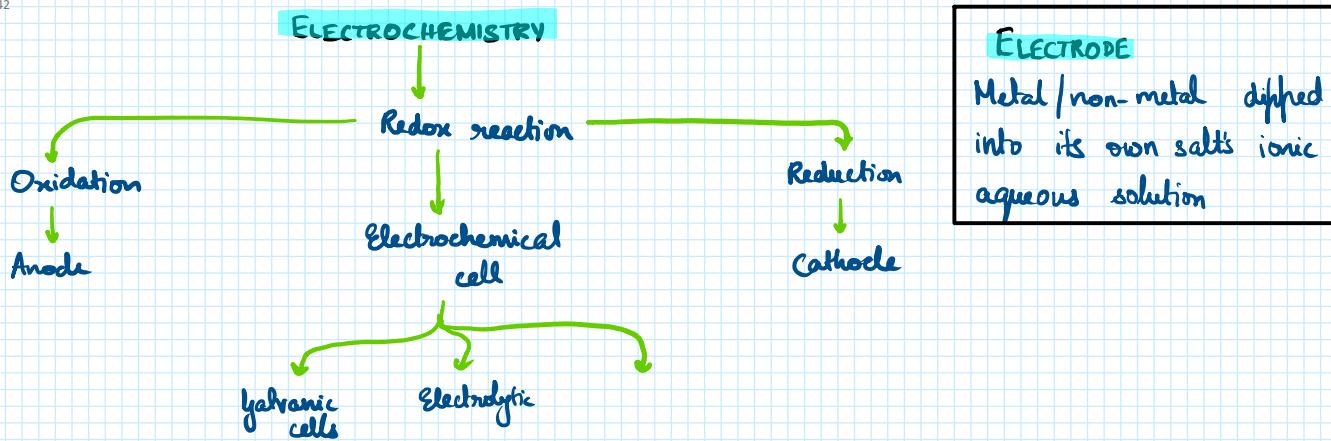


# 1. Electrode Potential, Free Energy, Origin of Electrode Potential

05 October 2023 09:42



## ELECTRODE POTENTIAL ( $E$ )

Electrical potential developed at the interface of the metal and its solution due to Helmholtz electrical double layer is called single electrode potential

## STANDARD ELECTRODE POTENTIAL ( $E^\circ$ )

Same as  $E$ , but with soln. of concentration 1 M at 25°C, 1 atm (101.3 kPa)  
This remains constant for any given electrode. [ $E_{Zn}^\circ = -0.76\text{ V}$ ,  $E_{Cu}^\circ = +0.34\text{ V}$ ]

## FREE ENERGY ( $\Delta G$ )

Measure of available energy which can be converted into useful work

$$\Delta G = \underbrace{\Delta H}_{\text{enthalpy}} - T \underbrace{\Delta S}_{\text{entropy}}$$

## STANDARD FREE ENERGY ( $\Delta G^\circ$ )

Free energy change when all participants in a reaction are in standard state: 25°C, 1 M conc., 1 atm

## EMF OF CELL

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

$$\Delta G = -nFE_{\text{cell}}$$

NOTE: Spontaneous / non-spontaneous

$\Delta G$  is -ve  $\rightarrow$  spontaneous reaction

$\Delta G$  is +ve  $\rightarrow$  non-spontaneous reaction

NOTE: Cell notation

anode || cathode  


Single line in half cell is used to represent phase boundary

## DIFFERENCE B/W GALVANIC AND ELECTROLYTIC

## Galvanic

- Chemical energy  $\rightarrow$  electrical
- Anode = -ve  
Cathode = +ve
- $\Delta G = -n e F$
- Spontaneous reaction

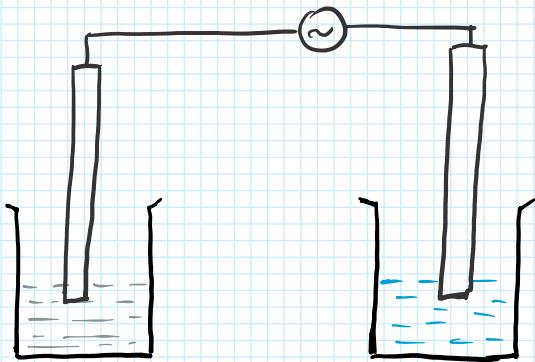
Eg: Battery

## Electrolytic

- Electrical  $\rightarrow$  chemical
- Anode = +ve  
Cathode = -ve
- $\Delta G = + n e F$
- Non-spontaneous reaction

Eg: Metallurgy

## Galvanic Cell



## HELMHOLTZ ELECTRICAL DOUBLE LAYER

When a metal is put into its soln,



Negative/ positive charges developed on metal

↓

Attract positive/ negative ions in soln.

