

PART B

ELECTROCHEMICAL EQUILIBRIUM

- Electrical energy \Rightarrow chemical energy
- Source of power - batteries
- corrosion - controlling is very crucial.
- Amount of resources gone into controlling corrosion is comparable to the amount spent on natural disasters.
- Three main requirements

1. Redox Reaction

- oxidation — loss of e^-
- reduction — gain of e^-

2. Electrodes

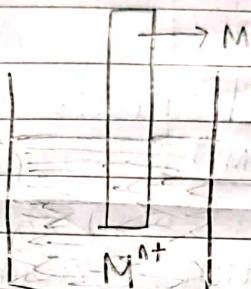
- surface for rxn to occur
- rxns should not occur at the same place; need to utilise energy
- anode — oxidation
- cathode — reduction
- simultaneously, in different compartments

3. Electrolyte

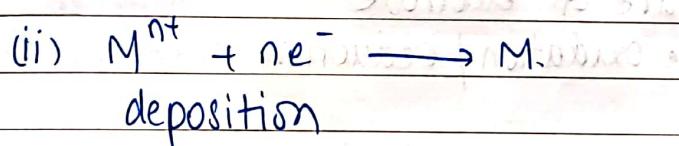
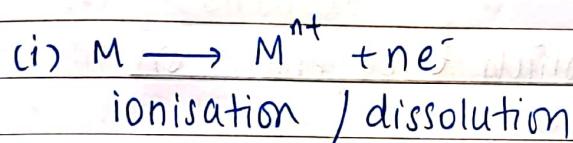
- electrons cannot move through electrolyte.
- ions are the charge carriers
- electrical wires provide electrons at electrodes.
- electrolytes offer high resistance
- electrodes carry electrons, electrolyte carries ion.
- cations — cathode] move towards anions — anode]
- substance that allows movement of ions

Electrode Potential

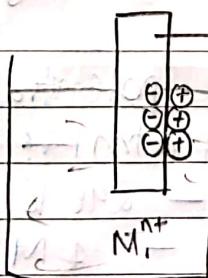
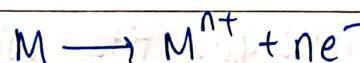
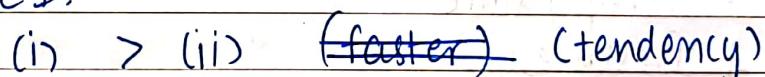
- The potential developed at the interface between the metal and the solution when it is in contact with a solution of its own ions, and it is denoted by E .



Two types of reactions on the electrode

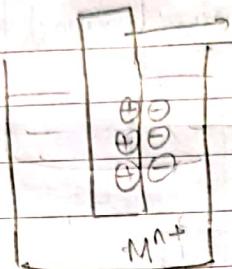
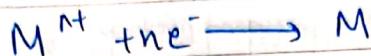


Case I:



- Electric double layer formed at surface due to charge separation
- Helmholtz double layer

- M^{n+} goes into solution, leaving -ve charge on the metal, attracting +ve charge from the solution

Case II(ii) \rightarrow (i)

- Helmholtz electric double layer

- M^{n+} from solution combines with e^- from the metal and deposits on the surface of the metal

Factors on which E depends on

1. Nature of electrode

- oxidation / reduction

2. Concentration of ions

3. Temperature

4. Pressure

- need to define new quantity with fewer variables

- standard electrode potential

Pressure - 1 atm

Temperature - 298 K

Concentration - 1 M

\therefore only depends on nature of electrode

Standard Electrode Potential (E°)

- The potential developed at the interface between the metal and the solution when it is in contact with a solution of its own ions at a concentration of 1 M (unit concentration), at 298 K and 1 atm, and is denoted by E° .
- At an electrode, only one of either oxidation or reduction occurs, not both
- But oxidation & reduction cannot occur independently
- Only working system can be a combination of 2 electrodes
- Measure potential difference
- One electrode has greater oxidation tendency, other has a greater reduction tendency

Cell Potential

- In an electrochemical cell, the difference in potential that causes electrons to flow from one electrode to another is called cell potential
- It is denoted by E_{cell} .

Standard cell Potential (E_{cell}°)

- E_{cell}° is defined as emf of a galvanic cell when reactants and products of the cell reaction are at unit concentration at 298 K at 1 atm pressure

- All cell reactions are due to E_{cell} .
- For spontaneity, ΔG must be negative

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

- E_{cell} must, therefore, be +ve

TYPES OF CELLS

Galvanic cell

- chemical \rightarrow electrical energy

- redox: spontaneous rxn

- uses: batteries, fuel cells

Electrolytic cell

- electrical \rightarrow chemical energy

- redox: non-spontaneous rxn; expend energy

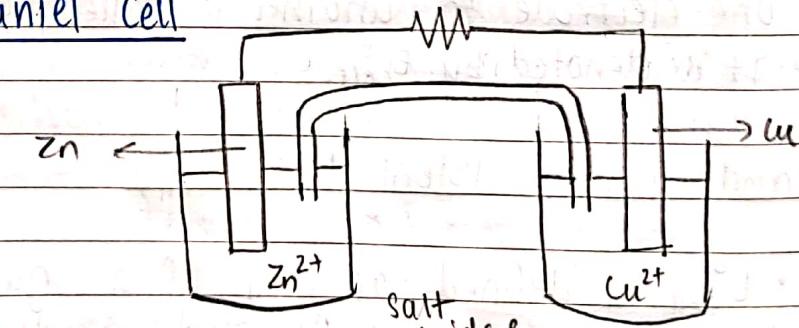
- uses: electroplating, electrorefining (Cu), electroforming

N.B.

- Galvanisation is NOT an electrolytic process

GALVANIC CELL

Daniel Cell



Phase separation
anode || cathode

$\text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt}$ → no phase separation between $\text{Fe}^{2+}, \text{Fe}^{3+}$

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

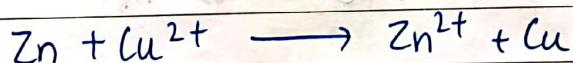
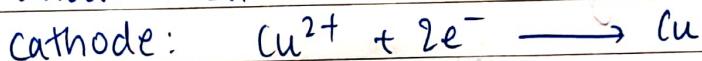
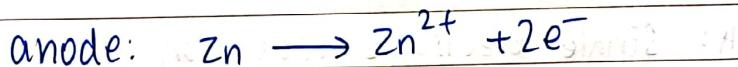
$$= E_{\text{RHS}} - E_{\text{LHS}}$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.34 \text{ V}$$

$$E_{\text{cell}}^{\circ} = +1.10 \text{ V} \quad \text{+ve value}$$

current runs is spontaneous cell reaction.



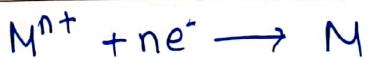
- series where standard electrode potentials have been tabulated

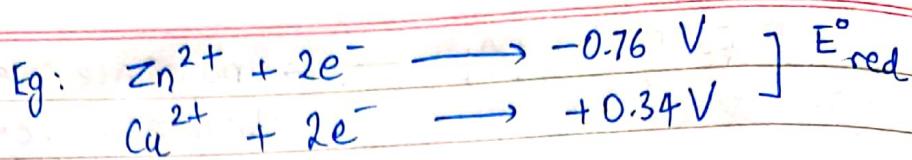
Electrochemical series

- In order to predict the electrochemical behaviour of electrode-electrolyte systems, the relative value of single electrode potential are listed in ascending order

- Standard potentials in ascending order.

- By convention, we use standard reduction potential.

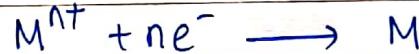




- Zn has a tendency to get oxidised, not reduced.
- Cu^{2+} has a greater tendency to undergo reduction
- Metal can never undergo reduction, only metal ions.
- Electrochemical series — standard conditions.
- Potential under nonstandard conditions

Q4: Derive Nernst Equation using thermodynamic principles

A: Single electrode reduction



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

- The max. work that can be obtained from a system is the decrease in free energy

W_{max} = total charge \times energy available per unit charge

$$W_{max} = nF \times E$$

$$-\Delta G = nFE$$

In standard conditions

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

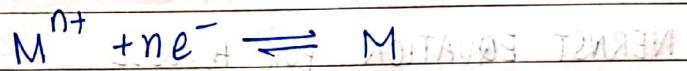
Vant Hoff Reaction Isotherm

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

- How the free energy changes from the standard value as the reaction proceeds.

