26

Polarography

26.1 Introduction

Polarography is a method of analysis in which the solution to be analysed is electrolysed in such a way that the graph of current against voltage shows what is in the solution and how much is present. The method was developed in 1922 by the Czech chemist Jaroslav Heyrovsky, who won the Nobel Prize for his discovery.

The basic idea is to pass the current between two electrodes, one large in area and other very small. Normally both electrodes are of mercury. The large electrode is a pool of mercury at the bottom of the cell. The small electrode is a drop of mercury coming out of a very fine capillary tube. Thus, if a steady increasing voltage is applied to such a cell, it is possible to construct a reproducible current-voltage curve. The electrolyte is an electroactive dilute solution of material to be analysed in a suitable medium containing an excess of different electrolyte called *base or supporting electrolyte.* The purpose of the latter electrolyte is to carry the bulk of the current and to raise the conductivity of the solution. From the current-voltage curve, information about the nature and concentration of the material may be obtained. *Thus polarography is that method of instrumental analysis, which consists of the measurement of potential difference as current flows in solution and the result obtained can thus be interpreted in terms of nature and concentration of many substances.* The value of current flowing through the cell at any applied voltage is measured with the help of an instrument known as *polarography* (Because the curves obtained are graphical representation of the polarisation of the dropping electrode) and the curves obtained with it are known as *polarograms.*

Virtually every element, in one form or another, is amenable to polarographic analysis. Also, the polarography can be used for the determination of several organic functional groups. The polarographic behaviour of any species is unique for a given set of experimental conditions. Therefore, it could be used for selective analysis.

26.2 Apparatus

A simple cell and electrical circuit of a polarograph are shown in Fig. 26.1.

In this apparatus, there is a *dropping* mercury electrode which consists of mercury reservoir from which mercury drops down as small drops through a capillary. This acts as a cathode and is generally known as *indicator* or micro electrode. The anode consists of mercury pool at the bottom of the reservoir, which acts as a reference electrode, and its area is larger, so that it is not polarised.

Both cathode and anode are connected across the appropriate ends of a battery. The applied voltage can be changed by adjusting the sliding contact along the potentiometer wire EF. P is the potentiometer by which E.M.F. up to three volts may be readily

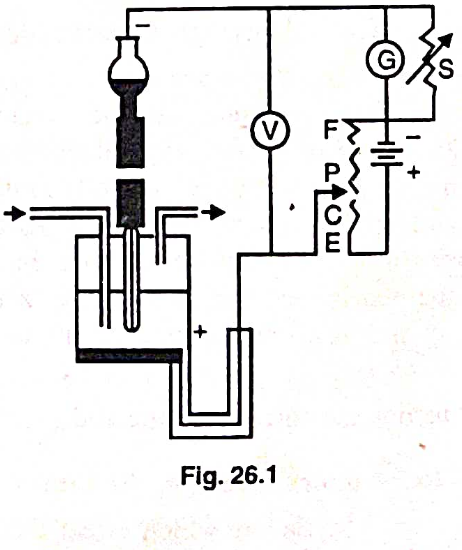

Fig. 26.1

applied to the cell, G is a galvanometer which measures the current strength and S is a shunt for adjustin the sensitivity of the galvanometer. The reservoir is provided for blowing nitrogen gas through the sample which removes dissolved oxygen from the sample. Although various micro-electrodes have been used bu the dropping mercury electrode is found best for obtaining the current-voltage curves due to the followin advantages:

(*i*) Its surface area is reproducible with any given capillary.

(*ii*) Mercury possesses the property of forming amalgams with many metals and therefore lowers the reduction potential.

(*iii*) The surface area can be calculated from the weight of the drops.

(*iv*) The diffusion current assumes steady value almost instantaneously and is reproducible.

(*v*) High overvoltage of hydrogen on mercury makes possible the depositions of ions which are difficu to be reduced.

The disadvantages of dropping mercury electrode are as follows:

(a) The area of the microelectrode is constantly changing as the size of the drop changes.

(b) Mercury may be easily oxidized and thus limits the feasible range of he electrode.

(c) The capillary may be easily plugged, the care must be taken to avoid touching the tip of the capillar with any foreign material.

Working. Consider a polarographic cell, containing a solution of cadmium chloride, to which a external E.M.F. is applied. The positively charged ions present in the solution will be attracted to th dropping mercury electrode by an electrical force, and by a diffusive force resulting from the concentratio gradient formed at the surface of the electrode. Thus, the total current flowing 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, a graph will be obtained which is shown in Fig. 26.2.

It can be seen from the Fig. 26.2 that from A to B, a small current flows. This is known as *residual current* and is carried by the supporting electrolyte and impurities present in the sample. At point B, the potential of the electrode becomes 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 increase 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 i_d.

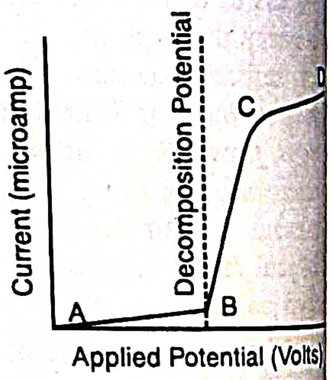

Fig. 26.2

The polarograph apparatus described above is a *manual* polarograph.

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 controlled rate by means of a constant speed motor, and simultaneously the chart paper is moved 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 the drops form and fall. (Fig. 26.3)

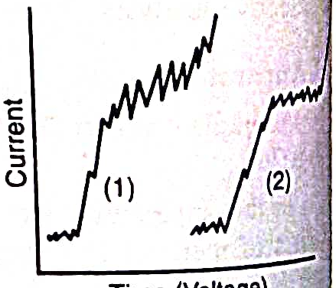

Fig. 26.3

The up and down movement that accompanies drop formation can be minimised by (*i*) using recorder with a long time and (*ii*) placing a high capacity condenser across the terminals of the recorde

26.3 Factors Affecting the Limiting Current

The factors which affect the current-voltage curve are as follows:

(*i*) Residual current
(*ii*) Migtation current
(*iii*) Diffusion current
(*iv*) Kinetic current

Let us discuss these one by one.

