# 2

General Principles of Analysis

The conventional methods of analysis were developed by the chemists by making use of chemical reactions entered into by different metals and non-metals with various reagents. In the field of geochemistry and mineral processing these methods were proved to be useful specially in assessing the grades of ores, minerals and products of ore dressing such as ore concentrates. These methods are simple in the sense that inexpensive equipment are employed for analysis and at the same time these are precise and accurate. A chemist can obtain accurate results by scrupulously following the step-by-step procedure with precaution to be taken therein for a particular ore. Before studying the various steps in analysis it will be advantageous for chemists to have some theoretical back up of the concepts on which the procedures of analysis have been developed.

SOME THEORETICAL CONSIDERATIONS

Law of Mass Action

Guldberg and Waage in 1867 have stated the *law of mass action* which is also sometimes called *law of chemical equilibrium*. The law states that the velocity of the chemical reaction is proportional to the product of the active masses of the reacting substances. The 'active mass' for instance shall interpret by concentration and express in mols per litre.

Let us consider a simple reversible reaction at constant temperature:

$$A + B \rightleftharpoons C + D$$
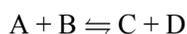
Applying the law of mass action, the velocity with which A and B react is proportional to their concentrations. Mathematically,

$$V_1 = k_1 \times [A] \times [B]$$

where k_1 is a constant known as the velocity coefficient, and [A] and [B] denote the molecular concentrations of reactants A and B respectively. Similarly, the velocity with which the reverse reaction occurs is given by

$$V_2 = k_2 \times [C] \times [D]$$

$$K = \frac{\alpha^2 c}{1 - \alpha}$$

This is known as **Ostwald's dilution law.**

From the point of view of quantitative inorganic analysis, sufficiently accurate values for the ionization constants of weak monoprotic acids may be obtained by using the classical Ostwald's dilution law expression; the resulting 'constant' is sometimes called the *'concentration dissociation constant'*.

Common Ion Effect

The name common ion suggests a particular ion is derived from two sources, thus the concentration of a particular ion already present in the solution is increased by addition of a reagent which on dissociation will give the same ion. The example of the application of principle of common ion is the precipitation of iron as hydroxide with ammonia solution. In ferric chloride solution a solid ammonium chloride is added followed by ammonia solution. The ammonium ion is derived from the ammonia solution and the ammonium chloride. The common ion effect provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte. It will become clear from the following example. Let us study the effect on degree of dissociation of the base when 0.5 mol of ammonium chloride is added to 1 litre of 0.1 M aqueous ammonia solution.

(Dissociation constant of ammonia (NH_3) in water = 1.8×10^{-5} mol/litre).

The aqueous ammonia will be ionized into NH_4^+ and OH^- ions. From Ostwald's dilution law, the ionization constant, $K = \alpha^2 c/1 - \alpha$, where α is the degree of ionization at equilibrium and c is the concentration in mols per litre. $(1 - \alpha)$ represents the amount of unionized electrolyte and may be taken as negligible, then

$K = \alpha^2 c$ and degree of ionization $\alpha = \sqrt{K/c}$.

In 0.1M ammonia solution, the degree of ionization

$\alpha = \sqrt{1.8 \times 10^{-5}/0.1} = 0.0135$.

Hence, $[OH^-] = [NH_4^+] = \alpha \cdot c$ mols/ltr = 0.00135 = 1.35×10^{-3}

and $[NH_3] = (1 - \alpha)c = 0.09865$ mols/ltr.

Let α' be the degree of ionization in presence of the added ammonium chloride, then $[OH^-] = \alpha' c = 0.1\alpha'$ and $[NH_3] = (1 - \alpha')c = 0.1$, since α' may be taken as negligibly small. The addition of completely ionized ammonium chloride will decrease the concentration of NH_4^+ derived from the base and increase the concentration of NH_3.

Say, $[NH_4^+] = 0.5$ approximately, then

$$K = \frac{[NH_4^+] \times [OH^-]}{[NH_3]} = \frac{0.5 \times 0.1\alpha}{0.1} = 1.8 \times 10^{-5}$$

$\alpha' = 3.6 \times 10^{-5}$ and $[OH^-] = 0.1 \times 3.6 \times 10^{-5} = 3.6 \times 10^{-6}$ mols/ltr

The addition of half a mole of ammonium chloride to a 0.1 M solution of aqueous ammonia has decreased the degree of ionization from 1.35 to 0.0036 per cent, and the hydroxide ion concentration from 1.35×10^{-3} to 3.6×10^{-6} mols/litre.

Solubility Product

It is an experimental fact that for sparingly soluble salts (i.e., those of which the solubility is less than 0.01 mols per litre) the product of total molecular concentration of ions is a constant at constant temperature. This product is termed as *solubility product*. For a binary electrolyte:
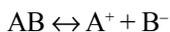
$$AB \leftrightarrow A^+ + B^-$$

$$K_{s(AB)} = [A^+] \times [B^-]$$

where, K_s is the solubility product. The solubility product constant (K_s) like all other equilibrium constants varies with temperature. For example, K_s of $PbCl_2$ at 25°C is 1.7×10^{-5}, while at higher temperature it is very high. The solubility product relation applies with sufficient accuracy for purposes of quantitative analysis only to saturated solutions of slightly soluble electrolytes and with small additions of other salts. In the presence of moderate concentrations of salts, the ionic concentration, and therefore the ionic strength of the solution will increase. This will, in general, lower the activity coefficients of both ions, and consequently the ionic concentrations (and therefore the solubility) must increase in order to maintain the solubility product constant. This effect, which is most marked when the added electrolyte does not possess an ion in common with the sparingly soluble salt, we may term it the *salt effect*.