Q = reaction quotient / extent of reaction

$$Q = \frac{[\text{Products}]}{[\text{Reactants}]}$$



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

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

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

- For a pure substance, $[M]$ is taken as 1 as the concentration doesn't change over time.

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

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

$E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}]$
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• At standard conditions

$$T = 298 \text{ K} \quad (\text{absolute temperature})$$

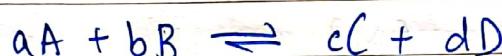
$$F = 96500 \text{ C mol}^{-1}$$

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

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

for the reduction of $M^{n+} + ne^- \rightarrow M$

NERNST EQUATION FOR A CELL



• To derive it for a cell,

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

$$W_{\max} = nFE$$

$$\Delta G = -nFE$$

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

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

$$-nFE = -nFE^\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E = E^\circ - \frac{RT}{NF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- At standard conditions

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

NERNST EQUATION FOR DANIEL CELL. (at 25°C)

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

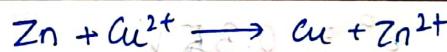
W_{\max} = total charge × energy available per unit charge

$$W_{\max} = nFE$$

$$-\Delta G = nFE$$

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

$Zn | Zn^{2+} || Cu^{2+} | Cu$ — Daniel cell.



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

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

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

$$-nFE = -nFE^\circ + RT \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

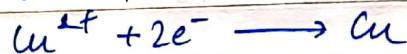
$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

- For ESA, write half reactions & full reactions.

Q5: Calculate standard potential of Cu^{2+}/Cu if its electrode potential at 25° is 0.296 V

$$[Cu^{2+}] = 0.015\text{ M}$$



A: $E = E^\circ + \frac{0.0591}{n} \log [Cu^{2+}]$

$$0.296 = E^\circ + \frac{0.0591}{2} \log (0.015)$$

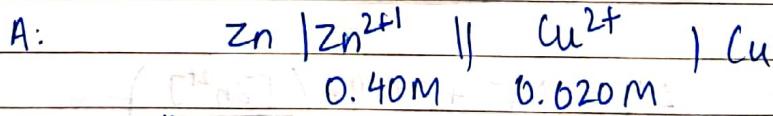
$$0.296 = E^\circ + \frac{0.0591}{2} (\log 1.5 - 2)$$

$$= E^\circ + \frac{0.0591}{2} (-1.8239)$$

$$0.296 = E^\circ - 0.05389$$

$$E^\circ = 0.35\text{ V}$$

Q6: Find emf of Daniel cell at 25°C



$$E_{cell}^\circ = 1.1\text{ V}$$



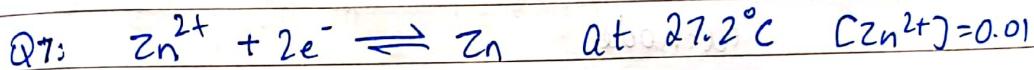
$$E = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 1.1 - \frac{0.0591}{2} \log \frac{0.4}{0.02}$$

$$= 1.1 - \frac{0.0591}{2} \log 20$$

$$= 1.1 - \frac{0.0591}{2} (1.3010)$$

$$E = 1.06 \text{ V}$$



$$E_{\text{Zn}}^{\circ} = -0.76 \text{ V}$$

A: $E = E_{\text{Zn}}^{\circ} + \frac{RT}{nF} \ln [\text{Zn}^{2+}]$

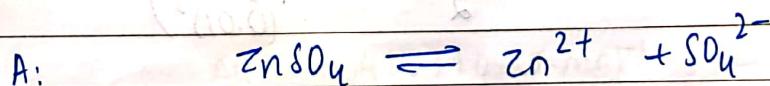
$$= -0.76 + \frac{(8.314)(300.2)}{(2)(96500)} \ln [\text{Zn}^{2+}]$$

$$= -0.76 + 0.0129 \ln [\text{Zn}^{2+}]$$

$$= -0.76 - 0.05955$$

$$E = -0.82 \text{ V}$$

Q8: Calculate E of Zn dipped in 0.05 M ZnSO_4
where $\alpha = 0.6$



$$0.05 \quad 0 \quad 0$$

$$0.05(0.4) \quad 0.05(0.6) \quad (0.05)(0.6)$$

$$[\text{Zn}^{2+}] = 0.05 \times 0.6 = 0.03$$

$$E = E^{\circ} + \frac{0.0591}{2} \log (0.03)$$

$$= -0.76 + \frac{0.0591}{2} (-1.52287) :$$

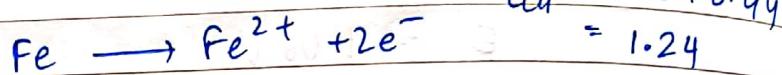
$$= -0.76 - 0.045$$

$$E = -0.805 \text{ V}$$

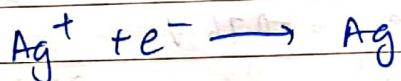
Q9: For the cell $\text{Fe} | \text{Fe}^{2+} (0.1 \text{ M}) || \text{Ag}^+ (0.01) | \text{Ag}$
at 298 K, calculate E & write rxn.

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \quad E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80$$

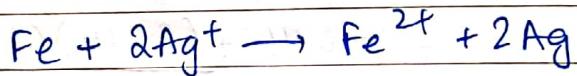
A: anode:



cathode



Cell equation



$$Q = \frac{[\text{Fe}^{2+}]}{[\text{Ag}^+]^2}$$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{Ag}^+]^2}$$

$$= E^\circ - \frac{0.0591}{2} \log \left(\frac{0.1}{(0.01)^2} \right)$$

$$= 1.24 - \frac{0.0591}{2} \log (10^3)$$

$$= 1.24 - \frac{0.0591 \times 3}{2} = 1.24 - 0.08865$$

$$E = 1.15 \text{ V}$$

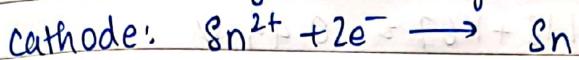
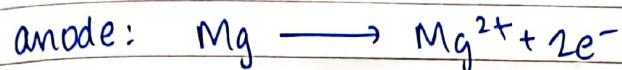
Q10: Calculate E° , E , ΔG° for the following reaction



$$[\text{Mg}^{2+}] = 0.045 \text{ M} \quad E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ V}$$

$$[\text{Sn}^{2+}] = 0.035 \text{ M} \quad E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14 \text{ V}$$

A:



$$E^\circ_{\text{cell}} = E^\circ_{\text{Sn}^{2+}/\text{Sn}} - E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -0.14 + 2.37 = \cancel{+1.23} \text{ V}$$

$$E^\circ_{\text{cell}} = +1.23 \text{ V}$$

$$E_{\text{cell}} = +1.23 - \frac{0.0591}{2} \log \left(\frac{0.045}{0.035} \right)$$

$$= 1.23 - \frac{0.0591}{2} \log \left(\frac{9}{7} \right)$$

$$= 1.23 - 3.225 \times 10^{-3}$$

$$= 1.23 - 0.003225$$

$$E_{\text{cell}} = 1.227 \text{ V}$$

$$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.23$$

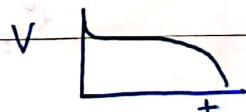
$$= -4.46 \times 96500$$

$$= -430390$$

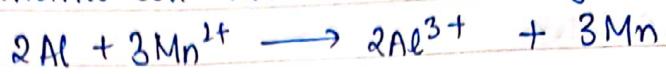
$$\Delta G^\circ = -430390 \text{ J mol}^{-1}$$

$$= -430.39 \text{ kJ mol}^{-1} \Rightarrow W = 430.39 \text{ kJ mol}^{-1}$$

- Difference between E and E° very little
- The reason why batteries give constant voltage (steady)
- Q value is constantly changing \therefore the contribution of second term is little



Q11: A galvanic cell uses the following reaction



$$E_{\text{Al}^{3+}/\text{Al}}^{\circ} = -1.67 \text{ V} \quad E_{\text{Mn}^{2+}/\text{Mn}}^{\circ} = -1.18 \text{ V}$$

