24

Measurement of pH

24.1 Introduction

The *p*H scale is a series of numbers. These numbers express the degree of acidity or alkalinity of a solution, as contrasted with the total quantity of acid or base in some substances as found by acid-base titrations. The term *p*H was introduced by Sorenseno, who defined it as

$$pH = -\log [H^+] \qquad (i)$$

In other words, it is the negative logarithm of hydrogen ion concentration expressed in molarity. Actually, it is the activity of hydrogen ion that is consistent with the thermodynamics. The activity definition of *p*H is

$$pH = -\log a_{H^+} \qquad (ii)$$

Operational Definition of pH. The definition employed should be capable of theoretical interpretation and for practical measurement. Of all the techniques available to measure free hydrogen ions in a solution of unknown composition, none will measure either concentration or activity. The definitions of *p*H given above are therefore not sufficient since *p*H is generally measured with glass electrode and a *p*H meter. The cell to be used is represented as :

$$\text{Glass} \mid H^+ \parallel \text{SCE}$$

where SCE is standard calomel electrode.

To compute the cell voltage, we will assume that the SCE is more positive than the glass electrode. Thus,

$$E_{cell} = E_{SCE} + E_J - E'_G - 0.059 \log [H^+]$$

where E_J is liquid junction potential

$$\text{or} \qquad E_{cell} = E^\circ - 0.059 \log a_{H^+}$$

$$= E^\circ - 0.059 \log C_{H^+} f_{H^+}$$

Now it is known that it is not possible to measure or compute f_{H^+} by itself. Moreover, f_{H^+} is very nearly equal to $f^{\pm}$ which can be measured by using the cell.

$$Pt, H_2/H^+, Cl^-, AgCl \mid Ag$$

Therefore, for practical purposes *p*H is defined as :

$$pH = -\log C_{H^+} f^{\pm}$$

or in terms of voltage

$$E_{cell} = E^\circ + 0.059\, pH$$

$$\text{or} \qquad pH = \frac{E_{cell} - E^\circ}{0.059} \text{ at } 25^\circ C$$

where E° is a constant and is different for different cells. This equation is the operational definition of *p*H.

The relationship between $[H_3O^+][OH^-]$, *p*H and *p*OH is given in Table 24.1.

Table 24.1 : Relationship between $[H_3O^+][OH^-]$, pH and pOH in aqueous solutions at 25°C

$[H_3O^+]$	*pH*	*pOH*	*[OH]*	*Remarks*
10^0	0	14	10^{-14}	strongly acid
10^{-1}	1	13	10^{-13}	
10^{-2}	2	12	10^{-12}	
10^{-3}	3	11	10^{-11}	weakly acid
10^{-7}	7	7	10^{-7}	neutral
10^{-11}	11	3	10^{-3}	weakly alkaline
10^{-12}	12	2	10^{-2}	
10^{-13}	13	1	10	
10^{-14}	14	0	10^0	strongly alkaline

24.2 Determination of pH

There are two methods which are generally used for determining the *p*H of a solution. These are:

1. Method of *p*H indicator.
2. Potentiometric method.

1. **Method of pH Indicator.** A number of organic substances are known which show distinctly different colours below and above a small *p*H range. Thus phenolphthalein, the common acid base indicator, is colourless below a *p*H of 8.3 and distinctly pink above 10.0. Over the *p*H range 8 to 10 it changes colour gradually through different shades of pink. Methyl organge shows a distinct red colour below *p*H 3.1 and a yellow colour above a *p*H of 4.4. The use of these two indicators could easily tell if the *p*H of a solution is below 3.1, between 3.1 and 4.4, between 4.3 and 10.0 and above 10.0.

Table 24.2 gives the various indicators in use and their working range in *p*H units.

Table 24.2

Indicator	*Colour Change*		*pH range*
	Acid	*Alkali*	
Thymol blue	Red	Yellow	1.2–2.8
Methyl yellow	Red	Yellow	2.9–4.0
Methyl orange	Red	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Bromo thymol blue	Yellow	Blue	6.0–7.6
Phenol red	Yellow	Red	6.8–8.4
Cresol red	Yellow	Red	7.2–8.8
Phenolphthalein	Colourless	Pink	8.3–10.0

To reduce the labour involved in the choice of appropriate indicator, several companies have marketed proprietory mixtures of indicators under trade names as *Universal Indicators*. From the colour developed with the universal indicator, one can easily fix the approximate value of the *p*H of a solution. Then a more appropriate indicator can be chosen such that approximate *p*H value of a solution under test falls within the working range of this indicator. By comparing the colour developed on mixing the indicator with the solution with already prepared standard colour plates or charts, the *p*H of the solution under test can be fixed with remarkable accuracy. For quickness and convenience, now we have *Indicator Papers* made from universal indicator as well as from short range indicators.

2. **Potentiometric Method.** This is the most accurate method of determining the pH of a solution. For finding the pH value of the solution we shall use an electrode reversible to H^+ ions. Following are some of the electrodes which can be used for this purpose:

(a) ***Hydrogen Electrode.*** A normal hydrogen electrode can be set up by bubbling pure hydrogen gas at a pressure of one atmosphere through a solution of an acid in which activity of hydrogen ions is unity. For detection of the electrode potential of this electrode a plate of an inert metal like gold or platinum is so placed that it dips partly in the acid and hydrogen gas bubbles on it at a slow rate. A platinized platinum plate is preferred as it permits the equilibrium value of potential to be reached quickly. When the two electrodes are coupled together to form a galvanic cell, the electrodes which has stronger tendency to lose electrons into external circuit acquires the negative polarity and becomes the negative pole. The other electrode then becomes the positive pole of the cell.

If a hydrogen electrode is immersed in a solution (the pH of which is to be measured), and the half cells are coupled with a normal hydrogen electrode by means of a saturated KCl bridge in order to eliminate the liquid junction potential, the E.M.F. of the resulting cell

$$Pt \mid H_2, H^+ (a=1) \parallel H_2, H^+ (a=x) \mid Pt$$

can be calculated potentiometrically.

The E.M.F. of the concentration cell at 25°C, is given by

$$E = E^\circ - \frac{RT}{nF} ln \frac{C_2}{C_1}$$

$$= 0 - \frac{0.0591}{1} \log \frac{1}{\left[H^+\right]} \qquad \left[\text{Because } E^\circ, \text{ standard potential} = 0\right]$$

$$= -0.0591\, pH$$

or $$pH = -\frac{E}{0.0591}$$

Thus simply by measuring the E.M.F. of the cell we can find out the value of pH. A simple arrangement for determining the pH value by using hydrogen electrode is shown in Fig. 24.1.

It is known that hydrogen electrodes give reproducible results, still the use of normal hydrogen electrode as a standard electrode or a half cell gives certain practical difficulties. It is therefore rarely used in routine pH measurements.

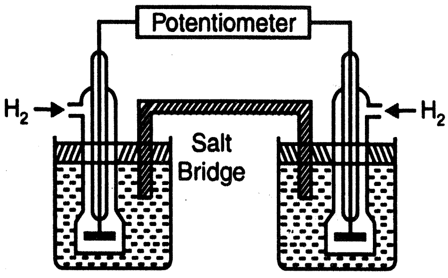

Fig. 24.1

Advantages of Hydrogen Electrode

(*i*) It is a fundamental electrode to which all measurements of pH are ultimately referred.

(*ii*) It can be used over the entire pH range.

(*iii*) It gives no salt error.

Disadvantages of Hydrogen Electrode

(*i*) It cannot be used in presence of air, dissolved oxygen, oxidising or reducing agents.

(*ii*) The platinum black coating deteriorates and hence it should be renewed from time to time. Sometimes it is poisoned due to the presence of compounds like alkaloids, sulphides, cyanides arsenic and antimony salts.

(*iii*) It is difficult to maintain the pressure of the hydrogen gas at a fixed value due to mechanical difficulties.

(*iv*) It is not easy to get pure hydrogen.

(b) **Quinhydrone Electrode.** This electrode was introduced by E. Billman in 1921. By the use of this electrode a rapid and easy determination of pH is possible. Quinhydrone is a 1:1 molar compound of quinone and hydroquinone and in solution it provides equimolecular quantities of these two substances.

$$\underset{\text{Quinhydrone}}{C_6H_4O_2.C_6H_4(OH)_2} \rightarrow \underset{\text{Quinone}}{C_6H_4O_2} + \underset{\text{Hydroquinone}}{C_6H_4(OH)_2}$$

Quinone and hydroquinone and hydrogen ions form a reversible redox system.

$$\underset{\text{Quinone (Q)}}{C_6H_4O_2} + 2H^+ + 2e^- \rightarrow \underset{\text{Hydroquinone }(QH_2)}{C_6H_4(OH)_2}$$

If an inert electrode such as platinum is immersed in this system, the electrode potential is given by:

$$E = E^\circ - \frac{2.303\,RT}{2F}\log\frac{[QH_2]}{[Q][H^+]^2} \qquad (\because n=2)$$

$$= E^\circ - \frac{2.303\,RT}{2F}\log\frac{[QH_2]}{[Q]} + \frac{2.303\,RT}{2F}\log\left[H^+\right]^2$$

Now in aqueous solution of quinhydrone,

$$[QH_2] = [Q]$$

$$\therefore \quad \log\frac{[QH_2]}{[Q]} = \log 1 = 0$$

Also $\log [H^+]^2 = 2 \log [H^+]$

Hence $$E = E^\circ + \frac{2.303\,RT}{2F} \times 2\log\left[H^+\right]$$

$$= E^\circ + \frac{2.303\,RT}{F}\log\left[H^+\right]$$

$$= E^\circ - \frac{2.303\,RT}{F}pH$$

$$= E^\circ - 0.0591\,pH \text{ at } 25°C$$

From the above equation it is clear that electrode potential will change with change in the concentration of hydrogen ions.

For convenience a calomel electrode often replaces the normal hydrogen electrode. The complete cell can be represented as :

$Hg \mid Hg_2Cl_2\,(s)$, KCl saturated $\parallel H^+$ (unknown) $Q.\,QH_2 \mid Pt$

In this cell the oxidation takes place on the calomel electrode while reduction takes place at the quinhydrone electrode. Using reduction electrode potential values, we have

$$E_{cell} = E_{quinhydrone} - E_{calomel} \text{ at } 25°C$$

Now $$E_{quinhydrone} = (0.6998 - 0.0591\,pH) \text{ volt}$$

and $$E_{calomel} = 0.2422 \text{ volt}$$

$$\therefore \quad E_{cell} = \{(0.6998 - 0.0591\,pH) - 0.2422\}$$

$$E_{cell} = 0.4576 - 0.0591\,pH$$

or $$pH = \frac{0.4576 - E_{cell}}{0.0591}$$

The electrode is set up by immersing a bright platinum wire or foil into the test solution containing excess of quinhydrone (0.5 to 1.0 per 100 ml of solution). The platinum wire must be cleaned with chromic acid and water. For preparing quinhydrone, dissolve 60 g of ferric alum in about 100 ml of water at about 60°C and pour it into a warm solution containing 5g of hydroquinone in 60 ml of water. Quinhydrone precipitates out as fine dark green needles. Cool using ice and filter by suction. After recrystallising from water, dry the crystals on filter paper.

The complete assembly for the measurement of *p*H using quinhyrone electrode is shown in Fig. 24.2.

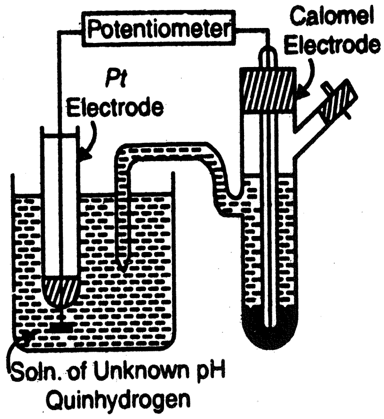

Fig. 24.2

Advantages of Quinhydrone Electrode

(*i*) It has a low resistance.
(*ii*) Equilibrium is reached quickly.
(*iii*) Its use is not affected by dissolved oxygen.
(*iv*) It can be used for micro-determinations.

Disadvantages of Quinhydrone Electrode

(*i*) It can be used for determining *p*H values less than 8 only.
(*ii*) The solution to be tested gets contaminated.
(*iii*) It suffers from salt error defect.
(*iv*) It cannot be used in presence of oxidising and reducing agents.
(*v*) It is not stable for long time, particularly above 30°C.
(*vi*) It alters the equilibrium between quinone and hydroquinone.

(c) **Glass Electrode.** When a glass surface is kept in contact with a solution, a potential is established between the glass and the solution. The value of potential is a function of H^+ ion concentration of the solution and the nature of the glass electrode. This observation was made by **Haber and Klemensiewiez** in 1909 and now forms the basis of a method for determining the *p*H of a solution.

The magnitude of the potential difference at 25°C is given by,

$$E_G = E^\circ_G - 0.0591 \log [H^+]$$
$$= E^\circ_G + 0.0591\, pH$$

where E_G is the potential of the electrode and E°_G is a constant for the given glass electrode depending upon the nature of the glass.

