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Learning Outcome of Module-5

LO	Learning Outcome (LO)	Course Outcome Code
LO1	To gain knowledge about Electrochemical Cell	BP102.5
LO2	To understand the different Electrodes, Methods of end point determination, Applications	BP102.5
LO3	To gain knowledge about Polarography	BP102.5
LO4	To understand the instrumentation of Polarography, advantages, applications	BP102.5

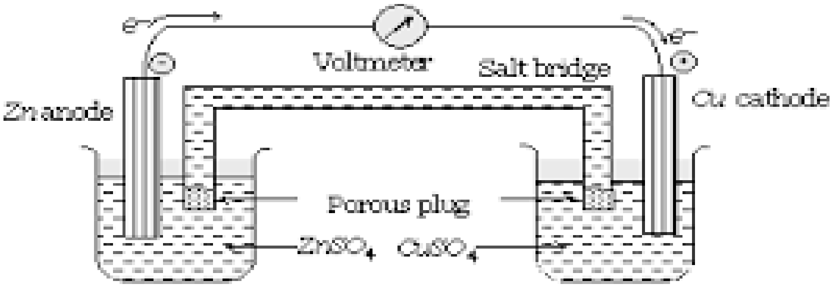
Module Content Table

Topic
• Electrochemical Cell • Construction and working of different electrodes • Applications. • Theory of Polarography • Different types of currents,Factors affecting limiting current • Instrumentation, Application

POTENTIOMETRY

Electrochemical cell

Potentiometry is one type of electrochemical analysis methods. Electrochemistry is a part of chemistry, which determines electrochemical properties of substances. An electrical circuit is required for measuring current (unit: ampere, A) and potential (also voltage, unit: volt (V)) created by movement of charged particles. Galvanic cell (electrochemical cell) serves as an example of such system.



Electrochemical cell consists of two solutions connected by a salt bridge and electrodes to form electrical circuit. Sample cell on figure consists of solutions of $ZnSO_4$ and $CuSO_4$. Metallic Zn and Cu electrodes are immersed in respective solutions. Electrodes have contacts firstly through wires connected to the voltmeter and secondly through solutions and a salt bridge, forming an electric circuit. Salt bridge consists of a tube filled with saturated salt solution (e.g. KCl solution). The ends of the tube are capped with porous frits that prevent solutions from mixing, but permit movement of ions.

Three distinct charge transfer processes are described for the system in Fig

1. Electrons move in electrodes and wires from zinc electrode to copper electrode.
2. Ions move in solutions:
   a. In solution on the left, zinc ions move away from the electrode and sulfate ions move towards it.
   b. In solution on the right, copper ions move towards the electrode and negatively charged ions (sulfate) away from it.
   c. In salt bridge positive ions move right and negative ions left.
3. On the surfaces of electrodes electrons are transferred to ions or vice versa:
   a. Zinc electrode dissolves: $Zn \rightarrow Zn^{2+} + 2e^-$

b. Metallic copper is deposited on the electrode surface: $Cu^{2+} + 2e^{-} \rightarrow Cu\downarrow$

Three processes mentioned above are important parts of a closed electrical circuit making the flow of electrical current possible. Potential on an electrode depends on the ions present in the solution and their concentration. These way electrochemical cells can be used to determine ions and their concentration in solution. The dependence of potential between electrodes from concentration of ions is expressed by Nernst equation:

$$E = E_0 – RT/nF.\ln a$$

E – Electrode potential,

E_0 – Standard potential of the electrode,

R – Universal gas constant (8.314 J/(K•mol)),

F – Faraday constant (96485 C/mol),

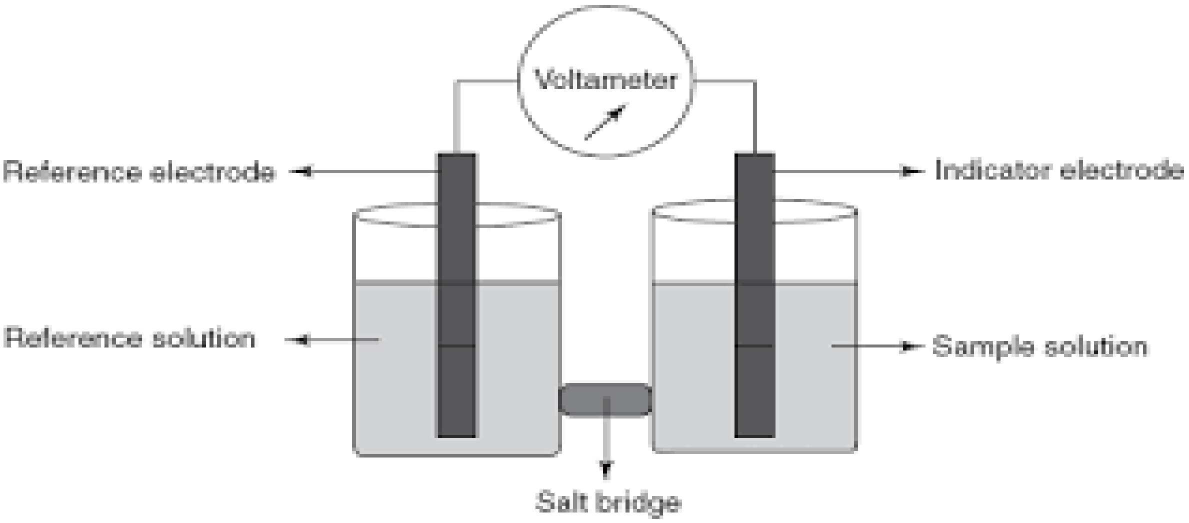
T – Temperature in kelvins,

n – Charge of the ion or number of electrons participating in the reaction,

a – activity of the ions. Activity of the ions is a function of concentration. For solutions with concentrations lower than about 0.1 mol/l, activity can be approximated to concentration. Thus a logarithmic dependence exists between potential and the activity (concentration) of ions in solution.

