure to air the solution may again become colourless, owing to the disulphide undergoing further oxidation to form thiosulphate.

Ammonium molybdate.—A solution obtained by dissolving 145 grm. ammonium molybdate in 700 c.c. of 8 per cent. ammonia, and slowly pouring this solution into 1800 c.c. of cold diluted nitric acid (900 c.c. concentrated acid diluted with 900 c.c. distilled water). After allowing the precipitate to settle, the clear liquid is decanted. Used in testing for phosphates.

Ammonium oxalate $(NH_4)_2C_2O_4$, H_2O.—A solution obtained by dissolving 20 grm. in the litre (0·3 N). Used as a soluble oxalate, specially for precipitating the metals of the calcium group.

Ammonium perchlorate, NH_4ClO_4.—A solution obtained by dissolving 120 grm. in the litre (N). Used in testing for potassium.

Ammonium phosphate, $(NH_4)_2HPO_4$.—A solution obtained by dissolving 40 grm. in the litre (N). Used along with ammonium chloride and ammonia, in testing for magnesium.

Barium nitrate, $Ba(NO_3)_2$.—A solution obtained by dissolving 25 grm. in the litre (0·2 N). Used in testing for acidic radicals, owing to the large number of its salts which are insoluble in water; of these, the sulphate alone is insoluble in dilute nitric acid.

Bleaching solution.—This solution contains calcium chloride, $CaCl_2$, and calcium hypochlorite, $Ca(ClO)_2$, and may be prepared by shaking up 100 grm. of bleaching powder with one litre of *cold* water, allowing the residue to settle, and siphoning off the clear liquid. The hypochlorite is the active constituent. Used as an oxidising agent; also as a source of chlorine, which is liberated on the addition of hydrochloric acid—the liquid may then be employed as **chlorine water**, since the calcium chloride and hydrochloric acid which are present are generally not objectionable. On exposure to air the calcium hypochlorite is decomposed, with liberation of hypochlorous acid and precipitation of calcium carbonate. In absence of air, it slowly changes at ordinary temperatures, or rapidly on heating, into a mixture of chlorate and chloride.

Calcium chloride, $CaCl_2$, $6\,H_2O$.—A solution obtained by dissolving 35 grm. in the litre (0·3 N). Used in testing for certain acidic radicals.

Calcium sulphate, $CaSO_4$, $2\,H_2O$.—A saturated solution of gypsum, containing about 2 grm. in the litre (0·02 N). Used for distinguishing calcium, strontium, and barium from one another. Another equally dilute sulphate solution would serve the same purpose; the calcium salt is chosen because it is impossible to prepare from it a solution which would be too concentrated.

Chlorine water.—A saturated aqueous solution of the gas (water dissolves about twice its volume at laboratory temperature). Unless the solution smells strongly of chlorine it is of no use as a reagent. Great care should be exercised in using this reagent owing to its irritant, poisonous nature. (See also Bleaching solution.)

Cupric sulphate, $CuSO_4$, $5\,H_2O$.—A solution obtained by

dissolving 30 grm. in the litre (0·25 N). Used in testing for arsenites, biuret, and albumen.

Fehling's solution is an alkaline solution of a cupric salt which is reduced by several of the sugars, when boiled with them, yielding a red precipitate of cuprous oxide. A reagent suitable for qualitative purposes can be obtained by employing the following solutions :—

A. 35 grm. of crystallised cupric sulphate dissolved in water and the solution made up to half a litre.

B. 170 grm. of sodium potassium tartrate and 60 grm. of sodium hydroxide dissolved in water and the solution made up to half a litre.

For use, *A* and *B* are to be mixed in equal proportions by volume. The mixture does not keep well, and should not be prepared in large quantity.

Ferric chloride, $FeCl_3$.—A solution obtained by dissolving 15 grm. ferric chloride (commercial solid) in water with addition of 10 c.c. of dilute hydrochloric acid and making the solution up to a litre. When used in testing for acidic radicals, such as formates and acetates, it should be neutralised by the addition of sodium hydroxide. It is also used in the preparation of ferric ferricyanide to test for reducing agents (see under test papers).

