CHM 432: ADVANCED ELECTROCHEMISTRY

CONTENTS

1.0. ELECTRICAL DOUBLE LAYER

ELECTRICAL DOUBLE LAYER

In heterogeneous systems, an electrode can only donate or accept electrons from species that is present in a layer of solution which is immediately adjacent to the electrode. Thus, this layer may have a composition that differs significantly from that of the bulk of solution.

Let's consider the structure of the solution immediately adjacent to an electrode when a positive potential is first applied to that electrode, immediately after impressing the potential, there will be a momentary surge of current, which rapidly decays to zero if no reactive species are present at the surface of the electrode. This current is a charging current that creates an excess (or a deficiency) of negative charge at the surface of the two electrodes. As a consequence of ionic mobility, however, the layers of solution immediately adjacent to the electrodes acquire an opposing charge.

The figure below is Electrical double layer formed at electrode surface as a result of an applied field potential.

*FIGURES 1a & b are not in this text

This effect is illustrated in figure (1a). The surface of the metal electrode is shown having an excess of positive charge as a consequence of an applied positive potential. The charged solution layer consists of two parts : (1) a compact inner layer (d_o to d_1) in which the potential decreases linearly with distance from electrode surface and (2) a diffuse layer (d_1 to d_2) in which the decrease is exponential (fig 1b).

The assemblage of charge at the electrode surface and the solution adjacent to the surface is termed an electrical double layer.

Faradaic and Non faradaic current

Two types of processes can conduct current across an electrode / solution interface. One kind involves a direct transfer of electrons via oxidation reaction at one electrode and a reduction at the other. Processes of this type are called faradaic processes because they are governed by faradaic laws which state that an amount of chemical reaction at one electrode is proportional to the current i.e. faradaic current.

To understand the basic difference between a faradaic and a non-faradaic current, imagine an electron travelling down the external circuit to an electrode surface when the electron reaches the solution interface, it can do one of only two things, it can remain at the electrode surface and increase the charge on the double layer which constitutes a non-faradaic current.

Alternatively, it can leave the electrode surface and transfer to a species in the solution, thus becoming a part of a faradaic current.

Mass Transfer in Cells with the Passage of Current

A faradaic current requires continuous mass transfer of reactive species from the bulk of the solution to the electrode surface. Three mechanism bring about this mass transfer; Convection, Migration and Diffusion.

Convection: Involves mechanical motion of the solution as a result of stirring or the flow of the solution past the surface of the electrodes.

Migration: is the movement of ions through the solution brought about by electrostatics attraction between the ions and the charged electrode.

Diffusion: is the motion of species brought about by a concentration gradient.

Mechanism of Mass Transport

It is important to investigate the mechanism by which ions or molecules transported from the bulk of the solution to a surface layer (or the reverse) because knowledge of these mechanisms provides insight into how concentration polarization can be prevented or induced as required. Recall that three mechanisms of mass transport can be recognised (1) Diffusion, (2) Migration, (3) Convection. Whenever a concentration difference develops between two regions of a solution, as it does when a species is reduced at a cathode surface (or oxidized at an anode surface) ions or molecules move from the more concentrated region to the more dilute as a result of diffusion. The rate of diffusion dC/dt is given by:

$$dC/dt = K(C - C_o) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

Where C is the reactant concentration in bulk of the solution, C_o is its equilibrium concentration at the electrode surface, K is proportionality constant. As shown earlier, the value of C_o is fixed by the potential of the electrode and can be calculated from the Nernst equation. As higher potentials are applied to the electrode, C_o becomes smaller and smaller and the diffusion rate becomes greater and greater, ultimately, C_o becomes negligible with respect to C; the rate then becomes constant, i.e. when $C_o \rightarrow 0$.

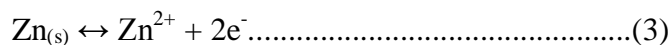$$dC/dt = kC \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

Under this condition, concentration polarization is said to be complete, and the electrode operates as an ideal polarized electrode. The process by which ions move under the influence of an electrostatic field is called Migration. It is often the primary process by which mass transfer occurs in a bulk of the solution in a cell. The electrostatic attraction (or repulsion) between a particular ionic species and the electrode becomes smaller as the total electrolyte concentration of the solution becomes greater. It may approach zero when the reactive species is but a small fraction, say 1/100, of the total concentration of ions with a given charge.
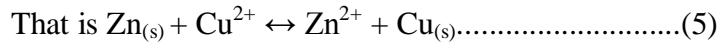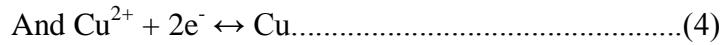
Reactants can also be transferred to or from an electrode by mechanical means. Thus forced convection such as stirring or agitation tends to decrease concentration resulting from temperature or density differences also contributes to material transport.