Potentiometry

Potentiometry is based on the measurement of the potential of an electrode system (e.g. electrochemical cell). Potentiometric measurement system consists of two electrodes called reference and indicator electrode, potentiometer and a solution of analyte (figure). Reference electrode is an electrode with potential which is a) independent of concentration of analyte (or other) ions in solution; b) independent of temperature. Potential of an indicator electrode depends mainly on the concentration of the analyte ions (in these case hydrogen ions). Potentiometric measurements enable selective detection of ions in presence of multitude of other substances. In case of figure, the potential of the indicator electrode is sensitive to hydrogen ions. In a system like this, the potential is measured in reference to a calomel electrode, e.g. calomel electrode functions as the reference electrode.



Reference Electrodes

Hydrogen electrode: Hydrogen electrode is the primary standard against which the potentials of other electrodes are measured. It can be used as indicator as well as reference electrode. It consists of a platinum foil coated with platinum black and has wire contacts through mercury. This assembly is enclosed in a glass covering through which hydrogen (99.8% purity adequate) is passed at 1 atmospheric pressure continuosly and dipped into the solution of standard acid or unknown solution. At all times, the electrode surface and the solution should be saturated with the gas.

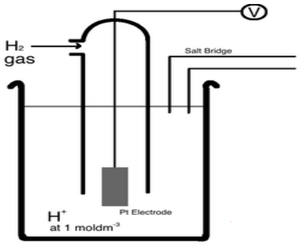
The potential of this electrode is given as follows:

$$E = E^0_H + 0.0592 \log [H^+]$$

$$= E^0_H - 0.0592 \text{ pH}$$

$$E = -0.0592 \text{ pH}$$

Since E^0_H is the standard potential of hydrogen electrode and is taken as 0



Merits

1. It is the primary reference standard against which the potentials of other electrodes are measured.

2. It can be used over the entire pH range.
3. It can be used as a reference electrode when dipped with standard acid solution and as an indicator electrode when dipped into a sample solution.

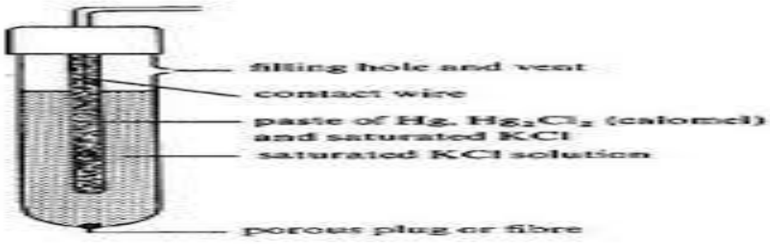
Demerits

1. Factors like purity of hydrogen and pressure of hydrogen affect the potential of this electrode.
2. It is affected by the presence of oxidizing or reducing substance.
3. Potential is affected due to poisoning of platinum surface.

Saturated calomel electrode

It consists of an inner jacket and outer sleeve. The inner tube (jacket) has wire contact with mercury and plugged with a mixture of calomel (Hg_2Cl_2) and KCl. This is surrounded by an outer sleeve and the tip is filled with crystals of KCl and porous plug of asbestos. The space between the inner jacket and outer sleeve is filled with either saturated KCl or 1N KCl or 0.1 N KCl on which the potential of the electrode depends upon. The potential of this half cell depends upon i) Concentration of potassium chloride used ii) Temperature as given as follows.

Calomel electrode when filled with	Potential in mV	
	At 20ºC	At 25ºC
Saturated KCl	250	246
1N KCl	286	285
0.1 N KCl	338	338



Merits of saturated calomel electrode

1. Ease of construction.
2. Stability of potential.

Silver-Silver chloride electrode

It is simply a silver wire coated electrolytically with silver chloride and dipped into potassium chloride. The potential of this half cell also depends upon temperature as well as concentration of potassium chloride used.

Silver-silver chloride electrode used with	Potential in mV at 25ºC
Saturated KCl	200
1 N KCl	235.5
0.1 N KCl	288

It has the advantage that it is easy to use, but the demerit is that it is difficult to prepare.

Indicator electrodes

Indicator electrode indicates the potential or pH of a solution in comparison to a reference electrode of a known potential. Examples for indicator electrode are hydrogen electrode, Antimony-antimony oxide electrode and Glass electrode.

1. Hydrogen electrode: Hydrogen electrode has been described in detail under reference electrode. It is used as reference electrode when dipped into a standard acid solution. Hydrogen electrode is used as indicator electrode when dipped into a unknown solution whose potential or pH has to be determined.

2. Antimony-Antimony oxide electrode: It consists of a Antimony rod dipped into a solution, whose potential or pH has to be determined. Antimony oxide (Sb_2O_3) is formed on exposure to air.

Reaction:

$$Sb + H_2O \longrightarrow SbO^+ + 2H^+ + 3e$$

Potential:

$$E = E^0 + 0.0592/3*\log[SbO^+] [H^+]^2$$

$$E = 0.255-0.0592 \text{ pH}$$

Advantages

1. It can be used from pH 3 to pH 8. It can be used even upto pH 12. If saturated solution of oxide is used.

2. It is not easily poisoned or damaged.

3. It can be used even with viscous fluids.

Disadvantages

This electrode cannot be used in the presence of dissolved oxygen, oxidizing agents, highly acidic or alkaline conditions or complexing agents.

