UNIT 2

Equilibrium

PART A

PHASE EQUILIBRIUM

- < 0°C : water is solid
  0°C – 100°C : water is liquid
  > 100°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 ~~at~~ 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

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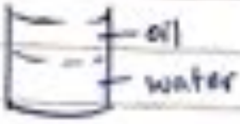
(i) Gaseous state
- gasses diffuse into each other
- form homogeneous solution
- all gases form one phase
- P = 1
- gases are completely miscible in each other

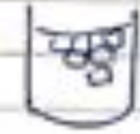
(ii) Liquid state
- P=1 for completely miscible liquids.
  eg: H_2O, CH_3CH_2OH
- P=1 for salt solutions (unless saturated)
- Otherwise, P = no. of layers of immiscible liquids



P=2

(iii) Solid state.
- P=1 for isomorphous alloys only (solid sol.)
- 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



Eg: 1. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

P=3
(each compound a different phase)

2. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

   P = 2

   - $NH_4Cl(s)$
   - $NH_3(g) + HCl(g)$

— Component

- It is the <u>smallest number</u> of independent chemical constituents by means of which composition of <u>each and every</u> phase can be expressed.
- When expressing in terms of components, 0 and negative quantities of components are permissible.
- C = 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 ⇌ liquid water
- P = 2, C = 1

- At boiling point, liquid water ⇌ water vapour
- P = 2, C = 1

- At triple point

  solid ice ⇌ liquid water ⇌ water vapour

  P = 3, C = 1

(ii) Two-component system

(a) Salt hydrate system
- water of crystallisation
- $Na_2SO_4 \cdot 10H_2O = Na_2SO_4 + 10H_2O$ — (1)
  $Na_2SO_4 \cdot 7H_2O = Na_2SO_4 + 7H_2O$ — (2)
  $Na_2SO_4 = Na_2SO_4 + 0H_2O$ — (3)
  $H_2O = 0Na_2SO_4 + H_2O$ — (4)

- 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

- $CuSO_4 \cdot 5H_2O(s) \xrightarrow{\Delta} CuSO_4 \cdot 3H_2O(s) \xrightarrow{\Delta} CuSO_4 \cdot H_2O(s)$
  (in lattice)
  $CuSO_4(s) \xleftarrow{\Delta \text{ severely}}$
- salt-hydrate systems are, therefore, two-component systems.
- 0 is also allowed.

(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
$P=3, C=2$

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

—— CaO, CO_2

$CaCO_3(s) = CaO + CO_2$
$CaO(s) = CaO + 0CO_2$
$CO_2(g) = 0CaO + CO_2$

—— $CaCO_3, CO_2$

$CaCO_3(s) = CaCO_3 + 0CO_2$
$CaO(s) = CaCO_3 - CO_2$
$CO_2(g) = 0CaCO_3 + CO_2$

- negative values allowed

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- only because of the equilibrium conditions
  - CaO, $CaCO_3$

  $CaCO_3(s) = CaCO_3 + 0\,CaO$

  $CaO(s) = 0\,CaCO_3 + CaO$

  $CO_2(g) = CaCO_3 - CaO$

- could have used 3 species, then $C=3$.
- ∴ min. number is $C=2$

(c) $NH_4Cl(s) \rightleftharpoons \underline{NH_3(g)} + HCl(g)$

$P=2$, $\boxed{C=2}$ ✗ closed system

$NH_4Cl(s)$: NH_4Cl

$NH_3(g) + HCl(g)$: NH_4Cl (same phase)

- could not be used to describe $CaCO_3$ because of different phase
- if $C=2$,

  $NH_4Cl = NH_3 + HCl$

  $NH_3 + HCl = NH_3 + HCl$
- 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 ⇌ liquid water (melting point)
0°C, 1 atm
either vary temperature or pressure
P depends on T as M.P. is defined
F = 1, P = 2

(c) solid ice ⇌ liquid water ⇌ water vapour
(triple point); cannot vary T or P
F = 0 Pressure: 4.58 mm Hg
Temp: 0.0098°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: Freeenrgy is an extensive property.
  - Define a new term: chemical potential

    chemical potential = μ = 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)

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

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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)

composition : $x_1^\alpha + x_2^\alpha + \ldots + x_c^\alpha = 1$

↳ requires C-1 components in one phase α

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

↳ requires C-1 components in phase β

⋮

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

↳ required C-1 components in phase P

total no. of variables <u>P(C-1) + 2</u>

(b) What are the equations?

$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \ldots = \mu_1^P$ P-1 equations

$\mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \ldots = \mu_2^P$ P-1 equations

⋮

$\mu_c^\alpha = \mu_c^\beta = \mu_c^\gamma = \ldots = \mu_c^P$ P-1 equations

total <u>C(P-1)</u> equations

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Degrees of freedom

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

$$F = P(C-1) + 2 - C(P-1)$$
$$= PC - P + 2 - CP + C$$

$$\boxed{F = C - P + 2}$$

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 → 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

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

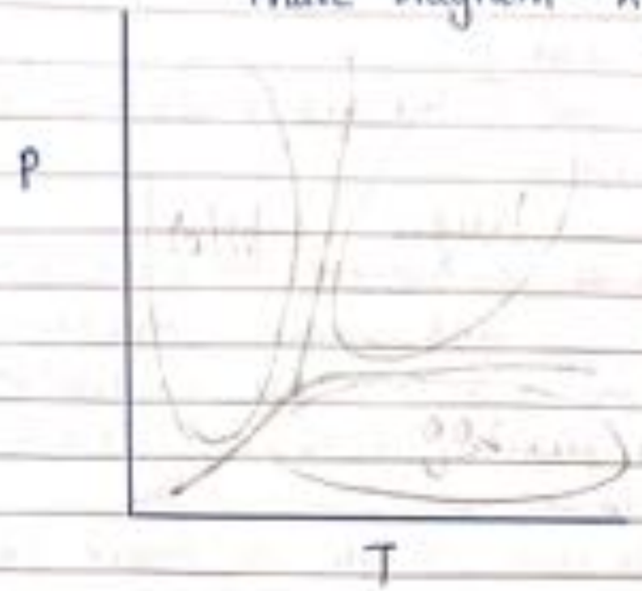
$\therefore F = 3 - P$

(a) 1 phase : $F = 2$
represented by an area
- solid - high P, low T
- gas - low P, high T
- liquid - in between

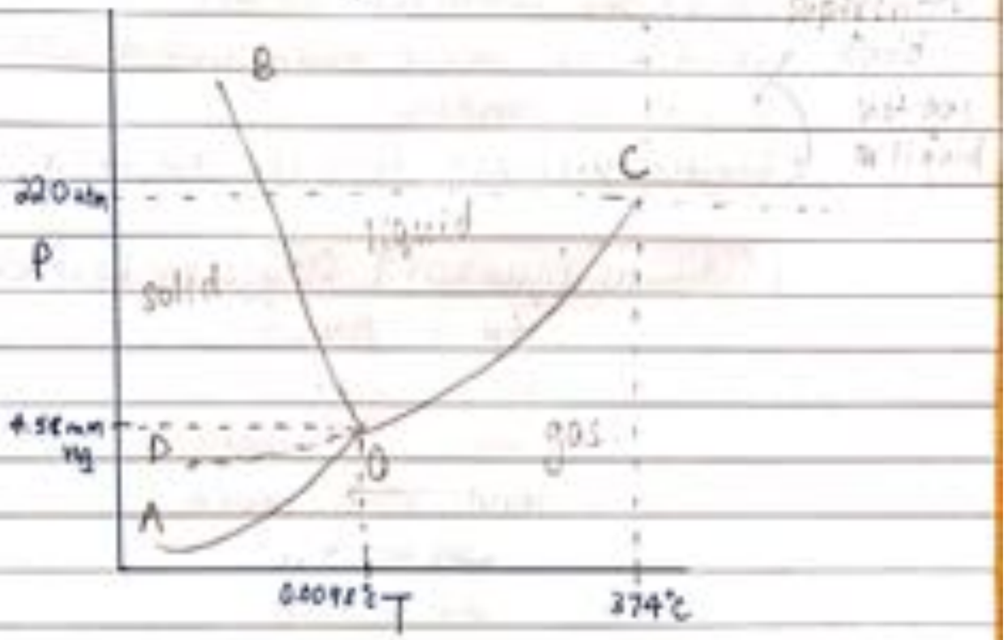
(b) 2 phases : $F = 1$
represented by a curve/line
- shows various MPs and BPs and SPs

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

Phase Diagram - Approximate



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

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- Aerosols & ⊖ electrolytes sprayed on clouds - cloud seeding
- supercooled water gets disturbed and starts precipitation

<u>Metastable curve</u>

- 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 OD line is above OA.

