Cambridge University Press
978-1-316-50983-8 - Qualitative Inorganic Analysis: Second Edition
A. J. Berry
Excerpt
More information

Part I

GENERAL

Chapter I

CERTAIN GENERAL PRINCIPLES

Introduction

The objects of the two main divisions of chemical analysis, namely qualitative analysis and quantitative analysis, are sufficiently indicated by the terminology; the former being concerned with the detection of substances, the latter with their determination. In volumetric and in gravimetric analysis, the reactions which are employed for effecting the determinations must proceed completely. Such, however, is not the case in qualitative analysis. In many of the tests which are employed in qualitative work, it is of little or no consequence whether the reactions proceed on quantitative lines or not, or even if the products which are formed for the recognition of substances are of definite composition.

Although the objects and many of the methods involved in the two branches of chemical analysis are widely different, it frequently happens that one branch of analysis must supplement the other. Occasionally, it is not possible to identify a highly complicated compound by qualitative methods alone, and it will then become necessary to make quantitative determinations of its constituents. Much more frequently, qualitative tests are required to check the accuracy of quantitative experiments. In volumetric analysis, for example, the end-point in some titrations is found by colour changes which are really of the nature of microchemical tests; and in gravimetric analysis, recourse to qualitative tests is often required to ascertain the completeness of a separation or the purity of a substance which is weighed. Hillebrand and Lundell have urged that "a little less attention be paid to the method of weighing and a little more to the thing that is weighed".*

THE GENERAL FUNCTIONS OF ACIDS AND BASES

According to the elementary theory of ionization, acids are supposed to derive their distinctive properties from their capacity to yield free hydrogen ions, or more correctly, free hydroxonium, H_3^+O, ions. Similarly, the characteristic properties of bases are identified with their property of yielding free hydroxyl ions. A closer study of these two classes of compounds, however, has shown that the undissociated molecules of both acids and bases have a definite *role* to play, particularly when the effects of the presence of neutral salts are examined.

Acids and bases may be classified as strong or weak according to the extent to which their distinctive properties are exercised. In terms of the classical theory of ionization, strong acids and bases are highly ionized, whereas weak acids and bases are ionized only to a very limited extent. It might therefore appear at first sight that two acids of identical strength should be equally efficient agents in bringing a substance into solution. Such, however, is by no means necessarily the case. Hydrochloric and nitric acids are of practically identical strength, yet many metallic oxides are more readily dissolved by the former than the latter. In the case of ferric oxide, the more powerful solvent action of hydrochloric acid is to be attributed to the formation of complex ferrichloride ions.

When discussing the concentration of an acid or base in solution, two wholly different meanings may be attached to the term concentration. The term may refer to the total quantity of acid or base in a specified volume of the solution, without drawing any distinction between the undissociated molecules and the ions. Alternatively, reference may be restricted to the ionized

---

* *Applied Inorganic Analysis*, p. 3.

fraction, i.e. to the actual free hydrogen or hydroxyl ions. In order to avoid the use of negative indices, the concentration of hydrogen or hydroxyl ions in a solution is always expressed logarithmically in terms of the so-called *p*H scale. On this scale, a neutral solution (i.e. a solution in which the concentrations of hydrogen and hydroxyl ions are equal) has a *p*H value of 7,* acid solutions have *p*H values numerically less than 7, and alkaline solutions have *p*H values which numerically are greater than 7. In many analytical operations, it is important to keep the *p*H value of a solution within certain limits, as the following example will show.

The precipitation of metallic hydroxides is frequently effected by adding a weak base such as ammonia to the solution. If ammonia be added to a solution of a mixture of an aluminium and a magnesium salt, the hydroxides of both metals are precipitated. But if ammonium chloride followed by ammonia is added to the mixture, aluminium hydroxide alone will be precipitated. The addition of ammonium chloride limits the precipitating power of the base. This action, known as buffer action, is considered to be due to suppression of the hydroxyl ions from the ammonium hydroxide in consequence of the considerable increase in the concentration of the ammonium ions derived from the strong electrolyte ammonium chloride.

Examples of the buffering of weak acids by adding one of their salts are common in analytical work. Thus hydrogen sulphide will not precipitate zinc sulphide from a solution of zinc sulphate. But if sufficient sodium acetate is added to a solution of zinc sulphate, zinc sulphide may be precipitated completely by passing in hydrogen sulphide. The basic ferric acetate method of separating phosphoric acid depends on the same principle.

