

**Handwritten Notes
On
ELECTROCHEMISTRY
(Part-2)**



CHARACTERISTICS OF ELECTROCHEMICAL SERIES

1. The values of SEP tell us the ease with which the given element will be reduced when compared to Hydrogen.
2. The tendency of an element to undergo reduction \uparrow from top to bottom i.e. power to act as reducing agent \downarrow ses.

\rightarrow The reduction of lithium ion into lithium atom i.e. $\text{Li}^+ + e \rightarrow \text{Li}$ is not feasible but its oxidation i.e. $\text{Li} \rightarrow \text{Li}^+ + e$ is feasible.

Li is the most powerful reducing agent.

Similarly, F has the greatest tendency to undergo reduction & thus it is the most powerful oxidising agent.

3. The element appearing prior to hydrogen in the series have the greater tendency to get oxidised and thus can act as better reducing agent than hydrogen.

4. The elements appearing first in the electrochemical series will displace all others below it from their aq. salt solution.

Thus in electrochemical series,

- (a) The tendency for redⁿ to occur or to gain e^- s & power to act as oxidising agent \uparrow from top to bottom.
- (b) The tendency for oxidⁿ to occur, tendency to lose e^- s & power to act as R.A \downarrow from top to bottom.

APPLICATIONS OF ELECTROCHEMICAL SERIES

- 1) Relative oxidising and Reducing Powers of Various Substances :-
 \rightarrow Substances with higher reduction potentials are strong oxidising agents while substances with lower reduction potentials are strong reducing agents.

- 2) Calculation of standard EMF of the cell (E°_{cell})

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

- 3) Predicting feasibility of Redox reaction

$\rightarrow E^\circ_{\text{cell}} = +ve$ for redox reaction to be feasible



4. Predicting the capability of metal to displace H_2 gas from acid :-

All metals lying above hydrogen in electrochemical series can liberate H_2 gas by reaction with acids. On the other hand, the metal lying below hydrogen in the e.c.s cannot undergo such a reaction.

5. The e.c.s provides a ready reference to select a reducing agent for the metallurgical processes of elements.
6. The series helps us to select a metal to be electroplated on an object made of some other metal.
7. The choice of O.A can be made by a quick survey of e.c.s.
8. The series can be used to select suitable electrodes for the construction of desired electrochem. cell.

NERNST EQUATION

→ The standard electrode potentials are measured in their standard states when the concentration of the electrolyte solutions fixed as 1M and temp is 298K. However in actual practice e.chem cells do not have always fixed conc. of the electrolyte solutions. The electrode potentials depend on the conc. of electrolyte solutions.

→ Nernst gave a ^{quantitative} relationship between electrode potential and the conc of electrolyte solutions. k/a Nernst equation

→ For a general electrode reaction:



Nernst eqⁿ can be written in 2 ways as

$$E_{(M^{n+}/M)} = E^{\circ}_{(M^{n+}/M)} + \frac{RT}{nF} \ln \frac{[\text{Oxidised state}]}{[\text{reduced state}]}$$

$$E_{(M^{n+}/M)} = E^{\circ}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[\text{reduced state}]}{[\text{oxidised state}]}$$

Converting natural logarithm (ln) to \log_{10} in 1st eq, we get

$$E_{(M^{n+}/M)} = E^{\circ}_{(M^{n+}/M)} + \frac{2.303 RT}{nF} \log \frac{[M^{n+}]}{[M]}$$



where; $E_{M^{n+}/M}$ = Electrode potential

$E_{M^{n+}/M}^{\circ}$ = standard electrode potential with reference to SHE when conc. of M^{n+} is 1 M.

$$R = 8.314 \text{ J K}^{-1} \cdot \text{mol}^{-1}$$

T = Temperature

$[M^{n+}]$ = Molar conc of ions

n = No of e's gained

$$F = 96500 \text{ C mol}^{-1} \text{ (Faraday constant)}$$

$[M]$ = Conc of metal

Substituting these values in eq 1, we get

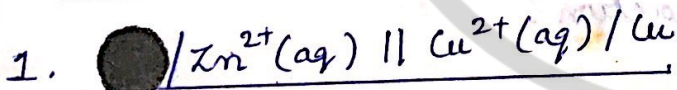
$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} + \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[M^{n+}]}{[M]}$$

In general, for any electrode,

$$E_{\text{red}} = E_{\text{red}}^{\circ} + \frac{0.059}{n} \log \frac{[\text{oxidised state}]}{[\text{Reduced state}]}$$

→ while using Nernst eqⁿ, the conc of solids i.e [solid] is taken to be unity while conc. of gases is expressed in terms of their partial pressures and conc of ionic species are taken in mol L⁻¹.

