

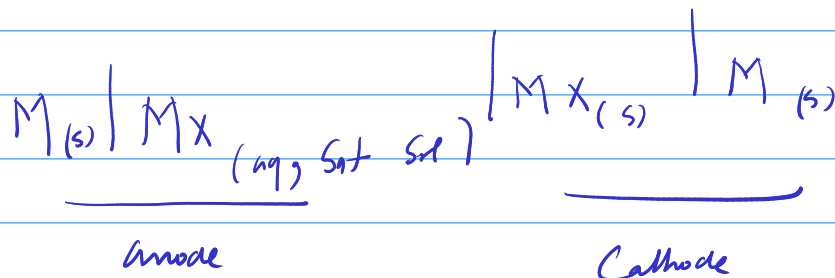
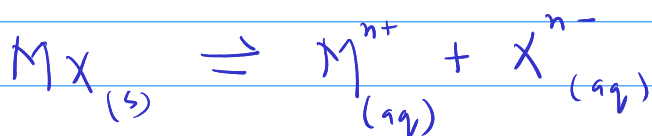
Determination of Solubility product Constant $\{K_{sp}\}$



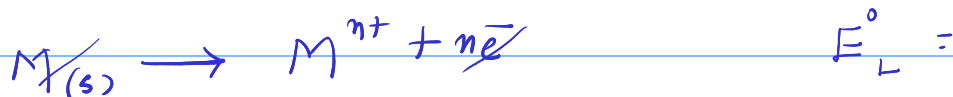
$$K_{sp} = a_{M^{b+}}^a \times a_{X^{a-}}^b$$

$$K = \frac{a_{M^{b+}}^a \times a_{X^{a-}}^b}{a_{M_a X_b} = 1} = a_{M^{b+}}^a \times a_{X^{a-}}^b$$

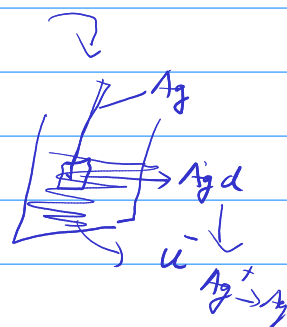
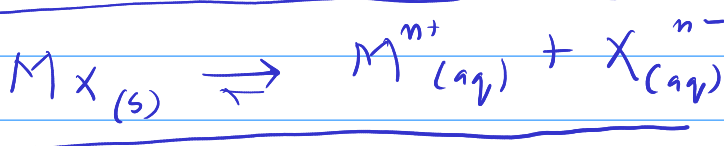
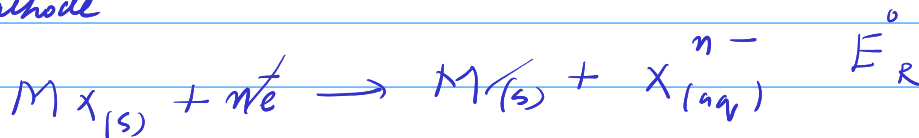
$$K_{sp} = K$$



