

# ELECTROCHEMISTRY

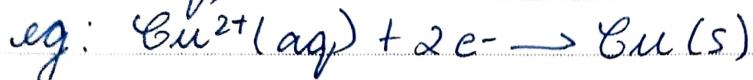
01/03/2024

- Electrochemistry is the branch of chemistry which deals with change in chemical energy into electrical and vice versa.

## Redox reaction

### Reduction

Gain of  $e^-$

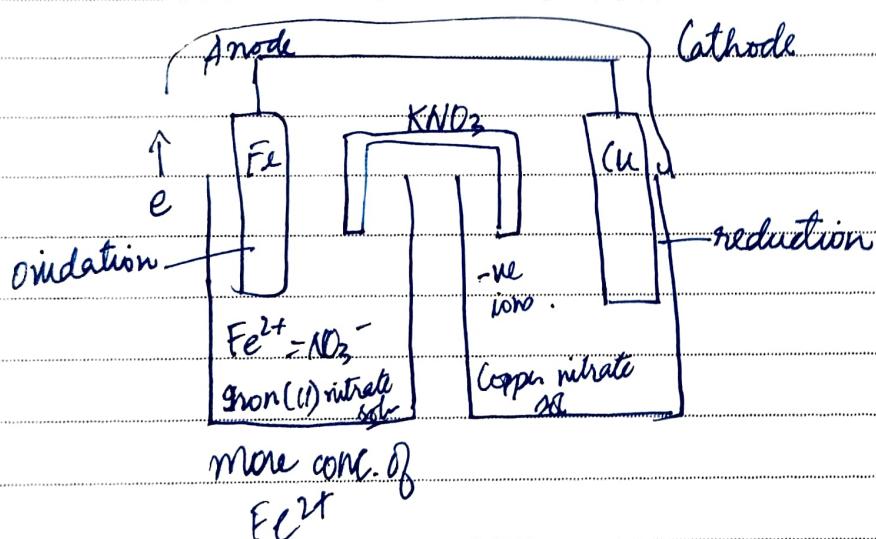


### Oxidation

Loss of  $e^-$



Electrochemical cells or galvanic cells or Daniel cell or Voltaic cell.



L - left side  
O - oxidation  
A - Anode  
N - Negative charge

Functions of salt bridge:

- It completes inner circuit
- It maintains electrical neutrality.

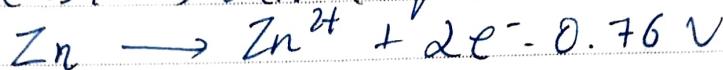
Q. Why in salt bridge  $KCl$  &  $KNO_3$  is used as electrolyte.

Ans They are having equal ionic mobility  
 $K^+ = NO_3^- = Cl^-$

Electrode Potential in a half cell.  
Tendency of an electrode to gain or lose  $e^-$ .

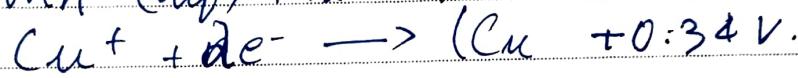
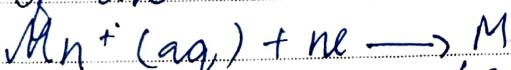
### i) Oxidation Potential:

Tendency of an electrode to lose  $e^-$ . its



### ii) Reduction Potential

Tendency of an electrode to gain  $e^-$ . its



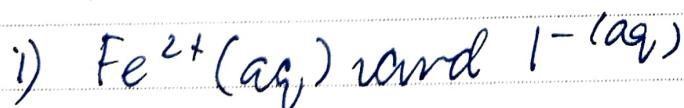
$$E^\circ_{\text{cell}} = E^\circ_C - E^\circ_A$$

$$= \underset{\substack{\text{reduction} \\ \text{potential}}}{E^\circ} - \underset{\substack{\text{oxidation} \\ \text{potential}}}{E^\circ}$$



Note: -ve sign in formula automatically change given reduction potential value into oxidation potential.