The glass electrode consists of a glass bulb with a long neck and is made of a special type of glass of relatively low melting point. A solution of 0.1 M HCl saturated with quinhydrone is filled up in the bulb. A platinum wire is inserted into the solution for making the electrical contact as shown in Fig. 24.3.

The glass bulb containing the solution is then dipped in the beaker containing the solution whose *p*H is to be determined.

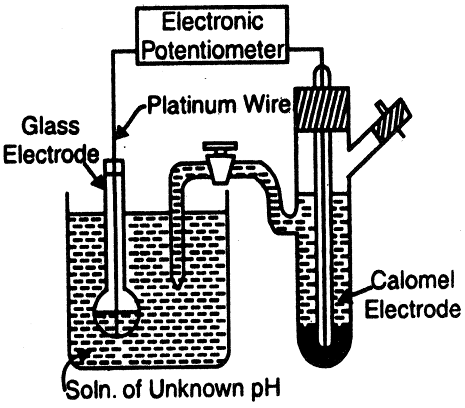

Fig. 24.3

For determining the *p*H of the solution, the above half-cell is joined with a reference electrode. The E.M.F. of such a cell can be determined by a potentiometer. The cell can be represented as:

Pt; 0.1 N HCl | Glass | Experimental solution | KCl (sat.), $Hg_2Cl_2(s)$ | Hg

The E.M.F. of the complete cell is given by

$$E_{cell} = E^{\circ}_{G} + 0.0591\,pH$$

The value of E°_{G} can be determined for this system by using a solution of known *p*H in the vessel containing the glass electrode and measuring the overall potential.

Advantages of Glass Electrode

(i) It may be used in the presence of strong oxidising and reducing solutions in viscous media and in presence of proteins which interfere with operation of other electrodes.

(ii) It can be used for solutions having *p*H values 2 to 10. With some special glass, measurements can be extended to *p*H values up to 14.

(iii) It is immune to poisoning.

(iv) It is simple to operate.

(v) The equilibrium is reached quickly.

Disadvantages of Glass Electrode

(i) In this electrode, the bulb is very fragile and therefore has to be used with great care.

(ii) As the glass membrane has a very high electrical resistance, the ordinary potentiometer cannot be used for measuring the potential of the glass electrode. Thus the electronic potentiometers are used.

(iii) Standardization has to be carried out frequently.

(iv) It cannot be employed in pure ethyl alcohol, acetic acid and gelatin.

(d) **Antimony–antimony Oxide Electrode.** This electrode also operates as an electrode reversible to hydrogen ion concentration. It consists of a rod of antimony placed in a solution having hydrogen ions. The antimony surface is cleaned and polished with fine emery paper. Antimony takes up a thin adhering layer of Sb_2O_3 almost instantaneously when exposed to air. This oxide is not dissolved by moderate acid concentrations.

The oxide gives an equilibrium concentration of Sb^{3+} ions in solution

$$Sb_2O_3 + H_2O \rightleftharpoons 2Sb^{3+} + 6OH^-$$

According to the above equation, the solubility product of Sb_2O_3 can be written as

$$K_{sp} = [Sb^{3+}]^2\,[OH^-]^6$$

or

$$\left[Sb^{3+}\right] = \frac{\left[K_{sp}\right]^{1/2}}{\left[OH^-\right]^3}$$

Also, from water equilibrium,

$$\left[OH^-\right] = \frac{Kw}{\left[H^+\right]}$$

The electrode reaction for antimony can be written as

$$Sb^{3+} + 3e^- \rightarrow Sb^0$$

$$E_{sb^{3+},\,sb} = E^{\circ} - \frac{RT}{3F}\ln\frac{[Sb]}{\left[Sb^{3+}\right]}$$

$$= E^{\circ} + \frac{RT}{3F}\,ln\,Sb^{3+} \quad [\because [Sb] = 1]$$

$$E_{sb}{}^{3+},{}_{sb} = E + \frac{RT}{3F} ln \frac{\left(K_{sp}\right)^{1/2}}{\left[OH^-\right]^3}$$

$$= E^\circ + \frac{RT}{3F} ln \left(K_{sp}\right)^{1/2} - \frac{RT}{3F} ln \left[OH^-\right]^3$$

$$E_{sb}{}^{3+},{}_{sb} = E^\circ + \frac{RT}{6F} ln\, K_{sp} - \frac{RT}{F} ln \frac{Kw}{\left[H^+\right]}$$

$$= E^\circ + \frac{RT}{6F} ln\, K_{sp} - \frac{RT}{F} ln\, Kw - \frac{2.303\, RT}{F} pH$$

This means that the values of E_{sb} can be used to determine the *p*H of the solution.

The antimony rod used is about 2-3 cm length. It is enclosed in an ebonite tube or glass sleeve and is soldered to a copper wire lead, one end of antimony rod protrudes out. This end is polished frequently. The electrode is stored in water for repeated use.

Advantages of Antimony Electrode

(i) It is robust and can be used as a probe for viscous solutions.
(ii) It can be used for determining *p*H in the range of 4 to 12.
(iii) It does not contaminate the solution to be tested.
(iv) It has a low resistance.

Disadvantages of Antimony Electrodes

(i) It cannot be used in presence of dissolved oxygen, oxidising agents, H_2S, heavy metal ions, highly acidic and alkaline solutions.
(ii) It is sensitive to temperature changes.

24.3 Ion Selective Electrode

Many types of membrane electrodes have been developed in which the membrane potential is selective toward a given ion or ions, in the same way as the potential of glass electrode is selective towards hydrogen ions. These electrodes are finding importance in the measurement of ions in small concentrations. None of these electrodes is specific for a given ion, but rather each will possess a certain selectivity toward a given ion or ions. Thus they are referred to as *ion-selective electrodes;* some of these electrodes are given below:

(*i*) **Glass Membrane Electrodes.** Those are similar in construction to the *p*H glass electrode. On varying the composition of the glass membrane the hydrated glass can acquire an increased affinity for various monovalent cations, with a much lower affinity for protons than the *p*H glass electrode has. The composition of the membrane will vary from manufacturer to manufacturer, but we can classify three general types of electrodes as follows:

(a) ***pH Type.*** This is the conventional *p*H glass electrode, and it has a selectivity order of $H^+ >>> Na^+ > K^+$, Rb^+, $Cs^+ >> Ca^{2+}$ responds to ions other than H^+
(b) ***Cation-Sensitive Type.*** This responds in general to monovalent cations, and the order of selectivity is $H^+ > K^+ > Na^+ > NH_4^+$, $Li^+ ... >> Ca^{2+}$
(c) ***Sodium-Sensitive.*** The selectivity order is $Ag^+ > H^+ > Na^+ >> K^+$ $Li^+ .... >> Ca^{2+}$.

(*ii*) **Precipitate Electrodes.** The construction of typical precipitate electrode is shown in Fig. 24.4.

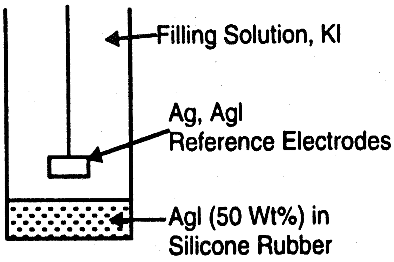

Fig. 24.4 : Precipitate impregnated membrane electrode.

They are used primarily for anion measurements, but are generally slow responding and subject to poisoning.

(iii) **Solid-State Electrodes.** The construction of these electrodes is shown in Fig. 24.5.

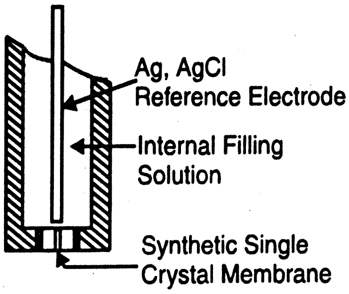

Fig. 24.5 : Crystal membrane electrode.

The most successful example is the fluoride electrode.

(iv) **Liquid-Liquid Electrode.** The construction of this electrode is shown in Fig. 24.6.

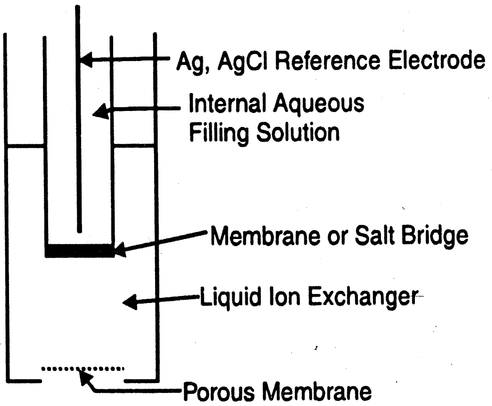

Fig. 24.6 : Liquid membrane electrode.

Here the potential determining "membrane" is a layer of a water-immiscible liquid ion exchanger held in place by an inert porous membrance.

(a) **Enzyme Electrodes.** Ion selective electrodes used in conjunction with immobilized enzymes can serve as the basis of electrodes that are selective for specific enzyme substrates.

24.4 Instrumentation

The glass electrode has high resistance, therefore, one electronic instrument called *p*H meter is generally used for determining the *p*H of the solution. There are two types of *p*H meters:

(*i*) Potentiometric type

(*ii*) Direct reading type

(*i*) **Potentiometric Type.** In this instrument, the glass electrode is incorporated in an ordinary potentiometric circuit and the off-balance currents are amplified electronically so that a milliammeter can be used to detect the balance point. The electronic amplifier in this manner acts as a null point indicator.

In this type a slide wire is adjusted until no meter deflection is obtained. This wire is calibrated directly in *p*H units and also in millivolts. The schematic diagram of electronic circuit is shown in Fig. 24.7.

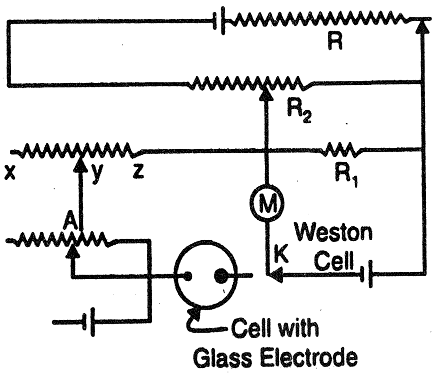

Fig. 24.7

XYZ is a potentiometer which is directly calibrated in *p*H units. The voltage corresponding to one division of the potentiometer should be adjusted according to the temperature of the solution. For making the temperature adjustments, the potentiometer XYZ is shunted with the resistance R_2. The current through the potentiometer is adjusted with resistance R_1 which is firstly calibrated against a Weston cell. The key k_1 is allowed to remain in position 1 by making the adjustment with variable resistance R. A is a potentiometer which is connected in series with the main potentiometer XYZ and acts to correct for variations in the constant *k* according to the equation

$$E = k + 0.0591\ pH$$

from one glass electrode to another. The resistance R_2 which is calibrated in °C must be set before R is adjusted.

When the *p*H meter is in operation, the E.M.F. developed by the glass and reference cell is opposed by E.M.F. obtained from XYZ. Any off balance is observed as deflection on the volt meter and the main potentiometer is then adjusted until the deflection is zero. Now for measuring unknown *p*H the instrument is first calibrated with a buffer solution of known *p*H and then for unknown *p*H and the position of Y is changed until balance is obtained in a position when *k* is in position 2.

(*ii*) **Direct Reading Type.** The basic circuit diagram of a typical reading type *p*H meter is shown in Fig. 24.8.

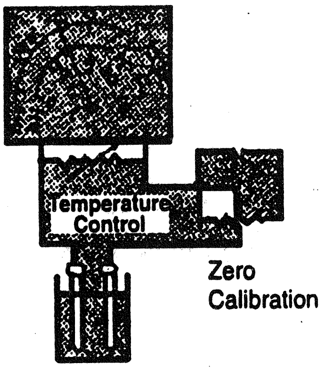

Fig. 24.8

The sensitivity of the meter (scale division/*m*V) is adjustable by a temperature control knob to allow for a change in the 0.059 factor with temperature. To read absolute *m*V rather than *p*H, the temperature control is disconnected entirely. The zero calibration knob changes the zero setting of the meter by

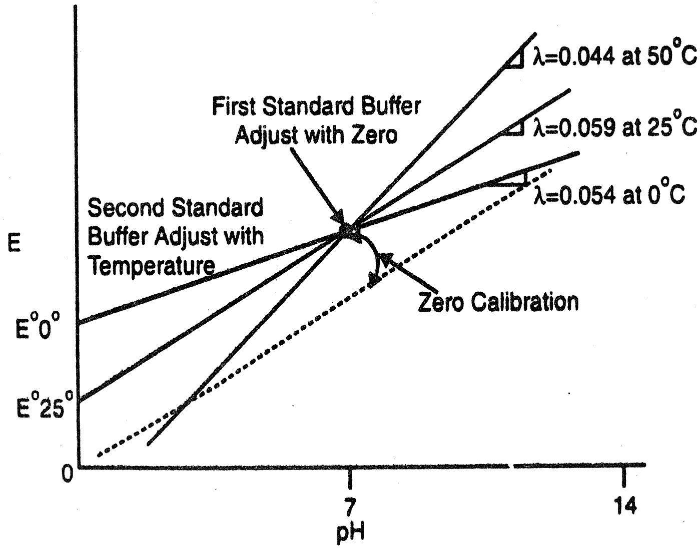

Fig. 24.9

introducing a bias voltage into the meter circuit so that the meter reading will correspond to the *p*H of the standard buffer.