When a solution of salt containing a common ion is added to a saturated solution of a slightly soluble salt, two situations may arise:

1. at moderate concentrations of the added salt, the solubility will generally decrease,
2. at higher concentrations of soluble salt, when the ionic strength of the solution increases considerably and the activity coefficients of the ions decrease, the solubility may actually increase. This is one of the reasons why a very large excess of the precipitating agent is avoided in quantitative analysis.

The concept of the solubility product has great importance in quantitative analysis due to its impact on precipitation from solution. The solubility product is the ultimate value which is attained by the ionic concentration product when equilibrium has been established between the solid phase of a difficultly soluble salt and the solution. In other words, when the solution is saturated, the ionic concentration product of slightly soluble salt is equal to the solubility product. If the experimental conditions are such that ionic concentration product is different from the solubility product, then two situations will arise:

1. when the ionic concentration product exceeds the solubility product, for example, by addition of salt with a common ion, the system will be adjusted in such a way which results in precipitation of the solid salt, provided supersaturation conditions are excluded;
2. when the ionic concentration product is less than the solubility product, then further quantity of solute can pass into the solution until the solubility product is attained, or if this is not possible, until all the solute has dissolved.

Quantitative Effect of a Common Ion

We have seen in the discussion of solubility product that the addition of common ion will decrease the solubility of the salt. This decrease in solubility by the common ion effect is of fundamental importance in gravimetric analysis. The solubility of a precipitate can be minimized to negligible extent by the addition of a suitable excess of a precipitating agent. An illustration of a specific case of determination of silver as silver chloride may help in understanding the effect.

The silver in solution is precipitated by adding chloride solution. If an exactly equivalent amount is added, the resultant saturated solution of silver chloride will contain 0.0015 gram/litre AgCl (the solubility of silver chloride is 0.0015 gram/litre). If 0.2 gram of silver chloride is produced and the volume of the solution and washings is 500 ml, the loss owing to solubility will be 0.00075 gram or $0.00075 \times 100/ 0.2 = 0.38$ per cent of weight of salt. If the precipitant (chloride solution) is added in excess, say to a concentration of 0.01 M, the solubility of silver chloride is reduced to 1.5×10^{-5} gram/litre and the loss will be $1.5 \times 10^{-5} \times 0.5 \times 100/0.2 = 0.0038$ per cent.

Factors Affecting the Solubility of a Precipitate

Effect of acids

When an acid is added to an aqueous suspension of sparingly soluble salt of strong acid, the effect will be similar to that of any other indifferent electrolyte. But the addition of an acid to sparingly soluble salt of weak acid has in general, a solvent effect upon it. This can be explained as under. Suppose hydrochloric acid is added to an aqueous suspension of sparingly soluble salt MA of weak acid HA. The following equilibrium will establish.

$$M^+ + A^- + H^+ \rightleftharpoons HA + M^+$$

If dissociation constant of acid HA is very small, the anion A^- will be removed from the solution to form undissociated acid HA. As a result, more of the salt will be dissolved to replace the anions removed in this way, and this process will continue until equilibrium is established, i.e., ionic product $[M^+] \times [A^-]$ becomes equal to solubility product of MA. The solubility of silver orthophosphate in dilute nitric acid is thus explained on the similar reasoning and is due to removal of PO_4^{3-} ion as HPO_4^{2-} and/or $H_2PO_4^-$

i.e., $PO_4^{3-} + H^+ \rightleftharpoons HPO_4^{2-}$

$HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$
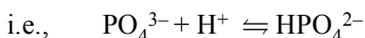
In case of salts of weak acids, such as carbonic acid, sulphurous acid and nitrous acid, the increased solubility is due to contribution of an additional factor that is actual disappearance of an acid from solution either spontaneously or on gentle warming. The solubility of sparingly soluble sulphites, carbonates, oxalates, phosphates, arsenites, arsenates, cyanides (exception of silver cyanide which is salt of strong acid), fluorides, acetates, and other organic acids in strong acid is thus explained. The weakness of second stage of ionization of sulphuric acid ($K_2 = 1.2 \times 10^{-2}$ mols/litre) contributes to the increased solubility of sparingly soluble sulphates (e.g., sulphates of barium, strontium and lead) in acids, although the effect is small as K_2 is comparatively large. This is why precipitation of barium

sulphate is carried out in slightly acid solution in quantitative separation. In this condition, the precipitate is more easily filterable and reduces coprecipitation.

Effect of temperature

In general, the solubility of precipitates is increased with rise in temperature. The influence of temperature varies with the substance. Thus, the solubility of silver chloride at 10 and 100°C is 1.72 and 21.1 mg/litre, whereas that of barium sulphate at these two temperatures is 2.2 and 3.9 mg/litre respectively. As we have already discussed, the common ion effect largely controls the solubility in many instances. Wherever possible it is advantageous to filter the solution in hot condition as it increases the rate of filtration and solubility of foreign substances, thus facilitates their removal form the precipitate more complete. The double phosphates of ammonium with magnesium, manganese or zinc as well as lead sulphate and silver chloride, are usually filtered at room temperature to avoid solubility losses whereas the precipitate of iron oxide is preferably filtered hot.

Effect of solvent

Addition of organic solvents such as methanol, ethanol, acetone, etc. helps in reducing the solubility of most inorganic compounds. The addition of about 20 per cent by volume of ethanol reduces the solubility of lead sulphate practically negligible.