## Galvanic and Electrolytic Cells

*FIGURE 2 is not in this text

Figure (2) refers to a galvanic electrochemical cell with salt bridge. The net cell reaction that occurs in the figure (2) above is the sum of the two half-cell reactions:-

$$Zn_{(s)} \leftrightarrow Zn^{2+} + 2e^- \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3)$$

And $Cu^{2+} + 2e^- \leftrightarrow Cu$..(4)

That is $Zn_{(s)} + Cu^{2+} \leftrightarrow Zn^{2+} + Cu_{(s)}$...........................(5)

The potential that develops in this cell is a measure of the tendency for this reaction to proceed towards equilibrium. Thus, as shown in this figure, when the copper and Zinc ion activities are 0.01M, a potential of 1.10V develops, which shows that the reaction is far from equilibrium. As the reaction proceeds, the potential becomes smaller and smaller, ultimately reaching 0.00V when the system achieves equilibrium.

Cells such as the one shown in this figure that are operated in a way that produces electrical energy. For example, the cell under discussion could be made electrolytic by connecting the negative terminal of a dc power supply to the Zinc electrode and the positive terminal to the copper electrode. If the output of the supply was made somewhat greater than 1.10V, the two electrode reactions would be reversed and the net cell reaction would becomes

$Zn^{2+} + Cu_{(s)} \leftrightarrow Zn_{(s)} + Cu^{2+}$
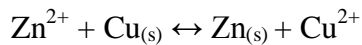
A cell in which reversing the direction of the current supply reverses the reaction at the two cell electrodes is termed a chemically reversed cell.

Anodes and Cathodes.

The cathode of an electrochemical cell is the electrode of which reduction occurs while the anode is the electrode where oxidation takes place in both galvanic and electrolytic cells.

For galvanic cell in figure 2, the copper electrode is the anode. In contrast, where this same cell is operated as an electrolytic cell, the copper electrode would be the anode and the Zinc electrode the cathode.

Ohmic Potential; IR Drop.

To develop a current in either a galvanic or an electrolytic cell, a driving force in the form of a potential is required to overcome the resistance of the ions to movement toward the anode and the cathode. Just as in metallic conduction, this force follows Ohm's law and is equal to the product of the current in amperes and the resistance of the cell in Ohms. The force is generally referred to as the ohmic potential or the IR drop.

The net effect of IR Drop us to increase the potential required to operate an electrolytic cell and to decrease the measured potential of a galvanic cell. Therefore, the IR drop is always subtracted from the theoretical cell potential. i.e.

$E_{cell} = E_{cathode} - E_{anode} - IR$......................................(6)

Polarization

Recall the equation $E_{cell} = E_{cathode} - E_{anode} - IR$

This equation predicts that at constant electrode potentials, a linear relationship should exist between the cell voltage and the current. In fact, departures from linearity are often encountered, under these circumstances, the cell is said to be polarized. Polarization may arise at one or both electrodes.

Ideal polarized and Non-polarized Electrodes and Cells

The ideal polarized electrode is one in which current remains constant and independent of potential over a considerable range.

Figure (3a) and (3b)

*FIGURES 3a & b are not in this text

Figure (3a) is a current-voltage curve for an electrode that behaves ideally in the region between A and B. Figure (3b) depicts the current-voltage relationship for a depolarized electrode that behaves ideally in the region A and B. Hence the potential is independent of the current.

Figure (4) Current-voltage curve for a cell showing real non-polarized behaviour between a and B (solid line) and polarised behaviour (dashed line).

*FIGURES 4 is not in this text

Because of the internal resistance of the cell, the current-voltage curve has a definite slope equal to R. (equation 6) rather than, the infinite slope for the ideal non-polarized electrode in fig. 4. Beyond point A and B, polarization occurs at one or both electrodes resulting in departures from the ideal straight line. Note that when polarization arises in an electrolytic cell, a higher potential is required to achieve a given current. Similarly polarization of a galvanic cell produces a potential that is lower than expected.

Concentration Polarization.

Concentration polarization is observed when diffusion, migration and convection are insufficient to transport the reactant to or from an electrode surface at a rate demanded by the theoretical current. Concentration polarization causes the potential of a galvanic cell to be smaller than the value predicted on the basis of the thermodynamic potential and the IR drop or ohmic potential (a driven force in galvanic or electrolytic cell that is equal to the product of the current in amperes and the resistance of the cell in ohms).