The acid or alkaline reaction of salts in solution arises as the result of hydrolysis, i.e. reaction between the ions of water with the ions of the salt, always tending to produce the least ionized product. Thus when sodium acetate is dissolved in water, the resulting solution has a *p*H value between 8 and 9, depending

---

* At room temperature.

on the concentration of the solution. The hydrogen ions derived from the water combine with the acetate ions to produce the feebly ionized acetic acid, the net effect of the equilibrium being to leave a small but decided excess of hydroxyl ions in the solution. Similarly, when ammonium chloride is dissolved in water, the pH value of the solution usually lies between 4 and 5. In this case, the hydroxyl ions derived from the water unite with some of the ammonium ions to produce the feebly ionized ammonium hydroxide, and equilibrium is established with a small excess of hydrogen ions in solution. Solutions of salts of which both cation and anion are constituents of strong bases and acids are neutral, because hydrolysis does not arise to an appreciable extent.

It may be added that some of the fundamental conceptions of acids and bases have undergone modifications in recent years. It is held by some chemists that the distinctive properties of weak acids and weak bases are to be considered as due not to the limited ionization of these substances, but to equilibria between pseudo acids and true acids and between pseudo bases and true bases, the true acids and bases being completely ionized. The apparent weakness is considered to be due, not to the intrinsic properties of the compounds, but to the extremely small concentration of hydrogen or hydroxyl ions which is in equilibrium with the pseudo form. In this connexion, it has been pointed out by Thiel that it is incorrect to describe carbonic acid as an extremely weak acid. The error has arisen as a consequence of regarding dissolved carbon dioxide as consisting wholly of carbonic acid and not partly of carbonic anhydride. Equilibrium between carbonic acid and its ions is established immediately, but the hydration of dissolved carbon dioxide is a time reaction. When the true ionization constant of carbonic acid is measured, the acid is estimated to be about twice as strong as formic acid.

An extended conception of the fundamental ideas about acids and bases was introduced by Brønsted and by Lowry in 1923, who defined acids as substances which can lose hydrogen ions and bases as substances which can acquire hydrogen ions. In this definition, Brønsted refers to the unhydrated hydrogen ion, the proton. It will be evident that this way of regarding acids and bases extends these terms to include substances which are not defined as acids or bases in the ordinary way, although their acidic or basic properties are none the less recognizable.*

THE POTENTIAL OR ELECTROCHEMICAL SERIES OF THE METALS

It is well known that metals differ very widely as regards their reactivity with acids. Thus with hydrochloric acid, magnesium readily dissolves with evolution of hydrogen in the dilute acid, zinc dissolves more slowly, indeed very slowly if the metal is fairly pure, while tin is practically without action upon the dilute acid, but dissolves in the concentrated acid on heating. Relevant to this behaviour is also the displacement of one metal from a solution of its salts by another metal. Thus zinc displaces copper from a solution of copper sulphate, and copper displaces mercury from a solution of mercurous nitrate. Such phenomena are due primarily to differences in the tendency of the metals including hydrogen, which in this respect resembles metals, to become ionized. When a metal is placed in a solution of its own ions, the tendency to assume the ionic condition is a measurable quantity which can be expressed in volts. This tendency is greatest with the alkali metals, and least with gold and platinum. If the metals are arranged in the order of ascending normal potential, as determined by electrochemical measurements, it will be found that the same order is followed with regard to diminution of electropositive character. The commoner metals become arranged in the following order:

K, Ca, Al, Mn, Zn, Fe, Cd, Co, Ni, Sn, Pb, H, Cu, Hg, Ag, Au.

A knowledge of the relative order of the metals in the potential series is of value in studying their analytical reactions, but it must be emphasized that the chemical behaviour of any parti-