These instruments are often constructed so that the true zero of the voltmeter is at *p*H 7 on the scale. In use, the *p*H meter should be first standardized with a *p*H 7 buffer, adjusting the zero calibration to give the correct reading. Then a second buffer, *p*H 4 or 10 is used and *p*H is adjusted to give the correct reading with the temperature control. This procedure establishes the correct linear relationship between E (*m*V) and *p*H (Fig. 24.9).

At least two points are required to establish the line, although for rough measurements one point and theoretical slope of 0.059 may be adequate for calibration.

24.5 Application of pH Measurement

1. **pH Measurement of Blood.** It is known that the equilibrium constants of the blood buffer systems change with temperature, the *p*H of blood at body temperature of 37°C is different than at the room temperature. Thus in order to obtain meaningful blood *p*H measurements that can be related to actual physiological conditions, the measurements should be made at 37°C and the samples should not be exposed to the atmosphere.

   Some important rules in measuring blood *p*H are given below:

   (*i*) Calibrate the electrode using a standard buffer at 37°C making sure to select the proper *p*H of the buffer at 37°C and to set the temperature knob on the *p*H meter at 37°C.

   (*ii*) Blood samples must be kept anaerobically to prevent loss or absorption of CO_2. The *p*H measurement should be made within 15 minutes after sample collection or the sample should be kept on ice and measurements should be made within 2 hours. The sample should be equilibrated to 37°C before measurement.

   (*iii*) To prevent the coating of the electrode, the sample from the electrode should be flushed with saline solution after each measurement. A residual blood film can be removed by dipping for a new minutes in 0.1 M NaOH followed by 0.1 M HCl and water or saline.

   It is common practice to take venous blood for *p*H measurement. For special applications arterial blood may be required. The 95% confidence limit range for arterial blood *p*H is 7.31 to 7.45 for all ages and sexes. Venous blood may differ from arterial blood by up to 0.03 unit.

pH Measurement in Nonaqueous Solvents

The measurement of *p*H in a nonaqueous solvent when the electrode is standardized with an aqueons solution has little significance in terms of possible hydrogen ion activity, because of the unknown liquid junction potential, which can be rather large depending on the solvent. The measurements carried out in this way are generally referred to as "apparent *p*H".

TEST YOUR KNOWLEDGE

Q.1. What is *p*H?

Q.2. What is a glass electrode? What is its principle?

Q.3. What is the acid error of glass electrode due to?

Q.4. Explain how the glass electrode functions as an indicator electrode for hydrogen ions.

Q.5. What assumptions are involved in the establishment of the conventional scale of *p*H? What is the uncertainty with which one can measure *p*H numbers?

Q.6. Will the *p*H reading of a soda-lime glass electrode be too high or too low in 0.1 M NaOH? Explain.

Q.7. Sketch and label a metal ion selective glass electrode.

Q.8. Describe the hydrogen electrode? What are its advantages and disadvantages?

Q.9. The response associated with the glass electrode is related to the *p*H of its environment by the expression

$$E = k + 0.059\,pH$$

What will be the uncertainty in pH that results from an uncertainty of 0.001 V in the measuremen of E?

Q.10. What is meant by an ion-selective electrode?

Q.11. How accurately can the pH of an unknown solution generally be measured? How much is this in terms of millivolts measured?

Q.12. Discuss the pH limitations of ion-selective electrodes.

Q.13. Explain how the mercury electrode serves as an indicator electrode for various metal ions.

25

Potentiometric Titrations

25.1 Introduction

Potentiometric methods include two major types of measurements. These are the direct measurement of an electrode potential from which the concentration of an active ion may be found and the changes in the E.M.F. of an electrolytic cell brought about by the addition of a titrant. These methods are based on the quantitative relationship of the E.M.F. of a cell as given by the following equation :

$$E_{cell} = E_{reference} + E_{indicator} + E_{junction}$$

The reference electrodes are expected to assume a potential which is independent of the composition of the solution. Moreover, the junction potential is assumed to remain almost constant. Under these conditions, the indicator electrode can give information about the nature or concentration of substances capable of exchanging electrons.

In the potentiometric titration, the course of titration reaction is followed by measuring the concentration of one or more of the species potentiometrically. The titration beaker becomes one of half-cell. It is important to distinguish between the titration reaction and the cell reaction. The reactants and products of the titration are all in same half-cell and the titration reaction is always at equilibrium. The cell reaction is normally not at equilibrium because it is not allowed to take place except for brief periods while balancing the potentiometer.

In potentiometric titrations, the change in the electrode potential upon the addition of the titrant are noted against the volume of the titrant added. At the end point the rate of the change of the potential is maximum. The end point is found by plotting a curve of potential versus the volume of the titrant.

The potentiometric end point has been applied to all types of chemical reactions. It can be used with colored or opaque solutions that mask observation of ordinary indicator changes. It is less subjective than indicator methods and inherently more accurate.

Ordinarily, the potentiometric titration is carried well beyond the end point.

25.2 Instrumentation

There are three types of instruments which are generally used for the measurement of potentials both for obtaining single potential measurements and for titrations. These are:

1. Non-electronic instruments.
2. Electronic instruments.
3. Automatic instruments.

We will discuss these one by one.

1. Non-Electronic Instruments

A potentiometer for titrations can be made from simple components as shown in Fig. 25.1.

In this apparatus B is the battery which supplies working current and consists of two dry cells in the series. R is a variable resistor and V is a voltmeter A glavanometer, G, of intermediate sensitivity is critically damped by the resistor R_D. A reversing switch S_2 helps in connecting the reference and indicator electrodes in either polarity. The instrument can be operated by dipping the electrodes in the sample solution, closing S_1 and adjusting B until there is no deflection in the galvanometer. Finally, the voltmeter reading is recorded. If balance point is not obtained, then S_2 is reversed and the process is repeated after each addition of reagent.

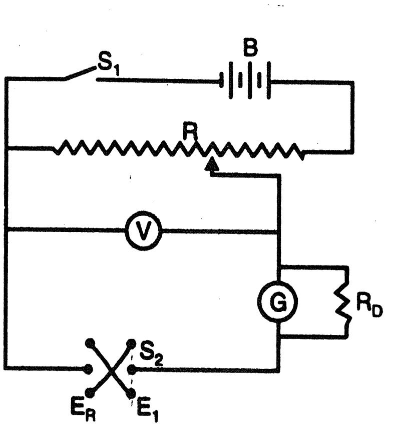

Fig. 25.1

2. Electronic Instruments

These instruments have many advantages over non-electronic instruments. Due to high resistance of the glass electrode, it cannot be used with a simple potentiometer. An electronic amplifier for use with a glass electrode is called a *p*H meter. These *p*H meters with glass electrodes and electronic voltameters for *p*H measurements and potentiometric titrations are commercially available. A schematic diagram of a circuit for vacuum triode null point detector is shown in Fig. 25.2.

The vacuum tube or triode consists of a cathode F, a plate P and a grid G. When the cathode F is heated by a source of low voltage, the electrons are thrown out. These electrons are attracted towards plate P by virtue of positive charge on P produced by its being connected to the positive pole of the battery B. The small current passing through the external plate is indicated by the milliammeter MA. The flow of electrons is repelled back from the cathode to the plate by impressing a negative charge on the grid G. This reduces the plate current indicated by milliammeter. The negative terminal of the cell X is joined to the grid, so that any unbalance between the potential of X and potentiometer will cause a deflection in millimeter. The balance is then restored by adjusting the potentiometer. The extent of adjustment necessary to restore the milliameter to the position corresponding to no charge on the grid gives the potential drop in X.

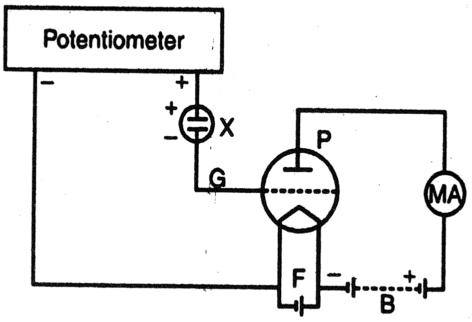

Fig. 25.2

3. Automatic Instruments

When used manually so as to give a detailed titration curve or merely to locate accurately an end point, a potentiometer titration is a time consuming and tedious job. Automatic instrument for performing and recording the titration curve provides a logical solution to the problem.

The basic features of commercial titrators are alike. In the delivery unit a short length of the flexible tubing is shut in some way, with no current passing through the solenoid. After setting the instrument and reading the burette level, a switch is pressed to start the titration. The solenoid is energized, the pressure on the tubing is released, and then the titrant is allowed to flow through the delivery tip. The titration proceeds at a fast rate until a predetermined distance from the end point, when the anticipation control automatically shows the delivery of the titrant. At the end point the delivery is stopped. A schematic circuit diagram of an automatic titrator is shown in Fig. 25.3.

The control unit has a calibrated potentiometer, a null-sensing amplifier, and an anticipator circuit. To operate, the potentiometer is set at the potential expected at the end point, the electrode

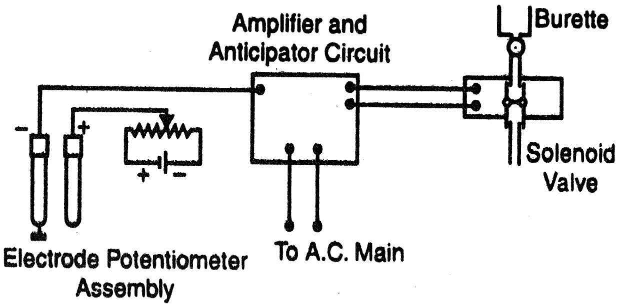

Fig. 25.3

assembly is immersed in the sample solution and the operating switch is pressed. The difference signal arising between the cell, E.M.F. and the present voltage on the potentiometer is amplified. As the end point is approached, the difference signal diminishes. When the two signals are matched, the delivery of the titrant is stopped.

The final category of automatic titrators are known as differential titrators. These instruments add titrants at a constant rate and electronically take the derivative of the potential versus time curve that is produced. The advantage of differential titrators is that equivalence point potential need not be known to employ these devices.

Finally it should be kept in mind that automatic titrators are no more accurate than manually performed titrations. Thus, they are most useful in those situations where speed is the predominant factor.

25.3 Types of Potentiometric Titrations

Potentiometric titrations may be applied to a variety of systems including those involving oxidation-reduction, precipitation, acid-base, and complexation equilibria reactions.

1. **Acid Base Titrations.** It is known that the neutralization of acids and bases is always accompanied by the changes in the concentration of H^+ and OH^- ions. It is evident that hydrogen electrode may be employed in these titrations. The reference electrode used in these titrations is N-calomel electrode.

The apparatus used for acid-base titrations is shown in Fig. 25.4.

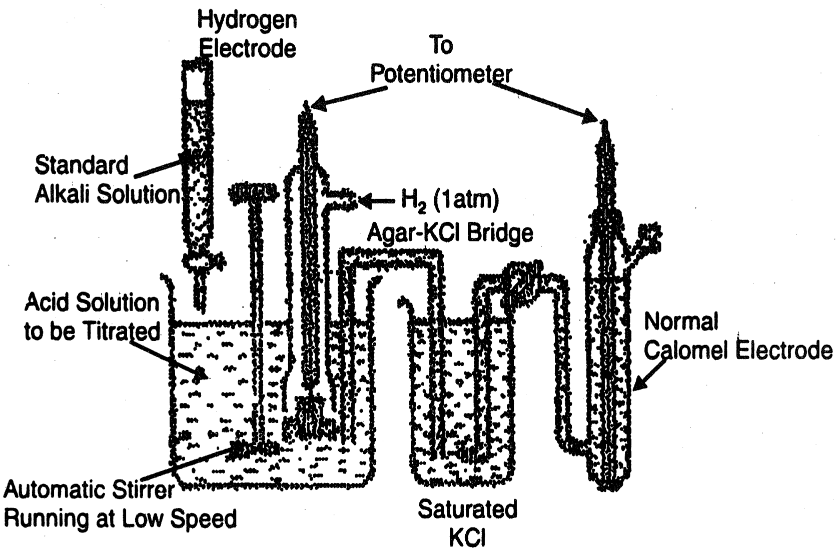

Fig. 25.4

A known volume of the acid to be titrated is kept in a beaker having an automatic stirrer. It also has a standard hydrogen electrode. It is connected to a N-calomel electrode through a salt bridge. The hydrogen and calomel electrodes are connected to a potentiometer which records the E.M.F. of the solution. After the each addition of base from burette into the beaker, the E.M.F. is measured. The values of the E.M.F. are then plotted against the ml of base added and a curve is obtained as shown in Fig. 25.5.