Glass electrode: Glass electrode is the most widely used indicator electrode. It is selective and responsive to change in concentration of hydrogen ions. The glass electrode consists of a glass tube with a thin pH sensitive glass bulb at its tip. It has a silver-silver chloride wire at the centre of the tube and the lower tip of the wire immerses into the 0.1 N hydrochloric acid filled in the glass tube. This assembly acts as an indicator electrode and is dipped into a solution whose pH or potential is to be known. The potential of the glass electrode is given by

$$E = k + 0.0592\ (pH_1 - pH_2) \text{ at } 25^{\circ}C$$

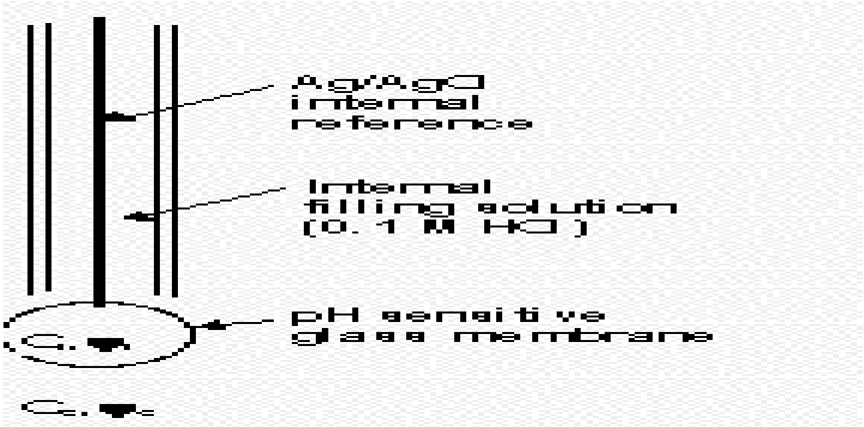
Where k = constant for the electrode

pH_1 = pH of solution inside the bulb

pH_2 = pH of test solution (outside)

$$E = k + 0.0592\ pH_1 - 0.0592\ pH_2$$

Since pH_1 = constant, $k + 0.0592\ pH_1$ is also another constant.



Advantages

1. It gives a rapid response.

2. It is chemically resistant to oxidizing and reducing agents, dissolved gases, colloids and salts etc.

3. When Lithia-silica glasses are used (it can be used over the entire pH range).

Disadvantages

1. It is extremely fragile, since it contains a very thin bulb.

2. Minute abrasions on the surface of the tip, damages the electrode.

3. It cannot be used with simple potentiometers, because of high resistance.

Membrane/ Ion Selective Electrodes

The glass electrode can be modified suitably to a selective ion/ membrane electrode. The composition of the membrane is changed by adding specific ions or synthetic substances or polymers thereby the electrode can be used for measuring cations or anions. For example,

1. Cation selective glass electrode is used in the determination of H^+, Li^+, Na^+, Ag^+ or K^+.

2. Divalent cation activity electrode can be used to measure the total hardness of water (response due to calcium/ magnesium or other divalent ions) and for complexometric titrations using EDTA.

3. Heterogenous membrane or solid state electrode can be used to measure concentrations of Cl^-, Br^-, I, CN^- etc.

Potentiometric titration

Principle

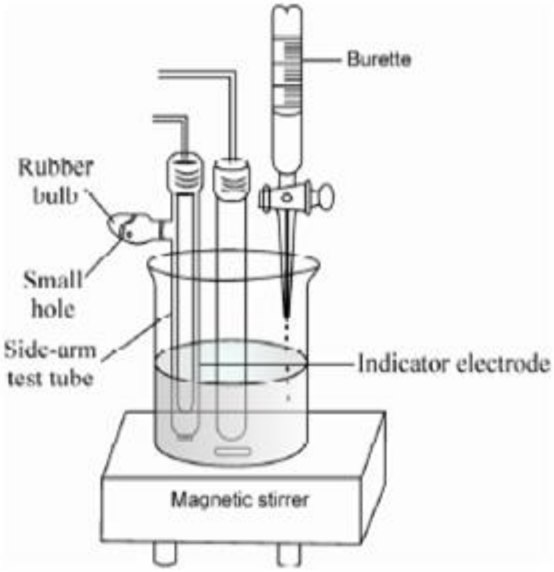
These are titrations in which the end point of titrations can be determined by measuring the potential or changes in the potential of a solution caused by the addition of titrant. Alternatively the pH can also be monitored during the titration to detect end point. In a titration, the addition of titrant causes changes in the concentration or activity of ions in solution.

Advantages

1. Coloured solutions dilute solutions or turbid suspensions can be titrated.
2. Actual potential of reference electrode need not be known since it is maintained as constant throughout the titration.
3. Titration can be automated.
4. Mixture of components can be titrated.
5. Inexpensive method with more accuracy.

Apparatus and Requirements

Titrations can be done manually or under automation. When it is done manually, a beaker with a stirrer and a pipette are sufficient. In case of automated models, a sample cell which can hold a pair of electrode, inlet for titrant and a stirrer for mixing the solution are essential. The pair of reference and indicator electrodes depends on the type of titration i.e. acid-base titration or redox titration. In most titrations, saturated calomel electrode is used as reference electrode. Only the indicator electrode varies with respect to the type of titrant.



Applications

The following types of titrations can be done by potentiometric method.

1. Acid-base titrations.
2. Redox titrations.
3. Diazotisation titrations.
4. Precipitation titrations.
5. Complexometric titrations.
6. Dead stop end point technique.

1. Acid-base titrations

Acid-base titrations can be done in aqueous as well as by non-aqueous medium.

Indicator electrode: Glass electrode

Reference electrode: Saturated calomel electrode

The potential (E) of such system is given by the following equation.

$$E = k - 0.0592 \text{ pH}$$

Where k is the asymmetry p1`otential, a constant which depends on the electrode system used.

Examples

a. Aqueous medium

i) All acid-base combinations (any strength – 0.01N, 0.1N, 1N)

Weak acid vs. Weak base e.g. CH_3COOH vs. NH_4OH

Weak acid vs. Strong base e.g. CH_3COOH vs. NaOH

Strong acid vs. Weak base e.g. HCl vs. NH_4OH

Strong acid vs. Strong base e.g. HCl vs. NaOH

ii) Mixture of acids vs. bases e.g. (CH_3COOH + HCl) vs. NaOH

Mixture of bases vs. acids e.g. (NH_4OH + NaOH) vs. HCl

iii) Poly basic acids vs. bases e.g. Citric acid vs. NaOH

e.g. Tartaric acid vs. NaOH

b. Non-aqueous medium

The same electrode system used for titration in aqueous medium is used.