---

* See *Inorganic Chemistry* by Niels Bjerrum, English edition, 1936, pp. 107 *et seq.*

cular metal may be much more complicated than its relative position in the potential series might at first sight appear to indicate. In this connexion the behaviour of certain metals, particularly zinc with dilute hydrochloric or sulphuric acid, is of much interest. Pure zinc is remarkably resistant to the attack of these acids, which may at first sight appear surprising, as the metal stands considerably above hydrogen in the potential series. The impure metal dissolves rapidly, and the pure metal also can be made to dissolve with equal rapidity if it is touched with a piece of silver or platinum under the surface of the acid. A completed Voltaic circuit is necessary for the metal to dissolve in and displace hydrogen from the acid. The action of copper upon acids is also instructive. As this metal follows hydrogen in the potential series, it would not be expected to displace hydrogen from acids, but only to be attacked by oxidizing acids such as nitric acid or by hot concentrated sulphuric acid, in which it dissolves with formation of reduction products of these acids. Copper is, however, dissolved when heated with hydriodic or hydrobromic acid with evolution of hydrogen, and if the experiments are carried out quantitatively, it will be found that the volume of hydrogen which is evolved corresponds with the *cuprous* equivalent of the metal. The action of these acids in dissolving the metal is due to the strong tendency of copper to form complex halogen anions of the type $\overset{-}{\mathrm{Cu}}\mathrm{X}_n$. If the solution obtained by the action of hydrobromic or hydriodic acid on copper is diluted with water, the complex anion is decomposed with separation of cuprous bromide or iodide. Even boiling concentrated hydrochloric acid has an appreciable solvent action upon copper, as may be seen by applying sensitive tests. The action of an acid upon a metal is determined not only by the tendency to discharge hydrogen ions, but to the capacity for producing complex ions.

Cambridge University Press
978-1-316-50983-8 - Qualitative Inorganic Analysis: Second Edition
A. J. Berry
Excerpt
More information

OXIDATION AND REDUCTION

The fundamental conception of oxidation is the addition of oxygen to a substance or the removal of hydrogen from it. In a similar sense, the term reduction expresses the addition of hydrogen to a substance or the removal of oxygen from that substance. The meaning of the terms has been extended beyond the original conceptions by considering other electro-negative elements as functioning similarly to oxygen, and electropositive elements as behaving similarly to hydrogen. Electrochemical definitions of the terms have been formulated in this more extended sense. Thus oxidation is frequently defined as increasing the ratio of the electronegative part to the electropositive part of a molecule, or diminishing the ratio of the electropositive to the electronegative part of the molecule. Reduction is similarly defined in reciprocal terms.

Remy has pointed out that oxidation and reduction when considered in the purely chemical sense may be in conflict with electrochemical definitions. Thus when calcium hydride is dissociated by heat, hydrogen is expelled. Is this change to be regarded as an oxidation or as a reduction? From the purely chemical standpoint, hydrogen is removed from the substance and therefore the change must be regarded as an oxidation. But since experiments on the electrolysis of calcium hydride have shown conclusively that hydrogen is the electronegative constituent of this compound, the chemical change of thermal dissociation must be regarded as a reduction when the electrochemical definitions of oxidation and reduction are taken as the standards. Rigid definitions of fundamental conceptions in chemistry are very difficult to formulate without complications arising as the science develops.

Reactions which involve oxidation and reduction in aqueous solution are sometimes accompanied with characteristic changes of colour. In subjecting a substance to a preliminary examination in qualitative analysis, it is frequently desirable to investigate its response to the action of oxidizing and reducing agents, and to note any colour changes. For example, zinc and dilute sulphuric acid will convert dichromates (orange) into green chromic and ultimately into the blue chromous salts. Under similar conditions, titanic salts which are colourless are converted into the violet titanous salts. Derivatives of quinquevalent vanadium (vanadic acid) undergo an interesting series of colour changes as reduction proceeds from a yellow colour through blue (vanadyl salts), then green (vanadic salts) and ultimately to the violet colour of vanadous salts.

Reactions which are concerned with oxidation and reduction can, of course, be expressed by ordinary chemical equations. An older way of doing this is to give expression merely to changes in the states of oxidation. Thus the oxidation of iron from the ferrous to the ferric condition by potassium dichromate in acid solution may be expressed by the "oxide" equation:

$$6\mathrm{FeO} + 2\mathrm{CrO_3} = 3\mathrm{Fe_2O_3} + \mathrm{Cr_2O_3},$$

or by an equation which is concerned with the resulting changes of valency:

$$3\mathrm{Fe(II)} + \mathrm{Cr(VI)} = \mathrm{Cr(III)} + 3\mathrm{Fe(III)}.$$

Both the "oxide" and the "valency" equations are accurate in so far as they furnish a quantitative statement of the actual state of affairs. They are however incomplete in one important particular. Free hydrochloric or sulphuric acid is concerned in the reaction, or, more generally, hydrogen ions are involved. The reaction may therefore be written:

$$\overset{--}{\mathrm{Cr_2O_7}} + 6\overset{++}{\mathrm{Fe}} + 14\overset{+}{\mathrm{H}} = 7\mathrm{H_2O} + 2\overset{+++}{\mathrm{Cr}} + 6\overset{+++}{\mathrm{Fe}}.$$