Ferrous sulphate, $FeSO_4$, $7\,H_2O$.—A solution obtained by dissolving 140 grm. in a litre of water (N), slightly acidified with sulphuric acid ; used chiefly in testing for nitrates, nitrites, and cyanides. On exposure to air oxidation takes place, and, in absence of acid, a rusty-looking precipitate is formed, consisting of basic ferric sulphate, $Fe_2O(SO_4)_2$. The presence of free acid does not prevent oxidation, but it prevents the precipitation, since soluble normal ferric sulphate is then formed.

Iodine, I_2.—Iodine does not dissolve to any great extent in pure water, but is easily soluble in solutions of iodides. A solution may be prepared by rubbing 2·5 grm. of iodine, and the same weight of potassium iodide, with a small quantity of water until completely dissolved, and then diluting to 1 litre (0·02 N). Used in testing for magnesium and for various reducing agents (sulphite, etc.).

Lead acetate, $Pb(C_2H_3O_2)_2$, $3\,H_2O$.—A solution obtained by dissolving 25 grm. in the litre (one-eighth N), slightly acidified with acetic acid. Used principally as a soluble lead salt in testing for a number of acidic radicals, and also for

detecting the presence of hydrogen sulphide (see under test papers).

Magnesia mixture.—For qualitative purposes this may be prepared by adding to magnesium sulphate solution (see below) about its own volume, first, of ammonium chloride solution, and then of ammonia solution. Used in testing for phosphates and arsenates.

Magnesium sulphate, $MgSO_4$, $7\,H_2O$.—A solution obtained by dissolving 25 grm. in the litre (0·2 N). Used for preparation of "Magnesia mixture."

Mercuric chloride, $HgCl_2$.—A solution obtained by dissolving 30 grm. in the litre (0·2 N). Used chiefly in testing for stannous salts and for iodides, and also employed in the preparation of Nessler's reagent.

Nessler's reagent.—For qualitative purposes this may be prepared when required by adding potassium iodide to mercuric chloride solution until the red precipitate of mercuric iodide is just dissolved in excess of potassium iodide, using as slight excess as possible. To the clear solution thus obtained, about its own volume of sodium hydroxide is then added; the resulting solution should be colourless, or, at most, pale yellow, without any distinct turbidity. Used in testing for ammonia and ammonium salts.

Potassium chromate, K_2CrO_4.—A solution obtained by dissolving 25 grm. in the litre (0·25 N). Used for precipitating chromates of the heavy metals and in the identification of barium, strontium, and calcium by means of the differences in solubility of the corresponding chromates; also, with addition of free acid, as a test for reducing agents.

Potassium ferricyanide, $K_3Fe(CN)_6$.—A solution obtained by dissolving 25 grm. per litre (0·2 N). Used chiefly for distinguishing ferric salts from ferrous; the former give a brown coloration only, the latter a blue precipitate. Also used for the preparation of ferric ferricyanide test paper (see p. 238).

Potassium ferrocyanide, $K_4Fe(CN)_6$, $3\,H_2O$.—A solution obtained by dissolving 25 grm. in the litre (0·2 N). Used for precipitating ferrocyanides. The ferrocyanides which are insoluble in water are insoluble in acids also, but are decomposed by alkalies, with formation of hydroxide unless this is itself soluble in the alkali. The reagent slowly decomposes on standing, and then gives a bluish coloration on the addition of acid.

Potassium iodide, KI.—A solution obtained by dissolving 15 grm. in the litre (0·1 N). Used chiefly in testing for the heavy metals and for the presence of oxidising gases (see under test papers).

Silver nitrate, $AgNO_3$.—A solution obtained by dissolving 12 grm. in the litre (0·07). Used in testing for acidic radicals and for various reducing agents (glucose, etc.).

Sodium carbonate, Na_2CO_3.—A solution obtained by dissolving 50 grm. of the anhydrous salt (or 140 grm. of the pure crystals, Na_2CO_3, 10 H_2O) in the litre (N).

