The generic term voltammetry commonly involves, studying the influence of voltage changes on the current, flowing in a cell, where one electrode is of relatively large surface area (known as counter electrode or auxiliary electrode) and the other has a very small surface area, which is often referred to as micro electrode or working electrode or indicator electrode. Polarography refers to that branch of the general field of which the micro electrode is a dropping mercury electrode.

Polarography incorporates the features of electrolysis and potentiometry but distinct from both. In electrolysis a chosen constituent is removed completely 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 polargraphy is of short duration and the electrode on which the constituents are plated out is a dropping mercury electrode so that the currents are very small. Hence, the changes produced by polargraphy are normally (with 5 to 20 ml test solution) not measurable and the polarographed solution can be recovered virtually unchanged.

The polarographic analysis of a test solution is carried out with the aid of current-potential curves. These curves are constructed by applying a steadily increasing voltage to a cell incorporating a relatively large anode (mercury pool or saturated calomel electrode) and a small dropping mercury cathode. 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; a 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. A polarogram can be potted between the current flowing through the polarographic cell against the increasing potential of the dropping electrode. A typical polarogram is depicted in **Fig.1.**
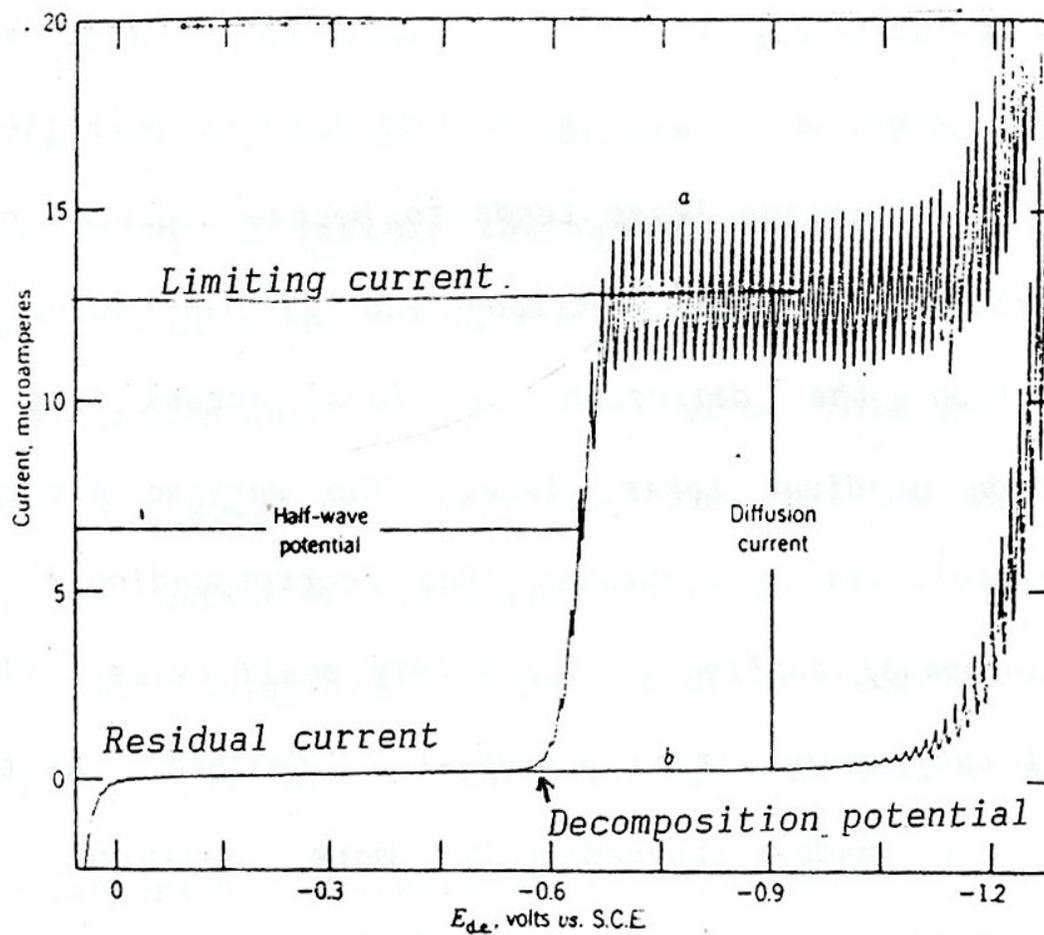
Fig.1 Typical polarogram obtained with the Dropping Mercury Electrode

The virtually flat upper portion of the polarographic wave is called its plateau and the total current which flows through the cell at a potential on the plateau is called the limiting current of the substance responsible for the wave. The difference between the limiting current and the residual current is called the diffusion current or wave height (i_d) of that substance and is a function of the concentration of the reacting material. The potential at which the current is one – half of the diffusion current is called half-wave potential designated as $E_{1/2}$. The half - wave potential of a reducible substance is independent of concentration and is the characteristic of the nature of the reacting material. This is essential basis of quantitative and qualitative polarographic analysis. A schematic diagram of a simple polarographic set up is shown in **Fig.2.**
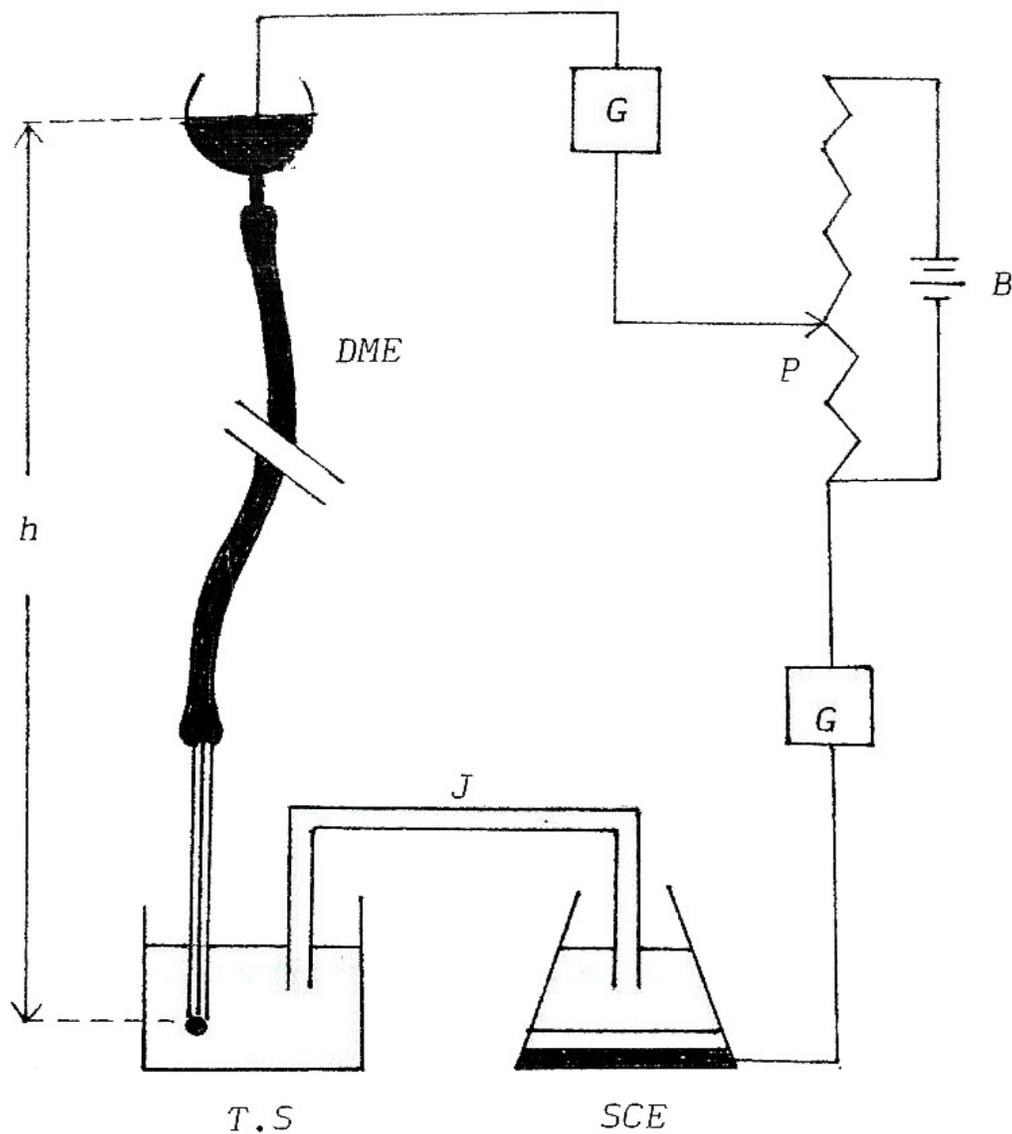
Fig.2 Schematic diagram of essentials for polarographic analysis

