

UNIT 2

L Equilibrium⁷

PART A

PHASE EQUILIBRIUM

- $< 0^\circ\text{C}$: water is solid
- $0^\circ\text{C} - 100^\circ\text{C}$: water is liquid
- $> 100^\circ\text{C}$: water is gaseous

] at 1 atm.

- Increase in pressure, B.P increases
- Most stable state under a certain set of conditions, hard to find
- Solid \rightleftharpoons liquid equilibrium; study phase transformation
- Phase with minimum free energy is most stable.
at 30°C , liquid H_2O has less free energy than solid H_2O , which is why H_2O is at its stablest in its liquid phase at room temperature.
- Phase diagram for each material - map
- Doping of semiconductors - phase diagram useful
- Doping in ppm, ppb.

—Phase—

- It is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite bounding surfaces.

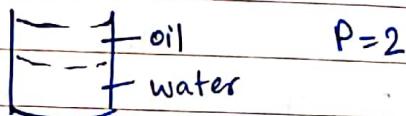
- P = number of phases

(i) Gaseous state.

- gasses diffuse into each other
- form homogeneous solution
- all gases form one phase
- $P = 1$
- gases are completely miscible in each other

(ii) Liquid state

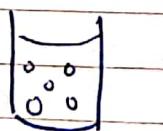
- $P = 1$ for completely miscible liquids.
eg: H_2O , CH_3CH_2OH
- $P = 1$ for salt solutions (unless saturated)
- Otherwise, $P = \text{no. of layers of immiscible liquids}$



(iii) Solid state.

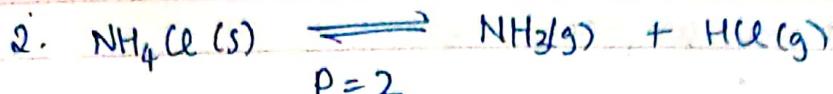
- $P = 1$ for isomorphous alloys only (solid stt.)
- each solid contributes to one phase
- each allotrope/polymorph contributes to one phase.

- Do not consider each particle as a phase.
- Ice cubes in water — only 2 phases
- Oil droplets in water — only 2 phases
- Mixture of sugar and sand — only 2 phases



$P=3$

(each compound a different phase)



$$P=2$$

- $\text{NH}_4\text{Cl}(\text{s})$
- $\text{NH}_3(\text{g}) + \text{HCl}(\text{s})$

Component

- It is the smallest number of independent chemical constituents by means of which composition of each and every phase can be expressed.
- When expressing in terms of components, 0 and negative quantities of components are permissible.
- $C = \text{no. of components}$.

(i) Single component system

- water where $P=1$
- either ice, water or water vapour
- $P=1, C=1$.

- At melting point, solid ice \rightleftharpoons liquid water
- $P=2, C=1$

- At boiling point, liquid water \rightleftharpoons water vapour
- $P=2, C=1$

- At triple point

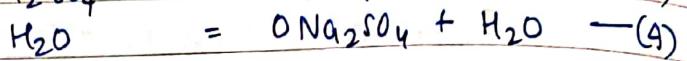
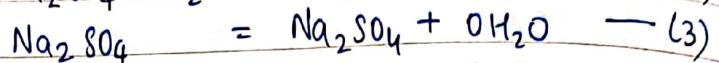
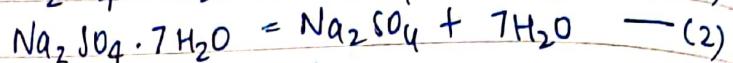
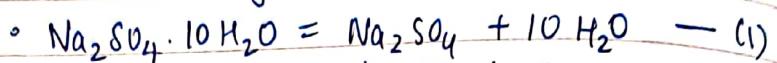
solid ice \rightleftharpoons liquid water \rightleftharpoons water vapour

$$P=3, C=1$$

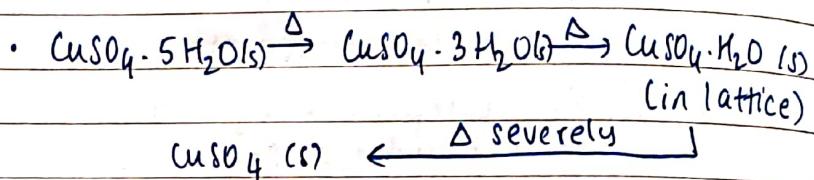
(ii) Two-component system

(a) Salt hydrate system

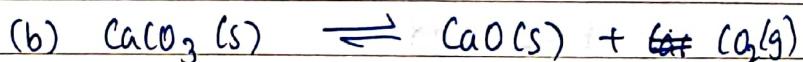
- water of crystallisation



- to describe all the phases, $C=1$ is insufficient as it fails to describe (1) and (2)
- $C=2$ is the minimum number to describe all the phases of the system



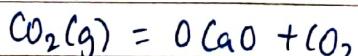
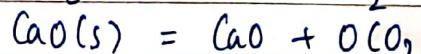
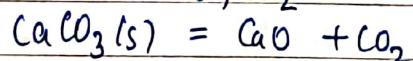
- salt-hydrate systems are, therefore, two-component systems.
- 0 is also allowed.



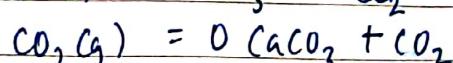
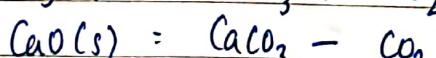
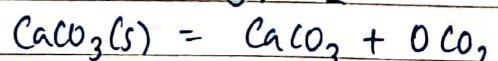
$P=3, C=2$

- if any two components are known, third can be found easily

CaO, CO₂

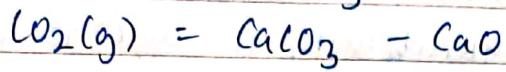
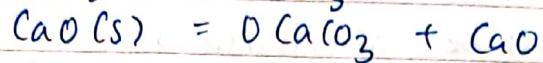
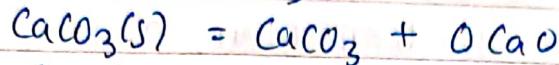
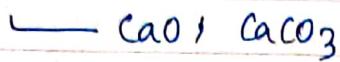


CaCO₃, CO₂



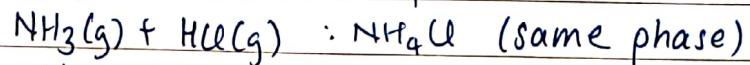
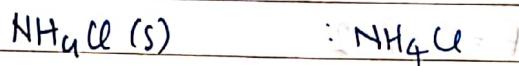
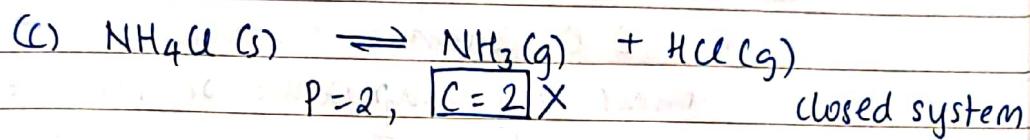
- negative values allowed

- only because of the equilibrium conditions



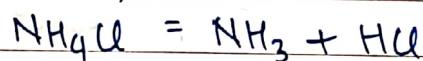
- could have used 3 species, then C=3.

- \therefore min. number is C=2



- could not be used to describe CaCO_3 because of different phase

- if C=2,



- one-component system

- add x amount of NH_3 , NH_4Cl cannot account for extra NH_3

- insufficient HCl

- Now, C=2 as C=1 is not good enough

- P=2 still holds

Degrees of Freedom

- the minimum number of independent variables such as temperature, pressure, composition that must be ascertained so that a given system in equilibrium is defined. (No. of degrees = F)

(a) liquid water: T & P can be varied independently
 $F=2, P=1$

(b) solid ice \rightleftharpoons liquid water (melting point)
 $0^\circ\text{C}, 1\text{ atm}$

either vary temperature or pressure
P depends on T as M.P. is defined.

$$F=1, P=2$$

(c) solid ice \rightleftharpoons liquid water \rightleftharpoons water vapour

(triple point); cannot vary T or P

$$F=0 \quad \text{Pressure: } 4.58 \text{ mm Hg}$$

$$\text{Temp: } 0.0198^\circ\text{C}$$

• Alternate definition: no. of variables that can be changed independently without altering the equilibrium.

• Also known as variance

• (c) is invariant system

(b) is univariant system

(a) is bivariant system.

GIBBS PHASE RULE

- correlation of P, C, F
- Gibbs, 1876
- Provided the equilibrium in a heterogeneous system is not influenced by external forces (gravity, electrical, magnetic), the number of degrees of freedom, F , is related to number of components, C , and number of phases, P , existing at equilibrium to one another by the equation

$$F = C - P + 2$$

Derivation

- All the components c are in all the phases P .
- Equilibrium:
 - (1) thermal equilibrium — T is constant.
 - (2) Mechanical equilibrium — P is constant
 - (3) Chemical/Material equilibrium — μ_i is constant

• Problem: Free energy is an extensive property.

• Define a new term : chemical potential

chemical potential $= \mu$ = partial molar Gibbs Free Energy

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j}$$

- Chemical potential of component c in all phases is constant (equal)

$$\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma}$$

At triple point

$$\mu_{\text{solid water}} = \mu_{\text{liquid water}} = \mu_{\text{gaseous water}}$$

At melting point

$$\mu_{\text{solid ice}} = \mu_{\text{liquid water}}$$

(a) What are no. of variables?

T const — 1 var

P const — 1 var

Composition — c components in all P phases
relative composition (mole fraction)

$$\text{composition} : x_1^\alpha + x_2^\alpha + \dots + x_c^\alpha = 1$$

↳ requires c-1 components in one phase α

$$x_1^\beta + x_2^\beta + \dots + x_c^\beta = 1$$

↳ requires c-1 components in phase β

:

$$x_1^P + x_2^P + \dots + x_c^P = 1$$

↳ required c-1 components in phase P.

total no. of variables $P(c-1) + 2$

(b) What are the equations?