Q. Predict if the reaction between the following is feasible?

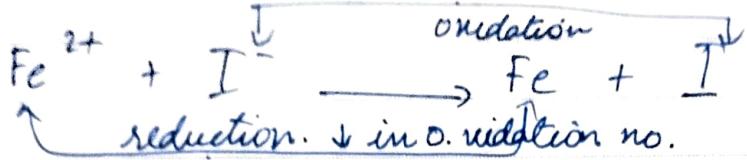


$$E^\circ(Fe^{2+}/Fe) = -0.44 \text{ V.}$$

$$E^\circ(I_2/I^-) = 0.54 \text{ V.}$$

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

red - oxidation ↑ in oxidation no.



$$\begin{aligned} &= -0.44 - 0.54 \\ &= -0.98 \text{ V.} \end{aligned}$$

$E^\circ_{\text{cell}}$  should be +ve for feasible process

$$(-n)F \Delta G = -nFE^\circ$$

## Electrolytic conduction

### Conductance

metallic  
conductor

ionic  
conductor

①  $e^-$  are responsible

① ions are responsible

② Solid state &  
molten

② Solid state &  
molten state

③  $\downarrow$  with ↑ in  
temp as ↑ in  
temp cause resistance  
for flow of  $e^-$  as  
metal atoms vibrates

③ ↑ with ↑ in temp  
as ↑ in temp ↑ rate  
of dissociation of salt

## Electrolytic conductance

### Ohm's law

$$R = \rho \frac{l}{A} \quad \text{where } R \text{ is resistance}$$

$\rho$  is resistivity

$$\frac{1}{\rho} = \frac{1}{R} \frac{l}{A} \quad l \text{ is length of cell}$$

$A$  is area of cross section

$$\frac{1}{\rho} = k = \text{specific conductance} \quad (k) \rightarrow \text{unit is } \Omega^{-1} \text{ cm}^{-1}$$

$\text{s cm}^{-1}$

$$G = \frac{1}{R} = \text{conductance}$$

$$k = G \frac{l}{A} = \frac{1}{R} \frac{l}{A}$$

$$\frac{l}{A} \rightarrow \text{cell constant} \rightarrow \text{unit is } \text{cm}^{-1}$$

### Molar conductance ( $\Lambda_m$ )

$$\Lambda_m = k \times \frac{1000}{M}$$

$M \rightarrow \text{molarity}$

$$= k \frac{\Omega^{-1} \text{ cm}^{-1}}{\text{molarity} \rightarrow \text{mol L}^{-1}}$$

$$1 \text{ L} = 1000 \text{ cm}^3$$

$$= \frac{\Omega^{-1} \text{ cm}^{-1} 1000 \text{ cm}^3}{\text{mol}}$$

$$= \frac{\Omega^{-1} \text{ cm}^{-2} \text{ mol}^{-1}}{\text{mol}}$$

8. The electrical resistance of a column of  $0.05 \text{ mol L}^{-1}$  NaOH solution of diameter 1 cm and length 50 cm is  $5.55 \times 10^3 \Omega \text{m}$ . Calculate its resistivity, conductivity and molar conductivity.

Sols ① Here given  $l = 50 \text{ cm}$   $\frac{d}{2} = r$

$$a = \pi r^2$$

$$= 3.14 \times (0.5)^2$$

$$= 3.14 \times 0.25$$

$$= 0.785 \text{ cm}^2$$

$$\frac{l}{2} = 0.5 \text{ cm}$$

$$R = \rho \frac{l}{a} \quad \frac{l}{a} = \frac{50}{0.785}$$

$$\rho = R \times \frac{a}{l} = 63.7 \text{ cm}^{-1}$$

$$= 5.55 \times 10^3 \times \frac{0.785}{50}$$

$$= 87.18 \Omega \text{ cm}$$

$$\textcircled{2} \quad k = \frac{1}{\rho} = \frac{1}{87.18} = \frac{1000}{8718} \times 10^{-2}$$

$$= 1.14 \times 10^{-2} \text{ S cm}^{-1}$$

$$\textcircled{3} \quad K_m = k \times \frac{1000}{m} = \frac{1.14 \times 10^{-2} \times 1000 \Omega \text{ cm}}{0.05 \times 100}$$

$$= \frac{114}{5} \times \frac{200}{100}$$

$$= 228. \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$$

Resistance of a conductivity cell filled with  $0.1 \text{ mol L}^{-1}$  KCl solution is  $100\Omega$ . If the resistance of the same cell when filled with  $0.02 \text{ mol L}^{-1}$  KCl solution is  $520\Omega$ , calculate the conductivity and molar conductivity of  $0.02 \text{ mol L}^{-1}$  KCl solution. The conductivity of  $0.1 \text{ mol L}^{-1}$  KCl solution is  $1.29 \text{ S/m}$ .