↓

layer of positive/negative ions formed around electrode  $\rightarrow$  Helmholtz electrical double layer

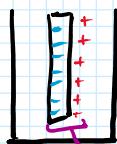
## ORIGIN OF ELECTRODE POTENTIAL

Definition of  $E$ : Potential developed at the interface of the metal electrode and its solution due to Helmholtz electrical double layer

Definition of  $E^\circ$  (1 M, 25°C): Potential developed at the interface of electrode and electrolyte when concentration of the electrolyte is unity, the temperature is 25°C and the pressure is 1 atm (101.3 kPa)

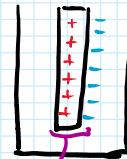


Oxidation reaction



Oxidation > Reduction

Reduction reaction



Reduction > Oxidation

Factors on which electrode potential depends:

Electrode potential depends upon:

## Factors on which electrode potential depends:

Electrode potential depends upon:

- Nature of metal
- Temperature
- Pressure
- Concentration of electrolyte

## ELECTROCHEMICAL SERIES

Element	Reduction eqn.	$E^\circ$
Li	$\text{Li} + e^- \rightarrow \text{Li}$	-3.05 V
K	$\text{K}^+ + e^- \rightarrow \text{K}$	-2.9 V
Zn	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.76 V
Fe	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.44 V
H <sub>2</sub>	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.0 V
Cu	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.34 V
Ag	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+0.8 V

## LKG PROBLEMS



Write half reactions, overall reactions. Calculate  $E_{\text{cell}}^\circ$ .

Ans: ①  $E^\circ(\text{Cu}) = +0.34 \text{ V}$        $E^\circ(\text{Ag}) = +0.8 \text{ V}$

↓                          ↓  
anode                    cathode



$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cath}}^\circ - E_{\text{anode}}^\circ \\ &= 0.8 - 0.34 \\ &= \underline{\underline{0.46 \text{ V}}} \end{aligned}$$

② E°

## NERNST EQUATION: DERIVATION

Based on reduction reaction



$$\varrho = \frac{[M]}{[M^{n+}]} = \frac{1}{[M^{n+}]}$$

Work done by the system

$$W_{max} = nEF$$

$$W_{max} = -\Delta G$$

$$\begin{aligned} \Delta G &= -nEF \\ \Delta G^\circ &= -nE^\circ F \end{aligned} \quad \left. \right\} \longrightarrow \textcircled{1}$$

Vant Hoff equation

$$\Delta G = \Delta G^\circ + RT \ln \varrho \quad \text{--- } \textcircled{2}$$

Substituting  $\textcircled{1}$ ,  $\varrho$  in  $\textcircled{2}$

$$-nEF = -nE^\circ F + RT \ln \left( \frac{1}{[M^{n+}]} \right)$$

Dividing both sides by  $-nF$

$$E = E^\circ - \frac{RT}{nF} \ln \left( \frac{1}{[M^{n+}]} \right)$$

$$E = E^\circ - \frac{2.303RT}{nF} \log \left( \frac{1}{[M^{n+}]} \right)$$

Solubility constants

$$E = E^\circ - \frac{0.0591}{n} \log \left( \frac{1}{[M^{n+}]} \right)$$

[OR]

$$E = E^\circ + \frac{0.0591}{n} \log ([M^{n+}])$$

Q.  $Zn|Zn^{2+}||Cu^{2+}|Cu$ . Derive Nernst eqn. for this reaction

Soln: Anode:  $Zn \longrightarrow Zn^{2+} + 2e^-$

Cathode:  $Cu^{2+} + 2e^- \longrightarrow Cu$



$$\varrho = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$W_{max} = nEF$$

$$W_{max} = -\Delta G$$

$$\begin{aligned} \Delta G &= -nEF \\ \Delta G^\circ &= -nE^\circ F \end{aligned} \quad \left. \right\} \longrightarrow \textcircled{1}$$

Vant Hoff eqn.