@ anode



@ Cathode



@ 298K

$$E = E^0 - \frac{0.0592}{n} \log K$$

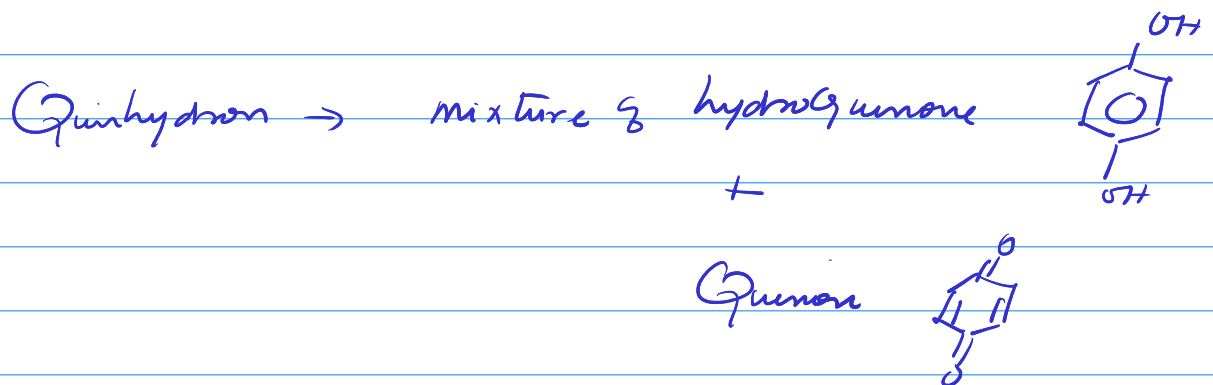
for sparingly soluble salt $K = K_{sp}$

$$E^{\circ} = \frac{0.0592}{n} \log K_{sp}$$

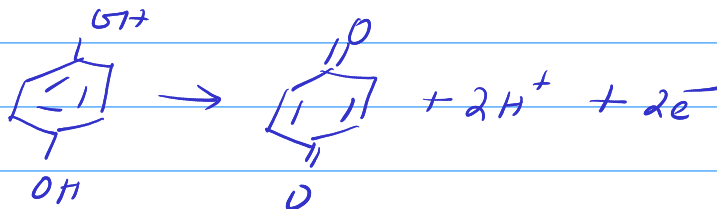
$$\log K_{sp} = \frac{E^{\circ} \times n}{0.0592}$$

$$K_{sp} = 10^{\left(\frac{E^{\circ} \times n}{0.0592} \right)}$$

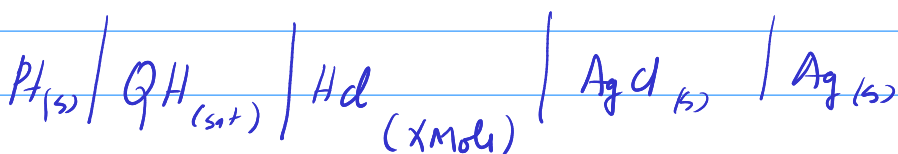
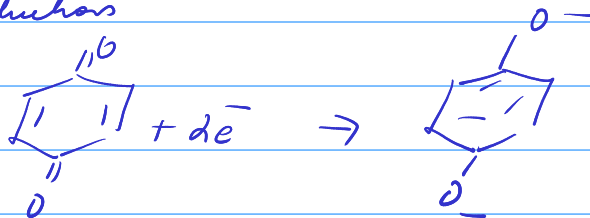
5) Determination of mean ionic activity Co-efficient of electrolyte



On Oxidation



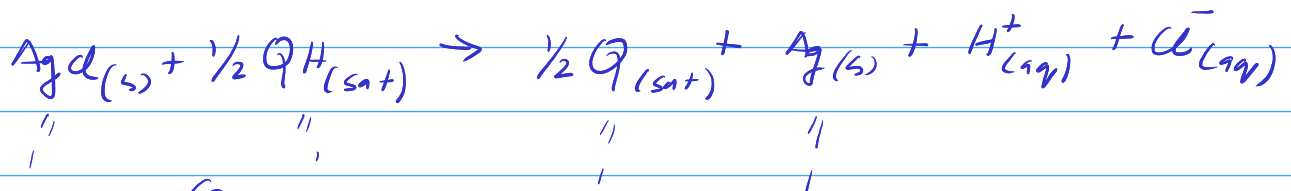
On Reduction



@ anode



@ Cathode



$$Q = a_{\text{H}^+} \times a_{\text{Cl}^-}$$

Potential of cell

$$E = E^0 - 0.0592 \log a_{\text{H}^+} \times a_{\text{Cl}^-}$$

We know that

$$a_+^x \times a_-^y = [a_{\pm}]^{x+y}$$

$$a_{\text{H}^+} \times a_{\text{Cl}^-} = (a_{\pm})^{1+1} = a_{\pm}^2 = \left(\gamma_{\pm} \times m \right)^2 = \gamma_{\pm}^2 \times m^2$$

