Salts and their reactions : a text-book of practical chemistry / by Leonard Dobbin and Hugh Marshall.

Contributors

Doddin, Leonard, 1858-
Marshall, Hugh, 1868-1913.

Publication/Creation

Edinburgh : James Thin ; London : Simpkin, Marshall, 1912.

Persistent URL

https://wellcomecollection.org/works/c5zvq258

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AND THEIR
REACTIONS

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A Class-Book of Practical Chemistry

BY

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REVISED EDITION

EDINBURGH
JAMES THIN, 54 AND 55 SOUTH BRIDGE
Publisher to the University
LONDON: SIMPKIN, MARSHALL, AND COMPANY, LIMITED
1912

PREFACE TO REVISED EDITION

A RE-ISSUE of this book having become necessary, advantage has been taken of the opportunity to make a variety of emendations and additions, which the experience of its use by numerous teachers, as well as some of the recent changes and extensions in the training of Arts and Science Students, seemed to render desirable. The plan of the book as a whole, however, remains unaltered, only a slight rearrangement in the experimental sections having been made. The chief additions include some simple qualitative and quantitative experiments designed to familiarise students with methods of chemical manipulation; the descriptions of a few processes in volumetric analysis by means of standard solutions, in addition to those in simple acidimetry and alkalimetry formerly given; notes on the more important reactions of tartrates and citrates; and some additional dry-way tests. It may be that some of the additions go slightly beyond the scope of the title of the book and of the purposes for which it was originally designed, as indicated in the preface to the original edition, but they do not make demands upon the student which cannot be overtaken during a first year's experimental course.

As in the original edition, no attempt has been made to lay down a particular order in which the experimental work should be carried out, since the individual teacher will arrange this to meet the special requirements of his mode of teaching the subject of Chemistry. Hence, while the matter is presented with sufficiently methodical sequence, the order in which the different experimental sections are taken may be varied as considered desirable.

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APPENDIX:

ERRATA

Page 72, line 2 from foot, *for* "0·3" *read* "0·03."
,, 101, ,, 21 ,, top, *for* "254" *read* "127."

THE NATURE AND PROPERTIES OF SALTS

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 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 criteria for the classification. That 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 one of the vitriols or with oil of vitriol; and "aqua fortis," similarly obtained by distilling saltpetre 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* appears to be 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 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; the *volatile* *alkali*, obtained by sublimation from dried animal matters (urine, etc.). Subsequently, it was discovered 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 (soda), 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, 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 thus 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 combustion and similar processes. The metallic calces were then found to be compounds formed by the union of the metals—elements—with oxygen—also 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 was restricted to those substances 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 could not at that time be 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.

It was further assumed 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 what would now be called acid anhydrides). Consequently the acid corresponding to common salt (then called muriatic acid or spirit of salt) was supposed 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.

Looked at from the point of view indicated above, salts were 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 early part of the nineteenth century. It was then recognised to be untenable, owing to the gradual accumulation of a mass of evidence which was entirely opposed to the assumption that muriatic acid and its salts contained oxygen, so that these substances had now to be looked upon as compounds of an elementary substance—chlorine—with hydrogen and the metals respectively. This view 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 the later view as to the composition of muriatic acid (or, as it then came to be called, hydrochloric acid), a distinction was drawn between those acids which contained oxygen (oxygen acids) and those which did not (hydracids); but in course of time this 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 anhydrous oxides 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, the only difference being that in them the hydrogen was united to a complex group instead of to a single element, as is the case with the hydracids. 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: sulphuric acid, H_2SO_4, having all its hydrogen replaceable by metal, had as its salt radical the group SO_4, unstable by itself and unknown in the free state, but occurring as an essential part of all sulphates. This view of the constitution of acids is the one now generally accepted.

It is to be noted here that many acids contain hydrogen which is not "acidic," *i.e.*, is not replaceable by metals; such hydrogen forms part of the salt 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 salt 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 an intermediate position between normal salts and the bases, just as the acid salts stand between the normal salts and the acids. The typical bases are metallic oxides and hydroxides, and it may therefore be said that a basic salt is one which still contains oxygen or hydroxyl replaceable by salt radical. Thus, lead hydroxide is $Pb(OH)_2$, normal lead nitrate is $Pb(NO_3)_2$, and there is an intermediate basic salt, lead hydroxy-nitrate, $PbOHNO_3$.

Just as a salt radical may be either elementary or compound, so also the other part of a salt may be either simple 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*), 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 salt 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 salt 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 salt 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 the formation of metallic radicals or of salt radicals. Many metals themselves can form part of salt radicals, as shown by the position of manganese in potassium permanganate, $KMnO_4$, where the metallic radical is K and the salt radical MnO_4. In ammonium bichromate, $(NH_4)_2Cr_2O_7$, the metallic radical is ammonium and the salt 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 salt 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 salt radicals, it always constitutes the metallic radical 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 salt 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 salt 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 salt radical have quite different properties. Analogous cases are known among salt radicals; the formula for potassium manganate is K_2MnO_4, and that for potassium permanganate is $KMnO_4$. The salt 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 metallic radical, and the other salt 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 salt radical. In other words, all those salts which have a metallic radical in common behave similarly under certain conditions, and those which have a salt 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 salt radical; and the reactions of a salt are, in general, those of its metallic radical *plus* those of its salt 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 salt 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. At first sight this might be supposed to represent a sulphate, owing to the presence of SO_4 in it. Such is not the case, however, for the compound, when dissolved in water, does not behave like a sulphate. On the other hand, it has all the properties of an ammonium salt, and its metallic radical is therefore ammonium, NH_4, and the remainder is the salt 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. It is possible to prepare 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 salt radical being SO_4, and the metallic radicals H (the acidic hydrogen) and the group NCH_6.*

Within recent years there has been propounded and elaborated a theory which offers an ingenious, and so far satisfactory, explanation of the peculiarities exhibited by salts. It is really a theory as to the nature of salts in solution, especially in aqueous solution; for it is only in aqueous solution that the peculiarities of salts are strongly marked. Before proceeding to a short general statement of this theory, it is advisable to look more fully at the general nature of the reactions into which salts most readily enter.

Solubility of salts in water.—Very many salts are easily soluble in water, and can be crystallised from their solutions by evaporation of the solvent; in some cases the salt thus obtained under ordinary conditions is anhydrous (*e.g.*, K_2SO_4, $NaNO_3$, NH_4Cl), in many other cases it is combined with a definite amount of "water of crystallisation" (*e.g.*, $Na_2SO_4,10H_2O$; $BaCl_2,2H_2O$; $Cu(NO_3)_2,3H_2O$). The degree of solubility varies very much with different salts; 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 well 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. When vast quantities of solvent have to be considered, however, the amount of substance actually taken up in such cases may be very considerable, as shown by many of the effects observed in nature. Barium sulphate is commonly spoken of as insoluble, yet there have been found very large naturally-formed crystals, some weighing as much as fifty kilograms, which have been apparently deposited from solution. Barium sulphate requires about four hundred thousand times its weight of water to dissolve it, and even in laboratory work this solubility, slight though it appears, is often by no means negligible.

As a rule, the solubility of a salt increases with rise of temperature, sometimes only to a small extent, sometimes very

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* This radical is called methyl-ammonium, and its formula is written NH_3CH_3, to indicate that it corresponds to ammonium with the methyl group (CH_3) in place of one atom of hydrogen.

greatly. 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.

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 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 the state of equilibrium is established. The most certain method of starting crystallisation in such cases is to bring some of the solid salt (the merest trace suffices) into contact with the supersaturated solution. 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 case of strontium sulphate.

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 salt 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 salt radical (assuming that it is not one which itself gives rise to coloured salts); the corresponding statement holds true for the different salts of any salt 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 hydrated salt has a colour at least approximating to that of the aqueous solution, the anhydrous salt may have a totally different colour.

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 (or of salt radicals) between two salts when they are brought together; thus, if AY and BZ be taken as general formulæ for any two salts, double decomposition between these means the formation of the other two salts AZ and BY, in accordance with the equation—

$$AY + BZ = AZ + BY.$$

If either AZ or BY 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: When solutions of a silver salt (say the nitrate), and of a chloride (say barium chloride) are mixed, a white precipitate of silver chloride immediately forms, and barium nitrate remains dissolved—

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

When solutions of a barium salt, say the 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 cases both of the resulting salts may be insoluble, and in these, if suitable proportions of the original salts are taken, the resulting liquid may be free from all but the merest traces of dissolved substance—

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

Double decompositions such as these take place practically instantaneously, the precipitate appearing immediately the solutions are mixed, provided the latter are fairly concentrated. With exceedingly dilute solutions the precipitate appears more gradually, and in some cases, if the new salt is 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—

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

the resulting solution, however, contains a considerable quantity of potassium salt and of sulphate. 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? This problem is difficult to solve with certainty, but it would appear that action does take place in all such cases. The solution obtained by mixing together solutions containing two salts AY and BZ in equivalent proportions, coincides exactly in all its physical and other properties with that obtained by mixing similar solutions of the two salts AZ and BY; it must therefore be assumed that in both these cases action takes place, and that the state of affairs in the mixture is a balance expressed by the equation—

$$AY + BZ \rightleftharpoons AZ + BY,$$

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—

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

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.

Closely related in some respects to double decomposition are those actions in which one metal displaces another in a salt. Thus, when metallic iron is immersed in a solution of cupric sulphate, ferrous 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 salt 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 general reactions in aqueous solution, and especially in the matter of double decompositions, acids generally behave just like soluble salts of the same salt radical, and therefore might be looked upon merely 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 (to take a still better example) of ammonium salts.

As a matter of fact, in practical work, acids are frequently employed in preference to the corresponding salts of some other 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 used for precipitation.

Bases as a particular class of salts.—On similar general grounds the typical basic substances—namely, the metallic hydroxides—may be looked upon as a special class of salts, in which the salt radical is the hydroxyl group, OH. The soluble hydroxides (the alkalies and alkaline earths) exhibit a set of reactions peculiar to themselves, and enter into double decompositions like other salts, giving rise to precipitates consisting either of insoluble hydroxide or of an insoluble salt of the metal previously united to hydroxyl. Thus, when solutions of silver nitrate and a hydroxide are mixed, there is an immediate precipitation of silver hydroxide—

$$AgNO_3 + KOH = AgOH + KNO_3;$$

when solutions of barium hydroxide and a 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, H OH; as we should expect, it is a neutral substance. There are chemical actions, however, in some of which water behaves like a very feeble acid, and in others like a very feeble base; these will be referred to later. The mutual 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; it is, therefore, unfortunate that it has become customary to speak of *weak* sulphuric acid when *dilute* sulphuric acid is meant, and to call the undiluted acid *strong* sulphuric acid. 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.

One of the various methods which have been adopted for definitely measuring the relative strengths of acids, consists in determining the amounts of calcium oxalate dissolved by their solutions. If HX be taken as a general formula to represent the acid under consideration, the action on calcium oxalate may be represented by the equation—

$$CaC_2O_4 + 2HX \rightleftharpoons CaX_2 + H_2C_2O_4.$$

Assuming that the new salt, CaX_2, remains dissolved, the change will not become complete, owing to the reverse action of the oxalic acid upon the dissolved calcium salt, which tends to precipitate calcium oxalate. A balance is therefore established, as indicated in the above equation. The stronger the acid HX is, so much the more will the direct action preponderate; that is to say, the greater will be the amount of calcium oxalate decomposed (or, the greater will be the amount of calcium salt in solution). In order that the results obtained by this, or by any other appropriate method, 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.

When the relative strengths of equivalent solutions of different acids are measured, the values obtained vary exceedingly in different cases. 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.

The following table gives the numbers actually obtained by means of the calcium oxalate method for a few monobasic acids, at two different concentrations. In each case the value for nitric acid is taken = 100.

Acid.	Normal Solution.*	Decinormal Solution.*
Nitric	100	100
Hydrochloric	90	97·9
Hydrobromic	85·4	99·0
Chloric	93·2	99·8
Formic	2·33	12·9
Acetic	0·94	7·35

A fact which is well brought out by these numbers is the remarkable increase in relative strength which the weak acids undergo on dilution, as compared with the strong acids; apparently acids all tend to become equally strong as their concentration becomes less.

There are several other methods employed for determining the relative strengths (or *affinities*) of acids. Although widely different in character, they all give results of the same general order, the agreement between them being, on the whole, surprisingly good. As determined by some of these other methods, the strengths of sulphuric acid and phosphoric acid are respectively about 60 per cent. and 7 per cent. of that of nitric acid.

The relative strengths of bases can be determined by suitable methods, more or less resembling some of those applicable to acids, and the general results are analogous to those obtained in the case of the latter. The strongest bases are the hydroxides of the alkali metals, but those of the alkaline earth metals are very slightly inferior to them. Ammonia is very much weaker, however, and so also are the compounds known as replaced ammonias; to the latter group belong the complex bases known as alkaloids (this name being given to them on account of their chemical character being similar to that of the alkalies). A considerable number of hydroxides of compound metallic radicals are known, however, which are practically as strong bases as the alkalies themselves.

Many of those metallic hydroxides which are practically insoluble in water are very feeble bases, especially those derived from trivalent metallic radicals. In some cases these feebly basic hydroxides can also, in the presence of very strong bases, act as exceedingly feeble acids. In consequence of this, certain of the metallic hydroxides dissolve in excess of potassium hydroxide or sodium hydroxide solution, because they interact with these substances to produce salt-like compounds; the hydroxides of lead, zinc, and aluminium are examples.

In many cases, very weak bases and very weak acids do not interact to form salts, or at least, not in aqueous solution; in

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* See p. 41.

some cases salts can be formed under other conditions, and it is then found that the salts so produced are decomposed by 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 the common aluminium, ferric, and cupric salts exemplify the former state of affairs. These cases are intermediate in their character between the salts which yield neutral solutions and those compounds referred to in the preceding paragraph; partial hydrolysis takes place, with liberation of strong acid or strong base, as the case may be, and this produces its characteristic reaction in the solution of the salt. (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.

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, however, the substances first set free would appear to be the metallic radical and the salt 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 salt 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 salt radical, which travels towards the anode, as the *anion.*

Solutions of acids and alkalies also conduct, and are decomposed by, the electric current—*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 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 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. This improved relative conductivity of dilute solutions can be easily demonstrated as follows: An electrolytic cell is built up in the form of a tall rectangular box, having the bottom and one pair of opposite sides composed of non-conducting material (glass), while the remaining pair of sides is composed of (or lined with) metallic silver; these sides have terminals for connecting with a battery, and form the electrodes of the cell. If this cell is filled with pure water, no current will be indicated on closing the circuit through a suitable galvanometer; but, on removing the water and substituting a small quantity of a somewhat concentrated solution of silver nitrate, a current will pass. If pure water is now added in successive equal portions, and the liquids mixed, the current strength increases with each dilution, but the successive increments steadily become less and less, and at last cease to be recognisable. This experiment shows clearly that the effect produced by a given quantity of salt, under the conditions of the experiment, increases with increasing dilution, and asymptotically approaches a maximum value as the dilution approaches infinity. The conditions which may be specially noted are—(1) the constancy of the quantity of solute between the electrodes; (2) the constancy of the distance separating the electrodes; and (3) the proportional increase of the area of the electrodes, with increasing dilution.

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.

The exact determination of the conductivity of a solution presents difficulties over and above those met with in the case of metallic conductors, one of the principal of these being due to the effect known as *polarisation*. When these difficulties are obviated, however, the results obtained show that electrolytes obey the same general laws as metallic conductors do—Ohm's law holds in all cases, within the limits of experimental error.

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 $HCl : NaCl : \frac{CaCl_2}{2} : \frac{FeCl_3}{3}$. In the same way, if a current is passed through a series of salts of the same metallic radical, the quantity of metal liberated is the same in all cases, irrespective of the salt 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 salt 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. On the other hand, salts, as a class, do not undergo other reactions with any particular readiness. Notwithstanding the rapidity with which silver chloride is formed when solutions of a silver salt and a chloride are mixed, there is no precipitation of silver chloride when silver nitrate is added to a solution of potassium chlorate, $KClO_3$, since the formation of the precipitate would in this case involve the breaking up of the salt radical, ClO_3. 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 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 only 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.

There are serious practical difficulties which render it exceedingly troublesome to obtain even moderately accurate direct measurements of the osmotic pressure exerted by a solute. There are, however, certain effects, resulting from osmotic pressure, which lend themselves to exact determinations, and the measurement of such effects is now a matter of considerable importance. An idea of how it is that some of these effects are related to the osmotic pressure may be obtained from the following considerations. The pressure exerted by gas or vapour resists any change tending to reduce the volume occupied; correspondingly, the osmotic pressure of a solute resists any change tending to reduce the volume of the solution. Reduction of the volume of a solution involves the removal of the solvent; this is generally effected by evaporation, but the same results 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 of 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 molcular 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 could be calculated if its (osmotic) pressure, temperature, and mass-concentration were known. As has already been indicated, the direct measurement of the osmotic pressure cannot at present be carried out simply and accurately, 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, 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

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* The *concentration* of a substance is the weight, or rather the mass, of that substance contained in unit volume; to avoid ambiguity this is later on referred to as *mass-concentration*. The molecular concentration of a substance would be the number of molecules of that substance contained in unit volume; the absolute number cannot, of course, be determined, but an expression for the *relative* molecular concentration is obtained by dividing the concentration by the molecular weight.

$$Concentration = \frac{mass}{volume}. \qquad Molecular\ concentration = \frac{concentration}{molecular\ weight}.$$

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.

These discrepancies correspond closely with the apparent irregularities observed, in certain cases, when the method of determining molecular weights by means of vapour densities is employed, and such exceptional cases were the cause of much dubiety until they received a simple and satisfactory explanation. For example, it was found that the density of the vapour obtained by heating ammonium chloride was little more than half that which was expected, and which was necessary to justify the formula NH_4Cl. However, as soon as it was shown that ammonium chloride undergoes dissociation into ammonia and hydrochloric acid when it is heated, all the difficulty vanished; the vapour density which was determined was 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 ammonium chloride. At first sight, a similar explanation of the discrepancies observed in the case of dissolved salts, such as sodium chloride, seems hardly possible, for in that case a simple decomposition would result in the production of *free atoms* of sodium and chlorine; the occurrence of a double decomposition between the salt and water, such as that represented by the equation

$$NaCl + H_2O = NaOH + HCl,$$

would certainly result in doubling the number of molecules of solute, but the assumption of any such double decomposition is futile as an explanation of the abnormality of sodium chloride, since sodium hydroxide and hydrochloric acid are themselves similarly abnormal.

The ionisation hypothesis.—The theory which gives the most satisfactory explanation of the peculiarities of salts in solution adopts what is practically a double decomposition view, in which it is assumed, however, that the salt interacts, not with a chemical substance, but with electricity. According to this hypothesis, when a salt dissolves in water some of its molecules are resolved there and then into ions, consisting not of the free radicals themselves, but of these *united each with a definite quantity of electricity*, the charge being positive in the case of the cation and negative in the case of the anion. The charges thus assumed to form ions, positive or negative as the case may be, are all exactly equal; but a radical in forming an *ion* may assume one, two, or more charges, according to its chemical character, just as it may unite with one, two, or more atoms of, say, a halogen, or of a univalent metal, to form a *molecule* of a salt. In this connection it is therefore sometimes convenient to speak of the charges as "atoms" of positive or of negative electricity, resulting from the splitting up of "molecules" composed of both, and therefore electrically neutral.

The process of the formation of ions which is thus supposed to take place when a salt dissolves in water is frequently called "electrolytic dissociation," but there are certain objections to this expression. *Ionisation* is a convenient name, and will be adopted here.

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, adopts 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—

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

In all such cases the equation gives no indication whatsoever of the *extent* to which ionisation takes place; this may vary within the widest limits.

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 salt radical, exhibit the same group of reactions, which are said to be the reactions of that particular metallic radical or salt 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 $Fe(CN)_6''''$, 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 do not become appreciably ionised when dissolved in water; such substances are found to differ from the true (ionised) salts of the same metal in many of their reactions. Mercuric cyanide is a good example of such a case [see p. 104].

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.

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, 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

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

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

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

Consequently, owing to this increase in the concentration of the chlorine ions, an increased proportion of sodium ions and chlorine 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 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 :—

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

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 $\mathrm{Na}^{\cdot}$ 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.

In the laboratory it is not unusual to purify chlorides and nitrates which are easily soluble in water, by adding to their concentrated aqueous solutions either hydrochloric acid or nitric acid, as the case may be. 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. In such cases, however, 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, and the SO_4'' ions are in great measure changed to HSO_4' ions. 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, 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. 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 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 re-arrangement 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 :—

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

It is easy to see from the above 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—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 would begin to crystallise out if the evaporation were 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 everyday 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 reprecipitation, 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 practically complete, if either of the products is practically insoluble, and is therefore precipitated 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, 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

$$\begin{tikzcd}
 & & & BX & \\
AX \arrow[r, leftrightharpoons] & A^{\cdot} & + & X' \arrow[u, leftrightharpoons] & \\
 & + & & + & \\
 & Y' \arrow[d, leftrightharpoons] & + & B^{\cdot} \arrow[r, leftrightharpoons] & BY \\
 & AY & & &
\end{tikzcd}$$

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 chlorine 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

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

which uses ionic symbols, is in some respects preferable, since the particular reaction under consideration is independent of the source of the silver ions or of the chlorine ions.