DME: Dropping Mercury Electrode ; T.S : Test Solutions ; J : Agar bridge

SCE : Saturated Calomel Half – Cell P ; Potentiometer or poloragraphy ;

B ; Battery ; G : Galvanometer ; h : Height of Mercury Column.

The success of polarography was largely attributed to the fact that the dropping mercury electrode has several advantages over solid metal such as platinum as an indicator electrode. One of the most important of these is, the high over potential for the evolution hydrogen on mercury. This makes it possible to study the reductions of many substances including even the alkali and alkaline earth metal ions, which could not possibly be deposited onto a platinum cathode without interference from the simultaneous reduction of water on hydrogen ion. Unlike a solid electrode, a mercury droplet has a perfectly smooth surface free from scratches or any other irregularities; this makes the accurate calculation of the electrode area a rather simple matter.

Since, a fresh surface of the electrode is renewed regularly, adsorbed or deposited materials cannot accumulate on the electrode surface. Hence numerous metals which are soluble in mercury usually behave more reproducibly and reversibly when amalgamated than in the pure solid state. During electrolysis with a dropping mercury electrode only negligibly small quantities of the substance are deposited in the vicinity of dropping electrode. For this reason there is no depletion of the depolariser in the solution and provided the volume of the electrolyzed solution is not too small, even after several runs the curves obtained are identical. Finally, the dropping mercury electrode is much less sensitive to mechanical disturbances than a stationary solid microelectrode because a shock which would cause the latter to vibrate for sometime merely dislodges one drop prematurely from a dropping electrode without having much effect on the next. An even more serious defect of a stationary solid micro electrode is that the concentration gradient resulting from the flow of current extends further and

further out into the solution as time goes on, so that ions must diffuse through a greater and greater distance to reach the electrode surface, resulting in a steady decrease of the current.

On the other hand, there are certain definite limitations associated with the dropping electrode. The dropping mercury electrode may be applied over the range +0.4 to about –2.0 volts with reference to the S.C.E. Above +0.4 volt mercury dissolves and gives an anodic wave; it begins to oxidise to mercury (I) ion. At potentials more negative than about –1.8 volts vs S.C.E., visible hydrogen evolution occurs in acid solution and the usual supporting electrolytes commence to discharge. The range may be extended to about   -2.6 volts vs S.C.E. by using supporting electrolytes having higher reduction potentials than the alkali metals. For work at potentials where mercury undergoes oxidation, other types of electrodes must therefore be sought. Form the stand point of analytical chemistry, the sensitivity of polargraphy is restricted by the charging current caused by the growth of the drop. From the theoretical point of view a serious complication in the mathematical formulation is introduced by the necessity of considering the growth of the drop.

The current varies between a minimum and maximum for each drop of mercury it forms, since there is periodic change in the surface area of the drop. Therefore, the graph lines obtained are actually not smooth lines but are saw toothed lines. The amplitude of the fluctuation is small, however, smooth lines can easily be drawn between them to represent the average current during the drop life.

In general, the total current, flowing through the polarographic cell can be regarded, as the sum of residual current, migration current and diffusion current. In order to obtain true current - potential curves, the residual and migration currents should absent. The residual current is defined as a small current that flows in the cell before the decomposition of a solution, containing an indifferent electrolyte, begins. This current increase almost linearly with the applied voltage and it is observed even when the purest, air-free solutions are used, so that it cannot be due to the reduction of impurities. It must therefore be considered a non-faradaic or condenser current, made appreciable by the continual charging of new mercury drops to the applied potential. In practice, one often finds that the indifferent electrolyte contains traces of impurities so that small, almost imperceptible currents are superimposed upon the condenser current. It is customary to include all these in the residual current. In practical polarographic work the residual current is subtracted from the total observed current by proper extrapolation and placement of tangents to the wave.

If the electroactive substance is ionic, there will be an electrostatic force between its ions and the electrode. The force may be one of either attraction or repulsion in either case it affects the rate at which the ions reach the electrode surface and undergo reduction or oxidation. The difference between the limiting current actually obtained and the limiting current that would be obtained in the absence of any electrostatic force is called the migration current. In all practical polarographic work the migration current is rendered negligible by the presence of a relatively large concentration of an indifferent electrolyte (base or ground solution or supporting electrolyte) whose ions serve to conduct current through the

solution and thus dissipate the electrostatic force, but are not reduced or oxidized over the range of potentials that is being studied.

The most important component of the total limiting current is the diffusion current. It reflects the rate at which the ions or molecules of the substance, responsible for the wave, reach the electrode surface under the sole influence of a diffusive force. On the plateau of the wave these ions or molecules are reduced (or oxidized) as rapidly as they reach the electrode surface and their concentration in the layer of solution, immediately adjacent to the electrode surface, is therefore virtually zero. Hence, there is a concentration gradient between the bulk of the solution and the layer at the electrode surface and it is this concentration gradient that is responsible for the existence of the diffusive force.

The diffusion current has great importance in polarographic analysis because most practical methods are based on its measurement.   The fundamental equation for the polarographic diffusion current was derived by the Czech chemist IIkovic in 1934 and is known as the Ilkovic equation. It is,

$$i_d = 607 \, nD^{1/2} \, C \, m^{2/3} \, t^{1/6} \qquad \qquad \dots (1)$$

Where id = Average diffusion current (in micro amperes)

N = Number of electrons consumed in the reduction of one ion or

Molecule of the substance responsible for the wave;

D = Diffusion coefficient of that substance (cm^2 per sec)

C = Concentration of the elecroactive material (millimoles per liter)

M = Rate of flow of mercury through the capillary (mg per sec)

t = Time (in seconds) which elapses between the fall of one drop and the fall of the next.

The quantities 'm' and 't' depend largely on the geometry of the capillary and are therefore called the capillary characteristics. The terms 'n', C and $D^{1/2}$ are determined by the properties of the solute and solution.

Under constant experimental conditions (supporting electrolyte composition, $E_{d.e}$ temperature etc.,) the quantities 'n' and 'D' in the Ilkovic equation are fixed for any reducible ion or molecule. However, C, m and 't' can all be varied. It is therefore convenient to rewrite the Ilkovic equation in the form

$$\frac{i_d}{cm^{2/3}t^{1/6}} = I = 607nD^{1/2}$$

... (2)

The quantity 'I' defined by this equation is called the 'diffusion current constant' and it has a characteristic value for anyone electrode process occurring under any defined set of experimental conditions.