The potential of any hydrogen electrode is given by

$$E = E^\circ - 0.0591 \log a_{H^+} \text{ at } 25^\circ C$$

where E° is the standard electrode potential. Also, $pH = -\log a_{H^+}$

$$\therefore \quad E = E^\circ + 0.0591\, pH$$

It can, therefore, be concluded that the change in electrode potential or E.M.F. of the cell is proportional to the change in pH during titration. The point where the E.M.F. increases rapidly gives the end point.

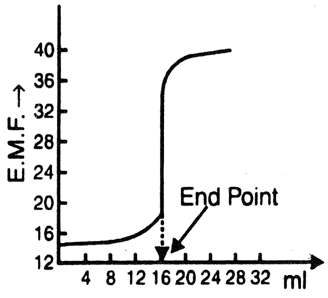

Fig. 25.5

A more sensitive and satisfactory method of finding the end point is to plot the slope of the curve, *i.e.*, $\Delta E/\Delta V$ against V. As the slope is maximum at the equivalence point, the maximum value gives the end point of the titration. This is shown in Fig. 25.6.

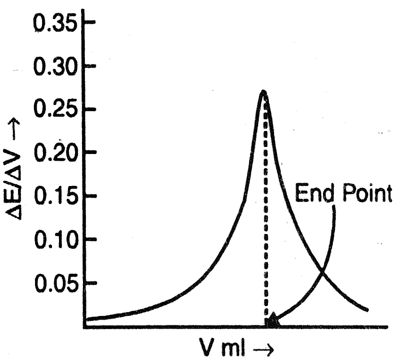

Fig. 25.6

2. **Complexometric Titrations.** Complexometric titrations can be followed with an electrode of the metal whose ion is involved in complex formation. For example, a silver electrode may be used to follow the titration of cyanide ion with a standard solution of silver. The silver ion concentration will be governed by the equilibrium constant for the complex formation reaction.

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^- \qquad (i)$$

$$K_c = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} \qquad (ii)$$

At the equivalence point,

$$2[Ag^+] = [CN^-]$$

Thus, the equation (ii) becomes

$$[Ag^+] = \sqrt[3]{\left(\frac{K_c}{4}[Ag(CN)_2^-]\right)} \qquad (iii)$$

In this case, solid silver cyanide begins to get precipitated soon after the equivalence point. The further addition of silver neither changes the concentration of the complex nor changes the silver ion to any extent, so that the titration curve has an almost horizontal portion shortly after the equivalence point (Fig. 25.7).

It should be kept in mind that in case of many complexometric reactions the situation cannot be handled so easily because more than one complex is formed. Thus, the reactions in the case of mercuric ion with cyanide are:

$$Hg^{2+} + 3CN^- \rightarrow Hg(CN)_3^-$$

$$Hg^{2+} + 4CN^- \rightarrow Hg(CN)_4^{2-}$$

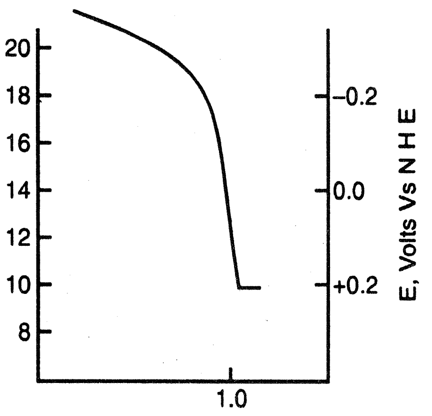

Fig. 25.7 : Titration of 0.1N cyanide with 0.1N silver solution.

However, these situations have become widely used because of the discovery of the metal chelating agents such as EDTA. Reilley has successfully applied potentiometric end point detection to EDTA titrations.

3. **Oxidation-Reduction Titrations.** Redox reactions can be followed by an inert indictor electrode. The electrode assumes a potential proportional to the logarithm of the concentration ratio of the two oxidation states of the reactant or the titrant which ever is capable of properly poising the electrode. These titrations involve the transfer of electron from the substance being oxidised to the substance being reduced. For example,

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

It is generally considered that such a reaction consists essentially of two *half reactions* whose standard potentials may be used to calculate the standard potential of the reactions.

$$Fe^{2+} \rightarrow Fe^{3+} + e,\ E^\circ = -0.76\ V \qquad (i)$$

$$Ce^{4+} + e \rightarrow Ce^{3+},\ E^\circ = +1.61\ V \qquad (ii)$$

$$\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{3+},\ \text{E}^\circ = +\ 0.85\ \text{V} \qquad (iii)$$

The equilibrium constant, K, of any reaction may be calculated from the following formula:

$$\text{E}^\circ = \frac{0.0591}{n}\log_{10}\text{K} \qquad (iv)$$

where n is the number of equivalents of electricity associated with one molar unit of reaction.

If an acidic ferrous solution is titrated with a standard ceric solution at 25°C, the potential (relative to the N.H.E.) of a platinum electrode in contact with the solution will be given by either of the following equations:

$$\text{E} = \text{E}^\circ_{Ce^{4+}/Ce^{3+}} - \frac{0.0591}{1}\log_{10}\left[\frac{\text{Ce}^{3+}}{\text{Ce}^{4+}}\right] \qquad (v)$$

$$\text{E} = \text{E}^\circ_{Fe^{3+}/Fe^{2+}} - \frac{0.0591}{1}\log_{10}\left[\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}}\right] \qquad (vi)$$

It would be more convenient to use the equation (vi) before the equivalence point, as the right hand erm of this equation could be easily found from the known extent of the titration. If equation (v) is used, hen the [Ce^{3+}]/Ce^{4+}) ratio has to be calculated by means of the equilibrium constant. After the equivalence oint, calculations are done by means of equation (v). From equation (vi) it is evident that the potential t the start of the titration should be—∞, because Fe^{2+} ions are the only ions present and there are no e^{3+} ions.

At the mid-point of the titrations, where [Fe^{2+}] = [Fe^{3+}], equation (vi) becomes:

$$\text{E} = \text{E}^\circ_{Fe^{3+}/Fe^{2+}} \qquad (vii)$$

At the equivalence point, the concentration of unchanged ferrous ions will be equal to the concentration f the unchanged ceric ions. Similarly, the concentration of cerous ions will be equal to the concentration f ferric ions.

Thus, it can be concluded that

$$\left[\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}}\right] = \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \qquad (viii)$$

Now,

$$\text{K} = \frac{[\text{Fe}^{3+}][\text{Ce}^{3+}]}{[\text{Fe}^{2+}][\text{Ce}^{4+}]} \qquad (ix)$$

At equivalence point,

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} = \sqrt{\text{K}} \qquad (x)$$

On combining equations (v) and (vi) with equation (x), we get

$$\text{E}_{ep} = \text{E}^\circ_{Ce^{4+}/Ce^{3+}} - \frac{0.0591}{2}\log_{10}\text{K} \qquad (xi)$$

$$\text{E}_{ep} = \text{E}^\circ_{Fe^{3+}/Fe^{2+}} + \frac{0.0591}{2}\log_{10}\text{K} \qquad (xii)$$

On adding, equations (*xi*) and (*xii*), we get

$$E_{ep} = \frac{E^{o}{}_{Ce^{4+}/Ce^{3+}} + E^{o}{}_{Fe^{3+}/Fe^{2+}}}{2}$$

where E_{ep} = End point potential.

Fig. 25.8 shows a theoretical titration curve according to the above procedure.

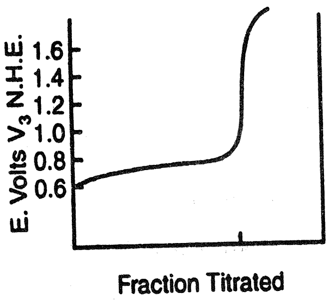

Fig. 25.8

Oxidation-reduction titrations may be used in procedures such as monitoring of cyanide wastes from metal plating industries or chlorine compounds in bleach compounds manufacturing, and the use of these bleach compounds in paper manufacturing. They are also extensively used in water pollution, sewage treatment, agricultural and biochemical studies.

4. **Precipitation Titrations.** Any precipitation titration that involves insoluble salts of metals such as mercury, silver, lead and copper may be followed potentiometricaly. The indicator electrode may be made of the metal involved in the reaction or may be an electrode whose potential is governed by the concentration of the anion being precipitated. The magnitude of the potential change at the end point depends on the solubility of the substance being precipitated as well as the concentration involved. The titration of chloride ions with a standard solution of silver nitrate using a silver metal indicator electrode is an example of a precipitation titration. The other electrode to complete the cell is unimportant, provided that it is a true reference electrode, *i.e.*, it maintains a constant potential. In the above case it will be assumed that the normal hydrogen electrode (N.H.E.) is used and this assumption is convenient because standard potential may be used directly. The potential of silver electrode will be governed by the appropriate Nernst equation:

$$E_{Ag^{+}/Ag} = E^{o}{}_{Ag^{+}/Ag} + \frac{0.0591}{1}\log_{10}\left[Ag^{+}\right] \qquad (i)$$

As soon as enough silver nitrate solution to precipitate Cl as AgCl has been added, the following equilibrium is established,

$$AgCl \rightleftharpoons Ag^{+} + Cl^{-} \qquad (ii)$$

The equilibrium constant for the above reaction is

$$K_{AgCl} = [Ag^{+}]\,[Cl^{-}] = 10^{-10} \qquad (iii)$$

If 0.1 N sodium chloride is titrated against 0.1 N silver nitrate, the silver ion concentration may be considered to be 10^{-9} N as soon as few drops of silver nitrate have been added. Equation (*i*) can be used to calculate the indicator electrode potential.

$$\begin{aligned} E_{Ag^{+}/Ag} &= 0.80\ V + 0.0551\ \log_{10} 10^{-9} \qquad (iv)\\ &= 0.2681 \end{aligned}$$

Similarly, half wave through the titration will be when the chloride ions concentration has been reduced to 0.033 N.

$$\begin{aligned} E_{Ag^{+}/Ag} &= 0.80\ V + 0.0591\ \log 10\ (3 \times 10^{-9})\\ &= 0.30\ V \end{aligned}$$

At the equivalence point, $[Ag^{+}] = [Cl^{-}] = 10^{-5}$ N

$$\begin{aligned} \therefore\ E_{Ag^{+}/Ag} &= 0.80\ V + 0.0591\ \log_{10} 10^{-5}\\ &= 0.50\ V \end{aligned}$$

Thus by using the Nernst equation the complete titration curve can be made as shown in Fig. 25.9.

5. **Non-Aqueous Solvents.** The potentiometric method has been found to be useful for carrying out titrations in non-aqueous solvents. The ordinary glass-calomel electrode system can be used. Generally, the millivolt scale of the potentiometer rather than the *p*H scale should be employed because the potentials in non-aqueous solvents may exceed the *p*H scale.

25.4 Variations in Potentiometric Titrations

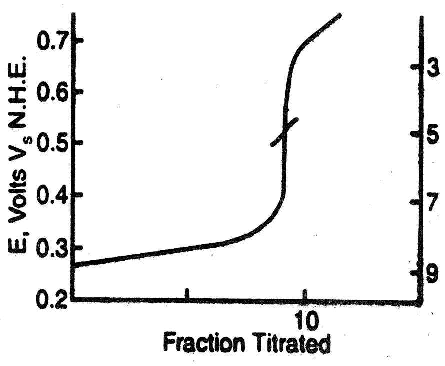

Fig. 25.9

The use of compensation electrode in place of reference calaomel electrode has been suggested by Pinkhof and Treadwell. The potential of such an electrode is exactly equal to the E.M.F. of the indicator electrode at the end point. The end point in such a setup is located by a sudden reversal of polarity. Thus, no potentiometric assembly is needed. A simple *capillary electrometer* can be employed instead of the galvanometer. The mercury in the electrometer moves in one direction when the titration is started and continues till the end point is reached when it stops to move. On further addition of the reagent, the mercury moves in the opposite direction. The main drawback of this method is that every titration requires its own electrode system.

The end points in the usual potentiometric titrations are dragged if equilibrium is not established quickly at the indicator electrode; in such cases titrations are carried out successfully at *constant current* which will result in a sharp change of potential at the end point. The titration of copper (II) using EDTA and a rotating platinum micro electrode at a constant current of 2 micro amperes has been reported by **Kolthoff. Svoboda** has employed constant current with two platinum electrodes in the titration of a series of organic amines with $HClO_4$ and obtained well defined peaks at the equivalence point.