Similarly, in an electrolytic cell, a potential more negative than the theoretical is required to maintain a given current. Concentration polarization is important in general elecctroanalytical methods. In some applications, steps are taken to eliminate it; in others however, it is essential to the method, and every effort is made to promote it. The degree of concentration polarization is influenced experimentally by:- (1) the reactant concentration, with polarization becoming more probable at low concentration, (2) the total electrolyte concentration, with polarization becoming more probable at high concentration, (3) mechanical agitation with polarization decreasing in well-stirred solutions and (4) electrode size with polarization effects decreasing as the electrode surface area increases.

There exist three regions of a half-cell where polarization can occur. These regions include the electrode itself, a surface film of solution immediately adjacent to the electrode, and the bulk of the solution. The overall electrode reaction is: $Ox + ne^- \leftrightarrow Red$.

Several factors limit the rate at which this overall reaction occurs and thus the magnitude of the current. One of this is mass transfer which involves movement of oxidized from the bulk of the solution to the surface film. When this step or the reverse mass transfer of reduced to the bulk limits the rate of the overall reaction and thus the current, concentration polarization is said to exist.

Concentration polarization arises when the rate of transport of reactive species to the electrode surface is insufficient to maintain the current determined by the equation:-

$$E_{cell} = E_{cathode} - E_{anode} - IR$$

For example, consider a cell made up of an ideal non-polarized anode and a polarized cathode consisting of a small Cadmium electrode immersed in a solution of Cadmium ions. The reduction of Cadmium ions is a rapid and reversible process so that when a potential is applied to this electrode the surface layer of the solution comes to equilibrium with the electrode essentially. Instantaneously i.e. a brief current is generated that reduces the surface concentration of cadmium ions to the equilibrium concentration C_o given by:-

$$E = E^o_{Cd} - (0.0592/2)\log[1/ C_o]...(7)$$

In summary concentration polarization is observed when diffusion, migration and convection are insufficient to transport the reactant to or from electrode surface at a rate demanded by the theoretical current. Concentration polarization causes the potential of a galvanic cell to be smaller than the value predicted on the basis of the thermodynamic potential and the IR drop. Similarly, in an electrolytic cell, a potential more negative than the theoretical is required to maintain a given current. Concentration polarization is important in general elecctroanalytical methods. In some applications, steps are taken to eliminate it; in others however, it is essential to

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Diffusion Coefficient

Recall that a faradaic current requires continuous mass transfer of reactive species from the bulk of the solution to the electrode surface above one of the three mechanisms that bring about this mass transfer is Diffusion. Diffusion is one main cause of band spreading. The diffusion coefficient measures the rate at which a substance moves randomly from a region of high concentration to a region of lower concentration, as shown below.

*FIGURES 5 is not in this text

This figure 5 shows spontaneous diffusion of solute across a plane with a concentration gradient dx/dc. The number of moles crossing each square metre per second called the flux (J), is proportional to the concentration gradient:- i.e.

Diffusion Coefficient = Flux[mol/m^{2}s] = J = -D[dc/dx]....................................(8)

The constant of proportionality (D) is the diffusion coefficient, and the negative sign is necessary because the net flux is from the region of high concentration to the region of low concentration. The above equation is called Fick's law of diffusion. The fick's law of diffusion states that the flux of molecules diffusing across a plane of unit area is proportional to the concentration gradient and to the diffusion coefficient. If the concentration is expressed as mol/m^3, the unit of D are m^2/s i.e.

J = -D[dc/dx]...(9)

Fick's laws are differential equations describing the flux or movement of substance and its concentration under diffusion control as function of time and position. Consider a particular location x. At time t, assume that N(x) molecules are to the left of this location and that N(x + dx) molecules are to the right. After a time increment, dt, the molecules originally at x will have moved an average distance dx. Because the driving force for the motion of these molecules is a random thermal process the same number goes to the right as to go to the left. The net number of molecules that move between x and (x + dx) is given by the difference between the number of molecules on the left and the number on the right. The net movement per unit time or flux through an area A is

[1/A]dN/dt = flux/area = {[N(x)/2] –[(N(x) + dx)/2]}/Adt................................(10)

Multiplying the right hand side of equation (10) by $(dx)^2/(dx)$ converts the number of molecules to the concentration, and noting that the concentration of the species is given by

C = N/(Adx)..(11)

One obtains

Flux = J = $[(dx)^2/dt]$[C(x + dx) – C(x)]/dx...............................(12)

The first term on the right-hand side of eqn (12) is a function of the average distance the molecules have moved, dx, in a given time, dt. It is a constant, characteristic of the particular system of solute and solvent molecules, and is called the diffusion Coefficient D. By allowing dx and dt approach zero, the differential form. Fick's first law is obtained.