Mean ionic activity coefficient concentration

We can write potential of cell as

$$E = E^0 - 0.0592 \log (\gamma_{\pm}^2 \times m^2)$$

$$= E^0 - 0.0592 \log \gamma_{\pm}^2 - 0.0592 \log m^2$$

$$= E^0 - 0.1184 \log \gamma_{\pm} - 0.1184 \log m$$

$$E + 0.1184 \log m = E^0 - 0.1184 \log \gamma_{\pm}$$

We can get

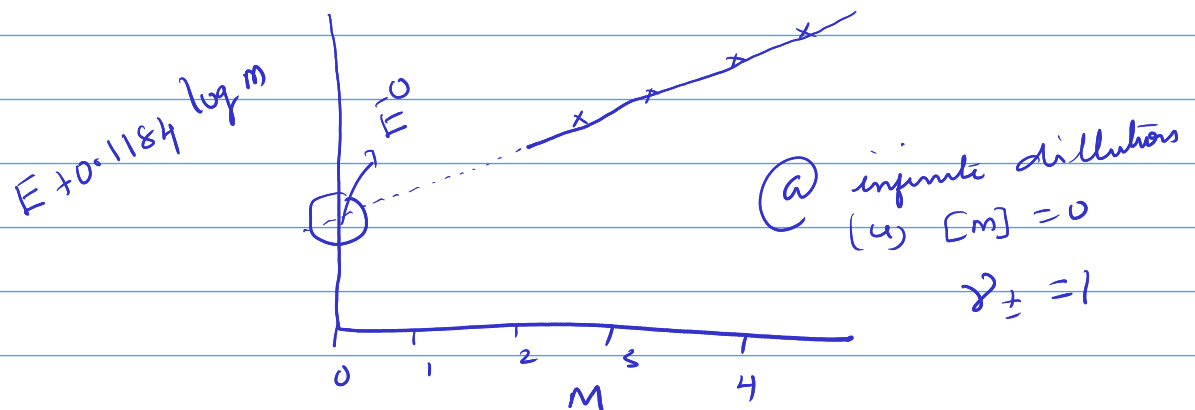
We know

Unknown

Unknown

Measure E @ different m & plot a graph

b/w $E + 0.1184 \log m$ Vs m



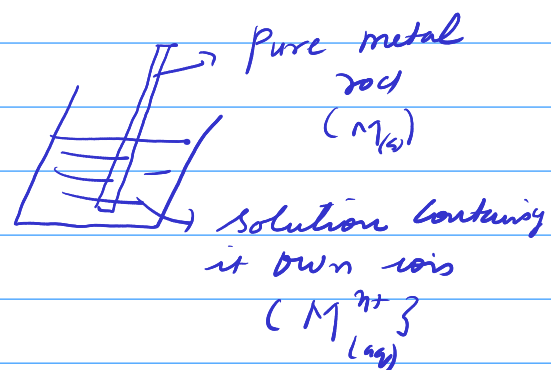
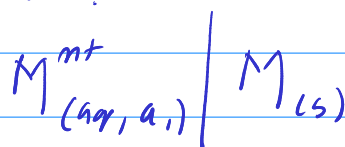
Once you get E^0 we can calculate/determine the γ_{\pm} @ any concentration.