<u>Slope of OB</u>

- 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) Clayperon Equation

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

$$\text{solid} \longrightarrow \text{liquid}$$

$$\Delta H = +ve$$

$$\Delta V = -ve$$

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

- As P increases, MP decreases

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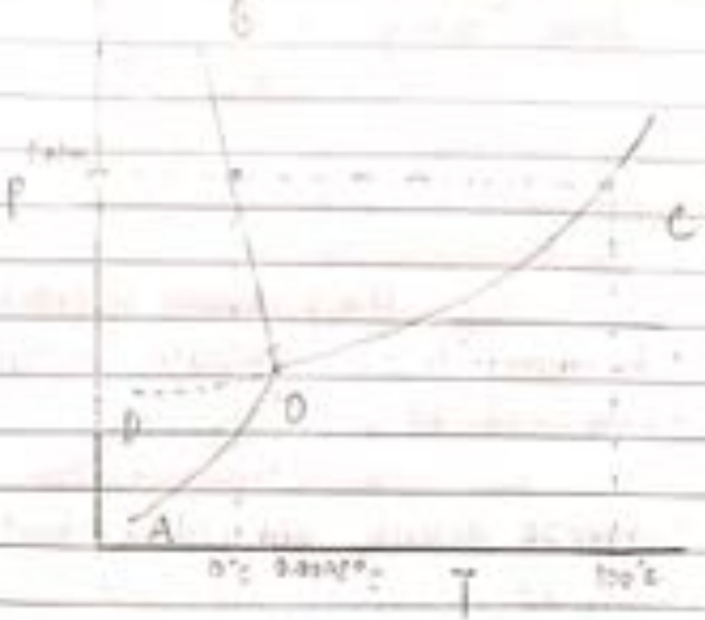
Normal conditions



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

solid → liquid
ΔH : +ve
ΔV : −ve
$\therefore \frac{dP}{dT}$ = −ve

slope is −ve, steep (ΔV is small)

vaporisation curve
liquid → gas
ΔH : +ve
ΔV : +ve
$\therefore \frac{dP}{dT}$ = +ve

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

Normal pressure : 1 atm
Normal MP and BP: draw a line at P = 1atm

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- 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 decrease
- 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

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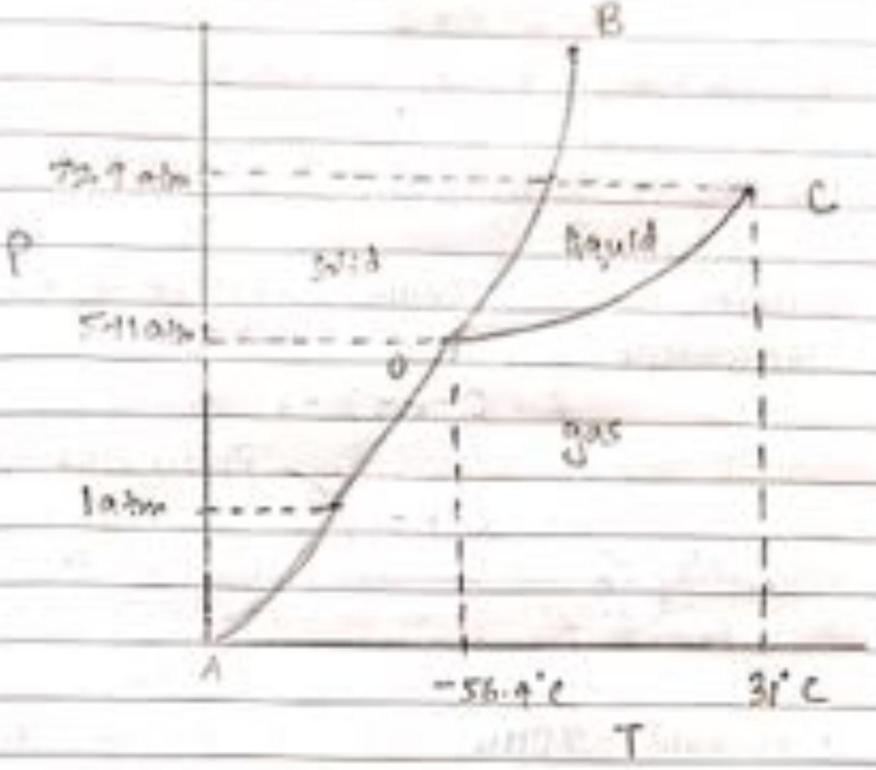
Phase Diagram of CO_2



- 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)

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

$$\boxed{F = C - P + 1}$$

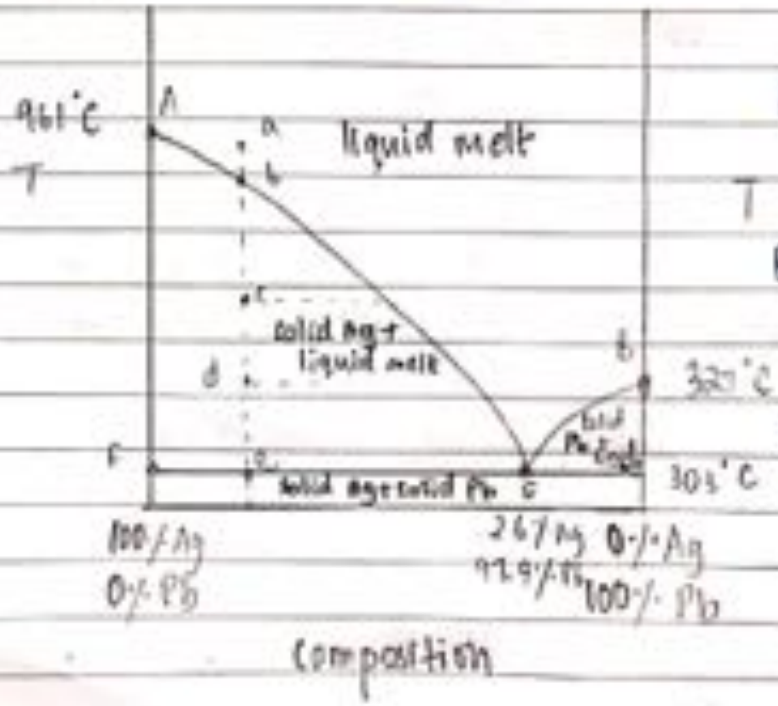
Phase rule for 2-component system (Reduced phase rule)

Also called condensed phase rule

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

(1) Ag-Pb system - simple eutectic system

$$F = C - P + 1$$



AE: MP of Ag with added Pb

BE: MP of Pb with added Ag

abcde: isopleth

— I: 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 ~~so~~ related to Azeotrophs
- At other temperatures, the mixture crystallises over a range.