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^r = \dots = \mu_1^P \quad P-1 \text{ equations}$$

$$\mu_2^\alpha = \mu_2^\beta = \mu_2^r = \dots = \mu_2^P \quad P-1 \text{ equations}$$

$$\mu_c^\alpha = \mu_c^\beta = \mu_c^r = \dots = \mu_c^P \quad P-1 \text{ equations}$$

total $(CP-1)$ equations

Degrees of freedom

- no. of variables that can be varied independently.
- no. of variables - no. of equations

$$\begin{aligned} F &= P(c-1) + 2 - CP - 1 \\ &= PC - P + 2 - CP + C \end{aligned}$$

$$F = C - P + 2$$

Eg: Water

$$C = 1$$

— single phase (liquid water/ice/water vapour)

$$P = 1$$

$$\therefore F = 2$$

• can change T, P independently

• Both T & P need to be specified to define system

— two phases (melting: ice \rightarrow water)

$$P = 2$$

$$\therefore F = 1$$

• can either change T or P; not both

— three phases (triple point: ice, water, vapour)

$$P = 3$$

$$\therefore F = 0$$

• neither T nor P can be varied

• invariant

At triple point, three phases are in equilibrium and it is an invariant system

PHASE DIAGRAM

- A phase diagram summarises the conditions at which a substance exists as solid, liquid or gas.
- It is a map that predicts the conditions under which each phase is stable and also enables us to predict transformation from one phase to another

1. Phase diagram of a 1-component system

$$C = 1$$

$$F = C - P + 2$$

$$\therefore F = 3 - P$$

(a) 1 phase : $F = 2$

represented by
an area

- solid - high P , low T
- gas - low P , high T
- liquid - in between

(b) 2 phases : $F = 1$

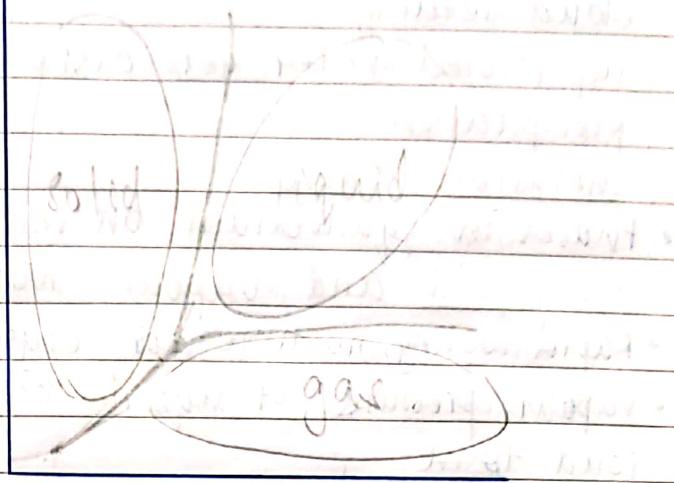
represented by
a curve/line

- shows various MPs and BPs and SPs

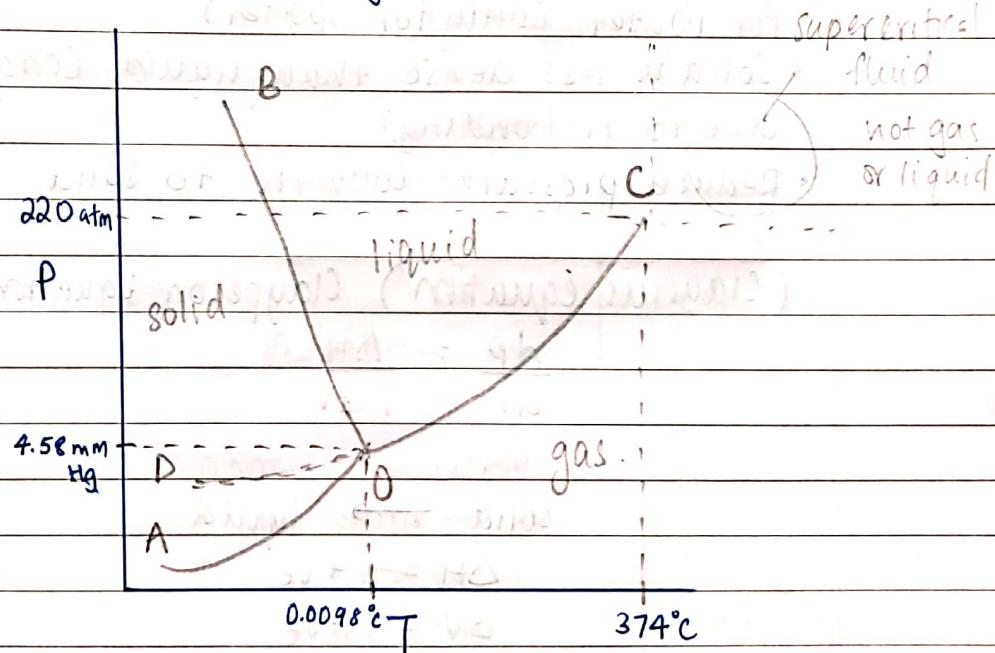
(c) 3 phases : $F = 0$
represents a point

Phase Diagram - Approximate

P



Phase Diagram of Water



OB: melting point curve / fusion curve

OC: boiling point curve / vaporisation curve

OA: sublimation curve

O: triple point

C: critical point (beyond C, no liquid)

cannot distinguish between liquid & gas

OD: metastable equilibrium (supercooled water)

liquid state below freezing point is at an unstable equilibrium; will ppt with disturbance

- Aerosols & electrolytes sprayed on clouds - cloud seeding

- supercooled water gets disturbed and starts precipitation

Metastable curve

- Phases in equilibrium on metastable curve are liquid and vapour, NOT SOLID
- Rapid cooling, no time for crystallisation
- Vapour pressure of liquid much higher than solid form
- That is why OB line is above OA.

Slope of OB

- Melting point curve has a negative slope for water (only for water)
- Solid is less dense than liquid (cage structure due to H-bonding)
- Reduce pressure, converts to solid.

(Clausius equation) Clapeyron Equation

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V}$$

Solid \rightarrow liquid

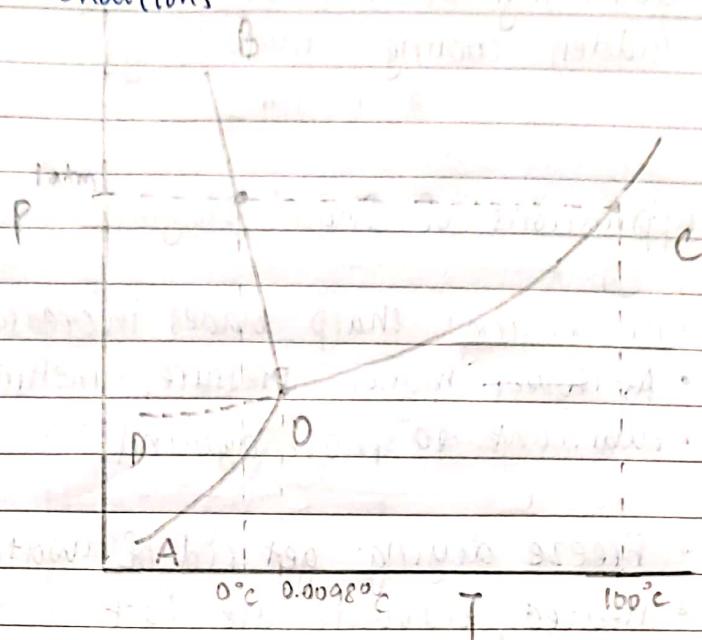
$$\Delta H = +ve$$

$$\Delta V = -ve$$

$$\therefore \frac{dp}{dT} = -ve = \text{slope of OB.}$$

- As P increases, MP decreases

Normal conditions



$$\text{fusion curve: } \frac{dP}{dT} = -\frac{\Delta H}{T\Delta V}$$

solid \rightarrow liquid

$\Delta H: +ve$

$\Delta V: -ve$

slope is -ve,
steep
(ΔV is small)

$$\therefore \frac{dP}{dT} = -ve$$

vapourisation curve

liquid \rightarrow gas

$\Delta H: +ve$

$\Delta V: +ve$

slope is +ve,
not as steep
(ΔV is large)

$$\therefore \frac{dP}{dT} = +ve$$

Normal pressure: 1 atm

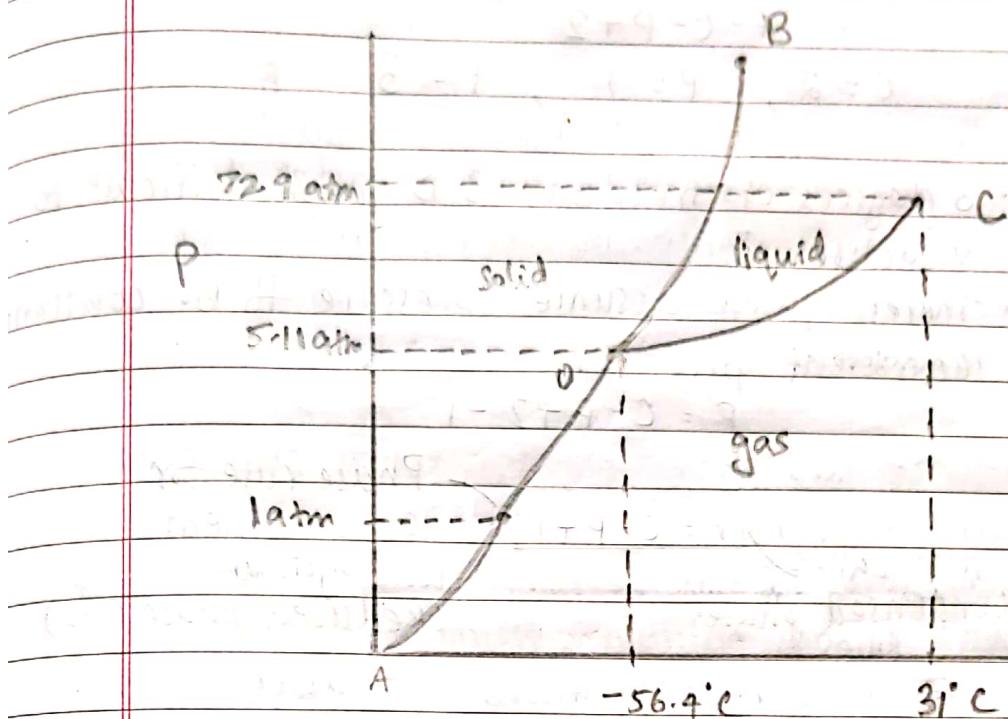
Normal MP and BP: draw a line at $P = 1 \text{ atm}$