Ans.  $0.1 \text{ mol L}^{-1}$

$$R = 100\Omega$$

$$R = \rho \frac{l}{a}$$

$$\frac{1}{\rho} \times R = \frac{l}{a}$$

$$k \times R = \frac{l}{a}$$

$$1.29 \times 100$$

$$129 = \frac{l}{a}$$

$$k = \frac{1}{R} \frac{l}{a}$$

$$= \frac{1}{520} \times 129$$

$0.02 \text{ mol L}^{-1}$

$$R = 520\Omega$$

$$\lambda_m = ?$$

$$k = ?$$

$$\lambda_m = \frac{k \times 1000}{M}$$

$$= \frac{1}{520} \times \frac{129 \times 1000}{0.02}$$

$$k = \frac{1290}{520} \times 10^{-3}$$

$$= 0.248$$

$$= \frac{0.248 \times 1000}{0.02}$$

$$= 12400$$

### Effect of dilution on molar conductance

Strong electrolyte

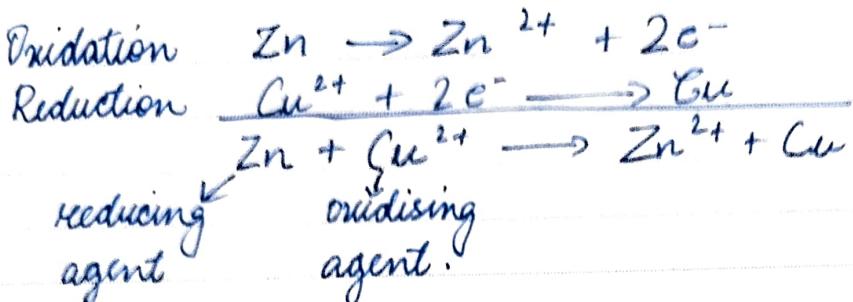
On dilution interionic attraction  $\downarrow$  as a result ionic mobility  $\uparrow$ .

Weak electrolyte

molar conductance  $\uparrow$  on dilution as rate of dissociation  $\uparrow$ .

Doms

ions can rejoin with that speed since rate of backward reaction increases.



Factors involving in reducing agent nature.

Reducing agent depends on



> Sublimation enthalpy

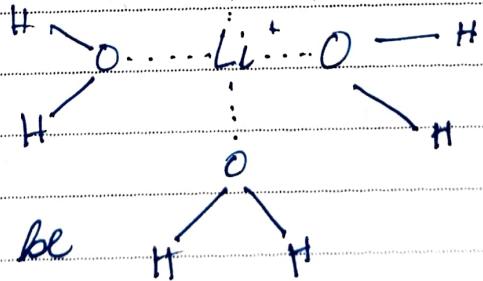
Amount of energy required to convert 1 mol of solid into gaseous phase. It is an endothermic process. [Bond breaking happens]

> Ionization enthalpy

Amount of energy required to remove  $e^-$  from outermost shell of an isolated gaseous atom. endothermic

> Hydration enthalpy

Amount of energy released when an ion is surrounded by water molecule. It is an exothermic process.



Smaller the ion, more will be hydration enthalpy.

Ion dipole interaction

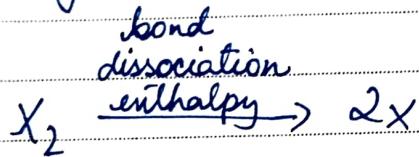


Why Lithium is strongest reducing agent? than Cs.

