Class XI

CBSE

Competitive Exams

IIT-JEE Mains
IIT-JEE Advanced
BITSAT

Chemistry

Physical, Organic and Inorganic

Notes

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Date 23 April 09

MOLE CONCEPT

Mole

It is a no.

It is the no. of atoms present in 12g of C^{12} isotope.

Denoted by N_A → Avogadro's Number

6.023×10^{23}

1 atom of C^{12} contains 1.99×10^{-23} g.

1.99×10^{-23} g → 1 atom

12g → $\frac{1}{1.99 \times 10^{-23}} \times 12$.

$= 6.022 \times 10^{23}$.

Atomic Weight (A)

Atomic weight is a relative weight. It represents the relative heaviness of an atom of the element w.r.t. standard wt.

$$\text{At. weight} = \frac{\text{Weight of 1 atom}}{\text{Standard weight}}$$

It has NO UNIT

Standard Weight = $\frac{1}{12}$ times wt. of 1 atom of C^{12} isotope.

Represented by a.m.u.

Date

1.66
1.99 × 10^-23
12 × 100

1 amu = 1.66 × 10^-24 is the standard weight.

$N_A \times C^{12} = 12g$,

1 atom of $C^{12} = \frac{12}{N_A}$.

Now,

1 amu $= \frac{12}{N_A \times 12}$

$= \frac{1}{N_A} = 1.66 \times 10^{-24} g$.

$A = \frac{\text{Wt. of 1 atom}}{1/12 \text{ wt. of an atom of } C^{12}}$

Q. On a non-conventional scale, 1 amu is defined as $\frac{1}{8}$ part by weight of an atom of C^{12}. Determine at. wt. of Al. if its at. wt. on conventional scale is 27.

$A_1 = \frac{w}{1/12\, w_C} = \frac{12w}{w_C} = 27$

$A_2 = \frac{8w}{w_C}$

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$\frac{3 \cancel{12}0}{\cancel{w_c}} = \frac{27}{A_2}$

$\frac{\cancel{2}\cancel{8}0}{\cancel{w_c}}$

$\Rightarrow \Rightarrow 18 = A_2$

★ $1\,amu = \frac{1}{N_A} g$

$amu \times N_A = 1g$

$Al = 27\,amu$

$= 27 \times \left(\frac{1}{12} w^c\right)$ amu

$= \cancel{27}^{9} \times \left(\frac{\cancel{2}\cancel{8}}{\cancel{12}\cancel{0}_{4}}\right)\left(\frac{1}{8}\right) w^c$

$= 18\,amu$

Q. At. wt. of Fe is 56 amu
On a non-conventional scale, At. wt. of Fe = 84
Determine how amu is defined.

$\frac{A_1}{A_2} = \frac{56}{84}$

$\frac{A_1}{A_2} = \frac{56}{84} \times \frac{1}{12} w^c$

$A_2 = 84$

$= \frac{w}{\frac{1}{12} w^c} \cdot \frac{w}{\frac{1}{x} w^c}$

$= \frac{56}{84} = \frac{12}{x}$

$\Rightarrow \frac{56}{84} = \frac{12}{x}$

$\Rightarrow x = \frac{12 \times 84}{56} = 18$

$1\,amu = \frac{1}{x} w^c$

$A = \frac{w}{\frac{1}{12} w^c} = \frac{12w}{w^c}$

$A' = \frac{w}{\frac{1}{x} w^c} = \frac{xw}{w^c}$

Date

☆ GRAM ATOMIC WEIGHT OR MOLAR MASS

It is the weight of N_A (1 mole) of atoms expressed in gram unit.

K A = 39.

39 = wt. of 1 atom of K / amu.

⇒ wt. of 1 atom = 39 amu.

⇒ N_A × wt. of 1 atom = 39 amu × N_A

= 39 g.

Atomic wt	GAW
Relative wt	Absolute/Exact weight

Q. Gram At. W. of Mg = 24 g. If a mole is defined differently as 4×10^{24}

$N_A = 4 \times 10^{24}$.

Determine GAW of Mg on new definition of mole.

~~24~~ = Mg = 24 amu × N_A

= $24 \times 1.66 \times 10^{-24} \times 4 \times 10^{24}$

= $24 \times \frac{160}{100} \times 4$

= 25

6.023×10^{23} atoms of Mg = 24g

$4 \times 10^{24} = \frac{24 \times 4 \times 10^{24}}{6.023 \times 10^{23}}$

$= \frac{24 \times 4 \times 10^{}}{6023}$

$= \frac{960000}{6023}$

$= 160$

Q. GAW of Ca = 40g

On a new scale, 1 mole is redefined and GAW on this new scale is found to be 240 g.

$40 \longrightarrow 6.023 \times 10^{23}$

$240 \rightarrow \frac{6.023 \times 10^{23} \times 240}{40}$

$= 36.6138 \times 10^{23}$

$= 3.6138 \times 10^{24}$

★ AVERAGE ATOMIC WEIGHT

Denoted by $\bar{A}$

$$\bar{A} = \frac{x A_1 + A_2 (100 - x)}{100}$$

Q. Fe has 3 isotopes → Fe^{54}, Fe^{56}, Fe^{57} and their relative abundance are 5%, 90%, 5% resp. Assuming mass of a proton and neutron to be equal, 1 amu each, determine A of Fe.

$$\frac{(54)5 + (56)90 + (57)5}{100}$$

$$= \frac{270 + 5040 + 285}{100}$$

$$= \frac{5595}{100}$$

$$= 55.95\ g.$$

5040
285
+ 270
5595

☆ Molecular Weight / Gram Molecular Weight.

Molecular weight is a relative weight and it is the relative heaviness of a molecule wrt standard wt.

Denoted by = A

$$A = \frac{\text{wt. of 1 molecule}}{\text{amu wt.}}$$

144
22
+176
342

Numerically
A (mol. wt.) = $\sum$ At. wt. of all atoms present in the molecule.

No. of moles = $\frac{\text{Weight}}{\text{Molar mass}}$
(n)

Date

Gram Molecular Weight is the wt. of N_A of molecules expressed in gram unit.

$CuSO_4 \cdot 5H_2O$

At.
Cu = 63.5
S → 32
O → 16
H → 1

= 249.5 g → 6.023×10^{23}

@ 12.067 4

20 → $\frac{6.023 \times 10^{23} \times 20 \times 10}{2495}$

$= 48.28 \times 10^{24}$

Q. Determine no. of atoms present in 8g of H_2O.

18g → $\frac{6.022 \times 10^{23} \times 8 \times 4}{18 \times 9}$

$= \frac{24.088}{9} \times 10^{23}$

$= 2.67 \times 10^{23}$.

$\frac{6 \times 10^{23} \times 4}{9 \times 3}$

$= \frac{8}{3} \times 10^{23}$

$= 2.66 \times 10^{23}$.

$= 8.01 \times 10^{23}$.

Date 26 April

(M)
Molar Mass is a generalised term for a gram. It is mass of N_A of particles which can be expressed as atom/molecule/ion.

Q. 5g of an element 'X' whose (M = 40) contains 4m atoms of X.
8g of other element 'Y' has 4m atoms
Determine molar mass of Y.

~~40 ——— 6.023×10^{23}~~

5g of X → 4m atoms.

40g → $\frac{4}{5} \times 40 = 32m$ atoms.

~~$32m = 6.023 \times 10^{23}$ atoms~~

4m atoms of Y = 8g.

32g → $\frac{8}{4} \times 32$

= 64g.

Q. ~~Q~~ Q. A metal sulphide has molecular formula MS_2 and it contains 40% Sulphur by weight. Determine molar mass of Metal.
M ≡ of S = 32g.

$1\,\text{Å} = 10^{-10}\,m$ Å → Angstrom → Used for smaller scale.

40% → 64

1 → 64 × 100 / 40

60% = 32 × 100 × 360 / 48 × 100

= 2

= 192 g.

Total Molar mass = M + 64.

40 g S in 100 g compound.

64 g S in $\frac{100}{40} \times 64$ g compound.

So, mass of 1 mole of compound = 160 g.

So, mass of metal = 96 g.

Q. Plant virus uniform & cylindrical in shape and its length is 5000 Å. Diameter of the virus is 150 Å & its specific volume of virus is $0.75\,g\,cm^{-3}\,g^{-1}$. Determine molar mass of the virus.

$\frac{22}{7} \times 3.14 \times (75)^2 \times 10^{-10} \times 5000$

$= 2766.250 \times 5000$

$= 13831250\,Å^3$

Volume of cylinder =

$$\pi \times 3.14 \times \left(\frac{150}{2} \times 10^{-8}\right)^2 \times \left(5 \times 10^{-5}\right)$$

$$= 3.14 \times (75)^2 \times 5 \times (10^{-21}) \text{ cm}^3$$

$$0.75 \text{ cm}^3 = 1 \text{ g}$$

$$1 \text{ cm}^3 = \frac{1}{0.75} \text{ g}$$

$$\text{Mass} = \frac{3.14 \times (75)^2 \times 5 \times (10^{-19})}{0.75}$$

Mass of 1 virus $= 3.14 \times 75 \times 5 \times 10^{-19}$

Molar mass of Virus $= 3.14 \times 75 \times 5 \times 6 \times 10^{4}$

$= 314 \times 375 \times 6 \times 10^{2}$

$= 7 \times 10^{7}$ g/mol

Q. HB contains Fe as the only metal and rest are non-metals. If it contains .072% iron by weight, determine minimum molar mass possible for HB if molar mass of Fe = 56 g/mol

$\frac{\text{wt.}}{\text{Molar mass}} = \text{no. of moles}$

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100 g ← 0.072 g Fe.

1 g → $\frac{100}{0.072}$

56 g → $\frac{100 \times 56 \times 1000}{72}$

$= \frac{7}{9} \times 10^5$ g.

$= 7.7 \times 10^4$

Mass of 1 Mole Hb = M

$M \times \frac{0.072}{100} = 56$

$\Rightarrow M = 7.7 \times 10^4$.

Q. A protein molecule contain Fe and Mg in equal weight ratio and the protein is 0.04% in metal by wt. if M of Fe = 56g, Mg → 24g. Determine min. M of protein.

Protein

Molar mass of metal = M.

$\left(\frac{50}{100}\right) 56 + \frac{50}{100} \times 24 = M$

$= 28 + 12 = M$

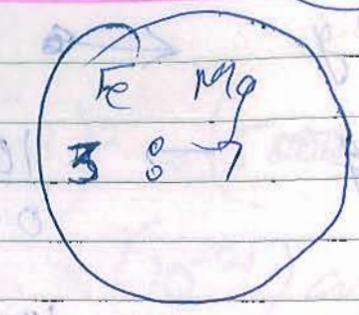
$= 40 = \text{Molar mass of protein}$.

$$n = \frac{\text{No. of atoms } (N)}{N_A}$$

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$$\frac{W}{M} = n.$$

Given



$$\frac{W_{Fe}}{W_{Mg}} = \frac{1}{1}$$

$$\Rightarrow \frac{n_{Fe}}{n_{Mg}} = \frac{1}{56} \times \frac{24}{1} = \frac{3}{7}$$

1 mole of protein $\rightarrow 168 \times 2\ g = 336\ g$ metal.

Molar mass of ~~protein~~ protein ~~metal~~ = M

$$M \times \frac{0.4}{100} = 336$$

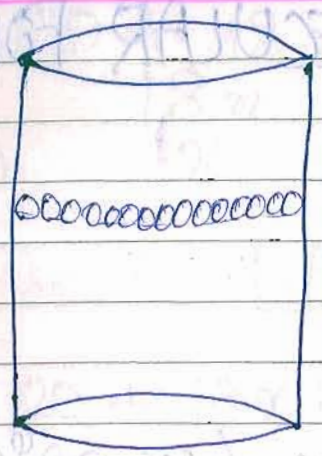
$$\Rightarrow M = \frac{336 \times 100}{0.4}$$

$$= 84000.$$

Q.1. 1 drop of an oily polymer with molecules spherical in shape is spilled in a bucket full of water. Polymer spread on the surface forming exactly monolayer of molecules covering the entire surface. Bucket is cylindrical with $r = 50$ cm and diameter of polymer molecule is $\sqrt{\pi}$ nm. Density of polymer is $0.6\ g/cm^3$ and 10 drops = 1 ml. Determine molar mass of polymer.

$1 mL = 1 cm^3$; $1 nm = 10^{-9} m$.
$= 10^{-7} cm$.

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SA of polymer $= \frac{2}{3} \pi r^2$

$= \frac{2}{3} \pi 2^2$.

No. of molecules of polymer

$= \frac{\pi \times 2500 \times 3}{2 \times \pi^2}$

Mass of 1 polymer $= 0.1 \times 0.6$
$= 0.006$.

SA of polymer $= (\sqrt{\pi}\, nm)^2$
$= \pi \times 10^{-14} cm^2$

No. of molecules $= \frac{2500\pi}{\pi} \times 10^{14}$

$\frac{6}{100} \times 2500 \times 10^{14}$

$= 25 \times 10^{16}$

$= 2.5 \times 10^{17}$

$2.5 \times 10^{17} \longrightarrow 0.06\ g$

$N_A = \frac{0.06 \times 6 \times 10^{23} \times 10^5}{2.5 \times 10^{17}}$

$= \frac{36 \times 10^5}{25}$

$= 144 \times 10^5$

$= 1.44 \times 10^3\ g$.

325
36
1150
75
000

325
06
150

Date

☆ MOLAR MASS — MOLECULAR FORMULA

64
136

Q. $MgSO_4 \cdot xH_2O$ on heating loses 23% of its weight. Determine formula of the salt, molar mass of Mg = 24
32
64
M of salt = 120

$$MgSO_4 \cdot xH_2O \xrightarrow{\Delta} MgSO_4 + xH_2O$$

$\frac{23}{100} \times 120 + 120 = Total$

$= 27.6 + 120 = Total$

$\Rightarrow Total = 147.6\ g$

23
27.6
120
147.6

100g → 77g + 23g

77g $MgSO_4$ → 100g $MgSO_4 \cdot xH_2O$

120g → $\frac{100}{77} \times 120$

$= \frac{12000}{77}$ 155.6 g

$120 + 18x = 155$

$\Rightarrow 18x = 35$

$\Rightarrow x \simeq 2$

OR

$(120 + 18x)\frac{23}{100} = 18x$

$\Rightarrow x \simeq 2$.

Q. 5g of a hydrated zinc sulphate $ZnSO_4 \cdot xH_2O$, on heating gives 3.2g of $ZnSO_4$. Deduce formula.

$M(Zn) = 65$ g

32

64

161

$161 + 18x = 161 + 18x$

$(161 + 18x)\frac{3.2}{10} = 18x$

$\Rightarrow 161 + 18x = \ldots$

$ZnSO_4 \cdot xH_2O \xrightarrow{\Delta} ZnSO_4 + xH_2O$

161 : 18x — 3.2 — 1.8

3.2 g $ZnSO_4$ = 1.8 g H_2O

161 g = $\frac{18x \times 161}{3.2}$ g H_2O

$= 90$ g.

161
32
322
1483
552

$18x = 90$

$\Rightarrow x = 5$

Q. 5g of a mixture of $CaSO_4 \cdot 5H_2O$ and $MgSO_4 \cdot 7H_2O$ on heating give 2.4g of solid residue. Determine composition of original wt. of each.

Ca → 40
Mg → 24

	40	24	120
	32	32	84
	64	64	84
$CaSO_4$ →	136	$MgSO_4$ → 120	1
	120		
$CaSO_4 \cdot 5H_2O = 226$	256		

226 g $CaSO_4 \cdot 5H_2O$ → $CaSO_4$ + $5H_2O$

x gm

246 $MgSO_4 \cdot 7H_2O$ → $MgSO_4$ + $7H_2O$

(5 − x) gm

226 g → 136

1 g → $\frac{136}{226}$

x → $\frac{136 \times x}{226}$

$= \frac{68x}{113}$

$$(5-x) = \frac{60}{120} \times (5+x)$$

$$= \frac{60}{123} \frac{20}{41} (5-x)$$

$$= \frac{100 - 20x}{41}$$

$$= \frac{2788x + 11300 - 2260x}{4633}$$

$$2.4 = \frac{528x + 11300}{4633}$$

$$= 11119.2 - 11300 = 528x$$

$$= 99892$$

Practick Exercise

Q.1 At. wt. of Ca = $\frac{40}{\frac{1}{10 N_A}}$

$= 400 N_a$

$= 400 \times 6.023 \times 10^{23}$

$= 24092 \times 10^{25}$

$= 2.4092 \times 10^{29}$ gram.

$10.01x + 10.1101 - 11.01x = 100$

~~Atm~~ amu = $\frac{1}{10}$ × mass of an atom of C^{12} isotope

Atomic weight =

☆ Emperical Formula and its determination

~~Ef~~ EF is the simplest formula of a compound with elements present in simple whole no. ratio.

eg

	Mol. Formula	Emperical formula	Factor (f)
Benzene	C_6H_6	CH	6
	H_2O_2	HO	2
	CH_4	CH_4	1
	$C_6H_{12}O_6$	CH_2O	6

(EFW) Emperical formula Weight : Σ of At. Wt. of elements.

(MW) Molecular wt. = f × EFW.

☆ EF Determination

	A	B	X	Y	
wt. or % wt.	W_A	W_B	W_X	W_Y	
n (mole)	n_A	n_B	n_X	n_Y	$\frac{W}{M}$
Simple ratio	1	n_B/n_A	n_X/n_A	n_Y/n_A	Let n_A is smallest

Application of EF

Q. A compound of N has EF → NX_3 and it contains 40% N by weight. Determine At. wt. of X.

N	X
40	60.
2.85 = 3	

$$\frac{14}{40} = \frac{14 + 3M_x}{100}$$

$$\Rightarrow M_x = 7.$$

N	X
40	60
n $\frac{40}{14} = 3$	$\frac{60}{X}$
SR. 1	$\frac{60}{X} \times \frac{14}{40} = 3$

$$\Rightarrow x = 7$$

Q An oxide of Titanium, EF → TiO_2 on heating converts into another oxide Ti_xO_y evolving $O_2(g)$

$$TiO_2 \xrightarrow{\Delta} Ti_xO_y(s) + O_2(g)$$

and 10% wt. loss is observed. At. wt. of Ti is 48. Determine EF of the product oxide.

$$\frac{10}{100}(80) = O_2$$

$$8g \rightarrow O_2$$

Date

$TiO_2 \xrightarrow{\Delta} Ti_xO_y(s) + O_2(g)$

$48+32=80$

60g Ti

30g O

80 → 48g Ti

100 → 12+48 ×5

= 60g

	Ti	O
	60	30
	1.25 = 1	1.8 ≈ 2
SR.	1	$\frac{15}{8} \times \frac{12}{15} = \frac{3}{2}$
	= 2	= 3

$= Ti_2O_3$

15	
60	
48	
+2	
1.25	
30	
16	
1.8	

Q. 4g of an organic compound on complete combustion produces 8.8g of CO_2 and 4.4g of H_2O. Assuming that the organic compound has C, H, O as the only elements, determine EF of the original compound.

$C_xH_y \xrightarrow{+O_2} CO_2 + H_2O$

8.8g CO_2 → 12g C

CO_2 → 32+12 = 44.

8.8g

$C_xH_yO_z + O_2 \longrightarrow CO_2 + H_2O$

$12+32=44$ $\quad 2+16=18$

$44g\ CO_2 \rightarrow 12g\ C.$

$8.8g\ CO_2 \rightarrow \frac{12}{44} \times \frac{88}{10} = 2.4g\ C.$

$18g\ H_2O \rightarrow 2g\ H.$

$4.4g\ H_2O \rightarrow \frac{2}{18} \times \frac{44}{10} 4.8 = 0.48g\ H.$

$O_2 \rightarrow 1.12g.$

$\frac{0.2 \times 1600}{1120}$

$2.40 + .48 = 2.88$

EF

C	H	O
2.4	0.48	1.12
0.2	1	0.07
		1600
		100
3	7	1

$= C_3H_7O$

Q. A complex compound of Fe has EF → $Fe_x(CO)_y$

The compound on heating in O_2 gives equal wt. of CO_2. Rxn to occur acc. to the following eqn.

At. of Fe → 56

$Fe_x(CO)_y + O_2 \rightarrow CO_2 + Fe_2O_3$

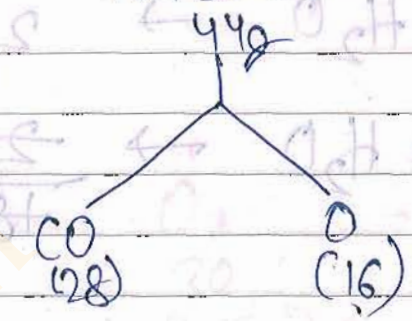
$12+32=44$ $112+48=160$

$\xleftarrow{44g}$

112
48
160

$CO \rightarrow 28g$

$Fe \rightarrow 112g$



Fe | CO

16 8 4 2 | 28 1

56 28 14 7 | 28

= 2 | 7

Fe_2CO_7

Q. 10g of a sample containing $CaCO_3$ and some non-volatile, inert impurity on heating gives 6g of solid ∈ residue. Determine %age pur of the original sample.

$10g\left[CaCO_3 + Imp\right) \xrightarrow{\Delta} \underbrace{CaO(s) + Imp.}_{6g} + CO_2(g)$

4g

Date

44g CO_2 ⟷ 100g $CaCO_3$.

4g CO_2 ⟷ $\frac{100}{44} \times 4$

$= 9.09$ g $CaCO_3$.

Impurity ↔ 0.1 g

10 → 9.09

100 → 90.9%

% age purity = 90.9%

Q. 10g of sample of $CaCO_3$ and volatile impurity on heating decomposes acc. to following Rxn.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

and produces 5g of solid residue. Determine % age purity.

56g ⟷ 100

5 → $\frac{100}{56} \times 5$.

$= \frac{125}{14}$ 8.92

= 8.92g.

8.92g → 10g $CaCO_3$

89.2% CaO → 100g $CaCO_3$.

% age = 89.2%.

40
16
14
28
112
14
89
126

Q. 10g of a mixture containing $CaCO_3$ and $MgCO_3$ on heating decomposes completely giving 5g of solid ~~residue~~ metal oxides. determine mass % of each carbonate in the mixture.

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$100 \qquad 56 \qquad 44$$
$$x\,g \qquad y\,g$$

$$MgCO_3 \longrightarrow MgO + CO_2$$
$$84 \qquad 40$$
$$(10-x)g \qquad (5-y)g$$

$100\,g\ CaCO_3 \longrightarrow 56\ CaO$

$x \longrightarrow \frac{56}{100}x = \frac{14}{25}x$

$84 \longrightarrow 40$

$10-x \longrightarrow \frac{40}{84}(10-x) = \frac{10}{21}(10-x)\,g\ CaO$

$$\frac{14}{25}x + \frac{10}{21}(10-x) = 5$$

$$\Rightarrow \frac{14}{25}x + \frac{100-10x}{21} = 5$$

$$\frac{294x + 2500 - 250x}{525} = 5$$

$$\Rightarrow 44x + 2500 = 2625$$

$$\Rightarrow 44x = 125$$

$\Rightarrow x = \frac{125}{44} \times 2.84$

$\Rightarrow x = 2.84\,g \rightarrow CaCO_3$.

$10 - x = 7.16\,g \rightarrow MgCO_3$

OR $\leftrightarrow$ Taking Residue

$\frac{44x}{100}\,g\ CO_2 + \frac{44(10-x)}{84}\,g\ CO_2 = 5$.

$= 44\left(\frac{x}{100} + \frac{10-x}{84}\right) = 5$.

$\Rightarrow x = 2.8\,g$

Mass % of $CaCO_3 \rightarrow \frac{2.8}{10} \times 100 = 28\%$ and $MgCO_3 \rightarrow 72\%$.

Q. A sample of clay contains Silica (SiO_2), 12% H_2O and some other N.V, inert impurity. On heating, dehydrates partially and a new sample containing 5% H_2O and 50% SiO_2. Determine mass % of Silica in the original sample.

$SiO_2 \not\rightarrow H_2O \rightarrow$

Suppose 100 g of sample.

