"Physical chemistry"

IIT Fresher batch

~~Roll no ⇒ 184805~~

Batch ⇒

1) Solid state
2) Chemical kinetics → 111
3) Electrochemistry → 361 to

~~11) Chemical ki~~
~~11) electrochemistry~~
1) Co-ordinate bonding

→ One thing you can't recycle is wasted time

→ हमको जितना पढ़ाना था उससे अधिक ही पढ़ा दिये हम जितना पढ़ा दिये AIR-1 के लिए भी काफी है लेकिन यह अब तुम पे depend करता है तुम्हारे मेहनत पर depend करता है कि तुम JEE में नंबर उठा पाते हो या नहीं -

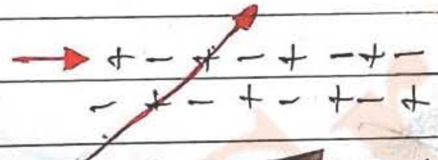
GB Sir :
(17/5/2012)

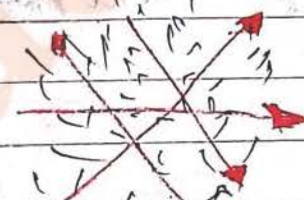
Start

Solid state

★ On the basis of arrangement of constituent particle solid can be classified into two categories.

1) Crystaline solid — or True solid	2) Amorphous solid — or Pseudo solid or super cooled liquid
a) In such type of solid their is regular arrangement of constituent particles.	a) Their is irregular arrangement of constituent particles.
b) They have long range order.	b) They have short range order.
c) They ~~are~~ are formed by slow cooling of liquid	c) They are form by rapid cooling of the liquid
d) Examples:- Diamond, Graphite, NaCl, ZnS etc.	d) Examples:- Glass, Plastic rubber etc.
e) Crystaline solid's are rigid in nature	e) Amorphous solid are non-rigid in nature.
f) Crystaline solid's have sharp melting point	f) They have range of melting point.
g) Crystaline solid's are also know as "True solid's"	g) Amorphous solid's are also known as Pseudo solid's or super cooled liquid or short range solid.
h) Crystaline solid shows ~~are~~ anisotropic behavior	h) Amorphous solid show's Isotrophic behavior.





Isotropic means they exhibit same physical properties in all the direction.

Example of Anisotropic :- The electric and thermal conductivities are different in different direction.

...s they ... physical properties in different direction.

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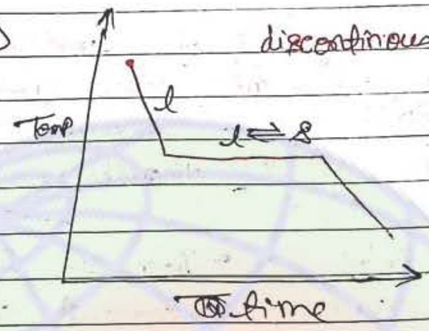
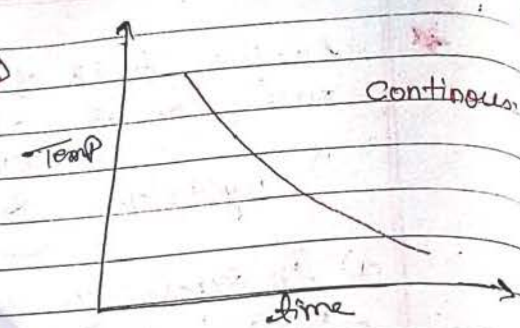
I) discontinous



I) Continous



J) Crystaline solid's have symmetric

याद रखें;
जब Rigid, symmetric, Anisotropic, Regular arrangement (जैसे Diamond, graphite, NaCl, ZnS वगैरह धीरे ठंडा करके (slow cooling) लंबा खिंचाव (long range order) तब ही sharp melting हो गईल (तथा ~~इसलिए~~ graph discontinuous बनेगा.)

(K) crystalline solid's can be Ionic, Covalent, molecular and metallic

J) Amorphous Solid do not have symmetric

(K) Amorphous silicon is used in Photo voltaic cell.

L) Amorphous Solid not show clevage Properties

Note: ➡ Silica (SiO_2) can be crystalline (quartz) as well as Amorphous. (see R.K. Page 622)

Types of crystaline solid ⟹

Depending upon the "nature of force of attraction" acting b/w the constituent particles crystaline solid can be divided into four categories :-

Type	Constituent particles	Interaction force	Example
1) Ionic	Ions	Ionic Bond electrostatic	NaCl, ZnS
b) covalent / Network	Atom	covalent bond	SiC, graphite, diamond, SiO_2, SiC
c) metallic	atom (+ve ions and electron)	metallic bond	Cu, Ag, Au
d) molecular	molecules	vander waal, H-Bond	$I_2(s)$, HCl, P_4H_{10}, $H_2O(s)$ H-bond

[for more must Read N.C.E.R.T Page→6]

* Crystal → A crystal is a homogenous portion of a solid substance made by regular patter of structural unit's bonded by plane surface making definite angles with each other.

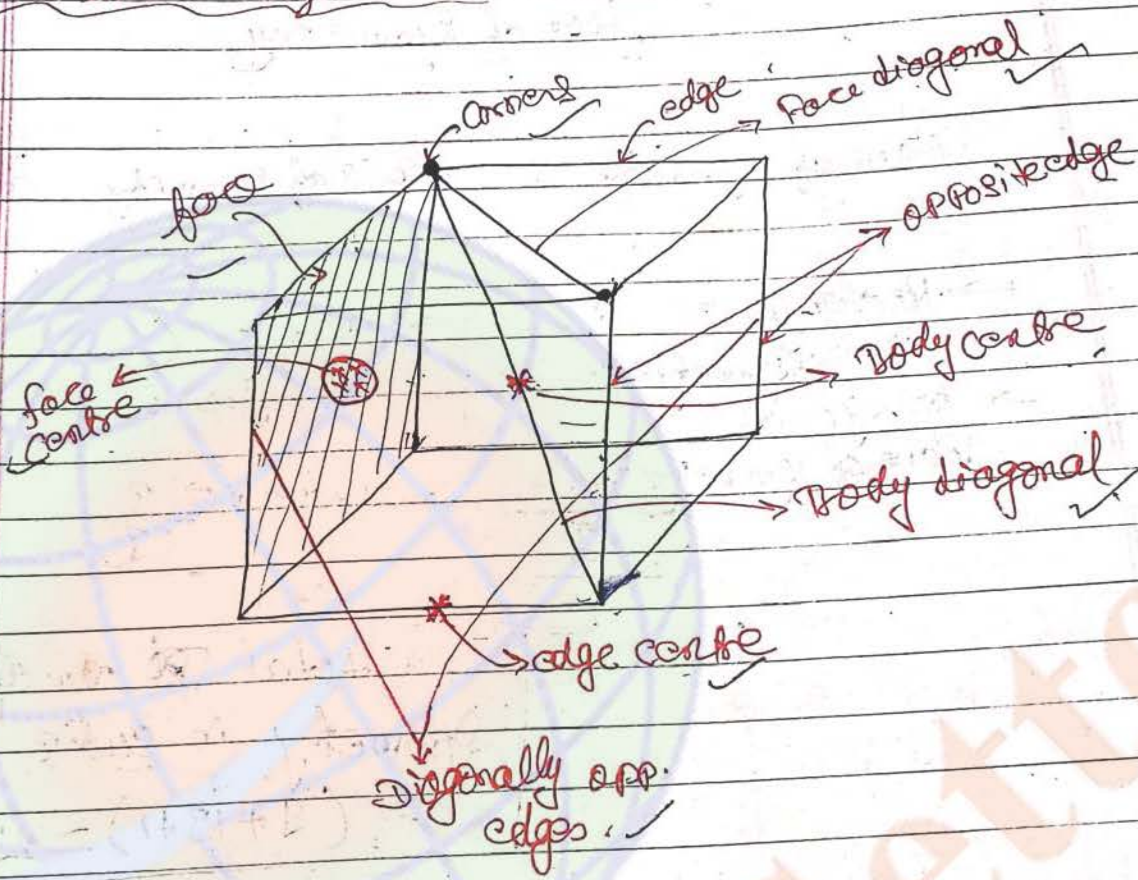
* Crystallography → ~~or~~ A branch of Physical science that deals with study of crystals, viz their sources, classifications, properties, structure etc. is called crystallography.

* Interfacial angles → The angle b/w the perpendicular ~~two~~ two Intersecting faces called Interfacial angle.

* Law of constancy of Interfacial angle → The Interfacial angles for all the crystal's of a given crystalline substance are always the same irrespective to the shape and size of crystal.
This is known as law of constancy of Interfacial angles.

* Amorphous silicon is one of the best "Photovoltaic material" or "Photovoltaic cell" available for conversion of sunlight into electricity.

★ Cubic crystal:→



corners → 8
edge - 12
face = 6
face diagonal = 12
body diagonal = 4

Law of Symmetry

- Plane of symmetry
  - Rectangular Plane of Symmetry ⇒ 3
  - Diagonal Plane of Symmetry ⇒ 6
  - ————
  - 9
- Axis of symmetry
  - Diad ⇒ 6
  - Triad ⇒ 4
  - Tetrad ⇒ 3
  - ————
  - 13
- Centre of Symmetry ⇒ 1

$\boxed{\text{So, total No. of symmetry in "cubic crystal" is } (9+13+1) = 23}$

याद रखें :→ 3 6 6 4 3 1

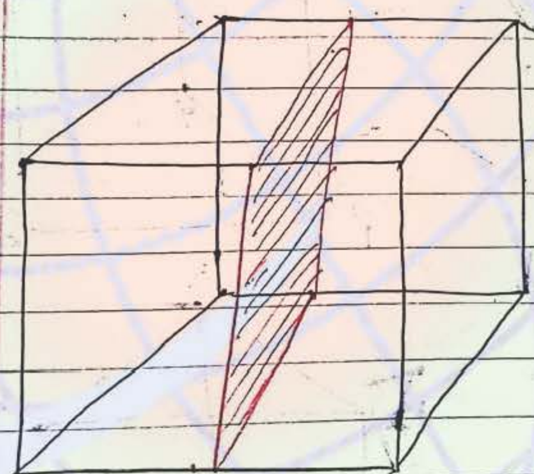
Notes:→ what is Bragg's equation is →

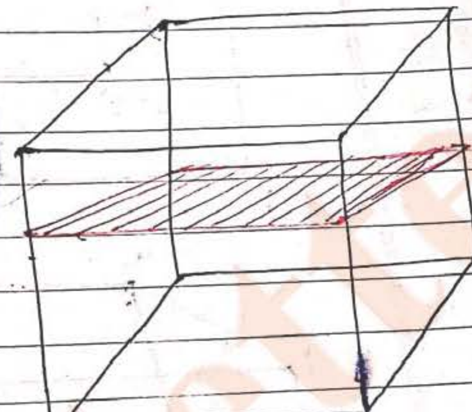
Soln:— Bragg's equation is $n\lambda = 2d\sin\theta$

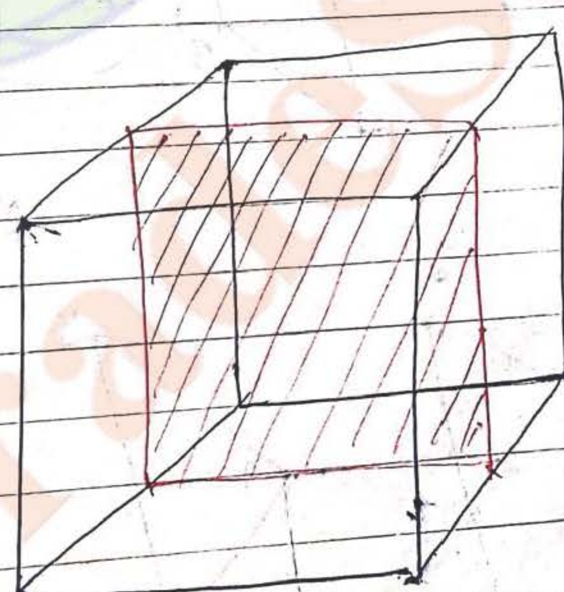
Laws of symmetry ⇒

1) Plane of symmetry → There are two types of plane of symmetry

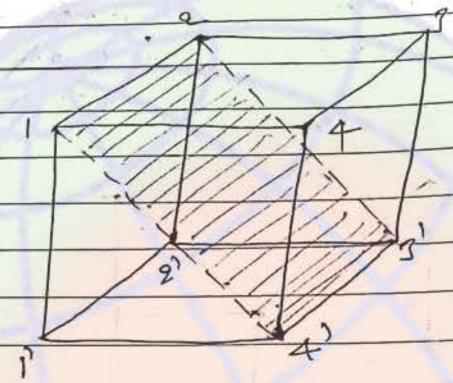
a) Rectangular plane of symmetry → By joining mid-point of opposite edges.
3

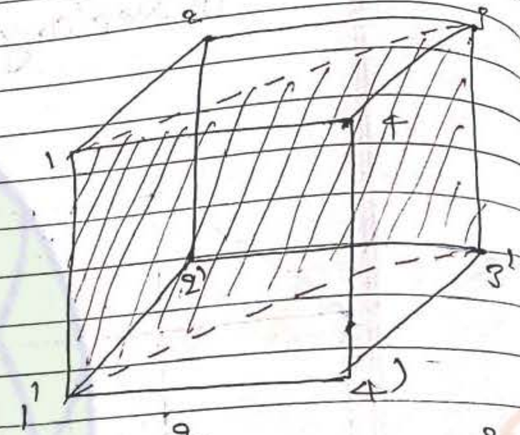


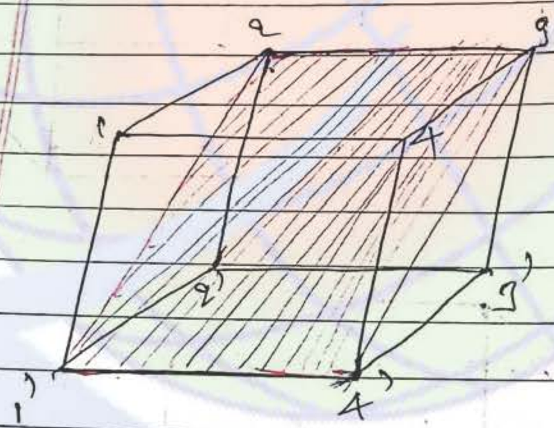


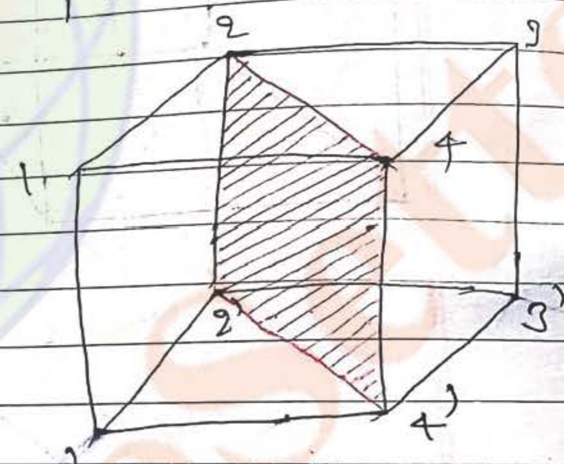


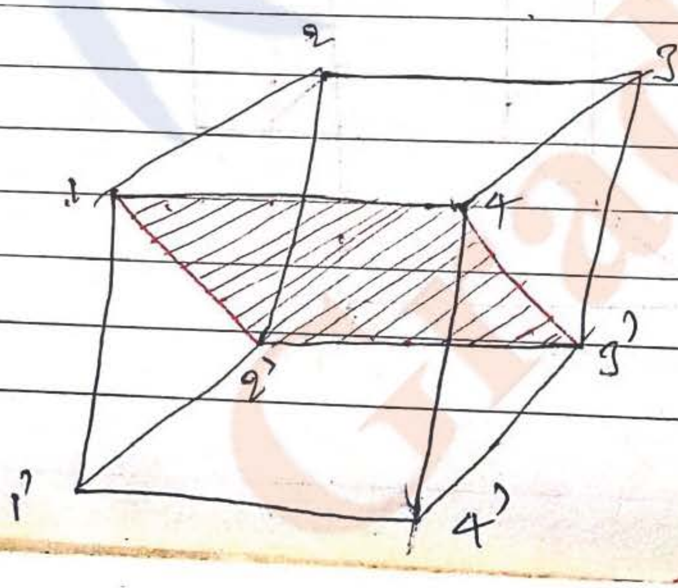
b) Diagonal Plane of Symmetry
By joining diagonally opposite edges.
"6"

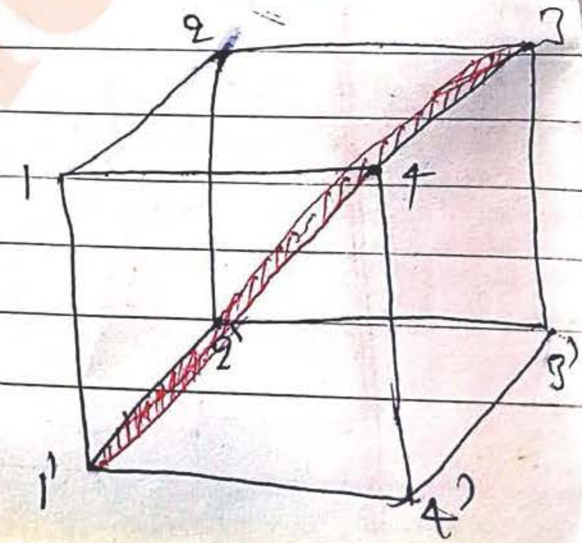


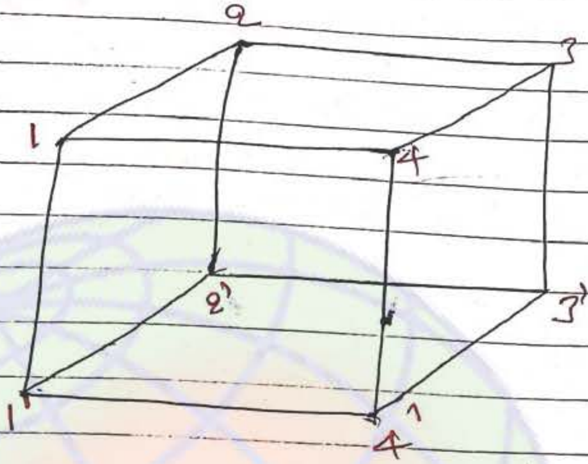












Possible number of diagonal plane of symmetry ⇒

- 12 – 3'4'
- 23 – 1'4'
- 34 – 1'2'
- 14 – 2'3'
- 11' – 33'
- 22' – 44'

So,
Total No. of plane of symmetry ⇒ 3+6
⇒ 9

2.) Axis of Symmetry → (on the basis of rotation)

Their are three axis of symmetry :-

a) Diad (two fold axis of symmetry) → ($\theta = 180$)
- → By joining mid point of diagonally opp. edges → "6"
- → original appereance is repeated twice in one rotation

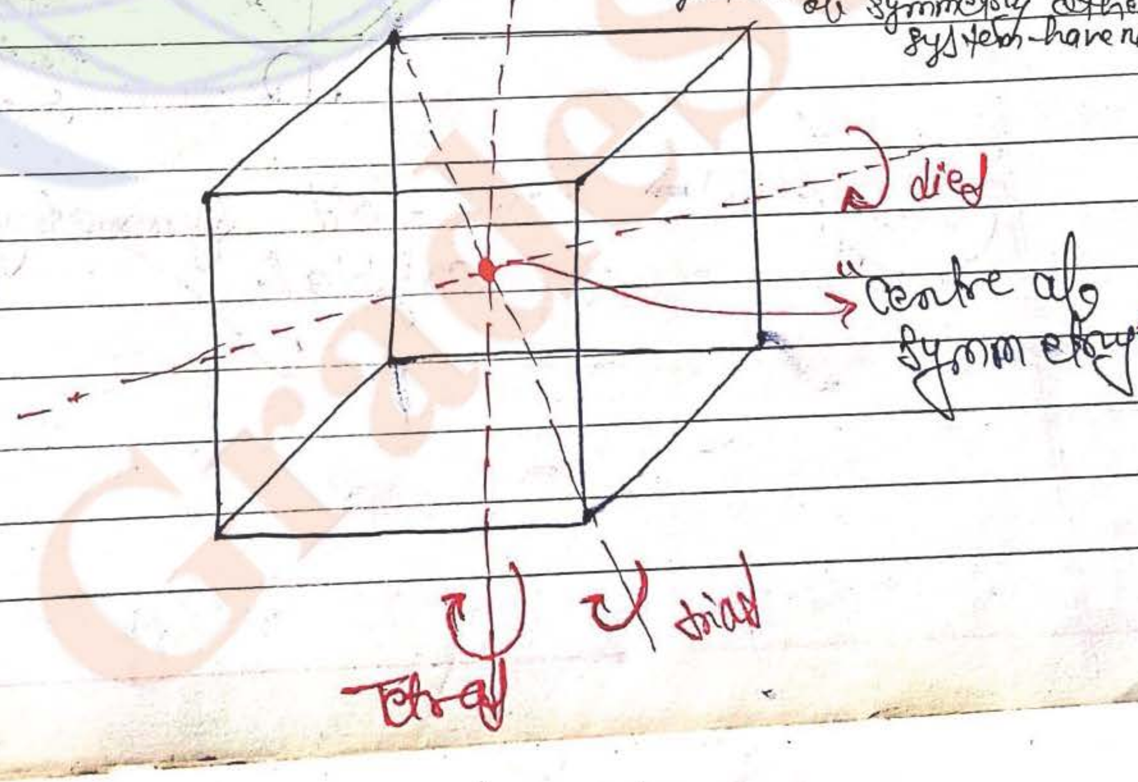
e (diad) → C (Triad) → f → Tetrad

b) Triad (Three fold axis of symmetry) → ($\theta = 120$)
- → By joining diagonally opp. corner → 4
- → original appereance is repeated thrice in one rotation

c) Tetrad (Four fold axis of symmetry) → ($\theta = 90°$)
- → By joining mid-point of opp. faces → "3"
- → original appereance is repeated four times in one rotation

Note! → Centre of symmetry = 1

→ only simple cubic system have one centre of symmetry other system have not



So,
Total elementary symmetry :-
= 9 Plane of symmetry
= 13 Axis of symmetry
= 1 centre of symmetry
= 23 elements of symmetry

Note →

* In Hexagonal structure, four fold symmetry (Hexad) are also present.

Number ⇒ "1"

$\theta = 60$

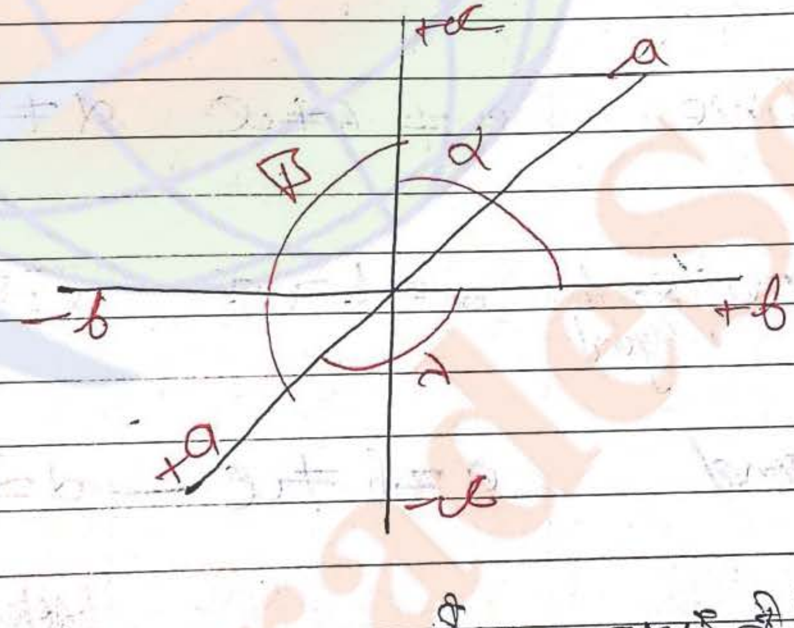
It mean's original appearance is repeated six times (60°) in one rotation of 360°.

Attention → Five fold symmetry is not found in crystal.

* Space lattice ⇒ The regular arrangement of constituent particle in three dimensional space is known as space lattice
eg:- बिल्डिंग

* Unit Cell ⇒ The smallest unit of space lattice which on repeation gives space lattice, and tell's us about all the properties of space lattice is known as unit cell
eg → ईंट

* Types of Crystal on the basis of Intercept on Crystallographic axis and Angle b/w them :→



Z और y-axis के बीच α-angle रहता है
आरेख से => x और y-axis के बीच β-angle बनाते हैं
और z और x " " " γ - " बनाते हैं

Zy α, → xy β, → Zx γ

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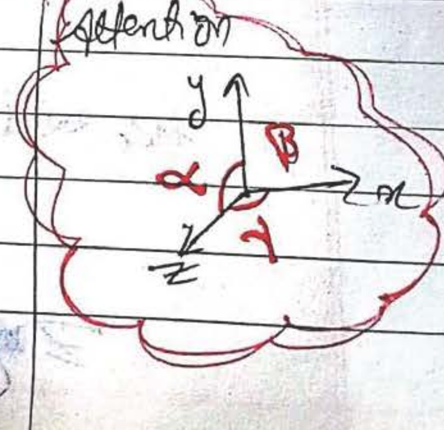
Type of Crystal	Relation b/w a, b, and c	Relation b/w α, β, and γ	Type of cell
(A) 1.) cubic	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$	Primitive SC, FCC, B
(B) 2.) Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90^\circ$	SC, BCC
(C) 3.) orthorombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90^\circ$	SC, BCC,
(F) 4.) monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90^\circ$, $\beta\neq 90^\circ$	SC, E
(G) 5.) Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90^\circ$	SC
(E) 6.) Trigonal/Rombohydral	$a=b=c$	$\alpha=\beta=\gamma\neq 90^\circ$	SC
(D) 7.) Hexagonal	$a=b\neq c$	$\alpha=\beta=90^\circ$, $\gamma=120$	SC

Attention



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Type of cell	Example -
Primitive SC, FCC, BCC → base centred cubic	NaCl, Zinc blende, Cu, KCl, diamond
SC, BCC	white tin, SnO_2, TiO_2, $CaSO_4$,
SC, BCC, FCC, ECC	Rhombic sulphur, KNO_3, $BaSO_4$, $CaCO_3$
SC, ECC	monoclinic sulpher, $Na_2SO_4 \cdot 10H_2O$,
SC	$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$, H_3BO_3
SC	calcite($CaCO_3$), HgS (cinnabar)
SC	Graphite, ZnO, CdS, Mg

क्यूबी टी और
ओ
हाथी कभी
मोनोक्लिनिक
ही था ही

Different arrangement of Particles.

⇒ Two dimensional arrangement

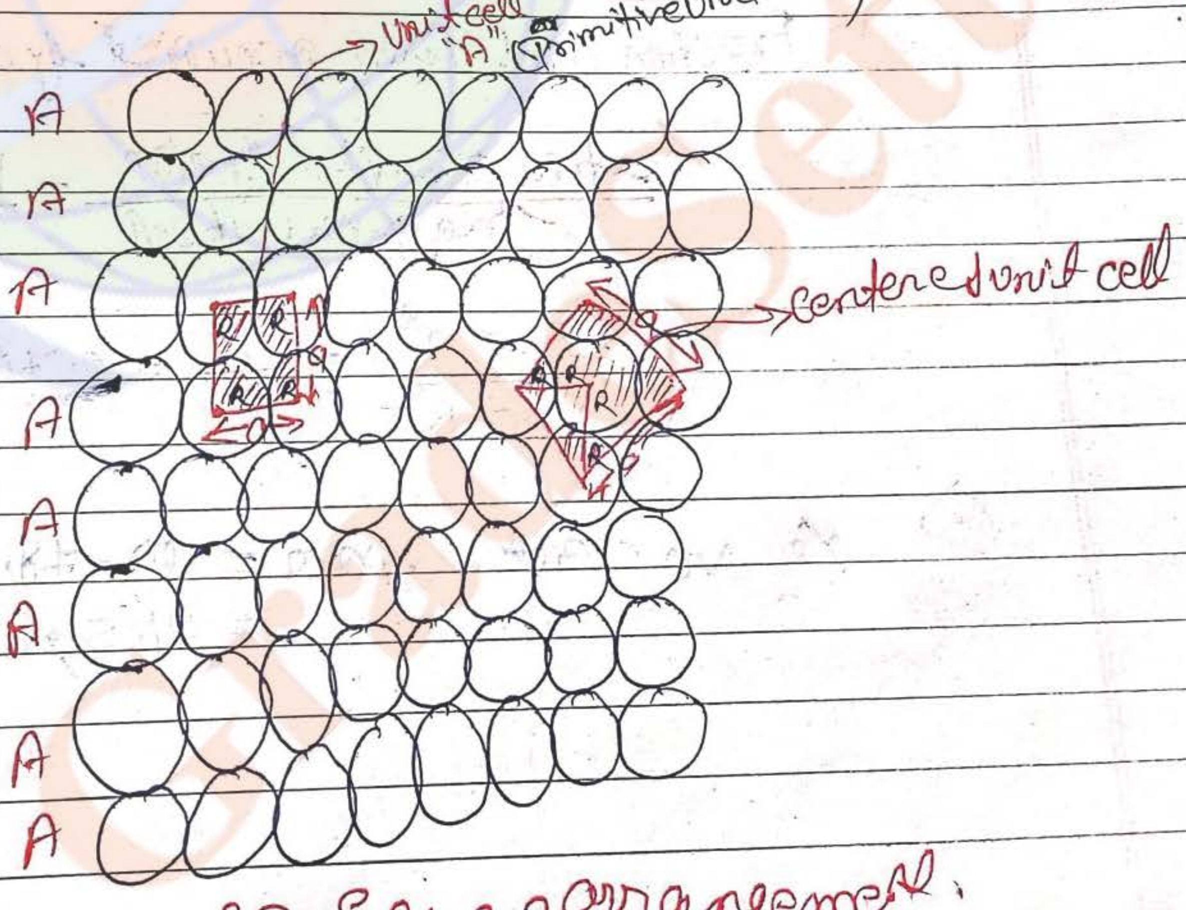
The definite arrangement of constituent particle in a plane is known as two dimensional arrangement.

There are two types of two dimensional arrangement.

I) Square arrangement → Primitive or simple unit cell; → centered unit cell

II) Hexagonal arrangement.

Square arrangement →



2D-Square arrangement.

B

* Primitive or Simple Unit cell

1) No. of atoms per unit cell (N)

$$N = 4 \times \frac{1}{4} = 1$$

2) Relation b/w edge length (a) and R

$$\boxed{a = 2R}$$

3) co-ordination Number (N) = 4

4) Area occupied by the atom per unit cell $= 1 \times \pi R^2$

5) Fraction of area occupied by atom =

$$\frac{\text{Area occupied by atom}}{\text{Area of per unit cell}} = \frac{1 \times \pi R^2}{a^2}$$

$$= \frac{\pi R^2}{4R^2} = \frac{\pi}{4} = 0.785 \text{ or } 78.5\%$$

6) % vaccant space = 100 − 78.5
= 21.5 %

Centered unit cell →

1) No. of atom's per unit cell (N)

$$N = 4 \times \frac{1}{4} + 1 = 2$$

2.) Relation b/w edge length (a) and R

$$a^2 = (2R)^2 + (2R)^2 \quad , \boxed{a = 2\sqrt{2}R}$$

3.) Co-ordination no. (Z) = 4

4.) Area occupied by the atom per unit cell $= 2 \times \pi R^2$

5.) fraction of area occupied by atom's =

$$= \frac{\text{Area occupied by atom}}{\text{Area of unit cell}} = \frac{2 \times \pi R^2}{a^2}$$

$$= \frac{2\pi R^2}{8R^2} = \frac{\pi}{4} \text{ or } 78.5\%$$

6) % vaccent space = 100 − 78.5
= 21.5%

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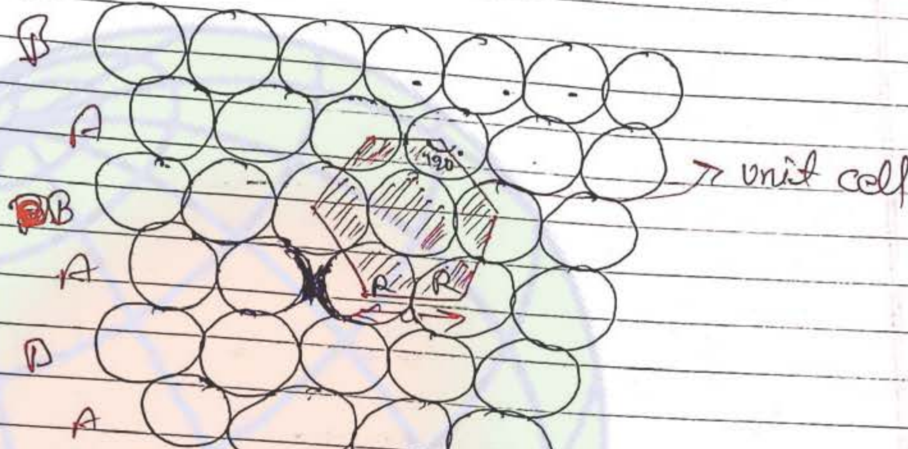
Hexagonal arrangement →



2D-Hexagonal arrangement.

1) No. of atom per unit cell (n) $= 6 \times \frac{1}{3} + 1 \times 1 = 3$

2) Relation b/w a and R

$$\boxed{a = 2R}$$

6) % vacant area = 9.4%

3) Co-ordination (Z) = 6

4) Area occupied by atom's $= 3\pi R^2$

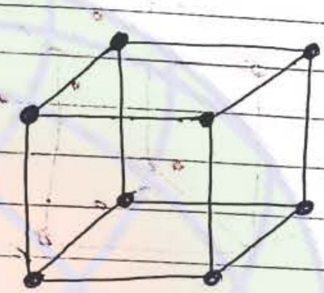
5) Area efficiency $= \frac{3 \times \pi R^2}{\text{area of hexagon}} = \frac{3\pi R^2}{6 \times \text{Area of } \Delta}$

$$\frac{3\pi R^2}{6 \times \frac{\sqrt{3}}{4} a^2} = \frac{\pi}{2\sqrt{3}} = 0.906 = 90.6\%$$

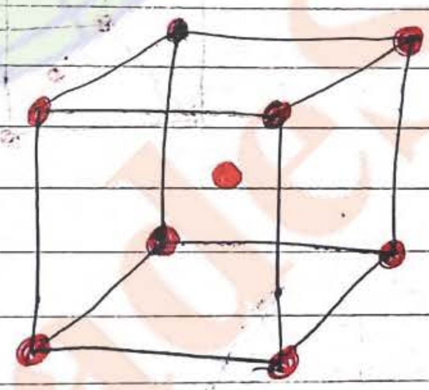
3D - arrangement ⇒ (Cubic crystal) -

1.) → Type of unit cell :-

1) Simple cubic unit cell (S.C) ⇒ In this type of unit cell atom's are present only at the corner of a cube

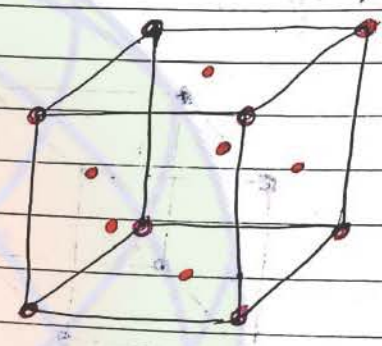


2.) ~~Base Cent~~ Body centred Cubic (BCC) →
In this type of unit cell atom's are present at each corner of the unit cell and one atom is present at body centre of a cube.

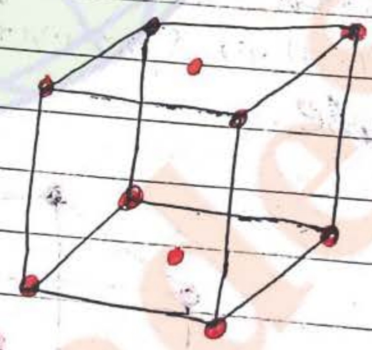


3) Face-centre cubic (FCC) →

In this type of unit cell atoms are present at each corner of the cube and at each base centre of a cube



4) End centred cubic (ECC) →



2) Contribution of various ~~point~~ atom →

a) corner atom contribution $= \frac{1}{8}$.

b) Face centre atom contribution $= \frac{1}{2}$.

c) Body centre atom contribution $= 1$

4) edge centre atom contribution $= \frac{1}{4}$

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3.) No. of atom's per unit cell →

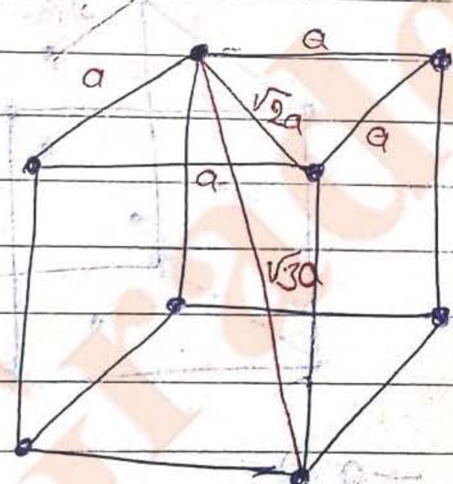
S.C ⇒ $N = \underset{\text{corner}}{8} \times \frac{1}{8} = 1$

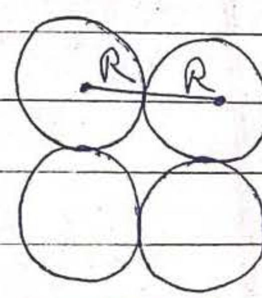
BCC ⇒ $N = \underset{\text{corner}}{8} \times \frac{1}{8} + \underset{\text{centre}}{\frac{1}{1}} \times 1 = 2$

FCC ⇒ $N = \underset{\text{corner}}{8} \times \frac{1}{8} + \underset{\text{(face centre)}}{6} \times \frac{1}{2} = 4$

★ Relation b/w edge length "a" and atomic radius "r" → (पीछे :→ Concept याद रखें "a" और "R" का Relation हो closest atom के बिच मे निकालते है। क्योंकि structural Packing मे closed atom मे ही formula लगाएँ)

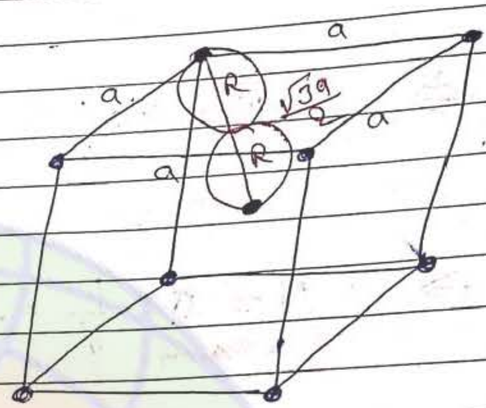
→ S.C





$\boxed{a = 2R}$

⇒ BCC

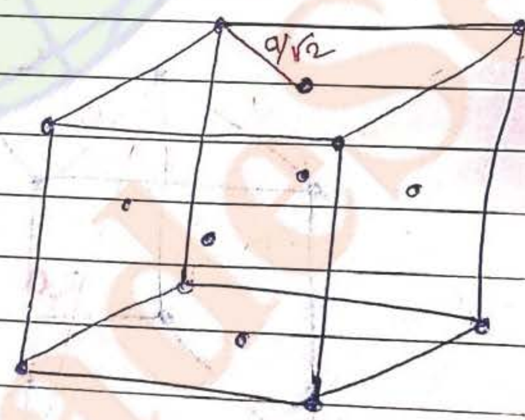


$$\frac{\sqrt{3}a}{2} = 2R$$

$$\boxed{\sqrt{3}a = 4R}$$

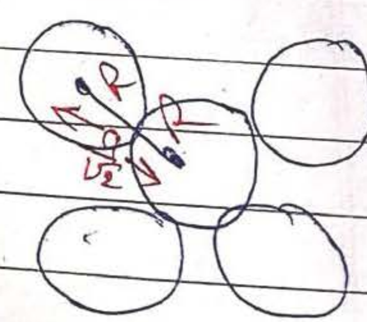
⇒ FCC

$\frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}}$



$$\frac{a}{\sqrt{2}} = 2R$$

$$\boxed{a = 2\sqrt{2}R}$$



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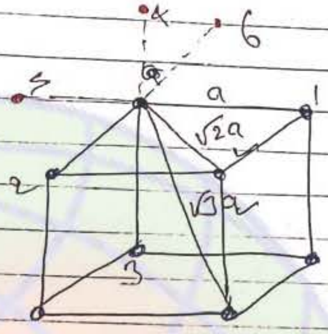
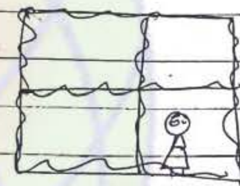
4) Co-ordination number →

⇒ S.C



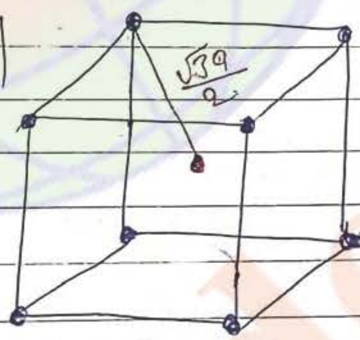
$\boxed{Z=6}$

मान लो room में पास-पास तीन कमरे फिर इस का co-ordination कहते हैं Simple cubic में इस आधार पर पता चलेगा कि जिस बीच में जो atom है वह √2a पर किसी atom से मिल सकता है और वही उसका co-ordination number होगा।



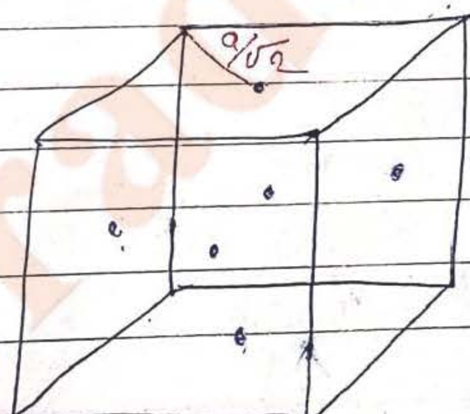
⇒ BCC

इसी प्रकार हम सभी का भी निकाल सकते हैं।



$\boxed{Z=8}$ $\left(\frac{1\times8}{1}\right)$

⇒ FCC



$\boxed{Z=12}$ $\left(\frac{3\times8}{2}\right)$

4 in it's plane
4 above and 4 below

और → "N" से Number of atom per unit cell दर्शाते है जबकि "Z" से co-ordinate संख्या को लिखते हैं।

5) Calculation of density for different type of cubic structure.

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

किसी भी solution में इसे लिखना ना भूलें क्योंकि है solution इसके बिना गलत हो सकता है इसलिए इसको ध्यान में रखें।

$$\boxed{d = \frac{N \times M}{a^3 \times N_A \times 10^{-30}}\ g/cm^3}$$

N = no. of atom per unit cell

(in g/mole) ← M = molecular weight / Atomic wt.

$N_A = 6.023 \times 10^{23}$

a = edge length (in pm)

so, $\boxed{\because 1\,pm = 10^{-10}\,cm}$

SC :→ VVI

$$d = \frac{1 \times M}{N_A \times a^3} \quad \{a = 2R\}$$

BCC → VVI

$$d = \frac{2 \times M}{N_A \times a^3} \quad \{\sqrt{3}a = 4R\}$$

face centred cubic

FCC → VVI

or

CCP — Cubical closed Packing

$$d = \frac{4 \times M}{N_A \times a^3} \quad \{a = 2\sqrt{2}R\}$$

याद रखें दोनों में double "C" है और F और "P" also same दिखते हैं

$\boxed{1 Å = 10^{-10} m}$, $\boxed{1 pm = 10^{-12} m}$, $\boxed{1 \text{ micron}(\mu) = 10^{-6} m}$

$\boxed{1 Å = 10^{2} pm}$ $cc \Rightarrow ml$

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Note → (इस chapter के सभी formula "Root" हैं इसलिए याद कर लें!)

In S.I unit :-

$$\text{density } (d) = \frac{N \times M}{a^3 \times N_A} \text{ kg m}^{-3}$$

Here:
"a" is in metres
"m" is in kg mole^{-1}

In C.G.S system :-

$$\text{density } (d) = \frac{N \times M}{a^3 \times N_A \times 10^{-30}} \text{ g/cm}^3$$

Here!
a is in pm
and m is in g/mole

So, edge of unit cell = a pm = $a \times 10^{-10}$ cm
volume of unit cell = $a^3 \times 10^{-30}$ cm^3

No. of atom = $\frac{\text{Given mass}}{\text{molar mass}} \times N_A$

= No. of atom of given compound × No. of molecules of compound

molar mass = mass of each atom × N_A

No. of unit cell = $\frac{\text{No. of atom}}{N}$

$1 nm = 10^{-9} m$

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Date: / /

Calculation of Packing efficiency (fraction) for different type unit cell →

Packing efficiency or Packing fraction

$$\eta = \frac{\text{volume occupied by atom's}}{\text{volume of unit cell}}$$

$$= \frac{N \times \frac{4}{3}\pi R^3}{a^3}$$

N → No. of atom's Per unit cell

a → edge length

SC →

$$\eta = \frac{1 \times \frac{4}{3}\pi R^3}{a^3} \quad \{a = 2R\}$$

$$= \frac{1 \times \frac{4}{3}\pi R^3}{8R^3}$$

$$= \frac{\pi}{6} = 0.524$$

or

52.4%

Now

% void = 47.6%

आवश्यक है 17 — 52 — 68 — 74

B

BCC →

$$\eta = \frac{2 \times \frac{4}{3}\pi R^3}{a^3} \quad \left\{ a = \frac{4R}{\sqrt{3}} \right\}$$

$$= \frac{2 \times \frac{4}{3}\pi R^3}{\frac{16R^3}{9\sqrt{3}}}$$

$$= 2 \times \frac{4\pi}{3} \times \frac{3\sqrt{3}}{16 \; 4}$$

$$= \frac{\sqrt{3}\pi}{8} = 0.68$$

or

68 %

% void = 32 %

FCC

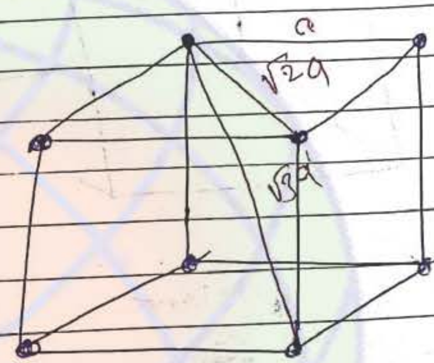
$$\eta = \frac{4 \times \frac{4}{3}\pi R^3}{32\sqrt{2}R^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

or 74 %

% void = 26 %

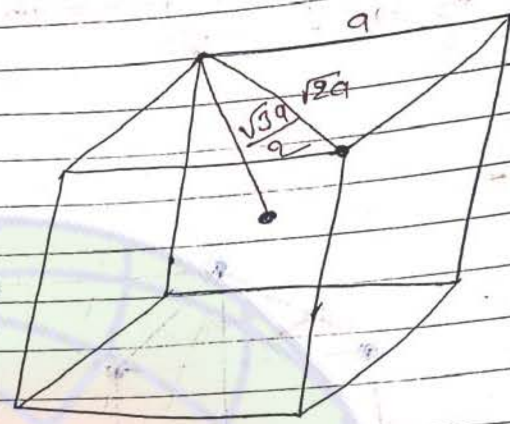
Calculation of nearest, next nearest, next to next nearest atom in different type of unit cell

⟹ S.C



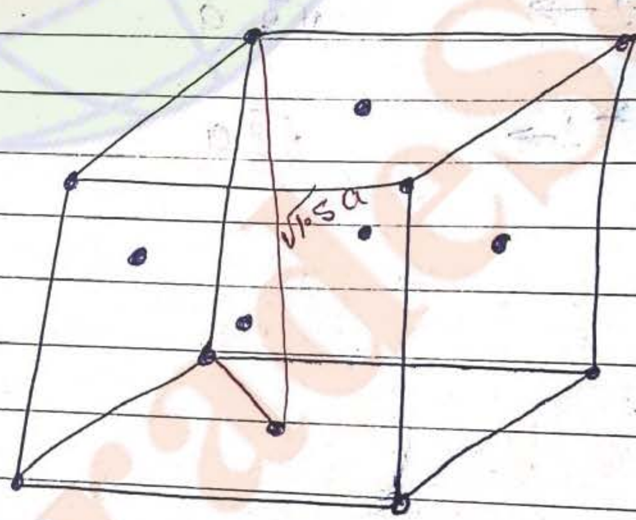
	distance	No. of atom
nearest :→	a	6
next :→	$\sqrt{2}\,a$	12 $\left(\frac{3\times8}{2}\right)$
next^2 :→	$\sqrt{3}\,a$	8 $\left(\frac{1\times8}{1}\right)$

⇒ BCC



	distance	no. of atom	
nearest	$\sqrt{3}a/2$	8	$\left(\frac{1\times 8}{4}\right)$
next	a	6	
next^2	$\sqrt{2}\,a$	12	

⇒ FCC



	distance	no of atom
nearest :-	$\frac{a}{\sqrt{2}}$	12
next :-	a	6
next^2 :-	$\sqrt{1.5}\,a$	24 $\left(\frac{3\times8}{1}\right)$
next^3 :-	$\sqrt{2}a$	12

Note →

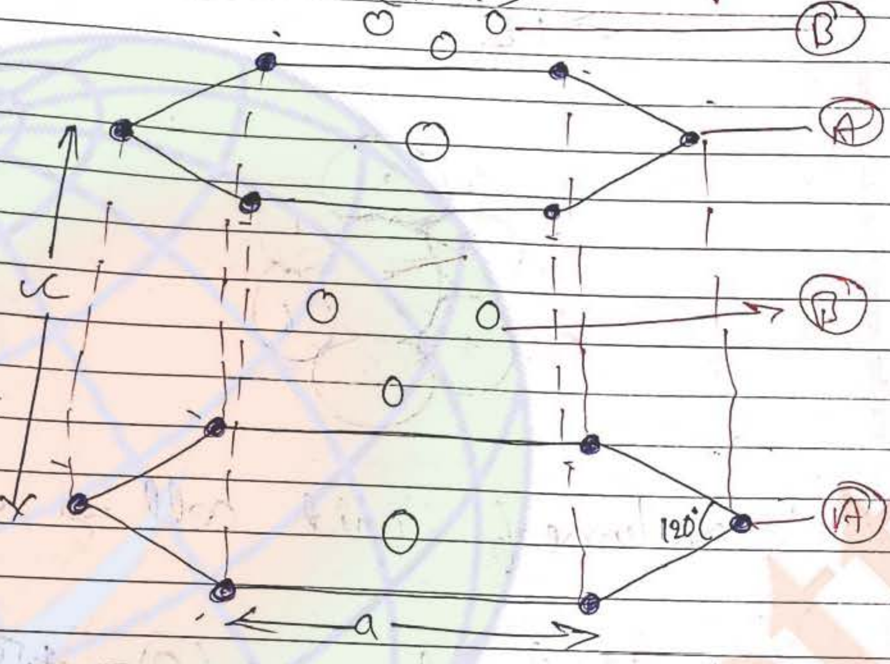
face → 12

Body diagonal → 8

edge → 6

Hexagonal closed Packing → (ABAB ---- Pattern)

(HCP)



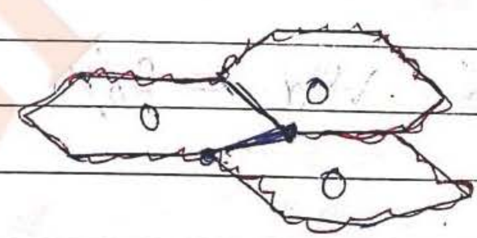
1) Relation b/w "a" and "R"

$$a = 2R$$

2) No. of atom per unit cell (N)

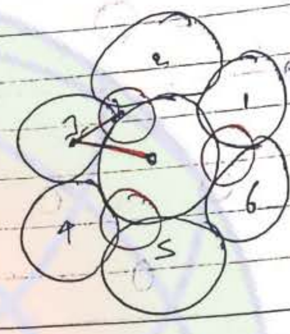
(corner)

$$N = 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 \times 1 = 6$$



3.) C. No (Z) → co-ordination number

$\Rightarrow 12$



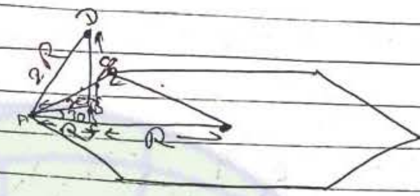
4.) volume of unit cell $\Rightarrow 24\sqrt{2}\,R^3$

5.) Height of hexagon (C) = "$\frac{4\sqrt{2}}{\sqrt{3}}R$"

6.) $\eta = \dfrac{6 \times \frac{4}{3}\pi R^3}{6 \times \frac{\sqrt{3}}{4} a^2 \times c}$

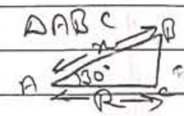
$= \dfrac{6 \times \frac{4}{3}\pi R^3}{6 \times \frac{\sqrt{3}}{4} \times 4R\,\frac{4\sqrt{2}R}{\sqrt{3}}} = \dfrac{\pi}{3\sqrt{2}} = 0.74$ or 74%

7.) % Void = 26%



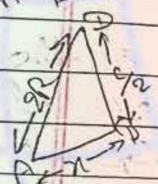
$$\cos 30^\circ = \frac{R}{x}$$

(from ΔABC



$$x = \frac{R}{\sqrt{3}/2} = \frac{2R}{\sqrt{3}}$$

from ΔABC



$$(2R)^2 = \left(\frac{c}{2}\right)^2 + x^2$$

(By Pythagoras theorem)

$$4R^2 = \frac{c^2}{4} + \frac{4R^2}{3}$$

$$\frac{c^2}{4} = \frac{8R^2}{3}$$

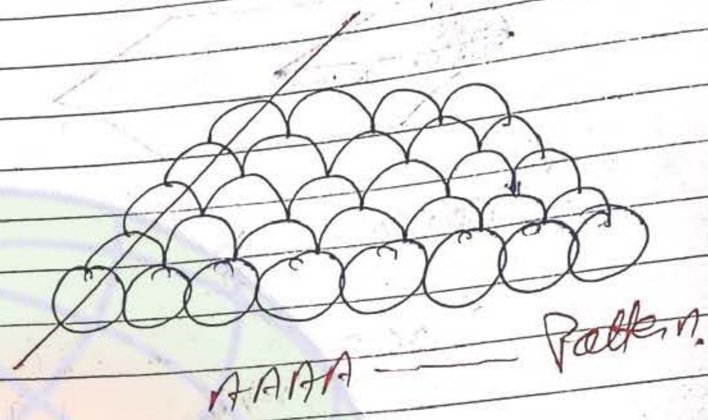
$$c^2 = \frac{32R^2}{3}$$

$$\boxed{c = \frac{4\sqrt{2}}{\sqrt{3}} R}$$

Note ⇒

FCC — ABCABC ---- Pattern
HCP — ABAB ---- Pattern
SC — AAAA ---- Pattern

SC ⇒



(D) only "tetrahedral voids" are found on the line passing through their centres of layer of AAA identical layer of atom (see sheet on 1 (Q=16)

(Exd. Q4) $Tl\,Al(SO_4)_2 \cdot xH_2O$

bcc $(N=2)$

$a = 1.22\times10^{-9}\,m$

$d = 2.32\,g/cm^3$

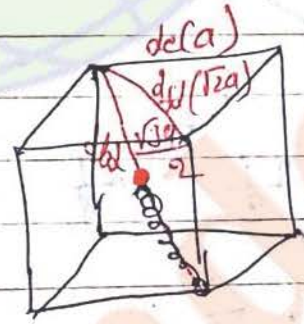
$$d = \frac{N \times m}{a^3 N_A}$$

g/cm^3 cm

$$\text{mol weight} = \frac{d\times a^3 \times N_A}{N}$$

$=$

(Exd. Q5) BCC, $N = 2$



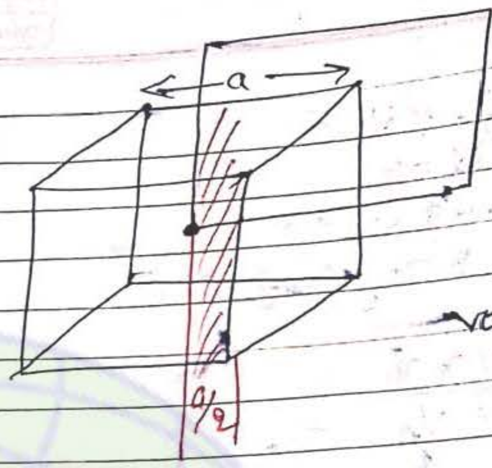
Q6)

$1-2 \Rightarrow a\sqrt{2}$

$2-3 \Rightarrow a/\sqrt{2}$

$1-3 \Rightarrow \sqrt{1.5}\,a$

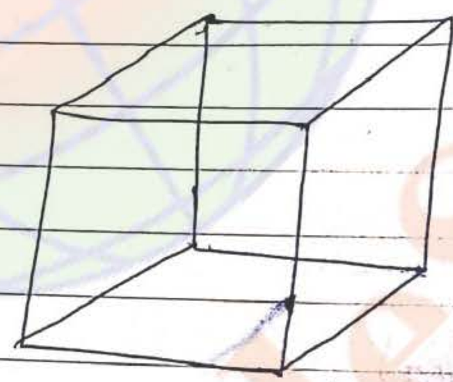
7)



$vol = \left(\frac{a}{2}\right)^3 = \frac{a^3}{8}$

8)

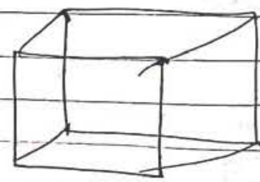
9)



$X_{7\times\frac{1}{8}}\ Y_{6\times\frac{1}{2}}\ Z_{1\times\frac{1}{8}}$

$\cancel{}X_{\frac{7}{8}}\ Y_{3}\ Z_{1/8}$

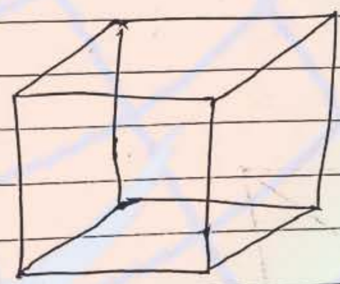
10.)