Types of electrodes

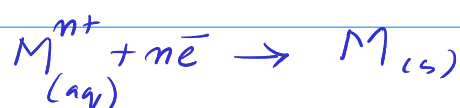
1. Metal-metal ion electrode
2. Metal-metal insoluble salt electrode
3. Metal amalgam electrode
4. Gas-ion electrode
5. Redox electrode

1. Metal-metal ion electrode:-

Representation:-



Reactions



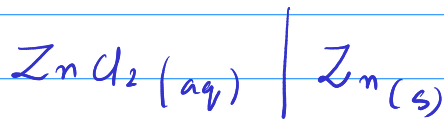
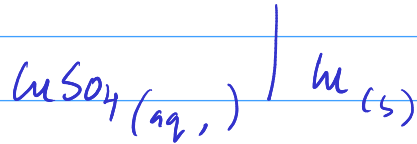
Potential of cell @ 298K

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{1}{a_{M^{n+}}}$$

$$E = E^{\circ} + \frac{0.0592}{n} \log a_{M^{n+}}$$

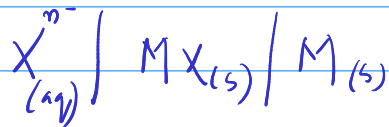
$$E \propto a_{M^{n+}}$$

Eg:-

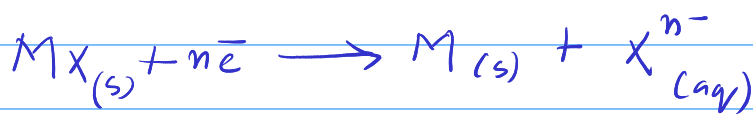


2. Metal - metal insoluble salt electrode

Representation



Reaction

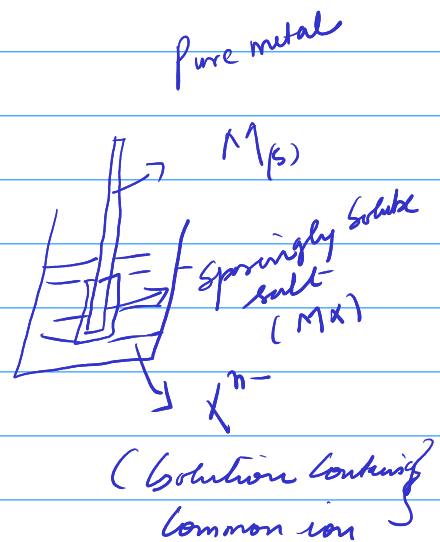
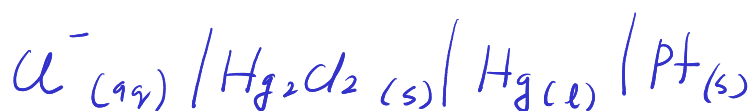
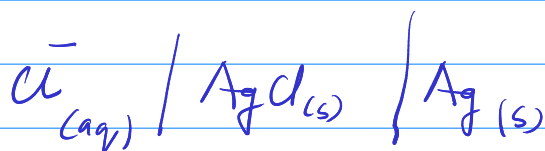


Potential @ 298K

$$E = E^{\circ} - \frac{0.0592}{n} \log a_{X^{n-}}$$

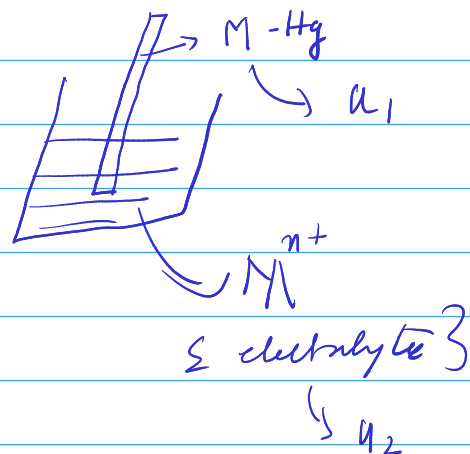
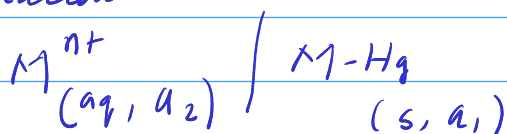
$$E \propto a_{X^{n-}}$$