(*i*) **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 ions 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 of 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 0.52 volt more negative than the saturated calomel electrode. In the case of electrolytes containing traces of impurities, a small faradic current is also superimposed upon the condenser current. It is a practice to include this in the residual current. Thus we can write:

Residual current = Faradic current + Condenser current.

(*ii*) **Migration Current.** The electroactive material reaches the surface of electrode by two processes:

(a) The first involves the migration of charged particles in the electrical field caused by the potential difference existing between the electrode surface and the solution.

(b) The second involves the diffusion of particles.

The current required for the above two processes is called migration current., Jaroslav 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 ions carry almost all the current. The following example will make the concept more clear.

Suppose a solution contains 0.1 M potassium chloride and 0.01 M cadmium ions. The current is carried through the cell by all the ions present. 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.

(*iii*) **Diffusion Current.** The maximum current as shown as I_1 and I_2 in Fig. 26.4, is known as *diffusion current.*

This current is directly proportional to the concentration of the substance being reduced or oxidised at the dropping mercury electrode. The current is given by the *Ilkovic equation:*

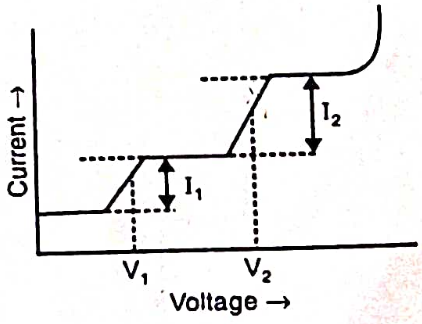

Fig. 26.4

$$i_d = 607\, nCD^{1/2}\, m^{2/3}\, t^{1/6}$$

where, i_d = the diffusion current in microamperes averaged over the lifetime of the drop,
n = number of electrons transferred per ion,
C = concentration in millimoles per litre,
D = diffusion coefficient of the reducible ion in $cm^2\ sec^{-1}$,
m = mass of mercury flowing per second in milligrams, and
t = drop time in seconds.

From the Ilkovic equation it follows that, "The observed diffusion current is directly proportional the concentration of the electroactive material. This is the basis of quantitative polarographic analy

The equation given by Ilkovic does not take into consideration the curvature of the electrode modified equation was, therefore, given by Lingane and Loveridge which is as follows:

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

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

(iv) **Kinetic Current.** The limited current may be affected by the rate of non-electrode reaction ca the *kinetic current.* The kinetic current will be proportional to the rate constant and to the volume of interface and, therefore, is a direct function of size of the mercury drop but is independent of the velo of the flow of mercury from the capillary. This current results if the oxidised or reduced form, of electroac species, is involved in a chemical equilibrium with other substances. It means that these are rate proces therefore, the current resulting from those is called the kinetic current.

26.4 Cells

Many cell designs have been proposed and cells of many types are sold commercially. A form of the cell that is convenient is shown in Fig. 26.5.

The left hand side of the cell contains saturated potassium chloride solution and a pool of mercury into which a stainless steel wire dips to make electrical contact. The horizontal tube that connects the two halves of the cell is closed at the right hand end by a porous sintered glass disc which is backed by a plug of agar gel 2-3 *cm* long. The capillary is mounted in a rubber stopper, a small groove is cut in the side of the stopper to let the nitrogen escape. The nitrogen inlet in provided with a stopcock (not shown in the figure) so that the gas stream can be stopped while readings are being taken.

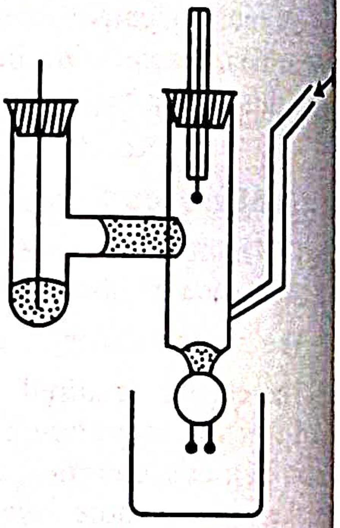

Fig. 26.5

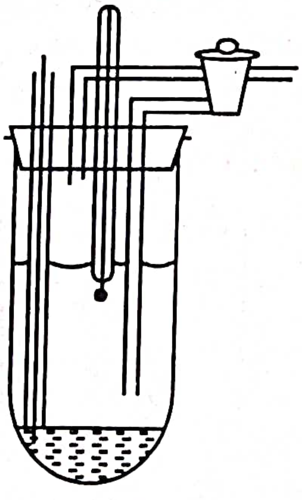

Fig. 26.6

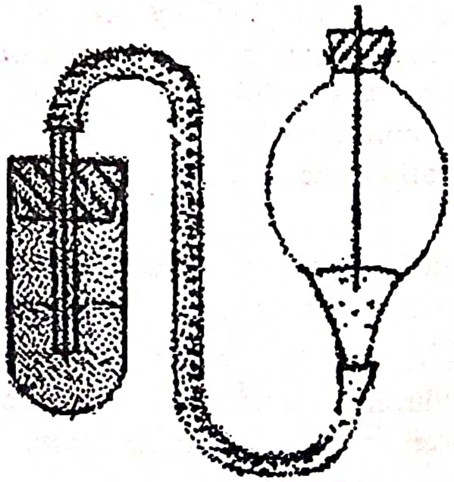

Fig. 26.7

Another simple form of the cell that needs no special glassware is shown in Fig. 26.6.

