Chapter ... 14

POLAROGRAPHY

♦ LEARNING OBJECTIVES ♦

- To understand the principle, instrumentation, working and applications of polarography.

14.1 INTRODUCTION

The polarographic method of analysis has been developed by Jaroslov Heyrovsky, a Czech chemist in 1922, who received Nobel prize in chemistry in 1952. Since then, this method has acquired immense importance in analytical chemistry for determination of metal ions and other electroactive organic compounds.

The term polarography is applied to the current voltage curves when dropping mercury electrode is used as an indicator electrode. This method comes under the category called as voltammetry, which is a general term used for all current voltage methods using micro-electrodes.

Polarography is essentially an electrolysis on a microscale for the solution of substances in a concentration range of 10^{-6} to 10^{-2} M. The method is based upon study of the current-voltage relationship by using polarographic apparatus. If a steadily increasing microvoltage is applied to a solution in a polarographic cell having a saturated calomel electrode or large mercury as an anode and dropping mercury electrode as a cathode, it is possible to obtain a current-voltage graph. The nature of graph (also known as polarographic wave) gives an idea about the nature and amount of material present in the solution. Thus, qualitative and quantitative analysis of substance is possible provided the substance under study is capable of undergoing cathodic reduction or anodic oxidation.

In polarography, dropping mercury is used as an indicator electrode. The reaction occurs at its surface. It is considered to be a polarised electrode. An electrode is called as polarised when it adopts a potential impressed upon it with no change of current. Once a chemical reaction has occured on the surface of electrode, it becomes depolarised. A large pool of mercury placed at the bottom of polarographic cell is a reference electrode. It is incapable of

being polarised. This type is called as non-polarizable electrode in which the potential is independent of the current flowing.

14.2 PRINCIPLE

Polarography is the study of the current voltage relationship using polarographic apparatus. Let us consider a typical polarogram for a solution containing 10^{-3} M Pb^{+2} in 1 M KCl (as supporting electrolyte) and applying increasing negative potential. The 'polarographic wave' as shown in the Fig. 14.1 is obtained.

It will be seen that initially there is a very small gradual rise in the current between A and B. It is known as residual current (i_r). Though no electrolysis process takes place before the applied potential upto B, no current should flow through the galvanometer. The small background current which is usually observed is known as residual current. It is sum of faradic current (i_f) and condenser current (i_c).

$$i_r = i_f + i_c$$

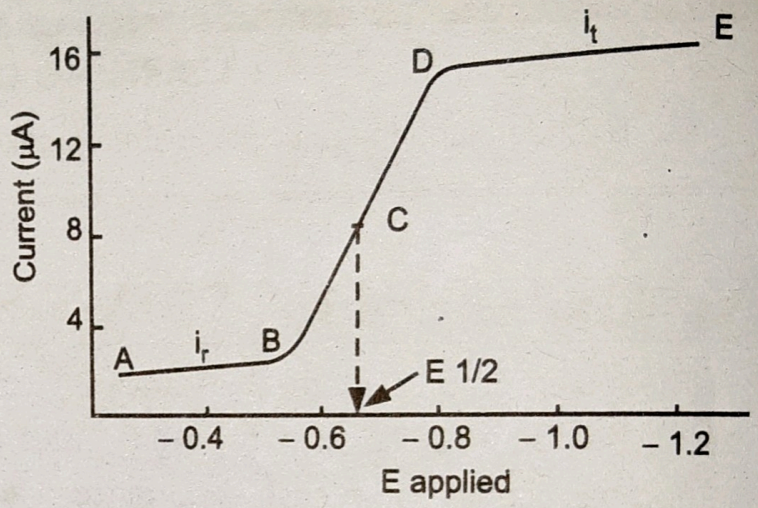

Fig. 14.1

The faradic current (i_f) is attributed to the reducible impurities present in the solution and condenser current because of the charge of each drop of mercury which it carries when it falls in the solution resulting in the formation of helmholtz double layer of positive and negative charged ions. This background or residual current should be deducted for diffusion current measurements. At point 'B' which corresponds to the decomposition potential of the electrolyte (Pb^{+2}) electrolysis commences and ions (Pb^{+2}) move to the electrode surface of DME and get reduced $Pb^{+2} + 2e = Pb^{o}$. At potential between – 0.3 V and – 0.5 V the current increases rapidly because more number of lead ion from the solution carries current. The ions get reduced to metal lead that forms an amalgam with the mercury of DME. In the region of the polarographic wave, the electrode becomes depolarised. It obeys the Nernst equation. The current which flows is the result of reduction of lead ion to give appropriate ratio of [Pb amalgam] / [Pb^{+2}] at the electrode surface.