Ionic Product of Water

It was found by Kohlrausch and Heydweiller that the highly purified water possesses a small but definite conductivity. This shows that the water must therefore be slightly ionized. The ionized form of water or electrolytic dissociation of water may be written as

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
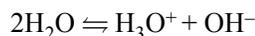
For sake of simplicity, the hydronium ion is written as H^+ and the more simple equation that is in practice is

$$H_2O \rightleftharpoons H^+ + OH^-$$

Applying the law of mass action, we obtain, for any given temperature:

$$\frac{[H^+] \times [OH^-]}{[H_2O]} = \text{Constant}$$

In pure water or in dilute aqueous solutions, the concentration of undissociated water may be considered constant. Hence,

$$[H^+] \times [OH^-] = K_w, \text{ a new constant.}$$

K_w is the *ionic product of water*. The ionic product of water varies with temperature. The value at about 25°C may be taken as 1×10^{-14} with the concentrations expressed in mol/litre. The concentrations of hydrogen and hydroxide ions are equal and therefore $[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7}$ mol/litre at about 25°C. A solution is said to be exactly neutral when concentrations of hydrogen and hydroxide ions are

equal, i.e., 10^{-7} mol/litre. If $[H^+]$ is greater than 10^{-7} mol/litre, the solution is acid and if less than 10^{-7} mol/litre, the solution is said to be alkaline (or basic).

Table 2.1: Ionic product of water at various temperatures

Temp. (°C)	$K_w \times 10^{-14}$	*Temp. (°C)*	$K_w \times 10^{-14}$
0	0.12	35	2.09
5	0.19	40	2.92
10	0.29	45	4.02
15	0.45	50	5.47
20	0.68	55	7.30
25	1.01	60	9.61
30	1.47		

The Hydrogen Ion Exponent (pH)

The Hydrogen Ion Exponent (pH) is defined by the relationships:

$$\text{pH} = \log_{10} 1/[H^+] = -\log_{10}[H^+], \text{ or } [H^+] = 10^{-\text{pH}} \qquad \text{..... (1)}$$

Substituting the value of $[H^+]$ in pure water (see the section of ionic product of water) then $\text{pH} = \log_{10} 1/10^{-7} = 7$. Thus, the solution with pH 7 is said to be neutral solution. The solution having hydrogen ion concentration of 1 mol/litre has $\text{pH} = -\log_{10} 1 = 0$ and a solution having hydroxide ion concentration of 1 mol/litre has $[H^+] = K_w/[OH^-] = 10^{-14}/10° = 10^{-14} = 14$. Thus, the acid solutions will be those with pH less than 7 and alkaline or basic solutions will be having pH greater than 7. The pH of the solution can be conveniently measured with the help of pH meter. The commonly available digital pH meters consist of a glass electrode or combination (glass plus reference) electrode and a unit for measuring pH and e.m.f. with digital read out. In the pH meter, the e.m.f. of the cell containing glass electrode is impressed upon a high resistance and the current flowing in the resistance is then amplified and applied to a sensitive moving coil meter. This is calibrated in millivolts so that the cell e.m.f. is recorded directly; the scale is also calibrated in pH units from 0 to 14 to facilitate direct measurement of pH. In most of the pH meters a selector knob is provided to select the pH or e.m.f. value for measurement. As the pH varies with temperature, a temperature selector is also provided. The glass electrode has an 'asymmetry potential' which makes it impossible to relate a measured electrode potential directly to pH of the solution, and therefore the calibration of electrode becomes necessary. For calibration, the buffer solutions of known pH are used and the scale is adjusted to the correct value.

On the line of equation (1) above, the hydroxide ion concentration may be expressed as:

$$\text{pOH} = -\log_{10}[OH^-] \text{ or } [OH^-] = 10^{-\text{pOH}}$$

Taking the logarithmic value of the ionic product, we may write

$$\log\{[H^+] \times [OH^-]\} = \log K_w = \log 10^{-14}$$

Then $\log[H^+] + \log[OH^-] = 14$

or $\text{pH} + \text{pOH} = 14$

The approximate pH value of solutions can be calculated using the following formulae.

Strong acid	$pH = -\log[\text{acid}]$
Strong base	$pH = 14 + \log[\text{base}]$
Weak acid	$pH = \frac{1}{2}\,pKa - \frac{1}{2}\log[\text{acid}]$
Weak base	$pH = 14 - \frac{1}{2}\,pKb + \frac{1}{2}\log[\text{base}]$
Salt of weak acid and strong base	$pH = 7 + \frac{1}{2}\,pKa + \frac{1}{2}\log[\text{salt}]$
Acid salts of dibasic acid	$pH = \frac{1}{2}\,pK_1 + \frac{1}{2}\,pK_2 - \frac{1}{2}\log[\text{salt}] + \frac{1}{2}\log(K_1 + [\text{salt}])$
Buffer solution consisting of a mixture of a weak acid and its salt	$pH = pKa + \log \dfrac{[\text{salt}] + [H_3O^+] - [OH^-]}{[\text{acid}] - [H_3O^+] + [OH^-]}$

Buffer Solutions

Before knowing about the buffer solutions it is necessary to know what buffer action is. An acid solution having definite concentration will have a definite pH, say a 0.0001 N hydrochloric acid solution should have pH equal to 4. This solution is extremely sensitive and if exposed to air or even stored in glass container pH of the solution will change due to absorption of traces of ammonia from air or alkali from glass container. The same phenomenon is applicable to alkali solutions which are sensitive to atmospheric carbon dioxide. If these solutions are made resistant to changes in hydrogen ion concentration upon addition of small quantity of acid or alkali, the action is termed *buffer action*. This can be achieved by addition of a solution which generally consists of definite proportion of weak acid or base and its salt. Such solutions which possess '*reserve acidity*' and '*reserve alkalinity*' and provide a solution a capacity of resistance to changes in its pH upon addition of small amount of acid or alkali are called *buffer solutions*. These buffer solutions are employed in the titrations to be performed at definite pH. For example, the EDTA complexometric titrations of calcium, magnesium, aluminium, zinc, etc.

