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# ELECTROCHEMISTRY

## TYPES OF CELL:-

Electrochemical cells:- Device used to convert chemical energy of a redox reaction into electrical energy. It is also known as galvanic cell.

Electrolytic cells:- Device which uses electricity to bring about a non-spontaneous redox reaction.

## DANIEL CELLS:-

- Cell Rxn; $Zn(s) + Cu^{+}(aq) \longrightarrow Zn^{+2}(aq) + Cu(s)$
- When external opposite potential is applied to the cell in standard state.

(a) $E_{ext} = 1.1\,V$, no flow of electron

(b) $E_{ext} > 1.1\,V$, electron flow from Cu → Zn

(c) $E_{ext} < 1.1\,V$, $e^-$ flow from Zn → Cu

## CELL POTENTIAL:-

Electrode potential - the potential diff. developed b/w the electrode and the electrolyte when the conc° of all species involved is unity is known as standard electrode potential.

Cell potential; The difference of potential b/w cathode and anode. $E_{cell} = E_{Right} - E_{left}$.

*In galvanic cells:-

Anode has negative potential wrt sol°

Cathode has positive potential wrt sol°

*Standard hydrogen electrode:-

↳ $H^+_{(aq)} + e^- \longrightarrow \frac{1}{2} H_2(g)$

$E^\circ = 0$ volt (ASSUMED).

## NERNST EQUATION

*For the Rxn; $M^{n+} + ne^- \longrightarrow M$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

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

* For the rxn; $aA + bB \longrightarrow cC + dD$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

*For eqb rxn:- $E_{cell} = 0$

* $E^\circ_{cell} = \frac{2.303}{nF} \log K_c = \frac{0.0591}{n} \log K_c$

## GIBBS ENERGY:-

↳ It is reversible work done by the gravitational.

↳ $\Delta_r G = -nFE_{cell}$

↳ $\Delta_r G^\circ = -nFE^\circ_{cell}$

↳ $\Delta_r G^\circ = -RT \ln K = -2.303\,RT \log K$.

## SOME OTHER:-

Resistance :- $R = \frac{\rho l}{A}$ unit = ohm

Conductance :- $G = \frac{1}{R} = \frac{\kappa A}{l}$ unit = $ohm^{-1}$

cell conductance; $G^* = \frac{l}{A}$ unit = $cm^{-1}$

Conductivity :- $\kappa = \frac{Gl}{A}$

Molar conductivity :- $\Lambda_m = \frac{\kappa \times 1000}{M}$

## ELECTROCHEMICAL:-

**ELECTROCHEMICAL SERIES**

A negative E° means that the redox couple is stronger reducing agent than the $H^+/H_2$ couple.

A positive E° means that the redox couple is a weaker reducing agent than the $H^+/H_2$ couple.

Increasing Strength of Oxidising Agent ↑

| Oxidised form | Reduced form | E°/V |
|---|---|---|
| $F_2(g) + 2e^-$ | $\rightarrow 2F^-$ | 2.87 |
| $Co^{3+} + e^-$ | $\rightarrow Co^{2+}$ | 1.81 |
| $Cl_2(g) + 2e^-$ | $\rightarrow 2Cl^-$ | 1.36 |
| $O_2(g) + 4H^+ + 4e^-$ | $\rightarrow 2H_2O$ | 1.23 |
| $Br_2 + 2e^-$ | $\rightarrow 2Br^-$ | 1.09 |
| $Ag^+ + e^-$ | $\rightarrow Ag(s)$ | 0.80 |
| $Fe^{3+} + e^-$ | $\rightarrow Fe^{2+}$ | 0.77 |
| $O_2(g) + 2H^+ + 2e^-$ | $\rightarrow H_2O_2$ | 0.68 |
| $I_2 + 2e^-$ | $\rightarrow 2I^-$ | 0.54 |
| $Cu^{2+} + 2e^-$ | $\rightarrow Cu(s)$ | 0.34 |
| **$2H^+ + 2e^-$** | **$\rightarrow H_2(g)$** | **0.00** |
| $Pb^{2+} + 2e^-$ | $\rightarrow Pb(s)$ | −0.13 |
| $Sn^{2+} + 2e^-$ | $\rightarrow Sn(s)$ | −0.14 |
| $Cr^{3+} + 3e^-$ | $\rightarrow Cr(s)$ | −0.74 |
| $Zn^{2+} + 2e^-$ | $\rightarrow Zn(s)$ | −0.76 |
| $2H_2O + 2e^-$ | $\rightarrow H_2(g) + 2OH^-(aq)$ | −0.83 |
| $Na^+ + e^-$ | $\rightarrow Na(s)$ | −2.71 |
| $Ca^{2+} + 2e^-$ | $\rightarrow Ca(s)$ | −2.87 |
| $K^+ + e^-$ | $\rightarrow K(s)$ | −2.93 |
| $Li^+ + e^-$ | $\rightarrow Li(s)$ | −3.05 |