Ans as its hydration lithium being smallest ion, its hydration enthalpy will be highest which can compensate high sublimation enthalpy as well as ionization enthalpy.

Lithium being smallest ion, its hydration enthalpy is too high which can compensate high sublimation enthalpy as well as ionization enthalpy

Oxidising agent depends on



i) Bond dissociation enthalpy

Process is endothermic.

Amount of energy required to break bond in a molecule



Why  $F_2$  is least unexpected bond dissociation

→ Unexpected bond dissociation due to interelectronic repulsion because of its smaller size.

ii) Electron gain enthalpy.

Process is exothermic

Amount of energy released when an  $e^-$  is added in outermost shell of an isolated gaseous atom.

Why  $e^-$  gain enthalpy is high / more negative for Cl than F<sub>l</sub>?

→ In case of F<sub>l</sub>, amount of energy

→ Due to smaller size of F<sub>l</sub>, it has more interelectronic repulsion for incoming  $e^-$  whereas for Cl, due to its bigger size, interelectronic repulsion is less hence more negative.

> Hydration enthalpy [emo]

Why F<sub>l</sub> is strongest reducing agent

→ Due to its low bond dissociation enthalpy and high hydration enthalpy.

Electrode Potential

Tendency of an electrode to gain or loose  $e^-$ .

Q1. Given that the standard electrode potential ( $E^\circ$ ) of metals are

$$K^+/K = -2.93 \text{ V}, Ag^+/Ag = 0.80 \text{ V}, Cu^{2+}/Cu = 0.34 \text{ V}$$
$$Mg^{2+}/Mg = -2.37 \text{ V}.$$

$K > Mg > Cu > Ag$ .

Strongest reducing agent

Arrange these metals in an increasing order of their reducing power

Standard Hydrogen Electrode

Reference electrode to find electrode potential of unknown half electrodes.

What is the effect of dilution of specific conductance?

Ans k decreases with dilution as no. of ions per unit volume decrease.

Q. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is  $0.146 \times 10^8 \text{ S cm}^{-1}$ .

$$\text{Ans } R = 1500 \Omega$$

$$k = 0.146 \times 10^8 \text{ S cm}^{-1}$$

$$R = \rho \frac{l}{a}$$

$$\Rightarrow \frac{1}{\rho} \times R = \frac{l}{a}$$

$$\Rightarrow k \times R = \frac{l}{a}$$

$$\Rightarrow 0.146 \times 10 \times 1500 = \frac{l}{a}$$

$$\begin{array}{r} 146 \\ \times 15 \\ \hline 730 \\ 146 \\ \hline 2190 \end{array}$$

$$\Rightarrow \frac{l}{a} = 2190 \text{ cm}^{-1}$$

Kohlrausch law of independent migrations of ions.

The law states that the limiting

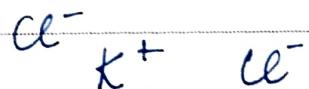
Molar conductance of an electrolyte is the sum of molar conductance of its ions.

## Application :

- i) Molar conductance at given concentration  $\lambda_m$
- ii) Molar conductance at infinite dilution  $\lambda_m^\circ$   
→ Means maximum molar conductance achieved after diluting a solution.

Molar conductance always increases with dilution.

For strong electrolyte, on dilution interionic attraction decreases hence ionic mobility increases



- a) Calculation of Molar conductance at infinite solution for weak electrolytes.

$$\lambda_{\text{H}_2\text{O}} = \lambda_{\text{HCl}} + \lambda_{\text{NaOH}} - \lambda_{\text{H}_2\text{O NaCl}}$$
$$\text{H}^+ \quad \text{OH}^- \quad \text{H}^+ \quad \text{Cl}^- \quad \cancel{\text{Na}^+ + \text{OH}^-} \quad \cancel{\text{Na}^+} \quad \text{Cl}^-$$

$\lambda_m^\circ$  for NaCl, HCl and NaAc are 126.4, 425.9 and 91.05  $\text{am}^2 \text{mol}^{-1}$  respectively. Calculate  $\lambda_0$  for HAc

Ans 425.9

$$\begin{array}{r} 91 \\ \hline 516.9 \\ - 126.4 \\ \hline 390.5 \end{array}$$

2) Calculation of degree of dissociation of weak electrolytes

$\alpha$  = degree of dissociation

$\gamma^c$  = molar conductance of solution at any conc.