The first of the above kinds of equations is used throughout the body of this book, but the student will find it an advantage to familiarise himself with the other kind by translating a considerable number of examples into the ionic form. In balancing such equations, it is necessary to pay particular attention to the electric 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 mostly ionised. Taking the case of hydrochloric acid and potassium hydroxide as an example, and representing it by the equation

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

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 them 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 ones obtained with strong acids and bases.

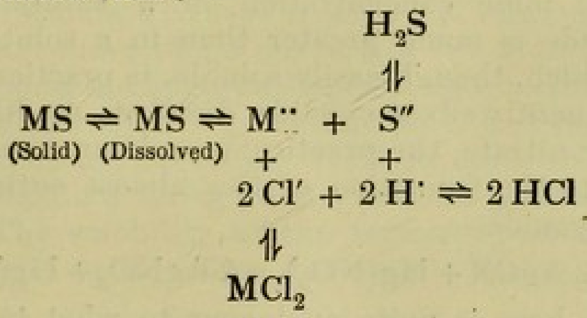
This particular kind of double decomposition is practically complete because one of the products—the water—is practically non-ionised. Perfectly pure water is an exceedingly poor conductor of electricity, but it is not absolutely non-conducting; for this and other reasons, it is necessary to assume the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

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 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 anions unite with the hydrogen ions of the acid present, 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 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, as referred to in connection with methods of measuring the relative strengths of acids.

While the great majority of such cases are quite simple of 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:—



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

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 $H^{\cdot}$ ions, so far diminish the ionisation of the hydrogen sulphide (see p. 26) that the latter becomes the least ionised product, whereupon the sulphide will begin to dissolve up.

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 salts "insoluble" in water is not due to a property peculiar to acids, but, as already mentioned (p. 29), 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 to what 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.

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

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 behave like a mixture of two cyanides, however. It contains $K^{\cdot}$ ions, but apparently practically no $Fe^{\cdot\cdot}$ ions or CN' ions; the metallic radical is potassium only, and the salt 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 further on in this book. Thus, practically all silver compounds (the only important exception is the sulphide) dissolve in solutions of thiosulphates and cyanides (*except mercuric cyanide*), giving rise to salts which do not behave as silver salts; in each case the silver forms part of the salt 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 $KAgS_2O_3$.

At first sight the double salts before referred to 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, on the other hand, a solution of the above-mentioned 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 one another, 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 uninterrupted varies with different salts, shows that different ions hold their charges with varying degrees of firmness.

It would appear from what has just been said 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. For reasons which need not be discussed here, they are of especial use in connection with acids.

Indicators.

Although weak acids are themselves very slightly ionised in solutions of such concentrations as are generally dealt with in laboratory work, the salts formed from them by means of strong bases are generally ionised to a far greater extent. The same is the case as regards weak bases and the salts formed from them by interaction with strong acids. This fact is of considerable importance in some respects; for example, in connection with its application to the theory of indicators, *i.e.*, of substances like litmus, the solutions of which change colour very decidedly when they are treated with a small quantity of acid or of alkali, and therefore indicate the presence of the one or the other in solution. The substances used practically as indicators are all highly complex carbon compounds, some of them (including those which have been long known) are derived from plants, but many now in use are artificially prepared dyes. The behaviour of some indicators is apparently due to special kinds of changes which cannot be discussed here, but probably in most cases it is due to the fact of the highly coloured substance being either a very weak acid or a very weak base. In either of these latter cases the solution will contain very few ions, and the colour will be due almost entirely to the non-ionised molecules of the substance itself. If the indicator has a feebly acid character, the addition of a small quantity of a strong base will result in the formation of a highly ionised salt, and the colour will now to a large extent come from the anions present in the solution; the change of colour will be the same for all strong bases. The addition of a strong acid to the solution will reproduce the non-ionised acid of the indicator, and the original colour will be restored. Similarly, if the indicator is a weak base, the addition of a small quantity of a strong acid will give rise to the formation of a highly ionised salt, and the colour of the solution will now be due chiefly to the complex cations of the salt; the change in this case will be the same for all strong acids, and will be reversed by any strong base. Generally speaking, therefore, any weak acid or base which has a colour sufficiently different from that of the ions derived from it in solution, may be used as an indicator. Some indicators appear to belong to the class of substances which can act as feeble bases towards strong acids and as feeble acids towards strong bases. In such cases three different colours may be observed :—that of the non-ionised compound in aqueous solution; that of the anions of the one class of salts, derived from it by interaction with strong bases; and that of the cations of the other class of salts, derived from it by interaction with strong acids. Some indicators are much more sensitive than others, that is to say, they show a distinct change of colour with a smaller addition of acid or of alkali; they may also indicate an acid or an alkaline reaction with substances which are apparently neutral to other indicators. These variations are in most cases due to the fact that the various indicators are not all equally weak acids or bases, as the case may be, and therefore are not all acted upon in exactly the same way by substances added to them.

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 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—

$$\begin{tikzcd}[row sep=small, column sep=tiny]
H_2O + Na_3PO_4 \rightleftharpoons 3\,Na^{\cdot} + & HPO_4'' \arrow[d, shift left] & + OH' \\
 & PO_4''' + H^{\cdot} \arrow[u, shift left] &
\end{tikzcd}$$

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—

$$\begin{tikzcd}[row sep=small, column sep=tiny]
 & NaOH \arrow[d, shift left] & & & \\
2\,Na^{\cdot} + & Na^{\cdot} \arrow[u, shift left] & + & PO_4''' & \rightleftharpoons Na_3PO_4 \\
 & + & & + & \\
H_2O \rightleftharpoons & OH' & + & H^{\cdot} \arrow[d, shift left] & \\
 & & & HPO_4'' \arrow[u, shift left] &
\end{tikzcd}$$

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.

In the preceding pages an attempt has been made to give a short and simple statement of the ionisation theory of salt solutions. There are many other interesting applications of the theory, to which it has been impossible to refer in limited space, and the discussion has therefore been confined as much as possible to points which have some bearing on the subsequent work.

ACIDIMETRY AND ALKALIMETRY.

The use of indicators, such as litmus, is not confined to the qualitative recognition of the presence of free acid, or of free alkali; by means of them we are enabled to determine exactly the quantity of the one or the other present in a solution.

In order to neutralise a given quantity of, say, sodium hydroxide, a definite quantity of, say, hydrochloric acid is necessary, the proportion being given by the equation:

$$\begin{array}{ccccccc} NaOH & + & HCl & = & NaCl & + & H_2O \\ 23+16+1 & & 1+35{\cdot}5 & & 23+35{\cdot}5 & & 2+16 \\ =40 & & =36{\cdot}5 & & =58{\cdot}5 & & =18 \end{array}$$

i.e., 40 grams of sodium hydroxide require 36·5 grams of hydrochloric acid. It is therefore possible, by means of hydrochloric acid solution of known concentration, to determine the concentration of a solution of sodium hydroxide, or of any other alkali, and *vice versa*, provided the volumes of the known and unknown solutions which mutually neutralise one another are ascertained.

Any solution of accurately known concentration is called a *standard solution*. For the purposes now under consideration it is convenient to have as much uniformity as possible in the standard solutions employed. This is secured by the use of what are called *normal solutions*. Normal solutions are prepared so as to be all of the same neutralising power, irrespective of the particular acid or alkali employed; 1 c.c. of normal hydrochloric acid neutralises the same quantity of alkali as 1 c.c. of normal nitric acid, or of normal sulphuric acid. Similar relationships hold among normal solutions of alkalies; and moreover, 1 c.c. of any normal alkali solution exactly neutralises 1 c.c. of any normal acid solution. Hence it follows that when the actual concentration of, say, normal hydrochloric acid has been defined, the actual concentrations of normal solutions of other acids and of alkalies can be deduced by very simple calculations based on the formula weights of the various acids and alkalies. Normal hydrochloric acid contains 36·5 grams of HCl per litre, and as 36·5 is the formula weight of HCl, it follows that one litre of a normal solution of any other monobasic acid contains the formula weight in grams of that acid; in the case of dibasic acids, where the quantity represented by the formula has twice the neutralising power of that represented by the formula for hydrochloric acid, only half the formula weight in grams will be contained in a litre of the normal solution. It is evident that similar simple relationships exist between normal solutions of alkalies. In general terms a normal solution of an acid might be defined as one containing one gram ($H = 1$) of replaceable hydrogen per litre, and a normal solution of an alkali as one containing seventeen grams ($OH = 16 + 1$) of basic hydroxyl per litre.

In determining the concentrations of unknown solutions of acids or alkalies by means of appropriate normal solutions, comparatively small quantities are employed, and it is convenient to express the neutralising power per cubic centimetre rather than per litre. From what has been already stated it is evident that one litre of any normal acid will neutralise 40 grams of sodium hydroxide, therefore 1 c.c. will neutralise $\frac{40}{1000}$, *i.e.*, 0·040 gram. The latter nnmber is sometimes called the *factor* for sodium hydroxide with reference to normal acid. Analogous factors can be deduced in a similar way for other hydroxides; and likewise for acids with reference to normal alkali.

To illustrate the method of calculation a definite example may be taken: It is found that 19·6 c.c. of a certain solution of sodium hydroxide are necessary for the neutralisation of 25 c.c. of normal acid; what is the concentration of the sodium hydroxide? As 1 c.c. of normal acid neutralises 0·040 gram of $NaOH$, 25 c.c. will neutralise $25 \times 0{\cdot}040$ gram; therefore, this quantity must be contained in the 19·6 c.c. of the above solution, and 1 c.c. of that solution will contain $\frac{25 \times {\cdot}040}{19{\cdot}6}$, *i.e.*, 0·0510 gram $NaOH$. If the result is desired in grams per litre the above quantity must be multiplied by 1000; this gives 51 grams $NaOH$ per litre of solution. Generally, if x represent the volume of normal acid, y the volume of the alkali solution necessary for neutralisation of that quantity of acid, and F the factor for the particular alkali, then the concentration, C, of the latter is given by the formula $C = \frac{x \times F}{y}$, where C represents the weight of the substance in 1 c.c. of solution. The same method and formula apply in the determination of the quantity of acid in a solution of unknown concentration by means of normal alkali solution; in this case x, as before, represents the volume of normal solution (in this case alkali), y the volume of the solution whose concentration is to be determined (in this case acid), and F the factor characteristic of the particular acid involved.

Instead of expressing the concentration of a solution in the manner just referred to, it is for some purposes convenient to state simply its relation to a normal solution. Thus, in the example already employed, where 25 c.c. of normal acid required 19·6 c.c. of sodium hydroxide solution, it is evident that the latter is more concentrated than a normal solution, and the ratio $\frac{25}{19 \cdot 6}$, *i.e.*, 1·275, expresses its concentration as compared with a normal solution. The concentration expressed in this way is called the *titre* of the solution; in the above case the titre is 1·275 normal. The process involved in the comparison of an unknown solution with a standard one is called *titration*.

For many purposes normal solutions are too concentrated to give the best results; in such cases more dilute solutions, such as semi-normal or deci-normal, are employed. The former have one-half, and the latter one-tenth, the neutralising power of a normal solution, *i.e.*, their titres are respectively 0·5 and 0·1 normal. Occasionally, also, standard solutions are employed whose concentrations bear no simple ratio to that of a normal one, but whose titres are accurately known. In calculating results obtained by means of solutions which are not of normal concentration, allowance must, of course, be made for the difference; this is effected simply by multiplying by the number representing the titre of the standard solution employed. If the titre be represented by T, then the formula already given is replaced by $C = \frac{x \times T \times F}{y}$. This form really includes the previous one as a particular case, for the titre of a normal solution is, of course, unity.

By taking certain precautions, some salts of very weak acids can be determined in a manner similar to that described for alkalies. This is the case with soluble carbonates, provided an indicator is employed which is not affected by carbonic acid (such as methyl orange), or the solution is heated sufficiently to decompose the whole of the carbonic acid and expel the carbonic anhydride produced.

Owing to the practical difficulty of obtaining most of the common acids and alkalies in a weighable form and free from admixture with other substances, standard solutions of these cannot, as a rule, be prepared by simply weighing out the necessary quantity and adding water to make up the appropriate volume, hence indirect methods of standardisation are necessary. These need not be considered here, as they are beyond the scope of the present work.

The quantitative determination of free acids and alkalies by the methods just sketched (*acidimetry* and *alkalimetry*) is a branch of volumetric analysis, which includes all methods of quantitative analysis by means of standard solutions. Such methods are applicable in all cases where the completion of a chemical change is sharply indicated in some way, with or without the employment of a special indicator other than the substances taking part in the reaction itself.

The apparatus employed for accurate volumetric analysis consists chiefly of graduated flasks and cylinders, used in making up solutions to definite volumes; pipettes, employed to deliver predetermined volumes of liquid, such as 10, 20, or 50 c.c.; and burettes, 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 commenced, and after it is completed.

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 there is good reason to believe that 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 sulphurous anhydride. Such complications do not occur with hydrochloric acid.

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

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 sulphurous anhydride—

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

$$PbO_2 + SO_2 = PbSO_4.$$

[At low temperatures manganese peroxide does not behave like lead peroxide towards sulphurous anhydride. 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 dissolves metals, the action 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 salt 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 sulphurous anhydride 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. The evolution of hydrogen takes place only when the acid is dilute, and is then the result of only one of several simultaneous reactions. 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 of course 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. In cases where such replacements are possible, the action may be used as a method for preparing salts. As a rule, however, such actions are carried out on the large scale principally as a means of obtaining the replaced metal, the new salt being only a bye-product—

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

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—

$$\mathrm{Fe} + \mathrm{Cl_2} = \mathrm{FeCl_2}.$$

$$2\ \mathrm{FeCl_2} + \mathrm{Cl_2} = 2\ \mathrm{FeCl_3}.$$

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 the bromine has been all 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.

$$2\ \mathrm{Al} + 3\ \mathrm{Br_2} = 2\ \mathrm{AlBr_3}.$$

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—

$$\mathrm{Fe} + \mathrm{I_2} = \mathrm{FeI_2}.$$

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 applicable when the acid liberated by the action is much more volatile than that which is added to the original salt, or when the former is very much weaker than the latter, though not much more volatile; or again, when the former is very easily decomposed, yielding volatile products which can be removed from the sphere of action. When more than one of these conditions is fulfilled, as is the case when carbonates serve as the starting-point, the method becomes a very important and general one. Carbonic acid is such a weak acid, and decomposes into carbonic anhydride and water at such slight concentrations, that its salts can be completely decomposed by the great majority of acids, even in presence of a considerable quantity of water. On this account most salts can be prepared from the carbonate of the metal, as easily as from the basic oxide, by the action of the appropriate acid. In addition to the new salt formed, the only other products are carbonic anhydride and water:—

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

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 prepared 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.) Frequently in practice this method is employed really for the preparation of the acid, and the new salt is simply a bye-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 completely decompose 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 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 reacting 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 grams of crystallised cupric sulphate ($CuSO_4,5H_2O$), and 244 grams of crystallised barium chloride ($BaCl_2,2H_2O$), 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 shall 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 is 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.

$$\underbrace{5\ CaCl_2 + Ca(ClO_3)_2}_{} + 2\ KCl = 6\ CaCl_2 + 2\ KClO_3.$$

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.

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.

8. When a metal forms two sets of salts, corresponding to two different basic oxides, methods of preparing the higher

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* 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.

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 salt radical, while the latter involves its removal.

Preparation of higher salts from lower ones.—In the case of halides the salt 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—

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

In the case of most salts other than the halides, the corresponding salt 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 salt 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 salt 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 salt radical unites with the lower salt.

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

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

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

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

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* Some salts undergo this change so readily that they are difficult to prepare, and every trace of free oxygen must be excluded from the solutions employed and from the atmosphere to which they are exposed. The chromous salts (those derived from the oxide CrO) are of this nature.

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 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—

$$2\ Cu + 2\ H_2SO_4(\mathit{dil.}) + O_2 = 2\ CuSO_4 + 2\ H_2O,$$
$$6\ Ag + 3\ H_2SO_4(\mathit{dil.}) + 2\ HNO_3 = 3\ Ag_2SO_4 + 2\ NO + 4\ H_2O.]$$

Preparation of lower salts from higher ones.—The removal of the extra proportion of salt 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 impossibility of easily 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.

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. Such cases are not of much practical importance.

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 salt 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, a 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.

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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 titre 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 saturated 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 saturated 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 (2·5 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 peroxide) 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 $H\bar{A}$.—A solution containing about 60 grams of the acid in the litre (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).

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 insoluble sulphides, especially from acid solution; it also acts as a reducing agent, generally with deposition of sulphur.

Alkalies—

Potassium hydroxide, KOH.—Solution containing about 55 grams per litre (N). Employed chiefly for precipitation of insoluble 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 carbonic anhydride from the air.

Sodium hydroxide, NaOH, is frequently employed in place of potassium hydroxide, as it serves equally well, though there are a few differences between them in some comparatively unimportant reactions (see p. 112). The normal solution contains 40 grams per litre.

Calcium hydroxide, $Ca(OH)_2$.—A saturated, but nevertheless very dilute, solution (lime water, 0·04 N). Used chiefly to test for carbonic anhydride; 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 potassium 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, otherwise the ammonia solution will merely float as a layer on the top of the other liquid, and not mix with it effectively. 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.

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 (N) may be prepared from this by dissolving 40 grams in a litre of water, and adding about 15 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 25 grams in the litre (0·5 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 oxalate, $(NH_4)_2C_2O_4,H_2O$.—A solution obtained by dissolving 35 grams in the litre (0·5 N). Used as a soluble oxalate, specially for precipitating the metals of the calcium group.

Barium nitrate, $Ba(NO_3)_2$.—A solution obtained by dissolving 25 grams in the litre (0·2 N). Used in testing for salt 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 grams of bleaching powder with *cold* water, allowing the residue to settle, siphoning off the clear liquid and adding sufficient water to bring the volume up to one litre. 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.

Calcium chloride, $CaCl_2$, 6 H_2O.—A solution obtained by dissolving 35 grams in the litre (0·3 N). Used in testing for certain salt radicals, especially for distinguishing between oxalate and borate.

Calcium sulphate, $CaSO_4$, 2 H_2O.—A saturated solution of gypsum, containing about 2 grams in the litre (·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.—See under Bleaching solution.

Cupric sulphate, $CuSO_4$, 5 H_2O.—A solution obtained by dissolving 30 grams in the litre (0·25 N). Used in testing for arsenites.

Ferric chloride, $FeCl_3$.—A suitable reagent may be obtained by diluting the *Liquor ferri perchloridi fortis* of the Pharmacopœia to twenty-five times its volume (0·5 N). Used in testing for a number of salt radicals, especially acetates; also for 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 40 grams in a litre of water (0·3 N), slightly acidulated 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 grams 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 grams in the litre (one-eighth N). Used principally as a soluble lead salt in testing for a number of salt 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 a quantity of magnesium sulphate solution 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 grams in the litre (0·2 N). Used for preparation of "magnesia mixture."

Mercuric chloride, $HgCl_2$.—A solution obtained by dissolving 15 grams in the litre (0·1 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 potassium 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 carbonate, K_2CO_3.—A solution obtained by dissolving 25 grams of the dried salt in the litre (0·3 N).

Potassium chromate, K_2CrO_4.—A solution obtained by dissolving 25 grams in the litre (0·25 N). Used for precipitating various insoluble chromates of the heavy metals, and especially for distinguishing among the members of the calcium group, owing to the marked difference in the solubility of the chromates of barium, strontium, and calcium; also, with addition of free acid, as a test for reducing agents.

Potassium ferricyanide, $K_3Fe(CN)_6$.—A solution obtained by dissolving 25 grams 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. 65).

Potassium ferrocyanide, $K_4Fe(CN)_6$, 3 H_2O.—A solution obtained by dissolving 25 grams in the litre (0·2 N). Used for precipitating various insoluble 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 grams 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).

Sodium hydrogen tartrate, $NaHC_4H_4O_6,H_2O$; $NaH\overline{T}$). —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 phosphate, $Na_2HPO_4,12\ H_2O$.—A solution obtained by dissolving 25 grams in the litre (0·2 N). Used, along with ammonium chloride and ammonia, in testing for magnesium.

Sodium sulphite, Na_2SO_3, 7 H_2O.—A solution obtained by dissolving 25 grams in the litre (0·2 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 grams 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 peroxide, 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, $NaNH_4HPO_4$, $3\,H_2O$, 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.—Dry 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.

The following varieties of test paper are referred to in the subsequent work :—

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 produces 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 filter 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, however; in this 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.

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 potassium 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 must on no account be employed, as this would almost certainly introduce objectionable matters. The vessel should simply be drained as thoroughly as possible, and allowed to dry in the air.

Platinum wires, which have become contaminated with substances which are not easily volatile, 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 one way or the other by tilting the wire in the appropriate direction, 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. 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.