$W_{8\times\frac{1}{8}}\ O_{12\times\frac{1}{4}}\ Na_1$

$W_1 O_3 Na$

11.)



$m = 100\ g/mole$

edge(a) = 400 pm

$d = \frac{N\,M}{a^3 \times N_a \times 10^{-30}}$

14.) $d = \cancel{40 g/mole}\ 1.68\ g/cm^3$ $\because d = \frac{m}{v}$

$V_T = 1\ cm^3$

V_{atom} = No. of atom × $V_{one\ atom}$

$= \cancel{Note}$ mole × $N_A \times \frac{4}{3}\pi R^3$

$= \frac{1.68}{40} \times N_A \times \frac{4}{3}\pi R^3$ ↓(cm)

$= 0.3564\ cm^3$

% empty space = $(1 - 0.3564)$

(Q2) Q20 $d = 11.34\ g/cm^3$

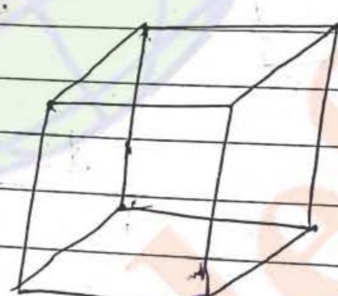
$(FCC = N = 4)$
$m = 208$

$d = \frac{N \times m}{N_A \times a^3}$

$a^3 = a(\ )^{1/3}$
volume of unit cell

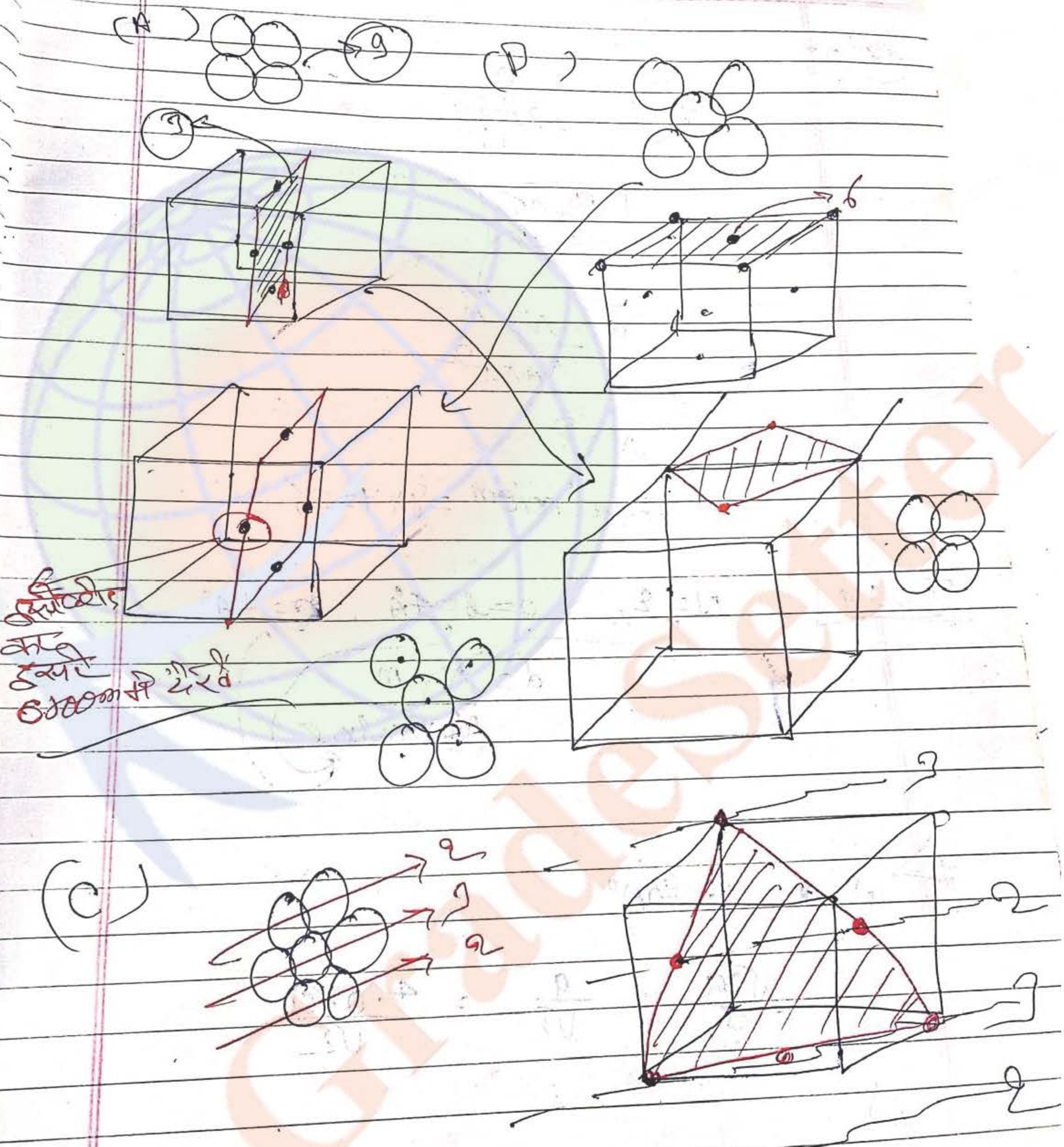
for fcc
$a = 2\sqrt{2}\, r$

22



23

A → (II), (IV)
B → (III), (IV)
C → (I)
D → (III)


(A)
9
(B)
6
(C)
2
2
2
3
2
2
2

(Ex 9) Q 9

Fe	O
$\frac{72.36}{56}$	$\frac{27.64}{16}$

7 atom

$\boxed{Fe_3O_4}$

$$d = \frac{N \times M}{N_A \times a^3}$$

$N = 8$

Total atom $= 8 \times 7 = 56$

$\boxed{\text{Ex 9) Q 4}}$ $N = 2$, $a = b = 4 Å$, $c = 7 Å$

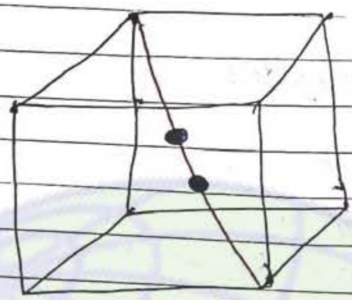
$$d = \frac{N \times M}{N_A \times a \times b \times c}$$

7) a) $a = 4.070 Å$

$$\frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}} = \frac{4.070}{\sqrt{2}}$$

b)

15.)



$N' = 8 \times \frac{1}{8} + 2 \times 1$

$= 1 + 2$

$= 3$

$a^3 = 24 \times 10^{-24}\ cm^3$

$d = 7.2\ g/cm^3$

$wt = 200\ gm$

$\boxed{\text{No. of atom} = \frac{200}{mol\ wt} \times N_A}$

$d = \frac{N \times m}{N_A \times a^3}$

$m =$

then we get answer.

16.) $\frac{a}{\sqrt{2}}$

$a = 2\sqrt{2}l$

19.) FCC = $N = 4$

$a = 200\ pm = 200 \times 10^{-12}\ m$

$d = ?$

$d = \frac{N' \times M}{N_A \times a^3}$

$wt = 200 gm$

No. of atom $= 24 \times 10^{23}$

$$d = \frac{N \times m}{N_A \times a^3}$$

$$n = \frac{wt}{m}$$

$$\frac{\text{No. of atom}}{N_A} = \frac{wt}{M}$$

21.)

$N = 2$

$m = 100$

$a = 400 \times 10^{-12} m$, $wt = 10 gm$

$$d = \frac{N \times m}{N_A \times a^3}$$

No. of atom $= \frac{10}{100} \times N_A = 0.1 N_A$

No. of unit cell $= \frac{0.1 N_A}{2}$

(Passage II) ⇒ (Q33 to 35)

33) Solid :-

$\boxed{\begin{array}{l} V_s = 100ml \\ d = 3.2 g/ml \\ m = 320 gm \end{array}} \rightarrow fcc$

$\eta = 0.74$

$V_{atom} = 74 ml$

liquid :-

$m = 320 gm$

$d = 3 g/ml$

$V_{liq} = \frac{320}{3} = 106.6 ml$

$\% \text{ empty} = \frac{106.6 - 74}{106.6} \times 100$

34 (Q 2 L)

$d = 10.5 g/cm^3$

$1cm^3 — \frac{10.5}{108} \times N_A$ No of atom

$1cm — (\quad)^{1/3}$

$1cm^2 — (\quad)^{2/3} \times 10^{-8}$

$10^{-12} m^2 \times 10^{-8} cm^2$

H.W 3 Q 4 'Sheets'

Q 5.) $\frac{d_{fcc}}{d_{bcc}} \Rightarrow \frac{N_{fcc} \times \cancel{M} \times a^3_{fcc} \times \cancel{N_A}}{N_{bcc} \times \cancel{M} \times a^3_{bcc} \times \cancel{N_A}}$

Q 10.) $\frac{d_2(fcc)}{d_2(bcc)} = \frac{N_{fcc}}{N_{bcc}} \times \frac{a^3_{bcc}}{a^3_{fcc}}$

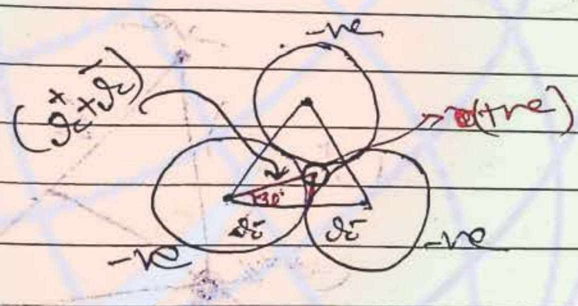
$$\frac{a_{fcc}}{\sqrt{2}} = \frac{\sqrt{3}\, a_{bcc}}{2}$$

$$\frac{a_{fcc}}{a_{bcc}} = \frac{\sqrt{3}}{\sqrt{2}}$$

☆ Study of Ionic crystal →

1. calculation of $\frac{r^+}{r^-}$ for different types of void's →

(a) Triangular void (2D, 3 co-ordinate) → C.No. ⇒ 3



यहाँ "-ve" atom का Radius "r^-" और "+ve" atom का radius "r^+" consider किये हैं।

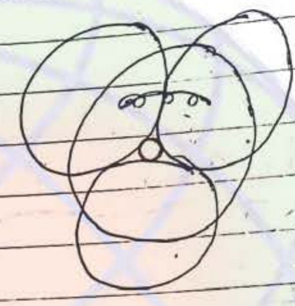
इस बात का ध्यान रखें यहाँ -ve atom बड़ा है और +ve atom छोटा है

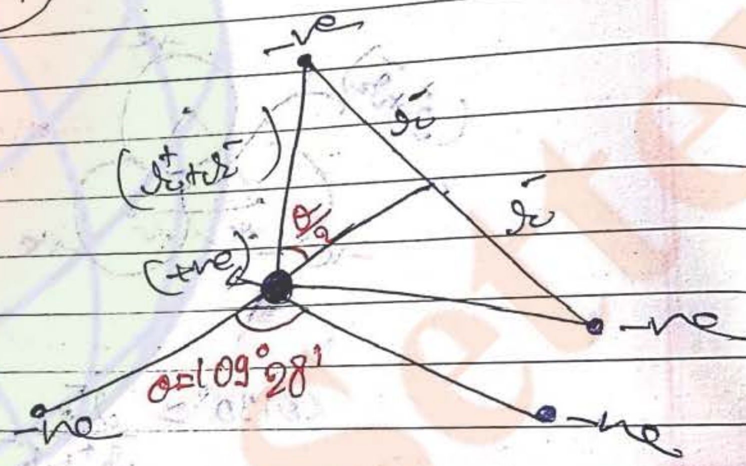
$$\cos 30° = \frac{r^-}{r^+ + r^-}$$

$$\frac{\sqrt{3}}{2} = \frac{r^-}{r^+ + r^-}$$

$$\boxed{\frac{r^+}{r^-} = 0.155}$$

b) Tetrahedral void (T-void)
3D, C.No = 4)





$$\sin \frac{109°28'}{2} = \frac{r^-}{r^+ + r^-}$$

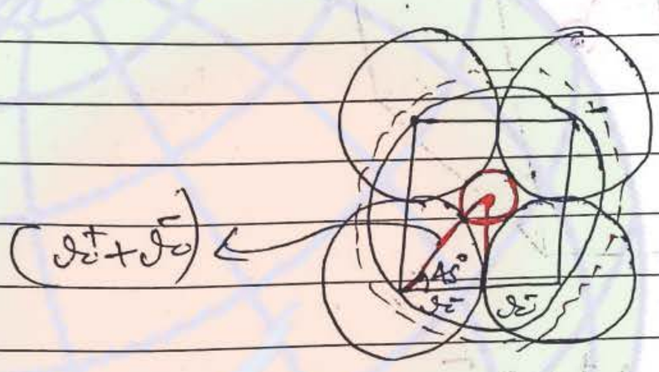
(चूंकि $\frac{\theta}{2}$)

$$0.8155 = \frac{r^-}{r^+ + r^-}$$

$$\boxed{\frac{r^+}{r^-} = 0.225}$$

c) Octahedral void (O-void)

(3D, C.No ⇒ 6)

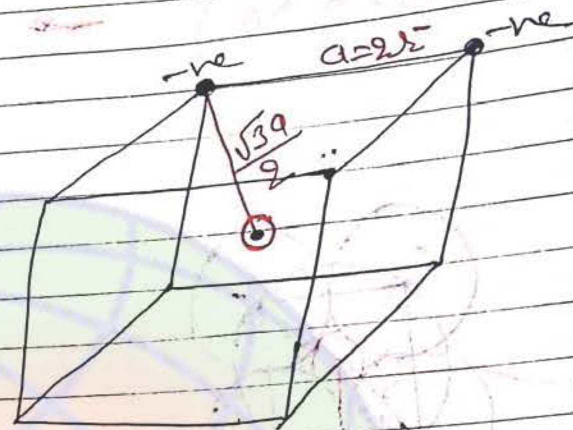


$$\cos 45^\circ = \frac{r^-}{r^+ + r^-}$$

$$\frac{1}{\sqrt{2}} = \frac{r^-}{r^+ + r^-}$$

$$\boxed{\frac{r^+}{r^-} = 0.414}$$

⑤ Cubical void (3D, C.No=8)



$$\frac{\sqrt{3}a}{2} = r^+ + r^-$$

$$a = 2r^-$$

$$\sqrt{3} = \frac{r^+ + r^-}{r^-}$$

$$1.732 = 1 + \frac{r^+}{r^-}$$

$$\boxed{\frac{r^+}{r^-} = 0.732}$$

Note →

1.)

$\frac{r^+}{r^-}$	Type of void	C. No (coordination number)
1) $0.155 \le \frac{r^+}{r^-} < 0.225$	Triangular	[illegible]
2) $0.225 \le \frac{r^+}{r^-} < 0.414$	T-void	4
3) $0.414 \le \frac{r^+}{r^-} < 0.732$	O-void	6
4) $0.732 \le \frac{r^+}{r^-} < 1$	Cubical void	8

equality sign

2.) $\boxed{\frac{\text{C. No. of cation}}{\text{C. No of anion}} = \frac{\text{charge on anion}}{\text{charge on cation}}}$ → दोनों case में निरंतर होते हैं

3.) "P ↑" "C. No ↑"

"T ↑" "C. No ↓"

4.) T- void < O-void < Cubical void

fcc and hcp

SC (for IIT) more Correct

but for {Board and AIEEE this is "BCC"} less Correct.

6.)

5.) Total no. of T-void and O-void →

(याद रखें → tetrahedral void अधिक होते हैं)

Total no. of T-void $= 2N$

" " " O-void $= N$

where

N = No. of atom's per unit cell.

fcc →

T-void $= 8$, O-void $= 4$

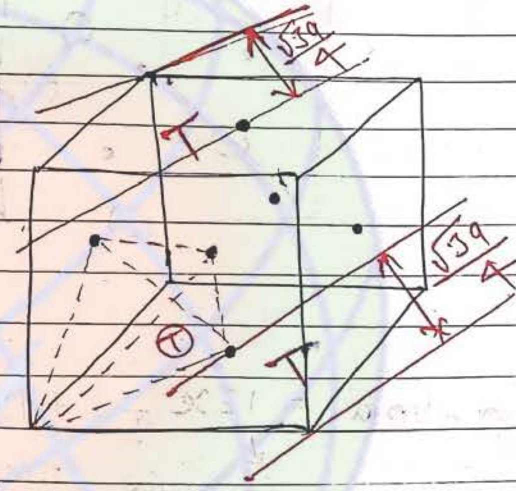
HCP →

T-void $= 12$ O-void $= 6$

ध्यान दें octa hedral void याद रखें और इसकी formula Note भी [illegible]

6.) Location of T-void and O-void in FCC unit cell →

T-Void →



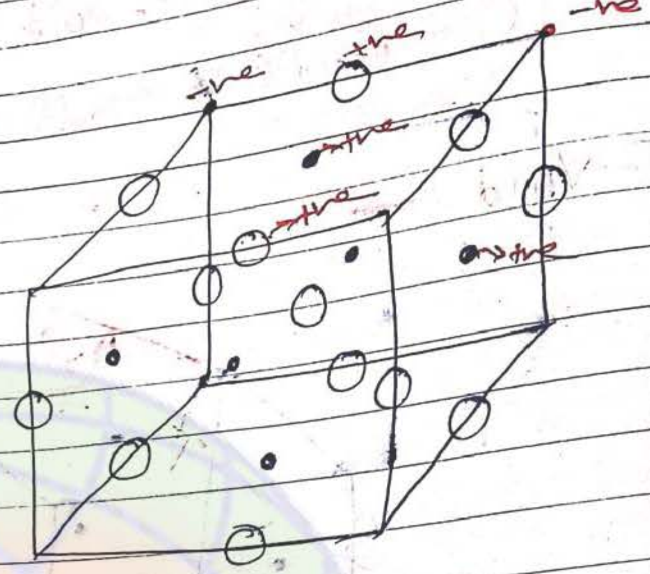
Per One body diagonal there are two T-void's

So,

Total no. of T-void's = "8"

Note:⇒ "$\frac{\sqrt{3}a}{4}$" is the distance b/w an octahedral and ~~tet~~ tetrahedral void in fcc lattice.

O-void's



$$\text{O-void} = \underbrace{12 \times \frac{1}{4}}_{\text{edgecentre}} + \underbrace{1 \times 1}_{\text{Body centre}} = 4$$

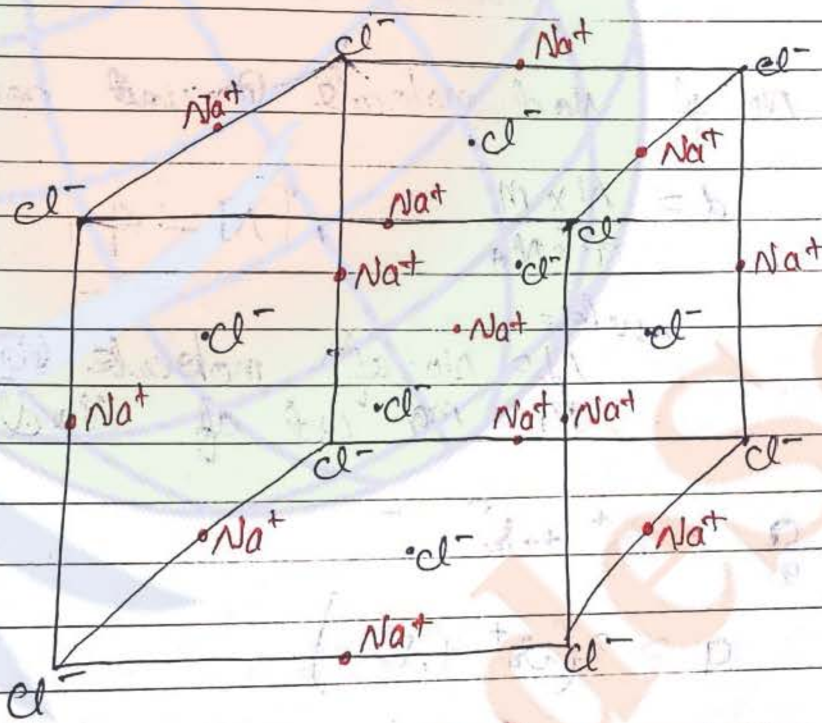
Study of Structure of different Ionic crystal's :→

NaCl में "Cl^-" FCC बनाता है और Na^+ octahedral void में fill होता है।

1) NaCl (Rock Salt Structure) →

या LiCl, KBr, RbI, AgCl, AgBr, MgO, CaO, TiO, NiO, SnAs, VC, SnS

$$0.414 < \frac{r^+}{r^-} < 0.732$$



1) Cl^- will form fcc unit cell

2) No. of Cl^- per unit cell $N_{Cl^-} = 4$ (Number of chloride ion)

3.) Na^+ will occupy all O-voids (To balance the charge)

4.) No of Na^+ per unit cell $N_{Na^+} = 4$

5.) C. No of $Na^+ = 6$

6.) C. No of $Cl^- = 6$

7.) 6:6 C.C
↳ coordination compound

8.) No. of NaCl molecule per unit cell "N = 4"

9.) $$d = \frac{N \times M}{a^3 \times N_A}, \quad \boxed{N = 4}$$

where
N = No. of molecule per unit cell
M = mol. wt of NaCl

10.) $$\frac{a}{2} = r^+ + r^-$$

$$a = 2(r^+ + r^-)$$

11.) $$\underset{6:6}{NaCl} \xrightarrow{P\uparrow} \underset{CsCl}{8:8}$$

Balance charge

12) No. of ion's w.r.t. Cl^-

	distance	No. of atom
Nearest	$a/2$	6
next	$a/\sqrt{2}$	12

13) No. of ion's w.r.t. Na^+

	distance	No. of atom
nearest	$a/2$	6
next	$a/\sqrt{2}$	12

14) Packing fraction :-

$$\eta = \frac{4\times\frac{4}{3}\pi r_+^3 + 4\times\frac{4}{3}\pi r_-^3}{a^3}$$

In general
where $a = 2\sqrt{2}r^-$

$\frac{r^+}{r^-} = 0.414$

In Ideal condition
जब कुछ नहीं दिया हो।

$$= \frac{\frac{16}{3}\pi\left(r_+^3 + r_-^3\right)}{16\sqrt{2}\,r_-^3}$$

$$= \frac{\pi}{3\sqrt{2}}\left(1+(0.414)^3\right)$$

$= 0.7934$ or 79.34%

15.) $\%$ void $= 100 - 79.34$

इन सबका 3-D visualisation, Shishir mittal में Page 1008 में अच्छी तरह दिखता है।

64

2.) CsCl → याद रखें ⇒ CsCl में Cl^- simple cubic बनाता है और "Cs^+" body centre पर होता है।

↳ CaS, TiSb, CsCN, CuZn

$$\boxed{0.732 < \frac{r^+}{r^-} < 1}$$

1) Cl^- will form S.C

2) No. of Cl^- per unit cell = 1

3) Cs^+ will occupy all cubical void

4) No. of Cs^+ per unit cell $N_{Cs^+} = 8 \times \frac{1}{8} = 1$

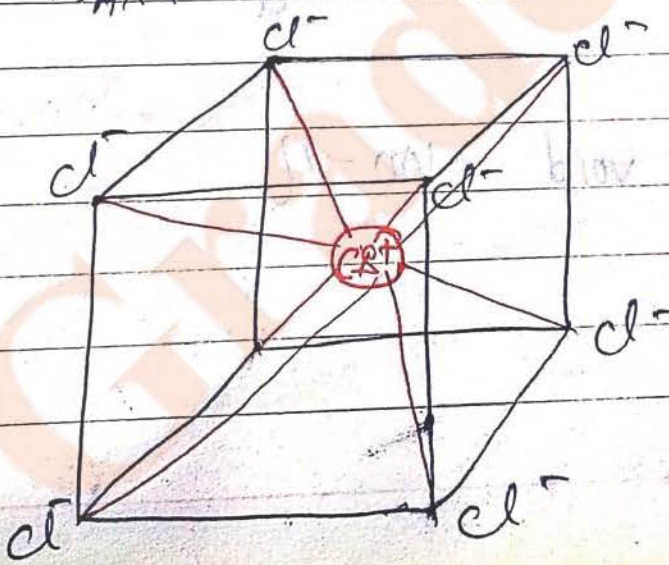
5) C. No. of Cs^+ = 8

6) C. No. of Cl^- = 8

7) 8 : 8 C.C

8) No. of CsCl per unit cell = 1

9) $d = \frac{N \times M}{N_A \times a^3}$, $\boxed{N = 1}$

10) 

10) $\boxed{\frac{\sqrt{3}\,a}{2} = (r^+ + r^-)}$

11) No. of ion's w.r.t. Cl^-

Nearest	$\sqrt{3}a/2$	8
next	a	6

12) No. of ion's Cs^+

nearest	$\frac{\sqrt{3}a}{2}$	8
next	a	6

13) $\underset{8:8}{CsCl} \xrightarrow{T\uparrow} \underset{6:6}{NaCl}$

14) $$\eta = \frac{1 \times \frac{4}{3}\pi r_1^3 + 1 \times \frac{4}{3}\pi r_2^3}{a^3}$$

15) % void $= 100 - \eta$

Zn

3.) $\overset{+2\ -2}{ZnS}$ (Zinc blend structure) →

→ CuCl, CdS, HgS, GaP, InAs

$$\boxed{0.225 < \frac{r^+}{r^-} < 0.414}$$

1) S^{-2} will form FCC

2) No. of S^{-2} per unit cell $= 8\times\frac{1}{8} + 6\times\frac{1}{2} = 1+3 = 4$

3) Zn^{2+} will occupy ~~all cubical void's~~ (half) alternate T-void's

4.) No. of Zn^{2+} per unit cell $N_{Zn^{2+}} = 4$

5) C. No. of $Zn^{2+} = 4$

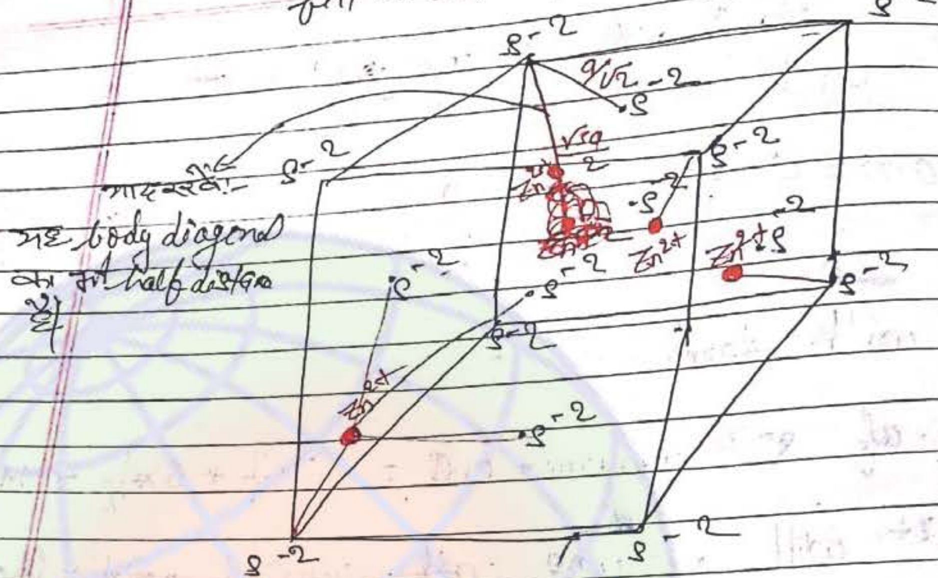
6) C. No. of $S^{-2} = 4$

7) 4 : 4 C.C

8.) No. of ZnS per unit cell = 4

9.) $d = \frac{N \times M}{a^3 \times N_A}$ $\boxed{N = 4}$

याद रखें ⇒ ZnS में (S^{-2}) FCC form करता है तो Zn^{2+} Half tetrahedal void को body के अंदर fill करता है।



10.) $\frac{\sqrt{3}a}{4} = r^+ + r^-$

11) No. of ion's w.r.t. S^{-2}

Nearest $\frac{\sqrt{3}a}{2}$ 4 → Attention

next $\frac{a}{\sqrt{2}}$ 12

12.) No. of ion w.r.t. Zn^{2+}

nearest $\frac{\sqrt{3}a}{4}$ 4 → Attention

next $\frac{a}{\sqrt{2}}$ 12

13.) $$\frac{4 \times \frac{4}{3}\pi r^3 + 4 \times \frac{4}{3} \times \pi r^3}{a^3}$$

$$\frac{r^+}{r^-} = 0.225$$

14.) $\eta = 100 - \eta$

$\boxed{\text{Note:} \Rightarrow \text{ZnS also form hcp structure.}}$

4.) CaF_2 (flourite structure)
↳ UO_2, $BaCl_2$, HgF_2, PbO_2

$$\boxed{0.225 < \frac{r^+}{r^-} < 0.414}$$

10.)

1.) ~~F_2^{2-} will form~~ Ca^{2+} will form FCC

11.)

2.) No. of Ca^{2+} per unit cell ⇒

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3 = 4$$

3.) F_2^- will occupy all T-voids

4.) No. of F_2^- per unit cell = 8

5.) C.NO $F^- = 4$

6.) C.NO $Ca^{2+} = 8$

7.) 8 : 4 C.C
cation anion

$$CaF_2 \quad 8 \quad 4 \quad 8$$

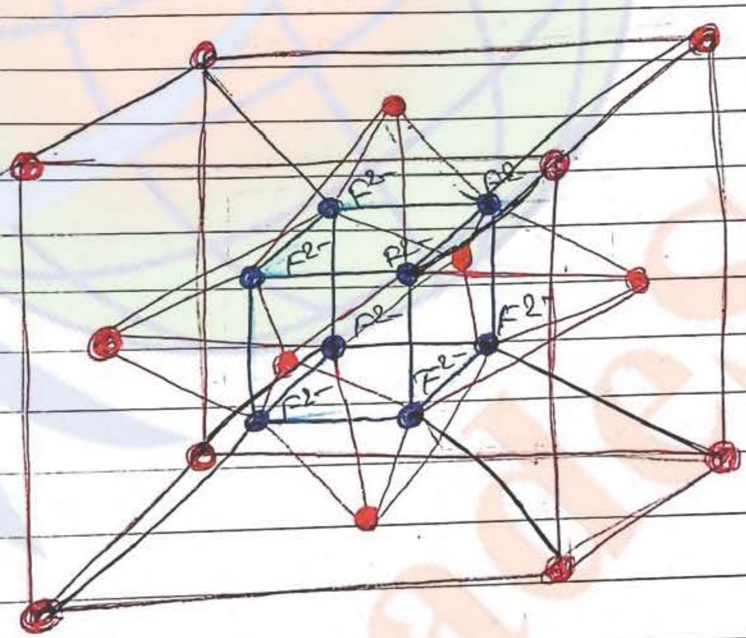
8.) No. of CaF_2 molecule per unit cell = 4

9.) $d = \frac{N \times M}{a^3 \times N_A}$ $\boxed{N = 4}$

10.) $\frac{\sqrt{3}a}{4} = r_+ + r_-$

11) $\eta = \frac{4\times\frac{4}{3}\pi r_+^3 + 8\times\frac{4}{3}\pi r_-^3}{(2\sqrt{2}\,r_+)^3}$

$\boxed{\frac{r^-}{r^+} = 0.225}$



● → Ca^{2+}

● → F_2^{2-}

अब यहाँ CaF_2 में Ca^{2+} FCC Structure बना रहा है और F^{2-} Ion simple cubic के रूप में body के अंदर है।

$\rightarrow K_2O, Na_2O, K_2S, Na_2Se, Na_2S$

5) Li_2O (Antifluorite Structure)

$$\boxed{0.225 < \frac{r^+}{r^-} < 0.414}$$

1) O^{-2} will form FCC

2) $N_{O^{-2}} = 4$

3) Li^+ will occupy all T-void's

4) $N_{Li^+} = 8$

5) C.No $Li^+ = 4$

6) C.No of $O^{-2} = 8$

7) 4:8 C.C

8) No. of Li_2O

याद रखें → Li_2O_1
$2\times 4 \quad 1\times 8$

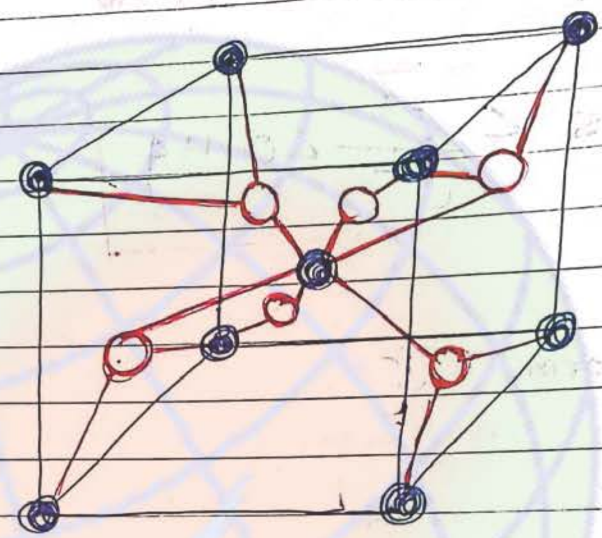
9) $d = \frac{N \times M}{a^3 \times N_A}$ $\boxed{N=4}$

10) $\frac{\sqrt{3}a}{4} = r^+ + r^-$

Note → The antifluorite structure is the Inverse of fluorite structure in the sense that the locations of cation and anion's are reversed.

6.) Rutile Structure (TiO_2) → MnO_2, SnO_2, WO_2, MgF_2, NiF_2

मात्र रहेंगे ⇒ Titanium (Ti) BCC



$$\boxed{0.414 < \frac{r^+}{r^-} < 0.732}$$

1) Ti^{4+} will form BCC Structure
2.) N Ti^{4+} = $8 \times \frac{1}{8} + 1 = 2$
3.) O^{2-} will

4.) No. of O_2 per unit cell = 6
5.) C.No. of Ti^4 = 6
6.) C.No. of O_2^{2-} = 3

7.) 6:3 C.C

$$TiO_2 \quad \left\{ \underset{1 \times 6}{Ti} \; \underset{2 \times 3}{O_2} \right.$$

6.) Diamond (Same as that of ZnS)

1) C will form FCC

2.) C will occupy all T-void

3.) $N_C = 8$

4.) $\frac{\sqrt{3}a}{4} = 2r = d_{C-C}$

5.) $\eta = \frac{8 \times \frac{4}{3}\pi r^3}{a^3} = \frac{8 \times \frac{4}{3}\pi r^3}{\left(\frac{8R}{\sqrt{3}}\right)^3} = 0.34$ or 34%

(imp) v.imp

Note! ⇒

7) Spine Structure →

$A\ B_2\ O_4$ → form of structure

Atom and charge: → $A \to +2$, $B_2 \to +3$, $O_4 \to -2$

eg: → $Zn\ Al_2O_4$, $Mg\ Al_2O_4$

- The spine structure, AB_2O_4, consist of an FCC array of O^{2-} ion in which the "A" cations occupy one eigth of the T-void and B-cation occupy O-voids.

Note →

Perovskite

$CaTiO_3$ → example of structure

$A\ B\ O_3$ → form of structure

$A \to +2$, $B \to +4$, $O_3 \to -6$

- eg: – $CaTiO_3$

In Perovskite structure:–

"A" form simple cubic

"B" is in BCC

"O" is in only face centre.

Defect's in Crystals (or Imperfection)

Page No. 8

This is also known as Atomic Imperfection or Point defects

Defect's (Ideal crystal) ⇒ 0°K

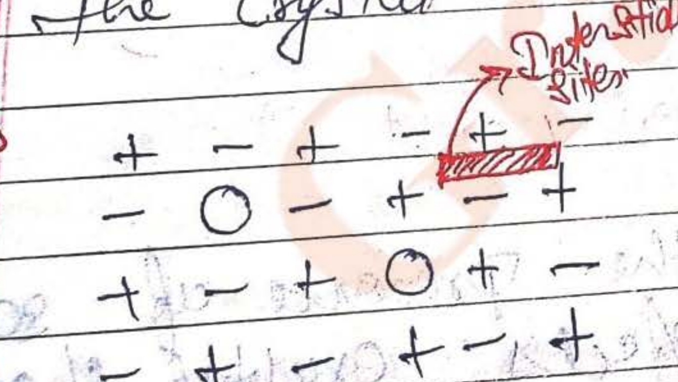
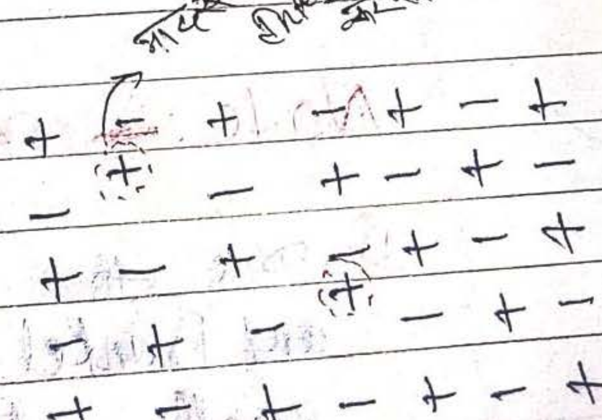
T↑ S↑ defect's↑

There are two types of defect's :-

i) Stoichiometry defect's
ii) Non-Stoichiometry defect.

1) Stoichiometry defect's

The defect in which the ratio of ~~anion~~ cation and anion as represented by the formula is known as Stiochiometry defects. There are two type's of Stoichiometry defect's →

i) Schottky (mean's short) याद रखें :- Don ने Short करना है	ii) Frenkel
1) In such type of defect equal no. of cation and anion are missing from the crystal.	1) In such type of defects cation's occupy Interstitial site. याद रखें cation (+ve) है Interstitial site occupy कर सकता है
2) 	2) 

3) Example: → NaCl, KCl, CsCl, CsBr (All are 1st group elements)	3) Eg: – ZnS, AgCl, AgBr, AgI
4) Found in those type of compound's which has high co-ordination number.	4) Found in those type of crystal's which have low value of co-ordination number
5) Found in those compound in which difference in size of cation and anion is less	5) Found in those crystal's in which difference in size of cation and anion is high
6) Crystal in which schotky deffect's are found have less density $\rho_{theoritical} > \rho_{experimental}$	6) Density of the crystal does not changes
7) $\%\ \text{missing site} = \frac{\rho_{theo} - \rho_{exp.}}{\rho_{theo}} \times 100$	

Note: → Common Point

1) Due to the presence of schotky and Frankel defect's crystal show small electric conductivity.

Solids Complete
sheet discussion
Date: Tuesday 8?

g) In "AgBr" crystal both Schottky and Frenkel are found.

2) Non-stoichiometry defect's →

1) Anion vacancy →

+ − + − + − +
− + (e⁻) + − + −
+ − + − + (e⁻) +
− + − + − + −

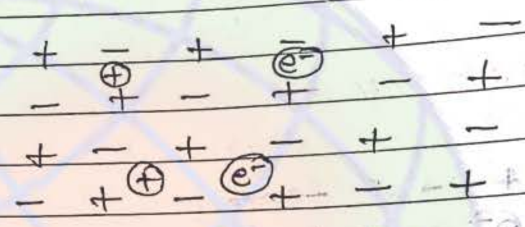
F-centre

a) Found in those type of crystal's which have Schottky defect's.
b) Due to the Presence of F-centre crystal is colourful in nature
c) As the number of F-centre Increases the Intensity of colour Increase.
d) extra charge is balanced by electron(e^-)

e) For example :→ excess of Sodium Ion in NaCl crystal makes the crystal yellow
excess of Potassium Ion in KCl crystal makes the crystal violet.

- excess of lithium Ion in LiCl crystal makes the crystal pink.

2) Extra cation occupy Interstitial sites →



a) Found in those type of crystal which have Frankel defects

b) Due to the presence of free electron (e^-) crystal will show less electrical conductivity.
Due to absorption spectrum; crystal is colourfull in nature.

c) examples → ZnO (yellow)

$$ZnO \xrightarrow{>850K} Zn^{+2} + O_2\uparrow + 2e^-$$

stoichiometric defects ← S.D (white)

N.S.D (yellow)

3.) Cation vaccancy (+ve) →

$+ \quad - \quad + \quad - \quad +^2 \quad -$
$- \quad O \quad - \quad + \quad + \quad -$
$+ \quad - \quad +^2 \quad - \quad + \quad -$
$- \quad + \quad - \quad O \quad - \quad +$

नोट ⇒ यदि "+ve" खाली हो जाएगा उसके स्थान पर ~~"+ve" charge आ जाएगा~~ क्योंकि तो कुछ -ve" charge अधिक हो जाएगा इस -ve charge को ballance करने के लिए कुछ +ve charge "square" हो जाएगा।

a) oxidation of some cation take's place to balance the -ve charge.

b) Examples ⇒ FeO, NiO, FeS

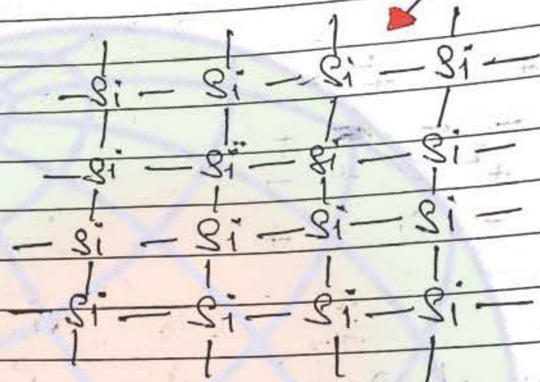
4.) Extra anion occupying Interstitial site →

This type of defect is non found in crystal.

The conductivity of pure silicon and germanium is very low at room temperature. The conductivity of silicon and germanium can be increased by adding appropriate amount of suitable impurity. The process is called doping.

Doping →

Impurity

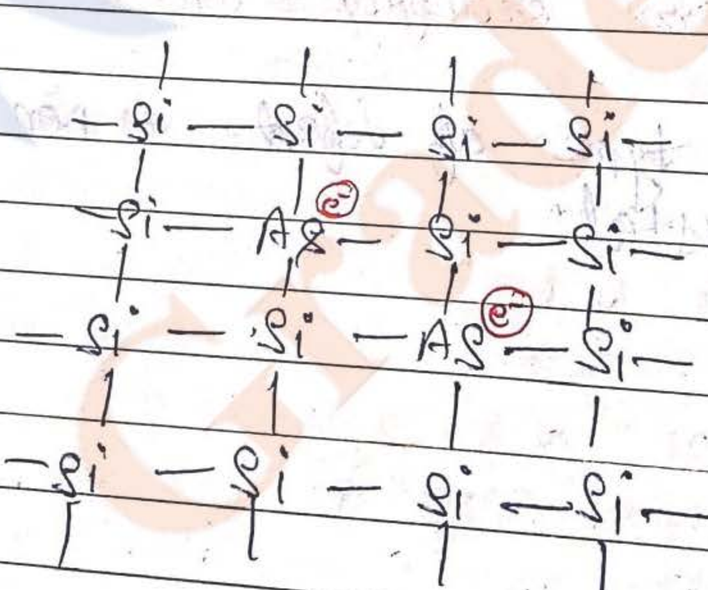


(Insulator) (group 14)

क्योंकि इसमें "n" और "p" नहीं है कुछ नहीं मिलता है

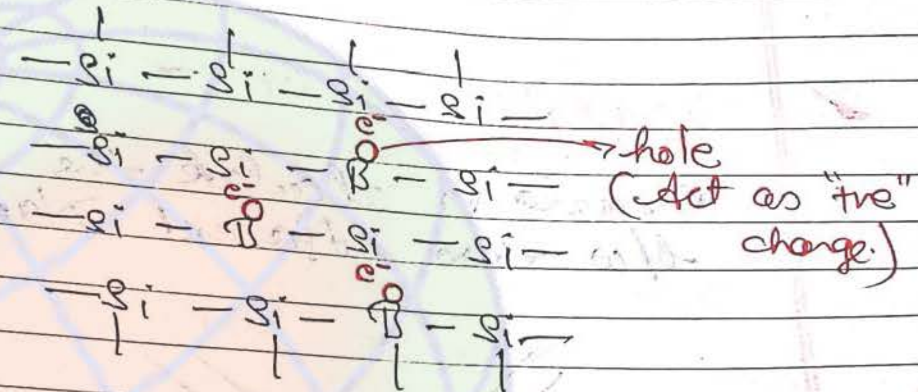
1) N-type Semiconductor →

By adding Impurity of higher group
eg. As (Arsenic)



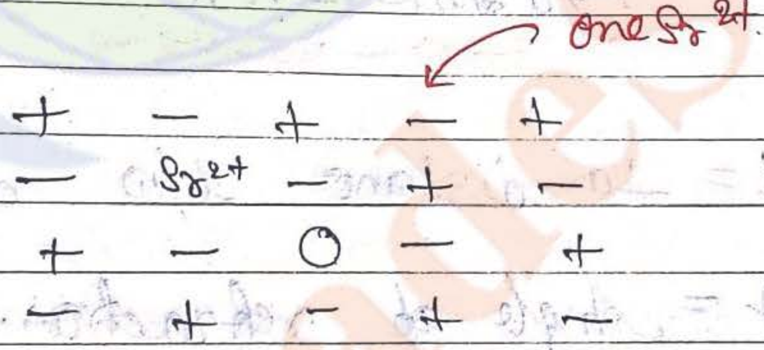
2) P-type semiconductor →

By Adding Impurity of lower group.
eg: → B, Al



[Q] If NaCl crystal doped with 10^{-3} mole% of Strontium chloride. Find the no. of cation vacancy

Sol^n



1 Sr^{+} creates one cation vacancy

10^{-3} mole % or 10^{-5} mole Sr^{+2} added

Sr^{2+} will create =

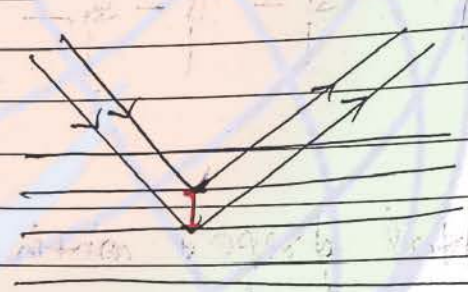
$10^{-5} \times N_A$ no. of ... $10^{-5} \times N_A$ no. of cation vacancy

$\frac{Br^{3}}{(2)} = \frac{96}{}$

$80|^{d}$

Bragg's equation →

Formula to calculate the ⊥ar distance b/w two adjacent plane.



$$\boxed{2d \sin\theta = n\lambda}$$

d = ⊥ar distance b/w adjacent plane

θ = Angle of refraction.

n ⇒ order of refraction

λ ⇒ wavelength of light Incident

Problem's based on non-stoichiometry defect.

(2013-06 [2]) The composition of a sample of coustite is $Fe_{0.93}O_{1.0}$. What percentance of Iron is present in the form of Fe (III)?

Sol^n

$Fe_{0.93}O$

+2 — +3

x — $0.93-x$

Total +ve = total −ve

$2x + 3(0.93 - x) = 2$

$x = 0.79$

$\% \; Fe^{+2} = \frac{0.79}{0.93} \times 100$

$= 84.95$

So,

% of Iron present in the form of Fe(III)

is $\Rightarrow (100 - 84.95)$

$\Rightarrow 15.05$

Problem's based on Bragg's equation →

(2011 Q-22 [2]) What will be the wavelength of X-rays which give a diffraction angle $(2\theta) = 16.80°$ for a crystal?