Eg:-



3) Metal amalgam electrode

Representation



Reaction:-

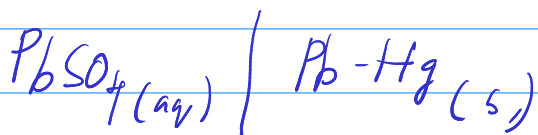


Potential of electrode @ 298K

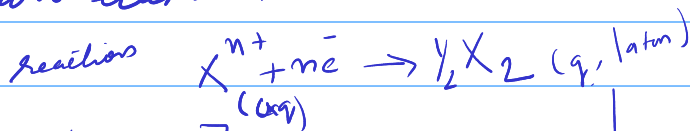
$$E = E^0 - \frac{0.0592}{n} \log \frac{a_1}{a_2}$$

$$E = E^0 + \frac{0.0592}{n} \log \frac{a_2}{a_1}$$

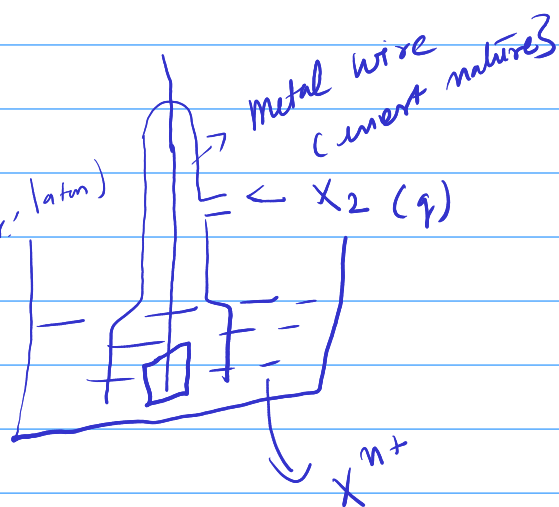
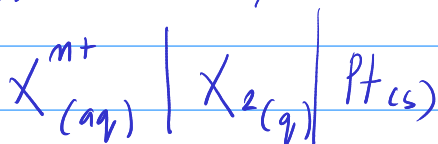
Eg:-



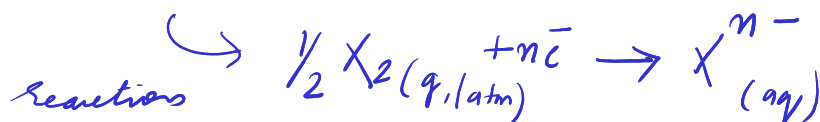
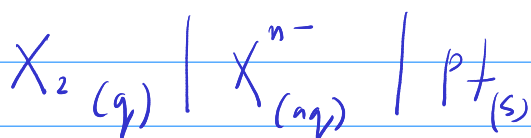
4) Gas-ion electrode:-



Representation



Sometimes



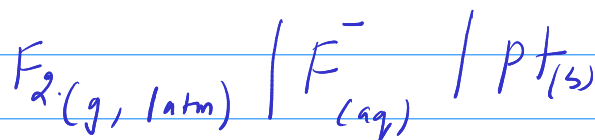
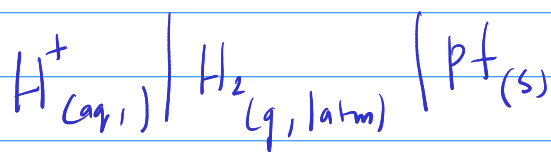
Potential @ 298K

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{1}{a_{X^{n+}}}$$

(or)