In observing reactions which are carried out in test tubes, the tube should be held securely, but not too tightly, between the thumb and 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 held in that way until the reagent has been added, when it is replaced. Stoppers should not be laid upon the bench, if it 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.

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 1-2 c.c. is a sufficiency for all ordinary reactions; sometimes a single drop is all that is necessary. 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 which is employed 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 overheating, 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. 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.

PRELIMINARY EXERCISES IN SIMPLE CHEMICAL MANIPULATION.

A. Qualitative.

1. *Ascertain that Common Salt dissolves in Water.*—Boil 2-3 grams of common salt with 20 c.c. water. Filter. Evaporate the filtrate to dryness. Record the result.

2. *Ascertain whether or not Sand dissolves in Water.*—Boil 2-3 grams of sand with 20 c.c. water. Filter. Evaporate the filtrate to dryness. Record the result.

3. *Separate Common Salt from Sand.*—Boil 2-3 grams of a mixture of common salt and sand with 20 c.c. water. Filter. Evaporate the filtrate to dryness. Dry the residue on the filter paper.

4. *Separate Common Salt from Ammonium Chloride.*—Place about a gram of a mixture of equal parts by weight of common salt and ammonium chloride in a dry test tube. Heat the mixture, gently at first and then more strongly; observe the formation of a sublimate, while a residue remains in the bottom of the test tube. Ascertain whether the residue or the sublimate consists of common salt.

5. *Recrystallise Cupric Sulphate to obtain well-formed Crystals.*—Dissolve 5-10 grams of cupric sulphate in hot water. If the resulting liquid is not quite clear, get rid of any suspended matter by filtering the hot 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.

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

7. *Recrystallise a mixture of Cupric Sulphate and Alum.*—Dissolve about 10 grams of a mixture of 2 parts by weight of cupric sulphate and 1 part by weight of alum in about 15 c.c. of hot water, and then proceed as in Experiment 5. Record the result.

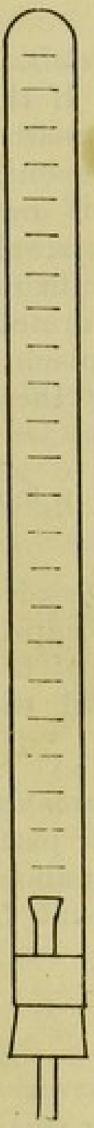
8. *Recrystallise a mixture of Cupric Sulphate and Ammonium Sulphate.*—Dissolve about 10 grams of a mixture of equal parts by weight of cupric sulphate and ammonium sulphate in about 15 c.c. of hot water, and then proceed as in Experiment 5. Record the result.

B. QUANTITATIVE.

1. *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 flask 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, filter a portion of the solution (not more than 2 or 3 grams) into this tared basin, 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 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, w = weight of basin and solution, and w' = weight of basin 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 grams of water is therefore $100(w' - b)/(w - w')$ grams.



‹ 2. *Determine the solubility of Calcium Sulphate at Room Temperature.*—Prepare a saturated solution of calcium sulphate by adding 2-3 grams of 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 grams) into a tared basin and weigh again. Evaporate to dryness and complete the determination as described under Experiment 1.

3. *Determine the ratio CuO : Cu.*—Carefully weigh a clean porcelain crucible and lid. Place in the crucible about 0·5-1 gram precipitated copper 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 CuO : Cu.

4. *Determine the Hydrogen Equivalent of Aluminium or of Magnesium.*

[For this experiment a 50 c.c. measuring tube fitted with perforated rubber stopper and narrow glass tube, as represented above in the figure, is required.]

Weigh off about 0·3 gram of aluminium, or magnesium,
.003 in the form of wire, ribbon, or foil, and attach it to the narrow

tube, between the widened upper end and the stopper, either by winding it round the tube or by means of a fine platinum wire. Pour about 15 c.c. of concentrated hydrochloric acid into the measuring tube and then carefully fill up the tube to the top with water, avoiding undue mixing of the hydrochloric acid with the water. Then introduce the stopper and tube with the attached metal, making sure that the interior of the narrow tube becomes filled completely with water as the stopper is pressed into position. Close the end of the narrow tube with the forefinger, invert the measuring tube, quickly place the end of the narrow tube under the surface of some water contained in a shallow vessel, and remove the forefinger. The dense solution of hydrochloric acid mixes rapidly with the water in the measuring tube, and the considerably diluted acid comes into contact with the metal; interaction between the metal and the acid takes place, hydrogen being liberated. Should any loss of particles of metal or of bubbles of gas occur, this can be obviated in a subsequent determination by tying a small piece of thin muslin over the widened end of the narrow tube before starting the experiment. When the evolution of hydrogen has ceased, transfer the measuring tube to a deep cylinder containing water at room temperature, remove the stopper below the surface of the water, support the tube by means of a clamp, and allow the whole to stand for ten minutes. Then, by raising or lowering the clamp, adjust the measuring tube so that the level of the liquid is the same outside and inside, and read off the volume of the hydrogen,* the temperature of the water in the cylinder, and the barometric pressure.

Let w = the weight of the metal employed (gram),
,, 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 (gram).

Then $v' = 273\,v(p-r)/760\,(t+273)$.

Since 1 c.c. hydrogen at 0° and 760 mm. weighs 0·000089 gram, $w' = v' \times 0{\cdot}000089$, and the hydrogen equivalent of the metal $= w/w'$.

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* For precautions, consult the chapter on Volumetric Analysis, p. 92.

EXPERIMENTS INVOLVING REACTIONS ILLUSTRATIVE OF THE FORMATION AND DECOMPOSITION OF SALTS.

1. In order to acquire some familiarity with the use of indicators 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:—Tear out a strip of each kind of paper and lay it on a clean sheet of paper on the bench; clean a glass rod, dip it into the solution to be examined, and, after withdrawing it, transfer a small drop of the solution to each strip of paper; note the effect. After washing the rod, repeat the experiment with a different solution, taking care to touch the paper on a part not already moistened; in this way one strip of paper will serve for a number of experiments. Another method is to dip the end of the strip into the solution, but the former is more expeditious and is preferable. If the second method is employed, the paper should not be dipped directly into the solution contained in the bottle; a small quantity should be first transferred to a test tube, watch-glass, or other suitable vessel.

Observe in this way the behaviour of the following ordinary reagents:—Acetic acid, hydrochloric acid, nitric acid, sulphuric acid (*dilute*); potassium or sodium hydroxide, calcium hydroxide, ammonium hydroxide (ammonia); sodium hydrogen tartrate (sodium bitartrate); cupric sulphate, ferric chloride; potassium 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.

2. Pour several 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, potassium 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. [Compare page 41.]

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 finger, 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 hydrochloric acid until the liquid is slightly acid. 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. 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. [Compare page 45.]

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 above, 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.

6. 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 [p. 187] 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.

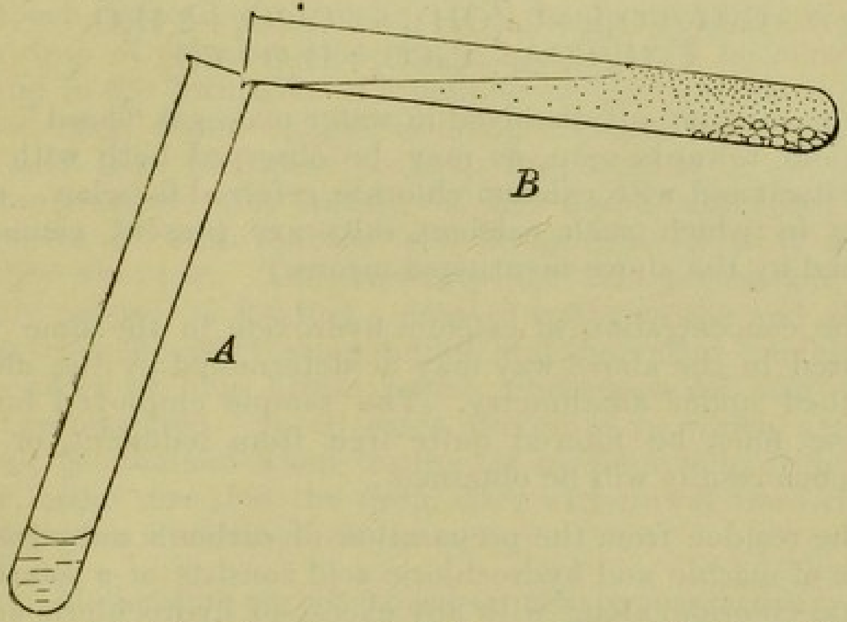
$$CaCO_3 = CaO + CO_2.$$
$$CaO + H_2O = Ca(OH)_2.$$

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 carbonic anhydride from the air.

Pour a fresh portion into a clean test tube and blow gently down into the tube; close the latter with the thumb and shake vigorously (repeat the operations if necessary); the liquid becomes turbid owing to the production of calcium carbonate by the action of the carbonic anhydride of the breath. (Expired air contains 4-5 per cent. of carbonic anhydride.)

In another clean tube place a fresh portion of lime water which has previously been diluted with its own volume of water, and pour into it carbonic anhydride 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 carbonic anhydride; the whole operation should be carried out as 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.



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* 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*.

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 such calcium salts 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. The sample employed for the purpose must be filtered quite free from sediment, or very erroneous results will be obtained.

The residue from the preparation of carbonic anhydride 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. [Compare page 51.]

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 $CaSO_4,2H_2O$ will be produced. This composition is the same as that of *gypsum*, the mineral from which plaster of Paris is prepared. [Compare page 52.]

Part of the calcium chloride solution may be diluted and examined for the reactions of calcium salts as described on page 131; the flame test [page 187] may be best observed with the undiluted solution.

Since carbonic anhydride 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 carbonic anhydride 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 carbonic anhydride in this way, make sure that the drop, after withdrawal from the tube, still gives a distinct alkaline reaction.

7. 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. Show

Warm a small quantity of magnesite with hydrochloric acid; note the effervescence due to the escape of carbonic anhydride; 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 ; solution will take place without effervescence, provided the magnesite was completely decomposed by heating.

Heat some powdered magnesite in a hard glass tube, and after a short time test for the presence of carbonic anhydride 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.†

To about 15 c.c. of dilute sulphuric acid add magnesium carbonate in successive small portions, waiting each time 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 ; should it not become clear, add a drop or two of dilute sulphuric acid. Pour the liquid 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, $MgSO_4,7H_2O$. 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 p. 132.

8. 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.

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* 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.

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. 164, 165]. When the metal has all dissolved, the solution thus obtained may also be tested for magnesium salt.

9. 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. 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 p. 108. [Compare page 48.]

NO
NO_2
N_2

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

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* 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.

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. [Compare page 52.]

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 sulphurous anhydride, the latter recognisable by its odour and its reducing action on ferric ferricyanide test paper [p. 65]; the gases are accompanied by sulphuric acid fumes. [Page 48.]

10. 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 carbonic anhydride. 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 carbonic anhydride. 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

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* 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 carbonate, formed by slow absorption of carbonic anhydride from the air.

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.

NOTE.—Lead or compounds of lead should on no account be heated on platinum apparatus in the flame, otherwise the apparatus will be destroyed, owing to the formation of a fusible alloy of the two metals.

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

Heat a quantity of dry "white lead" in a dry test tube: note the production of carbonic anhydride 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.

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

12. Prepare lead nitrate by heating together several grams of litharge and about 10 c.c. of nitric acid. If the solution does not become quite clear, filter it as quickly as possible, collecting the filtrate in a glass 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.

Slow

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.

13. Place some flowers of sulphur in a 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. 46]. 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. 65].

14. Warm together a small quantity of finely powdered *galena* (native sulphide of lead) and hydrochloric acid. The sulphide gradually dissolves with formation of lead chloride and evolution of hydrogen sulphide, which may be recognised as already indicated. 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 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.

15. "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 nitric acid in a test tube. Chemical action proceeds rapidly, with formation of brown insoluble peroxide of lead 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. 65].

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

16. Heat some dry peroxide of lead 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.

17. 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. [Compare page 48.] Slow

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. 110] 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 copper sulphate in solution, with evolution of nitric oxide [p. 55.]

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. [Compare page 47.]

Pour about 5 c.c. of concentrated sulphuric acid over 2-3 grams of copper turnings in a tube, and warm gently. Action soon begins, and sulphurous anhydride 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. 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," $CuSO_4,5H_2O$, 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 p. 109. [Compare p. 48.]

18. 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 crystallising dish. To the clear solution add a small quantity of nitric acid, and boil for a minute or two; then set aside to cool slowly. The crystals of hydrated zinc sulphate or "white vitriol," $ZnSO_4,7H_2O$, 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 mother liquor and dried between filter paper. An aqueous solution prepared from them may be examined for the reactions of zinc salts [see p. 119]. 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. [Compare page 55.]

Show

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 the action with hydrochloric acid and with acetic acid, giving rise to the evolution of hydrogen in each case, and also with nitric acid [see p. 48].

19. Warm 2-3 grams of iron wire—a small roll of iron gauze is a convenient form in which to employ 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 * 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," $FeSO_4,7H_2O$, 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. 122] or for the preparation of iron alum [see below].

Show

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* The ferrous 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.

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 of course immediately converted into nitrogen peroxide as soon as it mixes with the air. [Compare page 55.]

The ferric salt must be clear
& not strongly acid.

A saturated solution of ferrous sulphate may be employed for the preparation of ammonium iron alum—ammonium ferric sulphate, $(NH_4)_2Fe_2(SO_4)_4,24H_2O$—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.

Show

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 portions until it is found that effervescence (due to the escape of oxygen) takes place when the solid dissolves. The colour of the solution changes to reddish brown (becoming yellow on cooling), 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 purplish colour, and are octahedral in shape. They may be dissolved in water, and the solution employed for examining the reactions of ferric salts [p. 123]. The presence of the ammonium sulphate is, for this purpose, immaterial.

Iron dissolves easily in hydrochloric acid with evolution of hydrogen and formation of ferrous chloride. This salt is much more soluble in water than the sulphate is, 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 employing cold dilute nitric acid, it is possible to obtain ferrous nitrate, along with ammonium nitrate [see p. 49]. Neither ferrous nor ferric nitrate is suitable for preparation in the solid state on a small scale.

20. 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 easily obtained 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 gram of sheet aluminium with dilute sulphuric acid; action takes 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. When the action slackens, heat the liquid and keep it nearly boiling for a minute or two so as to use up nearly all the acid. A fine powder will be seen floating in the solution; it consists of minute particles of silicon, originally present as an impurity in the aluminium; to get rid of it as far as possible, the solution should be filtered, but probably only a part will be removed in this way. The aluminium sulphate thus obtained may be employed for the preparation of ammonium alum, $(NH_4)_2Al_2(SO_4)_4,24H_2O$, a double salt which can be easily obtained in large octahedral crystals. For this purpose add 2-3 grams of 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.

In this experiment the presence of hydrochloric acid greatly accelerates the rate at which the metal is dissolved, and a very small proportion mixed with the sulphuric acid is sufficient to reduce the time necessary for solution to a reasonable period.

An aqueous solution of ammonium alum may be employed for the examination of the reactions of aluminium salts [see p. 127]; 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 now 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, while a corresponding quantity of aluminium is dissolved—

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

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 seem to sprout from the surface of the metal. This property renders it impossible to employ aluminium for instruments in surgery when mercuric chloride solution is employed as an antiseptic.

21. Heat a small quantity of dry lead nitrate in a hard glass tube (the crystals obtained in Experiment 12 may be employed for this purpose). At first the salt decrepitates strongly, owing to the presence of small quantities of included mother liquor; 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.

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

22. 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 taper, 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.

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

23. 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.

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

24. Heat a small quantity of potassium chlorate in a hard glass tube. The salt fuses and soon begins to decompose, 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.

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

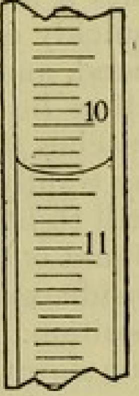
25. Heat a small quantity of sodium chloride (common salt) with concentrated sulphuric acid in a test tube. The hydrochloric acid gas which is evolved fumes when it comes in contact with moist air, forming a cloud composed of minute drops of hydrochloric acid solution. Hold a piece of blue litmus paper 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. [Compare p. 51.]

VOLUMETRIC ANALYSIS.

Practise manipulating and reading the burette, which is assumed to be of 25 c.c. capacity and graduated in 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 out 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 upwards 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. The lateral distance of this part 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 the case sketched in the illustration the level is about half-way between 10·3 and 10·4, and the reading would be 10·35. 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, as 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. Withdraw the pipette, still tightly closed, and hold it over the vessel into which the liquid is to be transferred, allowing the point to rest against the inside wall of the vessel, with the pipette itself in a vertical position. Remove the forefinger, and, when all the liquid has run down, blow gently through the pipette so as to remove the drop which remains in the bottom, the point being still in contact with the wall of the vessel. In order to allow for proper drainage, the nozzle of a pipette should have a very small opening, so that at least 40 seconds are required for the liquid to run out. The pipette should not be blown into until no more liquid will run out spontaneously.

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 (the exact level being noted), and then running in 10 c.c. of water from the pipette. On again reading the burette, the difference should amount to exactly 10 c.c. A further quantity of 10 c.c. should be again added and the level again read.

Graduated apparatus of a high degree of accuracy can nowadays be easily purchased, but for accurate work it is necessary to check the graduations by weighing the quantity of water either contained in the vessels (as in the case of graduated flasks) or delivered by them (as in the case of burettes and pipettes). If a flask or pipette is found inaccurate, a new mark can be made on it, or the true volume corresponding to the original mark may be noted. In the case of a burette, the slight errors cannot be corrected by altering the marks, and a "calibration table" has to be prepared for each instrument. This table gives the true volume corresponding to each graduation. The process of determining the true values of the marks on graduated instruments (including, for example, thermometers) is called *calibration*.

ACIDIMETRY AND ALKALIMETRY.

Using normal acid solution, 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 out with several cubic centimetres of the normal acid solution,* allowing this in its turn to drain away. 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 out with a small quantity of the alkaline solution which is to be tested;* then by means of it measure out 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 normal 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

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* The preliminary rinsings are to remove the water adhering to the walls of the instruments, which otherwise would slightly dilute the solutions employed.

† Many other indicators are in use at the present time for work of this kind; some are more suitable than others in particular cases. The discussion of their use is beyond the scope of the present volume.

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 out 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 normal 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,	11·32

The factor [p. 42] for sodium hydroxide is 0·040, so that in the above case 10 c.c. of the sodium hydroxide solution contains 11·32 × 0·040 gm. NaOH, and therefore 1 c.c. contains $\frac{11{\cdot}32 \times 0{\cdot}40}{10}$, *i.e.*, 0·04528 gm. NaOH; or the solution contains 45·28, say 45·3, gm. per litre.

Instead of measuring out the sodium hydroxide solution by means of the pipette, the latter might have been employed to measure out 10 c.c. of normal 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 determine the concentration of other alkaline reagents, such as potassium hydroxide or calcium hydroxide, employing the appropriate factor in the calculation.

1 c.c. of normal acid neutralises	0·017	gram	NH_3
	0·040	„	$NaOH$
	0·056	„	KOH
	0·037	„	$Ca(OH)_2$.

Also, using normal alkali solution, determine the concentration of the various dilute acids.

1 c.c. of normal alkali neutralises	0·0365	gram	HCl
	0·063	„	HNO_3
	0·049	„	H_2SO_4
	0·045	„	$H_2C_2O_4$.

Instead of employing normal alkali to determine the concentration of the acids, as above indicated, the solution of, say, potassium hydroxide, whose concentration has already been determined, may be used. In this case the titre of the hydroxide solution must be taken into account in calculating the results [p. 43].

NOTE.—In very accurate work the factors should be calculated from exact atomic weights; in the above tabulation they have been rounded off.

ANALYSIS OF AMMONIUM SALTS.

Weigh out accurately about 0·5-1 gram of, say, ammonium chloride in a beaker or other suitable vessel, dissolve it in 10-20 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 contents with normal acid solution. From the amount of residual alkali thus determined, the amount of alkali used up in decomposing the ammonium salt can be easily found, and the proportion of NH_4 radical in the salt calculated.

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O.$$

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.

ADDITIONAL METHODS OF VOLUMETRIC ANALYSIS.

Quantitative determinations by volumetric methods, with the aid of standard solutions, can be carried out in a great variety of other cases besides those involving merely the interaction of acids and alkalies. In order that an interaction which takes place between substances in solution may be employed in such volumetric methods, it is usually requisite that the occurrence of some change easily recognisable by the eye should indicate (as in the case of the litmus solution used in acidimetry and alkalimetry, see p. 95) the completion of the interaction. Thus, a marked change may take place in the colour of one of the interacting substances or of some specially added indicator; the first formation of a permanent precipitate may be noted; or the end-point may be indicated in some other appropriate way. Certain of these volumetric methods are of great value on account of their simplicity, rapidity, accuracy, and wide applicability, and this fact justifies the inclusion here of two of them.

STANDARD SOLUTION OF POTASSIUM PERMANGANATE.

