UNIT 2 POTENTIOMETRY-I

Structure

2.1 INTRODUCTION

You are already aware of the electrode potentials and how it can be calculated using Nernst equation from our discussion given in Unit 1. In this unit, we are going further to discuss how the electromotive force developed in a galvanic cell can be measured using a potentiometer. This method consists of measuring the potential between any two electrodes immersed in the solution to be analysed. For measuring the potential, we require two electrodes, an indicator electrode and a reference electrode along with a device called potentiometer. Potentiometric methods have many applications in the area of analytical chemistry. These methods can be used for direct and selective measurement of analyte concentrations, for determining end point in various types of titrations and for the determination of several types of equilibrium constants.

In this unit, you will know about different types of reference and indicator electrodes, a brief description about instrumentation and potentiometric titrations.

Objectives

After studying this unit, you should be able to:

- explain the principle of potentiometric methods of analysis,

- discuss the method of operation of a potentiometer,

- describe some common types of reference and indicator electrodes,

- calculate the equilibrium constants from cell potential,

- describe chemical reactions involved in potentiometric titrations,

- explain the principle of potentiometric titration, and

- state the experimental details of neutralisation, redox, precipitation and complexations reactions.

2.2 POTENTIAL

Let's recapitulate Nernst equation which you have studied in the previous unit. You have seen earlier when a metal is immersed in a solution containing its own ions, say

zinc rod in zinc sulphate solution, a potential difference is established between the metal and the solution.

$$M^{n+} + ne^- \longrightarrow M^o \qquad \qquad \ldots(2.1)$$

The potential difference E for an electrode reaction can be given by Nernst equation:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{a_{M^{n+}}} \qquad \qquad \ldots (2.2)$$

where R is gas constant, T is absolute temperature, F is Faraday Constant, n is the valency of ions, $a_{M^{n+}}$ is the activity of ions in the solution, and E^0 is a constant depending upon the metal.

In this equation no term for elemental metal is included in the logarithmic term because it is a pure solid and its activity is one. Eq. 2.2 can be simplified by introducing the known values of R, F, and T, and converting natural logarithms to base 10 by multiplying by 2.3; it then becomes:

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{a_{M^{n+}}} \qquad \qquad \ldots (2.3)$$

For most purposes in quantitative analysis, it is sufficiently accurate to replace a $a_{M^{n+}}$ with $[M^{n+}]$, the concentration of the metal ions in mol/dm^3.

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \qquad \qquad \ldots (2.4)$$

This is the simplest form of Nernst equation where E° is standard electrode potential of the metal, which is constant. Thus, the electrode potential varies linearly with the logarithm of the reciprocal of the metal ion concentration. This equation can be used to calculate potential of half-cell if we know the concentration of ions involved in half-cell reaction or calculate the concentration of ions in the solution if we know the potential and standard potential of the half-cell shown above. To further understand this try out following SAQs.

SAQ 1

Calculate the potential of a copper electrode immersed in 0.044 M CuSO$_4$

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SAQ 2

Calculate the potential of a zinc electrode immersed in 0.060 M ZnSO$_4$.

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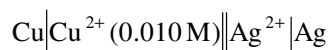...

SAQ 3

Calculate the cell potential for the cell made by combining the half-cell in SAQs 1 and 2 in the following way:

$$Zn \left| Zn^{2+} (0.060\,M) \right\| Cu^{2+} (0.044\,M) \left| Cu \right.$$

....

....

SAQ 4

The potential for the following cell is 0.462 V. Calculate the concentration of Ag^+ in its half-cell:

$$Cu\left|Cu^{2+}(0.010\,M)\right\|Ag^{2+}\left|Ag\right.$$

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2.2.1   Measurement of Potential

The electromotive force developed by a galvanic cell cannot be measured accurately by placing a simple dc voltmeter across the electrodes as shown in Fig. 1.3 of Unit 1, because a significant current is required for operation of the meter. Since current is drawn from the cell, a variation in concentrations of the reacting species will take place which leads top a change in the cell voltage. An additional factor is the development of ohmic potential drop due to the internal resistance of the cell, this opposes the potential due to the two electrodes of a galvanic cell. A truly significant value for the output of a cell potential can be attained only if the measurement is made with a negligible passage of current. A potentiometer is one type of instrument that meets this specification.

Potential Measurement with Potentiometer

Schematic diagram of a simple poetntiometer is given in Fig. 2.1. To understand the functioning of the instrument it can be divided into two parts: a voltage divider and the galvanic cell part.
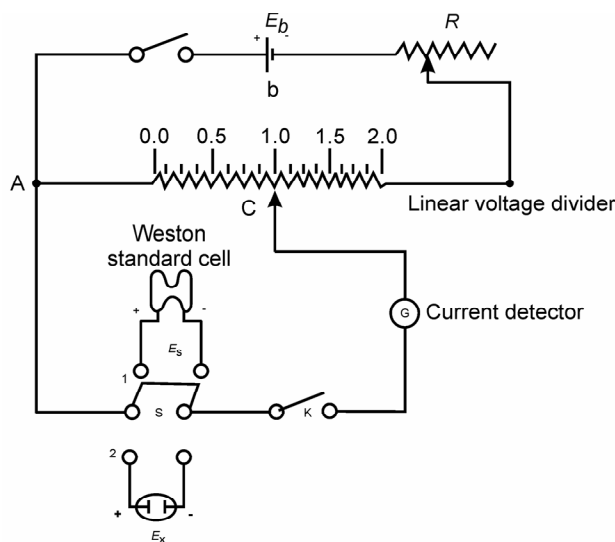

Fig. 2.1: Circuit diagram for a laboratory potentiometer

The working battery with potential E_b is connected to the terminals of a linear voltage divider AB. The electrical resistance, R_{AC}, from one end A to any point C, is directly proportional to the length AC of the resistor that is $R_{AC} \propto AC$ or $R_{AC} = kAC$, where k is a proportionality constant. In its simplest form the divider consists of a uniform resistance wire mounted on a meter stick. A sliding contact permits variation of the distance A and C and thus the output voltage. Divider is precision wire-wound resistor

formed in a helical coil. Included also is a sensitive current-detecting device G, which may be either a sensitive galvanometer or a dc amplifier, a tapping key, K, by which the circuit can be momentarily closed, and a double pole, double throw switch S to permit insertion of the unknown cell with potential, E_x or standard cell of known potential E_S into the circuit. The potential of working battery, E_b, is greater than that of E_x or of E_S.

Principles

A current, I, flows continuously from the battery through AB, causing a potential drop between A and B. From Ohm's law, this is given by:

$$E_{AB} = IR_{AB} \qquad \qquad \dots (2.5)$$

The current passing between A and C is also I and is given by the potential drop between A and C

$$E_{AC} = IR_{AC} \qquad \qquad \dots (2.6)$$

Resistance along resistor is linear. The above can also be written as

$$E_{AB} = IR_{AB} = kI.AB \qquad \qquad \dots (2.7)$$

$$E_{AC} = IR_{AC} = kI.AC \qquad \qquad \dots (2.8)$$

Dividing (2.8) by (2.7) and rearranging,

$$E_{AC} = E_{AB} \frac{AC}{AB} \qquad \qquad \dots (2.9)$$

Now there are three possibilities exist if the potential divider is adjusted to a position of E_{AC} and the key K is pressed. Two of these are when E_{AC} is greater than E_X (unknown potential) or E_s (potential of standard cell) electrons will be forced to flow from right to left through the unknown cell and the direction will be reversed if E_{AC} is less than E_x. The third case is where E_{AC} is equal to E_x, and for this situation no current flows through the galvanometer and galvanic cell. However, electrons will continue to flow through AB under these circumstances. In practice the key is tapped and C is moved until the galvanometer indicates no current flow. When this balance is found, the position on voltage divider is noted say AC_s. Similarly position on voltage divider with standard cell is also noted say AC_s.