CALCULATION OF CELL POTENTIAL USING NERNST EQUATION :-



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

$$\text{Nernst eq}^n \text{ for Cu electrode} : E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} + \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}]}$$

$$\text{Nernst eq}^n \text{ for Zn electrode} : E_{\text{Zn}^{2+}/\text{Zn}} = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Zn}]}$$

Substituting the values,

$$\text{cell potential} = \left(E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} + \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}]} \right) - \left(E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Zn}]} \right)$$

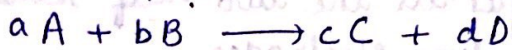
$$= E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}][\text{Zn}]}{[\text{Cu}][\text{Zn}^{2+}]}$$



Since conc. of solids is taken to be unity, $[Zn] = [Cu] = 1$

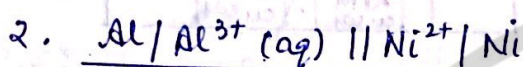
$$\text{Cell potential} = E_{\text{cell}}^{\circ} + \frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

In general, for a redox cell reaction involving the transference of n electrons

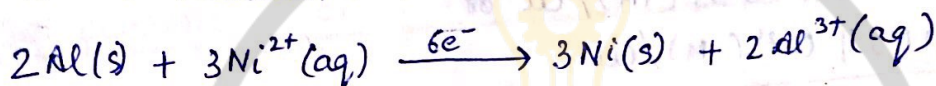


$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{RT}{nF} \ln \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.059}{n} \log \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

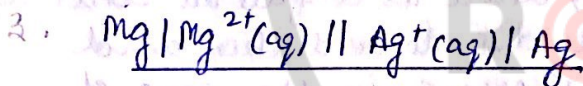


The cell reaction is:

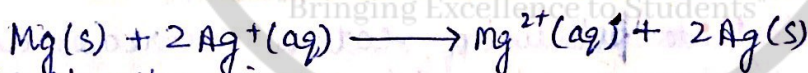


The Nernst eqⁿ is \rightarrow

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.059}{6} \log \frac{[Ni^{2+}]^3}{[Al^{3+}]^2} \text{ at } 298 \text{ K}$$

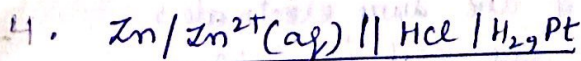


The cell reaction is:



The Nernst eqⁿ is \rightarrow

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.059}{2} \log \frac{[Ag^+(aq)]^2}{[Mg^{2+}(aq)]} \text{ at } 298 \text{ K}$$



The cell reaction is



The Nernst eqⁿ is

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.059}{2} \log \frac{[H^+(aq)]^2}{[Zn^{2+}(aq)]} \text{ at } 298 \text{ K}$$

NOTE: while applying Nernst equations, electrode potential is always taken as reduction potential.

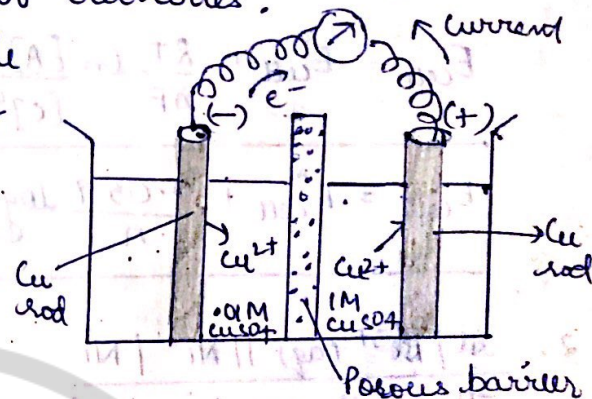


concentration cells

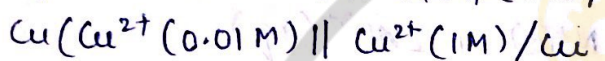
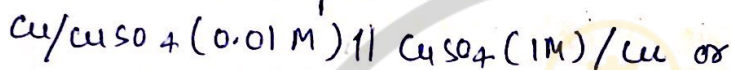
→ The galvanic cells in which electrodes are made of same metal but they are immersed in the electrolytes of diff. concentrations in two half cells are called concentration cells

→ The diff in conc. of electrolytes in the two half cells, creates pot. diff. across the two electrodes.