Titrations

i) Weak acids vs. Potassium or lithium methoxide e.g. Barbituric acid vs. LiOMe

ii) Weak bases vs. Perchloric acid

e.g. Ephedrine Hydrochloride, Quinine sulphate, Metronidazole or Chloroquine Phosphate vs. 0.1N $HClO_4$

B. Redox Titrations

The general equation of a redox titration can be given by

$$\text{Reductant} + ne \longrightarrow \text{oxidant}$$

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

Ce^{4+} is an oxidizing agent which oxidizes Fe^{2+} (ferrous) to Fe^{3+} (ferric ion). In this process Ce^{4+} (cerric) gets reduced to Ce^{3+} (cerrous) ions.

The potential (E) of redox titration can be represented by

$$E = E^{\circ} + 0.0592/n \log [ox]/[Red]$$

Where E^0 = standard potential

N = no. of electrons involved in the reaction

[ox] = conc. of oxidant

[Red] = conc. of reductant

Reference electrode: Saturated calomel electrode or Silver-silver chloride electrode

Indicator electrode: Platinum wire or foil.

For end point detection, mV scale is used and not pH.

Examples

Ferrous Ammonium Sulphate in dil. H_2SO_4 vs. $KMnO_4$

Ferrous Ammonium Sulphate in dil. H_2SO_4 vs. $K_2Cr_2O_7$

Sodium Arsenite vs. $KBrO_3$

Ferrous sulphate in 6N H_2SO_4 vs. Cerric Ammonium sulphate

Oxidising agents like $KMnO_4$, $K_2Cr_2O_7$, Cerric ammonium sulphate, Potassium iodate and Potassium bromated in the presence of Sulphuric acid or hydrochloric acid are used as titrants for several reducing agents.

C. Diazotisation titrations

Drugs or substances containing aromatic primary amino group can be titrated against Sodium nitrite in acidic medium. As these results in the formation of diazonium salt, this type of titration is called as diazotization titrations. One method of detecting end point is by using starch iodide paper (external indicator method). The other method, better than the external indicator method is by potentiometric method of determining end point.

Reference electrode: Saturated calomel electrode

Indicator electrode: Glass electrode

Examples

Alkaloids, Amines, Sulpha drugs and other drugs which contain aromatic primary amino group can be titrated against 0.1N Sodium Nitrite in hydrochloric acid.

D. Precipitation titrations

For the quantitative determination of several ions or elements, precipitating agents are used as titrants and the end point is determined by potentiometric method. The potential of such system is given by

$$E = E^0 + 0.0592/n \log [M^{n+}]$$

Where [M] = refers to the concentration of ions.

n = electronic state

Reference electrode: Saturated calomel electrode

Hydrogen electrode

Silver – silver chloride electrode

Indicator electrode: Silver wire electrode

Examples: Determination of Mercury, Silver, Lead, Copper and several other ions using precipitants to form insoluble salts.

E. Complexometric titrations

Several metallic ions (divalent) can br titrated against disodium edetate solutions by Potentiometric method. Measurements are made in mV scale. The reference electrode used is Saturated calomel electrode or reference electrode. The indicator electrode used is Silver electrode or Mercury electrode. E.g. Divalent ions, trivalent ions.

F. Dead stop end point technique (Biamperometry)

Classical example is the determination of water (Moisture content) by Karl Fischer reagent. It contains two platinum electrodes, between which a small emf is applied. No current flows till the solution is free from polarising substances. Current flows only when both electrodes are depolarised. Normally the titrant is added through an automatic burette and at the end point the stopper gets automatically closed and titrant stops flowing. This is because there is a sharp transition in the end point between one polarised electrode and complete depolarisation of both electrodes.

POLAROGRAPHY

Polarography is that branch of Voltammetry in which changes in current, resulting from the electrolysis of the solution under study are investigated using a renewable mercury droplet as the indicator electrode (cathode).

- The anode of the electrolytic cell called the reference electrode consists of either a mercury pool at the bottom of the cell or a calomel electrode.
- Voltammetry is essentially an electrolysis carried out on a micro scale, using a micro Working electrode and is concerned with the study of voltage-current-time relationships during electrolysis under controlled application of a potential to an electro active system in an electrolytic cell.
- The analytical species in solution are capable of being reduced or oxidized reproducibly at the working microelectrode surface.
- A continuously variable potential is applied to the working microelectrode and the Flow of current is monitored. The resulting current voltage curve is called aVoltammogram.

THEORY

- The theory and technique of Polarography have been developed only long time after Palmaer used the dropping mercury electrode in 1898.
- It was only in 1922, that JaroslavHerovsky studied the characteristics of voltage- Current curves obtained in the electrolysis of substances at the dropping mercury electrode under conditions of concentration polarization.
- Later, he was awarded a Nobel Prize in 1959 in recognition of its importance.
- Polarography is an electrochemical method of analysis incorporating features of electrolysis but distinct from it.
- In electrolysis the aim is to remove completely a chosen constituent from the solution by passing an electric current through it for a sufficient length of time.
- The electrodes have relatively large surfaces and the solution is stirred to facilitate transport of electroactive material to the electrode.
- In contrast to this, the electrolysis in Polarography is of short duration and the electrode on which the constituents are placed out is a dropping mercury electrode or other micro electrode so that the currents are very small.
- Hence the changes produced by Polarography are normally (with 5 to 20ml test solution) not measurable, and the polarographic solution can be recovered virtuall unchanged.
- The electro chemical technique Polarography used in analytical chemistry, involve measurements of current-voltage curves, obtained when voltage is applied to Electrodes immersed in the solution being investigated.
- One of the electrodes is an indicator electrode .It is a dropping mercury electrode, consisting of a mercury drop hanging at the orifice of a fine bore glass capillary.
- The capillary is connected to a mercury reservoir so that mercury flows through the capillary at a rate of few milligrams per second.
- The life time of each drop is usually 3 to 5 seconds. Each drop forms a new electrode, its surface is practically unaffected by processes taking place on the previous drop.
- Hence, each drop represents a well-reproducible electrode with fresh clean surface. The second electrode is a reference electrode; its potential remains constant during the measurement.

