

ELECTROCHEMISTRY I

The science concerned with the study of electron transfer across phase boundary

Electrode: Is a conducting material immersed in a media.

Electrode potential: Is the potential difference across formed across the phase boundary or the double layer.

Double Layer: Is the arrangement of positive and negative charges

Spontaneous process: Is a process that occurs naturally [Cold to Hot , Up to Down,]

Electrolytic Solution Pressure of a Metal P: Is the tendency of a metal to go into solution as ions.

Osmotic Pressure p: Is the tendency of the metal ions to deposit on the metal.

Example 1

$P > p$ The metal will continue to dissolve into ions and the electric field will increase around the electrode (at boundary) until equilibrium is reached.

If $p > P$ the ions will deposit until equilibrium is reached.

Sign Convention:

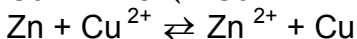
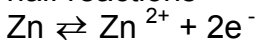
The SI units are used and hence the European convention [IUPAC] i.e. the electrode potential is given the sign of the charge on the metal side . Contrary to the American convention.

Example 2

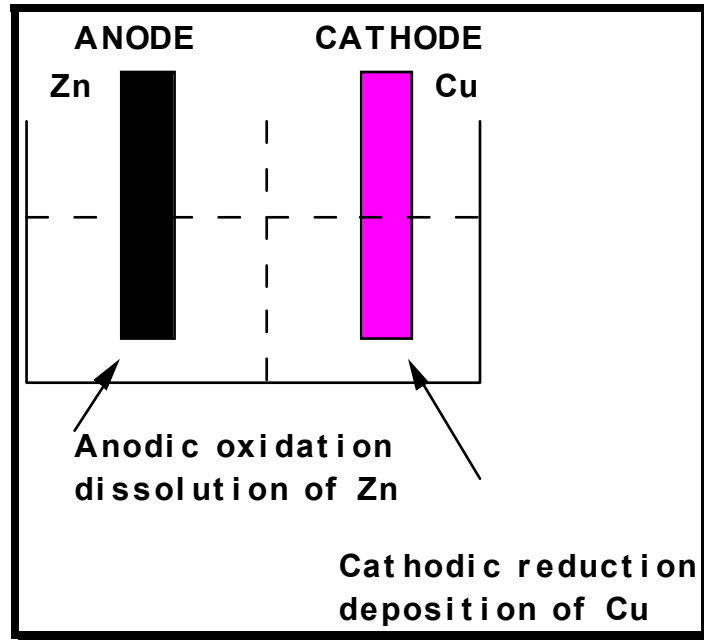
$\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2\text{e}^-$ $E_{\text{Zn/Zn}^{2+}}^{\circ}$ is -ve and equals - 0.76 v vs NHE

Anodes and Cathodes

Zn metal is more easily oxidized than Cu metal. Cu ions are more easily reduced than Zn ions. Thus the spontaneous reaction in a voltaic cell is the sum of two half reactions



The Zn in this example is the **anode** and the Cu is the **cathode** . The anode is the sight of oxidation while the cathode is the site of reduction. How could you tell in general which of two metals will be the cathode and which will be the



anode. The one with -ve value of potential in the e.m.s. is the anode when existing with one with +ve value of potential. The more -ve is the anode when the two are -ve. When the two are +ve the less positive is the anode.

TYPES [KINDS] OF REVERSIBLE ELECTRODES

1-Electrode of the first kind

An element in contact and in equilibrium with its ions

a- Metal-metal ions electrode M / M^{n+}

Ex. Zn / Zn^{2+} Ag / Ag^+

b- The Gas electrode

A gas in contact with its own ions in solution. In this case the electrode is not a conducting material Pt or another unattackable metal which can attain a rapid equilibrium with the gas is used for the purpose of contact.

H_2 / H^+ , Pt Cl_2 / Cl^- , Pt O_2 / OH^- , Pt

c- The Amalgam Electrode

An amalgam of a certain metal in contact with a solution containing its own ions

$Na(Hg) / Na^+$ $Cd(Hg) / Cd^{2+}$

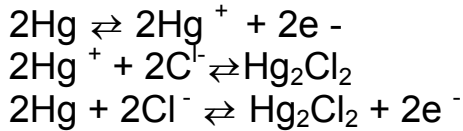
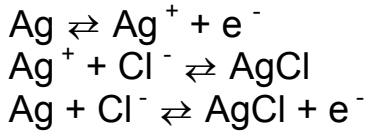
2-Electrode of the second kind

A metal covered with one of its sparingly soluble salt immersed in a solution containing the anions of this salt.