The rubber stopper carries two tubes for nitrogen, one to bubble it through the solution bef readings are taken, the other to pass nitrogen over the surface and protect the solution from air while current-voltage readings are taken. There is no groove in the side of the stopper to let the gas esca

Capillary tubes used in polarography are very fine, about 25 microns internal diameter. Special tu are used for making these capillary tubes. It comes in lengths of about 20 *cm*, and these are generally in two before use, with the freshly cut ends dipping into solution.

The end of the capillary should be kept clean. The mercury should be kept flowing continuously through a series of experiments and after the experiments are completed, the capillary is lifted out of the solution. This is then rinsed with distilled water, dried with the help of a filter paper and then placed in a tube containing mercury as shown in Fig. 26.7.

26.5 Form of Waves and Half Wave Potentials

We can learn something of the process at the mercury drop, and get a clue as to what is being reduced. The reduction is one of many processes that are possible. Processes like [$Cu^{2+} + e \rightarrow Cu^{+}$] give polarographic waves, and so do the reduction of many organic compounds.

The half wave potential in polarography is a characteristic property of the electroactive material. *This potential is found on the steeply rising portion of the current-voltage curve and is one half of the distance between the residual and limiting currents.* It is denoted by $E_{1/2}$. This is shown in Fig. 26.8.

The importance of the half wave potential can be followed by considering the reduction taking place at the dropping mercury electrode which may be represented as follows:

$$\text{Oxidant} + ne \rightleftharpoons \text{Reductant}$$

or for convenience, $ox + ne \rightleftharpoons \text{red}$

The reversible potential of the system as it exists at the electrode-solution interface of the drop will be recorded on the polarogram. This electrochemical equilibrium may be represented by :

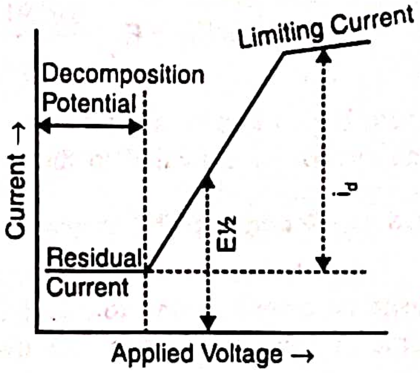

Fig. 26.8

$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{[ox]_0}{[\text{red}]_0} \tag{1}$$

where the subscripts represent concentration at the electrode solution interface.

Let us suppose that before the start of the current voltage curve, the solution at the electrode solution interface consists of oxidant only. As soon as the E.M.F. becomes larger enough to reduce it, the concentration of the oxidant at the electrode surface begins to decrease. Some ions will move in from the bulk of the solution by means of diffusion, as the concentration of the gradient builds up in the bulk of the volume around the electrode. The average current, *i*, flowing through the cell, at any point of the wave, is given by:

$$i = K[(ox) - (ox)_0]D_{ox}^{1/2} \tag{2}$$

where K includes capillary characteristics, the *n*, *m* and *t* are terms from the Ilkovic equation, (*ox*) is the concentration, of the reducible ions in the bulk of the solution, and $(ox)_0$ is the concentration of the oxidant at the electrode-solution interface.

When the current attains the limiting value represented by the diffusion current plateau, *i.e.*, the concentration of the oxidant at the electrodes solution interface is reduced to zero. Therefore, equation (2) becomes

$$i_d = K\,(ox)\,D_{ox}^{1/2} \tag{3}$$

From equations (2) and (3), we get

$$(ox)_0 = \frac{i_d - i}{KD_{ox}^{1/2}} \tag{4}$$

For those metals which form amalgams with the dropping electrode, the concentration of metal amalgam is directly proportional to the current on the current voltage curve, so

$$i = K[\text{red}]_0 D_{red}^{1/2} \tag{5}$$

Substituting equations (4) and (5) in (1), we get

$$E = E^{\circ} + \frac{0.0591}{n}\log\frac{i_d - i}{i} + \frac{0.0591}{n}\log\left[\frac{D_{red}}{D_{ox}}\right]^{1/2}$$

But by definition, the half wave potential is the point, where,

$i = i_d - i$ or $i = ½\, i_d$

The equation (6), therefore, becomes

$$E_{\frac{1}{2}} = E^{\circ} + \frac{0.0591}{n}\log\left[\frac{D_{red}}{D_{ox}}\right]^{1/2}$$

where $E_{1/2}$ is known as half wave potential. From the equation (7) it is clear that the polarographic hal wave potential is related to the standard reduction potential of oxidation-reduction system.

26.6 Applications of Polarography

The technique of polarography has been found to be a convenient technique for measuring th electrode potentials and for, studying electrode reactions. It has, therefore, large number of applications Some of these applications are discussed below.

(*i*) **Applications to Inorganic Compounds.** Polarography can be used for the estimations of cations and anions in the presence of interfering ions.

It is observed that the successful polarographic analysis of cations generally depends upon the employment of a suitable supporting electrolyte. Polarography of aqueous solutions of cations may be determined in the 10^{-2} to 10^{-6} M concentration range successfully.

Thus, lithium having a negative wave potential can be estimated in the presence of other alkali metals but the concentrations of other alkali metals should not be very high. Alkaline earth metals have been determined by Kimura, using alkaline solutions as supporting electrolytes.

In the separation of zinc and nickel, which have nearly identical half-wave potentials in neutral chloride solution, an alkali hydroxide can be used as the supporting electrolyte. Zincate ions are reducible, whereas nickel is precipitated as the hydroxide. A portion of the solution is then taken for analysis. In nickel and zinc, the two waves can be separated in a 1 N ammonia-aqueous ammonia buffer and appear at −1.06 and −1.33V respectively against the saturated calomel electrode.