With the standard cell and the unknown cell in the circuit, Eq. 2.9 becomes

$$E_S = E_{AC_S} = E_{AB} \frac{AC_s}{AB} \qquad \qquad \dots (2.10)$$

$$E_x = E_{AC_X} = E_{AB} \frac{AC_x}{AB} \qquad \qquad \dots (2.11)$$

where AC_S and AC_X represent the linear distances corresponding to balance point for the two cases. Dividing these two equations and rearranging, we get

$$E_x = E_s \frac{AC_x}{AC_s} \qquad \qquad \dots (2.12)$$

Thus E_x, the unknown potential of the cell, will be obtained by measuring the two distances with cell of unknown potential and the known emf of standard cell.
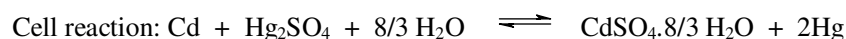
Standard Cell

In the previous sub-section you have seen that there is a need of standard source of potential for the measurement of potential of unknown electrolytic cell. The most

commonly used standard cell in potentiometry is the Weston Cell (Weston cadmium cell) which is depicted in Fig. 2.2 and can be represented by

$$Cd(Hg)|CdSO_4.8/3\ H_2O\ (s)\|\ Hg_2SO_4(s)|Hg \qquad \dots (2.13)$$

where Cd(Hg) represents the solution of cadmium in mercury. The two half-cell reactions occurring in this cell are

$$Cd\,(Hg) \rightarrow Cd^{2+} + Hg\,(1) + 2e \qquad \dots (2.14)$$

$$Hg_2^{2+} + 2e \rightarrow 2Hg(1) \qquad \dots\dots (2.15)$$

Cell reaction: $Cd + Hg_2SO_4 + 8/3\ H_2O \rightleftharpoons CdSO_4.8/3\ H_2O + 2Hg$

The potential of this Weston Cell is 1.0183 V at 20 ^oC. It is temperature dependent and is given by $1.0183 - 0.0000406\ (t - 20^0)$ at any other temperature t. Actually, in practice there are small variations in the emf of Weston Cells supplied by different manufacturers and it is essential to use the exact value quoted for the cell. While using it or preferably the value obtained by calibrations of the cell in use against a Weston Cell of known emf which is always kept reserved only for calibrations purposes. At no time current be drawn for longer times from a Weston Cell. A typical design of Weston cadmium cell is shown in Fig. 2.2.
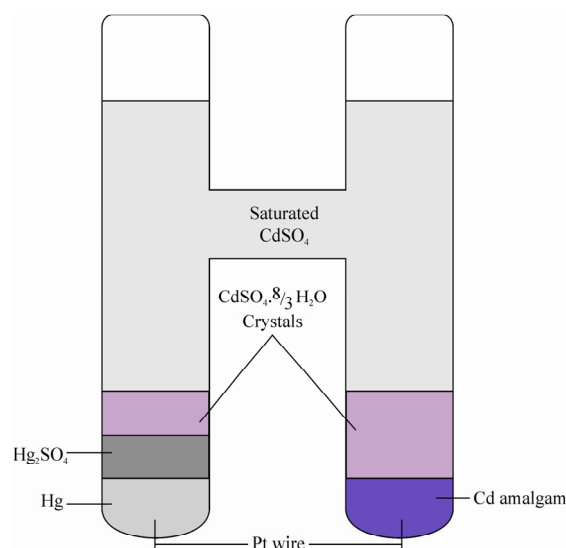

Fig. 2.2: The Weston cadmium cell

Potentiometric measurement using potentiometer discussed above is quite suitable if galvanic cell having internal resistance less than 10^3 Ω. Most of cells containing membrane electrode like glass electrode have high internal resistance (>10^9 Ω). To measure potential of such high resistance cell accurately, it is necessary that voltmeter device have resistance that is several order of magnitude greater than the resistance of the cell being measured. If the meter resistance is too low, the current is drawn from the cell, this result in lowering its output potential, thus creating a *negative loading error*. Because of this, digital voltmeters (dvm) are preferred for the measurement of potential as these offers the great advantage of having large internal resistance (10^{11} to 10^{12} Ω). Digital voltmeters are marketed as pH meters or ion meters.

2.3   DIRECT POTENTIOMETRY

Potentiometric methods of analysis may be grouped into direct reading method or direct potentiometry and potentiometric titrations. In this section we are taking up direct potentiometry in detail. In subsequent section, the potentiometric titrations will be discussed.

By convention, the indicator electrode is always treated as the right-hand electrode and reference electrode as the left-hand electrode.

The direct potentiometry is the method which makes use of the single measured electrode potential to determine the activity of the ion of interest (or concentration of the ion in case of dilute solution). This method is widely used for the determination of pH of the solution (using Hydrogen electrode) or determinations of other ions using different ion-selective electrodes.

In all the electroanalytical methods, two electrodes are required, the potential of one of the electrode be known, constant and is completely independent of the composition of the solution. This electrode is known as Reference electrode.

The second electrode whose potential is dependent on the concentration of the ion to be determined is called indicator electrode. For direct potentiometric measurement, the potential of the cell can be expressed in terms of the potential developed by the indicator electrode and the reference electrode:

$$E_{cell} = (E_{ind} - E_{ref}) + E_j \qquad \text{... (2.16)}$$

where E_j is a junction potential.

Consider the indicator electrode whose potential vary with cation activities or concentration, we can write Nernst Equation similar to Eq. 2.3 derived earlier for half cell reaction expressed by Eq. 2.1:

$$E_{ind} = E^o_{ind} + \frac{0.0591}{n} \log a_{M^{n+}} \qquad \text{... (2.17)}$$

Substitution of Eq. 2.17 into Eq. 2.16 yields:

$$E_{cell} = (E^o_{ind} + \frac{0.0591}{n} \log a_{M^{n+}}) - E_{ref} + E_j \qquad \text{... (2.18)}$$

On rearrangement

$$\log a_{M^{n+}} = \frac{n(E_{cell} - K)}{0.0591} \qquad \text{... (2.19)}$$

$$\text{or pM} = -\log a_{M^{n+}} = -\frac{n(E_{cell} - K)}{0.0591} \qquad \text{... (2.20)}$$

For anion A^{n-} Eq. 2.20 will have reversed sign

$$\text{pA} = -\log a_{A^{n+}} = \frac{n(E_{cell} - K)}{0.0591} \qquad \text{... (2.21)}$$

where pM and pA are the negative logarithm of the metal ion activity $a_{M^{n+}}$ and an anion $a_{A^{n+}}$, respectively. These terms are more general forms of the familiar term pH. K is summation of several constants, including standard electrode potential of metal ion or anion, potential of reference electrode, junction potential, asymmetrical potential if membrane electrode is involved.

All direct potentiometric methods are based on Eqs 2.20 and 2.21. Both these equations in terms of E_{cell} may be written as

$$E_{cell} = K - \frac{0.0591}{n} \text{pM} \qquad \text{... (2.22)}$$

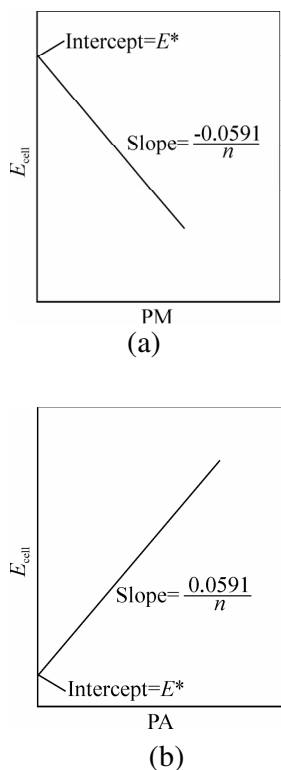$$E_{cell} = K + \frac{0.0591}{n} \text{pA} \qquad \text{... (2.23)}$$

Fig. 2.3: (a) A plot of Eq. 2.22 for a metal ion electrode; (b) A plot of Eq. 2.23 for an anion electrode

Using Eqs. 2.20 and 2.21,we can determine concentration of metal ions or cations and anions in terms of pM and pA, respectively. Further, Eq. 2.22 also indicates that for a metal ion-selective electrode, an increase in pM results in decrease in E_{cell} as shown in Fig. 2.3. But before that constant K should be known to us. As you know K is made up of several constants, including the junction potential, which cannot be measured directly or calculated from theory without assumptions. This problem can be overcome by electrode calibration method using standard solution of the analyte. Though calibration methods are simple, take less time and convenient to the continuous monitoring of pM or pA, but suffer somewhat limited accuracy because of uncertainty in junction potential.

In the electrode-calibration method, K is determined by measuring E_{cell} for one or more standard solution of known pM or pA. The calibration is performed just before the determination of pM or pA for the unknown. There is an assumption that K is unchanged when standard is replaced by the unknown analyte solution. Some time instead of calculating K using emf value of standard solution, a calibration graph is plotted using measured emf of standard solutions against log a (concentration), pM or pA. The sample is then treated in the same way as the standards and the concentration (or activity) read directly off the calibration graph. For getting fast results, a graph between cell potential and log a is plotted and for this we can use graph paper called semi-log paper for drawing calibration curve and concentration of a sample can be read off directly from the graph. To further understand this let's try following SAQ.

SAQ 5

Following emf readings are obtained for the standard solutions of Ca^{2+} ions in a potentiometry experiment. What is the concentration of a sample if its emf 33 mV?