Flux per unit area = - [1/A]dN/dt = - D(dC/dx)...............................(13)

Which states that the flux is proportional to the concentration gradient dc/dx which is decreasing as the electrode surfaces is approached. The net transfer of solute mass per unit time across a plane intersecting a concentration profile is proportional to the steepness of the profile concentration gradient, meaning that they diffuse in the direction in which the sign of dc/dx is negative from the molecules' frame of reference.

Fick's Second Law

This law involves the change in the concentration gradient as a function of time. It is derived from the first law by noting that the change in concentration at location x_2 is given by the differences in the flux into and the flux out of an element width dx.

(dc/dt) x_2 = [D(dc/dt) $_{x2-dx}$ - D(dc/dt) $_{x2 + dx}$]/dx..........................(14)

When dx and dt approach zero, and because D is assumed independent of x and t, for planar electrodes Fick's second law becomes

dc/dt = D$[d^2C/(dx)^2]$...(15)

Levich Equation

This equation deals with methods involving convective mass transport of reactants and products. These involve systems where the electrode is in motion or where there is forced solution flow past a stationary electrode these methods take advantage of enhanced sensitivity resulting from the enhanced mass transfer of electro active substance to the electrode that occurs under hydrodynamic conditions. A steady state is attained rather quickly and measurements can be made with high precision. At steady state, double layer charging does not enter into the measurement.

In a rotatory disk electrode (which consists of a disk of electrode material embedded in a rod of an insulting material with a platinum wire sealed in a glass tubing with the sealed end ground smooth and perpendicular to the rod axis. The addition of an independent ring surrounding the disk produces a ring disk electrode.

In this electrode, the spinning disk drags with it the fluid at its surface. The hydrodynamic flow pattern that results from rapid rotation of the disk moves liquid horizontally out of and away from the centre of the disk.

The fluid at the disk surface is replenished by an upward axial flow normal to the surface once the velocity profile has been determined, the convective-diffusion relationships can be solved to give the mass transfer- limited current by Levich equation:

$$I_{lim} = 0.620nFAD^{2/3}\omega^{1/2}V^{-1/6}C ....(16)$$

Where V is the kinematic viscosity (= viscosity/density) in cm^2/sec and w is the angular frequency of rotation (2π x rotation rate). The rotation rate should be faster than $10sec^{-1}$ but slow enough to maintain laminar flow because turbulent flow must be avoided. The rate at which the electrode potential is scanned must be slow with respect to the rotation rate to allow the steady state conditions to be achieved. For a totally reversible reaction, the shape of the current-potential wave is independent of the rotation rate. Deviation of the plot of i versus $w^{1/2}$ form a straight line that intersects the origin suggests that some kinetic step is involved in the electron-transfer reaction. When this arises, the plot will be curved and tend towards the kinetically limited current as the square root of the rotation rate approaches infinity. Plotting $1/i$ versus $1/\omega^{1/2}$ yields $1/i_k$ the kinetic current upon extrapolation. Determination of the kinetic current at different values of potential then allows determination of the kinetic parameters.

Ohmic Potential

Whenever current flows, three factors decrease the magnitude of the output voltage of a galvanic cell and increase the magnitude of the applied voltage needed for electrolysis. These factors are: The ohmic potential, concentration polarization and over potential.

Any cell has some electric resistance the voltage needed to force currents (ions) to flow through the cell is called ohmic potential given as

Ohmic potential = E_{ohmic} = IR.

In a cell with no current flowing, there is no ohmic potential because I = 0. If current is drawn from the cell, the output voltage decreases because part of the energy released by the chemical reaction is needed to overcome resistance inside the cell. The voltage applied to an electrolytic cell must be great enough to drive the chemical reaction and to overcome cell resistance.

Let's denote the voltage of a galvanic cell with zero current as E_{Nernst} which is a positive number, for a spontaneous reaction. If the reaction is reversed to make it an electrolytic cell, the voltage is $-E_{Nernst}$. In the absence of any other effects the voltage of a galvanic cell is decreased by IR and the magnitude of the applied voltage in an electrolytic cell must be increased by IR for current to flow.

Effect of Ohmic Potential

Output of galvanic cell; $E_{galvanic} = E_{nernst} - IR$.