In the case of determination of lead, Hubicki and Matysik have used ammonia-ammonium nitrate buffer as supporting electrolyte. The estimation was carried out at 0°C with dropping mercury cathode and a pool of mercury anode showed that the value of half wave potential was—0.35V and was independent of the concentrations of lead and anions used.

Ionic solution of various elements can be determined directly. The mixtures of the ions can be determined if half wave potentials of the ions are separated by 0.2V. This is essential in order to distinguish the height of two waves, otherwise the overlapping of the waves takes place. The various ions present can be estimated in a single run (Fig. 26.9).

Thus a series of reducible substances can be estimated in one solution.

The polarographic analysis is also used in the determination of anions such as bromate, iodate, vanadate, selenite, nitrite and dichromate provided the central atom has two or more oxidation states. It is found that the polarograms for these substances are affected by the pH of the solution because the hydrogen ion is a participant in the reduction process. As a result, strong buffering of the solutions to some fixed pH is necessary to obtain reproducible data.

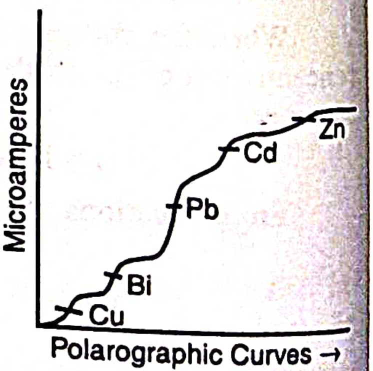

Fig. 26.9

The polarographic method can be used for the analysis of a few inorganic substances that exist as uncharged molecules in the solvent used.

The technique has also been used successfully in the determinations of large number of alloys.

(*ii*) **Applications to Organic Compounds.** The reactions of organic compounds at a microelectrode are slow and more complex than those of inorganic compounds. The theoretical interpretation of the polarographic data is more difficult or even impossible. Despite the handicaps, organic polarography has proved fruitful for the determination of structure, for the quantitative identification of compounds, and for the quantitative analysis of mixtures.

Reversible organic reductions are generally confined to quinones and some other functional systems such as phenylene diamines which resemble quinones in forming resonating systems. Most of the applications to organic compounds have involved irreversible reductions. Some of organic functional groups which are reducible are given in Table 26.1.

In organic polarography, solubility considerations demand the use of some solvent other than water. Aqueous mixtures having varying amounts of such miscible solvents as glycols, dioxane, alcohols, Cellosolve or glacial acetic acid have been employed. Supported electrolytes are often lithium salts or tetraalkyl ammonium salts.

In organic polarography, the Ilkovic equation applies to the diffusion current for electrode reactions that are non-reversible.

Table 26.1 : Reducible organic functional groups

Compound	*Group*	*Compound*	*Group*
Ketone	>C=O	Azoxy	–NO=N–
Aldehyde	–CHO	Nitro	$-NO_2$
Alkene	>C=C<	Hydroxylamine	–NHOH
Nitrite	–C≡N	Nitrite	–ONO
Azo	–N=N–	Nitrate	$-ONO_2$

The estimation of sugars have been carried out in the range of 10^{-3} to 10^{-2}M using *p*H of 2.3 and supporting electrolyte hydrazine sulphate polarographically. A single well formed hydrazone wave has been observed.

Organic electrode processes ordinarily involve hydrogen ions. The most common reaction may be represented as follows: (1)

$$R + nH^+ + ne \rightarrow RH_n$$

where R and RH_n are the oxidised and reduced forms of the organic molecule. From Eq. (1), it is evident that half-wave potentials for organic compounds are markedly *p*H dependent. Also, alteration of *p*H often changes the reaction products. For example, when benzaldehyde is reduced in basic solutions, a wave is obtained at about—1.4V, attributable to the formation of benzyl alcohol.

$$C_6H_5CHO + 2H^+ + 2e \rightleftharpoons C_6H_5CH_2OH$$

If *p*H of the solution is less than 2, a wave is obtained at about –1.0V which is just half the size of the foregoing one; in this reaction, hydrobenzoin is produced.

$$2C_6H_5CHO + 2H^+ + 2e \rightleftharpoons C_6H_5CHOHC_6H_5$$

At intermediate *p*H values, two waves are observed, indicating the occurrence of both reactions.

(*iii*) **Determination of Dissolved Oxygen.** The determination of dissolved oxygen in aqueous solution or in organic solvents can be carried out successfully with the help of polarography. In this method, the dissolved oxygen is not swept out with nitrogen gas, as with other samples. Instead the oxygen waves are measured and the dissolved oxygen determined.