→ The electrode placed in electrolyte of larger conc acts as cathode or +ve terminal, whereas that placed in lower electrolyte conc. acts as anode or -ve terminal.



→ Cell can be represented as



$$\rightarrow E_{\text{Cu}} = \frac{0.059}{n} \log \frac{C_2}{C_1} \quad (\text{For } E_{\text{cell}} \text{ to be +ve } C_2 > C_1)$$

NERNST EQUATION AND EQUILIBRIUM CONSTANT

→ As the cell reaction progresses, there is a fall in the conc. of cations around cathode due to reduction and at the same time there is an increase in the conc of metal cations around anode due to oxidation.

→ As a result, electrode potential of cathode decreases and that of anode increases. ultimately $E_{\text{cathode}} = E_{\text{anode}}$ becomes zero and the flow of e^- s stops.

→ At this situation the cell reaction attains eq^m .

→ At eq^m , the electrode potential of the two electrodes becomes equal so that e.m.f of the cell is zero.

→ Let us consider an example of a cell $\text{Zn}/\text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq})/\text{Cu}$.

→ cell reaction at eq^m



→ Considering the conc of $\text{Zn}(s)$ & $\text{Cu}(s)$ to be unity, the eq^m constant for the above reaction, K_c , is given by the expression $K_c = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$ [$\because [\text{Cu}] = [\text{Zn}] = 1$]



Applying Nernst eqⁿ,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}][\text{Zn}]}{[\text{Zn}^{2+}][\text{Cu}]} = E_{\text{cell}}^{\circ} + \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}][\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Since E_{cell} at eq^m is zero

$$0 = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log K_c$$

$$E_{\text{cell}}^{\circ} = \frac{0.059}{n} \log K_c$$

Significance of K_c :- The value of K_c gives the extent of cell reaction. If the value of K_c is large, the reaction proceeds to larger extent before attainment of eq^m conditions.

NOTE: At eq^m $E_{\text{cell}} = 0$ but E_{cell}° can not be zero.

ELECTROCHEMICAL CELL AND GIBB'S ENERGY

→ The electrical work or the electrical energy is equal to the product of EMF of the cell and the electrical charge that flows through the external wire.

$$W_{\text{elec}} = (\text{EMF}) \times (\text{Electrical charge flowing through the wire})$$

→ Now if n moles of e^- s are transferred in the cell reaction, then charge flowing through the wire = nF

→ If E_{cell} is the EMF of the cell, then,

$$W_{\text{elec}} = nF \times E_{\text{cell}}$$

→ The use in Gibb's energy ($-\Delta G$) of the cell reaction provides a measure of electrical work (W_{elec}) is ΔG for a reaction is a measure of the maximum useful work that can be obtained from a chemical reaction. ($\Delta G = \text{maximum work}$)

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

$$\Delta G = -nFE_{\text{cell}} \quad (\text{max. work})$$

→ The standard Gibb's energy change is given by,

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

Significance of this eqⁿ :- This eqⁿ help in predicting the feasibility of the cell reaction. For the cell reaction to be spontaneous, ΔG must be -ve & for +ve ΔG , the value of E must be positive.

→ The relationship b/w Gibb's free energy change & EMF of the cell act as a bridge b/w chemical thermodynamics & elec. Energy



Relationship b/w standard EMF & eq^m constant :-

$$\Delta G^\circ = -RT \ln K_c$$

$$\Delta G^\circ = -nF E^\circ_{\text{cell}}$$

$$nF E^\circ_{\text{cell}} = RT \ln K_c = 2.303RT \log K_c$$

$$E^\circ_{\text{cell}} = 2.303 \frac{RT}{nF} \log K_c$$