The salt potassium permanganate, $KMnO_4$, is met with in commerce in the form of shining, dark purple, prismatic crystals, which dissolve in water to produce an intensely dark purple solution. In admixture with a considerable excess of dilute sulphuric acid, this salt, even in dilute solution, acts as a powerful oxidising agent towards a large number of oxidisable substances; and as its colour is discharged when it is reduced to manganous salt, it is itself a sufficient indicator of the progress of the changes. The potassium and manganese of the permanganate unite with SO_4 radical from part of the added sulphuric acid, to form sulphates. In order that this may take place, however, the hydrogen of this sulphuric acid has to be oxidised by part of the oxygen of the permanganate, with the formation of water, while the balance of the oxygen is available for the oxidation of the reducing substance present. The proportion of the oxygen of the permanganate required for the former of these purposes and available for the latter is shown by the equation—

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5[O],$$

from which it appears that of the 8 oxygen atoms represented in the $2\,KMnO_4$, 3 are required to oxidise the 6 hydrogen atoms of the $3\,H_2SO_4$, with the formation of $3\,H_2O$, while 5 are available for other oxidation purposes.

The standard potassium permanganate solution is usually placed in the burette and added to the solution containing the oxidisable substance. When the oxidisable substance is already in the form of a solution, a measured volume of this solution is employed, and when it is a solid, a quantity of the solid is weighed off and dissolved in water; excess of dilute sulphuric acid is added, and the permanganate is run in from the burette until the last drop added just leaves a permanent pink coloration in the liquid (the operation being carried out either in the cold or after heating the solution of the oxidisable substance to the requisite temperature, as the case may be). The intense colour of the permanganate solution thus renders the use of any other indicator unnecessary. This colour also renders it somewhat difficult to read the bottom of the meniscus; in such cases it is usually easy to read the top edge, however.

It is to be noted that potassium permanganate does not give correct results in presence of hydrochloric acid, since this acid acts to some extent as a reducing agent towards the permanganate, even in cold dilute solutions. Care must also be taken that the amount of dilute sulphuric acid is largely in excess of the quantity represented in the equation, as, otherwise, the separation of a brown precipitate ($MnO(OH)_2$) may take place. If such a precipitate is produced in any determination, the experiment must be repeated, with the addition of a larger proportion of dilute sulphuric acid.

As previously stated on p. 41, a normal solution of an acid is one which contains 1 gram of replaceable hydrogen per litre. By convention, a solution of an oxidising agent which is capable of yielding 8 grams of available oxygen per litre (*i.e.*, the weight of oxygen requisite to form water with 1 gram of hydrogen) is also termed a normal solution.

As shown above, the quantity of potassium permanganate represented by $2KMnO_4$ yields $5[O]$, that is, $5 \times 16 = 80$ grams of available oxygen, or just ten times the quantity of oxygen required to yield a normal solution. Since $2KMnO_4 = 316$ grams, the normal solution would contain 31·6 grams of the salt. It has been found, however, that a normal solution has an inconveniently high concentration for many purposes, and hence a decinormal solution (containing 3·16 grams per litre) is very commonly used.

The oxidisable substances or mixtures for which potassium permanganate is an appropriate oxidising agent in acid solutions, are numerous: they include ferrous salts, oxalic acid, sulphurous acid, etc., but only the first two will be dealt with here.

Ferrous sulphate and dilute sulphuric acid form a reducing mixture which takes up oxygen with the production of ferric sulphate and water. The equation representing this change—

$$2FeSO_4 + H_2SO_4 + [O] = Fe_2(SO_4)_3 + H_2O,$$

shows that 56 parts by weight of iron as ferrous salt require 8 parts by weight of oxygen for conversion into ferric salt; that is, 1 litre of normal permanganate solution (capable of yielding 8 grams of available oxygen) will transform 56 grams of iron as ferrous salt into ferric salt, hence—

1 litre normal $KMnO_4$ solution is required for 56 grams ferrous iron;

∴ 1 litre *N*/10 $KMnO_4$ solution is required for 5·6 grams ferrous iron;

or 1 c.c. *N*/10 $KMnO_4$ solution is required for 0·0056 gram ferrous iron.

Oxalic acid and dilute sulphuric acid, at a temperature of about 60° C., also form a mixture which reduces potassium permanganate.

The equation—

$$H_2C_2O_4 + [O] = 2\,CO_2 + H_2O$$

shows that 90/2 gram of anhydrous oxalic acid (or 126/2 gram of the crystallised acid, $H_2C_2O_4, 2\,H_2O$) requires 8 grams oxygen for conversion into carbonic anhydride and water, hence—

1 litre normal $KMnO_4$ solution is required for 63 grams crystallised oxalic acid;

∴ 1 litre *N*/10 $KMnO_4$ solution is required for 6·3 grams crystallised oxalic acid;

or 1 c.c. *N*/10 $KMnO_4$ solution is required for 0·0063 gram crystallised oxalic acid.

Potassium permanganate of a high degree of purity can be purchased, and a solution, prepared by simply dissolving 3·16 grams in water and making up the volume of the solution to a litre, may be employed, without standardisation, for making approximate determinations. When the degree of purity of the permanganate is unknown, the volumetric solution must be standardised, however, before it is employed for purposes where highly accurate results are required. This may be done by means of weighed quantities of ammonium ferrous sulphate, $(NH_4)_2SO_4,FeSO_4,6H_2O$, a salt which is easily prepared in a pure state for the purpose, or by means of pure crystallised oxalic acid.

STANDARD SOLUTIONS OF SODIUM THIOSULPHATE AND IODINE.

The salt sodium thiosulphate is obtained from its aqueous solutions in colourless hydrated crystals which correspond to the formula $Na_2S_2O_3,5H_2O$. When dissolved in water, the salt interacts with great readiness with iodine (which may conveniently be dissolved in an aqueous solution of potassium iodide), forming sodium iodide, NaI, and sodium tetrathionate, $Na_2S_4O_6$.

The solution of iodine is coloured from dark brown to pale yellow, according to its concentration, and since solutions of sodium thiosulphate, iodide, and tetrathionate are all colourless, the progress of the interaction of an iodine solution with a thiosulphate solution may be followed by observing the diminishing intensity of the brown or yellow colour, and the completion of the interaction may be noted by the disappearance of the last trace of yellow colour from the liquid. Since iodine in presence of a dissolved iodide colours starch intensely blue, mucilage of starch is generally used as an indicator in iodine titrations, whereby the end-point is rendered more conspicuously noticeable.

The equation representing the interaction is—

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

from which it appears that 158 parts by weight of sodium thiosulphate (corresponding to 248 parts by weight of the crystallised salt, $Na_2S_2O_3,5\,H_2O$) interact with 254 parts by weight of iodine.

A standard solution of sodium thiosulphate is very commonly employed in conjunction with a standard solution of iodine, and it is convenient to prepare the latter solution of such a concentration that any given volume of it is exactly decolorised by an equal volume of the thiosulphate solution. A solution of iodine containing 127 grams per litre is called a normal solution, and, by convention, a solution containing 158 grams of sodium thiosulphate (corresponding to 248 grams of the crystallised salt) per litre, is also called a normal solution. Solutions of one-tenth these concentrations, or decinormal solutions, are more convenient for most purposes and are those usually employed.

A decinormal solution of iodine is prepared by shaking up 12·7 grams of pure iodine with the solution obtained by dissolving 20 to 25 grams of 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 grams of the crystals in water and making up the volume with water to a litre. It should be standardised from time to time by means of pure iodine.

Starch mucilage for use along with these solutions is prepared by rubbing about a gram of starch to a paste with a small quantity of cold water in a mortar, adding about 100 c.c. more water, heating the mixture to the boiling-point, and then allowing it to cool and settle, the clear upper liquid being poured off for use. As an indicator of the presence of iodine, this mucilage is much more delicate when freshly prepared than it is after having been kept for some time.

Standard solutions of sodium thiosulphate and of iodine find numerous and varied applications, of which the following may serve as an illustrative example.

Determination of the Copper in a solution of Cupric Sulphate.

Measure into a small flask 10 c.c. of the solution of cupric sulphate (which may be only very slightly acid with sulphuric or acetic acid, and must be free from nitric or hydrochloric acid), and add considerable excess of a solution of potassium iodide. Interaction gradually takes place with, eventually, complete precipitation of the copper as cuprous iodide [compare p. 110], in accordance with the equation—

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

from which it appears that for 126 parts by weight of copper converted into cuprous iodide, 254 parts by weight of iodine are liberated.

When the interaction is complete, run in decinormal sodium thiosulphate solution from the burette, until the colour of the liquid has almost disappeared; add a few drops of starch mucilage, and then, drop by drop, more thiosulphate solution until the blue colour just disappears. From the number of cubic centimetres of the sodium thiosulphate solution used, the weight of the liberated iodine can be ascertained, and from this the weight of copper which was converted into cuprous iodide can be calculated.

NOTE.—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 45 *et seq.*

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. It is also 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—

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

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.

✓ **Potassium hydroxide** produces a brown precipitate of silver hydroxide—

$$AgNO_3 + KOH = KNO_3 + AgOH.$$

This hydroxide decomposes very easily into silver oxide and water—

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

The precipitate is insoluble in excess of potassium 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.

d' J. Weber 21 [illegible] pp 3 1

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. 55, 56]. 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—

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

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

$$2\,HgNO_3 + 2\,KOH = 2\,KNO_3 + Hg_2O + H_2O.$$

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

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

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. 107].

Potassium chromate produces a red precipitate of mercurous chromate—

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

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* It is probable that these substances are really mixtures of the mercuric compounds [see p. 107] with metallic mercury.

Stannous chloride, if the solution does not contain a very large excess of hydrochloric acid [see p. 64], 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 or in ammonium hydrosulphide. 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.

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

$$HgCl_2 + 2\,KOH = 2\,KCl + HgO + H_2O.$$

Ammonia produces a white precipitate of a 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 salt 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.

Potassium 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. 81].

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

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.

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

$$Pb(NO_3)_2 + 2\,KOH = 2\,KNO_3 + Pb(OH)_2.^*$$

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

Potassium carbonate produces a white precipitate of lead carbonate—

$$Pb(NO_3)_2 + K_2CO_3 = 2\,KNO_3 + PbCO_3.$$

Potassium iodide produces a yellow precipitate of lead iodide—

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

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* 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 $Pb_2O(OH)_2$.

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 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 potassium 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 potassium hydroxide, and in concentrated solution of ammonium acetate, or of ammonium tartrate and ammonia.

$(NH_4)_2C_4H_4O_6$

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 carbonic oxide, 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—

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

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

$$CuSO_4 + 2\,KOH = K_2SO_4 + Cu(OH)_2.$$

Provided sufficient potassium hydroxide is added, the precipitate becomes black on boiling the liquid, 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 potassium cyanide.

Potassium 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. 73], 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 further on [p. 112].

REACTIONS OF SOLUTIONS OF STANNOUS SALTS.

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

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

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.

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

$$SnCl_2 + 2\,KOH = 2\,KCl + Sn(OH)_2.$$

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—

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

Stannic sulphide also dissolves in potassium 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—

$$3\,SnS_2 + 6\,KOH = 2\,K_2SnS_3 + K_2SnO_3 + 3\,H_2O.$$
$$2\,K_2SnS_3 + K_2SnO_3 + 6\,HCl = 3\,SnS_2 + 6\,KCl + 3\,H_2O.$$

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

$$H_4SnO_4 + 2\,KOH = K_2SnO_3 + 3\,H_2O.$$

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

Stannic chloride solution when kept for some time undergoes a gradual change with formation of what is called metastannic chloride solution. A similar solution is obtained by dissolving metastannic acid [see p. 49] in hydrochloric acid. There is reason to believe that metastannic acid is a polymer of stannic acid, probably corresponding to the formula, $H_{20}Sn_5O_{20}$. The reactions observed in such a solution do not, as a rule, differ greatly from those observed in the case of stannic chloride solution. One of the most marked exceptions is the behaviour with **sodium hydroxide**, which produces a precipitate with a metastannic solution, but does not redissolve it when added in excess; potassium hydroxide, however, behaves in a similar manner towards both solutions.

The change from stannic to metastannic solution may be recognised by the addition of **stannous chloride**, which produces a yellow coloration with the latter, but not with the former.

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.

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

$$Cd(NO_3)_2 + 2\,KOH = 2\,KNO_3 + Cd(OH)_2.$$

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—

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

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

$$BiCl_3 + 3\,KOH = 3\,KCl + Bi(OH)_3.$$

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

$$Bi(NO_3)_3 + 3\,NH_4OH = 3\,NH_4NO_3 + Bi(OH)_3.$$

Potassium 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 **potassium 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 cannot be obtained. 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.)

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 potassium hydroxide, in ammonia, and in ammonium carbonate, forming mixtures of arsenite and thiarsenite—

$$2\,As_2S_3 + 4\,KOH = KAsO_2 + 3\,KAsS_2 + 2\,H_2O.$$

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

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

Ammonia produces no precipitate.

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* With solution of arsenious acid, hydrogen sulphide produces colloidal arsenious sulphide which appears to remain dissolved, imparting 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 probably due to colloidal arsenious sulphide [see footnote on preceding page]. 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 precipitates arsenious sulphide from the arsenious compound produced.

The precipitate described above may be obtained immediately in the cold if a small quantity of a **thiosulphate** is added along with the other reagents.

H Cl. Arsen. chlor.
H S Arsen. Sul.
H [illegible] Ars in [illegible]

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— ho

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

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. 62] 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.

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—

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

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.

Tartar emetic is not an antimonious salt in the strict sense, as the metallic radical is potassium and the antimony forms part of the salt radical. Its composition is represented by the formula $KSbC_4H_4O_7$. It is one of the most important antimonious compounds, especially from a medical point of view, and a knowledge of its reactions is therefore desirable. These are given on page 119. Tartar emetic is soluble in water without decomposition.

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

The solution is strongly acid to **test paper** (see p. 117).

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 potassium hydroxide, forming a mixture of antimonite and thiantimonite. 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—

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

Potassium hydroxide produces a white precipitate of antimonious oxide—

$$2\,SbCl_3 + 6\,KOH = 6\,KCl + Sb_2O_3 + 3\,H_2O.$$

Antimonious oxide dissolves in potassium hydroxide, forming potassium antimonite.

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

Silver nitrate added to an alkaline solution of potassium 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 **potassium 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 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—

$$KSbC_4H_4O_7 + HCl = SbOCl + KHC_4H_4O_6.$$

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, orange antimonious sulphide is precipitated—

$$2\ KSbC_4H_4O_7 + 3\ H_2S = Sb_2S_3 + 2\ KHC_4H_4O_6 + 2\ H_2O.$$

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.

Potassium hydroxide produces, after some time, a white precipitate of antimonious oxide. 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 potassium 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 oxide is formed. The precipitate is insoluble in excess of ammonia.

Silver nitrate and **potassium 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 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—

$$ZnSO_4 + 2\,NH_4HS = (NH_4)_2SO_4 + H_2S + ZnS.$$

Potassium hydroxide produces a white precipitate of zinc hydroxide, soluble in excess—

$$ZnCl_2 + 2\,KOH = 2\,KCl + Zn\,(OH)_2.$$

The solution formed by dissolving zinc hydroxide in potassium 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.]

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.

Potassium carbonate produces a white precipitate of basic carbonate of zinc.

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—

$$MnSO_4 + 2\,NH_4HS = (NH_4)_2SO_4 + H_2S + MnS.$$

Potassium hydroxide produces a white precipitate* of manganous hydroxide, insoluble in excess—

$$MnSO_4 + 2\,KOH = K_2SO_4 + Mn(OH)_2.$$

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 prevented by the presence of a sufficiency of ammonium chloride.

Potassium carbonate produces a white precipitate of manganous carbonate—

$$MnCl_2 + K_2CO_3 = 2\,KCl + MnCO_3.$$

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 man-

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* 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 potassium hydroxide are boiled for some time, to expel this dissolved oxygen, before they are mixed.

ganite and hydroxide. The general nature of the change may be represented by the following equation—

$$3\,K_2MnO_4 + 2\,H_2O = 4\,KOH + 2\,KMnO_4 + MnO_2\ ;$$

but it is to be borne in mind that some of the hydroxide represented in the equation is really neutralised with formation of insoluble manganite. The decomposition 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—

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

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

In order that the permanganate may be reduced completely to manganous salt, and the formation of insoluble manganite avoided, it is necessary to add free acid considerably in excess of that represented in the equations.

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 [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].

Solutions of ferric salts 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—

$$FeCl_2 + 2\,NH_4HS = 2\,NH_4Cl + H_2S + FeS.$$

Potassium hydroxide produces a white precipitate of ferrous hydroxide, insoluble in excess—

$$FeCl_2 + 2\,KOH = 2\,KCl + Fe(OH)_2.$$

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. 121.]

✓ **Ammonia** produces a white precipitate of ferrous hydroxide, insoluble in excess. [See preceding paragraph.]

✓ **Potassium carbonate** produces a whitish precipitate of ferrous carbonate—

$$FeSO_4 + K_2CO_3 = K_2SO_4 + FeCO_3.$$

On exposure to the air ferrous carbonate becomes slowly oxidised into ferric hydroxide, carbonic anhydride being evolved. The oxidation takes place more slowly than in the case of ferrous hydroxide, but the colour changes observed are similar.

✓ **Potassium ferrocyanide** produces a white precipitate of ferrous ferrocyanide—

Much more [illegible]

$$2\,FeSO_4 + K_4Fe(CN)_6 = 2\,K_2SO_4 + Fe_2Fe(CN)_6.$$

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—

$$Fe_2S_3 + 4\,HCl = 2\,H_2S + 2\,FeCl_2 + S.$$
$$2\,FeS\,(+S) + 4\,HCl = 2\,H_2S + 2\,FeCl_2\,(+S).$$

Potassium hydroxide produces a reddish brown precipitate of ferric hydroxide, insoluble in excess—

$$FeCl_3 + 3\,KOH = 3\,KCl + Fe(OH)_3.$$

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. 65.]

Potassium thiocyanate produces a deep red solution. 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.

REACTIONS OF SOLUTIONS OF COBALTOUS SALTS.

With salts derived from weak acids **hydrogen sulphide** produces a black precipitate of cobaltous sulphide, insoluble in dilute acids—

$$Co\overline{A}_2 + H_2S = 2\,H\overline{A} + CoS.$$

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—

$$Co(NO_3)_2 + 2\,NH_4HS = 2\,NH_4NO_3 + H_2S + CoS.$$

Potassium hydroxide produces a blue precipitate of basic salt, insoluble in excess, but becoming reddish on boiling, owing to its conversion into hydroxide—

$$Co(NO_3)_2 + 2\,KOH = 2\,KNO_3 + Co(OH)_2.$$

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.

Potassium 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.

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 **potassium 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.

With salts derived from weak acids, **hydrogen sulphide** produces a black precipitate of nickel sulphide, insoluble in dilute acids—

$$Ni\overline{A}_2 + H_2S = 2H\overline{A} + NiS.$$

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 nickel sulphide, insoluble in dilute acids—

$$NiSO_4 + 2\,NH_4HS = (NH_4)_2SO_4 + H_2S + NiS.$$

Potassium hydroxide produces a pale green precipitate of nickel hydroxide, insoluble in excess—

$$NiSO_4 + 2\,KOH = K_2SO_4 + Ni(OH)_2.$$

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.

Potassium carbonate produces a pale green precipitate of basic nickel carbonate.

Bleaching solution produces, somewhat slowly, a black precipitate of nickelic hydroxide $Ni(OH)_3$. When excess of bleaching solution is added and the mixture warmed, oxygen is evolved, due to the decomposition of the hypochlorite.

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 **potassium 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**], nitrate, chloride [**5, 6**], bromide [**5**], acetate.

REACTIONS OF SOLUTIONS OF ALUMINIUM SALTS.

Potassium hydroxide produces a white gelatinous precipitate of aluminium hydroxide, soluble in excess—

$$Al_2(SO_4)_3 + 6\,KOH = 3\,K_2SO_4 + 2\,Al(OH)_3.$$

From the solution obtained by dissolving the precipitate in excess of potassium hydroxide, ammonium chloride, if added in sufficient quantity, reprecipitates aluminium hydroxide. The reason of this is that ammonium chloride interacts with potassium hydroxide, forming water, potassium chloride, and ammonia, in which mixture aluminium hydroxide is almost insoluble. The solution of aluminium hydroxide in potassium hydroxide gives no precipitate on the addition of a small quantity of hydrogen sulphide; but if the latter reagent is added until all the potassium hydroxide is converted into potassium hydrosulphide the whole of the aluminium hydroxide is reprecipitated, because it is insoluble in potassium hydrosulphide. [Compare the Reactions of Zinc Salts.]

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—

$$Al_2(SO_4)_3 + 6NH_4HS + 6H_2O = 3(NH_4)_2SO_4 + 6H_2S + 2Al(OH)_3.$$

Potassium carbonate produces a white precipitate of aluminium hydroxide or of basic aluminium carbonate, with evolution of carbonic anhydride.

After acidifying with **hydrochloric acid, potassium ferrocyanide** produces no precipitate. [Compare the Reactions of Zinc Salts.]

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**], 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.