- (a) calculate E_{cell}° under standard conditions
- (b) calculate E_{cell} when $[\text{Al}^{3+}] = 1.5 \text{ M}$, $[\text{Mn}^{2+}] = 0.1 \text{ M}$
- (c) Work done in case (b)

A:

$$(a) E_{\text{cell}}^{\circ} = -1.18 + 1.67 = 0.49 \text{ V}$$

$$(b) E_{\text{cell}} = 0.49 - \frac{0.0591}{6} \log \left(\frac{(1.5)^2}{(0.1)^3} \right)$$

$$= 0.49 - \frac{0.0591}{6} (3 + 2\log 1.5)$$

$$E_{\text{cell}} = 0.457 \text{ V}$$

$$= 0.45698 \text{ V}$$

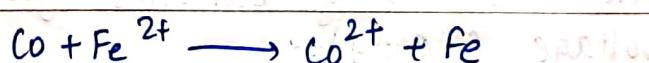
$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Mn}^{2+}]^3} \quad n = 6.$$

$$(c) \Delta G = -nFE = -6 \times 0.45698 \times 96500$$

$$\boxed{\Delta G = -264.6 \text{ kJ mol}^{-1}}$$

$$W = 264.6 \text{ kJ mol}^{-1}$$

Q12: Predict whether the following rxn proceeds spontaneously at 298 K when the following concentrations are present



$$[\text{Co}^{2+}] = 0.15 \text{ M} \quad [\text{Fe}^{2+}] = 0.68 \text{ M}$$

$$E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \quad E_{\text{Co}^{2+}/\text{Co}}^{\circ} = -0.28$$

$$A: E_{\text{cell}}^{\circ} = -0.44 + 0.28 = -0.16 \text{ V}$$

$$E_{\text{cell}} = -0.16 - \frac{0.0591}{2} \log \left(\frac{0.15}{0.68} \right)$$

$$= -0.16 + 0.01939$$

$$E_{\text{cell}} = -0.1406$$

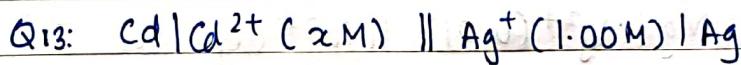
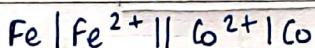
$$\Delta G = -nFE = +2 \times 96500 \times 0.1406$$

$$= 27136 \text{ J mol}^{-1}$$

$\therefore \Delta G$ is +ve & the rxn is non spontaneous

(E_{cell} is -ve \Rightarrow rxn not feasible)

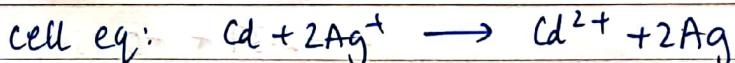
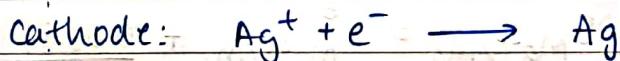
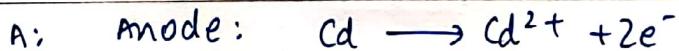
Correct cell:



$$E_{\text{cell}}^{\circ} = 1.2022 \text{ V}$$

$$E_{\text{cell}} = 1.2871 \text{ V}$$

$$[\text{Cd}^{2+}] = ? \text{ at } 298$$



$$1.2871 = 1.2022 - \frac{0.0591}{2} \log \left(\frac{x}{12} \right)$$

$$2 \times 0.0849 = -0.0591 \log x$$

$$x = 1.339 \times 10^{-3} \text{ M}$$

$$x = 1.34 \text{ mM}$$

Q14: Zn electrode in 0.101 M $ZnSO_4$ has
 $E = -0.7912 \text{ V}$ at temp $T = ?$ $E^\circ = -0.76$

$$\text{A: } E = E^\circ + \frac{RT}{nF} \ln [Zn^{2+}]$$

$$-0.7912 + 0.76 = \frac{8.314 T}{2 \times 96500} \ln (0.101)$$

$$\frac{-0.0312 \times 2 \times 96500}{8.314} = \ln (0.101) T$$

$$T = \frac{-724.27}{\ln (0.101)} = 315.9 \text{ K}$$

$$\boxed{T = 315.9 \text{ K}} \quad C = 42.9^\circ \text{C}$$

Q15: $Mg | Mg^{2+}(0.01) \parallel Cu^{2+}(C_1) | Cu$.

$$E = 2.78 \text{ V at } 298 \text{ K}$$

$$E^\circ_{Mg^{2+}/Mg} = -2.37 \text{ V} \quad E^\circ_{Cu^{2+}/Cu} = ?$$

$$\text{A: } E_{Mg^{2+}/Mg} = E^\circ_{Mg^{2+}/Mg} + \frac{0.0591}{2} \log (0.01)$$

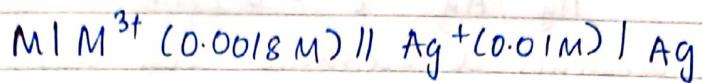
$$= -2.37 + -0.0591$$

$$E_{Mg^{2+}/Mg} = -2.4291$$

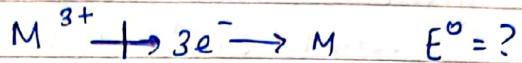
$$E_{cell} = 2.78 = E_{Cu^{2+}/Cu} + 2.37 - 2.4291$$

$$E_{Cu^{2+}/Cu} = 0.409 \text{ V}$$

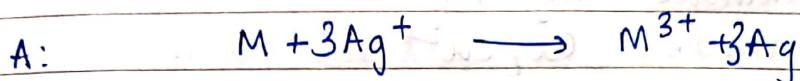
$$= 0.3509 \text{ V}$$

Q16: $M^{3+} | M$ 

$$E_{cell} = 0.42 \text{ V}$$



$$E^\circ_{Ag^+/Ag} = 0.80 \text{ V}$$



$$Q = \frac{[M^{3+}]}{[Ag^+]^3}$$

$$E_{Ag^+/Ag} = 0.80 + 0.0591 \log (0.01)$$

$$= 0.80 - 0.1182$$

$$E_{Ag^+/Ag} = 0.6818 \text{ V}$$

$$E_{M^{3+}/Mg} = E_{Ag^+/Ag} - E_{cell}$$

$$= 0.80 - 0.42 = 0.38$$

$$E_{M^{3+}/Mg} = 0.6818 - 0.42$$

$$0.2618 = E^\circ + \frac{0.0591}{3} \log (0.0018)$$

$$0.2618 = E^\circ - 0.054$$

$$E^\circ = 0.3158 \text{ V}$$

$$\text{Q17: } \text{Cu}^{2+}/\text{Cu} : E^\circ = 0.337 \text{ V},$$

$$\text{Ag}^+/\text{Ag} : E^\circ = 0.799 \text{ V}$$

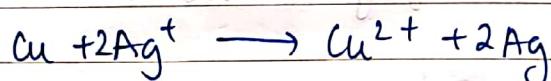
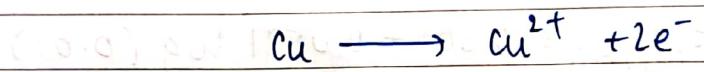
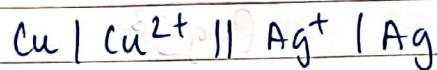
construct a galvanic cell using the values given.

For what $[\text{Ag}^+]$ does $E_{\text{cell}} = 0$ at 25°C when $[\text{Cu}^{2+}] = 0.01 \text{ M}$

cathode: Ag^+/Ag

anode: Cu/Cu^{2+}

cell:



$$Q = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$E_{\text{cell}}^\circ = 0.799 - 0.337 = 0.462 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{2} \log \left(\frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \right)$$

$$\text{Let } x = [\text{Ag}^+]$$

$$0.462 = \frac{0.0591}{2} \log \left(\frac{0.01}{x^2} \right)$$

$$\log \left(\frac{0.01}{x^2} \right) = 15.6345$$

$$-2 - 2 \log x = 15.6345$$

$$-\frac{17.6345}{2} = \log x = -8.81725$$

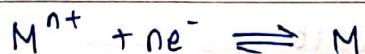
$$x = 1.5 \times 10^{-9} \text{ M}$$

TYPES OF ELECTRODES

- So far, only spoken of metal rod dipped in its own solution

1. Metal-metal ion electrode

- when a metal rod is dipped in a solution of its own ions
- M^{n+}/M
- eg: Zn^{2+}/Zn , Ag^+/Ag



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

2. Metal-insoluble salt of metal-ion

- Calomel electrode: Hg_2Cl_2/Cl^-
- ion to which the salt is reversible
- insoluble / sparingly soluble salt

Calomel: ~~not a~~ not ion.