The Ilkovic equation is important because, it accounts quantitatively for the many factors which influence the diffusion current. The diffusion current in turn depends on number of other factors including the diffusion coefficient of the depolarizing substance and its concentration in the body of the solution, number of Faradays consumed in one mole of the electrode reaction, the area of the electrode and the transfer coefficient.

The Ilkovic equation is valid only if the wave obtained is solely due to diffusion of ions from the body of the solution to the electrode surface. This equation fails if the wave obtained is partly or wholly controlled by the kinetics of the reaction, the presence of catalytically active substances in solution or the adsorption of either the oxidized or reduced ion or groups on the surface of

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mercury drop. So the validity of this equation is decided by considering whether the polarographic wave obtained is diffusion controlled or not. To decide this, the following factors are to be considered:

1. The diffusion current i_d is proportional to $m^{2/3}$ $t^{1/6}$ when the other factors in the Ilkovic equation are constant. The drop time depends upon the height of mercury column. Hence, if the wave is diffusion controlled $i_d/\sqrt{h} = K$. This is the frequently used method to ascertain whether the height of the wave is diffusion controlled or not. If 'K' is not constant within the limits of the experimental error over a wide range of the mercury heights, it may be concluded that the rate of some process other than the diffusion of metal ions.

2. 'D' the diffusion coefficient in the Ilkovic equation is given by the Nernst equation as:

$$D = \frac{RT}{ZF^2} \lambda^{\infty} \qquad \dots \ (3)$$

Where

R	=	the gas constant in volt-coulombs per degree;
T	=	Absolute temperature
λ^{∞}	=	the equivalent conductance at infinite dilution
Z	=	the charge of the ion
F	=	the number of coulombs per Faraday.

The conductivity of the solution varies rapidly with temperature causing changes in 'D' and hence in value 'i_d'. Normally 'D' and 'i_d' values increase by 2 and 3 per cent, respectively per degree rise in temperature. High deviations from these values are common tests for kinetic and catalytic currents.

3.   When other factors in the Ilkovic equation remains constant, the diffusion current i_d is directly proportional to the concentration of the reduciable or oxidizable substances.   Hence, a graph plotted between the diffusion current and concentration of the substance should give a straight line if the wave is diffusion controlled.   This forms the quantitative aspect of polarography.

Complexation of a metal ion decreases the diffusion current if the ligand is bigger in size to the water molecules it replaces and shifts the half-wave potential to more cathodic value. These two variables induced by increasing concentration of ligand allow the determination of coordination number, size and stability constants of complexes in solution or serve to elucidate the kinetics of the rate determining step depending upon the type of the electrode reaction.

OXYGEN REMOVAL

Dissolved oxygen undergoes a two-step irreversible reduction at the dropping electrode, the H_2O_2 produced in the first step is reduced to H_2O in the second. Two waves of equal size result, the first with a half-wave potential at about –0.14 V and the second at about –0.9 V (vs SCE). The two half – reactions are somewhat slow. As a consequence, the waves are drawn out over a considerable potential range.

While these polarographic waves are convenient for the determination of oxygen in solutions, the presence of this element often interferes with the accurate determination of other species. Thus, oxygen removal is ordinarily the first step in a polarographic analysis. Deaeration of the solution for several minutes with an inert gas accomplished this end. A stream of the gas, usually nitrogen, is passed over the surface during the analysis to prevent reabsorption.

POLAROGRAPHIC MAXIMA

In polarographic measurements, if no special precautions are taken, sharply defined peaks or humps, called polarographic maxima, may appear on polarograms. The occurrence of maxima is ascribed to the increased transport of depolarizer towards the electrode by a streaming motion of the solution. Such maxima, which are reproducible are called streaming maxima and according to their occurrence and properties, are divided into maxima of the first kind and maixma of the second kind.

The appearance of maxima interferes with analysis by distorting the shape of the wave and hampering the determination of wave heights. The presence of maximum not only leads to serious errors in the measurement of the half-wave potential, but also make it impossible to ascertain whether a wave is reversible or not. To avoid polarographic maxima and obtain normal polarograms, surface-active substances are added to the solution under study. The mechanism of their action can be explained with the aid of electocapillary curves. The surface-active substances adsorb on to the surface of a dropping electrode and keep the surface tension practically constant over a wide range of potentials, and cannot provide an intensive tangential motion of the surface layers of the mercury. The ability of a particular surface-active substance to suppress polarographic maxima is linearly dependent on its concentration in the solution. Usually lower concentration of maximum suppressor is recommended. At higher concentration, they render interpretation of polarograms difficult by diminishing the limiting current of the substance itself. The effectiveness of a suppressor can be expressed as the maximum dilution or the minimum necessary for complete suppression of a given maximum. The substances that have been used to suppress maxima are both numerous and varied. They include such materials as proteins and related substances (gelatin, glue, gum arabic, agar, peptone and gum ghatti), dyes (methyl red, fuchsin, methylene blue, bromophenol blue), cationic and anionic soaps (dodecyltrimethyl ammonium and hexadecyl ammonium bromides and the sodium salts of lauric, myristic and dodecyl sylphonic acids), non-ionic detergents (Trition-x-100) and such miscellaneous materials as thymol, camphor, tylose, methylcellulose and even the substances introduced into a solution by passing it through filter paper or bringing it in contact with a cork stopper.

REVERSIBLE AND IRREVERSIBLE PROCESS

Electrode reactions at d.m.e can be broadly divided into reversible and irreversible processes. Reversible reactions are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. On the other hand, irreversible reactions are so slow that they proceed only a fraction of the way towards equilibrium during the life of each drop. For these reactions, it is the rate of the electron transfer process and the manner in which this is influenced by the electrode potential that governs the relationship between the current and potential. Between these two electrode reactions, there is an intermediate class of reactions that are fast enough to approach the equilibrium during the drop life, but not quite so fast that they appear to reach it within the experimental error of measurements. This type of electrode reactions are known as quasi-reversible reactions. The values of standard rate constant, K_s of these three types of reactions are given as follows:

1.   Reversible processes where $K_s > 2 \times 10^{-2}$ cm sec^{-1}
2.   Irreversible process $K_s < 10^{-5}$ cm sec^{-1}
3.   Quasi-reversible process $K_s = 2 \times 10^{-2}$ to 10^{-5} cm sec^{-1}

The theory of reversible process was well-established in the early stages of the development of the field.

Consider a reversible reduction of an oxidant to a reductant occurring at the dropping mercury electrode which may be represented as

Oxidant + n electrons $\rightleftharpoons$ Reductant

    Ox   + ne $\rightleftharpoons$ Red   **. . . .** (4)
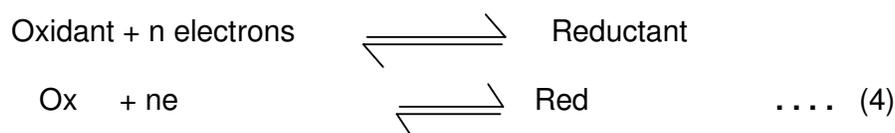
The electrode potential is given by

$$E = E^0 - \frac{RT}{nF} \ \ln \frac{a_{Re\,d}}{a_{OX}} \qquad \qquad \text{.... (5)}$$

Where a_{ox} and a_{red} are the activities of the oxidant and reductant respectively as they exist at the electrode surface, R is the gas constant, T the absolute temperature, n the number of electrons involved in the reaction and F the Faraday constant. E^0 is the electrode potential of the system when the activities of the oxidant and the reductant are equal. Writing concentration terms for activities, equation 5 becomes as

$$E = \overset{o}{E} \quad \frac{RT}{nF} \ - \quad \ln \frac{[Re\,d]_s}{[OX]_s} \qquad \qquad \text{.... (6)}$$