- Quenching: don't want a crystal to form; sudden cooling - metallurgy

Applications of Phase Diagram

- Ice skating: sharp blades increase the pressure
- At lower higher pressure, melting point decreases
- Lubricant to move around
- Freeze drying: get rid of water to preserve
- Heated, flavours are lost
- Below 4.58 mm Hg, ice directly vaporises
- Becomes dry
- Keep food below triple point, directly sublimes
- Note: lowest pressure for liquid water is 4.58 mm
- Phase diagram of Carbon
- Graphite can be converted to diamond (200,000 atm, 4000 K)
- Only in a volcano
- Practically impossible
- (10^4 atm, 1000 K) most practical conditions - synthetic diagram
- Graphite more stable than diamond (lower ΔG)
 - All diamond slowly converts to graphite, kinetically impossible
- Diamond is metastable equilibrium

Phase Diagram of CO_2



- CO_2 sublimes at normal pressure as triple point pressure is 5.11 atm, which is greater than 1 atm.

PHASE DIAGRAM OF A TWO-COMPONENT SYSTEM

$$F = C - P + 2$$

$$C = 2, \quad P = 1, \quad F = 3$$

- 3 degrees of freedom; 3-D graph difficult to visualise
- Therefore, we assume pressure to be constant (ambient pressure)

$$F = C - P + 2 - 1$$

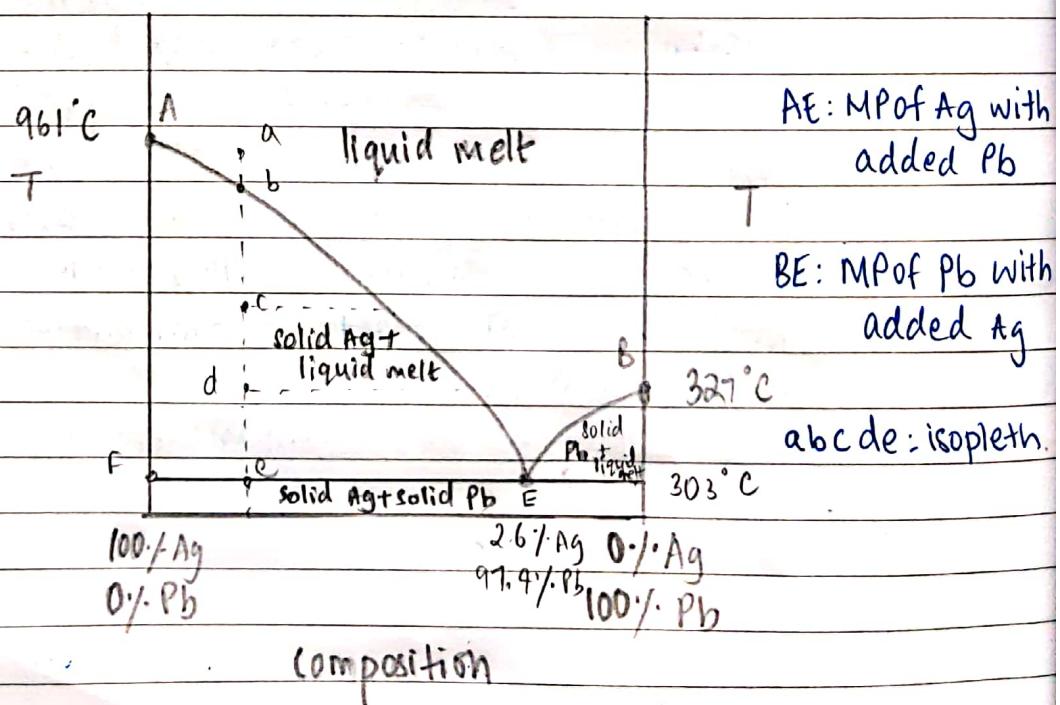
Phase rule for
 2-component
 system
 (Reduced phase rule)

Also called
 Condensed phase
 rule

- Assume pressure changes do not affect equilibrium
- solid, liquid equilibria (condensed systems)

(1) Ag-Pb system - simple eutectic system

$$F = C - P + 1$$



— E: Eutectic point

- Eutectic means easily melting - Greek

— Liquid melt

- in the liquid melt, Pb & Ag are completely miscible (single phase)

— Solid form

- Pb & Ag are completely immiscible.

EUTECTIC POINT

- Eutectic or Eutectic mixture is a mixture of two or more phases at a composition that has the lowest melting point and where the phases simultaneously crystallise from the molten solution at this temperature

At Eutectic Point,

$$C = 2$$

$$P = 3$$

$$F = C - P + 1$$

$$F = 0$$

$\therefore E$ is invariant;

fixed point

(fixed temperature,
composition)

- at a particular pressure, Eutectic point is an invariant
- 2.6% Ag and 97.4% of Pb
- Temperature remains constant until all the liquid melt gets converted into solid form
- Usually happens only for pure compounds.
- People thought a compound was being formed due to sharp melting point.
- An indication that this was a mixture was the fact that it changed with a change in pressure

- If impurities are added, melting point should decrease
- But, from E to 100% Pb, MP increases.
- Liquid behaves like a pure compound at Eutectic point — sharp MP.
- Can be related to Azeotrope
- At other temperatures, the mixture crystallises over a range.

- Eutectics are similar to Azeotropes
- cannot separate Ag & Pb any further
- Best composition has 2.6% Ag

- Can calculate amount of Ag ppt- out using Lever rule

• Even though AEF is an area, degrees of freedom $F=1$ (solid Ag + liquid melt)

Q: Why doesn't Pb ppt at 327°C when coming from 100% Ag side?

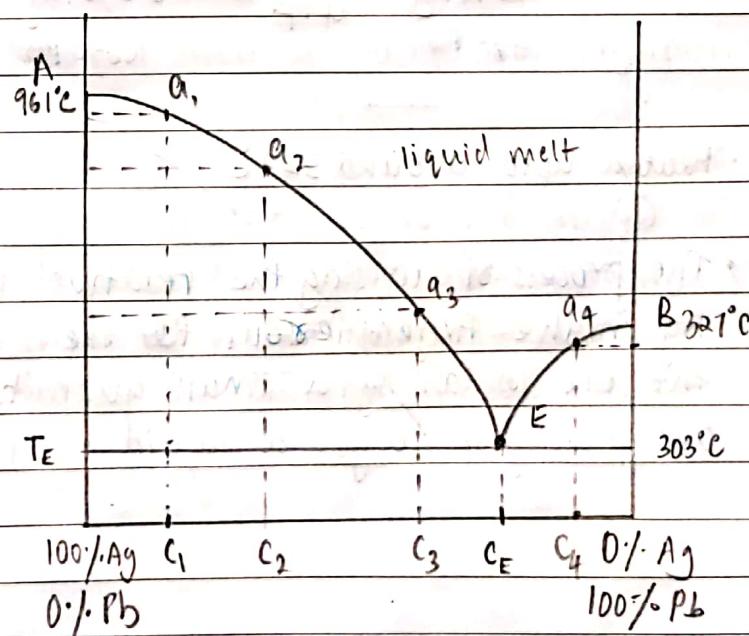
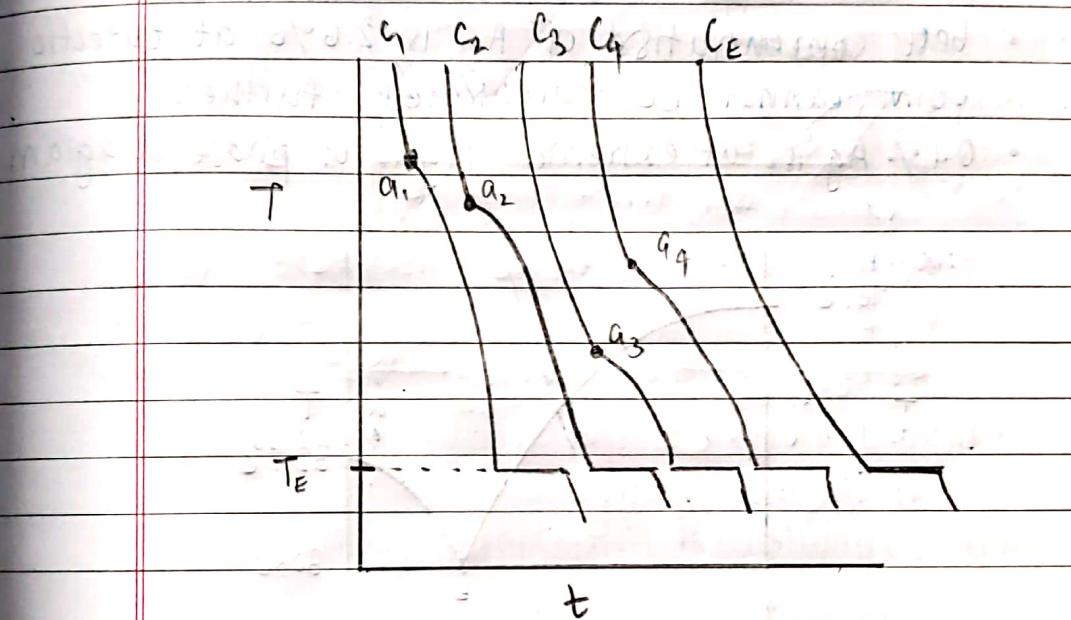
A: Have to reach MP of Pb in the mixture of the composition

Q: Three salient features of Eutectic point.