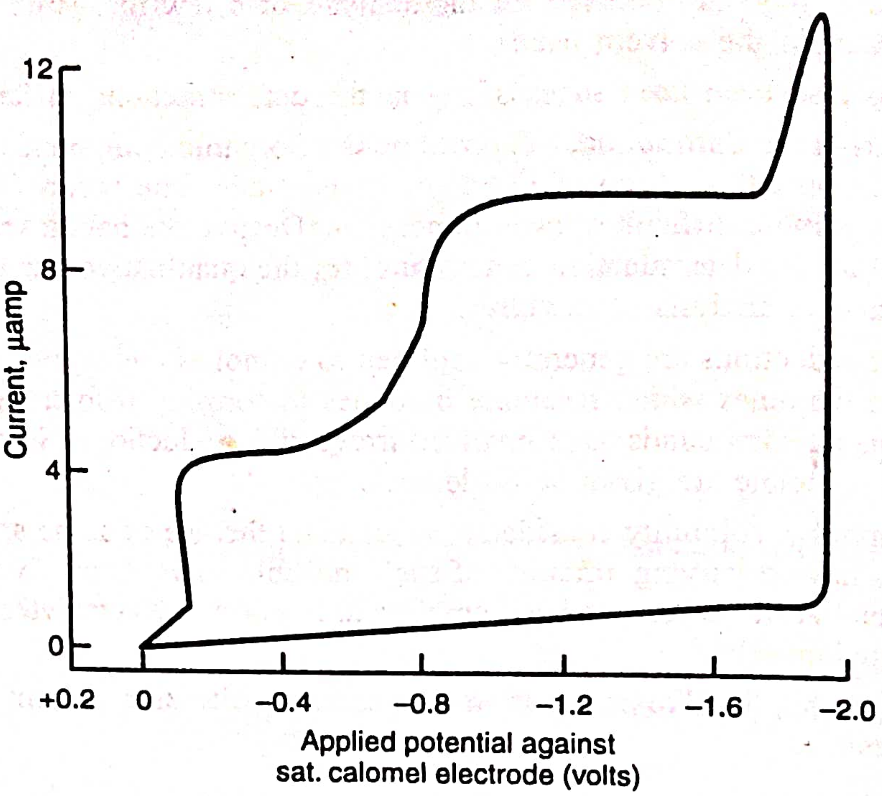

Fig. 26.10 : Polarogram for the reduction of oxygen in an air-saturated 0.1 M KCl solution. The lower curve is for 0.1 M KCl alone.

Dissolved oxygen produces two reaction waves (Fig. 26.10) corresponding to

$$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2$$

and $$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$$

It is the first of these two reactions which is used in oxygen meter.

In the sensing probe for the oxygen meter, there are two inert metal electrodes which are separ from each other but contained in a single cylindrical tubing. The leads go through one end of tube to the recording system. The other end of the tube is sealed with a thin plastic membrane w is permeable to dissolved oxygen as well as some other gases. This system detects the concentra of the oxygen, in 0-50 ppm range, which passes through the membrane.

The method suffers no interference from combined oxygen in the sample. For example in the of aqueous solution, the oxygen combined in the H_2O molecule does not take part in a reaction. is a distinct advantage over other methods of analysis of oxygen.

However, the halogens and sulphur dioxide interfere in this measurement. Oxygen meters are primarily for the study of water as in timnology, ecology, pollution control, and oceanography

(*iv*) **Studies of the Complexes.** Polarography is a powerful tool in the study of the composition complexes if the simple metal ion and complex of that metal ion in the same oxidation state reversible electrode processes and involve the same number of electrons.

(*v*) **Determination of Plant Contents.** The determination of plant contents is in general preceded by extraction. A polarographic analysis of the contents of essential oils can be carried out in most ca by dissolving the oil in ethanol and diluting with a suitable aqueous buffer solution. In this way total content of the mixture is obtained. Thus, a separation prior to polarographic analysis necessary if the contents of individual components are to be determined.

(*vi*) **Applications to Pharmaceuticals.** Medicines like epinephrine and norepinephrine are oxidized periodate to iodoadrenochrome and iodonoradrenochrome respectively. The oxidation proce quantitatively within a few minutes and well developed waves are obtained in acetate buffer solutio In this way epinephrine has been determined in injection solutions containing 2 to 20μg/ml.

Some of the local anaesthetists are directly reduced at the dropping mercury electrode. Among these are basic ketones propipocaine and dyclonine showing waves at negative potentials, the wave height being proportional to the concentration.

Indirect polarographic determinations have been studied for frequently used analgesics and antipyretics phenacetin and phenazone involving nitration. Polarograms can be recorded in the nitration solution immediately after diluting with a buffer solution.

Tetracyclines including half synthetic derivatives may also be determined polarographically, but the steps are not very predictable and the experimental conditions must remain constant. The use of A.C. polarography according to Breyer has proved advantageous in the analysis of tetracyclines, because of the increased sensitivity and better resolution of peaks as compared with D.C, polarography. With A.C. polarography it is possible to analyse oxytetracycline and chlorotetracycline together.

Sulphonamides can be determined in solutions of tetraalkylammonium salts, due to the hydrogen reduction step of the acid proton of the nitrogen. Moreover polarographic behaviour of the vitamins has also been studied in detail.

27

Amperometric Titrations

27.1 Introduction

Polarography can be used as the basis of amperometric titration method comparable with th potentiometric, the conductometric, and the photometric methods. In amperometric titrations, the voltag applied across the indicator electrode and the reference electrode is kept constant and the diffusion curre (which is equal to limiting current-residual current) passing through the cell is measured and plotted again the volume of the reagent added.

From polarographic technique, it is known that current is independent of applied voltage impresse upon dropping mercury electrode or any other electrode. Now if we take an excess of supporting electroly the factors affecting the limiting current is the rate of diffusion of electroactive material from the bulk o the solution to the electrode surface. This is because the migration current is eliminated under suc conditions. Thus, diffusion current is proportional to the concentration of electro active-material in th solution. If by any method, some of the elctro-active material is removed by interaction with any reagen the diffusion current will naturally decrease. This forms the fundamental basis of amperometric titration derived from ampere, the unit of current. As the diffusion current is because of polarisation at a micr electrode, the technique is also known as polarometric or polarographic titration.

The amperometric method is considered to be more accurate than the polarographic method becaus it is less dependent upon the characteristics of the capillary and the supporting electrolyte.

Amperometric and conductometric titrations are similar in the respect that the data for each ar collected well away from the equivalence point. Therefore, the reactions that are relatively incomplete ca be employed.

27.2 Apparatus Used for Amperometric Titrations

The equipment used in the case of amperometirc titrations is simple. Although it may be same as used for polarography, several simplifications are possible. The titrations may be performed either with the dropping mercury electrode or with rotating platinum electrode. For dropping mercury electrode, the usual polarographic equipment is used with cells modified to allow the addition of titrating reagent (Fig. 27.1).