- Eutectics are similar to Azeotrophs
- 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.
A: - Invariant point (97.4% Pb, 2.6% Ag, 303°C)
  - Lowest MP of all Ag-Pb mixtures
  - Sharp MP

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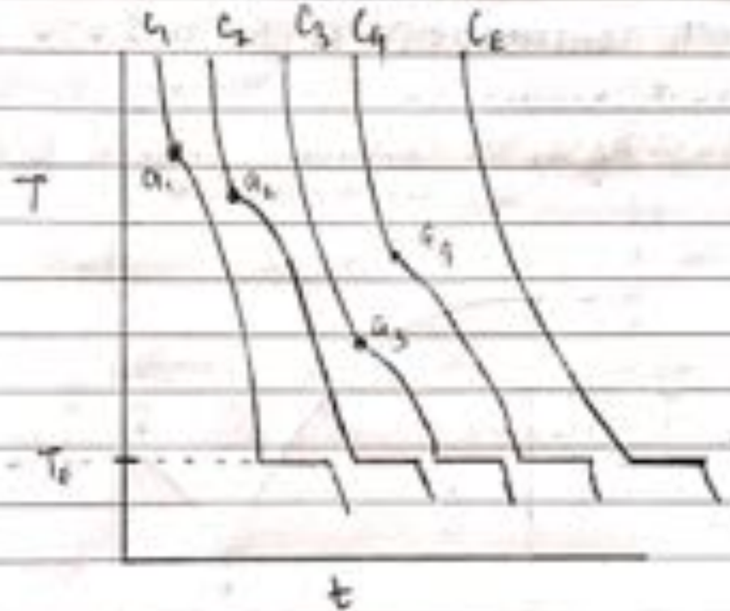
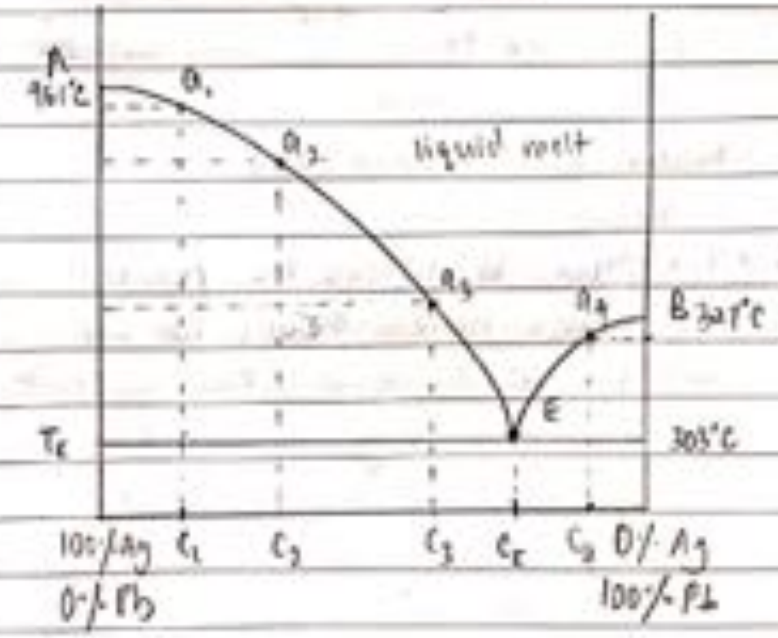
Thermal Analysis

- Cooling curve: a graph of T vs t
- constructed experimentally
- In the lab, we take naphthalene, biphenyl and ~~permit~~ perform expeliments
- Both MPs below 100°C & both are simple eutectics
- keep recording T every 30s.

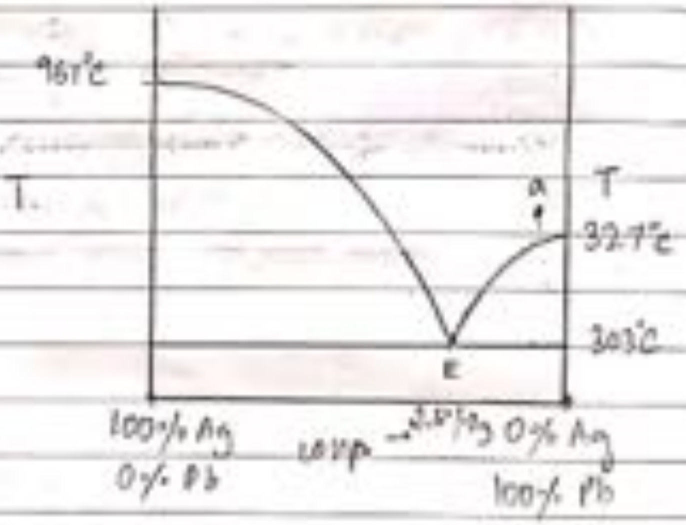




Application of Ag-Pb Phase Diagram

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

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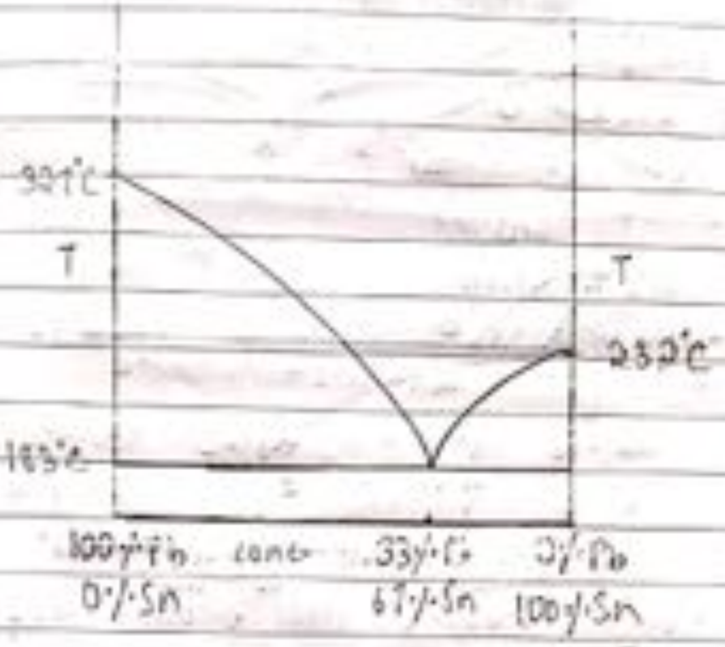
(2) Solder - Pb-Sn system (simple eutectic)