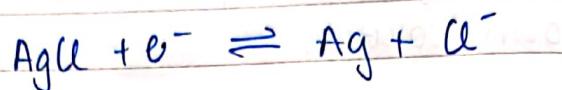
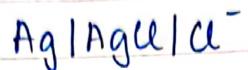


$$E = E^\circ - \frac{0.0591}{2} \log ([Cl^-]^2)$$

$$E = E^\circ - 0.0591 \log ([Cl^-])$$

- The potential of calomel electrode depends on $[Cl^-]$
- Reversible to the chloride ion.
- metal in contact with insoluble salt in contact with ion that the electrode is reversible to.

eg 2: Silver-silver chloride electrode

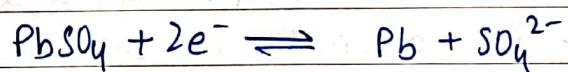
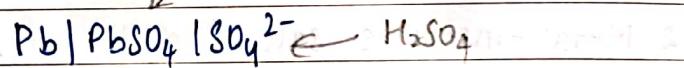


$$E = E^\circ - \frac{0.0591}{1} \log [c\text{Cl}^-]$$

- to make previous kind of Ag electrode (metal-metal), use soluble salt of silver like AgNO_3
- to make insoluble salt kind of electrode, insoluble salt
- $\text{Ag}|\text{AgNO}_3$ is reversible to Ag^+

eg 3: Pb and PbSO_4 (insoluble salt)

↙ insoluble



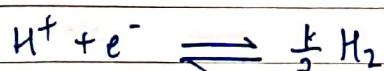
$$E = E^\circ - \frac{0.0591}{2} \log [\text{SO}_4^{2-}]$$

3. Gas electrode

- Hydrogen electrode
- gas being bubbled around an inert electrode dipped in a solution of gas in which the gas is reversible (ions to which gas is reversible)

eg 1: $\text{H}^+ | \text{H}_2 \text{ (gas)} | \text{Pt}$

(cm) (p atm)



$$E = E^\circ - \frac{0.0591}{1} \log \left(\frac{(P_{H_2})^{1/2}}{[H^+]} \right)$$

- P_{H_2} is always P_{H_2}/P_0 (reference), relative partial pressure

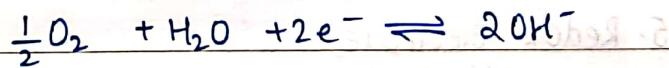
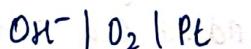
eg 2: Chlorine electrode.



$$E = E^\circ - \frac{0.0591}{2} \log \frac{[Cl^-]^2}{(P_{Cl_2})}$$

- role of Pt: provides electrical contact, provides reaction surface (platinised platinum)

eg 3: oxygen electrode

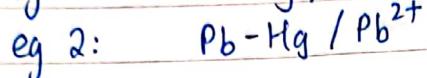
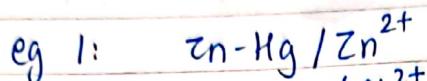


- shows oxygen reduction in alkaline medium

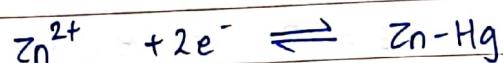
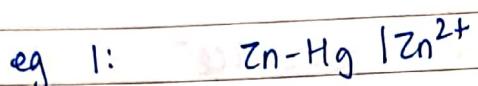
$$E = E^\circ - \frac{0.0591}{2} \log \frac{[OH^-]^2}{(P_{O_2})^{1/2}}$$

4. Amalgam electrode

- metal in contact with metals ions but metal in the form of its amalgam.
- used for Na electrode, etc, to be able to work with



- can control the activity of the electrodes

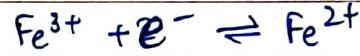
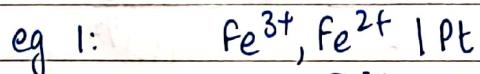


$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn-Hg}]}{[\text{Zn}^{2+}]}$$

- we always take pure metals as 1.
- in Amalgam electrodes, % Zn cannot be ignored
- used to reduce activity of electrodes, control inertness with surrounding (eg: active metals)

5. Redox electrode

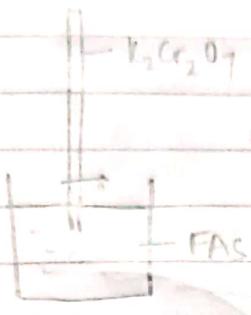
- oxidised & reduced species present together
- one would want to change to the other
- if wire placed, potential formed.



$$E = E^\circ - \frac{0.0591}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

- Fe³⁺, Fe²⁺ | Pt used in potentiometric titration for Haematite in the lab

Fe^{2+} as well as Fe^{3+} in the solution at the same time.



Pt wire causes potential to form

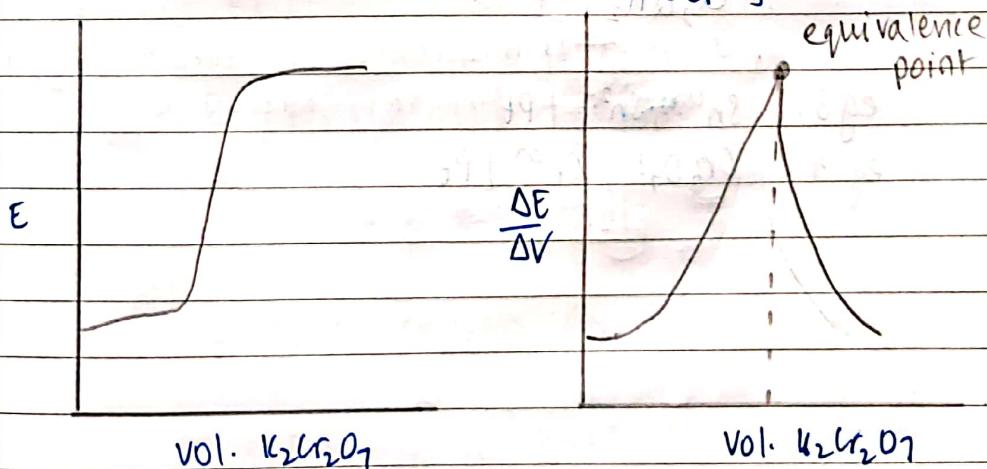
- As more and more $\text{K}_2\text{Cr}_2\text{O}_7$ added, $[\text{Fe}^{3+}] \uparrow$ and $[\text{Fe}^{2+}] \downarrow$
- $\therefore E_{\text{electrode}}$ increases
- At end point, almost all $[\text{Fe}^{3+}]$ and no $[\text{Fe}^{2+}]$
- After no more Fe^{2+} , electrode does not exist
- With excess $\text{K}_2\text{Cr}_2\text{O}_7$, Cr^{6+} introduced to Cr^{3+} which is already in solution
- After end point, new electrode $\text{Cr}^{6+}, \text{Cr}^{3+} \mid \text{Pt}$ introduced

$$E^\circ \text{ of } \text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt} = 0.77 \text{ V}$$

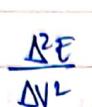
$$E^\circ \text{ of } \text{Cr}^{6+}, \text{Cr}^{3+} \mid \text{Pt} = 1.33 \text{ V}$$

$$E^\circ = E^\circ - \frac{0.0591}{3} \log \frac{[\text{Cr}^{3+}]}{[\text{Cr}^{6+}]}$$

activity; dimensionless

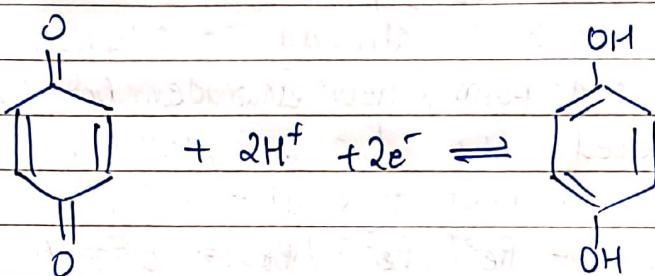


- use $\frac{\Delta^2 E}{\Delta V^2}$ if unsure of $\frac{\Delta E}{\Delta V}$



Vol. $\text{K}_2\text{Cr}_2\text{O}_7$

eg 2: Quinhydrone electrode



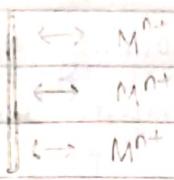
quinone hydroquinone

Q, QH_2 IPT

eg 3: $\text{Sn}^{4+}, \text{Sn}^{2+} \mid \text{Pt}$

eq 4: $\text{Cr}_2\text{O}_7^{2-}$, Cr^{3+} | Pt

6. Ion selective electrode



membrane capable of exchanging only one particular ion.