Differential Titrations. The plotting of ΔE/ΔV versus V (Fig. 25.11) gives better result than the step curve obtained by plotting E versus V (Fig. 25.10). The value of ΔE/ΔV can be directly obtained by a simple but ingenious device due to Hall *et.al.*

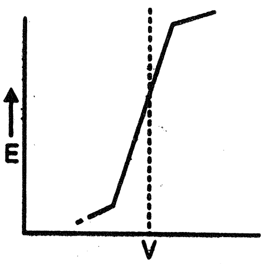

Fig. 25.10

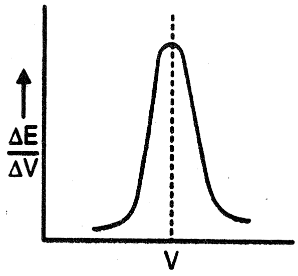

Fig. 25.11

In this arrangement, one electrode is maintained in the main bulk of the titrant, while the other electrode in a small volume of the titrant which is one increment ΔV behind the main bulk. If the potential difference between the two electrodes is now measured that will directly yield the value of ΔE/ΔV. After each increment, the nipple is pressed in order to expel the enclosed quantity of liquid and a fresh lot is drawn in from the bulk. The end point will be located by the maximum value of ΔE/ΔV.

The main advantage of a differential method is the elimination of the reference electrode and salt bridge. The end points are ordinarily sharply defined.

25.5 Advantages of Potentiometric Titrations

The potentiometric titrations have several advantages over indicator methods. Some of these are given below:

1. The apparatus required is generally inexpensive, reliable and readily available.
2. It is easy to interpret titration curves.
3. The method can be used for coloured solutions.
4. The method is applicable for analysis of dilute solutions.
5. Several components can be titrated in the same solution without the possibility of indicators interfering with each other. For instance, bromide and iodide may be titrated together.

TEST YOUR KNOWLEDGE

Q.1. What are the advantages of a potentiometric titration over direct potentiometry?

Q.2. Explain the principle and operation of the null-balance potentiometer.

Q.3. Describe the experimental set-up required for the potentiometric titration of V^{2+} with MnO_4^-.

Q.4. Explain the principle used in the measurement of EMF by the potentiometric method. Explain with the help of a diagram the principle involved in potentiometric titrations.

Q.5. What are the advantages of potentiometric titrations over indicator methods?

Q.6. What is the principle underlying potentiometric titrations?

Q.7. How will you carry out acid-base titrations by potentiometry?

Q.8. Which electrode is used in oxidation-reduction titrations?

Q.9. What are the different variations in potentiometric titrations?

22

Conductometric Measurements

22.1 Introduction

Conductometric analysis is based on the measurement of the electrical conductivity of the solution. *The electrical conductivity is entirely due to the movement of ions.* Thus, in a cell shown in Fig. 22.1, the transport of positive charge from left to right can be obtained either by the movement of positive ions from left to right or the movement of negative ions in the reverse direction. Actually, such charge transport involves both these processes. The movement of the ions occurs in such a way that the solution remains electrically neutral throughout. The ability of any ion to transport charge depends on the mobility of the ion. *The mobility of an ion is essentially its rate of movement through the solution under the influence of an imposed force which could be an electrical field or a concentration gradient.* The mobility of an ion is affected by factors such as the *charge, size, mass* and *extent of solvation.* The difference in rates of diffusion of ions gives rise to liquid junction potential.

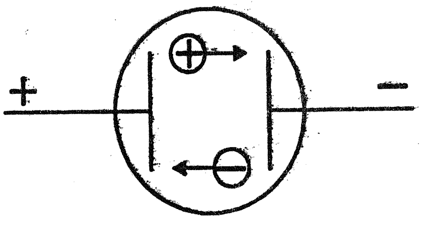

Fig. 22.1

The conductometry is used in direct and indirect methods of physico-chemical analysis. It is widely used in complexometric titrations, chemical kinetics, precipitation titrations and plant laboratories. It is appropriate at this point to discuss certain related terms.

22.2 Some Important Laws, Definitions and Relations

(a) **Ohm's Law.** Ohm's law is obeyed by metallic as well as by electrolytic conductors. According to this law, *the strength of current (I) flowing through a conductor is directly proportional to the potential difference (E) applied across the conductor and inversely proportional to the resistance (R) of the conductor."* Mathematically, the law can be represented as

$$I = \frac{E}{R}$$

The current is measured in amperes, potential difference in volts and electrical resistance in ohms.

(b) **Conductance.** In the case of electrolytes, the term conductance (C) is generally used. *It implies the ease with which the current flows through a conductor.* Thus, the conductance is the reciprocal of resistance. Mathematically,

$$C = \frac{1}{R}$$

It is expressed in units of reciprocal ohms or mhos.

c) **Specific Resistance.** The resistance R of the conductor is directly proportional to its length (l) and inversely proportional to its area (a) of cross section. Thus,

$$R \propto l \text{ and } R \propto \frac{1}{a}$$

or $$R \propto \frac{l}{a}$$

or $$R = \rho \frac{l}{a}$$

where ρ is a constant called the "specific resistance" or "resistivity". If l=1 cm, and a=1 sq. cm. then ρ=R ohms.

Thus specific resistance is defined as *"the resistance of a uniform column of the material of the conductor having a length of 1 cm and area of cross section of 1 sq. cm"*. We know that

$$\rho = R\frac{a}{l} = \text{ohm.} \ \frac{(\text{cm})^2}{\text{cm}} = \text{ohm} \cdot \text{cm}$$

Hence specific resistance is expressed in *ohm-cm.*

d) **Specific Conductance.** *The specific conductance of any conductor is the reciprocal of specific resistance* and is denoted by k (Greek, small kappa).

Now we know that $$R = \rho \frac{l}{a}$$

or $$R = \frac{l}{k} \times \frac{l}{a}$$

or $$k = \frac{1}{R} \times \frac{l}{a} \text{ohm}^{-1} \text{ cm}^{-1}$$

If l=1 and a=1 sq. cm, then the above equation can be written as

$$k = \frac{1}{R} = \rho$$

Thus in simple words specific conductance can be defined as "the conductivity offered by a solution of length 1 cm and area of 1 sq. cm cross section." It is expressed in mhos/cm.

(e) **Equivalent Conductance.** This may be defined as *"the conductance of a solution containing 1 gm equivalent of an electrolyte when placed between two sufficiently large electrodes which are 1 cm apart."* It is denoted by λ_v, where V is the volume in c.c. containing 1 gm equivalent of electrolyte dissolved in it and is measured in *reciprocal ohms or mhos.*

(f) **Molecular Conductance.** This may be defined as *"the conductance of a solution containing 1 gm mole of the electrolyte when placed between two sufficiently large electrodes placed 1 cm apart."* It is denoted by μ_v and is measured in mhos.

(g) **Relation between Specific Conductance and Equivalent Conductance.** Consider a rectangular metallic vessel with opposite sides exactly 1 cm apart (Fig. 22.2).

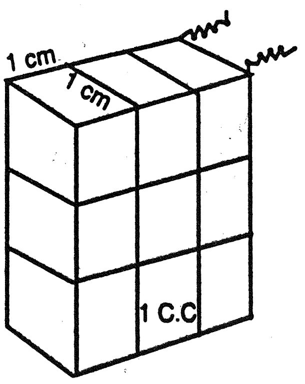

Fig. 22.2

If 1 c.c. of the solution is now placed in this vessel, the areas of the opposite faces of the cube covered by the solution will be 1 sq. cm. Thus, the measured conductance of the solution will be its specific conductance. If 1 c.c. of the solution is placed in the above vessel containing 1 gm equivalent of the electrolyte, then the measured conductance will be equal to the equivalent conductance.

$$\therefore \quad \lambda = k$$

Now dilute this 1 c.c. of the solution to 10 c.c. by adding 9 c.c. of pure solvent. The measured conductance will still be equivalent conductance. The equivalent conductance however will be 10 times as specific conductance.

$$\therefore \quad \lambda = k \times 10.$$

Similarly if the solution is diluted 100 times its volume, the measured conductance will still be equivalent conductance, but will be 100 times the specific conductance.

Thus, $\lambda = k \times 100.$

If the solution containing 1 gm equivalent of the electrolyte is dissolved in V c.c. of the solution, then

$$\lambda = k \times \text{V}$$

Hence Equivalent conductance = specific conductance × volume of solution in c.c. containing 1 gm equivalent of the electrolyte.

(h) **Relation between Molecular Conductance and Specific Conductance.** The relation which exists between molecular conductance and specific conductance is quite similar to the relation between equivalent conductance and specific conductance. Thus,

$$\mu_v = k \times \text{V}$$

or molecular conductance = specific conductance × volume of solution in c.c. containing 1 gm mole of the electrolyte.

22.3 Effect of Dilution

(a) **On the Conductance.** It is already mentioned that the conductance of a solution is due to the presence of ions. Moreover the degree of dissociation of electrolyte is increased on dilution which means more ions are produced in solution. It is, therefore, expected that the conductance of a solution should increase on dilution.

(b) **On the Specific Conductance.** It is already discussed that the specific conductance depends on the number of ions present per c.c. of the solution. The degree of dissolution of electrolyte is increased on dilution but the number of ions per c.c. decreases. It is, therefore, expected that the specific conductance of solution should decrease on dilution.

(c) **On the Equivalent and Molecular Conductance.** The equivalent conductance increases on dilution. This increase is because of the fact that equivalent conductance is the product of specific conductance and the volume V of the solution containing 1 gm equivalent of the electrolyte. The decreasing value of specific conductance is more than compensated by the increasing value of V, therefore, the equivalent conductance will increase on dilution.

Similarly molecular conductance will also increase on dilution.

The variation of equivalent conductance with the dilution is shown in Fig. 22.3.

In this figure the equivalent conductance at various dilutions is plotted against square root of the concentration of the solutions in moles. It is clear from the Fig. 22.3 that the equivalent conductance tends to become maximum as the concentration decreases or dilution increases. It can also be observed that in case of strong electrolytes like KCl, the maximum conductivity is reached at comparatively higher concentrations or lower dilutions than in case of weak electrolytes like CH_3COOH.

The maximum value of equivalent conductance of an electrolyte obtained at very high dilutions is called the equivalent conductance at infinite dilution. By infinite dilution we mean that the solution is already so dilute that further dilution will not produce any change in the equivalent conductance. The equivalent conductance at infinite dilution is denoted by λ_∞. The equivalent conductances of ions at infinite dilution at 25°C are given in Table 22.1.

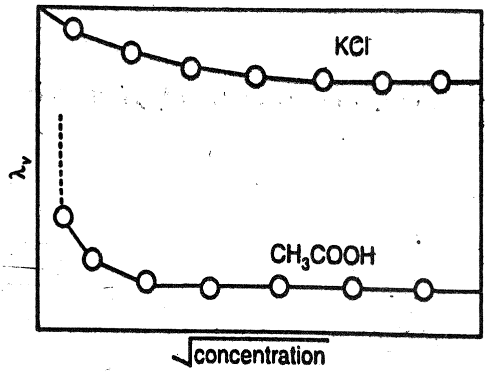

Fig. 22.3

Table 22.1 : Equivalent conductances of ions at infinite dilution at 25°C

Cation	*Equivalent conductance*	*Anion*	*Equivalent conductance*
H^+	349.8	OH^-	198.6
Li^+	39	F^-	55
Na^+	50	Cl^-	76.35
K^+	74	Br^-	78
NH_4^+	73	I^-	77
Ag^+	61.92	NO_3^-	71
Mg^{2+}	53	IO_4^-	55
Ca^{2+}	60	HCO_3^-	45
Sr^{2+}	59	SO_4^{2-}	80
Ba^{2+}	64	CO_3^{2-}	69
Zn^{2+}	53	$C_2O_4^{2-}$	74
Hg^{2+}	53	CrO_4^{2-}	82
Cu^{2+}	54	PO_4^{3-}	80
Pb^{2+}	73	$HCOO^-$	55
Co^{2+}	55	CH_3COO^-	41
Fe^{2+}	54	$C_6H_5COO^-$	32

22.4 Conductance Measurements

The conductance of a solution can be expressed by

$$\frac{1}{R} = x\left(c_1\lambda_1 + c_2\lambda_2 + c_3\lambda_3......+c_i\lambda_i\right)$$

Here c_i terms are the concentrations of various ions in solution, λ_i terms are numerical constants characteristic of the ions and x is a proportionality factor that takes account of the geometry of the cell. Because of interionic interactions and solvent-ion interactions, the values of λ_i depend slightly on concentration, and extrapolation to infinite dilution is required to obtain values that are physical constants of ions. Thus with proper calibration, a single measurement can give the concentration of any electrolyte.

The conductance of a solution can be measured by finding out the resistance by means of Wheatstone bridge arrangement. Some of the conductance bridges are described below:

(*i*) **Kohlrausch Conductance Bridge.** It is the simplest bridge which is used for the measurement of conductance of different solutions (Fig. 22.4).