$Ag / AgCl / Cl^-$ (Silver-Silver chloride electrode)

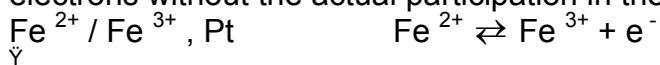
$Hg / Hg_2Cl_2 / Cl^-$ (Calomel electrode)

Mechanisms



3-Electrode of the third type

It is an inert electrode immersed in a solution containing two oxidation states of a same species. It is important to notice that the inert electrode takes and gives electrons without the actual participation in the electrode reaction.



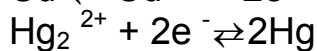
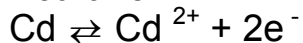
STANDARD CELLS

A standard cell can be easily prepared in a laboratory, can be stored without any change in EMF and is nearly temperature independent.

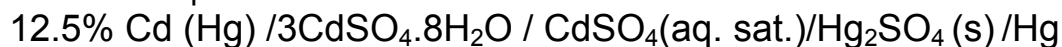
Weston Cadmium Cell

This is an H type cell consisting of two limbs. The LHS limb contains Cd amalgam covered with crystals of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$. The RHS contains Hg with solid Hg_2SO_4 and covered with crystals of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$. The whole cell is filled with a saturated solution of CdSO_4 . The EMF of this cell is 1.01807 v at 25 °C and decrease about 4×10^{-5} v / degree.

Mechanism



The cell is represented as follows



DERIVATION OF THE NERNST EQUATION

The Nernst equation can be derived in several ways two ways are discussed. The derivation on Thermodynamic basis and the derivation on kinetic basis.

Thermodynamic Basis

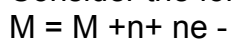
The activity is related to the free energy by

$$dG = RT d \ln a$$

$$G = G^\circ + RT \ln a \quad (1)$$

G° is the free energy of the system when the activity is unity and is known as the standard free energy.

Consider the following equation



Applying equation 1

$$G_m = G_m^{\circ} + RT \ln a_m, \quad G_{m^{n+}} = G_{m^{n+}}^{\circ} + RT \ln a_{m^{n+}}$$

$$\Delta G = G_p - G_r$$

$$\Delta G = (G_{m^{n+}} = G_{m^{n+}}^{\circ} + RT \ln a_{m^{n+}}) - (G_m = G_m^{\circ} + RT \ln a_m)$$

$$\Delta G = (G_{m^{n+}}^{\circ} - G_m^{\circ}) + RT \ln a_{m^{n+}} / a_m$$

$$\Delta G = \Delta G^{\circ} + RT \ln a_{m^{n+}} / a_m \quad (2)$$

Since $\Delta G = -nFE$

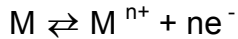
deviding 2 by $-nF$

One obtains the Nernst equation

$$E = E^{\circ} + RT/nF \ln a_{m^{n+}} / a_m$$

Kinetic Basis

Consider the following equation



The rate of the forward reaction $v_f = k a_m e^{\alpha nFE/RT}$

The rate of the backward reaction $v_b = k' a_{m^{n+}} e^{-(1-\alpha)nFE/RT}$

at equilibrium $v_f = v_b$

and hence the following series of equation can be derived

$$k a_m e^{\alpha nFE/RT} = k' a_{m^{n+}} e^{-(1-\alpha)nFE/RT}$$

$$e^{\alpha nFE/RT} / e^{-(1-\alpha)nFE/RT} = k' / k \cdot a_{m^{n+}} / a_m$$

$$e^{nFE/RT} = k' / k \cdot a_{m^{n+}} / a_m$$

$$nFE/RT = \ln k' / k + \ln a_{m^{n+}} / a_m$$

$$E = RT/nF \ln k' / k + RT/nF \ln a_{m^{n+}} / a_m$$

$$E = E^{\circ} + RT/nF \ln a_{m^{n+}} / a_m$$

The generalized form of Nernst equation is

$$E = E^{\circ} + RT/nF \ln \Pi a(\text{Oxidant}) / \Pi a(\text{Reductant})$$

or

$$E = E^{\circ} + 2.303RT/nF \log \Pi a(\text{Oxidant}) / \Pi a(\text{Reductant})$$