If the interplanar distance in the crystal is 0.200 nm and only first order diffraction is observed ($\sin 8.40 = 0.1461$)

Sol^n Given → $2\theta = 16.80$

so $\theta = 8.40$,

$d = 0.200$ nm

$n = 1$

Now, By using Bragg's equation —

$2d\sin\theta = n\lambda$

$2 \times 0.200 \times \sin 8.40 = 1 \times \lambda$

so,

$\lambda = (2 \times 0.200 \times 0.1461)$ nm

$= (0.400 \times 0.1461)$ nm

$= (0.05844)$ nm

$= 0.05844 \times 100$

N.G.A $= 5.84$ pm

DPFAF → डिपुक; फुका ~~[illegible]~~ अप्रव फिर ~~[illegible]~~

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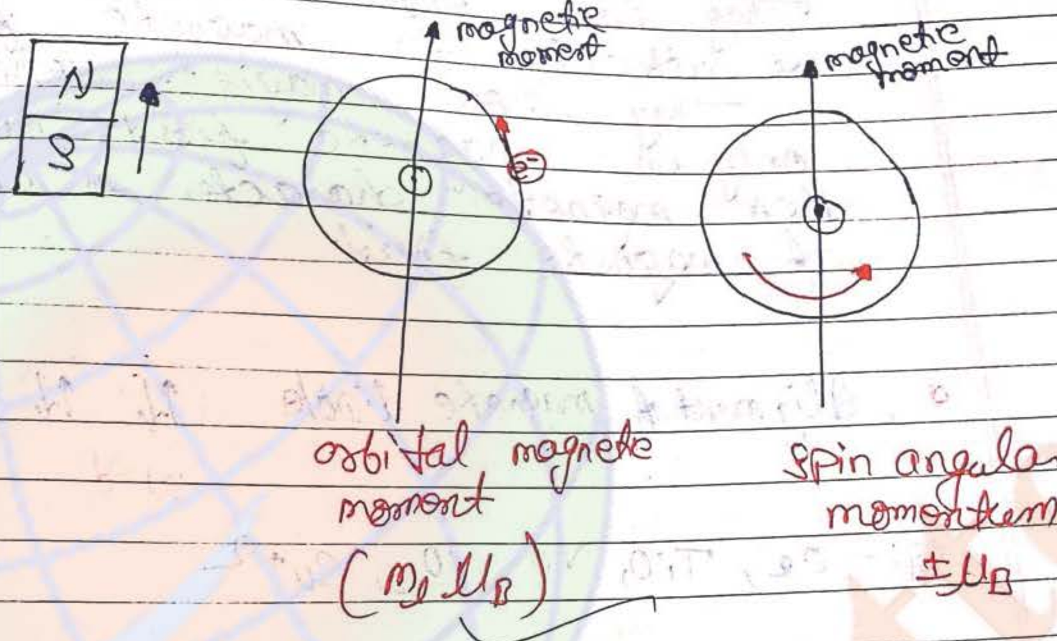
Date: / /

☆ magnetic Properties of Substance →



1) Dimagnetic →

Those substance which do not have unpaired e^- and are repelled in magnetic field are known as dimagnetic substance.

Alignment of magnetic dipole ⇅ ⇅ ⇅
Paired

eg: → TiO_2, NaCl, V_2O_5, C_6H_6

2) Paramagnetic substance →

They have unpaired "e⁻" Present and are attracted in magnetic field.
They show magnetic behavior only in magnetic field but loose their magnetic character in absence of magnetic field.

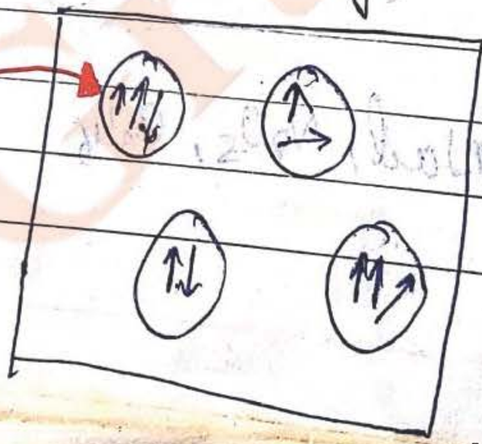
- Alignment of magnetic dipole (↑↓) (↑↓) ↑↑
paired

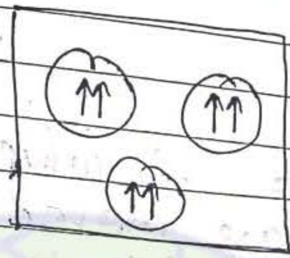
eg:- O_2, TiO, VO, VO_2, Cu^{+2}

3) Feromagnetic substance →

These substance have unpaired e^- and are strongly attracted by magnetic field.
but they do not loose their magnetic properties even in the absence of magnetic field.

Domain





Aligment of magnetic dipole ↑↑↑↑↑↑↑↑↑

eg: → Fe, Co, Ni, CrO_2

4) Antiferomagnetic substance →

These compound's have unpaired e^- but the aligment of magnetic dipole are such that the resultant magnetic moment are zero

Aligment of magnetic dipole ↑↓↑↓↑↓↑↓

eg: - MnO

5) Ferrimagnetic:-
Those substance in which no. of unpaired e^- are moved but magnetic dipoles are arranged in such a manner (Parallel and Anti-Parallel) the the net value of magnetic moment is less or non zero.

Alignment of magnetic dipole ↑↓↑↑↓↑↑↑↓↓

eg:- Fe_3O_4, $MgFe_2O_4$, $ZnFe_2O_4$

Formula to calculate the no. of Schottky defect present in the crystal containing "N" ion's at temperature "T".

$$n = N e^{-E/2kT}$$

Here, $n \Rightarrow$ No. of schotky defect
$N \Rightarrow$ Total no. of Ion's
$K \Rightarrow$ Boltzman Constant

$$\frac{R}{N_A} = \frac{8.314}{N_A}$$

$E \Rightarrow$ Energy required to produce Schocky defect.

Formula to calculate the number of Frankel defect present in a crystal at a temperatee "T", which contain's "N" Ion's and "Ni" number of Interstitial sites

$$n = \left(\frac{N}{N_i}\right)^{1/2} e^{-E/2kT}$$

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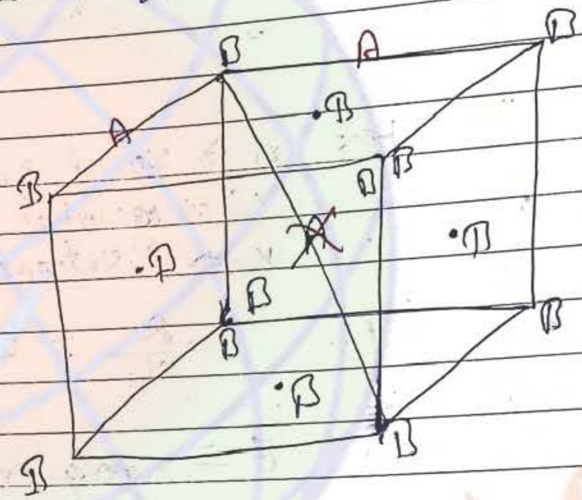
→ 5:00 PM to 7:00 PM

Ex) AB lattice is same as that of NaCl lattice. If the atoms lying on one of the body diagonal axis is removed. What would be the molecular formula of defective lattice.

Sol



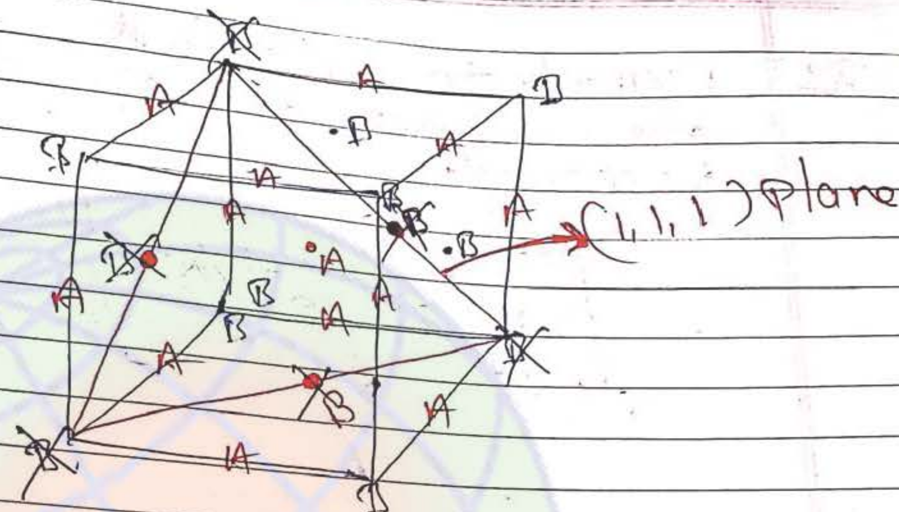
$$B_{6\times\frac{1}{8} + 6\times\frac{1}{2}} = \frac{15}{4}$$

$$A_{12\times\frac{1}{4}}$$

$$A_3 \quad B_{\frac{15}{4}}$$

$$\boxed{A_{12} B_{15}}$$ Ans

Q.



AB has the same lattice structure like that of NaCl. If the atom's lying on the plane are completly removed what would be the molecula formula of defective lattice.

80/

$A_4 \quad B_{3\times\frac{1}{2}+5\times\frac{1}{8}}$

$A_4 \quad B_{\frac{3}{2}+\frac{5}{8}}$

$A_4 \quad B_{17/8}$

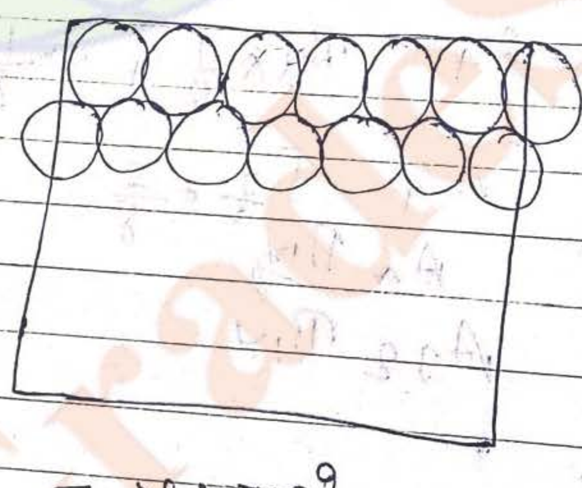
$A_{32}B_{17}$

☆ Formula to calculate fraction of ~~cc~~ ~~Sood~~ crystal the surface of the vacancies

$$\boxed{\frac{n}{N} = e^{-E/RT}}$$

Example - You ~~have~~ are given marbles of diameter 10mm. they are to be placed such that their centres are lying in a square bound by four lines each of length 40mm.
Find the maximum no. of marbles that can be placed ~~Inside this area~~ per unit area.

Sol^n



$$\eta = \frac{N \times \pi R^2}{area}$$

Now:

$$0.906 = \frac{N \times \pi R^2}{16}$$

$$0.906 = \frac{N \times 3.14 \times 0.25\,cm}{16}$$

$$N \Rightarrow \frac{16 \times 0.906}{0.25 \times 3.14}$$

$$\Rightarrow 18$$

start'

Chemical kinetics

Page No. 1
Date: / /

This chapter tell us about the rate of the chemical reaction, mechanism by which reaction is taking place and factor's affecting the rate of reaction.

* Types of reaction on the basis of rate →

1) Instantinious reaction or very fast reaction →
The reaction which get completed as shown as the reactant's are brought in contact with each other are known as Instantaneous reaction.
These reaction's are ionic in nature and ~~cation~~ the time required for the completion is very lone (10^{-14} to 10^{-16} seconds)

The rate of such reaction's can not be determined practically.

eg:-
(i) Precipitation Reaction-

$$AgNO_3 + HCl \rightarrow AgCl\downarrow + HNO_3$$

(ii) Nutilisation reaction

$$HCl + NaOH \rightarrow NaCl + H_2O$$

(iii) Redox Reaction

2.) very slow reaction →

The reaction which takes a very long time to show a considerable change in the concentration of reactant or Product are known as very slow reaction.

eg 1→ Rusting of Iron

eg 2→ $H_2 + O_2 \xrightarrow{\text{Room temperate}} H_2O(l)$

• ⇒ $C(s) + O_2(g) \xrightarrow{R.T} CO_2(g)$

• we can not

3) moderate reaction →

The Reaction which occure at measurable rate are known as moderate reaction's those reactions are molecular in nature and the rate of such reaction's can be determined Practically.

eg 1→
(i) Decomposition of H_2O_2

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

(ii) decomposition of N_2O_5

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

Hydrolysis of ester

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Rate of Reaction :→

$$\boxed{\text{Rate} = \frac{\text{change in some quantity}}{\text{Time required for the change}}}$$

There are two types of rate of reaction →

1) Average rate (r_{avg}) →

The rate of reaction in a particular time interval is known as average rate of reaction.

$$A \longrightarrow B$$

→ for A

$$r_{avg} = \frac{-\text{decrease in conc. of A}}{\text{Time required}}$$

यह भी +ve रहे आएगा -ve और -ve मिलकर +ve आएगा हो जाएगा।

$$= \frac{-\Delta[A]}{\Delta t} = \frac{-\Delta[A_f - A_i]}{\Delta t}$$

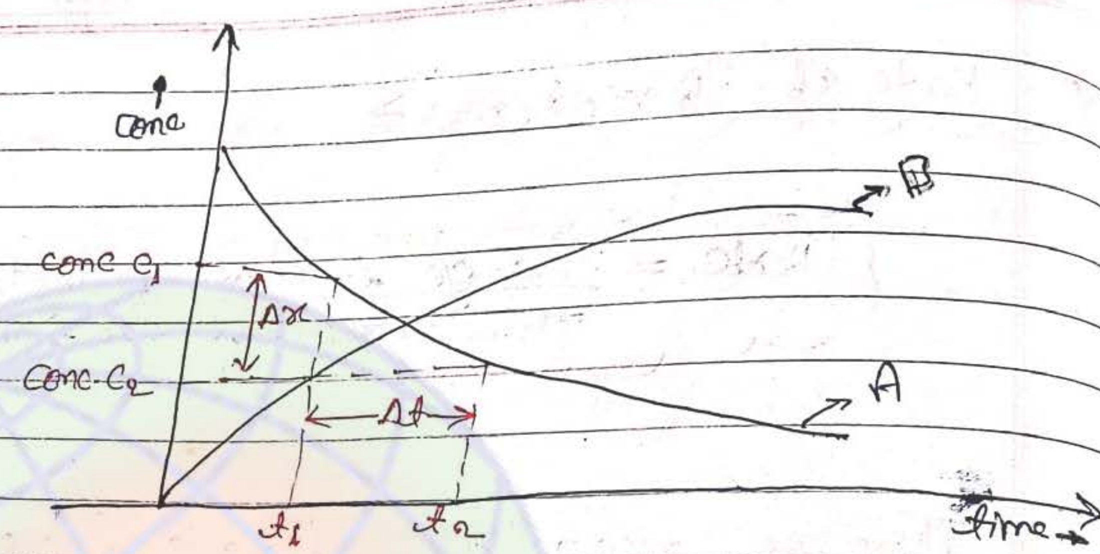
→ for B

$$r_{avg} = \frac{\text{Increase in concentration of B}}{\text{time required}}$$

→ final conc. of B
→ Initial conc. of B

$$= +\frac{\Delta[B]}{\Delta t} = \frac{\Delta[B_f - B_i]}{\Delta t}$$

(#) Rate can never be "-ve".



$$\boxed{\text{slope} = \frac{-\Delta x}{\Delta t} = r_{avg}}$$

RQ1

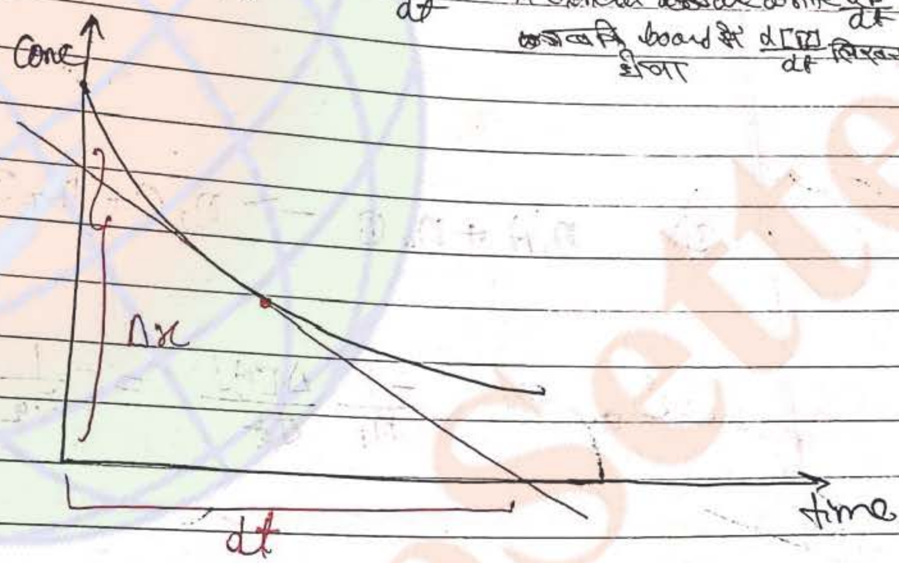
2) Instantinious rate →

The rate of reaction at the particular Instand is known as Instantinious reaction

$$r_{inst} = \lim_{\Delta t \to 0} -\frac{\Delta(A)}{\Delta t} = -\frac{d[A]}{dt}$$

$$r_{inst} = \lim_{\Delta t \to 0} +\frac{\Delta(B)}{\Delta t} = \frac{d[B]}{dt}$$

→ Board में [ ] है । It mean in General we write $\frac{dB}{dt}$ जबकि board में $\frac{d[B]}{dt}$ लिखना होगा



$$\boxed{Slope = \frac{-\Delta x}{\Delta t} = r_{inst}}$$

Notes →→

1) unit of rate of reaction — RQ1

$$r = \frac{mole/litre}{time} = mole\ litre^{-1}\ time^{-1}$$

$\Rightarrow$ mole lit^{-1} time^{-1}

$\Rightarrow$ mole lit^{-1} sec^{-1}

$\Rightarrow$ mole lit^{-1} min^{-1}

2.) $nA \longrightarrow B$

rate of reaction (r) :-

$$r = \frac{1}{n}\left\{\frac{-d[A]}{dt}\right\} = \frac{1}{n}\left\{\frac{-dA}{dt}\right\}$$

In board

Rate of disapperance of "A" (chemistry में ऐसे लिखते हैं)

3) $n_1A + n_2B \longrightarrow n_3C + n_4D$

$$r_{av} = \frac{-1}{n_1}\frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2}\frac{\Delta[B]}{\Delta t} = \frac{1}{n_3}\frac{\Delta[C]}{\Delta t} = \frac{1}{n_4}\frac{\Delta[D]}{\Delta t}$$

$$r_{inst.} = \frac{-1}{n_1}\frac{dA}{dt} = \frac{-1}{n_2}\frac{dB}{dt} = \frac{1}{n_3}\frac{dC}{dt} = \frac{1}{n_4}\frac{dD}{dt}$$

4)

$$r = \pm\frac{dc}{dt}$$

$$PV = nRT$$

$$P = \frac{n}{V}RT$$

$$P = CRT$$

$$\frac{dP}{dt} = \frac{dc}{dt} RT$$

$\frac{dP}{dt}$ → Rate of reaction (atm/sec)

$\frac{dc}{dt}$ → Rate of R^n (molarity/second)

5) $$r = \pm \frac{dc}{dt}$$

$$= \pm \frac{d}{dt}\left(\frac{n}{V}\right)$$

$$= \pm \frac{1}{V} \cdot \frac{dn}{dt}$$

6) $$PV = nRT$$

$$\frac{dP}{dt} \cdot V = \frac{dn}{dt} RT$$

$$\frac{dn}{dt} = \frac{V}{RT} \frac{dP}{dt} \Rightarrow \frac{dn}{dt} \cdot \frac{1}{V} = \frac{1}{RT} \frac{dP}{dt}$$

$$\because r = \pm \frac{1}{V} \frac{dn}{dt}$$

$$r = \pm \frac{1}{RT} \frac{dP}{dt}$$

Date: / /

7.) $2H_2O_2 \rightarrow 2H_2O + O_2$

$$-\cancel{\tfrac{1}{2}}\frac{dH_2O_2}{dt} = \cancel{\tfrac{1}{2}}\frac{dH_2O}{dt}$$

Rate of disapp. of H_2O_2 = Rate of appearance of H_2O

$$\frac{1}{2}\left\{-\frac{dH_2O_2}{dt}\right\} = \frac{dO_2}{dt}$$

$$-\frac{dH_2O_2}{dt} = \frac{2dO_2}{dt}$$

Rate of disappearance of H_2O_2 = 2 × rate of app. of O_2

(Important concept) VV imp

$2H_2O_2 \longrightarrow 2H_2O + O_2$

2gm/sec — rate of H_2O formation

$$\frac{dn\,H_2O_2}{dt} = \frac{dn\,H_2O}{dt}$$

सबसे पहले mass से रहे है उसे mole में change कर ले।

$$2/34 = \frac{dn\,H_2O}{dt}$$

$$\frac{dw_{H_2O}}{dt} = \frac{2}{34}\times 18$$

Factor's affecting the rate of reaction →

1) ~~Nature~~ Physical state of Reactant :->

Solid < liquid < gas

→ Rate of reaction

2) Concentration of reactant "↑" rate of Rxn "↑"

3) Temp of Reaction (Rxn) "↑" Rate of Reaction "↑"

4) Catalysis

→ +ve catalyst ; activation energy (E_A) ↓ rate of reactn ↑

→ -ve catalyst ; Activation energy (E_A) ↑ rate of reactn ↓

याद रखें :-> जो Rate of Rxn को बढ़ा देते हैं उन्हें +ve catalyst कहते हैं।

5) Lesser is the no. of bond's to be broken and lesser is the bond dissociation energy more will be the rate of reaction.

अधिक bond तोड़ना होगा तो bond dissociation energy भी अधिक होगा

(No. of bond's to be broken & bond dissociation energy $\propto \frac{1}{\text{Rate of reaction}}$)

6) As the surface area of the reactant increase, the rate of Reaction increases.

(Surface area of reactant $\propto$ rate of Reaction)

7) Effect of Radiation :-> (only applicable for photochemical Reaction)

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

Note →

1) Rate of Reaction $\propto \dfrac{1}{\text{Activation energy}}$

2.)

Rate law and Rate law expression →

Expressing the rate of reaction in terms of concentration of reactant is known as rate law.

It is an experimentally determined quantity.

$$aA + bB \longrightarrow \text{Product}$$

$$r \propto [A]^a [B]^b$$

Rate law expression → $\boxed{r = K [A]^a [B]^b}$ → on the base of law of mass action

Here

$K \Rightarrow$ Rate constant/velocity constant

- If $[A] = [B] = 1\,M$

$$\boxed{r = K}$$

specific reaction rate

- Rate of reaction at unit concentration of reactant is known as "Specific Reaction Rate".

Note →

1) The value of rate constant ("K") does not depend's upon concentration of reactant

ant as long as temp. remain constant, the value of rate constant (K) remain constant.

$\boxed{K \propto Temp.}$

Rate constant/vel. const

नोट ⇒ याद रखे।

Rate of Reaction जो है वह temp. बढ़ाने से समानुपात में बढ़ता और Conc. बढ़ाने पर बढ़ता है
लेकिन Rate constant/vel. constant temp. बढ़ाने पर बढ़ता है लेकिन Conc. का कोई भी effect नहीं पड़ता है।

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★ molecularity of Reaction →

1.) For a single step reaction or elementary reaction → molecularity is equal the total no of reactant molecules taking part in a balanced chemical reaction.
(molecularity = No. of reactant molecules)

eg:→ Elementary reaction –

$\underbrace{PCl_5}_{1\ molecule} \rightarrow PCl_3 + Cl_2$, molecularity = 1
(Unimolecular Reaction)

$\underbrace{2HI}_{2\ molecule} \rightarrow H_2 + I_2$; (molecularity = 2)
(Bimolecular reaction)

$\underbrace{\underbrace{2SO_2}_{2\ molecule} + \underbrace{O_2}_{1\ mole}}_{3\ molecule} \rightarrow 2SO_3$; molecularity = 3
(Trimolecular reaction)

2.) For complex reaction or multistep reaction molecularity is equal to the total no. of reactant molecules taking part in slowest step (or Rate determining step) of the reaction

eg:→ $2H_2O_2 \rightarrow 2H_2O + O_2$

इस तरह से exam में दिया रहेगा — mechanism:→ $H_2O_2 \rightarrow H_2O + O$ (slow) — Rate determin rate
$O + O \rightarrow O_2$ (fast)

molecularity = 1 (याद रखें – molecularity Rate determining step or slow step से पता होता। fast से पता नहीं चलता है)

Note ⇒

1) molecularity of reaction is a theoritical concept.

2) molecularity of reaction can not have zero, -ve, fractional, Infinite and Imaginary value. (molecularity of reaction only have natural number → 1, 2, ...)

theoritical है। [illegible] phenomena [illegible]

molecularity of reaction can not have value greater than "three" (3)

H.W & sheet करो
D.P.P & neet

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Date: / /

Order of reaction

It is an experimently determined quantity and it is equal to the sum of powers of concentration term involved in rate law expression.
(order of reaction = sum of powers of concentration)

$$aA + bB \longrightarrow \text{Product}$$

By experiment →

$$\boxed{r = K[A]^n[B]^m}$$

Order of Reaction = $n+m = a+b$
or $\neq a+b$

(m+n और a+b equal हो सकते हैं और नहीं भी हो सकते हैं)

Note ⇒

1) order of reaction can have value greater than "3".

2) order of reaction can be zero, -ve, fractional but infinite and imaginary value are not possible.

or (order of reaction can have rational number, -ve, 0, +ve, fraction)

नोट :- molecularity एक theoritical concept है लेकिन order of reaction एक experimental concept है इसलिए ये समान है।

1) Pseudo order Reaction ⇒

$$A + 2B + 3C \rightarrow \text{Product}$$
(excess)

~~Rate~~ $\cancel{r = K[A]^1[B]^2[C]^0}$

$$r = K[A]^1[B]^2[C]^0$$

(order = 3)

The reaction whose order is found to be different when ~~dd~~ derived using rate law expression, is known as pseudo order reaction.

☆ some Important examples ⇒

Ex.1) The decomposition of N_2O_5 is given by the equation N_2O_5 is changing into $2NO_2 + \frac{1}{2}O_2$

If during the certain time interval the rate of decomposition of N_2O_5 is 1.8×10^{-3} mole/litre min

what will be the rate of formation of NO_2 and O_2 in same time Interval.

Sol^n

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

$$r = 1.8 \times 10^{-3} \text{ mole/litre minute}$$

$$\frac{-dN_2O_5}{dt} = 1.8 \times 10^{-3}$$

$$\frac{-dN_2O_5}{dt} = \frac{1}{2}\frac{dNO_2}{dt}$$

So

$$\frac{dNO_2}{dt} = 2 \times \left\{\frac{-dN_2O_5}{dt}\right\}$$

$$= 2 \times 1.8 \times 10^{-3}$$

$$= 3.6 \times 10^{-3}$$

Now

$$\frac{-dN_2O_5}{dt} = 2\frac{dO_2}{dt}$$

So,

$$\frac{dO_2}{dt} = \frac{1}{2}\left\{\frac{-dN_2O_5}{dt}\right\}$$

$= \frac{1}{2} \times 1.8 \times 10^{-3}$

$= 0.9 \times 10^{-3}$

Ex 2.) NH_3 and O_2 reacts at high temperature as

$NH_3 + 5O_2 \longrightarrow NO + H_2O$

in an experiment the concentration of NO Increases by 1.08×10^{-2} mole/litre in 3 second calculate

i) rate of reaction

ii) rate of disappearance of NH_3

iii) rate of formation of H_2O

Sol^n

$\frac{dNO}{dt} = 1.08 \times 10^{-2}$

$t = 3$ sec

Attention :→ Examiner अक्सर Unballance eq^n देता है। इस तरह के case में आप उस eq^n को देखें यदि unballance होगा तो सबसे पहले ballance कर लें।

First ballance the reaction.

$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$

Ans

i) 3×10^{-4}

ii) 3×10^{-4}

iii) 5.4×10^{-4}

$\frac{d[NO]}{dt} = \frac{\overset{36}{\cancel{108}} \times 10^{-2}}{\cancel{3}\ sec \times 100}$

$= 3.6 \times 10^{-4}$

$$r = \frac{1}{4} \times \frac{dNO}{dt} = 9\times10^{-4}$$

ii) None

$$\frac{1}{4}\left[\frac{-dNH_3}{dt}\right] = \frac{1}{4}\frac{dNO}{dt}$$

$$\frac{-dNH_3}{dt} = 9\times10^{-4}\times4$$

$$= 36\times10^{-4}$$

iii) self solve

$$\frac{1}{6}\left[\frac{dH_2O}{dt}\right] = \frac{1}{4}\frac{dNO}{dt}$$

$$\frac{dH_2O}{dt} = 6\times 9\times10^{-4}$$

$$= \cancel{56\times10^{-4}} \Rightarrow 54\times10^{-4}$$

$$\frac{dP}{dt} = \frac{dC}{dt} RT$$

$$\frac{dC}{dt} = \frac{dP}{dt} \times \frac{1}{RT}$$

$$= \frac{2-1}{50 \times 60} \times \frac{1}{0.821 \times 298}$$

$$\frac{2-1}{50 \times 60} = \frac{dc}{dt} \times 0.821 \times 298$$

Q6. For the reaction

$$2NH_3 \rightarrow N_2 + 3H_2$$

$$\frac{-d[NH_3]}{dt} = K_1 [NH_3]$$

$$+\frac{dN_2}{dt} = K_2 [NH_3]$$

$$+\frac{dH_2}{dt} = K_3 [NH_3]$$

find the relation b/w K_1, K_2 and K_3

Ans $\boxed{3K_1 = 6K_2 = 2K_3}$

Sol^n ~~$\frac{1}{2} K_1 [NH_3] = K_2 [NH_3] = \frac{1}{3} K_3 [NH_3]$~~

$$-\frac{1}{2}\frac{dNH_3}{dt} = \frac{dN_2}{dt} = \frac{1}{2}\frac{dH_2}{dt}$$

$$\frac{1}{2} K_1 [\cancel{NH_3}] = K_2 [\cancel{NH_3}] = \frac{1}{3} K_3 [\cancel{NH_3}]$$

Now multiply each term by 6

$$3K_1 = 6K_2 = 2K_3$$

[Q7] For the following reaction

$$xA \longrightarrow yB$$

$$\log\left[\frac{-dA}{dt}\right] = \log\left[\frac{dB}{dt}\right] + 0.3$$

find $x:y$.

a) 2:1 b) 1:2 c) 2:3 d) 1:3

So^n $$\frac{1}{x}\left[\frac{-dA}{dt}\right] = \frac{1}{y}\left[\frac{dB}{dt}\right]$$

$\boxed{\text{Ans } 1:2}$ (a)

$$-\frac{dA}{dt} = \frac{x}{y}\frac{dB}{dt}$$

$$\log\left[\frac{-dA}{dt}\right] = \log\frac{dB}{dt} + \underbrace{\log\frac{x}{y}}_{0.3}$$

$$\log\frac{x}{y} = 0.3$$

$$\frac{x}{y} = (10)^{0.3}$$

(Q8) For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$

rate of reaction $= 10^2[N_2][H_2]^3 - 10^{-3}[NH_3]^2$

$\left(r \text{ or } \frac{dx}{dt}\right)$

find the value of equillibrium constant 'k'.

Sol^n $r_f = K_f[N_2][H_2]^3$ (forward, backward; f, b)

$r_b = K_b[NH_3]^2$

at eq, $\because r = \underbrace{10^2}_{K_f}[N_2][H_2]^3 - \underbrace{10^{-3}}_{K_b}[NH_3]^2$

$r_f - r_b = 0$

$r = K_f[N_2][H_2]^3 - K_b[NH_3]^2$

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$$K_a = \frac{K_f}{K_b} = \frac{10^2}{10^{-3}} = 10^5 \text{ Ans.}$$

Eg.) The experimental data for the reaction

$$2A + B_2 \longrightarrow 2AB$$

[A]	[B]	Rate
0.5	0.5	1.6×10^{-4}
0.50	1.00	3.2×10^{-4}
1.00	1.00	3.2×10^{-4}

find order of Reaction?

Sol/ⁿ

$\cancel{1.6 \times 10^{-4} = k}$

$$r = K [A]^x [B_2]^y$$

$$1.6 \times 10^{-4} = K [0.5]^x [0.5]^y \quad \text{—(i)}$$

$$3.2 \times 10^{-4} = K [0.5]^x [1]^y \quad \text{—(2)}$$

$$3.2 \times 10^{-4} = K [1]^x [1]^y \quad \text{—(3)}$$

Here

from eq ① ÷ eq ②

$$\frac{\cancel{1.6\times10^{-4}}}{\cancel{3.2\times10^{-4}}} = \frac{\cancel{K}\,\cancel{[0.5]^{x}}\,[0.5]^{y}}{\cancel{K}\,\cancel{[0.5]^{x}}\,[1]^{y}}$$

$$\frac{1}{2} = \frac{[0.5]^{y}}{[1]^{y}}$$

~~now~~ $\frac{1}{2} = \left[\frac{05}{10}\right]^{y}$

$$\left(\frac{1}{2}\right) = \left(\frac{1}{2}\right)^{1}$$

so,

$y = 1$

from eq ② & eq ③

$x = 0$, we get

$r = K [A]^0 [B_2]^1$

w.r.t. A order = 0

w.r.t. B_2 order = 1

overall order = 1

☆ Unit of Rate constant "K" ⇒

Rate constant or vel. constant

$$K = \left(\frac{1}{conc}\right)^{n-1} sec^{-1} \equiv \left(\frac{mole}{litre}\right)^{1-n} sec^{-1}$$

Here

n = order of Reaction

eg:→

Zero order of Reaction, n = 0

$$K = \left(\frac{1}{conc}\right)^{-1} sec^{-1}$$

First order of Reaction, n = 1 → $K = sec^{-1}$

$$K = \left(\frac{litre}{mole}\right)^{-1} sec^{-1}$$

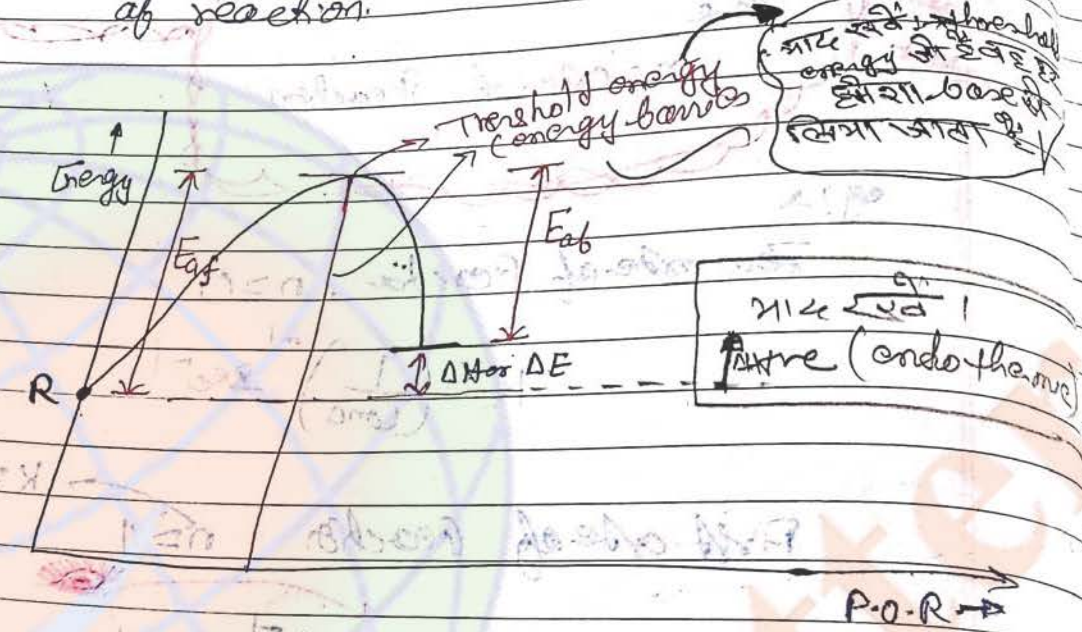
$$= mol\ litre^{-1} sec^{-1}$$

Note ⇒

From the unit of "K" we can find the order of reaction

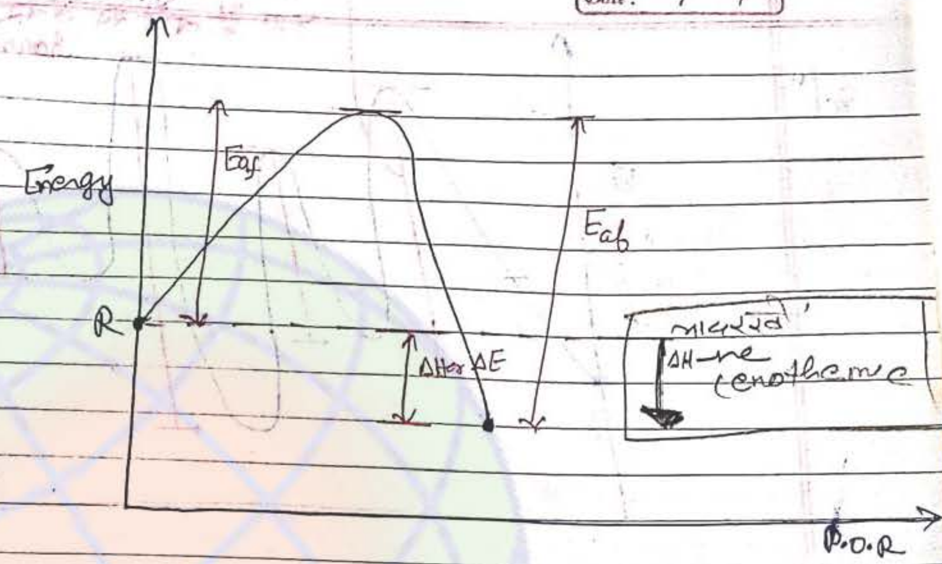
Activation energy (E_a)

Greater is the value of activation energy for a given reaction less will be the rate of reaction.



Endothermic reaction

$\Delta E = E_{a_f} - E_{a_b}$ or $E_P - E_R$ } ⇒ the इस लिए मात्र सबसे जिसमें Product ऊपर ही बन जाता है। वह endothermic curve है। क्योंकि ($E_{af} - E_{ab}$)



Exothermic Reaction.

$$\left.\begin{array}{l}\Delta E \text{ or } \Delta H = E_{af} - E_{ab} \\ \quad\quad \text{or} \\ \quad\quad E_P - E_R\end{array}\right\} \Rightarrow -ve$$

Q. For a Reaction (ΔH = –ve)

mech :-

$A \longrightarrow B$	(slow)	($E_a \uparrow$)
$B + C \longrightarrow B + D$	(fast)	($E_a \downarrow$)
$D \longrightarrow E + F$	(slow)	($E_a \uparrow$)
$F \longrightarrow G$	(fast)	($E_a \downarrow$)

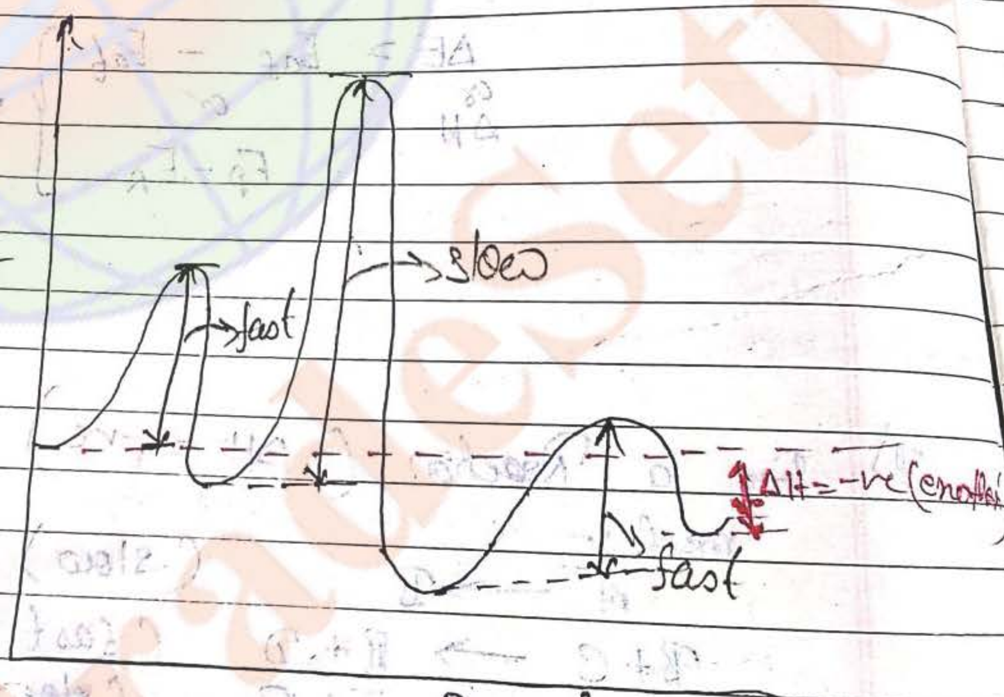
80/4 एक concept याद रखें → जब Activation energy (E_a) अधिक होगा तब reaction slow होगा और vice versa. इसका उल्टा भी कह सकते हैं कि जब reaction slow होगा तब E_a अधिक होगा।

fd, S, f, Endo

नोट:>> इसे यह सही देखना है (अर्थात Ea देखना है) मतलब graph जहाँ से ऊपर जा रहा है वहाँ से लेकर max. energy barrier तक देखना

80/4

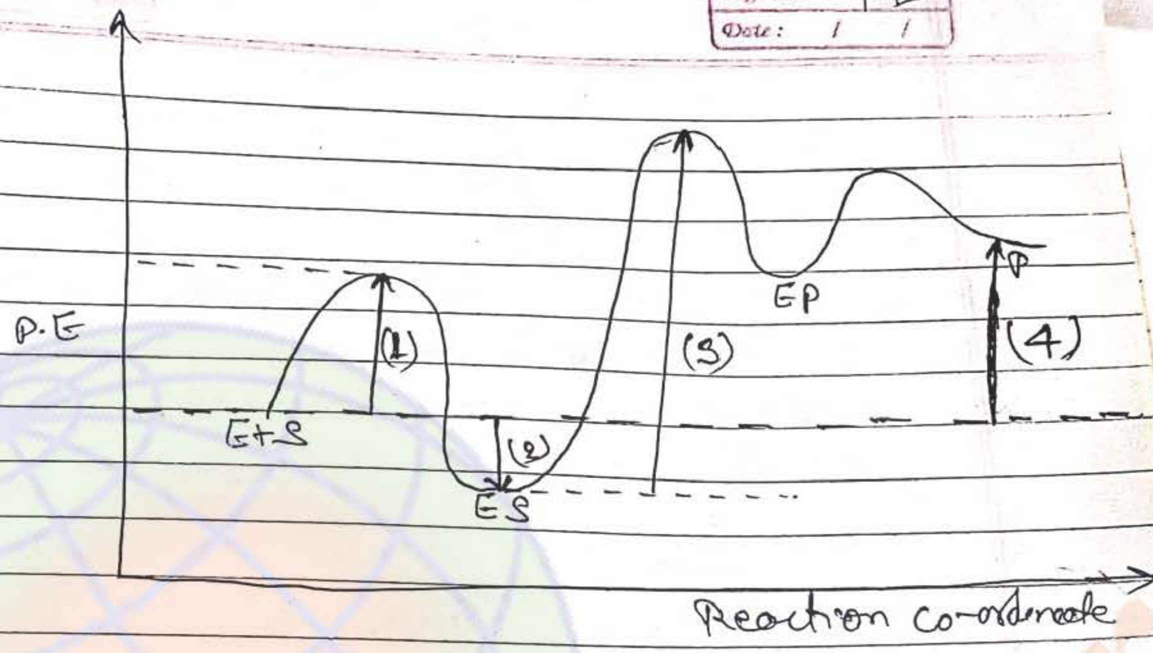
Ex-2 Q.16



(80, option A)

Exp 2

[illegible]17



(1)	(2)	(3)	(4)
E_a for	ΔE for	E_a for	$\Delta E_{overall}$ for
$E+S \rightarrow ES$	$E+S \rightarrow ES$	$ES \rightarrow EP$	$E+S \rightarrow P$

Zero order reaction

1) The reaction whose rate is directly proportional to zero power of concentration term is known as zero order reaction

2)
$$A \longrightarrow \text{Product}$$

$$r = K[A]^0$$

$$\boxed{r = K}$$

Since rate of reaction is "Independent" of concentration of reactant's therefore zero order reaction occur's at constant rate or average rate.

3)
$$A \longrightarrow \text{Product}$$

$t=0$ $\quad C_0$

$t=t$ $\quad C_t$

Now

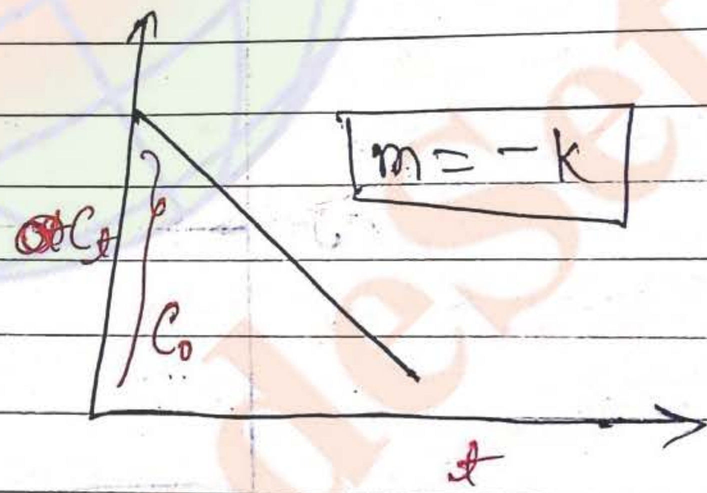
$$r = -\frac{[C_t - C_0]}{t}$$

$$k = \frac{-C_t + C_0}{t}$$

$$\boxed{C_t = C_0 - kt}$$

C_t: Conc. of reactant at any time "t"

C_0: Initial conc. of reactant.



$$\boxed{m = -k}$$

4) Amount of Reactant that get Converted into Product at time "t".

$$A \longrightarrow \text{Product}$$

$t=0$ $\quad a$ or C_0

$t=t$ $\quad (a-x)$ or C_t

$$r = K[A]^0_t$$

$$\frac{-d(a-x)}{dt} = K(a-x)^0$$

$$\boxed{\frac{dx}{dt} = K = K[A]^0}$$

$$\cancel{\int \frac{dx}{dt} = K}$$

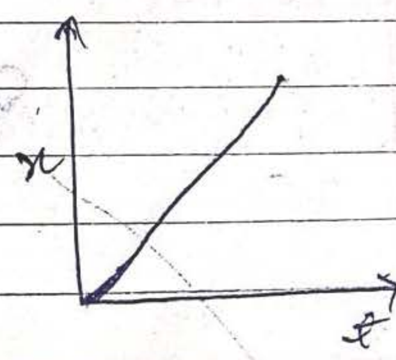
$$\int dx = K\int dt$$

$$\boxed{x = Kt + C}$$

$t=0$, $x=0$, $C=0$

$$\boxed{x = Kt}$$

Amount of reactant that get converted into product



5) Time required for completition of Zero order order reaction →

For Zero order reaction

$$C_t = C_0 - Kt$$

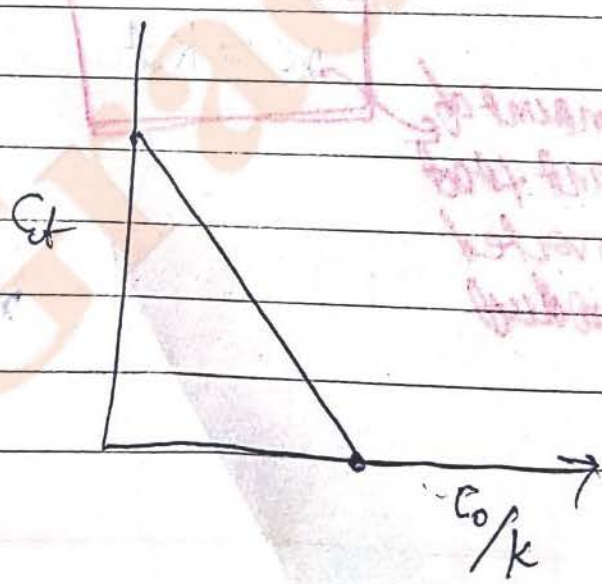
$$A \longrightarrow \text{Product}$$

$t = 0$	4m	a or C_0
$t = 10s$	3m	
$t = 20s$	2m	
$t = 30s$	1m	C_t
$t = 40s$	0m	

$t = t_{comp}$ $\quad C_t = 0$

$$0 = C_0 - K t_{comp}$$

$$\boxed{t_{completion} = \frac{C_0}{K}}$$



6.) Half life of Zero order reaction

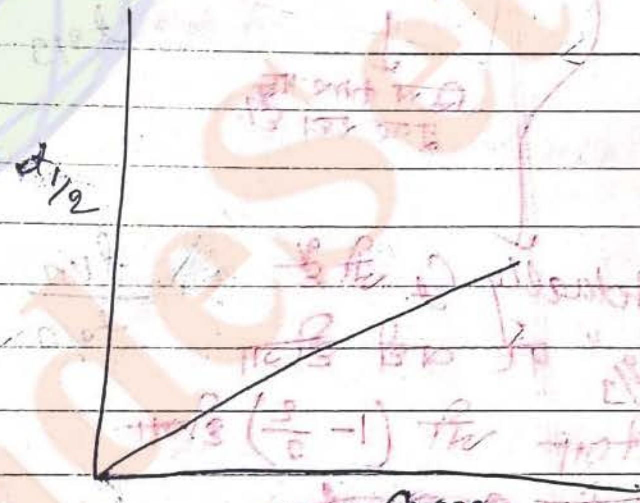
"The time in which concentration of the "reactant" becomes half of it's initial concentration is known as half life of the reaction.