So, H_2O (12 g) $\xrightarrow{\Delta}$ 5 g % H_2O

$x\,g \rightarrow SiO_2$ $\xrightarrow{\Delta}$ 50 % SiO_2

$(88 - 7x)\,g \rightarrow$ Imp. $\xrightarrow{\Delta}$ 45 % Imp.

Since The ratio of SiO_2 and Impurity will remain constant -

$$\frac{x}{88-x} = \frac{50}{45} \quad \frac{10}{9}$$

$$\Rightarrow x = \frac{880 - 10x}{9}$$

$$\Rightarrow 9x = 880 - 10x$$

$$\Rightarrow 19x = 880$$

$$\Rightarrow x = \frac{880}{19} = 46.3$$

$$\Rightarrow x = 46.3\%.$$

19 | 880 | 46.3
76

119
114

60
57

3

Q. 10g of a sample containing $CaCO_3$, SiO_2 and some water on heating loses 3.9g of its wt. If all $CaCO_3$ is decomposed during heating and water is removed partially, the residue was found to contain 20% silica and 4% H_2O Determine % age composition of original sample.

$$CaCO_3 \rightarrow CaO + CO_2$$

100 56 44

Wt. of product = 10 - 3.9

= 6.1 g

20% SiO_2 = 1.22 g

4% H_2O = 0.244 g

76% $CaCO_3$ = 4.636 g

Eqn →

$$CaCO_3 + SiO_2 + H_2O \xrightarrow{\Delta} CaO + CO_2 + SiO_2 + H_2O$$

NAME

Date

$\frac{16.6}{100} \times 228$

$= \frac{1100.20}{35.50} \rightarrow Cl.$

3 99

$n_{Cl.} = 4.$

$MCl_3 \rightarrow (1)$

$M \rightarrow$ ~~146~~

$= 121.5$

$\frac{2.88}{392} \times 14.3$

24
+5
29
02
58
+16
74

10g

$CaCO_3 \rightarrow 8.2 \rightarrow 82\%$

$SiO_2 \rightarrow 1.22g \rightarrow 12.2\%$

$H_2O \rightarrow 0.58g \rightarrow 5.8\%$

$\xrightarrow{\Delta}$ CaO 20% SiO_2 4% H_2O $\quad CO_2 \uparrow \; H_2O \uparrow$

$CaCO_3 \rightarrow CaO + CO_2$

4.6g.

56 → 100

4.6 → $\frac{100}{56} \times \frac{46}{10}$ = 8.2g $CaCO_3$

105
106
630
103
288
+104
392
110
4
4355
09
3195
2355
04
288
−142
146
−106.5
40.10
−8.2
32

1143
1228
0465
1140
13687
2526
1100 20
1065
3520
3195
3250

1355
03
1065

8.2
+1.22
9.462
58.

Date 3 May

☆ Calculations based on CHEMICAL EQN.

Based on ↓

Laws of Chemical Combination

Law of Indestructivity of Matter OR Conservation of Mass.

☆ Imp Law of Definite (Constant) Proportion

$1\,H_2 + (\tfrac{1}{2})\,O_2 \rightarrow 1\,H_2O$

Stoichiometric Coefficients

$H_2 + \tfrac{1}{2}O_2 \rightarrow 1\,H_2O$

n : 1 : ½ : 1

m : 2g : 16g : 18g

1 : 8

☆ Elements combine in a fixed mass ratio in a given chemical eqn. irrespective of supplied mass ratio

☆ Reactant which is less than its stoichiometric requirement is called Limiting Reagent

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* Limiting Reagent is that reactant which is less than the stoichiometric requirement. In a chemical rxn, limiting reagent is consumed 1st and determines the amount of product.

eg $3H_2 + N_2 \longrightarrow 2NH_3$

n : 3 1 2

m : 6 28

Ratio : = 3g : 14g $\longrightarrow$ 17g NH_3

Supplied mass : 5g & 5g $\longrightarrow \frac{17}{14} \times 5 = 6.07g$ (Unitary Method)

(L.R) (E.R)

5/3 Limiting R. $\rightarrow N_2$

Excess R. $\rightarrow H_2$

1.6 How much $\rightarrow$ ~~EG~~ 2

$N_2 \rightarrow$ L.R $\rightarrow$ mass $\rightarrow$ 5g

$NH_3 \rightarrow$ mass $\rightarrow$ 6.07g

$H_2 \rightarrow$ mass $\rightarrow$ 10 - 6.07 = 3.93 g

10.00
- 6.07
3.93

CALCULATIONS BASED ON MASS-MASS RELATIONSHIP

Q. Determine the mass of Chloroethane (C_2H_5Cl) produced by Rxn of 2g of Ethane with 4g of Cl. acc. to the following $\longrightarrow$

$C_2H_6 + Cl_2 \longrightarrow C_2H_5Cl + HCl$.

2g 4g

168 → 44

25 ↔ $\frac{44 \times 25}{168}$

$= \frac{1100}{168}$

44g CO_2 → 100 $CaCO_3$

$\frac{44 \times 25}{168}$ CO_2 → $\frac{100}{44} \times \frac{44 \times 25}{168}$

$= \frac{2500}{168}$ 14.8g

$= 14.8g$

OR

$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$

1 1 1 2

$\frac{25}{84 \times 2}$ mol 25g of $NaHCO_3$

$= \frac{25}{84}$ mol.

$CaCO_3 \longrightarrow CO_2 + CaO$

1 1

Moles of CO_2 = Moles of $CaCO_3$

So, moles of $CaCO_3 = \frac{25}{84 \times 2}$

Mass of $CaCO_3 = \frac{25}{168} \times 100$

$= 14.8g$.

1044
025
1100
168
668
1176
14
1-258
-168
820
16
168
84
2

Q. Determine the mass of Fe metal which must be dissolved in excess of dil. H_2SO_4 to produce sufficient H_2 required for complete exn. with 8g of O_2 gas producing H_2O.

Fe → 56 g.

32
64
+2
98

$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$
56 98 ~~1g~~ 2

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
1g 8g

2 ⟶ 56
1 ⟶ $\frac{56}{2} = 28g$

OR

$OH_2 + \frac{1}{2}O_2 \rightarrow H_2O$.
0.50 mol $8g = \frac{8}{32} = 0.25 mol$.

$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$
0.5 mol. 0.5 mol

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

$\Rightarrow m = 0.5 \times 56$
$= 28g$.

$P_4 + 6\,3O_2 \longrightarrow \underset{220}{P_4O_6}$ x g

$P_4 + 5O_2 \longrightarrow \underset{284}{P_4O_{10}}$ $(4-x)$ g

0 4g

220 g P_4O_6 → 124 g P_4

x g P_4O_6 → $\frac{124}{220} \times x$ g P_4

$\frac{31}{55}$ g P_4

$(4-x)$ g P_4O_{10} → $\frac{124}{284}(4-x)$ g

$= \frac{31}{71}(4-x)$ g

$\frac{31}{55}x + \frac{31}{71}(4-x) = 2$

$\Rightarrow 31\left(\frac{x}{55} + \frac{4-x}{71}\right) = 2$

$31\left(\frac{71x + 220 - 55x}{3905}\right) = 2$

$\frac{31}{62}\cdot\frac{16x + 220}{3905} = \frac{2}{31}$

$\Rightarrow 8x + 110 = \frac{3905}{31}$

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=) $x = \left(\frac{3905}{31}\right) - 110$ $\quad (x = 1.8)$

$$= \frac{125.9 - 110}{8}$$

$$= \frac{15.9}{10} \quad 1.9$$

$$= 1.9\,g$$

125.9
−110.0
15.9

13.54
+.46
4.00

OR

2
124

96 62 31

1.54g

124 → 96
2 → 96/124 × 2

3.54g

P_4 L.R. + $3O_2$ → P_4O_6

O_2 left

consumed fully

220
64

P_4O_6 + $2O_2$ → P_4O_{10}

3.54 0.46g 4g

(2 − 1.54)

64 → 220

1.54 → 2.2

$64\ O_2 \longrightarrow 220\,g\ P_4O_6$

$0.46 \rightarrow \frac{220}{64} \times \frac{46}{100}$

32. 23

506 16

320 ×10

$= 1.58\,g\ P_4O_6$

$3.54 - 1.58g = 1.96g$ → mass of P_4O_6 left

Mass of $P_4O_{10} = 4 - 1.96 = 2.04\,g$.

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Q. 5g of each C, H and F, are mixed together when following rxn. takes place.

$$2C + 2H_2 + F_2 \longrightarrow C_2H_4F_2$$

F = 19

24 4 38 66g

Determine the max. mass of product which can be obtained in the rxn.

n: 2 + 2 + 1 → 1

m: 24 4 38 → 66

Supplied mass: 5 5 5

$\frac{38}{19} \times 5 = \frac{165}{19} = 8.6\,g$

Q. Determine the mass of Zn metal which must be reacted with excess of dil H_2SO_4 to produce sufficient H_2 gas required for complete rxn. of O_2 gas produced from complete decomposition of 20g of $KClO_3$ acc. to the following rxn.

Zn = 65
K = 39
Cl → 35.5

$$KClO_3 \longrightarrow KCl + \frac{3}{2}O_2$$

122.5 74 48

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

65 98 161

$\frac{3}{2} \times 32$ 16 64 165

122.5 ——— 48

20 → 48 × 200 / 1225 = 48 × 8 / 49

= 48 × 8 / 49 g.

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

2 — 16 — 18

20 ——— 16 ⟶ 2

48 × 8 / 49 → 2 × 48 × 8 / 49

= 48 / 49 g.

2 ⟶ 65.

48 / 49 → 65 × 48 × 24 / 49 × 2

= 1560 / 49

= 32 (approx.)

265
24
260
130×
560
49
032
98
1478
1568

HYDROLYSED, HYDROLYSIS → reaction with H_2O ★★★

Date

OR

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$\frac{1}{3} KClO_3 \longrightarrow \frac{1}{3} KCl + \frac{1}{2} O_2$$

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$$

$\frac{1}{3}$ mol. of $KClO_3$ ≡ 1 mole of zinc.
122.5

★★ $\frac{20}{122.5}$ mol.

1 mol. of $KClO_3$ ⇒ 3 mol. of Zn.

$\frac{20}{122.5}$ mol. $KClO_3$ = $\frac{3 \times 20}{122.5}$

Mass of Zn = $\frac{3 \times 20 \times 65 \times 2}{225}$

$\frac{245}{45}$

3

= $\frac{104}{3}$ 31.6 g.

★ Check

39, 8, 37, 53, 74

213
104

~~C_3H_4~~

Date 10 May 09

Q. Determine the mass of CaC_2 (Calcium Carbide) which must be HYDROLYSED to produce sufficient Acetylene gas req. for producing 1 Kg of Polyethylene.

$$\underset{\frac{1000}{28}}{CaC_2} + 2H_2O \longrightarrow \underset{\text{Ethyne}\ \frac{1000}{28}}{C_2H_2} + Ca(OH)_2$$

$$\underset{\frac{1000}{28}}{C_2H_2} + H_2 \longrightarrow \underset{\text{Ethene}}{C_2H_4}$$

$$n\,C_2H_4 \longrightarrow \underset{\text{Polyethylene}\ 1\,Kg}{-(CH_2-CH_2)_n-}$$

$\frac{1000}{28}$ g mol

$$\frac{1000}{28} \times 64.16 = 2.285\,Kg$$

Q. Consider the following rxn.

$$CoF_2 + 2F_2 \longrightarrow CoF_6 \quad \Rightarrow n = 10$$

$100\,n \rightarrow M = 1000$

$$4n\,CoF_6 + \underset{\text{P.E}}{-(CH_2-CH_2)_n-} \longrightarrow \underset{\text{Teflon}\ 1000\,g}{-(CF_2-CF_2)_n-} + 4nHF + CoF_4$$

Determine mass of & Fluorine req for preparing 1kg of Teflon.

$CoF_6 \longrightarrow CoF_4 + 2F_2$

$\Rightarrow 4n\,CoF_6 \longrightarrow 4n\,CoF_4 + 8n\,F_2$

Since $n = 10$.

$\Rightarrow 40\,CoF_6 + \left(CH_2 - CH_2\right)_n \longrightarrow$

$\underset{1000g}{\left(CF_2 - CF_2\right)_n} + 4n\,HF + 4n\,CoF_4$

$CoF_2 + 2F_2 \longrightarrow 1C_2F_6$

80 mol. 40 mol.

Mass of $F_2 \rightarrow 80 \times 19$

$=$

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⑧ ✱ Mass - Volume Relationship

✱ STRENGTH OF SOLUTION

Amount ~~Mass~~ of solute present in a ~~given~~ unit volume of solution is expressed in the form of strength of solution. Its also called CONCENTRATION OF SOLUTION

Date

5 TYPES

1) %age Strength 2) Molarity (M) 3) Molality (m) 4) PPm Strength 5) Normality (N)

1) Percentage Strength (% Strength): %age strength is the amount of Solute (g unit) present in 100g of solution.

5% NaCl Solution - or - 5% NaCl (w/v) (wt./Vol.)



5g in 100 mL.

or

3% ethanol (v/v)

⇒ 3 mL ethanol in 100 mL of soln.

* 2) MOLARITY (M): It is the no. of moles of solute present in 1 L of solution.

If 'n' mol of solute in V Litre of solution.

So, $M = \frac{n}{V}$

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Q. A glucose soln is 6% in glucose by wt. (w/v).
Determine M of glucose soln.

6g glucose ... 100g soln.

$C_6H_{12}O_6$
$72 + 12 + 96$
180

$\frac{6}{180}$

30

n of Glucose $= \frac{1}{30}$

$M = \frac{1}{30} \div 100\ mL$

$= \frac{1}{30} \times \frac{10}{100}$

$= \frac{1}{300}$

$= \frac{1}{3} = 0.33\ M$

(read as: 0.33 molar)

Q. A NaCl soln contains 5% NaCl by wt. and its density is (1.12 g/mL). Determine molarity of soln.

$23 + 35.5 = 58.5$

58.5 g → 1

1.12 g → 1 mL

1 g → $\frac{5 \times 100}{112}$

$= \frac{500}{112} = 4.4\ mL$

$= 0.0044$

$112 \times 5 = 560$

$448 \times 1 = 448$

$560 - 448 = 112$

~~50~~ 0.08
~~58.5~~

~~0.08~~ 0.
~~4.40~~

$\frac{0.08}{.004 \times 4} = \frac{800}{44}$

OR

1 Lit. soln = 1120g

mass of NaCl = $1120 \times \frac{5}{100} = 56g$

$n(NaCl) = \frac{56}{58.5}$

$= 0.95\ M$

Q. An aq. soln of H_2SO_4 has density of 1.32 g/ml. It contains 30% H_2SO_4 by wt. Determine molarity of soln.

$1320 \times \frac{30}{100} = \frac{396}{98}$ 4.04 M

$= 4M$ (approx.)

$M = \frac{n}{V}$

$T = 27°C$

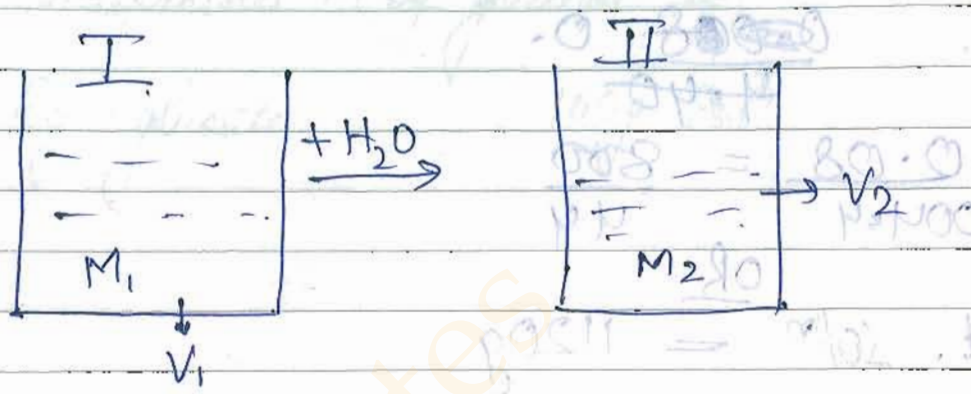
1 L. NaCl.

2 M

⇔ Temp. affects Molarity

Date

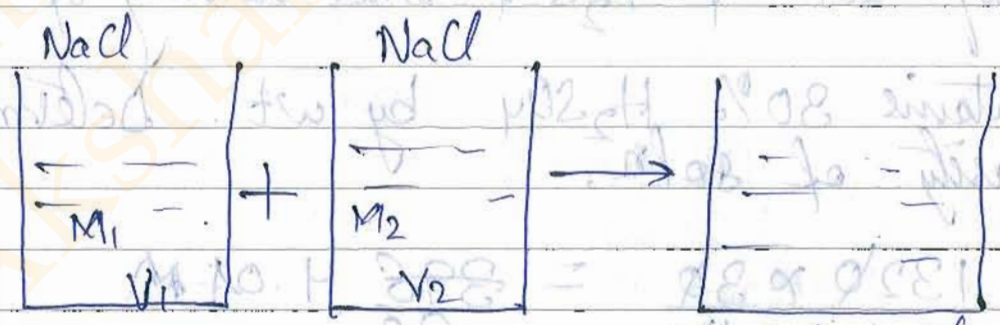
☆ DILUTION LAW



$n = M_1V_1$ $\quad n = M_2V_2$

$\Rightarrow M_1V_1 = M_2V_2$

☆ MIXING LAW.



$n_1 = M_1V_1$ $\quad n_2 = M_2V_2$

$V_1 + V_2 = V_3$

$n_3 = M_1V_1 + M_2V_2$

$$M_3 = \frac{M_1V_1 + M_2V_2}{V_3}$$

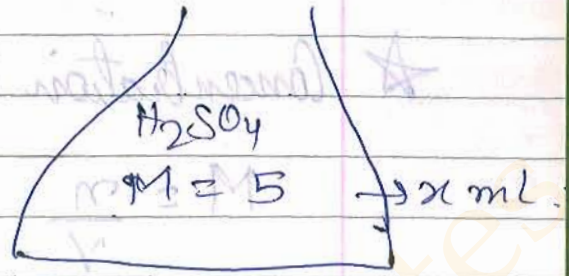
$M_3V_3 = M_1V_1 + M_2V_2$

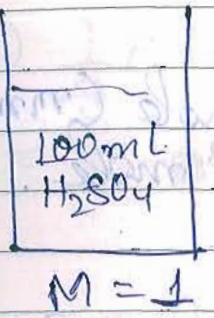
So $MV = \sum_{i=1}^{n} M_iV_i$

Q. What volume of a 5 molar H_2SO_4 soln must be added to a 100 mL 1M H_2SO_4 soln in order to obtain a 2 M H_2SO_4 soln.

$M_3V_3 = M_1V_1 + M_2V_2$

$2(100+x) = 5x + 100$





$\Rightarrow \frac{5x}{1000} + \frac{100}{1000} = \frac{200+2x}{1000}$

$\Rightarrow x = \frac{100}{3}$ mL.

Q. You have available 2 L, 2 M, H_2SO_4 & 3 L, 5 M H_2SO_4. What max. vol. of 3 M H_2SO_4 can we prepare?

$4x + 15 = 3x$

$\Rightarrow x = 15$

$= 6.3$ L.

$4x + 15 = 5x$

$\Rightarrow x = 15$

$= 3.8$

2L 2M H_2SO_4

3L 5M H_2SO_4 → x L.

$2 \times 2 + 5(x) = 3(2+x)$

$\Rightarrow x = 1$ L.

Total volume = 3 L.

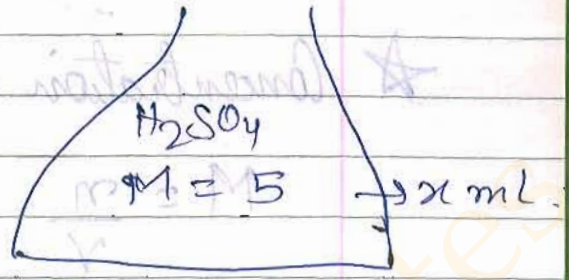
M = 3M.

Date

Q. What volume of a 5 molar H_2SO_4 soln must be added to a 100 ml 1M H_2SO_4 soln in order to obtain a 2 M H_2SO_4 soln.

$M_3V_3 = M_1V_1 + M_2V_2$

$2 \times (100+x) = 5x + 100$



100 ml H_2SO_4	$\Rightarrow \frac{5x}{1000} + \frac{100}{1000} = \frac{200+2x}{1000}$
M = 1	$\Rightarrow x = \frac{100}{3}$ ml.

Q. You have available 2 L, 2 M, H_2SO_4 & 3 L, 5M H_2SO_4. What max. vol. of 3 M H_2SO_4 can we prepare?

$4x + 15 = 3x$	$4x + 15 = 5x$
$\Rightarrow \frac{15}{3} = x$	$\Rightarrow \frac{15}{5} = x$
$= 6.3$ L	3 L

2L 2M H_2SO_4

3L 5M H_2SO_4 → x L

$2 \times 2 + 5(x) = 3(2+x)$

$\Rightarrow x = 1$ L.

Total volume = 3 L.

M = 3M.

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14 May 2009

☆ Concentration : Molarity.

$M = \frac{n}{V}$, $MV = n$

Q. 15 mL, 0.2 M NaCl = 3 millimole (mmol)
Or 3×10^{-3} mole.

Q. $\underset{10\,mL;\,0.1\,M}{BaCl_2} + \underset{20\,mL;\,0.15\,M}{2AgNO_3} \longrightarrow 2AgCl + Ba(NO_3)_2$
1 mmol, 3 mmol

After rxn. 0, 1 mmol, 2 mmol

(i) ~~what max mass of AgCl can be produced?~~
2×10^{-3} mol $\times$ 143.5.
$= 287 \times 10^{-3}$ g.

143.5
$\times 2$
287.0

(ii) Determine molarity of AgCl in remaining Soln?

$V_{final} = 30$ mL.
$n = 1$ mmol.
$M = \frac{1}{30}$ $AgNO_3$.

Q. 10 mL 0.1 M $BaCl_2$ soln is mixed with 30 mL 0.1 M Na_3PO_4 soln. Determine the max. mass of $Ba_3(PO_4)_2$ which can be formed.

At. wt. → Ba → 137
P → 31

CR → $BaCl_2$ 31 + 64 = 95 | 95 × 2 = 190 | 137 + 71 = 208 | 411 | 190 | 601

$3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 6NaCl$

10 mL 0.1 M — 30 mL 0.1 M — $\frac{1}{3}$ mmol.

1 mmol. — 3 mmol.

B

$n \times M = g$.

$\Rightarrow \frac{1}{3} \times 10^{-3} \times$ ~~501 167~~ 601 $\times$ 200.3

$= 0.02$ g.

Q. 2.5 g of a sample containing Na_2CO_3, $NaHCO_3$ & some non-volatile inert impurity on strong heating loses 20% of its weight. The residue is dissolved in water and diluted to 100 mL. 10 mL portion of this stock sol^n required 15 mL 0.1 M $BaCl_2$ sol^n for complete precipitation of carbonates. Determine mass %age of Na_2CO_3 & $NaHCO_3$.

FACT

1) Alkali metal carbonates are stable to heat while alkaline earth metal carbonates are unstable, decomposes on heating to metal oxides & CO_2.

2) All bicarbonates are unstable.

i.e $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$

↳ decomposes to become stable.

$Ca(HCO_3)_2 \longrightarrow CaO + H_2O + 2CO_2$

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$2 \times 84 = 168$ — 8 mmol — 62

Soln. $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$

Na_2CO_3

62 ——— 168.

N.V. of Imp. 0.5 → $84 \times \frac{468}{62} \times \frac{5}{10}$ — $\frac{2.84}{420}$ — 31

20 — 0.5g — 31

10 — 2.5 — 1.3

5

$NaHCO_3 \rightarrow 1.3g$.

→ 10 mL.

100 mL — 15 mmol Na_2CO_3 — Stock solution.

$BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3 \downarrow + 2N$

15 mL 0.1 M. — 1.5 mmol in 10 mL.

62g wt. loss for 1000 mmol Na_2CO_3 formed

0.5g ——— $\frac{1000}{62} \times \frac{0.5}{10} = \frac{250}{31}$

$= 8.06$

$\simeq 8$ mmol.

$\frac{31}{217}$ — 31g

31 g Original Na_2CO_3 → 7 mmol.