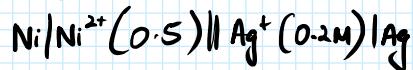
$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$-nEF = -nE^\circ F + RT \ln \left( \frac{[Zn^{2+}]}{[Cu^{2+}]} \right)$$

$$E = E^\circ - \frac{RT}{nF} \ln \left( \frac{[Zn^{2+}]}{[Cu^{2+}]} \right)$$

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Q. Given cell



$$E_{Ni^{2+}/Ni}^\circ = -0.25V$$

$$E_{Ag^+/Ag}^\circ = 0.8V$$

(i) Write half reaction and overall reaction

(ii) Derive Nernst eqn.

(iii) Calculate  $E_{cell}^\circ$ ,  $E_{cell}$  at  $25^\circ C$

(iv) Calculate  $\Delta G$

(v) Predict the nature of the reaction

Soln: (i) Anode:  $Ni \rightarrow Ni^{2+} + 2e^-$

Cathode:  $\underline{(Ag^+ + e^- \rightarrow Ag)} \times 2$



$$(iii) E_{cell}^\circ = E_{cath}^\circ - E_{anode}^\circ$$

$$= 0.8 - (-0.25)$$

$$= 1.05V$$

$$E_{cell}(25^\circ C) = 1.05 - \frac{0.0591}{2} \log \left( \frac{0.5}{0.2} \right)$$

$$= 1.017V$$

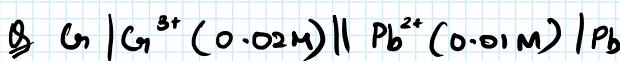
$$(iv) \Delta G = -nEF$$

$$| F = 96500C$$

$$= -2 \times 1.017 \times 96500$$

$$= -196281J$$

(v) Spontaneous reaction



$$E_{Cu|Cu^{3+}}^\circ = -0.744V$$

$$E_{Pb^{2+}/Pb}^\circ = -0.126V$$

Soln. Anode:  $\underline{(Cu \rightarrow Cu^{3+} + 3e^-) \times 2}$

Cathode:  $\underline{(Pb^{2+} + 2e^- \rightarrow Pb) \times 3}$





$$E_{\text{cell}}^{\circ} = E_{\text{c}}^{\circ} - E_{\text{A}}^{\circ}$$

$$= -0.126 - (-0.744)$$

$$= \underline{\underline{0.618 \text{ V}}}$$

$$\begin{aligned} E_{\text{cell}}(25^\circ\text{C}) &= E_{\text{cell}}^{\circ} - \frac{0.0591}{6} \log \frac{(0.02)^2}{(0.01)^3} \\ &= 0.618 - \frac{0.0591}{6} \log \frac{(0.02)^2}{(0.01)^3} \\ &= \underline{\underline{0.5923 \text{ V}}} \end{aligned}$$

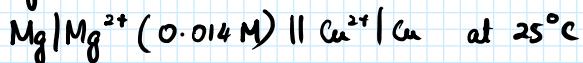
$$\Delta G_f = -nEF$$

$$= -6(0.5923)(96500)$$

$$= \underline{\underline{-342941.7 \text{ J}}}$$

Since  $\Delta G_f$  is -ve  $\longrightarrow$  non-spontaneous reaction

Q. Emf of the cell is 2.78 V.



$$\text{Measured } E_{\text{Mg}}^{\circ} = -2.37 \text{ V}$$

Calculate electrode potential of Cu.

$$\begin{aligned} \text{Given } E_{\text{cell}} &= E_{\text{c}}^{\circ} - \frac{0.0591}{2} \log \frac{1}{0.014} \\ &= -2.37 - \frac{0.0591}{2} \log \frac{1}{0.014} \\ &= -2.425 \end{aligned}$$

$$E_{\text{cell}} = E_{\text{c}} - E_{\text{A}}$$

$$2.78 = E_{\text{cu}} - (-2.425)$$

$$2.78 - 2.425 = E_{\text{cu}}$$

$$\underline{\underline{E_{\text{cu}} = 0.355 \text{ V}}}$$