$t = t_{1/2}$ $\quad C_t = \frac{C_0}{2}$

$$\frac{C_0}{2} = C_0 - K\, t_{1/2}$$

$$\boxed{t_{1/2} = \frac{C_0}{2K}}$$

$t_{1/2}$



7.) Q) $\frac{t_{1/3}}{t_{2/3}}$

$t_{1/3} \Rightarrow C_t = C_0 - Kt$

(याद रखें → C_t में changing हो रहा है C_0 में नहीं)

$\frac{2}{3}C_0 = C_0 - Kt_{1/3}$ → लेकिन मात्र time में कोई change नहीं होगा time तो समान रहेगा

$\boxed{\left(1-\frac{1}{3}\right)=\frac{2}{3}}$

(जिस time पर पूछ रहा है)

$t_{1/3} = \frac{C_0 - \frac{2C_0}{3}}{K}$

$= \frac{C_0}{3K}$

$t_{2/3} \Rightarrow C_t = C_0 - Kt$

$\frac{1}{3}C_0 = C_0 - K\,t_{2/3}$

$\boxed{\left(1-\frac{2}{3}\right)=\frac{1}{3}}$

जिस time पर पूछ रहा है

$t_{2/3} = C_0 - C_{0/3} / K$

$= \frac{2C_0}{3K}$

Actually C_t जो है "$t_{2/3}$" पर वही होगा होगा जो $\left(1-\frac{2}{3}\right)$ होगा

अर्थात ~~Conc~~

Conc. at time "t" is $\frac{1}{3}$ of Initial Concentration (C_0)

$\frac{t_{1/3}}{t_{2/3}} = \frac{C_0/3K}{2C_0/3K} = \frac{1}{2}$

b) $\frac{t_{3/4}}{t_{1/4}} = \frac{3}{1}$

c) $\frac{t_{50\%}}{t_{75\%}} = \frac{2}{3}$

d) $\frac{t_{25\%}}{t_{50\%}} = \frac{1}{2}$

$t_{25\%} \Rightarrow C_t = C_0 - kt$	$t_{50\%} \Rightarrow C_t = C_0 - kt$
$\boxed{100-25 = 0.75} \rightarrow 0.75\,C_0 = C_0 - Kt_{0.25}$	$0.50C_0 = C_0 - Kt_{0.50}$
$\frac{75}{100}C_0 - C_0 = -K\,t_{25\%}$	$\frac{50}{100}C_0 - C_0 = -Kt_{50\%}$
$\cancel{-}\frac{25}{100}C_0 = \cancel{-}K\,t_{25\%}$	$\cancel{-}\frac{50}{100}C_0 = \cancel{-}Kt_{50\%}$
$t_{25\%} = \frac{25C_0}{100K}$	$t_{50\%} = \frac{50C_0}{100K}$

Now

$$\frac{t_{25\%}}{t_{50\%}} = \frac{\cancel{25}C_0}{100K} \times \frac{100K}{50C_0}$$

$$= \frac{1}{2}$$

8) Examples of Zero order Reaction (याद होना चाहिए)

a) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

b) $2HI(g) \xrightarrow{Au} H_2(g) + I_2(g)$

c) $2NH_3(g) \xrightarrow{W/Mo} N_2(g) + 3H_2(g)$

For above reaction experimentally determined law →

$$r = \frac{K_1[NH_3]}{1 + K_2[NH_3]} \quad \{K_1 \text{ and } K_2 << 1\}$$

Case 1st → " ↓ "

$K_2[NH_3] <<< 1$

$r = K_1[NH_3]^1$ → 1st order Reaction

Case 2nd → " ↑ "

$K_2[NH_3] >>> 1$

$$r = \frac{K_1\cancel{[NH_3]}}{K_2\cancel{[NH_3]}} = \frac{K_1}{K_2}[NH_3]^0$$ → Zero order Reaction

9.) $3A \longrightarrow$ Product , Zero order , find $t_{1/2}$

$$r = K[A]^0$$

$$\frac{1}{3}\frac{dx}{dt} = K[A]^0$$

$$\int dx = 3K\int dt$$

$$\boxed{x = 3Kt}$$ $x = nKt$

$$C_t = C_0 - 3Kt$$

$$t = t_{\frac{1}{2}} , \quad C_t = \frac{C_0}{2}$$

$$\boxed{t_{1/2} = \frac{C_0}{6K}}$$ or $t_{1/2} = \frac{C_0}{2nK}$

Imp 80,

In General! –
$nA \longrightarrow$ Product , Zero order

$$\boxed{C_t = C_0 - nKt}$$ → लेकिन याद रखेंगे ~~यहा~~ formula ~~को~~ ~~कोई~~ derive ही जाएगा। ("t" भी इतना ही रहा है।)

10.)

$$A + 2B \longrightarrow \text{Product}$$

Initial conc.: a b 0 $r = k[A]^0[B]^0$

$$(C_t)_A = C_0 - kt = a - kt$$

$$(C_t)_B = C_0 - 2kt = b - 2kt$$

$$(t_{1/2})_A = \frac{a}{2k}$$

$$(t_{1/2})_B = \frac{b}{4k}$$

Ratio of conc. of A and B so that half life becomes equal

$$\frac{a}{2k} = \frac{b}{4k}$$

$$\frac{a}{b} = \frac{1}{2} \Rightarrow \boxed{b = 2a}$$

Concept →

If the Initial conc. of the reactant are taken in their respective stoichiometric ratio; than their half life will be equal irrespective of their order.

sheet: $\binom{v_e > 1}{a > 2}$

$$-\frac{d P_A}{dt} = k' P_A^2 \qquad -\frac{1}{V}\frac{dn_a}{dt} = kC_A^2$$

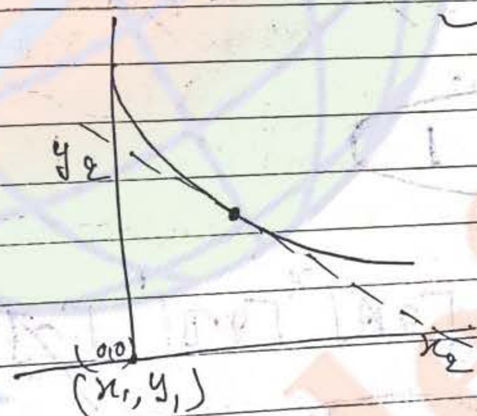
$$\frac{-d}{dt}(C_A RT) = k'(C_A RT)^2 \qquad -\frac{dC_A}{dt} = kC_A^2$$

$$RT\left(\frac{-dC_A}{dt}\right) = k'C_A^2(RT)^2$$

$$k' C_A^2 RT = kC_A^2$$

Q.4.)

$$r_{inst} = \text{slope of range} = \frac{y_2 - y_1}{x_2 - x_1}$$



5.) $2NO + O_2 \longrightarrow 2NO_2$

$$r = k[NO]^2[O_2]$$

$$r' = k\left[\frac{NO}{2}\right]^2\left[\frac{O_2}{2}\right]$$

8) $r = K C_A^2 C_B^{1/2}$

$8r = K(\ )^2(\ )^{1/2}$

9.) $C_6H_5N_2^+Cl^- \longrightarrow \_\_ + N_2$

$r = K[C_6H_5N_2Cl]^1$

10) $$\frac{\cancel{r} = \cancel{K}[A]^x [B]^y [\cancel{C}]^z}{2\cancel{r} = \cancel{K}[\cancel{A}]^x [2B] [\cancel{C}]^z}$$

$y = 1$

$2\cancel{r} = K[2A]^x [2B]^1 [\cancel{C}]^z$

$x = 0$

$4r = K[2B]^1 [2C]^z$

$z = 1$

5) $r = K[A]^2$

$A = \sqrt{r/K}$

Ex-2

Q1) $A + 2B \xrightarrow{K} C$

$r = K[A]^x [B]^y$ —(1)

$2.82r = K[2A]^x [B]^y$ —(2)

$9r = K[A]^x [3B]^y$ —(3)

eq(1) ÷ eq(2) , $x =$ ✓

eq(1) ÷ eq(3) , $y =$ ✓

3. $K_{app} = \frac{k_1 C}{1+\alpha C}$

$K_{app} = \frac{0.9 k_1 C}{\alpha C}$

$\frac{\cancel{k_1 C}}{1+\alpha C} = \frac{0.9 \cancel{k_1 C}}{\alpha C}$

$0.9(1+\alpha C) = \alpha C$

4)
$$-r = \frac{K_1 C_A}{1 + K_2 C_A}$$ → Neglect this

$$= \frac{K_1 C_A}{1}$$

ii) $A \rightleftharpoons 2B$, $K_f = 1.5 \times 10^{-3}$

$$\frac{10^{-5}}{10} \qquad \frac{100}{10}$$

$$10^{-6} \qquad 10$$

$$K_{eq} = \frac{K_f}{K_b} \Rightarrow \frac{[B]^2}{[A]}$$

K_b ?

13)

a → (i)

b → (i), ii

c)

$\boxed{\frac{[x]}{O.N.O \Rightarrow 2}}$ ⇒

I II III

$k_1[A] = k_2[A]^2 = k_3[A]^3$

↓ 1m ↓ 1m ↓ 1m

→ mol/litre

$k_1 > k_2 > k_3$

$k_1\left[\frac{1}{10^{-3}}\right] = k_2\left[\frac{1}{10^{-3}}\right]^2 > k_3\left[\frac{1}{10^{-3}}\right]^3$

First order reaction ⇒

1) $A \longrightarrow$ Product

$t=0$ $\quad a$ or C_0 $\quad$ —

$t=t$ $\quad (a-x)$ or C_t $\quad$ —

$r = K[A]^1$

$\frac{dx}{dt} = K(a-x)$ ← ये step याद रखें

$\int \frac{dx}{dt} = K\int dt$

$-\ln(a-x) = Kt + c$

$t=0, \; x=0, \; C = -\ln a$ ← ये step याद रखें

$-\ln(a-x) = Kt - \ln a$

$K = \frac{1}{t}\ln\frac{a}{a-x}$

or

$K = \frac{1}{t}\ln\frac{C_0}{C_t}$

$$\boxed{K = \frac{2.303}{t}\log\frac{C_0}{C_t}} \text{ or } \boxed{K = \frac{2.303}{t}\log\frac{a}{a-x}}$$

→ C_0 or a

→ C_t or $a-x$

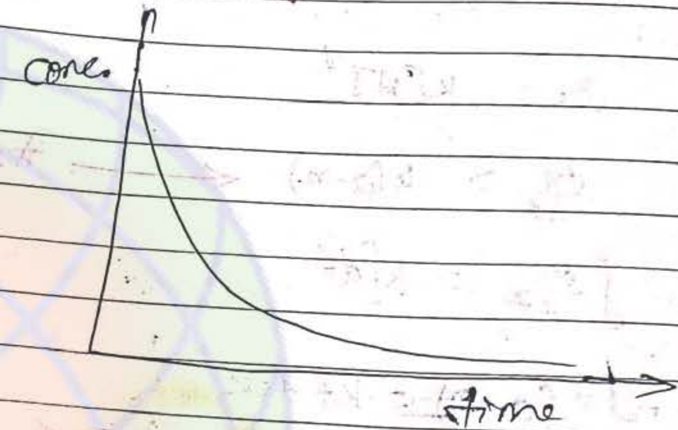
2) WILHELMY FORMULA

$K = \frac{1}{t}\ln\frac{C_0}{C_t}$

$Kt = \ln\frac{C_0}{C_t}$

$$\frac{C_0}{C_t} = e^{Kt}$$

$$\boxed{C_t = C_0 e^{-Kt}}$$



3.) Interval formula ⇒

$$A \longrightarrow \text{Product}$$

$t = t_1$ C_1
$t = t_2$ C_2

$$\boxed{K = \frac{2.303}{(t_2 - t_1)} \log \frac{C_1}{C_2}}$$

4) Time required for completion of first order reaction

$$K = \frac{2.303}{t} \log \frac{C_0}{C_t} \text{ or } \frac{a}{a-x}$$

t = temp, $C_t = 0$ or $x = a$

$$\boxed{t_{comp.} = \infty}$$

5.) Calculation of degree of dissociation of the reactant →

$$\alpha = \frac{\text{No of moles dissociated}}{\text{Initial no of moles}} = \frac{x}{a}$$

	$A \longrightarrow$	Product
$t=0$	a	0
$t=t$	$(a-x)$	—

$$k = \frac{1}{t}\ln\frac{a}{a-x}$$

$$kt = \ln\frac{a}{a-x}$$

$$e^{kt} = \frac{a}{a-x}$$

$$e^{-kt} = \frac{a-x}{a} = 1-\alpha$$

$$\boxed{\alpha = 1 - e^{-kt}}$$

6.) calculation of half life of first order reaction →

$(\because c_0 = a,\ c_t = a-x)$

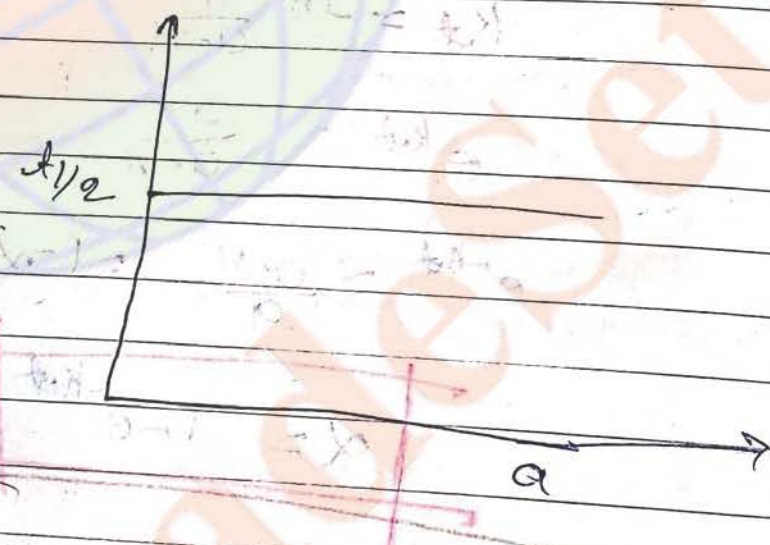
$$K = \frac{2.303}{t} \log \underbrace{\frac{c_0}{c_t}}_{} \text{ or } \underbrace{\frac{a}{a-x}}_{}$$

$t = t_{1/2}$, $c_t = \frac{c_0}{2}$ or $x = a/2$

$$K = \frac{2.303}{t_{1/2}} \log \frac{c_0}{c_0/2}$$

$$t_{1/2} = \frac{2.303}{K} \log 2$$

$$\boxed{t_{1/2} = 0.693/K} \quad \text{or} \quad \boxed{t_{1/2} \propto (a)^0 \text{ or } c_0}$$



Fact

Notes:- Half life of 1st order reaction is Independent of Initial concentration eg: →

$$\underset{100gm}{A} \xrightarrow[t_1]{50\%} \text{Product}$$

$$\underset{100gm}{A} \xrightarrow[t_2]{50\%} \text{Product}$$

$$\boxed{t_1 = t_2}$$

Time required for a particular percentage of reactant to decompose is independent of initial conc. of reactant in case of first order reaction.

7.) Conc. of Reactant after "n" half life →

$$A \longrightarrow \text{Product}$$

$t = C_0$

Conc. of Reactant after one half life $= \frac{C_0}{2}$

" " " " two " " $= \frac{C_0}{4} = \frac{C_0}{2^2}$

" " " " three " " $= \frac{C_0}{8} = \frac{C_0}{2^3}$

conc. ~~after "n" life~~

Conc. after "n" half life :-

$$\boxed{C_t = \frac{C_0}{2^n}}$$

8) Average life → (T_{avg})

The time in which the conc. of the reactant becomes "$\frac{1}{e}$" of Initial conc. of reactant is known as average life of the reaction.

~~at 68~~

$$t = T_{avg}, \quad C_t = \frac{C_0}{e}$$

$$C_t = C_0 e^{-Kt}$$

$$\frac{C_0}{e} = C_0 e^{-K T_{avg}}$$

$$e^{-1} = e^{-K T_{avg}}$$

$$\boxed{T_{avg} = \frac{1}{K}}$$

(1) Conc. of Reactant after one T_{avg}

$$C_t = C_0 e^{-Kt}$$

$$T = T_{avg} = \frac{1}{K}$$

$$C_t = C_0 e^{-K \times \frac{1}{K}} = \frac{C_0}{e}$$

(2) Conc. of Reactant after 2 Tavg

$$2\,T_{avg} = 2 \times \frac{1}{K}$$

$$C_t = C_0 e^{-Kt}$$

$$= C_0 e^{-K \times 2/K} = \frac{C_0}{e^2}$$

So,

$$\boxed{\text{Conc. of Reactant after "n" } T_{avg} = \frac{C_0}{e^n}}$$ → e पर power 'n'

Q. Or.

$$\frac{t_{1/2}}{t_{3/4}} = \frac{1}{2} \quad \because \quad \frac{t_{1/2} = \frac{2.303}{K} \log \frac{C_0}{C_0/2}}{t_{3/4} = \frac{2.303}{K} \log \frac{C_0}{C_0/4}} = \frac{\log 2}{\log 4} = \frac{1}{2}$$

$$\frac{t_{75\%}}{t_{50\%}} = 2 \quad , \quad \frac{t_{75\%} = \frac{2.303}{K} \log \frac{a}{a - 0.75a}}{t_{50\%} = \frac{2.303}{K} \log \frac{a}{a - 0.50a}} =$$

$$\frac{t_{99\%}}{t_{99.9\%}} = \frac{2}{3} \quad \frac{t_{99\%} = \frac{2.303}{K} \log \frac{a}{a - 0.99a}}{t_{99.9\%} = \frac{2.303}{K} \log \frac{a}{a - 0.999a}} = \frac{2}{3}$$

$$\frac{t_{7/8}}{t_{1/2}} = 3 \quad , \quad \frac{t_{7/8} = \frac{2.303}{K} \log \frac{a}{a - \frac{7}{8}a}}{t_{1/2} = \frac{2.303}{K} \log \frac{a}{a - a/2}} = 3$$

Note → Here use formula

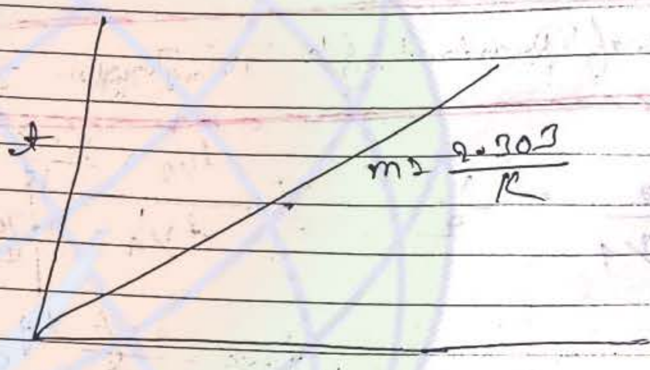
$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{or} \quad t = \frac{2.303}{K} \log \frac{a}{a-x}$$

(iv) Graph of first order reaction →

a) $K = \frac{2.303}{t} \log \frac{C_0}{C_t}$

$t = \frac{2.303}{K} \log \frac{C_0}{C_t}$

$y = mx$



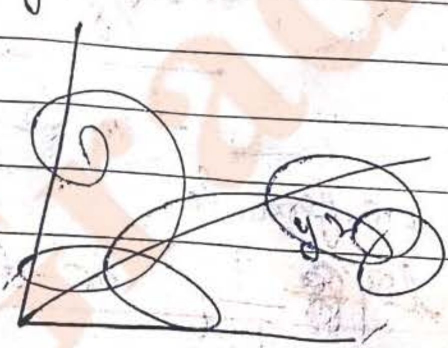
$\log \frac{C_0}{C_t}$

b) $K = 2.303 \log \frac{C_0}{C_t}$

$\log \frac{C_0}{C_t} = \frac{Kt}{2.303}$

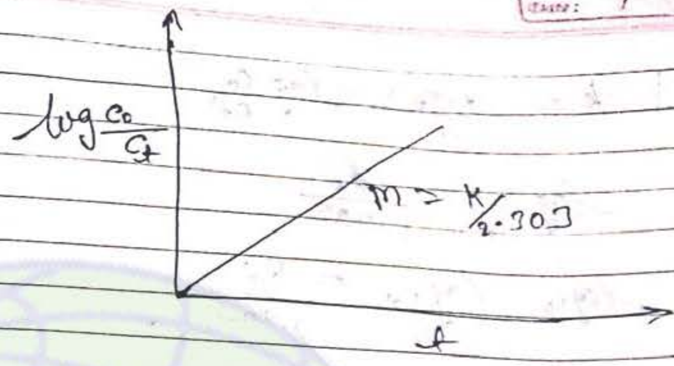
$y = mx$

मान रखिए case में $y = mx + c$, original equation से निकाल है। इसलिए suitable होगा।



नोट → मान रखो - "$\log \frac{C_0}{C_t}$" और "t" की बीच graph ऐसा बनेगा।

और आप इस तरह slope निकाल लें $y = mx + c$ से।

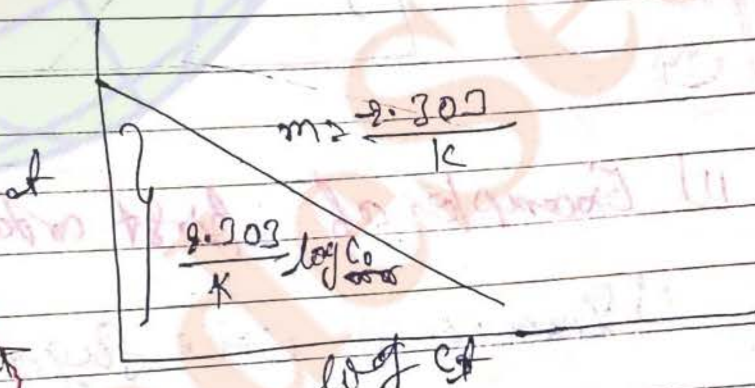


c) $K = \frac{2.303}{t}\log\frac{C_0}{C_t}$

$t = \frac{2.303}{K}\left[\log C_0 - C_t\right]$ → (याद रखे "C_0" वाला y-intercept है) v.v.i

$t = \frac{2.303}{K}\log C_0 - \frac{2.303}{K}\log C_t$

$y = c + mx$



नोट → याद रखे।
"$\log C_t$" और "t" के बिच graph ऐसा बनेगा

और आप इस तरह slope(m) तथा intercept (c)
याकि $y = mx$ के उपयोग से निकाल लें।

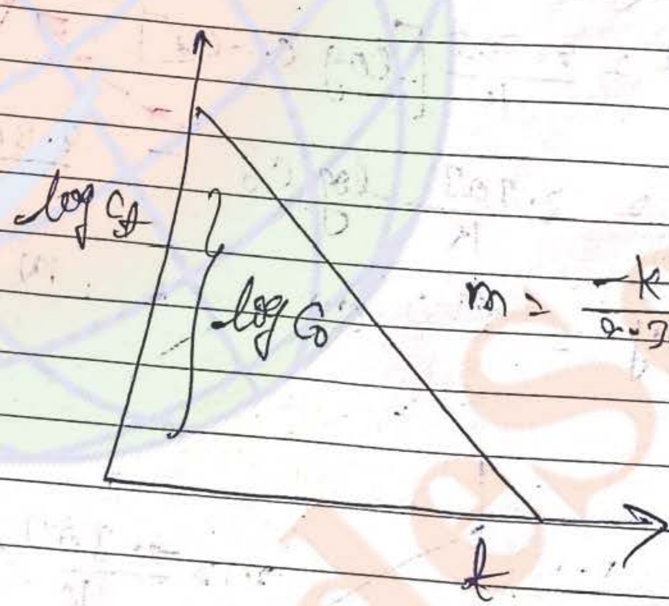
d) $k = \frac{2.303}{t} \log \frac{C_0}{C_t}$

$\log \frac{C_0}{C_t} = \frac{kt}{2.303}$

$\log C_0 - \log C_t = \frac{kt}{2.303}$

$\log C_t = \log C_0 - \frac{kt}{2.303}$

$y = c + mx$



ii) Examples of first order reactions

i) Inversion of cane sugar

$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

(Sucrose) Glucose (fructose)

2.) Hydrolysis of ester.

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

ester.

3.) Decomposition of H_2O_2

$2H_2O_2 \longrightarrow 2H_2O + O_2$

4.) De-composition of N_2O_5

$N_2O_5(g) \longleftrightarrow N_2O_4(g) + \frac{1}{2}O_2(g)$

12.)

$3A \longrightarrow$ Product, Ist order Reaction.

$t=0, \quad a \qquad 0$

$t=t \quad (a-x)$

$$\frac{1}{3}\frac{dx}{dt} = K(a-x)$$

$$\int \frac{dx}{a-x} = 3K\int dt$$

$$-\ln(a-x) = 3Kt + c$$

$t=0, \quad x=0, \quad c = -\ln a$

$\Rightarrow -\ln(a-x) = 3kt - \ln a$

$$\boxed{K = \frac{1}{3t}\ln\frac{a}{a-x}}$$

or

$$\boxed{K = \frac{2.303}{3t}\log\frac{a}{a-x}}$$

$t = t_{1/2}, \quad x = \frac{a}{2}$

महत्वपूर्ण बात याद रखें कि Half life में conc. of reactant आधा हो जाता है अपने ही Initial से

$$K = \frac{2.303}{3t_{1/2}}\log 2$$

$$\boxed{t_{1/2} = \frac{2.303}{3K}\log 2}$$

Degree of dissociation ⇒

$$K = \frac{1}{3t}\ln\frac{a}{a-x}$$

$$e^{3Kt} = \frac{a}{a-x}$$

$$e^{-3Kt} = \frac{1-\alpha}{1}$$

$$\boxed{\alpha = 1 - e^{-3kt}}$$

~~NOTE~~

$nA \longrightarrow$ Product

$$K = \frac{1}{nt} \ln \frac{a}{a-x} \text{ or } \frac{2.303}{nt} \log \frac{a}{a-x}$$

$$\alpha = 1 - e^{-nkt}$$

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Example For the first order reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

A) The concentration of the reactant decreases exponentially with time.

B) The half life of the reaction decreases with increasing temp.

C) The half life of the reaction depend's on the initial concentration of the reactant.

D) The reaction proceed's to 99.6% completion in eight half-life duration.

Sol^n A, (see page 163 with help formula)

B, (see page 123 and 166)

D,

Similar to P-164 (Point)

14. Remaining Reactant after 'n' half life:-

For a 1st order reaction, If "x" moles of reactant is taken Initially, after 'n-half' life,
Reactant Remaining is given by

$$\boxed{\text{\% of Remaining reactant} = x\cdot\left(\frac{1}{2}\right)^n}$$

— to find % remaining reactant generally we take 100 moles.

★ First order ~~group~~ Growth kinetics →

Bacteria / Population – (follows 1st order reaction)

$t = 0 \qquad a \qquad C_0$

$t = t \qquad (a+x) \qquad C_t$

$$\boxed{r = k\,[\text{Bac/Pop. etc.}]^{1}_{t=0}}$$

→ जो बढ़ रहा है (उसका Initial ~~group~~ concentration या number आदि)

$$r = k(a+x)^1$$

$$\frac{d}{dt}(a+x) = k(a+x)$$

$$\frac{dx}{dt} = k(a+x)$$

$$\int \frac{dx}{dt} = k\int dt$$

$$\ln(a+x) = kt + c$$

$$t = 0, \quad x = 0, \quad c = \ln a$$

$$\ln(a+x) = kt + \ln a$$

$$\boxed{k = \frac{1}{t}\ln\frac{a+x}{a}}$$

or

$$\boxed{k = \frac{2.303}{t}\log\frac{C_t}{C_0}}$$

Note:- Degree of dissociation / degree of association is not defined in case of 1st order reaction

[Ex-3] Passage-III

33) (A) 1st order reaction

34) See own copy Page-191

35) See own copy Page-191

Study of different type of Ist order reaction ⇒ or Pseudo Ist order reaction
Progress of

1) Gaseous reaction:-

$$\begin{array}{llll} & A(g) & \longrightarrow B(g) & + C(g) \\ t=0 & P^0 & 0 & 0 \\ t=t & P^0-P & P & P \\ t=\infty & 0 & P^0 & P^0 \end{array}$$

Let the total pressure at time "t" = P_T
" " " " " , " "∞" = P_∞

Ist two condition:-

$$P^0 - \cancel{P} + \cancel{P} + P = P_T$$

$$P = P_T - P^0$$

$$K = \frac{1}{t} \ln \frac{P^0}{P^0 - P}$$

$$K = \frac{1}{t} \ln \frac{P^0}{P^0 - (P_T - P_0)}$$

$$\boxed{K = \frac{1}{t} \ln \frac{P^0}{2P^0 - P_T}}$$

Last two conditions:-

$$P^0 - \cancel{P} + \cancel{P} + P = P_T$$

$$P = P_T - P_0$$

$$P^\infty = 2P^0$$

$$P^0 = P^\infty/2$$

$$K = \frac{1}{t} \ln \frac{P^0}{P^0 - P}$$

$$= \frac{1}{t} \ln \frac{P_\infty/2}{P_\infty/2 - (P_T - P^0)}$$

$$= \frac{1}{t} \ln \frac{P_\infty/2}{\frac{P_\infty}{2} - P_T + P_\infty/2}$$

$$\boxed{K = \frac{1}{t} \ln \frac{P_\infty}{2(P^\infty - P_T)}}$$

$\boxed{\text{Ex 25, Q15}}$

$$A \rightarrow P + C$$

$t = 0 \quad p^0 \quad 0 \quad 0$

$t = t \quad p^0 - p \quad p \quad p$

$t = \infty \quad 0 \quad p^0 \quad p^0$

$$p^0 - p + p + p = P_2$$

$$p^0 + p = P_2$$

$$p = P_2 - P_0 \quad \text{---(i)}$$

$$2p^0 = P_3$$

$$P_0 = \frac{P_3}{2} \quad \text{---(ii)}$$

$$K = \frac{1}{t} \ln \frac{P_0}{P_0 - p}$$

from eq (i) and (ii) putting value of p and P_0 we get the answer

Alt — we know that

$$K = \frac{1}{t} \ln \frac{P_\infty}{2(P_\infty - P_t)}$$

$$= \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$$

Ans.

Alt

$$A \rightarrow B + C$$

$t = 0 \quad p^0 \quad 0 \quad 0$

$t = t \quad p^0 - p \quad p \quad p$

$t = \infty \quad 0 \quad p^0 \quad p^0$

$2p = P_2 \qquad p = \frac{P_2}{2}$

$2p^0 = P_3 \qquad P_0 = P_3/2$

we know that

$$K = \frac{1}{t} \ln \frac{P_0}{P_0 - P_t}$$

$$= \frac{1}{t} \ln \frac{\frac{P_3}{2}}{\frac{P_3}{2} - \frac{P_2}{2}} = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$$

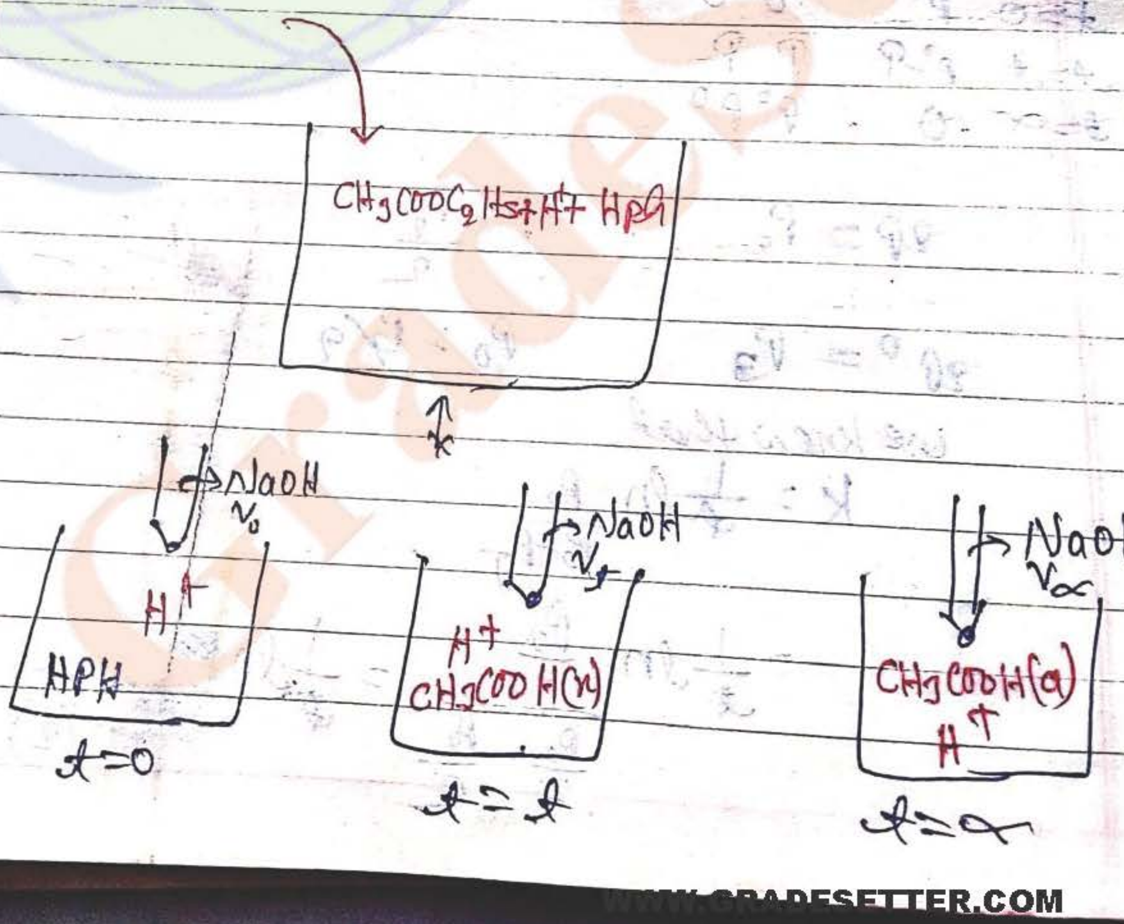
2) Hydrolysis of ester in acidic medium

$$CH_3COOC_2H_5 + \underset{\text{excess}}{H_2O} \xrightarrow{[H^+]} CH_3COOH + C_2H_5OH$$

	$CH_3COOC_2H_5$	H_2O	CH_3COOH	C_2H_5OH
$t=0$,	a	0	0	0
$t=t$,	$a-x$	–	x	x
$t=\infty$	0	–	a	a

The progress of this reaction is studied by time taking the reaction mixture where standard NaOH soln using pheopthalen as Indicator.

The volume of NaOH used in titrate is is directly proportion to amount of ester hydrolysed.



Let the volume of NaOH used at $t=0$ is $V_0 \propto H^+$
" " " " " $t=t$ "

$V_t \propto CH_3COOH + H^+$

$V_t \propto x + V_0$

$\boxed{x \propto V_t - V_0}$

Let the volume of NaOH used at $t=\infty$ is ~~V~~

$V_\infty \propto CH_3COOH + H^+$

$V_\infty \propto a + V_0$

$\boxed{a \propto V_\infty - V_0}$

$$a-x \propto V_\infty - \cancel{V_0} - V_t + \cancel{V_0}$$

$$a-x \propto V_\infty - V_t$$

$$K = \frac{1}{t} \ln \frac{a}{a-x}$$

Imp

$$\boxed{K = \frac{1}{t} \ln \frac{V_\infty - V_0}{V_\infty - V_t}}$$

Notes→
If V_∞ is not given in the question then it's value equal to zero
and similarly V_0 and V_t is not given
then $V_0 = 0$, $V_t = 0$

3) Decomposition of N_2O_5 in Inert Solvent →

$$N_2O_5(g) \xrightarrow{Solvent} N_2O_{4(l)} + \frac{1}{2}O_2(g)$$
$$\rightleftharpoons$$
$$NO_2(l)$$

$t=0$	a	0
$t=t$	$a-x$	$x/2$
$t=\infty$	0	$a/2$

The progress of this reaction is studied by measuring the volume of "O_2" at different time interval.

The volume of O_2 evolved is directly proportion to decomposition of N_2O_5

Let

V_0 is the volume of oxygen evolve at $t=0$ $V_0 \propto$ Zero

V_t " " " " O_2 " " $t=t$, $V_t \propto \frac{x}{2}$,

$x \propto 2V_t$

V_∞ " " " " " " $t=\infty$ =

$V_\infty \propto a/2$ ∴ $a \propto 2V_\infty$

$$K = \frac{1}{t}\ln\frac{a}{a-x} = \frac{1}{t}\ln\frac{2V_\infty}{2(V_\infty - V_t)}$$

$$\boxed{K = \frac{1}{t} \ln \frac{V_\infty}{V_\infty - V_t}}$$

Decomposition of H_2O_2 ⇒
The progress of this reaction is studied by titrating the reaction mixture with $KMnO_4$ solution using a suitable Indicator at different time Interval

$$H_2O_2(l) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g) \uparrow$$

$t=0$	a	—	0
$t=t$	$a-x$	—	$x/2$
t	0	—	$a/2$

Let vol. of $KMnO_4$ used at $t=0$ is $V_0 \propto a$
" " " " $t=t$ is $V_t \propto a-x$
" " " " $t=\infty$ is $V_\infty \propto$ Zero

$$K = \frac{1}{t} \ln \frac{a}{a-x}$$

$$\boxed{K = \frac{1}{t} \ln \frac{V_0}{V_t}}$$

(जो नहीं हो उसे Zero मान लें)

$\boxed{Q=17}$

$$A \rightarrow B + C$$

$t=0$	a	0	0
$t=t$	$a-x$	x	x
$t=\infty$	0	a	a

$$V_1 \propto a$$

$$V_2 \propto a - x + x + x$$

$$V_2 \propto a + x$$

$$x \propto V_2 - V_1$$

$$k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{1}{t} \ln \frac{V_1}{V_1 - (V_2 - V_1)}$$

$\boxed{Q=18}$

$$A \longrightarrow 2B + 3C$$

$t=0$	a	0	0
$t=t$	$a-x$	x	x
$t=\infty$	0	a	a

$$a - x + 2x + 3x \propto V_2$$

$$a + 4x \propto V_2$$

$$5a \propto V_3$$

$$\therefore a \propto \frac{V_3}{5}$$

$$4x \propto V_2 - a$$

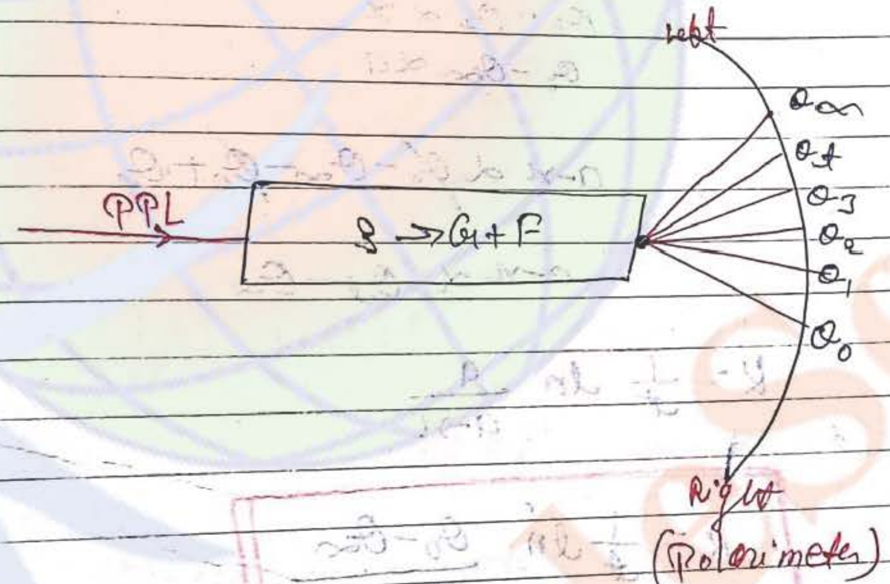
$$x \propto \frac{V_2 - a}{4} \propto \frac{V_2 - V_3/5}{4} \propto \frac{5V_2 - V_3}{20}$$

so $\left(k = \frac{1}{t} \ln \frac{a}{a-x} \right)$ 'S'

5) ✲ Inversion of Cane Sugar ⇒

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

	Sucrose (dextro)	excess (right side)	glucose (dextro)	fructose (levo) → slightly more effect.
$t=0$	a	—	0	0
$t=t$	$a-x$		x	x
$t=\infty$	0		a	a



The progress of this reaction is studied by measuring the angle of rotation at different time interval. The angle of rotation is i.e. the change in the angle of rotation is directly proportion to amount of sucrose hydrolyzed.

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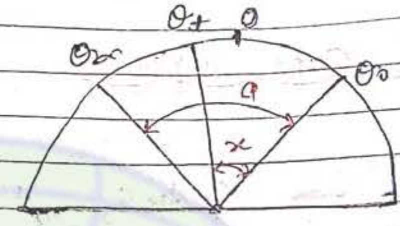


Let θ_0 is Initial angle of rotation
θ_t is angle of rotation at time $t = t$
θ_∞ " " " " " $t = \infty$

$$\theta_0 - \theta_t \propto x$$
$$\theta_0 - \theta_\infty \propto a$$

$$a - x \propto \cancel{\theta_0} - \theta_\infty - \cancel{\theta_0} + \theta_t$$

$$a - x \propto \theta_t - \theta_\infty$$

$$K = \frac{1}{t} \ln \frac{a}{a-x}$$

$$\boxed{K = \frac{1}{t} \ln \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}}$$

Put the value with sign

(V) If θ_∞ is not given then take it's value equal to zero

(V) The value of θ_t will be equal to zero when reading of polarimeter is zero.

Q=3
Passage II Bd

33) ans. (i) 1st order reacho

34) ans

$$K = \frac{2.303}{t} \log \frac{C_t}{C_0}$$

$$= \frac{2.303}{15} \log \frac{200}{100}$$

so,

$$K = \frac{2.303}{15} \times 0.301 = 0.0462 \ min^{-1}$$

35) ans $r = K [\ \ ]_{t=0}$

$= K[100]$

$= 0.0462 \times 100$

$= 4.62$ bacteria per min

Q=5
aNo=6

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

$$r = k[N_2O_4]$$

4/5/201

Q.No=4

Q.No.=4

1st order reaction.

Initial conc = 0.1(m)

$t = 40s$

final conc = 0.025(m)

$r = K[0.01]^1$

$K = \frac{2.303}{t} \log \frac{C_0}{C_t}$

Q.No.10

$r = 0.04$ mol litre^{-1} s^{-1}

$t = 10$ min

$K = \frac{2.303}{t_2 - t_1} \log \frac{C_1}{C_2}$

Q.No.14

$A = 4B$

$A \xrightarrow{5min} 2M \xrightarrow{5min} 1M \xrightarrow{5min} 1/2$

$B \xrightarrow{15min} 1/2$

4/5/2012

Second order Reaction

1)

$A \longrightarrow$ Product or $A+A \longrightarrow$ Product

$t=0$ a 0

$t=t$ $a-x$ $-$ $a-x$ $a-x$

$$r = k(a-x)^2$$

$$\frac{dx}{dt} = k(a-x)^2$$

$$\cancel{\int \frac{dx}{dt} = k(a-x)^2}$$

$$\int \frac{dx}{(a-x)^2} = k\int dt$$

$$\boxed{\int \frac{dx}{(a-x)^n} = \frac{1}{(n-1)(a-x)^{n-1}}}$$

$$\frac{1}{a-x} = kt + c$$

$t=0$ $x=0$ $c = \frac{1}{a}$

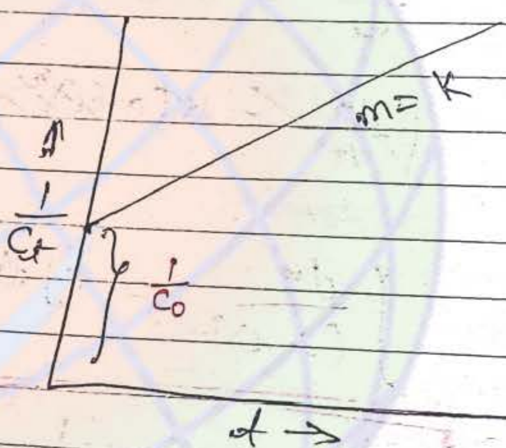
$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$\frac{1}{a-x} - \frac{1}{a} = kt$$

$$\frac{1}{C_t} - \frac{1}{C_0} = Kt$$

$$\boxed{\frac{1}{C_t} = \frac{1}{C_0} + Kt}$$

$$y = C + mx$$



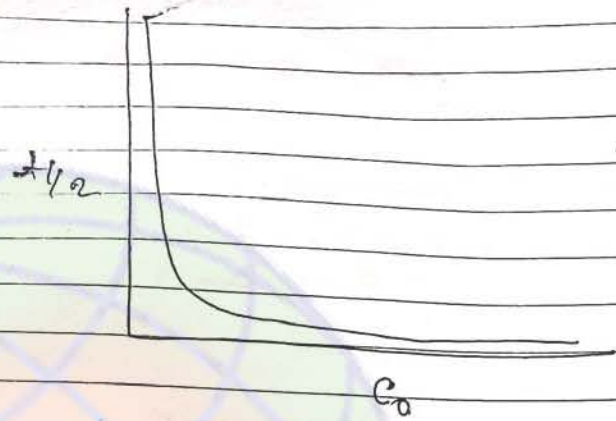
Half life →

$t = t_{1/2}$, $C_t = C_0/2$

$$\frac{2}{C_0} - \frac{1}{C_0} = K \cdot t_{1/2}$$

$$K t_{1/2} = \frac{1}{C_0} \quad \text{so,} \quad \boxed{t_{1/2} = \frac{1}{KC_0}}$$

$$t_{1/2} \propto \frac{1}{C_0}$$



Case IInd →

	$A + B$		$\longrightarrow$ Product
$t=0$	a	b	0
$t=t$	$a-x$	$b-x$	$-$

$$r = K(a-x)(b-x)$$

$$\int \frac{dx}{(a-x)(b-x)} = K\int dt$$

$$\boxed{K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}}$$

nth order Reaction →

$$A \longrightarrow \text{Product},$$

$t=0$ a 0

$t=t$ $a-x$ $-$

$$r = k(a-x)^n$$

$$\cancel{\frac{t_{1/4}}{t_{1/2}} = a}$$

$$\frac{dx}{dt} = k(a-x)^n$$

$$\cancel{\int \frac{dx}{dt} = k}$$

$$\int \frac{dx}{(a-x)^n} = k\int dt$$

$$\frac{1}{(n-1)(a-x)^{n-1}} = kt + C$$

$$t=0, \quad x=0 \quad C = \frac{1}{(n-1)\,a^{n-1}}$$

$$\frac{1}{(n-1)(a-x)^{n-1}} = kt + \frac{1}{(n-1)a^{n-1}}$$

$$\frac{1}{(n-1)}\left\{\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right\} = Kt$$

$$\boxed{\frac{1}{n-1}\left\{\frac{1}{a^{n-1}} - \frac{1}{C_0^{n-1}}\right\} = Kt}$$

$t = t_{1/2}$, $C_t = C_0/2$

$$\frac{1}{(n-1)}\left[\frac{1}{(C_0/2)^{n-1}} - \frac{1}{C_0^{n-1}}\right] = K\,t_{1/2}$$

$$\frac{1}{\cancel{(n-1)}}\left[\frac{2^{n-1}-1}{\cancel{C_0^{n-1}}}\right] \cancel{=K}\, t_{1/2} \quad \text{—— (1)}$$

$t = t_{3/4}$, $C_t = C_0/4$

$$\frac{1}{(n-1)}\left[\frac{1}{(C_0/4)^{n-1}} - \frac{1}{C_0^{n-1}}\right] = K\,t_{3/4}$$

$$\frac{1}{\cancel{(n-1)}}\left[\frac{4^{n-1}-1}{\cancel{C_0^{n-1}}}\right] \cancel{=K}\, t_{3/4} \quad \text{—— (2)}$$

$$\boxed{\frac{t_{3/4}}{t_{1/2}} = \frac{4^{n-1}-1}{2^{n-1}-1}}$$

$$= \frac{4^{n-1}-1}{2^{n-1}-1} \times \frac{2^{n-1}+1}{2^{n-1}+1}$$

$$\frac{t_{3/4}}{t_{1/2}} = 2^{n-1}+1$$

In general for n^{th} order Reaction

$$\boxed{t_{1/2} \propto \frac{1}{C_0^{\,n-1}} \propto \frac{1}{P^{n-1}}}$$

Ex. $4A(g) \longrightarrow 2(g) + B(g)$
decomposition of A follows first order kinetic if Initially the pressure of "A" was 800 mm hg and after 10 minutes pressure is found to be 650 mm Hg what is the half life of "A".

80/4

$$4A(g) \longrightarrow 2(g) + B(g)$$

$t=0$ 800 0 0

$t=t$ $800-4P$ $2P$ P

$$800-4P+2P+P = 650$$

$$P = 150$$

$$K = \frac{2.303}{10} \log \frac{800}{200}$$

$$t_{1/2} = \frac{0.693}{K}$$

$$\boxed{t = 5 \text{ minutes}}$$ Ans.

(see concept on self copy p> 127)

☆ Method to Determine the "order of reaction"

1) Vant Hoff method →

$$A \longrightarrow \text{Product}$$

t	Conc	Rate
0	a_1	r_1
10	a_2	r_2
20	a_3	r_3

$$r = K[A]^n$$

$$\frac{r_1}{r_2} = \frac{\cancel{K}[a_1]^n}{\cancel{K}[a_2]^n}$$

$$\frac{r_1}{r_2} = \left(\frac{a_1}{a_2}\right)^n$$

$$\boxed{n = \frac{\log r_1/r_2}{\log a_1/a_2}} \quad \text{or} \quad n = \frac{\log r_1/r_2}{\log a_1/a_2}$$

order of reaction

2) Half life method →

$$A \longrightarrow \text{Product}$$

$t_{1/2}$	10	20	30
Conc.	a_1	a_2	a_3

नोट याद यह रखें

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

और इससे यह निकाल लें और फिर इससे

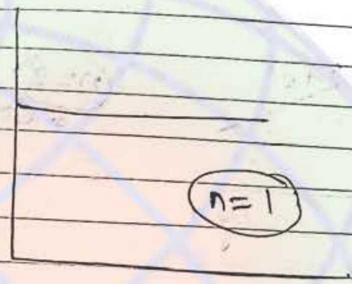
$$\boxed{\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}}$$

निचे वाला नA निकाल लो (याद सिर्फ यह रखें कि इस Conc की log नA लेना ही है)

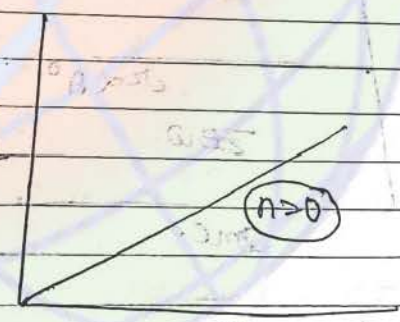
$$\frac{\log (t_{1/2})_1}{\log (t_{1/2})_2} = (n-1) \log \frac{a_2}{a_1}$$

$$\boxed{n = \frac{\log (t_{1/2})_1 - \log (t_{1/2})_2}{\log a_2 - \log a_1} + 1}$$

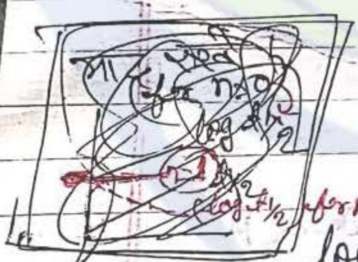
3) Graphical method ⇒

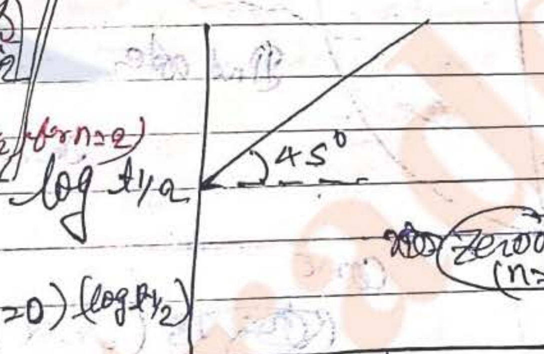


$t_{1/2} \propto \frac{1}{a^{n-1}}$



$t_{1/2} \propto \frac{1}{a^{n-1}}$





$t_{1/2} = \frac{K}{a^{n-1}}$

$t_{1/2} = K a^{1-n}$

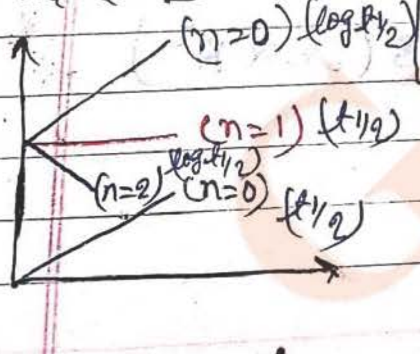
$\log t_{1/2} = \log K + (1-n)\log a$

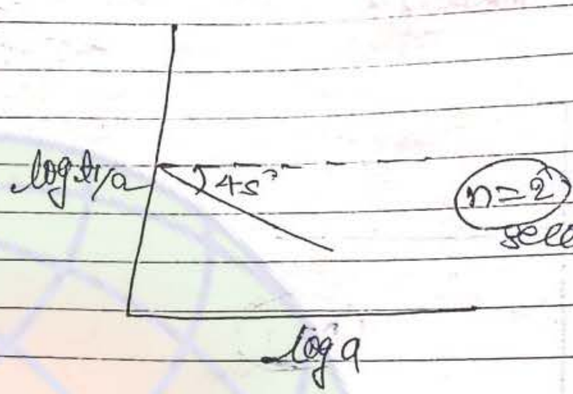
$y = c + mx$

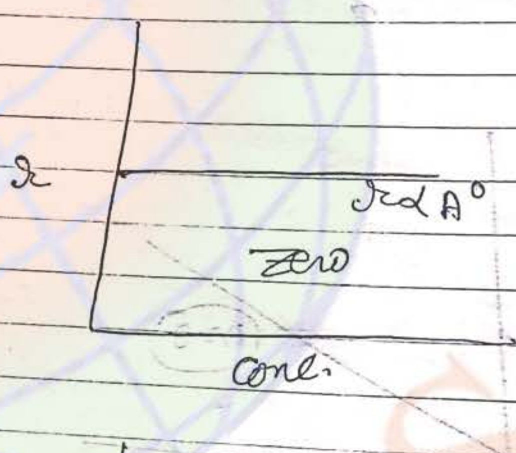
$m = 1-n$ so, n=0

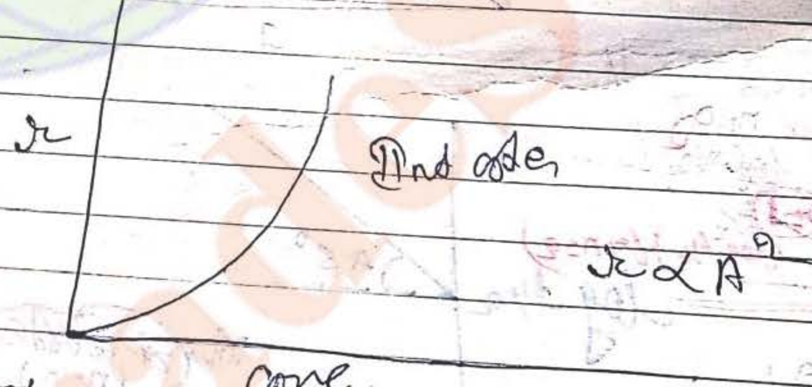
$1 = 1-n$

याद रखें :-

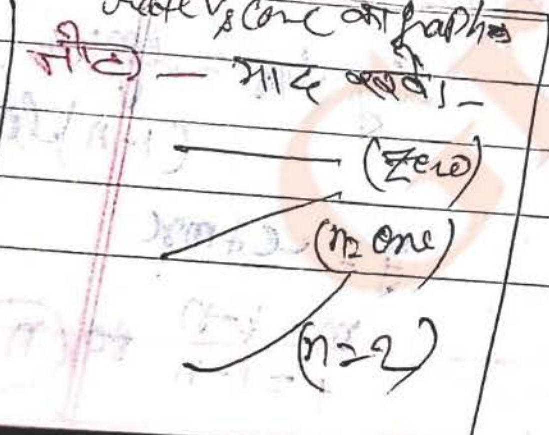


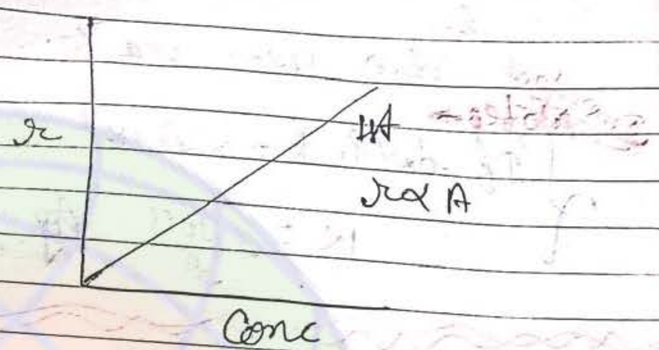






(n=2) $(r \propto A^2)$





4) Heat and trial method →

Conc	C_1	C_2	C_3	C_4
time	10	20	30	40

In this type of method we first assume the order of the reaction and then calculate the value of "k" at different time interval.
If the value of "k" come same in different time interval our assumption is correct otherwise we assume next order reaction.