At a point 'C' the corresponding voltage is half-wave potential ($E_{1/2}$). At this point, the concentration of oxidised and reduced forms at electrode surface is equal (Pb^{+2}) = (Pb^{o}). This potential is characteristic of the nature of reducing substance and is used for identification of unknown substance.

The straight line DE is known as limiting current (i_l) or diffusion current (i_d) in absence or presence of supporting electrolyte used. At the point 'D' electroreducible substance is reduced as rapidly as it reaches the electrode surface. Depending upon the concentration of reducing species (Pb^{2+} ions) the limiting stage of current is reached.

The reducible ions are supplied to the electrode surface by two independent forces:

1. a diffusion force which is proportional to the concentration gradient of ions at electrode surface and bulk of solution (i_d) and
2. electrical force which is due to the opposite electrical charge of ion. This is also called as electrical migration (i_m).

Thus, $i_l = i_d + i_m$

If a sufficient quantity of inert electrolyte (which is known as ground electrolyte or supporting electrolyte) is added to the solution under study the influence of electrical migration is reduced to zero ($i_m = 0$) then limiting current (i_l) becomes diffusion current (i_d). $i_l = i_d$. Thus, at potentials between – 0.5 to 0.9 V the current is limited by the rate of diffusion and is called as diffusion current (i_d).

The substance reducing at the electrode moves only through a thin diffusion layer because of concentration gradient and not because of electrical migration (attraction). No further increase in current beyond point E is observed unless there is another electrolyte undergoing reduction at higher applied voltage. For example, analysis of solution of lead 10^{-3} M and zinc 10^{-3} M concentration in 0.1 M KCl is shown in Fig. 14.2.

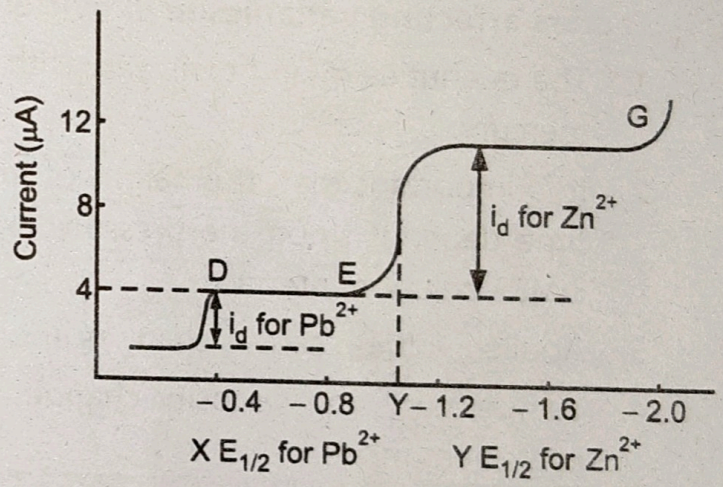

Fig. 14.2

The first wave on the polarogram is the reduction of lead ion to form lead-mercury amalgam $Pb^{2+} + 2e^- \rightarrow Pb - Hg$ (amalgam). The second wave is the reduction of zinc ion to metal zinc which also forms amalgam with mercury of DME.

$$Zn^{2+} + 2e^- \rightarrow Zn - Hg \text{ (amalgam)}$$

Between the points D and E no further increase in current occurs until the impressed voltage exceeds the decomposition potential of zinc ions (– 1.0 V). Finally, current rises (after G) near – 2.0 V caused by the reduction of potassium ion used as supporting electrolyte.

For the reducible ions, often part of its charge gets reduced and the product is capable of further reduction at higher potential. This gives two steps polarogram.

For example,

$$Cr^{3+} + e^- \rightarrow Cr^{2+} \quad \ldots (14.1)$$

$$Cr^{2+} + 2e^- \rightarrow Cr \quad \ldots (14.2)$$

Ilkovic Equation: The diffusion current at the DME is given by Ilkovic equation :

$$i_d = 607\ n\ D^{1/2}\ c\ m^{2/3}\ t^{1/6}$$

where i_d = the average diffusion current during the life of drop, in amperes.

607 = a constant of various numerical factors including π, the Faraday constant, density of mercury etc.

n = the number of electrons involved in the electrode reaction.

D = the diffusion coefficient of the substance in cm^2/sec.

c = the concentration of the substance in m.moles/litre.

m = the rate of mercury flowing through the capillary in mg/sec;

t = the drop time in seconds.

The Ilkovic equation holds for drop time of about 2 to 8 seconds. For this, adjustment of capillary length and mercury pressure is made to bring the drop time within the range. Accordingly, with all other factors as constant (of drop assembly) i_d is proportional to the concentration or $i_d = kc$ wherein k = overall constant. The linear relationship fails when drop time is too short (fast falling) or too slow or when there is a stirring effect.