The current 'i' at any point on the wave is determined by the rate of diffusion of the oxidant form the bulk of the solution to the electrode surface under a concentration gradient [Ox] to $[Ox]_s$.

$$i = K([Ox] - [Ox]_s) \qquad \qquad \text{.... (7)}$$

When $[Ox]_s$ is reduced to almost zero, equation may be written:

$$i = K[Ox] = i_d \qquad \qquad \text{.... (8)}$$

Where i_d is the diffusion current. From equations (7) & (8) and, it follows that

$$[Ox]_s = \frac{i_d - i}{k} \qquad \qquad \text{.... (9)}$$

If the reductant (Red) is soluble in water and none was originally present with the oxidant, it will diffuse from the surface of the electrode to the bulk of the solution.   The concentration of $[Red]_s$ at the surface at any value of 'i' will be proportional to the rate of diffusion of the reductant from the surface of the

electrode to the solution (under a concentration gradient $[Red]_s$) and hence, also the current

$$i = K[Red]_s \qquad\qquad \dots (10)$$

If the reductant is insoluble in water, but soluble in the mercury (amalgam formation) equation (10) still holds. Substituting the values of $[Red]_s$ and $[Ox]_s$ in equation (6) it follows that :

$$E = E^o - \frac{RT}{nF} \ln \frac{K}{K} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \qquad\qquad \dots (11)$$

When 'i' is equal to $i_d / 2$, equation (11) reduces to

$$E = E_{1/2} = E^{O'} - \frac{RT}{nF} \ln \frac{K}{K} \qquad\qquad \dots (12)$$

Where $E^{o'}$ is the formal potential of the half-reaction under the experimental conditions employed.

The potential at the point on the polarographic wave where the current is equal to one-half, the diffusion current is termed as half-wave potential and is designated by $E_{1/2}$. It is quite clear from equation 12 that $E_{1/2}$ is a characteristic constant for a reversible oxidation-reduction system and that its value is independent on the concentration of the oxidant [Ox] in the bulk of the solution. It follows from equation 11 & 12 and that at 25^oC

$$E = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \qquad\qquad \dots (13)$$

This equation represents the potential as a function of the current at any point on the polarographic wave. It is sometimes termed the equation of the polarographic wave.

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The above equation indicates that a plot of $\log \dfrac{i}{i_d - i}$ versus E should

give a straight line with slope equal to $\dfrac{0.0591}{n}$ which is the most common

criterion for thermodynamic reversibility. The intercept at which the log term is

equal to zero gives the half-wave potential. Even though, this linear relationship is

usually taken as an important criterion for establishing reversibility of the

polarographic process it should be used with great caution. Very often a linear

plot is obtained for irreversible processes. However, in such cases, the value of

'n' is non-integer. Sometimes, the observed slope of such plot for a reversible

wave may differ from theoretical value by 3-5 mV, but any difference greater than

this is a proof for irreversibility.

The other factors which can be considered to decide the reversibility of an

electrode process are given below. Tom's method requires the measurement of

$E_{3/4}$ and $E_{1/4}$ i.e., the potentials at which the current is equal to three-fourths and

one-fourths of the diffusion current respectively. At $E_{1/4}$, we have:

$$E_{1/4} = E_{1/2} - \frac{0.0591}{n} \log \frac{i_d / 4}{i_d - i_d / 4} \qquad \text{.... (14)}$$

$$= E_{1/2} - \frac{0.0591}{n} \log 1/3 \qquad \text{.... (15)}$$

and at

$$E_{3/4} = E_{1/2} - \frac{0.0591}{n} \log 3 \qquad \text{.... (16)}$$

so that

$$E_{3/4} - E_{1/4} = - \frac{0.0591}{n} \log 9 \qquad \text{.... (17)}$$

$$= - \frac{0.0564}{n} \qquad \text{.... (18)}$$

Consequently the value for a reversible cathodic wave $E_{3/4} - E_{1/4}$ is equal to

$-\dfrac{56.4}{n}$ mV, for a reversible anodic wave, it is equal to $+\dfrac{56.4}{n}$ mV

The most conclusive proof of reversibility of a reaction is secured when the cathodic wave obtained with the oxidized from alone, the anodic wave obtained with the reduced form alone, and the composite wave obtained with a mixture of the two must all have the same half-wave potential.

In addition to those common criteria of reversibility, there are several others that are less often used, partly because special information must be obtained to permit their application and the important among these are temperature coefficient values and drop time. The temperature coefficient of the half-wave potential of a reversible wave is usually small, typically between –2 and +2 mV/degree. Irreversible waves often have half-wave potentials with similarly small temperature coefficients but there are some whose temperature coefficients are positive and exceed several millivolts per degree. A large positive temperature coefficient of the half-wave potential, therefore, usually signifies that the half-reaction is irreversible. The half-wave potential of a reversible wave is nearly independent of the drop time, while that of an irreversible cathodic wave becomes more positive as the drop time is increased. For a totally reversible wave, the relationship between the half-wave potential and the drop time can be written as

$$\frac{\Delta E_{1/2}}{\Delta \log t} = \frac{0.02957}{\alpha\, n_a} \qquad \text{.... (19)}$$

Where the values of $\alpha\, n_a$ ranging from about 0.1 to 2.0 for different processes and correspondingly the values of $\Delta E_{1/2} / \Delta \log t$ may range from about 300 to 15

mV. The values of $\Delta E_{1/2} / \Delta \log t$ will usually be only a few tenths of a millivolt for a reversible wave, but for irreversible reactions the value of $\Delta E_{1/2} / \Delta \log t$ exceeds very much.

APPLICATIONS OF POLAROGRAPHY:-

Polarographic analysis can be used directly for the determination of any substance – solid, liquid or gaseous, organic or inorganic, ionic or molecular that can be reduced or oxidized at dropping mercury electrode. One of the most important advantages of polarography is the determination of two or more substances by obtaining a single current – potential curve. Another important technique which involves polarographic measurements is the amperometric titration. In addition to analytical uses, polarography is one of the most fruitful techniques of research in physical, inorganic and organic chemistry. This technique is spreading more widely in subsidiary fields like biochemistry, pharmaceutical chemistry, environmental chemistry and others. It has been used to study such diverse topics as hydrolysis, solubility, complex formation, adsorption, the stoichiometry and kinetics of chemical reactions, the mechanisms of electrode reaction and of chemical reactions accompanying them, standard and formal potentials, molecular dimensions, the effects of structure on reactivity and many others of interest and importance.

The advantages of the polarographic methods of analysis can be summarized as follows:

1. Several components in a mixture can be detected and determined with an accuracy of about $\pm$ 3% which under extremely favourable conditions can be increased to $\pm$ 1.0.%

2. With the usual experimental arrangement, the volume of the electrolysed solution can be limited to 1.0 or 0.5 ml, but with special precautions the volume can be reduced to 0.005 ml. The detections limit can then be of the order 0.0001μg

3. A polarographic record can be carried out in a relatively short time, ranging from 2 to 8 minutes. The full advantage of the speed of polarographic methods is made use of in those instances in which the preparations of the solution from the sample is simple and fast. In series analysis, the preparation of the sample can often be carried out during the time in which the curve is automatically recorded. With economic sample handling, up to 12 samples an hour may be analysed

4. In polarographic analysis, a polarogram is objectively recorded that can be easily quantitatively evaluated and then filed for further reference.