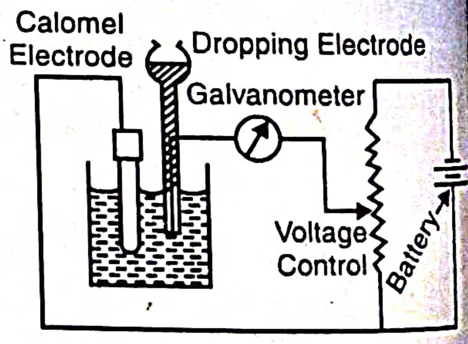

Fig. 27.1

Calomel electrode is used as a reference electrode. The galvanometer measures the current and th series of rheostat may be used for changing the sensitivity of the galvanometer. In order to carry out th amperometric titrations, the voltage applied to the indicator electrode and the reference electrode is ke constant. The sensitive galvanometer indicates the value of diffusion current after each addition of th titrant. It is to be noted that generally the potential of a reference electrode will lie in the permissible rang so that it is necessary only to short-circuit the indicator electrode through a suitable current measuri instrument to a reference electrode of relatively large area. Some of suitable reference electrodes are give in Table 27.1.

Table 27.1 : Electrode potentials in volts of reference electrodes as a function of temperature in °C

Temperature	*0.1M* Calomel	*Saturated* Calomel	*1.0M* Ag/AgCl
10	0.3362	0.2528	0.2314
15	0.3360	0.2508	0.2286
20	0.3358	0.2476	0.2256
25	0.3356	0.2444	0.2223
30	0.3353	0.2417	0.2190
40	0.3345	0.2379	0.2131
50	0.3315	0.2308	0.2045

Instead of dropping mercury electrode, a rotating platinum micro-electrode can be used. The latter possesses the following advantages over the dropping mercury electrode :

(*i*) It is simple to construct.

(*ii*) It increases the workable range on the positive voltage side upto 0.9V. Thus it can be used at positive potentials whereas the mercury electrode may not be used.

(*iii*) The technique is more sensitive because the rotation of the electrode increases the value of diffusion current as much as 20 time the value in polarography.

The rotating platinum micro-electrode was introduced by H.A. Laitinen and I.M. Kolthoff in 1941. It consists of glass tube of about 15-20 cm in length and 6 mm in diameter. A short length of platinum wire extends 5-10 mm from the wall of the glass tube (Fig. 27.2). The electrode is mounted in the shaft of a motor and rotated at a constant speed of about 600 rotations per minute.

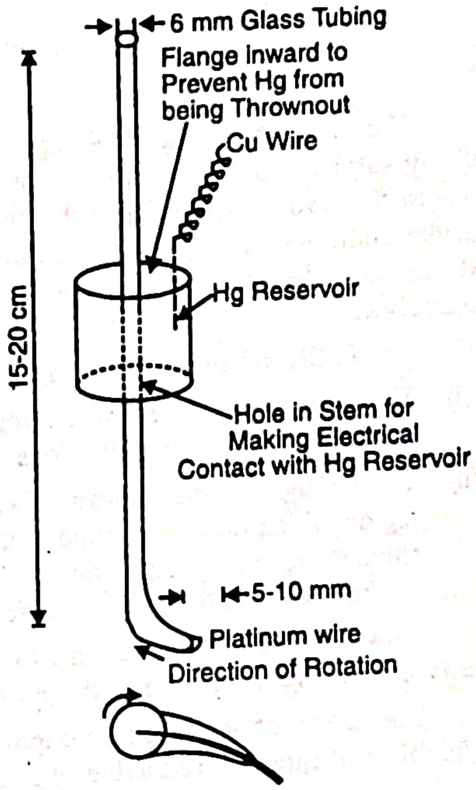

Fig. 27.2

A simple rotatory platinum electrode arrangement used in amperometric titrations is shown in Fig. 27.3.

In amperometric titrations removal of oxygen is necessary, if the electrolysis is carried out at an E.M.F. at which oxygen would have a diffusion current. Removal of oxygen is done by bubbling purified nitrogen before the commencement of the titration and for about 1 minute after each addition of the titrant.

27.3 Technique of Amperometric Titrations

The technique of amperometric titrations may be illustrated by considering the titration of a reducible ion, like Pb^{2+}. Lead ions being reducible at the cathode, give a diffusion current whereas the sulphate ion being non-reducible shows no diffusion current. The concentration of the reducible Pb^{2+} ions is steadily decreased as the SO_4^{2-} ions removes some of the electro-active Pb^{2+} ions. A polarogram of a solution containing lead ions is represented by curve A in Fig. 27.4.

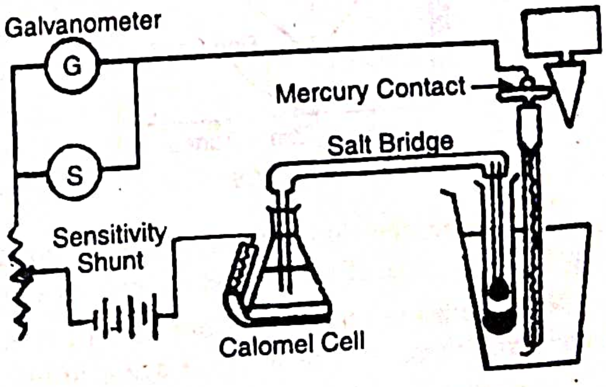

Fig. 27.3

If the voltage is kept constant at any value of diffusion current plateau, the limiting current value will be represented by i_0 corresponding to C_0, the initial concentration of lead ions. At this stage the titra exhibits no diffusion current at the applied E.M.F.