$\gamma^\circ$  = molar conductance of infinite dilution

$$\alpha = \frac{\gamma^c_m}{\gamma^\circ_m}$$

3) Calculation of dissociation constant of weak electrolytes

$k$  = dissociation constant

$\alpha$  = degree of dissociation

$C$  = concentration.

$$k = \frac{C\alpha^2}{1-\alpha}$$

$$\alpha = \frac{\gamma^c_m}{\gamma^\circ_m}$$

If  $1 > \alpha$

$$k = C\alpha^2$$

Q. The molar conductivity of  $0.025 \text{ mol L}^{-1}$  methanoic acid is  $46.1 \text{ S cm}^2 \text{ mol}^{-1}$ . Calculate its degree of dissociation and dissociation constant. Given  $\gamma^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$  and  $\gamma^\circ(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$ .

Ans.

molarity

$$C = 0.025 \text{ mol L}^{-1}$$

$$\eta_m = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\eta^\circ(H^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\eta^\circ(HCOO^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\eta_m^\circ(HCOOH) = 349.6 + 54.6 \\ = 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\eta_m}{\eta^\circ_m}$$

$$= \frac{46.1}{404.2}$$

$$= 0.114$$

$$\begin{array}{r} 0.114 \\ 404.2 | 46.10 \\ -4 \quad \quad \quad 4042 \\ \hline 12 \quad 26 \quad 5680 \\ \quad \quad \quad 4042 \\ \hline 16380 \\ 1.000 \quad 16188 \\ -0.114 \quad \quad \quad 212 \\ \hline 0.886 \end{array}$$

$$K = \frac{C\alpha^2}{1-\alpha}$$

$$= \frac{(0.025)(0.114)^2}{1 - 0.114}$$

$$= \frac{0.025 \times 12996}{0.886}$$

$$= \frac{0.00314900}{0.886}$$

$$= 3.55 \times 10^{-4} \text{ mol/L}$$

$$0.114$$

$$1141$$

$$458$$

$$114$$

$$\begin{array}{r} +114 \\ \hline 12996 \end{array}$$

$$\times 258$$

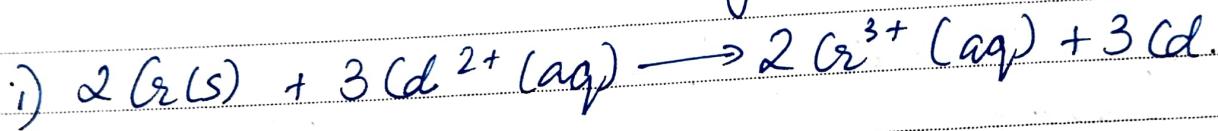
$$\begin{array}{r} ,6419180 \\ +25992 \\ \hline 314900 \end{array}$$

Q. Write the net eq<sup>n</sup> and calculate the emf of the given cell at 298 K.

Electrochemical cell  
Cell which convert electrical energy to chemical energy.

Iron on electrode at anode

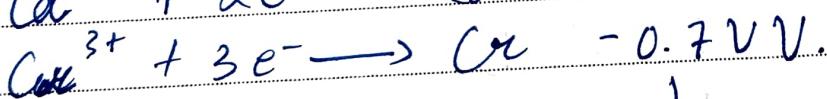
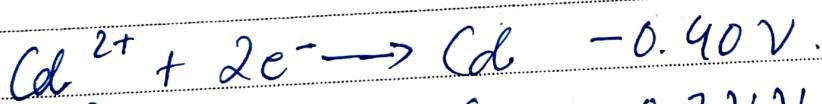
Q. Calculate the standard cell potential of galvanic cell in which the following reactions take place:



Given.  $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74\text{ V}$ ,  $E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.40\text{ V}$

$E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80\text{ V}$ ,  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77\text{ V}$ )

$$E^\circ_{\text{cell}} = E^\circ_{\text{C}} - E^\circ_{\text{A}}$$



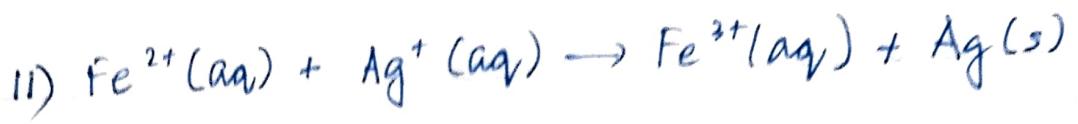
↓

+ 0.74.