$= 7 \times 10^{-3}$ mol. $\times 106 = 0.742$ g.

1.742 — 4 — 2.968

$\frac{1.3}{25} \times \frac{106}{4}$ — $\frac{0.742 \times 100}{25}$

52% → $NaHCO_3$.

29.68% → Na_2CO_3

19% → Imp

Ag → 108 u

(III) 40 + 71 = 111 Due.

35.5 × 2 = 71.0

Q) 1 g sample containing $CaCl_2$ & some inert impurity is dissolved in H_2O & diluted to 100 mL. 10 mL portion of this sol^n on treatment with excess of $AgNO_3$ sol^n produced 0.15 g AgCl (ppt.) Determine mass %age of $CaCl_2$ in the original sample.

35.5 | 5.5 mmol. $CaCl_2 + H_2O$ | 100 mL.

10 mL.

$CaCl_2 + 2AgNO_3 \longrightarrow$

0.55 mmol

$2AgCl \downarrow + Ca(NO_3)_2$

108 + 35.5 = 143.5

0.15 g / 143.5

1.1 mmol.

150 / 1435 × 100

2 → 1

1 ↔ 1/2

1.1 → 1/2 × 11 × 5.5

$M = \frac{n}{V}$

$CaCl_2 = 0.55$ m mol.

$n = \frac{G}{M}$

5.5 — 5.5 × 10^{-3} × 1000 / 111

0.4 = 0.00004

5.5 m mol $CaCl_2$ = 5.5 × 10^{-3} × 111

555 × 10^{-3}

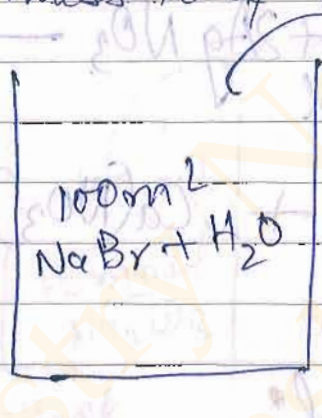
6105 = 0.61 g

= 61%

$Br \rightarrow 80$ $\quad \begin{array}{r} 23 \\ +80 \\ \hline 103 \end{array}$

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Q. 1.5g of a sample containing NaBr & some inert impurity is dissolved in H_2O & diluted to 100 mL. 10 mL portion of this soln is mixed with 15 mL 0.1 M $AgNO_3$ soln (1.5 & AgBr (ppt) is filtered-off. Filterate required 3 mL 0.1 M (0.3 mmol) NaCl soln for ppt. of unreacted $AgNO_3$. Determine mass % of NaBr → original.



100 mL
$NaBr + H_2O$

$NaBr + AgNO_3 \longrightarrow NaNO_3$
1.2 mmol. 1.2 mmol.
$+ AgBr.$

$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl.$
0.3 mmol 0.3 mmol.

$\frac{12 \times 100}{1.5}$ $\quad 12 \times \frac{20}{100}$ $\quad \begin{array}{r} 103 \\ 612 \\ \hline 1236 \end{array}$

$\frac{12360 \times 3}{15}$

$\frac{41.200 \times 2}{1000}$

$82.4\ \%$

Date

★ MOLALITY (m) :- It is the no. of moles of solute present in 1 Kg (1000 g) of solvent.

If w_2 g of solute in w_1 g of solvent.

$\downarrow$

$\frac{w_2}{M_2}$ → n_2

$$m = \left(\frac{w_2}{M_2}\right) \times \frac{1000}{w_1}$$

$$\Rightarrow m = \frac{n_2 \times 1000}{w_1}$$

★ It is temp. independent conc. unit.
★ It is independent ~~on any~~ of any physical parameter.

Q. MOLE FRACTION (x)

$n_1 \rightarrow A$, $n_2 \rightarrow B$.

Mole fraction → A → $\frac{n_1}{n_1 + n_2} = x_1$

Mole fraction of B → $\frac{n_2}{n_1 + n_2} \Rightarrow x_2$



$$\rightarrow x_i = \frac{n_i}{\sum n_i} \quad , \sum x_i = 1$$

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Q. In a water - ethanol mixture, mole fraction of C_2H_5OH is 0.1 Determine m of this ethanol - water sol^n

$$\frac{n_1}{n_1+n_2} = 0.1$$

Let us assume 1 mol of this mixture

So, 0.9 mol $\rightarrow H_2O$

0.1 mol $\rightarrow C_2H_5OH$

$$\frac{0.1}{0.9 \times 18} \times 1000$$

$$= \frac{1000}{162} = 6.1$$

2 | 18
6 | 3 | 162
6 | 6
1 | 2

★ Mole-fraction — Derivation

$$x_2 = \frac{n_2}{n_1+n_2}$$

★ $\Rightarrow \frac{n_1}{n_2} + 1 = \frac{1}{x_2}$

$\Rightarrow \frac{n_1}{n_2} = \frac{1-x_2}{x_2}$

Now,

$$m = \frac{n_2}{w_1} \times 1000$$

$M_1 \rightarrow$ Molar mass of solvent.

$$= \frac{n_2}{n_1} \times \frac{1000}{M_1}$$

$$\Rightarrow m = \left(\frac{x_2}{1-x_2}\right)\left(\frac{1000}{M_1}\right)$$

Date

Q. 50g $CaSO_4 \cdot 5H_2O$ is dissolved in 100g H_2O. Determine molality of resultant.

$226 \longrightarrow 90.$

$50 \longrightarrow \frac{90}{226} \times 50.$

$= \frac{4500}{226} = 19.9$

$H_2O \rightarrow 120.$

$\frac{50}{136} \times \frac{25}{120}$

$66 \quad 63$

$= \frac{625}{198} = 3.15$

OR

$\frac{50}{226} = 0.221$

$CaSO_4 \cdot 5H_2O \longrightarrow CaSO_4 + 5H_2O$

$\frac{50}{226} \qquad \frac{50}{226}$

$m = \frac{50}{226} \times \frac{1000}{120} = 1.8 \text{ molal}$

Date

Q. 50g of $Na_2SO_4 \cdot xH_2O$ is dissolved in 50g H_2O & resulting sol^n has molality 2.25. Determine x.

$$Na_2SO_4 \cdot xH_2O + H_2O \longrightarrow Na_2SO_4 \cdot xH_2O$$
$$50g \qquad 50g \qquad 100g$$

46
32
64
142 + 18x → 142
50 → $\frac{142}{142+18x} \times 50$

$\Rightarrow \frac{142 \times 50}{2(71+9x)}$

$\Rightarrow \frac{3550}{71+9x} \rightarrow Na_2SO_4$

Wt. of water = $\frac{142}{1} - \frac{3550}{71+9x}$

Now $\frac{142(71+9x)-3550}{71+9x}$

2.25 =

50 g $Na_2SO_4 \cdot xH_2O$ 50g H_2O

142 18x

$\frac{50}{142+18x} \longrightarrow 50 + \frac{50 \times 18x}{142+18x}$

$2.25 = \frac{x}{\frac{50}{142+18x}} \times 1000$

$\frac{50+50 \times 18x}{142+18x}$

$\Rightarrow 2.25 = \frac{50}{50(142+18x)+(50\times 18x)} \times 1000$

$\Rightarrow x = 8$ (approx.)

Q. An aq. soln of Na_2SO_4 is 4 molal & its density is 1.15 g/mL. Determine molarity (M) of soln.

$Na_2SO_4 \rightarrow 142$

$1\,L \rightarrow 1150\,g$ soln.

$\Rightarrow Na_2SO_4 = 8.1$ moles.

$4 = \frac{8.1}{x}$

$\Rightarrow x = 2$ g solvent.

$M = \frac{n}{V}$

4 mole solute $\rightarrow$ 1 Kg solvent.

soln
4 mol solute
1000 g solvent

$\frac{1568\,g}{1.15}$ soln. $\frac{15\,g}{1150}$

$M = \frac{n}{V} = \frac{4 \times 1.15 \times 1000}{1568 \times 100}$

$= \frac{1150}{392} = 2.9M$

Q. Density of an aq. soln of ethanol in H_2O is 1.2 g/mL. If Molarity of soln is 4, determine Molality (m) of soln.

Let 4 moles of ethanol

So, 1 L of ~~H_2O~~ solution.

1.2000 g → ~~H_2O~~ solution

1016 ~~1000~~ g → solvent.

$$m = \frac{n}{(\text{wt. of solvent})}$$

$$= \frac{4}{\frac{4000}{1016}\,3.5}$$

$$\Rightarrow m = 3.9 \text{ molal}$$

$$= 4 \text{ molal}$$

☆ PPM STRENGTH.

It is the parts of solute present in millionth part of SOLUTION

eg. 1000 ppm NaCl.

↓

1000 g NaCl in 10^6 g of soln.

eg 2000 ppm (v/v) [Default → w/w i.e if nothing is given]

i.e

2000 mL of solute in 10^6 mL of soln.

eg 3000 ppm of NaOH (w/v)
i.e 3000g NaOH in 10^6 ml of soln.

Q. Concentration of $CaCl_2$ in sea water is 5 ppm i.e $(5 \times 10^{-6}\ M)$. If density of sea water is 1.12 g/mL determine ppm strength of $CaCl_2$ in sea water.

$n = 5 \times 10^{-6}$ M
$\Rightarrow$ 1L of soln $\rightarrow$

$\Rightarrow$ Mass of 1L = 1120g.

555×10^{-6} g $\rightarrow CaCl_2$.

ppm strength $= \frac{5 \times 10^{-6} \times 111 \times 10^6}{1120 \times 10}$

$= \frac{224}{111}$

$= 0.548$ ppm.

40
71
111

2
224
5
1120

☆ When conc. is very small, we express in ppm. so that it becomes significant.

Q. NaCl soln $\rightarrow$ 1000 ppm. S $\rightarrow$ 1.2 g/mL. determine M of soln.

23
35.5
58.5

NaCl $\rightarrow$ 58.5 g.
1L $\rightarrow$ $\frac{1200}{585}$ g

M = 12

$n = \frac{1000}{585}$ NaCl $\rightarrow$ $\frac{10^6}{1.2}$ g Soln. (1.2 g/mL)

$\Rightarrow n = \frac{1000}{585}$ NaCl $\rightarrow$ $\frac{1000}{1.2}$ L.

$$M = \frac{1000}{58.5} \times \frac{1.2}{1000}$$

$$= \frac{12}{585}$$

$$\simeq 0.02\ M.$$

☆ PRECIPITATION R.X.N.

Process

GRAVIMETRY

NaCl (inert imp.) $\xrightarrow{H_2O}$ 100 mL → 10 mL

$NaCl + AgNO_3 \rightarrow \underset{m}{AgCl}\downarrow + NaNO_3$

Add Precipitating agent ☆ ($AgNO_3$ & $BaCl_2$)

☆ Reason for making $AgNO_3$ as PPt. agent.
- all salts of Ag are insoluble in sol^n except $AgNO_3$.

GRAVIMETRY: Process in which we express wt. of —

Q. A 2g sample containing $CaCl_2$ & some inert impurity is dissolved in H_2O & diluted to 100 mL. A 10 mL portion of this sol^n when treated with excess of $AgNO_3$ produced 0.0-2.5 g of ppt. Determine % purity of original sample.

Soln → $CaCl_2$ 100 mL. → 10 mL

$CaCl_2 + 2AgNO_3 \rightarrow 2AgCl + Ca(NO_3)_2$

$\frac{0.025}{143.5 \times 2}$ $\frac{0.025}{143.5}$.

108
35.5
143.5
×2
2870

$\frac{0.25}{287}$ 100 mL.

$\frac{0.25}{287} \div 2 \times \frac{1}{2} \times 100$

1287
×2
574

2

$\frac{25}{287 \times 2} = \frac{25}{574}$

$\frac{0.25 \times 111}{287 \times 2} \times 100$

$= \frac{25 \times 111}{574}$

$= \frac{2775}{574}$ 4.9%

$= 4.9\%$

23
+35.5
58.5

25
×111
25
25×
25××
2775
3594
65
2870

616
2775
2296
4790 2296

25
2574
84.

Q. 2g of a sample containing NaCl and some inert imp. is dissolved in H_2O & diluted to 100 ml A 10 ml portion of this soln required 20 mL 0.1 M $AgNO_3$ soln for complete precipitation. determine % purity of NaCl sample.

NaCl 100mL → 10mL

$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl$.

n = 2 mmol n = 2 mmol n = 2.

2×10^{-3}

585 0.0117 g

$= \frac{1.17\,g}{2\,g} \times 100$

$= 5850 \times 10^{-2}\ \%$

$= 58.5\ \%$

∴ $BaCl_2$

☆ Majority of salts of Ba are water insoluble except $BaCl_2$ & $Ba(NO_3)_2$

☆ All nitrates & ammonium salts are all soluble in water.

$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl.$

Q A 1g, 75% $Al_2(SO_4)_3$ sample is dissolved in H_2O & diluted to 100 mL. Determine volume of 0.02 M $BaCl_2$ sol^n required for complete ppt. of SO_4 from 10 mL of a stock sol^n.

$\frac{0.75\,g}{342} \quad \frac{750}{342}$.

$Al_2(SO_4)_3$ 100 mL —10 ml→

$Al_2(SO_4)_3 + 3BaCl_2 \longrightarrow 3BaSO_4 + 2AlCl_3$

$\frac{750}{342}$ mmol $\quad 0.63$ mmol $\quad \frac{3 \times 750}{342}$ SO_4 mmol.

$3 \times 2 = 1\,SO_4$ mmol.

$= 0.63\ SO_4$ mmol.

2.191 mmol

54 — 32 + 64 = 96 — 3 — 126 + 54 = 342

3

$\frac{.63}{196}$

$0.02 \times V = n.$

$\Rightarrow V = \frac{0.63}{0.02}\ 31.5$

$\Rightarrow V = 31.5$ mL.

Date

☆ PRECIPITATE EXCHANGE RXN.

more soluble than ↑ gCl / gBr

$$NaCl + AgNO_3 \rightarrow \underset{(143.5)}{AgCl\downarrow} + NaNO_3$$
1 mol, excess, 1 mol

$$AgCl(s) + NaBr \rightarrow AgBr(s) + NaCl.$$
excess, 1 mol. (188)

Halide

F^-
Cl^-
Br^-
I^-

↓ Down the groups, solubility decreases

eg

A sample ↓ NaCl, NaBr, inert impurity

$\xrightarrow{AgNO_3}$ excess.

$\overbrace{AgCl}^{m_1} + AgBr \xrightarrow{NaBr} \overbrace{AgBr}^{m_2}$

$AgCl$: $\frac{x}{143.5}$; $AgBr$: $\frac{m_1 - x}{188}$; $AgBr$: $\frac{m_2}{188}$

Q. 2 g of a sample containing NaCl, NaBr & some inert impurity is dissolved in H_2O & treated with excess of $AgNO_3$ soln. & resulting in formation of 3 g of ppt. The ppt. was filtered, dried & treated with excess of NaBr to produce 3.75 g of final ppt. Determine mass % of NaCl & NaBr in original sample.

$$\frac{x}{143.5} + \frac{3-x}{188} = \frac{3.75}{188}$$

$$\Rightarrow \frac{x}{143.5} = \frac{3.75}{188} - \frac{(3-x)}{188}$$

$\Rightarrow \frac{x}{143.5} = \frac{3.75 - 3 + x}{188}$

$\Rightarrow \frac{188x}{143.5} = 609.75 + x.$

$\Rightarrow 188x = 609.875 + 143.5x$

$\Rightarrow 44.5x = 609.875$

$\Rightarrow x = \frac{609.87}{4450}$

13.07

$\Rightarrow x = -13.07$

$\Rightarrow 44.5x = 107.625$

$\Rightarrow x = 2.4$

$\frac{2.4}{143.5}$ moles of NaCl.

$143.5\,g \rightarrow 58.5\,g$

$2.4 \rightarrow \frac{58.5 \times 2.4}{143.5}$

$= 1\,g$ (approx)

AgCl = 50%

$188 \rightarrow 103$

$0.6 \rightarrow \frac{103 \times 63}{188}$

94

$= \frac{309}{94 \times 10}$ 3.2

$= 0.32 \times 100$

AgBr = 32%,

2.1435

6425

7175

12870

15740

609875

60

188.0

143.5

44.5

2

14450 | 56098

4450

64

17800

16487

14450

1337

3137

13359

2143.5

9875

7178

100450

107625

80

+23

103

1.94

2309

282

27

2.82

OR

$AgCl \xrightarrow{NaBr} AgBr$

AgBr	AgBr
3g	3.75g

$AgCl \longrightarrow AgBr$

$143.5g \longrightarrow 188\,g$

Need, gain of mass = 44.5g

44.5g mass gain $\equiv$ 58.5g NaCl (1 mol NaCl)
(For 1 mol AgCl)

44.5 mass gain for 58.5g NaCl. 3 mol

0.75g mass gain $\rightarrow \frac{58.5}{44.5} \times \frac{0.75}{100}$ g NaCl.

$= \frac{1 \cdot 89}{89} \quad \frac{3}{4}$

$= \frac{351}{356}$

$= 1$ mol approx NaCl

$\frac{3.75}{188}$ → Total moles of AgBr.

→ Standard Temp. & Pressure.

★ STP: Under STP condition 22.4 l. of an ideal gas contains 1 mole / N_A of molecules.

★ NTP: Normal Temp. & Pressure.
Pertains to 0°C, 1 atm. conditions.

1 mol CH_4
1 mol N_2
1 mol CO_2
} 22.4 l

Q. 1·8 g of a mixture of $CuCl_2$ & $CuBr_2$ when treated with 1·85 g of AgCl

21 May 2009

~~EQUIA-EQ~~

Ch: Equivalent Weight and Neutralization Titration

Q. 10 g of a sample containing $NaHCO_3$ & some non-volatile inert impurity on heating gives off 320 ml of CO_2 gas under STP condition. Determine %age purity of the original sample.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + 6H_2O + CO_2$$

N.V.I. 320 ml at STP

22400 ml $\longrightarrow$ 1 mol.

320 $\longrightarrow$ $\frac{1}{22400} \times 320$ ~~$\times 1$~~

~~22400~~

~~1120~~

~~560~~

~~280~~

70.

$= 0.014$

$= 1/35$ or 0.028 mol.

Mass $= \frac{1}{35} \times 84 = 2.4\,g = 24\,\%$

Ch. Equivalent Weight and Neutralization Titration.

☆ Equivalent Weight :

(1) Equivalent wt. of an element : It is that part by wt. which combines with either 1 g of H_2 or 8 g of O_2 or 35.5 g of Cl_2 in a given chemical rxn.

eg $Ca + Cl_2 \longrightarrow CaCl_2$

40 g $\quad$ 35.5×2 g

(20 g) ✓ Equivalent wt. of Ca.

eg $Ca + H_2 \longrightarrow CaH_2$

40 $\quad$ 1×2 g

(20)

eg $2Al + 3O_2 \longrightarrow 2Al_2O_3$

$\frac{2\times27}{6} \quad \frac{3}{2}\times\frac{32}{6} = 8$

$= 9$

☆ Equivalent wt. of an element is defined in a rxn. MAY VARY for an element in different rxns. if the element show variable valency.

$Fe + \frac{1}{2}O_2 \longrightarrow FeO$

56 g $\quad$ 16 g

(28 g) $\quad$ 8 g

→ EW.

Date

$AlCl_3 \rightarrow \frac{56}{3} + \frac{35.5}{1}$

$9 + 35.5 = 44.5$

★ Valency : It is called net +ve charge or net -ve charge in a compound. On that basis, $CaCl_2$

Ca^{+2} $2Cl^{-}$ → (2)

345.5
03
1065
22
33.5

$EW = \frac{\text{Molar mass}}{\text{Valency}}$

$\overset{+6}{Al_2}\overset{-6}{(SO_4)_3} = 6$

SO_4^{-2} $EW = \frac{M}{6}$

Q. 5 g of Al is allowed to react with 15 g of Cl. What max. mass of $AlCl_3$ can be obtained?
M → Al → 27.

$2Al + 3Cl_2 \rightarrow 2AlCl_3$

$\frac{2 \times 27}{3}$ $\frac{3 \times 35.5}{}$

$= 9$ eq > $\frac{15}{35.5}$ eq

$\frac{15}{35.5}$ eq. $AlCl_3$

$= \frac{15}{35.5} \times (9 + 35.5)$

$= \frac{15}{35.5} \times 44.5$

$2Fe + \frac{3}{2}O_2 \longrightarrow Fe_2O_3$

$\frac{1}{2} * 56 \qquad \frac{48}{6}$

$\frac{63}{}$

$= \frac{56}{3}$

☆ H, O, & Cl were taken because these 3 are the ones most common which react with almost all elements of periodic table.

So, EW of other elements can be found in terms of H, O & Cl.

☆ No. of Gram Equivalents (denoted - eq)

$eq = \frac{W(\text{Given mass})}{EW}$

☆ Imp LAW OF CHEMICAL EQUIVALENCE:

Acc. to law of chemical Equivalence, in a chemical rxn. same no. of gram equivalence of reactants combine to produce same no. of gram equivalent of products.

$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6NaCl$

☆ Equivalent Weight of Compound: It is sum of Equivalent wt. of element present in that compound.

$CaCl_2$ $M = 40 + 2(35.5) = 111$

$EW = 20 + 35.5 = 55.5$

Q. 5g of a metal when heated in a stream of Cl_2 gas produced 13g of ~~MCl~~ metal chloride. Determine EW of metal chloride.

$$M + Cl_2 \longrightarrow M_xCl_y$$

5g | $35.5 \times 2 = 8g$ | 13g

$8 \longrightarrow 5$

$35.5 \longrightarrow \frac{5}{8} \times 35.5$

$= \frac{177.5}{8} = 22.18$

$M = 22.18\ g$

EW of $MCl_x = 57.68\ g$

$35.5 + 22.18 = 57.68$

Q. 0.183g of a metal MCl_x when heated with excess of O_2 gas gives 0.105g of metal oxide. Determine EW of metal.

$$MCl_x + O_2 \longrightarrow M_2O_x + Cl_2$$

$\frac{0.183}{4}$ | $\frac{2 \times 16}{4}$ | 0.105

EW of $MCl_x = \frac{0.183}{4}$

EW of $M = x$.

$x + 35.5$

$eq \rightarrow \frac{0.183}{x + 35.5} = \frac{0.105}{x + 8}$

$\Rightarrow 0.183x + 1.464 = 0.105x + 3.7275$

$OH \leftarrow {}^{-}HO + {}^{+}H$ Date

$\Rightarrow (0.183 - 0.105)x = 3.7275 - 0.1464$

$x = \frac{0.5811}{0.078}$

$= \frac{5811}{780} \frac{16937}{260}$

$3.7275 - 1.4640 = 2.2635$

$\frac{0.2}{x+35.5} = \frac{0.105}{x+8}$

$\Rightarrow 0.2x + 1.6 = 0.105x + 3.7275$

$\Rightarrow 0.2x - 0.105x = 3.7275 - 1.6$

$\Rightarrow 0.095x = 2.1275$

$\Rightarrow x = \frac{2.1275}{0.095}$

$\Rightarrow \frac{21275}{950} \frac{4255}{190} \frac{851}{38}$

$= 2.2635$

$= \frac{22635}{280} \frac{4527}{156} \frac{52}{}$

$= 29.01$ Ans

$\frac{S}{EW} = \frac{8}{35.5}$

$EW = 50.35$

MAV MAM.

0.183 − 0.105 = 0.078

3.7275 − 0.1464 = 0.5811

1260 ÷ 2 = 322

2355 ÷ 10 = 1776

355 × 9 = 3195

3727.5

0.200 − 0.105 = 0.095

3.7275 − 1.6000 = 2.1275

138 ÷ 2 = 26

152 ÷ 2 = 104

468 − 150 − 104 = 469

785 − 76 = 709

738 ÷ 2 = 342

Date

☆ BASICITY OF AN ACID:

It is the no. of hydrogen $^{+}$ ion which can be produced per molecule of acid in a given neutralisation rxn.

Monobasic	Basicity	Dibasic	Basicity
HCl	1	H_2SO_4	2
HX	1	H_2SO_3	2
HNO_3	1	H_2CO_3	2
HNO_2	1	H_3PO_3 ☆	2
R-COOH (Acid group)	1	H_2S	2
		COOH / COOH (oxalic acid)	2

Tribasic	Basicity
H_3PO_4	3
H_3AsO_4 (Arsenic acid)	3

H_2SO_4 (98) $\rightarrow 2H^+ + SO_4^{-2}$.