- also called membrane electrode
- application - water pollution, blood sample
- sensitive for quantifying

e.g. 1: glass electrode

- membrane sensitive to H⁺
- able to quantify and detect H⁺

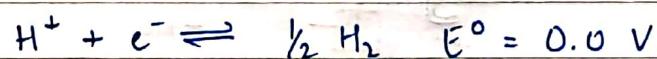
Reference Electrodes

- single electrode potential cannot be measured.
- Reference electrodes are electrodes that have a potential that is accurately known and is constant and with respect to these electrodes, potential of other electrodes can be determined or assigned.

Primary Reference Electrode

SHE (Standard Hydrogen Electrode)

Pt | H₂ (1 atm) | H⁺ (1 M)



- Hydrogen chosen for convenience

- To find E[°]_{Zn²⁺/Zn}, Zn | Zn²⁺ || H⁺ | H₂ | Pt.

$$E_{\text{cell}}^\circ = 0.0 - E_{\text{Zn}^{2+}/\text{Zn}}^\circ \Rightarrow E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -E_{\text{cell}}^\circ$$

must be +ve

- For Cu²⁺/Cu : Pt | H₂ | H⁺ || Cu²⁺ | Cu

$$E_{\text{cell}}^\circ = E_{\text{Cu}^{2+}/\text{Cu}}^\circ - 0.0 \Rightarrow E_{\text{Cu}^{2+}/\text{Cu}}^\circ = E_{\text{cell}}^\circ$$

Problems / Limitations of SHE

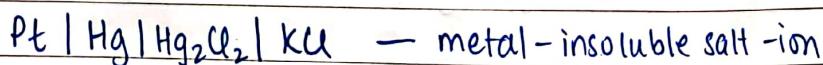
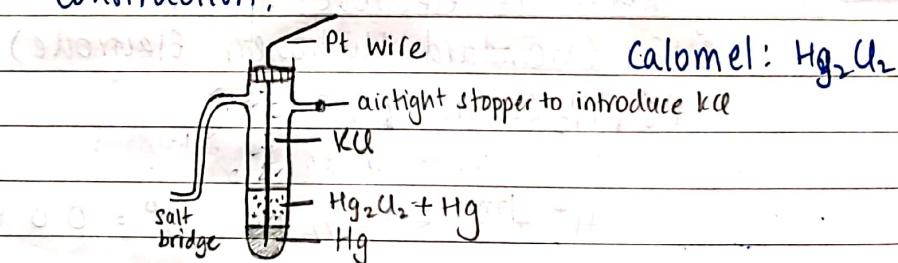
- construction and working is difficult and as maintaining concentration unity and maintaining pressure of the gas uniformly is difficult. (gas electrode)
- Active sites get blocked; Pt is highly susceptible to poisoning.
- cannot be used in the presence of oxidising agents

Secondary Reference Electrode

- Since SHE is difficult to repair & maintain, it is replaced by different secondary electrodes which are convenient to handle, easy to assemble & have a stable potential that is accurately known.
- With respect to these electrodes, potential of other electrodes can be measured.

CALOMEL ELECTRODE

Construction:

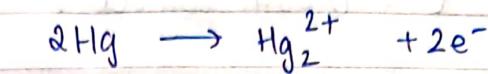


Three types of Calomel electrodes based on [KCl]

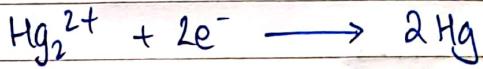
1. 0.1 N — deionized calomel electrode
2. 1 N — normal calomel electrode
3. Saturated solution — saturated calomel electrode (SCE) : most used

Working:

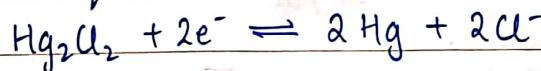
When it acts as the anode



When it acts as the cathode



Nernst Equation



at 298 K

$$E = E^\circ - \frac{0.0591}{2} \log [\text{Cl}^-]^2$$

$$E = E^\circ - 0.0591 \log [\text{Cl}^-]$$

- electrode is reversible to Cl^-
- electrode potential depends on $[\text{Cl}^-]$
- $E_{\text{calomel}}^\circ = E_{\text{IN}}$

E for standard electrodes at 298 K.

$$1. 0.1 \text{ N}, E = 0.334 \text{ V}$$

$$2. 1 \text{ N}, E = 0.281 \text{ V}$$

$$3. \text{ SCE}, E = 0.2422 \text{ V}$$

Q18: Find $[Cl^-]$ for calomel electrode given the three electrode potentials.

$$E = E^\circ - 0.0591 \log [Cl^-]$$

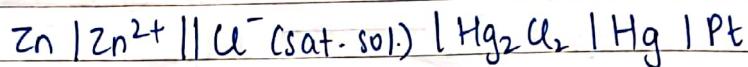
$$0.2422 = 0.281 - 0.0591 \log [Cl^-]$$

$$-0.0388 = -0.0591 \log [Cl^-]$$

$$\log [Cl^-] = 0.6565$$

$$[Cl^-] = 4.53 M$$

Representation of Zn electrode



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

cannot use E°

as $[Cl^-]$ not 1M

$$E_{\text{cell}} = 0.2422 - E_{Zn^{2+}/Zn}$$

if $[Zn^{2+}] = 1 M$ (standard)

$$E_{\text{cell}} = 0.2422 + 0.76 = 1.0022$$

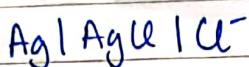
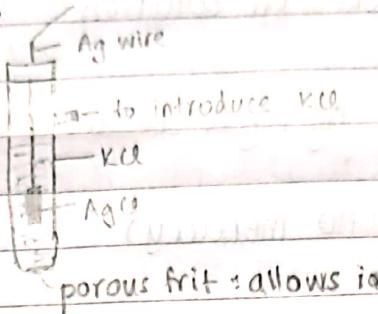
Advantages of Calomel Electrode

1. Simple to construct
2. Electrode potential is reproducible and constant over a long period of time
3. Electrode potential does not vary much with temperature.

SILVER - SILVER CHLORIDE ELECTRODE

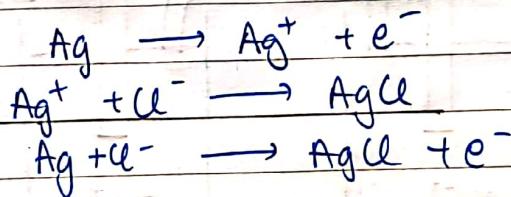
Construction:

(no Pt. required)

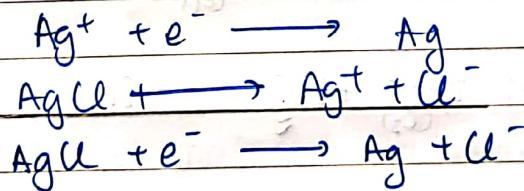


Working:

When it acts as anode



When it acts as cathode



Nernst Equation

$$E = E^\circ - 0.0591 \log [\text{Cl}^-] \quad \text{at } 298$$

• E of standard electrodes:

$[\text{KCl}]$	E at 298 K
0.1N	0.289 V
1N	0.223 V = E°
saturated sol.	0.199 V

Note:

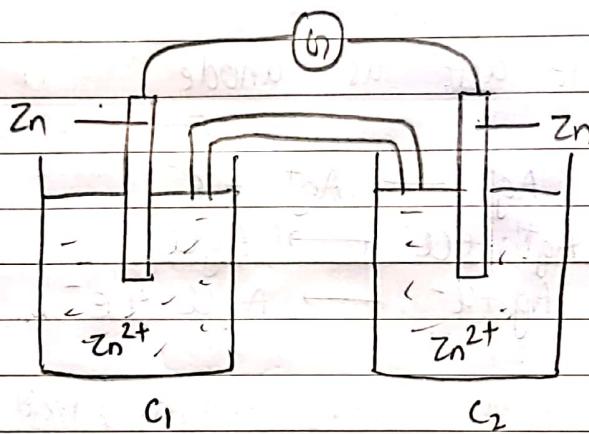
reversible to an ion \Rightarrow can find concentration of said ion in solution

Advantages of Ag-AgCl Electrode Over Calomel

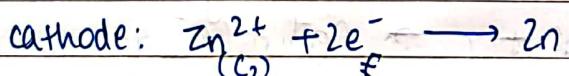
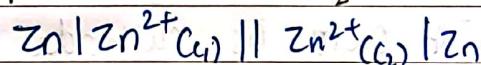
1. Inexpensive
2. Non-toxic (no mercury)

- We continue to use Calomel as it is very versatile

CONCENTRATION CELLS



Driving force:
trying to equalise
the concentration



Derive the cell potential

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

$$= \left(E_{Zn^{2+}/Zn}^{\circ} + \frac{2.303RT}{NF} \log [Zn^{2+}]_{C_2} \right)$$

$$- \left(E_{Zn^{2+}/Zn}^{\circ} + \frac{2.303RT}{NF} \log [Zn^{2+}]_{C_1} \right)$$

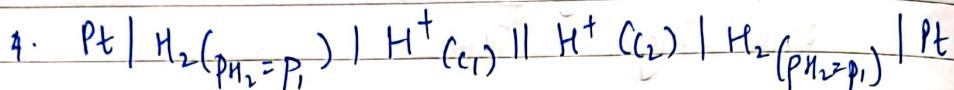
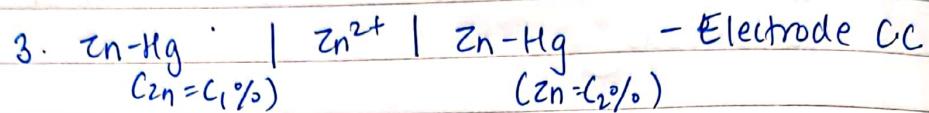
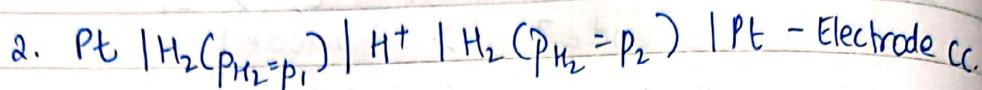
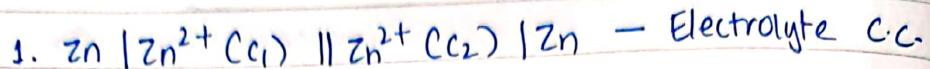
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{[C_2]}{[C_1]}$$

1. • We understand that $C_2 > C_1$
 • $\therefore [\text{cathode}] > [\text{anode}]$
 • E_{cell} is +ve if $C_2 > C_1$ and the rxn is spontaneous.
2. • $E_{\text{cell}} \propto \log \frac{C_2}{C_1} \Rightarrow$ if diff. in conc. is high,
 E_{cell} is high.
3. • If $C_2 = C_1$, cell does not give you any potential, $E_{\text{cell}} = 0.0V$
4. • Cannot be used to generate power as the contribution of E° is absent
 • Usually in the order of mV.
5. • The reason $C_2 > C_1$ is because the anode tries to increase $[Zn^{2+}]$ and cathode tries to reduce $[Zn^{2+}]$.

Definition.

cells that consist of two electrodes of the same electrodic material in contact with the same electrolyte of different concentrations and emf arises due to difference in concentration.

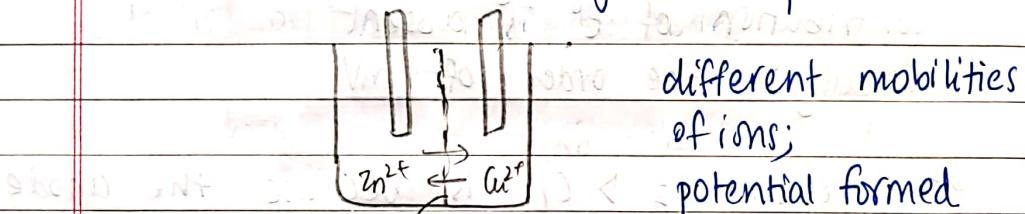
TYPES OF CONCENTRATION CELLS



Electrolyte C.C.

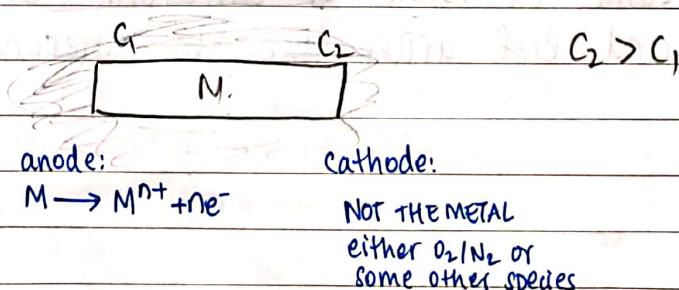
Reason for using salt bridge,

- Prevent formation of junction potential



- KCl: transport no. of $K^+ \approx Cl^-$
- no junction potential formed.

Phenomenon Observed in Corrosion

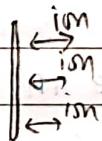


- cathode part is completely unaffected by corrosion
- make metal into cathode to protect

- Nerve signalling, $[Na^+]$ and $[K^+]$ different; cell membrane separates.
- Each cell gives $\approx 65\text{ mV}$ of potential
- ECG detects this (the Matrix utilises this)

Ion Selective Electrode

- very sensitive; can detect upto ppm.
- Electrodes which can selectively detect and quantitatively measure a particular chemical species in a mixture while ignoring others.
- The potential developed is a measure of the concentration of the species of interest.
- It is also called a membrane electrode as the membrane of the electrode is what is sensitive to the particular ions. (capable of exchanging)



Types of ISE

(a) Crystalline

1. Single crystal - LaF_3 (Lanthanum fluoride)

- sensitive to F^-
- membrane is LaF_3
- used for water pollution detection
- fluoride toothpaste (in ppm); too much causes enamel decay

2. Polycrystalline - Ag_2S

- sensitive to S^{2-}

(b) Non-crystalline

1. Glass Silicate,

- responds to H^+ , Na^+

2. Liquid membrane

- ion exchanger placed in organic solvent (dissolved)
- placed on porous disc
- responds to Ca^{2+}
- immobilised ion exchanger

3. Immobilised ion exchanger on polymer matrix

- PVC
- responds to Ca^{2+} , NO_3^-

Potential of Ion Selective Electrode

external reference electrode		analyte solution	internal reference solution	internal reference electrode
		$[M^{n+}] = C_1$ (unknown)		$[M^{n+}] = C_2$

- Due to difference in $[M^{n+}]$, boundary potential

$$E_b = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

$$= k + \frac{2.303RT}{nF} \log C_1 \quad (k = \frac{2.303RT}{nF} \log C_2)$$

- If E_b is known, C_1 can be found
- Internal reference electrode to be able to find the boundary potential

$$\begin{aligned} E_M &= E_b + E_{int-ref.} \\ &= k + \frac{2.303RT}{nF} \log C_1 + E_{int-ref.} \end{aligned}$$

$$E_M = E_M^{\circ} + \frac{2.303 RT}{nF} \log C_1$$

where $E_M^{\circ} = k + E_{\text{int. ref. electrode}}$

$$E_{\text{cell}} = E_M - E_{\text{ext. ref. electrode}}$$

- there is no redox process
- only exchange of ions
- E_M° is not a constant, but is constant for a particular electrode
- membrane has a very high resistances; ordinary potentiometers cannot detect/measure the potential — problem with ISEs ($10^8 \Omega$)
- special, expensive potentiometers must be used.