Standard Solutions

In titrimetric analysis and most of the instrumental analysis a chemist has to come across the standard solutions. A standard solution is one of which concentration or strength is known. In other words, it is a solution which contains a known weight of substance in a definite volume of solution. The concentrations of such solutions are generally expressed in terms of molarity or normality. The concentrations are also expressed in percentage and even in terms of parts per million or billion when substance present is in minute quantity. In conventional analysis, we are mostly concerned with the molar or normal solutions. The molarity may be defined as the number of moles of solute per litre of solution. A molar solution will be that which contains weight in grams equal to the molecular weight of the substance in one litre of solution. Likewise the normality may be defined as number equivalents per litre. These definitions are not absolutely correct because as per the definition of mole, it is no longer a unit of mass but is one of amount of substance. The definition of mole is given below:

'*The mole* is the amount of substance which contains as many elementary units as there are atoms in 0.012 kilogram of carbon-12. The elementary unit must be specified and may be an atom, a molecule, an ion, a radical, an electron or other particle or a specified group of such particles.'

However, the use of terms equivalent or normal solution are found to be practically advantageous. The IUPAC has suggested the following definition of equivalent.

'The equivalent of a substance is that amount of it which, in a specified reaction, combines with, releases or replaces that amount of hydrogen which is combined with 3 grams of carbon-12 in methane $^{12}CH_4$.'

In the above definition, the amount of hydrogen referred to may be replaced by one equivalent of any other substance, but the reaction to which the definition is applied must be clearly specified. Although the terms mole and equivalent as now defined refer to an amount of substance, each definition does in fact refer to a specified mass of carbon-12, and hence we can say for example,

1 mole of NaCl has a mass of 59.4428 g.

1 mole of $Na_2CO_3.10H_2O$ has a mass of 286.004 g.

1 mole of H_2SO_4 has a mass of 98.078 g.

1 equivalent of $Na_2CO_3.10H_2O$ has a mass of 143.002 g.

1 equivalent of H_2SO_4 has a mass of 49.039 g.

In the light of above discussions the earlier definitions of molarity and normality, therefore, require modification. A *molar solution* is thus defined as one containing one mole of a defined species per litre and the *normal solution* is one containing one equivalent of a defined species per litre.

The quantity of the term 'equivalent' used in the definition of normal solution varies with the type of reaction. Hence, for determining the equivalent of a substance the specific reaction involved is necessary to consider. The concept is elaborated in discussion of different types of reactions.

Neutralization reactions: In these reactions the acid is neutralized by a base and vice versa by reacting hydrogen ion and hydroxide ion to form water and salt. The acid releases the hydrogen ion and thus equivalent of an acid is that mass of it which contains 1.0078 gram of replaceable hydrogen. In monoprotic acids only one hydrogen is available for replacement and therefore the equivalent of monoprotic acid is identical with the mole. The equivalent of hydrochloric acid is equal to 36.461 gram, and that of nitric acid is 31.0139 gram. The diprotic acids or dibasic acids such as sulphuric acid, oxalic acid have two replaceable hydrogens and therefore the equivalent will be ½ of the mole. Likewise an equivalent of a triprotic acid will be 1/3 of the mole as it contains three replaceable hydrogens. A normal solution of hydrochloric acid contains 36.461 grams of HCl in one litre of solution, a normal solution of sulphuric acid contains 49.039 gram in one litre of solution, and so on.

In a base, the replaceable species is hydroxide ion and therefore the equivalent of a base is that mass of it which contains one hydroxyl group, i.e., 17.008 grams of ionisable hydroxyl. The equivalents of sodium and potassium hydroxide (one replaceable hydroxyl group) are the mole, that of calcium hydroxide $Ca(OH)_2$ (two replaceable hydroxyl groups) is half a mole.

Table 2.2

Substance	Partial ionic equation	Equivalent
Oxidants		
Potassium permanganate (acid)	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	$MnO_4^-/5 = KMnO_4/5$
Potassium dichromate	$Cr_2O_7^{2-} + 14\,H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	$Cr_2O_7^{2-}/6 = K_2Cr_2O_7/6$
Cerium (IV) sulphate	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	$Ce^{4+}/1 = Ce(SO_4)_2/1$
Sodium bismuthate	$BiO_3^- + 6H^+ + 2e^- \rightleftharpoons Bi^{3+} + 3H_2O$	$BiO_3^-/2 = Na\,BiO_3/2$
Reductants		
Oxalic acid	$C_2O_4^{2-} \rightleftharpoons 2CO_2 + 2e^-$	$C_2O_4^{2-}/2 = H_2C_2O_4/2$
Ferrous sulphate	$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$	$Fe^{2+}/1 = FeSO_4/1$
Sodium thiosulphate	$S_2O_3^{2-} + H_2O \rightleftharpoons S_4O_6^{2-} + 2e^-$	$S_2O_3^{2-}/2 = Na_2S_2O_3/2$

The other method, i.e., oxidation number method for calculation of the equivalents of the substances is based on the changes in valency of the element in a particular compound in a reaction. The oxidation number of the element in a particular compound is that number which is required to convert one atom of the element in free state to that in the compound. The oxidation numbers are both positive and negative. The effective change indicates oxidation and reduction. The effective positive change in oxidation number indicates oxidation while the reduction is indicated by negative change. For determination of oxidation numbers the following rules are observed.