Substances may be classified as oxidizing or as reducing agents according to their behaviour with certain types of substances. Some compounds can function as oxidizing agents in some reactions and as reducing agents in others. Thus nitrous acid would be described as an oxidizing agent when it reacts with potassium iodide, since iodine is liberated, but nitrous acid will decolorize potassium permanganate, and in those circumstances it would be classed as a reducing agent. Hydroxylamine normally acts as a powerful reducing agent, but it can also oxidize freshly precipitated ferrous hydroxide to ferric hydroxide. In acid solution the reaction is reversed, ferric salts being reduced to the ferrous condition.

Catalysed and Induced Reactions. Numerous reactions which involve oxidation and reduction are profoundly influenced by the presence of traces of substances which exert a catalytic action. A test for tartrates depending on the catalytic action of a trace of ferrous ion was discovered many years ago by Fenton. In the presence of this catalyst, tartaric acid is oxidized to dihydroxymaleic acid by hydrogen peroxide, whereas, without a trace of ferrous salt, no obvious oxidation takes place. The course of the oxidation of thiosulphates by hydrogen peroxide has been shown by Abel to be capable of variation according to the experimental conditions. In dilute acetic acid solution, particularly in presence of a trace of iodide ion, oxidation proceeds to the tetrathionate stage, whereas in neutral solution with a trace of ammonium molybdate as catalyst, the oxidation proceeds to sulphate. More recently, Feigl has devised a useful test for silver which depends upon the catalytic action of the metal on the reduction of a ceric salt (see p. 30).

Induced reactions resemble catalytic reactions in many respects. A solution of sodium sulphite is slowly oxidized to sulphate by exposure to atmospheric oxygen. A solution of sodium arsenite, on the other hand, is remarkably stable to atmospheric oxygen. But if air is passed through a solution of the two salts, *both* are oxidized. Many similar examples are known. A most interesting application of this principle has been applied by Feigl and Krumholz to increasing the sensitiveness of the alkaline stannite test for bismuth. Bismuth salts are rapidly reduced to the metallic condition by a solution of sodium stannite (see p. 40). The sensitiveness of the test may, however, be increased one hundredfold as follows. Lead salts are reduced to the metallic state very slowly by sodium stannite. In the presence of a concentration of one part of bismuth in five million, the lead salt is rapidly reduced.

COLLOIDAL PHENOMENA IN ANALYSIS

When substances react together in solution in such a way as to form an insoluble product, it sometimes happens that a precipitate is not produced at once. This may arise as a result of supersaturation, or it may be due to the substance being held in colloidal solution. Examples are frequently to be encountered in analytical work. Thus when hydrogen sulphide is passed through a solution of arsenious acid, the solution becomes yellow, but arsenious sulphide is not actually precipitated unless hydrochloric acid or some other suitable electrolyte is present. The yellow liquid which is produced in the absence of electrolytes contains arsenious sulphide in colloidal solution. Under some conditions aluminium hydroxide may remain partly in colloidal solution when ammonia is added to a solution of an aluminium salt in the absence of ammonium salts.

When some insoluble precipitates are washed for a long time with water, a point may be reached when there is a marked tendency for the insoluble substance to pass through the filter. If the washing is conducted with a dilute solution of an electrolyte instead of with water, this does not arise. If thallous iodide is washed with water, after some time the liquid assumes a pale yellow colour. This phenomenon is known as peptization, and is due to the solid passing into colloidal solution. If the washing is conducted with a dilute solution of potassium iodide, the washings remain colourless.

Colloids are usually classified broadly into two types, formerly termed suspensoids and emulsoids, and now usually distinguished as lyophobic colloids and lyophilic colloids. In the former type, there is no tendency for the dispersed substance to unite with the "solvent", whereas in the latter type there is a more or less strong tendency for the colloidal substance to enter into a somewhat ill-defined combination with the solvent. The distinction between lyophobic and lyophilic colloids is, however, not a rigid one.

Colloidal solutions differ from true solutions in various respects. In consequence of the very small concentration of the