Concentration of Ca^{2+}/mol dm^{-3} (M)	emf/mV
1.00×10^{-4}	– 2
5.00×10^{-4}	+16
1.00×10^{-3}	+25
5.00×10^{-3}	+43

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....

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2.3.1   Reference Electrodes

So far you have seen that galvanic cells are composed of two half cells and their potential can be measured using instrument called potentiometer. One of the half-cells of galvanic cell is consisted of the solution under investigation and the indicator electrode. The potential of this half is varied in accordance with the Nernst equation and the activity of the relevant ion. For the potential of the cell as a whole to reflect the indicator half-cell potential it is necessary to keep the potential of the other half-cell a constant. As mentioned earlier, we call this second half-cell the reference electrode. In this sub-section, we are going to take up some reference electrodes which are commonly used in potentiometry. But before that you should know the features to be considered when constructing or selecting a reference electrode. Some important one are:

- The potential of the electrode should remain constant; even some current is passed through it.

- The potential should be reproducible.

- The electrode should be easily prepared from readily available materials.

- The potential of the electrode should not change with temperature.

- It should be cheap.

Hydrogen Electrode

You know well that all the standard electrode potentials are quoted with reference to the standard Hydrogen Electrode, which is the most important primary reference electrode and whose potential is equal to zero under fixed conditions namely hydrogen gas at 1 atm. pressure and unit activity of Hydrogen ions in the solution in contact with the electrode. Upon connecting the standard Hydrogen electrode with a metal electrode (a metal in contact with its ions in a solution of unit activity) through a bridge, the standard electrode potential of the metal may be obtained from the following.

The hydrogen ions of the solution and the gaseous hydrogen are kept in equilibrium and platinum (pt) electrode coated with a thin film of pt-black. The platinum electrode is cleaned with hot chromic acid and thoroughly washed with distilled water. Then it is electrolytically plated from a solution of chloroplatinic acid with pt foil as anode. It is important that a thin jet black deposit is formed and thick deposits are not satisfactory for use as hydrogen electrodes. After platinizing, the electrode is to be freed from traces of chlorine. The most convenient source of hydrogen is the compressed gas available in the market in cylinders. The gas is purified by passing through all glass wash bottles containing 0.2 M $KMnO_4$, alkaline Pyrogallol, dilute H_2SO_4 and distilled water before passing on to the electrode surface. Fig. 2.4 shows typical designs of commonly used hydrogen electrodes.
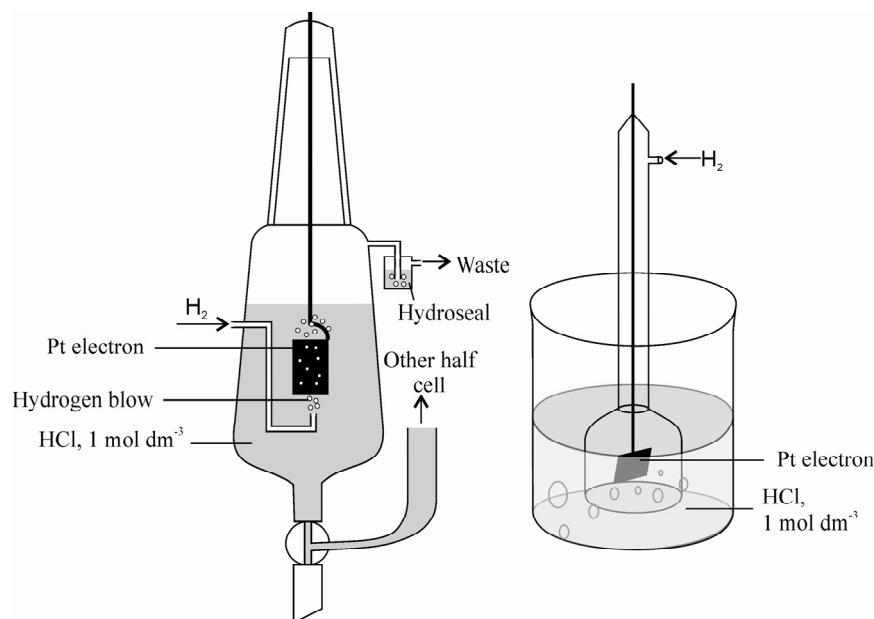

Fig. 2.4: Common design of Hydrogen Electrodes

Even though the hydrogen electrode is first and primary reference electrode developed, now-a-days, many other subsidiary standard electrodes, which can be easily prepared and permanently set up, are available for practical use and are preferred because of easiness to set up in comparison with hydrogen electrode, which is more complicated and require rigorous experimental conditions.

Hydrogen electrode is inconvenient for use in practical routine laboratory experiments since it has got the following practical problems.

1. It requires a large gas cylinder.

2. Hydrogen and air mixture is highly explosive.

3. Catalyst is easily poisoned.

Hence for routine laboratory use some other reference electrodes are commonly employed for measuring the potentials of other half-cells. The potentials of these reference electrodes have been measured against standard hydrogen electrode (SHE) and in potentiometry, the potential of any system is expressed as if it is measured with reference to the potential of standard hydrogen electrode (SHE)

The simple and common reference electrodes widely used are calomel electrode and silver-silver chloride electrode. These two are preferred because of their easy fabrication and maintain a constant and reproducible potential.

Calomel Electrode

The calomel electrode is the most widely used electrode due to its ease of preparation and constancy of potential. A calomel half-cell is one in which mercury and calomel [mercury (I) chloride] are covered with aqueous KCl solution of definite concentration (this may be 0.1M, 1.0 M, or saturated). If the KCl solution is saturated with the calomel, the electrode is called the saturated calomel electrode. The electrode potential of such electrode is +0.2412 V at 25 °C as determined against SHE. If the KCl solution is exactly 1.0 M, the potential is +0.2801 V; this is sometimes called Standard Calomel Electrode (SCE). Electrode potential of different types of calomel electrodes are given in Table 2.1.

Table 2.1: Specifications of Calomel Electrodes

Name	Concentration of		Potential vs SHE at 25 °C (V)
	Hg_2Cl_2	KCl	$Hg_2Cl_2(s) + 2e \rightarrow 2Hg^{2+} + 2Cl^-$
Saturated	Sat.	Sat.	+ 0.2412
Normal	Sat.	1.0 M	+ 0.2801
Decinormal	Sat.	0.1 M	+ 0.3337

The half-cell reaction for this electrode is:

$$Hg_2^{2+} + 2e \rightarrow 2Hg \qquad \qquad \text{… (2.24)}$$

It may be recalled that mercury (I) is a dimeric species, i.e. we are dealing with Hg(I) but ion in the solution is Hg_2^{2+}. According to Nernst equation, the potential is given by

$$E = E^o - \frac{0.0591}{2} \log \frac{1}{[Hg_2^{2+}]} \qquad \qquad \text{… (2.25)}$$

Hg_2^{2+} is also involved in another equilibrium : Hg_2Cl_2 is a slightly soluble salt, for which we may write a solubility product constant, K_{sp}.

$$K_{sp} = [Hg_2^{2+}] [Cl^-]^2 \qquad \qquad \text{… (2.26)}$$

Rearranging, we obtain

$$[Hg_2^{2+}] = \frac{K_{sp}}{[Cl^-]^2} \qquad \qquad \text{… (2.27)}$$

and substitution into the Nernst equation above yields

$$E = E^\circ - \frac{0.059}{2} \log \frac{[Cl^-]^2}{K_{sp}} \qquad \dots (2.28)$$

Since E^0 and K_{sp} are constants, it is seen that the potential reflects the concentration of Cl^-.