- Invariant point (97.4% Pb, 2.6% Ag, 303°C)
- Lowest MP of all Ag-Pb mixtures
- Sharp MP

Thermal Analysis

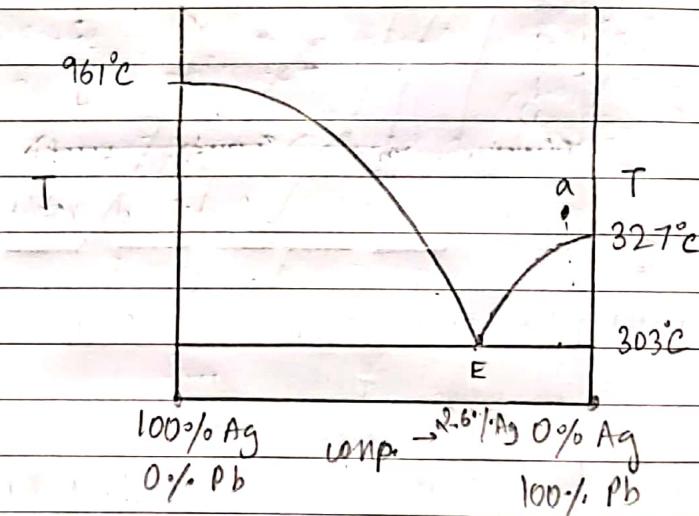
- Cooling curve: a graph of T vs t
- constructed experimentally
- In the lab, we take naphthalene, biphenyl and perform experiments
- Both MP's below 100°C & both are simple eutectics.
- keep recording T every 30s.



Application of Ag-Pb Phase Diagram

* Pattinson's Process - Desilverisation of Pb

- Argentiferous Pb ore - 0.1% silver
- mix heated to above curve and then cooled
- Pb precipitates and liquid melt is more concentrated in Ag
- increase [Ag] from 0.1% to 2.6%
- best concentration of Ag is 2.6% at Eutectic point, cannot be concentrated further.
- 0.1% Ag is at extreme right of phase diagram

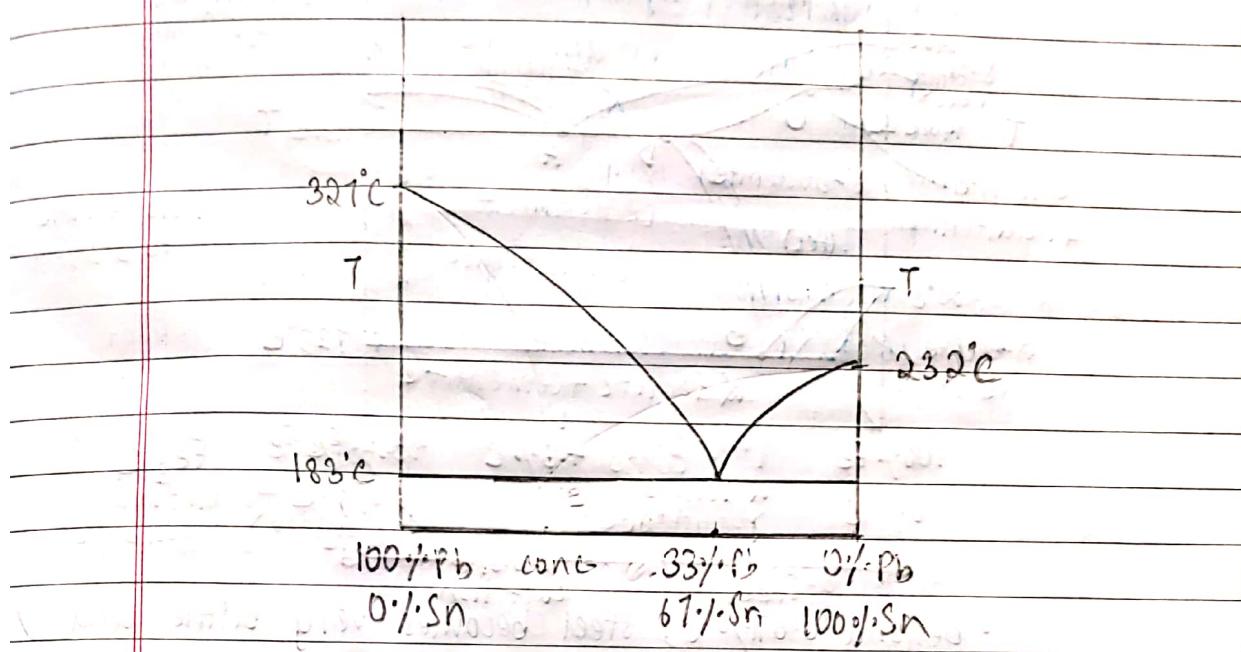


• heated upto around 327°C

• The process of raising the relative proportion of Ag in the Argentiferous Pb ore by heating the ore containing a small quantity of Ag (0.1%) and cooling it to get a liquid melt richer in Ag.

(2) Solder - Pb-Sn system (simple eutectic)

- lowest MP of mixture = 183°C
- Eutectic composition = 67% Sn, 33% Pb
- Pure MP: Pb = 327°C , Sn = 232°C



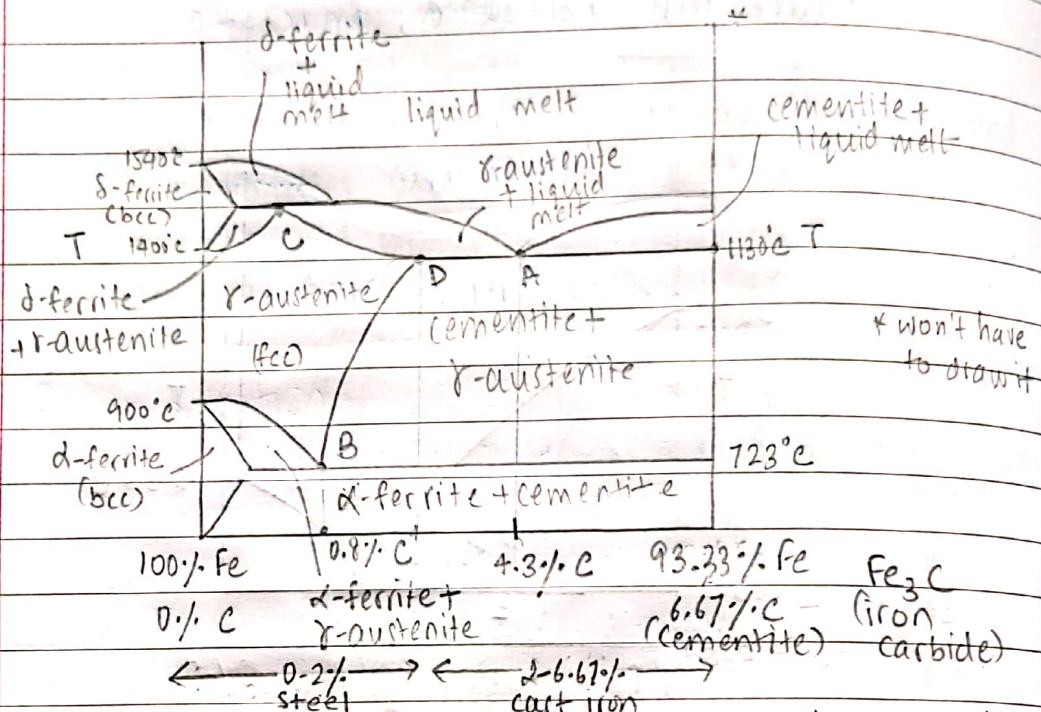
- Eutectic composition is always chosen for soldering electrical joints
- Lowest MP, least energy used
- Sharp melting point / solidify point
- Can solidify fast.
- Earlier, pipes used to be soldered at a different composition (~50%)
- No sharp MP, melts over range, get more time to work with the pipe
- Some Pb will precipitate in the process

(3) Fe-C system (steel & more)

reduced phase rule

$$F = C - P + 1$$

draw tie-lines

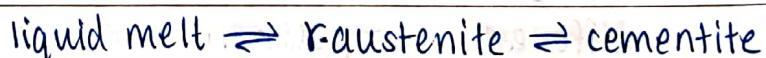


- beyond 6.67% C, steel becomes very brittle and is of no use to us

- As Fe is heated, crystal structure changes.

Point A:

- three phases in equilibrium ($P=3$)
- liquid melt $\rightarrow \gamma$ -austenite + cementite



$$\bullet F = C - P + 1 = 2 - 3 + 1 = 0$$

$\therefore F = 0$; invariant system at A.

• Eutectic temperature = 1130°C

Eutectic composition = 4.3% Carbon

Point B:

- three phases in equilibrium
- γ -austenite \rightarrow α -ferrite + cementite
- γ -austenite \rightleftharpoons α -ferrite \rightleftharpoons cementite
- $F = C - P + I = 2 - 3 + 1 = 0$
- $\therefore F = 0$; invariant system at B

• Eutectic temperature: } NOT A EUTECTIC;
 Eutectic composition: } NO LIQUID SOLIDIFIES/
 MELTS

• Correct word: Eutectoid

• Eutectoid temperature: 723°C
 Eutectoid composition: 0.8% Carbon.