$EW = \frac{98}{2} = \frac{MW}{Basicity}$

☆ EW of a base is that part of a wt. which combines with 1g of H^+ ion in a given neutralisation rxn.

$NaOH + HCl \longrightarrow NaCl + H_2O$

(40) (1g)

$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$

(23+16=39, 46+16=62) (2g) $2 \longrightarrow 62$, $1 \longrightarrow 31$

Neutralization Rxn.

$H^+ + OH^- \longrightarrow H_2O$

Date

☆ EQUIVALENT WEIGHT OF ACIDS AND BASES

☆ Eqn Ew of an acid: It is that part by wt. which produces 1g of H^+ ion in a given neutralization rxn.

$2 \times 36.5g$

$2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O$

$\downarrow 2Cl^-$ $\downarrow Ca^{+2}$

$2H^+ + 2OH^- \longrightarrow H_2O$

2g

$Ew = 36.5$

eg: $3 + 31 + 64 = 98g$

$H_3PO_4 + 3NaOH \longrightarrow Na_3PO_4 + 3H_2O$

$\downarrow$

$3H^+$

3g

$Ew \rightarrow \frac{98}{3} = 32.67$

98

$H_3PO_4 + 2NaOH \longrightarrow Na_2HPO_4 + 2H_2O$

$\downarrow HPO_4^{-2}$

$2H^+$

2g

$Ew = 49g$

So, Ew of acid MAY VARY

Date

ACIDITY :

Acidity of a base is the no. of H^+ ions req. for complete neutralisation of 1 molecule of a base.

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

54 + 48 = 102

102 g ——— 6 g

1 g ——— $\frac{6}{102}$ g ——— 17 g

$EW = 17 g = \frac{M}{\text{Acidity}}$

So, EW of a base $= \frac{M}{\text{Acidity}}$

NORMALITY (Denoted : N)

It is the no. of gram equivalent of solute present in 1 L of solution.

$$N = \frac{eq}{V(\text{in } L)}$$

Q An aq. sol^n of H_2SO_4 has density 1.3 g/ml & it is 45% H_2SO_4 by wt. Determine N of sol^n

32 + 64 = 96

98 = 2 × 49

$H_2SO_4 = 1.3 \times \frac{10}{13} \times \frac{45}{100}$ g

1 L of sol^n ⟶ $1300 g \times \frac{45}{100}$

$= \frac{13 \times 45}{49} = \frac{585}{49} \approx 12$ eq in 1 L.

$Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$

$Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$

Date

So, its N will be 12 N. (read as 12 normal)

Q. Determine mass of Na_2O req. for preparing 250 mL 0.5 N NaOH soln.

$Na_2O + H_2O \longrightarrow 2NaOH$

250 mL. 0.5 N.
= 0.25 L.
0.125 g eq.

1.46
16
62

eq. of Na_2O = 0.125
wt. = 3.875 g

125
63
125
375
3.875

24 May 09

Q. Determine mass of K_2O req. for preparing 250 mL 0.15 N KOH soln.

KOH → 37.5 meq

7.25
015
37.50

$K_2O + H_2O \longrightarrow 2KOH$

37.5 meq

$N = \frac{eq}{V}$

$N \times V_{mL}$ = meq (milli equivalent)

$\frac{37.5}{1000} \times \frac{M}{2} = 1.76 g$

with the help of this we can interconvert

$n \sim EW$

Date

★ $n = \frac{w}{M}$, $eq = \frac{w}{EW}$, $\frac{eq}{n} = \frac{M}{EW} = n\ factor$

The factor which when multiplied to EW gives M.

n factor = Normality / Molarity

— For acid.

$EW = \frac{M}{Basicity}$, $\frac{M}{EW} = Basicity$

— For base:

$EW = \frac{M}{Acidity}$

$\frac{M}{EW} = Acidity$

— Salt:

$EW = \frac{M}{Valency}$, $\frac{M}{EW} = valency$

★

H_2SO_4 soln 0.5 M

If 1 L soln = 0.5 mol H_2SO_4

$= 0.5 \times 98\ g\ H_2SO_4$

$= 0.5 \times \frac{98}{49}\ eq.\ H_2SO_4$

$= 1\ eq.\ H_2SO_4$

$= 1N$

Molarity = 0.5

Normality = 1.0

OR

$M = \frac{n}{V}$, $N = \frac{eq}{V}$.

$\Rightarrow \frac{N}{M} = \frac{eq.}{n} = n\ factor$.

Q. What volume of a 5 mole M H_2SO_4 sol^n should be added to a 250 ml, 2N H_2SO_4 sol^n in order to make a 4N H_2SO_4 sol^n.

$H_2SO_4 \Leftrightarrow$ 5 meq

Molarity = 5 M.

$M = \frac{N}{n \text{ factor}}$

$5 = \frac{4}{n \text{ factor}}$

$\Rightarrow$ n factor $\times$ M = N.

N = 10 N.

$m_1V_1 + m_2V_2 = m_3V_3$

$\Rightarrow 10V_1 + \frac{4}{1000}$



$N_1V_1 + N_2V_2 = N_3V_3$

$\Rightarrow 10V_1 + 2(0.25) = 4(0.25 + V_1)$

$\Rightarrow 10V_1 + 0.5 = 1 + 4V_1$

$\Rightarrow 6V_1 = 1 - 0.5$

$\Rightarrow V_1 = \frac{0.5}{6}$ l

$= 83$ ml

Q. Determine mass of ~~NaOH~~ Na_2O which must be added to 150 ml 0.5 M NaOH sol^n in order to make 1N NaOH sol^n.

Date

Na_2O + [150 mL, 0.5 M NaOH] → 2N NaOH

$NaOH + HCl \rightarrow NaCl + H_2O$

$N = 0.5\ N$ NaOH

$V \rightarrow 150$ mL.

80.75 meq NaOH ← Na_2O

146 / 146 / 62

146 / 146 / 62

[150 mL, 1N NaOH] → 150 meq NaOH

$\frac{75 \times 62}{1000} = \frac{31}{2}$

$= 2.325$ g

175 / 031 / 175 / 350 / 2325

Q. Determine mass of SO_3 which must be absorbed in a 200 mL 1.6 M H_2SO_4 soln in order to increase its Normality to 6 N.

$SO_3 + H_2O \rightarrow H_2SO_4$

20 meq

N of H_2SO_4 → 3.2 N.

meq → 20 meq.

$N \times 0.2 = Eq$

3.2 / 32 / 40 / .6

[200 mL, 3.2 N.] $\xrightarrow{SO_3}$ 200 mL, 6N

640 meq → 1200 meq

Diff → 560 meq of H_2SO_4 needs to be added.

* mostly acids & bases are colourless

Date

Difference = 560 meq

$\frac{eq}{n}$ = n factor.

= 280 mmol H_2SO_4

$SO_3 + H_2O \longrightarrow H_2SO_4$

280 mmol 280 mmol

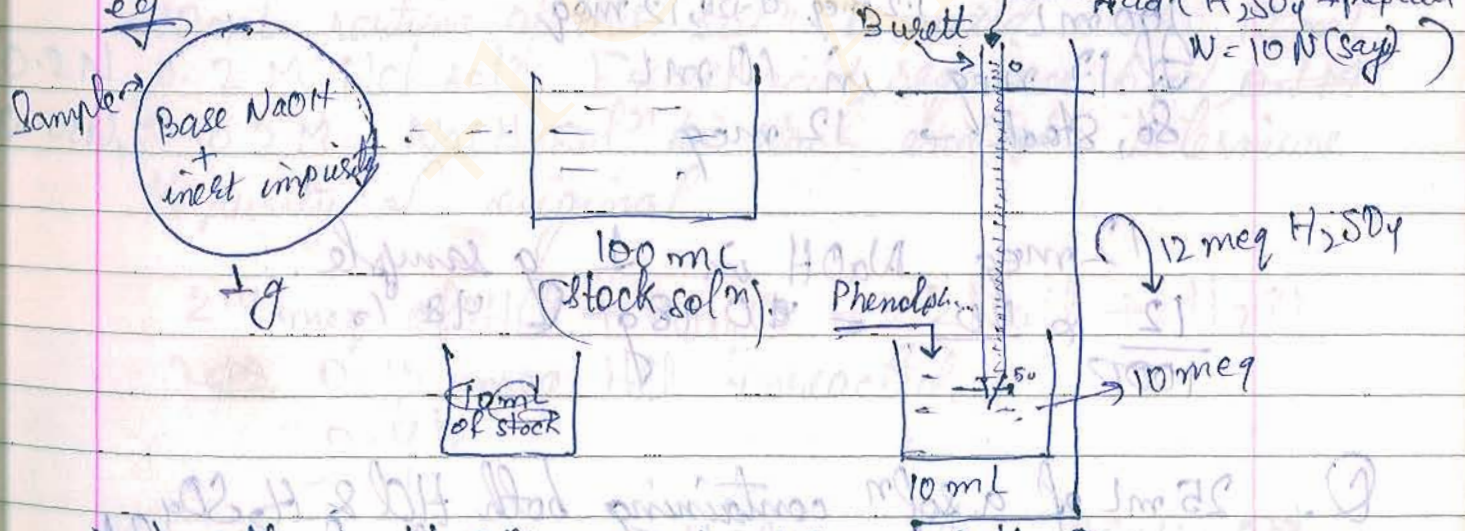
$80 \times \frac{280}{1000} = 22.4$ g

Neutralization Titration
OR
Acid - Base Titration

* Titration : Volumes are used in analysis.

Objective : To determine the amount of acid-base in an unknown sample through volumetric method

eg



$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

10 meq ; 10 mmol 1 drop - 1 drop

* Stop adding acid from Burett when base is completely neutralised. Now, note the reading of Burett.

☆ ~~The point at which~~

☆ In a Neutralization Titration END POINT indicate the completion of Neutralization Rxn. & at the end point G. eq of Acid = G. eq. of base

☆ Indicator changes its colour at the end point & ∴ indicates the attainment of END POINT

Q. 1 g of a sample containing NaOH & some inert impurity is dissolved in H_2O & diluted to 100 mL. A 10 mL portion of this solution required 10 mL of 0.6 M H_2SO_4 soln to reach end pt. Determine % purity of NaOH

1g NaOH → 100 mL → 10 mL

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

1·2 meq, 0·12N, 12 meq

If 12 meq in 10 mL

So, Stock → 12 meq.

12 meq. NaOH in 1 g sample.

$\frac{12}{1000} \times 40 = 0.48$ g ≡ 48 %

Q. 25 mL of a soln containing both HCl & H_2SO_4 required 40 mL, 0·02 M NaOH soln for complete neutralisation. The neutralised soln required 12 mL, 0·2 M $BaCl_2$ soln for complete precipitation of SO_4. Determine Normality of both HCl & H_2SO_4 in the original soln.

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$.

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N of NaOH = 0.2 N

$HCl + NaOH \rightarrow NaCl + H_2O$

3.2 meq — 40 mL

25 mL

$2H_2SO_4 + NaOH \rightarrow Na_2SO_4 + 2H_2O$

4.8 meq

0.4 N.

$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$

4.8 meq — 0.2 M, 12 mL

4.8 meq.

meq ($HCl + H_2SO_4$) = 8.

$\frac{4.8}{25}$ → N of H_2SO_4, $\frac{3.2}{25}$ → N of HCl.

Q. 1 g of a sample containing Na_2O & some inert impurity is dissolved in H_2O & diluted to 100 mL. A 10 mL portion of this sol'n is mixed with 12 mL 0.2 N, 0.2 M HCl sol'n. Excess acid required 6 mL 0.1 M. 0.02 N, 0.02 M NaOH sol'n to reach end pt. Determine % purity of original.

$2HCl + Na_2O \rightarrow 2NaCl + H_2O$

2.4 meq of HCl

0.12 meq HCl unreacted.

2.4

− .12

2.28 meq. HCl react with Na_2O

2.28 meq. of Na_2O

Date

10mL NaOH

x meq. + 2.4 meq. HCl + 0.12 meq. NaOH ⟶ End

Base Acid

$\Rightarrow x + 0.12 = 2.4$ meq.

$\Rightarrow x = 2.28$ meq. NaOH in 10mL

Total meq of NaOH = 22.8 meq.

So meq of Na_2O = 22.8 meq.

$$m(Na_2O) = \frac{22.8}{1000} \times \frac{62}{2}$$

$$= 0.7068\ g$$

$$= 70.68\%$$

Q. 1g of an alkane is burnt completely & all CO_2 gas was absorbed in 200 mL x 2 N NaOH sol^n. Excess base required 60 mL 0.5 M H_2SO_4 sol^n for complete neutralization determine formula of alkane.

$$C_nH_{2n+2} + O_2 \rightarrow n\,CO_2 + (n+1)H_2O$$

1 g

$M = 14n + 2$

$n = \frac{1}{14n+2} \longleftarrow \frac{n}{14n+2}$ mol CO_2

$n\,CO_2 + 2\,NaOH \longrightarrow NaHCO_3$

$\frac{200}{1000}$ mol

0.2×40

$= 8\ g$

Date

$C_nH_{2n+2} + O_2 \rightarrow nCO_2 + nH_2O$

1g → $\frac{n}{14n+2}$ mol.

$14n+2$.

$nCO_2 + 2NaOH \rightarrow Na_2CO_3$

70 mmol. 200 ~~mEq~~ meq. = 200 mmol NaOH

$Eq = \frac{E}{A}$ — 60 = 140 mmol.

$NaOH + H_2SO_4$

60 meq. 60 ml 0.5 M

1 N.

$\frac{n}{14n+2} = \frac{70}{2000}$ So, $C_nH_{2n+2} = C_7H_{16}$

$\Rightarrow 100n = 98n + 14$

$\Rightarrow 2n = 14$

$\Rightarrow n = 7$.

Q. 0.5g Sample → ~~NaCl, KCl & Imp.~~ Na_2O & K_2O —HCl→ NaCl, KCl —$AgNO_3$→ AgCl

x (0.118 − x) g

0.118 g.

0.2451 g

23 + 35.5

$\frac{x}{58.5} + \frac{0.118 - x}{74.5} = \frac{0.2451}{143.5}$

$Na_2O \rightarrow 2NaCl$

62 58.5

x

139 + 35.5 = 74.5

$K_2O \rightarrow 2KCl$

94 149

(0.118 − x)

108 + 35.5 = 143.5

Q. M of H_2O? $\rho = 1000\ Kg/m^3$

$1000\ Kg / 1000\ L$

$\frac{1000 \times 1000}{18}\ g.$

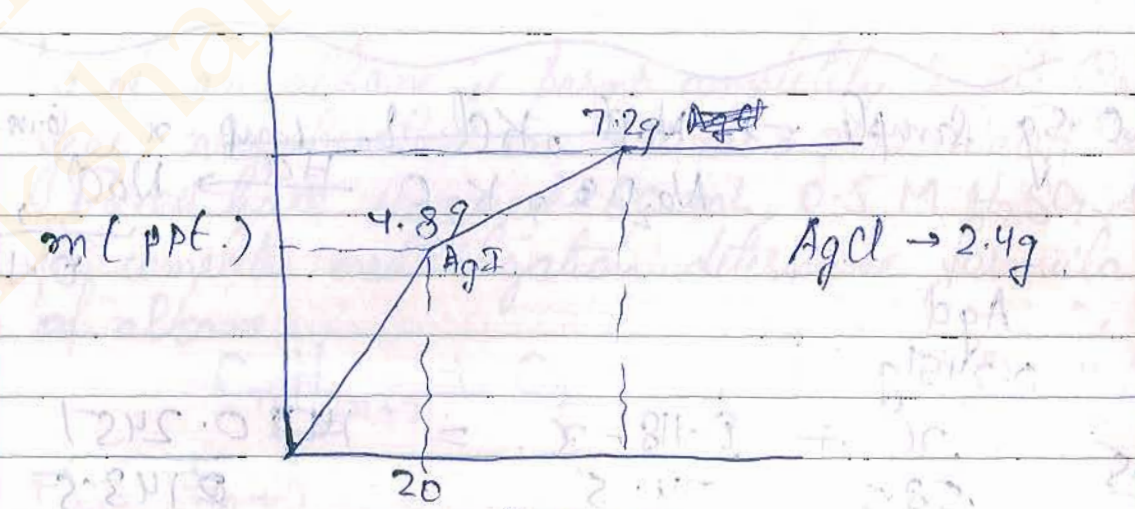
18×1000

$= \frac{1000 \cdot 500}{18\ 9}$

~~852 g of P_4O_{10}~~

TEST PAPER

Comprehension 1



4g

$NaCl$, MI_2

(a) $\frac{2.4}{143.5} \times 58.5$ → $\frac{4 - NaCl\ mass}{4} \times 100$: % age

$n(AgI) = \frac{4.8}{235}$ = mole of $AgNO_3$

(b) $I^- + AgNO_3 \rightarrow AgI$

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$\frac{4.8 \times 1000}{235}$ = 20 × molarity of $AgNO_3$

(c) $MI_2 + 2Ag^+ \longrightarrow 2AgI + M^{2+}$

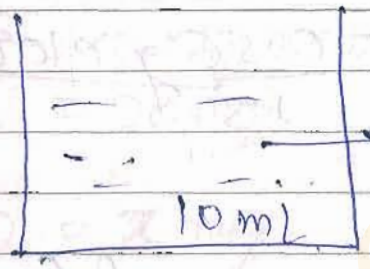
$\frac{4.8}{235 \times 2} = \frac{m(MI_2)}{MW}$ $\qquad$ $\frac{4.8}{235}$ × mol

~~$MW + 127 \times 2 = MW(MI_2)$~~

$\frac{Wt.\ of\ MI_2}{MW} = \frac{4.8}{235 \times 2}$

$\Rightarrow MW = \frac{Wt.\ of\ MI_2 \times 235 \times 2}{4.8}$

Q 32



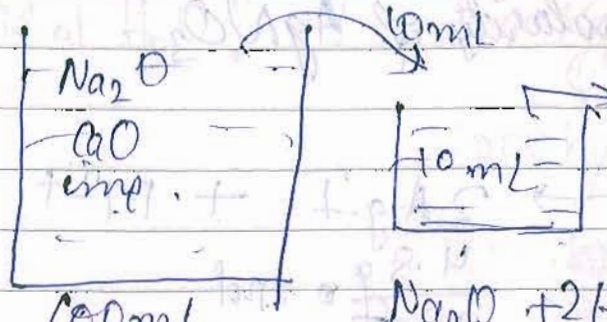
2.4 M $Al_2(SO_4)_3$ 2.4 mmol

$2Al^{+3} + 3SO_4^{2-}$

4.8 mmol 7.2 mmol

28 May 09

Q. 1.5 g of a sample containing Na_2O_2 CaO & some inert inp. is dissolved in H_2O & diluted to 100 ml A 10 ml portion of this sol^n required 12 ml 0.2 M HCl sol^n for complete neutralisation. A neutral sol^n when treated with excess of ~~NaOH~~ Na_2CO_3 resulting in formation of 0.1 g of $CaCO_3$ ↓. Determine mass % age of Na_2O_2 & CaO in the original sample.



$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$

4.8 meq 4.8 meq

$CaO + 2HCl \rightarrow CaCl_2 + H_2O$

~~4.8 meq~~ ~~4.8 meq~~

$CaCl_2$

~~NaCl~~ + $Na_2CO_3 \rightarrow NaCl + CaCO_3$

0.1 g / 100 = ~~0.001 mol~~

EW = 50 = 0.1

$\frac{0.1}{50}$ eq = 2 meq

meq. of CaO = 20

$m(CaO) = \frac{20}{1000} \times \frac{56}{2} = \frac{0.56\ g \times 100}{15}$

For 10 ml sol^n.

meq. of HCl used = 2.4 = meq. of (CaO + Na_2O)

2 0.4

So, $Na_2O \rightarrow 0.4$ meq $\rightarrow$ 10 mL

So, 4 meq $Na_2O \rightarrow$ 100 mL

$= \frac{4}{1000} \times 31 = \frac{0.124\ g \times 100}{15}$ % age.

Q. 4.06g of a mixture of BaO & an unknown MCO_3 on heating gives 3.62g of solid residue which contains only BaO & MO. The residue was dissolved in 100 mL 1 M HCl sol^n. Excess acid required 16 ml 2.5 M

NaOH soln for neutralization. Determine MW of unknown metal

Ba : 137

~~BaO~~ → 3.06

MCO_3 (BaO) (MCO_3) → 1g. $\xrightarrow{\Delta}$ BaO, MO + HCl

4.06g. 3.62g. 100mmol 100meq

0.01mol 0.01mol.

4.06 − 3.62 = 0.44

$MCO_3 \xrightarrow{\Delta} MO + CO_2$

BaO BaO

$\frac{0.44g}{44} = \frac{1}{100} = 0.01$ mol

$\boxed{\frac{eq}{n} = n\text{ factor}}$

MO = 0.01 × 2 × 1000 meq

= 20meq.

NaOH

16ml 25ml

40meq

BaO = x meq.

(20 + x) meq = 60

x = 40meq of BaO.

BaO = $\frac{137+16}{2} = \frac{153}{2}$ EW of BaO.

$m(BaO) = \frac{40}{1000} \times \frac{153}{2} = \boxed{3.06g}$

153 : 2 :: 3.06

MCO_3 0.01 mol mass → 1g.

1 mol → 100g mass

So, molar mass of MCO_3 → 100 = M + 60

So, MW of M = 40, Ca.

$Na_2SO_4 + HCl$. $NaOH + CH_3COOH \rightarrow CH_3COONa$

Date

✡ ANALYSIS OF ACIDIC / BASIC SALTS :

	Acid	Base	Salt	Ex
(1)	St	St	Neutral	NaCl, Na_2SO_4, KNO_3, KCl,
(2)	WK	St	Basic.	NaF, CH_3COONa Na_2CO_3, $NaNO_2$
(3)	St	WK	Acidic	NH_3, $R-NH_2$ am $(NH_4)_2SO_4$, NH_4NO
(4)	WK	WK	Acidic / Basic = Amphoteric	CH_3COONH_4, NH_4F $(NH_4)_2CO_3$

✡ Strong acids are : ~~HCl~~ HX (Except HF)
~~H_2SO_4~~ H_2SO_4, HNO_3, $HClO_4$
~~HNO_3~~ HIO_4

✡ Oxides & Hydroxides of group 1 & group 2 metals are all strong base. ~~Exp~~ Except all metals are weak base

✡ Stronger compound (Acid / Base) governs the nature of salt

✡ EW of Acidic / Basic Salt.

Na_2CO_3

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2\uparrow$

$EW = \frac{M}{2}$

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

$EW = M$

$Mg(OH)_2 + HCl \rightarrow$ Date

★ $\begin{matrix} COONa \\ | \\ COONa \end{matrix}$ = $Na_2C_2O_4$ Sodium Oxalate.
(Basic Salt)

~~$(NH_4)_2SO_4 + 2HCl \longrightarrow H_2SO_4$~~

$(NH_4)_2SO_4 \rightarrow SO_4^{2-} + (2)NH_4^+$

$NH_4^+ \rightarrow NH_3 + (H^+)$

Basicity = 2.

★ $\frac{eq}{n}$ = n. factor = Acidity / Basicity

Q. 2.5g @ of a sample containing NaOH, Na_2CO_3 & some inert imp. is dissolved in H_2O & diluted to 250 mL. A 25 mL portion of this sol^n req 20mL 0.12 M HCl sol^n to reach the end pt.

In a separate experiment, 25 mL portion of the same stock when treated with excess of $CaCl_2$ gives 0.08 g of $CaCO_3 \downarrow$.

Determine mass % age of NaOH & Na_2CO_3 in the original sample.

meq of $NaOH + Na_2CO_3 = 2.4$

25 mL → 0.8 meq

NaOH
Na_2CO_3
250 mL

$NaOH + HCl \rightarrow NaCl + H_2O$

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3$

meq of $Na_2CO_3 = \frac{0.08}{50} \times 1000 = 1.6$ meq

Meq of NaOH = 8 meq
Na_2CO_3 → 16 meq.