Calomel electrodes may be fabricated in a variety of sizes and shapes, some of these are shown in Fig. 2.5. Some calomel electrodes are small enough to be inserted into blood vessels of experimental animals through syringe needles. It should be emphasized that the potential of an electrode does not depend upon its size. Likewise, the liquid junction between the test solution and the KCl solution in the electrode may be physically established in various ways. Sometimes it involves an agar plug or a sintered glass frit, sometimes a pinhole, sometimes a small wet fiber, the point is to permit the migration of ions without allowing excessive solution to pour across the interface. Although the contamination from calomel electrodes is inconsequential for most purposes, in critical cases it must be remembered that a small amount of KCl may leak into the test solution. Similarly, a test solution with a large hydrostatic head may contaminate the contents of a calomel electrode.
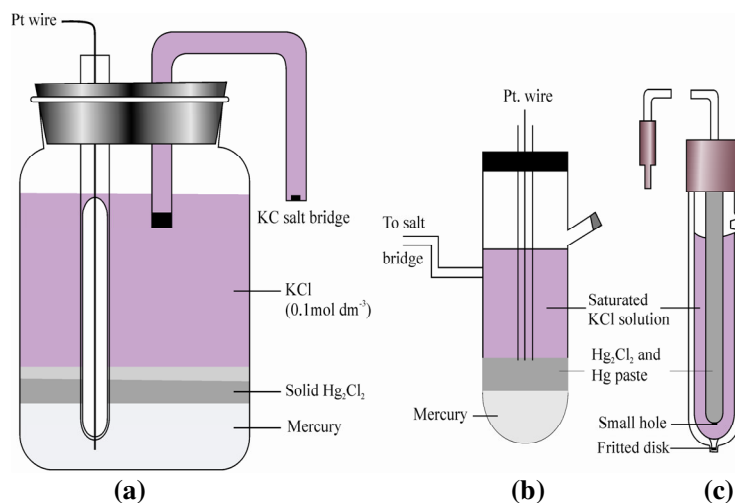
Fig. 2.5: A typical (a) & (b) laboratory-made saturated calomel reference electrodes; (c) commercial calomel electrode

For special purpose, modification of the calomel electrode may be preferred. Thus, if it is necessary to avoid the presence of potassium ions, the electrode may be prepared with sodium chloride replacing the potassium chloride. In some cases, the presence of chloride ions may be inimical and a mercury (I) sulphate electrode may then be used, this is prepared in a similar manner to a calomel electrode using mercury (I) sulphate and potassium or sodium sulphate solution.

Silver-Silver Chloride Electrodes

This electrode is similar to the one given above. It consists of a silver wire or a silver plated platinum wire coated with a thin layer of silver chloride, immersed in a solution of potassium chloride of a known concentration. It can be represented by:

$$AgCl \text{ (sat.)}, KCl \text{ (}x\text{ M)} \mid Ag \qquad \dots (2.29)$$

and the half-cell reaction is :-

$$AgCl \text{ (s)} + e \rightarrow Ag \text{ (s)} + Cl^- \qquad \dots (2.30)$$

Normally this electrode is prepared with saturated potassium chloride solution and its potential at 25 °C is + 0.199 V (vs) SHE while the potentials with 1.0 M and 0.1 M KCl are +0.237 and + 0.290 V (vs) SHE, respectively.

This electrode can be easily constructed and is as shown in Fig. 2.6. The electrode is contained in a glass tube fitted with a 10 mm fritted glass disk or porous plug (A). A layer of agar-KCl gel (B) is placed on the top of the disk to prevent loss of solution from the half-cell. A portion of the hot suspension is poured into the tube, which on cooling solidified into a gel with a low electric resistance. A layer of solid KCl (C) is placed on the gel and the tube is filled with saturated KCl (D). A drop or two of 0.1 M Ag NO_3 is added and a heavy gauge Ag wire (E) is inserted in the solution.

KCl solution
+2 drops
$AgNO_3$

Silver wire
coated with
AgCl

Porous disc
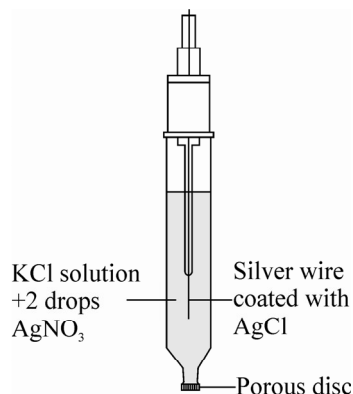
Fig. 2.6: A typical silver-silver chloride reference elctrode

2.3.2 Indicator Electrodes

An indicator electrode of a cell is one whose potential is dependent on the activity of a particular species whose concentration is to the determined. Several metals like silver, copper, mercury, lead and cadmium that show reversible half reactions are used for the construction of indicator electrodes. The potentials developed are reversible and reflect the activities of these ions in solution.

Among the metals; some metals like nickel, cobalt, tungsten do not give reproducible potentials due to some chemical or physical reactions and hence are not used as indicator electrodes.

Usually these metal electrodes are constructed from coils of wire, flat metal, metal plates or button set in plastic or glass (see Fig. 2.7). Large surface area is preferable because of rapid attainment of equilibrium. Metal surface is to be thoroughly cleaned. Usually it is achieved by dipping in concentrated nitric acid followed by repeated rinsing with distilled water.
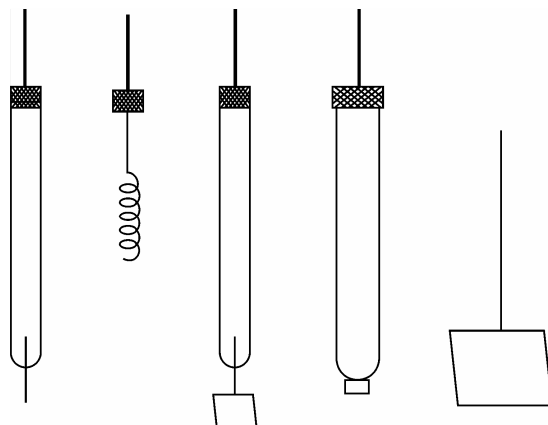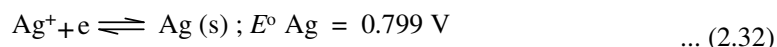

Fig. 2.7: Typical indicator electrode designs

In addition to the above where the metal electrode is used as an indicator electrode for its own cations, it can also be used indirectly; where it becomes responsive to anions that form slightly soluble precipitates with cations of the metal. For this application it is necessary to saturate the solution under study with the sparingly soluble salt, e.g. the potential of a silver electrode will accurately reflect the concentration of iodide ion in a solution that is saturated with silver iodide.

The reactions involved in this equilibrium are:

$$AgI\,(s) \rightleftharpoons Ag^+ + I^- \qquad \qquad \text{… (2.31)}$$

$$Ag^+ + e \rightleftharpoons Ag\,(s)\,;\, E^o\,Ag\, =\, 0.799\;V \qquad \text{... (2.32)}$$

Combining these two equations

$$AgI\,(s) + e \rightleftharpoons Ag\,(s) + I^-$$

$$E^o_{AgI}\, = - 0.151\;V \qquad \qquad \text{... (2.33)}$$

Applying Nernst equation to this half reaction, we get the following relationship between the electrode potential and the anion activity.

$$E = - 0.151 \; - \; 0.0591 \log [I^-] \qquad \text{... (2.34)}$$

This type of electrode, where silver is serving as an indicator electrode for iodide as called an electrode of the second order because it measures the concentration of an ion that is not directly involved in the electrode process.

If it is used for determination of silver ion then it is an electrode of the first order, because the potential is directly dependent on the participant ion in the electrode process.

Mercury Electrodes

Another important second order electrode used for the measurement of EDTA and its anion Y^{4-}, is based on the response of mercury electrode in the presence of a small concentration of stable Hg (II) EDTA complex.

The half-cell reactions for this electrode process are similar to the one given above and may be written as

$$HgY^{-2} + 2e \rightleftharpoons Hg\,(1) + \; Y^{-4} \;(E^o \, = \, 0.21\;V) \qquad \text{… (2.35)}$$
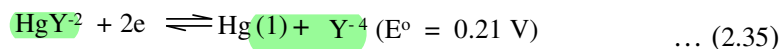
for which

$$E = 0.21 - \frac{0.0591}{2} \log \frac{[Y^{4-}]}{[HgY^{-2}]} \qquad \text{… (2.36)}$$

For this electrode system, a small concentration of HgY^{2-} is introduced into the analyte solution. The complex is so stable, that the dissociation to form Hg^{2+} is minimal ($K_f = 6.3 \times 10^{21}$ for $Hg\,Y^{2-}$) and the concentration of the complex remains constant over a wide range of Y^{4-}. Hence, the above equation may be simplified as

$$E = K - \frac{0.0591}{2} \log [Y^{-4}] \qquad \text{… (2.37)}$$

where the constant K is equal to

$$K = 0.21 - \frac{0.0591}{2} \log \frac{1}{[HgY^{2-}]} \qquad \text{… (2.38)}$$

This electrode is largely used in complexometric titrations using EDTA.

Membrane or Ion-selective Electrode:

There are another category of electrodes called membrane or ion-selective electrodes. These electrodes preferentially respond to a single chemical species. The potential between the indicator electrode and the reference electrode varies as the concentration or activity of that particular species varies. Unlike the inert indicator electrodes, ion-selective electrodes do not respond to all species in the solution. Glass membrane electrode or glass electrode is a typical example of ion selective electrodes. Functioning and principle of glass electrode will be discussed in detail in next unit of this course.

2.4 DETERMINATION OF EQUILIBRIUM CONSTANTS

From electrode potential measurements, we can calculate numerical values of many equilibrium constants such as solubility-product constant, dissociation constants and formation constants. One important advantage of this method is that the measurements can be made without disturbing any equilibria that may exist in the test solution.