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

$$= (-0.40) - (-0.74)$$

$$= 0.34\text{ V}$$



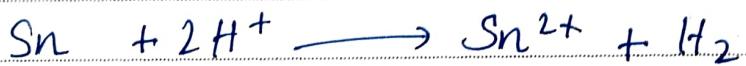
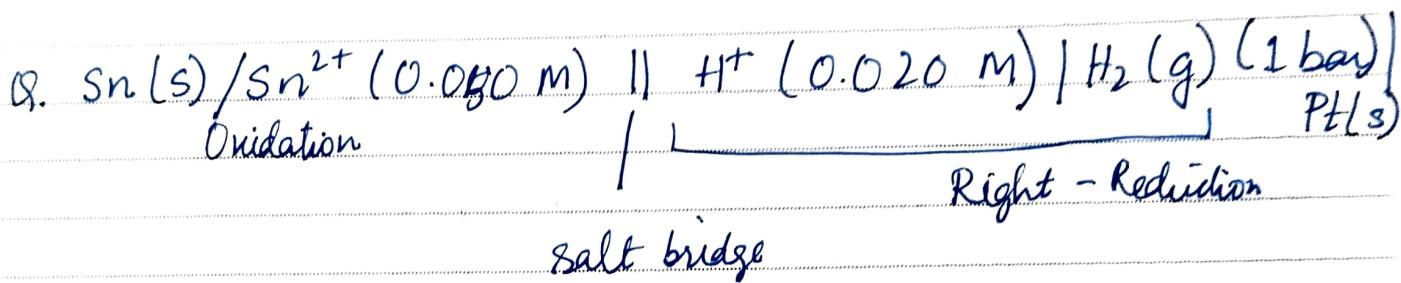
$$\epsilon_{\text{cell}}^\circ = \epsilon_C^\circ - \epsilon_A^\circ$$

$$= 0.80 - (-0.77)$$

$$= 0.03 \text{ V}$$

Nernst eq<sup>n</sup>

$$\epsilon_{\text{cell}} = \epsilon_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[P]}{[R]}$$



$$\epsilon_{\text{cell}}^\circ = \epsilon_C^\circ - \epsilon_A^\circ$$

$$= 0 - (-0.14)$$

$$= +0.14.$$

$$\epsilon_{\text{cell}} = \epsilon_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2}$$

$$= 0.14 - 0.0295 \log \frac{0.05}{(0.02)^2}$$

Note  $\rightarrow$  stoichiometric coefficient are the power of conc. in nernst eq<sup>r</sup>.

$$E_{\text{cell}} = 0.14 - 0.0295 \log \frac{0.05}{(0.02)^2}$$

$$\begin{aligned}\log 4 &= 0.602 \\ \log 5 &= 0.699\end{aligned}$$

$$= 0.14 - 0.0295 \log \frac{0.05}{0.02 \times 0.02}$$

$$= 0.14 - 0.0295 \cancel{\log 5} \times \frac{100\%}{4} \cancel{\times 100}$$

$$= 0.14 - 0.0295 (\log 5 + \log 10^2 - \log 4)$$

$$= 0.14 - 0.0295 (0.699 - 0.681)$$

$$= 0.14 - 0.0295 \times 2.097$$

$$= 0.14 - 0.06195$$

$$= 0.09$$

$$* \Delta G^\circ = -nFE^\circ$$

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



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

$$= -6 \times 96500 \times 0.34.$$

$$= 196860$$

$$= 196.86 \text{ kJ J/mol}$$

$$E_{\text{cell}}^\circ = E_C^\circ - E_A^\circ$$

$$= 0.74 - 6.0$$

$$= -0.4 - (-0.74)$$

$$= +0.34$$

$$\Delta G = -nFE_{\text{cell}}^\circ \quad \text{--- (1)}$$

$$\text{Feasibility} - E_{\text{cell}}^\circ = +ve$$

Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[P]}{[R]} \quad \text{--- (2)}$$