IT 2010
[4×4]
Ques no => 13

solute
we find order of the reaction by heat and trial method →
Let the order of reaction is zero

$$\boxed{C_t = C_0 - Kt}$$

$0.75 = 1 - K \times 0.05$ $\qquad K = 5$

$0.40 = 1 - K \times 0.12$ $\qquad K = 5$

So, Zero order reactn.

Important Notes →

If both k = s. is not same then we

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

Ex-3
Q. No → 26

$n_1 A \longrightarrow n_2 B$

$C_t = C_0 \, e^{-n_1 K t}$

$n_1 A \longrightarrow n_2 B$

$a \qquad 0$

$a - x \qquad \frac{n_2}{n_1} x$

$C_t = C_0 \, e^{-n_1 K t}$

$(a - x) = a \cdot e^{-n_1 K t}$

$a - x = a e^{-n_1 K t}$

$a - a e^{-n_1 K t} = x$

$x = a\left(1 - e^{-n_1 K t}\right)$

$n_T = a - x + \frac{n_2}{n_1} x$

Nenti → D.P.P.S

$$n_T = a + \left(\frac{n_2}{n_1} - 1\right) x$$

$$PV = n_T RT$$

$$V = \frac{n_T RT}{P}$$

$$V = a\left\{\left(1 + \left(\frac{n_2}{n_1} - 1\right)\left(1 - e^{-n_1 kT}\right)\right\}\frac{aRT}{P}$$

$$V = V_0\left\{1 + \left(\frac{n_2}{n_1} - 1\right)\left(1 - e^{-n_1 kt}\right)\right\}$$

$$\text{Conc.} = \frac{a - x}{V}$$

$\boxed{K_0 = ?}$ $\boxed{0.1b - ?}$

$A \longrightarrow 2B + C$, first order Reactn

$T = 100^\circ C$

$t = 10\,min$ 176 mm Hg

$t = \infty$ 240 mm Hg

Exe 1, Q. No 3 4
208

Exe 1
Q. No → 8

$$A \longrightarrow 2B + C$$

$t=0 \quad P^0 \quad 0 \quad 0$

$t=10 \quad P^0 - P + 2P + P = 176 \quad -(1)$

$t=\infty \quad 0 \quad 2P^0 + P^0 = 270 \quad -(11)$

P^0 and P

$$K = \frac{2.303}{t} \log \frac{P_0}{P^0 - P}$$

Exe 1
Q. No → 4

$$+\frac{dA}{dt} = K[A]^{1/2}$$

$$+\int \frac{dA}{A^{1/2}} = K \int dt$$

$$\frac{1}{(1/2 - 1)} \frac{1}{(a-x)^{1/2 - 1}} = Kt + C$$

$$-2(a-x)^{1/2} = Kt + C$$

Ans $\frac{\sqrt{2}(\sqrt{2}-1) A_0^{1/2}}{K}$

method to finding the Rate का law →

In boards Determination of Rate law with the help of given mechanism for a reaction → (जब slow और fast दिया हुआ रहे तब उस case में)

1) Rate law is written from the slowest step of the given mechanism.

2) In the rate law expression concentration term of only reactant should be used but in some cases concentration of product can also appear.

very Imp 3) In the rate law expression Intermediate should never appear. (किसी भी mechanism में given reaction के compound के अलावा कोई भी compound होगा तो वह Intermediate का काम करेगा।)

Case III → For elementary Reaction →

eg.

$$A + 2B \longrightarrow C + D$$

$$r = K[A][B]^2$$

eg 2. ⇒ $A + 2B + C \longrightarrow D + E$
(excess)

$$r = K[A][C]$$

case 2nd ⇒ For Complex Reaction

Q1.) $H_2(Para) \longrightarrow H_2(ortho)$

mech ⇒

$H_2(Para) \xrightleftharpoons{K_{eq}} 2\boxed{H}$ (fast)

$H_2(Para) + \boxed{H} \xrightarrow{K_1} H_2(ortho) + \boxed{H}$ (slow)

Intermediate

सबसे पहले Intermediate पहचानें फिर rate law expression लिखें।

rate law expression.

Sol^n

rate concept page 125

$r = K_1 [H_2]_{Para} [H] = K_1 \sqrt{K_{eq}} [H_2]^{3/2}_{Para}$

order $= \frac{3}{2}$ ⇒ order का concept page 127 (own copy)

$K_{eq} = \frac{[H]^2}{[H_2]_{Para}}$

$[H] = \sqrt{K_{eq}} \sqrt{H_2\ Para}$

Q2.) $A_2 + B_2 \longrightarrow 2AB$

mech ⇒

$A_2 \xrightleftharpoons{K_{eq}} \boxed{A} + \boxed{A}$ (fast)

$\boxed{A} + B_2 \xrightarrow{K_1} AB + \boxed{B}$ (slow)

$A + \boxed{B} \xrightarrow{K_2} AB$ (fast)

Intermediate

find rate law (r) = ?

Sol^n

~~$r = K_1 [A][B_2]$~~ $r = K_1 [A][B_2]$

~~$r = K_1 \frac{[AB][B]}{[A][B_2]}$~~

$= K_1 \sqrt{K_{eq}} \sqrt{A_2} [B_2]$

Ans order $= 3/2$

$$K_{eq} = \frac{[A][A]}{[A_2]} \Rightarrow [A] = \sqrt{K_{eq}}\sqrt{A_2}$$

$$\cancel{K_1 = \frac{[AB][D]}{[A][B_2]}}$$

$$\cancel{K_2 = \frac{[AB]}{[A][B]}} \Rightarrow \cancel{A}$$

so, $r = K_1 \sqrt{K_{eq}}\sqrt{A_2}\,[B_2]$

order $= \frac{1}{2} + 1 = \frac{3}{2}$

नोट :- सबसे पहले slow step से Rate law expression लिखते और और फिर Rate law expression में जो-जो Intermediate आ रहा है उसे fast step (chemical eqn) की सहायता से हटा देते हैं।

O_3) $2O_3 \rightleftharpoons 3O_2$

mech :-

$$O_3 \underset{}{\overset{K_{eq}}{\rightleftharpoons}} O_2 + \boxed{O} \text{ (fast)}$$

Intermediate

$$O_3 + \boxed{O} \xrightarrow{K_1} 2O_2 \text{ (slow)}$$

$$r_0 = \cancel{\frac{[O_2]^2}{[O_3][O]}} \quad \cancel{K_1 K_{eq} [O_3]^2 [O_2]^{-1}}$$

$$r = K_1 [O_3][O]$$

$$K_{eq} = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \frac{K_{eq}[O_3]}{[O_2]}$$

so, $r = K_1 \dfrac{[O_3]\,K_{eq}[O_3]}{[O_2]}$, order $= 2 + (-1) = 1$ (slow)

Ra, Ra

2007 (must do again)

eg 4 Ra

$NH_4OCN \longrightarrow (NH_2)_2CO$

Sol^n

mech →

$NH_4^+ + OCN^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} NH_3 + \boxed{HOCN}$ (fast)

$NH_3 + \boxed{HOCN} \xrightarrow{K_2} (NH_2)_2CO$ (slow)

$$\boxed{r = K_2 \times \frac{K_1}{K_{-1}} [NH_4^+][OCN^-] \quad \text{order} = 1}$$

Sol^n
Intermediate का value निकालते जाए और फिर put करते जाए यदि इसको है कुछ intermedial आपस में cancel हो जाती है

$r = K_2 [NH_3][HOCN]$

यदि दोनों तरफ का हिस्सा हुआ रहे तब ही फिर ऊपर नीचे करके लिखना होगा। और यदि नीचे कुछ नहीं इसका मतलब "1" है

$$\frac{K_1}{K_{-1}} = \frac{[NH_3][HOCN]}{[NH_4^+][OCN^-]}$$

so $\boxed{r = K_2 \times \frac{K_1}{K_{-1}} [NH_4^+][OCN^-]}$ Ra

order = 1

order ⇒ 2 की जगह "1" इस लिए हुआ क्योंकि $[NH_4^+][OCN^-] = [NH_4OCN]$

eg 5.

$CO + Cl_2 \longrightarrow COCl_2$

mech –

$Cl_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2\boxed{Cl}$ (fast)

$\boxed{Cl} + CO \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} \boxed{COCl}$ (fast)

$\boxed{COCl} + Cl_2 \xrightarrow{K_3} COCl_2 + Cl$ (slow)

$r = ?$

order = $\frac{5}{2}$

Sol^n

$r = k_3 [COCl][Cl_2]$

$\frac{K_2}{K_{-2}} = \frac{[Cl][CO]}{[COCl]}$ $\frac{[COCl]}{[Cl][CO]}$

Now $r = k_3 \times \frac{K_2}{K_{-2}} [Cl][CO][Cl_2]$

$\frac{K_1}{K_{-1}} = \frac{[Cl]^2}{[Cl_2]}$

Now

$r = k_3 \times \frac{K_2}{K_{-2}} \times \sqrt{\frac{K_1}{K_{-1}}} \sqrt{Cl_2} [CO][Cl_2]$

so

$r = K [CO][Cl_2]^{3/2}$

order $= 1 + \frac{3}{2}$

$= \frac{5}{2}$

Not in board but approach 5% to 8% in IIT

2.) ★ Study State Approximation → (S.S.A) (mech तो दिया रहेगा पर slow या fast नहीं दिया रहे) | 217

Determination of rate law with the help of given mechanism for a reaction (जब slow fast नहीं दिया हुआ रहे)

Q.) $2O_3 \rightarrow 3O_2$

mech.>>

$O_3 \xrightarrow{K_a} O_2 + \boxed{O}$ → Intermediate form हो रहा है।

Intermediate Disappear हो रहा है।

$O_2 + \boxed{O} \xrightarrow{K_a'} O_3$

$O_3 + \boxed{O} \xrightarrow{K_b} 2O_2$

find rate law.

So/n Study state of Approximation (S.S.A) on Intermediate

$$r_f = r_d$$
(formation) (disapp)

यहाँ हमें S.S.A लगाने [O] का Rate of formation और disappearance निकालना है।

$$K_a[O_3] = K_a'[O_2][O] + K_b[O_3][O]$$

$$[O] = \frac{K_a[O_3]}{K_a'[O_2] + K_b[O_3]}$$

Attention> इसमें S.S.A में rate जो है वह main given eqn से प्राप्त होगा (जबकि यदि slow और fast दिया हो तो slow step से प्राप्त होता है)

$$r = -\frac{1}{2}\frac{d[O_3]}{dt}$$

(नोट:>> main given chemical eqn में देखें कि कौन से compound की सहायता से हमें कम expression को solve करना होगा और उसे select कर लें।)

$$\frac{d[O_3]}{dt} = \frac{-d[O_3]}{dt}\Big|_1 + \frac{d[O_3]}{dt}\Big|_2 - \frac{d[O_3]}{dt}\Big|_3$$

$\frac{d[O_3]}{dt}$ mechanism की सहायता से निकाल लें

$$= -K_a[O_3] + K_a'[O_2][O] - K_b[O_3][O]$$

$$= -K_a[O_3] + K_a'[O_2]\frac{K_a[O_3]}{K_a'[O_2]+K_b[O_3]} - K_b[O_3]\frac{K_a[O_3]}{K_a'[O_2]+K_b[O_3]}$$

$$\overline{K_a'[O_2]+K_b[O_3]}$$

Now

$$\frac{d[O_3]}{dt} = \frac{-2K_a \cdot K_b[O_3]^2}{K_a'[O_2]+K_b[O_3]}$$

$$r = -\frac{1}{2}\frac{d[O_3]}{dt}$$

$$= \frac{+1}{\cancel{2}} \times \frac{\cancel{2}K_a K_b [O_3]^2}{K_a'[O_2]+K_b[O_3]}$$

$$\boxed{r = \frac{K_a K_b [O_3]^2}{K_a'[O_2]+K_b[O_3]}}$$

→ इसे याद नहीं करना है यह इस question का final answer है।

[Q9.] $2N_2O_5 \longrightarrow 4NO_2 + O_2$

mech ⇒

$N_2O_5 \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} NO_2 + \boxed{NO_3}$ → Intermediate

$NO_2 + \boxed{NO_3} \xrightarrow{k_b} NO + NO_2 + O_2$ → Intermediate

$\boxed{NO_3} + NO \xrightarrow{k_c} 2NO_2$

find rate law?

Sol^n Study State of approximation on Intermediate.
on NO

$r_f = r_d$
(formation) (disapp.)

$$k_b [NO_2][NO_3] = k_c [NO_3][NO]$$

$$\boxed{[NO] = \frac{k_b}{k_c}[NO_2]}$$

S.S.S on NO_3

$$r_f = r_d$$

$$k_a [N_2O_5] = k_a' [NO_2][NO_3] + k_b [NO_2][NO_3] + k [NO_3][NO]$$

$$[NO_3] = \frac{K_a[N_2O_5]}{K_a'[NO_3] + K_b[NO_2] + K_c[NO]}$$

$$[NO_3] = \frac{K_a[N_2O_5]}{(K_a' + K_b)[NO_2] + \cancel{K_c} \times \frac{K_b}{\cancel{K_c}}[NO_2]}$$

$$[NO_3] = \frac{K_a[N_2O_5]}{[K_a' + 2K_b][NO_2]}$$

$$r = \frac{d[O_2]}{dt} = K_b[NO_2][NO_3]$$

$$= \frac{K_b\cancel{[NO_2]}\,K_a[N_2O_5]}{(K_a' + 2K_b)\cancel{[NO_2]}}$$

$$\boxed{r = \frac{K_a K_b [N_2O_5]}{K_a' + 2K_b}}$$

[illegible] formula [illegible]

Q.3.) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

mech:-

$$N_2O_5 \underset{Ka'}{\overset{Ka}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{K_b} NO + NO_2 + O_2$$

$$NO + N_2O_5 \xrightarrow{Kc} 3NO_2$$

find rate law?

Sol:

$$r = \frac{d[O_2]}{dt} = K_b [NO_2][NO_3]$$

S.S. A on $[NO_3]$

$$r_f = r_d$$

$$Ka[N_2O_5] = Ka'[NO_2][NO_3] + K_b[NO_2][NO_3]$$

$$[NO_3] = \frac{Ka[N_2O_5]}{(Ka' + K_b)[NO_2]}$$

Now

$$\boxed{r = K_b [NO_2] \frac{Ka[N_2O_5]}{(Ka' + K_b)[NO_2]}}$$

Q→ Q No→ 24
P→ 2001

$$A + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \boxed{C} \xrightarrow{K_3} D$$

Intermediate.

Sol[n]

S.S.A on C

$$r_f = r_d$$

$$K_1 [A][B] = K_2 [C] + K_3 [C]$$

$$[C] = \frac{K_1 [A][B]}{K_2 + K_3}$$

$$r = K_3 [C]$$

$$\boxed{r = \frac{K_3 K_1 [A][B]}{K_2 + K_3}}$$

Ans.

Q→ Q No→ 5

$$\cancel{K = \frac{dN_2O_5}{dt}}$$

Sol[n]

$$K = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

0.008, 20, 16

V_0 → Zero

Q→ Q No→ 6

$$V_0 = 22.8$$

$$V_t = 13.8 \quad , t = 10$$

$$V_t = 8.25 \quad t = 2$$

D.P.P.S-10 → Q 4,18 not do, other do

Page No. 223

$$K = \frac{2.303}{t} \log \frac{v_0}{v_t}$$

a) $t = 10$, $v_t = 13.8$, $v_0 = 22.8$, $K = \checkmark$

$t = 20$, $v_t = 8.25$, $v_0 = 22.8$, $K = \checkmark$ 1st order

b) $t_{1/2} = \frac{0.693}{K}$

c) $\alpha = 1 - e^{-Kt}$ → 25 min

$\boxed{\begin{matrix} P \to 7 \\ P \to 31 \end{matrix}}$ Passage 1st

$A \longrightarrow B + C$, $K_{eq} = 0.5 = \frac{K_f}{K_b}$

$r = K[A]^x$

$0.05 = K[0.170]^x$

$0.1 = K[0.34]^x$

27 a)

order ← $\boxed{x = 1}$

28 b) $r = K_f[A]^1$

$0.05 = K_f\ [0.170]$

$K_f = \frac{0.05}{0.170}$

Now

$$0.5 = \frac{K_f}{K_b}$$

$$K_b = \frac{0.5}{0.170 \times 0.05}$$

29.) $Keq = \frac{K_f \downarrow}{K_b \uparrow} = 0.5 \downarrow$

12/5/2012

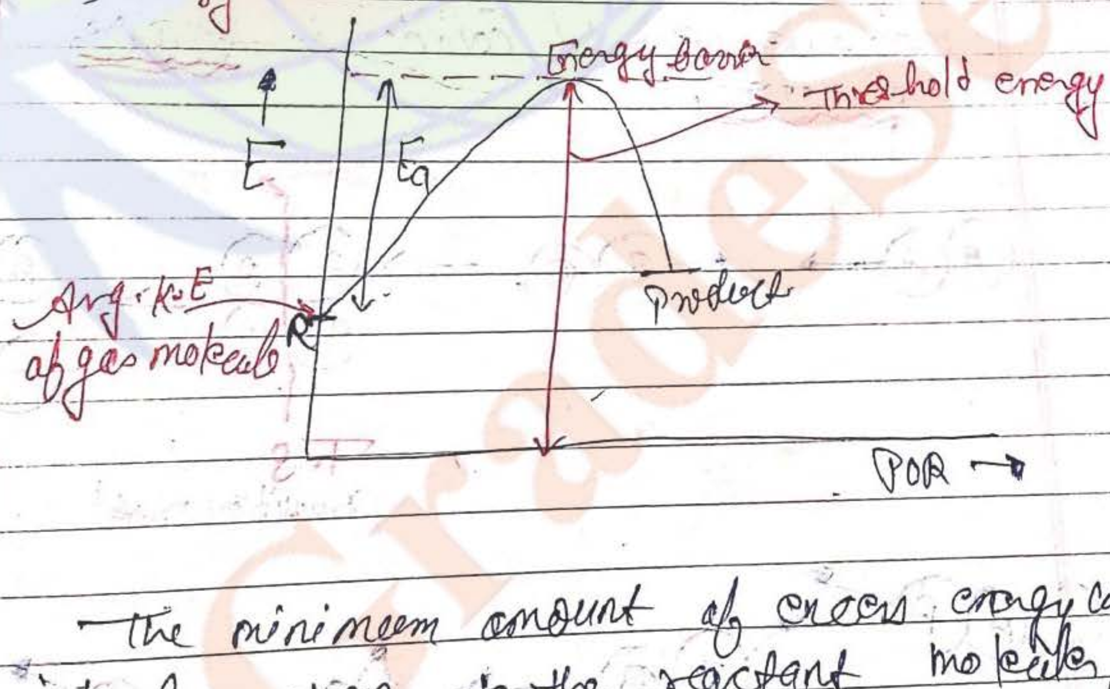
Collison theory of reaction rate →

Page No. 225
Date: / /

1) Collison frequency (Z) ⇒ It is defined as the total number of collison's taking place per second per unit volume of reaction mixture.
It value is very high of the order 10^{25} to 10^{28} but the rate of reaction is low as compare to the value of "Z".

2) Effective collison →
The collison after which reactant get converted into product is known as effective collison. for the collison to be effective it has to overcome two barrier's :-
a) Energy barrier
b) orientation barier.

(a) Energy barrier



The minimum amount of excess energy which is to be given to the reactant molecule so that it get converted into product (show that they can take part in chemical reaction is known as activation energy

Activationenergy → effective collision → rate of reaction

$\Rightarrow E_a$ "↑" Z_{eff} "↓" r "↓"

$\Rightarrow E_a$ "↓" Z_{eff} "↑" r "↑"

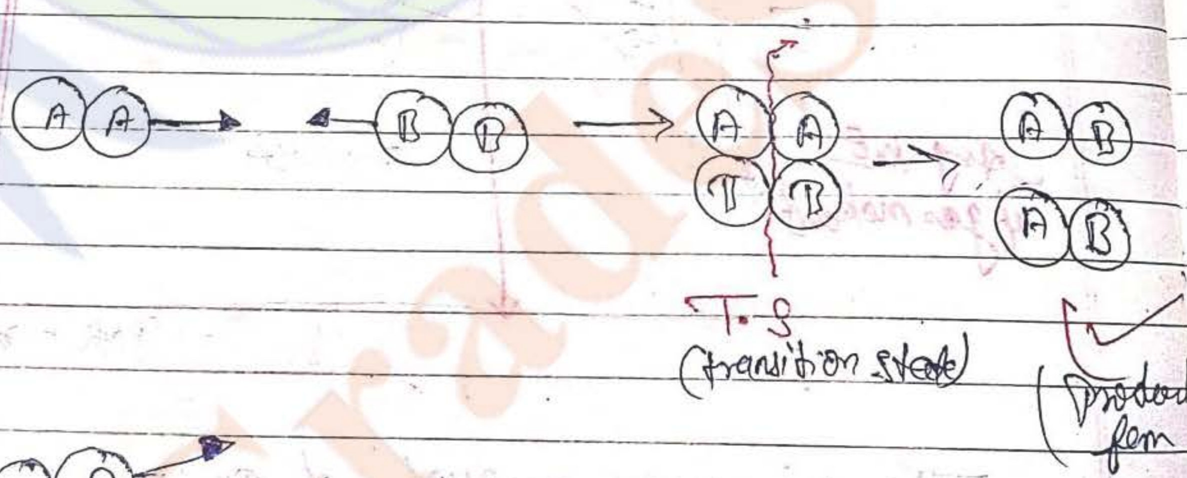
rate ∝ Effective collision

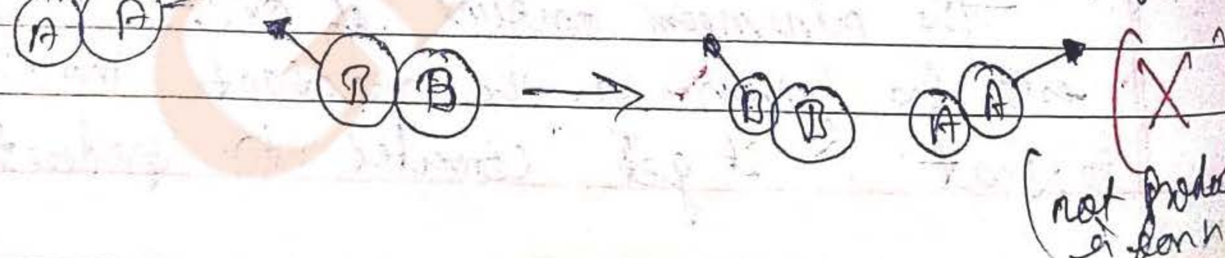
and

$E_a \propto \frac{1}{Z_{eff}}$

b) orientation factor →

Energy along do not decides the effectiveness of the collision for a collision to be effective → the two molecules should collide in proper direction.





A ⟶ Product

Specific rate of reaction (r) ⇒ ($r = K$)

$$\boxed{r = Z \times P \times f}$$

$$\boxed{\Rightarrow r = K[A]^n}$$

Here:-

Z = Collision frequency
P = orientation factor
f = fraction of molecules having energy greater than or equal to Ea
↓
Boltzman maxwell equation
↓
$$\boxed{e^{-Ea/RT}}$$

Note

$r = Z \times P \times e^{-Ea/RT}$

$$\boxed{r = A e^{-Ea/RT}}$$ → Arrhenius equation.

or

$$\boxed{K = A e^{-Ea/RT}}$$

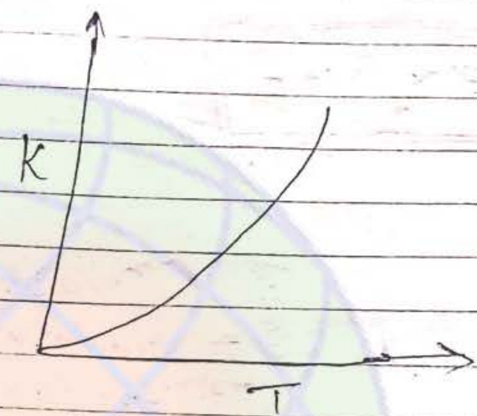
A = freq. factor or Pre exponential factor (sec^{-1})

K → specific rate constant ($r = K$)

R → 8.314 or 2 cal

Note ⇒

1) $K = Ae^{-E_a/RT}$



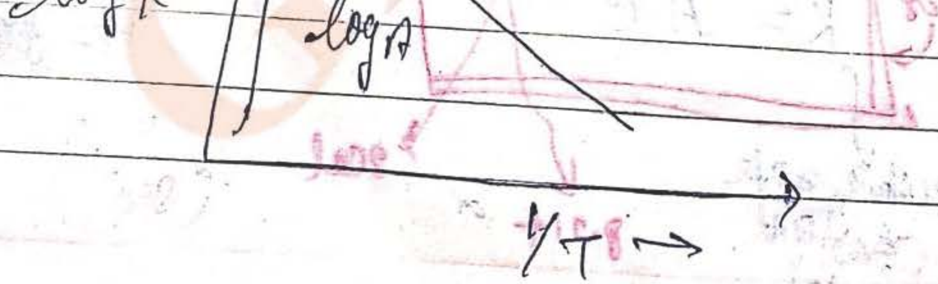
Here the rate constant (K) Increases exponentially wit (temp

2.) $K = Ae^{-E_a/RT}$

$\ln K = \ln A - \frac{E_a}{RT}$

$\log K = \log A - \frac{E_a}{2.303RT}$

$y = c + mx$



3. $\boxed{\ln K = \ln A - \frac{E_a}{RT}}$

diff. w.r.t. T

$$\boxed{\frac{d \ln K}{dT} = \frac{E_a}{RT^2}}$$

4. $\boxed{\log K = \log A - \frac{E_a}{2.303RT}}$

$T = T_1$ $\quad \log K_1 = \cancel{\log A} - \frac{E_a}{2.303RT_1}$ —(i)

$T = T_2$ $\quad \log K_2 = \cancel{\log A} - \frac{E_a}{2.303RT_2}$ —(ii)

$$\boxed{\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

$(T_2 > T_1)$

Note → i) "Ea" of the reaction is Independent of temperature.

ii) "Ea" of the reaction depend on

Presence of catalyst and nature of reactant.

5.) $A \xrightarrow[r_1, T_1]{Ea_1}$ Product

$B \xrightarrow[r_2, T_1]{Ea_2}$ Product

$(Ea_1 > Ea_2)$

(Same temperature)

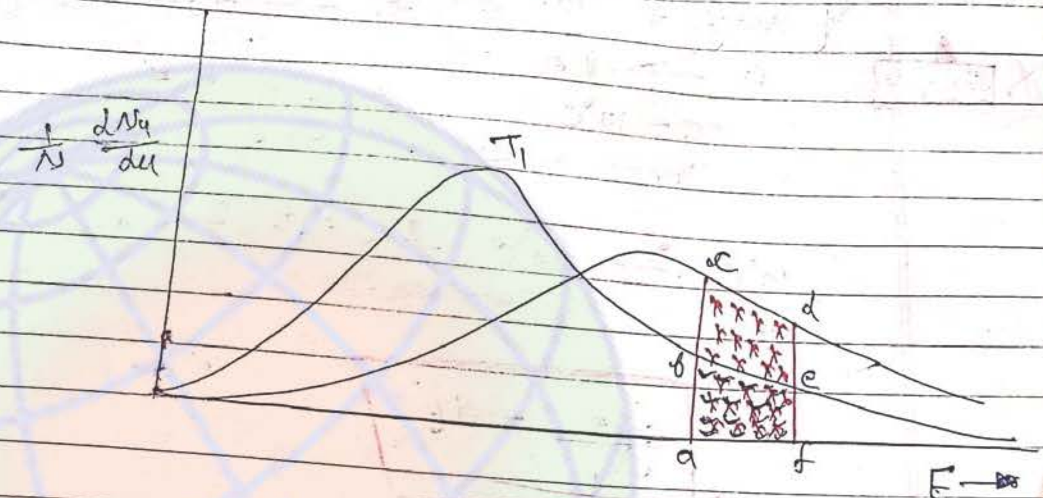
If temp. of both reaction is increase from T_1 to T_2 than % increase in value of "K" will be more for that reaction which have "more" value of "Ea".

$$K = Ae^{-Ea/RT}$$

$$\frac{dK}{dT} = \underbrace{Ae^{-Ea/RT}}_{K} \frac{Ea}{RT^2}$$

$$\boxed{\frac{1}{K}\frac{dK}{dT} \propto Ea}$$

6-) maxwall Boltzman curve →



Temperature coefficient (μ) →

It is defined as the ratio of rate constant of a reaction which differ's by "10°C"

A ⟶ Product

$t = T \quad K_1$

$t = T+10 \quad K_2$

$$\boxed{\mu = \frac{K_{T+10}}{K_T} = 2 \text{ to } 3}$$

Temp. coff. (μ) for most of the reaction comes b/w 2 to 3 which mean's that for every 10° rise in temp. the rate of

GRAPH → the reaction becomes 2 to 3 time
{ लेकिन याद रखो → ऐसा तब होगा जब वह Activation energy को पार कर चुका होगा। यदि ये पार किया नहीं है तो इसके पहले थोड़ा न कुछ होगा है। }

Example: $A \rightarrow \text{Product}$, $\mu = 2$

$T_1 = 10^\circ C$, $T_2 = 50^\circ C$
r_1 , r_2

$$\underset{\text{"}r\text{"}}{10^\circ C} \xrightarrow{2} 20^\circ C \xrightarrow{2} 30^\circ C \xrightarrow{2} 40^\circ C \xrightarrow{2} \underset{\text{"}16r\text{"}}{50^\circ C}$$

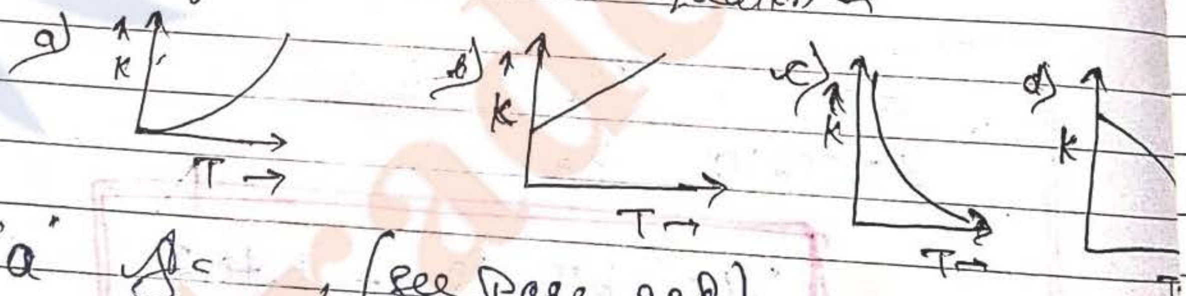
$$\boxed{\frac{r_2}{r_1} = 16}$$

Imp.

$$\boxed{\frac{K_2}{K_1} = \frac{r_2}{r_1} = (\mu)^{\frac{T_2 - T_1}{10}}}$$ → This is formula

IIT 2010 (A)

Plot's showing the variation of the rate constant (K) with temperature (T) are given below. The plot that follows Arrhenius equation is



Sol/n "a" Ans, (see page 228)

Catalyst

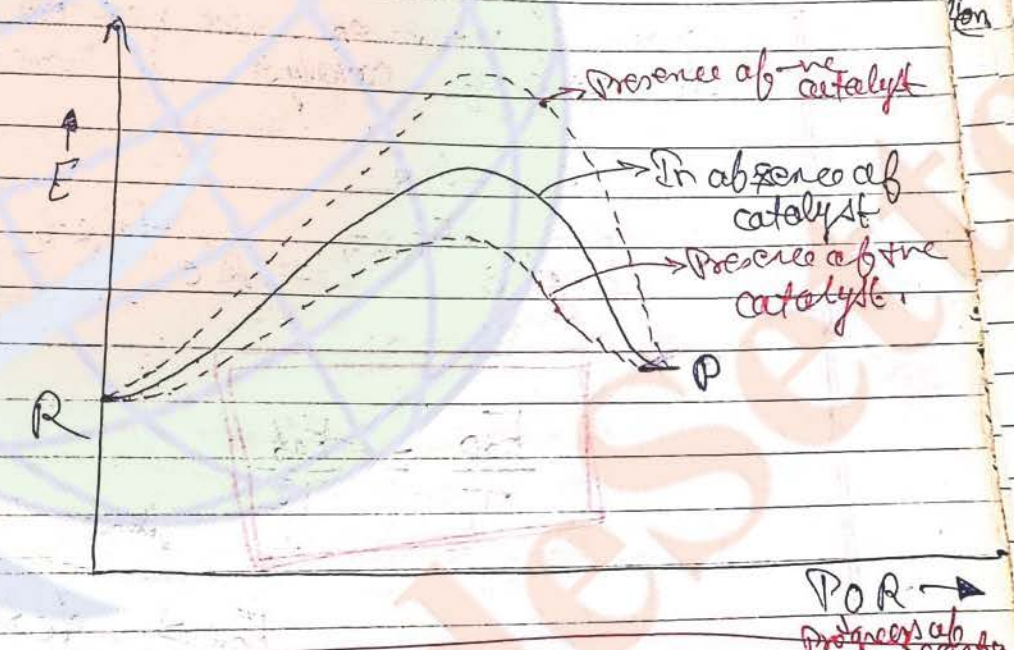
1)

+ve catalyst
(जब कुछ नहीं लिखा है तो +ve मानें)

$\boxed{E_a \downarrow \ r \uparrow}$

-ve catalyst

$\boxed{E_a \uparrow \ r \downarrow}$



$\Delta U, \Delta G, \Delta H \rightarrow$ value are not changed by use of catalyst.

activation energy in presence of catalyst.

2.) $A \xrightarrow[\text{In presence of the catalyst}]{T_1,\ E_{aP},\ r_1} \text{Product}$

$A \xrightarrow[\text{In absence of catalyst}]{T_1,\ E_{ab},\ r_{2}} \text{Product.}$

Case 1st ⟹

Rate of both the reaction can be made equal if Temp. of the reaction taking place in absence of catalyst is increased from $T_1 \rightarrow$

$$r_1 = r_2$$

$$\cancel{A}\, e^{-E_{aP}/RT_1} = \cancel{A}\, e^{-E_{ab}/RT_2}$$

$$\boxed{\frac{E_{aP}}{T_1} = \frac{E_{ab}}{T_2}}$$

Here

$E_{aP} \Rightarrow$ Activation energy in presence of catalyst

$E_{ab} \Rightarrow$ Activation energy in absence of catalyst.

D.P. P $\geq$ 10^3, 12 $\Rightarrow$
DP.P $\geq$ 12
305

Case IInd $\rightarrow$

$$\frac{r_1 = \cancel{A} e^{-E_{ap}/RT_1}}{r_2 = \cancel{A} e^{-E_{ab}/RT_1}}$$

$$\frac{r_1}{r_2} = e^{(E_{ab} - E_{ap})/RT_1}$$

$$\boxed{\frac{K_1}{K_2} = \frac{r_1}{r_2} = e^{(E_{ab} - E_{ap})/RT_1}}$$

~~ghost~~
~~Bad~~
~~Desorage $\rightarrow$ T~~
P $\rightarrow$ T1

$\boxed{\text{Ex}^2 1,\ Q \to 26}$

$t_{1/2} = 10\ min$

$t = 60 min$

$C_t = \frac{C_0}{2^6}$

$\boxed{\text{Ex}^2 1,\ Q.16}$

$$2A \longrightarrow B + 3C$$

	$2A$	B	$3C$
$t=0$	P^0	0	0
$t=10$	$P^0 - 2P$	P	$3P$
~~$t=\infty$~~	~~0~~	~~P^0~~	~~$3P^0$~~

$$P^0 - 2P = 200$$

$$P^0 - 2P + P + 3P = 300$$

$$K = \frac{1}{t}\ln\frac{P_0}{P_0 - 2P}, \text{ find } P_0 \text{ and}$$

$t \to 10$

$\boxed{\text{Ex}^2 1,\ Q = 17}$

$$K = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

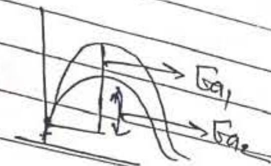
$V_\infty \to 42.03$, $V_0 \to 19.2$, $t \to 75$, $V_\infty \to 42.03$, $V_t \to 24.2$

$\boxed{\text{Ex}^2 1,\ Q = 18}$

$$K = \frac{2.303}{t}\log\frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}$$

$\theta_\infty \to 100$, $\theta_t \to 50$, $\theta_\infty \to 100$

प्र॰ 2
Q.N. 38



$Ea_1 \uparrow$ $\qquad$ $Ea_2 \downarrow$

$K_1 \downarrow$ $\qquad$ $K_2 \uparrow$

$\Downarrow$ $\qquad$ $\Downarrow$

$K_1' \uparrow$ (ज्यादा बढ़ा) $\qquad$ $K_2' \uparrow$ (कम बढ़ा)

$$\boxed{\frac{K_1'}{K_1} > \frac{K_1'}{K_2}}$$

Po and B

प्र॰ 2
Q.N. 19

$$K = \frac{2.303}{t} \log \frac{C_0}{C_t}$$

$t \rightarrow 2.71$, $C_0 \rightarrow 1$, $C_t \rightarrow 0.25$

very Imp (Most Imp must asked)

Parallel 1st order Reaction →

$$A \xrightarrow[\text{1st Path}]{E_1, K_1} B$$

$$A \xrightarrow[\text{2nd Path}]{E_2, K_2} C$$

$t = 0$ a or A_0

$t = t$ $a-x$ or A_t

Overall Reaction K_T, E_T

List of Important formula →

1.) $K_T = K_1 + K_2 + \text{-----} + K_n$

2.) $E_T = \dfrac{K_1 E_1 + K_2 E_2 + \text{-----} + K_n E_n}{K_1 + K_2 + \text{-----} + K_n}$

3.) $\dfrac{1}{(t_{1/2})_{overall}} = \dfrac{1}{(t_{1/2})_1} + \dfrac{1}{(t_{1/2})_2} + \text{-----} + \dfrac{1}{(t_{1/2})_n}$

4.) $t = \dfrac{2.303}{K_1 + K_2 + \text{---} + K_n} \log \dfrac{a}{a-x}$ or $\boxed{t = \dfrac{2.303}{K_T} \log \dfrac{a}{a-x}}$

5.) $\dfrac{[B]_t}{[C]_t} = \dfrac{K_1}{K_2}$

Note $K = \frac{1}{\tau}$ and $K = \frac{0.693}{t_{1/2}}$

So $\boxed{\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2}}$

6. $K_1 = x\% \; K_T$

7. $\frac{1}{(t_{1/2})_1} = \frac{x}{100} \times \frac{1}{(t_{1/2})_{overall}}$

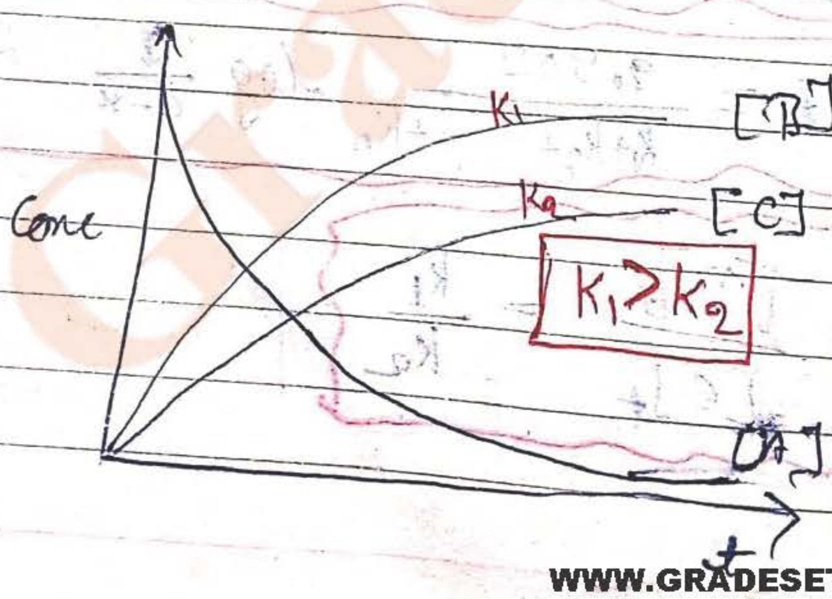
8. $\% B = \frac{k_1}{k_1 + k_2} \times 100$

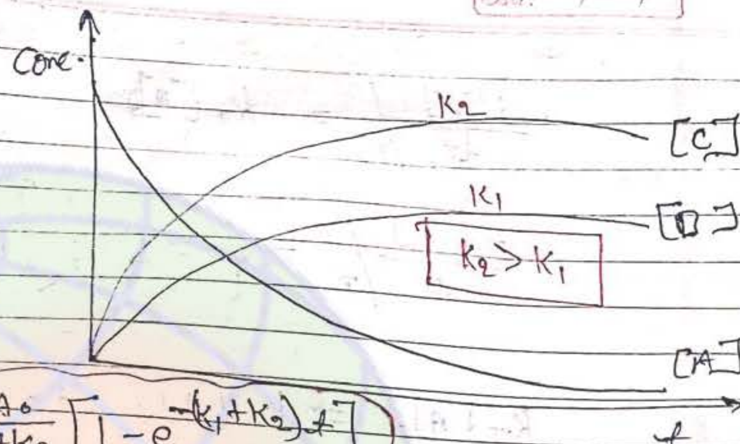
9. $\% C = \frac{k_2}{k_1 + k_2} \times 100$

10. $\frac{[B]_t}{[A]_t} = \frac{k_1}{k_1 + k_2} \left[e^{(k_1 + k_2)t} - 1 \right]$

11. $\frac{[C]_t}{[A]_t} = \frac{k_2}{k_1 + k_2} \left(e^{(k_1 + k_2)t} - 1 \right)$

12.





13. $[B]_t = \frac{K_1 A_0}{K_1+K_2}\left[1 - e^{-(K_1+K_2)t}\right]$

14. $[A]_t = A_0 e^{-(K_1+K_2)t}$

15. $[C]_t = \frac{K_2 A_0}{K_1+K_2}\left[1 - e^{-(K_1+K_2)t}\right]$

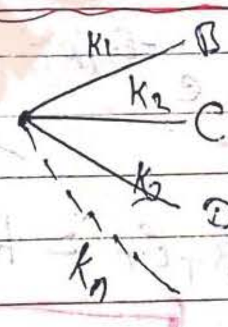
⇒ Derivation ⇒

1) Rate of disapp. of "A" in path I →

$$\frac{-d[A]}{dT}\Big/_1 = K_1 [A]_t$$

Rate of disapp. of A in path II

$$\frac{-dA}{dt}\Big/_2 = K_2 [A]_t$$



$K_T = K_1 + K_2 + K_3 + \dots + K_n$

so,

Total rate of disapp. "A"

$$\left.\frac{-d[A]}{dt}\right|_T = k_T[A]_t$$

$$\left.\frac{-d[A]}{dt}\right|_T = \left\{\left.\frac{-dA}{dt}\right|_1\right\} + \left\{\left.\frac{-dA}{dt}\right|_2\right\}$$

$$k_T[A]_T = k_1[A]_t + k_2[A]_t$$

$$\underline{k_T = k_1 + k_2}$$

2.)

$$k_T = k_1 + k_2$$

$$\cancel{A_T e^{-E_T/RT}} = \cancel{A_1 e^{-E_1/RT}} + \cancel{A_2 e^{-E_2/RT}}$$

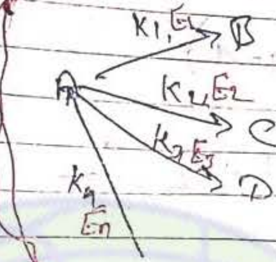
$$A_T e^{-E_T/RT} = A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT}$$

diff w.r.t T

$$A_T e^{-E_T/RT}\left(\frac{E_T}{\cancel{RT^2}}\right) = A_1 e^{-E_1/RT}\left(\frac{E_1}{\cancel{RT^2}}\right) + A_2 e^{-E_2/RT}\left(\frac{E_2}{\cancel{RT^2}}\right)$$

$$k_T E_T = k_1 E_1 + k_2 E_2$$

$$\boxed{E_T = \frac{k_1 E_1 + k_2 E_2 + \cdots\cdots k_n E_n}{k_1 + k_2 + \cdots\cdots + k_n}}$$



$$K_T E_T = k_1E_1 + k_2E_2 + \dots k_nE_n$$

$$E_T = \frac{k_1E_1 + k_2E_2 + \dots k_nE_n}{K_T}$$

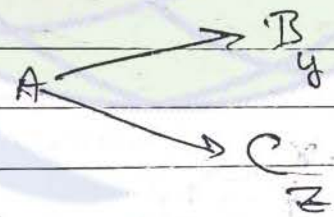
$$E_T = \frac{k_1E_1 + k_2E_2 + \dots k_nE_n}{k_1 + k_2 + \dots + k_n}$$

3.) $K_T = k_1 + k_2$

$$\frac{0.693}{(t_{1/2})_T} = \frac{0.693}{(t_{1/2})_1} + \frac{0.693}{(t_{1/2})_2}$$

$$\boxed{\frac{1}{(t_{1/2})_T} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2} + \dots}$$

4)



$t = 0 \quad a$

$t = t \quad a - x$

$$-\frac{d[A]}{dt}\Big|_{ove} = K_T[A]_t$$

$$-\frac{d}{dt}(a - x) = K_T(a - x)$$

$$\frac{dx}{dt} = k_T (a-x)$$

$$\int \frac{dx}{a-x} = (k_1+k_2)\int dt$$

$$\boxed{t = \frac{2.303}{k_1+k_2+\dots+k_n} \log \frac{a}{a-x}}$$

5.)

$$A \xrightarrow{k_1} \overset{x}{B}$$
$$A \xrightarrow{k_2} \overset{y}{C}$$

$t=0$ $\quad A_0$

$t=t$ $\quad A_t$

$$\frac{1}{x}\frac{d[B]}{dt} = k_1[A]_t$$

$$\frac{1}{y}\frac{d[C]}{dt} = k_2[A]_t$$

$$\frac{d[B]}{d[C]} = \frac{k_1}{k_2} \times \frac{x}{y}$$

$$\int_0^t d[B] = \frac{x}{y}\frac{k_1}{k_2}\int_0^t d[C]$$

$$\boxed{\frac{[B]_t}{[C]_t} = \frac{x k_1}{y k_2}}$$

$$A \xrightarrow{k_1} xB$$
$$A \xrightarrow{k_2} yC$$
$$A \xrightarrow{k_3} zD$$

$$\frac{[C]_t}{[D]_t} = \frac{y\,k_2}{z\,k_3}$$

$$\frac{[B]_t}{[D]_t} = \frac{x\,k_1}{z\,k_3}$$

6.)

Rate of formation of B = x% of total rate of diss. of A

$$\frac{d[B]}{dt} = x\%\left\{\frac{-dA}{dt}\right\}_T$$

$$k_1\,\cancel{[A]_t} = x\%\;k_T\,\cancel{[A]_t}$$

$$\boxed{k_1 = x\%\;k_T}$$

x% ⇒ कितना % B बना है यह बताता है

7) ~~$K_1 = x\% \, R$~~

$$K_1 = x\% \; K_T$$

$$\frac{0.693}{(t_{1/2})_1} = \frac{x}{100} \times \frac{0.693}{(t_{1/2})_{overall}}$$

$$\boxed{(t_{1/2})_{overall} = \frac{x \times (t_{1/2})_1}{100}}$$

8) $K_1 = x\% \, KT$

$$x\% = \frac{K_1}{KT}$$

$$\boxed{\% \, B = \frac{K_1}{K_1 + K_2} \times 100}$$

10) WILHELMY FORMULA

$$C_t = C_0 e^{-Kt}$$

$$[A]_t = A_0 e^{-(K_1 + K_2)t}$$

$$\frac{d[B]}{dt} = K_1 [A]_t$$

$$\frac{d[B]}{dt} = k_1 \, A_0 \, e^{-(K_1+K_2)t}$$

$$\int_0^t dB = K_1 A_0 \int_0^t e^{-(K_1+K_2)t} \, dt$$

$$[B]_t = K_1 A_0 \left[\frac{e^{-(K_1+K_2)t}}{-(K_1+K_2)} \right]_0^t$$

$$[B]_t = \frac{K_1 \cancel{A_0}}{-(K_1+K_2)} \left[e^{-(K_1+K_2)t} - 1 \right]$$

$$[A]_t = \cancel{A_0} \, e^{-(K_1+K_2)t}$$

$$\frac{[B]_t}{[A]_t} = \frac{K_1}{K_1+K_2} \frac{\left[1 - e^{-(K_1+K_2)t} \right]}{e^{-(K_1+K_2)t}}$$

$$\frac{[B]_t}{[A]_t} = \frac{K_1}{K_1+K_2} \frac{\left[1 - \frac{1}{\cancel{e^{(K_1+K_2)t}}} \right]}{\frac{1}{\cancel{e^{(K_1+K_2)t}}}}$$

$$\boxed{\frac{[B]_t}{[A]_t} = \frac{k_1}{k_1+k_2}\left[e^{(k_1+k_2)t} - 1\right]}$$

Passage (V)

39.)

$$A \longrightarrow 2B \quad (2x)$$

$$A \longrightarrow 3C \quad (3y)$$

$t=0$: a

$t=t$: $a-x-y$, $2x$, $3y$

→ A के लिए अलग अलग mole disappear करवाएँगे और तब फिर stoichiometry का उपयोग करते हुए Product की लिखेंगे।

$[A_0] = a$

$[A]_t = a-x-y$

$[B]_t = 2x$

$[C]_t = 3y$

Now put the value find L.H.S = R.H.S

(C.)

$$a = a - x + \frac{2x}{2} + \frac{3x}{3}$$

$$2 \neq a - x + 2x$$

$$\neq a + x$$

$$a = a - x - y + \frac{2x}{2} + \frac{3y}{3}$$

$$a = a - \cancel{x} \cancel{+y} + \cancel{x} + y$$

$$a = a$$

40.)

$$x \begin{array}{l} \nearrow y \\ \searrow z \end{array}$$

$$\frac{X_t}{Y_t + Z_t} \quad or \quad \frac{A_t}{B_t + C_t}$$

$$\frac{A_t}{B_t + C_t} = \frac{\cancel{A_0}\, e^{-(K_1+K_2)t}}{\frac{K_1 \cancel{A_0}}{K_1+K_2}\left[e^{-(K_1+K_2)t} - 1\right] + \frac{K_2 \cancel{A_0}}{K_1+K_2}\left[e^{-(K_1+K_2)t} - 1\right]}$$

$$= \frac{e^{-(K_1+K_2)t}}{\frac{(K_1+K_2)}{(K_1+K_2)}\left[e^{-(K_1+K_2)t} - 1\right]}$$

41.)

Ex-3
Passage - IV

$$k' = \frac{2k_2}{k_3}\left(\frac{k_1}{k_5}\right)^{1/5}$$

36)

$$\cancel{E_a' = \frac{2E_{a_2}}{E_{a_3}}\left(\frac{E_{a_1}}{E_{a_5}}\right)^{1/5}}$$

$\cancel{E_{a_3} =}$

$$A' e^{-E_a'/RT} = \cancel{\left(\frac{2A_2 e^{-E_{a_2}/RT}}{A_3 e^{-E_{a_3}/RT}}\right)}$$

$$A' e^{-E_a'/RT} = \frac{2 A_2 e^{-E_{a_2}/RT}}{A_3 e^{-E_{a_3}/RT}}\left(\frac{A_1 e^{-E_{a_1}/RT}}{A_5 e^{-E_{a_5}/RT}}\right)^{1/5}$$

By solving we get

$$E_a' = E_{a_2} - E_{a_3} + \frac{1}{5}E_{a_1} - \frac{1}{5}E_{a_5}$$

37)

$$\boxed{A' = \frac{2A_2}{A_3}\left(\frac{A_1}{A_5}\right)^{1/5}}$$

$$e^{-E_a'/RT} = e^{\frac{-E_{a_2} + E_{a_3} - E_{a_1}^{1/5} + E_{a_5}^{1/5}}{RT}}$$

$$\frac{-E_a'}{\cancel{RT}} = \frac{-E_{a_2} + E_{a_3} - E_{a_1}^{1/5} + E_{a_5}^{1/5}}{\cancel{RT}}$$

36

$$\boxed{E_a' = E_{a_2} - E_{a_3} + \frac{1}{5}E_{a_1} - \frac{1}{5}E_{a_5}}$$

Do all sheet
sheet Discussion

Ex-3
Passage - II

sheet Ex
Ex 1.

30) $N_2O_5(g) \longrightarrow 2NO_2 + O_2(g)$

0.2 mole
$V = 2L$
$T = 200K$

$$\frac{E_a}{2.303R} = 6670$$

$R \to 8.314$

Divide by the above and get answer.