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



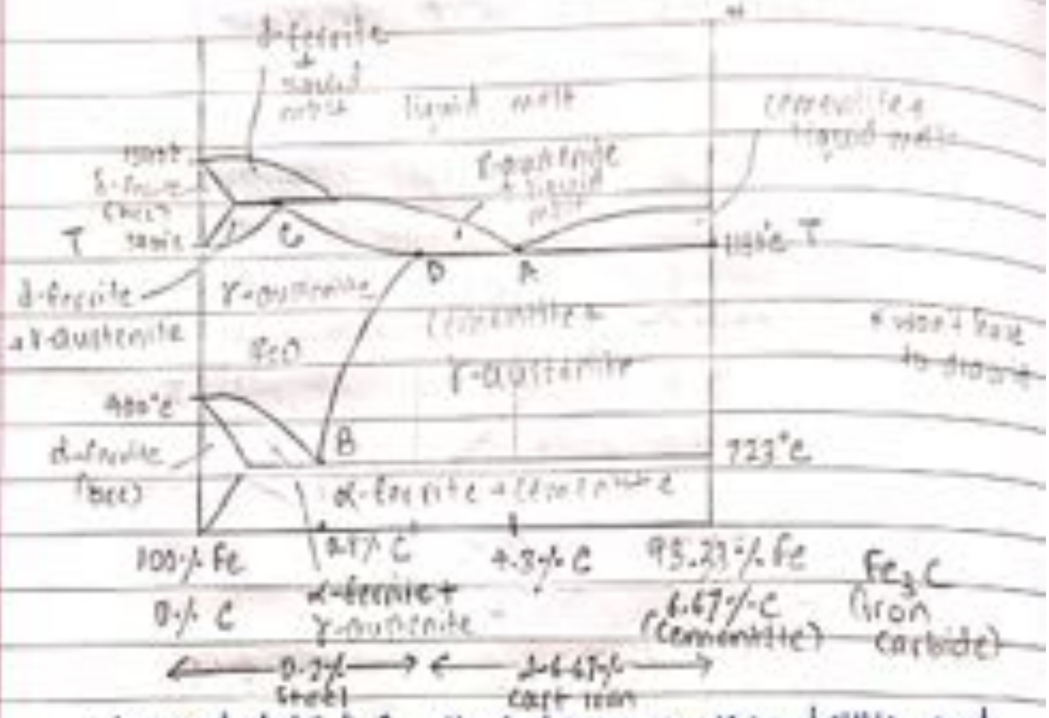
- Eutectic composition is always chosen for soldering electrical joints
- Lowest MP, least energy used
- Sharp melting point / solidify point
- Can solidify fast.
- Earlier, pipes used to be soldered at a different composition (~50%)
- No sharp MP, melts over range, get more time to work with the pipe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

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

reduced phase rule

$$F = C - P + 1$$

draw the 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 ⟶ γ-austenite + cementite

liquid melt ⇌ γ-austenite ⇌ cementite

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

  ∴ F = 0 ; invariant system at A.

- Eutectic temperature = 1130°C
  Eutectic composition = 4.3% Carbon

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Point B:

- three phases in equilibrium
- γ-austenite $\rightarrow$ α-ferrite + cementite
- γ-austenite $\rightleftharpoons$ α-ferrite $\rightleftharpoons$ cementite
- $F = C - P + 1 = 2 - 3 + 1 = 0$
  $\therefore F = 0$; 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-austentite?
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

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PART B

ELECTROCHEMICAL EQUILIBRIUM

- Electrical energy → 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.
   - $\left.\begin{array}{l}\text{cations — cathode} \\ \text{anions — anode}\end{array}\right]$ move towards
   - 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 <u>own ions</u>, and it is denoted by E.

Two types of reactions on the electrode

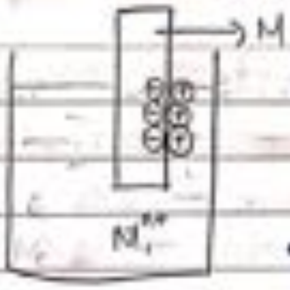
(i) $M \longrightarrow M^{n+} + ne^-$
ionisation / dissolution

(ii) $M^{n+} + ne^- \longrightarrow M$.
deposition

Case I:

(i) > (ii) ~~(faster)~~ (tendency)

$M \longrightarrow M^{n+} + ne^-$



- 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

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Case II

(ii) > (i)

$M^{n+} + ne^- \longrightarrow M$

- 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

∴ 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 combinatio 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 concentratio at 298 K at 1atm pressure

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

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

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

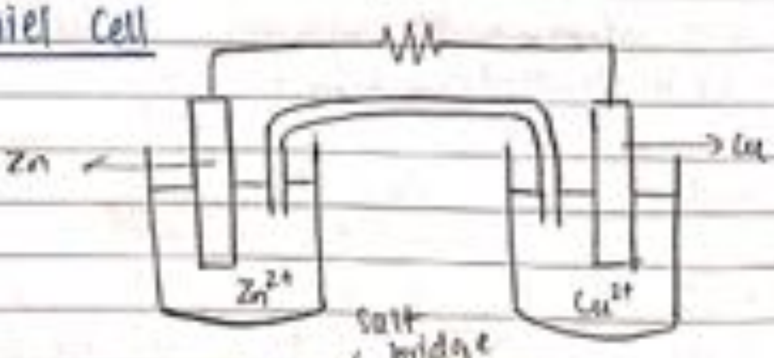
TYPES OF CELLS

Galvanic cell	Electrolytic cell
• chemical energy → electrical energy	• electrical energy → chemical energy
• redox: spontaneous rxn	• redox: non-spontaneous rxn; expend energy
• uses: batteries, fuel cells	• uses: electroplating, electrorefining (Cu), electroforming

N.B.
- Galvanisation is NOT an electrolytic process

GALVANIC CELL

Daniel Cell



salt bridge

$Zn | Zn^{2+} || Cu^{2+} | Cu$

phase separation

anode || cathode

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$Fe^{3+}, Fe^{2+} | Pt$ ⟶ no phase separation between Fe^{2+}, Fe^{3+}

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

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

$E^\circ_{Zn^{2+}/Zn} = -0.76\,V$

$E^\circ_{Cu^{2+}/Cu} = +0.34\,V$

$E^\circ_{cell} = +1.10\,V$ — +ve value

∴ rxn is spontaneous

cell reaction

anode: $Zn \longrightarrow Zn^{2+} + 2e^-$
cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

- 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.

$M^{n+} + ne^- \longrightarrow M$

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Eg: $$\left.\begin{array}{l} Zn^{2+} + 2e^- \longrightarrow -0.76\ V \\ Cu^{2+} + 2e^- \longrightarrow +0.34\ V \end{array}\right] E^{\circ}_{red}$$

- 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

$$M^{n+} + ne^- \longrightarrow M$$

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

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

$$W_{max} = \text{total charge} \times \frac{\text{energy available}}{\text{unit charge}}$$

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

$$-\Delta G = nFE$$

In standard conditions

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

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Van't 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

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

$$M^{n+} + ne^- \rightleftharpoons M$$

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

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

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

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

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

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

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

- At standard conditions

  $T = 298\,K$ (absolute temperature)
  $F = 96500\ C\ mol^{-1}$
  $R = 8.314\ J\ K^{-1}\ mol^{-1}$

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

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

NERNST EQUATION FOR A CELL

$$aA + bB \rightleftharpoons cC + dD$$

- To derive it for a cell,

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

$$W_{max} = nFE$$

$$\Delta G = -nFE$$

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

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

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

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

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

- 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)

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

$$W_{max} = \text{total charge} \times \frac{\text{energy available}}{\text{unit charge}}$$

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

$$-\Delta G = nFE$$

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

$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$ — Daniel cell

$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$$

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

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

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

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

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

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

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

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

A: $$E = E^0 + \frac{0.0591}{n} \log [Cu^{2+}]$$

~~00~~ $$0.296 = E^0 + \frac{0.0591}{2} \log (0.015)$$

$$0.296 = E^0 + \frac{0.0591}{2} (\log 1.5 - 2)$$

$$= E^0 + \frac{0.0591}{2} (-1.8239)$$

$$0.296 = E^0 - 0.05389$$

$$E^0 = 0.35 \text{ V}$$

Q6: Find emf of Daniel cell at 25°C

A: $$Zn \,|\, \underset{0.40M}{Zn^{2+}} \,||\, \underset{0.020M}{Cu^{2+}} \,|\, Cu$$

$E^0_{cell} = 1.1$V

~~$Zn^{2+} + Cu \longrightarrow Cu^{2+}$~~

$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$$

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

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

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

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

$$E = 1.06\ V$$

Q7: $Zn^{2+} + 2e^- \rightleftharpoons Zn$ at 27.2°C $[Zn^{2+}] = 0.01$

$E^{\circ}_{Zn} = -0.76\ V$

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

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

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

$$= -0.76 - 0.05955$$

$$E = -0.82\ V$$

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

A: $$ZnSO_4 \rightleftharpoons Zn^{2+} + SO_4^{2-}$$

$ZnSO_4$	Zn^{2+}	SO_4^{2-}
0.05	0	0
0.05(0.4)	0.05(0.6)	(0.05)(0.6)

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

$$E = E^{0} + \frac{0.0591}{2} \log (0.03)$$

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

$= -0.76 - 0.045$

$E = -0.805\text{ V}$

Q4: For the cell $Fe|Fe^{2+}(0.1M)||Ag^{+}(0.01)|Ag$ at 298 K, calculate E & write rxn.