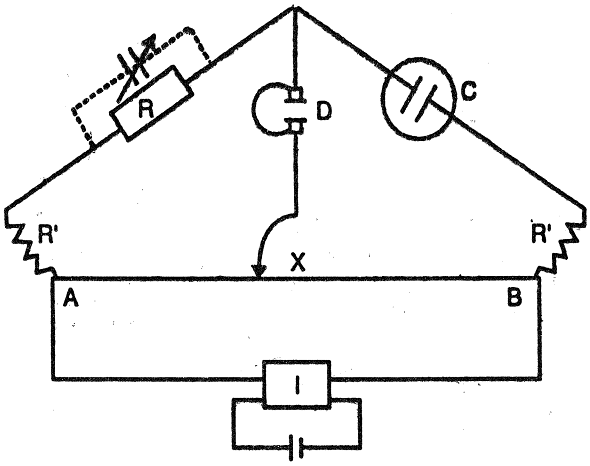

Fig. 22.4

It consists of a metre bridge wire AB, with a fixed resistance R' at both ends to increase the effective length of the wire, a resistance box R, a conductance cell C, head phone D and a small induction coil I which is operated by means of a battery.

(*ii*) **Direct Reading Conductance Bridges.** In these instruments the head phone is replaced by a magic eye which is an electronic device.

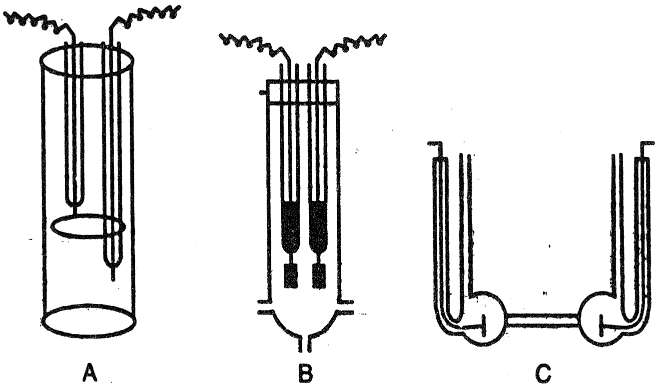

Fig. 22.5

Conductivity Cell. The solution whose conductivity is to be measured is taken in a cell called *conductivity cell.* Different types of conductivity cells are used for different purposes. However, the fundamental requirement is for a pair of electrodes that are firmly located in a constant geometry with respect to one another. The three types of cells which are generally used are shown in Fig. 22.5.

(*i*) Type A cell consists of smaller electrodes separated by larger distance and is useful for the measurement of high conductance accurately.

(*ii*) Type B cell is a simple dipping cell and is used in conductometric titrations.

(*iii*) Type C cell consists of larger electrodes separated by the smaller distance and is useful for the measurement of low conductance accurately. The cells are usually made of pyrex glass or quartz and are fitted with platinum electrodes. The electrodes are platinum plates coated with finely divided platinum to reduce the polarisation effect. These are welded to platinum wires which are sealed through two glass tubes. These tubes are firmly fixed in an ebonite cover so that the distance between the electrodes is not altered during the experiment. The electrodes of conductivity cell may be connected to the circuit by means of mercury placed in the tubes.

Electrodes. The electrodes are generally made of two parallel sheets of platinum foil which do not bend readily. The relative positions of these electrodes are fixed by sealing the connected tubes into the side of the conductivity cell. Although alternating current is employed to remove the polarisation yet it may occur to small extent when smooth platinum electrodes are used. In order to remove the polarisation, the electrodes are coated with finely divided platinum black.

The platinisation is carried out by taking 2 to 3% solution of chloroplatinic acid and 0.02 to 0.03 gm of lead acetate in the cell. The amount of the solution should be enough to dip the electrodes. Now pass the current for about 15-20 minutes. The electrolysis of chloroplatinic acid takes place and the electrodes get blackened because of the coating of finely divided platinum. The electrodes are then washed repeatedly with distilled water and finally with conductivity water. When not in use, then also these should be kept in conductivity water.

Conductivity Water. It is observed that the conductivity of solution of any electrolyte is very sensitive to the presence of impurities. It is, therefore, essential that water used in the measurements of conductance should be of high degree of purity, *i.e.,* has no conductance due to dissolved impurities. For this reason ordinary water is not suitable for conductance measurements because it may contain dissolved CO_2. Thus for most purposes conductivity water is used in conductance measurements. It can be prepared by distilling distilled water containing small amounts of sodium hydroxide and potassium permanganate. The distillation is generally carried out in a pyrex glass apparatus and conductivity water is collected in a receiver fitted with sodalime tube.

Source of A.C. An induction coil is the most simple source of A.C. but it is noisy in operation and does not give a symmetrical alternating current. It is, therefore, generally used in conductance measurements where much accuracy is not required. In 1913 Washburn used a mechanical high frequency A.C. generator. Taylor and Acree suggested in 1916 the use of an oscillator as a source for generating A.C. This oscillator consists of a double mercury arc arrangement capable of giving a symmetrical sinewave of A.C. of constant frequency. Hall and Adams in 1919 suggested a vacuum tube oscillator for conductivity measurements. The essential circuit for any oscillator is shown in Fig. 22.6.

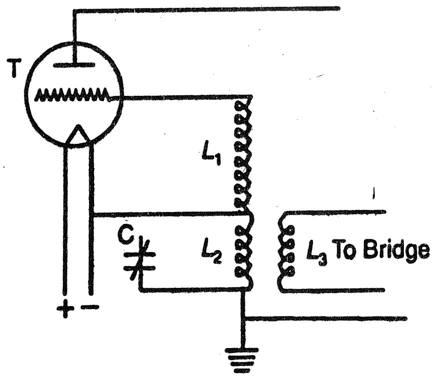

Fig. 22.6

The grid circuit of the vaccum tube T contains a grid coil L_1 and connected to the oscillator coil L_2 in parallel with the variable condenser C. The coil L_3 which is an output coil is coupled with L_2 inductively and conveys the oscillations to the conductance bridge. The vacuum tube oscillator is better than other oscillators because it is silent in operation and gives alternating current of constant frequency.

Method of Conductance Measurement

The apparatus used for conductance measurement is a modified form of the Wheatstone bridge and is shown in Fig. 22.7.

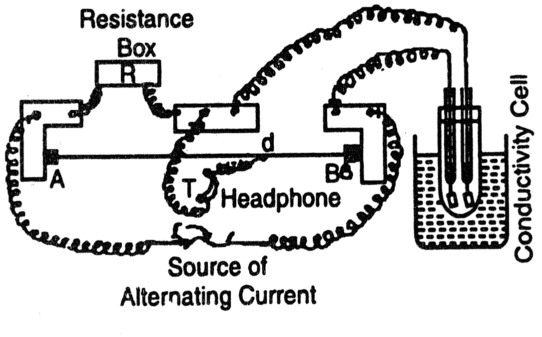

Fig. 22.7

The solution, whose conductance is to be measured, is taken in the conductivity cell. It is known that conductance varies with temperature. It is, therefore, necessary to keep the temperature of the solution constant throughout the experiment. This is achieved by placing the conductivity cell in the thermostat. The cell is connected to a resistance box R on one side and to a long thin wire AB stretched along a scale on the other side. Now some known resistance 'R' is taken out of the resistance box. An alternating current is passed through the solution with the help of an induction coil. The sliding contact *d* is moved on the wire AB so that minimum or no sound is heard in the head phone. At this point, the following relationship holds good:

$$\frac{\text{Resistance of solution}}{\text{Resistance R}} = \frac{\text{length B}d}{\text{length A}d}$$

Thus knowing R, A*d* and B*d*, the resistance of the solution can be calculated.

$$\text{Since conductivity of the solution} = \frac{1}{\text{Resistance of the solution}}$$

Therefore knowing resistance of the solution, the conductivity of the solution can be calculated.

Determination of the Cell Constant

The electrodes in the cell are not exactly one cm apart and may not have surface area of one sq. cm. Thus, the value of observed conductivity is not equal to specific conductivity but proportional to it. It is important to calculated a factor for the conductivity cell, known as cell constant. The cell constant when multiplied by the observed conductivity gives the value for specific conductivity. It is already mentioned that

$$R = \rho\frac{l}{a}$$

or $$R = \rho x \left[\text{where } x = \frac{l}{a} = \text{cell constant}\right]$$

or $$x = \text{cell constant} = \frac{R}{\rho} = \frac{\dfrac{1}{\text{observed conductivity}}}{\dfrac{1}{\text{specific conductivity}}}$$

or $$\text{specific conductivity} = \text{cell constant} \times \text{observed conductivity}$$

The cell constant is determined by substituting the value of specific conductivity of N/50 KCl solution at 25°C. This value as determined by Kohlrausch was found to be 0.002765 mhos. The value of conductivity is then observed with the given cell using N/50 KCl solution. The cell constant is then calculated by using the following relation:

$$\text{cell constant} = \frac{0.002765}{\text{observed conductivity}}$$

Temperature Control. As the temperature coefficient for conductance measurements is about 2 per cent per degree Celsius, some temperature control is essential during a conductometric titration. The usual practice is to immerse the cell in a large bath of water or oil maintained at room temperature.

22.5 Applications of Conductance Measurements

There are many applications of conductance measurements. Some of these are discussed below:

1. **Basicity of Organic Acids.** After conducting the studies on the sodium salts of a large number of organic acids, **Ostwald** gave empirical relation:

$$B = \frac{\lambda_{1024} - \lambda_{32}}{10.8}$$

where λ_{1024} and λ_{32} are the equivalent conductances of the salt at 25°C and dilutions of 1024 litres and 32 litres per gm equivalent respectivity and B is the basicity of the acid.

To prepare N/32 solution of the sodium salt of an acid, firstly N/16 NaOH solution is prepared. A known volume of this solution, say 100 ml, is then neutralised by adding a concentrated solution of the acid, using a suitable indicator. When the neutralisation is complete, the volume is made upto 100 ml. This gives N/32 solution of the salt. After this N/1024 solution can be prepared by accurate dilution of N/32 solution. The equivalent conductivities of N/32 and N/1024 solutions of the salt, are measured and then basicity, B can be calculated by using the above relation.

It should be noted that this method fails when applied to very weak acids whose salts are considerably hydrolysed in solution.

2. **Solubility of Sparingly Soluble Salts.** It is a simple fact that the saturated solution of a sparingly soluble salt is so soluble that the electrolyte present in it may be regarded as completely ionised. The relation between the equivalent conductance λ, the specific conductance k, and the concentration C is given by the equation

$$\lambda = k \times \frac{1000}{C}$$

The solution being saturated, C represents the solubility (in gm equivalents per litre).

Suppose the problem is to find out the solubility of AgCl at 25°C. The soluble impurities in the AgCl are readily removed by washing with conductivity water. The salt (AgCl) is then suspended in conductivity water, warmed and then kept at 25°C. A small amount of the substance will dissolve and the remaining will settle down. The solution so obtained can be said to be a saturated solution at 25°C. The conductivity of this solution can be measured at this temperature by usual method. Since a minute amount of AgCl is present in the solution, the value of λ_v can be considered to be equal to λ_∞, *i.e.*, the equivalent conductance at infinite dilution. Thus, we can say

$$\lambda_v = \lambda_\infty = k_v \times V$$

where V is the volume of 1 gm equivalent of the solute. According to **Kohlrausch's** law:

$$\begin{aligned}\lambda_\infty &= \lambda_{\infty(cation)} + \lambda_{\infty(anion)}\\ &= \lambda_\infty(_{Ag}{}^{+}) + \lambda_\infty(_{Cl}{}^{-})\\ &= 61.92 + 76.35 \qquad \textbf{(From Tables)}\\ &= 138.27\end{aligned}$$

Thus by knowing λ_∞ and k_v, the volume V containing 1 gm equivalent can be determined and hence the solubility S can be calculated.

Thus, solubility $S = \frac{1000}{V} \times E$ gm / litre

where E = Equivalent weight of the substance.

or $S = \frac{1000 \times E \times k_v}{\lambda_\infty}$ $\left(\text{Because } V = \frac{\lambda_\infty}{k_v}\right)$

$$= \frac{1000 \times 143.5 \times k_v}{138.27}$$

Thus, knowing k_v the solubility of sparingly soluble salts can be calculated.

3. **Ionic Product of Water.** Pure water ionises to a very small extent and the ionisation can be represented as:

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

$$\therefore \qquad \text{K (ionisation constant)} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Since water ionises to very small extent, concentration of unionised water may be considered almost constant, *i.e.*,

$$K_w = [H^+]\,[OH^-]$$

In other words, the product of ionic concentration of H^+ and OH^- expressed in gm moles per litre is constant at a constant temperature and is known as ionic product of water (K_w).