Potassium hydroxide produces a bluish or greenish grey precipitate of chromic hydroxide, which dissolves in excess forming a green solution—

$$CrCl_3 + 3\,KOH = 3\,KCl + Cr(OH)_3.$$

The green solution obtained by dissolving chromic hydroxide in excess of potassium hydroxide gives a green precipitate of chromic hydroxide on boiling, provided only a slight excess of potassium 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—

$$CrCl_3 + 3\,NH_4HS + 3\,H_2O = 3\,NH_4Cl + 3\,H_2S + Cr(OH)_3.$$

Potassium 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—

$$2\,K_2CrO_4 + 2\,HCl = 2\,KCl + H_2O + K_2Cr_2O_7.$$

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[*] 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.

Reducing agents along with **free acid** produce chromic salt, and the colour of the solution changes to bluish purple or green. **Hydrogen sulphide, sulphurous acid, alcohol,** and **stannous chloride** may be taken as examples of such reducing agents. In some cases it is necessary to heat the mixture.

$$2\,K_2CrO_4 + 5\,H_2SO_4 + 3\,H_2S = Cr_2(SO_4)_3 + 2\,K_2SO_4 + 8H_2O + 3S.$$

$$2\,K_2CrO_4 + 2\,H_2SO_4 + 3\,H_2SO_3 = Cr_2(SO_4)_3 + 2\,K_2SO_4 + 5\,H_2O.$$

$$2\,K_2CrO_4 + 5\,H_2SO_4 + 3\,C_2H_6O = Cr_2(SO_4)_3 + 2\,K_2SO_4 + 8\,H_2O + 3\,C_2H_4O.$$

$$2\,K_2CrO_4 + 16\,HCl + 3\,SnCl_2 = 2\,CrCl_3 + 4\,KCl + 3\,SnCl_4 + 8\,H_2O.$$

✓ **Silver nitrate** produces a red precipitate of silver chromate, soluble in nitric acid and in ammonia— see Ag)

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

✓ **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.

REACTIONS OF SOLUTIONS OF BARIUM SALTS.

✓ **Ammonium carbonate** produces a white precipitate of barium carbonate, soluble in dilute acids with evolution of carbonic anhydride—

$$Ba(NO_3)_2 + (NH_4)_2CO_3 = 2\,NH_4NO_3 + BaCO_3.$$

✓ **Potassium hydroxide,** even if quite free from carbonate, produces in concentrated solutions, a white precipitate of barium hydroxide— N.B.

$$BaCl_2 + 2\,KOH = Ba(OH)_2 + 2\,KCl.$$

Commercial potassium hydroxide, or potassium hydroxide solution which has been exposed to the air, always contains potassium carbonate, and this interacts even with dilute solutions of barium salts, producing a white precipitate of barium carbonate—

$$Ba(NO_3)_2 + K_2CO_3 = 2\,KNO_3 + BaCO_3.$$

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—

$$Ba(NO_3)_2 + (NH_4)_2C_2O_4 = 2\ NH_4NO_3 + BaC_2O_4.$$

[See also p. 187.]

STRONTIUM.

Basic oxide, SrO.

Examples of soluble strontium salts [**1, 6**]:—Nitrate, chlorate, acetate, chloride, bromide, iodide.

REACTIONS OF SOLUTIONS OF STRONTIUM SALTS.

Ammonium carbonate produces a white precipitate of strontium carbonate, soluble in dilute acids with evolution of carbonic anhydride—

$$SrCl_2 + (NH_4)_2CO_3 = 2\ NH_4Cl + SrCO_3.$$

Potassium hydroxide, even if quite free from carbonate, produces in concentrated solutions a white precipitate of strontium hydroxide—

$$SrCl_2 + 2\ KOH = Sr(OH)_2 + 2\ KCl.$$

Potassium hydroxide containing potassium carbonate as impurity, produces a white precipitate of strontium carbonate. [See under Reactions of Barium Salts.]

Ammonia, if quite free from ammonium carbonate, does not produce any precipitate.

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—

$$SrCl_2 + (NH_4)_2C_2O_4 = 2\ NH_4Cl + SrC_2O_4.$$

[See also p. 187.]

CALCIUM.

Basic oxide, CaO.

Examples of soluble calcium salts [6]:—Nitrate, chlorate, acetate, chloride, bromide, iodide, sulphate.

REACTIONS OF SOLUTIONS OF CALCIUM SALTS.

Ammonium carbonate produces a white precipitate of calcium carbonate, soluble in dilute acids with evolution of carbonic anhydride—

$$CaCl_2 + (NH_4)_2CO_3 = 2\ NH_4Cl + CaCO_3.$$

Potassium hydroxide, even if quite free from carbonate, produces in moderately concentrated solutions, a white precipitate of calcium hydroxide—

$$CaCl_2 + 2\ KOH = Ca(OH)_2 + 2\ KCl.$$

Potassium hydroxide containing potassium carbonate as impurity, produces a white precipitate of calcium carbonate. [See under Reactions of Barium Salts.]

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. [See under Reactions of Barium and Strontium Salts.] In concentrated solutions partial precipitation takes place on boiling.

Ammonium oxalate produces a white precipitate of calcium oxalate, insoluble in acetic acid but soluble in hydrochloric acid—

$$CaCl_2 + (NH_4)_2C_2O_4 = 2\ NH_4Cl + CaC_2O_4.$$

[See also p. 187.]

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.

Potassium carbonate produces, on warming, a white precipitate of basic magnesium carbonate.

Potassium hydroxide produces a white precipitate of magnesium hydroxide, insoluble in excess—

$$MgSO_4 + 2\ KOH = K_2SO_4 + Mg(OH)_2.$$

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 **sodium phosphate** produce a white precipitate of ammonium magnesium phosphate—

$$MgSO_4 + Na_2HPO_4 + NH_3 = Na_2SO_4 + MgNH_4PO_4.$$

The ammonium chloride is added to prevent the precipitation of magnesium hydroxide by the ammonia alone.

Iodine and then **potassium hydroxide** (the latter in very small quantity) produce a dark brown precipitate which consists of magnesium hydroxide coloured by free iodine. Excess of potassium 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 **potassium hydroxide** ammonia gas is evolved—

$$(NH_4)_2SO_4 + 2\,KOH = K_2SO_4 + 2\,NH_3 + 2\,H_2O.$$ ✓

The ammonia can be recognised by its odour and by its action on moist turmeric paper. [See note on p. 140.]

With very concentrated solutions **sodium hydrogen tartrate** may produce a white precipitate of ammonium hydrogen tartrate— nil

$$NH_4Cl + NaH\overline{T} = NaCl + NH_4H\overline{T}.$$

With very dilute solutions **Nessler's reagent** 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.

$$NH_4Cl + 2\,KHgI_3 + 4\,KOH = NH_2Hg_2OI + 5\,KI + KCl + 3\,H_2O.$$

In moderately concentrated solutions **chloroplatinic acid** produces a yellow precipitate of ammonium chloroplatinate—

$$2\,NH_4Cl + H_2PtCl_6 = 2\,HCl + (NH_4)_2PtCl_6.$$

The precipitate is somewhat soluble in water, insoluble in alcohol.

POTASSIUM.

Basic oxide, K_2O.

The majority of the potassium salts are readily soluble in water, potassium hydrogen tartrate being one 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** 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 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 acid 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 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—

$$KNa\overline{T} + NaH\overline{T} + KH\overline{T} + Na_2\overline{T}.$$

[See also p. 187.]

In moderately concentrated solutions chloroplatinic acid produces a yellow precipitate of potassium chloroplatinate—

$$2\,KNO_3 + H_2PtCl_6 = 2\,HNO_3 + K_2PtCl_6.$$

The precipitate is slightly soluble in water, insoluble in alcohol.

✓ 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 ten cubic centimetres of alcohol, a yellow precipitate of potassium bismuth thiosulphate is produced, easily soluble on the addition of water.

SODIUM.

Basic oxide, Na_2O.

The sodium salts of all the usually occurring salt 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 p. 187.

Classification of the commoner Metallic Radicals from the point of view of the Reactions of their Salts.

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. $As^{\cdot\cdot\cdot}$, $Sb^{\cdot\cdot\cdot}$, $Ag^{\cdot}$, $Hg^{\cdot}$, $Hg^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Sn^{\cdot\cdot}$.

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: $Fe^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Mn^{\cdot\cdot}$.

C. Metallic radicals, the sulphides of which are soluble in water or cannot be prepared from the salts in the wet way: $Cr^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $K^{\cdot}$, $Na^{\cdot}$, $(NH_4)^{\cdot}$.

A may be divided into the following three groups:—

I. The sulphides are thio-anhydrides, and dissolve in ammonium hydrosulphide: $As^{\cdot\cdot\cdot}$, $Sb^{\cdot\cdot\cdot}$.

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: $Ag^{\cdot}$, $Hg^{\cdot}$. (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: $Hg^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Sn^{\cdot\cdot}$.

B need not be further divided.

C may be divided into the following four groups:—

I. Ammonium hydrosulphide precipitates the hydroxide: $Cr^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$. These hydroxides are soluble in potassium hydroxide; while the sulphides of class **B** are insoluble in potassium hydroxide.

II. The carbonates are insoluble in water, and very sparingly so in ammonium chloride: $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ca^{\cdot\cdot}$.

III. The carbonate is insoluble in water, but easily soluble in ammonium chloride: $Mg^{\cdot\cdot}$.

IV. The carbonates and phosphates are soluble in water: $(NH_4)^{\cdot}$, $K^{\cdot}$, $Na^{\cdot}$.

PART II.—DEALING WITH THE REACTIONS DUE TO THE SALT 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 carbonic anhydride escapes with effervescence; the latter may be detected by means of **calcium hydroxide,** as described on p. 79.

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

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 sulphurous anhydride, and the latter may escape with effervescence—

$$H_2SO_3 = H_2O + SO_2.$$

In cases where there is no effervescence, a quantity of sulphurous anhydride 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.

Hydrochloric acid and **hydrogen sulphide** produce a yellowish 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 salt radical—

I N
S A

$$Na_2SO_3 + 2\ AgNO_3 = 2\ NaNO_3 + Ag_2SO_3.$$
$$Ag_2SO_3 + Na_2SO_3 = 2\ NaAgSO_3.$$

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 sulphurous anhydride 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 sulphurous anhydride 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 in which silver forms part of the salt 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 purplish 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.

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—

$$(NH_4)_2S + 2\,AgNO_3 = 2\,NH_4NO_3 + Ag_2S.$$

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 107. 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.

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 in which silver forms part of the salt 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 **potassium 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 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—

$$HCN + (NH_4)_2S_2 = NH_4HS + NH_4CNS.$$

HYPOCHLORITES AND "BLEACHING SALTS."

Hypochlorous acid, $HClO$; monobasic.

Pure hypochlorites are difficult to prepare and are of very little practical importance. 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 carbonic anhydride 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 under Reactions of Iodides.]

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 under Reactions of Cobaltous Salts.]

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. 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—

$$KNO_2 + AgNO_3 = KNO_3 + AgNO_2.$$

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, $H\overline{A}$ or $HC_2H_3O_2$; 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 characteristic 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.

Barium nitrate produces no precipitate.

Silver nitrate produces no precipitate.

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—

$$K_2SO_4 + Pb\bar{A}_2 = 2K\bar{A} + PbSO_4.$$

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.

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 di-hydrogen 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 produces a white precipitate of ammonium magnesium phosphate—

$$Na_2HPO_4 + MgCl_2 + NH_3 = 2\,NaCl + MgNH_4PO_4.$$

Ammonium molybdate in nitric acid solution produces, on warming, a bright yellow precipitate of a complex salt.

OXALATES.

Oxalic acid, $H_2C_2O_4$; dibasic.

Examples of soluble oxalates: — Oxalates of potassium, sodium, and ammonium.

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—

$$K_2C_2O_4 + CaCl_2 = 2\,KCl + CaC_2O_4.$$

Solid oxalates when heated with **concentrated sulphuric acid** are converted into sulphates, with evolution of a mixture of carbonic oxide and carbonic anhydride—

$$K_2C_2O_4 + H_2SO_4 = K_2SO_4 + H_2O + CO + CO_2.$$

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, $Na_2B_4O_7$, 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 **potassium hydroxide** the colour is changed to dark green.

If a solid borate is moistened with **concentrated sulphuric 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.

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 peroxide and **concentrated sulphuric acid** liberate chlorine, which can be recognised by its odour and colour, and by its action on **potassium iodide** test paper—

$$2\,KCl + MnO_2 + 2\,H_2SO_4 = K_2SO_4 + MnSO_4 + 2\,H_2O + Cl_2.$$

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.

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* The drying is best effected by wrapping the paper round the outside of a test tube containing hot water.

REACTIONS OF SOLUTIONS OF BROMIDES.

Silver nitrate produces a slightly yellowish curdy precipitate of silver bromide, insoluble in nitric acid, but soluble in ammonia—

(large [illegible]
only

$$KBr + AgNO_3 = AgBr + KNO_3.$$

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 peroxide 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; monabasic.

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 pale 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 peroxide 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 sulphurous anhydride—

$$2\,H_2SO_4 + 2\,KI = K_2SO_4 + 2\,H_2O + SO_2 + I_2.$$

Lead acetate produces a yellow precipitate of lead iodide.

Mercuric chloride produces a red precipitate of mercuric iodide, as described under the reactions of mercuric salts.

See [illegible] no ppt with $AgNO_3$

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—

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

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.

ARSENITES.

ARSENATES.

Arsenic acid, H_3AsO_4; tribasic.

CHROMATES.

Chromic acid, H_2CrO_4; dibasic.

Reactions of solutions of the above salts have been described already at pages 116 and 128.

col
Sol in h.s. ~ HHG$_3$, col
> NH$_4$

Classification of the commoner Salt Radicals, from the point of view of the Reactions of their Salts.

A. Salt 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', $C_2H_3O_2'$.

B. Salt radical, of which the barium salt is insoluble in water and in dilute acids:—SO_4''.

C. Salt 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'', BO_2', AsO_3''', CrO_4''.

D. Salt radicals, of which the silver salts are insoluble in water and in dilute nitric acid:—Cl', Br', I', CN', S''.

E. Salt radicals, of which all the normal salts are soluble in water:—NO_3', ClO_3', $C_2H_3O_2'$.

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.

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).

* It is difficult to get a precipitate by the action of sulphurous anhydride when the experiment is carried out in the manner described on p. 79.

SCHEME

FOR THE

SYSTEMATIC APPLICATION OF THE FOREGOING ANALYTICAL REACTIONS TO THE DETECTION OF A SINGLE SALT IN SOLUTION.

SCHEME.

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.

I.—EXAMINATION FOR THE METALLIC RADICAL:—

Note that although the tests here applied are intended for the detection of the metallic radical, reactions will, in some cases, be observed which are due to the salt radical. In these cases it is advisable to follow up the indications thus obtained, and determine the salt radical before continuing the examination for the metallic radical.

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 is produced (which does not dissolve on adding more hydrochloric acid). See **A.**

(*b*) A white or pale yellow precipitate of sulphur is produced. See **B.**

(*c*) A recognisable gas [see p. 150] is evolved in the cold, or on gently warming. See **C.**

(*d*) A precipitate is not produced, or if produced, it dissolves in excess of hydrochloric acid, and no recognisable gas is evolved even on warming. See **2.**

2. To the same solution (containing **hydrochloric acid**) add **hydrogen sulphide** until the mixture, after shaking, smells of the reagent.

(*a*) A yellow precipitate is produced. See **D.**

(*b*) An orange precipitate is produced. See **E.**

(*c*) A dark brown or black precipitate is produced. See **F.**

(*d*) A yellow precipitate is produced slowly on warming. See **G.**

(*e*) A white or pale yellow precipitate, consisting of sulphur only, is produced. See **H.**

(*f*) No precipitate is produced even on warming. See **3.**

3. I. To the same solution (containing **hydrochloric acid** and **hydrogen sulphide**) add **ammonia** until the mixture, after shaking, smells of the reagent: Or, II. If a precipitate of sulphur has been produced by the action of hydrogen sulphide (2, *e*), 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 is produced. See **J.**

(*b*) A buff precipitate is produced. See **K.**

(*c*) A black precipitate is produced. See **L.**

(*d*) A bluish-grey or green precipitate is produced. See **M.**

(*e*) No precipitate is produced. See **4.**

4. To a fresh portion of the original solution add **ammonium chloride, ammonia** until the mixture, after shaking, smells of it, and **ammonium carbonate.**

(*a*) A white precipitate is produced. See **N.**

(*b*) No precipitate is produced. See **5.**

5. To the same solution (containing **ammonium chloride** and **ammonia**) add **sodium phosphate.**

(*a*) A white precipitate is produced. See **O.**

(*b*) No precipitate is produced. See **P.**

II.—EXAMINATION FOR THE SALT RADICAL:—

Note that, in some cases, information respecting the salt radical will have been obtained during the systematic examination for the metallic radical. What follows contains a scheme for the examination for those salt 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.

6. To a portion of the original solution add **barium nitrate,** and if a precipitate is produced add **nitric acid.**

(*a*) A white precipitate remains undissolved. See **Q.**

(*b*) A precipitate is not produced, or, if produced, it dissolves in nitric acid. See **7.**

7. To a fresh portion of the original solution add **silver nitrate,** and if a precipitate is produced add **nitric acid.** (Note that silver oxalate (white) requires a considerable quantity of nitric acid to dissolve it.) [See footnote, p. 160.]

(*a*) The precipitate dissolves. See **R.**

(*b*) The precipitate does not dissolve. See **S.**

(*c*) No precipitate is produced. See **T.**

A. The WHITE PRECIPITATE, consisting of a chloride, indicates the presence of a silver, a mercurous, or a lead salt.

To the precipitate add **ammonia** in excess :

Silver chloride dissolves ; confirm* **SILVER** by means of **potassium iodide** [p. 104].

Mercurous chloride is blackened ; confirm **MERCUROUS** by means of **stannous chloride** [p. 106].

Lead chloride is changed into white basic salt which remains undissolved ; confirm **LEAD** by means of **potassium iodide** [p. 108].

B. The WHITE OR PALE YELLOW PRECIPITATE is produced somewhat slowly in the cold, but more rapidly on warming, and sulphurous anhydride is simultaneously evolved. (An immediate precipitate of sulphur indicates polysulphide ; see below.) This indicates the presence of a thiosulphate ; confirm **THIOSULPHATE** by means of **silver nitrate** [p. 138]. (If thiosulphate is proved to be present, resume testing for the metallic radical at **4**, p. 153.)

C. The recognisable gases and the salt radicals which they indicate are as follows :—

CARBONIC ANHYDRIDE indicates carbonate ; confirm **CARBONATE** by means of **barium nitrate** and **silver nitrate** [p. 136]. (Resume at **P**, p. 159.)

SULPHUROUS ANHYDRIDE, if evolved without simultaneous precipitation of sulphur, indicates a sulphite ; confirm **SULPHITE** by means of **silver nitrate** [p. 137]. (Resume at **4**, p. 153.)

SULPHUROUS ANHYDRIDE, with simultaneous PRECIPITATION OF SULPHUR, indicates thiosulphate. [See **B**.]

HYDROGEN SULPHIDE indicates sulphide or hydrosulphide ; confirm **SULPHIDE** or **HYDROSULPHIDE** by means of **silver nitrate** [p. 139]. (Resume at **4**, p. 153.)

NOTE that in the case of polysulphides the evolution of hydrogen sulphide is accompanied by the formation of a white precipitate of sulphur.

HYDROCYANIC ACID indicates cyanide ; confirm **CYANIDE** by means of **silver nitrate** and the **Prussian blue test** [p. 140]. [See also **S**.] (Resume at **4**, p. 153.)

NOTE that MERCURIC CYANIDE is exceptional in its reactions.

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[*] **All confirmatory tests are to be applied to fresh portions of the original solution.**

HYPOCHLOROUS ACID or CHLORINE indicates hypochlorite; confirm **HYPOCHLORITE** by means of **cobaltous nitrate** [p. 141]. (Resume at **4**, p. 153.)

" EUCHLORINE " indicates chlorate; confirm **CHLORATE** by means of **concentrated sulphuric acid** [p. 142]. [See also **T.**] (Resume at **2**, p. 152.)

NITROGEN PEROXIDE indicates a nitrite; confirm **NITRITE** by means of **potassium iodide** and **acetic acid**, and of **ferrous sulphate** [p. 143]. (Resume at **3**, II., p. 153.)

ACETIC ACID indicates an acetate; confirm **ACETATE** by means of **ferric chloride** [p. 143]. [See also **T.**] (Resume at **2**, p. 152.)

D. The 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 **potassium hydroxide** and of **ammonia** [p. 113].

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 **potassium hydroxide** or of **ammonia** [p. 115]. 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. 116]. (If arsenite is proved to be present, resume testing for the metallic radical at **P**, p. 159).

E. The ORANGE PRECIPITATE, consisting of antimonious sulphide, is insoluble in **ammonia,** and indicates the presence of an antimonious salt or of tartar emetic.

If the original solution is strongly acid to **test paper,** antimonious salt is indicated, but if neutral then tartar emetic is indicated; confirm **ANTIMONIOUS** or **TARTAR EMETIC,** as the case may be, by means of **potassium hydroxide,** of **ammonia,** and of **hydrogen sulphide** alone [pp. 118, 119].