Sodium hydrogen tartrate, $NaHC_4H_4O_6$, H_2O; ($NaH\bar{T}$).—A saturated solution of the salt in water (0·4 N). This reagent is used only in testing for potassium salts, with which it gives a white crystalline precipitate. If the original solution is alkaline, the reagent must be added until the mixture becomes decidedly acid.

Sodium nitroprusside, $Na_2Fe(NO)(CN)_5$, 2 H_2O.—A solution obtained by dissolving 15 grm. in the litre (0·1 N). Used in testing for sulphides. Being unstable, the solution should be prepared as required.

Sodium sulphite, Na_2SO_3, 7 H_2O.—A solution obtained by dissolving 50 grm. in the litre (0·4 N). Used as a reducing agent (generally in presence of acid). The solution undergoes oxidation on exposure to the air, and changes to sulphate.

Stannous chloride, $SnCl_2$, 2 H_2O.—The reagent (0·5 N) is conveniently obtained by dissolving 30 grm. of metallic tin in a litre of dilute (2 N) hydrochloric acid, when a considerable excess of hydrochloric acid will remain in the solution. Used as a powerful reducing agent, especially in testing for salts of mercury. The solution undergoes oxidation to the stannic condition on exposure to the air, and, in absence of free acid, would deposit a basic salt on standing.

Borax, $Na_2B_4O_7$, 10 H_2O.—Finely powdered solid salt. Used for bead reactions.

Manganese dioxide, MnO_2.—The powdered solid; it must be free from admixed chlorides, which are often present in commercial samples. Used in testing for halides.

Microcosmic salt, $NaNH_4HPO_4$, 4 H_2O, used like borax.

Potassium nitrate, KNO_3.—Finely powdered dry solid. Used as oxidising agent in sodium carbonate bead tests.

Sodium carbonate, Na_2CO_3. — Anhydrous salt finely powdered. Used for bead reactions.

TEST PAPERS.

For some purposes reagents are most conveniently applied in the form of test papers, *i.e.* strips of absorbent paper (filter paper) which have been dipped in a solution of the reagent. Certain varieties of test paper can be dried and preserved for an indefinite time, but others are best prepared freshly as required; the former may be purchased in the form of small books or rolls ready for use.

When a solution is being examined by means of test paper, there are two methods of procedure available: (1) the end of a strip of the appropriate paper may simply be dipped into a small quantity of the solution; or (2) a clean, thin glass rod may be dipped into the solution, so that a small drop will adhere when it is withdrawn, and this drop is brought into contact with a piece of the test paper.

When a gas is to be examined, the *moist* paper should be held with its free end just inside the mouth of the test tube or other vessel in which the gas is being evolved, care being taken that the paper never touches the walls of the tube. For the sake of convenience and certainty of manipulation, only the very tip of the paper strip should be moist, so that the greater part of the strip remains stiff; further, the strip should be decidedly narrower than the test tube—a width of about 5 mm. is ample. If the paper is supplied in sheets, it should be cut up cleanly with a knife or scissors, not torn into irregular pieces.

Ready-made Papers.

Blue litmus paper. Paper dipped in solution of litmus, and dried. Used to test for the presence of free acid, which produces a red stain.

Red litmus paper. Paper dipped in solution of litmus which has been reddened by the addition of the minimum quantity of acid, and dried. Used to test for free alkali, which produces a blue stain.

Turmeric paper (yellow). Paper dipped in solution of turmeric, and dried. Used to test for free alkali, which pro-

duces a brown stain; also for boric acid, which produces a reddish stain, which, in its turn, is changed to a greenish-black by alkalies.

Starch paper. Paper dipped in thin starch paste, and dried. (Many samples of paper contain starch as a dressing, and may be employed without being specially treated.) Used to test for free iodine, which produces a blue stain; also used, after moistening with potassium iodide solution, to test for oxidising gases which liberate iodine, and so produce a blue stain also.

Ready-made test papers must be preserved dry and clean.

Papers to be prepared as required.