Point C:

• Peritectic point - fixed point

• three phases in equilibrium

Q1: Lowest T at which γ -austenite can exist,

(b) liquid melt can exist

A: (a) 723°C (b) 1130°C

Q2: What is the maximum concentration of C in γ -austenite?

A: Max. solubility of C in γ -austenite is point D, at 2% C

Q3: What is the most stable structure of Fe at room temp.

A: α -ferrite

- Purest form of Fe available - 0.008% C (wrought iron)
- used for swords, Iron pillar in Delhi, 1600 years old.
- Built by King Chandra

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

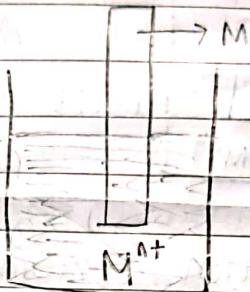
- surface for rxn to occur
- rxns should not occur at the same place; need to utilise energy
- anode — oxidation
- cathode — reduction
- simultaneously, in different compartments

3. Electrolyte

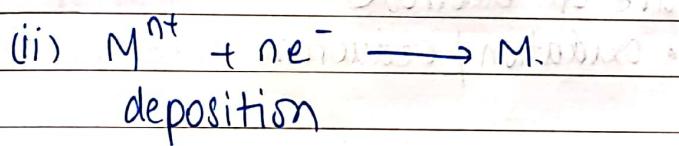
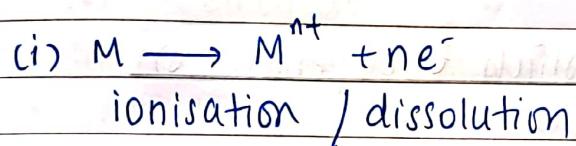
- electrons cannot move through electrolyte.
- ions are the charge carriers
- electrical wires provide electrons at electrodes.
- electrolytes offer high resistance
- electrodes carry electrons, electrolyte carries ion.
- cations — cathode] move towards anions — anode]
- substance that allows movement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

Electrode Potential

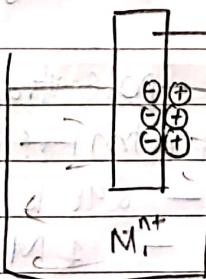
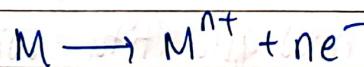
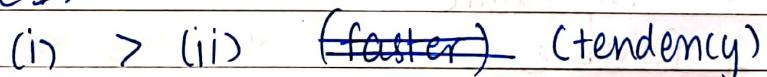
- The potential developed at the interface between the metal and the solution when it is in contact with a solution of its own ions, and it is denoted by E .



Two types of reactions on the electrode

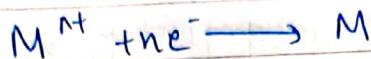


Case I:



- 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

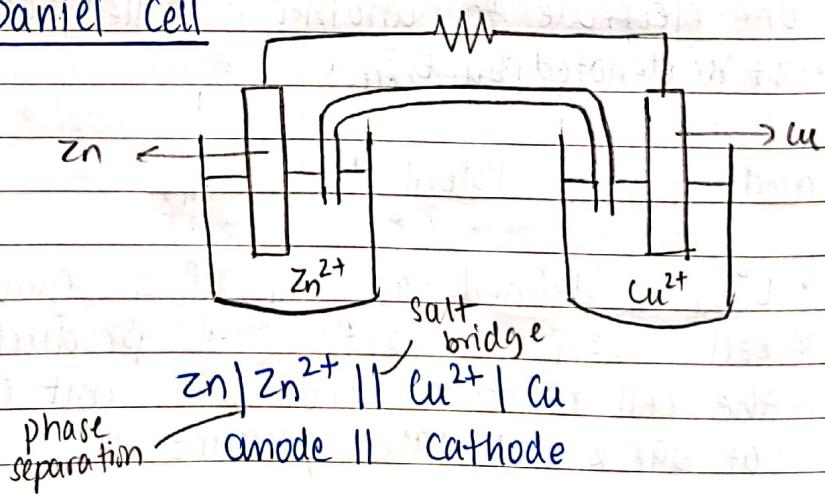
- electrical \rightarrow chemical energy
- redox: non-spontaneous rxn; expend energy
- uses: electroplating, electrorefining (Cu), electroforming

N.B.

- Galvanisation is NOT an electrolytic process

GALVANIC CELL

Daniel Cell



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

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

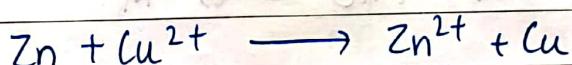
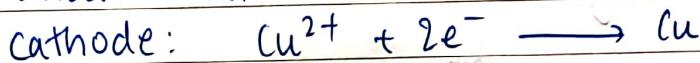
$$= E_{\text{RHS}} - E_{\text{LHS}}$$

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

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

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

current is spontaneous
cell reaction.



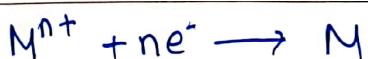
- series where standard electrode potentials have been tabulated

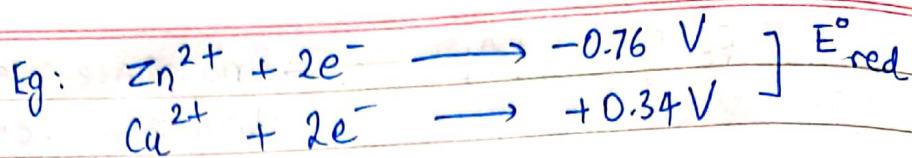
Electrochemical series

- 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.

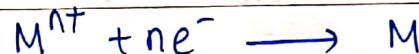




- Zn has a tendency to get oxidised, not reduced.
- Cu^{2+} has a greater tendency to undergo reduction
- Metal can never undergo reduction, only metal ions.
- Electrochemical series — standard conditions.
- Potential under nonstandard conditions

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

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

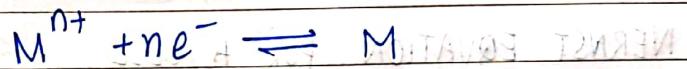
Vant Hoff Reaction Isotherm

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

- 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.

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

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

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

• At standard conditions

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

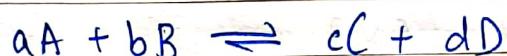
$$F = 96500 \text{ C mol}^{-1}$$

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

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

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

NERNST EQUATION FOR A CELL



• To derive it for a cell,

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

$$W_{\max} = nFE$$

$$\Delta H = -nFE$$

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

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

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

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

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

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

- 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

$$W_{\max} = n F \times E$$

$$-\Delta G = nFE$$

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



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

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

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

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

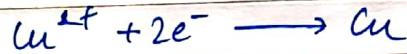
$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

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

- 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

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



$$A: E = E^\circ + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{1}$$

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

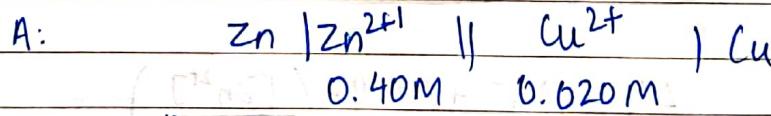
$$0.296 = E^\circ + \frac{0.0591}{2} (\log 1.5 - 2)$$

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

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

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

Q6: Find emf of Daniel cell at 25°C



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



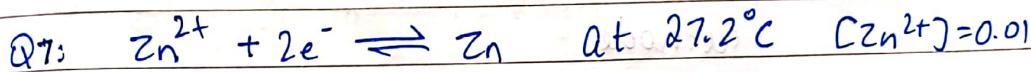
$$E = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

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

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

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

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



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

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

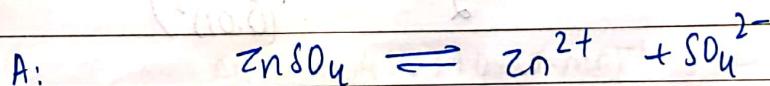
$$= -0.76 + \frac{(8.314)(300.2)}{(2)(96500)} \ln [\text{Zn}^{2+}]$$

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

$$= -0.76 - 0.05955$$

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

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



$$0.05 \quad 0 \quad 0$$

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

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

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

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

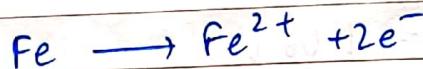
$$= -0.76 - 0.045$$

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

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

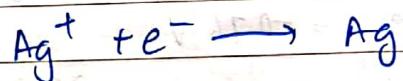
$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \quad E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80$$

A: anode:

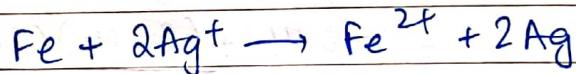


$$E^\circ_{\text{cell}} = 0.80 + 0.44 = 1.24$$

cathode



Cell equation



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

$$[\text{Ag}^+]^2$$

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

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

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

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

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

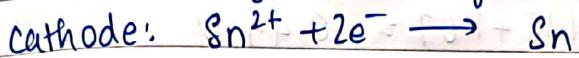
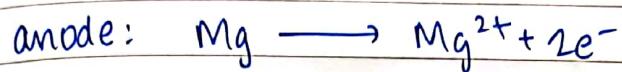
Q10: Calculate E° , E , ΔG° for the following reaction