Input to electrolysis cell; $E_{electrolysis} = - E_{nernst} - IR$

Consider the cell; $Cd_{(s)}/CdCl_2$ (aq. 0.167M)/$AgCl_{(s)}$/Ag in which the spontaneous chemical reaction is

$Cd_{(s)} + 2AgCl_{(s)} \rightarrow Cd^{2+} + 2Ag_{(s)} + 2Cl^-$
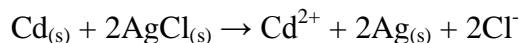
The Nernst equation tell us that the cell voltage is $E_{nernst} = 0.764V$

(a)   If the cell has a resistance of 6.42Ω and a current of 28.3mA is drawn, what will be the cell voltage?
(b)   What voltage must be applied to operate the same cell in reverse as an electrolytic cell.

Solution: with a current of 28.3mA, the voltage will decrease to.

Concentration Polarization

Concentration polarization occurs when the concentration of a species created or consumed at an electrode is not the same at the surface of the electrode as it is in bulk solution. Concentration polarization decreases the magnitude of voltage available from a galvanic cell and increases the magnitude of the voltage required for electrolytic cell.

Consider the cadmium anode for which the oxidation is $Cd_{(s)} \rightarrow Cd^{2+} + 2e^-$ eqn ....(1)

Figure 6

*FIGURE 6 is not in this text

Here (in this figure 6). The potential of the Cd^{2+}/ Cd couple depends on the concentration of the Cd^{2+} in the layer surrounding the electrode.

If the Cd^{2+} ions move rapidly away from the electrode by diffusion or convection, the concentration of Cd^{2+} is uniform throughout the entire solution. The potential for reaction

$Cd_{(s)} \leftrightarrow Cd^{2+} + 2e^-$ depends on $[Cd^{2+}]_s$ and not $[Cd^{2+}]_o$. Let's write the Nernst equation for all half reactions as reductions. And reverse the direction of equation. The anode potential is:

$$E_{(anode)} = E^o_{(anode)} - (0.05916/2)\log[(1/[Cd^{2+}]_s)] \quad ....(2)$$

If $[Cd^{2+}]_s = [Cd^{2+}]_o$, the anode potential is consistent with bulk Cd^{2+} concentration. If the current flows so fast that Cd^{2+} cannot escape from the vicinity of the electrode as fast as it is made, $[Cd^{2+}]_s$, will be greater than $[Cd^{2+}]_o$. This is concentration polarization.

The anode potential in eqn (7) becomes more positive and the cell voltage $E = E_{(cathode)} - E_{(anode)}$ becomes more negative.

Consider the Figure (7) below.

*FIGURE 7 is not in this text

This figure (7) shows the behaviour of a galvanic cell illustrating concentration polarization that occurs when $[Cd^{2+}]_s > [Cd^{2+}]_o$. The resistance of the cell is 6.42 Ω. The straight line shows the behaviour expected from ohmic potential. Deviation from the straight line at high currents is due to concentration polarization.

Concentration polarization decreases the magnitude of voltage available (output) from a galvanic cell and increases the magnitude of the voltage required (input) for electrolytic cell.

Note that when ions are not transported to or from an electrode as rapidly as they consumed or created, concentration polarization exists and $[X]_s = [X]_o$ where X is concentration of electro active species.

Effects of Ohmic potential and Concentration polarization

Output of galvanic cell; $E_{galvanic} = E_{nernst} - IR - E_{conc.}$

Input to electrolysis cell; $E_{electrolysis} = -E_{nernst} - IR - E_{conc.}$

Where $E_{conc.}$ = additional voltage.

Ions move by diffusion, convection and electrostatic forces, raising the temperature increases the rate of diffusion and thereby decreases concentration polarization. Mechanical stirring transports species through the cell. Increasing ionic strength decreases electrostatic forces between ions and electrode. These factors all affect the degree of polarization. Also the greater the electrode surface area, the more current can be passed polarization.

To decrease concentration polarization:

(a) Raise the temperature

(b) Increase stirring

(c) Increase electrode surface area

(d) Change ionic strength to increase or decrease attraction between the electrode and the reactive ion.

Figure (8).

*FIGUREs 8 is not in this text

This figure (8) is showing the behaviour of Pt and Ag cathodes at which reduction of H_3O^+ occurs at pH 3.2 in O_2-free, aqueous H_2SO_4 using saturated calomel electrode.