The ionic product of water can be calculated by knowing the specific as well as equivalent conductances at infinite dilution. The equivalent conductance at infinite dilution λ_∞ is represented by the equation

$$\lambda_\infty = \frac{k_\infty}{C} \times 1000$$

where k_∞ is the specific conductance at infinite dilution and C is the concentration in gm equivalent per litre. The experimental value of specific conductance of pure water is found to be 5.54×10^{-8} mhos cm^{-1} at 25°C. This can be regarded as a solution of ionised water at infinite dilution. The value of equivalent conductances of the two ions of water at infinite dilutions are

$$\begin{aligned} \lambda_\infty (_H^+) &= 349.8 \text{ mhos cm}^2 \\ \lambda_\infty (_{OH}^-) &= 198.6 \text{ mhos cm}^2 \\ \therefore \quad \lambda_\infty (_{H_2O}) &= \lambda_\infty (_H^+) + \lambda_\infty (_H^-) \\ &= 349.8 + 198.6 \\ &= 548.4 \text{ mhos-cm}^2 \end{aligned}$$

Substituting the values of K_∞ and λ_∞ in the equation:

$$\lambda_\infty = \frac{k_\infty}{C} \times 1000$$

we get the value of $[H^+]$ and $[OH^-]$ concentrations.

$$\text{Thus} \qquad [\text{H}^+] = \frac{1000 \times 5.54 \times 10^{-8}}{548.4} = 1.01 \times 10^{-7}$$

$$\text{and} \qquad [\text{OH}^-] = \frac{1000 \times 5.54 \times 10^{8}}{548.4} = 1.01 \times 10^{-7}$$

Hence the ionic product of water,

$$\begin{aligned} K_w = [H^+]\,[OH^-] &= [1.01 \times 10^{-7}] \times [1.01 \times 10^{-7}] \\ &= 1.02 \times 10^{-14} \end{aligned}$$

4. **Degree of Dissociation of Weaker Electrolytes.** The degree of dissociation of weak electrolyte is given by

$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

where λv = equivalent conductance at a given dilution V and λ_∞ = equivalent conductance at an infinite dilution. But the value of λ_∞ can be found from the equivalent conductance table at infinite dilution and λv can be found experimentally. Hence the degree of dissociation of weak electrolytes can be calculated.

5. **Degree of Hydrolysis.** When a salt of weak acid or base is dissolved in water, the conductance of solution will be partly due to the ions of the salt and partly due to H^+ or OH^- ions of the acid or base

formed by hydrolysis. An excess of the weak acid or base in the presence of its salt can be regarded as completely unionised. Thus, the addition of weak acid or base to the salt solution suppresses the hydrolysis, but the ionisation will be unaffected.

Let us consider aniline hydrochloride, $C_6H_5NH_3^+Cl^-$ which is a salt of weak base and a strong acid. When this compound is hydrolysed, α equivalents of free acid and base are produced and (1–α) equivalents of salt is not hydrolysed. Here α is degree of hydrolysis. This can be represented as

$$\underset{(1-\alpha)}{C_6H_5NH_3^+} \rightleftharpoons \underset{\alpha}{C_6H_5NH_2} + \underset{\alpha}{H^+}$$

The weak undissociated base aniline does not contribute to the total equivalent conductance, λ, of the solution. This can be written as

$$\lambda = (1-\alpha)\,\lambda_c + \alpha.\lambda_{HCl}$$

or

$$\alpha = \frac{\lambda - \lambda_c}{\lambda_{HCl} - \lambda_c}$$

where λ_c = Equivalent conductance of unhydrolysed salt.

λ_{HCl} = Equivalent conductance of free acid

Now λ_c can be determined by measuring the equivalent conductance of $C_6H_5NH_3^+Cl^-$ in presence of excess of aniline. The values of λ_{HCl} at concentrations of M/32, M/64 and M/128 are 393, 399 and 401. Thus, α can be calculated. Now hydrolysis constant K_h is given by

$$K_h = \frac{\alpha^2 C}{1-\alpha}$$

Since α and C are known, hydrolysis constant can be calculated.

6. Determination of Vanillin in a Vanilla Essence. Commercial vanilla essence contains about 1% of vanillin, though this concentration may vary widely. Coumarin is also likely to be present and the cheaper flavouring essences may contain very little vanillin. It may be possible to titrate the essence directly, after diluting it with water. If the commercial products contain other materials, then the separation should be done firstly. Now take 10 ml of the essence in a graduted cylinder, and mix it with 40 ml of water containing about 5 gm of common salt, which will help in decreasing the miscibility of water and ether. Now transfer the contents to a separating funnel and add 6N hydrochloric acid and 40–60 ml of ether and shake. After the separation of phases, run off as much of the water as possible. Then wash the ether layer with distilled water. Finally decant the clean ether layer into a beaker and evaporate the ether on a steam bath.

Dissolve the only residue in 10 ml of ethyl alcohol, and about 75 ml of water and titrate conductometrically.

Before titrating the essence it is best to titrate a sample of pure vanillin to become acquainted with the shape of the curve and slopes of the two sections.

7. Conductometric Titrations. These can be carried out in those titrations in which there is a sharp change in the conductivity at the end point. In other words we can say that the determination of the end point of a titration with the help of conductivity measurements is termed as conductometric titration.

In a conductometric titration the titrant is added from the burette and the conductivities are followed during the course of titration. The values of the conductivities are then plotted against the volume of the titrant in c.c. Since the measured conductivity is a linear function of the concentration of ions present, two lines will be obtained which will intersect each other at a point, known as "end point" or "equivalence point".

When the reaction is not quantitative, there may be some curvature in the curve or in line near the end point which may be due to hydrolysis, dissociation of the product or appreciable solubility in case of precipitations. In these cases the end point can be determined by extrapolating these portions of lines or curves.

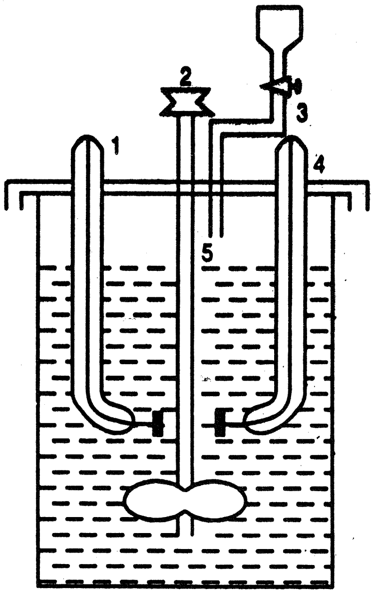

Fig. 22.8 : 1.4=Dipping electrodes, 2=Electric driven-motor, 3=Burette and 5=Stirrer

It must be remembered that the conductivity of a solution is affected by changes in temperature. The resistance decreases by about 1% to 2% for each degree increase in temperature. It is therefore, desirable to carry out measurement at constant temperature. A number of titration cells have been used in conductometric titrations. The simplest cell mostly consists of a dipping electrode, a beaker of the suitable size and a mechanical stirring device (Fig. 22.8).

In the case of precipitation titrations, the electrodes are mounted vertically to prevent excessive amounts of precipitate from collecting on the electrode surfaces.

It is known that a large effective surface area minimises polarisation, most of the electrodes used in conductometric titrations, therefore, are coated with platinum black. The platinisation of the electrodes also helps in the establishment of a sharp balance point. It should also be remembered that the platinised electrodes have a great tendency to adsorb electrolytes from solution. In order to remove such difficulties in dilute solutions or solutions containing surface active agents, bright platinum or lightly platinised electrodes are used in such case.

If absolute measurements are to be made, a constant temperature bath, *i.e.*, thermostat should be used.

In order to get straight line graphs, it is essential that the total volume of the solutions remains constant during the titration. The concentration of the titrant must be 10 times as the solution being titrated. This is done to keep the volume change small. Whenever necessary a correction to the reading can also be applied.

$$\text{Thus, Actual conductivity} = \left(\frac{v+V}{V}\right) \times \text{observed conductivity}$$

where v = Volume of the titrant or reagent added.

V = Initial volume

$v + V$ = Final volume.

The correction presupposes that conductivity is a linear function of dilution. In the interest of keeping v small, the reagent for a conductometric titration is ordinarily several times more concentrated than the solution being titrated.

Apparatus for Conductometric Titrations

(a) ***Measuring Circuits.*** In order to prevent concentration changes due to reactions at the electrodes, the conductivity of the solution is generally measured with alternating currents at frequencies from 60 to 1000 cps. Most of the circuits used are of the Wheatstone bridge type.

(b) ***Commercial Apparatus.*** The commercially available equipment is accurate enough for routine conductometric titrations. The important advantage of this equipment is that it is convenient and can be set up and used without the knowledge of electronics or electricity.

(c) ***Other Methods.*** Many workers have shown that conductance can also the measured by using D.C. provided that the cell has two unpolarisable electrodes, such as Ag/AgCl electrode. Eastman has shown that direct-current method is capable of yielding results within 0.01% of the usual alternating-current method. Stock has published an excellent review of the equipment used for conductometric titrations.

22.6 Types of Conductometric Titrations

(a) **Acid-base Titrations.** These are particularly well adapted to the conductometric end point because of the very high conductance of the hydroxide and hydronium ions compared with the conductance of reaction products.

(*i*) *Strong Acid with a Strong Base.* Let us consider the titration of HCl with NaOH.

$$[H^+ + Cl^-] + [Na^+ + OH^-] \rightarrow [Na^+ + Cl^-] + H_2O.$$

At the start of the titration, the acid solution has a high conductivity due to highly mobile hydrogen ions. The share due to chloride ions will be smaller because of less mobility as compared to hydrogen. When NaOH is added to HCl, the highly mobile hydrogen ions are replaced by less mobile sodium ions. This will result in the decrease of conductivity rapidly. The solution at neutralisation, *i.e.*, at the end point containing only sodium and chloride ions, will have a minimum conductivity. Now if more NaOH is added, the conductivity will increase owing to the pre-presence of OH^- ions, because OH^- ions have more mobility as compared to Na^+ ions.

Thus, if the titration is carried out at constant temperature and the conductivity is plotted against the volume of sodium hydroxide added, Fig. 22.9 will be obtained. The point of intersection of the two lines gives the end point.

In actual practice the lines may be slightly curved because of (*i*) Variation in temperature due to heat of neutralisation, (*ii*) Interionic effect, and (*iii*) Increase in the volume of the solution because of the addition of the reagent. In spite of these, the inflection is sharp enough to get the exact end point.

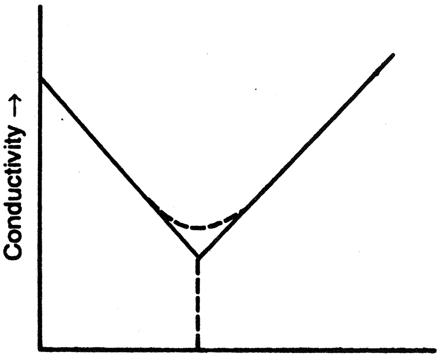

Fig. 22.9

An important advantage of the conductometric titrations is that the relative change in conductivity is almost independent of the concentration of strong acid being titrated. Thus, dilute solution can be titrated with almost the same accuracy as concentrated solutions.

The earlier titrations involving strong acid and strong bases were attempted by conductometric method but this method is not much used for such determinations. The reason for this is that large number of indicator methods are available.

(*ii*) *Strong Acid with a Weak Base.* Let us consider the titration of HCl (strong acid) with NH_4OH (weak base). When ammonium hydroxide is added to hydrochloric acid, the conductivity decreases because of the replacement of the fast moving H^+ ions by slow moving NH_4^+ ions.

$$[H^+Cl^-] + [NH_4^+OH^-] \rightarrow [NH_4^+ Cl^-] + H_2O$$

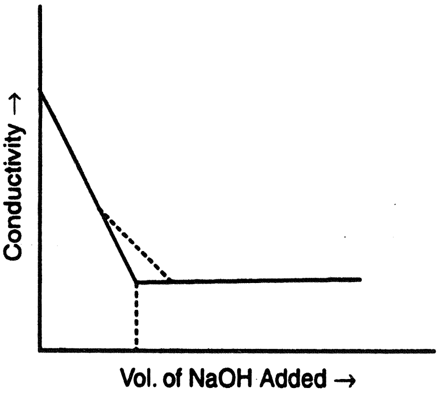

Fig. 22.10

The addition of NH_4OH after end point does not change the conductance because NH_4OH, a weakly ionised electrolyte, has a very small conductivity compared with that of the acid or its salt (Fig. 22.10).

(*iii*) *Weak Acid with a Strong Base.* Let us consider the titration of weak acid (CH_3COOH) with strong base (NaOH), when a small amount of NaOH is added to CH_3OOH, the conductivity decreases initially and then increases with the further addition of NaOH.

$$[CH_3COO^- + H^+] + [Na^+ + OH^-] \rightarrow [CH_3COO^- + Na^+] + H_2O$$

When the neutralization of acid is complete, further addition of alkali produces excess of OH^- ions. The conductance of the solution, therefore, starts increasing more rapidly (Fig. 22.11).