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

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

A:



$$E^\circ_{\text{cell}} = E^\circ_{\text{Sn}^{2+}/\text{Sn}} - E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -0.14 + 2.37 = 2.23 \text{ V}$$

$$E^\circ_{\text{cell}} = 2.23 \text{ V}$$

$$E_{\text{cell}} = 2.23 - \frac{0.0591}{2} \log \left(\frac{0.045}{0.035} \right)$$

$$= 2.23 - \frac{0.0591}{2} \log \left(\frac{9}{7} \right)$$

$$= 2.23 - 3.225 \times 10^{-3}$$

$$= 2.23 - 0.003225$$

$$E_{\text{cell}} = 2.227 \text{ V}$$

$$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 2.23$$

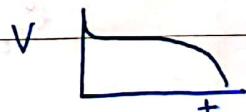
$$= -4.46 \times 96500$$

$$= -430390$$

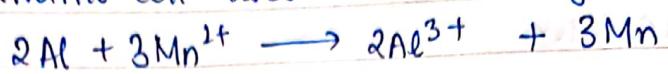
$$\Delta G^\circ = -430390 \text{ J mol}^{-1}$$

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

- 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:

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

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

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

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

$$= 0.45698 \text{ V}$$

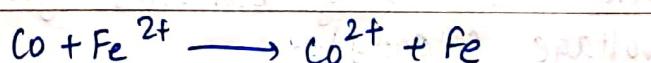
$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Mn}^{2+}]^3} \quad n = 6.$$

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

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

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

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

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

$$= -0.16 + 0.01939$$

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

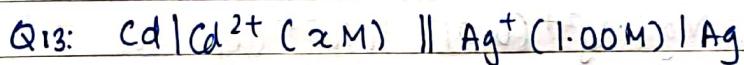
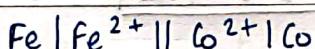
$$\Delta G = -nFE = +2 \times 96500 \times 0.1406$$

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

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

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

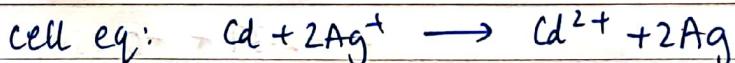
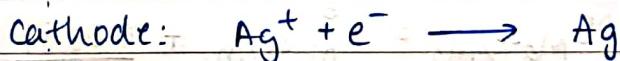
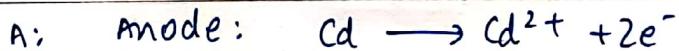
Correct cell:



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

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

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

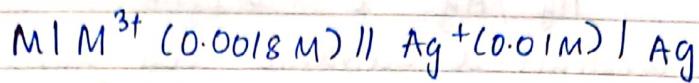
$$= -2.37 + -0.0591$$

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

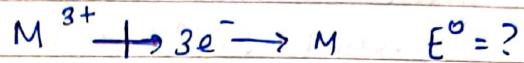
$$E_{cell} = 2.78 = E_{Cu^{2+}/Cu} + 2.37 - 2.4291$$

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

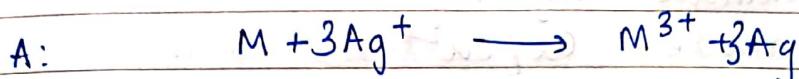
$$= 0.3509 \text{ V}$$



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



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



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

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

$$= 0.80 - 0.1182$$

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

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

$$= 0.80 - 0.42 = 0.38$$

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

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

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

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

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

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

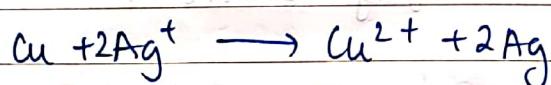
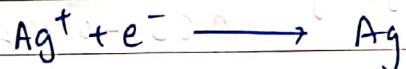
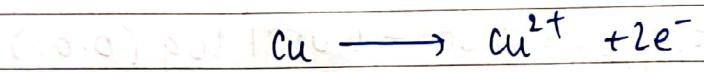
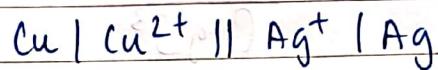
construct a galvanic cell using the values given.

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:



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

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

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

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

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

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

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

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

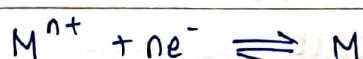
$$x = 1.5 \times 10^{-9} \text{ M}$$

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.

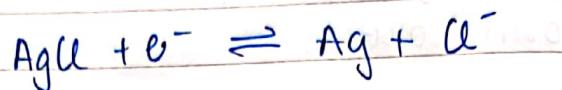
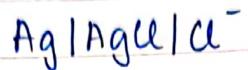


$$E = E^\circ - \frac{0.0591}{2} \log ([Cl^-]^2)$$

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

- 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.

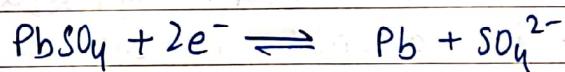
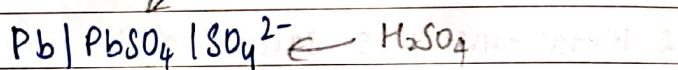
eg 2: Silver-silver chloride electrode



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

- 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)



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

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

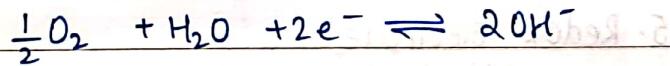
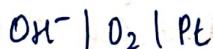
eg 2: Chlorine electrode.



$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Cl}^-]^2}{(P_{\text{Cl}_2})}$$

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

eg 3: oxygen electrode

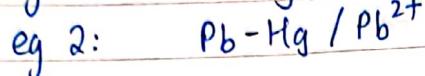
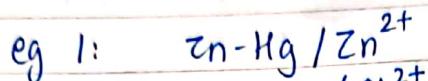


- shows oxygen reduction in alkaline medium

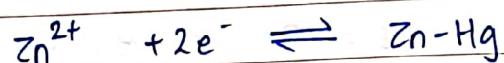
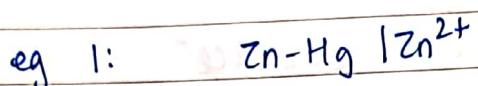
$$E = E^\circ - \frac{0.0591}{1/2} \log \frac{[\text{OH}^-]^2}{(P_{\text{O}_2})^{1/2}}$$

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

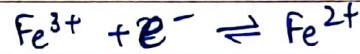
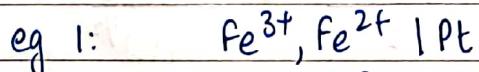


$$E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn-Hg}]}{[\text{Zn}^{2+}]}$$

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

5. Redox electrode

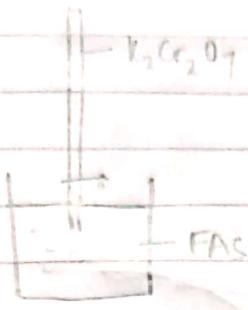
- oxidised & reduced species present together
- one would want to change to the other
- if wire placed, potential formed.



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

- $\text{Fe}^{3+}, \text{Fe}^{2+} / \text{Pt}$ 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

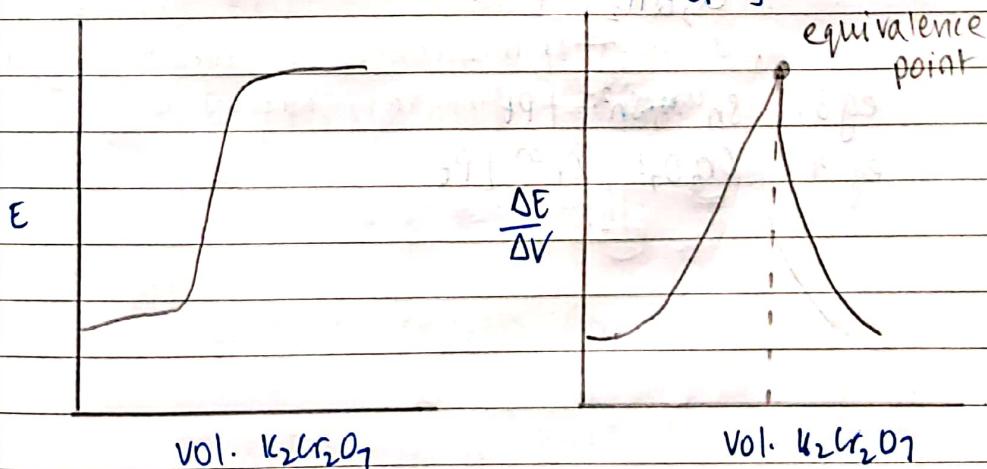
- As more and more $\text{K}_2\text{Cr}_2\text{O}_7$ added, $[\text{Fe}^{3+}] \uparrow$ and $[\text{Fe}^{2+}] \downarrow$
- $\therefore E_{\text{electrode}}$ increases
- At end point, almost all $[\text{Fe}^{3+}]$ and no $[\text{Fe}^{2+}]$
- After no more Fe^{2+} , electrode does not exist
- With excess $\text{K}_2\text{Cr}_2\text{O}_7$, 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

$$E^\circ \text{ of } \text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt} = 0.71 \text{ V}$$

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

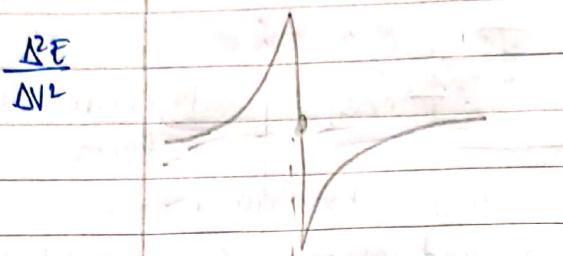
$$E^\circ = E^\circ - \frac{0.0591}{3} \log \frac{[\text{Cr}^{3+}]}{[\text{Cr}^{6+}]}$$