$E^{\circ}_{Fe^{2+}/Fe} = -0.44$ $E^{\circ}_{Ag^{+}/Ag} = 0.80$

A: anode:

$Fe \longrightarrow Fe^{2+} + 2e^{-}$

$E^{\circ}_{cell} = 0.80 + 0.44$
$= 1.24$

cathode

$Ag^{+} + e^{-} \longrightarrow Ag$

Cell equation

$Fe + 2Ag^{+} \longrightarrow Fe^{2+} + 2Ag$

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

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

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

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

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

$E = 1.15\text{ V}$

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

$$Mg + Sn^{2+} \longrightarrow Mg^{2+} + Sn$$

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

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

A:

anode: $Mg \longrightarrow Mg^{2+} + 2e^-$

cathode: $Sn^{2+} + 2e^- \longrightarrow Sn$

$$E^\circ_{cell} = E^\circ_{Sn^{2+}/Sn} - E^\circ_{Mg^{2+}/Mg} = -0.14 + 2.37\ ~~[illegible]~~ V$$

$$E^\circ_{cell} = ~~[illegible]~~\ 2.23\ V$$

$$E_{cell} = \overset{2.23}{\cancel{+19}} - \frac{0.0591}{2} \log\left(\frac{0.045}{0.035}\right)$$

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

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

$$= 2.23 - 0.003225$$

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

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

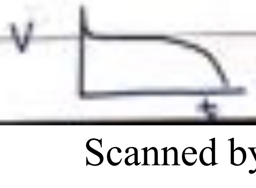
$$= -4.46 \times 96500$$

$$= -430390$$

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

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

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



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Qu: A galvanic cell uses the following reaction

$$2Al + 3Mn^{2+} \longrightarrow 2Al^{3+} + 3Mn$$

$$E^\circ_{Al^{3+}/Al} = -1.67\ V \qquad E^\circ_{Mn^{2+}/Mn} = -1.18\ V$$

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

A:

(a) $E^\circ_{cell} = -1.18 + 1.67 = 0.49\ V$

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

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

$$E_{cell} = 0.457\ V$$
$$= 0.45698\ V$$

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

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

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

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

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

$$Co + Fe^{2+} \longrightarrow Co^{2+} + Fe$$

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

$E^\circ_{Fe^{2+}/Fe} = -0.44$ $\qquad$ $E^\circ_{Co^{2+}/Co} = -0.28$

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

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

$= -0.16 + 0.01939$

$E_{cell} = -0.1406$

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

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

∴ ΔG is +ve & the rxn is non spontaneous

(E_{cell} is -ve ⇒ rxn not feasible)

Correct cell:

$Fe|Fe^{2+}||Co^{2+}|Co$

Q13: $Cd|Cd^{2+}(xM)\ ||\ Ag^{+}(1.00M)|Ag$

$E^{0}_{cell} = 1.2022V$

$E_{cell} = 1.2871\ V$

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

A: anode: $Cd \longrightarrow Cd^{2+} + 2e^{-}$

cathode: $Ag^{+} + e^{-} \longrightarrow Ag$

cell eq: $Cd + 2Ag^{+} \longrightarrow Cd^{2+} + 2Ag$

$$1.2871 = 1.2022 - \frac{0.0591}{2} \log\left(\frac{x}{1^2}\right)$$

~~0.4~~

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

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

$x = 1.34\ mM$

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

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

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

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

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

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

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

$E = 2.78$ V at 298 K

$E^\circ_{Mg^{2+}/Mg} = -2.371$ $\qquad E_{Cu^{2+}/Cu} = ?$

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

$$= -2.37 + -0.0591$$

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

$E_{cell} = 2.78 = E_{Cu^{2+}/Cu} +$ ~~2.371~~ 2.4291

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

$= 0.3509$ V

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

$M | M^{3+} (0.0018\,M) || Ag^{+} (0.01\,M) | Ag$

$E_{cell} = 0.42\,V$

$M^{3+} + 3e^{-} \longrightarrow M \qquad E^{\circ} = ?$

$E^{\circ}_{Ag^{+}/Ag} = 0.80\,V.$

A: $M + 3Ag^{+} \longrightarrow M^{3+} + 3Ag$

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

$E_{Ag^{+}/Ag} = 0.80 + 0.0591 \log(0.01)$
$= 0.80 - 0.1182$

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

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

~~$= 0.80 - 0.42 = 0.38$~~

$E_{M^{3+}/Mg} =$ ~~0.38 V~~ $0.6818 - 0.42$
$= 0.2618$

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

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

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

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Q17: Cu^{2+}/Cu : $E^\circ = 0.337V$,
Ag^+/Ag : $E^\circ = 0.799V$

construct a Galvanic cell using the values given.
For what $[Ag^+]$ does $E_{cell} = 0$ at 25°C when $[Cu^{2+}] = 0.01\ M$

cathode : Ag^+/Ag
anode : Cu/Cu^{2+}

cell:

$$Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$$

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

$$Ag^+ + e^- \longrightarrow Ag$$

$$Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$

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

$$E^\circ_{cell} = 0.799 - 0.337 = 0.462\ V$$

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

Let $x = [Ag^+]$

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

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

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

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

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

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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

$$M^{n+} + ne^- \rightleftharpoons M$$

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

2. Metal-insoluble salt of metal-ion
   - Calomel electrode : $Hg \mid Hg_2Cl_2 \mid Cl^-$
   - ion to which the salt is reversible
   - insoluble / sparingly soluble salt

Calomel:

eg 1: $Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + \overset{\text{not ion}}{2Cl^-}$

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

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

- 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

$Ag | AgCl | Cl^-$

$AgCl + e^- \rightleftharpoons Ag + Cl^-$

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

- 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
- $Ag | AgNO_3$ is reversible to Ag^+

eg 3: Pb and $PbSO_4$ (insoluble salt)

insoluble

$Pb | PbSO_4 | SO_4^{2-} \leftarrow H_2SO_4$

$PbSO_4 + 2e^- \rightleftharpoons Pb + SO_4^{2-}$

$E = E^\circ - \frac{0.0591}{2} \log [SO_4^{2-}]$

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: $\underset{(cM)}{H^+} | \underset{(p\ atm)}{H_2(gas)} | Pt$

$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2$

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

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

eg 2: Chlorine electrode

$$Cl^- | Cl_2 | Pt$$

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$$

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

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

eg 3: oxygen electrode

$$OH^- | O_2 | Pt$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightleftharpoons 2OH^-$$

- 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

eg 1: $Zn\text{-}Hg / Zn^{2+}$
eg 2: $Pb\text{-}Hg / Pb^{2+}$

- can control the activity of the electrodes

eg 1: $Zn\text{-}Hg | Zn^{2+}$

$$Zn^{2+} + 2e^- \rightleftharpoons Zn\text{-}Hg$$

$$E = E^0 - \frac{0.0591}{2} \log \frac{[Zn\text{-}Hg] \text{ — } C\%}{[Zn^{2+}]}$$

- 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

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

eg 1: $Fe^{3+}, Fe^{2+} | Pt$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$$

$$E = E^0 - \frac{0.0591}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

- $Fe^{3+}, Fe^{2+} | Pt$ used in potentiometric titration for Haematite in the lab