Chromic acid paper. Paper dipped in a mixture of potassium chromate solution and dilute sulphuric acid. Used to test for reducing gases, which produce a greenish stain; the greenish colour may be so faint as to be scarcely noticeable, in which case it appears as if the reddish-yellow colour had simply been bleached. This test paper is not so sensitive as the ferric ferricyanide paper.

Ferric ferricyanide paper. Paper dipped in the brown solution obtained by mixing together ferric chloride and freshly prepared solution of potassium ferricyanide. Used to test for reducing gases, which produce a dark stain of Prussian blue.

Lead acetate paper. Paper dipped in solution of lead acetate. Used to test for hydrogen sulphide, which produces a black stain of lead sulphide.

Potassium iodide paper. Starch-free paper dipped in solution of potassium iodide. Used to test for oxidising gases, which produce a brown stain of free iodine; some of these, such as chlorine and bromine, subsequently bleach the stain, oxidising the iodine to iodic acid, which is colourless. (See also under Starch Paper.)

In preparing the papers noted in the last four paragraphs, the paper strip should *not be dipped* into the solution contained *in the reagent bottle.* Either a small quantity of the solution should be poured out into a watch-glass or other small vessel, and the paper dipped into this, or a drop of it should be allowed to fall directly on the paper to be moistened.

SET OF APPARATUS.

12 Test tubes, 6″ × ⅝″.
12 Test tubes, 6″ × ¾″.
Test tube brush.
Test tube stand.
2 Filter funnels. 2½ .
Flask, 500 ml. (wash bottle complete).
Flask graduated, stoppered, 100 ml.
Flask conical, 250 ml.
2 Flasks, 500 ml., 250 ml.
2 Beakers, 250 ml., 100 ml.
2 Watch glasses, 2″.
2 Crystallising dishes, 2¾″, 2″.
Burette, 30 ml.
Pipette, 10 ml.
Measuring cylinder, 25 ml.
2 Porcelain basins, 3½″, 3″.
2 Porcelain crucibles, 1½″, and lids.
Crucible holder.
Crucible tongs.
Pipeclay triangle, 2¼
2 Files, triangular and round.
2 Glass rods, 8″, 6″.
Rubber baton (for rod).
Silica spoon.
Blue glass.
Spatula, vulcanite, 4
Platinum wire.
Bottle, stoppered, 250 ml.
100 Filter papers, 9 cm., in box.
50 Labels, 2″ × 1″ in box.
Sponge.
Glass cloth.
2 Litmus books (red and blue).
Wire gauze, 6″ × 6″.
Set of weights, 50 grm. 0·01 grm., and rider.
*Retort stand.
*2 Bosses.
*Clamp (burette).
*2 Retort rings, 4″, 2

* Apparatus used in common by the several students (*e.g.* three) who occupy the same working bench at different hours.

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J. AND J. GRAY, PRINTERS, EDINBURGH

TABLE OF ATOMIC WEIGHTS.

Element.	Symbol.	Atomic Weight.
Aluminium	Al	27·0
Antimony	Sb	121·8
Arsenic	As	74·9
Barium	Ba	137·4
Bismuth	Bi	209·0
Boron	B	10·8
Bromine	Br	79·9
Cadmium	Cd	112·4
Calcium	Ca	40·1
Carbon	C	12·0
Chlorine	Cl	35·5
Chromium	Cr	52·0
Cobalt	Co	58·9
Copper	Cu	63·5
Fluorine	F	19·0
Hydrogen	H	1·0
Iodine	I	126·9
Iron	Fe	55·9
Lead	Pb	207·2
Lithium	Li	7·0
Magnesium	Mg	24·3
Manganese	Mn	55·0
Mercury	Hg	200·6
Nickel	Ni	58·7
Nitrogen	N	14·0
Oxygen	O	16·0
Phosphorus	P	31·0
Potassium	K	39·1
Silicon	Si	28·1
Silver	Ag	107·9
Sodium	Na	23·0
Strontium	Sr	87·6
Sulphur	S	32·0
Thallium	Tl	204·4
Tin	Sn	118·7
Titanium	Ti	47·9
Tungsten	W	184·0
Uranium	U	238·2
Vanadium	V	51·0
	Zn	65·4