At eq<sup>m</sup>

$$E_{\text{cell}} = 0 \quad R \rightarrow P$$

$$E_{\text{cell}}^\circ = \frac{0.059}{n} \log K_C^{\text{eq}} \xrightarrow{K_C^{\text{eq}} / K_C} \frac{[P]}{[R]} \quad \text{--- (3)}$$

$K_C$  is eq<sup>m</sup> constant.

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log \frac{[P]}{[R]}$$

R is gas constant  $[8.314 \text{ JK}^{-1} \text{ mol}^{-1}]$

$$T = 298 \text{ K}$$

$$\frac{2.303RT}{F} = 0.059.$$

$$\begin{array}{r}
 96500 \\
 - 341 \\
 \hline
 388000 \\
 - 2895 \\
 \hline
 675500 \\
 - 64 \\
 \hline
 53000
 \end{array}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303}{nF} RT \log \frac{[P]}{[R]}$$

At eq<sup>m</sup>  $E_{\text{cell}} = 0 \quad \frac{[P]}{[R]} = K_c$

$$E_{\text{cell}}^{\circ} = \frac{2.303 RT}{nF} \log K_c \quad \text{--- (4)}$$

$$\Delta G = -nFE_{\text{cell}}^{\circ} \quad \text{--- (5)}$$

Put  $E_{\text{cell}}^{\circ}$  value in eq<sup>n</sup> (3)

$$\Delta G = -nF \times \frac{2.303 RT}{nF} \log K_c$$

$$\Delta G = -2.303 RT \log K_c$$

$$= -2.303 \frac{RT}{1} \log K_c$$

$$-19686 \text{ L} = -2.303 \times 8.314 \times 298 \log K_c$$

$$\frac{-19686 \text{ L}}{2.303 \times 8.314 \times 298} = \log K_c$$

$$\Rightarrow 34.5 = \log K_c$$

Taking antilog on both sides.

$$K_c = \text{antilog } 34.5$$



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

$$= 0.80 - (-0.77)$$

$$= 0.03 \text{ V.}$$

$$\Delta G = -nFE^\circ_{\text{cell}}$$

$$= -1 \times 96500 \times 0.03$$

$$= 2895 \text{ J/mol.}$$

$$\log K_c = 1 \times 0.03$$

$$\Delta E^\circ_{\text{cell}} = -\frac{0.059}{n} \log K_c$$

$$\log K_c = \frac{n E^\circ_{\text{cell}}}{0.059}$$

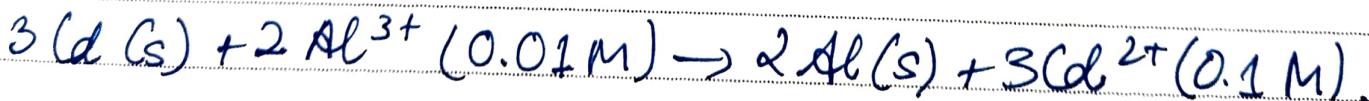
$$= \frac{1 \times 0.03}{0.059}$$

$$= 0.508$$

Taking antilog on both side

$$K_c = 3.22$$

Q. Represent the cell in which the following reaction takes place. The value of  $E^\circ$  for the cell is 1.260 V. What is the value of  $E_{\text{cell}}$ ?