Factors affecting variables in Ilkovic equation:

1. The quantities m and t will vary with the capillary, its length and with the pressure of mercury.
2. It is important that, the height of mercury column remains constant since the drop time depends upon the pressure exercised by the column of mercury at the tip of DME - solution interface.
3. Applied voltage causes changes in the surface tension, a drop at the tip of electrode.
4. Temperature and viscosity changes should be minimum since it disturbs diffusion coefficient most.

14.3 THE POLAROGRAPHIC APPARATUS

A typical polarographic apparatus is shown in Fig. 14.3.

There are two main units of polarographic apparatus, a polarographic cell and an electrical instrument. Polarographic cells are of numerous types and different forms are available commercially. Simplest one consists of a beaker type of glass cell with a lid. A large pool of mercury at the bottom of cell has an electrical connection. This mercury electrode acts as an anode terminal. The lid has glass bend tubes for passing nitrogen gas and tip of dropping mercury electrode.

The dropping mercury electrode (DME) consists of a dropping funnel for mercury reservoir (about 100 ml capacity). It is connected to capillary tube of fine bore. The connection is made either by using heavy walled rubber tubing of about 80 cm long or by Neoprene tubing. The effective glass capillary tube has a length of about 5-10 cm and a bore diameter of about 0.05 mm. The outer diameter of capillary tube may be of 6-8 mm. The tip of capillary is cut fine and horizontal. The overall adjustment of DME is such that with a pressure of about 50 cm of mercury produces a drop weighing about 6-10 mg in a full time of 3-6 seconds.