31) $\cancel{\frac{2.303}{K} = 1.2\times10^2}$ $\quad \frac{K}{2.303} = 1.2\times10^2$

$\cancel{K = \frac{2.303}{1.2\times10^2}}$ $\quad K = 1.2\times2.303\times10^2$

$\cancel{t_{1/2} = 0.693}$ $\quad t_{1/2} = \frac{0.693}{K} = 2.5\times10^{-3}$

$\to t_{1/2}$

32) $t = 5\times10^{-3}$

$t = 2\,t_{1/2}$

$$C_t = \frac{C_0}{2^2} = \frac{0.1}{2^2} = \frac{0.1}{4}$$

$r = K[C]_t$

$\to 1.2\times2.303\times10^2$

Sheet Ex. 1

Ex1.) A substance undergoes first order decomposition. The decomposition follows two parallel first order reaction as:-

$$A \xrightarrow{k_1} B \quad \text{and } k_1 = 1.26 \times 10^{-4}\ sec^{-1}$$
$$A \xrightarrow{k_2} C \quad k_2 = 3.80 \times 10^{-5}\ sec^{-1}$$

The % distribute of B and C are?

Sol^n

$$\% B = \frac{k_1}{k_1 + k_2} \times 100$$

$$= \frac{1.26 \times 10^{-4}}{1.26 \times 10^{-4} + 3.80 \times 10^{-5}} \times 100 = 76.83\%$$

$$\% C = \frac{k_2}{k_1 + k_2} \times 100$$

$$= 23.17$$

Alt

$$\% C = 100 - 76.83$$
$$= 23.17\ \%$$

Ex2.) for the following 1st order parallel chain reaction

$$A \rightarrow B$$
$$A \rightarrow C$$
$$A \rightarrow D$$

If the half life of A is 25 sec. then find out

The half lives of B, C, and D. Given that the rate of formation of ~~B, C and D~~ B and C is 15% and 30% of the rate of decomposition of "A" respectively?

Sol

Sequenctial first order Reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$t=0$	a	0	0
$t=t$	x	y	z

1) WILHELMY formula

$$C_t = ae^{-k_1 t}$$

$$\boxed{x = ae^{-k_1 t}}$$

2) Rate of formation of B

w.imp

$$\boxed{\frac{d[B]}{dt} = k_1 x - k_2 y}$$

$$\frac{dy}{dt} = k_1 x - k_2 y$$

1st order differential equation (Euler method)

$$\boxed{\frac{dy}{dt} = k_1 ae^{-k_1 t} - k_2 y}$$

Also

$$\boxed{y = \frac{k_1 a}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]}$$

most imp Disp 9.

Time at which conc of B is max →

$$y = \frac{k_1 a}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]$$

for maxima, $\frac{dy}{dx} = 0$

$$\frac{dy}{dt} = \underbrace{\frac{k_1 a}{k_2 - k_1}}_{\neq \text{ zero}}\underbrace{\left[e^{-k_1 t}(-k_1) - e^{-k_2 t}(-k_2)\right]}_{= 0} = 0$$

(zero नहीं हो सकता)

$$e^{-k_1 t}(\cancel{-}k_1) = e^{-k_2 t}(\cancel{-}k_2)$$

$$\frac{k_1}{k_2} = e^{(k_2 - k_1)t_{max}}$$

$$\boxed{\ln\frac{k_2}{k_1} = (k_2 - k_1)t_{max}}$$

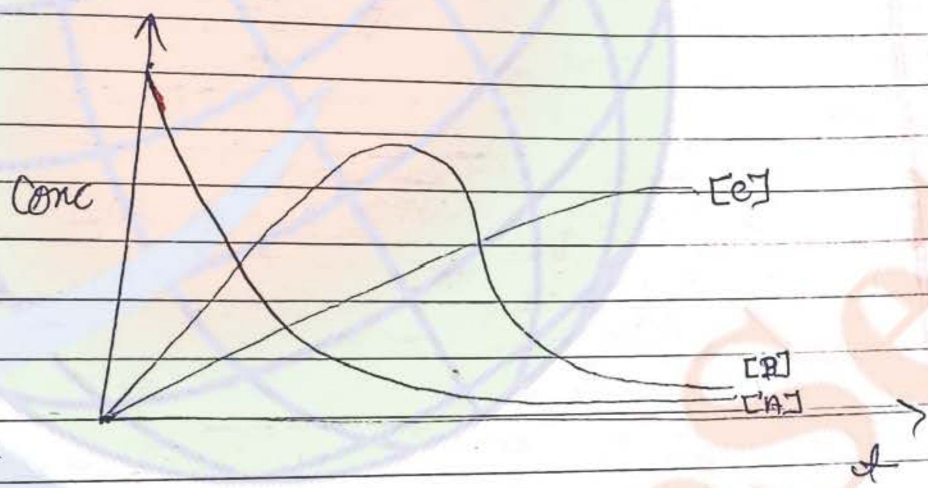
$$\boxed{t_{max} = \frac{1}{K_2 - K_1} \ln \frac{K_2}{K_1}}$$

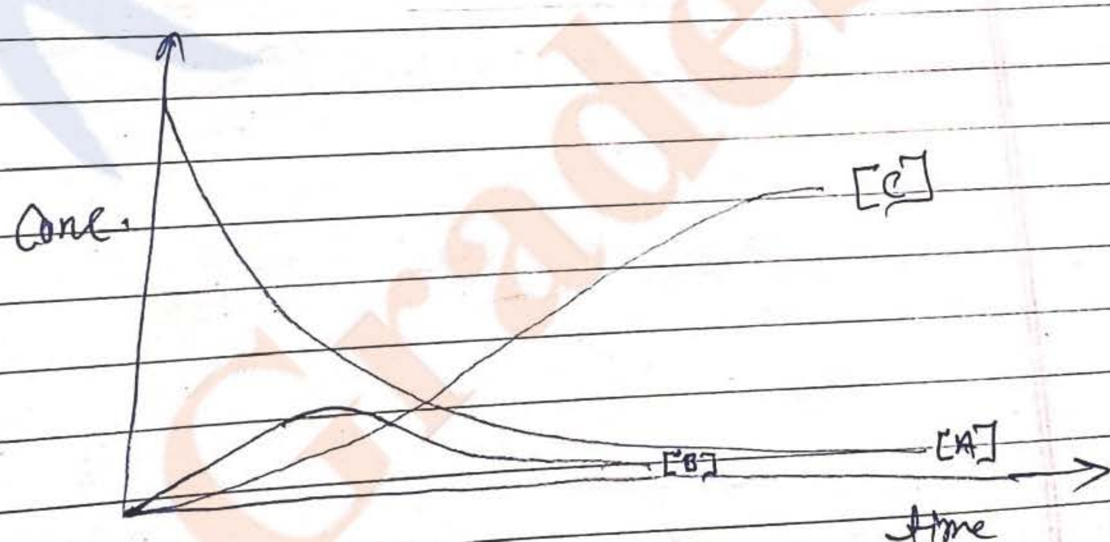
or

$$\boxed{t_{max} = \frac{2.303}{K_2 - K_1} \log \frac{K_2}{K_1}}$$

Imp

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$





Reversible 1st order Reaction

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$t=0$	a	0
$t=t$	$a-x$	x
$t=t_{eq}$	$a-x_e$	x_e

1) $$\boxed{K_{eq} = \frac{k_f}{k_b} = \frac{x_e}{a-x_e}}$$

so,

$$k_b = \frac{a-x_e}{x_e} k_f$$

2) Rate of formation of B

$$\frac{dB}{dt} = k_f(a-x) - k_b(x)$$

$$\frac{dx}{dt} = k_f(a-x) - k_f\frac{(a-x_e)}{x_e}x$$

$$= k_f\left(\frac{ax_e - \cancel{xx_e} - ax + \cancel{xx_e}}{x_e}\right)$$

$$\frac{dx}{dt} = k_f \, a \frac{(x_e - x)}{x_e}$$

$$\int \frac{dx}{x_e - x} = \frac{k_f a}{x_e} \int dt$$

$$-\ln(x_e - x) = \frac{k_f a}{x_e} t + c$$

$t = 0$, $x = 0$, $c = -\ln x_e$

$$\ln \frac{x_e}{x_e - x} = \frac{k_f a}{x_e} t$$

$$k_f = \frac{x_e}{at} \ln \frac{x_e}{x_e - x}$$

$$\boxed{k_f = \frac{2.303 \, x_e}{at} \log \frac{x_e}{x_e - x}}$$

3)

$$\frac{k_f}{k_b} = \frac{x_e}{a - x_e}$$

$$1 + \frac{k_f}{k_b} = 1 + \frac{x_e}{a - x_e}$$

$$\frac{K_f + K_b}{K_b} = \frac{a}{a - x_e}$$

$$(K_f + K_b) = \frac{a}{a - x_e} \times K_b \quad (1)$$

$$K_b = \frac{a - x_e}{\cancel{x_e}} \times \frac{2.303\,\cancel{x_e}}{at} \log \frac{x_e}{x_e - x}$$

$$K_b = \frac{2.303(a - x_e)}{at} \log \frac{x_e}{x_e - x}$$

$$(K_f + K_b) = \frac{\cancel{a}}{\cancel{(a - x_e)}} \times \frac{2.303\cancel{(a - x_e)}}{\cancel{a}t} \log \frac{x_e}{x_e - x}$$

So,

$$\boxed{(K_f + K_b) = \frac{2.303}{t} \log \frac{x_e}{x_e - x}}$$

Q1.) $A \xrightarrow{K_1} B \xrightarrow{K_2} C$

If $(t_{1/2})_A = 4min$

$(t_{1/2})_B = 2min$

find $(t_{max})_B = ?$

Sol^n $t_{max} = \frac{2.303}{K_2 - K_1} \log \frac{K_2}{K_1}$ (Ans = 4 min)

& $K_2 = \frac{0.693}{2}$

$K_1 = \frac{0.693}{4}$

Put value of K_1 and K_2 and find t_{max} ?

~~Q2)~~ $\cancel{A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B}$ $\cancel{K_f = 10^{-2} sec^{-1}}$

Q9) $A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$, $K_f = 10^{-2} sec^{-1}$

$\frac{[B]_{eq}}{[A]_{eq}} = 4$ $[A]_0 = 0.01M$

conc. of "B" after 30 sec.

Sol^n

$$t = \frac{2.303}{K_f + K_b} \log \frac{x_e}{x_e - x}$$

$t \rightarrow 30$, $x \rightarrow ?$

$$K_{eq} = \frac{B_{eq}}{A_{eq}} = 4 = \frac{K_f}{K_b}$$

$$K_b = \frac{10^{-2}}{4}$$

$$= 2.5 \times 10^{-3}$$

$K_{eq} = \frac{x_e}{a - x_e}$, $K_{eq} \rightarrow 4$, $a \rightarrow 0.01$

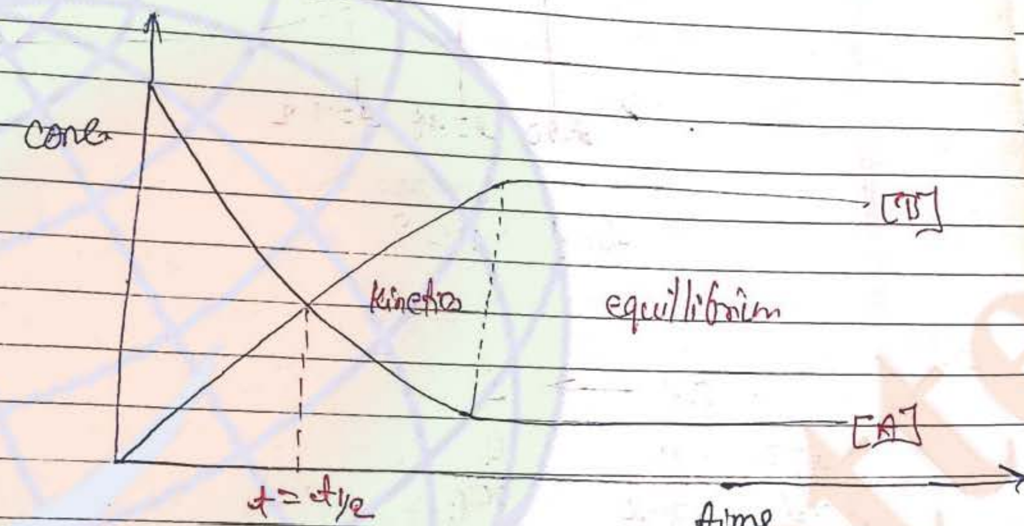
$x_e = 0.008$

Note →

1) $A \longrightarrow B$

$a \qquad 0$

$a-x \qquad x$



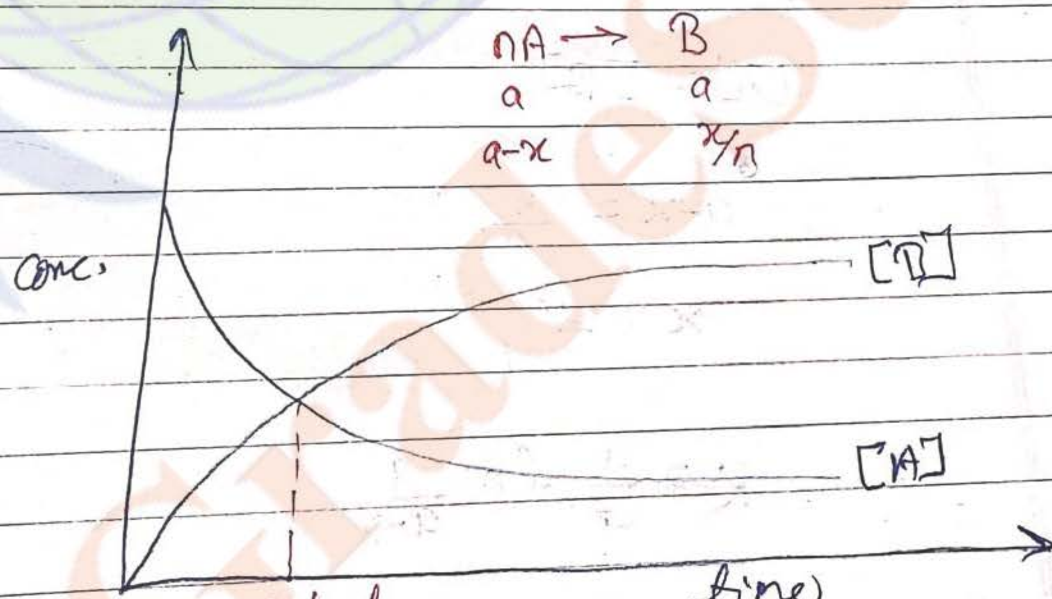
$t = t_{1/2}$

$[A] = [B]$

2.) $nA \longrightarrow B$

$a \qquad a$

$a-x \qquad x/n$

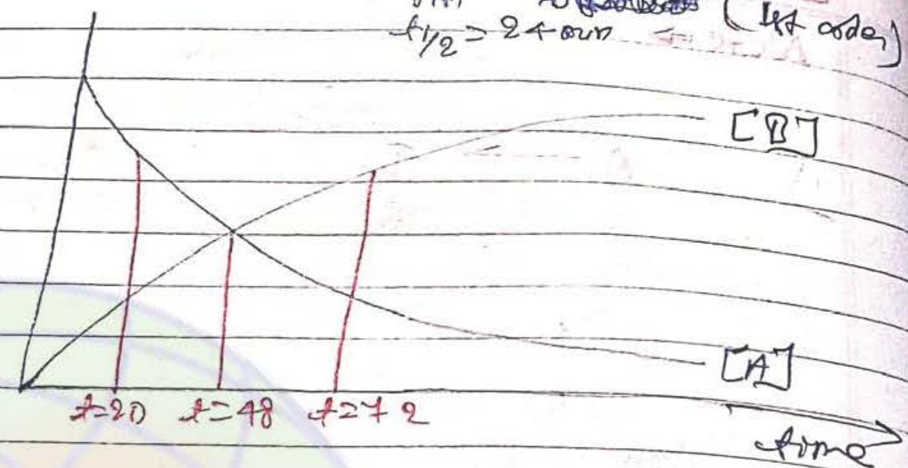


$t \neq t_{1/2}$

$[A] = [B]$

$nA \longrightarrow B$ (1st order)
$t_{1/2} = 24\ min$

Example–



find $n = ?$

Sol^n

$$\begin{array}{lcc} & nA \longrightarrow & B \\ t=0 & a & 0 \\ t=t & a-x & x/n \end{array}$$

$$t = 48\ min$$

$$[A] = [B]$$

$$a - x = \frac{x}{n}$$

$$x = \frac{an}{n+1}$$

$$K = \frac{1}{t} \ln \frac{a}{a-x}$$

$$\frac{\ln 2}{24} = \frac{1}{48} \ln \frac{a}{a - \left(\frac{an}{n+1}\right)}$$

$$\ln 2 = \frac{1}{2} \ln(n+1)$$

$$\ln_2 = \frac{1}{2} \ln(n+1)$$

Concept

$$A + 2B \longrightarrow \text{Product}$$

$t=0$	a	$2a$	$-$
$t=t$	$a-x$	$2a-2x$	

$$\frac{-d[B]}{dt} = k\sqrt{A}\,\sqrt{B}$$

find $t_{1/2}$ of R_n^x

S^n_1

$$\frac{-d}{dt}(2a-2x) = k(a-x)^{1/2}(2a-2x)^{1/2}$$

$$\frac{2dx}{dt} = k\sqrt{2}\,(a-x)$$

$$\frac{dx}{dt} = \frac{k}{\sqrt{2}}(a-x)$$

$$\int \frac{dx}{a-x} = \frac{k}{\sqrt{2}} \int dt$$

$$-\ln(a-x) = \frac{kt}{\sqrt{2}} + C$$

$$\ln \frac{a}{a-x} = \frac{Kt}{\sqrt{2}}$$

$$2.303 \log \frac{a}{a-x} = \frac{Kt}{\sqrt{2}}$$

for, $t = t_{1/2}$, $x = \frac{a}{2}$

$$t_{1/2} = \frac{\sqrt{2} \times 0.693}{K}$$

Do all sheet questio
Read must sheet

Date: / 349

Q1.) In a gaseous phase reaction

$$A_2(g) \longrightarrow B(g) + \frac{C}{2}(g)$$

The pressure increases from 100 mm to 110 mm in 5 minutes.
Find the rate of dissaperance of A_2 in mm/min.

Acid
metre
the
, taken
-80°
reaction
5°
-20°

80|n

$\frac{d[A_2]}{dt}$

$$A_2(g) \longrightarrow B(g) + \frac{C}{2}(g)$$

$t=0$	100	0	0
$t=5$	$100-P$	P	$P/2$

$$\text{Increase} = \frac{P}{2} = \frac{110-100}{5}$$

$$= \frac{10}{5} = 2$$

~~Example~~ An optically active compound "A" upon Acid catalise hydrolysis give two optically active compound B and C pseudo Ist order kinetic. The observed rotation of the mixture after 20 min was $5°$, while after completion of reaction it was $-20°$. If optical rotation per mole of A, B and C are $60°$, $40°$ and $-80°$ respectively, calculate the half life of the reaction.

Sol/n

$$A \longrightarrow B + C$$

$$\begin{cases} t = 20 & 5° \\ t = \infty & -20° \end{cases}$$

	A	B	C
$t=0$	a	0	0
$t=t$	$a-x$	x	x
$t=\infty$	0	a	a

~~$a(60) = \theta_0$ — (i)~~

$t=0 \qquad a(60) = \theta_0 \qquad$ — (i)

$t=t \qquad 60(a-x) + 40x - 8x = 5°$

$$40a - 80a = -20 \qquad \text{— (ii)}$$

$$k = \frac{2.303}{t} \log \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}$$

from eq (i) and (ii)

$$a = \frac{1}{2}$$

so, $\theta = 30°$ of

Electro chemistry

- Electrochemical Cell or Galvanic cell
  - Reversible
  - Irreversible
  - fuel cell
- Electrolytic Cell
- conductance

1 → Electro chemical cell → It is a device in which a ~~red~~ redox reaction is carried out so as to convert chemical energy into electrical energy is known as electro chemical cell.

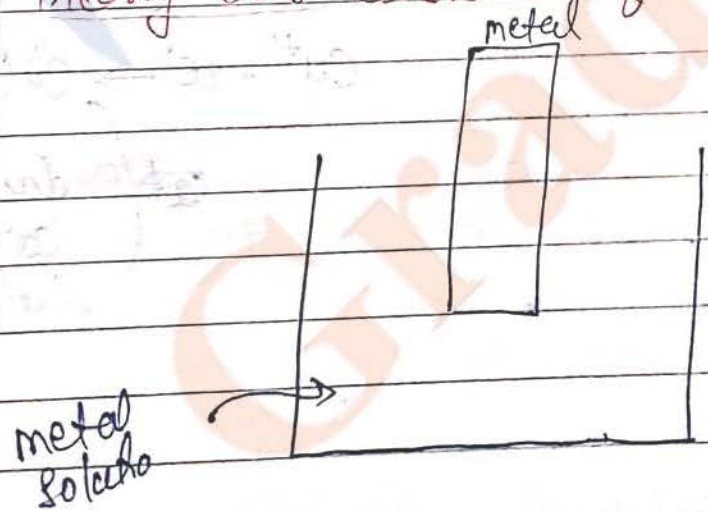
Electro chemical cell are of two types—

a) Reversible cell or Galvanic cells or voltaic cell
b) Irreversible cell or dry cell

a) Reversible cell or secondary cell :- cell that can be recharged
eg → Daniel cell, Lead storage battery, Nickel cadmium battery

b) Irreversible cell or primary cell :- cell that can't be recharged.
eg → Dry cell, mercury cell

Theory and Construction of electrochemical cell →



(**) your confusion so you remove it by reading this

→ An anode is the electrode at which oxidation

An cathode is the electrode at which reduction

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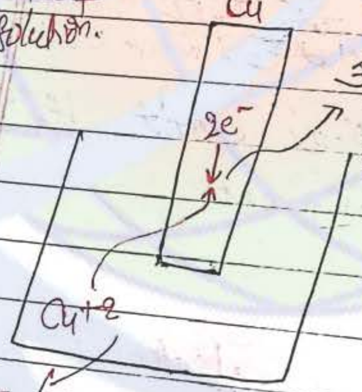
when an electrode is depth in it's salt solution than the metal accuires either +ve or -ve charge with respect to the solution due to which a electrical double layer is form at the Interface of metal electrode and it's salt solution.

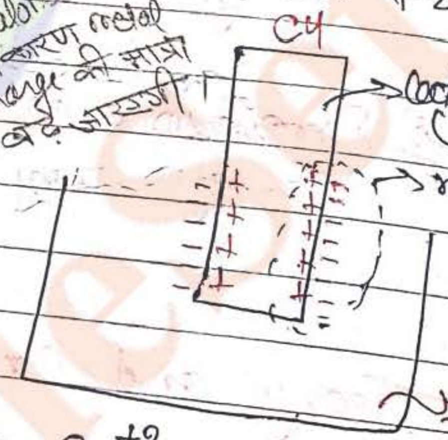
The potential developes is known as electrode potential.

oxidation →

$Zn(s) \rightarrow Zn^{+2} + 2e^-$



Reduction →



$Cu^{+2} + 2e^- \rightarrow Cu(s)$

(Reduction / cathode half cell)

LOAN
L →
O →
A →
N →
Ze →

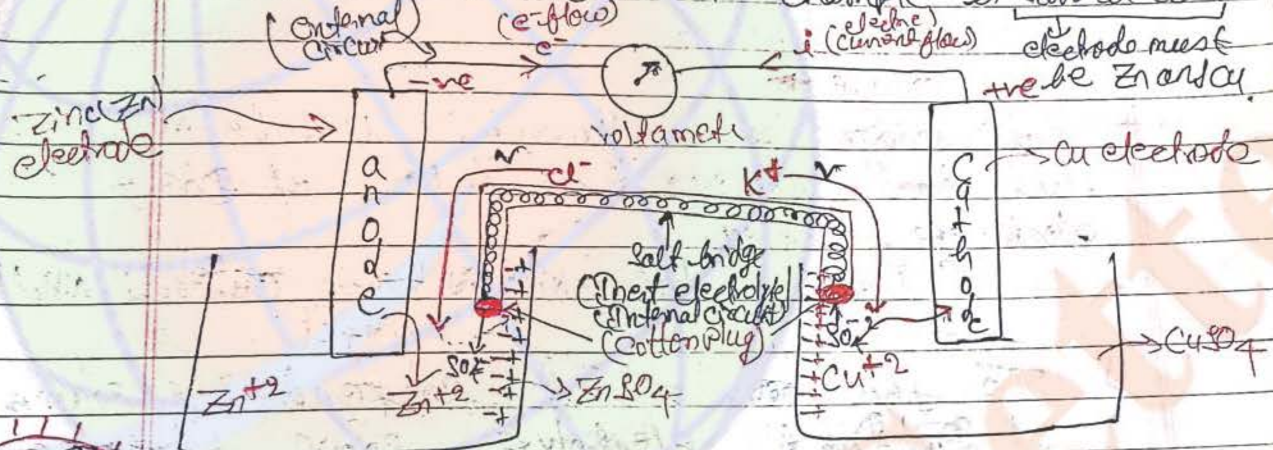
नोट :> e^- के opposite direction में electric current (i) flow करता है

Electrode potential are of two type →

I) Oxidation Potential (O.P)
II) Reduction potential (R.P)

For any electrode (except H_2O)
$R.P = -O.P$ — great formula

If we join the two half cell through wire then it will form a electrochemical cell and the most common example is danial cell.



मदरस्व
"LOAN" Ze
L → left
O → oxidation
A → Anode
N → Negative
Ze → Zinc

anode →
$Zn(s) \rightarrow Zn^{+2} + 2e^-$
(oxidation)

cathode →
$Cu^{+2} + 2e^- \rightarrow Cu(s)$
(Reduction)

Note $Zn + Cu^{+2} \rightarrow Cu + Zn^{+2}$

Danial cell

observation →

1) oxidation of ~~cathode~~ anode take place whereas reduction of cathode take place.
2) with the passage of time conc. of Zn^{+2} ion's Increase in anodic half cell whereas Cu^{+2} ion's decreases in cathodic half cell.

3) There is flow of e^- from anode to cathode
4) The weight of anode decreases whereas the weight of cathode increases with time.
5) Chemical energy is being converted into electrical energy.

Salt bridge →

Salt bridge is a Inverted U-tube in which hot and concentrated solution of Inert electrolyte is filled.

(Inert electrolyte → KCl, KNO_3, CH_3COOLi, NH_4NO_3, NH_4Cl

1) To this hot and concentrated solution of Inert electrolyte some gelatinous agar-agar powder is added so that solution of cooling set's in a form of gel.

2) The cation's and anion of Inert electrolyte used in salt bridge should have same Ionic ~~mobility or velocity~~ velocity, mobility.

3) If our anode or cathodic compartment contains silver Ion's (Ag^+) or mercurous Ion (Hg^{2+}) then in salt bridge KCl

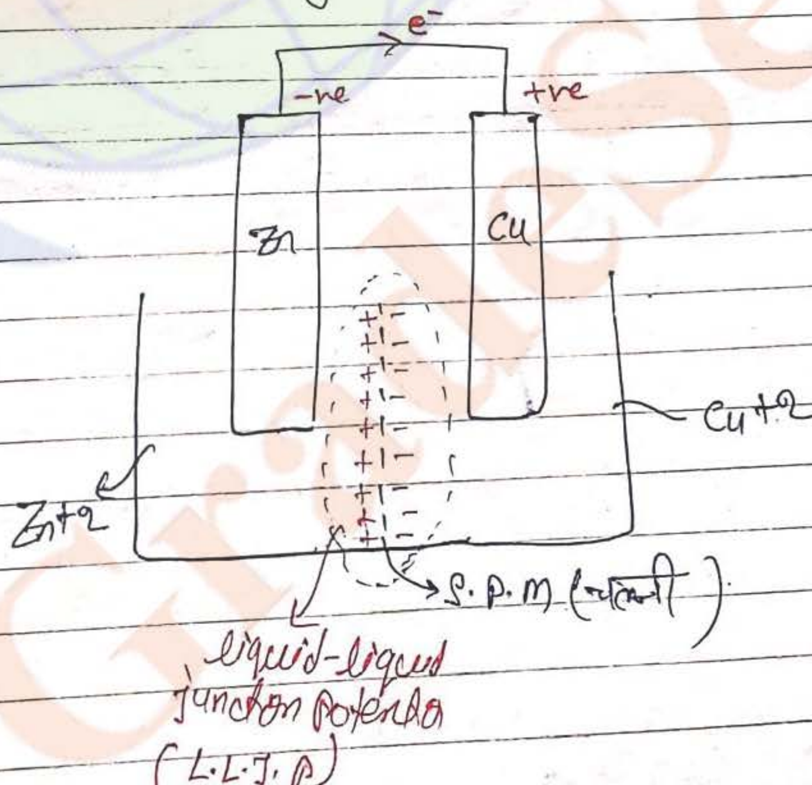
should not be used because after reaction it forms ppt. which close the mouth of salt bridge.

Function of Salt Bridge →

1) It maintains electrical neutrality in both the half cell's.

2) It complete the Internal circuit by passing the Ion's through it
(In external circuit e^- is flow while in Internal ~~cell~~ circuit Ion's is flow.)

3) It minimises liquid-liquid junction potential which ~~acts~~ act's against the emf of the cell



Note याद रखें → Right side the charge O.P होगा

IUPAC notation of electrode potential and electro chemical cell

a) Representation of electrode potential →

very important symbol.

$E_{Zn/Zn^{+2}}$ → O.P (oxidation potential) of Zn electrode

$E_{Zn^{+2}/Zn}$ → Reduction potential of Zn electrode

$E_{Fe^{+2}/Fe}$ → " " " Fe "

(loose of e^- is known as oxidation and gain of e^- is known as Reduction)

b) Cell notation

In cell notation or representation anode is written on the left ~~hat~~ hand side whereas cathode is written on right hand side.

The salt which connects the two half cell cell is represented by two vertical line (||)

conc. "C_1" → इलेक्ट्रोलाइट का conc. C_2 है।

$$\underbrace{Zn(s)\,|\,Zn^{+2}(C_1)}_{\text{Anode}}\ \underbrace{||}_{\text{salt bridge}}\ \underbrace{Cu^{+2}(C_2)\,|\,Cu(s)}_{\text{cathode}}$$

or

$$Zn(s);\ Zn^{+2}(C_1)\ ||\ Cu^{+2}(C_2)\ ;\ Cu(s)$$

or

$\overset{\ominus}{Zn(s)} / Zn^{+2}(C_1) \| Cu^{+2}(C_2) / \overset{\oplus}{Cu(s)}$

Standard electrode →

For a electrode to be in it's standard condition it has to fullfil two condi

i) The concentration of Ion or Solution in which it is dipped should be "1 M"

ii) If any gas is used in the formation of electrode then it's pressure should be "1 atm"

Note: The temperature at which the above two condition are satisfied at that temperature electrode will be in it's standard condition.

but during the process temperature should remain constant.

Representation of standard electrode potential

Standard electrode potential are of two types

i) Standard oxidation potential. (SOP)

ii) Standard reduction potential (SRP)

$$\boxed{\begin{array}{c}\text{For any electrode (except } H_2O\text{)} \\ SOP = -SRP\end{array}}$$

so,

Representation of Standard electrode potential

$E^\circ_{Zn/Zn^{+2}} \longrightarrow$ S.O.P of Zn electrode

$E^\circ_{Zn^{+2}/Zn} \longrightarrow$ S.R.P of Zn electrode

$E^\circ_{Fe^{+3}/Fe} \longrightarrow$ S.R.P. of Fe electrode.

Note ⟶ calculation of electro motive force (emf) of cell (E_{cell}) ⟶

Danial cell ⟶

$$E_{cell} = \underset{\text{anode}}{\underset{(a)}{O.P}} + \underset{\text{cathode}}{\underset{(c)}{R.P}} \qquad \{R.P = -O.P\}$$

$$E^\circ_{cell} = \underset{(a)}{S.O.P} + \underset{(c)}{S.R.P} \qquad \{S.R.P = -S.O.P\}$$

Note

Also teachers Don't use this formula (answer नहीं आ पायेगा) क्योंकि book में इस formula का उपयोग करके किसी question को solve किया गया होगा जबकि हम (G.A) वाले इस formula का उपयोग नहीं करवाएंगे)

Daniell cell -

use this possible

इस (Cu/Zn) इस formula का उपयोग करेंगे इसलिए ध्यान पूर्वक याद करो।

$$E_{cell} = \underset{(c)\,\to\,cathode}{R.P} - \underset{(a)\,\to\,anode}{R.P}$$

$$= E_{Cu^{+2}/Cu} - E_{Zn^{+2}/Zn}$$

"gain of e^-"

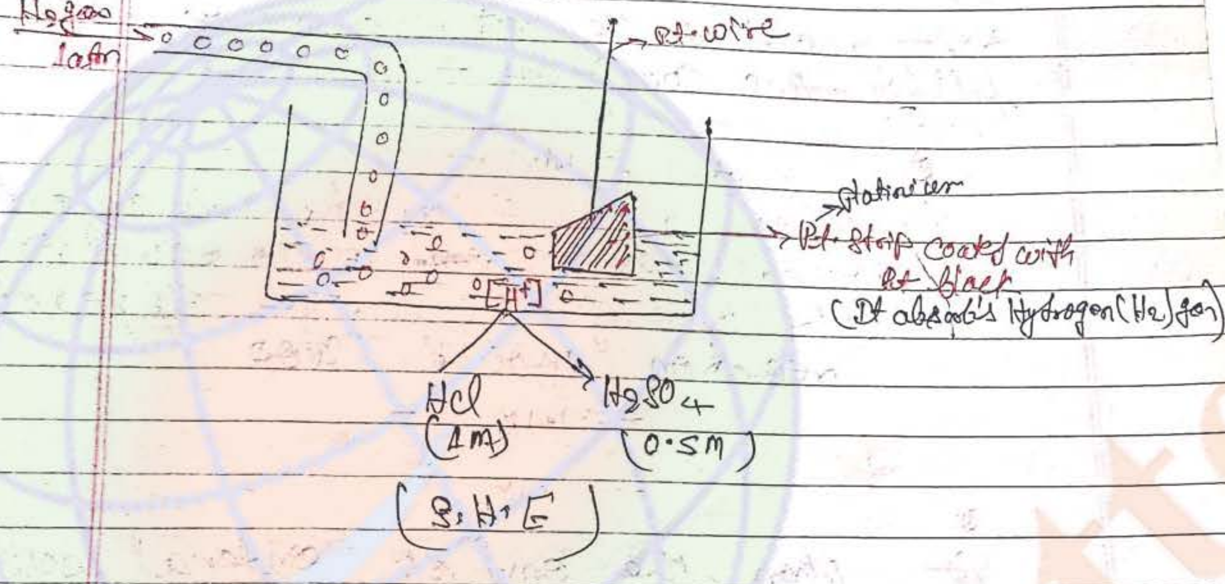
$$E^{0}_{cell} = \underset{(c)\,\to\,cathode}{S.R.P} - \underset{(a)\,\to\,anode}{S.R.P}$$

$$= E^{0}_{Cu^{+2}/Cu} - E^{0}_{Zn^{+2}/Zn}$$

Attention →

For a cell to function it's E_{cell} value and E^{0}_{cell} value should be ~~negative~~ +ve.

Standard Hydrogen electrode (S.H.E)
or gas-Ion-electrode.



anode: →

$$H_2(g) \longrightarrow 2H^+ + 2e^- \qquad E^\circ_{\underset{1atm}{H_2}/\underset{1M}{H^+}/Pt} = 0.00V$$

cathode: →

$$2H^+ + 2e^- \longrightarrow H_2(g) \qquad E^\circ_{Pt/\underset{1M}{H^+}/\underset{1atm}{H_2}} = 0.00V$$

1) The electrode whose S.R.P is to be determined is coupled with S.H.E. to form a electrochemical cell

2) The S.R.P of diff^n electrodes are determines practically by combining them S.H.E and these electrodes are arrange in a series (according to their S.R.P) which is known as "electro chemical series"

Note →

Reversible and Irreversible cell.

For a cell to be reversible it has to fullfill two conditions:—

1) when a cell is connected to an external source having emf equal to the emf of cell. The cell reaction should stop

$+ E = 1.1V -$

$- E = 1.1V +$

2) when the emf of external source is greater than cell emf the cell reaction should be reversed

The cell do not fullfill the above two condition is known as Irreversible cell

Electro chemical Series → Best Reducing agent (अर्थात् इ अपचायक का oxidation होगा)

Page No. 37?

Element		electrode Reaction	S.R.P (T = 298 K)
Li	(लिइइइ	$Li^{+} + e^{-} \rightarrow Li$	−3.05 V
K	के रव अभाज	$K^{+} + e^{-} \rightarrow K$	−2.93 V
Na	ना	$Na^{+} + e^{-} \rightarrow Na$	−2.71
H_2O	H_2O	$2e^{-} + H_2O \rightarrow H_2 + 2OH^{-}$	−0.83
Zn	जन	$Zn^{+2} + 2e^{-} \rightarrow Zn$	−0.76
S.H.E $\boxed{H_2}$	H_2	$2H^{+} + 2e^{-} \rightarrow H_2$	0.00
Cu	को	$Cu^{+2} + 2e^{-} \rightarrow Cu$	0.34
I_2	उनाइ	$I_2 + 2e^{-} \rightarrow 2I^{-}$	0.54
Ag	अगट	$Ag^{+} + e^{-} \rightarrow Ag$	0.80
Cl_2	काल	$Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$	1.36
F_2	फिर देखना	$F_2 + 2e^{-} \rightarrow 2F^{-}$	2.87

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ध्यान दें यह सभी अलग है

Oxidation Reduction of H_2O ⇒

Reduction (cathode) ⇒

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

$S.R.P = -0.83V$

Oxidation → (anode) ⇒

$$H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

$S.O.P = -1.23V$

Note ⇒

"Li" → $\boxed{-3.05}$ ⇒ (i) max. tendency to lose e^-

(ii) It acts as best reducing agent

(iii) इस चीज का ख्याल रखें ~~कि~~ Ecell value +ve आना चाहिए। ⇒ $E_{cell} \rightarrow SRP_{(C)} - SRP_{(a)}$

(iv) ऊपर वाला metal नीचे वाले metal को हटायेगा

Application of electro chemical series :-

Lithium is the best reducing agent.

1) The electrode which has greater -ve value of S.R.P has max. tendency to lose e^- so it act as best reducing agent.

Florine is best electronegative element

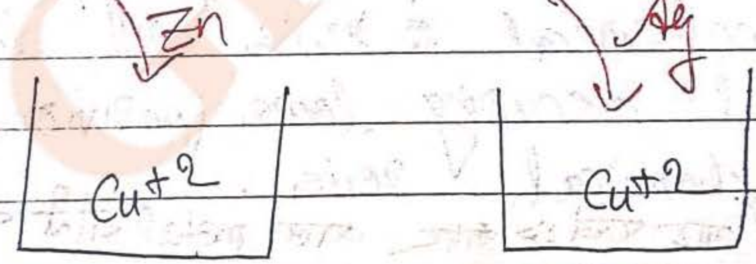
2) The electrode which has greater value of S.R.P has max. tendency to gain e^- so it acts as best oxidising agent.

very Important

In making a electrochemical cell the electrode having less value of S.R.P should be taken as anode and the electrode having greater value of S.R.P should be taken as cathode so that E°_{cell} comes to be +ve.

4) The electrode having -ve value of S.R.P when joint with S.H.E will act as anode whereas the electrode having +ve value of S.R.P when joint with S.H.E will act as cathode.

5)

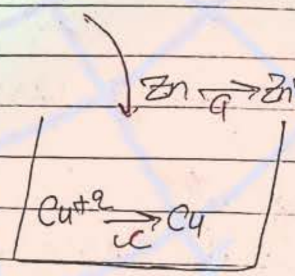


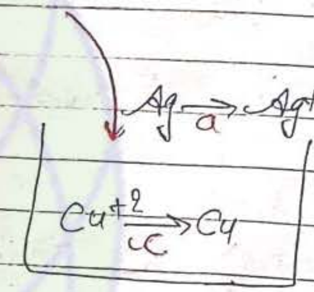
The metal having lower value of S.R.P can displace another metal ion from it's salt solution having greater value of S.R.P

5.)

Now

$$E^0_{cell} = S.R.P_{c} - S.R.P_{a}$$





✓ (Correct)

X (Not correct)

because -

$$E^0_{cell} = S.R.P_{(c)} - S.R.P_{(a)}$$

$$= E^0_{Cu^{+2}/Cu} - E^0_{Zn^{+2}/Zn}$$

$$= 0.34 - (-0.76)$$

$$= +ve$$

because -

$$E^0_{cell} = S.R.P_{c} - S.R.P_{a}$$

$$= 0.34 - 0.80$$

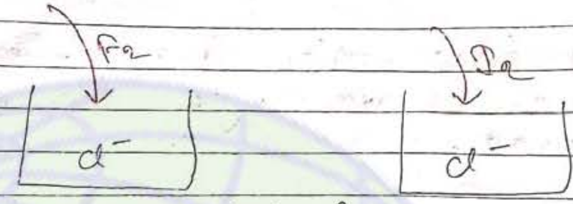
$$= -ve$$

It can also be written as:-

The metal occuping higher position in electrochemical series will displace another metal occuping lower position in electrochemical series

(याद रखो ऊपर वाला metal नीचे वाले metal को हटाएगा।)

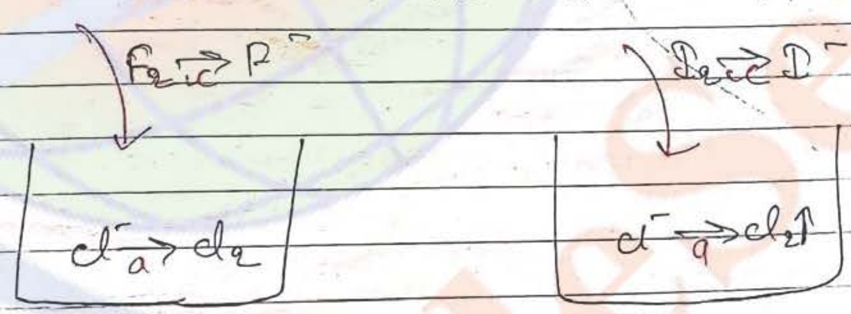
5.)



The non-metal having greater value of S.R.P will displace another non-metal from it's solution which has low value of S.R.P.

or.

The ~~most~~ non-metal occuping lower position in electrochemical series can displace another non-metal occuping higher position in electrochemical series. याद रखें ⇒ नीचे वाला non-metal ~~~~ ऊपर वाला non-metal को हटाएगा।



$E^o_{cell} = SRP_{(c)} - SRP_{(a)}$ (✓) Correct

$E^o_{cell} = S.R.P_{(c)} - S.R.P_{(a)}$ (✗) Incorrect

(c) The electrode which have -ve value of S.R.P can liberate H_2 gas from dilute acid solution.

$E^0 \rightarrow$ electrode potential
$E^0 \rightarrow$ " " of cell

7.) When a electrode reaction is multiplied or divided by any factor than it's E^0 value or S.R.P value does not changes but the value of ΔG^0 changes accordingly.

$Ag^+ + e^- \longrightarrow Ag$ $\quad E^0_{Ag^+/Ag} = 0.80V$ $\quad \boxed{\Delta G^0 = -n_1 FE^0}$

$2Ag^+ + 2e^- \longrightarrow 2Ag$ $\quad E^0_{Ag^+/Ag} = 0.80V$ $\quad \Delta G^0 = -n_2 FE^0$

$n =$ no. of e^- taking part in electron Reaction
$n_1 = 1$
$n_2 = 2$, $E^0_{Ag^+/Ag} = 0.80$

$F \rightarrow$ one faraday charge $= 96500\ C$

Calculation of electrode potential of a single electrode with the help of given electrode potential.

Q1.) If $E^0_{Fe^{+2}/Fe} = x_1$, $E^0_{Fe^{+3}/Fe} = x_2$
then
$E^0_{Fe^{+3}/Fe^{+2}} = ?$

Sol/ⁿ

$Fe^{+2} + 2e^- \longrightarrow Fe$, $E_1^0 = x_1$

$Fe^{+3} + 3e^- \longrightarrow Fe$ $E_2^0 = x_2$

Target equation → $Fe^{+3} + e^- \longrightarrow Fe^{+2}$ $E_3^0 = x_2 - x_1$

This is wrong method

If $E^0_{Fe^{+2}/Fe} = x_1$ (E_1^0) , $E^0_{Fe^{+3}/Fe} = x_2$ (E_2^0)

① — $Fe^{+2} + 2e^- \longrightarrow Fe$ (n_1) $\Delta G_1^0 = -n_1 E_1^0 F$

2 — $Fe^{+3} + 3e^- \longrightarrow Fe$ (n_2) $\Delta G_2^0 = -n_2 E_2^0 F$

Target equation ③ — $Fe^{+3} + e^- \longrightarrow Fe^{+2}$ (n_3) $\Delta G_3^0 = -n_3 E_3^0 F$

eq ③ = eq ② − eq ①

Now

$$\Delta G_3^0 = \Delta G_2^0 - \Delta G_1^0$$

$$-n_3 E_3^0 \cancel{F} = -n_2 E_2^0 \cancel{F} - (-n_1 E_1^0 \cancel{F})$$

$$n_3 E_3^0 = n_2 E_2^0 - n_1 E_1^0$$

$$E_3^0 = \frac{n_2 E_2^0 - n_1 E_1^0}{3} \Rightarrow \frac{3x_2 - 2x_1}{1}$$

$\boxed{Eo=3}$ e·NO-5

Q. E.M.F diagram for Iron is given as —

$$Fe^{+6} \xrightarrow{2.20} Fe^{+3} \xrightarrow{.77} Fe^{+2} \xrightarrow[-0.445]{} Fe^0$$

$Fe^{+6} \to Fe^{+2}$: $E^0 = ?$

Sol^n:

$E^0_{Fe^{+6}/Fe^{+3}} \to +2.20$ E_1^0

$E^0_{Fe^{+3}/Fe^{+2}} \to 0.077$ E_2^0

$E^0_{Fe^{+2}/Fe^0} \to -0.445$

(1) — $Fe^{+6} + 3e^- \to \cancel{Fe^{+3}}$ ($3e^- \to n_1$) $\quad \Delta G_1^0 = -n_1 E_1^0 F$

(11) — $\cancel{Fe^{+3}} + e^- \to Fe^{+2}$ ($e^- \to n_2$) $\quad \Delta G_2^0 = -n_2 E_2^0 F$

(3) — $Fe^{+6} + 4e^- \to Fe^{+2}$ ($4e^- \to n_3$) $\quad \Delta G_3^0 = -n_3 E^0 F$

$$\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0$$

$$-4FE_3^0 = -(3FE_1^0 + FE_2^0)$$

$$E_3^0 = 6.6 + 0.77 = \frac{7.37}{4} = 1.8475\,V$$

$\boxed{\dfrac{S_6 = 3}{Q.No - 24}}$

Date: / /

Exp) Given that

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

$E^\circ_{H^+/H_2} = 0.00V$

Predict whether the given reaction is spontaneous or non-spontaneous

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

Sol^n

E° $Cu^{+2} + 2e_a$

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

ccw then,

$E^\circ_{cell} = S.R.P_{(C)} - S.R.P_{(a)}$

$= E^\circ_{H^+/H_2} - E^\circ_{Cu^{+2}/Cu}$

$= 0 - (0.34)$

$= -ve$

$\Rightarrow$ (Non-spontaneous)

Exp) $E^\circ_{Fe^{+2}/Fe^{+3}} = -0.77V$ } S.O.P

$E^\circ_{I_2/2I^-} = +0.54V$

$2Fe^{+3} + 2I^- = 2Fe^{+2} + I_2$

Rxn is ~~possible~~ feasible or not

Page No.
Date. / /

Sol^n $2Fe^{+3} + 2I^- = 2Fe^{+2} + I_2$

$E^\circ_{cell} = E^\circ_{Fe^{+3}/Fe^{+2}} - E^\circ_{I_2/I^-}$

$= 0.77 - 0.54$

$E^\circ_{cell} \Rightarrow +ve$

feasible

Q02.) Determine the standard reduction potential for the half cell reaction

$Cl_2 + 2e^- \longrightarrow 2Cl^-$, $E^\circ = ?$

given

$E^\circ_{cell} = 0.50V$

$Pt^{+2} + 2Cl^- \longrightarrow Pt + Cl_2$, $E^\circ_{cell} = -0.15V$

$Pt^{+2} + 2e^- \longrightarrow Pt$, $E^\circ = 1.2V$

$\cancel{E^\circ = 1.2V}$

Sol^n $\cancel{E^\circ_{cell}}$

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

or

$Zn^{+2} + 2e^- \Rightarrow Zn$

$E^\circ = -0.76V$

$Pt^{+2} + 2Cl^- \longrightarrow Pt + Cl_2$,

cell reactn

$E^\circ_{cell} = S.R.P_{(c)} - S.R.P_{(a)}$

$-1.5 = 1.2 - E^\circ_{Cl_2/Cl^-}$

Ex 4) Red ~~Rad~~ hot carbon can remove oxygen from the oxide "XO" and "YO" but ~~to~~ not from "ZO".

why ~~co~~ can remove oxygen from "XO"
Find the order of activity of three metal X, Y and Z. Putting the most ~~ms~~ reactive metal first.

Soln $\boxed{Z > Y > X}$ ✓

Since "C" ~~can~~ can reduce X and Y it means S.R.P of carbon is ~~less than~~ X and Y

while

C XO YO

ZO

Ques) A gas "X" at 1 atm is ~~@~~ pass ~~into~~ through the solution containing the mixture of 1M Y and 1M Z at 25°C if the reduction potential are $Z > Y > X$

then

a) Y will oxidise X and not Z
b) " " " Z " " X
c) " " " both ~~x~~ X and Z
d) " " Y reduce " " "

Sol^n Attention:- "X" ए metal नहीं है यह gas है

X
Y
Z ↓

Ans ≥ (a)

Ex6) A cell is maid from two electrodes from "A" and "B"

Electrode "A" :-> $Cr_2^{+6}O_7^{2-}/Cr^{+3}$ $E^o = 1.33V$

Electrode "B" :-> Fe^{+3}/Fe^{+2} $E^o = 0.77V$

which of the following statement are correct.

a) e^- flow from B to A when cell is made

b) $E^o_{cell} = 0.56V$

c) "A" will be +ve electrode

d) current flow from A to B.

Sol^n

Electrode B → Anode

Electrode A → Cathode

$$\overset{-ve}{Fe^{+2}/Fe^{+3}} \;||\; \overset{+ve}{Cr_2O_7^{-2}/Cr^{+3}}$$

$\underbrace{Fe^{+2}/Fe^{+3}}_{\text{anode (B)}}$ cathode (A)

$$E^o_{cell} = \underset{(c)}{S.R.P} - \underset{(a)}{S.R.P}$$

Ans a, b, c, d

$= 1.37 - 0.77$

$= 0.56$

Ex-4) If $Co^{+3} + e^- \longrightarrow Co^{+2}$, $E^\circ = 1.82V$
and

$E^\circ_{H_2O/O_2} = -1.23V$

then

Co^{+3} is

a) Stable in aqueous solution
b) Unstable in "
c) Can't be Predicted.