In Unit 1, it was shown that the change in free energy for a reaction can be given by the equation 1.23:

$$\Delta G = \Delta G^o + RT \ln \frac{a_P^p \, a_R^r}{a_A^a \, a_B^b}$$

$$\text{or } \Delta G = \Delta G^o + 2.3RT \log K \qquad \qquad \dots (2.39)$$

where K is equilibrium constant.

In equilibrium condition $\Delta G = 0$,

$$\Delta G^o = -2.3RT \log K$$

According to Eq.1.24, $\Delta G^o = -nFE^o$

Combining both above equations yields

$$-nFE^o = -2.3RT \log K$$

and

$$\log K = \frac{nFE^o_{cell}}{2.3 \, RT} \qquad \qquad \dots (2.40)$$

Substitution for F, R and T, leads to

$$\log K = \frac{nE^o_{cell}}{0.0591} \qquad \qquad \dots (2.41)$$

Let's try following SAQ to know how the potential can be used in calculating equilibrium constants.

SAQ 6

Calculate the equilibrium constant for the reaction between Fe (II) and Ce (IV).

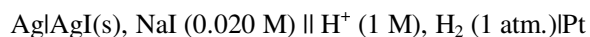(Use Appendix I for standard potentials of involved ions)

....

....

....

....

SAQ 7

Calculate the solubility product for AgI in the following cell, if cell develops a
potential of 0.048 V.

Ag|AgI(s), NaI (0.020 M) || H$^+$ (1 M), H$_2$ (1 atm.)|Pt

....
....
....
....
....

2.5   POTENTIOMETRIC TITRATIONS

The potential of a suitable indicator electrode is conveniently employed to establish
the equivalence point for a titration (a potentiometric titration). A potentiometric
titration provides different information from a direct potentiometric measurement
rather than involving absolute potentials or potentials with respect to standard half-
cells, the measurements are made while the titration is in progress. The equivalence
point of the reaction will be revealed by a sudden change in potential in the plot of emf
readings against the volume of the titrating solution. One electrode must be maintained
at a constant, but not necessarily known, potential; the other, electrode must serve as
an indicator of the changes in ionic concentration and must respond rapidly. The
solution must, of course, be stirred during the titration.

In contrast to direct potentiometric measurements, potentiometric titrations generally
offer increased accuracy and precision. Accuracy is increased because; measured
potentials are used to detect rapid changes in activity that occurs at equivalence point
of the titration. Furthermore, it is a change in emf versus titre volume rather than
absolute value of emf. Thus, the influence of liquid-junction potentials and activity
coefficients is minimised.

Potentiometric titrations may be applied to a variety of systems including those
involving oxidation-reduction, precipitation, acid-base, and complexation equilibria
reactions. We will discuss all these systems in detail in subsequent sections.

Further, potentiometric end-point detection also provides more accurate result than the
corresponding method employing indicators. It is particularly useful for titration of
coloured or opaque solutions and for detecting the presence of unsuspected species in
a solution. Titrations of more dilute solutions are possible using potentiometry.
Unfortunately, it is more time consuming than a titration performed with an indicator.
Simple arrangement for potentiometric titration are given in Fig. 2.8.

Ordinarily the titration involves measuring and recording a cell potential after each
addition of a reagent.

The titrant is added in large increments at the outset. As the end-point is approaching
(as indicated by larger potential changes per addition), the increments are made
smaller. Sufficient time must be allowed for the attainment of equilibrium after each
addition of reagent. Precipitation reactions may require several minutes for
equilibration, particularly in the vicinity of the equivalence points. A closed approach
to equilibrium is indicated when the measured protential ceases to drift by more than a
few millivolts. Good stirring is frequently effective in hastening the achievements of
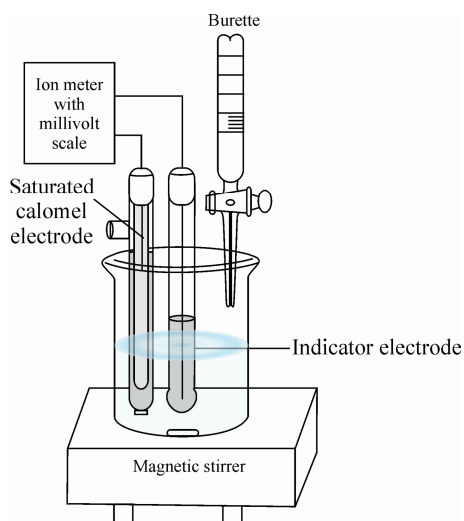equilibrium.

Fig. 2.8: Typical apparatus for potentiometric titration

A number of commercial "potentiometric titration units" are available which comprise an electrode system (frequently a selection of electrode is offered) together with a special stand providing supports for the electrodes, and one or two burette holders. The base of the stand incorporates in magnetic stirrer and in some cases a hot plate, so that if necessary the solution to be titrated may be heated. A separate unit embodies a potentiometer and a compact galvanometer or if the potentiometer is designed for the portion from the a.c. mains, the balance point indicator may be 'magic eye' electronic indicates similar to that used in mains operated conductivity bridges.

2.5.1 Location of End Points

In potentiometric titration the end-point is detected by determining the volume at which a selectively large change in potential occurs as the titrant is added. The method can be employed for all the reactions used for titrimetric purposes: acid -bases, redox, precipitation and complex formation. The titration may be performed manually or the procedure may be automatic.

In manual titrations, the potential is measured after the addition of each successive increment of titrant and the resulting readings are plotted on graph paper vs the volume of titrant to give the titration curve shown in Fig. 2.9 (a). You can see, this increase is not linear and a sigmoid shaped curve is obtained as shown the figure. The greater change in emf occurs around the equivalence point. In fact the equivalence point of maximum change in emf with volume added. This is formed the point of inflexion. The equivalence point is determined by dropping vertical line from this point. Fig. 2.9 (b) shows a plot of slope of a titration curve i.e. the rate of change of potential, with a change in volume ($\Delta E/\Delta V$) against volume of titrant, the resulting curve rises to maxima at equivalent point. The volume at equivalence point is determined by dropping a vertical line from the peak to volume axis. The more complete the reaction, the sharper the peak and hence more accurate the location of equivalence point.

Fig. 2.9 (c) shows a plot of the change in the slope of a titration curve ($\Delta^2 E/\Delta V^2$) against the volume of titrant. At the point where the slop $\Delta^2 E/\Delta V^2$ is a maximum, the derivative of the slope is zero. The end-point is located by drawing a vertical line from the point at which $\Delta^2 E/\Delta V^2$ is zero to the volume axis. Portion of the curve joining

the maximum and minimum values of $\Delta^2 E/\Delta V^2$ is steeper, the more complete the titration reactions.
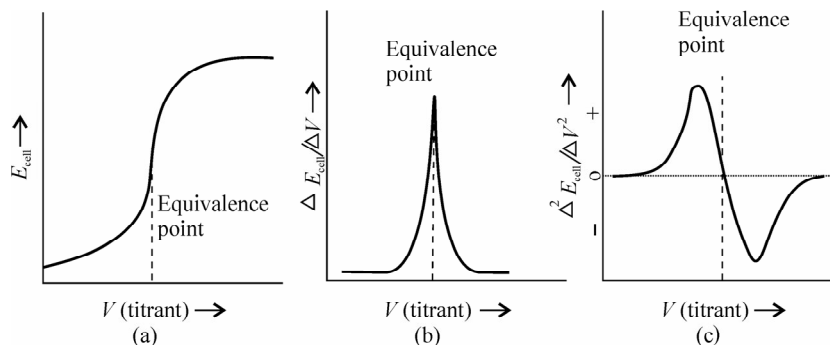

Fig. 2.9: Titration curves : (a) typical plot of emf vs volume; (b) typical first derivative titration curve; and (c) typical second derivative titration curve

2.5.2 Types of Potentiometric Titrations

The majority of potentiometric titrations involve chemical reactions such as neutralisation, oxidation-reduction, precipitation and complexation.

1. **Neutralisation Titrations**: Potentiometric neutralisation titrations are particularly useful for the analysis of mixture of acids or polyprotic acids or bases because discrimination between the end-points can often be made. An approximate numerical value for dissociation constant of the reactant species can also be estimated from potentiometric titration curves in theory. This quantity can be obtained from any point along the curve as a practical matter. It is most easily calculated from the pH at the point of half-neutralisation e.g. in the titration of weak acid HA, we may ordinarily assume that at the mid-point $[HA] \cong [A^-] + [H^+]$ and therefore :

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \ldots (2.42)$$

$$\log K_a = \log H^+ + \log \frac{[A^-]}{[HA]}$$

$$-\log K_a = -\log H^+ - \log \frac{[A^-]}{[HA]}$$

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

At half neutralization of the acid

$$[A^-] \text{ (salt) } = [HA] \text{ (acid)} \qquad \ldots (2.43)$$

Therefore, $pK_a = pH - \log 1$ $\qquad$ (log 1 = 0)

or $pK_a = pH$ $\qquad \ldots (2.44)$

This is the midway point to the equivalence pint. Therefore, pKa values can also be directly read from the titration curves.