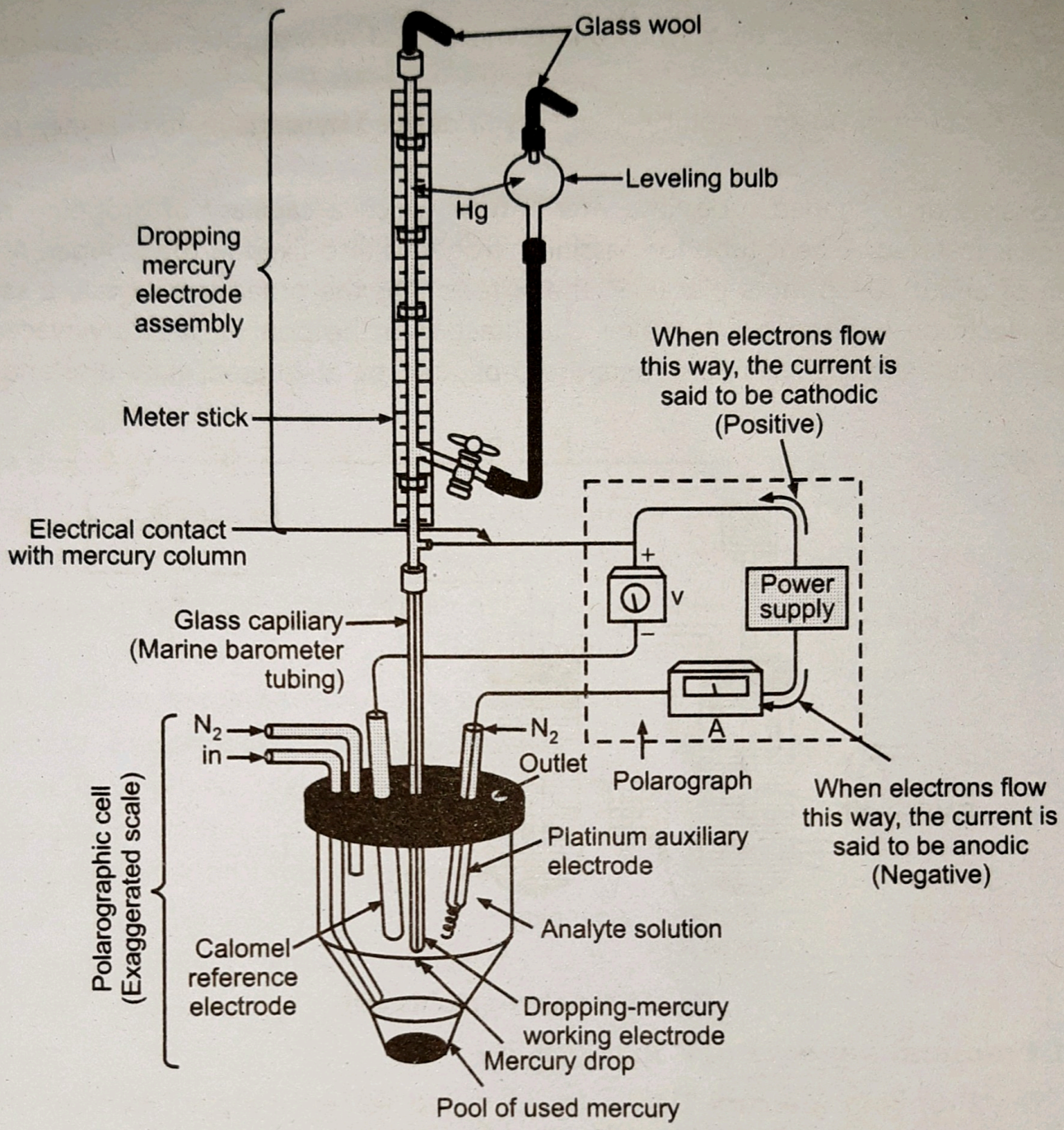

Fig. 14.3: Dropping mercury electrode

The DME is fitted to the cell and the cell is mounted on a heavy stand on a platform free from vibrations. The instrument part consists of standard power supply from a battery, a variable potentiometer, emf indicating voltmeter and a galvanometer for measuring current.

A solution to be analysed along with solution of ground-inert electrolyte and maxima suppressor is placed in the cell. The anode and cathode are joined to the positive and negative terminals of a potentiometer slide wire. This enables a variable potential difference to be applied between the anode and cathode which is indicated by a voltmeter (V). The current flowing through the cell is indicated by the galvanometer (G). Air from the cell is driven off by passing a current of nitrogen before the measurement of current-voltage is made. The record of current-voltage (known as polarogram) is obtained by slowly increasing the applied voltage and measuring the current. In modern instruments, the applied voltage is

supplied at a constant rate by a synchronous motor and record obtained on an automatic recorder.

The other form of polarographic cell of H-type deviced by Lingane and Laitinen is shown in Fig. 14.4.

It consists of H shaped tube, into one arm of which a capillary of dropping mercury electrode is inserted. A bent tube for passing nitrogen is also fixed in the stopper. A sample solution of about 10–50 ml is placed in the H tube into the other arm of cell, a saturated calomel electrode is fitted which makes a contact with the pool of mercury placed at its bottom. The two arms or compartments are separated by a sintered glass disc and a agar plug.

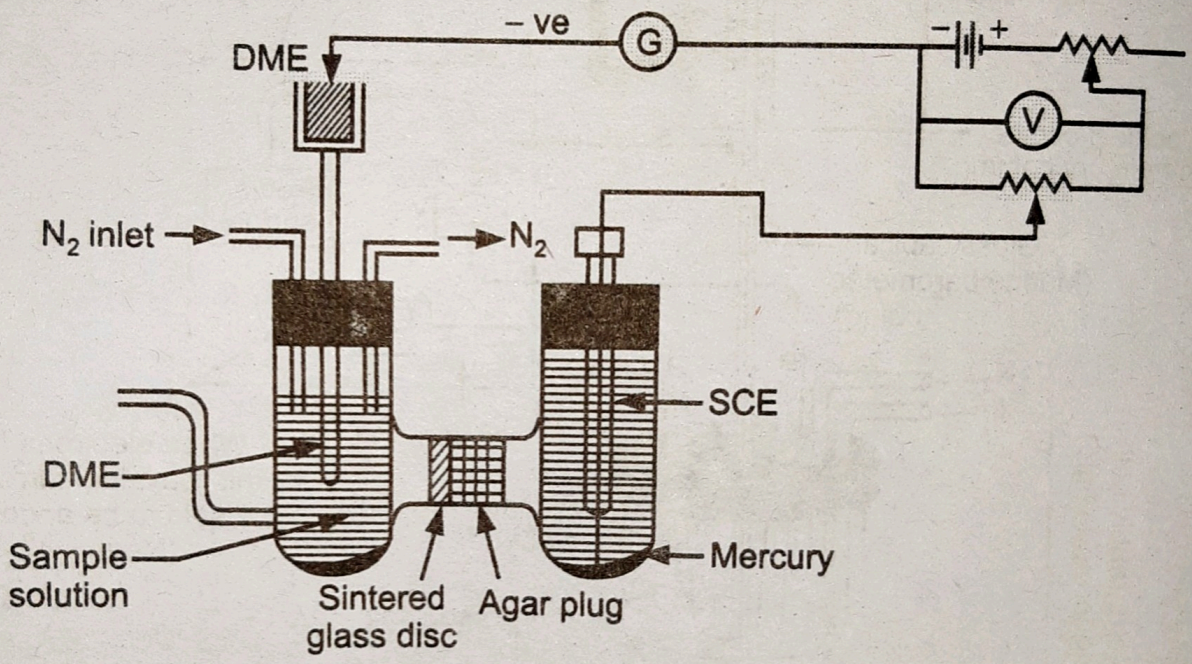

Fig. 14.4: Polarographic cell

14.3.1 Practical Aspects of Polarography

1. The Dropping Mercury Electrode: As stated earlier dropping mercury electrode (DME) is used as an indicator electrode for its unique nature.