Sol^n

$E^\circ_{H_2O/O_2} = -1.23V$ → यह anode की होगा।

$E^\circ\ Co^{+3} + e^- \longrightarrow Co^{+2}$ $E^\circ = 1.82V$ → Cathode

$$E^\circ_{cell} = \underset{(C)}{SRP} - \underset{(a)}{SRP}$$

$= +ve$

$Co^{+3} + H_2O \longrightarrow Co^{+2} + O_2$, $E^\circ_{cell} = +ve$

Ans (b)

Ex-5) 0 No. Reg

$M + X \longrightarrow M^+ + X^-$ (c, a)

$$E^\circ_{cell} = \underset{(C)}{SRP} - \underset{(a)}{SRP}$$

$= 0.33 - 0.44 = -ve$ (X)

$M^+ + X^- \longrightarrow M + X$ (c, a)

$$E^\circ_{cell} = \underset{(C)}{SRP} - \underset{(a)}{SRP}$$

$X^- + Y_2 \longrightarrow Y^- + X_2$

S.R.P↓ SRP↑

$E_{X_2/X^-} < E_{Y_2/Y^-}$ → S.R.P

$E_{X^-/X_2} > E_{Y^-/Y_2}$ → S.O.P

Z^- X_2

SRP↓ S.R.P↑

SOP↑ SOP↓

$E^\circ_{Z^-/Z_2} > E^\circ_{X^-/X_2}$

$W^- + Y_2 \longrightarrow X$

SRP↑ SRP↓

1.5024

Q.No-8

NO_3^- → cathod

V

9

$E^\circ_{cell} = S.R.P - SRP$

(C) 9

$= 0.96 - (0 - 1.1)$

$= +ve$

i) cell Rn^n में Redox होता है (oxidat + Redn both)
ii) Electrode Rn^n में only oxidatn या Redn होता है

Page No. 384

Q.) Given than

$E^\circ_{Cu^{+2}/Cu^+} = 0.15V$

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

which of the following statement are correct
a) Cu^+ goes disproportanation Rn^n in solution
b) Cu^+ goes comproportanation Rn^n in solution
(c) Cu^+ shows no Reaction Rn^n in solution
(d) Cu^+ does not goes disproportanation Rn^n in solu

Sol^n a and b can also be write it on—
a) $Cu^+ \longrightarrow Cu + Cu^{+2}$ → Disproportional में एक state की दोनों अधिक
b) $Cu + Cu^{+2} \longrightarrow Cu^+$ → Comproportanation Rn^n में दो या अधिक एक में change होता है

None

$$E^\circ_{Cu^{+2}/Cu} = 0.15V$$

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

disproportanation reaction

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

oxidato(a)

Reducto(c)

→ यह cell Rn^n है

$$E^\circ_{cell} = \underset{(c)}{SRP} - \underset{(a)}{SRP}$$

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

$$= 0.53 - 0.15$$

$= 0.38 > 0$

Note

$Cu^{+2} + e^- \xrightarrow{n_1} Cu^+ \qquad \Delta G_1^\circ$

$Cu^{+2} + 2e^- \xrightarrow{n_2} Cu \qquad \Delta G_2^\circ$

$Cu^{+2} + e^- \xrightarrow{n_3} Cu \qquad E^\circ_{Cu^+/Cu} = 0.53$

$$\Delta G_3^\circ = \Delta G_2^\circ - \Delta G_1^\circ$$

$$-n_3 E_3^\circ \cancel{F} = -n_2 E_2^\circ \cancel{F} - (-n_1 E_1^\circ \cancel{F})$$

$$-n_3 E_3^\circ = -n_2 E_2^\circ + n_1 E_1^\circ$$

$$E_3^\circ = \frac{n_2 E_2^\circ - n_1 E_1^\circ}{n_3}$$

$$= 0.53\,V$$

Ans ⇒ "a"

~~NERST EQual~~

Nernst equation (calculation of emf of cell)

let us consider a reversible reaction taking place in a electrochemical cell

$$n_1 A + n_2 B \rightleftharpoons n_3 C + n_4 D$$

$$\Delta G = \Delta G^\circ + 2.303RT \log Q$$

$$\Delta G = \Delta G^\circ + 2.303RT \log \frac{C^{n_3} D^{n_4}}{A^{n_1} B^{n_2}}$$

max. useful work that can be

$$\Delta G^\circ = -nFE^\circ_{cell}, \qquad \Delta G = -nFE_{cell}$$

$$-nFE^\circ_{cell} = -nFE_{cell} + 2.303RT \log \frac{[P]}{[R]}$$

This equation is known as nernst

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{2.303\,RT}{nF} \log \frac{[P]}{[R]}}$$

→ मैन equation यही है।

→ Applicable at all all temperature

Now

$T = 298K$, $F = 96500C$, $R = 8.314 JK^{-1} mol^{-1}$, $\frac{2.303RT}{F} = 0.0591$

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}}$$

→ Applicable only at $T = 298 K$

$$\boxed{E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}}$$

$\begin{pmatrix} R.P & - R.P \\ (c) & a \end{pmatrix}$ $\quad$ $\underset{(c)}{S.R.P} - \underset{(a)}{S.R.P}$

Notes:→

1) Here
n → is equal to the number e⁻ cancelled out in making nernst cell equation.

2) The active mass of solid and liquid are taken as unity.

eg:→

$Zn(s) \,|\, Zn^{+2}(C_1) \,||\, Cu^{+2}(C_2) \,|\, Cu(s)$

anode (oxidation) $\quad$ Cathode (Reduction)

anode:→

$Zn(s) \longrightarrow Zn^{+2}(C_1) + \cancel{2e^-}$

Cathode

$Cu^{+2}(C_2) + \cancel{2e^-} \longrightarrow Cu(s)$

cell Rn: $Zn(s) + Cu^{+2}(C_2) \rightleftharpoons Zn^{+2}(C_1) + Cu(s)$ {n=2}

ie a Redox Rn which no e⁻ is coming

$$E_{cell} = E^{\circ}_{cell} - \frac{.0591}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

(+ve)

$E^{\circ}_{cell} \rightarrow$ SRP − SRP
(c) (a)

$(E^{\circ}_{Cu^{+2}/Cu} - E^{\circ}_{Zn^{+2}/Zn})$

$$E_{cell} = E^{\circ}_{cell} + \frac{.0591}{2} \log \frac{[Cu^{+2}]\downarrow}{[Zn^{+2}]\uparrow}$$

cell is ~~reversible~~ reversible w.r.t. $[Cu^{+2}]$ and $[Zn^{+2}]$

discharging

Q1-> $Cu(s)/Cu^{+2}(C_1)||Ag^{+}(C_2)/Ag(s)$
anode cathode

Anode:-
$Cu(s) \longrightarrow Cu^{+2}(C_1) + \cancel{2e^-}$

Cathode:-
$[Ag^{+}(C_2) + \cancel{e^-} \longrightarrow Cu(s)] \times 2$

cell Rnⁿ:-> $Cu(s) + Ag^{+2}(C_2) \rightleftharpoons Cu^{+2}(C_1) + Cu(s)$

$n=2$

$$E_{cell} = E^{\circ}_{cell} - \frac{.0591}{2} \log \frac{[Cu^{+2}]}{[Ag^{+}]^{2}}$$

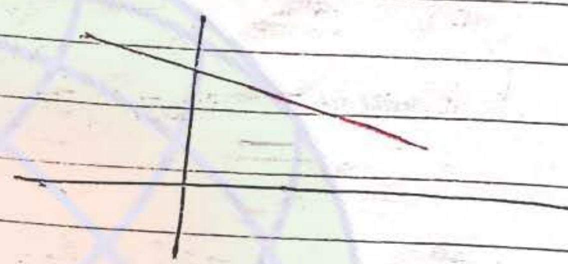
reversible w.r.t. Ag^{+} and Cu^{+2}

$$E_{cell} = E^{\circ}_{cell} + \frac{0.0591}{2} \log \frac{[Ag^{+}]^{2}\downarrow}{[Cu^{+2}]\uparrow}$$

[X2]
02-10-24

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

$$y = C + mx$$



Application of Nernst equation →

1) Calculation of single ~~electrode~~ electrode potential or potential of a electrode.

Case (1) → This electrode is working as cathode

$$M^{n+} + ne^- \longrightarrow M(s)$$

solid का active mass "1" मानते हैं

$$\cancel{E_{M^{n+}/M} = E^{0}_{M^{n+}}}$$

$$E_{M^{n+}/M} = E^{0}_{M^{n+}/M} - \frac{.0591}{n} \log \frac{[P]}{[R]}$$

सिर्फ R.P वाला याद रखेंगे और इससे ही O.P का भी formula बना लेंगे

$$\boxed{R.P = S.R.P - \frac{.0591}{n} \log \frac{1}{[M^{n+}]}}$$

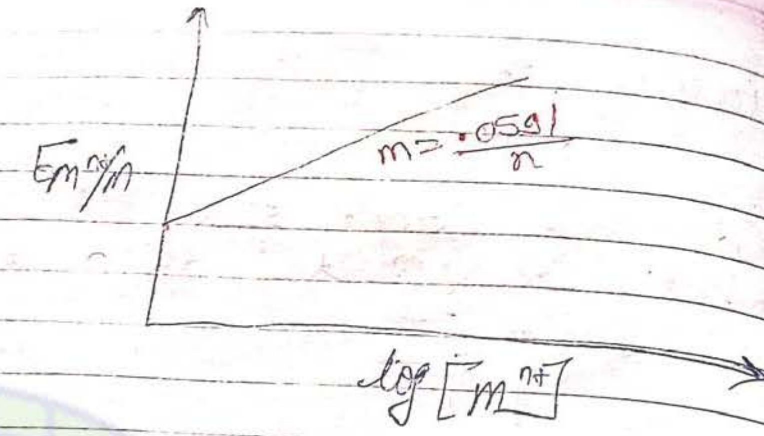
the

reversible w.r.t. $[M^{n+}]$

$$y = c + mx$$

or

$$\boxed{R.P = S.R.P + \frac{0.0591}{n} \log [M^{n+}]}$$



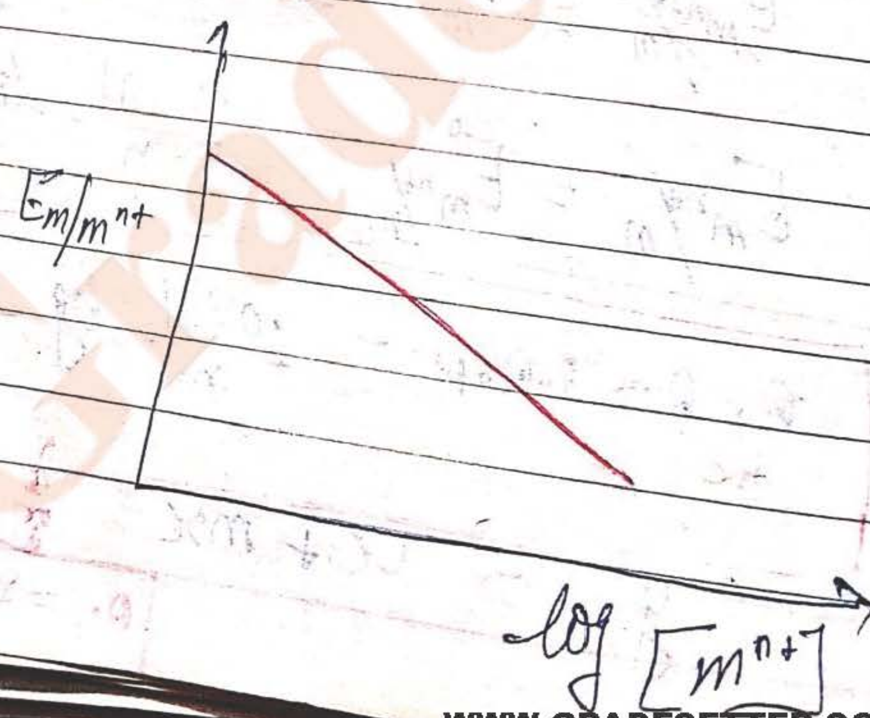
Case 2nd:- The electrode is working as anode

$$M(s) \longrightarrow M^{n+} + ne^-$$

$$\boxed{O.P = SOP - \frac{.0591}{n}\log[M^{n+}]}$$

$$E_{M/M^{n+}} = E^\circ_{M/M^{n+}} - \frac{.0591}{n}\log[M^{n+}]$$

$$y = c + mx$$



2.) Calculation of maximum useful work that can be obtained by a electrochemical cell :-

$$\Delta G = -nFE_{cell} \quad \left(\underset{(c)}{R.P} - \underset{(a)}{R.P}\right)$$

change in gibbs free energy

$$\Delta G^{\circ} = -nFE^{\circ}_{cell} \quad \underset{(c)}{S.R.P} - \underset{(a)}{S.R.P}$$

change in standard gibbs free energy.

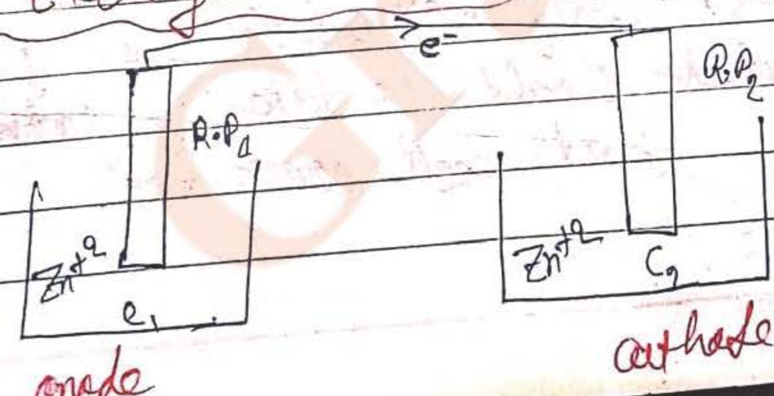
n ⇒ Number of e^- cancelled out in making cell Reaction.

3.) Concentration cell :-> $(E^{\circ}_{cell} = 0)$

Electrolytic conc. cell (diff. concentration)

Electrode conc. cell (diff. pressure)
electrode बनाते समय ही शुरू में ही कुछ change कर दिया।

a) Electrolytic concentration cell $(E^{\circ}_{cell} = 0)$



anode:- $Zn(s) \longrightarrow Zn^{+2}(C_1) + \cancel{2e^-}$

cathode:-

$Zn^{+2}(C_2) + \cancel{2e^-} \longrightarrow Zn(s)$

cell Rxn:- $Zn^{+2}(C_2) \rightleftharpoons Zn^{+2}(C_1)$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{+2}](C_1)}{[Zn^{+2}](C_2)}$$

$$E_{cell} = (SRP_c - SRP_a) - \frac{0.0591}{2} \log \frac{C_1}{C_2}$$

$$\boxed{E_{cell\,(+ve)} = \frac{0.0591}{2} \log \frac{C_2}{C_1}}$$

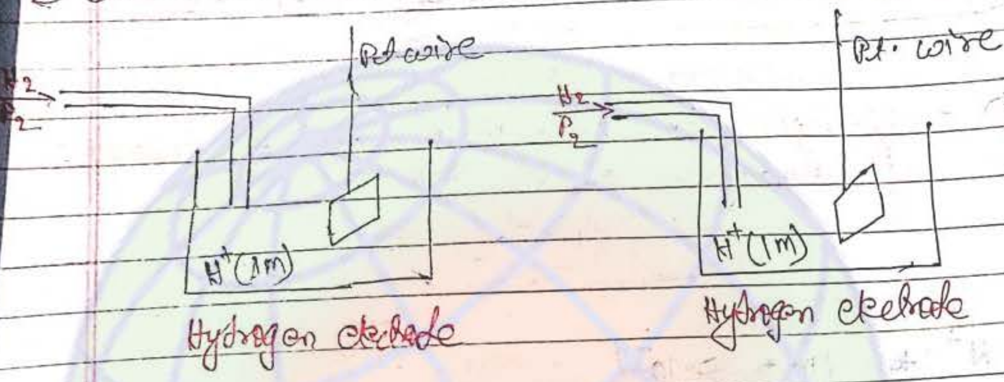
[For cell to be +ve, $C_2 > C_1$]

Note:- जिस cell का Conc. ज्यादा है उसे cathode लेना है।

Conclusion:-

(a) In making electrolytic concentration cell the half cell which has greater concentration should be taken as cathode so that Ecell comes "+ve".

(b) Electrode Concentration cell →



$$Pt \,|\, \underset{P_1}{H_2} \,|\, \underset{1m}{H^+} \,||\, \underset{1m}{H^+} \,|\, \underset{P_2}{H_2} \,|\, Pt$$

anode –

$$H_2(P_1) \longrightarrow \underset{1m}{2H} + \cancel{2e^-}$$

cathode –

$$\underset{1m}{2H^+} + \cancel{2e} \longrightarrow H_2(P_2)$$

$$\text{cell Rn}^n \rightarrow \quad H_2(P_1) \rightleftharpoons H_2(P_2) \quad \{n=2\}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[H_2]}{[H_2]}$$

$$= 0 - \frac{0.0591}{2} \log \frac{P_2}{P_1}$$

$$\boxed{\underset{+ve}{E_{cell}} = \frac{0.0591}{2} \log \frac{P_1}{P_2}} \quad (P_1 > P_2)$$

(*) This cell is reversible w.r.t. Pressure of hydrogen gas.
$P_1 > P_2$

Ex-2
QNO-5

$H^+ \quad 1M \longrightarrow 10^{-4}$

$MnO_4^- + 8H^+ + 5e^- = Mn^{+2} + 4H_2O$

$$R.P = S.R.P - \frac{0.0591}{5} \log \frac{1}{[H^+]^8}$$

$$R.P = S.R.P + \frac{0.0591}{5} \times 8 \log [H^+]$$

$$R.P_1 = SRP + \frac{0.0591 \times 8}{5} \log [1]$$

$$R.P_2 = SRP + \frac{0.0591 \times 8}{5} \log [10^{-4}]$$

$$R.P_2 - R.P_1 = \frac{-0.0591 \times 8 \times 4}{5}$$

Calculation of Equillibrium Constant (K) for a cell reaction →

{ नोट याद रखें → equillibrium constand के case में ($E_{cell} = 0$) होता है }

$$n_1 A + n_2 B \rightleftharpoons n_3 C + n_4 D$$

$$\Delta G = \Delta G^\circ + 2.303 RT \log Q$$

at eq

$$\Delta G = 0 , \quad Q = K$$

$$\Delta G^\circ = -2.303 RT \log K$$

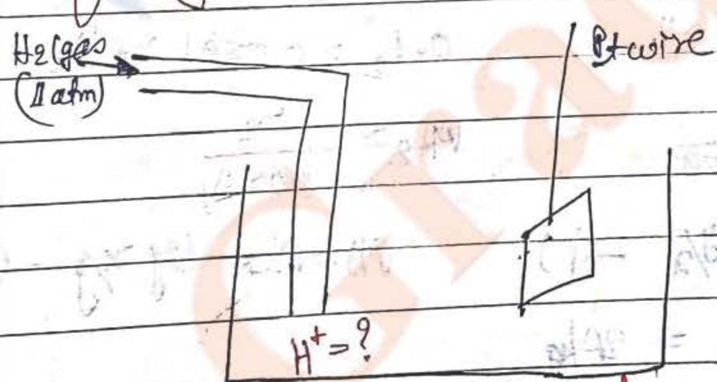
$$-nF E^\circ_{cell} = -2.303 RT \log K$$

$$\boxed{E^\circ_{cell} = \frac{2.303 RT}{nF} \log K}$$

$T = 298 K$

$$\boxed{E^\circ_{cell} = \frac{0.0591}{n} \log K}$$

Calculation of ~~Ph~~ of P_H of the solution of Hydrogen electrode →



Hydrogen electrode

Let this electrode is working as cathode

$$2H^+ + 2e^- \longrightarrow H_2(g)$$

$$R\cdot P = S\cdot R\cdot P - \frac{0.0591}{2} \log \frac{\overset{\to 1\,atm}{P_{H_2}}}{[H^+]^2}$$

$$R\cdot P = 0 + \frac{0.0591}{\cancel{2}} \log [H^+]^{\cancel{2}}$$ $\because RP = -$

$$R\cdot P = 0.0591 \times \log [H^+]$$ $\boxed{Ph = -\log H^+}$

$$\boxed{R\cdot P = -0.0591 \times P_H}$$

$$\boxed{O\cdot P = +0.0591 \times P_H}$$ $\boxed{R\cdot P = -O\cdot P}$

$E_0 = 2$
$OAJO = 10$

$CH_3COOH + CH_3COONa$
$x : y$
H^+ pH_1
H-electrode

buffer
$CH_3COOH + CH_3COONa$
$y : x$
H^+ pH_2
H-electrode

$$O\cdot P_1 = 0.0591 \times pH_1$$

$$O\cdot P_2 = 0.0591 \times pH_2$$

$$pH_1 = \frac{E_1}{0.0591}$$

$$pH_2 = \frac{E_2}{0.0591}$$

$$pH_1 = pK_a + \log y/x \quad \text{—(i)}$$

$$pH = pK_a + \log x/y \quad \text{—(ii)}$$

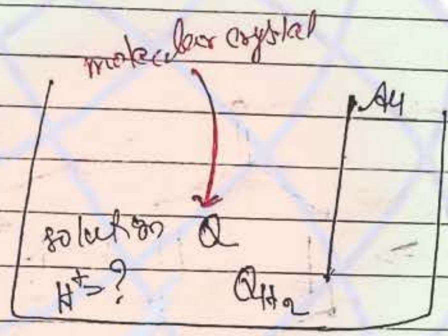
$$pH_1 + pH_2 = 2pK_a$$

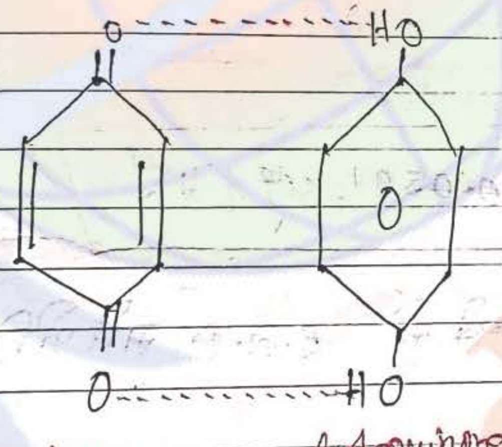
$$pK_a = \frac{pH_1 + pH_2}{2} = \frac{E_1 + E_2}{2 \times 0.0591}$$

Cathode

Quinhydrone electrode →

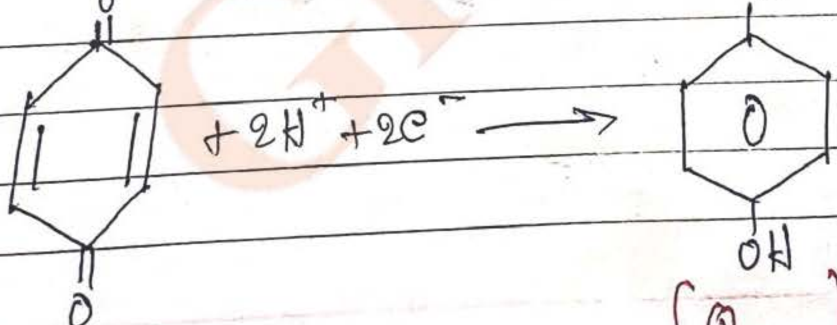
Quin-hydrone is ~~the~~ the name given to a molecular ~~co~~ crystal in which ~~quinon and hydro~~ quinone (Q) and hydroquinone (QH_2) are present in equimolar amount.





quinone (Q) hydroquinone (QH_2)

⇒ cathode :-

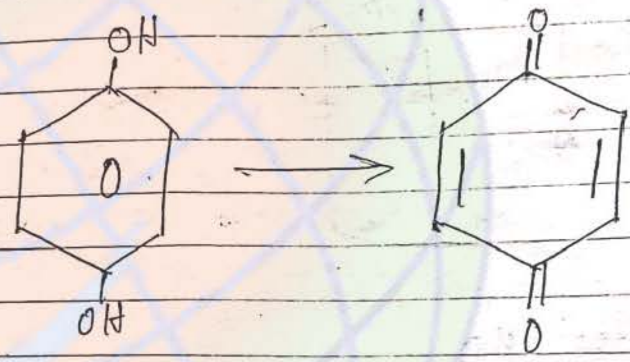


(Q) (QH_2)

$$R.P = S.R.P - \frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$

$$\boxed{R.P = S.R.P + 0.059 \log [H^+]}$$

Anode →



$+ 2H^+ + 2e^-$

$$\boxed{O.P = SOP - 0.0591 \log [H^+]}$$

प्र० 01
04 Nov 21

जब कुछ नहीं लिखे तो S.R.P माने लेकिन यहाँ दिया हुआ है

$$O.P = S.O.P - \frac{0.0591}{2} \log [H^+]^2$$

$$= 1.30 - \frac{0.0591}{1} \log [0.10^{-2}]$$

~~Calculation of solubility product (K_{sp}) of a sparingly soluble salt →~~

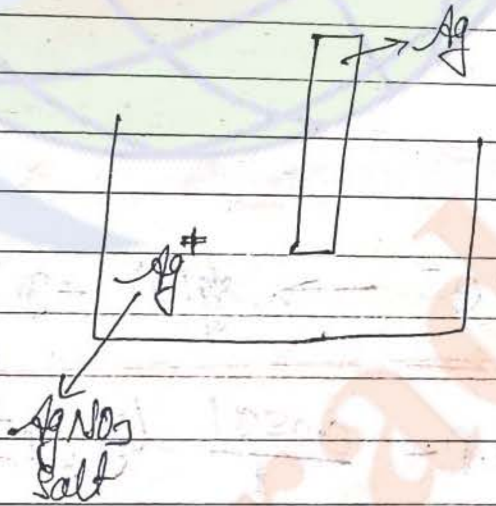
~~Case IV~~

~~Calculate the K_{sp} of AgI ?~~

~~$Ag(s) \,|\, AgI(s),\ 0.05\,M\ KI \,||\, AgNO_3 (0.05\,M) \,|\, Ag(s)$, $E_{cell} = 0.788$~~

Calculation of Reduction Potential of metal, metal in soluble ~~solid~~ salt ~~sol~~ electrode →

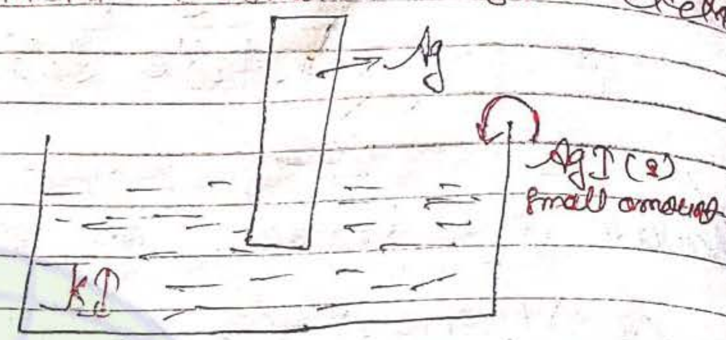
⟹ metal-metal soluble salt electrode ($E_{Ag^+/Ag}$)



cathode → $Ag^+ + e^- \rightleftharpoons Ag$

$$\boxed{R.P = SR.P - \frac{0.0591}{1} \log \frac{1}{[Ag^+]}}$$

⟹ metal - metal insoluble salt electrode



secondary reference electrode

Anode

$E_{Ag(s)/AgI(s)/I^-}$

anode -

$I^- + Ag(s) \longrightarrow AgI(s) + e$

cathode

$E^\circ_{I^-/AgI/Ag}$

cathode -

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

cathode -

$$AgI\,(s) + e^- \longrightarrow Ag(s) + I^-$$

rev. w.r.t I^-

$$\boxed{R.P = S.R.P - \frac{0.0591}{1}\log[I^-]}$$

Secondary reference electrode –

$E_{Pb(s)/PbS(s)/S^{-2}}$ anode :⇒ $S^{-2} + Pb(s) \rightarrow PbS(s) + 2e^-$

$E_{Pb(s)/PbSO_4/SO_4^{-2}}$ anode :⇒ $Pb(s) + SO_4^{-2} \rightarrow PbSO_4(s) + 2e^-$

$E^0_{Ag(s)/AgI/I^-}$ anode :⇒ $Ag(s) + I^- \rightarrow AgI(s) + e^-$

Note ⇒

$E^0_{H^+/H_2/Pt} \longrightarrow$ Ion-gas half cell

$E^0_{Fe^{+2}/Fe^{+3}} \longrightarrow$ Redox electrode

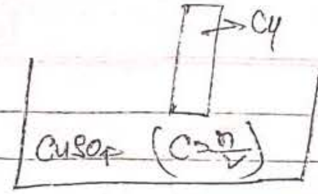
(a)

$Fe^{+2} \rightarrow Fe^{+3} + e$

(c)

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

$\boxed{\frac{[x]=4}{O.No \to 2.2}}$



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

$$R.P = SRP + \frac{0.0591}{2} \log [Cu^{+2}]$$

$$R.P_1 = SRP + \frac{0.0591}{2} \log [10]$$

$$R.P_2 = SRP + \frac{0.0591}{2} \log [1]$$

$$R.P_2 - R.P_1 = -\frac{0.0591}{2}$$

$\boxed{\frac{[x]=2}{O.No \to 2}}$ anode (a)

$$H_2 \longrightarrow 2H^+ + 2e^-$$

cathode (C) $\left. AgI + e^- \longrightarrow Ag + I^- \right] \times 2$

cell $H_2 + 2AgI \longrightarrow 2H^+ + 2Ag + 2I^-$

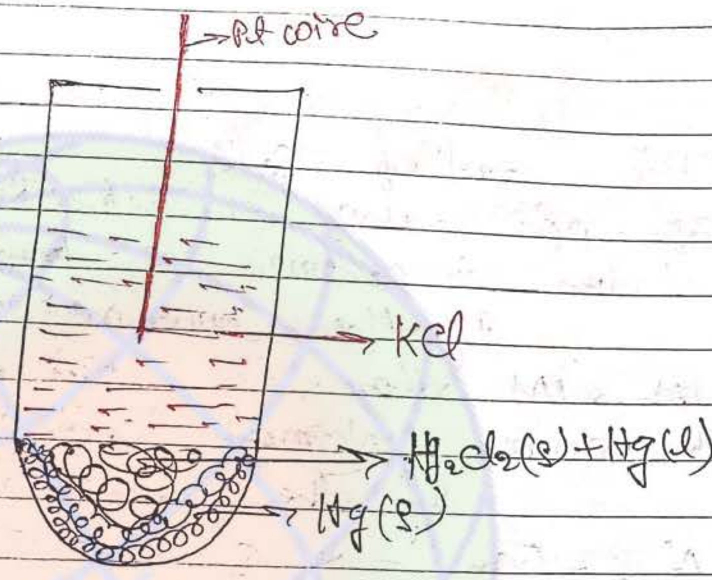
1M

$$E_{cell} = \underbrace{E^0_{cell}}_{\left(SRP_{(C)} - SRP_{a}\right)} - \frac{0.0591}{2} \log [H^+]^2$$

$$0 = \{(-0.151) - zero\} + 0.0591 \times P_H$$

$P_H = 1$ ✓

calomel electrode or (secondary refrence electrode)



Cathode: $E^0_{Cl^-/Hg_2Cl_2(s)/Hg(l)}$

$$2e^- + Hg_2Cl_2(s) \longrightarrow 2Hg(l) + 2Cl^-$$

Reversible w.r.t. Cl^-

$$\boxed{R.P = S.R.P - \frac{0.0591}{\cancel{2}} \log [Cl^-]^{\cancel{2}}}$$

Anode

$E^0_{Hg(l)/Hg_2Cl_2/Cl^-}$

$$2Hg(l) + 2Cl^- \longrightarrow Hg_2Cl_2(s) + 2e^-$$

$$O.P = SOP + \frac{0.0591}{\cancel{2}} \log [Cl^-]^{\cancel{2}}$$

$$\boxed{O.P = S.O.P + 0.0591 \log [Cl^-]}$$

The emf of calomel electrode depends upon the concentration of KCl taken in calomel electrode.

If the concentration of KCl is 1N then this electrode is known as Normal calomel electrode.

If the concentration of KCl is $\frac{N}{10}$ then the electrode is known as deci normal calomel electrode (DNCE)

and

If the KCl solution taken is saturated then this electrode is known as saturated calomel electrode (S.C.E)

calculation of solubility product (KSP) of a sparingly soluble salt →

Case II
Example → Calculate the Ksp of AgI ?

Ag(s) | AgI(s), KI (0.05M) || AgNO$_3$ (0.05M) | Ag(s) ; Ecell = 0.788V

Solution

When E°_{cell} is not given in the question than treat the above cell as concentration cell.

$$Ag \,|\, Ag^+ \,||\, \underset{(0.05M)}{Ag^+} \,|\, Ag$$

anode:
$Ag \rightarrow Ag^+_{(a)} + e^-$

cathode:
$Ag^+_{(c)} + e^- \rightarrow Ag$

cell → $Ag^+(c) \rightarrow Ag^+(a)$

$$E_{cell} = 0 - \frac{0.0591}{1} \log \frac{[Ag^+]_a}{[Ag^+]_c}$$

$$0.788 = 0 - \frac{0.0591}{1} \log \frac{[Ag^+]_a}{[Ag^+]_c}$$

$$[Ag^+]_a = 2.2 \times 10^{-15}$$

$$K_{sp}\,AgI = [Ag^+][I^-]$$

$$= 2.2 \times 10^{-15} \times 0.5$$

Case 2nd

Example → Calculate the Ksp of AgI from the following standard reduction potential

$E^\circ_{Ag^+/Ag} = 0.80V$ (SRP) $E^\circ_{I^-/AgI/Ag} = -0.$ (SRP)

Solution →

If in the question Ecell is not given then we consider above cell at equilibrium so that

$E_{cell} = 0$ and $Q = K$

$\underbrace{Ag(s) / AgI, I^-}_{a} \,||\, \underbrace{Ag^+ / Ag}_{c}$

anode →

$Ag(s) + I^- \longrightarrow AgI(s) + \cancel{e^-}$

cathode →

$Ag^+ + \cancel{e^-} \longrightarrow \cancel{Ag(s)}$

cell → $Ag^+ + I^- \longrightarrow AgI(s)$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{1} \log \frac{1}{[Ag^+][I^-]}$ → IP, Q

cell at eq., $E_{cell} = 0$, $Q = K_{SP}$ or I.P

$$0 = E^{\circ}_{cell} - \frac{0.0591}{1} \log \frac{1}{K_{SP}}$$

$$0 = E^{\circ}_{cell} + \frac{0.0591}{1} \log K_{SP}$$

$$\boxed{E^{\circ}_{cell} = -\frac{0.0591}{1} \log K_{SP}}$$ $$\boxed{pK_{SP} = -\log K_{SP}}$$

$\left(SRP_{(c)} - SRP_{(a)} \right)$

So,

$0.80 + 0.15 = 0.0591 \times pK_{SP}$

$pK_{SP} = $ ✓

then find K_{SP} by using $pK_{SP} = -\log K_{SP}$

Ex 2 Q ONO-3 $E^{\circ}_{Ag^+/Ag} = 0.799$ $E^{\circ}_{AgI/Ag/I^-} = -0.151$

$$E^{\circ}_{cell} = -0.0591 \log K_{SP}$$

Ex=3 Q.No-28

(Ex=3 QNo=28) Calculate ~~the~~ the ratio of Br^- and Cl^- so that E_{cell} is zero.

or

Example→ Consider the cell $Ag|AgBr(s)|Br^-||AgCl(s)|Ag$ at 25°C. The solubility product constant of AgBr and AgCl are respectively 5×10^{-13} and 1×10^{-10}. For what ratio of the concentrations of Br^- and Cl^- ions would the emf of the cell be zero.

Solution $\frac{[Br^-]}{[Cl^-]} = ?$ $E_{cell} = 0$

$E^\circ_{cell} = 0$

$$Ag|AgBr|Br^-||AgCl|Ag|Cl^-$$

$$K_{sp}\,AgBr = 5\times10^{-13} = [Ag^+]_a[Br^-]$$

$$K_{sp}\,AgCl = 1\times10^{-10}$$

anode→

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

Cathode :→

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

Now

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{1} \log \frac{[Ag^+]_a}{[Ag^+]_c} \text{ or } \frac{Ksp\ AgBr / Br^-}{Ksp\ AgCl / Cl^-}$$

$$0 = 0 - \frac{0.0591}{1} \log \frac{5\times10^{-13} / [Br^-]}{1.8\times10^{-10} / [Cl^-]}$$

(Exam, ONO=30)
Example- K_d for complete dissociation of $[Ag(NH_3)_2]^+$ into Ag^+ and $2NH_3$ is 6×10^{-8}. calculate E° for the following half reaction -

$$Ag(NH_3)_2^+ + e^- \longrightarrow Ag + 2NH_3$$

$$Ag^+ + e^- \longrightarrow Ag, \quad E^{\circ} = 0.799\ V$$

Solution-

anode → $\cancel{Ag} \longrightarrow Ag^+ + \cancel{e^-}$

cathode → $Ag(NH_3)_2^+ + \cancel{e^-} \longrightarrow \cancel{Ag} + 2NH_3$

$$Ag(NH_3)_2^+ \longrightarrow Ag^+ + 2NH_3 \ ; \quad K_d = 6\times10^{-8}$$

$$\cancel{E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{1} \log Q}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{1} \log Q$$

$E_{cell} = 0$, $Q \Rightarrow K_d$

DPP 27

Page No. 7

$$0 = \left(\underset{(C)}{SRP} - \underset{9}{SRP}\right) - \frac{0.0591}{1} \log (6 \times 10^{-8})$$

$$0 = (x - 0.799) - \frac{0.0591}{1} \log 6 \times 10^{-8}$$

Calculation of enthalpy change and entropy change for a cell reaction

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \quad \text{---(1)}$$

$$G = H - TS$$

$$G = (E + PV) - TS$$

$$dG = \underbrace{\cancel{dE + PdV}}_{dq} + Vdp - \underbrace{\cancel{TdS}}_{dq} - SdT$$

$$dG = Vdp - SdT$$

at constant pressure, $Vdp = 0$

$$dG_p = -SdT$$

$$\frac{d}{dt}(G)_p = -S$$

$$\frac{d}{dT}(\Delta G)_p = -\Delta S \quad \text{---(2)}$$

Gibb's HELMOLTZ equation →

$$\boxed{\Delta G = \Delta H + T\frac{d}{dT}(\Delta G)_p \quad \text{or} \quad \Delta G = \Delta H + T\frac{\partial}{\partial T}(\Delta G)_p}$$

change in gibb's free energy.

calculation of ΔH →

$$\Delta H = \Delta G - T\frac{\partial}{\partial T}(\Delta G)_P$$

$$\Delta H = -nFE_{cell} - T\frac{\partial}{\partial T}(-nFE_{cell})_P$$

$$\boxed{\Delta H = nFT\left(\frac{\partial E}{\partial T}\right)_P - nFE_{cell}}$$

change in enthalpy

same

इसमें "T" पर Ecell की value Pcel करते है

Here

$\frac{\partial E}{\partial T}$ → Temp. co-efficient for a cell

→ show variation of cell emf w.r.t

→ $\frac{\partial E}{\partial T} = \frac{E_2 - E_1}{T_2 - T_1}$ $\left\{ \begin{array}{l} T_1 \to E_1 \\ T_2 \to E_2 \end{array} \right.$

→ If $\left(\frac{\partial E}{\partial T}\right)_P > 0$, $\Delta H > 0$,

R_{x}^{n} is endothermic

→ If $\left(\frac{\partial E}{\partial T}\right)_P < 0$, $\Delta H < 0$

R_{n}^{x} is exothermic

→ $E = a + bT + CT^2$

$$\left(\frac{\partial E}{\partial T}\right)_P = b + 2CT$$

Calculation of $\Delta S \rightarrow$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G - \Delta H = -T\Delta S \quad —(1)$$

$$\Delta G - \Delta H = T\frac{\partial}{\partial T}(\Delta G)_P \quad —(2)$$

$$\frac{\partial}{\partial T}(\Delta G)_P = -\Delta S$$

$$\frac{\partial}{\partial T}(\Delta G)_P = -\Delta S$$

$$\frac{\partial}{\partial T}(+nFE_{cell})_P = +\Delta S$$

$$\boxed{\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P}$$

change of entropy,

Ex 1 / QNo-26

$$\frac{\partial E}{\partial T} = 0.00065$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$$

$$= 2 \times 96500 \times -0.00065$$

Ex 1 / QNo-27

$$\Delta H = nFT\left(\frac{\partial E}{\partial T}\right) - nFE$$

$$= 2 \times 96500 \times 298 \times \left(\frac{E_2 - E_1}{T_2 - T_1}\right) - 2 \times 96500 \times 0.6753$$

Ex 1 Q.No-28

$$E^0 = 1.1028 - 0.641 \times 10^{-3} T + 0.72 \times 10^{-5} T^2$$

$$\frac{\partial E^0}{\partial T} = 0 - 0.641 \times 10^{-3} + 2T \times 0.72 \times 10^{-5}$$

2.5

$$\Delta S^0 = nF \left(\frac{\partial E^0}{\partial T} \right)_P$$

2 96500

Ex1) $Zn(s) + 2AgCl(s) \rightleftharpoons ZnCl_2\ (0.555M) + 2Ag(s)$

E at $0^\circ C = 1.015\ V$

$\frac{\partial E}{\partial T} = -4.02 \times 10^{-4}$ volt per degree

find ΔG, ΔS and ΔH for cell Rn^x.

80/n

$Zn(s) + 2AgCl(s) \rightleftharpoons ZnCl_2 + 2Ag$

$\cancel{\Delta H = 0.555 \times 1.015}$ $n=2$

$\Delta H = nFT\left(\frac{\partial E}{\partial T}\right)_P - nFE$

T, n = 2

$= 2 \times 96500 \times 273(-4.02 \times 10^{-4}) - 2 \times 96500 \times 1.015$

$=$

$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$

$= 2 \times 96500 \times (-4.02 \times 10^{-4})$

$=$

$\Delta G = \Delta H - T\Delta S$

$=$

[Ex 2] For the reaction

$H_2(g) + 2AgCl(s) + 2H_2O(l) \rightarrow 2Ag(s) + 2H_3^+O(aq) + 2Cl^-$

at 25°C standard free energy formation of $AgCl(s)$, $H_2O(l)$ and $(H_3O^+ + Cl^-)$ are -109 kJ, -237.2 and -368.4 kJ/mole respectively. Find the value of E°_{cell}.

Ans -43 kJ

Sol^n

$$\Delta G^\circ_{Rn^x} = \sum G^\circ_{f(P)} - \sum G^\circ_{f(R)}$$

$$= \left\{2G^\circ_f(Ag) + 2G^\circ_{f}(H_3^+O + Cl^-)\right\} - G^\circ_f(H_2) - 2G^\circ_f(AgCl) - 2G^\circ_f(H_2O)$$

$$= -43 \times 10^3 \text{ J}$$

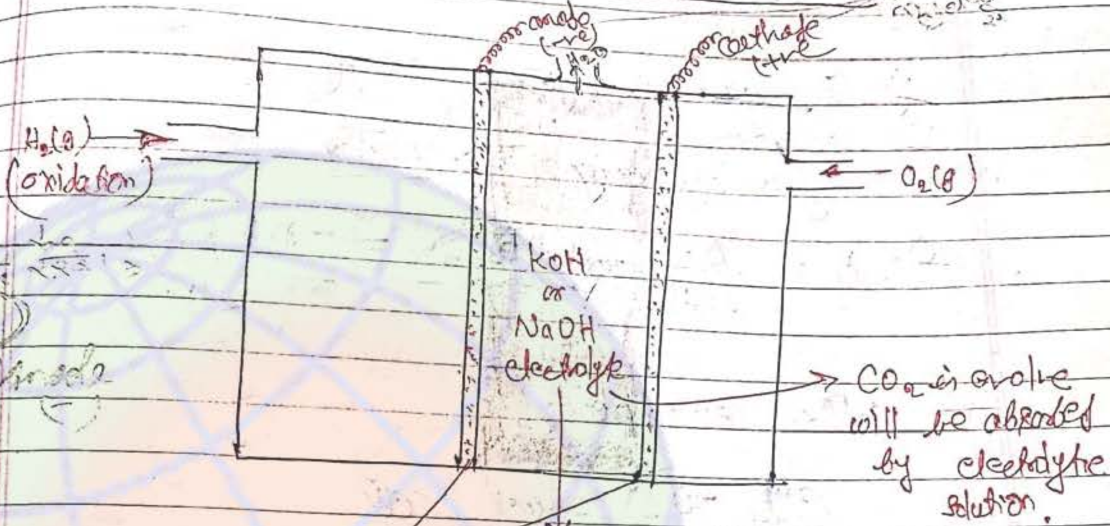
$\Delta G^\circ = -nFE$

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

$$-43 \times 10^3 = -2 \times 96500 \times E^\circ_{cell}$$

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

H_2-O_2 fuel cell (BACON cell)



It acts as medium in presence of which oxidation and reduction take place

Porous carbon electrode platinum
(Some Pt or Pd → Palladium added which acts as catalysis)

Reaction →

anode → $\cancel{H_2O} + H_2 \longrightarrow \cancel{H_2O} + 2H^+ + 2e^-$
$2OH^-$ $\quad$ $2OH^-$

$$\left. H_2 + 2OH^- \longrightarrow 2H_2O + 2e^- \right\} \times 2 \quad \text{—(i)}$$

cathode → $4e^- + 4H^+ + O_2 \longrightarrow 2H_2O$
$4OH^-$ $\quad$ $4OH^-$

$$\cancel{4e^-} + \cancel{2H_2O} + O_2 \longrightarrow \cancel{4OH^-} \quad \text{—(ii)}$$

cell Rxn $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ $\{n=4\}$

→ By product

 the efficiency of thermal power plant in ~40%.

Advantages :-

i) Continuous supply of energy
ii) pollution free working
iii) high efficiency $\boxed{70-75\%}$

iv) $\eta = \frac{\Delta G^\circ}{\Delta H^\circ} = \frac{-nFE^\circ_{cell}}{\Delta H^\circ}$

v) other example -

$CH_4 - O_2$ fuel cell

$C_3H_8 - O_2$ " "

$C_2H_5OH - O_2$ " "

CO_2

Alkane C_nH_{2n+2}

fuel.

vi) No used in daily life because it is not economical because catalyst (Pt or Pd) used are very costly

{while in rocket this is used}

Ex1.) If for Propane-oxygen fuel cell ($C_3H_8-O_2$) Ecell value is found to be nearly 0.8V. Find the max^n value of useful work that can be obtained from the cell.

Sol^n

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

Anode:>

$H_2O + C_3H_8 \longrightarrow 3CO_2 + 20H^+ + 20e^-$

cathode:> $4e^- + 4H^+ + O_2 \longrightarrow 2H_2O$ → यह स्थिति Reaction में अनुपात same रहता है।

$4OH^- \qquad 4OH^-$

$[4e^- + 2H_2O + O_2 \longrightarrow 4OH^-] \times 5$

Cell:- $C_3H_8 + 5O_2 \longrightarrow 4H_2O + 3CO_2 \; \{n = 20\}$

So, $n = 20$

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

$= -20 \times 96500 \times 0.8$ Ans.

Note For CH_4-O_2 fuel cell

Anode:> $2H_2O + CH_4 \longrightarrow CO_2 + 8H^+ + 8e^-$

Cathode:> $4e^- + 4H^+ + O_2 \longrightarrow 2H_2O$

cell → $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O(l)$

Batteries

Primary batteries or Primary cells

(It can't be recharged)

example ⇒

1) Dry cell or (Lechlanche cell) (cell potential ≈ 1.5V)

Anode ⇒

$Zn(s) \longrightarrow Zn^{+2} + 2e^-$

Cathode ⇒

oxidation states 4 → 3

$MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

2) mercury cell (cell potential = 1.35V)

Anode ⇒

$Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

cathode ⇒

$HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

cell ⇒

$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

Secondary batteries or secondary cells

(It can be recharged)

must read (Read sheet Page 40)

1) The lead storage battery

overall reaction

$Pb(s) + PbO_2(s) + 2H_2SO_4 \longrightarrow 2PbSO_4(s) + 2H_2O$

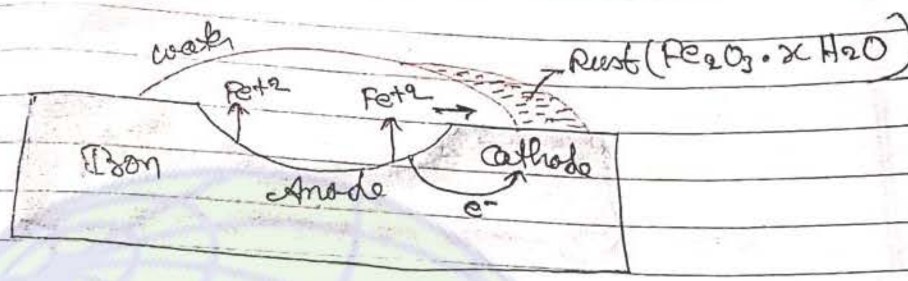
and 38% solution of sulphuric acid is used as an electrolyte.

2) Nickel cadmium battery ⇒

overall reaction

$Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O$

mechanism of corrosion



Oxidation :> $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$ —(i)

Reduction :> $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$ —(ii)

Now

The net reaction of the corrosion cell can be obtained by adding eq (i) and (ii)

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

$E^{\circ}_{cell} = 1.67\,V$

The ferrous ion's so formed move through electrolyte and come at the surface of Iron object where these are further oxidised to ferric state by atmospheric oxygen and constitute rust which is hydrated Iron (III) oxide

$$2Fe^{+}(aq) + \frac{1}{2}O_2(g) + 2H_2O(l) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$$

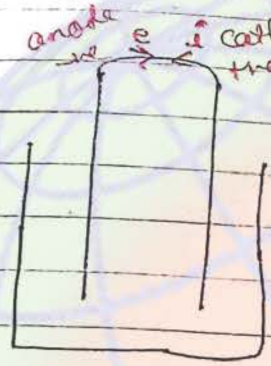
$$Fe_2O_3 + x\cdot H_2O \longrightarrow Fe_2O_3 \cdot xH_2O$$

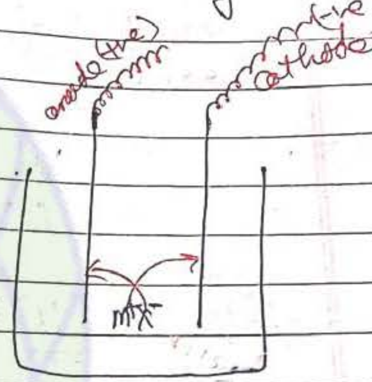
(Rust)

Elect.

Electrolytic cell

It is a device in which a Redox reaction is carried out by passing current into the cell.
It is reverse of electrochemical cell.
when a electrochemical cell is subjected to charging then it behaves as electrolytic cell.





Electrochemical cell	electrolytic cell
LOAN anode(-ve) → oxid.	anode (+ve) → oxidatn
cathode (+ve) → reductn	cathode (-ve) → reductn
e^- flow ; a → c	e^- flow ; a → c

Faraday law's of electrolysis -

1) charge on one $e^- \Rightarrow 1.6\times10^{-19}$ C
2) charge on one mole $e^- \Rightarrow 1.6\times10^{-19}\times N_A$
$\Rightarrow 96500C$
$= 1F$

$\boxed{\text{1F is charge on one mole of } e^-}$

3) Faraday's Ist law of electrolysis

According to this law the amount of substance deposited or evolved on a electrode is directly proportion to the amount of charge passed in electrolyte solution.

$$W \propto Q$$

$$W \propto i \times t$$

$$\boxed{W = Zit}$$

Confusion → molecular weight or "mass"

The amount of substance deposited/released/produced

where

Z = electrochemical equivalent of substance

$$= \frac{E}{96500}$$ { E = eq. wt of substance.

$$W = Zit$$

$$W = \frac{Eit}{96500}$$

$$\boxed{\frac{W}{E} = \frac{i \times t}{96500}}$$

No. of eq = No. of faraday

i.e. No. of eq. of substance deposited or evolve is equal to the no. of faraday passed in electrolyte solution

$$\left\{ E = eq.\,wt = \frac{mol.\,wt}{v.f\,(n)} \right\}$$

v.f = valency factor.

$$\frac{w}{m/n} = \frac{i \times t}{96500}$$

$$\frac{w}{m} = \frac{i \times t}{n \times 96500}$$

$$\boxed{No.\ of\ moles = \frac{i \times t}{n \times 96500}}$$

$$\boxed{N = m \times v.f}$$ ***

$$\boxed{No.\ of\ eq = no.\ of\ mole \times v.f}$$

$Ag^+ + e^- \rightarrow Ag$; v.f = 1

$Cu^{+2} + 2e^- \rightarrow Cu$; vf = 2

$2Cl^- + 2e^- \rightarrow Cl_2$; vf = 2 ****

valency factor (v.f) →
It is equal to the no. of e⁻ taking part in a electrode reaction when one mole of substance get deposited or evolved at electrode.