It is important to note that a dissociation constant determined from a potentiometric titration curve may differ from that shown in the table of

dissociation constant in the literature by a factor of 2 or more because the latter is based upon the activities while the former is not.

2. **Oxidation-Reduction Titrations:** Indicator electrodes for oxidation-reduction are generally fabricated from platinum, gold mercury or silver. The metal chosen must be un-reactive with respect to the components of the reaction. It is merely a site for electron transfer. Platinum electrode is most widely used for oxidation-reduction titrations. It should be recalled that the curves for many oxidation-reduction titrations are not symmetric. Thus, the equivalence point potential may be significantly different from the potential corresponding to the point of inflection in the curve.

The determining factor in the values of potential is the ratio of the activity or concentration of the oxidised and reduced forms of certain ion species.

Take a general equation

$$\text{Oxidised form} + n\text{e} \rightleftharpoons \text{reduced form}$$
$$\text{… (2.45)}$$
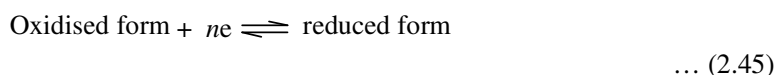
the potential acquired by the indicator electrode at 25 $^\circ$C is given by

$$E = E^0 + \frac{0.0591}{n} \log \frac{a_{\text{oxidised form}}}{a_{\text{reduced form}}} \qquad \text{... (2.46)}$$

where E^0 is the standard potential of the system. The potential of the immersed electrode is controlled by the ratio of these activities or concentration. In redox reactions, reducing agent is oxidised or oxidising agent is reduced and the ratio and the potential therefore changes more rapidly at the end point of the reaction. Thus titrations involving such reactions like Fe (II) with potassium permanganate or potassium dichromate or ceric sulphate may be followed potentiometrically and equivalence points can be obtained.

3. **Precipitation titrations:** Titrations involving the precipitation reactions are not nearly so numerous in titrimetric analysis for as those involving redox or acid - base reactions. One of the reasons for limited use of such reactions is the lack of suitable indicators. In some cases, particularly in the titration of dilute solution, the rate of reaction is too slow for convenience of titrations. As the equivalence point is approached and the titrant is added slowly, a high degree of super-saturation does not exist and the precipitation may be very slow. Another difficulty is that the composition of the precipitate is frequently not known because of co-precipitation effects. Although the latter can be minimised or partially corrected for by processes such as ageing the precipitate. This is not possible in direct titrations involving the formation of precipitate.

The indicator electrode for a precipitation titration is frequently the metal from which the reacting cation was derived. Membrane electrodes that are sensitive to one of the ions involved in the titration may also be employed.

Theoretical curves for a potentiometric titration are readily derived. For example, we may describe the potential of a silver electrode during the titration of iodide with silver ion by the expression.

$$E_{\text{Ag}} = -0.151 - 0.0591 \log [\text{I}^-] \qquad \text{… (2.47)}$$

Where -0.151 is the standard potential for the half reaction

$$\text{Ag I (s)} + \text{e} \rightleftharpoons \text{Ag (s)} + \text{I}^- \qquad \text{… (2.48)}$$

Alternatively, the potential is given by

$$E_{Ag} = 0.799 - 0.0591 \log 1/[Ag^+] \qquad \ldots (2.49)$$

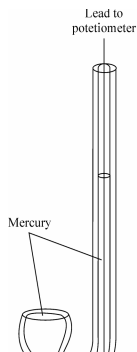where 0.799 is the standard potential for the reduction of silver ion.

4. **Complex Formation Titrations:** Both metal electrodes and the membrane electrodes can be used to detect end point in reactions that involve formation of a soluble complex. The mercury (Hg) electrode given in Fig. 2.10 is particularly useful for EDTA titrations. It will function as an indicator electrode for the titration of cations forming complexes that are less stable than HgY^{2-}.

5. **Differential Titrations:** This titration requires the use of two identical indicator electrodes, one of which is well-shielded from bulk of solution. Fig. 2.11 given below illustrates a typical arrangement. Here one of the electrodes is contained in a small side-arm test-tube. Contact with the bulk of the solution is made through a small hole in the bottom of the tube. Because of the restricted access, the composition of the solution surrounding the shielded electrode will not be immediately affected by an addition of titrant to the bulk of the solution. The resulting difference in solution composition gives rise to a difference in potential ΔE between the electrodes. After each potential measurement, the solution is homogenised by squeezing the rubber bulb several times, where upon ΔE again becomes zero. If the volume of the solution in the tube that shields the electrode is kept small, the error arising from failure of final addition of reagent to react with this portion of the solution can be shown to be negligibly small. The main advantage of a differential method is the elimination of the need for the reference electrode and salt bridge.

Lead to potetiometer

Mercury

Fig. 2.10: Mercury electrode

Burette

Rubber bulb

Small hole

Side-arm test tube

Indicator electrode

Magnetic stirrer
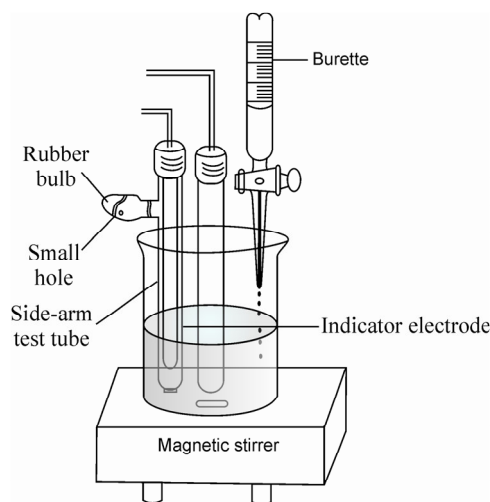
Fig. 2.11: Apparatus for differential potentiometric titration

Automatic Titrations

Now-a-days large number of automatic titrators based on the principle of potentiometry have come into the market. These are highly useful in those places, where a large number of routine analysis are required. These may not be more accurate than the manual techniques, but are quite rapid and decrease the time needed to perform the experiment and thus offer some economic advantages. Two different automatic titrators are available:

1. The first type gives titration curves of V vs E or $\Delta E/\Delta V$ vs V. The end point is obtained from the curve by inspection.

2. In the second type of titrators, the titration is stopped automatically when the potential of the electrode system reaches a predetermined value and the volume of reagent delivered is read at the operators convenience or printed on a tape. These titrators usually employ a burette system with a solenoid-operated value to control the flow or alternately it makes use of a syringe, the plunger of which is activated by a motor driven micrometer screw.
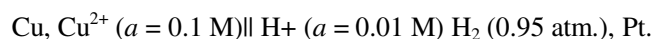
2.6   SUMMARY

In this unit, you have learnt about electrode potentials, principles of potentiometer and measurement of potential, different types of reference electrodes : such as Hydrogen Electrode, Calomel Electrode, Silver-Silver Chloride Electrode and different types of indicator electrodes. You have also learnt about the measurement of potential and location of end points from the graphs obtained from the experimental values of emf and volume of titrant.

Different type of tirations such as acid-base titrations, redox titrations, precipitation titrations, complexometric titration and differential titrations were also explained in detail.

2.7   TERMINAL QUESTIONS

1. What is an electrode potential?

2. Why the absolute value of electrode potential cannot be determined ?

3. What is a reference electrode? Give some examples.

4. Explain liquid-junction potential. How can it be eliminated?

5. What is a Standard Cell? Give the reaction in case of Weston Standard Cell.

6. Calculate the EMF of the following electrochemical cell at 25°C:

    Cu, Cu^{2+} (a = 0.1 M)|| H+ (a = 0.01 M) H_2 (0.95 atm.), Pt.