Advantages of DME:

(i) It provides a smooth, fresh surface for the reaction.
(ii) Each drop remains unaffected and does not become contaminated by the deposited metal.
(iii) Mercury forms amalgam with most metals.
(iv) Mercury has a high hydrogen overvoltage.
(v) Diffusion equilibrium is readily established at mercury-solution interface.

Disadvantages of DME:

(i) Surface area of a drop of mercury is never constant.
(ii) Applied voltage produces changes in surface tension and hence change in drop size.
(iii) Mercury has limited applications in analysis of more positive potential range; and
(iv) Mercury is poisonous so care should be taken in its handling.

Precautions:

In using dropping mercury electrode following care should be taken.

(i) The DME assembly should be mounted vertical on a heavy stand to be free from vibrations.

(ii) Tip of DME should be always immersed in water when not in use.

(iii) Tip of DME should be cleaned by dipping in 50% nitric acid.

(iv) It is essential to use clean and dust free tubing while setting the DME.

(v) Pure and triple distilled mercury should be used in DME.

(vi) There should be sufficient mercury in reservoir so that the pressure changes are negligible.

The Supporting Electrolyte : The role of supporting electrolyte in polarographic analysis is to eliminate the influence of electrical migration on the reducing ions. The high concentration (10 to 20 times that of ions under study) of inert supporting ions eliminates the attraction or repulsion forces between the electrode and the analyte. The inert electrolyte ions are not electrolysed at the applied potential range. Potassium chloride, potassium nitrate or sodium chloride solutions are often used for this purpose.

Maxima Suppressors: In the polarographic studies, it is observed that instead of S-shaped polarographic wave there is a distortion. The wave shows a sharp peak or a rounded hump as shown in Fig. 14.5.

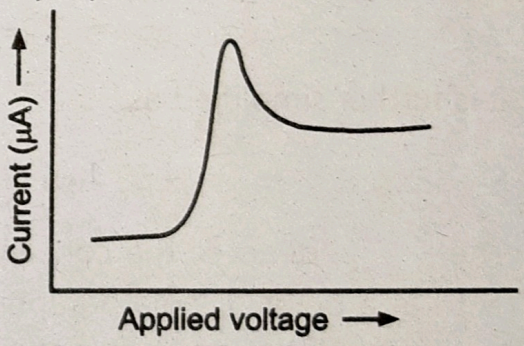

Fig. 14.5

(1) 0.001 M lead nitrate solution (without suppressor) with 0.01% gelatin as maxima suppressor.

This is known as polarographic maxima. The maxima phenomena is not completely understood. It is believed to be related to the phenomena of electrostatic stirring of the electrode surface and adsorption. The maxima can be suppressed by adding a small amount of surface active substance such as gelatin or agar in 0.005 % or using Trition x-100 in 0.002%. These substances are known as maximum suppressors. They are supposed to form a adsorbed layer on aqueous side of mercury solution interface which resists compression. This prevents maxima. Care must be taken not to add too much of maxima suppressors otherwise diffusion current may be suppressed.

Removal of Oxygen: Dissolved oxygen in water is reduced in two steps, first to H_2O_2 and then to H_2O. In the first step in acidic conditions $O_2 + 2H^+ + 2e \rightarrow H_2O_2$ occurs at about − 0.1 V. In the second step, reduction takes at 0.09 V,

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$$

The interference of oxygen is eliminated by bubbling high-purity nitrogen through the solution for 5 to 10 minutes. A nitrogen atmosphere is maintained above the solution in cell while the polarogram is run.

In alkaline conditions reduction occurs as under :

$$O_2 + 2H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$$

$$H_2O_2 + 2e^- \rightarrow 2OH^-$$

Reference Electrode: A large pool of mercury at the bottom of cell is a anode and acts as reference electrode. Often saturated calomel electrode (SCE) is also used as reference electrode by connecting to the pool of mercury. This provides an accurately known potential of 0.245 mV. The potential (in mV) of polarised DME (E_m) at mercury solution is given by expression.

$$E_m = E_{ref} - (V - iR)$$

where E_{ref} is the potential of reference electrode (0.245 mV). V is the applied potential, i is current flowing through cell and R is the resistance.