/ activity;
dimensionless

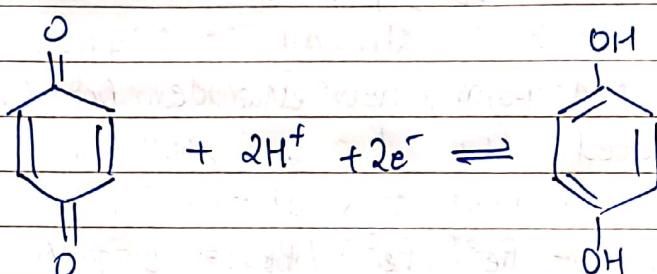


- use $\frac{\Delta^2 E}{\Delta V^2}$ if unsure of $\frac{\Delta E}{\Delta V}$

$$\frac{\Delta E}{\Delta V^2}$$

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

eg 2: In an acidic soln. $\text{Q} \rightarrow \text{QH}_2$
Quinhydronne electrode

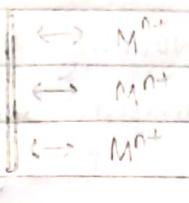


quinone

hydroquinone

 $\text{Q}, \text{QH}_2 | \text{Pt}$ eg 3: $\text{Sn}^{4+}, \text{Sn}^{2+} | \text{Pt}$ eg 4: $\text{Cr}_2\text{O}_7^{2-}, \text{Cr}^{3+} | \text{Pt}$

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

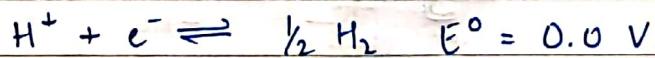
- membrane sensitive to H^+
- able to quantify and detect H^+

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)
 $Pt | H_2 (1 \text{ atm}) | H^+ (1 \text{ M})$



- Hydrogen chosen for convenience

- To find $E^\circ_{Zn^{2+}/Zn}$, $Zn | Zn^{2+} || H^+ | H_2 | Pt$.

$$E^\circ_{cell} = 0.0 - E^\circ_{Zn^{2+}/Zn} \Rightarrow E^\circ_{Zn^{2+}/Zn} = -E^\circ_{cell}$$

must be +ve

- For Cu^{2+}/Cu : $Pt | H_2 | H^+ || Cu^{2+} | Cu$

$$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - 0.0 \Rightarrow E^\circ_{Cu^{2+}/Cu} = E^\circ_{cell}$$

Problems / Limitations of SHE

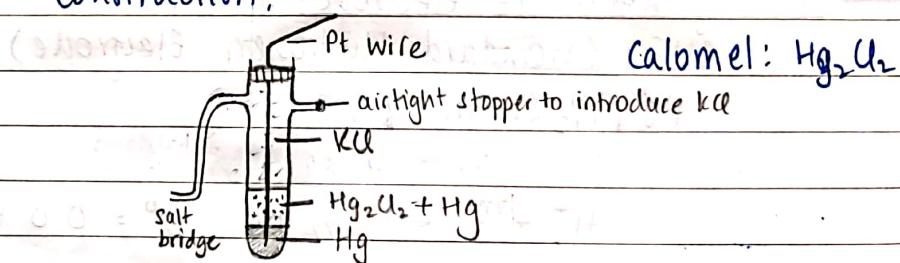
- construction and working is difficult and as maintaining concentration unity and maintaining pressure of the gas uniformly is difficult. (gas electrode)
- Active sites get blocked; Pt is highly susceptible to poisoning.
- cannot be used in the presence of oxidising agents

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:



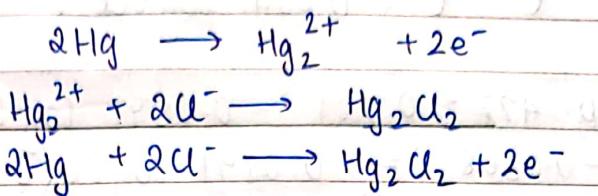
$\text{Pt} \mid \text{Hg} \mid \text{Hg}_2\text{Cl}_2 \mid \text{KCl}$ — metal-insoluble salt-ion

Three types of Calomel electrodes based on $[\text{KCl}]$

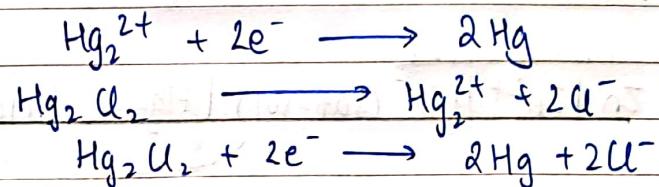
1. 0.1 N — deionized calomel electrode
2. 1 N — normal calomel electrode
3. Saturated solution — saturated calomel electrode (SCE) : most used

Working:

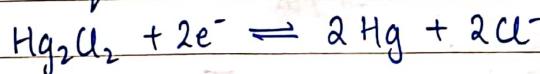
When it acts as the anode



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.

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

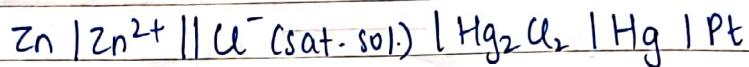
$$0.2422 = 0.281 - 0.0591 \log [Cu^-]$$

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

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

$$[Cu^-] = 4.53 \text{ M}$$

Representation of Zn electrode



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

cannot use E°
as $[Cu^-]$ not 1M

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

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

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

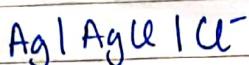
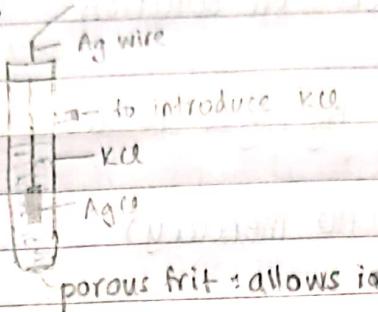
Advantages of Calomel Electrode

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

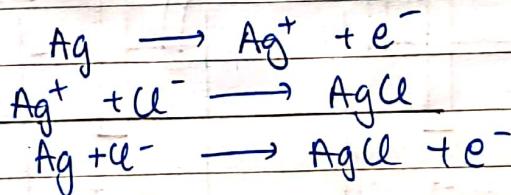
Construction:

(no Pt. required)

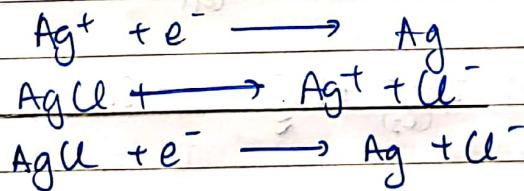


Working:

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:

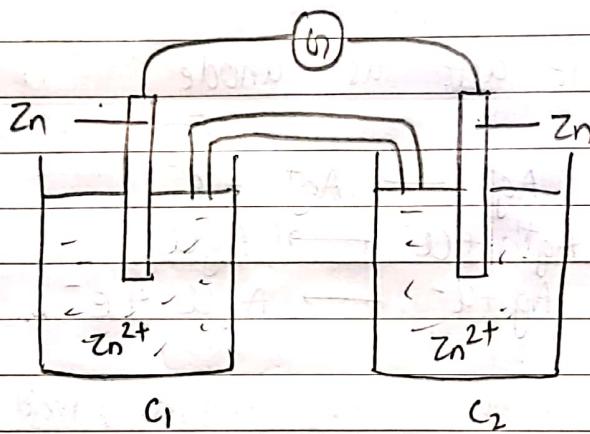
reversible to an ion \Rightarrow can find concentration of said ion in solution

Advantages of Ag-AgCl Electrode Over Calomel

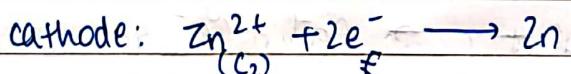
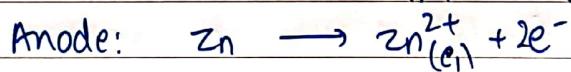
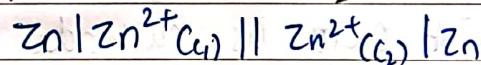
1. Inexpensive
2. Non-toxic (no mercury)

- We continue to use Calomel as it is very versatile

CONCENTRATION CELLS



Driving force:
trying to equalise
the concentration



Derive the cell potential

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

$$= \left(E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{2.303RT}{NF} \log [\text{Zn}^{2+}]_{\text{C}_2} \right)$$

$$- \left(E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \frac{2.303RT}{NF} \log [\text{Zn}^{2+}]_{\text{C}_1} \right)$$

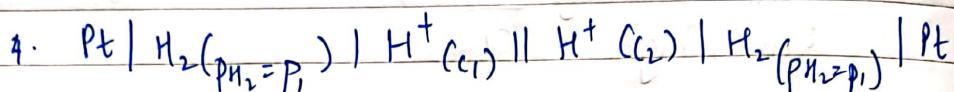
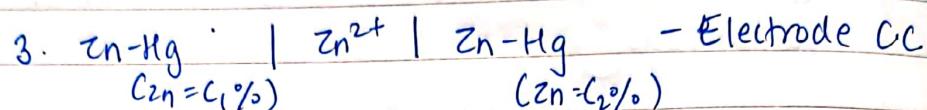
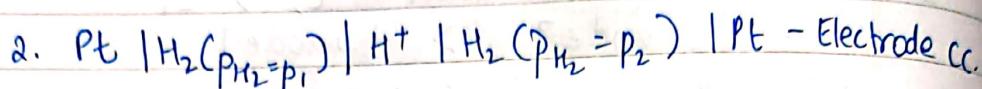
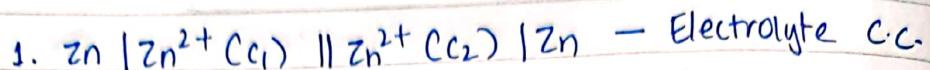
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

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.