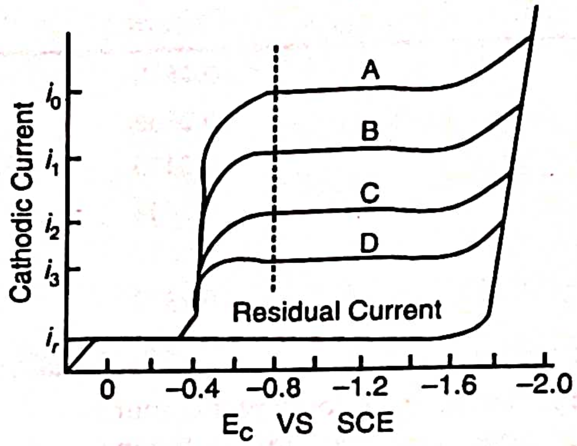

Fig. 27.4

The curve A in Fig. 27.4 represents the current i_0 of the solution of lead ions before the additi of any sulphate ions. The curve labelled B represents the current i_1 after the addition of some sulpha ions to the lead ions. Similarly the curves C and D represent the currents i_2 and i_3 which correspond further additions of sulphate ions. Finally i_r is the point at which the lead ions have completely reacte At this stage the only current flowing is a residual current and its value is characteristic of the supporti electrolyte.

The following inferences can be drawn from Fig. 27.4.

(i) The decrease in current with decrease in the concentration forms the basis of amperometric titrations.

(ii) The voltage on the plateau of voltage curve illustrates the voltage region which may be applied in the case of titration of lead ions with sulphate ions amperometrically. The range –0.8 volt is selected out of the range –0.6 to –1.2 volt for this titration.

Now if we plot the diffusion current against the volume of the titrant, the type of curve which we with get is shown in Fig. 27.5.

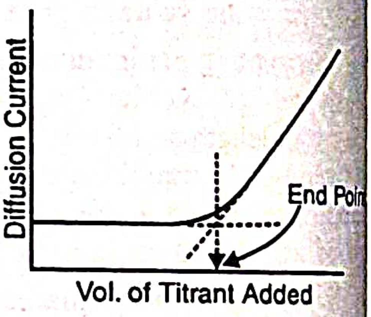

Fig. 27.5

The intersection of the extrapolated portions gives the end point. When the titrated ion is n reducible and titrant is reducible, the amperometric curve will be of the type shown in Fig. 27.6.

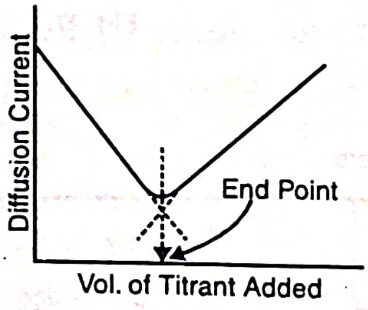

Fig. 27.6

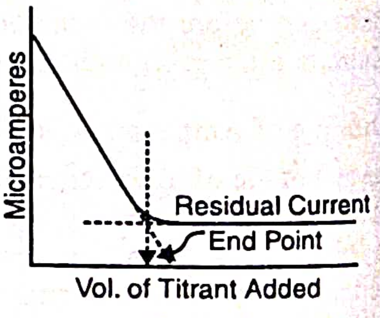

Fig. 27.7

In this case, the titration curve is a horizontal line, which starts to rise after the end point. Anoth example of this type of titration is of lead ions with dichromate ions at 0.0 volt.

When both the titrated ion and titrant ion are reducible at the cathode, the current will drop to t end point and there will be increase again to give a V shape titration curve as shown in Fig. 27.7.

This type of curve is obtained when lead ions are titrated with dichromate ions and the titration performed at a voltage of –0.8 volt. The current decreases as the lead ions are removed from the solut and then increases as the lead ions are removed from the solution and then increases after the end point because of the increase in concentration of dichromate ions. A similar type of curve was also obtained, when molybdenum was titrated against lead nitrate at a constant voltage of −0.8 V, by Aylward.

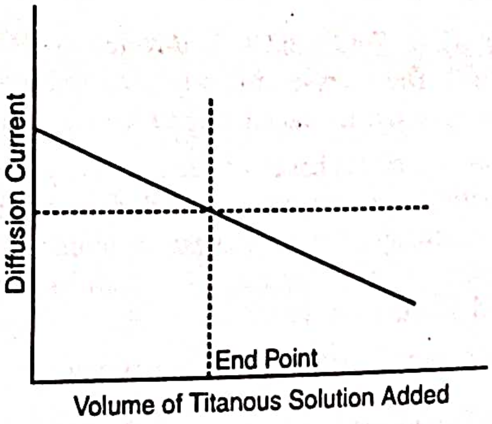

Fig. 27.8

Redox titrations can also be carried out by amperometric method. In an oxidation reduction system, where both oxidising and reducing agents give diffusion current, the titration curve obtained is of the type shown in Fig. 27.8.

In the case of ferric ions titrated against titranous ions, the diffusion current decreases linearly with the addition of titrant (Ti^{3+} ions) to the ferric ions until it attains the zero value at the end point. At this point ferric ions have completely reacted. When more titrant is added after the end point, a diffusion current caused by the oxidation of titranous ions is set up. A change in slope caused by the difference in diffusion coefficients is usually evident as the lines cross the zero axis. The point of intersection of the two lines gives the end point.

Certain titrations involving neutralization and complex ion formation have also been successfully carried out by amperometric method. Neuberger has modified the amperometirc method for the study of precipitation reactions. He has used reagents like dimethylglyoxime, salicyaldoxime etc. for such type of studies.

Laitiner, Jennings and Parks have titrated iodide, bromide and chloride at a less negative potential, because in these titrations the indicator reaction is the deposition of silver from aquo-silver ions. Micro-molecular solutions of cadmium against E.D.T.A. have been studied amperometrically by Nickelley and Cooke in 1956.