7. Calculate the potential for the cell given below:

    $$Pt\left|Fe^{2+} (0.010\,M), Fe^{3=} C(0.010\,M), HCl\,(1M)\right|\left|\begin{array}{l}Cr_2O_7^{2-} (0.020\,M), Cr^{3+} (0.005\,M),\\ HCl\,(o.100\,M)\end{array}\right|Pt$$
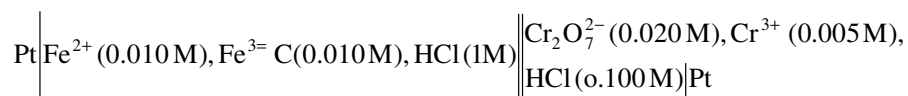
8. Calculate the solubility product of AgCl from the data

    $Ag^+ + 1e \longrightarrow Ag\,(s)$ $E^0_{Ag^+,Ag}$ =+ 0.799 V

    $AgCl\,(s) + 1e \longrightarrow Ag\,(s) + Cl^-$ $E^O_{AgCl,Ag}$ =+ 0.222 V
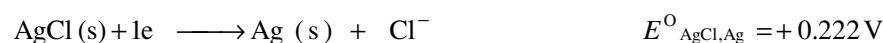
9. 25 cm^3 of a solution of HCl (0.1M) is being titrated potentiometrically against a std. (0.1 M) sol. of NaOH using a hydrogen electrode as the indicator electrode and saturated calomel electrode (S.C.E.) as the reference electrode. (a) What would be the emf of the cell initially and after the addition of 20, 24.9, 25.10, 30.00 cm^3 of NaOH solution? (b) Also calculate the potential at equivalent point and after the addition of 0.05 cm^3 of NaOH.

10. Calculate the potential of the indicator electrode at 25°C relative to S.C.E. at the equivalence point of the titration of 25.00 cm^3 of 0.010 M Fe^{2+} with 0.010 M $Cr_2O_7^{2-}$ in a sol. that is buffered at pH 3.50.

2.8 ANSWERS

Self Assessment Questions

1. Half-cell reaction : $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

    Nernst equation : $E = E^\circ - \dfrac{0.0591}{2} \log \dfrac{1}{[Cu^{2+}]}$

    No term of elemental Cu is included in the logarithmic term because it is a pure solid.

    or $\qquad E = E^\circ + \dfrac{0.0591}{2} \log[Cu^{2+}]$

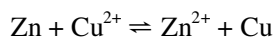 E° for Cu electrode is +0.337 (from Table 1 Appendix 1), therefore,

    $E = 0.337 + \dfrac{0.0591}{2} \log 0.044$

    $E = 0.297$ V

2. You have to follow the same steps as shown for SAQ 1.

    $E = -0.799$ V

3. For this cell chemical reaction is:

    $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

    $E_{cell} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$

    $\qquad = 0.297 - (-0.799) = 1.096$ V

4. For this cell chemical reaction is

    $Cu + 2Ag^+ \rightleftharpoons Cu^{2+} + Ag$
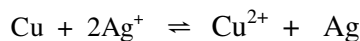
    $E_{cell} = E_{Ag^+/Ag} - E_{Cu^{2+}/Cu}$

    $E_{cell} = \left[E^\circ + \dfrac{0.0591}{1} \log[Ag^+]^2 \right] - \left[E^\circ + \dfrac{0.0591}{2} \log[Cu^{2+}] \right]$

    Substitute the value of the standard potentials, cell potential and concentration of copper ions.

    $0.463 = \left[0.799 + \dfrac{0.0591}{1} \log[Ag^+]^2 \right] - \left[0.337 + \dfrac{0.0591}{2} \log 0.010 \right]$

    Concentration of $Ag^+ = 0.104$ M

5. Draw a calibration graph using the data given in SAQ 5 on special type of graph paper called semi-log (or log/mm) paper. The calibration graph is shown in Fig. 2.12. You can find the concentration of sample from this graph is 2.1×10^{-3} M.

6. The two half-cells can be written as

    $Ce^{4+} + 1e \rightarrow Ce^{3+}; \qquad E^0_{Ce^{4+},Ce^{3+}} = 1.70 \, V$

    $Fe^{3+} + 1e \rightarrow Fe^{2+}; \qquad E^0_{Fe^{3+},Fe^{2+}} = 0.771 V$

    For these two half-cells, final reaction can be written as:
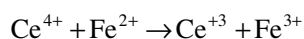
$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{+3} + Fe^{3+}$$

$$K = \frac{[Ce^{3+}][Fe^{3+}]}{[Ce^{4+}][Fe^{2+}]}$$

$$\log K = \frac{n(E^0_{right} - E^0_{left})^*}{0.0591}$$

$$\log K = \frac{(1)(1.70 - 0771)}{0.0591} = 15.69$$

$$K = 10^{15.69} = 4.90 \times 10^{15}$$

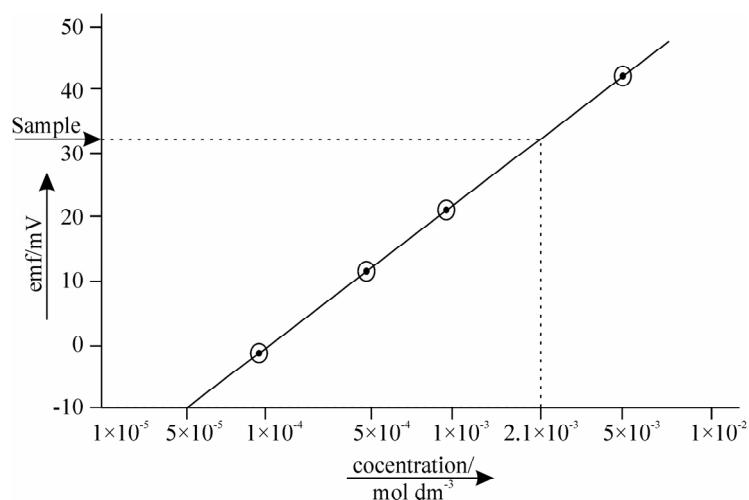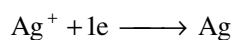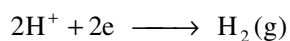**Fig. 2.12 : Calibration curve for calcium ion selective electrode**

7.   Half-cell reactions are
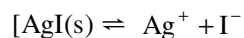
$$2H^+ + 2e \longrightarrow H_2(g)$$

$$Ag^+ + 1e \longrightarrow Ag$$

$$E_{cell} = E_{H^+,H_2} - E_{Ag^+,Ag}$$

$$E_{cell} = E^0_{H^+,H_2} - \frac{0.0591}{2}\log\frac{P_{H_2}}{[H^+]^2} - \left[E^0_{Ag^+,Ag} - \frac{0.0591}{1}\log\frac{1}{[Ag^+]} \right]$$

$$0.0480\,V = 0.00\,V - \frac{0.0592}{2}\log\frac{1}{[1]^2} - 0.799\,V + \frac{0.592}{1}\log\frac{1}{[Ag^+]}$$

$$[Ag^+] = 4.16 \times 10^{-15}$$

$$[AgI(s) \rightleftharpoons Ag^+ + I^-$$

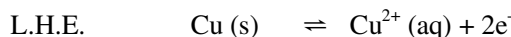$$[I^-] = 2.00 \times 10^{-2}\,M$$

$$K_{sp} = [Ag^+][I^-]$$

$$K_{sp} = [4.16 \times 10^{-15}][2.00 \times 10^{-2}] = 8.32 \times 10^{-17}$$

Terminal Questions

1. This is the tendency of an electrode to get oxidised or reduced. But as per the IUPAC conventions, it is the reduction potential of the electrode.

2. Because oxidation or reduction cannot take place independently.

3. A standard electrode with reference to which the potential of an indicator electrode is determined is called "reference electrode." Some examples are Standard Hydrogen Electrode (S.H.E.); Saturated Calomel Electrode (S.C.E.).

4. This is the potential which is set up at the junction of two solutions because of difference in the speeds of ions moving across the boundary. It can be eliminated by using a salt bridge containing KCl, since K^+ and Cl^- move with almost equal speeds.