Because of the sensitivity of the polarographic method, certain impurities can affect the course and accuracy of the procedures. It is therefore necessary to take precautions to ensure sufficient purity of the chemicals and glassware used.

In the preparation of solutions, the recommendations devised for the preparation of volumetric standards have provided useful.

In conclusion, it may be stated that the polarographic technique has also been widely used for a wide variety of non-analytical studies such as (a) measurements of rates of reactions, where often concentrations of both reactants and products can be followed; (b) evaluation of thermodynamic constants, such as oxidation-reduction potentials and equilibrium constants of chemical reactions occurring at the electrode surface or in the bulk of the solutions; (c) determination of diffusion co-efficients of different chemicals species in solution; (d) elucidation of reaction mechanism and equilibria, including the detection of reaction intermediates.

Cations bound in a complex can also be reduced to the metallic state or to a lower valency state as:

$$M^{n+} + ne \rightleftharpoons M \qquad \qquad \ldots \ (20)$$

$$M^{n+} + Xe \rightleftharpoons M^{+(n-x)} \qquad \ldots \ (21)$$

The interpretation of the polarographic waves obtained for such reductions was discussed by Lingane [1] in a review article. In the presence of complexing agent the characteristics of the polarographic reduction wave for metal ions in solution are altered in two distinct ways. Firstly, the half-wave potential is shifted usually to more negative values and secondly, the diffusion current becomes smaller. Generally this is ascribed to the more bulky nature of the complexed ion (compared to aqua metal ion) requiring more energy in order to undergo reduction process at the dropping mercury electrode. However, the electron exchange process remains relatively fast with respect to that of diffusion process so that the latter is still rate determining. This results in a reversible polarographic reduction of the complexed metal ion. Measurement of shift in the half-wave potential as a function of concentration of ligand can be used determine the formula and the stability constant of the complex. It should be emphasised that this information can only be obtained when the reduction or oxidation of the metal complex is reversible at the dropping mercury electrode.

Under these reactions two methods are discussed for the determination of stability constants and coordination number of metal complexes. The first one is that of Lingane, which is applicable to metal-ligand system in which a single complex species is formed to the virtual exclusion of all others over the entire ligand concentration working range. The second one is the DeFord and Hume [3]

method for the study of consecutively formed complex ions, whose stabilities differ to such an extent from one another, that each tends to predominate between fairly and sharply defined limits of ligand concentration. It is a method of mathematical analysis of the shift of half-wave potentials with ligand concentration, which makes possible the identification of successive complex ions formed and the evaluation of formation constants.

Method of Lingane

Lingane **[1]** has considered the case where reduction of the complex to the metal (soluble in mercury) at the dropping electrode. The electrode reaction for such reduction of a complexed one to the metallic state is given as

$$MX_j^{(n-jm)+} \rightleftharpoons M^{n+} + JX^{m-}$$

$$ne, E^0$$

$$M \qquad \qquad \textbf{....} \quad (22)$$
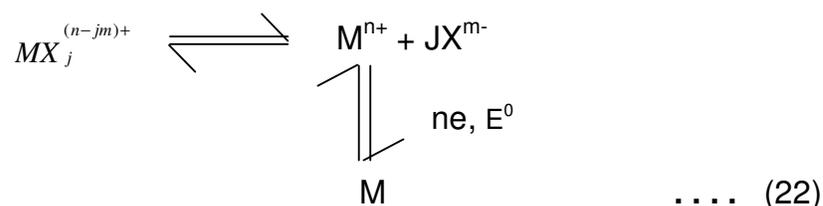
If these processes take place reversibly and much more rapidly than the rate of natural diffusion of ions to the electrode surface, then the potentials of the d.m.e at all points on the polarographic wave may be given by

$$E = E^0_A - \frac{RT}{nF} \ln \frac{c^0_A \gamma_A}{c^0_M \gamma_M} \qquad \qquad \textbf{....} \quad (23)$$

Where C^0_A is the concentration of amalgam formed on the surface of the d.m.e. and γ_A its activity coefficient. c^O_M is the concentration of the metal ion M in the solution at the drop surface and γ_M its activity coefficient, E^0_A is the standard potential of the amalgam.

The overall thermodynamic stability constant, β_{MX_j} of the complex MX_j (charges are omitted for clarity) is given by

$$\beta_{MX_j} = \frac{[MX_j]}{[M][X]^j} \qquad \ldots (24)$$

Where the terms in brackets represent activities. The concentration of the complex in the bulk of the solution, for a given concentration of metal ion and ligand, may then be written as

$$C_{MX_j} = \frac{\beta MX_j . C_M \gamma_M [X]^j}{\gamma_{MX_j}} \qquad \ldots (25)$$

At the electrode surface the metal ion will have a concentration given by

$$C^0{}_{MX_j} = \frac{\beta_{MX_j} . C_M^O \gamma_M [X]^j}{\gamma_{MX_j}} \qquad \ldots (26)$$

Now substituting the value for $c_M^o \; \gamma_M$ from equation 26 into equation 23, we have

$$E = E_A{}^0 - \frac{RT}{nF} \ln \frac{c_A^0 \gamma_A \beta_{MX_j}[X]^j}{\gamma_{MX_j} c_{MX_j}^o} \qquad \ldots (27)$$

If the complexed ions arrive at the electrode by diffusion only, the mean current at any part of the reduction wave may be given by

$$i = KI_{MX_j}(c_{MX_J} - c_{MX_j}^O) \qquad \ldots \quad (28)$$

Where K and I_{MX_j} are the capillary constant ($m^{2/3}\, t^{1/6}$), and the diffusion current

constant ($607\, n\, D^{1/2}$) of the species MX_j respectively. The limiting mean current

value as $c^O_{MX_j}$ approaches zero, will be given by:

$$i_d = KI_{MX_j} c_{MX_J} \qquad\qquad \ldots\; (29)$$

A similar relation holds in terms of the concentration of metal atoms within the

mercury, namely,

$$i = KI_A\; C^0_A \qquad\qquad ` \qquad\qquad \ldots\; (30)$$

Where I_A is the diffusion current constant of metal atoms in the amalgam.

Substituting the value for C^0_A from equation 30 into equation (27) gives

$$E = E^0 - \frac{RT}{nF}\; \ln \frac{i\gamma_A}{kI_A}\; \frac{\beta_{MX_j}[X]^j}{\gamma_{MX_j}C^0_{MX_j}} \qquad\qquad \ldots\; (31)$$

From equations we have

$$C^O_{MX_j} = \frac{i_d - i}{KI_{MX_j}} \qquad\qquad \ldots\; (32)$$

Substituting for $C^0_{MX_j}$ in equation (31)

$$E = E_A^0 - \frac{RT}{nF}\; \ln \frac{I_{MX_j}\gamma_A}{I_A}\left(\frac{i}{i_d - i}\right)\; \frac{\beta_{MX_j}[X]^j}{\gamma_{MX_j}} \qquad\qquad \ldots\; (33)$$

By substituting the condition $i = i_d/2$, the expression for half-wave potential of

reduction wave for the complex ion

$$(E_{1/2})_C = E_A{}^0 - \frac{RT}{nF} \ln \gamma_A \frac{I_{MXj}}{I_A} \frac{\beta_{MX_j}[X]^j}{\gamma_{MX_j}} \qquad \dots \ (34)$$

The corresponding equation for the half-wave potential of a simple metal ion is given by

$$(E_{1/2})_S = E_A{}^0 - \frac{RT}{nF} \ln \frac{\gamma_A}{\gamma_M} \frac{I_M}{I_A} \qquad \dots \ (35)$$