Half-Wave Potential: Qualitative analysis by polarography is based on the 'Half wave potential' known as $E_{1/2}$ which is the potential at a point on polarographic wave where the current is one half of the diffusion current for a given substance.

Let us consider the reversible reduction of oxidant (metal ion) at the DME. This may be written as

$$E = E^\circ + \frac{RT}{nf} \log \frac{[OX]_o}{[Red]_o} \quad \text{... (14.3)}$$

It is further simplified as:

$$E = E^\circ + \frac{0.0591}{n} \log \frac{[OX]_o}{[Red]_o} \quad \text{... (14.4)}$$

The $[\quad]_o$ denotes the concentration of oxidant or reductant at electrode surface. The current i at a point of polarographic wave is determined by the rate of diffusion of oxidant from bulk of solution to electrode surface under the concentration gradient

$$[OX] \rightarrow [OX]_o \quad \text{... (14.5)}$$

Thus,
$$i = k\left([OX] - [OX]_o\right) \quad \text{... (14.6)}$$

where k includes capillary characteristic and n, m and t terms of Ilkovic equation as constant.

When $[OX]_o = 0$

$$i = k\,[OX] = i_d \frac{1}{2} \quad \text{... (14.7)}$$

Now, if reductant is water soluble or soluble in mercury (forming amalgam) its concentration at electrode surface is given by $[Red]_o \rightarrow [Red]$ under concentration gradient.

Thus,
$$i = k\,[Red]_o \quad \text{... (14.8)}$$

Since [Red] is zero, now if

$$i = i_d \frac{1}{2} \text{ as per the Halfwave-potential}$$

the equation becomes

$$E = E^\circ + \frac{0.0591}{n} \log \frac{\left(i_{d_{(1/2)}}\right)}{\left(i_{d_{(1/2)}}\right)} \quad \text{... (14.9)}$$

or $$E = E_{1/2} + \frac{0.0591}{n} \log \frac{\left(i_{d_{(1/2)}}\right)}{\left(i_{d_{(1/2)}}\right)} \quad \ldots (14.10)$$

Thus, the potential at point i when the diffusion current is half known as $E_{1/2}$, the concentration of oxidant and reductant at this point remains equal. This potential is a characteristic of electro-reducible species and remains constant and is used for its identification.

2. Rotating Platinum Electrode:

Initially Kolthpff and Harris described a specific argentometric titration of mercaptans with silver nitrate using a rotating platinum electrode in 1946. That titration was employed for the determination of sulfhydry group. Later in 1948 Benesch and Benesch and Werssman et al in 1950 had modified this method in order to determine sulfhydryl groups in amino acids, proteins and in serum respectively. In those methods, satisfactory electrical contact was not made with the rotating platinum electrode when operating at high speeds. Frank J. Herbert and Jack R. Denson in 1952 proposed another type of rotating platinum electrode to overcome the difficulties of previously reported methods. In this alternative method, they demonstrated a modified RPE in which the motor is not completely insulated from the electrode, thus electrical interference results.

Construction:

According to the initial design proposed by Kolthpff, a vertical steel shaft is attached to a motor shaft. A platinum wire is attached into this shaft at right angle. A motor was used to rotate the shaft into a mercury pool kept at the bottom. A rigid side arm was attached to the shaft using a clamp system into a stone wall. This arm set up is used to maintain the shaft rigidly. The electrical contact to the platinum wire is made via the shaft through the side flanges. Ceresin was used to insulate the shaft which was scraped away from the wired to provide the platinum electrode surface. However, this electrode has the disadvantage that satisfactory electrical contact was not made with the rotating platinum electrode.

Hence, in later stages a modified version of RPE was designed by Frank and Jack. This version consists of two parts.

1. A glass well
2. A glass tube with a bell shaped rotating top.

The glass well is a fixed tubing that measures 40 mm and 16 mm diameter. A 8 mm tubing acts as a side arm which has a 20 mm length of platinum wire sealed through the end. The electrode is made from pyrex tubing, the inside diameters of which are 8 mm and 28 mm. At the bottom of the electrode, a platinum wire is sealed and extends to the outer edge of the bell. The platinum wire is fastened with household cement to the side of the bell, and a portion is allowed to be is contact with the mercury. The mercury bath is filled to a height of 6 to 10 mm. The glass bell is placed upto a depth of not more than 3 mm into the mercury in order to prevent excessive splashing of mercury at high speeds.