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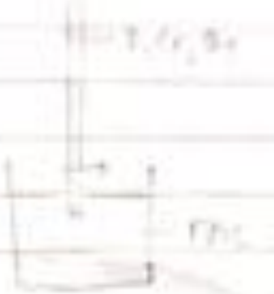
- 

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

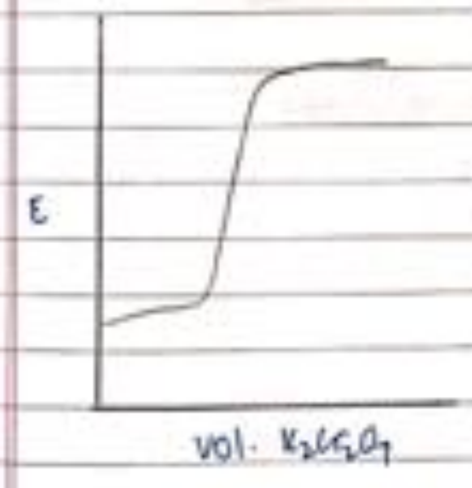
Pt wire causes potential to form

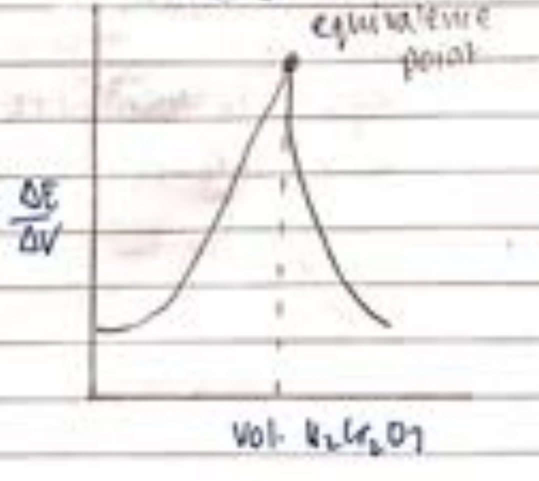
- As more and more $K_2Cr_2O_7$ added, $[Fe^{3+}]$ ↑ and $[Fe^{2+}]$ ↓
- ∴ $E_{electrode}$ increases
- At end point, almost all $[Fe^{3+}]$ and no $[Fe^{2+}]$
- After no more Fe^{2+}, electrode does not exist
- With excess $K_2Cr_2O_7$, Cr^{6+} introduced to Cr^{3+} which is already in solution
- After end point, new electrode $Cr^{6+}, Cr^{3+} | Pt$ introduced

$$E^\circ \text{ of } Fe^{3+}, Fe^{2+} / Pt = 0.77 \text{ V}$$
$$E^\circ \text{ of } Cr^{6+}, Cr^{3+} | Pt = 1.33 \text{ V}$$

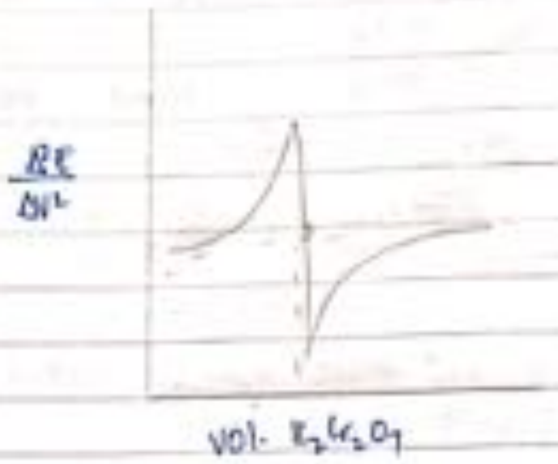
activity, dimensionless

$$E^0 = E^0 - \frac{0.0591}{3} \log \frac{[Cr^{3+}]}{[Cr^{6+}]}$$

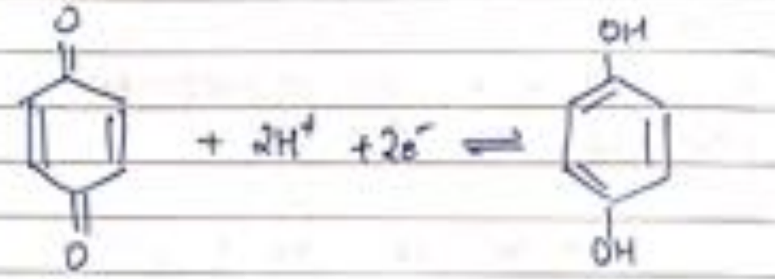




- use $\frac{\Delta^2 E}{\Delta V^2}$ if unsure of $\frac{\Delta E}{\Delta V}$



eg 2:
Quinhydrone electrode

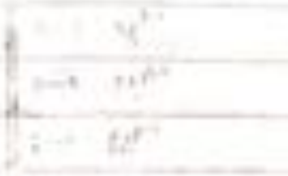


quinone hydroquinone

$Q, QH_2 | Pt$

eg 3: $Sn^{4+}, Sn^{2+} | Pt$
eg 4: $Cr_2O_7^{2-}, Cr^{3+} | Pt$

6. Ion selective electrode



membrane capable of exchanging only one particular ion

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

eg 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)

$Pt \mid H_2 (1 atm) \mid H^+ (1 M)$

$$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2 \quad E^\circ = 0.0 \text{ V}$$

- Hydrogen chosen for convenience

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

$$\underbrace{\boxed{E^\circ_{cell}}}_{\text{must be +ve}} = 0.0 - E^\circ_{Zn^{2+}/Zn} \Rightarrow E^\circ_{Zn^{2+}/Zn} = - E^\circ_{cell}$$

- For Cu^{2+}/Cu : $Pt \mid H_2 \mid H^+ \parallel Cu^{2+} \mid Cu$

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

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Problems / Limitations of SHE.

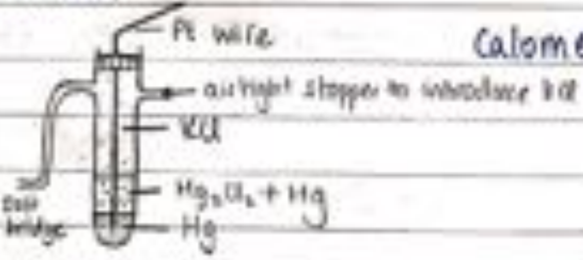
- construction and working is difficult ~~and~~ as maintaining concentration unity and maintaing pressure of the gas uniformly is difficult. (gas electrode)
- Active sites get blocked ; Pt is highly susceptible to poisoning.
- Cannot be used inthe presence of oxidising agents

— 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:



Calomel: Hg_2Cl_2

$Pt \mid Hg \mid Hg_2Cl_2 \mid KCl$ — metal - insoluble salt - ion

Three types of Calomel electrodes based on [KCl]

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

Working:

When it acts as the anode

$$2Hg \longrightarrow Hg_2^{2+} + 2e^-$$
$$Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2$$
$$\overline{2Hg + 2Cl^- \longrightarrow Hg_2Cl_2 + 2e^-}$$

When it acts as the cathode

$$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$$
$$Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^-$$
$$\overline{Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-}$$

Nernst Equation

$$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$$

at 298 K

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

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

- electrode is reversible to Cl^-
- electrode potential depends on $[Cl^-]$
- $E^\circ_{calomel} = E_{1N}$

E for standard electrodes at 298K

1. 0.1 N , E = 0.334 V
2. 1 N , E = 0.281 V
3. SCE , E = 0.2422 V

Q18: Find [saturated sol] for calomel electrode given the three electrode potentials.