1. The oxidation number of free or uncombined element is zero.
2. The oxidation number of hydrogen is +1 in all its compounds except in certain hydrides (such as ionic metal hydrides, e.g., $Na^{+1}H^{-1}$ where it is –1).
3. The oxidation number of oxygen is –2 except in peroxides where it is –1.
4. The oxidation number of fluorine is –1 in all its compounds.
5. The oxidation number of a metal in combination is usually positive except in hydrides.
6. The oxidation number of a radical or ion is equal to the electrical charge on it.
7. The oxidation number of a compound is always zero, and is determined by the sum of the oxidation numbers of the individual atoms each multiplied by the number of atoms of the element in the molecule.

The following illustration will help in understanding the concept of oxidation number. Calculate the oxidation number of Cr in $K_2Cr_2O_7$ and that of Mn in $KMnO_4$.

Applying the above rules,

O. N. of K = +1

O. N. of each O = –2

Now, let the oxidation number of Cr in $K_2Cr_2O_7$ be x then $2 + 2x + [7 \times (-2)] = 0$.

Hence, $x = +6$. The oxidation number of Cr in $K_2Cr_2O_7$ is +6.

Likewise the oxidation number of Mn in $KMnO_4$ may be calculated and it is +7.

The equivalent of an oxidizing agent is determined by the change in oxidation number taken place in the process of its reduction. For example, in reduction of potassium permanganate in the presence of dilute sulphuric acid reduces to manganese sulphate, the change in oxidation number of manganese is 5 $\overset{+1}{K}\overset{+7}{Mn}\overset{-8}{O_4} \to \overset{+2}{Mn}\overset{+6}{S}\overset{-8}{O_4}$, i.e., Mn (+7) to Mn (+2). The equivalent of potassium permanganate is therefore 1/5 mole.

Similarly, the equivalent of a reducing agent is determined by the change in oxidation number taken place in the process of its oxidation. For example, in oxidation of ferrous sulphate [Fe(II)] to ferric sulphate [Fe(III)] the change in oxidation number per atom of iron is 1unit (i.e., from +2 to +3) and hence the equivalent of ferrous sulphate is 1 mole.

Complex formation and precipitation reactions: In these reactions the equivalent is the mass of the substance which reacts with cation divided by the valency of the cation. Thus, the equivalent of the substance would be 1 mole of univalent cation, ½ mole of bivalent cation and 1/3 mole of trivalent cation. The equivalent of a salt in a precipitation reaction is the mole divided by total valency of the reacting ion. The equivalent of silver nitrate in the titration of chloride ion is one mole as the total valency of the chloride ion is one.

Standard Substances

The substances used for preparation of standard solutions are categorized into two: (1) *primary standard substances* and (2) *secondary standard substances*. The primary standard substances are those which are used for standardization of the solution of unknown strength. A substance to be used as primary standard should satisfy the following requirements:

1. It must be in pure form, i.e., purity of the substance should be at least 99.95%.

2. It must be easy to dry and preservable in pure state.

3. The substance should remain unaffected in air during weighing, i.e., it should neither absorb moisture, nor react with oxygen or carbon dioxide from air. The hygroscopic substance such as sodium hydroxide does not meet this criterion and hence cannot be considered primary standard. The composition of the substance should remain unchanged during weighing and storage.

4. The substance should have already been tested otherwise should be capable of being tested for impurities.

5. It should be readily soluble under the conditions in which it is employed.

6. The reaction with standard solution should be stoichiometric and practically instantaneous. The titration error should be negligible, or easy to determine accurately.

A secondary standard is a substance which is standardized and whose content of active ingredient has been determined by comparision against a primary standard.

Obtaining an ideal primary standard meeting the above ideal requirements is difficult in practice, and usually a chemist has to compromise with some of the ideal requirements in selection of primary standards. The following are some of the substances which are usually used as primary standards.

Table 2.3

Substances	*Molecular formula*
Sodium carbonate	Na_2CO_3
Sodium tetraborate	$Na_2B_4O_7$
Potassium hydrogen-phthalate	$KH(C_8H_4O_4)$
Constant-boiling-point hydrochloric acid	HCl
Benzoic acid	$H(C_7H_5O_2)$
Silver nitrate	$AgNO_3$
Potassium dichromate	$K_2Cr_2O_7$
Potassium bromate	$KBrO_3$
Sodium oxalate	$Na_2C_2O_4$
Arsenic (III) oxide	As_2O_3
Spectroscopic grade metals	

Sampling

The important stage in analysis is to obtain a sample which should represent the original lot in true sense. In other words, the sample taken for analysis must represent the essential physical and chemical characteristics of the original material. The accuracy of the analytical results largely depends on accurate sampling of the material to be analyzed. The most refined analytical techniques cannot give consistently good results if the samples are biased or liable to a large random error.

Preparation of Sample

At the time of original sampling stage as well as at the stage of preparing the smallest amount to be used by the analyst in the test, the thorough mixing of the material, the range of particle sizes and the presence of interfering impurities are all significant factors. The methods of sampling necessarily vary considerably depending on the nature and complexity of the material to be sampled. In order to do the whole job properly, it is necessary to know about the nature, physical and chemical properties of the material to be sampled and the knowledge of tools to be used in sampling. The knowledge of the element or radical to be determined also plays important role in selecting the tools of sampling. For example, in the sampling of ore in which iron is to be determined the use of iron mortar or pulverizer should be avoided, similarly the quartz should not be pulverized in agate or silica mortar as there are chances of contamination from the pulverizer. In sampling of ores and the like, a large sample is usually obtained which is then reduced to a laboratory sample. In general, the sample is first crushed to a reasonable size, a portion is taken by quartering or similar procedures. This portion is again crushed to somewhat smaller size and again divided. The operations are repeated until a sample is obtained that is large enough for the analyses to be done. The quantity of the sample at this stage should not be so large as to cause needless work in its final preparation. The sample is then crushed to a size that will minimize error in sampling at the balance and is fine enough for easy decomposition.