$m(NaOH) \rightarrow \frac{8}{1000} \times 40$

$= .32\ g$

$m(Na_2CO_3) = \frac{16 \times 53}{1000}$

$= \frac{8.48}{2.5} \times \frac{1000}{1000}\ 40$

$= \sim 34\%$

30 May

Q. 2.5 g of a sample containing Na_2CO_3, $NaHCO_3$ & some non-volatile inert impurity on strong heating produces ~~100~~ 112 mL of CO_2 gas measured under STP condition. The residue obtained is dissolved in H_2O & diluted to 100 mL. A 10 mL portion of this stock sol^n required 24 mL of 0.12 M HCl sol^n for complete neutralisation. Determine mass %age of Na_2CO_3 & $NaHCO_3$ in the original sample. Assume that during heating only HCO_3 is affected & gets converted into CO_3.

$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$

10 mmol × 84 — 5 mmol — 112 mL

$= \frac{0.84\ g.}{2.5} \times \frac{1000}{40}$ — $= 0.112\ L$ — 5 mmol

$= 33.6\%$

Date

Na_2CO_3 (Sol.) + Na_2CO_3 (Pr.) — 100 mL

10 mL → $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$

24 mL, 0.12 M

23.12
48
+1
84
×2
168

22400 mL CO_2 ⟶ 2 mole $NaHCO_3$

⟶ 168 g $NaHCO_3$ ≡ 112

$= \frac{84}{168} \times 112 \times \frac{22400}{100} \times 10^{-3} = 0.84$ g

Moles of $CO_2 \rightarrow \frac{112}{22400} = 5$ mmol.

2.50
84
1.66 g Na_2CO_3

466
664
$\frac{1.66 \times 100}{25} = 66.4\%$

Let the moles of Na_2CO_3 in the original sample be x.
So, in residue,
(x+5) mmol Na_2CO_3 ↓ 10 mL

$\frac{24 \text{ mL} \cdot 0.12 \text{ HCl}}{} = 2.88$ meq $Na_2CO_3 \rightarrow 10$ mL

So, ~~mmol~~ meq of $Na_2CO_3 \rightarrow 100$ mL → 28.8 meq

$(x+5)2 = 28.8$

$\Rightarrow x = 9.4$ mmol.

Mass $= \frac{9.4 \times 106}{1000} \approx 1$ g (approx.)

$= 40\%$

146
12
48
146

AMPHOTERIC SALT

Date

(Q) $NaHCO_3$ ← Amphoteric salt

It has a weak acid & a weak base.

(as base) $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

(as acid) $NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$

(Q) 2g of a sample containing Na_2CO_3, $NaHCO_3$ & NaCl is dissolved in H_2O & diluted to 100mL. A 10mL portion of this sol^n required 12mL 0.1M NaOH sol^n to reach end pt. The sol^n thus obtained was then titrated against 0.1M H_2SO_4 sol^n ~~for complete neut^n~~ & its 15mL was required for complete neutralisation. Determine mass % age of $NaHCO_3$, Na_2CO_3 in the original sample.

$NaHCO_3 + Na_2CO_3 + NaCl$ (2) — 100mL

10mL

$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$ (1)

1.2 mmol, 1.2 meq

12mL 0.1M

$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$

(1) + (2) 0.75 meq

1.5 mmol, meq

1.2 meq $NaHCO_3$.

$146 \div 2 = 73$; $73 + 48 = 106$

$123 \div 1.3 = 84$; $84 + 48 = 132$

$12 \times 84 = 1008$; $1008 \div 2 = 504$; $504 \div 1000 = 0.504$ g

$= 50.4\%$

$1.20 + .75 = 1.95$

$1.95 \times 106 \times 100 \div (100 \times 2 \times 1000) = 195 \times 53 \div 1000$

$= 10335 \div 1000$

$= 10.335$ g

$2 - 0.504 - 10.335 = 1.161$ g

STR

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$= \frac{10335}{1000} = 10.335\%$

Let 10 mL contain x mL Na_2CO_3 (original)

$(1.2 + x)$ meq $Na_2CO_3 \longrightarrow 10mL = 3(15 \times 2)$

$\Rightarrow x = 1.8$ meq Na_2CO_3

$= 18$ meq $\rightarrow 100mL$

$\frac{9 \cancel{18} \times 100 \times 53}{\cancel{2000}\ 10}$

$= 47.7\%$

253
9
477

☆ USE OF 2 INDICATORS

eg. Let [$NaHCO_3$ + Na_2CO_3] + HCl.

y mmol, x mmol, x mmol

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ rxn. complete, then

$(x+y)$ mmol $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

(original + produced) $(x+y)$ mmol

☆ Strong Acid – Strong Base react & neutralise 1st. When their rxn. is complete, strong base is consumed fully, then the left acid reacts with the weaker base (in the reaction of 2 bases & 1 acid).

☆ In neutralisation titration, if the sol^n contains more than 1 base or more than 1 acid, stronger component is neutralised 1st, then weaker component START neutralising

RT 2

Date

☆ SALTS ARE ~~Aw~~ always weaker acid than pw & weaker base than pure acid & pure base

☆ Phenolphthalein — Transition pH 9

Methyl Orange — ~~pH < 4~~ ~~pH > 4~~ pH

pH > 4 yellow

pH < 4 red (orange)

1) Na_2CO_3 (aq.) pH > 11

2) $NaHCO_3$ (aq.) pH < 9 or 7 < pH < 9

pH > 7

Phe' Phenolphthalein (1 drop)

Na_2CO_3 → x mmol $NaHCO_3$ → y mmol	$HCl + Na_2CO_3 \rightarrow NaHCO_3 + NaCl$ x mmol x mmol x

mmol of Na_2CO_3 present = mmol of H^+ ion req. to complete reach phenolphthalein end pt.

Methyl orange $2NaHCO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

(x+y) mmol

after rxn. → Red color due to $CO_2 + H_2O$ ⇌ H_2CO_3

x 5 mmol Na_2CO_3 7 mmol $NaHCO_3$	+ Me. Or. $\xrightarrow{HCl}$ yellow

$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$

5 mmol 5 mmol 5 mmol x

$NaHCO_3$ + HCl
12 mmol 12 mmol
x+y. (required)

So, total mmol of HCl required = 17 mmol.
= 2x+y.

Q. 1.5g of a sample containing Na_2CO_3, $NaHCO_3$ & NaCl is dissolved in H_2O & V diluted to 100mL. A 10mL portion of this sol^n required 8mL 0.1M HCl sol^n to reach phenolphalein end pt. Methyl orange is then added and further 10mL 0.05M H_2SO_4 sol^n is required to reach end pt. Determine mass %age of Na_2CO_3, $NaHCO_3$ in the original sample.

10mL + PP
x mmol $NaHCO_3$ (original)

$NaHCO_3$ + Na_2CO_3 + NaCl
1.5g

$NaHCO_3$ + HCl → $NaHCO_3$ + NaCl
0.8 mmol 0.8 mmol 0.8 mmol
10mL

100mL

$NaHCO_3$ + H_2SO_4

Na_2CO_3 → 8 mmol 100mL

$\frac{8 \times 106}{1000} = \frac{0.848g \times 100}{1.5}$

106
08
848

= 56%

(Me Or)

$NaHCO_3$ + $2H^+$ → Na^+ + H_2O + CO_2
(x + 0.8 mmol) 10mL 0.05M
= 0.5 mmol.

x → 0.2 mmol

$\frac{2 \times 84}{1000} = \frac{0.1689 \times 100}{1.5}$

$= 11.____\%$

Q. A mixed sol^n contains both Na_2CO_3 & $NaHCO_3$ & its 25 ml require 16 ml 0.1 M HCl sol^n to reach phenolphthalein end pt. Another 25 ml portion of the same stock sol^n required 40 ml 0.1 M HCl in the presence of Me OR indicator to reach end pt. Determine PARTIAL molarity of the sol^n w.r.t Na_2CO_3 & $NaHCO_3$

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$.

1.6 mmol. 1.6 mmol. 1.6

25 ml sol^n →

x mmol Na_2CO_3

y mmol $NaHCO_3$.

$NaHCO_3 + HCl$.

(x + 1.6) mmol. 4 mmol.

$\frac{1.60}{1060} = \frac{16}{1060} = \frac{8}{530} = \frac{4}{265}$

$0.1 \quad \frac{16}{100} \quad \frac{64}{250} \quad 25 \times 10$

$= 0.064\ M$

4.00

− 1.6

2.4 mmol $NaHCO_3$

$= \frac{2.4}{250} = \frac{24}{25 \times 10} \quad 0.96$

$= 0.096\ M$

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

1.6 3.2

$NaHCO_3 + HCl \rightarrow NaCl \rightarrow H_2O + CO_2$

x x

$3.2 + x = 4$ mmol
$= 0.8$ mmol $NaHCO_3$

$\frac{8}{250} = 0.032\ M$

Q. 2g of a sample containing Na_2CO_3, NaOH & some NaCl is dissolved in H_2O & diluted to 100 mL. A 10mL portion of this sol^n required 30mL 0.1M HCl sol^n to reach the end pt. In another titration 10mL of the same stock sol^n 40mL 0.1M HCl to reach MeO end pt. Determine mass %age of NaOH & Na_2CO_3 in the original sample.

$NaOH \rightarrow 3$ mmol

$NaOH + HCl \rightarrow NaCl + H_2O$
3mmol. 3mmol.

$Na_2CO_3 + 2HCl \rightarrow 2NaCl$
2 mmol 4mmol.

$\frac{0.12}{2} \times 100 = 6\%$

23
+17
40

Na_2CO_3, NaOH → 100mL

Ph. 10mL

$NaOH + HCl \rightarrow NaCl + H_2O$

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

Let x mmol NaOH, y mmol Na_2CO_3

$x + y = 3$

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
y 2y

$x + 2y = 4$ $\quad y = 1, x = 2$

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20 mmol NaOH × 40 / 1000
= 0.8 g = 40%

10 mmol Na_2CO_3 × 106 / 1000
= 1.06 g
= 53 %

4 JUNE

☆ %age Strength of OLEUM ($H_2S_2O_7$) (CN)

↓
$H_2SO_4 \cdot SO_3$

☆ Oleum is a physical mixture which we prepare. It can have SO_3 & H_2SO_4 in any molar ratio.

☆ It absorbs H_2O & gets converted into H_2SO_4

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

100 g. So, 166% oleum. 100 g (say)

☆ %age Strength of oleum: It is the wt. of sulphuric acid obtained on complete hydrolysis of 100 g of oleum.

☆ Oleum hydrolysis can be recwritten as

$H_2SO_4 \cdot SO_3 + H_2O \rightarrow H_2SO_4 \cdot H_2SO_4$

i.e $SO_3 + H_2O \rightarrow H_2SO_4$

80 g 18 g

$18 - \frac{80}{183} \times 61 = \frac{80}{3}$ % SO_3 in oleum

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Q. Determine the %age strength of oleum which contain 20% SO_3 by wt.

$SO_3 + H_2O \rightarrow H_2SO_4$

80 — 18

16g

$\frac{20}{100} \times 80 = 16$

80 — 18

16 → $\frac{18}{80} \times 16 = 3.6$ g.

100g $H_2SO_4 \cdot SO_3$

$SO_3 + H_2O \rightarrow H_2SO_4$

20g.

80 — 18

20 → $\frac{18}{80} \times 20 = 4.5$

So., Oleum = 100 + 4.5g = 104.5g.

Q. %age strength of oleum = 120%.

SO_3 %age ?

80 — 18 → $\frac{80}{18} \times 20 = \frac{800}{9} = 88.8$

= 88.8%

Q. What could be the max. %age strength of oleum.

$SO_3 + H_2O$

100

80 — $\frac{18}{80} \times 100 = \frac{45}{2} = 22.5$

42

= 122.5%

Q. 5g of a 115% oleum is dissolved in H_2O & diluted to 250 mL. A 20 mL portion of this soln is titrated using 0.2 M NaOH soln. What volume of NaOH will be req. to reach end pt.

115% Oleum 5g.
250 mL

100g Oleum → 115g H_2SO_4

5 → $\frac{115}{100} \times 5$ = 5.75

$0.2 = \frac{5.75 \text{ g } H_2SO_4}{98 \times 250 \times 100}$

$H_2SO_4 + NaOH$

0.2×10^{-3} mmol 0.2×10^{-3} mmol

$H_2SO_4 \rightarrow 5.75$g

$N = \frac{5.75}{49} \times \frac{1000}{250} \times 4$

$= \frac{575}{50 \times 100} \times 4$

$= 0.46$ N.

N = 0.46 20mL

$N = \frac{eq}{V}$

meq H_2SO_4 $\Rightarrow 20 \times 0.46 = 0.2 \times V$

$\Rightarrow V = 46$ mL.

Date

Ch-3 Redox Reaction

☆ Redox → Reduction & Oxidation

Oxidation: It is a process of addition of O_2 or removal of H_2

eg:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

Fe is oxidised.

eg $CH_4 \xrightarrow{\Delta} C$ (graphite) $+ 2H_2\uparrow$

CH_4 is oxidised.

Reduction: It is addition of H_2 or removal of O_2.

eg: $2C + 3H_2 \rightarrow C_2H_6$, C is reduced.

$TiO_2 \xrightarrow{\Delta} Ti + O_2\uparrow$, TiO_2 is reduced.

simultaneous

☆ Redox Rxn is a continuous process in which Oxidation & Reduction occur simultaneously.

i.e either Oxidation or Reduction cannot be done in isolation.

2nd DEFINITION

Redox Rxn as an electron transfer process

Oxidation: loss of electron is called oxidation.

Reduction: Gain of electron is called reduction.

eg: $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$

Oxalic acid : $H_2C_2O_4$

Date

$Na(s) \longrightarrow Na^+ + e^- \longrightarrow$ Oxidation (Oxidⁿ)

Process – loss of electron.

$\frac{1}{2}Cl_2 + e^- \longrightarrow Cl^- \longrightarrow$ Reduction (Redⁿ)

+

☆ Redox rxn. is an electron transfer process in which e^- produced by one is consd consumed by the other.

Here,

Na is reducing Cl, so, it is reducing agent

Cl is oxidising Na, " " " Oxidising "

☆ Reducing agent is the reagent which reduces others by oxidising itself.

In a redox rxn. reducing agent undergoes gain in valency.

☆ Oxidising agent is the reagent which oxidises others by reducing itself.

In a redox rxn. oxidising agent undergoes decrease in valency.

Redox rxn.

ex:

$KMnO_4 + \underbrace{H_2C_2O_4}_{\text{oxalic acid}} + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$

Oxalic acid : $H_2C_2O_4$

Date

$Na(s) \longrightarrow Na^+ + e^- \longrightarrow$ Oxidation (Oxidⁿ)

Process - loss of electron.

$\frac{1}{2}Cl_2 + e^- \rightarrow Cl^- \longrightarrow$ Reduction (Redⁿ)

+

☆ Redox rxn. is an electron transfer process in which e^- produced by one is consd consumed by the other.

Here,

Na is reducing Cl, so, it is reducing agent

Cl is oxidising Na, " " " Oxidising "

☆ Reducing agent is the re-agent which reduces others by oxidising itself.

In a redox rxn. reducing agent undergoes gain in valency.

☆ Oxidising agent is the reagent which oxidises others by reducing itself.

In a redox. rxn oxidising agent undergoes decrease in valency.

Redox rxn.

ex:

$KMnO_4 + \underbrace{H_2C_2O_4}_{\text{oxalic acid}} + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$

Date

✱ MODERN IUPAC DEFINITION

✱ Redox Rxn in terms of OXIDATION NO. (ON.)

* Oxidation is a process of increase in oxidation no.
* Reduction is a process of decrease in ON.

✱ OXIDATION NUMBER (always indicated by sign +, −)

It is the average charge possessed by an element in a molecule of ion.

eg $K_2Cr_2O_7 \rightarrow 6$ (Cr)

~~$2 + 14 + 2x + 0 = 12$~~

✱ RULES FOR ASSIGNING ON.

1) ON of an atom in its elemental state is always zero.
   eg $Na(s)$ ON → 0
   Cl_2 → Cl atom's ON → 0
   N_2 → N atom's ON → 0
   P_4 → P atom's ON → 0

2) ON of alkali metal in all its compound is always +1.
   ON of all alkaline earth metals in compound is always +2.
   ON of Al in compound is always +3

3) ON of Hydrogen in all its compound is +1.
   EXCEPTION occurs in case of METAL HYDRIDES, where, its ON is −1
   H with metal → ON → −1
   H with non-metal → ON → +1

4) ON of Oxygen in all its compound is −2
   ~~EXCEPT~~

$Cr_2O_7^{-2}$ → Dichromate. S^{-2} → Sulphide

CrO_4^{-2} → chromate. $C_2O_4^{-2}$ → Oxalate (From oxalic acid)

EXCEPTION occur in the following cases —

(a) in peroxide (O_2^{-2}) = −1

(b) in Superoxide (O_2^{-1}) = −1/2

(c) in OF_2 ON of Oxy → +2

5) O.N of Hallogens in Metal Hallides = −1 (always)

eg: $ZnBr$ → −1.

6) O.N of an ion is always equal to its valency

Cl^{-1} SO_4^{-2} PO_4^{-3}

Ca^{+2} NO_3^{-1}

7) O.N of a neutral molecule is always ZERO.

Q. SO_4^{-2}

$x + 4(-2) = -2$

$\Rightarrow x - 8 = -2$

$\Rightarrow x = +6$

Q. $S_4O_6^{-2}$

$4x + 6(-2) = -2$

$\Rightarrow 4x - 12 = -2$

$\Rightarrow x = \frac{5}{2} = +2.5$

Q. NH_4NO_3

$x + 4(1) + x + 3(-2) = 0$

$\Rightarrow 2x + 4 - 6 = 0$

$\Rightarrow 2x - 2 = 0$

$\Rightarrow x = +1$

Alkali Metals

Li +

Na

K

Rb

Cs

Fr

Medium is always req. in Redox Rxn. & Medium (Acid/Base) is never ~~reacted~~ counted in O.N (Not involved in Redox Rxn)

Q. $MnO_2Cl_2^{-1}$

$x + (-4) + (-2) = -1$

$\Rightarrow x - 6 = -1$

$\Rightarrow x = +5$

Q. PO_4^{-3}

$x + (-8) = -3$

$\Rightarrow x = +5$

$2 + 2x - 8 = 0$

$\Rightarrow -6 + 2x = 0$

$\Rightarrow x = +3$

- $\underset{\text{Reducing agent}}{\overset{-1}{KI}} + \underset{\text{OA}}{\overset{+7}{KMnO_4}} + \underset{\text{Medium}}{H_2SO_4} \rightarrow K_2SO_4 + \overset{+2}{MnSO_4} + \overset{0}{I_2} + H_2O$

- $\underset{\text{RA}}{Na_2\overset{-2}{S}} + \underset{\text{OA}}{K_2\overset{+6}{Cr}O_4} + H_2SO_4 \rightarrow \overset{+4}{SO_2} + K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + H_2O + Na_2SO_4$

- $\underset{\text{RA}}{Cu_2\overset{+1}{S}} + \underset{\text{OA}}{KMnO_4} + H_2SO_4 \rightarrow \overset{+2}{CuSO_4} + \overset{+4}{SO_2} + \overset{+2}{MnSO_4} + K_2SO_4 + H_2O$

If $(-4) = 0$, $x = 4$

- $\underset{\text{Ferrous oxalate RA}}{\overset{+2}{Fe}C_2O_4} + \underset{\text{OA}}{KMnO_4} + H_2SO_4 \rightarrow \overset{+3}{Fe_2}(SO_4)_3 + CO_2 + \overset{+2}{MnSO_4} + K_2SO_4 + H_2O$

$2x - 2 = 0$

$\Rightarrow x = 1$

$x - 2 = 0$

$-2 - 8 = 0$

$x \Rightarrow x$

$x - 2 = 0$

$2x - 2 = 1$

$\Rightarrow x = 1$

$-2 - 8$

$x - 4 = 0$

$2x - 2 = 0$

$2x - 8 = -2$

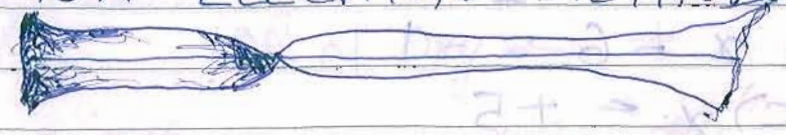
$\Rightarrow x = +3$

* MnO_4^{-1} → Permanganate

Date

☆ BALANCING OF REDOX RXN:

ION-ELECTRON METHOD



STEPS

S1

The method is applicable to ionic rxn. If the rxn is neutral, convert it into ionic rxn by dropping the ions ~~to the~~ whose ~~on~~ ON are not changing.

eg ~~K~~ $(K)MnO_4 + (K_2)C_2O_4 + (H_2SO_4) \longrightarrow$

$MnSO_4 + (K_2SO_4) + CO_2 + (H_2O)$

$\overset{+7}{MnO_4^-} + \overset{+3}{C_2O_4^{-2}} \longrightarrow \overset{+2}{Mn^{+2}} + \overset{+4}{CO_2}$

~~Oxi~~ Reduced (O.A) Oxidised (R.A)

S2

Identify Oxidising & Reducing agent. & Split the redox rxn into 2 reactions — Oxid^n half rxn & red^n half rxn

$2x$ (−6) A ON=5

$[8H^+ + 5e + \overset{+7}{MnO_4^-} \longrightarrow \overset{+2}{Mn^{+2}} + 4H_2O$ (−2) Red^n

$\times 5\ [\overset{+6}{C_2O_4^{-2}} \longrightarrow \overset{+8}{2CO_2} + 2e$ Oxid^n

$2x - 8 = -2$

$2x = 6$

Now balance the 2 half reactions independently as follows —

a— Balance the elements other than H & O.

* b- Balance the change in ON by adding electrons on the side higher in ON

S3
CHARGE BALANCE : It depends on nature of medium (Acidic / Basic)

(a) If acidic, excess +ve charge is balanced by adding H^+ ion on appropriate side

(b) If basic, excess -ve charge is balanced by adding OH^- ion on appropriate side

S4
Balance H & O using H_2O on appropriate side.

S5
Equalise the electrons in the 2 half rxns by multiplying with simple common factor & add them to obtain the balanced redox rxn.

$$2MnO_4^- + 5C_2O_4^{-2} + 16H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$

Balanced Rxn:

$$2KMnO_4 + 5K_2C_2O_4 + 8H_2SO_4 \longrightarrow 2MnSO_4 + 10CO_2 + 8H_2O + \boxed{6K_2SO_4}$$

→ Balance the left compound by hit & trial

Q. $K_2Cr_2O_4 + KI + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + I_2 + H_2O$

$$CrO_4^{-2} + I^- \longrightarrow Cr^{+3} + I_2$$

$$\overset{+6}{CrO_4^{-2}} + 3e + 8H^+ \longrightarrow \overset{+3}{Cr^{+3}} + 4H_2O \quad]\times 2$$

(Red^n)

$$2I^- \longrightarrow I_2 + 2e^- \quad]\times 3$$

(Oxid^n)

IO_3^{-1} = iodate

Date

⇒ $2CrO_4^- + 6I^- + 16H^+ \rightarrow 2Cr^{+3} + 3I_2 + 8H_2O$

⇒ $2K_2CrO_4 + 6KI + 8H_2SO_4 \rightarrow 5K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 \uparrow 8$

Q. $FeSO_4 + H_2SO_4 + NaIO_3 \rightarrow I_2 + Na_2SO_4 + Fe_2(SO_4)_3 + H_2O$

$Fe^{+2} + NaIO_3 \rightarrow I_2 + Na^{+2} + Fe^{+6}$

Fe^{+2} (Oxidn) $\rightarrow Fe^{+3} + 1e^-$] × 10

$12H^+ + 10e^- + NaIO_3 \rightarrow I_2 + 6H_2O$ (Redn)

⇒ $10FeSO_4 + 2NaIO_3 + 6H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + I_2 + 6H_2O + Na_2SO_4$

Q $NaNO_3 + Zn \rightarrow Zn(OH)_2 + NH_4NO_3 + NaOH$

+5 NO_3^{-1} → NO_3^{-1}

H_2O $+5$ -3

$8e^- + NO_3^- \longrightarrow NH_4^+ + 10(OH)^-$ Redⁿ

$Zn^0 \longrightarrow Zn^{+2} + 2e^-$] 4 Oxidⁿ

$\Rightarrow$ ~~$NaNO_3 + 4Zn \rightarrow 4Zn(OH)_2 + NH_4NO_3$~~

$= 4Zn + NO_3^- + 7H_2O \rightarrow 4Zn^{+2} + NH_4^+ + 10(OH)^-$

$4Zn + 2NaNO_3 + 7H_2O \rightarrow 4Zn(OH)_2 + NH_4NO_3 + 2Na(OH)$

Q. $Fe_2O_3 + Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + FeSO_4 + SO_2 + H_2O$

$1e + Fe^{+3} \longrightarrow Fe^{+2}$] ×6 Redⁿ

~~$S^{-2} \longrightarrow S^{+4} + 6e^-$~~ Oxidⁿ

c) $6Fe_2O_3 + Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + 6FeSO_4 +$

$2H_2O + S^{-2} \longrightarrow SO_2^{+4} + 6e^- + 4H^+$

3 ~~$6Fe_2O_3 + Na_2S + 2H_2SO_4 \rightarrow Na_2SO_4 + 6FeSO_4 + SO_2 + 2H_2O$~~

$3Fe_2O_3 + Na_2S + 2H_2O \rightarrow 6FeSO_4 + SO_2 + 2H_2SO_4 + 7H_2SO_4 + Na_2SO_4$

Date

Q. $\overset{+2\ +3}{FeC_2O_4} + \overset{+7}{KMnO_4} + H_2SO_4 \rightarrow \overset{+3}{Fe_2(SO_4)_3} + \cancel{KA}$

$\overset{+2}{MnSO_4} + \overset{+4}{CO_2} + H_2O$

$+ K_2SO_4$

$Fe^{+2} \longrightarrow Fe^{+3} + e$

$C_2O_4^{-2} \longrightarrow 2CO_2 + 2e^-$

$FeC_2O_4 \rightleftharpoons Fe^{+3} + 2CO_2 + 3e^-$] ×5 oxidn.

