

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

$$E_{(\text{anode})} = E^{\circ}_{(\text{anode})} - (0.05916/2)\log[(1/[\text{Cd}^{2+}]_s)] \dots\dots\dots(2)$$

If $[\text{Cd}^{2+}]_s = [\text{Cd}^{2+}]_o$, 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, $[\text{Cd}^{2+}]_s$ will be greater than $[\text{Cd}^{2+}]_o$. This is concentration polarization.

The anode potential in eqn (7) becomes more positive and the cell voltage $E = E_{(\text{cathode})} - E_{(\text{anode})}$ 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 $[\text{Cd}^{2+}]_s > [\text{Cd}^{2+}]_o$. The resistance of the cell is 6.42Ω . 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; $E_{\text{galvanic}} = E_{\text{nernst}} - IR - E_{\text{conc}}$.

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

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 $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow 1/2\text{H}_2 + \text{H}_2\text{O}$

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; $E_{\text{galvanic}} = E_{\text{nernst}} - IR - E_{\text{conc.}} - E_{\text{over}}$.

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

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).

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

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 than does a static surface (such as platinum electrode) whose characteristics changes with use.

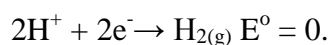
Secondly mercury electrode can operate at more negative potentials than most other electrodes.

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.

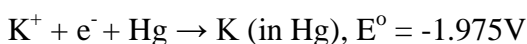
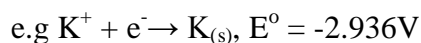
The classical dropping-mercury electrode consists of a long glass capillary tube connected to a mercury reservoir. The drop rate, which is typically one drop in 1-6 sec, is controlled by raising or lowering the levelling bulb.

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.

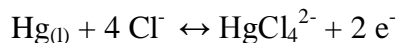
With any other working electrode (such as Pt) current depends on the electrode surface condition. The vast majority of reactions studied with the mercury electrode are reductions. At a Pt surface reduction of solvent competes with reduction of many analytes especially in acidic solutions.



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.



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^- .



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 polarograms (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 coefficient of the analyte D in cm^2/s and the diffusion variables are taken into account in the Ikovic equation;

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

Where $(I_d)_{\max}$ = 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

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

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

$$E = E_{1/2} - (0.0592/n)\log[(i/i_1-i)]$$

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 Voltametric wave would look like below: (Figure 12)

*FIGURE 12 is not in this text

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

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

Question:- The measurements shown in the table were made on a reversible dc polarographic wave for the reduction of $3.5 \times 10^{-3}M$ Nitrate in dimethylformamide at $25^\circ C$. The limiting diffusion current was $3.30\mu A$ 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.

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

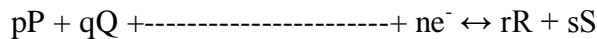
E(V vs SCE)	i/ μA
-0.519	0.40
-0.520	1.02
-0.531	1.55
-0.538	2.01
-0.548	2.56
-0.560	3.01
-0.568	3.20

3.0 EMF OF CELLS

- **Effect of Activity on electrode Potential E°**

- **The Standard Electrode Potential E°**
 - **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**

Let us consider the half-reaction



Where P,Q,R,S are reacting species, e^- = no of electrons and p,q,r,s are number of moles.

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

At room temperature, (298K)

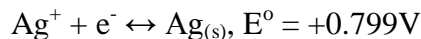
$$RT/nF = 0.05916/n$$

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

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°

Consider the potential for the process



$$\text{The nernst equation is; } E = 0.779 - (0.05916/n)\log[aAg/aAg^+] \text{-----(3)}$$

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 Br₂. Given that the half-cell reaction is:-

$\text{Br}_{2(l)} + 2e^- \leftrightarrow 2\text{Br}^-$, $E^\circ = 1.065\text{V}$, 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 Br₂. Given that the half-reaction

$\text{Br}_{2(l)} + 2e^- \leftrightarrow 2\text{Br}^-$, $E^\circ = 1.087\text{V}$,

Thermodynamic data from cell E.M.F

To relate ΔG° to E° , combine $E^\circ = (RT/F)\ln K$ with the expression $\Delta G^\circ_m = -RT\ln K$, the

$\Delta G^\circ_m = -nFE^\circ$, 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°C the std e.m.f of the cell $\text{Hg}/\text{Hg}_2\text{Cl}_{2(s)} \text{HCl}_{(aq)} \text{H}_2, \text{Pt}$ is 0.2692V and at 30°C it is 0.2660V. Find the values of ΔG_m , ΔH_m , and ΔS_m at 25°C.

The cell reaction is $1/2\text{Hg}_2\text{Cl}_{2(s)} + 1/2\text{H}_{2(g)} \leftrightarrow \text{Hg}_{(l)} + \text{HCl}_{(aq)}$

Corresponding to a 1-electron transfer.

Answer:- $\Delta G^\circ_m = -nFE^\circ$

$$\begin{aligned}\Delta G^\circ_{m(293K)} &= -(9.649 \times 10^4) \times (0.2692\text{V}) \\ &= -25.98\text{kJmol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{And } \Delta G^\circ_{m(303K)} &= -(9.649 \times 10^4) \times (0.2660\text{V}) \\ &= -25.67\text{kJmol}^{-1}\end{aligned}$$

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

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

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

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

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

$$\text{And } \Delta H_m^\circ = \Delta G_m^\circ + T\Delta S_m^\circ$$

$$= -25.82 + (298)\times(-31.00)/1000$$

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

Note that: For the reaction $\text{Hg}_2\text{Cl}_2(\text{s}) + 1/2\text{H}_2(\text{g}) \leftrightarrow 2\text{Hg}(\text{l}) + 2\text{HCl}(\text{aq})$ simply these values by 2.
Then at 298K $\Delta G_m^\circ = -51.64 \text{ kJmol}^{-1}$, $\Delta H_m^\circ = -62 \text{ kJmol}^{-1}$ and $\Delta S_m^\circ = -70.12 \text{ JK}^{-1}\text{mol}^{-1}$.