The reaction is $H_3O^+ + e^- \rightarrow 1/2H_2 + H_2O$

The reaction begins in earnest at approximately -0.35V at a Pt cathode and at approximately -0.8V at Ag. Question may be asked; what is going on here? If the chemistry is the same, why doesn't it require the same voltage for different electrodes? To make matter worse, when a mercury electrode was used in the same experiment, reduction did not begin until -1.3V.

Even when concentration polarization is absent and ohmic potential is taken into account, some electrolysis requires a greater than expected applied voltage than one anticipated. The difference between the expected voltage (after accounting for IR drop and concentration polarization) and the observed voltage is called the over potential ($E_{over.}$). The faster you wish to drive on electrode reaction, the greater the over potential that must be applied.

Effects of over potential, Concentration polarization

Output of galvanic cell; $E_{galvanic} = E_{nernst} - IR - E_{conc.} - E_{over.}$

Input to electrolysis cell; $E_{electrolysis} = - E_{nernst} - IR - E_{conc.} - E_{over.}$

Over potential can be traced to the activation energy barrier for the electrode reaction. The activation energy reactants can be converted to products. The higher the temperature, the greater the number of molecules with sufficient energy to overcome the barrier and faster the reaction proceeds.

Figure (9a) and (9b)

*FIGURES 9a & b are not in this text

The above figures shows schematic energy profile for electron transfer from a metal to H_3O^+ (a) with no applied potential (b) after a potential is applied to the electrode. The over potential increases the energy of the electrons in the electrode.

Figure (a) shows a high barrier preventing electron transfer from a metal electrode to H_3O^+, and the rate is very slow. If an electric potential (the over potential) is applied to the electrode, the energy of the electrons in the electrode is increased. In figure (b). The applied potential decreases the barrier that must be overcome and increase the rate of electron transfer. Over potential is the voltage needed to sustain a particular rate of electron transfer. The greater the rate, the higher the over potential must be. Thus over potential increases as current density (A/m^2) increases. The activation energy for the chemical reaction is different for different metals, which explains the different behaviours of a Pt and Ag electrodes in Figures (8).

his is the voltage that must be applied to drive the electrolysis in the absence of ohmic potential and over potential. It is called – E_{nernst} (rather than E_{nernst}) because, not the spontaneous galvanic reaction. The required electrolytic voltage is $E_{electrolysis} = - E_{nernst} – IR – $ over potentials

1.0.　　　　　　POLAROGRAPHY
- **Polarogram**
- **Diffusion current at dropping electrodes**
- **Half-wave Potential**
- **Current Potential Curves**

Polarography

In polarography, the current between the mercury (Hg) working electrode and an inert auxiliary electrode e.g. platinum electrode is being measured. Voltage is measured between the mercury electrode and a reference electrode e.g. calomel electrode. A mercury electrode gives more reproducible behaviour that does a static surface (such as platinum electrode) whose characteristics changes with use.

Secondly mercury electrode can operate at more negative potentials than most other electrodes.

Polarography is a technique by which the relationship between current and voltage is observed during electrochemical processes which involved the use of dropping-mercury electrode.

The classical dropping-mercury electrode consists of a long glass capillary tube connected to a mercury reservoir. The drop rate, which is typically one drop in 1-6 sec, is controlled by raising or lowering the levelling bulb.

The mercury drop grows continuously until it falls off; then a new one begins. A mercury electrode is used because the freshly exposed mercury surface yields reproducible current-potential behaviour.

With any other working electrode (such as Pt) current depends on the electrode surface condition. The vast majority of reactions studied with the mercury electrode are reductions. At a Pt surface reduction of solvent competes with reduction of many analytes especially in acidic solutions.

$2H^+ + 2e^- \rightarrow H_{2(g)}$ $E^o = 0$.
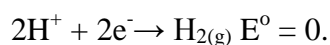
There is a large over potential for reduction of H^+ at the Hg surface. Therefore reactions that is thermodynamically less favourable than reduction of H^+ can be carried out without competitive reduction of H^+. In neutral or basic solutions, even alkali metal (Group I) cations are reduced more easily than H^+, despite their lower standard potentials. This phenomenon is partly because of the over potential for H^+ reduction and partly because reduction of a metal into a mercury amalgam is more favourable than reduction to the solid state.

e.g $K^+ + e^- \rightarrow K_{(s)}$, $E^o = -2.936V$

$K^+ + e^- + Hg \rightarrow K$ (in Hg), $E^o = -1.975V$
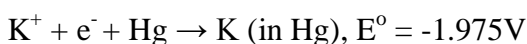
Mercury is not very used for starting oxidation reaction because Hg itself is easily oxidized. In a non complexing medium, Hg is oxidized near +0.25V (versus SCE). If the concentration of Cl^- is 1M, Hg is oxidized near 0Volt because Hg is stabilized by Cl^-.