Π means the product of activities of various species

Example



$$E = E^\circ + \frac{2.303 RT}{nF} \log \frac{(aC)^c (aD)^d}{(aA)^a (aB)^b}$$

APPLICATION OF NERNST EQUATION ON DIFFERENT TYPES OF ELECTRODES

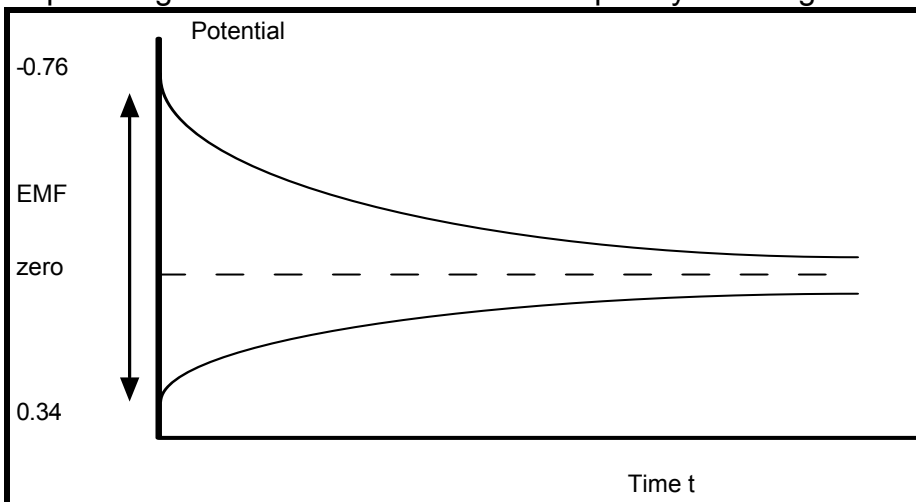
TYPES OF GALVANIC CELLS

An assembly of two electrodes or in another word of two half cells produces what so called a galvanic cell or voltaic cell that has the ability of producing an electric current. Each of the half-reaction contributes to the total voltage of the cell. |

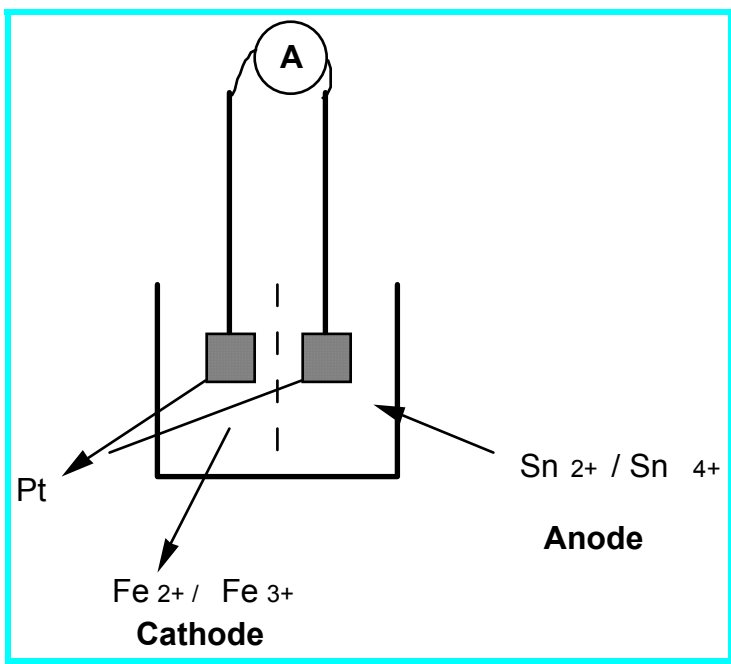
An example of a simple galvanic cell is the Daniel cell composed of two compartments (half-cells) Zn and Cu . As Cu is less reactive than zinc with a standard emf of +0.34 it acts as the cathode , on the other had Zn -0.76 acts as the anode the net emf E of the cell(if $a_{Cu^{2+}}$ and $a_{Zn^{2+}}$ are both unity) is thus equal to