5. This is a cell which gives constant and reproducible emf and has very small temperature coefficient. An important example is Weston Standard Cell in which the cell reaction is

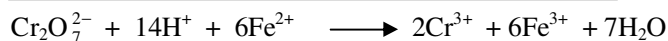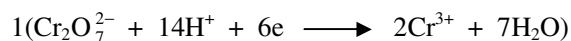 $Cd (Hg) + Hg_2SO_4(sat.) + 8/3 H_2O (l) \rightleftharpoons CdSO_4 8/3 H_2O (sat.) + 2 Hg (l)$

6. The half-cell reactions are :

    $$R.H.E. \qquad 2H^+ + 2e^- \rightleftharpoons H_2 (g)$$

    $$L.H.E. \qquad Cu (s) \rightleftharpoons Cu^{2+} (aq) + 2e^-$$

    Overall reaction : $Cu(s) + 2H^+ \rightleftharpoons Cu^{2+} (aq) + H_2 (g)$
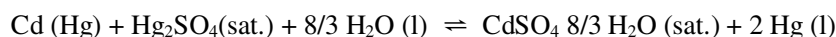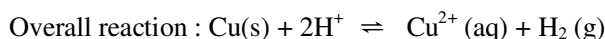
    $$E°_{cell} = E° = E°_R - E°_L = -0.34 \text{ V}$$

    The EMF of the cell is given by,

    $$E = E° - \frac{0.0591}{2} \log \frac{a_{cu^{2+}} \times a_{H_2}}{(a_{H^+})^2} \text{ at } 25°C$$

    $$= -0.337 - \frac{0.0591}{2} \log \frac{(0.1)(0.95)}{(0.01)^2}$$

    $$= -0.337 - 0.088 = -0.425 \text{ V}$$

7. Reaction for this cell can be written as:

    $$1(Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O)$$

    $$6(Fe^{2+} \longrightarrow Fe^{3+} + 1e)$$

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

    Cell potential :

    $$E_{cell} = E_{Cr_2O_7^{2-}/Cr^{3+}} - E_{Fe^{3+}/Fe^{2+}}$$
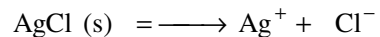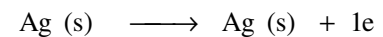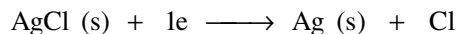
    $E_{cell} = \{ E^0_{CrO_7^{2-}/Cr^{3+}} - \frac{0.0591}{6} \log [Cr^{3+}]^2 / [Cr_2O_7^{2-}][H^+]^{14} \} - \{ E^o_{Fe^{3+}/Fe^{2+}} - $

    $\frac{0.0591}{1} \log \{[Fe^{2+}]\}/ \{[Fe^{3+}]\}$

    Substitute the values of standard potentials from Table 1, Appendix A, concentrations:

$E_{cell} = \{1.33 - \dfrac{0.0591}{6} \log [0.005]^2 / [0.020] [0.010]^{14}\} - \{0.771 - \dfrac{0.0591}{1} \log \{[0.010]\}/ [0.001]\}$

$E_{cell} = 1.33 - 0.109 - 0.771 + 0.0591 = 0.509$ V

8. Cell reaction can be written as:

$AgCl$ (s) + $1e \longrightarrow Ag$ (s) + Cl

$\dfrac{Ag \ (s) \longrightarrow Ag \ (s) + 1e}{AgCl \ (s) = \longrightarrow Ag^+ + Cl^-}$

$\log K_{sp} = \dfrac{1[0.222 - (+0.799)]}{0.0591}$

$K_{sp} = 1.82 \times 10^{-10}$

9. a) The galvanic cell can be represented as follows :

Pt, H_2 (1 atm.), H^+ (c, unknown) ‖ KCl sat. soln.,$Hg = Cl_2(s)$, Hg. The EMF of the cell is given by,

$E_{cell} = E_{SCE} - E_{hydrogen}$
$= 0.2422 - 0.0591 \log H^+$
$= 0.2422 + 0.0591 pH$ at 25°C
Initial pH of the titration solution viz., 0.1 M HCl $= - \log [H^+]$
$= - \log (0.1) = 0.1$
so that $E = 0.3013$ V

Since the product of volume of the solution in cm^3 and the concentration in mol dm^{-3} of a solute gives the amount of the solute in millimoles (mmol), hence, Amount of HCl initially present in the titration solution
$= 25 \times 0.1 = 2.5$ mmol

The amount of NaOH in 20 cm^3 of 0.1 M solution added during titration $= 20 \times 0.1 = 2.0$ mmol.

Amount of HCl left in the titration solution on adding 20 cm^3 of NaOH $= 2.5 - 2.0 = 0.5$ mmol.

Total volume of titration solution $= 25 + 20 = 45$ cm^3

Conc. of HCl or of H^+ ions in the solution

$\dfrac{\text{No. mmol HCl remain after addition of NaO}_4}{\text{Total volume of the solation}}$

$= \dfrac{0.5}{45}$ mol dm^{-3}

pH of the titration solution $= - \log [H^+]$

$= - \log (0.5/45) = 1.95$

The corresponding value of E is $0.2422 + 0.0591 \times 1.95 = 0.3574$ V. Proceeding as above the pH values of the titrant on the addition of 24.90, 25.10 and 30.00 cm^3 of NaOH solution come out to 3.70, 10.30 and 10.96,

respectively and hence the corresponding values of E are 0.4609, 0.8510 and 0.8900 V respectively.

b) On the addition of 25 cm^3 of NaOH, the acid is completely neutralised giving NaCl. The pH of the resulting solution is therefore 7 and E = 0.6560 V.

On additng 25.05 ml of NaOH, the excess volume of NaOH = 0.05 cm^3

Amount of NaOH in 0.05 cm^3 solution = 0.05 × 0.1
$$= 0.005 \text{ mmol}$$

Conc. of NaOH or OH$^-$ ions = 0.005 / 50.05 mol dm^{-3}
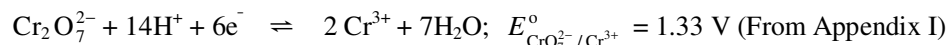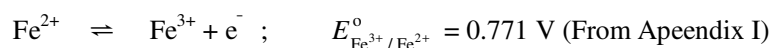
Since [H$^+$] [OH$^-$] = 10^{-14} at 25°C

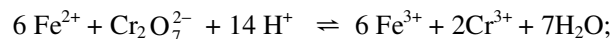$$\square[H^+] = \frac{10^{-14} \times 50.05}{0.005} \text{ mol dm}^{-3}$$

Hence pH = 10.0

The corresponding E is 0.833V.

10. The half-cell Potentials in this case are

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^- \; ; \qquad E^o_{Fe^{3+}/Fe^{2+}} = 0.771 \text{ V (From Apeendix I)}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2\,Cr^{3+} + 7H_2O; \quad E^o_{CrO_7^{2-}/Cr^{3+}} = 1.33 \text{ V (From Appendix I)}$$

The overall Potential is

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

The potential of the indicator electrode, relative to the S.H.E. is given by,

$$E_{In} = 0.771 - 0.0591 \log \{[Fe^{2+}]\}/\{[Fe^{3+}]\} \qquad \dots (1)$$

and by $$E_{In} = 1.33 - \frac{0.0591}{6} \log \{[Cr^{3+}]^2 / [Cr_2O_7^{2-}][H^+]^{14}\} \quad \dots (2)$$

We must combine these two equations in such a manner as to eliminate the concentration of the reactants that cannot be calculated at the equivalence point.

In this titration, neither [Fe^{2+}] nor [Cr$_2$O$_7^{2-}$] can be calculated at the equivalence point without prior knowledge of the equilibrium constant for the reaction. Hence, multiplying Eq. (2) by 6 and then adding with Eq. (1), we obtain,

$$7E_{In} = 8.75 - 0.0591 \log \frac{[Fe^{2+}][Cr^{3+}]^2}{[Fe^{3+}][Cr_2O_7^{2-}][H^+]^1} \qquad \dots (3)$$

At the equivalence point,

$$[Fe^{2+}] = 6\,[Cr_2O_7^{2-}]$$

Hence Eq. (3) simplifies to,

$$7E_{cell} = 8.75 - 0.0591 \log \frac{6[Cr_2O_7^{2-}] \, [Cr^{3+}]^2}{[Fe^{3+}] \, [H^+]^{14}} \qquad \ldots (4)$$

$$= 8.75 - 0.0591 \log \frac{6 \, [Cr^{3+}]^2}{[Fe^{3+}] \, [H^+]^{14}} \qquad \ldots (5)$$

Let x be the volume of $Cr_2O_7^{2-}$ added at the point of equivalence.
Since at the equivalence point,

$[Fe^{2+}] = 6 \, [Cr_2O_7^{2-}]$, hence

$(0.01 \text{ mmol/cm}^3) \times 25 \text{ cm}^3 = 6 \, (0.01 \text{ mmol/cm}^3) \times x$

$x = 4.16 \sim 4.2 \text{ cm}^3$

$$[Fe^{3+}] = \frac{0.010 \, \text{mmol}/\text{cm}^3 \times 25.0 \, \text{cm}^3}{25.0 \times 4.2 \text{ cm}^3}$$

At the equivalence point

$[Cr^{3+}] = [Fe^{3+}] \times 2/6 = 2.9 \; x \times 10 \text{ M}$

since, pH = 3.50, hence $[H^+] = 3.2 \times 10^{-4}$ M
Substituting these values in Eq. (4) and simplifying, we obtain

$E_{In} = 0.855$ V

Hence, the potential of the indicator electrode relative to SCE is

$E = 0.855 - 0.242 = 0.613$ V

as reduction potential of saturated calomel electrode is 0.242 V.