$Hg_{(l)} + 4\,Cl^- \leftrightarrow HgCl_4^{2-} + 2\,e^-$
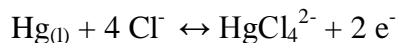
To study oxidation reactions by voltammetry Pt, au, or C working electrodes in appropriate solvents provides a wide range of accessible redox potentials.

POLAROGRAM

The graph of current versus potential in polarography is called a polarogram.

The figure 10 below shows the reduction of Cd^{2+} recorded by using the dropping-mercury electrode.

*FIGURE 10 is not in this text

Figure (10) Shows classical direct current polarogramms (old one) of (a) 5mM Cd^{2+} in 1M HCl and (b) 1M HCl alone. Note that voltage becomes more negative to the right and the scale of current is in microamperes.

The mercury electrode suspends a static drop of mercury with a fixed size and then measures current and voltage with this drop. Then the next drop is suspended and the next measurements are made. The constant size drops give the smooth curve in the figure below.

Figure (11) shows a sampled current polarograms mercury of (a) 5mM Cd^{2+} in 1M HCl alone.

*FIGURE 11 is not in this text

Diffusion current at dropping electrodes

In deriving an equation for polarographic diffusion currents, it is necessary to take into account the rate of growth of the spherical electrodes, which is related to the drop time in seconds t and the rate of flow of mercury through the capillary m, in mg/s and the diffusion coeffi9cient of the analyte D in cm^2/s and the diffusion variables are taken into account in the Ikovic equation;

$(Id)_{max} = 706nD^{1/2}m^{2/3}t^{1/6}C$

Where $(Id)_{max}$ = Maximum current in microamperes

C = the analyte concentration in mill moles per litre. To obtain an expression for the average current rather than the maximum, the maximum, the constant in the foregoing equation becomes 607 rather than 706. That is

$(Id)_{avg} = 607nD^{1/2}m^{2/3}t^{1/6}C$

Note that either the average or the maximum current can be used in quantitative polarography. The product $m^{2/3}t^{1/6}$ in the Ikovic equation called the capillary constant, described the influence of dropping electrode upon the diffusion current, both m and t are readily evaluated experimentally. Comparison of diffusion currents from the different capillaries is thus possible.

Half-wave Potential

$E = E_{1/2} - (0.0592/n)\log[(i/i_l-i)]$

Where $E_{1/2}$ = half-wave potential

I_l = limiting current

A plot of E against $\log[(i/i_l-i)]$ gives a straight line with the slope = $-$ (0.0592/n) and the intercept = $E_{1/2}$

Current Potential Curves

If both the oxidant and reductant are initially present and both are in solution, then a Volta metric wave would look like below: (Figure 12)

*FIGURE 12 is not in this text

The anodic current $(-id)_a$ arises when the reduced form is being oxidized at the electrode under these conditions the current potential relation assumes the form:

$$E = E_{1/2} + (0.0592/n)\log[((id)_c-i/i-(id)_a]$$

Question:- The measurements shown in the table were made on a reversible dc polarographic wave for the reduction of 3.5 x 10^{-3}M Nitrate in dimethylformamide at 25°C. The limiting diffusion current was 3.30µA on the plateau of the polarographic wave, the drop time was 43.7 seconds for 10 drops and 30 drops had a mass of 0.1962g.

(a)   What number of electrons was involved in the electrode reaction?
(b)   What is the half-wave potential for these reactions?
(c)   Calculate D for Nitrate in the dimethylformamide.

| E(V vs SCE)	i/ µA
-0.519	0.40
-0.520	1.02
-0.531	1.55
-0.538	2.01
-0.548	2.56
-0.560	3.01
-0.568	3.20

3.0 EMF OF CELLS

- **Effect of Activity on electrode Potential E^o**

- **The Standard Electrode Potential E^o**

- **Effect of Activity on electrode Potential**
- **Thermodynamic data from cell E.M.F**
- **The Temperature-dependence of the E.M.F**
- **Effect of Activity on electrode Potential**

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Let us consider the half-reaction

$pP + qQ +$----------------------$+ ne^- \leftrightarrow rR + sS$
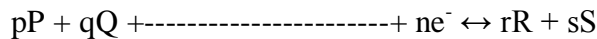
Where P,Q,R,S are reacting species, e^- = no of electrons and p,q,r,s are number of moles.