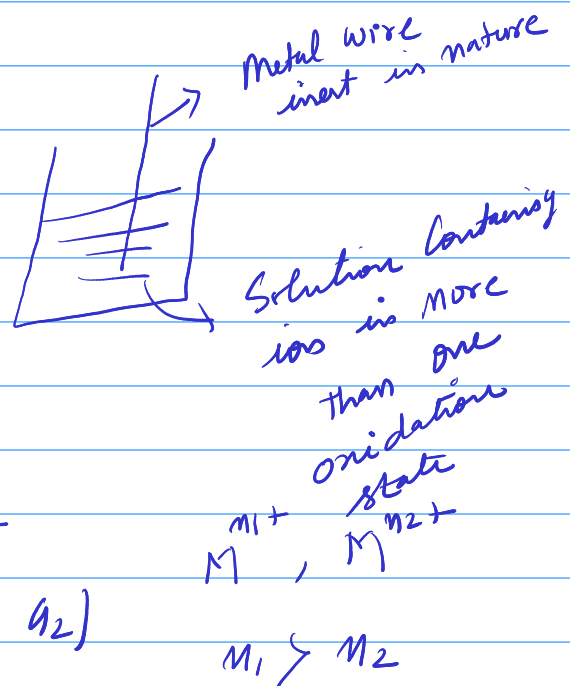
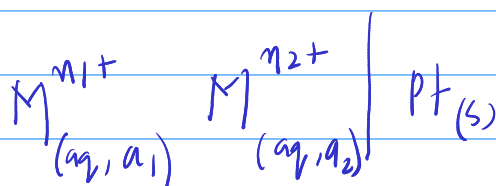
$$E = E^{\circ} - \frac{0.0592}{n} \log a_{X^{n+}}$$

Example:-

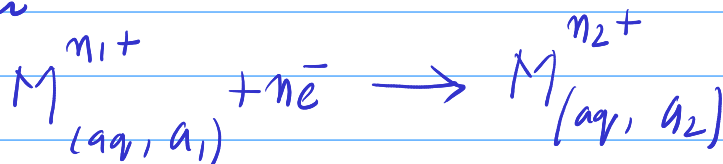


5) Redox electrode:-

Representation



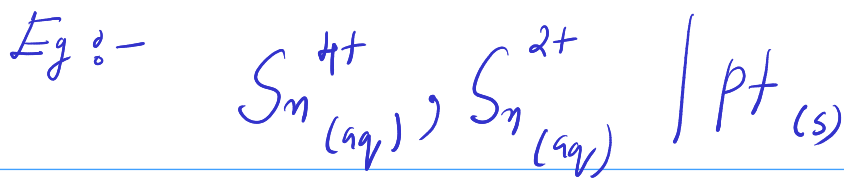
Reaction



Potential @ 298K

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{a_2}{a_1}$$

$$E = E^{\circ} + \frac{0.0592}{n} \log \frac{a_1}{a_2}$$



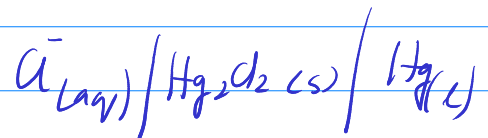
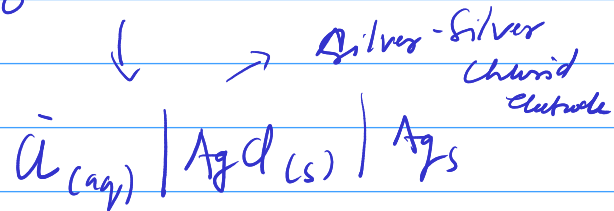
Reference electrode

1° reference electrode

↓
SHE

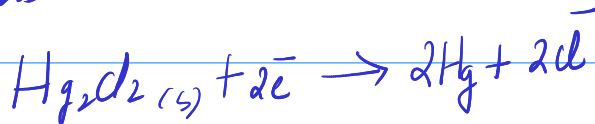
↓ not
we do^{n't} use it now a days

2° reference electrodes



Calomel electrode

Reactions



Potential @ 298K

$$E = E^{\circ} - \frac{0.0592}{2} \log a_{\text{Cl}^{-}^2}$$

$$E = E^{\circ} - 0.0592 \log a_{\text{Cl}^{-}}$$

$$E \propto a_{\text{Cl}^{-}}$$

Common Concentrations of KCl used

$$0.1\text{M KCl} \rightarrow E = 0.334\text{V}$$

$$1.0\text{M KCl} \rightarrow E = 0.28\text{V}$$

$$\text{Sat. KCl} \rightarrow 0.24\text{V}$$