## DILUTION EFFECT :-

→ conductivity always decreases with decrease in concentration (means on dilution) both for weak and strong electrolytes.

↳ For weak electrolytes, molar conductivity increases steeply on dilution.

→ For strong electrolyte, molar conductivity increases slowly with dilution.

## KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS:-

- Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte at infinite dilution.
- If an electrolyte on dissociation given $\nu_+$ cations and $\nu_-$ anions then $\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$
  - $\lambda^\circ_m$: $H^+ > Ca^{2+} > Mg^{2+} > K^+ > Na^+$
  - $\lambda^\circ_m$: $OH^- > SO_4^{2-} > Br^- > Cl^- > CH_3COO^-$
  - For a weak electrolyte : $\alpha = \Lambda_m/\Lambda^\circ_m$
  - For acetic acid : $K_a = \frac{C\alpha^2}{1-\alpha} = \frac{C\Lambda_m^2}{\Lambda^\circ_m(\Lambda^\circ_m - \Lambda_m)}$

## FARADAY'S LAW

**FARADAY'S LAW OF ELECTROLYSIS**

- **First law :** $w = ZQ = ZIt = \frac{E}{96500} \times It$
- **Second law :** $\frac{w_1}{w_2} = \frac{E_1}{E_2}$
- 1F = Charge on 1 mol electron = 96487 C = 96500 C

## PRODUCTS OF ELE

**(11) PRODUCTS OF ELECTROLYSIS**

- Molten NaCl : Anode : $Cl_2$, Cathode : Na
- Aqueous NaCl : Anode : $Cl_2$, Cathode : $H_2$
- Dilute $H_2SO_4$ : Anode : $O_2$, Cathode : $H_2$
- Concentrated $H_2SO_4$ : Anode : $S_2O_8^{2-}$, Cathode : $H_2$

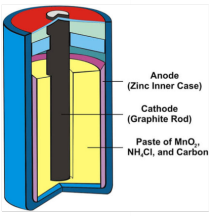
## BATTERIES:-

*Primary Batteries:-

1. Dry cell (Leclanche cell)

Anode → $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Cathode → $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$




2. Mercury cell →

cell potential (≈ 1.35 V) remains constant during its life.

Anode - $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

Cathode - $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

*Secondary batteries:-

lead storage battery:-

$Pb(s) + PbO_2(s) + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O$

Nickel cadmium cell:- It has a long life than the lead storage battery

$Cd(s) + 2Ni(OH)_3 \rightarrow CdO(s) + 2Ni(OH)_2 + H_2O$

*Fuel cells:-

→ galvanic cell that convert energy produced during combustion of fuel directly into electrical energy.

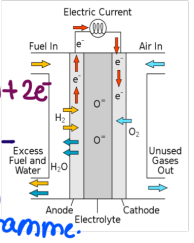
Anode:-

$H_2 + 2OH^- \longrightarrow 2H_2O(l) + 2e^-$

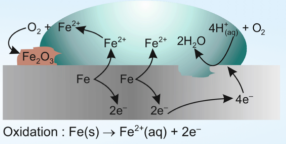
Cathode:-

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

The cell was used in apollo space programme.




## CORROSION:-




Oxidation : $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Reduction : $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Atmospheric oxidation : $2Fe^{2+}(aq) + 2H_2O(l) + 1/2O_2(g) \rightarrow Fe_2O_3 + 4H^+$

Fig. Corrosion of iron in atmosphere

→ It slowly coats the surface of metallic objects with oxides or other salts of metals.

→ Corrosion of iron is called as Rusting.

→ Rust is $Fe_2O_3 \cdot xH_2O$

→ Prevention of rusting can be done by:-

→ Covering the surface with metals and chemicals. Eg. Bisphenol, Zn etc.

→ Provide a sacrificial electrode of other metal (Mg, Zn) etc.

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