General Procedure of Sampling

1. Soils – Dry the sample in air, break up the clods with a wood rolling pin and pass the sample through a 2 mm mesh sieve. Pour the sieved soil in a pile on a heavy wrapping paper. Mix thoroughly and quarter. Discard the opposite quarters and repeat the process until a sample of 3 to 5 gram remains. Pulverize the small sub-sample in a multimortar to an impalpable powder.

2. Rocks – Break the rock fragments into small chips with a plattener diamond mortar and pass the sample through a 2 mm mesh sieve, crushing the portion that remains on sieve until the entire sample has passed through the sieve. Mix thoroughly and quarter. Discard the opposite quarters and repeat the process until a sample of 3 to 5 gram remains. Powder this in a multimortar to a fine powder.

Preparation of the Sample for Weighing

Before weighing, a care in general should be taken for removal of foreign matters such as pieces of wood fibre, metal piece or pieces of plastic introduced during sampling or from container. No general rule can be given for drying of sample. If the results of the analyses are to be reported on dry basis the sample should be dried at temperature 105° to 110°C. In some cases, as in the analyses of certain rocks, it is preferred to analyze the sample as it is. In some cases drying of sample requires higher temperature as for example, pyrolusite and bauxite require temperatures 125°C and 140°C, respectively. Some materials oxidize slowly when heated and require drying in a non-oxidizing atmosphere. For determination of moisture in the given sample, the sample should be weighed as it is.

Decomposition

The first and foremost step of the analysis by conventional method is decomposition of the sample. The different elements in the sample are brought into solution in the form of their salts and at the same time this step is utilized for separation of silica from the other constituents. The mode of attack depends on the nature of sample. A sample of basic nature is subjected to attack by acids, while the sample of acidic nature is attacked by alkalies. Similarly, samples containing easily oxidizable and reducible elements can be attacked by oxidizing and reducing agents respectively. Fusion methods are also used based on the same principles. The fluxes used for fusion are acidic and alkaline as well as oxidizing and reducing.

The precaution that has to be taken at this stage of analysis is to ensure complete decomposition of the sample. It has been observed in general that decomposition of the sample having finer particle size is easier than the coarse material. Generally, a particle size of sample powder passing through a 200 mesh sieve is recommended. After the attack and digestion of the sample it is always imperative to examine the residue in the solution for presence of any unattacked material. In case, some material is left unattacked, then filter the solution, wash the residue and treat it with suitable reagents preferably the same one used initially for complete decomposition. Certain elements may volatilize off during acid digestion, fusion and ignition. Some examples are loss of antimony, boron and trivalent arsenic during evaporation with hydrochloric acid. If these are suspected, other methods of attack should be followed.

As a general guideline for decomposition of sample it is advisable to test the solubility of a small amount of material in a test tube, using water if the material is salt or hydrochloric acid in case of an

9. **Perchloric acid** – is a powerful oxidizing and also dehydrating agent when hot and concentrated. The majority of the perchlorates are soluble in water which makes it a desirable solvent. The perchlorates in general are soluble in organic solvents such as alcohols, ketones, aldehydes, ethers and esters. Anhydrous perchloric acid is a dangerous substance because it interacts with oxidisable matter to cause violent explosion. With proper care, the use of perchloric acid is without hazards. The evaporation of alcoholic solution of perchloric acid must be avoided.

III. Fusions

The decomposition of some ores particularly silicate is effected by fusion with appropriate flux. The insoluble residue remaining from acid treatment of an ore is also generally brought into solution by fusion with suitable flux. The fusions are made in crucibles of silica, iron, nickel, silver, "palau" (gold – palladium 80 : 20) or platinum.

Potassium bisulphate fusion may be carried out in silica or glass as well as in platinum crucibles; sodium carbonate fusions may be made in iron, nickel, "palau" and platinum while for hydroxide or peroxide fusions crucibles made of iron, nickel or silver are recommended. For carrying out the fusion with the flux of sodium carbonate – potassium nitrate platinum crucible may be used but care should be taken while dissolving the fused mass. Hydrochloric acid should be avoided for dissolving the fused mass as the chlorine liberated attacks the platinum. Do not use platinum crucible for hydroxide fusion as alkali attacks platinum metal.

The various fluxes which are commonly used for fusion are given below:

1. **Sodium carbonate** – decomposes silicates of aluminium, calcium, cerium, chromium, etc.; halides of silver; sulphates of barium, lead, etc.

2. **Sodium and potassium carbonates** – This flux fuses at lower temperature than sodium carbonate alone. It can be used for fusion of silicates of aluminium, fluorine, iron, nickel, selenium, tellurium, etc.

3. **Sodium carbonate with oxidizing agents** such as potassium chlorate, potassium nitrate, sodium peroxide, zinc oxide, magnesium oxide – Ores of antimony, arsenic, chromium, iron, molybdenum, vanadium, zirconium, sulphides, pyrites, etc. may be decomposed using this flux.

4. **Sodium peroxide** – is strong oxidizing agent and to be handled carefully as it catches fire and explosion may occur with combustible substance. The fusion takes short time and should be done at very low temperature. Ores of antimony, arsenic, chromium, iron, molybdenum, nickel, vanadium, tin and uranium can be decomposed by fusion with sodium peroxide.

5. **Sodium bisulphate** – The flux is useful for fusion of ores of aluminium, antimony, copper, chromium, cobalt, iron, manganese, nickel, rhodium, tantalum, titanium, tungsten. Silica is not made soluble. Certain refractory oxides require the addition of reducing agent such as carbon from filter paper to assist the bisulphate flux. It is better to make two or more fusions on resulting residues remaining from an acid extraction of the melt, rather than to increase the amount of flux in the first charge.