$$E = E^\circ_c - E^\circ_a = E_R - E_L = 0.34 - 0.76 = 1.1 \text{ v}$$

If these electrodes are connected externally through a resistance and a galvanometer , the equilibrium is disturbed and a current flows through the circuit. This flow of current is accompanied by an increase in Zn^{2+} concentration and a consecutive decrease in Cu^{2+} concentration will occur As the Zn^{2+} concentration increases the electrode potential of this half- cell will increase and thus will shift to more +ve potential. As the Cu^{2+} concentration decreases, the potential becomes less than 0.34 and thus will shift to more -ve potential. After a time t the EMF of this cell will decrease until it reaches zero and the current will stop flowing and the cell is said to be completely discharged.



Oxidation-Reduction Cells



These are cells in which the electrodes are redox electrodes.

Anodic reaction is $\text{Sn}^{2+} \rightleftharpoons \text{Sn}^{4+} + 2e^-$

Cathodic reaction is $2\text{Fe}^{3+} + 2e^- \rightleftharpoons 2\text{Fe}^{2+}$

The net reaction $\text{Sn}^{2+} + 2\text{Fe}^{3+} \rightleftharpoons \text{Sn}^{4+} + 2\text{Fe}^{2+}$

This means that Sn^{2+} reduces Fe^{3+} since it has higher oxidation potential.

EMF of the cell =

$$E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.77 - (-0.15) = 0.92 \text{ V}$$

$$\text{EMF} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= \left(E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}} + \frac{RT}{2F} \ln \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} \right) - \left(E^\circ_{\text{Sn}^{2+}/\text{Sn}^{4+}} + \frac{RT}{2F} \ln \frac{a_{\text{Sn}^{4+}}}{a_{\text{Sn}^{2+}}} \right)$$

$$= \left(E^{\circ}_{\text{Fe}^{2+}/\text{Fe}^{3+}} - E^{\circ}_{\text{Sn}^{2+}/\text{Sn}^{4+}} \right) - \frac{RT}{2F} \ln \frac{a_{\text{Fe}^{3+}} \cdot a_{\text{Sn}^{4+}}}{a_{\text{Fe}^{2+}} \cdot a_{\text{Sn}^{2+}}}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{2F} \ln K$$

$$\text{where } K = \frac{a_{\text{Fe}^{3+}} \cdot a_{\text{Sn}^{4+}}}{a_{\text{Fe}^{2+}} \cdot a_{\text{Sn}^{2+}}}$$

Multiply by $-2F$, EMF of the cell $\Delta G = -nFE$ K : is the equilibrium constant of the cell reaction.

At equilibrium $\Delta G = \text{Zero}$

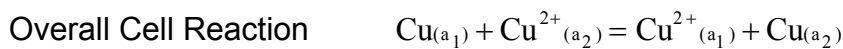
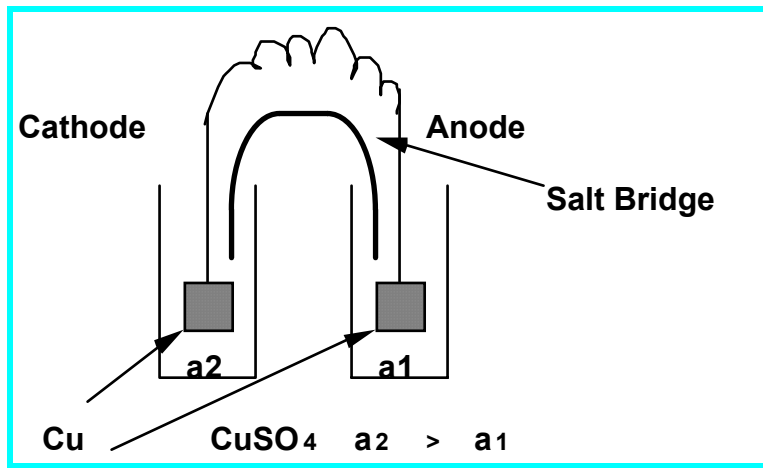
$$\Delta G^{\circ} = RT \ln K$$

$$\text{but } \Delta G^{\circ} = -nFE^{\circ}$$

$$nFE^{\circ}_{\text{cell}} = RT \ln K$$

Since n , F , E° , R and T are known, we can calculate the equilibrium constant of the cell reaction " K ".