- The potential at the indicator electrode varies in the course of measurement of the current-voltage curve, because of the change of the applied voltage.
- In view of the relative surface areas of the two electrodes, it follows that at the large auxiliary electrode the current density will be very small, while at the working electrode, it is hundreds of time higher.
- In consequence, the large or the counter electrode is not readily polarized and when small currents flow through the cell, the concentration of the ions in the electrode layer (i.e, the layer of solution immediately adjacent to the electrode) remains virtually equal to the concentration in the bulk solution and the potential of the electrode is maintained at a constant value.
- By contrast, at the micro electrode, the high current density causes its potential to deviate considerably from the equilibrium value (i.e., it assumes any potential applied to it from an external source the micro electrode is then said to be polarized) and consequently the electrode layer tends to become depleted of the ions being discharged at the electrode and if the solution is not stirred, then the diffusion of ions across the resultant concentration gradient takes place.
- The working electrode being perfectly polarisable assumes the correspondingly increasing negative potential applied to it; very small current flows in the cell until the decomposition potential is reached.
- As the cathode potential is made progressively more negative, than the decomposition potential, current suddenly commences to increase until the current approaches a steady limiting value.
- Inspite of the fact that the reducible ion in the bulk of the solution diffuses slowly towards the electrode, a point is reached where the reducible ion or compound is nearly depleted at the electrode, a further increase in e.m.f causes practically no increase in current unless a second compound able to depolarize the working electrode is present in the solution.

Half-wave Potentlal

Half-wave potential is the important constant in the polarography. The half-wave potential is defined as the difference between the total current and the residual current which is equal to the one-half of the limiting current. This is denoted by E1/2. This is obtained from the current-voltage curve which shows the inflection. This is mainly used in the identification of the substances.

The polarographic electrode reactions are divided into the following:

1. Reversible reactions.
2. Irreversible reactions.

The half-wave potential is equal to the oxidation-reduction potential.

The half-wave potential is determined by the following equation:

$$E_{app}= E_{1/2}+(0.0592/n) \log (i_d-i)/i$$

Where Eapp is the applied potential; E1/2 is the half-wave potential; n is the number electrons; i_d is the diffusion current; I is the current at the applied potential.

The following are the factors which affect the half-wave potential:

- Temperature of the analyte solution.
- Nature and concentration of the support electrolyte solution.
- Complex formation.
- Rate of electron transfer.
- Salt concentration.

CURRENT VOLTAGE CURVE (BASIS OF POLAROGRAPHY)

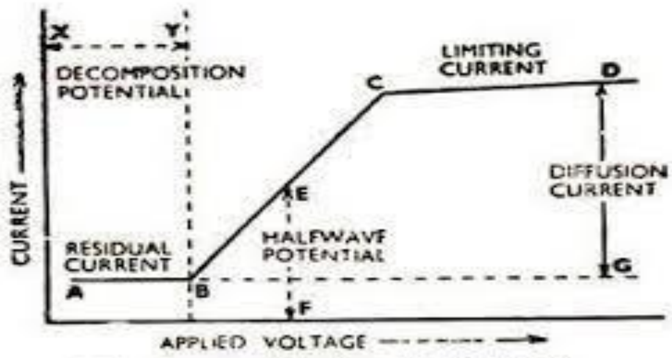


Fig. 1. Current-applied voltage curve (Polarogram)

Potentials in polarography as a convention are referred to versus Standard Calomel Electrode (SCE). The relationship used to change potentials vs SCE to the corresponding potential vs Standard Hydrogen Electrode (SHE) and vice versa is

$$E_{\text{vs}}\ \text{SCE} = E_{\text{vs}}\ \text{SHE}^{-0.242}$$

Thus we place a 10^{-3} M Cd $(NO_3)_2$ solution for its electrolysis at a microelectrode(such as DME) in a polarographic cell and apply a voltage difference between Droping Mercury Electrode (DME) working electrode and' an auxiliary electrode using a reference SCE electrode and make the microelectrode negative relative to SCE the electrode reaction will be :

$$Cd^{2+} + 2e^{-} \longrightarrow Cd \qquad E^{o} = -0.403V$$

The minimum electrode potential needed for DME to begin reducing cadmium ions 1.e, back emf required to force the reaction, may be calculated from the Nernst Equation:

$$E_{\text{vs}}\ \text{SCE} = -0.403 - 0.0591/2 \log 1/\ 10\text{-}^{3}\text{-}0.242 = 0.556V$$

This is called decomposition potential.

Consider a polarographic cell, containing a cadmium chloride, to which an external EMF is applied.

The positively charged ions present in the solution will be attracted to the dropping Mercury electrode by an electrical force, and by a diffusive force resulting from the concentration gradient formed at the surface of the electrode.

Thus, the total current following through the cell may be regarded as the sum of electrical and diffusive forces. When the applied voltage is increased and the current is recorded. The point from A to B a small current flow this known as Resudial current and is carried by supporting electrolyte and impurities present in the sample.

At point B, the potential of the electrode become equal to the decomposition potential of the Cd^{2} ion. The current then increases along the curve BC. At point C current no longer increases linearly with applied voltage but reaches a steady limiting value at point D.

After this no increases in current is observed at higher cathode potentials. Thus, the Current corresponding to the curve CD is known as limiting current. The difference between the residual current and the limiting current is called Diffusion current and is generally denoted by ia.

There are other types of polarographs also which are known as recording Polarographs. These record current voltage curves automatically.

More correctly they record current time curves. The applied voltage is increased at a Steady control rate by means of a constant speed motor, and simultaneously the Chart paper is removed at a steady rate. The recording pen moves in accordance with the current passing through the cell.Since the pen is recording current against time, the graph which it traces moves up and down as a drop from the fall. The up and down movement that accompanies drop formation can be minimized by

1.Using a recorder with a long time

2. Placing a high capacity condenser across the terminals of the recorder

FACTORS AFEECTINGTEE LIMITING CURRENT

He factors which affect the current voltage curve are as follows

1. Residual current

2. Migration current

3. Diffusion current

4. Kinetic current

Residual current

- The current is not zero when no reducible ions are present. As the mercury drop Grows, ions from supporting electrolyte gather around it.
- If the drop is negatively charged, these ions are positively charged. Consider potassium chloride solution, the potassium in it will be attracted to the drop.