$E = E^o - (RT/nF)\ln[(aR)^r \times (aS)^s/(aP)^p \times (aQ)^q]$--------------------(1)

At room temperature, (298K)

$RT/nF = 0.05916/n$

Hence $E = E^o - (0.05916/n)\log[(aR)^r \times (aS)^s/(aP)^p \times (aQ)^q]$--------(2)

Equation (2) is a general statement of the Nernst equation which can be applied to both half-cell reaction or cell reactions

The Standard Electrode Potential E^o

Consider the potential for the process

$Ag^+ + e^- \leftrightarrow Ag_{(s)}$, $E^o = +0.799V$
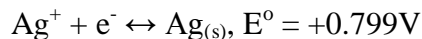
The nernst equation is; $E = 0.779 - (0.05916/n)\log[aAg/aAg^+]$------------(3)

Since the activity of Ag is unity, since it is a solid eqn (3) becomes

$E = 0.779 - (0.05916/n)\log[1/aAg^+]$

Example 1: What is the electrode potential for half-cell consisting of a cadmium electrode immersed in a solution that is 0.0150M in Cd.

Example 2: Calculate the potential for a platinum electrode immersed in a solution prepared by saturating a 0.0150M solution of KBr with Br_2. Given that the half-cell reaction is:-

$Br_{2(l)} + 2e^- \leftrightarrow 2Br^-$, $E^o = 1.065V$, and state any assumption made. Where (L) indicates saturated solution

Example 3:- Calculate the potential for a platinum electrode immersed in a solution that is 0.015M in KBr and 1.00×10^{-3} in Br_2. Given that the half-reaction

$Br_{2(l)} + 2e^- \leftrightarrow 2Br^-$, $E^o = 1.087V$,

Thermodynamic data from cell E.M.F

To relate ΔG^o to E^o, combine $E^o = (RT/F)lnK$ with the expression $\Delta G^o_m = -RTlnK$, the

$\Delta G^o_m = -nFE^o$, where F = Faraday, n = no of mole of electrons

The Temperature-dependence of the E.M.F

The variation of ΔG with temperature is given by $(dE/dT)_p = \Delta S_m/F$

The measurement of the gradient of the e.m.f of a cell with respect to temperature gives the values of the entropy change (ΔS_m) of the cell rxn.

Since $\Delta G = \Delta H - T\Delta S$, the two results can be combined to give the enthalpy change in the reaction $\Delta H_m = \Delta G_m + T\Delta S_m = -F[E-T(dE/dT)_p]$.

Question:- At 20^oC the std e.m.f of the cell $Hg/Hg_2Cl_{2(s)}$ $HCl_{(aq)}$ H_2, Pt is 0.2692V and at 30^oC it is 0.2660V. Find the values of ΔG_m, ΔH_m, and ΔS_m at 25^oC.

The cell reaction is $1/2Hg_2Cl_{2(s)} + 1/2H_{2(g)} \leftrightarrow Hg_{(l)} + HCl_{(aq)}$

Corresponding to a 1-electron transfer.

Answer:- $\Delta G^o_m = -nFE^o$

$\Delta G^o_{m(293K)} = -(9.649 \times 10^4) \times (0.2692V)$

$= -25.98kJmol^{-1}$

And $\Delta G^o_{m(303K)} = -(9.649 \times 10^4) \times (0.2660V)$

$= -25.67 kJmol^{-1}$

Hence $\Delta G^o_{m(298K)} = \Delta G^o_{m(298K)} + \Delta G^o_{m(303K)}/2$

$$= -25.82 \text{ kJmol}^{-1}$$

And $[d\Delta G^o_m/dT]_{298K} = [-25.67-(25.98)]/[303-293]$

$$= 31.00 \text{JK}^{-1}\text{mol}^{-1}$$

It follows that $\Delta S^o_m = (d\Delta G^o_m/dT)_{298K} = -31.00 \text{JK}^{-1}\text{mol}^{-1}$

And $\Delta H^o_m = \Delta G^o_m + T\Delta S^o_m$

$$= -25.82 + (298)\text{x}(-31.00)/1000$$

$$= -35.06 \text{ kJmol}^{-1}$$

Note that: For the reaction $Hg_2Cl_{2(s)} + 1/2H_{2(g)} \leftrightarrow 2Hg_{(l)} + 2HCl_{(aq)}$ simply these values by 2. Then at 298K $\Delta G^o_m = -51.64 \text{ kJmol}^{-1}$, $\Delta H^o_m = -62 \text{ kJmol}^{-1}$ and $\Delta S^o_m = -70.12 \text{ JK}^{-1}\text{mol}^{-1}$.