27.4 Dead stop and Point Method

Or

Titrations with two Indicator Electrode

This technique is a modification of the classical amperometric titration. This method is applicable only when the oxidation-reduction system is involved before and after the end point. In this method two similar platinum electrodes are immersed in the titration cell. Then a small and constant voltage is applied to these two electrodes.

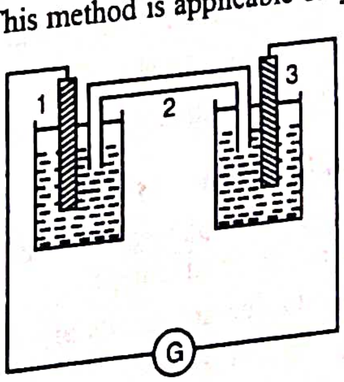

Fig. 27.9

An electrometric titration apparatus with the two electrodes dipping in two different vessels and linked through a salt bridge is shown in Fig. 27.9.

The amount of oxidized form reduced at the cathode is equal to that formed by oxidation of the reduced form at the anode, when the reactant involves a reversible system. At this stage with electrodes are depolarized until either the oxidized or the reduced member has been consumed by the titrant. After the end point only one electrode remains depolarized as if the titrant does not involve a reversible system. Thus the current becomes zero or very close to zero at the end point and this shoots up as shown in Fig. 27.10.

The method was introduced by C.W. Foulk and A.T. Bawden in 1926, under the name *"dead spot end point"*. The reverse of this type of end point is called *"kick off"* and resembles a reversed L-shaped amperometric curve.

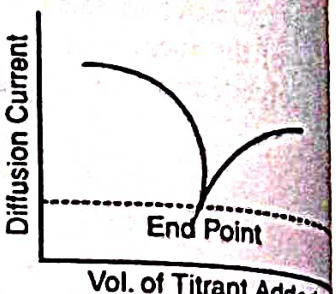

Fig. 27.10

Amperometric methods with two electrodes have not been fully exploited and there are few oxidation-reduction systems to which this end-point technique could be applied with advantage. Most of these titrations involve iodine. However, a titrations with reagents such as bromine, +3 titanium and +4 cerium have been reported. An important is in the titration of water with Karl Fischer reagent.

The principal advantage of the two electrodes is its simplicity.

27.5 Advantages of Amperometric Titrations

These titrations have a number of advantages over other methods, therefore some of these are gi below :

(*i*) The apparatus used is simple and the characteristics of electrodes are less important.

(*ii*) The method is relative, therefore, fewer disturbing factors are prevalent.

(*iii*) The accuracy is higher than in polarography and the error in the determination of the end p depends on the ability of the student.

(*iv*) The temperature need not be known provided it remains constant throughout the experiment.

(*v*) The range and the sensitivity of the technique are more than conductometric or potentiomet titrations. In reality, the amperometric methods are best for the determination of traces of eleme with good precision. The concentrations ranging from 0.1 to 0.0001 M and even in certain cases 0.000,001 M can be measured accurately.

(*vi*) It is not necessary to have capillary characteristics of the dropping electrode.

(*vii*) It is not necessary to maintain constant current throughout the titration.

(*viii*) It is immaterial whether the reaction which occurs during the titration is reversible or irreversib

(*ix*) The depolarising substances which cannot be determined very accurately by polarography, can successfully determined by amperometric titrations. For such substances, a suitable titrant is selec which gives a diffusion current. Moreover some other systems which do not possess measura equilibrium potentials can be estimated amperometrically. An interesting example is that magnesi which does not give the diffusion current curve, can be determined by using 8-hydroxyquinol which gives a reduction curve.

(*x*) These titrations can be carried out rapidly because the end point is found graphically.

(*xi*) The presence of foreign salts does not interfere, instead these act as supporting electrolytes.

(*xii*) Dilute solutions can be titrated with high degree of accuracy.

(*xiii*) The method is one of the few methods which are generally applicable to precipitation titrations.

27.6 Disadvantages of Amperometric Titrations

Inspite of large number of advantages as discussed earlier, the amperometirc titrations possess t following disadvantages :

(*i*) Inaccurate results are sometimes obtained because of coprecipitation.

(*ii*) The foreign substances which do not interfere in the amperometric titration should not be prese in larger concentrations than the substance to be titrated. In their presence, the relative curre becomes smaller.

27.7 Applications of Amperometric Titrations

The amperometric and point has been mostly confined to titrations in which a slightly soluble precipitate is the reaction product. Some selected applications are listed in Table 27.2.

Table 27.2 : Some Precipitation Titrations Employing the Amperometric End Point

Electrode	*Reagent*	*Substance Determined*
Dropping mercury	K_2CrO_4	Pb^{2+}, Ba^{2+}
	$Pb(NO_3)_2$	SO_4^{2-}, MoO_4^{2-}, F^-, Cl^-
	8-hydroxyquinoline	Mg^{2+}, Zn^{2+}, Cu^{2+}
	Cupfferron	Cu^{2+}, Fe^{2+}
	Dimethylglyoxime	Ni^{2+}
	$K_4Fe(CN)_6$	Zn^{2+}
Rotating platinum	$AgNO_3$	Cl^-, Br^-, I^-, CN^-

Amperometric electrodes are finding important applications as microdetectors in liquid chromatography for following the elution of electroactive substances.

Twin silver microelectrodes have been employed for end-point detection in which silver ion is a precipitant. For example, in the titration of silver ion with a standard solution of chloride ion, currents proportional to the metal ion concentration would result from the reactions :

Cathode, $Ag^+ + e \text{ —— } Ag$

Anode $Ag \text{ —— } Ag^+ + e$

With the effective removal of silver ion by the analytical reaction, cathodic polarisation would occur and the current would approach zero at the end point.