- They are not reduced to potassium atoms (unless the negative potential is very high) but remain close to the mercury surface forming the electrical double layer.
- The effect is like charging up a condenser. When the drop falls off, a new drop forms and a new condenser is charged up.
- This causes a continuous flow of electric current which increases as the potential or the drop is increased.
- It is Observed that the charging current is zero at the point at which the surface tension is maximum.
- This happens at about 0.52volt negative than the calomel electrode. In this case of electrolyte containing traces of impurities, a small fradic current is also superimposed upon the condenser current.
- It is a practice to include this in the residual currect. Thus we can write

Residual current = Faradic current + Condensor current

Migration current

The electro active material reaches the surtace of electrode by 2 processes

1. The first involves the migration of the charged particles in the electric field Potential difference existing between the electrode surface and the solution.
2. The second involves the diffusion of particles.

The current required for the above two process 1s called migrationcurrent. Jaroslas. Heyrovsky proved that the migration current can be almost eliminated if an indifferent electrolyte is added to the solution in a concentration so large that its irons carry almost all the current. The following example will make the concept more clear.

Suppose a solution contains 0.1M potassium chloride and 0.01M cadmium ions. The Current is carried through the cell by all the ions presernt. The fraction of total current carried By each ion depends upon its relative concentration compared with other ions and transport number. In present case about 90% of the current will be transported to the cathode by the potassium ions. If the concentration of potassium ions is increased to more than 99% of the total cations present, the relative currents carried by other cations are reduced practically to Zero. Thus all the current through the cell will be transported by the potassium ions.

Diffusion current

- The maximum current as shown as I and Ih is known as diffusion current.
- This current is directly proportional to the concentration of the substance being Reduced are oxidized at the dropping mercury electrode. The current is given by the IIkovic equation

$$Ia=607nCD/2m2/3t1/6$$

Where, i_d=The diffusion current in microamperes average over the life time of the drop

n=Number of electrons transferred per ion

C-Concentration in millimoles per liter

D=Diffusion coefficient of the reducible ion in cm2 sec

m=Mass of mercury flowing per second in milligrams

t=Drop times in seconds,

- From the Ilkovicequation it follows that, The observed diffusion current is directly proportional to the concentration of the electro active material. This is the basis of quantitative polarographic analysis.
- The equation given by the lkovic does not take into consideration that curvature of the electrode.
- A modified equation was, theretore, given by Lingane and Loveridge which is as follows

$$i_d= 607nCD^{1/2}m^{2/3}t^{1/6}1+39D^{1/2}m^{-1/3} t^{1/6}$$

- The term in the bracket corresponds to the difference between linear and spherical diffusion.
- This correction term is not large having values 2 to 6% of the total current. This equation is generally used for accurate work.

Kinetic current

- The limited current may be affected by the rate of non-electrode reaction called the Kinetic current.
- The kinetic current will be proportional to the rate constant and to the volume of the interface and therefore, is a direct function of size of the mercury drop but is independent of the velocity of the flow of mercury from the capillary.
- This current results if the oxidized or reduced form, of electro active species, is involved in a chemical equilibrium with the other substances.
- It means that these are rate processes; therefore, the current resulting from those is called the kinetic current.

DROPPING MERCURY ELECTRODE (DME)

- In aqueous solution DME vs SCE (Saturated calomel electrode) used over the range +0.3 to-2.8V.
- In polarography, potential EDME is measured as well as reported against the SCE. At potential more positive than 0.3V, Hg is oxidized and produces an anodic wave.
- The most positive potentials may be obtained in the presence of noncomplexing anions which give soluble Hg () and Hg(II) salts such as NO_3^-or ClO_4 ions.
- The anions which produce insoluble mercury salts or stable complexes shift the anodic dissolution potential to more negative values.
- At potentials more negative than -1.2V, the evolution of H_2 occurs visibly in IM HCL solutions and at 2.0V, the usual supporting electrolytes of alkali salts start discharging.
- The most negative potentials are produced in solution in which a quaternary ammonium hydroxide is the supporting electrolyte, e.g. with $(C_4H_9)_4$ NOH, a negative potential, -2.7V may be attained.

Advantage of DME:

1. The surface area exposed to the solution is reproducible With any given capillary and is continually renewed with fresh HHg and thus removes passivity or poisoning effects of the surface.

2. A new metal surface is generated continuously, which makes the behavior of the DME independent of its previous history. Thus each Hg-drop formed is unaffected by the reactions which took place at the surface of the previous drop.
3. Mercury readily forms amalgams with most of the metals. The amalgam formation lowers the activity of the metal, thereby facilitating the reduction of the metal ion.
4. The unusually high over voltage of Hg associated with the reduction of H^+ ions makes the analyses to be carried out in acid solutions. Thus metal ion such as Zn^+ and Cd2+ can be deposited from acidic solutions, although their thermodynamic potentials suggest that deposition of these metals without H_2 formation is impossible.
5. A reproducible average current is generated instantly on changing the applied potential. In other words the diffusion current is rapidly attained (reproducible) at the Hg- solution interface.

Disadvantage of DME:

1. The surface area of the Hg- drop is never constant.
2. An important disadvantage of the DME is the magnitude of the residual current. A part of this may be faradic, resulting from the impurities present in trace levels such as oxygen or easily reduced metal ions.
3. Changes in the applied voltage produce changes in the surface tensions of Hg and hence changes in the drop size occur.
4. The addition of surface active reagents such as gelation or Triton X- 100 etc., produces changes in the size of the Hg-drop and the adsorption of surface active agents can interfere with the electrode reactions.
5. The toxicity of mercury may prove harmful for certain biological studies.