The top of the well is fitted with large cork and the inside walls of the two small corks are fastened permanently to the glass well. All corks are covered with cement to give a smooth surface. The upper small cork should extend above the glass wall and slope outward to provide a run off for any mercury that splashes up inside the bell. To prevent the electrode from wobbling at high speed the glass electrode is fitted loosely into the two small corks but with no more than 1/32 inch clearance. An electric power-driven variable speed laboratory stirrer was used with this electrode. It is important to realize that the three corks play a leading role in the operation of this electrode. The corks should be aligned and the electrode tested by hand before attaching it to the motor. The glass well is clamped to the same stand as the stirrer. A short piece of rubber tubing connects the glass tubing of the electrode to the shaft of the motor. Minor adjustments may then be necessary for efficient operation of the electrode. A short tube of paper extends from the top cork in order to stop the mercury from creeping out of the well. A glass bead near the platinum wire protects it from being broken off. Once the electrode is in operating position it need not be removed except for repairs.

Oxidized mercury will form on the inside wall of the well and on the bell but it has not been found to interfere with the function of the electrode. The electrode could be operated at speeds from 100 to 1200 rpm for long period of time.

Advantages:

1. RPE can measure the micro concentration of ion due to its larger diffusion current which is 20 times larger than DME
2. The positive potential of the rotating platinum electrode can be used up to + 0.9 against the +0.4 volt to −2.0 Volt of DME.
3. The construction of RPE is very simple compared to DME and it has rapid steady diffusion state.

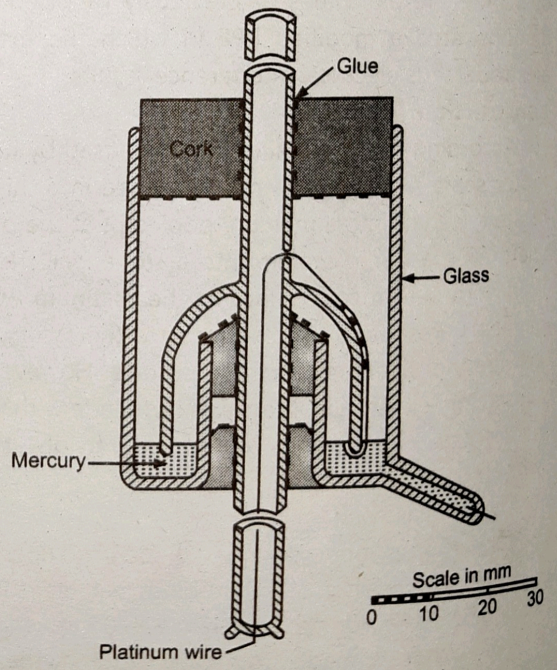

Fig. 14.6: Rotating platinum electrode

14.3.2 Measurement of Waveheights

For the quantitative evaluation of polarogram precise measurement of the height of each wave need be carried out. With the smooth polarographic wave the residual current plateau and limiting current plateau are almost parallel and measurement of diffusion current is simple. Subtracting the residual current from the limiting current by extrapolation of lines gives the measure of diffusion current. For measurement of wave height of diffusion current an extrapolation method as shown in Fig. 14.7 is carried out. As shown in the Fig. 14.7 the lines are constructed on the graph of current-voltage to find a point F for determining half wave potential. The height G for the diffusion current is also determined for quantitative work.

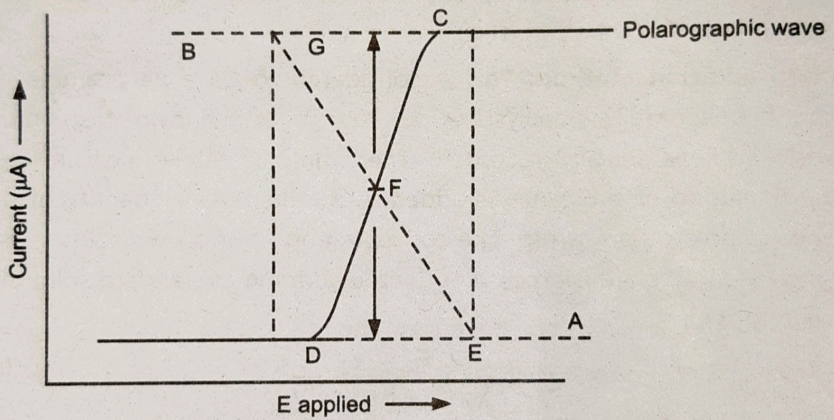

Fig. 14.7

14.3.3 Quantitative Polarographic Methods

There are various methods by which quantitative estimation of drugs, metal ions etc. is made. Some such methods are described as under :