F. The 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 acidulated 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. 106]. In the case of lead salts the precipitate is often reddish-brown at first, and becomes black on further addition of the reagent [p. 108].

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. 107].

NO PRECIPITATE, indicates stannous; confirm **STANNOUS** by means of **mercuric chloride** [p. 111].

A YELLOW PRECIPITATE, soluble in boiling water, indicates lead; confirm **LEAD** by means of **potassium chromate** [p. 109].

A YELLOW PRECIPITATE RAPIDLY CHANGING TO PINK, and soluble in excess of potassium iodide, indicates mercuric; confirm **MERCURIC** by means of **stannous chloride** [p. 107].

A YELLOW SOLUTION, or

A BROWN PRECIPITATE, soluble in considerable excess of potassium iodide to form a yellow solution, indicates **BISMUTH** [p. 114].

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. 110].

G. The YELLOW PRECIPITATE, consisting of sulphur and arsenious sulphide, indicates the presence of an arsenate; confirm **ARSENATE** by means of **silver nitrate** [p. 117]. (Resume at P, p. 159.)

H. The WHITE or PALE YELLOW PRECIPITATE of sulphur is produced by the oxidation of hydrogen sulphide. Such oxidation occurs when one of the following is present:—

(*a*) Salts which in virtue of their salt radicals yield an oxidising mixture when treated with hydrochloric acid. Of these, the following should have been already detected [**C**], if present:—sulphite, thiosulphate, hypochlorite, chlorate, nitrite; and only chromate remains to be considered.

In the case of chromate the original solution is coloured yellow; it becomes reddish 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. 129]. (Resume at **3**, II., p. 153.)

(*b*) Ferric salt [p. 123]. The ferric salt is reduced to ferrous, and the yellow solution becomes practically colourless [see **3**, II., p. 153].

J. The 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 observing that a *small* quantity of **hydrogen sulphide** precipitates the solution obtained by adding excess of **potassium hydroxide** to the original solution [p. 120].

Aluminium solution gives no precipitate; confirm **ALUMINIUM** by observing that a small quantity of **hydrogen sulphide** does not precipitate the solution obtained by adding excess of **potassium hydroxide** to the original solution [p. 127].

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. 152]

K. The BUFF PRECIPITATE, consisting of the sulphide, indicates the presence of a manganous salt; confirm **MANGANOUS** by means of **bleaching solution** [p. 121].

L. The 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. 123, 124].

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 **potassium hydroxide** and of **ammonia** [pp. 125, 126].

M. The BLUISH GREY or GREEN PRECIPITATE, consisting of chromic hydroxide, indicates the presence of a chromic salt ; confirm **CHROMIC** by means of **bleaching solution** [p. 128].

N. The 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. 130], and the **flame test** [p. 187].

Strontium solution gives a white precipitate on standing some time or on boiling ; confirm **STRONTIUM** by means of **potassium chromate** [p. 131], and the **flame test** [p. 187].

Calcium solution does not give any precipitate, even on boiling ; confirm **CALCIUM** by means of **potassium chromate** [p. 132], and the **flame test** [p. 187].

O. The WHITE PRECIPITATE, consisting of ammonium magnesium phosphate, indicates the presence of a magnesium salt ; confirm **MAGNESIUM** by means of **iodine** and **potassium hydroxide,** adding the latter drop by drop [p. 132.]

P. To a fresh portion of the original solution add **sodium hydrogen tartrate** till decidedly acid [see p. 133], and set aside; do not warm.

In another fresh portion test for ammonium by means of **potassium hydroxide** [p. 133, but see note on p. 140]; confirm **AMMONIUM** by means of **Nessler's reagent** applied to a single drop of the solution.

If ammonium is proved to be absent, examine the solution to which sodium hydrogen tartrate was added; a white crystalline precipitate indicates potassium; confirm **POTASSIUM** by means of the **flame test,** using the cobalt-blue glass [p. 187].

If ammonium and potassium are both proved to be absent, test for **SODIUM** by means of the **flame test** [p. 187].

Q. The WHITE PRECIPITATE of barium salt indicates the presence of a sulphate; confirm **SULPHATE** by means of **lead acetate** [p. 144].

R. I. The original precipitate of SILVER SALT IS WHITE, indicating the presence of a borate or an oxalate (or a carbonate. See note below).

To the original solution add **hydrochloric acid** and test the mixture by means of **turmeric paper,** subsequently drying the latter if necessary:

Borate gives a reddish stain, turned dark green by potassium hydroxide; confirm **BORATE** by means of **calcium chloride** and **acetic acid** [p. 146].

Oxalate gives no stain; confirm **OXALATE** by means of **calcium chloride** and **acetic acid** [p. 145].

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.

II. The original precipitate of SILVER SALT IS YELLOW, indicating the presence of a phosphate or an arsenite. The latter should have been already detected when testing for the metallic radical [see **D.**]. If hydrochloric acid and hydrogen sulphide have given no precipitate, confirm **PHOSPHATE** by means of **magnesia mixture** [p. 145].

III. The original precipitate of SILVER SALT IS BROWN, indicating the presence of an arsenate; confirm **ARSENATE** by means of **magnesia mixture** [p. 117]. (The presence of an arsenate might have been detected earlier [**G**]).

IV. The original precipitate of SILVER SALT IS CRIMSON, indicating the presence of a chromate; confirm **CHROMATE** by means of lead acetate [p. 129]. (The presence of a chromate might have been detected earlier [**H**]).

S. A BLACK PRECIPITATE of silver salt indicates sulphide or hydrosulphide; confirm **SULPHIDE** or **HYDROSULPHIDE** by means of **hydrochloric acid** and **lead acetate** test paper [p. 139].

A WHITE or YELLOW PRECIPITATE of silver salt indicates the presence of a cyanide (white), a chloride (white), a bromide (very pale yellow), or an iodide (pale yellow).

To the original solution add **chlorine water**:

The liberation of bromine indicates bromide; if necessary, confirm **BROMIDE** by means of **manganese peroxide** and **concentrated sulphuric acid** [p. 147].

The liberation of iodine indicates iodide; confirm **IODIDE** by means of **mercuric chloride** [p. 148].

A negative reaction indicates cyanide or chloride. In this case test the original solution by means of **silver nitrate** * in small quantity:

A locally formed precipitate which dissolves on shaking the liquid indicates cyanide; confirm **CYANIDE** by means of the **Prussian blue test** [p. 140].

A persistent white precipitate indicates chloride; confirm **CHLORIDE** by means of **manganese peroxide** and **concentrated sulphuric acid** [p. 146].

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 peroxide 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.

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* This second addition of silver nitrate to the original solution may be avoided if due attention is paid when adding it as group reagent at **7**, p. 153.

T. Taking a fresh portion of the original solution for each experiment, test for

NITRATE, by means of **ferrous sulphate** and **concentrated sulphuric acid** [p. 148].

CHLORATE, by means of **concentrated sulphuric acid** [p. 142].

ACETATE, by means of **ferric chloride** [p. 143].

EXAMINATION OF SOLID SUBSTANCES.

The solid may be examined in the first place by means of the dry-way reactions described on pages 187 *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 do not come within the scope of the present work.

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 gram) 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 off 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 152 *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 reduction products which might introduce possible complications, as nitric acid does; 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 salt radicals included in the general scheme. The reason for this is that, when they are dissolved in acid, the resulting solution contains *two* salt 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 salt 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, and the tube re-inverted 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 carbonic anhydride 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.

Peroxides, when warmed with not too dilute hydrochloric acid, yield either chlorine (PbO_2, MnO_2) or oxygen (BaO_2). 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 carbonic anhydride, recognisable by means of lime water; after effervescence ceases the solution should be boiled to expel all carbonic anhydride, 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 sulphurous anhydride, 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 work. 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 salt radical should have been detected by recognising the gas evolved on dissolving in acid.

APPENDIX

CONTAINING

THE REACTIONS OF SOME OF THE RARER METALLIC RADICALS AND INORGANIC SALT RADICALS, TOGETHER WITH SOME OF THE MORE IMPORTANT DRY-WAY REACTIONS.

APPENDIX.

I. METALLIC RADICALS.

CERIUM.

Basic oxides :—Cerous oxide, Ce_2O_3 ; ceric oxide, CeO_2.
The ceric salts are of little importance, and will not be considered here.
Examples of soluble cerous salts :—Sulphate, nitrate, chloride.

REACTIONS OF SOLUBLE CEROUS SALTS.

Potassium hydroxide produces a white precipitate of cerous hydroxide, $Ce(OH)_3$, insoluble in excess. The precipitate gradually turns yellow on exposure to the air, owing to the formation of ceric hydroxide, $Ce(OH)_4$.

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

Ammonium hydrosulphide produces a white precipitate of cerous hydroxide, insoluble in excess.

Potassium carbonate produces a white precipitate of cerous hydroxide, insoluble in excess.

Ammonium oxalate produces a white precipitate of cerous oxalate, insoluble in excess and in dilute hydrochloric acid.

A hot saturated solution of **potassium sulphate** produces a white precipitate of potassium cerous sulphate, $K_3Ce(SO_4)_3$, sparingly soluble in cold water, but readily soluble in hot water and in dilute hydrochloric acid. The precipitate is insoluble in potassium sulphate solution.

GLUCINUM (or BERYLLIUM).

Basic oxide, GlO.
Examples of soluble glucinum salts :—Chloride, nitrate, sulphate, acetate.

REACTIONS OF SOLUTIONS OF GLUCINUM SALTS.

Ammonium hydrosulphide produces a white precipitate of glucinum hydroxide, insoluble in excess—

$$GlCl_2 + 2\,NH_4HS + 2\,H_2O = 2\,NH_4Cl + 2\,H_2S + Gl(OH)_2.$$

Glucinum hydroxide dissolves in hydrochloric acid, forming a yellow solution which becomes colourless on dilution with water.

Potassium hydroxide produces a white precipitate of glucinum hydroxide, soluble in excess. If the addition of unnecessary excess of potassium hydroxide has been avoided, glucinum hydroxide is reprecipitated on boiling the alkaline solution, especially after dilution with water. Glucinum hydroxide is also reprecipitated from the alkaline solution on the addition of ammonium chloride in sufficient quantity.

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

Ammonium carbonate produces a white precipitate of glucinum carbonate, soluble in excess. From the solution obtained by adding excess of ammonium carbonate, a basic glucinum carbonate is precipitated on boiling.

GOLD.

Basic oxides:—Aurous oxide, Au_2O; auric oxide, Au_2O_3. These oxides are very weak bases, but some salts corresponding to each of them are known. Auric oxide also behaves as an acid anhydride, dissolving in solutions of alkali hydroxides to form aurates. On gentle heating, both oxides decompose into gold and oxygen. Gold salts are very easily decomposed when heated and when treated with reducing agents, gold usually separating. Auric chloride, $AuCl_3$, when very gently heated, yields chlorine and aurous chloride, AuCl, and the latter decomposes at a higher temperature into chlorine and gold. Auric chloride is formed (apparently as a product of the decomposition of aurous-auric chloride, Au_2Cl_4) when chlorine is passed over gold in fine powder at 200° to 300°. Auric chloride unites with hydrochloric acid to form chlorauric acid, $HAuCl_4$, the salts of which are crystalline. Gold is not dissolved by any of the ordinary acids, but it dissolves in aqua regia with formation of chlorauric acid. Finely divided gold dissolves in dilute solution of potassium cyanide in presence of air or of certain oxidizing agents. Most auric salts and chloraurates are soluble in water and yield yellow solutions.

REACTIONS OF A SOLUTION OF AURIC CHLORIDE (OR OF CHLORAURIC ACID).

The solution of chlorauric acid is strongly acid to test paper.

Hydrogen sulphide produces in cold solutions a black precipitate of aurous-auric sulphide—

$$8\,AuCl_3 + 9\,H_2S + 4\,H_2O = 24\,HCl + H_2SO_4 + 4\,Au_2S_2.$$

In boiling solutions a brown precipitate of metallic gold is produced—

$$8\,AuCl_3 + 3\,H_2S + 12\,H_2O = 24\,HCl + 3\,H_2SO_4 + 8\,Au.$$

Aurous-auric sulphide is insoluble in hydrochloric acid and also in nitric acid, even when the latter is concentrated. Aqua regia decomposes it with formation of chlorauric acid. It dissolves with difficulty in yellow ammonium sulphide, but more readily in yellow potassium sulphide, thiaurate being formed—

$$Au_2S_2 + K_2S_2 = 2\,KAuS_2.$$

Even the finely divided metallic gold is dissolved by heating with yellow potassium sulphide and sulphur, thiaurate being formed—

$$2\,Au + K_2S_2 + 2\,S = 2\,KAuS_2.$$

The addition of hydrochloric acid to the solution of thiaurate produces a yellowish brown precipitate, which consists of aurous-auric sulphide and sulphur—

$$2\,KAuS_2 + 2\,HCl = 2\,KCl + H_2S + Au_2S_2 + S.$$

Potassium hydroxide produces, in moderately concentrated solutions, a reddish brown precipitate of auric hydroxide, soluble in excess with the formation of potassium aurate—

$$HAuCl_4 + 4\,KOH = 4\,KCl + H_2O + Au(OH)_3\,;$$
$$Au(OH)_3 + KOH = 2\,H_2O + KAuO_2.$$

The precipitate redissolves in excess of potassium hydroxide with great readiness, and its formation cannot be observed when the gold solution employed is very dilute.

Ammonia produces a yellowish precipitate of "fulminating gold," soluble in excess. When dry, the precipitate explodes violently on heating or on being struck.

Reducing agents, such as **ferrous sulphate, sulphurous acid,** and **oxalic acid,** produce a yellowish or brownish precipitate of metallic gold—

$$HAuCl_4 + 3\,FeSO_4 = Fe_2\,(SO_4)_3 + FeCl_3 + HCl + Au\,;$$
$$2\,HAuCl_4 + 3\,H_2SO_3 + 3\,H_2O = 3\,H_2SO_4 + 8\,HCl + 2\,Au\,;$$
$$2\,HAuCl_4 + 3\,H_2C_2O_4 = 6\,CO_2 + 8\,HCl + 2\,Au.$$

Stannous chloride, containing some **stannic chloride,** produces a reddish purple precipitate of metallic gold associated with stannic oxide (Purple of Cassius).

LITHIUM.

Basic oxide, Li_2O.

The majority of the lithium salts are readily soluble in water, but lithium carbonate and lithium phosphate are sparingly soluble.

REACTIONS OF SOLUTIONS OF LITHIUM SALTS.

In moderately dilute solutions **sodium phosphate** produces, on boiling, a white precipitate of lithium phosphate. In order that the precipitation may be as complete as possible, sufficient **sodium hydroxide** should also be added—

$$3\,LiCl + Na_2HPO_4 + NaOH = 3\,NaCl + H_2O + Li_3PO_4.$$

Sodium hydroxide is here preferable to ammonia, as lithium phosphate is distinctly more soluble in solutions of ammonium salts.

In concentrated solutions, **potassium carbonate** produces a white precipitate of lithium carbonate—

$$2\,LiCl + Na_2CO_3 = 2\,NaCl + Li_2CO_3.$$

The precipitation is hastened by gentle warming; it is interfered with by the presence of much chloride of ammonium, sodium, or potassium.

[See also p. 187.]

PLATINUM.

Basic oxides:—Platinous oxide, PtO; platinic oxide, PtO_2. These oxides are very weak bases, but some salts corresponding to each of them are known. Platinic oxide also behaves as an acid anhydride, giving rise to the formation of platinates. Both oxides, and all the platinum salts, are very easily decomposed when heated, and certain reducing agents decompose the salts with separation of platinum. Platinic chloride, $PtCl_4$, loses half its chlorine when very gently heated, yielding platinous chloride, $PtCl_2$, which breaks up at a higher temperature into chlorine and platinum. Platinum dissolves in aqua regia, yielding a solution of chloroplatinic acid, H_2PtCl_6. The reagent commonly called platinic chloride is really a solution of this acid in water, together with some hydrochloric acid.

REACTIONS OF A SOLUTION OF CHLOROPLATINIC ACID.

The solution is strongly acid to test paper.

Hydrogen sulphide produces, slowly in the cold, more rapidly on warming, a dark brown precipitate of platinic sulphide—

$$H_2PtCl_6 + 2\,H_2S = 6\,HCl + PtS_2.$$

Platinic sulphide dissolves with difficulty in ammonium hydrosulphide, more readily in yellow ammonium (or potassium) sulphide. Hydrochloric acid reprecipitates platinic sulphide from the solution of thio-salt formed. Platinic sulphide is not soluble in hydrochloric acid or in nitric acid separately, but it is decomposed by aqua regia with formation of chloroplatinic acid.

Potassium chloride produces a yellow precipitate of potassium chloroplatinate—

$$H_2PtCl_6 + 2\,KCl = 2\,HCl + K_2PtCl_6.$$

Potassium chloroplatinate is slightly soluble in water and dilute acids, but is practically insoluble in alcohol. The dry precipitate is decomposed when heated to a high temperature, potassium chloride and platinum remaining, while chlorine is evolved. In presence of reducing agents, such as organic matter, it decomposes at a much lower temperature. In the presence of water it is slowly reduced by hydrogen in the cold, more rapidly on warming, platinum being precipitated.

Ammonium chloride produces a precipitate of ammonium chloroplatinate, which closely resembles the corresponding potassium compound, but is slightly more soluble. It is more easily decomposed on heating, and leaves a residue of platinum only.

Potassium hydroxide, added in small quantity, produces a precipitate of potassium chloroplatinate. The precipitate dissolves when excess of potassium hydroxide is added and the mixture is heated.

Sodium hydroxide produces no precipitate in the cold.

Ammonia, added in small quantity, produces a precipitate of ammonium chloroplatinate, which dissolves when heated with excess of ammonia.

From neutralised or alkaline solutions, certain **reducing agents (formates**, for example) precipitate platinum—

$$Na_2PtCl_6 + 6\,NaOH + 2\,NaHCO_2 = 6\,NaCl + 2\,Na_2CO_3 + 4\,H_2O + Pt.$$

THALLIUM.

Basic oxides :—Thallous oxide, Tl_2O ; thallic oxide, Tl_2O_3.

Thallic oxide is only feebly basic ; its salts very readily undergo hydrolysis, but can be dissolved in water containing the corresponding acid. They are relatively unimportant, and can be easily converted into thallous salts by means of suitable reducing agents, such as hydrogen sulphide or sulphurous acid. Thallous oxide is very strongly basic ; the hydroxide is soluble in water and forms a strongly alkaline solution.

Examples of soluble thallous salts :—Sulphate, nitrate, carbonate, phosphate, acetate.

REACTIONS OF SOLUTIONS OF THALLOUS SALTS.

In moderately concentrated solutions **hydrochloric acid** produces a white precipitate of thallous chloride, soluble when heated with a considerable quantity of water—

$$TlNO_3 + HCl = HNO_3 + TlCl.$$

Hydrogen sulphide produces a brownish precipitate of thallous sulphide—

$$Tl_2SO_4 + H_2S = H_2SO_4 + Tl_2S.$$

A strong acid such as sulphuric acid, even when dilute, prevents the precipitation of thallous sulphide by hydrogen sulphide, therefore the thallous salts of strong acids are only partially decomposed by hydrogen sulphide owing to the formation of acid by the action. Thallous salts of weak acids, such as acetic acid, can, on the other hand, be completely decomposed by hydrogen sulphide. If a sufficient quantity of sulphuric acid is added to the solution of any thallous salt before adding hydrogen sulphide, no precipitation takes place.

Ammonium hydrosulphide produces a brownish precipitate of thallous sulphide, which dissolves easily in dilute sulphuric acid, but not in acetic acid—

$$Tl_2SO_4 + 2\,NH_4HS = (NH_4)_2SO_4 + H_2S + Tl_2S.$$

Potassium iodide produces a bright yellow precipitate of thallous iodide, very sparingly soluble in hot water—

$$Tl_2SO_4 + 2\,KI = K_2SO_4 + 2\,TlI.$$

Potassium chromate produces a yellow precipitate of thallous chromate—

$$Tl_2SO_4 + K_2CrO_4 = K_2SO_4 + Tl_2CrO_4.$$

Chloroplatinic acid produces a yellow precipitate of thallous chloro platinate—

$$Tl_2SO_4 + H_2PtCl_6 = H_2SO_4 + Tl_2PtCl_6.$$

[See also p. 187].

TITANIUM.

The only important oxide of titanium is the dioxide, TiO_2. This compound plays the part both of a feebly basic oxide and of an acid anhydride. Solutions of titanium salts readily undergo hydrolysis, and in some other respects resemble the stannic salts. The most important soluble salts are the chloride, $TiCl_4$, and the sulphate, $Ti(SO_4)_2$. Crystallised titanium dioxide is insoluble in most acids, but it can be converted into the sulphate by fusion with potassium hydrogen sulphate. There are two acids derived from titanium dioxide: orthotitanic acid, H_4TiO_4, and metatitanic acid, H_2TiO_3. The titanates generally are insoluble in water.

REACTIONS OF SOLUTIONS OF TITANIUM SALTS.