Precautions:

1. The DME is used in first time, an extremely clean, dry and dust free tubing glass Reservoir, capillary and metallic Hg, triple distilled Hg should be used.
2. When not in use, the tip of the capillary is kept immersed in water so that the traces of dust do not reach the tip, which cause capillary to behave erratic. The tip of the capillary, if how

some has become impurity affected, it should be dipped under 50% HNO_3 and then washed several times with distilled water before experimentation.

3. The Hg- reservoir must not be lowered unless the tip of the capillary has been perfectly washed and immersed in water. When the Hg-reservoir is lowered, it should be in such a position that the mercury just stops flowing.
4. The end of the capillary becomes dirty after a long use. It is cleaned by immersing it periodically in 50% (v/v) $HNO_3$with the mercury flowing and then washing perfectly with a jet of water.

ROTATING PLATINUM ELECTRODE

- The dropping mercury electrode cannot be used at markedly positive potentials (say, above about 0.4 volt us S.C.E.) because of the oxidation of the mercury.
- By replacing the dropping mercury electrode by an inert platinum electrode, it was hoped to extend the range of polarographic work in the positive direction to the voltage approaching that at which oxygen is evolved, namely, 1.1 volts.
- The attainment of a steady diffusion current is slow with a stationary platinum electrode, but the difficulty may be overcome by rotating the platinum electrode at constant speed: the diffusion layer thickness is considerably reduced, thus increasing the sensitivity and the rate of attainment of equilibrium.
- Difficulties, however, arise in obtaining reproducible values for the diffusion currents from day to day, but nevertheless, it is suitable as an indicator electrode in Amperometric titrations.
- The larger currents (about 20 times those at the dropping mercury electrode) attained with the rotating platinum electrode allow correspondingly smaller currents to be measured without loss of accuracy and thus very dilute solutions (up to 0.1 – 4M) may be titrated.
- In order to obtain a linear relation between current and amount of reagent added, the Speed of stiring must be kept constant during the titration: a speed of about 600 revolutions per minute is generally suitable.

- The electrode is constructed from a standard ‘mercury seal. About 5 mm of platinum wire (0.5 mm diameter) protrudes from the wall of a length of 6 mm glass tubing. The latter is bent at an angle approaching a right angle a short distance from the lower end.
- Electrical connection is made to the electrode by a stout amalgamated copper wire passing through the tubing to the mercury covering the sealed-in platinum wire; the upper end of the copper wire passes through a small hole blown in the stem of the stirrer and dips into mercury contained in the ‘mercury seal.
- A wire from the latter is connected to the source of applied voltage.
- The tubing forms the stem of the electrode, which is rotated at a constant speed of 600 revolutions per minute (r.p.m).

Advantages over DME

1. Rotating electrode decreases the thickness of the diffusion layer by increasing the sensitivity; steady diffusion state is also reached fastly.
2. It can be used upto +0.9V vs SCE
3. The charging current produced by the detachment of Hg-drop in DME is eliminated.
4. Because of large currents (20 times greater than DME), very dilute solutions (10^{4+} M) may be treated with such an electrode. Further, the residual current with this electrode is reduced largely.

INSTRUMENTATION

The main parts of a polarographicanalyser are:

1. The polarographic cell

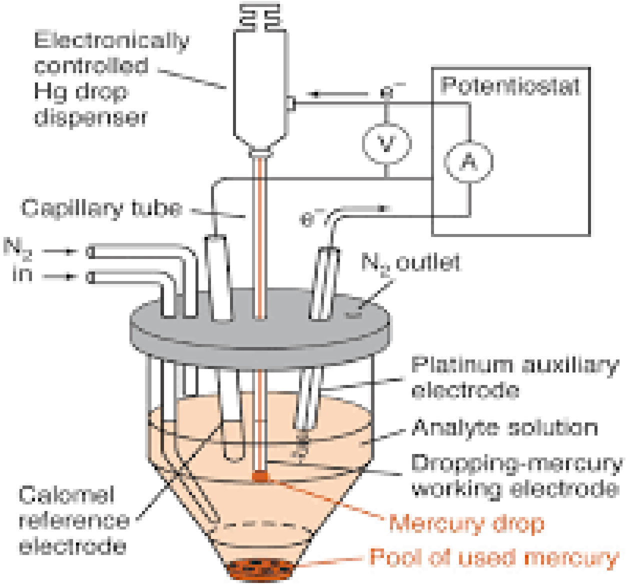
2. The potentiostat

3. PC with the application software

- The polarographic cell is a glass or teflon vessel in which are inserted a tube for the bubbling of nitrogen and three electrodes:
- The working electrode A capillary connected with a mercury container or a solid electrode.

- The reference electrode- A simply Ag/AgCl, saturated KCI electrode.
- The auxiliary electrode-A platinum wire inserted on a teflon rod.
- The stirring of the sample solution is allowed by a magnetic stirrer and a magnetic rod.
- The potentiostat allow imposing the desired potential scanning between working and reference electrodes while the current flowing in the circuit is recorded between working and auxiliary electrodes.
- The PC is interfaced to measuring system and the software has the following functions

1. Send to the potentiostaticanalyser the scanning parameters
2. Check if the execution of the scanning is correct or not
3. Handle the output data (current and potential).



Types of Polarography

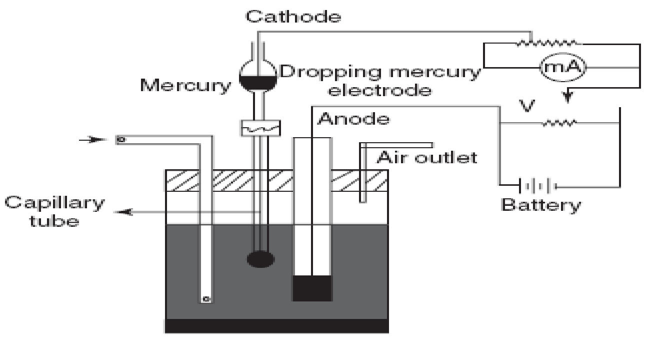
There are several types of the polarographic methods but the important types are the following

1. Rapid direct current polarography: In this, the mercury drop rhythmatically falls from the electrode.
2. Sampled direct current polarography: Initially the potential is increased and maintained constantly throughout the process.