$MnO_4^- + 5e + 8H^+ \longrightarrow Mn^{+2} + 4H_2O$] ×3

$\Rightarrow 5FeC_2O_4 + 3KMnO_4 + 12H_2SO_4 \rightarrow \frac{5}{2}Fe_2(SO_4)_3 + 10CO_2$

$+ 3MnSO_4 + \cancel{12}H_2O$

$+ \frac{3}{2}K_2SO_4$

Q. $\overset{+1\ -2}{Cu_2S} + \overset{+4}{MnO_2} + H_2SO_4 \longrightarrow \overset{+2}{CuSO_4} + \overset{+2}{MnSO_4} + \overset{+4}{SO_2} +$

H_2O

$2Cu^{+1} \longrightarrow 2[Cu^{+2} + e^-]$

$S^{-2} \longrightarrow \overset{0}{SO_2} + 6e^-$

$2H_2O + Cu_2S + \cancel{2H_2O} \rightarrow 2Cu^{+2} + 8e + SO_2 + \cancel{4H^+}$

$2e^- + Mn^{+4}O_2 \longrightarrow Mn^{+2} + 2e^- + 2H_2O$] × 4

$Cu_2S + 12H^+ + 4MnO_4^- \longrightarrow 2Cu^{+2} + SO_2 + 4H^+ + 4Mn^{+2} + 6H_2O$

$Cu_2S + 4MnO_2 + 6H_2SO_4 \longrightarrow 2CuSO_4 + 4MnSO_4 + SO_2 + 6H_2O$

$\overset{0}{Br_2} + NaOH \longrightarrow \overset{-1}{NaBr} + \overset{+5}{NaBrO_3} + H_2O$

DISPROPORTIONATION RXN.

These Disproportionation Rxns. are the redox Rxns in which similar reagent is oxidised as well as reduced.

Todo ↓

$Br_2^* + Br_2 + NaOH \longrightarrow \overset{-1}{NaBr} + \overset{+5}{NaBrO_3} + H_2O$

$12(OH)^- + Br_2 \longrightarrow 2BrO_3^- + 10e^- + 6H_2O$

$2e^- + Br_2 \longrightarrow 2Br^-$] × 5

$6Br_2 + 12NaOH \rightarrow 10NaBr + 2NaBrO_3 + 6H_2O$

$3Br_2 + 6NaOH \rightarrow 5NaBr + NaBrO_3 + 3H_2O$

SHORTCUT TO BALANCE

Date

12 JUNE

~~BALANCING OF DISPROPORTIONATION RXN.~~

Change in ON 5 — 2 → Cross & multiply.

$2KMnO_4 + 5K_2C_2O_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H$

S1
See which ~~of~~ ~~compound~~ is oxidised & which is reduced.

S2
Balance ~~or~~ ON on both sides of Mn, C here.

S3
Write change in ON above compounds. Cross multiply.

Done → half.

ΔON ~~6~~ 3 — ~~2~~ 1

12 — 4

Q. $1K_2Cr_2O_7 + 3Na_2SO_3 + H_2SO_4 \rightarrow K_2SO_4 + Na_2SO_4 + Cr_2(SO_4)_6 + H_2O$

-14
+2
= -12

-6+2x=0
=> 6

-6+2=4

— IDENTIFY
- which is oxidised — reduced.
- 1 mole OA which oxidise how many moles of RA.

~~ΔON~~ 2 — 3

Q. $H_2O + 3Na_3AsO_3 + 2KMnO_4 \rightarrow Na_3AsO_4 + MnO_2 + 4KOH$

+3 — 7 — +5 — 4

Date

Q.5 $\overset{+2}{Fe}\overset{+6}{C_2}O_4 + 3K\overset{+7}{Mn}O_4 + H_2SO_4 \rightarrow \frac{1}{2}\overset{+3}{Fe_2}(SO_4)_3 + \overset{+2}{Mn}SO_4 + 2\overset{+8}{CO_2} + H_2O +$

3 × 5

$\Delta \rightarrow 2+1$

$+ K_2SO_4$

Q.3 $\overset{+2}{Fe}\overset{+3}{(NO_2)_2} + 5K_2\overset{+6}{Cr}O_4 + H_2SO_4 \rightarrow \overset{+5}{K}NO_3 + \overset{+3}{Fe}(SO_4)_3 + K_2SO_4 +$

$\Delta 1 \quad \Delta 4 \qquad \Delta 3$

5

$\frac{1}{2}\overset{+3}{Cr_2}(SO_4)_3 + H_2O.$

1 mole $K_2CrO_4 \longrightarrow$ mole $Fe(NO_2)_2$?

$\overset{+3}{NO_2^-} \longrightarrow \overset{+5}{NO_3^-}$ $\quad 5 \rightarrow 3$

$\Delta\ 2$

$2\,NO_2 \longrightarrow \Delta 4$

★ CONCEPT

STOICHIOMETRY OF REDOX RXN.

* EQUIVALENT WT. OF OA/or RA

$$EW = \frac{MW}{\text{Change in ON per formula unit.}}$$

(formula unit = single molecule)

i.e $\frac{MW}{EW}$ = n factor

☆ COMMON OA — n factor

*1) MnO_4^- (-7) + H^+ → Mn^{+2} (+2), $\Delta 5$ — 5

Acidic medium

Permanganate

Permanganate in every acidic medium gives n factor → 5

*2) MnO_4^- + OH^- → MnO_2 (4) — 3

Alkaline medium

Chromium

*1) $Cr_2O_7^{-2}$ (+12) + H^+/or OH^- → $2Cr^{+3}$ (+6) — 6

2) CrO_4^{-2} + H^+/or OH^- → Cr^{+3} — 3

3) CrO_3 $\xrightarrow[OH^-]{H^+}$ Cr^{+3} — 3

$X \rightarrow Cl^-, Br, I$ (+5)

1) XO_3^- + H^+ → X_2 (0) — 5

$X \rightarrow Cl, Br, I$

1) X_2 + H^+ → $2X^-$ — 2

H_2O_2 (-2) $\xrightarrow[OH^-]{H^+}$ H_2O (-4) — 2

Hydrogen Peroxide

$2O^{-2} \xleftarrow[2]{KI} O_2^{-2} \xrightarrow[2]{KMnO_4} O_2$ Date

☆ COMMON RA — n factor

☆ 1) $I^- \xrightarrow[OH^-]{H^+} \frac{1}{2} I_2$ — 1

2) $\overset{+6}{C_2}O_4^{-2} \xrightarrow[OH^-]{H^+} \overset{8}{2CO_2}$ — 2

3) $Fe^{+2} \xrightarrow[OH^-]{H^+} Fe^{+3}$ — 1

☆ 4) $\overset{+4}{Na_2S_2O_3} \xrightarrow[OH^-]{H^+} \frac{1}{2} Na_2\overset{+5}{S_4}O_6$ — 1

Sodium Thiosulphate
(Hypo solution)

5) $SO_3^{-2} \xrightarrow[OH^-]{H^+} SO_4^{-2}$ — 2

6) $H_2O_2 \xrightarrow[OH^-]{H^+} H_2O$ — 2

$\frac{MW}{EW} = n\text{ factor} = \frac{eq}{n} = \frac{N}{M}$

$eq = \frac{w}{EW}$ $\quad N = \frac{eq}{V}$ $\quad \frac{N}{M} = \frac{eq}{n} = n\text{ factor}$

$n = \frac{w}{M}$ $\quad M = \frac{n}{V}$

$\frac{eq}{n} = \frac{MW}{EW}$

FORMULAE

Q. $K \to 39$, $Mn \to 55$, $O_4 \to 16$

Determine mass of $KMnO_4$ req. to be dissolved for preparing 250 mL 0.1 N acidified Soln.

$KMnO_4 + H^+ \longrightarrow MnO_2$

25 meq $\quad$ 250 mL, 0.1 N $\quad$ 25 meq

$eq = \frac{w}{EW}$

$= \frac{25}{1000} \times \frac{158}{5} = 0.75$ g

$2 \times 39 = 78$, $4 \times 58 = 232$, $78 + 232 = 310$

$\frac{310}{2} = 155$, $\frac{155}{5} = 31$, $31 \times 25 = 775$, $\frac{775}{1000} = 0.775$

Q. Determine mass of Fe_2O_3 req. to be dissolved in dil. H_2SO_4 sol^n which, on red^n with Zn metal will give 250 mL 0.15 M Fe^{+2} sol^n.

MW Fe → 56

$Fe_2O_3 \longrightarrow 2Fe^{+3}$

37.5 mmole

$Fe^{+3} + Zn \longrightarrow Fe^{+2}$

0.15 N
250 mL
0.15 M
37.5 mmol Fe^{+2}

2 — 1

37.5 → $\frac{1}{2} \times 37.5$ mmol = 18.75 mmol

$\frac{18.75 \times 160}{1000 \times 100} = 3\ g$

REDOX TITRATION

1g sample MnO_2 ⟶ [ ] 250 mL.

[ ] 25 mL + $C_2O_4^{-2}$ ⟶ At end pt.

OA RA

$MnO_2 + C_2O_4^{-2} \xrightarrow{H^+} Mn^{+2} + CO_2$

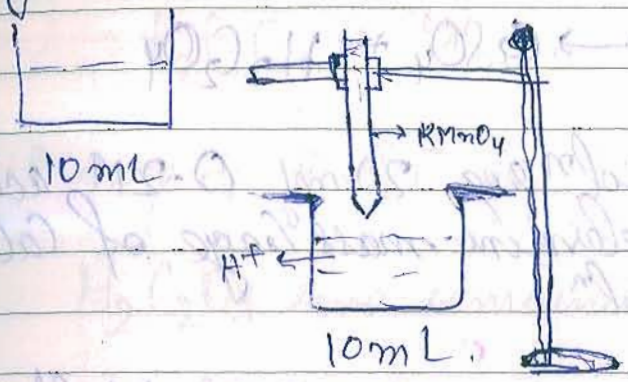
eq of $C_2O_4^{-2}$ = eq of MnO_2 in 25 mL

★ $KMnO_4$ d titration does not require any external indicator. $KMnO_4$ is called INTERNAL INDICATOR

Date

In Redox Titration, at end pt, g eq of OA = g eq of RA.

Q. lg $K_2C_2O_4$ + imp. ⟶ [ ] 100 ml



MnO_4^- ⟶ Mn^{+2}
Purple

$C_2O_4^{-2}$ ⟶ CO_2

Q. lg of a sample containing Fe_3O_4 & some inert imp is dissolved in dil. H_2SO_4 & treated with Zn pwdr which reduced all iron to Fe^{+2}. The resulting sol^n req. 40 mL 0.03M acidified $KMnO_4$ sol^n for complete oxid^n of Fe^{+2}. Determine mass % age of Fe_3O_4 in the original sample.

Fe_3O_4 + H^+ $KMnO_4$ → 0.15 N.
= 6 Meq

Fe_3O_4 + H^+ ⟶ $3Fe^{+2}$
2 mmol 6 mmol.

= 46.4 %

56
03
168
64
232
46.4

Q. 2.5 g of a mixture of ~~sample containing~~ $CaCl_2$ & NaCl is treated with excess of $Na_2C_2O_4$ (sol^n resulting in pptation of all Ca into CaC_2O_4. The ppt. is filtered & dissolved in dil. H_2SO_4 where C_2O_4 reacted with acid.

$$CaC_2O_4 + H_2SO_4 \longrightarrow CaSO_4 \downarrow + H_2C_2O_4$$

If the resulting sol^n req 20 mL 0.2 M acidified MnO_4^- sol^n. Determine mass%age of $CaCl_2$ in the original sol^n.

NaCl

$$CaCl_2 + Na_2C_2O_4 \longrightarrow CaC_2O_4 \downarrow + NaCl$$

10 mmol — 10 mmol

$$CaC_2O_4 + H_2SO_4 \longrightarrow CaSO_4 + H_2C_2O_4$$

10 mmol — 10 mmol

$$MnO_4^- + H_2C_2O_4$$

1 M — 20 meq.

~~20 mmol~~ — 10 mmol.

4 mmol

20 meq

$$\frac{10}{1000} \times 111 = \frac{21.1}{2.5} = 44.4\%$$

40
F11

Q. ~~0.6~~ g of a sample of Pyrolusite (MnO_2 ore) containing MnO_2 is dissolved in 200 mL 0.1 M $H_2C_2O_4$ sol^n & diluted to 500 mL. Excess $H_2C_2O_4$ in 100 ml of sol^n req 50 mL $\frac{1}{30}$ N $KMnO_4$ sol^n. Determine mass %age of MnO_2 in the original sample.

Mn → 55

$\frac{40-25}{3} = \frac{95}{3}$

Date

+4 +2
$MnO_2 + H_2C_2O_4 \rightarrow Mn^{+2}$

40 mmol
10 meq

500 mL

$H_2C_2O_4 + MnO_4^- \rightarrow Mn^{+2}$

5 meq of MnO_4^- for 100 ml $= \frac{5}{3}$ meq of $H_2C_2O_4$ remaining in 100 mL

meq of $C_2O_4^-$ remaining total $= \frac{25}{3}$ (500 mL)

meq of $H_2C_2O_4$ reacted with $MnO_4^- \Rightarrow \frac{95}{3}$

Mass of $MnO_2 \rightarrow \frac{95}{3} \times \frac{87}{2} \times 10^{-3}$

$= 1.377$ g

$\frac{0.65}{1.3} \times 100 = 65\%$

14 JUNE

✡ REDOX TITRATION

Q. 0.75 g of a sample containing KI & some inert imp. is treated with 50 mL of 0.1N KIO_3 sol^n. & the resulting sol^n is boiled till all I_2 evaporate out. The sol^n was cooled to room temp. & excess of

[redacted] n factor = 1

$2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

KI crystal is added. Liberated I_2 req. 16 mL of 0.1N $Na_2S_2O_3$ sol^n. Determine %age purity of original sample

I → 127.

$$\underset{3.4\text{ meq}}{[KI]} + \underset{5\text{ meq}}{[KIO_3]} \longrightarrow I_2 \uparrow \xrightarrow[\text{room temp}]{\text{cool to}} [KI\downarrow]$$

x meq KIO_3 remaining unreacted

$\longleftrightarrow$ I_2 = meq. Hypo

x meq

So, $x = 1.6$ meq

Wt. of KI = $\frac{18.6}{0.56}$ g × 100 = 318.6 = 74.4 %

Q 0.15g of a pure $(NH_4)_2SO_4$ is dissolved in H_2O & treated with excess of $BaCrO_4$. resulting in formation of insoluble $BaSO_4$. $BaSO_4$ & unreacted $BaCrO_4$ were removed by filtration & filtrate was treated with excess of KI. What volume of 0.5 M $Na_2S_2O_3$ sol^n would be req. for complete red^n of liberated I_2

$$\underset{0.15\text{g}}{(NH_4)_2SO_4} + \underset{\text{excess}}{BaCrO_4\downarrow} \longrightarrow \underset{x\text{ mol}}{BaSO_4\downarrow} + \underset{x\text{ mol}}{(NH_4)_2CrO_4}$$

moles of $(NH_4)_2CrO_4$ → $\frac{0.15}{132} = 0.0011$ mol

= 1.13 mmol

22.4 → 1
5 → 3.21

Date

6. $Cr_2O_7^{-2}$ + I^- → Cr^{+3} + I_2
1.13 mmol
3.39 meq
3.39 meq = 0.5 × V ; V = 6.8 mL

✱ VOLUME STRENGTH OF H_2O_2

Hydrogen Peroxide

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

✱ Volume Strength of H_2O_2 is → which is the volume of O_2 gas, measured at STP, produced on complete decomposition of UNIT volume of H_2O_2.

i.e 1 L → ? L
1 mL → ? mL.

eq $\frac{5}{5.6}$ eq

H_2O_2 (1 L) → $H_2O + \frac{1}{2}O_2$ (5 L O_2 at STP)

22.4 L → 32 g
5 L → $\frac{32}{22.4} \times 5$ g

$eq = \frac{32 \times 5}{22.4 \times 8}$

$eq = \frac{w}{EW}$

$= \boxed{\frac{5}{5.6}}$ = eq of O_2

So, N of $H_2O_2 = \frac{5}{5.6}$ N

vol. st. of H_2O_2 → 5
= 5 V H_2O_2

So, $\boxed{N = \frac{V.st.}{5.6}}$

Date

$KI \rightarrow H_2O_2 \xrightarrow{1 \text{ e}} \frac{6 \text{ meq}}{5.6}$

$KI \rightarrow KIO_3 \rightarrow I_2 \xrightarrow{Na_2S_2O_3}$

$Na_2S_2O_3 \rightarrow 0.6 \text{ meq}$

$= 0.6 + \frac{6}{5.6} \text{ meq} = 1.66 \text{ meq}$

$KI = 1.66 \times 166 \text{ g}$

$= 0.275 \text{ g} = 27.5\%$

Ques. 3g of a sample coal containing Fe_2O_3, Fe_3O_4 & some inert imp. is dissolved in dil H_2SO_4 & treated with excess of KI which reduced all iron to Fe^{+2}, oxidising itself to I_2. The sol^n is diluted to 100 ml & I_2 from its 20 ml req. 11 ml 0.5 M $Na_2S_2O_3$ sol^n. In a second titration, 50 ml of the stock sol^n was made free from I_2 & I^- & then req. 12.8 ml of 0.25 M acidified $KMnO_4$ sol^n for complete oxid^n of Fe^{+2}. Determine % age of Fe_2O_3 & Fe_3O_4 in the original sample.

$Fe_2O_3 \xrightarrow[n\text{ factor}=2]{KI} 2Fe^{+2}$ (2x mmol) + I_2

$Fe_3O_4 \xrightarrow[n\text{ factor}=2]{KI} 3Fe^{+2}$ (3y mmol) + I_2

x mmol = 2x meq

y mmol = 2y meq

(2x+2y) meq I_2 in 100 ml

5.5 meq I_2 in 20 ml.

$2(x+y) = 11 \times 0.5 \times 5$

$= 27.5 \rightarrow (1)$

$2x - 6 = +2$; $V.F = 3 + 3x \rightarrow \frac{3}{3}$

$\Rightarrow 3$; $\leftarrow 2$

Date

Q. A MnO_2 sample is only 60% pure. First 0.5 g of this sample is dissolved in dil. H_2SO_4 & titrated with H_2O_2 sol^n, 12 ml of H_2O_2 was req. to reach end pt. Determine V. st. of H_2O_2 sol^n.

55
32
87

$\frac{60}{100} \times \frac{5}{10}$ .3g.

$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O_2$

$\frac{0.3g \times 1000 \times 2}{87}$ meq

$= 6.89$ meq $=$ meq $H_2O_2 = 12 \times N$.

600/87

$\Rightarrow N = \frac{6.8}{12}$

200/29 6.89

V. st $= \frac{6.8 \times 5.6}{12 \times 5} = 3$

Q. 1g of a sample of KI is treated with 60 mL of H_2O_2 sol^n & the sol^n was heated to remove all I_2. The remaining sol^n was cooled & treated with excess of KIO_3 sol^n. & liberated I_2 req. 6mL 0.1M $Na_2S_2O_3$ sol^n to reach end pt. If V. st. of H_2O_2 sol^n is 1V. Determine mass %age of KI in the original sample. K → 39

I → 127

$KI + H_2O_2 \rightarrow I_2 + KIO_3 + K_2O + H_2O$

60 mL

$KI + H_2O_2 \rightarrow I_2 +$

Date

$Fe^{+2} + MnO_4^- \longrightarrow Mn^{+2} + Fe^{+3}$

$(2x + 3y)$ meq
$= (2x + 3y)$ mmol

$2x + 3y = 12.8 \times 0.25 \times 5 \times 2 \longrightarrow (2)$
$= 32.$

$\Rightarrow y = 4.5$
$x = 9.25$

Chemistry Notes
Akshansh

Ch

1. Atomic Structure
2. Periodic Table
3. Chemical Bonding

ATOMIC STRUCTURE

TOPICS

- Discovery of Fundamental Particles
- Atomic models.
- Bohr's model
- Emission Spectrum of H atom.
- Dual nature of e⁻
- Uncertainty Principle
- Quantum Nos.
- Orbitals and their shape
- Electronic Configuration.

Date

DISCOVERY OF ELECTRON

Discovery of electron occured in a discharged-tube experiment performed by Faraday which is commonly known as Cathode ray discharged tube experiment

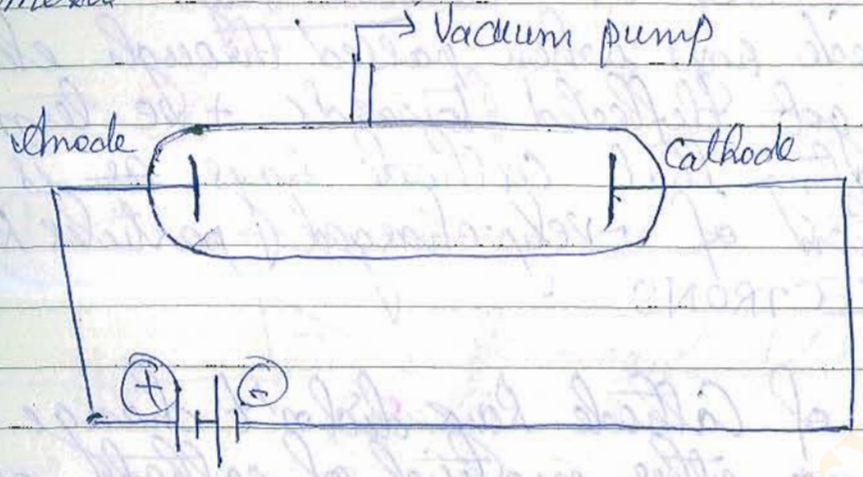


Fig: Cathode ray discharge-tube (CRDT)

In CRDT, high voltage electric discharge was produced b/w electrodes in a scaled glass tube containing gas at very low pressure.

As the circuit is completed, light rays start coming out of the surface of -ve electrode. Existence of this light rays was established as true by taking a perforated anode & coated the inner wall of glass tube with a phosphorescent (ZnS) material behind that anode.



Glowing up of the ZnS coating indicate that light rays are produced from Cathode surface.

Since these light rays are produced from cathode surface, they were called — cathode rays.