Concentration Cells



$$\text{EMF} = E_c - E_a$$

$$= E^\circ + \frac{RT}{2F} \ln a_2 - E^\circ - \frac{RT}{2F} \ln a_1$$

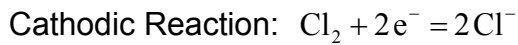
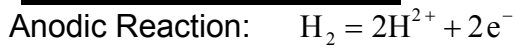
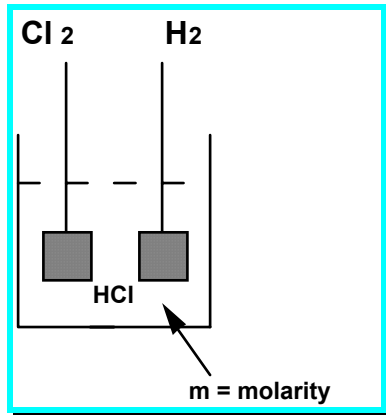
$$= \frac{RT}{2F} (\ln a_2 - \ln a_1) = \frac{RT}{2F} \ln \frac{a_2}{a_1}$$

$$\text{EMF} = \frac{RT}{2F} \ln \frac{a_2}{a_1}$$

$$\text{If } a_1 = a_2 = \ln \frac{a_2}{a_1} = \text{Zero}$$

\therefore EMF = Zero i.e. no current pass.

Concentration Cell (Chlorine-Hydrogen Cell)



$$E_{\text{H}_2/\text{H}} = E^\circ_{\text{H}_2/\text{H}^+} + \frac{RT}{2F} \ln \frac{a_{\text{H}^+}^2}{P_{\text{H}_2}} \quad \text{anode}$$

$$= \frac{RT}{2F} \ln a_{\text{H}^+}^2$$

$$E_{\text{Cl}_2/\text{Cl}} = E^\circ_{\text{Cl}_2/\text{Cl}^-} + \frac{RT}{2F} \ln \frac{P_{\text{Cl}_2}}{a_{\text{Cl}^-}^2} \quad \text{Cathode}$$

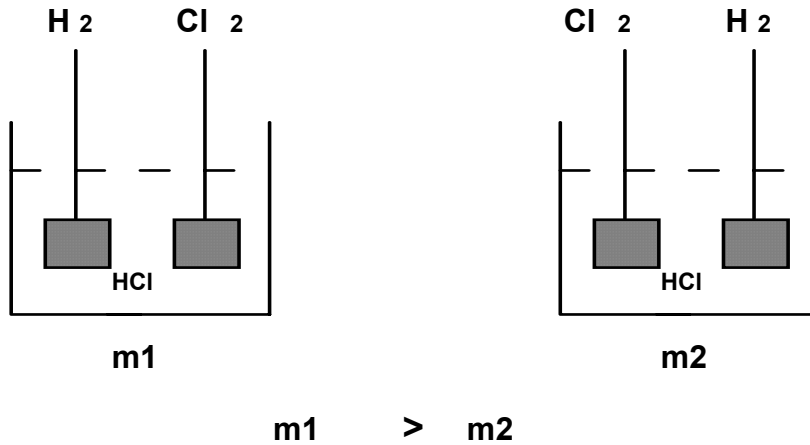
$$= E^\circ_{\text{Cl}_2/\text{Cl}^-} - \frac{RT}{2F} \ln a_{\text{Cl}^-}^2$$

$$\begin{aligned} \text{EMF} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E^{\circ}_{\text{Cl}_2/\text{Cl}^-} - \frac{RT}{2F} \ln a_{\text{Cl}^-}^2 - \frac{RT}{2F} \ln a_{\text{Cl}^+}^2 \end{aligned}$$

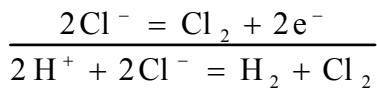
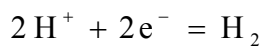
assume that $\gamma_{\text{H}^+} = \gamma_{\text{Cl}^-}$

$$\begin{aligned} \text{EMF} &= E^{\circ}_{\text{Cl}_2/\text{Cl}^-} - \frac{RT}{F} \ln [\text{H}^+][\text{Cl}^-] \text{ since } [\text{H}^+] = [\text{Cl}^-] = m \\ &= E^{\circ}_{\text{Cl}_2/\text{Cl}^-} - \frac{2RT}{F} \ln m^2 \\ &= E^{\circ}_{\text{Cl}_2/\text{Cl}^-} - \frac{2RT}{F} \ln m \text{ where "m" is the molarity of HCl} \end{aligned}$$