1. **Direct comparison method:** In the direct comparison method measurements of current of a standard solution of test ion with that of unknown or test ion is carried under the same condition of experiment. Then, using the Ilkovic equation, the diffusion current quotient i_d/C can be found out. The height of unknown wave when divided by quotient gives the concentration of unknown (test) ion. For accuracy of this method, the conditions employed in experiment should be the same.
2. **Calibration curve method:** Various concentrations of standard solutions are analysed for determining their diffusion current. A plot of diffusion current vs. concentration is plotted. Diffusion current of unknown (test) sample is determined under the same conditions of experimentation of standard solution and the concentration of unknown is found out from the graph. This method gives accurate

results provided same conditions are kept with respect to capillary characteristic, temperature, flow rate of mercury, concentration of maxima suppressors etc.

3. **Internal Standard (Pilot ion) Method:** This method is deviced by Forche. It is based on the fact that relative diffusion currents i are independent of capillary characteristic. For the pilot ion (standard ion) $i_{d_1} = I_1 \cdot C_1 m^{2/3} \cdot t^{1/6}$ where $I_1 = 607n.D^2$

and for test ion $i_{d_2} = I_2\, C_2\, m^{2/3}\, t^{1/6}$.

Thus, ratio of $\frac{i_{d_1}}{i_{d_2}} = \frac{I_1 C_1}{I_2 C_2}$ the ratio of $\frac{I_1}{I_2}$ is known as pilot ion ratio, such a ratio of few concentrations of pilot (standard) ions with those of test ions are determined to find the concentration of unknown (test) solutions.

4. **Standard addition method:** This is considered to be a very simple and reliable method in polarographic analysis. A polarogram of unknown (test) solution with a known volume is initially recorded. Then, an accurately measured quantity of standard solution of substance is added to another same quantity of test solution and second polarogram is run. The concentration of unknown solution is found out from increase in the diffusion current (by the addition of standard solution) using the following formula.

$$C_1 = \frac{C_2\, i_2\, V_2}{V_1\, (i_2 - i_1) + i_2\, V_2}$$

where C, V and i are concentration, volume and diffusion current and subscript 1 and 2 refers to test and standard solution.

For maximum precision, the amount of standard solution added should be sufficient to give about double the original wave height.

Analytical Applications:

Applications of polarography are limited to those species both organic and inorganic that can be oxidised or reduced at electrode. The potential range is limited to the positive direction by the oxidation of electrode material. Use of platinum micro electrode extends the anodic region considerably especially employing some non-aqueous solvents. Most of the metal ions and many inorganic anions are readily determined alone as well as in mixture.

Polarographic methods are applicable to several class of organic compounds possessing:

(i) Conjugated double bonds,
(ii) Aromatic ring system,
(iii) Carbonyl,
(iv) Aldehyde,
(v) Nitro and
(vi) Nitroso,
(vii) Quaternary ammonium groups,
(viii) Halogen groups.

Many compounds which contain carbon-nitrogen, nitrogen-oxygen, sulphur-sulphur, carbon-sulphur bonds can be analysed polarographically. From pharmaceutical point of view the drugs like acetazolamide, chlorthiazide, nitrofurantoin, chloramphenicol etc. are polarographically analysed.

14.3.4 Recent Advances in Polarography

In recent years, some significant and useful advances in polarographic techniques have been reported. Some such advances are given below:

1. **Alternating current polarography:** This method has been developed in an attempt to have more rapid and accurate determination of half wave potential. The method enables estimation of small concentration of ion in presence of other reducible substances. In this technique, alternating current is supplied to the electrode.
2. **Oscillographic polarography:** This method utilises alternating current coupled with oscillograph. The method is adapted for analysis of pharmaceutical products like antibiotics, vitamins, hormones from various materials.
3. **Chronopotentiometry:** This method involves measurement of potential time pattern. In this method, the working electrode is polarised with constant current and potential of indicator electrode with respect to reference electrode is observed as a function of time. Thus, chronopotentiometry is the study of time relation with the potential of working electrode during the electrolysis which occurs through the cell due to high current. Sand (1951) derived the following relationship

$$r_{1/2} = \frac{E^{1/2}\, nf\, D^{1/2}\, C}{2\, I}$$

where, r = Transition time (when concentration of species at electrode is zero.)

E = Potential

C = Bulk concentration in mole/lit.

I = Current density in amp/sq. cm.

Thus, $r_{1/2}$ is proportional to C (conc. of analyte sample). In instrumentation, a source of constant current, a device of recording potential as a function of time, a suitable cell/electrode system and galvanometer (ammeter) are required.

The analytical application of chronopotentiometry includes study of irreversible electrode process, study of mechanism of complex ions, in adsorption studies etc.