☆ PROPERTIES OF Cathode Rays

1) Cathode rays when passed through electric field got deflected towards +ve terminal indicating that cathode rays, as is a collection of -vely charged particles known as ELECTRONS.

2) Nature of Cathode Rays didn't change on changing either material of cathode or the gas in the discharged tube.
It was deduced that electrons are present in all matter & have same property in all of them i.e it is an atomic particle present inside the atom of all matter.

3) ~~Electrons~~ Cathode Rays when passed through magnetic field, it got deflected, indicating that it has magnetic property.

4) When a thin metal foil is placed in the path of cathode ray, it got heated.
It indicated that the cathode ray has kinetic energy.

5) When a frictionless, mass-less, rotating paddle when placed in the path of Cathode ray, it start rotating. It indicated that electron has got momentum. So, it also has mass. (mv)

Date

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✡ THOMSON'S EXPERIMENT / e/m determination.

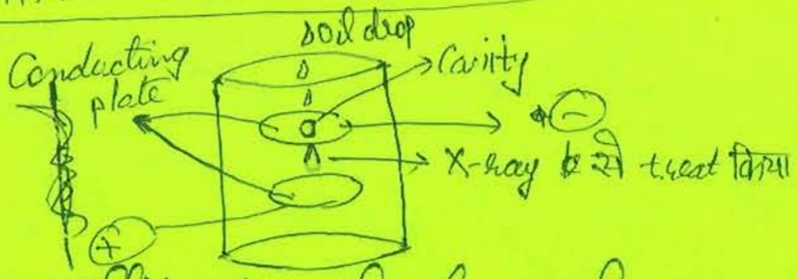
Thomson performed experiment on cathode ray in the same discharged tube under the influence of variable electric & magnetic field. & deflections under different conditions ~~co~~ were used to determine the charge to mass (e/m) ratio.



In the ~~Thomson~~ Thomson's experiment, electric & magnetic field, ⊥ to one another. and also, ⊥ to the path of cathode ray were applied ~~& the electric & ma~~ simultaneously. The strength of magnetic & electric field were adjusted in order to produce 0 deflection in the path of cathode ray & ~~et~~ equated to determine the e/m ratio.

✡ $\frac{e}{m} = 1.75 \times 10^{11}\ C\ kg^{-1}$

✡ MILLIKAN'S OIL-DROP EXPERIMENT TO DETERMINE ELECTRONIC CHARGE



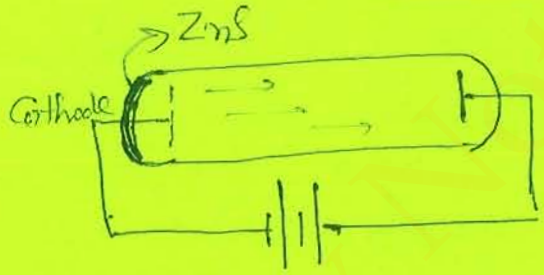
From the Millikan's oil-drop ~~eb~~ exp., charge on an e^- was measured to be 1.602×10^{-19} C.

$\star (e^-)_{mass} = \frac{e}{e/m} = m = 9.1 \times 10^{-31}$ kg ★

2 JULY

★ Discovery of Anode (Canal ray) or Protons -

GOLDSTEIN EXPERIMENT



- Discovery of Anode ray
In the discharged tube exp., when perforated cathode was used & the inner wall of the tube behind the cathode was coated with ZnS, flashes of light were observed on ZnS screen on producing discharge (completing circuit) in the tube. This indicated that some light rays originating from Anode surface are travelling towards cathode. ∴ They are called Anode rays.

On analysis anode rays were found to be +vely charged.

★ PROPERTIES OF Anode rays in Electric & Magnetic field were found to be completely opposite to the properties of Cathode rays. Unlike cathode rays, properties of anode rays also depends on the nature of anode surface & the nature of gas present in the discharged tube.

Date

☆ DISCOVERY OF NEUTRON (CHADWICK)

In his alpha particle exp. on Be foil, light rays were produced which was found to be electrically neutral ∴ named - NEUTRON RAYS. The particles of the rays were called neutrons. He established that neutrons are emitted from all type of atoms (except H.)
∴ neutrons it is also a basic particle present in atom of all matters.

☆ ATOMIC MODEL

Thomson's model

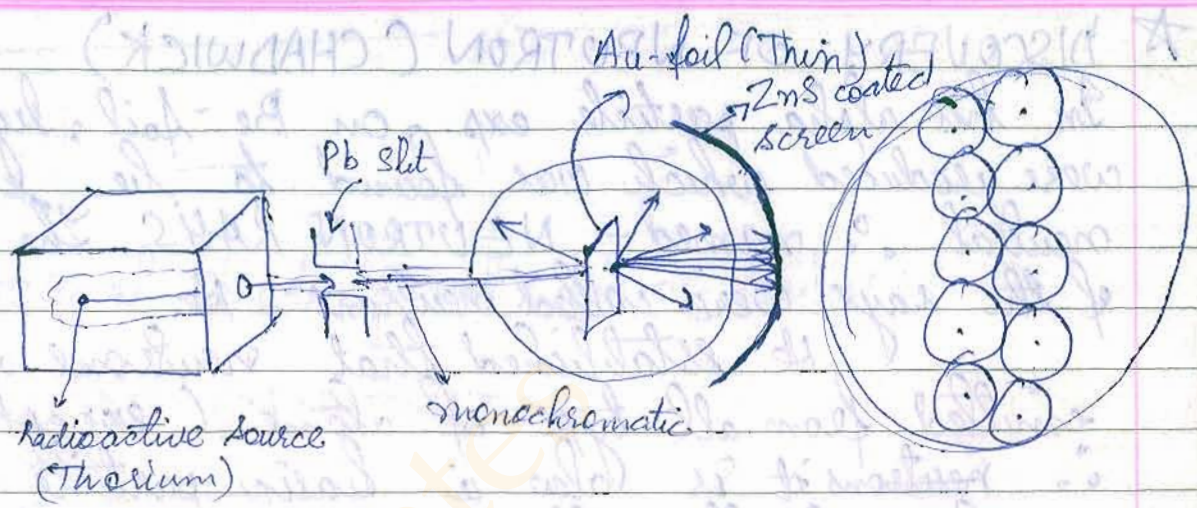
Acc. to Thomson's model atoms are all spherical with +ve charge uniformly distributed in the entire atom. To maintain the electro-neutrality of atom, -vely charged electrons are embedded like seeds in watermelon.

Rutherford's Model of Atom (Nuclear model)

Rutherford's model of atom is BASED ON an Expt. knowns as Alpha Particles Scattering expt.

↓

In this expt., α-particles (He^{+2} - doubly ionized Helium) from a radioactive source where were bombarded on a thin gold foil & then observed on a flourescent screen (ZnS coating)



Q ✱ Why thin gold foil was used?

A → In α- ray exp^t., it was intended that the α-ray encounter just 1 atom on its passes through foil so that the observation could reveal the structure inside the atom appropriately ∴ THIN gold foil is essential to make encounter of 1 atom with α-ray.

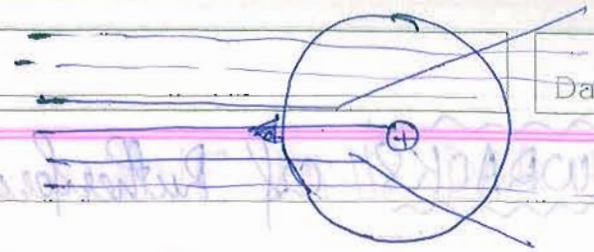
✱ lead is used to produce monochromatic α-rays so that rays go in one single dirn, that's why slit was also used of lead.

OBSERVATIONS

FIRST Most of the α-rays passed undeflected from the thin gold foil. 

2nd Some α-rays suffered small deflection from its original path.

3rd Very few (1 out of approx. 20,000) ~~α-part~~ α-particle bounced back on its original path.



Date

CONCLUSION

FIRST → On the basis of 1st observation, Rutherford concluded that most part of the atom is empty.

2nd On the basis of 2nd & 3rd observations, Rutherford concluded that ∃ highly dense, +vely charged centre in the atom which he called NUCLEUS. When +vely charged α-particles passes in the vicinity of this nucleus, they are deflected away due to repulsion b/w the like charges. When α-particles directly collide with nucleus, they returned back on its original path.

3rd Entire mass of the atom is concentrated in the nucleus.

On the basis of α-particle scattering expt, Rutherford proposed a model of atom. Acc. to Rutherford,

atom is spherical with a +vely charged, highly densed nucleus. Size of the nucleus is negligible in comparison to the size of atom.

* Atomic radius is in the order of $1 Å = 10^{-10} m$.
Radius of nucleus = $10^{-15} m$.

To make the atom neutral, electron revolve around the nucleus in circular orbit exactly like planets revolving around the Sun in solar system.
So, his model is also called PLANETARY MODEL

Date

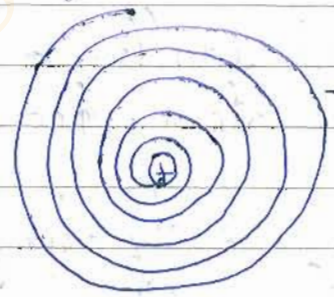
☆ DRAWBACKS of Rutherford's Model

FAILURE

1+ Acc. to classical mechanics, an object revolving in a circular path experiences accⁿ (due to change in dirn at every pt.

2+ Acc. to classical theory of electromagnetic radiation, an accelerating charge particle loses energy in the form of radiation during its motion.

+3 Based on the above theories, it is concluded that revolving electrons in circular orbit loses energy continuously.



→ Spiral path of decreasing curvature

+4 On the basis of the classical theory, electrons in Rutherford's model describes a spiral path of decreasing curvature & finally falls into the nucleus.

+5 ∴ Rutherford proposed a model of unstable atom & was discarded.

+6 Rutherford model of atom couldn't explain the arrangement of electrons in the atom (how they are arranged)

Date

☆ LIGHT AS WAVE AND PARTICLE

- Light is an electromagnetic wave characterized by wavelength (λ) & frequency (ν). They 2 are related as –

$$\nu = \frac{c}{\lambda} \rightarrow c \text{ is speed of light}$$
$$c = 3 \times 10^8 \text{ m/s}$$

☆ PLANK THEORY

According to Plank's Quantum Theory, light is a form of energy & energy occur in the form of packets known as Photon.



Acc. to Plan's Quantum theory energy of photon is directly proportional to frequency of light.

$$E \propto \nu$$
$$\Rightarrow \boxed{E = h\nu} \text{ Plank's eqn.}$$

h = Plank's constt.

Plank's constt. = 6.626×10^{-34} JS.

Now,

$$\boxed{E = \frac{hc}{\lambda}}$$

Q. In H_2 molecule, there is a single covalent bond b/w H_2 atom which can be broken (cleave) by light. If bond energy of H_2 is 436 KJ/mol. & 1 photon can break only 1 bond, determine the max. wavelength of light which can bring about dissociation of H_2.

Soln:

$$H \xrightarrow{e} H^+ + e$$

Min. energy req. to break bond = 436 KJ/mol.

$$E \propto \frac{1}{\lambda}$$

$$e = \frac{436 \times 10^3}{N_A} J = \frac{436 \times 10^3}{6 \times 10^{23}} = 73 \times 10^{-20} J$$

(e) → min Energy

$$E = \frac{hc}{\lambda}$$

$$73 \times 10^{-20} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{\lambda}$$

$$\Rightarrow \lambda = \frac{6.625 \times 3 \times 10^{-26}}{73 \times 10^{-20}}$$

$$= \frac{19.875 \times 10^{-6}}{73} m$$

$$= 2.7 \times 10^{-7} m$$

$$= 2.7 \times 100 \times 10^{-9}$$

$$= 2700 nm$$

or 2700 Å

16.625 / 1987.5 / 1.73 / 02 / 1.56 / 198 / 156 / 427

Q. Efficiency of a 60 W bulb is just 10% & it produces a light of $\lambda \rightarrow 600$ nm. Determine the no. of photons emitted by this bulb / hr.

$E = h\nu$

$E = \frac{hc}{\lambda}$

$P = \frac{E}{t}$

$E = 60$ J/s

$E = 6$ J/s (10%)

1 → 6 J

60 → 6 × 60 × 60

Total energy = 21600 J in 1 hr.

$$E = \frac{6.625 \times 10^{-34} \times 3 \times 10^{8}}{600 \times 10^{-9}}$$

$$= \frac{19.875 \times 10^{-26}}{600 \times 10^{-9}}$$

$$= \frac{19.875 \times 10^{-19}}{600}$$

$$E_\lambda = 3.312 \times 10^{-19}\ J$$

No. of photons $= \frac{21600}{3.312 \times 10^{-19}}$

$$= \frac{21600 \times 10^{19}}{3.312}$$

$$= \frac{21600 \times 10^{22}}{3312}$$

$$6\frac{72}{92} \times 10^{22}$$

$$\frac{92}{92}$$

$$6.5 \times 10^{22}$$

∴ No. of photons $= \boxed{6.5 \times 10^{22}}$

☆ BOHR'S MODEL (Very Imp)

Bohr's model is a modification of Rutherford's Nuclear Model.

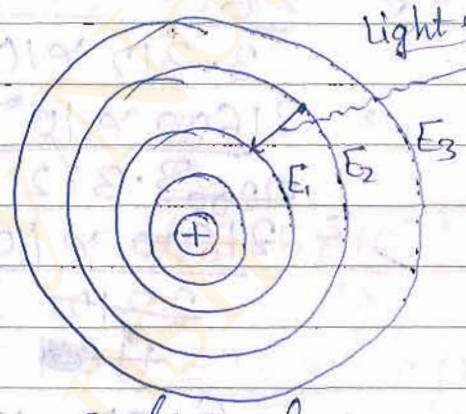
Bohr's model of atom is based on certain assumptions known as POSTULATES OF BOHR MODEL. (assumption)

POSTULATES

1) Acc. to Bohr model, electrons do not revolve in any arbitary orbit. Rather, they revolve only in certain fixed circular orbit known as 'STATIONARY ORBITS' (SO.)

(2) As long as electron revolves in a stationary orbit, it doesn't radiate energy.

(3) Electron loses energy only when it jumps from a higher S.O. to lower S.O. — known as Electronic Transition. Energy released in an electronic transition is always = difference in the energy of S. Orbits.

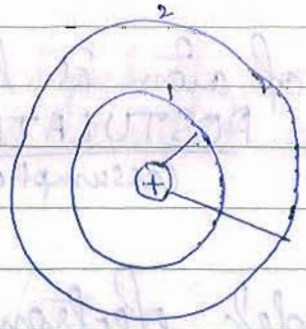


Note:

☆ An electron in the atom can be promoted in the higher orbit by absorption of energy. Energy ~~als~~ absorbed will be = the energy diff. of ~~the~~ S.O.

5 JULY

☆ Bohr's Radius



Acc. to Bohr model, Angular momentum of an electron in a stationary orbit is quantized (electron can only have energy in the form of $\frac{h}{2\pi}$)

ϵ_0 → epsilent → permitivity of vacuum

Date

& it is integral multiple of $\left[\frac{h}{2\pi}\right]$

Mathematical deduction of POSTULATE 1:

$$mvr = n\left[\frac{h}{2\pi}\right]$$

$n = 1, 2, 3, 4 \ldots \infty$

n = Orbit number.

$h = 6.625 \times 10^{-34}$.

* Centrifugal force working on outside of an e^- is exactly balanced by an electrostatic force in the inward dirn.

$$\text{Centrifugal force} = \frac{mv^2}{r}$$

Electrostatic force of attraction b/w 2 charged particles (F) $\propto \frac{q_1 q_2}{r^2}$

☆ LIMITATIONS

1) Bohr model is applicable only to H_2 & ~~light~~ like species: (Atom or ion containing 1 electron only) were considered in Bohr model.

Electrostatic attraction b/w so & nucleus.

$$F = \left(\frac{1}{4\pi\epsilon_0}\right)\left(\frac{q_1 q_2}{r^2}\right)$$

$q_1 = ze$ (charge on nucleus)

$q_2 = e$ (charge on electron)

$$\Rightarrow \left[F = \left(\frac{1}{4\pi\epsilon_0}\right)\left(\frac{ze^2}{r^2}\right)\right], \quad z \rightarrow \text{no. of proton}$$

$\epsilon_0 = 8.85 \times 10^{-12}$ ~~C~~ $N m^2 C^{-2}$

Date

Now,

$$F = \left(\frac{1}{4\pi\epsilon_0}\right)\left(\frac{Ze^2}{r^2}\right) = \frac{mv^2}{r} \quad \text{(centrifugal force)}$$

$$mvr = n\frac{h}{2\pi} \rightarrow (1)$$

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \rightarrow (2)$$

Very Imp

From (1),

$$v^2 = \frac{n^2h^2}{4\pi^2 m^2 r^2}$$

Using (1) in (2)

$$\Rightarrow m\left(\frac{n^2h^2}{4\pi^2 m^2 r^2}\right) = \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\Rightarrow r = \frac{n^2h^2\epsilon_0}{m\pi Ze^2}$$

Const^{tt} $\rightarrow 8.85 \times 10^{-12}$ $N m^2 C^{-2}$

$m \rightarrow$ mass of e^-

$$\Rightarrow r = \frac{n^2\left(\frac{h^2\epsilon_0}{e^2 m\pi}\right)}{Z}$$

LEARN

$n \rightarrow$ orbits

$Z \rightarrow$ no. of protons

$h \rightarrow$ Const^{tt}.

$\epsilon_0 \rightarrow$ Const^{tt}. (Permittivity of vacuum)

$e^2 \rightarrow$ charge of e^- $\rightarrow$ Const^{tt}.

$m \rightarrow$ mass of e^- $\rightarrow$ Const^{tt}.

$\pi \rightarrow$ Const^{tt}.

$$\Rightarrow r = a_0\left(\frac{n^2}{Z}\right); \quad a_0 = \frac{h^2\epsilon_0}{\pi m e^2}$$

a_0 = First Bohr radius of H-atom (Read as)

$a_0 = 0.53\ \text{Å} = 53\text{pm}$

r_n (n^{th} Bohr radius) $= \frac{a_0 (n^2)}{Z}$

Q. Determine 3rd Bohr radius of He^{+}

$Z = 2$

$= 2.385\ \text{Å}$

$53 \times 45 = 265 + 212 = 2385$

n^{th} Bohr radius of H = x (n^{th} Bohr radius of Li^{+2})

$r_n(H) = a_0\left(\frac{n^2}{1}\right) = x \cdot r_n(Li^{+2})$

$= x\, a_0 \left(\frac{n^2}{3}\right)$

$a_0\left(\frac{n^2}{1}\right) = x\,(a^0)\left(\frac{n^2}{3}\right)$

$Li = 3$

$\Rightarrow \boxed{x = 3}$

So, 1st Bohr rad. of Li^{+2} ion = $\frac{1}{3}$rd of 1st Bohr rad. of H atom

So, $r_n(H) = Z\, r_n(A)$ → ion of that atom

at. no. of atom

★ SPEED OF ELECTRON

$mvr = \frac{nh}{2\pi}$

$\Rightarrow v = \frac{nh}{2\pi m r}$

Now, $r = a_0\left(\frac{n^2}{Z}\right)$

$\Rightarrow v = \frac{nh(Z)}{2\pi m (a_0)(n^2)} \Rightarrow \frac{hZ}{2\pi m a_0 n}$

Imp: $\Rightarrow \boxed{v = \left(\frac{h}{2\pi m a_0}\right)\left(\frac{Z}{n}\right)}$

Date

$$\Rightarrow \boxed{v = \left(\frac{h}{2\pi m a_0}\right)\left(\frac{Z}{n}\right)}$$

$$\Rightarrow \boxed{v = (2.18 \times 10^6)\left(\frac{Z}{n}\right) \text{ m/s}}$$

∴ If 2 ~~atoms~~ electrons of same shell are compared, so value of Z (at. no.) will decide speed of electron.

MP

★ For the same atom/ion, speed of e⁻ decreasing on increasing n. i.e, as we move away from nucleus, speed of e⁻ decreases.

★ For diff. species in the same orbit, higher the at. no., greater the speed.

Q. Determine the no. of revolutions made by an e⁻ in the second Bohr orbit of H atom in 1 min.

$r = 0.53$ Å $= 0.53 \times 10^{-10}$ m.

$v = \frac{2.18 \times 10^6}{2}$

$v = 1.09 \times 10^6$ m/s.

$2\pi r = 2 \times 3.14 \times 0.53 \times 10^{-10}$.

$= 3.33 \times 10^{-10}$ m.

1.09×10^6 m → 1 sec

1.09×10^6 m → 1sec

12
6 ⊛ 66×10^6 m → 1min

⊛ $\frac{66 \times 10^6 m}{3.18 \times 10^{-10}}$

$= \frac{66 \times 10^{16}}{3.18}$

$= \frac{3366 \times 10^{18}}{318}$

$= \frac{33}{109} \times 10^{18}$

109
103
327

$= 0.302 \times 10^{18}$

$= 3.02 \times 10^{17}$

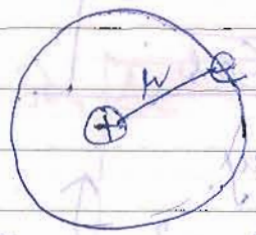
OR

$\ell pm = \frac{V \times 60}{2\pi r}$

$= \frac{V_0 (Z/n) 60}{2\pi a_0 \frac{n^2}{Z}} = \frac{2.18 \times 10^6 \times 60}{2 \times 3 \times 0.53 \times 10^{-10}} \times \frac{Z^2}{n^3}$

$= 5 \times 10^{16}$ rpm.

★ ENERGY

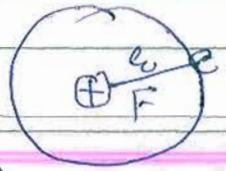


E = K.E + P.E

K.E = $\frac{1}{2} mv^2$.

$\frac{1}{2} \frac{mv^2}{r} = \frac{1}{2} \frac{Ze^2}{4\pi\epsilon_0 r^2}$ ⇒ $\frac{1}{2} mv^2 = \frac{1}{2} \frac{Ze^2}{8\pi\epsilon_0 r}$ → ①

★ K.E



Date

☆ Potential Energy of an electron in a Bohr orbit : It is -ve of of work done involved in moving e⁻ from distance to ∞.

$$P.E. = -\int F\,dr$$

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}$$

$$= -\frac{Ze^2}{4\pi\epsilon_0}\int_r^\infty \frac{dr}{r^2}$$

$$= \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right)_r^\infty$$

$$= \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{\infty}\to 0 - \frac{1}{r}\right)$$

$$\Rightarrow \boxed{P.E. = -\frac{Ze^2}{4\pi\epsilon_0 r}}$$

$x^3 \to 3x^2$

$$\int_{x_1}^{x_2}\frac{dx}{x^2} = \left(\frac{-1}{x}\right)_{x_1}^{x_2}$$

$$E = K.E + P.E$$

$$= \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$= \frac{Ze^2}{4\pi\epsilon_0 r}\left(\frac{1}{2} - 1\right)$$

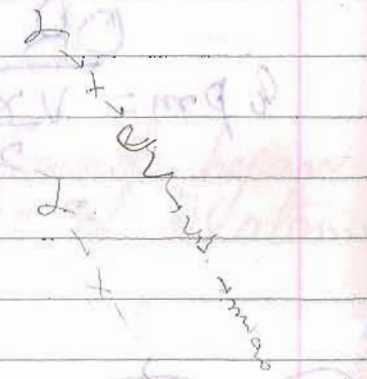
$$\Rightarrow \boxed{E = -\frac{Ze^2}{8\pi\epsilon_0 r}}$$

Total energy.

Now, $r = a_0\frac{n^2}{Z}$

$$\Rightarrow E = -\frac{Z^2e^2}{8\pi\epsilon_0 a_0 n^2}$$

$$\Rightarrow \boxed{E = \left(\frac{-e^2}{8\pi\epsilon_0 a_0}\right)\left(\frac{Z^2}{n^2}\right)}$$ Imp.