In case of gases faraday's Ist law of electrolysis can be written as: —

$$\text{No. of eq} = \frac{i \times t}{96500}$$

for gases

volume ← $\boxed{\dfrac{V}{V_e} = \dfrac{i \times t}{96500}}$

equivalent volume

where →

V_e → equal to the equivalent of gas

$\boxed{V_e = \dfrac{\text{molar volume}}{v.f}}$

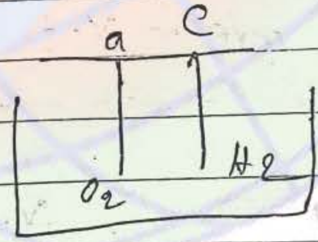
see p = 4+2 mobile C.15

H_2 ; $v.f = 2 \times 1 = 2$

Cl_2 ; $v.f = 2 \times 1 = 2$

O_2 ; $v.f = 2 \times 2 = 4$

$\boxed{\dfrac{G_o = 4}{ONO > 20}}$



eq O_2 = eq H_2

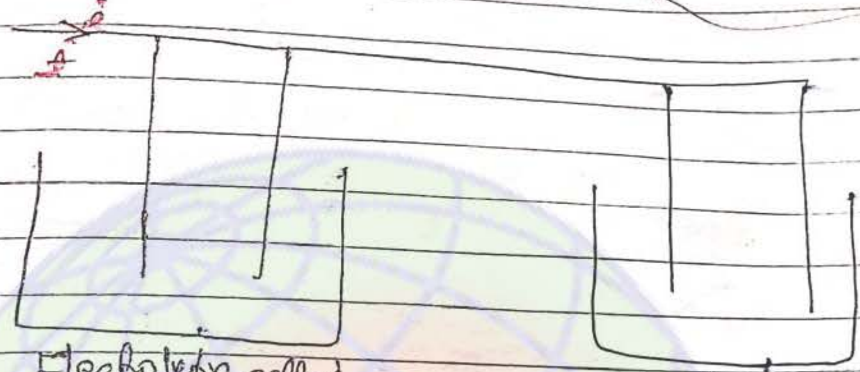
$$\frac{V_{O_2}}{22.4/4} = \frac{V_{H_2}}{22.4/2} \quad \text{Ans}$$

$\boxed{\dfrac{G_o = 1}{ONO > 30}}$

$$\frac{w}{E} = \frac{i \times t}{96500}$$

$$\frac{w}{63.5/2} = \frac{2.5 \times (360 + 265)}{96500}$$

Faraday's 2nd law of electrolysis



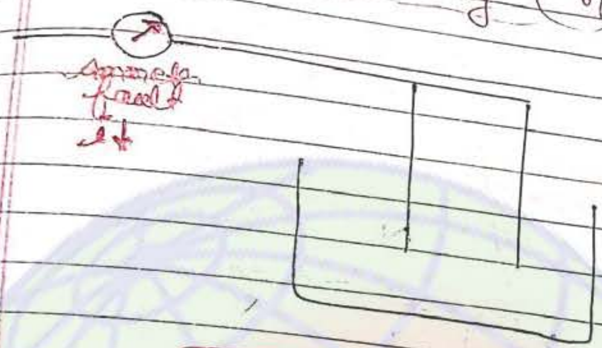
Electrolytic cell-1 Electrolytic cell-2

~~A/a to this~~

According to this law if same amount of current is passed through different electrolytic cell connected in series then the number of equivalent of the substance evolve or deposited on diffⁿ electrode will be equal.

$$\boxed{\frac{w_1}{E_1} = \frac{w_2}{E_2} = \cdots\cdots = \frac{w_n}{E_n}}$$

Q Current efficiency (η)



$$\boxed{\eta = \frac{i_{ammeter}}{i_{actual}} \times 100}$$

If current efficiency is given in the question than the formula will be

$$\boxed{\frac{w}{E} = \frac{i \times t}{96500} \times \eta}$$

और η यदि नहीं देते तो 1 मान लें।

$\boxed{\frac{\Delta O = 2}{O.N.O = 2}}$

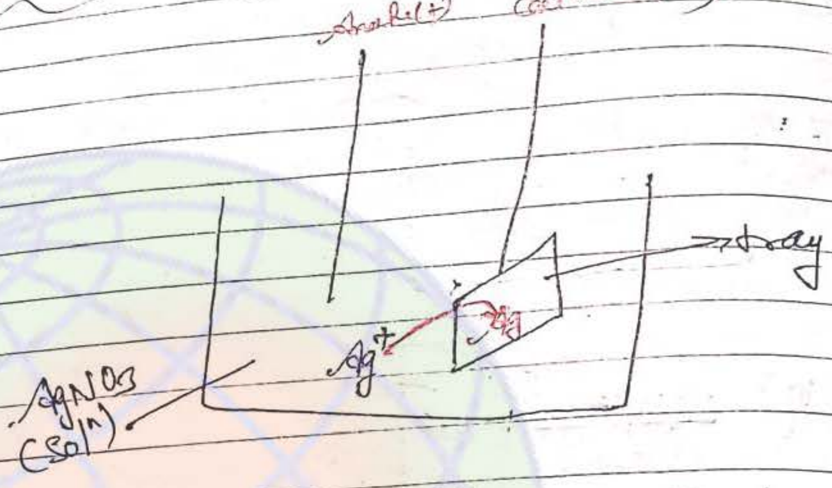
$$\overset{+2}{Mn}SO_4 \longrightarrow \overset{+4}{Mn}O_2$$

$n\text{-}f = 2$

$$\frac{w}{E} = \frac{i \times t}{96500} \times \eta$$

$$\frac{1000}{\frac{mol \cdot wt\ MnO_2}{2}} = \frac{27 \times 24 \times 60 \times 60}{96500} \times \eta$$

Q. Application of electrolysis (Electro plating)



Let the area of tray to be coated = (a×b)
Let the thickness of film to be coated = "c"

volume of tray to be coated = $(a \times b \times c) cm^3$

Let the density of substance to be coated = "d" g/cm^3

wt. of substance used = $v \times d$
$= (a \times b \times c) \times d$ g

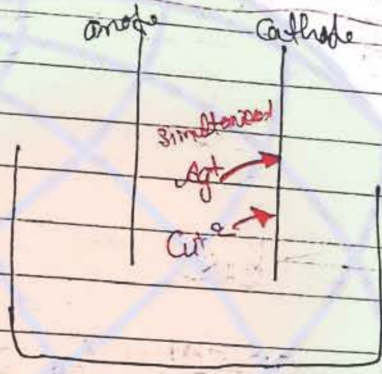
$$\frac{w}{E} = \frac{i \times t}{96500}$$

$$\boxed{\frac{(a \times b \times c) \times d}{E} = \frac{i \times t}{96500}}$$

Ex 2.1 → 9 to 25 | 440 | DPP-1 → 14 | sheet

~~Simultanies~~
~~Simultaneous~~

Simultaneous deposition of of two metal ion on a same electrode →



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

$$R.P_1 = \underbrace{SRP_1}_{fixed} + \frac{0.0591}{1}\log[Ag^+]$$

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

$$R.P_2 = \underbrace{SRP_2}_{fix} + \frac{0.0591}{2}\log[Cu^{+2}]$$

$$\boxed{\begin{array}{l} R.P_1 = R.P_2 \text{ for simultaneous} \\ S.R.P_1 + \frac{0.0591}{1}\log[Ag^+] = S.R.P_2 + \frac{0.0591}{2}\log[Cu^{+2}] \end{array}}$$

Ex 2.21 / Q.No 3/20

$\frac{\partial E}{\partial T} = -0.00015 \; V/deg$

Ex 2.2 / Q.No → 15

$\frac{(9 \times 1.6 \times 60) \times d}{63.5/2} = \frac{i \times t}{96500}$

100×10^{-2} 8.94

Ex 2.2 / Q.No → 18

$2H^{+} + 2e^{-} \longrightarrow H_2(g)$

1M

$R.P = SRP - \frac{0.0591}{2} \log P_{H_2}$

$R.P_1 = S.R.P - \frac{0.051}{2} \log[1] = 0$

$R.P_2 = S.R.P - \frac{0.0591}{2} \log[100]$

$R.P_2 - R.P_1 = -ve$

Ex 2.1 / Q.No → 7

$5e^{-}$

$\overset{+7}{Mn}O_4^{-} \longrightarrow Mn^{+2}$

$Mn^{+7} + 5e^{-} \longrightarrow Mn^{+2}$

1 mole $Mn^{+7} \longrightarrow Mn^{+2} \longrightarrow$ 5 mole

0.05 mole $\longrightarrow$ 5×0.05

$= 0.25 F$

$\boxed{1.6 \times 10^{-19} \times 6.022 \times 10^{23} = 96500}$

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Q.No→92

Q.No 31
Q.No→53

$\overset{+3}{AlCl_3} \longrightarrow \overset{0}{Al}$ $AlCl_3$ - $Al^{+3} + 3e^- \rightarrow Al$

$Al^{+3}Cl_3 + 3e^- \longrightarrow Al$

$\frac{W}{E} = \frac{I \times t}{96500}$

$\frac{13.5}{27/3}$ A.

94) $i = 0.75A$

$\frac{V}{V_e} = \frac{I \times t}{96500}$

$\frac{V}{5.6} = \frac{0.75 \times 10 \times 60}{96500}$

$V =$

H_2; $V_e = \frac{22.4}{2} = 11.2$

Cl_2; $V_e = \frac{22.4}{2} = 11.2$

O_2; $V_e = \frac{22.4}{4} = 5.6$

12/6/2019

35) MCl_x , 3.283

$$\frac{w}{E} = \frac{i \times t}{96500}$$

$$\frac{3.283}{197/x} = \frac{4825}{96500}$$

16) $i = 9.65 A$, $t = 1 hour$

Eq Zn = eq Cu

eq Cu = eq Zn = No. of eq = No. of faraday = $\frac{9.65 \times 3600}{96500}$

$$\text{No. of eq Zn} = \frac{9.65 \times 3600}{96500} = \frac{w_{Zn}}{65.4/2}$$

12/6/2019 Electrolysis

1) Greater is the S.R.P value of the given cation more will be it's tendency to get reduced at cathode.
Similarly, Greater is the S.O.P value of anion more will be it's tendency to get oxidized on anode.

2) In the competition of oxidation and reduction water will also take part and in some cases there can be exceptions to the give rule and it is due to ova voltage or ova potential.

3) The product of electrolysis depend's upon:—
i) Nature of electrolyte solution.

molten solution, (No. water (H_2O))

Aqueous solution (H_2O will take part)

ii) Concentration of solution

(concentrated sol^n) Conc. sol^n (No. salt)

Aqueous sol^n (Red. and oxidation of H_2O will take part + salt)

dilute solution (No salt) Red^n and oxidation of H_2O will take place.

3) Nature of electrode →

i) Non attackable electrode.

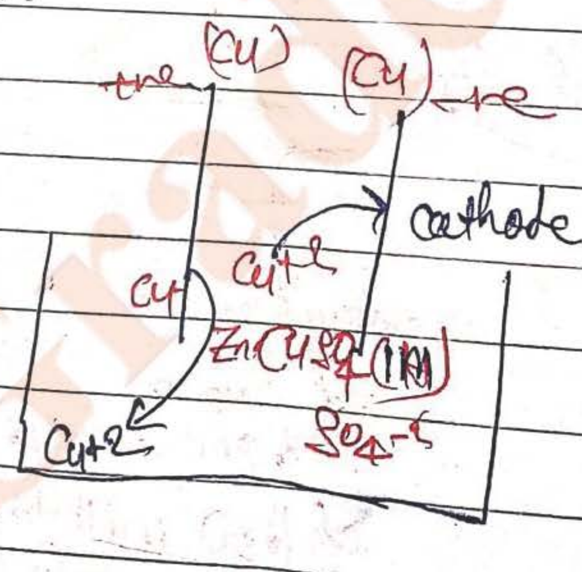
The electrode which do not take part in electrolysis is know as non attackable electrode.

eg → Pt

Notes → Platinum (Pt) and gold and also Pd (Pladium) are Inert electrode.

ii) Attackable electrode

The electrode which take part in electrolysis are known as attackable electrode.



If the electrolysis is carried out in presence of attackable electrode then before and after the electrolysis the conc^n of sol^n remain same.

eg:> electrolysis of copper surface solution in presence of Cu-electrode.

Goal
DMO> 32

Method to determine the Product of electrolysis (aquous solution)

~~eg1 → (Pcot)~~

~~Electrolysis~~

I^{st}, II^{nd} group, Al^{+3}	H_2O	Cu^{+}, Zn^{+2} all cation
In preferene to these ion reduction of H_2O take place		Reduction of these cation take place

F^-	H_2O	Cl^-, Br^-, I^-	SO_4^{-2}, NO_3^-, $C_2O_4^{-2}$ etc
oxidation of H_2O take place		oxidation of these ion's take place	molecula ion. oxidation of H_2O take place and these ion's remain in solution as such

Electrolyte sol^n	electrode	anode	cathode
NaCl (molten)	Pt	Cl ↑	Na ↓
NaCl (aq)	"	Cl ↑	H_2 ↑
NaCl (dilute)	"	$H_2O - O_2$ ↑	$H_2O - H_2$ ↑

$CuSO_4$ (aq)	Pt	$H_2O - O_2 \uparrow$	$Cu \downarrow$
$CuSO_4$ (aq)	Cu	$Cu - Cu^{+2}$	$Cu^{+2} - Cu \downarrow$
High charge density $H_2SO_4 \rightarrow H^+ + SO_4^{\ominus}$ (conc. sol)	Pt	$2HSO_4 \rightarrow H_2S_2O_8 + 2e^-$; $H_2O \longrightarrow O_2 \uparrow$; $\boxed{\text{eg: } H_2S_2O_8 + H_2O \rightarrow SO_4\ H_2}$	$H^+ \rightarrow H_2 \uparrow$; $H_2O \rightarrow H_2 \uparrow$
low charge density H_2SO_4 (aq) $\rightarrow (SO)$	Pt	$H_2O \longrightarrow O_2 \uparrow$	$H_2O - H_2 \uparrow$
NaF (aq)	Pt	$O_2 \uparrow$	$H_2 \uparrow$

F_2 can't be produced by electrolysis of it's aq. solution

Carbon … ele… Hg el… cathod… anod… Lec…

Special method to prepare "F_2" →

Electrolysis of KHF_2 (90% w/w in only HF)

anode: $F^- \longrightarrow F_2 \uparrow$

cathode: $K^+ + e^- \longrightarrow K$

$K + HF \longrightarrow KF + H_2 \uparrow$

450

(8) Castener kellers process →
electrolysis of NaCl solution in presence of Hg electrode

cathode ⇒ $Na^+ + e^- \longrightarrow Na$
$Na + Hg \longrightarrow Na\text{-}Hg$ (amalgam)

anode ⇒ $Cl^- \longrightarrow Cl_2 \uparrow$

imp

Lead storage battery (Secondary battery / Rechargable battery).

Electrolyte use ⇒ 38% H_2SO_4 (w/w)

anode ⇒
$Pb + SO_4^{-2} \longrightarrow PbSO_4 + \cancel{2e}$

Cathode ⇒ $PbO_2 + 4H^+ + SO_4^{-2} \longrightarrow PbSO_4 + 2H_2O$

Rn ⇒ $Pb(s) + PbO_2(s) + 2H_2SO_{4(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O(l)$

during discharging $[H^+] \downarrow$

during charging $[H^+] \uparrow$

DPP.8(15) → 3, 4, 5, 6, 7, 8, 9, 10, 11
DPP.8(16) → 8, 9

4-5

V.f of $H_2SO_4 = 1$

Eq. wt $H_2SO_4 = 98/1$

Ex=3
QNO→4

anode ; $Fe \rightarrow Fe^{+2} + 2e^-$

cathode ; $Cd^{+2} + 2e^- \rightarrow Cd$

cell ; $Fe(s) + \underset{1M}{Cd^{+2}} \rightarrow \underset{1M}{Fe^{+2}} + Cd$

$[Fe^{+2}] \uparrow = 1.8 M$

$[Cd^{+2}] \downarrow = 0.2 M$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{1.8}{2}$ Ans.

Ex=3
QNO→15

a) $H_2 \rightarrow 2H^+ + \cancel{2e^-}$

c) $Hg_2Cl_2 + \cancel{2e^-} \rightarrow 2Hg + 2Cl^-$

cell $H_2(g) + Hg_2Cl_2(s) \rightarrow 2Hg(l) + 2H^+ + \underset{1m}{Cl^-}$

$E_{cell} = E^\circ_{cell} - \frac{0.059}{\cancel{2}} \log \frac{[H^+]^2}{P_{H_2}}$ → 4

~~$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log [H^+]^2$~~

$0.6885 = 0.28 + 0.0591 \times P_H$

$P_H =$ ____

$\boxed{Ex = 3 \quad Q.No \to 423}$

$[OH^-] = \sqrt{K_b \cdot c} = \sqrt{5 \times 10^{-12}} = 7 \times 10^{-7}$

Aniline ($C_6H_5NH_2$) (E) 0.5×10^{-3}, $K_b = 10^{-9}$

$(E^\circ_{cell} = 0)$

HCl $n = 2.5 \times 10^{-3}$ $[H^+]$

$[H^+] = \frac{2.5 \times 10^{-3}}{0.5}$

500ml H_2O 500ml H_2O

$[H^+] = \frac{10^{-14}}{[OH^-]}$

H-electrode H-electrode

$$a)\quad H_2 \longrightarrow 2H^+ + 2e^-$$
$$c)\quad 2H^+ + 2e^- \longrightarrow H_2$$
$$\text{cell: } 2H^+(c) \longrightarrow 2H^+(a)$$

$$E_{cell} = 0 - \frac{0.0591}{\cancel{2}} \log \frac{[H^+]_a^{\cancel{2}}}{[H^+]_c^{\cancel{2}}}$$

$\boxed{Ex = 3 \quad Q.No \to 452}$

Zn^{+2} 1m

Cu^{+2} 1m $\leftarrow NH_3$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{+2}] \to 1M}{[Cu^{+2}] \to \frac{1}{16 \times 10^{12}}}$$

$$Cu^{+2} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{+2} \quad K_f = 10^{12}$$

	Cu^{+2}	$4NH_3$	$[Cu(NH_3)_4]^{+2}$
$t=0$	1	4	0
	0		1
$t = t_{eq}$	x	$4x$ 2M	$(1-x) \approx 1M$

$$10^{12} = \frac{1}{x(2)^4}$$

$$x = \frac{1}{16 \times 10^{12}}$$

[Ex-3] Q.No → 16

$i = \frac{W}{V} = \frac{200}{110}$

[Ex-3] Q.No → 20

$Zn^{+2} + 2e^{-} \rightarrow Zn$

$n = 2$

$\frac{w}{E} = \frac{\frac{200}{110} \times 30 \times 60}{96500}$

[Ex-3] Q.No → 19

$\frac{w}{\frac{65.4}{2}} = \frac{20 \times 18}{11 \times 965} = \frac{360}{965 \times 11}$

[Ex-3] Q.No → 20

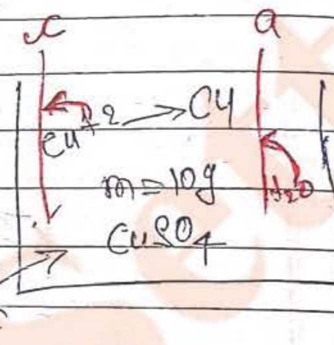
$w = \frac{360}{965 \times 11} \times \frac{65.4}{2}$

[Ex-3] Q.No → 18

10g

$CuSO_4 \rightarrow Cu^{+2} + SO_4^{2-}$

$i = 0.01F$



No. of equivalent = No. of faraday

$0.01F \rightarrow 0.01 eq = \frac{w}{eq wt}$

$0.01 = \frac{w}{63.5/2}$

$w_{deposite} = \frac{x}{\cancel{\quad}} \Rightarrow 10 \quad 10-x$

$2e^{-} + 2H^{+} + \cancel{H_2O} \rightarrow H_2 + \cancel{H_2O}$

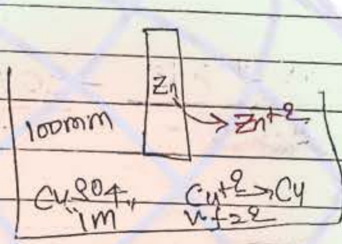
Ex-3
QNo→20

~~density = 8.94 g/ml~~

Ex-2
QNo→19

$$\frac{(a\times b\times c)\times d}{E} = \frac{i\times t}{96500}$$

Ex-2
QNo→20



$$(Cu^{+2})_i = 1\ M \qquad [Cu^{+2}]_f = 0.8M$$

a) $[SO_4^{-2}] = 1M$ ⇒ same

b) $n_{i\,(Cu)} = \frac{1\times 100}{1000}$, $n_f = \frac{0.8\times 100}{1000}$

$$n_{dep} = \frac{20}{1000}$$

$$\text{no. of eq} = \frac{20\times 2}{1000} = 0.04$$

deposite (Cu)

$$\text{Zn eq evolve} = 0.4 = \frac{w_{Zn}}{65.4/2}$$

$$w_{Zn} = x$$

evolve

Ex 23 Q No 32

$x = \left(\frac{w}{w}\right)\%$

Remember: d = density in g/ml = x g/ml = specific gravity

specific gravity = density of solution / density of H_2O

$$\boxed{\text{molarity} = \frac{x \times d \times 10}{\text{mol. wt}}}$$

$n = m \times V$

No of eq = $n_f - n_i$ (v.f = 1)

$$= \left[\frac{39 \times 1.294 \times 10}{9.8} - \frac{20 \times 1.39 \times 10}{98}\right] \times 0.5 = \frac{i \times t}{96500}$$

Ex 23 Q No 2

Do all questions of specific gravity जान कर भी density वाले Problem की कीजिए

Ex 24 Passage II

a) $2Cl^- \longrightarrow Cl_2 + 2e^-$
2 mole → 1 mole

c) $Na^+ + e^- \longrightarrow Na$
2 → 2

$Na + Hg \longrightarrow Na\text{-}Hg$
2 + 2 → 2

wt = 2(23 + 200)

NaCl, m = 4
V = 500
$n_{NaCl} = 2$

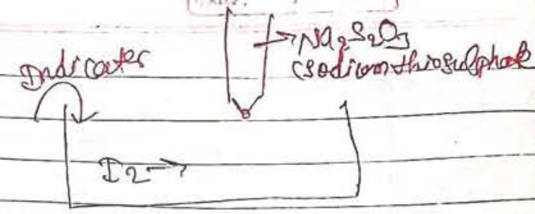
Na^+	Cl^-
2	2

No. of mole of Na deposite = 2 ($Na^+ \to Na$)
v.f = 1

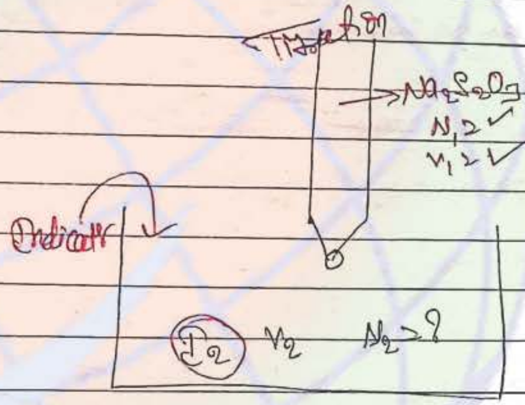
No. of eq = 2 = No. of F

$\boxed{Eq>) \; QNO\text{-}26}$

$$eq\ I_2 = eq\ X = \frac{0.617}{E}$$



$$eq\ I_2 \Rightarrow eq\ Hypo \quad (v.f = 1)$$
$$= M \times V$$
$$= \frac{46.3 \times 0.124}{1000}$$



$$2S_2O_3^{-2} \longrightarrow S_4O_6^{-2} + 2e^-$$
$v.f = 1$

$$2e^- + I_2 \longrightarrow 2I^-$$
$v.f = 2$

$$eq\ I_2 = eq\ Na_2S_2O_3$$
$$= N \times V = n_{\text{mole of } Na_2S_2O_3}$$
Hypo

$v.f = 2$
$$2I^- \longrightarrow I_2 + 2e^-$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{-2} + 2e^-$$
$v.f = 1$

Electrolytic conductance

1) conductor's

- metallic (due to flow of "e^-")
- Electrolyte (due to flow of "Ion's")

⇒ law of resistance and ohm's law is equally applicable on both type of conductor's.

2)

$$R \propto l$$

$$\propto \frac{1}{a}$$

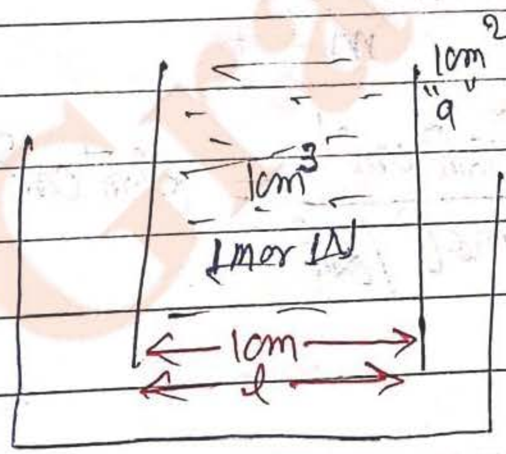
$$\boxed{R = \frac{\rho l}{a}}$$

$l = 1cm, \quad a = 1cm^2$

$$\boxed{R = \rho}$$

$R \to ohm$

$\rho \to ohm\,cm$



3) conductance (κC)

$$\boxed{C = \frac{1}{R}}$$

Unit $\Rightarrow ohm^{-1}$

4) Specific conductan (K) → चालकता

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

called as चालकता

$\frac{l}{a} = x =$ cell constant

$$\boxed{x = K \times R}$$

unit $\Rightarrow ohm^{-1} cm^{-1}$

5) molar conductance (λ_m or Λ_m)

$$\boxed{\lambda_m = \frac{1000 \times K}{M}}$$

Here, M = molarity

$$Unit = \frac{ohm^{-1} cm^{-1}}{mole / cm^{3}} = ohm^{-1} cm^{2} mol^{-1}$$

6) equivalent conductance (λ_E or Λ_E)

$$\boxed{\uparrow \lambda_E = \frac{1000 \times k\downarrow}{N\downarrow}}$$

$$\text{Unit} = \frac{ohm^{-1} cm^{-1}}{eq/cm^{3}}$$

$$= oh^{-1} cm^{2} eq^{-1}$$

7) Relation b/w λ_m and λ_E

$$\frac{\lambda_E}{\lambda_m} = \frac{M}{N} = \frac{M}{M \times v.f}$$

$$\boxed{\lambda_E = \frac{\lambda_m}{v.f}}$$

Imp

$$\boxed{\text{dilution } (V) \uparrow \quad \lambda_M \uparrow \quad \lambda_E \uparrow \quad k\downarrow \quad M\downarrow \quad N\downarrow}$$

(याद रखें K, M, N घटते रहते हैं)

Variation of molar conductance with concentration →

1) Strong electrolyte →

The molar conductance of strong electrolyte is found to obey Deby Huckle onsager equation:

$$\boxed{\lambda_m = \lambda_m^{\infty} - b\sqrt{c}}$$

$$y = c + mx$$

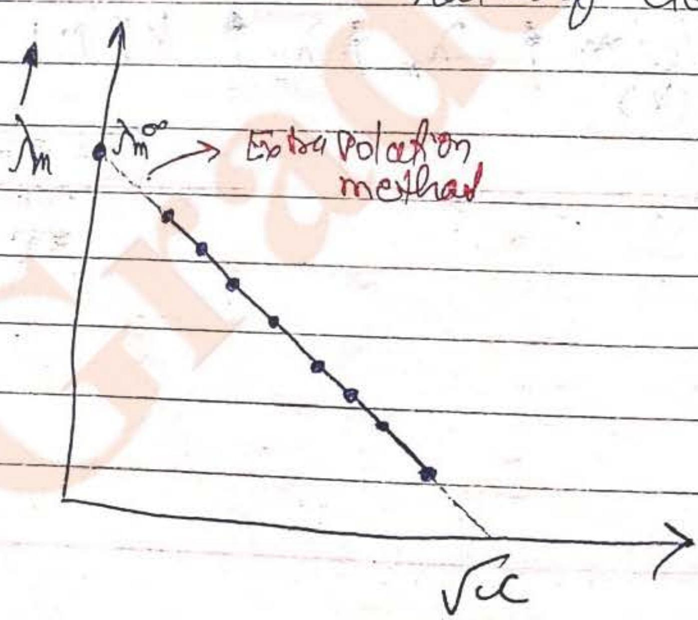
λ_m = molar conductance of solution of given

λ_m^{∞} = " " " " " ∞ dil or $\left(c = \frac{n}{V}\right)$

λ_m^{0} = " " " " " zero conc

c = Conc. of solution

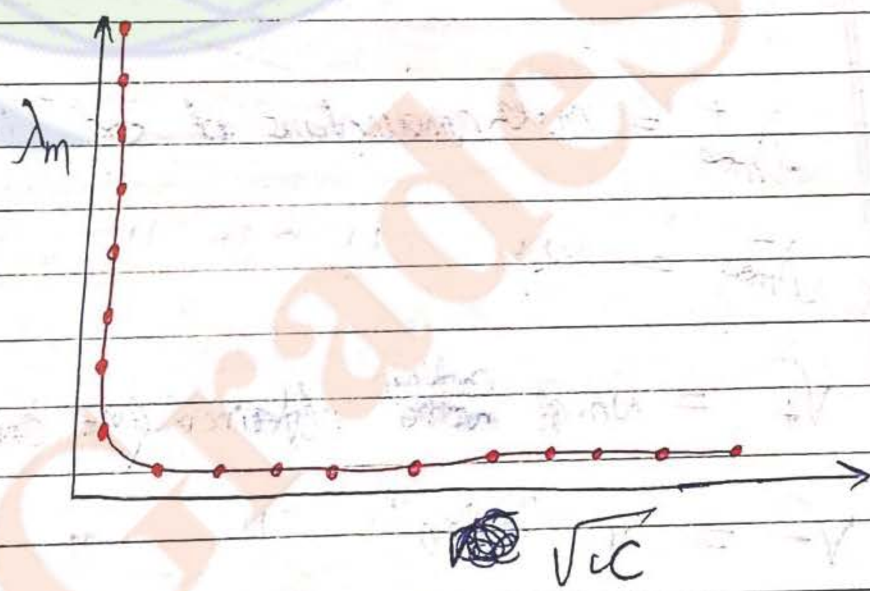
b = Constant, it's value depend upon nature of electrolyte



The value of "λ_m^∞" for strong electrolyte can be calculated graphically by extrapolation method.

2) weak electrolyte →

The solution of weak electrolyte do not obey Deby Huckle onsager equation and the graph b/w λ_m and $\sqrt{c}$ for weak electrolyte is found to be rectangula hyperbola
Therefore the value of λ_m^∞ for weak electrolyte can't be calculate graphically.



~~Colorsas law of~~

Kaulauraush law of Independent migration of Ion's :=>

According to this law at Infinite dilution the molar conductance of the solution is equal to the sum of conductance of all the Ion's present in the solution.

→ This law is applicable on weak electrolyte and strong electrolyte equally.

must read this concept of Λ_m^∞

$$\boxed{\Lambda_m^\infty = (\nu_+)\cdot \lambda_{m}^{\infty +} + (\nu_-)\cdot \lambda_m^{\infty -}}$$

$\lambda_{m\infty}^{+}$ = molar conductance at ∞ dilution of cation

$\lambda_{m\infty}^{-}$ = " " " " " anion

ν_+ = No. of cation obtained by "one" molecule of electrolyte

ν_- = " "anion" " " " " "

Example ⇒

i) $\lambda_{m\,NaCl}^{\infty} = \lambda_{m^{\infty}}^{Na^+} + \lambda_{m^{\infty}}^{Cl^-}$

ii) $\lambda_m^{\infty}\,BaCl_2 = \lambda_m^{\infty}Ba^{+2} + 2\lambda_m^{\infty}Cl^-$

must read this imp concept of λ_m^{∞}

iii) $\lambda_m^{\infty}\,Al_2(SO_4)_3 = 2\lambda_m^{\infty}Al^{+3} + 3\lambda_m^{\infty}SO_4^{2-}$

Important formula

$$\boxed{\lambda_E^{\infty} = \lambda_E^{\infty +} + \lambda_E^{\infty -}}$$

☒ Relation b/w λ_E^{∞} and λ_m^{∞} ⇒

$$\lambda_{E\,NaCl}^{\infty} = \lambda_E^{\infty}Na^+ + \lambda_E^{\infty}Cl = \frac{\lambda_m Na^+}{1} + \frac{\lambda_m Cl^-}{1}$$

$$\lambda_E^{\infty}\,BaCl_2 = \lambda_E^{\infty}Ba^{+2} + \lambda_E^{\infty}Cl^- = \frac{\lambda_m Ba^{+2}}{2} + \frac{\lambda_m^{\infty}Cl^-}{1}$$

$$\lambda_E^{\infty}\,Al_2(SO_4)_3 = \lambda_E^{\infty}Al^{+3} + \lambda_E^{\infty}SO_4^{-2} = \frac{\lambda_m Al^{+3}}{3} + \frac{\lambda_m^{\infty}SO_4^{2}}{2}$$

~~λ_E^{∞}~~

~~$\lambda_E^{\infty}\,Al_2(SO_4)_3$~~

$$\boxed{\lambda_E^{\infty} = \frac{\lambda_m^{\infty}}{v.f \; (Z^+ \text{ or } Z^-)}}$$

or

So, $\boxed{\lambda_E^{\infty} = \frac{\lambda_m^{\infty}}{v.f}}$

v.f cation या anion किसी का भी.

Application of Kohlrausch law

1) Calculation of molar conductivity of weak electrolyte at "∞" dilution.

$$\boxed{\lambda_m^\infty = (\nu_+) \cdot \lambda_m^{\infty +} + (\nu_-) \cdot \lambda_m^{\infty -}}$$

Eg.) $\lambda_m^\infty\ CH_3COOH = ?$

$\lambda_m^\infty\ HCl = 426$

$\lambda_m^\infty\ NaCl = 126$

$\lambda_m^\infty\ CH_3COONa = 91$

Sol^n

$\lambda_m^\infty\ HCl = 1 \cdot \lambda_m^\infty H^+ + 1 \cdot \lambda_m^\infty Cl^-$ — (i)

$\lambda_m^\infty\ NaCl = 1 \cdot \lambda_m^\infty Na^+ + 1 \cdot \lambda_m^\infty Cl^-$ — (ii)

$\lambda_m^\infty\ CH_3COONa = 1 \cdot \lambda_m^\infty CH_3COO^- + 1 \cdot \lambda_m^\infty Na^+$ — (iii)

$\lambda_m^\infty\ CH_3COOH = \lambda_m^\infty CH_3COO^- + \lambda_m^\infty H^+$ — (4)

eq (4) = eq (1) + eq (3) − eq (2)

$= 426 + 91 - 126$

$= 391$ Ans.

2) Calculation of degree of dissociation of weak electrolyte →

$$HA \rightleftharpoons H^+ + A^-$$

$$C \quad\quad 0 \quad 0$$

$$C(1-\alpha) \quad C\alpha \quad C\alpha$$

$$\boxed{K_a = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2}$$ → when $1-\alpha \approx 1$

$$\boxed{[H^+] = C\alpha = \sqrt{K_a \cdot C}}$$

$$\boxed{\alpha = \frac{\lambda_m^c}{\lambda_m^\infty} \text{ or } \lambda_m^c \text{ or } \frac{\lambda_E}{\lambda_E^\infty}}$$

Example: For Propanoic acid

$\lambda_E^\infty = 386.6 \quad K_a = 1.6 \times 10^{-5} \quad C = 0.05N$

$\lambda_E = ? \quad pH = ?$

Solⁿ

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.6 \times 10^{-5}}{0.05}}$$

$$\alpha = \frac{\lambda_E}{\lambda_E^\infty} \quad \lambda_E = \alpha \lambda_E^\infty = \sqrt{\frac{1.6 \times 10^{-5}}{0.05}} \times 386.6$$

$$[H^+] = C\alpha = 0.05 \times \sqrt{\frac{1.6 \times 10^{-5}}{0.05}}$$

$$P_H = -\log[H^+]$$

3) Calculation of Solubility Product of Sparingly Soluble Salt →

The solution of sparingly soluble salt is Infinitely diluted at every given concentration. Therefore for sparingly soluble salt λ_m can be taken to λ_m^∞

(पानी का solubility same होगा चाहिए पानी से या इसकेलिक पानी है)

$$\boxed{\lambda_m \text{ or } \lambda_m^\infty = \frac{1000 \times K_{sol}}{m \text{ or } S}}$$

$\because K_{sp} = S \times S = S^2$

If in the question specific conductivity K of the water is given then

$$\boxed{\lambda_m \text{ or } \lambda_m^\infty = \frac{1000 \times (K_{sol} - K_{H_2O})}{m \text{ or } S}}$$

Example > $K_{sp} = BaSO_4 = ?$, calculate the solubility product of barium sulphate if

$K_{BaSO_4} = 4.44 \times 10^{-6}$

$K_{H_2O} = 1.34 \times 10^{-6}$

$\lambda_m^{\infty} Ba^{+2} = 127.28$

$\lambda_m^{\infty} SO_4^{-2} = 159.6$

so, $\left(\lambda_m^{\infty} Ba^{+2} + \lambda_m^{\infty} SO_4^{-2} \right) = \dfrac{1000 \times (4.44 - 1.34) \times 10^{-6}}{S}$

$\dfrac{127.28 + 159.6}{80} = \dfrac{3.10 \times 10^{-3}}{S}$

$S = 11.07 \times 10^{-6}$ —(i)

$\cancel{K_{sp} = S \times S = S^2}$

so,

$K_{sp} = [Ba^{+2}][SO_4^{-2}]$

$= S \cdot S$

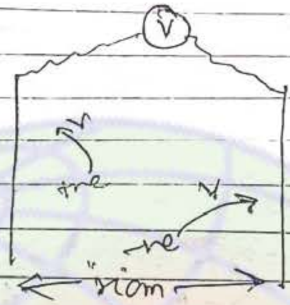
$= S^2$

so, from eq (i)

$K_{sp} = (11.07 \times 10^{-6})^2$

Ionic mobility (u)

→ Speed of Ions per unit in electric field
Its unit is 'cm² v⁻¹ sec⁻¹'



$$\boxed{U = \frac{\text{velocity of Ion's}}{\text{Potential gradient}} = \frac{u}{V/x} = \frac{\text{speed}}{\text{Electric field}}}$$

$$\text{Unit} = \frac{cm/sec}{volt/cm} = cm^2\ volt^{-1}\ sec^{-1}$$

Ionic mobility ←

$$\boxed{U = \frac{\lambda_m^\infty \text{ or } \lambda_E^\infty}{96500}}$$

Example →

$\lambda_{H^+}^\infty = 349.8$

$V = 5$ volt

$x = 3$ cm

u_{H^+} and U_{H^+}

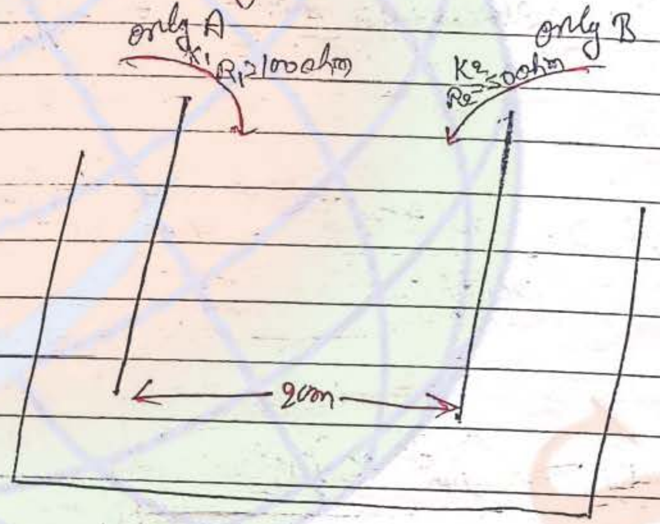
Sol^n

$$U_{H^+}^\infty = \frac{\lambda_{H^+}^\infty}{96500} = \frac{349.8}{96500}$$

$$U_{H^+}^{\infty} = \frac{U_{H^+}}{5/3}$$

$$\frac{349.8}{96500}$$

Calculation of Resistance of mixture so[l] in conducting cell



$$x = KR$$

$$K = \frac{x}{R}$$

only (A) $K_1 = x \times \frac{1}{R_1}$

only (B) $K_2 = x \times \frac{1}{R_2}$

{ Here K = kappa (कप्पा)
x = cell constant
R = Resistance
(see p- 459)

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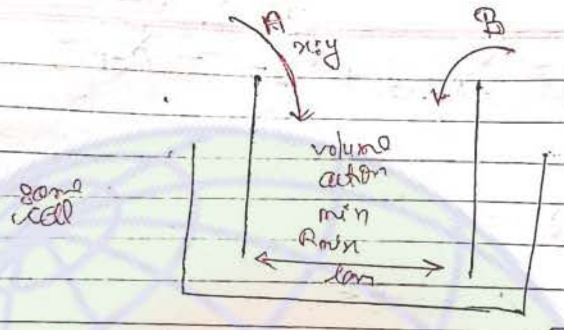

$$\left\{ k_1' = \frac{k_1 x}{x+y} \right\} \quad \left\{ k_2' = \frac{k_2 y}{x+y} \right\}$$

और इसमें प्रश्न की formula यहीं यह

$$\boxed{(k_1' + k_2') = x \times \frac{1}{R_{min}}}$$

इसलिए ये हमें याद रखें

or

$$\boxed{\left(\frac{k_1 x}{x+y} + \frac{k_2 y}{x+y} \right) = x \times \frac{1}{R_{min}}}$$

मैन formula यही है

equal volume ration "1:1"

$$\boxed{\frac{1}{2}(k_1 + k_2) = x \times \frac{1}{R_{min}}}$$

इसे भी याद रखें और इसकी सहायता से हम निकाल हैं। 1:1 के लिए

$$\frac{1}{2}\left(\frac{\cancel{x}}{100} + \frac{\cancel{x}}{50} \right) = \cancel{x} \times \frac{1}{R_{min}}$$

$R_{min} = 1$

Note:-
If electrodes are half dipped in electrolyte solution then in calculation their Area is taken half

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Q. 24 / Q.NO → 6

$\lambda^{\infty}_{NH_4OH} = \lambda^{\infty}_{NH_4Cl} + \lambda^{\infty}_{OH^-} - \lambda^{\infty}_{Cl^-}$

Q. 21 / Q.NO → 8

$\alpha = \frac{7}{390.8}$ $K_a = C\alpha^2$

Q. 21 / Q.NO → 44

$5e^- + Mn^{+7} \longrightarrow Mn^{+2}$

1 mole → 5F

0.5 → 5 × 0.2 = 2.5 F

Q. 22 / Q.NO → 20

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

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

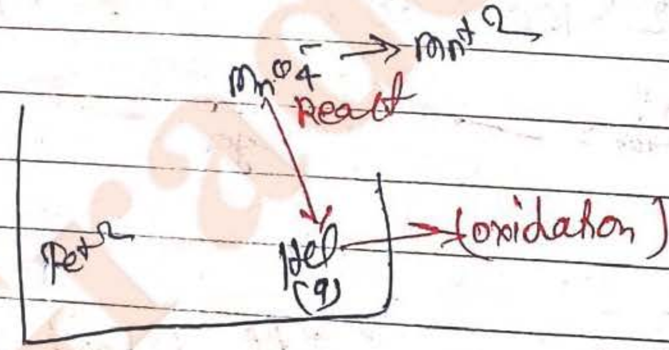
Q. 24 / Q.NO → 2

$Li^+_{(aq)} > Na^+_{(aq)} > K^+_{(aq)}$ $\boxed{\text{Size}}$

biggest ... smallest

< < $\boxed{\text{conductance}}$

Q. 4 / Q.NO → 3



$E^\circ_{cell} = SRP_{(C)} - SRP_{(A)}$

$1.51 - 1.4 = +ve$

Q. 4
01/10/10

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2} \log Zn^{+2}/Cu^{+2}$$

$$\cancel{E_1 = E^{\circ}_{cell} - \frac{0.0591}{2} \log Zn^{+2}/Cu^{+2}}$$

$$\cancel{E_1 + 0.05 = E^{\circ}_{cell} - \frac{0.0591}{2} \log Zn^{+2}/0.05}$$

Q. 5

1)

$$2Hg + 2Fe^{+3} \rightleftharpoons Hg_2^{+2} + 2Fe^{+2}$$

10^{-3} 0   0

$10^{-3} \times \frac{5}{100}$ $10^{-3} \times \frac{95}{100} \times \frac{1}{2}$ $10^{-3} \times \frac{95}{100}$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2} \log \frac{[Hg_2^{+2}][Fe^{+2}]^2}{[Fe^{+3}]^2}$$

2)

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

$$R.P = SRP + \frac{0.0591}{2} \log [Cu^{+2}]$$

SRP = 0.34

$$K_{sp}\, Cu(OH)_2 = [Cu^{+2}][OH^-]^2$$

$$10^{-19} = [Cu^{+2}] \quad (1)$$

pH = 14

pOH = 1

$[OH^-] = 1$

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5.) $2Fe^{+3} + 3I^- \rightleftharpoons 2Fe^{+2} + I_3^-$

$E_{cell} > 0$

6) $C_6H_5NO_2 \rightarrow C_6H_5NH_2 + 2H_2O$

v.f = 6

$\frac{W}{E} = \frac{i \times t}{96500} \times \eta$

$\frac{12.3}{mol\ wt/6} = \frac{Q}{96500}$

18) $a \times b \times c$

[Q2 3]

QNo = 10

$Co_2[Fe(CN)_6] \rightarrow 2Co^{+2} + [Fe(CN)_6]^{-4}$

2S S

$K_{sp} = (2S)^2(S) = 4S^3$

$2\lambda_m^\infty Co^{+2} + \lambda_m^\infty Fe(CN)_6^{-4} = \frac{1000 \times (K_{sol} \times K_{H_2O})}{S}$

S = ?

[Q2 3]

QNo = 22

$eq_{NaOH} = eq_{Cu}$

$\frac{wt}{40/1} = \frac{31.75}{63.5/2}$

$wt = 40$

$n = M \times V$

$= 0.6$

$n = 0.6 \times 4$

$= 2.4$

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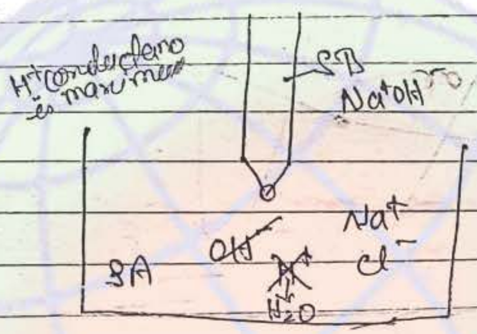
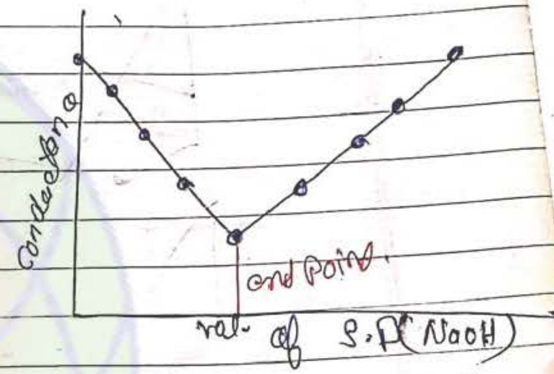
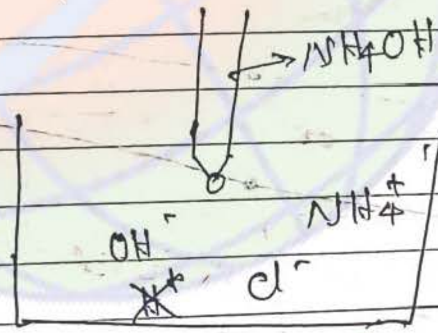
Condometric titration
conductometric

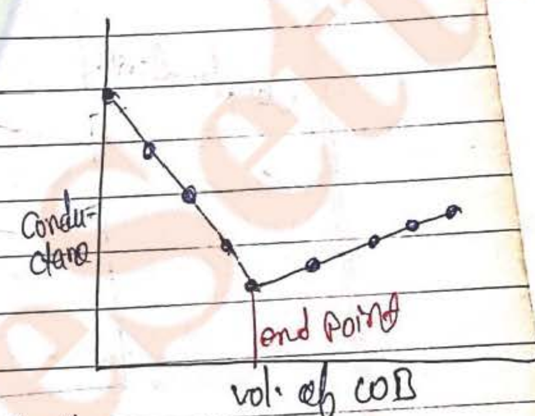
1) SA V/S S.B



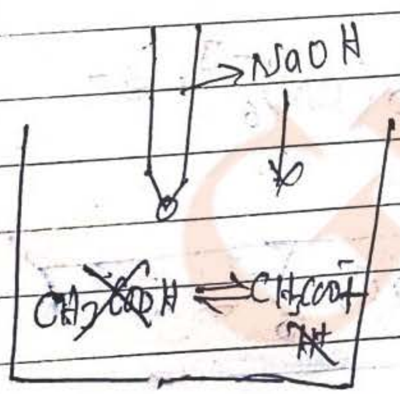


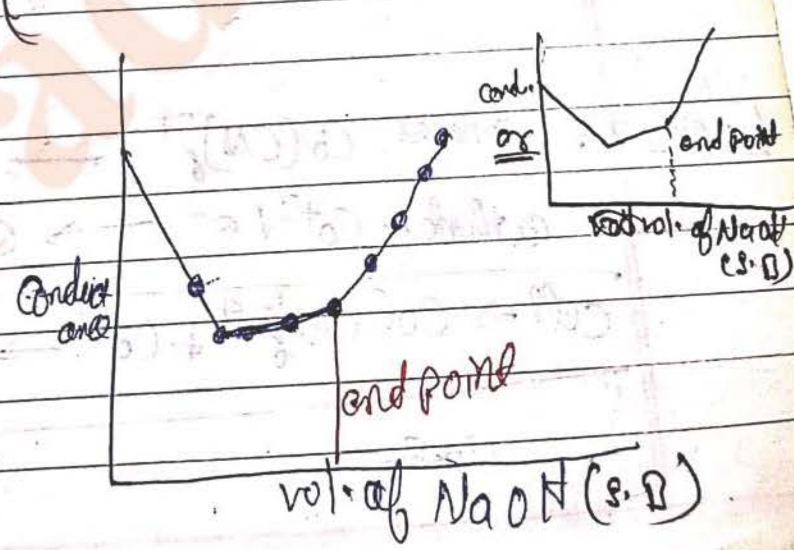
2) SA V/S WB



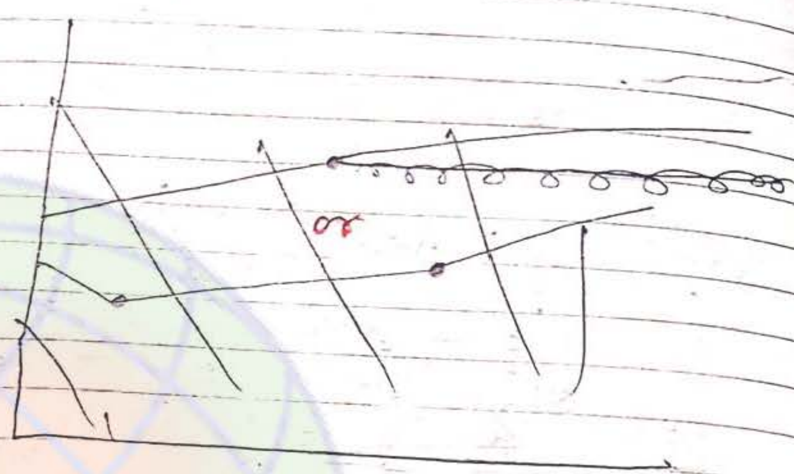


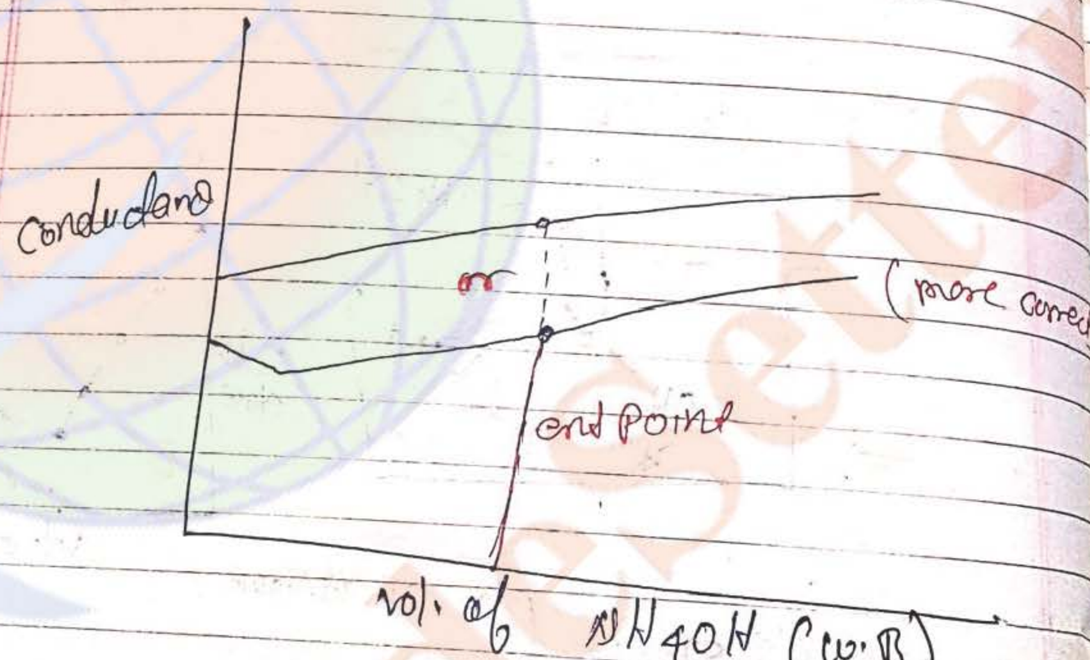
3.) WA V/S S.B (CH_3COOH V/S NaOH)





4.) WA v/s WB





Exp-7
Q No-32

anode: $Co(CN)_6^{-4} \longrightarrow Co(CN)_6^{-3} + e^-$

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

cell: $Co(CN)_6^{-4} + Co^{+3} \longrightarrow Co(CN)_6^{-3} + Co^{+2}$

No

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$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{1}\log\frac{[Co(CN)_6^{-3}][Co^{+2}]}{[Co(CN)_6^{-4}][Co^{+3}]}$$

$\Downarrow$

0

$\frac{K_{f_2}}{K_{f_1}}$ $\Rightarrow$?

$$6CN^- + Co^{+2} \longrightarrow [Co(CN)_6^{-4}]$$

$$K_{f_1} = \frac{[Co(CN)_6^{-4}]}{[CN^-]^6(Co^{+2})} = 10^{19}$$

$$6CN^- + Co^{+3} \longrightarrow [Co(CN)_6^{-3}]$$

$$K_{f_2} = \frac{[Co(CN)_6^{-3}]}{[Co^{+3}][CN^-]^6} = ?$$

Date: / /

$\boxed{\text{Q NO 321}}$

v.f = 1 v.f = 2

$Ag/Ag^+ // Cu^{+2}/Cu$

1 M 1 M

a c

1+x 1-y

$\frac{\omega}{E} = \frac{i \times t}{96500}$

$\text{No. of eq} = \frac{9.65 \times 3600}{96500}$

mole of Ag = No. of eq Ag = x

mole of Cu = No. of eq/2 = y

$\boxed{\text{Q NO 317}}$

H_2O → 4

Cu^{+2} → 3

Hg_2^{+2} → 2

Ag^+ → 1

Mg^{+2}

जब पानी ही खत्म हो जाएगा तभी electrolysis होगी