Thus, the shift in half-wave potential, produced by the presence of an excess of ligand, can be represented by the

$$(E_{1/2})_S - (E_{1/2})_C = \Delta E_{1/2}$$

$$= \frac{2.303RT}{nF} \log \frac{\gamma_M I_{MX_j}}{I_M} \frac{\beta_{MX_j}(X)^j}{\gamma_{MX_j}} \qquad \dots \ (36)$$

Assuming the diffusion current constants I_M and I_{MXj} to be approximately equal, and dropping the activity coefficients i.e., $\dfrac{\gamma_M \gamma_X{}^j}{\gamma_{MXj}} = 1$ equation 36 can be simplified as

$$\Delta E_{1/2} = \frac{0.0591}{n} \log \beta_{MX_j} + j \frac{0.0591}{n} \log C_X \qquad \dots (37)$$

Where C_X refers to the analytical concentration of the ligand

Equation (34) is written in the simplified form

$$(E_{1/.2})_C = E_A{}^0 - \frac{0.0591}{n} \log \beta_{MX_j} - j \frac{0.0591}{n} \log C_X \qquad \dots \ (38)$$

27

Hence the rate of change of half-wave potential with ligand concentration may be expressed as

$$\frac{d(E_{1/2})_C}{d \log C_x} = - j \ \frac{0.0591}{n} \ \text{(at 25}^0 \text{ C)} \qquad \qquad \text{. . . . (39)}$$

Thus, a plot of $(E_{1/2})_C$ vs log C_x should be linear of slope -j (0.0591/n) from which the coordination number j, of the complex MX_j can be found. Substituting the value of j in equation the stability constant β_{MX_j} can be determined. The Lingane method can be successfully employed for the determination of stability constant β and the formula of the metal complex (MX_j) in solution provided, the solution contains a singly complex species or more complex species or more complex species having stability constant differing by at least a power of 10.

Deford and Hume Method

De Ford and Hume [3] developed a method for determining consecutive formation constants of complex ions from polarographic data. It is a method of mathematical analysis of the shift of half-wave potentials with ligand concentration which makes possible the identification of successive complex ions formed and the evaluation of formation constants.

The reduction process of the step-equilibria between successively formed complexes can be represented as

$$M^{n+} \rightleftharpoons MX \rightleftharpoons MX_2 \rightleftharpoons \ldots\ldots\ldots \rightleftharpoons MX_n$$

$$E^o n$$

$$M(Hg) \qquad \ldots\ (40)$$
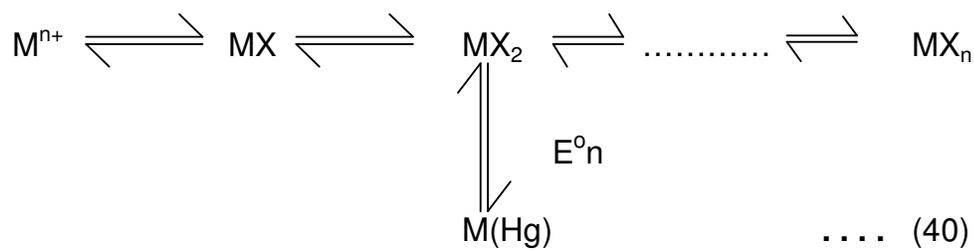
The concentration of each complex species, for a given free ligand concentration, is given by expressions of the from of equations (25) & (26) here, however, equation (26) must be summed overall possible species, so that the equation (26) becomes

$$_o^M \Sigma c^o_{MX_j} = c^o_M \gamma_M {}_o^N \Sigma \frac{\beta_{MX_J} [X]^j}{\gamma_{MX_j}} \qquad \ldots\ (41)$$

Here j = 1,2,3……….N

So equation 27 can be written as

$$E = E^o_A - \frac{RT}{nF} \ln C^o_A \gamma_A \frac{{}_o^N \Sigma \beta_{MX_j} [X]^j}{{}_o^N \Sigma c^O_{MXj} \gamma_{MX_j}} \qquad \ldots\ (42)$$

29

In terms of currents, equations of the form (28), (29) and (30) hold except that now the total current must be expressed in terms of the concentration from each species.

Thus

$$i = {}^M_O\Sigma i_{MX_j} = K {}^N_O\Sigma I_{MX_j}(c_{MX_j} - c^o_{MX_j})$$ .... (43)

Where k is the capillary constant and I_{MX_j} is the individual diffusion current constants. Alternatively,

$$i = K I_c {}^N_O\Sigma (C_{MX_j} - C^O_{MX_j})$$ .... (44)

Where I_C is the experimental mean value of the diffusion current constant for the mixture of complexes which in terms of the value for each individual species, is expressed by

$$I_c = \frac{{}^N_O\Sigma I_{MX_j}\beta_{MX_J}[X]^j/{}^\gamma MX_j}{{}^N_O\Sigma \beta_{MX_j}[X]^j/{}^\gamma MX_j}$$ .... (45)

Equation (33) becomes

$$E = E^o_A - \frac{RT}{nF}\ln\frac{I_C \gamma_A}{I_A}(\frac{i}{i_d - i}){}^N_O\Sigma\frac{\beta_{MX_J}[X]^j}{\gamma_{MX_j}}$$ .... (46)

This shift in half-wave potential is

$$\Delta E_{1/2} = \frac{2.0303\ RT}{nF}\log\left(\gamma_M\frac{I_C}{I_M}{}^N_O\Sigma\frac{\beta_{MX_j}[X]^j}{\gamma_{MX_j}}\right)$$ .... (47)

Rearranging the equation in order to calculate the individual overall constants,

$$F_O[X] = \beta_o + \beta_1[X]\frac{\gamma_M\gamma_X}{MX} + \beta_2[X]^2\frac{\gamma_M(\gamma_X)^2}{MX_2} +$$

$$... \beta_N \frac{[X]^N\gamma_M(\gamma_X)^N}{\gamma_{MX_N}}$$

$$= \text{anti log}\left(\frac{0.4343nF}{RT}\Delta E_{1/2} + \log\frac{I_M}{I_C}\right) \qquad \text{. . . (48)}$$

The symbol $F_O[X]$ if introduced for convenience to represent the experimentally measurable quantity on the right-hand side of the equation. Maintaining constant ionic strength, the activity coefficients in equation may be dropped and the equation becomes

$$F_O[X] = 1 + \beta_1[X] + \beta_2[X]^2 + ... \beta_n[X]^N \qquad \text{. . . . (49)}$$

After recording the shift in $E_{1/2}$ the various $F_O[X]$ functions are determined for each value of [X]

In order to determine $\beta 1$ ------------ $\beta_{M'}$ Leden's [R] extrapolation method is applied. It is apparent from equation that a plot of $F_O[x]$ vs [x] will be a steeply rising curve. However, as [x] approaches zero the graph will have a limiting slope of β_1 and an intercept on the $F_O[x]$ axis, of 1. Thus a preliminary value of β_1 is obtained.