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

$$0.2422 = 0.281 - 0.0591 \log[Cl^-]$$
$$-0.0388 = -0.0591 \log[Cl^-]$$
$$\log[Cl^-] = 0.6565$$
$$[Cl^-] = 4.53 \text{ M}$$

Representation of Zn electrode

$$Zn \mid Zn^{2+} \parallel Cl^- (\text{sat-sol}) \mid Hg_2Cl_2 \mid Hg \mid Pt$$

cannot use E° as [Cl⁻] not 1M

$$E_{cell} = E_{cathode} - E_{anode}$$
$$E_{cell} = 0.2422 - E_{Zn^{2+}/Zn}$$

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

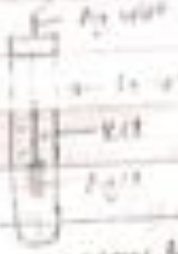
$$E_{cell} = 0.2422 + 0.76 = 1.0022$$

Advantages of Calomel Electrode

1. Simple to construct
2. Electrode potential is reproducable and constant over a long period of time (replenish the solution)
3. Electrode potential does not vary much with temperature

SILVER - SILVER CHLORIDE ELECTRODE

Construction: (coPL required)



porous frit - allows ions to move

Ag | AgCl | Cl^-

Working:

When it acts as anode

$$\begin{aligned} Ag &\longrightarrow Ag^+ + e^- \\ Ag^+ + Cl^- &\longrightarrow AgCl \\ \hline Ag + Cl^- &\longrightarrow AgCl + e^- \end{aligned}$$

When it acts as cathode

$$\begin{aligned} Ag^+ + e^- &\longrightarrow Ag \\ AgCl &\longleftrightarrow Ag^+ + Cl^- \\ \hline AgCl + e^- &\longrightarrow Ag + Cl^- \end{aligned}$$

Nernst Equation

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

- E of standard electrodes:

[KCl]	E at 298 K
0.1N	0.289 V
1N	0.223 V = E°
saturated sol.	0.199 V

Note:

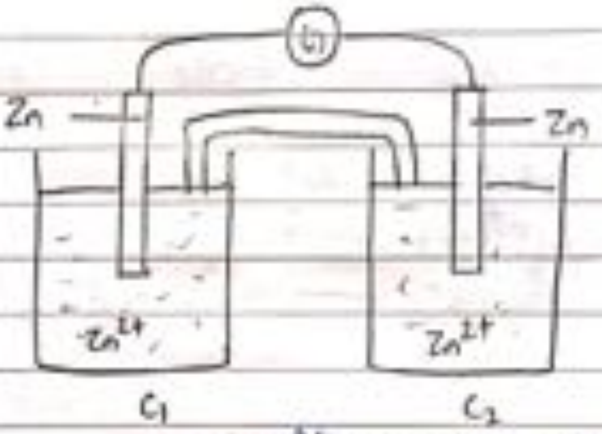
reversible to an ion => can find concentrati
of said ion in solution

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

$$Zn \mid Zn^{2+}{}_{(C_1)} \parallel Zn^{2+}{}_{(C_2)} \mid Zn$$

Anode: $Zn \longrightarrow Zn^{2+}_{(C_1)} + 2e^-$

cathode: $Zn^{2+}_{(C_2)} + 2e^- \longrightarrow Zn$

Derive the cell potential

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

$$= \left(\cancel{E^\circ_{Zn^{2+}/Zn}} + \frac{2.303RT}{nF} \log [Zn^{2+}]_{C_2}\right)$$

$$- \left(\cancel{E^\circ_{Zn^{2+}/Zn}} + \frac{2.303RT}{nF} \log [Zn^{2+}]_{C_1}\right)$$

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

1. • We understand that $C_2 > C_1$
   • ∴ [cathode] > [anode]
   • E_{cell} is +ve if $C_2 > C_1$ and the rxn is spontaneous.

2. • $E_{cell} \propto \log\frac{C_2}{C_1}$ ⇒ if diff. in conc. is high, E_{cell} is high.

3. • If $C_2 = C_1$, cell does not give you any potential, $E_{cell} = 0.0\,V$

4. • Cannot be used to generate power as the contribution of $E°$ is absent
   • Usually in the order of mV.

5. • The reason $\overset{cat}{C_2} > \overset{an}{C_1}$ 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 concentratio

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TYPES OF CONCENTRATION CELLS

1. $Zn \mid Zn^{2+}(c_1) \parallel Zn^{2+}(c_2) \mid Zn$ – Electrolyte C.C.

2. $Pt \mid H_2(p_{H_2} = p_1) \mid H^+ \mid H_2(p_{H_2} = p_2) \mid Pt$ – Electrode C.C.

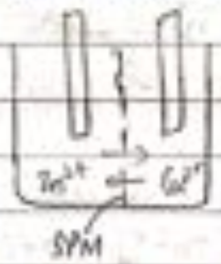
3. $\underset{(Zn = c_1\%)}{Zn\text{-}Hg} \mid Zn^{2+} \mid \underset{(Zn = c_2\%)}{Zn\text{-}Hg}$ – Electrode C.C.

4. $Pt \mid H_2(p_{H_2} = p_1) \mid H^+(c_1) \parallel H^+(c_2) \mid H_2(p_{H_2} = p_1) \mid Pt$

Electrolyte C.C.

Reason for using salt-bridge

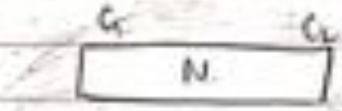
- Prevent formation of junction potential



different mobilities of ions; potential formed

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

Phenomenon Observed in Corrosion



$C_2 > C_1$

anode:
$M \longrightarrow M^{n+} + ne^-$

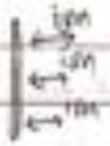
cathode:
NOT THE METAL
either O_2/H_2 or
some other species

- 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 $\sim$65 mV of potential
- ECG detect this (the Matrix utilised this)

Ion selective Electrode

- very sensitive; can detect upto ppm
- Electrodes which can selectively detect and quantitavely 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-}

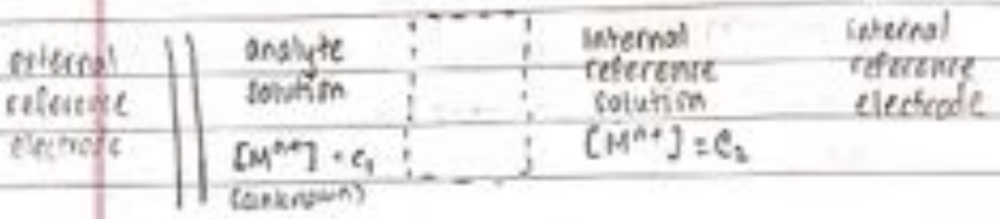
(b) Non-crystalline

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



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

$$E_b = \frac{2.303RT}{nF} \log \frac{c_1}{c_2}$$

$$= k + \frac{2.303RT}{nF} \log c_1 \quad \left(k = -\frac{2.303RT}{nF} \log c_2 \right)$$

- If E_b is known, c_1 can be found
- Internal reference electrode to be able to find the boundary potential

$$E_M = E_b + E_{int.ref.}$$
$$= k + \frac{2.303RT}{nF} \log c_1 + E_{int.ref.}$$

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$$\boxed{E_M = E^\circ_M + \frac{2.303RT}{nF} \log c_1}$$

where $E^\circ_M = k + E_{\text{int. ref. electrode}}$

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

- 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+} ppms

2. Can determine the concentrations of anions
   - S^{2-}, F^-, CN^-

3. pH measurement
4. Gas sensing probes: NH_3, H_2S, CO_2

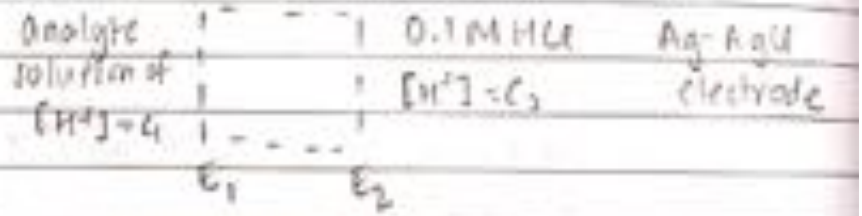
GLASS ELECTRODE

Construction:

Ag | AgCl | 0.1 M HCl | glass

- Corning 015 glass used for thin bulb membrane

Electrode potential

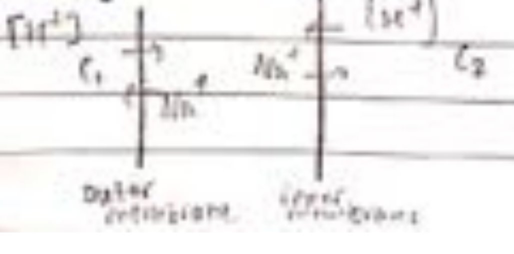


$$E_b = E_2 - E_1$$

$$Na^+Gl^- + H^+ \rightleftharpoons H^+Gl^- + Na^+$$

- Glass: SiO_4^{4-} network (tetrahedron)
- $Na^+, K^+, Li^+, Ca^{2+}, Al^{3+}$ inside the tetrahedron

- When glass dipped into $[H^+]$ ion solution, Na^+ exchanges with H^+



NOT LIKE A CONCENTRATION CELL

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

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

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

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

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

third component

asymmetric potential

- asymmetric potential
- Inner & outer membrane structures will be different
- responce 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

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

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

$$\boxed{E_g = E_g^{\circ} - 0.0591 \text{ pH}}$$

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

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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.

from NaOH

$$Na^+Gl^- + H^+ \rightleftharpoons H^+Gl^- + \boxed{Na^+}$$

electrode becomes more sensitive to Na^+ ions, instead of H^+ ions, as $[H^+]$ 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.

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DETERMINATION OF pH USING GLASS ELECTRODE

- Using saturated Calomel electrode.

ext. ref. electrode || glass electrode

Cell representation.

~~Pt | Hg | Hg_2Cl_2 | $\underset{(sat.)}{KCl}$ || $[H^+]$ | glass | 0.1M HCl | AgCl | Ag~~

$$Pt \,|\, Hg \,|\, Hg_2Cl_2 \,|\, \underset{(sat.)}{KCl} \,||\, [H^+] \,|\, glass \,|\, 0.1M\ HCl \,|\, AgCl \,|\, Ag$$

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

$$E_{cell} = E^\circ_G - 0.0591\ pH - E_{SCE}$$

$$pH = \frac{E^\circ_G - E_{cell} - E_{SCE}}{0.0591}$$

$$\boxed{pH = \frac{E^\circ_G - E_{cell} - E_{SCE}}{0.0591}}$$

- To determine E°_G, we use a buffer solution to find out E°_G. (known $[H^+]$)
- Instrument used as pH-meter is a potentiomete
- Calibrate instrument for pH

Q19: The cell given below gives E = 0.2094 when the buffer sol^n has pH = 4.006. When the buffer is replaced by unknown sol^n, gives ~~pH =~~ E = 0.1163, find pH, [H⁺].

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

Pt | Hg | Hg_2Cl_2 | KCl || H⁺ (x M) | glass | 0.1M HCl | AgCl | Ag

$pH = 4.006 \quad E = 0.2094$

$E_{cell} = E^\circ_G - 0.0591\,pH - E_{SCE}$

$0.2094 = E^\circ_G - (0.0591)(4.006) - 0.2412$

$E^\circ_G = 0.687\ V$

$pH = \dfrac{0.687 - 0.1163 - 0.2412}{0.0591}$

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

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

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

$[Zn^{2+}] = 0.732M \quad E^\circ_{Cal} = 0.281\ V \quad E^\circ_{Zn} = -0.763V$

anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

cathode: $\underline{Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-}$

$Zn + Hg_2Cl_2 \longrightarrow Zn^{2+} + 2Hg + 2Cl^-$

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

$E^\circ_{cell} = 0.281 + 0.763 = 1.044\ V$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log Q$

$= 1.044 - \frac{0.0591}{2} \log \left(0.732 \times 0.01\right)$

$= 1.044 + \frac{0.0591}{2} \times 2.135$

$= 1.044 - 0.063 = 0.981\ V$

Q21: $Fe | Fe^{2+} (0.1M) \| H^+ (0.02M) | H_2 (2atm) | Pt$ at 298K

Find E°_{cell}, E_{cell}. $E^\circ_{Fe^{2+}/Fe} = -0.44$

anode: $Fe \longrightarrow Fe^{2+} + 2e^-$

cathode: $H^+ + e^- \longrightarrow \frac{1}{2} H_2$

$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$

$Q = \frac{[Fe^{2+}](P_{H_2})}{[H^+]^2}$

$E^\circ_{cell} = 0.44\ V$

$E_{cell} = 0.44 - \frac{0.0591}{2} \log \left(\frac{(0.1)(2)}{(0.02)(\underset{0.01}{\cancel{0.02}})} \right)$

$= 0.44 - \frac{0.0591}{2} \log 500$

$= 0.44 - 0.0797 = 0.36\ V.$

Q21: $E^\circ_{Fe^{3+}, Fe^{2+} | Pt} = 0.771\ V$, $E^\circ_{Pt | I_2 | I^-} = 0.5355\ V$

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

Find E_{cell} at 298 K.

$Pt | I_2(s) | I^- \| Fe^{3+}, Fe^{2+} | Pt$

anode: $I^- \longleftrightarrow \frac{1}{2} I_2 + e^-$

cathode: $Fe^{3+} + e^- \longrightarrow Fe^{2+}$

$I^- + Fe^{3+} \longrightarrow \frac{1}{2} I_2 + Fe^{2+}$

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

$E^{\circ}_{cell} = 0.771 - 0.5355 = 0.2355$ V

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

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

$= 0.2355 - 0.1491$

$= 0.0864$

$= 0.0864$ V

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

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

$E^{0}_{Cu^{2+}/Cu} = 0.34$ V　　$E_{cal.} = 0.199$ V

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

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

$E_{cell} = 0.3104 - 0.199$

$E_{cell} = 0.1114$ V

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Q28: $Al \mid Al^{3+} (0.2\,M) \parallel Al^{3+} (0.5\,M) \mid Al$

$E^\circ_{Al^{3+}/Al} = -1.27\ V$

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

cathode: 0.5 M   anode: 0.2 M

$$E_{cell} = E^\circ_{cell} \frac{+0.0591}{3} \log \frac{C_2}{C_1}$$

$$= \frac{+0.0591}{3} \log\left(\frac{5}{2}\right) = \frac{0.0591}{3} \log 2.5$$

$$= 0.0078\ V \quad = 7.839\ mV$$

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

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

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

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

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

$$= -1.56\ mV$$

∴ the cell rxn is non-spontaneous

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Q24: Ag | Ag^+ (x M) || Ag^+ (1M) : Ag

E_{cell} = 0.26 V at 298 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
∴ Δ conc is very high

Q25: 2 Chlorine electrodes P_{Cl_2} = 2 atm
$[Cl^-]$ = 0.2 and 0.1

Derive an expression for E_{cell}.

Pt | Cl_2 (2 atm) | Cl^- (an[illegible] || Cl (cathode) | (Cl_2 [illegible]) |

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

~~$E_{cathode} = E^\circ_{cathode} - \frac{0.0591}{n} \log \frac{P_{Cl_2}}{Cl}$~~

cathode: $\frac{1}{2}Cl_2 + e^- \longrightarrow Cl^-$
anode: $\frac{1}{2}Cl_2 + e^- \longrightarrow Cl^-$
] reduction rxns.

classmate

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

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

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

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

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

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