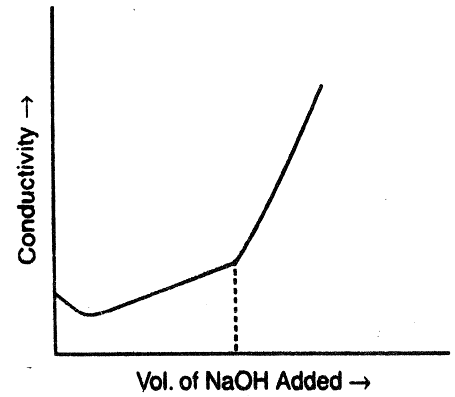

Fig. 22.11

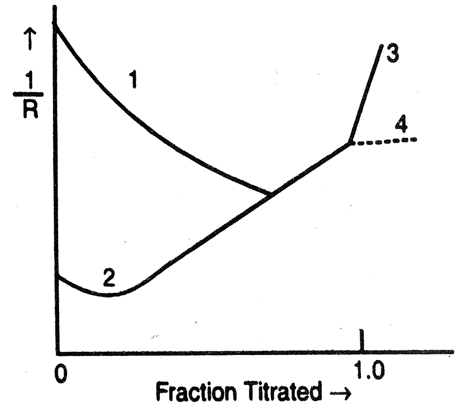

Fig. 22.12

(*iv*) *Weak Acid with a Weak Base.* When weak acid are titrated with weak bases, curves such as 1 and 2 shown in Fig. 22.12 are obtained.

The conductivity is governed by the extent of ionisation and concentration, before the end point. It decreases firstly as the anion formed suppresses the ionisation, passes through a minimum and then increases upto the end point. This is because of the conversion of non-conducting weak acid into its conducting salt. The effect of the dissociation constant on the titration curves has been compiled by Britton, Bruni and Eastman. These authors have also carried out mathematical analysis of the titration curves of weak electrolytes.

It is observed that the graphs of such titrations are generally curved because the incompleteness of reaction allows extra hydroxide ions (or hydrogen ions if a weak base is being titrated) to be present. This results in the increase in the conductivity. It is observed that with more incompleteness of the reaction, the more curvature is observed in the graph.

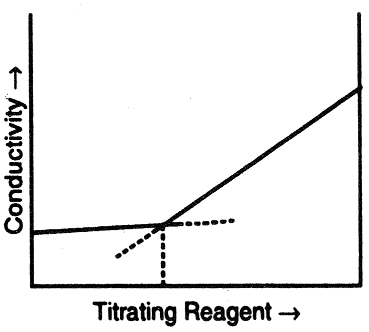

Fig. 22.13

(b) Replacement Titrations. When a strong acid reacts with sodium or potassium salts of weak acids, the weaker acid will be replaced first. Consider the titration of sodium acetate with hydrochloric acid.

$$[CH_3COO^- + Na^+] + [H^+ + Cl^-] \rightarrow [CH_3COO^-H^+] + [Na^+Cl^-]$$

In this titration only a slight increase in conductance is obtained up to the end point. This is because of the fact that chloride ion has higher conductance than the acetate ion. After the end point, it increases more rapidly, owing to the addition of excess of hydrochloric acid (Fig. 22.13). The end point can be determined by the interaction of two lines.

Similarly, titration of strong acid (NH_4Cl) can be carried out with NaOH.

$$[NH_4^+Cl^-] + [Na^+ + OH^-] \rightarrow [NH_4^-OH] + [Na^+Cl^-]$$

The main application of replacement titrations is in the determination of alkaloids. As alkaloids are weak bases and are often insoluble in water, and thus indicator methods are not applicable.

(c) **Precipitation Titrations.** The precipitation titrations cannot be carried out so effectively as the acid-base titrations. This is so because the acid-base titrations are characterised by sharp breaks because both the hydrogen and hydroxyl ions have very high equivalent conductances. In the case of precipitation titrations, one pair of ions is substituted for another and as the student has choice of reagents, good results can generally be obtained. If a cation is to be precipitated, a titrant whose cation has the smallest possible mobility, is selected. Similarly if an anion is to be precipitated, a titrant whose anion has very small mobility is selected. In this way the maximum possible change in conductance during the titration is assumed.

Let us consider the titration between silver nitrate and potassium chloride. The reaction which is taking place can be represented as,

$$[K^+ + Cl^-] + [Ag^+ + NO_3^-] \rightarrow [K^+ + NO_3^-] + AgCl.$$

In the initial stages of the titration, with the addition of silver nitrate, the conductance does not change much. This is because the Cl^- ions are replaced by NO_3^- ions and both have almost same ionic conductance. After the end point, the excess of silver nitrate added causes a sharp increase in the conductance. The "equivalent point" or the "end point" of the titration can, therefore the determined, (Fig. 22.14).

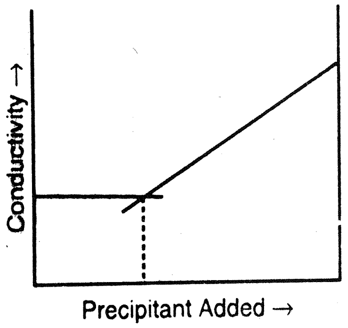

Fig. 22.14

When both the products of the reaction are sparingly soluble, the curve obtained takes up the shape as shown in Fig. 22.15. The conductrometric titration between $MgSO_4$ and Ba $(OH)_2$ is an example of the titration in which both the products are sparingly soluble. In this type of titrations, conductivity decreases in the beginning but increases after the end point because of the presence of excess of barium hydroxide.

The precipitation titrations cannot be performed very accurately because of the following reasons:

(*i*) Slow separation of precipitate and

(*ii*) Absorption of the ions on precipitate.

To eliminate the above errors the precipitation conductometric titrations should be carried out at elevated temperatures, *i.e.*, in boiling solution.

(d) **Redox (oxidation-reduction) Titrations.** In the case of oxidation-reduction titrations, there is a decrease in the hydrogen ion concentration. This is clear from the following equation.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

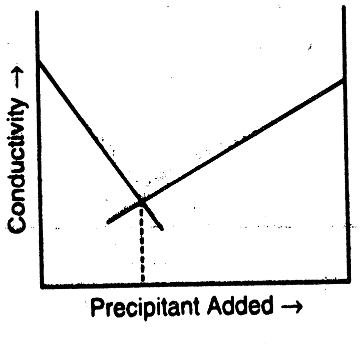

Fig. 22.15

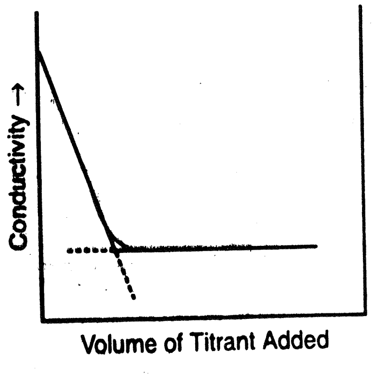

Fig. 22.16

Since the mobility of hydrogen ions is high, therefore, a sharp decrease in the conductance is expected during the initial part of the titration. It has been observed that when the initial concentration of acid is moderately high, the relative change in hydrogen ion concentration is very small.

The redox titrations give good results only when the initial concentration of acid is low. The curve for the titration of ferrous iron with dichromate in acidic medium is shown in Fig. 22.16.

(e) **Complexometric Titrations.** Conductivity has been used since long for the study of complex compounds very successfully. Werner supported many of the postulates of his coordination theory with the help of conductivity measurements.

Conductometric titrations have been used in the study of formulae of complex compounds. Job titrated roseo-cobaltic sulphate $[Co(NH_3)_5H_2O]_2(SO_4)_3$, with barium hydroxide and obtained two breaks in the titration curve.

In the titration of KCl with Hg $(ClO_4)_2$, two breaks are obtained in the curve. This is shown in Fig. 22.17.

The first break is due to the formation of $HgCl_4^{2-}$ and the second one at the completion of reaction due to the formation of K_2HgCl_4. These reactions can be represented as follows:

$$Hg(ClO_4)_2 + 4KCl \rightarrow HgCl_4^{2-} + 2K^+ + 2KClO_4$$

$$HgCl_4^{2-} + 2K^+ \rightarrow K_2HgCl_4$$

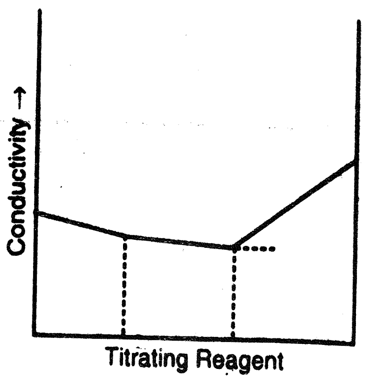

Fig. 22.17

Remark. Conductometric titrations based upon precipitation or complex-formation reactions are not so useful as those involving neutralisation processes. Conductance changes during these titrations are generally not as large as those observed with acid-base titrations. The factors such as a slowness of reaction and coprecipitation are further source of difficulty with precipitation reactions.

(f) Another application of conductivity for the determination of atmospheric sulphur dioxide was developed by Nash. The apparatus used for this purpose is shown in Fig. 22.18.

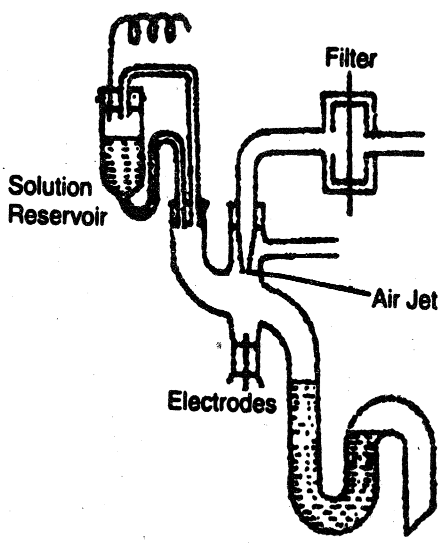

Fig. 22.18 : Conductivity cell for determination of atmospheric contaminants.

A low velocity jet of air impinges on a dilute solution of hydrogen peroxide contained in a conductivity cell. The gas is not only absorbed, but the jet induces rapid microcirculation that provides adequate mixing of electrolyte. The peroxide oxidizes the sulphur dioxide to sulphuric acid in the interim.

The apparatus is further provided with a reservoir into which a slow stream of electrolyte drips. This reservoir, above the cell, periodically siphons its contents into the latter, flushing out the old solution and introducing fresh electrolyte. Each time this happens the cell resistance increases abruptly to a high value, which gradually decreases, according to the rate at which sulphuric acid accumulates. The cell is connected to a Wien bridge oscillator whose output is passed to a recorder.

The record consists of sawtooth traces with slopes defining the instantaneous concentration and with the difference between readings, at two points corresponding to the total amount of gas collected between the indicated times.

The technique is applicable to the measurement of sulphur dioxide concentrations in air in the range 0.01–10ppm.

Similar to the above determination small amounts of nitrogen in biological materials can be determined by an ordinary kjeldahl digestion with sulphuric acid followed by distillation of the ammonia into a boric acid solution. The conductance of the resulting ammonium borate solution can then be related to the percentage of nitrogen in the sample.

(g) Conductance measurements have been widely used in measuring the salinity of sea water in oceanographic work.

22.7 Advantages of Conductometric Titrations

The main advantages of conductometric titrations are:

(*i*) They can be used in the case of coloured liquids where ordinary indicators cannot work.

(*ii*) They can be used for the analysis of dilute solutions and also for very weak acids.

(*iii*) It is not necessary to measure the actual conductance value because we can use any quantity that is proportional to it *e.g.*, the reading on a Wheatstone bridge. This can be directly plotted against the volume of the titrant used.

22.8 Disadvantages of Conductometric Titrations

The technique has its limitations. These are as follows:

(*i*) It becomes less accurate and less satisfactory with increasing total electrolytic concentration. Actually the change in conductance due to the addition of titrant can become largely masked by high salt concentrations in the solution being titrated; under these circumstances, the method cannot be used.

(*ii*) Although the method is potentially adaptable to all types of volumetric reactions, the number of useful applications to oxidation-reduction systems is limited. The reason for this is that the substantial excess of hydronium ion typically needed for such reactions tends to mask conductivity changes associated with the volumetric reaction.

TEST YOUR KNOWLEDGE

Q.1. Define specific conductance and equivalent conductance.

Q.2. Distinguish between equivalent conductance and molar conductance.

Q.3. What are the units of specific conductance and equivalent conductance?

Q.4. What is effect of dilution on (*i*) conductance (*ii*) specific conductance (*iii*) equivalent conductance and (*iv*) molecular conductance?

Q.5. How is conductivity water prepared? Why is it prepared?

Q.6. What are various types of conductivity cells? Why is a platinisation of electrodes done?

Q.7. How is the basicity of organic acids determined by conductance measurement?

Q.8. What are conductometric titrations? What are its various types?

Q.9. What are the advantages of conductometric titrations?

Q.10. What is the relation between molecular conductance and specific conductance?

Q.11. Calculate theoretical specific conductances of the mixture after the following addition of reagent: 0.00, 2.00, 4.00, 6.00, 8.00, 10.00, 12.0, 14.0, 16.0 ml.

(*i*) NaOH with HCl (*ii*) Phenol with NaOH (use $Ka=1.0 \times 10^{-10}$ and $\lambda^{o}=30$) (*iii*) Sodium acetate with HCl (for acetic acid $Ka=1.00 \times 10^{-5}$) (*iv*) Ag NO_3 with NaCl.