A new function $F_1[x]$ is then defined as

$$F_1[X] = \left[\frac{F_O[X]-1}{[X]}\right]$$

$$= \beta_1 + \beta_2[X] + ------- \beta_N[X]^{N-1} \qquad \text{. . (50)}$$

The derived values of F_1 [x] against corresponding values of [x] can be plotted which will have a limiting slope of β_2 as [x] tends to zero, and an intercept on the F_1 [x] axis of β_1. Thus a confirmative estimation of β_1 is possible and in addition a preliminary value of β_2 is obtained. Similarly a function F_2 [x] is defined as

$$F_2[X] = \left[\frac{F_1[X] - \beta_1}{[X]} \right]$$

$$= \beta_2 + \beta_3[X] + -------- + \beta_N[X]^{N-2} \qquad \text{.. (51)}$$

This procedure is followed until all N complexes have been accounted for . For the penultimate complex, MX_{N-1}

$$F_{(N-1)}[X] = \left[\frac{F_{N-2}[X] - \beta_{N-1}}{[X]} \right]$$

$$= \beta_{N-1} + \beta_N[X] \qquad \text{.... (52)}$$

Here the plot of $F_{(N-1)}$[x] Vs [x] will be a straight line indicating the formation of penultimate complex. The final function, F_N [x], will be independent of ligand concentration and thus,

$$F_N[X] = \left[\frac{F_{N-1}[X] - \beta_{N-1}}{[X]} \right] = \beta_N \qquad \text{.... (53)}$$

So the plot will have a straight line, parallel to the x-axis is obtained giving the value of β_N.

The mathematical from of the De Ford and Hume method has several interesting consequences. It is observed that plot of F[x] vs [x] for the last complex will be a straight line with a positive slope and all previous F[x] function

plots will show curvature. These characteristics aid in establishing the number of complex lions formed and also provide a qualitative check on the validity of data.

The application of the method requires that the concentration of complexing ligand must be large in comparison with the metal ion concentration. DeFord and Hume method is best suited for the study of series of complexes of moderate and comparable stability.

A polarographic process is termed irreversible when the electron exchange process is quite slow. Nevertheless the rate limiting step may still be a diffusion process. Such a process is referred to as irreversible diffusion controlled process. Nernst equation cannot be applied in the interpretation of current-potential curves which are irreversible. The half-wave potentials in case of irreversible waves are far different from the standard potentials depending upon ' η ', the over voltage which is equal to the potential at which the reaction occurs minus the potential calculated from Nernst equation.

The Shapes of the polarograms expected for a reversible and an irreversible reduction are shown in **(Fig.3)**. In an irreversible process the current is controlled mainly by the electrode reaction rate over a large part of the curve. However, at more negative potentials the electrode reaction becomes quite rapid and consequently the diffusion process becomes rate determining. Thus the Ilkovic equation is equally applicable to the limiting currents of both reversible and irreversible processes. In the case of irreversible process the half-wave potentials corresponding to the two processes that is oxidation and reduction are quite distinct and lie on different sides of the standard potential E_0 of the depolariser. The greater the degree of irreversibility the greater is the separation. On the other hand for reversible process the cathodic and anodic half-wave potentials coincide.

In its simplest form of mechanism responsible for a totally irreversible wave may be described by the equation.
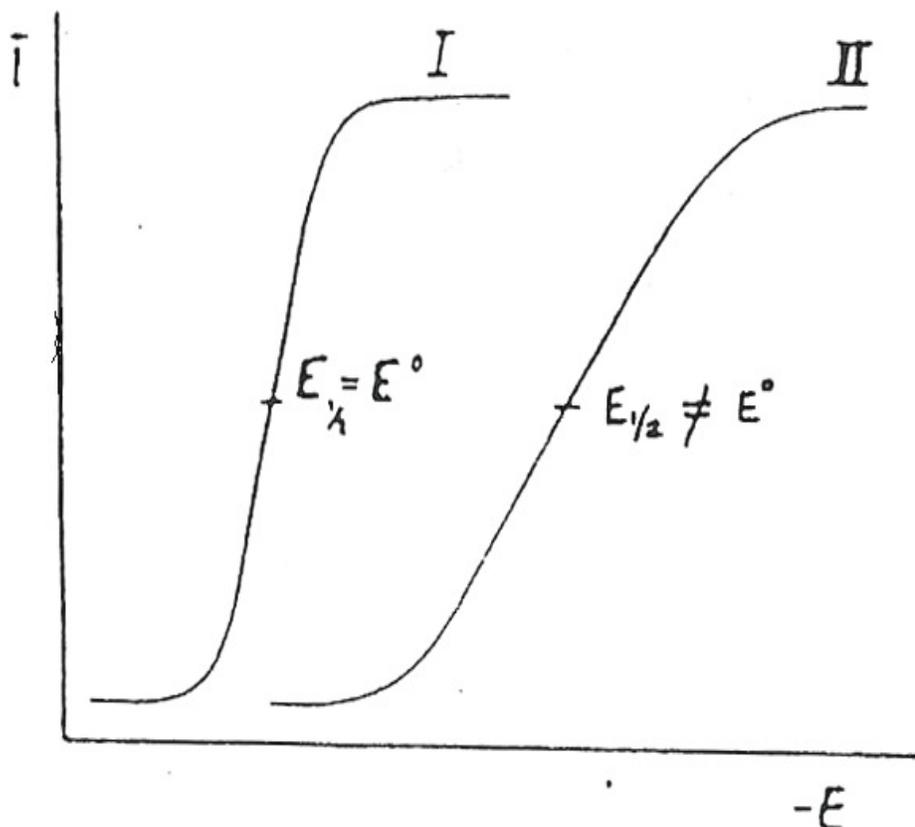
$$O \quad + \quad ne \longrightarrow R \qquad\qquad \textbf{....} \quad (54)$$

Fig.3 A reversible (I) and a totally irreversible wave (II)

Rates of forward reaction K_f and the backward reaction K_b are given by

$$K_f = K_f^o \ \exp(-afE) \qquad\qquad \dots\ (55)$$

$$K_b = K_b^O \ \exp(1-\alpha)fE \qquad\qquad \dots\ (56)$$

Where

$$f = \frac{nF}{RT};\ E = \text{potential and}\ \ \alpha = \text{transfer coefficient}$$

Superscript 'O' refers to the rate constant at E = 0. The standard rate constant is related to the individual rate constants as

$$K_S = K_f^o \exp(-\alpha fE^O) = K_b^O \exp[(1-\alpha)fE^O] \qquad\qquad \dots\ (57)$$

Hence

$$k_f = k_s \exp[-\alpha f (E - E^O)] \ and \qquad \text{.... (58)}$$

$$k_b = K_s \exp[(1-\alpha) f (E - E^o)] \qquad \text{.... (59)}$$

K_s is a fundamental parameter characteristic of the couple and it is the value of the K_s that determines whether the half-reaction is reversible or irreversible.

For a totally irreversible process the rate of a reaction expressed in moles of the substance transformed per unit time per unit area is given by

$$-\frac{dN_O}{dt} = k_f C_O^o - k_b\, C_R^o \qquad \text{.... (60)}$$

The product of flux, the area of the electrode and number of Faradys involved in the reaction gives the average polarographic current 'i' which is given by the equation

$$i = nFA\ (k_f C_O^o - k_b C_R^o) \qquad \text{.... (61)}$$

The concentration at the electrode surface can be obtained from Ilkovic equation

$$I = (i_d)_C - 607 n D_O^{1/2} C_O^o m^{2/3} t^{1/6} \qquad \text{.... (62)}$$

$$= 607\ n\ D_R^{1/2} C_R^o m^{2/3} t^{1/6} - (i_d)_a \qquad \text{.... (63)}$$

Though K_s is more useful for describing the behaviour of a particular couple, it is k_f^o (or $k_{f,h}^o$) that is more useful for comparing the behaviours of different totally irreversible couples. Moreover, it is impossible to calculate K_s unless the formal potential is known or can be calculated from data obtained on both the cathodic and anodic waves for a couple. All too often, however, the formal potential is unknown, and unless both the cathodic and anodic waves appear on polarograms there is no hope of calculating the formal potential of K_s. Therefore, the parameter has $k^0_{f,h}$ has always been evaluated for irreversible waves from polarographic data.