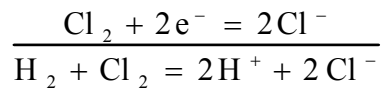
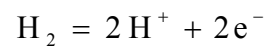
Concentration Cell without Transport (Helmholtz double Cell)



This cell will react to decrease m_1



This cell will react to increase m_2



$$E_1 = E^\circ - \frac{2RT}{F} \ln m_1$$

$$E_2 = E^\circ - \frac{2RT}{F} \ln m_2$$

$$\text{EMF (Combination)} = E_2 - E_1 \quad (E_2 > E_1)$$

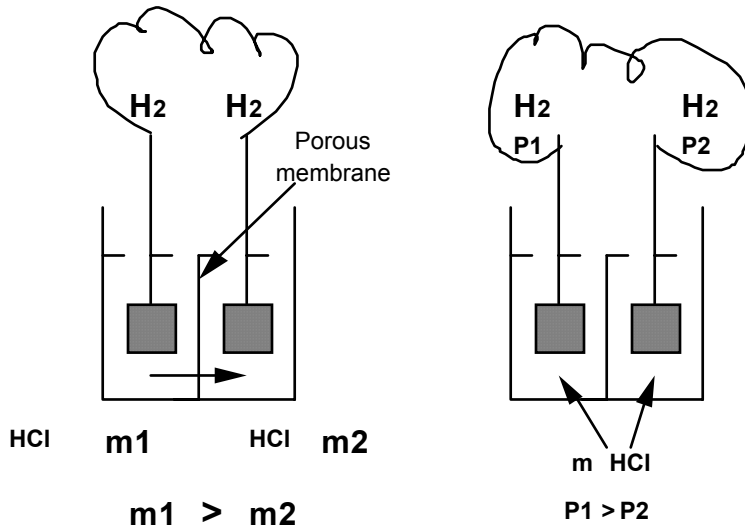
$$= \frac{2RT}{F} \ln \frac{m_1}{m_2}$$

N.B.

Free energy of dilution $\Delta G = -nFE$ of concentration cell without transport

$$\Delta G = -2RT \ln \frac{m_1}{m_2}$$

Concentration Cell with Transport



(a) $m_1 > m_2$

Cathodic Reaction $2H^+ + 2e^- = H_2$

Anodic Reaction $\frac{H_2 = 2H^+ + 2e^-}{\text{No Net Reaction}}$

Cl^- is transported by diffusion and or migration from cathode compartment to anode compartment.

t_{Cl^-} is the transport number which is defined as the fraction of the total current which is carried by the particular ion.

Therefore, the EMF of concentration cell with transport would be:

$$E = \frac{2RT}{F} t_{Cl^-} - X \ln \frac{m_1}{m_2}$$

(b)

$$P_1 > P_2$$

$$e_a = e^\circ + \frac{RT}{2F} \ln \frac{a_{H^+}^2}{P_{1H_2}}$$

$$e_c = e^\circ + \frac{RT}{2F} \ln \frac{a_{H^+}^2}{P_{2H_2}}$$

$$\text{EMF of the cell} = e_c - e_a$$

$$= \frac{RT}{2F} \ln \frac{P_2}{P_1}$$

THERMODYNAMICS OF GALVANIC CELLS

The factors which influence the EMF of the cell are usually the concentration, pressure and temperature

1- Concentration (Pressure) effect on EMF

$$E = E^\circ + \frac{RT}{nF} \ln \frac{\prod a_{\text{oxidant}}}{\prod a_{\text{reductant}}}$$

If the concentration is varied in either oxidant or reductant the EMF will consequently vary. The pressure variation acts similarly for gas reactions.