6. **Basic flux** – Sodium hydroxide, potassium hydroxide (with or without potassium fluoride)

   The flux is used for decomposition of oxidized antimony ore, ores of chromium, tin, zinc, zirconium, sulphides and sulphates in sulphur determinations.

dilute solutions should be used. The compound formed should be somewhat soluble in the beginning of its formation. The precipitation takes place slowly and gradually with small crystals and in time tends to grow in their crystal size with reduction in their solubility. The crystal lattice tends to become more perfect especially in hot condition. Thus, the conditions for proper precipitation are that it should be slow, it should be heated if taking place at room temperature and allowed sufficient time for crystallization.

2. Filtration

The second stage of gravimetric analysis is filtration. Filtration is done for separation of the precipitate containing the element of interest, from the solution. Any error at this stage affects the results of analysis seriously. The possible source of error in this operation is loss of precipitate by passing out through the filter paper. To avoid this possibility, filter paper used for filtration should be of correct porosity leaving negligible or no ash on ignition. In case of doubt or for very accurate work, the exact ash content of the filter paper should be accurately determined and deducted from the weight of precipitate on ignition. It is advised to choose a filter paper of correct size according to size of funnel. In any case the edge of the filter paper should remain below the edge of funnel when fitted. The funnel should not be filled up with filtering solution more than 3/4th the volume of filter paper and in any case volume of filtering solution should not cross the edge of filter paper.

3. Washing of precipitate

The precipitate is washed for removal of adsorbed impurities and co-precipitate. Washing of precipitate for more number of times with small volumes is more effective than for less number of times with large volumes of wash solution. The wash solution should contain recommended electrolytes to prevent peptization of the precipitate. For high accuracy, the precipitate after washing should be dissolved and precipitated again, filtered and washed.

4. Ignition of precipitate

The filter paper containing precipitate should be dried in an oven before ignition. This is necessary in the case of gelatinous precipitates like Fe_2O_3 and Al_2O_3 to prevent spurting during ignition. Ignition should be done initially at low temperature for removal of carbon by oxidation to prevent the formation of carbide and then increased gradually or strongly heated on burner.

5. Cooling and weighing of precipitate

The crucible containing precipitate must be cooled in a desiccator filled with proper desiccant. Some compounds tend to absorb moisture; the weighing of such compounds should be done fast after cooling. The heating, cooling and weighing should be done till constant weight is obtained.

Volumetric Method

The volumetric method of analysis also called *volumetry* refers to the quantitative analysis carried out by measuring the volume of solution of known strength required for reaction with test solution quantitatively. The process of addition of standard solution (solution of known strength) to the test

solution until the equivalence point or end point is reached is called titration and hence the analysis is often called *titrimetric analysis*. To determine the end point an auxiliary reagent known as an *indicator* is added to the test solution which gives a clear visual change (either a colour change or formation of turbidity) in the solution being titrated at the point of equivalence. In some cases either standard solution or test solution acts as self indicator.

Conditions for Titrimetric Analysis

In titrimetric analysis a reaction must fulfill the following conditions:

1. The reaction occurred in the titration must be simple and can be expressed by a chemical equation.

2. The substance to be determined should react completely with the reagent in stoichiometric and equivalent proportions.

3. The reaction should be practically instantaneous or proceed with very great speed. In some cases addition of catalyst increases the speed of reaction.

4. There must be a marked change in free energy leading to alteration in some physical or chemical property of the solution at equivalence point.

5. An indicator should be available which by a change in physical properties (colour or formation of precipitate) should sharply define the end point of the reaction.

   In absence of a visible indicator, the end point can be determined by using the following instrumental techniques.

   (a) Potentiometric titration: In this technique potential (e.m.f.) between an indicator electrode and a reference electrode is measured after each addition of *titrant* (standard solution) to the test solution (*titrand*). The end point is determined from the graph plotted between values of potential and the volume of titrant added. This is normally detected by an abrupt change in e.m.f. at certain volume of titrant added.

   (b) Conductometric titration: This titration is also performed in the same line but electrical conductivity of the solution is measured after each addition of titrant. The end point is determined graphically as the point of intersection of two straight lines giving the change of conductivity before and after the equivalence point.

   (c) Amperometric titration: In amperometric titrations the current which passes through the titration cell between an indicator electrode (e.g., the dropping mercury electrode) and the appropriate depolarized reference electrode (e.g., the saturated calomel electrode) at a suitable applied e.m.f. is measured as a function of the volume of the titrant.

The titrimetric methods are generally fast and simple; tedious difficult separations can be avoided. The results obtained are highly precise.

Types of Reactions Involved in Titrimetric Analysis

As earlier said, the titrimetric analysis is based on the chemical reactions taking place during the course of analysis. The chemical reactions employed in volumetric analysis are categorized as under.

$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$$
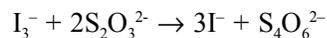
The sources of error in titrations involving iodine are (1) loss of iodine due to its appreciable volatility; and (2) air oxidation of iodide solutions.

$$4I^- + O_2 + 4H^+ = 2I_2 + 2H_2O$$
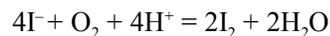
The error of loss of iodine due to volatility can be controlled as the volatility is decreased markedly through the formation of tri-iodide ion, in presence of excess of iodide. At room temperature the loss of iodine by volatilization from a solution containing at least 4% of potassium iodide is negligible provided the titration is not prolonged unduly. In order to prevent the loss, titration should be performed in cold solutions in conical flasks and not in beakers. Special type of flask called iodine flask with stopper are available for these titrations. If the solution is to stand it should be kept in a glass-stoppered vessel. The atmospheric oxidation of iodide is negligible in neutral solution in the absence of catalyst, but the rate of oxidation increases rapidly with decreasing pH. The reaction is catalysed by certain metal ions of variable valency (particularly copper), by nitrite ions and also by strong light. For this reason titrations should not be performed in direct sunlight, and solutions of iodide should be stored in amber glass bottles. Furthermore, the air oxidation of iodide ion may be induced by the reaction between iodide and the oxidizing agent, especially when the main reaction is slow. Hence, the oxidizing agent such as nitric acid used in dissolution of copper should be neutralized by adding small portions of sodium bicarbonate which also helps in displacing the air from the titration vessel. The vessel should be covered immediately with glass stopper after adding potassium iodide.