Potassium hydroxide produces a white gelatinous precipitate of orthotitanic acid, insoluble in excess, but easily soluble in hydrochloric acid—

$$TiCl_4 + 4\,KOH = 4\,KCl + Ti(OH)_4.$$

On warming, the precipitate is decomposed with formation of metatitanic acid, which is more granular than orthotitanic acid, and dissolves only with difficulty even in concentrated hydrochloric acid.

Ammonia produces a white precipitate of orthotitanic acid, insoluble in excess.

Ammonium hydrosulphide produces a white precipitate of orthotitanic acid.

Sodium acetate produces, on boiling, a white precipitate of metatitanic acid.

When the solution is diluted with much water, and boiled, complete hydrolysis takes place with the precipitation of metatitanic acid.

Hydrogen peroxide produces a yellow or orange coloration which does not disappear on adding more of the reagent. The coloration is due to the formation of titanium peroxide, TiO_3.

Sodium phosphate produces a white precipitate of basic titanium phosphate, soluble in hydrochloric acid, but insoluble in acetic acid—

$$Ti(SO_4)_2 + 3\,Na_2HPO_4 + H_2O = 2\,Na_2SO_4 + 2\,NaH_2PO_4 + TiOHPO_4.$$

Zinc and **hydrochloric acid** produce a blue or violet coloration due to the formation of a chloride corresponding to a lower oxide of titanium.

URANIUM.

Basic oxides :—Uranous oxide, UO_2 ; uranic oxide, UO_3. The salts corresponding to uranous oxide are comparatively unimportant. The uranium salts usually met with are derived from uranic oxide, which possesses the characters both of a basic oxide and of an acid anhydride. The two sets of derivatives referable to this oxide—the uranyl salts and the uranates — correspond to the hydroxide, $UO_2(OH)_2$. The uranyl salts, such as uranyl sulphate, UO_2SO_4, are of the nature of basic salts, having only the hydroxyl groups of the uranyl hydroxide replaced by salt radicals. In the uranates, such as sodium uranate, $UO_2(ONa)_2$, the hydrogen of the uranyl hydroxide is replaced by metal. There is also another well marked set of salts—the biuranates (or anhydro-uranates), such as sodium biuranate—which bear the same relation to the uranates that the bichromates do to the chromates.

Examples of soluble uranyl salts :—Chloride, nitrate, sulphate, acetate.

REACTIONS OF SOLUTIONS OF URANYL SALTS.

Ammonium hydrosulphide produces a brown precipitate of uranyl sulphide—

$$UO_2(NO_3)_2 + 2\,NH_4HS = 2\,NH_4NO_3 + H_2S + UO_2S.$$

Uranyl sulphide is easily soluble in dilute acids and in ammonium carbonate.

Potassium hydroxide produces a yellow precipitate of potassium biuranate (or anhydro-uranate), insoluble in excess—

$$2\,UO_2(NO_3)_2 + 6\,KOH = 4\,KNO_3 + 2\,H_2O + K_2U_2O_7.$$

Ammonia produces a yellow precipitate of ammonium biuranate, insoluble in excess. The alkali uranates and biuranates are insoluble in ammonium chloride, but dissolve easily in carbonate of ammonium, potassium, or sodium.

In concentrated solutions, **potassium carbonate** produces a yellow precipitate of potassium uranyl carbonate, soluble in excess to form an intensely yellow solution—

$$UO_2(NO_3)_2 + 3\,K_2CO_3 = 2\,KNO_3 + 2\,K_2CO_3, UO_2CO_3.$$

Sodium phosphate produces a yellowish precipitate of uranyl hydrogen phosphate, insoluble in acetic acid, soluble in hydrochloric acid—

$$UO_2(NO_3)_2 + Na_2HPO_4 = 2\,NaNO_3 + UO_2HPO_4.$$

Potassium ferrocyanide produces a brownish-red precipitate of potassium uranyl ferrocyanide—

$$UO_2(NO_3)_2 + K_4Fe(CN)_6 = 2\,KNO_3 + UO_2K_2Fe(CN)_6.$$

ZIRCONIUM.

Basic oxide :—ZrO_2. This oxide also possesses feebly acid characters.

Examples of soluble zirconium salts :—Sulphate, nitrate.

REACTIONS OF SOLUBLE ZIRCONIUM SALTS.

Potassium hydroxide produces a white precipitate of zirconium hydroxide, $Zr(OH)_4$, insoluble in excess ; soluble in dilute hydrochloric or sulphuric acid, provided the precipitate has not been warmed.

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

Ammonium hydrosulphide produces a white precipitate of zirconium hydroxide, insoluble in excess.

Ammonium carbonate produces a white precipitate of basic carbonate, soluble in excess, reprecipitated on boiling.

Oxalic acid produces a white precipitate of zirconium oxalate, soluble in large excess, especially on warming ; soluble in ammonium oxalate.

Concentrated solution of **potassium sulphate** produces a white precipitate of potassium zirconium sulphate, very sparingly soluble in water and in dilute acids. The composition of the precipitate is variable.

Concentrated solution of **hydrogen peroxide** produces a white precipitate of zirconium pentoxide, Zr_2O_5, insoluble in dilute acetic acid, and in very dilute sulphuric acid.

II. SALT RADICALS.

BROMATES.

Bromic acid, $HBrO_3$; monobasic.

Examples of soluble bromates :—Bromates of potassium, sodium, and ammonium.

REACTIONS OF SOLUTIONS OF BROMATES.

Silver nitrate produces a white precipitate of silver bromate, which is very sparingly soluble in water and in dilute nitric acid, soluble in ammonia.

Barium nitrate produces no immediate precipitate, but a crystalline precipitate of barium bromate is formed on standing.

Potassium iodide and dilute sulphuric acid (*i.e.* **hydriodic acid**) reduce the bromate, iodine being liberated.

$$KBrO_3 + 6\,KI + 3\,H_2SO_4 = 3\,K_2SO_4 + KBr + 3\,H_2O + 3\,I_2.$$

Sulphurous acid liberates bromine, which excess of the reagent converts into hydrobromic acid.

Solid bromates are decomposed when strongly heated, generally with evolution of oxygen and leaving a residue of bromide. In some cases the reaction is more complex, bromine as well as oxygen being evolved.

DITHIONATES.

Dithionic acid, $H_2S_2O_6$; dibasic.

All the known dithionates are soluble in water.

REACTIONS OF SOLUTIONS OF DITHIONATES.

Hydrochloric acid liberates dithionic acid, which is decomposed on boiling, with formation of sulphuric acid and sulphurous anhydride—

$$H_2S_2O_6 = H_2SO_4 + SO_2.$$

Barium nitrate produces no precipitate.

Silver nitrate produces no precipitate.

Mercurous nitrate produces no precipitate.

By the prolonged action of **bromine** in presence of **hydrochloric acid**, the sulphur of dithionates may be completely oxidised to sulphuric acid.

Solid dithionates decompose when heated, evolving sulphurous anhydride, and leaving a residue of sulphate.

FERRICYANIDES.

Hydroferricyanic acid, $H_3Fe(CN)_6$; tribasic.

Examples of soluble ferricyanides :—Ferricyanides of potassium, sodium, and ammonium.

REACTIONS OF SOLUTIONS OF FERRICYANIDES.

Silver nitrate produces an orange precipitate of silver ferricyanide, insoluble in dilute nitric acid, but readily soluble in ammonia.

Barium nitrate produces no precipitate.

Ferrous sulphate produces a dark blue precipitate of ferrous ferricyanide (Turnbull's blue), insoluble in dilute hydrochloric acid.

Ferric chloride produces a brown solution, due to the formation of ferric ferricyanide.

Cupric sulphate produces a brownish-yellow precipitate of cupric ferricyanide.

Dilute sulphuric acid, when boiled with the solution, liberates hydrocyanic acid.

FERROCYANIDES.

Hydroferrocyanic acid, $H_4Fe(CN)_6$; tetrabasic.

Examples of soluble ferrocyanides :—Ferrocyanides of potassium, sodium, and ammonium.

REACTIONS OF SOLUTIONS OF FERROCYANIDES.

In moderately concentrated solutions, **concentrated hydrochloric acid** produces a white precipitate of hydroferrocyanic acid, easily dissolved on the addition of water. The precipitate rapidly becomes blue on exposure to the air.

Silver nitrate produces a white precipitate of silver ferrocyanide, insoluble in dilute nitric acid and in ammonia, soluble in ammonia in presence of nitrates.

Barium nitrate produces no precipitate.

Ferrous sulphate produces a white precipitate of ferrous ferrocyanide, which rapidly becomes blue owing to oxidation. (Compare p. 123.)

Ferric chloride produces a dark-blue precipitate of ferric ferrocyanide (Prussian blue), insoluble in dilute hydrochloric acid; soluble in oxalic acid; decomposed by potassium hydroxide with formation of ferric hydroxide.

Cupric sulphate produces a brown precipitate of cupric ferrocyanide, insoluble in dilute acids.

Dilute sulphuric acid, when boiled with the solution, liberates hydrocyanic acid—

$$2\,K_4Fe(CN)_6 + 3\,H_2SO_4 = 3\,K_2SO_4 + K_2FeFe(CN)_6 + 6\,HCN.$$

FLUORIDES.

Hydrofluoric acid, HF ; monobasic (or H_2F_2 ; dibasic).

Examples of soluble fluorides :—Fluorides of silver, potassium, sodium, and ammonium.

REACTIONS OF SOLUTIONS OF FLUORIDES.

Silver nitrate produces no precipitate.

Barium nitrate produces a white precipitate of barium fluoride, soluble in considerable quantities of dilute nitric acid and of ammonium salts.

Calcium chloride produces a white precipitate of calcium fluoride, soluble with difficulty in dilute nitric acid, and practically insoluble in acetic acid.

Solid fluorides, when heated with **concentrated sulphuric acid**, yield hydrofluoric acid—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\,HF.$$

The presence of a fluoride may be recognised by liberating hydrofluoric acid and observing the etching action of the latter upon glass. To carry out the test, proceed as follows :—Coat the convex side of a watch-glass with wax, and draw some characters through the wax by means of a pin, so as to expose the glass. Thoroughly mix some of the solid substance to be tested with concentrated sulphuric acid in a lead or platinum basin. Cover the basin with the watch-glass, convex side down, and place some cold water in the watch-glass to prevent the melting of the wax ; then heat the basin very gently. After some time, say ten to twenty minutes, remove the watch-glass and clean off the wax. The glass will be found to be etched at the places which were exposed to the hydrofluoric acid.

When a solid fluoride is mixed with **silica** prior to heating with **concentrated sulphuric acid**, or if the treatment with sulphuric acid is carried out in a glass vessel, or, generally, in presence of a silicate, silicon fluoride is produced—

$$SiO_2 + 2\,CaF_2 + 2\,H_2SO_4 = SiF_4 + 2\,CaSO_4 + 2\,H_2O.$$

The silicon fluoride may be recognised by its action upon water, a gelatinous pellicle of silicic acid being formed when a drop of water, held on the end of a glass rod or other appropriate support, is kept for some time in contact with the gas—

$$3\,SiF_4 + 4\,H_2O = H_4SiO_4 + 2\,H_2SiF_6.$$

FLUOSILICATES.

Fluosilicic acid, H_2SiF_6 ; dibasic.

Most fluosilicates are readily soluble in water. Barium and potassium fluosilicates are sparingly soluble.

REACTIONS OF SOLUTIONS OF FLUOSILICATES.

Ammonia added in excess produces a white precipitate of gelatinous silicic acid.

Silver nitrate produces no precipitate.

In moderately concentrated solutions, **barium nitrate** produces a white crystalline precipitate of barium fluosilicate.

In moderately concentrated solutions, **potassium chloride** produces a white precipitate of potassium fluosilicate, almost insoluble in presence of excess of the precipitant, easily soluble in ammonium chloride.

Solid fluosilicates are decomposed on heating, and yield silicon fluoride and a metallic fluoride. When heated with **concentrated sulphuric acid**, they yield hydrofluoric acid, silicon fluoride, and a metallic sulphate.

HYPOPHOSPHITES.

Hypophosphorous acid, H_3PO_2; monobasic.

Most hypophosphites are soluble in water.

REACTIONS OF SOLUTIONS OF HYPOPHOSPHITES.

Barium nitrate produces no precipitate.

Silver nitrate produces a whitish precipitate of silver hypophosphite, which darkens slowly on standing, rapidly on heating, with separation of metallic silver.

Mercuric chloride, in presence of **hydrochloric acid**, gradually produces a white precipitate of mercurous chloride, or a grey precipitate of mercury, depending upon the relative quantities of hypophosphite and of mercuric chloride present.

Cupric sulphate, in presence of **dilute sulphuric acid**, produces, on warming with concentrated solutions, a reddish-brown precipitate of copper hydride.

In dilute solutions, excess of **sulphurous acid** and a small quantity of aqueous solution of **ammonium molybdate** produce slowly a blue coloration, which gradually increases in intensity; it is due to the reduction of the molybdate.

Concentrated sulphuric acid, when warmed with a moderately concentrated solution, is reduced, with evolution of sulphurous anhydride.

Zinc and **dilute sulphuric acid** liberate hydrogen phosphide, mixed with hydrogen. When the mixed gas is burned at a jet, the presence of the hydrogen phosphide is indicated by the green colour of the flame.

When solid hypophosphites are strongly heated in the open air, hydrogen phosphide is liberated, which takes fire and burns with a luminous flame.

IODATES.

Iodic acid, HIO_3; monobasic.

Examples of soluble iodates:—Iodates of potassium, sodium, and ammonium.

REACTIONS OF SOLUTIONS OF IODATES.

Silver nitrate produces a white precipitate of silver iodate, which is almost insoluble in water and in dilute nitric acid, soluble in ammonia.

Barium nitrate produces a white precipitate of barium iodate, very slightly soluble in water, even on boiling, and only slowly dissolved by dilute nitric acid.

Potassium iodide and **dilute sulphuric acid** (*i.e.* **hydriodic acid**) liberate iodine.

$$KIO_3 + 5\,KI + 3\,H_2SO_4 = 3\,K_2SO_4 + 3\,H_2O + 3\,I_2.$$

Sulphurous acid liberates iodine, which excess of the reagent converts into hydriodic acid.

$$2\,KIO_3 + 5\,H_2SO_3 = 2\,KHSO_4 + 3\,H_2SO_4 + H_2O + I_2.$$

Solid iodates are decomposed when strongly heated, frequently with evolution of oxygen and leaving a residue of iodide. In many cases, however, the reaction is more complex, iodine as well as oxygen being evolved.

METAPHOSPHATES.

There are several modifications of metaphosphoric acid, all of which are represented by the empirical formula HPO_3. Corresponding to these acids, there are salts which are called metaphosphates, dimetaphosphates, trimetaphosphates, etc. The sodium salts of the different acids are all represented by the general formula $Na_n P_n O_{3n}$. The reactions of the salts of the various acids differ considerably, and present complications with which it is outside the scope of this book to deal.

All metaphosphates are converted into orthophosphate by boiling with nitric acid.

MOLYBDATES.

Molybdic acid, H_2MoO_4; dibasic.

Examples of soluble molybdates :—Molybdates of potassium, sodium, and ammonium.

In addition to the normal salts of molybdic acid, there are also a number of what are called acid molybdates, some of which correspond to other acids derived from molybdic anhydride, MoO_3. As a matter of fact the molybdate most commonly employed is the ammonium salt represented by the formula $(NH_4)_6Mo_7O_{24},4\,H_2O$; this might, however, be looked upon as an acid salt $[(NH_4)_6H_8(MoO_4)_7]$ of the acid H_2MoO_4.

REACTIONS OF SOLUTIONS OF MOLYBDATES.

Hydrochloric acid produces a white precipitate of molybdic acid, soluble in excess; also soluble in ammonia and in a large quantity of water—

$$(NH_4)_6Mo_7O_{24} + 6\,HCl + 4\,H_2O = 6\,NH_4Cl + 7\,H_2MoO_4.$$

Hydrogen sulphide produces first a bluish coloration, and then, very slowly, a brown precipitate of molybdenum trisulphide (molybdic thioanhydride), soluble in ammonium hydrosulphide. It is difficult to obtain complete precipitation with hydrogen sulphide when applied in this way, but the precipitation can be rapidly effected by adding hydrochloric acid to a solution of a molybdate which has been previously mixed with a sufficient quantity of ammonium hydrosulphide.

Nitric acid and a very small quantity of **ammonium phosphate** produce, somewhat slowly in the cold, more rapidly on warming gently (do not boil), a bright yellow precipitate of ammonium phospho-molybdate, the composition of which is represented approximately by the formula $(NH_4)_3PO_4,12\,MoO_3$.

In presence of **acid**, reducing agents, such as **zinc**, **stannous chloride**, etc., produce a blue coloration which becomes greenish and ultimately brown. The blue coloration is best observed when the molybdate solution is added to dilute hydrochloric acid containing a mere trace of stannous chloride.

Potassium thiocyanate and then **stannous chloride**, in presence of hydrochloric acid, produce a transient red coloration due to the formation of molybdic thiocyanate, $Mo(SCN)_3$. If the solution is shaken up with ether, this thiocyanate dissolves in the ether and imparts to it a red colour.

Barium nitrate produces a white precipitate of barium molybdate, soluble in nitric acid.

Silver nitrate produces a slightly yellowish precipitate of silver molybdate, soluble in nitric acid and in ammonia.

PERCHLORATES.

Perchloric acid, $HClO_4$; monobasic.

All the perchlorates are soluble in water ; potassium perchlorate is very sparingly soluble.

REACTIONS OF SOLUTIONS OF PERCHLORATES.

Barium nitrate produces no precipitate.

Silver nitrate produces no precipitate.

Potassium nitrate, unless the solutions are very dilute, produces a white crystalline precipitate of potassium perchlorate.

Solid perchlorates are decomposed when strongly heated, evolving oxygen, and leaving a residue of chloride unless the latter is itself volatile.

PERSULPHATES.

Persulphuric acid, $H_2S_2O_8$; dibasic.

All the known persulphates are soluble in water ; the most important are the potassium salt, which is the least soluble, and the ammonium and sodium salts, which are very soluble.

REACTIONS OF SOLUTIONS OF PERSULPHATES.

In presence of moisture persulphates gradually decompose with formation of sulphate and evolution of oxygen—

$$2\,K_2S_2O_8 + 2\,H_2O = 4\,KHSO_4 + O_2\ ;$$

consequently most solutions, unless freshly prepared from pure persulphate, give a white precipitate on the addition of **barium nitrate** ; pure solutions give a precipitate of sulphate slowly, on boiling.

Hydrochloric acid is decomposed, slowly in the cold but rapidly on warming, with evolution of chlorine.

$$K_2S_2O_8 + 2\,HCl = 2\,KHSO_4 + Cl_2.$$

Potassium iodide is similarly decomposed, with liberation of iodine.

Sulphuric acid, on warming, causes decomposition with evolution of oxygen and ozone.

Ferrous sulphate is converted into ferric sulphate, the solution becoming dark reddish brown when hot.

$$K_2S_2O_8 + 2\,FeSO_4 = K_2SO_4 + Fe_2(SO_4)_3.$$

In solutions which are not too acid, **silver nitrate** produces a more or less marked precipitate of a black silver salt, $AgHSO_5$, which increases in quantity if the liberated acid is neutralised by means of potassium hydroxide. This salt is a derivative of a sulphur acid, known as monopersulphuric acid or Caro's acid, H_2SO_5, formed from the one under consideration, by loss of SO_3.

$$K_2S_2O_8 + AgNO_3 + H_2O = KHSO_4 + KNO_3 + AgHSO_5.$$

In the case of the ammonium salt, this silver salt gradually oxidises the nitrogen to nitric acid, so that when solution of ammonium persulphate, or of other persulphate mixed with ammonium sulphate, is warmed with **silver sulphate,** the resulting solution gives a marked nitrate reaction with the ferrous sulphate test. On the other hand, free ammonia is oxidised only to nitrogen, so that a persulphate solution rendered strongly alkaline with ammonia rapidly decomposes with effervescence when warmed with silver nitrate.

Manganous sulphate, on warming, produces a dark brown precipitate of manganite.

PHOSPHITES.

Phosphorous acid, H_3PO_3; dibasic.
Examples of soluble phosphites :—Phosphites of potassium and sodium.

REACTIONS OF SOLUTIONS OF PHOSPHITES.

Barium nitrate produces a white precipitate of barium phosphite, soluble in dilute nitric or acetic acid.

Silver nitrate produces a white precipitate of silver phosphite, which darkens on warming, with separation of metallic silver.

In presence of **hydrochloric acid, mercuric chloride** is slowly reduced, with production of a white precipitate of mercurous chloride. When excess of phosphite is present, a black precipitate of mercury is eventually produced.

Cupric sulphate produces a blue precipitate of cupric phosphite, soluble in dilute nitric acid.

Concentrated sulphuric acid, when warmed with a moderately concentrated solution, is reduced, with evolution of sulphurous anhydride.

Zinc and dilute sulphuric acid liberate hydrogen phosphide, mixed with hydrogen. When the mixed gas is burned at a jet, the presence of the hydrogen phosphide is indicated by the green colour of the flame.