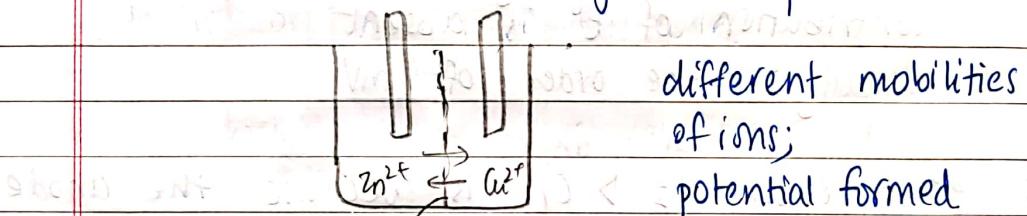
TYPES OF CONCENTRATION CELLS



Electrolyte C.C.

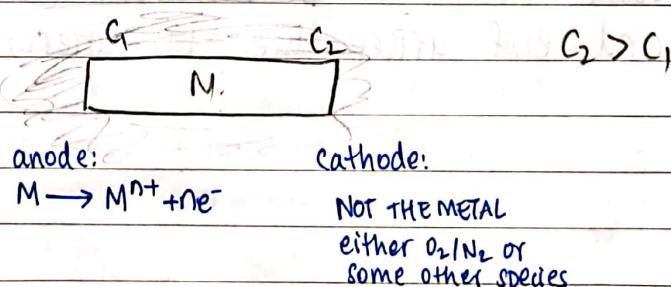
Reason for using salt bridge,

- Prevent formation of junction potential



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

Phenomenon Observed in Corrosion

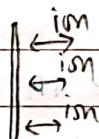


- cathode part is completely unaffected by corrosion
- make metal into cathode to protect

- 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

$$E_M = E_b + E_{int-ref.}$$

$$= k + \frac{2.303RT}{nF} \log C_1 + E_{int-ref.}$$

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

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

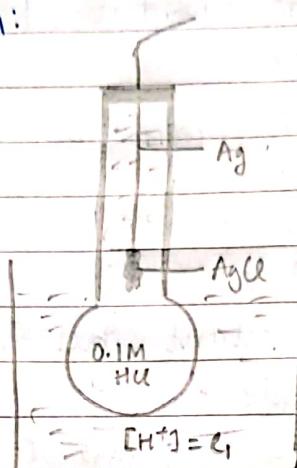
- S^{2-} , F^- , CN^-

3. pH measurement

4. Gas sensing probes: NH_3 , H_2S , CO_2

GLASS ELECTRODE

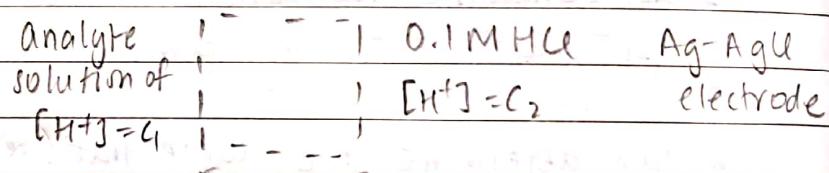
Construction:



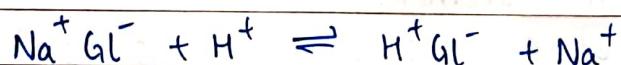
$\text{Ag} | \text{AgCl} | 0.1\text{M HCl} | \text{glass}$

- Corning 015 glass used for thin bulb membrane

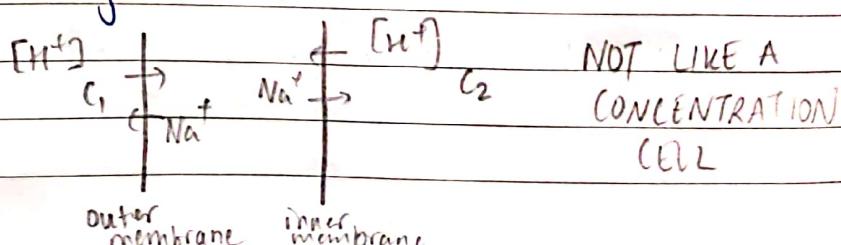
Electrode potential



$$E_b = E_2 - E_1$$



- 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 due to two membranes

- 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

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

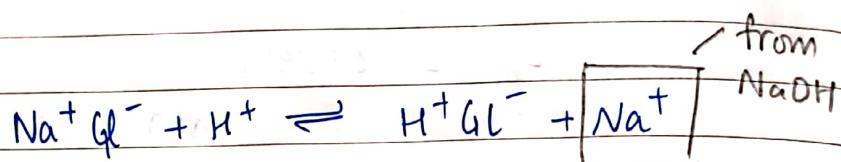
$$= L' + 0.0591 \log C_1 + E_{\text{int. ref.}} + E_{\text{asy.}}$$

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

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

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

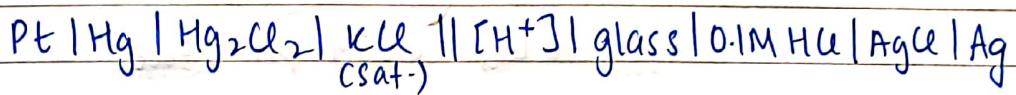
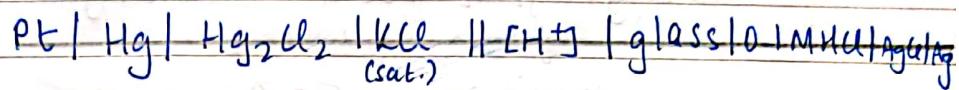
1. Beyond pH of 9, shows alkaline error so special equipment is required.
2. Membrane is very fragile
3. Glass offers very high resistance.

DETERMINATION OF pH USING GLASS ELECTRODE

- Using saturated calomel electrode.

ext. ref. electrode || glass electrode

cell representation.



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

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

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

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

$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$

- To determine E_{Hg}° , we use a buffer solution to find out E_{Hg}° . (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 , $[\text{H}^+]$.

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

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

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

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

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

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

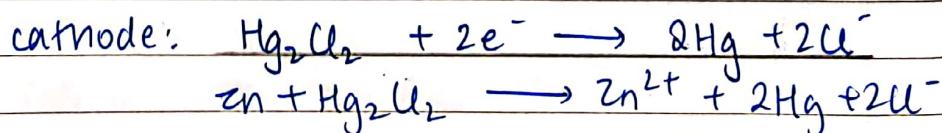
$$\text{pH} = \frac{0.687 - 0.1163 - 0.2412}{0.0591}$$

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

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

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

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



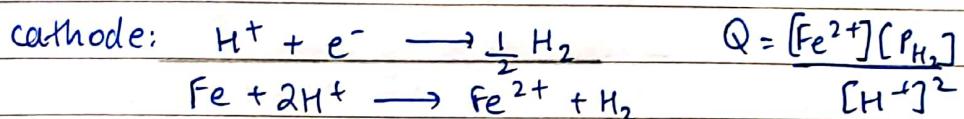
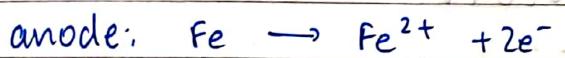
$$Q = [\text{Zn}^{2+}] [\text{Cl}^-]^2$$

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

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

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 298 K

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



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

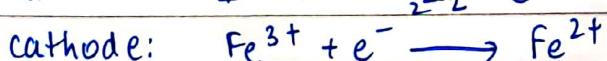
$$\begin{aligned} E_{\text{cell}} &= 0.44 - \frac{0.0591}{2} \log \left(\frac{(0.1)(2)}{(0.02)(0.01)} \right) \\ &= 0.44 - \frac{0.0591}{2} \log 500 \\ &= 0.44 - 0.0797 = 0.36 \text{ V.} \end{aligned}$$

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

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

Find E_{cell} at 298 K.

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



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

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

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

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

$$= 0.2355 - 0.1491$$

$$= 0.0864$$

$$= 0.0864 \text{ V}$$

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

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

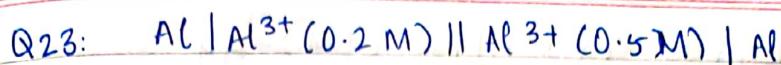
$$E_{Cu^{2+}/Cu}^{\circ} = 0.34 \text{ V} \quad E_{\text{sat.}} = -0.199 \text{ V}$$

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

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

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

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



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

E_{cell} at 298 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.

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

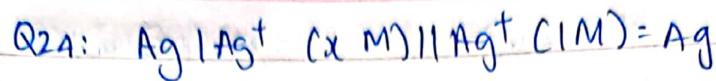
$$[\text{Anode}] = 0.2$$

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

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

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

\therefore the cell rxn is non-spontaneous



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

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

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

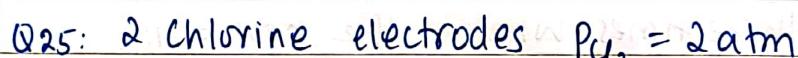
$$\log x = -4.399$$

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

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

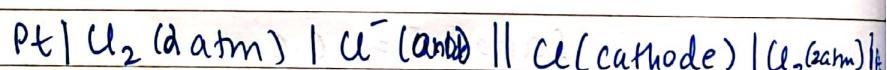
E_{cell} of 0.26 V is very high for conc. cell.

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



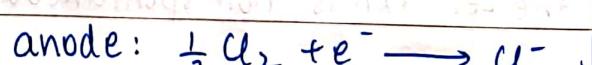
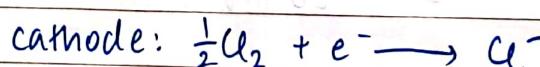
$$[\text{Cl}^-] = 0.2 \text{ and } 0.1$$

Derive an expression for E_{cell} .



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

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



reduction rxns.

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

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

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

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

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