Applications of ISEs

1. Can determine the concentrations of cations

- Li^+ , Ca^{2+} , Cd^{2+} , Pb^{2+} ppm

2. Can determine the concentrations of anions

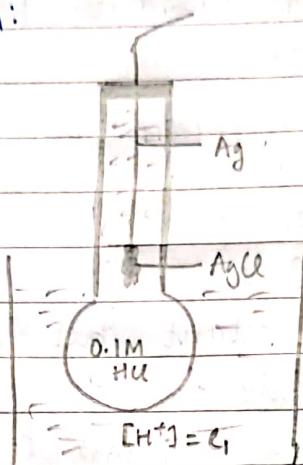
- S^{2-} , F^- , CN^-

3. pH measurement

4. Gas sensing probes: NH_3 , H_2S , CO_2

GLASS ELECTRODE

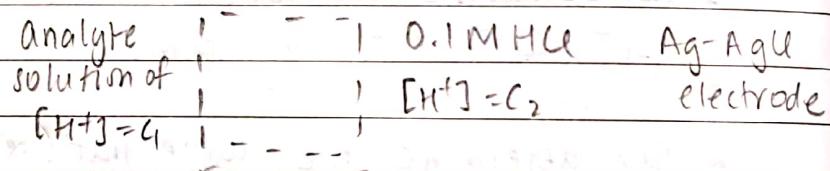
Construction:



$\text{Ag} \mid \text{AgCl} \mid 0.1\text{M HCl} \mid \text{glass}$

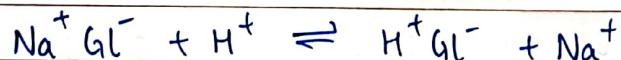
• Corning 015 glass used for thin bulb membrane

Electrode potential

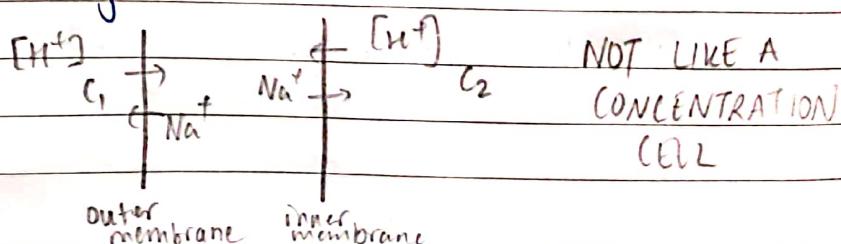


$$E_1 \quad E_2$$

$$E_b = E_2 - E_1$$



- Glass: SiO_4^{4-} network (tetrahedron)
- $\text{Na}^+, \text{K}^+, \text{Li}^+, \text{Ca}^{2+}, \text{Al}^{3+}$ inside the tetrahedron.
- When glass dipped into $[\text{H}^+]$ im solution, Na^+ exchanges with H^+



- No crossover of H^+ ions from outer membrane to inner membrane
- Potential due to membrane is not because of a redox reaction

$$E_b = \frac{0.0591}{n} \log \frac{C_1}{C_2}$$

$$= L' + 0.0591 \log [H^+] \quad (L' = 0.0591 \log C_2)$$

$$E_b = L' - 0.0591 \text{ pH}$$

$$E_b = E_b + E_{\text{int. ref. electrode}} + E_{\text{asy.}}$$

third component.

• Asymmetric potential

- inner & outer membrane structures will be different
- response of the inner & outer surfaces to the exchange differs.
- gives rise to small potential.

- if $C_1 = C_2$, no potential should be observed, but it is due to the difference in the structure of the two membranes

$$E_b = E_b + E_{\text{int. ref. electrode}} + E_{\text{asy.}}$$

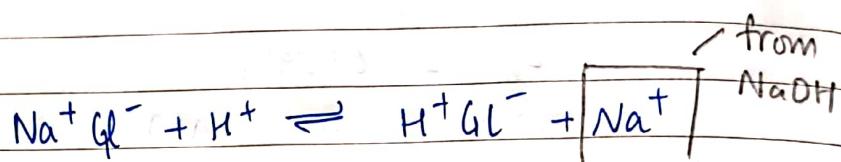
$$= L' + 0.0591 \log C_1 + E_{\text{int. ref.}} + E_{\text{asy.}}$$

$$E_b = E_b^\circ - 0.0591 \text{ pH}$$

$$E_{\text{cell}} = E_b - E_{\text{ext. ref. electrode}}$$

Advantages of Glass Electrode & Limitations

- Can be used in the presence of oxidising and reducing substances and metal ions
- Can be used even for very small volumes of liquid
- Electrode does not get poisoned (unlike SHE)
- Accurate results can be obtained in the pH range of 1-9, beyond which it shows the alkaline error.



electrode becomes more sensitive to Na^+ ions, instead of H^+ ions, as $[\text{H}^+]$ is very low and reverse rxn is favoured.

pH that is being shown is wrong.

(Special type of glass is used by adding Li^+ , Ca^{2+} etc.)

- It is simple to operate and can be used in portable instruments.
- Extensively used in chemical, industrial, biological and agricultural

Limitations

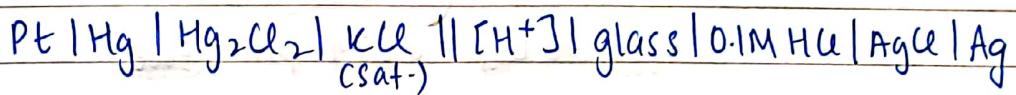
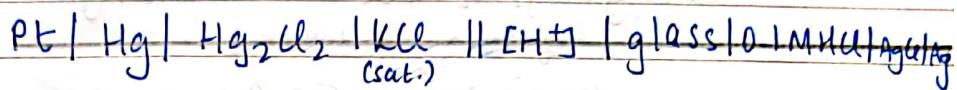
1. Beyond pH of 9, shows alkaline error so special equipment is required.
2. Membrane is very fragile
3. Glass offers very high resistance.

DETERMINATION OF pH USING GLASS ELECTRODE

- Using saturated calomel electrode.

ext. ref. electrode || glass electrode

cell representation.



$$E_{\text{cell}} = E_{\text{Ag}} - E_{\text{ext. ref. electrode}}$$

$$E_{\text{cell}} = E_{\text{Ag}}^{\circ} - 0.0591 \text{ pH} - E_{\text{SCE}}$$

$$\text{pH} = \frac{E_{\text{Ag}}^{\circ} - E_{\text{cell}} - E_{\text{SCE}}}{0.0591}$$

$$\boxed{\text{pH} = \frac{E_{\text{Ag}}^{\circ} - E_{\text{cell}} - E_{\text{SCE}}}{0.0591}}$$

- To determine E_{Ag}° , we use a buffer solution to find out E_{Ag} . (known $[\text{H}^+]$)
- Instrument used as pH-meter is a potentiometer
- Calibrate instrument for pH

Q19: The cell given below gives $E = 0.2094$ when the buffer solⁿ has $\text{pH} = 4.006$. When the buffer is replaced by unknown soln gives $\text{pH} \rightarrow E = 0.1163$, find pH , $[\text{H}^+]$.