3. Pulse polarography: The potential pulse is imposed at the end of the process. These are of two types:
    A. Differential pulse polarography.
    B. B. Normal pulse polarography.

Apparatus and the Methods

- The apparatus consists of a dropping mercury electrode which acts as a cathode and as a working electrode.
- The anode used is the pool of mercury at the bottom of the reservoir which acts as a reference electrode.
- The reference electrode potential is constant. These two electrodes are placed in sample solution which contains the both anions and cations.
- Then these anode and cathode are connected to the battery, voltammeter and the Galvanometer.
- Then apply the constant voltage and record the current-voltage curves using recorders. The sample cell is made of glass with tapering edge to place the mercury.
- The cathode capillary is dipped into the sample solution by setting the drop time of about 2-7 s.
- To control the movement of the ions to the surface on the electrode, the supporting electrolytes such as saturated potassium chloride solution are used.
- The oxygen present in the sample solution is removed by the alkaline pyrogallol solution.
- The determined diffusion current is directly proportional to the concentration of the sample solution.



APPLICATIONS

Every oxidizable or reducible substance that can be dissolved in an appropriate solvent can be analysed by Voltammetry, using appropriate conditions (supporting electrolyte, kind of electrode, scanning technique and scanning parameters) for its discharge. The Application field of the voltammetric techniques is the trace analysis of heavy metal in several different matrix like water, food, soil, air, industrial product, pharmaceutical, biology and so on.

Example:

1. Inorganic anions detectable with voltammetric techniques.

i. Cl-,ClO-, ClO_2, ClO_3^-, Cl_2, Br^-, I, $1O_3$, I_2

ii. S_2^-, SO_3^{2-}, S:OP, SCN, $S_2O_8^{2-}$

ii. NO_2^-, NO_3^-

iv. PO_4^{3-}

v. SiO_3^-

vi. CN^-

vii. BO_3

2.Main functional organic groups detectable with voltammetric techniques

Double Bond	**Triple Bond**
Aromatic	Alcohols, Phenols, ether
Aldehyde and Ketone	Quinones and quinhydrones
Conjugated Carboxylic Acid	Aromatic Carboxylic acids
Sulphides and disulphides Sulphonic salts	Thiocyanates
Sulphonates	Chloride,Bromide and Iodide Etherocycles
Organometallic Peroxides	Imines, Oximes nitriles Nitro, nitroso compounds Diazo compounds Amines

Qualitative Analysis

Voltammetry is not dedicated to the quantitative analysis. In fact the peakpotential or the Half wave potential can vary depending on the sample matrix, the type of supporting electrolyte and on the presence of chelating reagents. When necessary the presence/absence of an analyte is proved by the enrichment technique,namely, by adding an aliquot of Standard solution.

Quantitative Analysls

Quantitative analysis is than performed considering the peak (or wave) height and using the (Single or multiple) standard addition method. This is in fact the best method for lowering the matrix interference. When the sample matrix is very simple or reproducible the Calibration curve methods could be used.

MULTIPLE CHOICE QUESTIONS

1. **In polarography, when the limiting current is achieved, Which one of the following processes takes place.**
   - A) The rate of electron transfer just matches the rate of mass transfer.
   - **B) The rate of electron transfer is slower than the rate of mass transfer.**
   - C) The rate of electron transfer becomes independent of the rate of mass transfer.
   - D) The rate of electron transfer far exceeds the rate of mass transfer.
2. **Which one of the following is used as an indicator electrode in polarography**
   - A) Glass
   - **B) Dropping Mercury**
   - C) Platinum
   - D) Silver
3. **Ilkovic equation in Polarography D^2 cm^2 is**
   - A) id=706n $D^{1/2}$ cm$^{1/2}$ $t^{1/3}$
   - B) id=706n$^{1/3}$ $t^{1/3}$
   - **C) id=607n CD$^{1/2}$ m$^{2/3}$ t$^{1/6}$**
   - D) id=607n $D^{1/2}$ cm$^{1/3}$ $t^{2/3}$
4. **For Qualitative analysis by polarography, characteristics parameters used is**
   - A) Diffusion current
   - **B) Half wave potential**
   - C) Voltage
   - D) None of the above
5. **Limiting current is sum of diffusion current and**
   - A) Residual Current
   - **B) Faradic Current**
   - C) Migration Current
   - D) Additional Current
6. **Gradual rising in current in polarography is called**

A) Weak Current
B) Higher Current
C) Migration Current
D) **Residual Current**

7. **Use of mercury as a microelectrode in polarography is due to**
    A) Reproducible surface area with any given capillary
    B) Mercury forms amalgam with many metals
    C) Mercury may be early oxidized
    D) Both a,b and c
8. **Reason for generationof migration current in poalrogram is**
    A) Migartion of diffusion of charged particles
    B) Migration of charged particles
    C) Diffusion of charged particles
    D) None of the above
9. **The D and L isomeric form can be distinguished by**
    A) Polarimetry
    B) Refractrometry
    C) Potentiometry
    D) Conductometry
10. **Sodium vapour lamp used in Polarimeter emits light of wavelength(in Angstorm)**
    A) 5890 &5896
    B) 4368 & 4916
    C) 5770 & 5791
    D) 5461 & 4368

SHORT ANSWER QUESTION

1. What is Polarography?
2. Define half wave potential
3. Write about the parts of the apparatus used for the polarographic analyaser
4. What are the different type of current?
5. Give Ilkovic equation

6. What is diffusion current?
7. Write any two advantages of Dropping mercury electrode.
8. What are the different types of polarography

LONG ANSWER QUESTIONS

1. Explain the working principle of dropping mercury electrode?
2. Add a note on different types of current.
3. Explain about the working of Rotating Platinum electrode.
4. Write the applications of Polarography