When solid phosphites are strongly heated in the open air, hydrogen phosphide is liberated, which takes fire and burns with a luminous flame.

PYROPHOSPHATES.

Pyrophosphoric acid, $H_4P_2O_7$; tetrabasic.

Examples of soluble pyrophosphates :—Pyrophosphates of potassium, sodium, and ammonium.

REACTIONS OF SOLUTIONS OF PYROPHOSPHATES.

Silver nitrate produces a white precipitate of silver pyrophosphate, soluble in dilute nitric acid, and in ammonia.

Barium nitrate produces a white precipitate of barium pyrophosphate, soluble in dilute nitric acid.

Magnesium sulphate produces a white precipitate of magnesium pyrophosphate, soluble in excess of the soluble pyrophosphate and of the precipitant.

When boiled with dilute **acids**, pyrophosphates are converted into orthophosphate.

SILICATES.

Orthosilicic acid, H_4SiO_4; tetrabasic. Metasilicic acid, H_2SiO_3; dibasic.
Most silicates are insoluble in water. Potassium and sodium silicates are almost completely hydrolysed by water, with formation of potassium

and sodium hydroxides, and of dissolved silicic acid. The silicic acid in such a solution can be more or less completely coagulated into a white gelatinous mass by the addition of hydrochloric acid, or of ammonium chloride or other ammonium salt.

All solid silicates are attacked by hydrofluoric acid, with formation of silicon fluoride and metallic fluorides. Heated in a lead or platinum basin, with calcium or ammonium fluoride and concentrated sulphuric acid, they yield silicon fluoride and metallic sulphates. The presence of silicon fluoride may be detected by observing its action upon water. [See under Fluorides, p. 177.]

TETRATHIONATES.

Tetrathionic acid, $H_2S_4O_6$; dibasic.

Most tetrathionates are soluble in water.

REACTIONS OF SOLUTIONS OF TETRATHIONATES.

Hydrochloric acid produces no immediate precipitate, even on boiling. After some time sulphur is liberated, more quickly the more concentrated the solution; sulphurous anhydride is simultaneously evolved.

Barium nitrate produces no precipitate.

Silver nitrate produces a yellowish precipitate, which darkens on standing or on warming, and eventually becomes black. The black precipitate is a mixture of silver sulphide and sulphur.

Mercurous nitrate produces a bright yellow precipitate, the composition of which apparently has not been determined.

By the action of **bromine**, tetrathionate can be easily and completely oxidised, with formation of sulphate.

THIOCYANATES.

Thiocyanic acid, HSCN ; monobasic.

Examples of soluble thiocyanates:—Thiocyanates of potassium, sodium, and ammonium.

REACTIONS OF SOLUTIONS OF THIOCYANATES.

Silver nitrate produces a white curdy precipitate of silver thiocyanate, insoluble in dilute nitric acid, soluble in ammonia.

Barium nitrate produces no precipitate.

Ferric chloride produces an intensely deep-red coloration, due to the formation of soluble ferric thiocyanate. The colour is not sensibly altered by the addition of a moderate quantity of dilute hydrochloric acid, but it disappears on the addition of mercuric chloride. If the red solution is shaken up with ether, the ferric thiocyanate dissolves in the latter and imparts a red colour to it.

Cupric sulphate produces a bright green coloration; the subsequent addition of sulphurous acid produces a white precipitate of cuprous thiocyanate.

$$2\,KSCN + CuSO_4 + H_2O + H_2SO_3 = 2\,KHSO_4 + H_2SO_4 + 2\,CuSCN.$$

TUNGSTATES.

Tungstic acid, H_2WO_4 ; dibasic.

Examples of soluble tungstates :—Tungstates of potassium and sodium.

In addition to the normal salts of tungstic acid, many salts are known which correspond to other acids derived from tungstic anhydride, WO_3 ; thus sodium metatungstate is represented by the formula $Na_2W_4O_{13}$, and sodium paratungstate by $Na_{10}W_{12}O_{41}$.

REACTIONS OF SOLUTIONS OF TUNGSTATES.

Hydrochloric acid produces a white precipitate of hydrous tungstic acid, insoluble in excess of the dilute acid, but soluble in concentrated hydrochloric acid and in alkalies. When the mixture is boiled, the precipitate turns yellow owing to the loss of water, tungstic acid, H_2WO_4, being formed.

Hydrogen sulphide, in presence of **hydrochloric acid,** produces a blue precipitate slowly on warming. The precipitate is a reduction product intermediate in composition between WO_2 and WO_3.

Ammonium hydrosulphide produces a soluble thiotungstate; on acidifying the solution with **hydrochloric acid** a brown precipitate of tungsten trisulphide (tungstic thioanhydride) is produced. This sulphide is slightly soluble in pure water. It dissolves easily in ammonium hydrosulphide.

Stannous chloride produces a yellow precipitate. On then adding **hydrochloric acid** and warming, a deep blue precipitate is formed as a reduction product.

A blue precipitate, similar to the above, is also produced by reducing with **zinc** and **hydrochloric acid.**

Barium nitrate produces a white precipitate of barium tungstate, which is decomposed by hydrochloric acid with the production of (insoluble) tungstic acid.

Silver nitrate produces a slightly yellowish precipitate of silver tungstate, soluble in ammonia, and decomposed by nitric acid with production of tungstic acid.

VANADATES.

Vanadates are known corresponding to a number of distinct acids related to vanadic anhydride, V_2O_5. Three of these acids resemble the phosphoric acids, but there are several others of more complex constitution. Orthovanadic acid itself is not known, and the salts corresponding to it are very unstable. The vanadates usually met with are metavanadates, MVO_3, and pyrovanadates, $M_4V_2O_7$, the former being the most stable of all.

Examples of soluble vanadates :—Vanadates of potassium, sodium, and ammonium.

REACTIONS OF SOLUTIONS OF VANADATES.

Hydrochloric acid produces an intense orange coloration, owing to the formation of polyvanadate ; this coloration gradually disappears on standing.

Hydrogen sulphide (or **ammonium hydrosulphide**) produces a yellow or brownish coloration, due to the formation of soluble thiovanadate.

The subsequent addition of **hydrochloric acid** produces a brown precipitate of vanadium pentasulphide (vanadic thioanhydride), soluble in ammonium hydrosulphide with formation of a red or brown solution.

In presence of **hydrochloric acid, hydrogen sulphide** reduces the dissolved vanadic acid, with the precipitation of sulphur and the production of divanadyl chloride $(V_2O_2)Cl_4$, which imparts a blue colour to the solution.

Other **reducing agents** besides hydrogen sulphide, such as **stannous chloride** or **sulphurous acid**, also produce a blue coloration due to the formation of divanadyl compounds.

In presence of **hydrochloric acid, zinc** reduces the vanadic acid first to divanadyl chloride, producing a blue coloration, then to green vanadium trichloride, VCl_3, and finally to violet vanadium dichloride, VCl_2.

In acid solutions, **hydrogen peroxide** produces a red coloration which disappears on adding excess of the reagent. The red colouring matter is not extracted by ether.

Saturated solution of **ammonium chloride** slowly produces a white crystalline precipitate of ammonium metavanadate, NH_4VO_3. By adding solid ammonium chloride to the slightly warmed solution, complete precipitation may be effected.

Barium nitrate produces a yellow precipitate which becomes colourless on standing.

Silver nitrate produces a yellow precipitate which becomes colourless on standing.

TARTRATES.

Tartaric acid, $H_2C_4H_4O_6$, or $H_2\overline{T}$; dibasic.

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 SOLUTIONS OF TARTRATES.

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 thorough washing with water on the filter paper) is dissolved in the smallest possible quantity of very dilute ammonia and the solution is digested in a test tube at a moderate temperature (about 60°-70° C.), a shining mirror of metallic silver is deposited on the inside of the tube within about a quarter of an hour. 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

Oxidation of Citric ~~& tartrate~~ with $KMnO_4 + H_2SO_4$ does not take place so rapidly as that of oxalic

$Ca(OH)_2$

H_2SO_4

Sh. Sd

alone. [Compare the reaction of potassium salts with sodium hydrogen tartrate, page 133.]

$$Na_2\overline{T} + KCl + H\overline{A} = KH\overline{T} + NaCl + Na\overline{A}.$$

Solid tartrates, when heated alone, char and give off fumes having an odour resembling that of burnt sugar.

When a solid tartrate is heated with **concentrated sulphuric acid**, darkening takes place somewhat rapidly (much more rapidly than is the case with a citrate), and a considerable separation of carbon occurs.

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.

CITRATES.

Citric acid, $H_3C_6H_5O_7$, or $H_3\overline{Ci}$; tribasic.

Examples of soluble citrates:—Citrates of potassium, sodium, and ammonium.

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°-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. 184.]

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], ~~but an immediate precipitate of calcium citrate is obtained when a few drops of ammonia solution are added.~~ When 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,

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* 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.

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.

Solid citrates, when heated alone, char and give off fumes having an odour resembling that of burnt sugar.

When a solid citrate is heated with concentrated sulphuric acid, darkening takes place slowly (much more slowly than in the case of a tartrate), and on prolonged heating a considerable separation of carbon occurs.

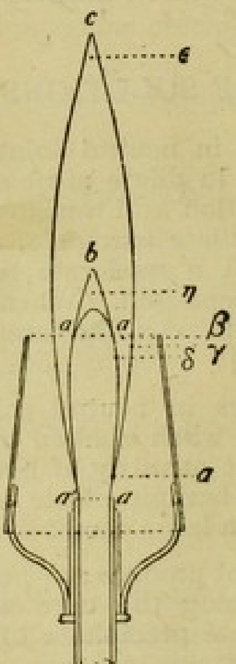

Fig. 1.

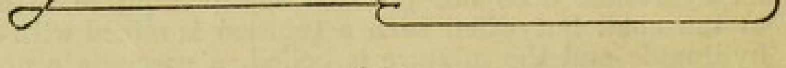

Fig. 2.

DRY-WAY REACTIONS.

FLAME COLORATION TESTS.

THE compounds of certain metals when introduced, on the end of a fine platinum wire, 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 (α, Fig. 1), where the temperature is comparatively low, and afterwards in the hottest part of the flame (β, Fig. 1). 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.

FILM TESTS.

A small quantity of the solid substance to be tested is taken up on a piece of 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 (η, Fig. 1). 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.

---

[*] 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.

[†] The film of mercury is grey and scattered.

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, *c*, 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 below:—

	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

The iodide films referred to above are obtained by exposing the oxide films to the fumes of hydriodic acid, produced by the action of atmospheric moisture on phosphorus iodide. 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 ammonia solution.

The white oxide films obtained from antimony and arsenic compounds may be distinguished from each other by moistening 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, at the position marked γ, Fig. 1. 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 (η, Fig. 1) 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

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* 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.

   $$Na_2B_4O_7 + CuO = Cu(BO_2)_2 + 2NaBO_2.$$

   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.

If microcosmic salt is used instead of borax for examining substances by means of bead tests, the colour effects produced are generally similar to those obtained with borax. 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—

$$2(NaNH_4HPO_4, 4H_2O) = 10H_2O + 2NH_3 + 2NaPO_3.$$

Fused sodium metaphosphate dissolves metallic oxides, forming orthophosphates—

$$NaPO_3 + CuO = NaCuPO_4.$$

Microcosmic salt is specially useful in testing for titanium compounds, which yield a characteristic violet colour on prolonged heating in the reducing flame in a bead prepared from this salt. Particles of silica are unattacked when strongly heated in the bead obtained by fusing microcosmic salt, and remain in the clear bead in an opaque form. Silicates undergo decomposition when heated in the bead, but leave an easily-recognised "skeleton" of undissolved silica, which has the shape of the particle of silicate employed.

SODIUM CARBONATE BEAD TESTS.

On the end of a fine platinum wire, which should be looped as shown in Fig. 2, p. 186, 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 and of manganese yield characteristic beads as follows :—

METAL.	COLOUR OF BEAD.	DUE TO FORMATION OF
Chromium	Yellow	Chromate
Manganese	Green	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.

Note respecting Sodium Carbonate Beads:

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.]

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. Next, mix on a watch-glass a small quantity of the solid substance to be examined with a few drops of the same liquid. Place this mixture on the coated end of the prepared match, 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, 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:—

Ductile 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 carbonic oxide and carbonic anhydride, 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). 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. *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, 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*) *Carbonic anhydride:* From cyanates, oxalates, certain carbonates, etc.; is sometimes mixed with carbonic oxide.

(*g*) *Carbonic oxide* (burns with a blue flame; darkens paper moistened with solution of palladium chloride): From oxalates and formates; is often mixed with carbonic anhydride, 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*) *Sulphurous anhydride:* 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 anhydride	White; part, at least, crystalline	Black shining sublimate
Arsenious sulphide	Reddish-yellow	
Ammonium chloride and some other ammonium salts	White	Smell 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 187].

(*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.
[illegible] Cadmium	Reddish-brown. Consists of cadmium oxide. The outer portions sometimes show a great variety of colours.
[illegible] 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. often [illegible]

Compounds of certain metals yield metallic beads. [Compare the character of the beads obtained in the match tests, page 191]. 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).

Magnes. Whl oxid

Al. Whl oxide fuse when heated

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.

<table>
<tr>
<td rowspan="6">Precipitate.
Dissolve in NH_4OH $AgCl$
$HgCl$
Sol. hot aq. → $PbCl_2$
(Silver Group).</td>
<td colspan="7">To the Filtrate add saturated H_2S water in excess, and shake well. Filter. Wash the precipitate.</td>
</tr>
<tr>
<td colspan="2" rowspan="3">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.</td>
<td colspan="5">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. Warm gently. Filter. Wash the precipitate.</td>
</tr>
<tr>
<td rowspan="4">Precipitate.
br. $Fe(OH)_3$
blue $Cr(OH)_3$
Colorless $Al(OH)_3$
(Iron Group).</td>
<td colspan="4">To the Filtrate add NH_4HS in slight excess. Filter. Wash the precipitate.</td>
</tr>
<tr>
<td rowspan="3">Precipitate.
white ZnS
buff. MnS
Black NiS
Black CoS
(Zinc Group).
HCl dissolves MnS but not ZnS.</td>
<td colspan="3">To the Filtrate add $(NH_4)_2CO_3$ in excess and warm gently. Filter. Wash the precipitate.</td>
</tr>
<tr>
<td rowspan="2">Residue.
Dissolve in HNO_3 $\left\{\begin{array}{l}HgS\\CuS\end{array}\right.$
Boil with dil HCl $\left\{\begin{array}{l}PbS\\Bi_2S_3\end{array}\right.$
Yellow → CdS
(Copper Group).</td>
<td rowspan="2">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.]</td>
<td rowspan="2">Precipitate.
$BaCO_3$
$SrCO_3$
$CaCO_3$
(Barium Group).
Flame.</td>
<td colspan="2">To the Filtrate add $(NH_4)_2HPO_4$ in excess. Filter. Wash the precipitate with dilute ammonia.</td>
</tr>
<tr>
<td>Precipitate.
NH_4MgPO_4
(Magnesium).
Crystals in dilute amorphous in concentrated</td>
<td>Filtrate.
Evaporate to dryness, and drive off ammonium salts by gentle ignition. Test for K and Na in the residue.</td>
</tr>
</table>

Test for NH_4 in the original substance by boiling with NaOH solution.

When sol. is too bulky boil down.

APPARATUS.

As it is advisable that each student should possess his own set of apparatus, care has been taken, in drawing up the course of practical work, to exclude any experiment which could not be carried out by means of very simple apparatus. The following is a list of all that is necessary for performing the experiments and reactions; if bought as a complete set, the cost of it should not exceed a few shillings.

Test tubes.—Thin-walled glass tubes, closed and rounded at one end, and lipped at the other. One dozen of medium size (150 mm. by 15 mm.). Test tubes containing liquid may be heated directly in the flame without breaking, but are easily crushed if handled carelessly.

Test tube brush.—Used for cleaning the above and other apparatus; it is cylindrical, mounted on wire, and should terminate below in a tuft of fibre or a piece of sponge, not in bare wire. After the brush has been used, the apparatus to be cleaned must be rinsed out several times with water.

Hard glass tubes.—Tubes of hard and difficultly-fusible glass, shaped like test tubes, but thicker in the wall. Three, measuring about 100 mm. by 10 mm. Used for heating dry solids to a high temperature.

Glass flask.—A thin-walled flask, of about 80-100 c.c. capacity, flat-bottomed. May be used for containing, and for heating, quantities of liquid too large to be dealt with in a test tube.

Porcelain basin.—A white glazed porcelain basin, with round bottom, about 75 mm. diameter. Used for evaporation of solutions to small bulk or to dryness, in which case it should be heated over a piece of wire gauze. Also used for titrations, as the white porcelain makes a good background for observing changes of colour.

Crystallising dishes.—Shallow, cylindrical glass vessels, thin-walled, and provided with spout. One about 40 mm. diameter, and one about 55 mm., are convenient sizes. Used for holding solutions from which crystals are expected to separate, either by slow cooling of a hot solution or by gradual evaporation of a cold solution.

Glass rod.—A thin glass rod, about 150 mm. by 2-3 mm., with both ends rounded off in the flame. Used for stirring liquids, and also for withdrawing and manipulating small quantities of liquid.

Burette.—An apparatus for measuring the volume of solution employed in carrying out chemical reactions. The simplest form consists of a cylindrical glass tube, which should be of uniform diameter, drawn out at the lower end to fit a narrow rubber tube. The greater part of the tube, with the exception of the ends, is marked off at intervals, representing cubic centimetres and fractions, and is graduated from above downwards. A jet is fitted to the lower end by means of a short piece of rubber tube, on which a spring clip is placed. Liquid in the burette can be allowed to run out by pressing open the clip. For many purposes it is preferable to use a burette fitted with a glass stopcock in place of the rubber tube and pinchcock.

Pipette.—A vessel to measure out a definite quantity of solution. It consists of a short, wide piece of tube contracted at its ends, to which are fused longer pieces of narrow tube; one of these (the lower stem) is drawn out at its free end to a fine point, while the other is merely rounded off. The upper stem has a mark etched upon it in such a position that if the pipette is filled (by suction) to this mark, and then allowed to drain (see p. 94), the volume of liquid delivered by it will be that marked on the bulb. One pipette of 10 c.c. will suffice.

Watch glass.—An ordinary watch glass, about 40-50 mm. in diameter, is convenient for holding small quantities of solids or of liquids; it also serves as a cover for a crystallising dish.

Funnel.—A glass funnel, about 50 mm. in diameter, for filtering.

Filter paper.—Pure unsized paper, cut into discs of convenient diameter. Used for filtering; also for drying crystals, and, when cut into narrow strips, for preparing special test-papers. When used for filtering purposes, a sheet is first folded exactly in two, and this doubled portion is again folded in two, at right angles to the previous fold, so as to form a fourfold quadrant. This is then opened out into a cone, and fitted into the funnel; while held in place in the funnel it is thoroughly wetted with water, after which it will retain its shape and position. Fifty sheets, 90 mm. in diameter.

Labels.—A small packet of blank gummed labels, for affixing to crystallising dishes, etc., containing substances set aside for subsequent use or examination.

Platinum wires.—Two pieces of thin platinum wire, about 50 mm. in length, mounted in handles of glass rod. Used for holding small quantities of substances to be heated in the flame, especially for flame coloration and bead reactions.

Platinum foil.—A strip of thin platinum foil, about 50 mm. by 10 mm., for holding substances to be heated in the flame when wire is not sufficient.

Cobalt blue glass.—A piece of deep blue glass, not less than 50 mm. by 25 mm. Used for recognition of potassium (by the flame coloration) in presence of sodium. Before using, each piece of glass should be tested by examining through it the flame given by a pure sodium salt; if the coloration is not completely cut off, the glass is to be rejected.

Forceps.—A pair of brass forceps, for lifting small fragments of material, holding platinum foil, etc.

Spatula.—A small paper knife, or "envelope opener," of bone, horn, or ebonite (not celluloid). Used for lifting powdered substances, etc.

In addition to the above apparatus, each working place should be provided with the following:—

Bunsen burner, giving a non-luminous gas flame for heating purposes.

Retort stand, with two rings of about 50 and 70 mm. diameter, the larger covered with wire gauze. The smaller ring serves for holding the funnel during filtration; the larger for holding vessels, other than tubes, when being heated, and as a support for the receiving vessel during filtration.

Test tube stand, of wood, to hold at least six tubes.

A duster, or cloth of some kind, is also desirable (it must not be used for drying the *inside* of apparatus, however).

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$As_2O_3 + 2NaOH = 2NaAsO_2 + H_2O$

$As_2S_3 + 2NaSH = 2NaAsS_2 + H_2S.$

Thiobase. Thiosalt.

$2NaAsS_2 + 2HCl = As_2S_3 + 2NaCl + H_2S.$

$SnS + 2NH_4HS + S = (NH_4)_2SnS_3 + H_2S.$

Brown

$(NH_4)_2SnS_3 + 2HCl = H_2S + SnS_2 + 2NH_4Cl.$

Yellow

Oxal   Sol in H_2O.

Sol. St.   [illegible]. [illegible]

forms: [illegible]. [illegible] [illegible]

no clear.

H_2SO_4

[illegible]