SCE || $\text{H}^+(x\text{M})$ | glass electrode. $E_{\text{SCE}} = 0.2412\text{V}$

$\text{Pt} | \text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{KCl} || \text{H}^+(x\text{M}) | \text{glass} | 0.1\text{M}\text{HgCl}_2 | \text{AgCl/Ag}$

$$\text{pH} = 4.006 \quad E = 0.2094$$

$$E_{\text{cell}} = E_{\text{Hg}}^{\circ} - 0.0591 \text{ pH} - E_{\text{SCE}}$$

$$0.2094 = E_{\text{Hg}}^{\circ} - (0.0591)(4.006) - 0.2412$$

$$E_{\text{Hg}}^{\circ} = 0.687 \text{ V}$$

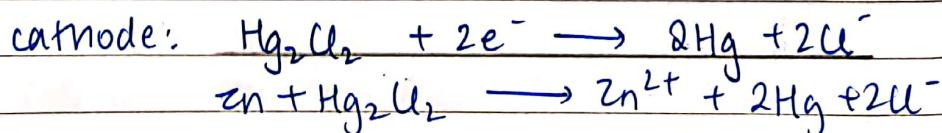
$$\text{pH} = \frac{0.687 - 0.1163 - 0.2412}{0.0591}$$

$$\text{pH} = 5.58 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 2.66 \times 10^{-6} \text{ M}$$

Q20: Zn electrode is coupled with deionized calomel electrode at 298 K

$$[\text{Zn}^{2+}] = 0.732 \text{ M} \quad E_{\text{cal}}^{\circ} = 0.281 \text{ V} \quad E_{\text{Zn}}^{\circ} = -0.763 \text{ V}$$



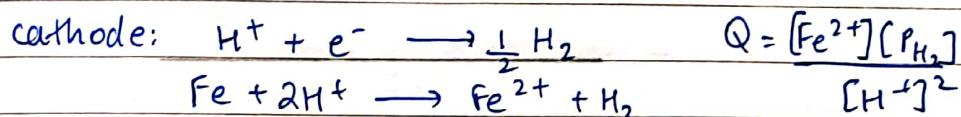
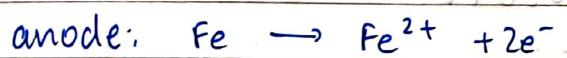
$$Q = [\text{Zn}^{2+}][\text{Cl}^-]^2$$

$$E_{\text{cell}}^{\circ} = 0.281 + 0.763 = 1.044 \text{ V}$$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log Q \\ &= 1.044 - \frac{0.0591}{2} \log (0.732 \times 0.01) \\ &= 1.044 - \frac{0.0591}{2} \times 2.135 \\ &= 1.044 - 0.063 = 0.981 \text{ V} \end{aligned}$$

Q21: $\text{Fe} | \text{Fe}^{2+}(0.1 \text{ M}) || \text{H}^+(0.02 \text{ M}) | \text{H}_2(2 \text{ atm}) | \text{Pt}$ at 298K

Find E_{cell}° , E_{cell} . $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44$



$$E_{\text{cell}}^{\circ} = 0.44 \text{ V}$$

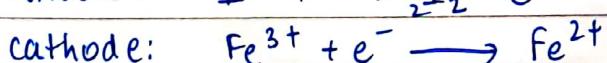
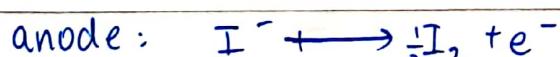
$$\begin{aligned} E_{\text{cell}} &= 0.44 - \frac{0.0591}{2} \log \left(\frac{(0.1)(2)}{(0.02)(0.01)} \right) \\ &= 0.44 - \frac{0.0591}{2} \log 500 \\ &= 0.44 - 0.0797 = 0.36 \text{ V.} \end{aligned}$$

Q21: $E_{\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}}^{\circ} = 0.77 \text{ V}$, $E_{\text{Pt} | \text{I}^{\pm}}^{\circ} = 0.5355 \text{ V}$

$$[\text{I}^-] = 0.03 \text{ M}, [\text{Fe}^{3+}] = 0.1 \text{ M}, [\text{Fe}^{2+}] = 1 \text{ M}$$

Find E_{cell} at 298 K.

$\text{Pt} | \text{I}_2(s) | \text{I}^- || \text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$



$$Q = \frac{[Fe^{2+}]}{[Fe^{3+}]Cl^-} \quad (\text{no } I_2 \text{ = solid})$$

$$E_{\text{cell}}^{\circ} = 0.771 - 0.5355 = 0.2355 \text{ V}$$

$$E_{\text{cell}} = 0.2355 - 0.0591 \log \left(\frac{1}{(0.1)(0.03)} \right)$$

$$= 0.2355 - 0.0591 \log \left(\frac{1000}{3} \right)$$

$$= 0.2355 - 0.1491$$

$$= 0.0864$$

$$= 0.0864 \text{ V}$$

Q22: A saturated solution Ag-AgCl electrode coupled with Cu electrode.

$$[Cu^{2+}] = 0.1 \text{ M} \quad E_{\text{cell}} \text{ at } 298 \text{ K.}$$

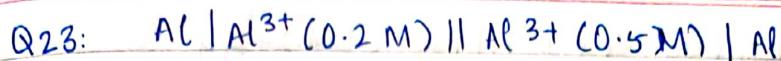
$$E_{Cu^{2+}/Cu}^{\circ} = 0.34 \text{ V} \quad E_{\text{sat.}} = -0.199 \text{ V}$$

$$E_{Cu^{2+}/Cu} = 0.34 + \frac{0.0591}{2} \log (0.1)$$

$$E_{Cu^{2+}/Cu} = 0.3104$$

$$E_{\text{cell}} = 0.3104 - 0.199$$

$$E_{\text{cell}} = 0.1114 \text{ V}$$



$$E_{\text{Al}^{3+}/\text{Al}}^{\circ} = -1.27 \text{ V}$$

$$E_{\text{cell}} \text{ at } 298 \text{ K} = ?$$

cathode: 0.5 M anode: 0.2 M

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.0591}{3} \log \frac{C_2}{C_1}$$

$$= -1.27 + \frac{0.0591}{3} \log \left(\frac{5}{2} \right) = \frac{0.0591}{3} \log 2.5 \\ = 0.0078 \text{ V} = 7.839 \text{ mV}$$

If the solution at the cathode is diluted three times, what is the new E_{cell} ? Comment on the spontaneity.

$$[\text{Cathode}] = \frac{0.5}{3} = 0.167$$

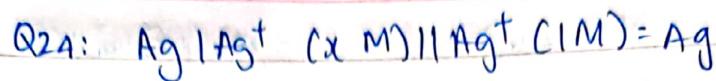
$$[\text{Anode}] = 0.2$$

$$E_{\text{cell}} = \frac{0.0591}{3} \log \left(\frac{5}{3 \times 2} \right)$$

$$= \frac{0.0591}{3} \log \frac{5}{6}$$

$$= -1.56 \text{ mV}$$

\therefore the cell rxn is non-spontaneous



$$E_{\text{cell}} = 0.26 \text{ V at } 298 \text{ K}$$

$$0.26 = \frac{0.0591}{1} \log \frac{1}{x}$$

$$0.26 = -0.0591 \log x.$$

$$\log x = -4.399$$

$$x = 3.99 \times 10^{-5} \text{ M}$$

$$x = 0.039 \text{ mM}$$

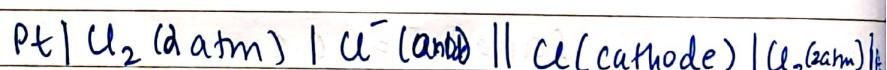
E_{cell} of 0.26 V is very high for conc. cell.

$\therefore \Delta \text{conc}$ is very high



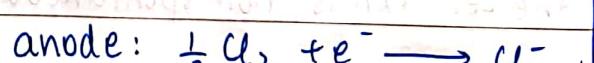
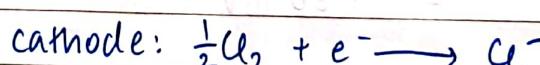
$$[\text{Cl}^-] = 0.2 \text{ and } 0.1$$

Derive an expression for E_{cell} .



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

$$E_{\text{cathode}} = E_{\text{cathode}}^{\circ} - \frac{0.0591}{n} \log \frac{P_{\text{Cl}_2}}{P_{\text{Cl}}}$$



reduction rxns.

$$E_{\text{cell}} = \theta \left(E_{\text{cathode}}^{\circ} - \frac{0.0591}{1} \log \frac{[Cl^-]_{\text{cat.}}}{(P_{Cl_2})^{1/2}} \right)$$

$$- \left(E_{\text{anode}}^{\circ} - \frac{0.0591}{1} \log \frac{[Cl^-]_{\text{an.}}}{(P_{Cl_2})^{1/2}} \right)$$

$$= \frac{0.0591}{1} \log \frac{[Cl^-]_{\text{anode}}}{[Cl^-]_{\text{cathode}}}$$

$$E_{\text{cell}} = 0.0591 \log \frac{0.2}{0.1} = 0.0178 \text{ V}$$

$$E_{\text{cell}} = 0.0178 \text{ V}$$