2- Effect of Temperature on EMF

$$(\delta G/\delta T)_p = -S \quad (\delta \Delta G/\delta T)_p = -\Delta S \quad \text{but } \Delta G = -nFE \quad \therefore nFE(\delta E/\delta T)_p = \Delta S$$

$$\text{and since } \Delta G = \Delta H - T\Delta S \quad \therefore \Delta G = \Delta H - TnF(\delta E/\delta T)_p \quad nFT(\delta E/\delta T)_p = \Delta H - \Delta G$$

$\delta E/\delta T$ is the temperature coefficient. ΔH , is the heat content change in the reaction which is the measure of the chemical energy produced by the cell. ΔG is the free energy change and its a measure for the quantity of useful electrical work which is produced by the cell reaction. $\Delta G = -nFE$.

$$\text{If } \delta E/\delta T = 0 \quad \therefore \Delta G = \Delta H$$

i.e. Quantitative conversion of the chemical energy change into useful electrical energy.

If $\delta E/\delta T > 0$ i.e. the EMF of the cell increase with rise of temperature $\therefore \Delta H > \Delta G$

But $-\Delta H$ is the chemical energy change of the reaction and $-\Delta G$ is the electrical energy or useful work thus $-\Delta G > -\Delta H$ therefore the useful work is more than the chemical work of the cell reaction, thus the cell absorbs heat from the surrounding and transfer it to electrical energy.

If $\delta E/\delta T < 0 \therefore \Delta H < \Delta G \therefore \Delta H > -\Delta G$ in this case the cell heats i.e. the conversion of the chemical energy into electrical energy is not quantitative and some of the chemical energy is lost to the surrounding the form of heat energy.

ELECTROCHEMISTRY OF IRREVERSIBLE PROCESSES



In a reversible reaction there is always a dynamic equilibrium . The reaction does not stop but proceeds with equal rates in both forward and backward directions at the same time. Thus for an electrode dipped in its ions the number of electrons generated by an anodic reaction at a certain time is equal to the number of electrons consumed by the cathodic reaction hence no net current is observed at equilibrium i.e. no net charge flow exists across the electrical double layer. Now if this system is subjected to any disturbance , the rate of one process will exceed the other and thus a net flow of electrical charge across the phase boundary will exist until another equilibrium is reached or achieved under the new conditions.

Polarization Overpotential - Overtension

The overpotential is defined as the magnitude of the difference of the electrode potential when current flows from the reversible value. At equilibrium there is no net current flowing in the electrode and what we measure is the equilibrium or reversible electrode potential, on the other hand when a net current anodic or cathodic flows out of the electrode or into the electrode the potential becomes different from the equilibrium potential , the magnitude of this difference is the overpotential. If the irreversible potential is more anodic as compared , to the equilibrium potential the electrode is said to be Anodically Polarized and the polarization is known as Anodic Polarization. The contrary is true if the irreversible electrode potentials less anodic or cathodic, the electrode is then Cathodically Polarized and the polarization is called Cathodic Polarization.

The magnitude of polarization is given by η

$$\eta = E_{irrev} - E_{rev} \text{ where } \eta \text{ is the overpotential or polarization}$$

THE VOLMER - TAFEL RELATION

The current is given by Faraday's law

$$I = n F \cdot \text{rate}$$

Thus the anodic current expression is given by

$$i_a = n F a_r k_f e^{(1-\alpha)nFE/RT}$$

$$i_c = nF a_p k_b e^{-\alpha n F E / R T}$$

at equilibrium $E = E_{rev}$ and $i_a = i_c$ and no net current flow in the circuit . This current at equilibrium is called the exchange current i_o , thus one can write

$$i_o = n F a_r k_f e^{(1-\alpha)n F E / R T} = nF a_p k_b e^{-\alpha n F E / R T}$$

and since $E = E_{rev} + \eta$ one can write the following

$$i_a = n F a_r k_f e^{(1-\alpha)n F (E_{rev} + \eta) / R T}$$

$$i_a = \frac{n F a_r k_f e^{(1-\alpha)n F (E_{rev}) / R T}}{i_o} e^{(1-\alpha)n F \eta / R T}$$

$$\therefore i_a = i_o e^{(1-\alpha)n F \eta / R T}$$

By the same way one may say

$$i_c = i_o e^{-\alpha n F \eta / R T}$$

and the net current is given by

$$i_{net} = i_a - i_c = i_o [e^{(1-\alpha)n F \eta / R T} - e^{-\alpha n F \eta / R T}]$$

The Volmer - Tafel relation is obtained thisw relation simply gives the net current under polarization in terms of kinetic parameters.

↔