Numerous methods are available for the determination of the transfer coefficient and the standard rate constant which will help the understanding the kinetics of irreversible process. They are method of Matsuda and Ayabe **[14],** Koryta **[17],** Gellings **[20],** Randles **[18],** Koutecky **[12]** and Meites and Israel **[16].** The stability constants and Ligand number of metal complexes which undergo irreversible reductions at the dropping mercury electrode can also be determined by Schwarzenbach **[6,11]** and Ringbom and Eriksson methods **[8,9].**

Koutecky Method

The method of Koutecky is applicable to totally irreversible processes. By taking into account the growth of the mercury drop Koutecky **[7,12]** developed a rigorous treatment which is applicable to totally irreversible process.

Neglecting the effect of backward reaction the equation for a purely cathodic wave is given in the form **[19]**

$$i_{irr} = i_{rev} \frac{F(\chi)}{1 + \exp f} \qquad \qquad \text{.... (64)}$$

Where F(χ) is a function of χ and

$$\chi = (\frac{12\tau}{7D})^{1/2} (1 + \exp f\eta) k_f \qquad \qquad \text{.... (65)}$$

Where f=$\frac{nF}{7D}$ and $\eta = E - E_f^{o'}$ and other terms have usual significance.

In the case of totally irreversible waves (where $\eta_{1/2}$ exceeds 200mV for a one electron reduction) $\exp f\eta$ in negligible and equation (64) and (65) can be written as

$$i_{irr} = i_{rev} F(\chi) \qquad \qquad \text{.... (66)}$$

And

$$\chi = (\frac{12\tau}{7D_O})^{1/2} K_f \qquad \qquad \text{. . . . (67)}$$

The correction factors for the curvature of the dropping mercury electrode was calculated by Koutecky and Cizek and the more rigorous equation is

$$\frac{i_{irr}}{i_{rev}} = F(\chi) - \xi H_c(\chi) = F'(\chi) \qquad \qquad \text{. . . .} \quad (68)$$

Where

$$\xi = 50.4 D^{1/2} \; \Upsilon^{1/6} m^{-1/3} \qquad \qquad \text{. . . .(69)}$$

From the known values of D, Υ and m, ξ can be calculated using the equation (69) values of F(x) and H_C(x) calculated by Kouteck'y and Cizek for assigned values of χ are given for ready reference

F' (χ) can be calculated from the equation (68). Utilizing F' (χ) and ξ values 'i' can then be obtained and the corresponding value of 'E' is read from the polarogram. The transfer coefficient and the rate constants for the forward reaction can be calculated from equation (67). The standard rate constant can be calculated from a knowledge of standard potentials. A plot of log K_f Vs E should result in a straight line with a slope equal to $-0.0591/\alpha$n volt at 25°, from which the transfer coefficient can be calculated. Extrapolation to O V gives the value of k_f^o and standard rate constant can be obtained at the standard potential.

Meites and Israel Method

For a totally irreversible process whose rate is governed by a single electron transfer were studied by several authors and equations for the polarographic current potential curves were given. The most rigorous solution was given by Koutecky [7,12]. Delahay and Strassner [4,5] devised a graphical method, which yielded essentially identical values for the parameters n and $k^0_{f,h}$ From Koutecky's treatment, Kern [10] has shown that a plot of $E_{d.e}$ Vs log i/i_d-i employing average currents in the log term should be linear with a slope of –0.0591/n volt at 25^0C. These results were accepted by some of the workers concerned with the subject [13,15].

A simple and most vulnerable method was developed by Meites and Israel [16] by taking into account the numerical deductions from Koutecky's method. They have suggested the use of maximum current at the end of a drop life for the calculations of αn and $k^O_{f,h}$ from polarographic data. This procedure is more convenient in general and is better adopted to the particular case in which the drop time varies appreciably over the rising portion of the wave than the relationship based on average current that was deduced by kern. The derivation of their equation is described below.

Koutecky gave values for the function F(χ) where χ and the subsidiary variable λ that is used here for the sake of convenience are defined as

$$\lambda = \sqrt{\frac{7}{12}} \quad \chi = k_{f,h} \frac{t^{1/2}}{D_O^{1/2}} \qquad \qquad \dots \quad (70)$$

Assuming that diffusion to the electrode surface to be linear, the value of

$F(\chi)$ is equal to the ratio i/i_∞ for a polarographic wave on which the current, i,

is determined by the rate of a single electron – transfer step. The quantity i_∞ is

the current that would flow at the same potential if the rate of over all process is

strictly controlled by diffusion. Both i and i are defined as maximum currents

during a drop life. Equation (70) can be given for the totally irreversible process in

which the rate of backward reaction is negligibly small over the entire rising

portion of the wave. Then i_∞ will be equal to the diffusion current i_d, when the

potential first becomes sufficiently negative to cause 'i' to deviate significantly from

Zero.

On neglecting changes in the structure of the electrical double layer

$$k_{f,h} = k^o_{f,h} \exp(-\alpha nFE/RT) \qquad\qquad .... (71)$$

Which, when combined, with equation (70) yields

$$E = \frac{0.434\,RT}{\alpha nF} \log \frac{K^O_{f,h} t^{1/2}}{D^{1/2}_O} - \frac{0.434\,RT}{nF} \log \lambda \qquad\qquad .... (72)$$

On the basis of the values given Kouteck'y it may be shown that $\log \lambda$ is a

linear function of log i/i_d –i over nearly entire rising portion of the wave in which the

straight line represents the equation

$$\log \lambda = \text{-0.1300+0.9163 log } i/i_d - 1 \qquad\qquad ... (73)$$

On combining equations (72) & (73) it follows from Koutecky's results that

an irreversible wave of the above type must obey the equation (at $25^o c$)

$$E_{d.e} = \frac{0.05915}{\alpha n} \log \frac{1.349\,K^O_{f,h} t^{1/2}}{D^{1/2}_O} - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i} \qquad\qquad .... (74)$$

Hence, if 't' is constant and independent of potential, a plot of $E_{d.e}$ versus log i/(i$_d$-i) for such a wave should be linear and should have a slope equal to $-0.0542/\alpha n$ volt. Then

$$E_{d.e} = E' - \frac{0.0542}{\alpha n} \log \frac{i}{i_d - i} \qquad \dots (75)$$

$$E' = -0.2412 + \frac{0.05915}{\alpha n} \log \frac{(1.349\ K^{o}_{f,h} t^{1/2})}{D^{1/2}_{O}} \qquad \dots (76)$$

In these equations both $E_{d.e}$ and E' are referred with respect to SCE. Meites and Israel observed that except in unusual circumstances a plot of $E_{d.e}$ Vs log i(i$_d$-i) will be linear over nearly the entire rising portion of the wave. It was also found that the slope of such a plot depends to some extend t on the drop time employed. Hence it was suggested by them the use of the equation (75) in the form

$$E_{d.e} = E' - \frac{0.0542}{\alpha n}[\log i/(i_d - i) - 0.546 \log t] \qquad \dots (77)$$

Is preferable, where

$$E' = -0.2412 + \frac{0.05915}{n} \log \frac{1.349}{D^{1/2}_{O}} K^{o}_{f,h} \qquad \dots (78)$$

]

A plot of $E_{d.e}$ Vs [logi/i$_d$-i)) -0.546 logt] will have a slope of $-54.2 / \alpha$n mV, and an intercept where the quantity being plotted along the abscissa is zero which is equal to the parameter E' defined by the equation from which $k^{o}_{f,h}$ is calculated. The parameter n is best obtained from the slope. For waves occurring between '0' and -1.0 volts Vs SCE the variation in drop time 't' may generally be ignored but outside this region it becomes much larger and correction for 't' is necessary.

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