$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Al}^3]^2}{[\text{Cd}^{2+}]^3} \quad \cancel{E_{\text{cell}} = E_C - E_A}$$

$$E_{\text{cell}} = 1.26 - \frac{0.059}{6} \log \frac{(0.01)^2}{(0.1)^3}$$

$$= 1.26 - \frac{0.059}{6} \frac{(0.01)^2}{(0.1)^3} \frac{(10^{-2})^2}{(10^{-1})^3}$$

$$= 1.26 - 0.0295 \log \frac{10^{-3}}{\cancel{10^{-3}}} \times 10^7$$

$$= 1.26 - 0.0295 \log 10$$

$$= 1.26 - 0.0295 (-1)$$

$$= 1.25$$

### Faraday's 1<sup>st</sup> Law.

It states that the amount of a substance that is liberated or deposited at electrodes is proportional to the quantity of electricity passed through the electrolyte.

$$w \propto q \quad m \propto q.$$

$$m = \frac{M It}{96500}$$

$$m = Z It$$

$$m = \frac{M}{n} \times \frac{Ixt}{96500} \quad \begin{matrix} m \rightarrow \text{mass} \\ \text{where } M \rightarrow \text{atomic mass} \\ n \rightarrow \text{valency} \end{matrix}$$

$I \rightarrow \text{current}$

$t \rightarrow \text{time}$ .

## 2<sup>nd</sup> Faraday Law.

When the same quantity of electricity is passed through electrolytic solution, the weight of different substances produced at the electrodes ratios of their equivalent masses.

$$\frac{M_{Ag}}{M_{Cu}} = \frac{\frac{M}{n} \times \frac{Ix t}{96500}}{\frac{M}{n} \times \frac{Ix 2}{96500}}$$

$$\frac{M_{Ag}}{M_{Cu}} = \frac{\text{eq. mass. Ag}}{\text{eq. mass. Cu}}$$

## Batteries

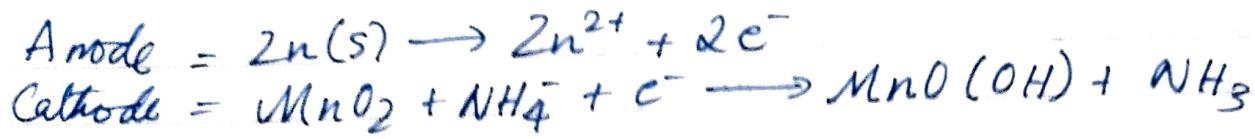
Primary batteries → reaction occurs only once and after use over a period of time battery becomes dead & cannot be reused again.

Leclanche cell is used commonly in our transistors & clocks.

The cell consists of a zinc container that also acts as anode & the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide & carbon.

The space b/w the electrodes is filled by a moist paste of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) & zinc chloride ( $\text{ZnCl}_2$ ).

Ammonia produced in the reaction forms a complex with  $\text{Zn}^{2+}$  to give  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ . The cell has a potential of nearly 1.5 V.



Mercury cell suitable for low current devices like hearing aids, watches, etc.

- Consists of zinc - mercury amalgam as anode & a paste of  $\text{HgO}$  & carbon as the cathode.

The electrolyte is a paste of  $\text{KOH}$  &  $\text{ZnO}$ . The overall reaction is represented by



The cell potential is approx. 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose conc. can change during its lifetime.

Role of ENL in Leclanche cell.

Ammonia produced in the reaction forms a complex with  $\text{Zn}^{2+}$  to give  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ . The cell has a potential of nearly 1.5 V.

Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.



$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^\circ = \frac{0.059}{1} \log \frac{1}{[H^+]} \\ &= 0 - 0.059 \log \frac{1}{10^{-10}} \quad \text{pH} = 10 = -\log [H^+] \\ &= -0.059 \log 10^{20} \quad -10 = \log [H^+] \\ &\approx -0.059 \times 10 \log 10 \quad \text{Taking antilog on both sides} \\ E_{\text{cell}} &= 0.59 \quad \text{antilog } (-10) = [H^+] \\ &\qquad\qquad\qquad 10^{-10} = [H^+] \end{aligned}$$

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$  in aqueous solution  
get hydrated

being smaller most highly hydrated become heavy hence ionic mobility decrease / conductivity  $\downarrow$

$Cs^+$  biggest cation & hence least hydrated hence ionic mobility increases.

17. Soln of 2 electrolytes A & B are diluted. The  $\eta_m$  of B increases 1.3 times while that of A increases 25 times. Which of the two is a strong electrolyte? Justify your ans.

Ans B.