INSTRUMENTAL METHODS OF ANALYSIS

The instrumental methods of analysis can be divided into four categories: (1) electroanalytical methods, (2) spectroscopic methods, (3) thermal analysis, and (4) radio-analytical methods.

1. The electroanalytical methods are:
   (i)   electrogravimetry
   (ii)   colorimetry
   (iii) potentiometry
   (iv)   conductometry
   (v)   voltametry or polarography
   (vi)   amperometry.

2. The spectroscopic methods of analysis are:
   (i)   spectrophotometry
   (ii)   fluorimetry
   (iii) nephelometry and turbidimetry
   (iv)   atomic absorption spectrometry
   (v)   flame photometry
   (vi)   atomic emission spectrometry (Inductively Coupled Plasma Atomic Emission Spectrophotometer)
   (vii) atomic emission spectrographic analysis
   (viii) X-ray spectrometry.

3. The thermal analytical methods are:
   (i)   thermogravimetry
   (ii) differential thermal analysis
   (iii) differential scanning calorimetry.
4. The radio-analytical method is:
   (i)   neutron activation analysis.

The scope of this book is limited to methods of analysis of ores, and minerals. In analysis of these materials although the above methods find their utility but all are not used in practice. Some commonly used instrumental methods are discussed below in short.

Colorimetry and Spectrophotometry

The colorimetric method of analysis is based on comparison of the intensity of colour of unknown compound in solution with that of known standards. The technique works in visible range of light, i.e., between wavelength 400 and 760 nm (approximately). In this technique a soluble coloured complex of a metal or radical is formed and the intensity of the colour is matched with the standards of different concentrations of the metal or radical. Here the comparison is done with naked eyes. This technique is less accurate. The modified technique is photometer where light source is used and its resolution is done with the help of filters. The colour comparison is done by photocell or phototube instead of eyes. The modified version of the colorimeter is spectrophotometer. In spectrophotometer a monochromator is used for resolution of light beam and measurement of absorption of light by the solution is done by sensitive detectors like photomultipliers. Nowadays sophisticated spectrophotometers are available which provide the source of light in the range of ultraviolet to infrared region, i.e., wavelength from 200 to 1500 nm (approximately) and hence facilitate measurement of absorbance of colourless solutions also. Some instruments are controlled by microprocessor with the facility of automatic adjustment of parameters, automatic calibration and direct reading of concentration. In the modern sophisticated instruments the time for analysis is reduced and accuracy of results increased.

The technique is based on the principle known as Beer-Lambert law. These are two separate laws governing absorption of light. **Lambert's law** states that when a beam of monochromatic light is allowed to pass through a transparent medium, the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of the medium. The **Beer's law** states that the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically. Combination of these two laws forms the basis of colorimetry and spectrophotometry.

Atomic Absorption Spectrometry

The analytical technique, atomic absorption spectrometry, is based on the measurement of the amount of monochromatic light absorbed by the ground state atoms. When a solution containing metallic species is introduced into a flame, the vapours of metallic atoms are formed. These atoms are called ground state atoms and are capable of absorbing the light of their resonant wavelength and get excited.

This method is very useful in the analysis of trace metals in geological samples. A good experience is required for use of this method. The accuracy and precision are not as high as spectrophotometric methods.

X-ray Spectrometry

The technique works on the principle that when a beam of X-ray is directed on the surface of the specimen containing atomic species, a secondary or fluorescent radiation is emitted which is characteristic of each element present in the specimen. Two types of the technique: (1) wavelength dispersive and (2) energy dispersive are available. In the former, the secondary radiation is converted into a parallel beam and directed on to an analyzing crystal, in order to separate out the wavelength. The separated spectra of different wavelength are reflected into a scanning radiation detector. At certain angles, which correspond to each different wavelength present, a peak of radiation intensity is obtained. The angle at which peak occurs is uniquely related to a particular element. The intensity of the peak is proportional to the concentration of that element in the sample. In the latter technique, i.e., energy dispersive X-ray spectrometry, the specimen containing elements is bombarded by X-rays or the beam electron. The interaction of the beam with the specimen results into release of an X-ray photon, whose energy is characteristic of the element from which it originated. Individual photons are collected by a detector made of lithium drifted silicon which can be built into an X-ray spectrometer or electron microscope column. This converts the energies of photons into electrical pulses, measurement of which provides a means of identifying the specimen's constituent elements. The relative quantity of each element is established by measuring the count of photons. The X-ray spectrometric technique facilitates multi-element analysis simultaneously.

Neutron Activation Analysis

It is one of the radio-analytical methods used in analysis of geological samples for determination of various elements particularly rare earth elements. The principle of the technique is the formation of radioactive isotope of the elements present in the sample with known nuclear characteristics by neutron irradiation. Each source of induced radioactivity is separated and identified. The intensity of induced radioactivity is measured for determining the quantity of the original element present in the irradiated sample. The isotopes of the element formed by bombardment are identified by the characteristic energy emitted and half-life period of the radioactive element produced.