Imp:

Date

⇒ $E = -K\frac{Z^2}{n^2}$; $K = \frac{e^2}{8\pi\epsilon_0 a_0}$ J ; $K = 2.18\times10^{-18}$ J

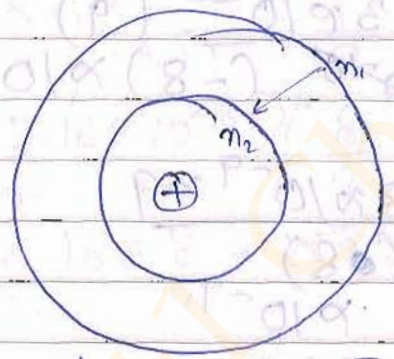
$= 13.6$ eV

(-) ~~Sign indicates restoring~~.

-ve sign of energy of so, indicates restoring nature of energy i.e supplying energy = $\left|\frac{KZ^2}{n^2}\right|$ will make e⁻ independent of nucleus.

तात्पर्य → KZ^2 की Energy आधार electron को दे तो वो nucleus n^2 से बाहर हो जाएगा।

☆ TRANSITION ~~ELEMENTS~~ ENERGY



Energy released = $E_2 - E_1 = \Delta E$ (Transition energy)

$\Delta E = KZ^2\left(\frac{1}{(n')^2} - \frac{1}{(n^2)^2}\right)$; $n_1 > n_2$

So, $\Delta E = KZ^2\left(\frac{1}{(n')^2} - \frac{1}{(n^2)^2}\right) < 0$

i.e energy is evolved

$\Delta E = KZ^2\left(\frac{1}{(n')^2} - \frac{1}{(n^2)^2}\right)$

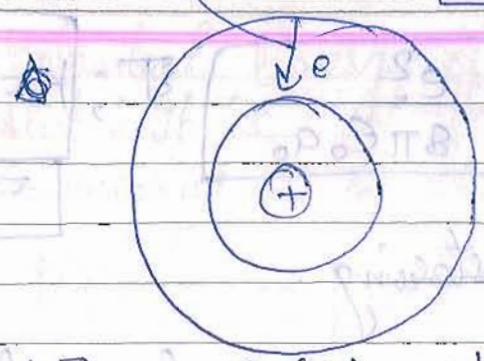
; $n_1' < n_2$

energy is absorbed

Imp:

$\frac{1}{\lambda} = \bar{\nu}$

Date



$$\Delta E = KZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu$$

Q. Determine the wavelength of light emitted when an electron from the 3rd orbit of H-atom return to 1st-orbit.

$$\Delta E = (2.18\times10^{-18})(1)^2\left(\frac{1}{1} - \frac{1}{9}\right) = \frac{6.625\times10^{-34}\times3\times10^{8}}{\lambda}$$

$$\Rightarrow \lambda = \frac{6.625\times3\times10^{-8}\,(9)}{2.18\times10^{-18}\,(-8)\times10}$$

$$\Rightarrow \lambda = \frac{6.625\times3\times10^{-9}\times9}{218\times(8)}$$

$$= \frac{9.78875}{1744}\times10^{-9}$$

$$= 100\,nm$$

$$\frac{hc}{\lambda} = KZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Rightarrow \frac{1}{\lambda} = \left(\frac{K}{hc}\right)(Z^2)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$\frac{K}{hc}$ → const^{n} (R_H)

Imp: Eqn for transition wavelength.

Imp: $\frac{1}{\lambda} = \bar{\nu}$ (wave number) $= R_H Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Imp: $R_H = 1.079\times10^{7}\,m^{-1}$ RYDBERG'S EQUATION

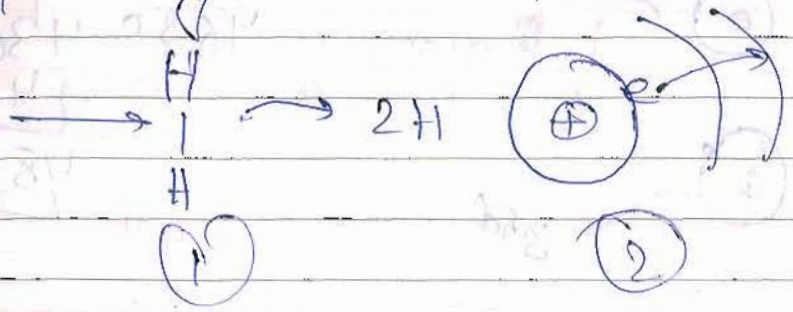
1 1 1 1 1 1
46625
0271
46375
9325
9325
978875
1218 6
08
1744

★ The orbit closest to nucleus is called Ground state orbit.
★ Other orbits are called excited state. eg: $n=2$ = 1st excited state.

Date

Q. Quartz bulb contain H_2 gas 1 mole of H gas. Bond energy of H_2 is 436 KJ/mol. Determine the total energy req. for complete dissociation of H_2 into atoms followed by transition of electrons in the 3rd orbit.

(a)



(1) Dissociation of H_2

So, $E = 436$ KJ. → (2)

(2) Transition energy.

$\Delta E = K(1)^2\left(\frac{1}{1} - \frac{1}{9}\right)$

$= \left(2.18 \times 10^{-18}\right)\left(\frac{8}{9}\right)$ J/atom.

$= \left(2.18 \times \frac{8}{9} \times 10^{-18} \times 6 \times 10^{23}\right)$ J/mol. (2)

$= 2.18 \times \frac{8}{4} \times 6 \times 2 \times 10^5$ — 2H atom, 2 moles

$= \left(\frac{2.18 \times 32}{3} \times 10^5\right)$ J/mol.

$= \left(\frac{69.76}{3} \times 10^5\right)$ J/mol.

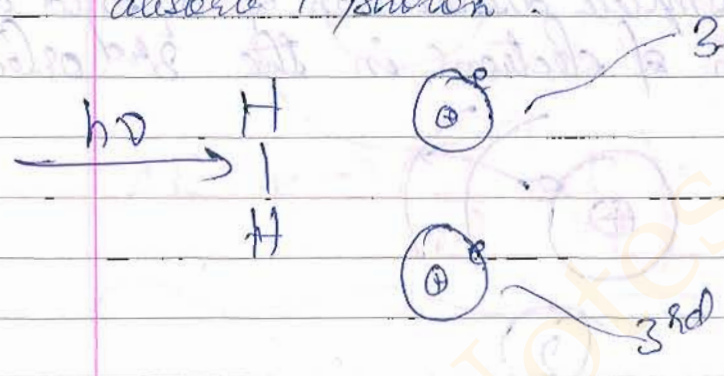
$= 23.25 = 3 \times 10^5$ J/mol.

$= 2.325 \times 10^6$ J/mol. → (1)

$E =$ (1) + (2)

218
e32.
436
654
6976

(b) Determine the max. λ light which can bring about this change assuming that 1 molecule of H absorb 1 photon.



436000
46500
482500

We know

E. of photon = (Bond. E) + (2× Transition E)

$\Rightarrow \frac{hc}{\lambda} = 436\ kJ + 2(2.325 \times 10^{4}\ J/mol)$

$\Rightarrow \frac{hc}{\lambda} = 436000 + 4.650 \times 10^{4}\ J/mol$

$\Rightarrow \frac{6.625 \times 10^{-34} \times 3 \times 10^{8}}{4.65 \times 10^{4}} = \lambda$

$\Rightarrow \lambda = \frac{6.625 \times 10^{-34} \times 3 \times 10^{8}}{482500}$

$\Rightarrow \lambda = \frac{6.625 \times 10^{-26} \times 3}{4.82500}$

$= \frac{19.875 \times 10^{-21}}{4.825}$

$\Rightarrow \lambda = \frac{19875 \times 10^{-21}}{4825}$

$\Rightarrow \lambda = 4.1 \times 10^{-21}\ m$

16.625
e3
19875
34825
e4
19300
19875
19300
5700

Date

9 JULY

1) $\Delta E = -K Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$K = 2.18 \times 10^{-18}$ J

2) $\frac{1}{\lambda} = \bar{\nu} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$R_H = 1.079 \times 10^7\ m^{-1}$

Q. A Hydrogen like species is in some excited state. When it returns back to the 1st excited state, light of energy E (photon) → 27.2 eV is emitted. Same species when return back from same excited state but to 2nd excited state, photon of E → 10.2 eV is emitted. Determine the orbit no. in which the electron is present originally & at. no. 'Z' of species...

$$27.2\,eV = 13.6 (Z^2) \left(\frac{1}{n_1^2} - \frac{1}{2^2}\right)$$

$$\Rightarrow \frac{27.2}{13.6} = Z^2 \left(\frac{1}{n_1^2} - \frac{1}{4}\right)$$

$$\Rightarrow Z^2 \left(\frac{4 - n_1^2}{4 n_1^2}\right) = 2 \longrightarrow (1)$$

Now,

$$10.2\,eV = 13.6 (Z^2) \left(\frac{1}{n_1^2} - \frac{1}{9}\right)$$

$$\Rightarrow \frac{10.2}{13.6} = Z^2 \left(\frac{9 - n_1^2}{9 n_1^2}\right)$$

68

$$\Rightarrow z^2 = \frac{51\,(9n_1^2)}{68\times(9-n_1^2)} \quad \&$$

$$z^2 = \frac{2\,(4n_1^2)}{(4+n_1^2)} = \frac{51}{68}\,\frac{(9n_1^2)}{(9+n_1^2)}$$

$$\Rightarrow \frac{8\times 68}{(n_1^2-4)} = \frac{51\times 9}{68\,(n_1^2-9)}$$

Or

$$\frac{27.2}{10.2} = \frac{\left(\frac{1}{4}-\frac{1}{n^2}\right)}{\left(\frac{1}{9}-\frac{1}{n^2}\right)}$$

$$136$$

$$\Rightarrow \frac{272}{102} = \frac{0.25-1/n^2}{0.11-1/n^2}$$

$$51 \qquad 12.75$$

$$\Rightarrow 14.96 - \frac{136}{n^2} = 12.75 - \frac{51}{n^2}$$

$$\Rightarrow 2.21 = \frac{85}{n^2}$$

(Check)

$$\Rightarrow n^2 = \frac{8500}{221}$$

$$\Rightarrow n = 6.$$

So, $27.2 = 13.6\,z^2\left(\frac{1}{4}-\frac{1}{36}\right)$

$$\Rightarrow 27.2 = 13.6\,z^2\left(\frac{36-9}{36}\right)$$

$$\Rightarrow \frac{2}{z^2} = \frac{27}{36}+\frac{3}{8}$$

$$\Rightarrow \frac{8}{3} = z^2$$

$$\Rightarrow z = 3.$$

14.96
12.75
2.21

225
5.1
25
125
125
12.75

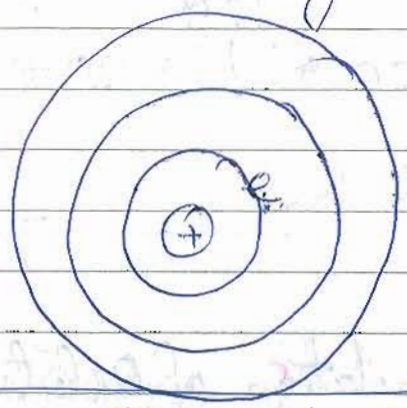
136
51
85

122 | 6.
13 26

Date

☆ IONIZATION ENERGY (IE)

Ionisation energy is the min. energy req. to remove the most ~~loost~~ loosely held e^- from ground state of a gaseous atom or a gaseous ion



$H_2(g) \xrightarrow{IE} H^+(g) + e^-$

$1m + e^-$, $IE = KZ^2\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = KZ^2$.

(APPLICABLE FOR EVERY ONE e^- SPECIES)

$He(g) \xrightarrow{IE_1}$ (To remove 1st e^-) $He^+(g) + e^-$

$He^+(g) \xrightarrow{IE_2}$ (To remove 2nd e^-) $He^{+2}(g) + e^-$

13.6, e^4, 54.4 ✓ Applicable for Bohr model

So, $IE_2 = KZ^2\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$

$\Rightarrow IE_2 = KZ^2$ ✓ $= 13.6 \times 4 = 54.4$

Q Consider the following ionization reaction.

~~$Li^{+3}(g)$~~

$Li(g) \rightarrow Li^{+3}(g) + 3e^-$, $E = 14000$ KJ/mol of $Li(g)$

If 1st IE_1 of Li is 520 KJ/mol Determine its 2nd IE_2.

$IE_3 = 122.4 \times N_A$

$= 734.4$

$2.18 \times 10^{-18} \times 9 \times N_A$

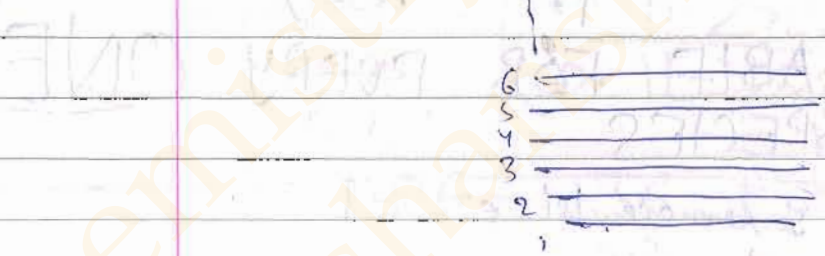
$= 11772 \times 10^{-18} \times 10^{23}$

$= 11772 \times \frac{10^5}{1000} = 11772$ KJ/mol.

$IE_2 = \frac{1}{4} \times 1000 \times [520 + 11772]$

$= 1708$ KJ.

☆ Easier representation of Orbits of atoms



$\Delta E = kz^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

(A) $\Delta E_{n \to 1} = kz^2 \left(1 - \frac{1}{n^2}\right)$

$\Delta E_{\substack{n \to 1 \\ min}} = kz^2 \left(1 - \frac{1}{4}\right)$

$\Rightarrow \boxed{\Delta E_{\substack{n \to 1 \\ min}} = \frac{3}{4} kz^2}$

(B) $\Delta E_{n \to 2} = kz^2 \left(\frac{1}{4} - \frac{1}{n^2}\right)$

$\Delta E_{\substack{n \to 2 \\ max}} = kz^2 \left(\frac{1}{4} - \frac{1}{\infty}\right)$

$\Rightarrow \boxed{\Delta E_{\substack{n \to 2 \\ max}} = \frac{1}{4} kz^2}$

CONCLUSION

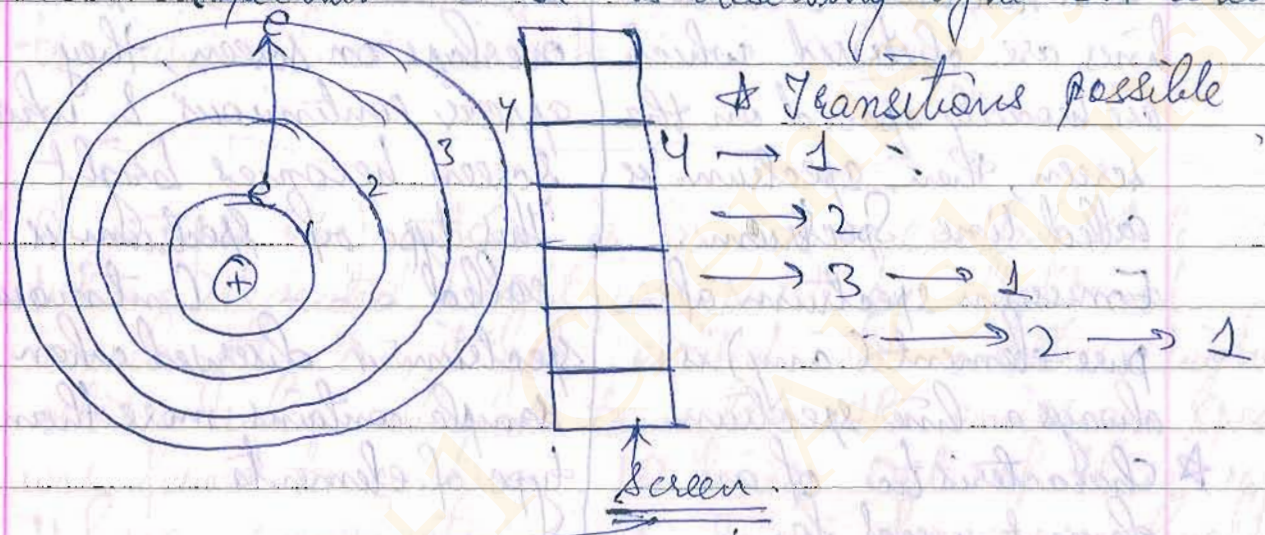
Date

(1) ☆ When e⁻ comes in lower orbit, photons of ☆ higher E is emitted, irrespective of the initial orbit no. involved in electronic transition.

(2) As we move away from nucleus S.O. comes closer & closer i.e energy gap b/w adjacent S-orbits ~~increases~~ decreases on increasing n.

☆ EMISSION & ABSORPTION SPECTRUM

Spectroscopy - Study of spectrum.
Spectrum ↔ It is observing light on screen.



☆ Transitions possible

Properties

It has lines → ~~many~~ drawn of (microscopic) which detects wavelength & when the light of wavelength ~~so~~ intersects with wavelength of screen → same, then, light of that λ would diffract.

☆ When only ~~so~~ few lines are observed on Spectrum → LINE SPECTRUM.

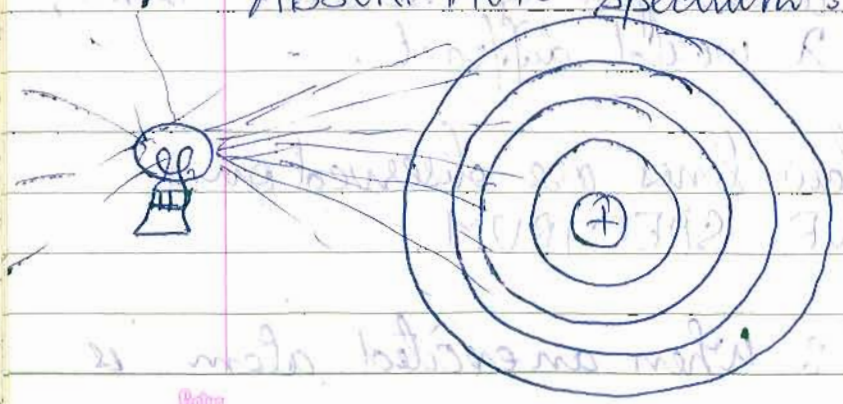
☆ Emission spectrum : When an excited atom ~~is~~

Give energy to atom & Excitation
Remove external energy from atom & Relaxation

allowed to relax, light rays are emitted. Since, only certain fixed transitions occur in an atom. Light rays of certain fixed wavelengths are emitted from excited atom. When these light rays are observed on a diffraction grating (screen), certain bright linings are observed). This type of spectrum is known as EMISSION SPECTRUM.

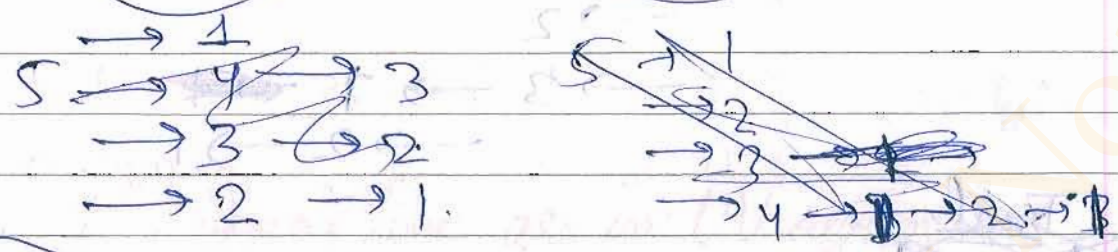
Line	Continuous
~~☆ Emission Spectrum of pure atom is called~~ When only certain lines are observed which are broadly spaced on the screen, then spectrum is called Line Spectrum. Emission spectrum of pure element (any) is always a line spectrum. ☆ Characteristic of an element used for finger printing of that element.	When the emission lines overlaps on screen, they apear continuous & whole screen becomes bright. This type of spectrum is called. Continuous spectrum is observed when sample contains more than 1 type of elements.

☆ ABSORPTION Spectrum:



When light from a source is made to incident on a sample of atom, certain wavelengths are absorbed for Electronic transition to higher orbit. Those

wavelengths are not observed on the screen. Missing wavelengths appears on the screen as dark line on bright background. This type of spectrum is called ABSOAPTION SPECTRUM. It can also be line Spectrum or Continuous Spectrum like Emission Spectrum.



☆ For any excited atom, the max. no. of ~~excite~~ transition lines will be $\rightarrow \frac{n(n-1)}{2}$.

Q. ☆ A sample of H-atom is in some excited state 'n'. When irradiated (light was put) by light of wavelength λ, it gets excited into another higher orbit. When allowed to relax, the emission spectrum was found to contain 10 lines. Out of these 10 lines, 4 have wavelengths $< \lambda$ & 5 have wavelengths $> \lambda$

Q.1 ☆ Determine the final orbit no.
Q.2) Determine original orbit no.
Q.3) Determine value of λ.

$10 = \frac{n(n-1)}{2} \Rightarrow n = 5$

So final orbit no. = 5

We know

$E \propto \frac{1}{\lambda}$



Date incident energy

So, 4 wavelengths of more energy than 5
5 " " less " " " .

5 → 1
→ 2
→ 3
→ 4 → 1
→ 2
→ 3 → 1
→ 2 → 1

Let $n = 4$

Ans-2 Originally e⁻ was in 2

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{4} - \frac{1}{25}\right)$$

$$\Rightarrow \lambda = \frac{100}{(R_H)\,21}$$

$$= \frac{100 \times 10^{-7}}{1.079 \times 21}$$

$$= \frac{4.8 \times 10^{-7}}{1.01}$$

$$= 480 \times 10^{-9}$$

$$= 480\ nm.$$

★ EMISSION SPECTRUM OF H-atom

⇒ Emission Spectrum of H-atom was investigated by several scientists in the diff. regions of electromagnetic radiations as follows:

Date

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

400 - 700 nm

UV	Visible	IR

(A) LYMAN SERIES

All transitions to 1st orbit are known as LYMAN Transitions & corresponding lines in the Emission spectrum are called LYMAN lines.

i.e

$$\frac{1}{\lambda}\Big|_{Lyman} = R_H Z^2 \left(\frac{1}{1^2} - \frac{1}{n^2}\right), \quad n = 2, 3 \text{ ---} \infty$$

Lyman lines are in UV region.

(B) BALMER SERIES

All transitions to 2nd orbit are called Balmer Transitions & corresponding lines in Emission Spectrum → Balmer lines.

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{4} - \frac{1}{n^2}\right), \quad n = 3, 4, 5 \text{ ---} \infty$$

Observed in Visible region of EMR (Electro Magnetic Radiation)

(C) PASCHEN SERIES

All transitions to 3rd bord orbit → Paschen Transitions, corresponding ——— → Paschen lines.

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{9} - \frac{1}{n^2}\right), \quad n = 4, 5, 6 \text{ ---} \infty.$$

Observed in IR region of EMR.

D. BRACKETT SERIES

All transitions ~~to~~ - 4th orbit are called ~~Br~~ Brackett transitions. Corresponding lines → Brackett lines.

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{16} - \frac{1}{n^2}\right), \quad n = 5, 6, 7 \text{ ---} \infty$$

Observed in IR region of EMR.

Date

(E) PFUND-SERIES

All transitions to 5th orbit → PFUND transitions
Corresponding lines → PFUND lines.

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{25} - \frac{1}{n^2}\right), \quad n = 6, 7 \ldots \infty$$

IR region

★ Imp: Did After 5 orbits, orbit becomes very close & corresponding lines are not separated on Spectrum.

12 | JULY | 09

Q Determine the shortest wavelength of transition in Balmer series & longest λ of transition in Paschen series.

B

$1.08 \times 10^7 \, m$

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{4} - \frac{1}{n^2}\right)$$

$$= R_H \left(\frac{1}{4} - \frac{1}{n^2}\right)$$

$$\Rightarrow \frac{1}{\lambda} = 1.08 \times 10^7 \left(\frac{n^2 - 4}{4n^2}\right)$$

$$\Rightarrow \frac{1}{\lambda} = 0.27 \times 10^7 \left(n^2 - 4\right)$$

$$\Rightarrow \frac{1}{\lambda} = 0.27 \times 10^7 n^2 - 1.08 \times 10^7$$

Taking $n^2 \to \infty$,

then $R_H \left(\frac{1}{4} - 0\right]$ will be max.

So λ would be min. $\lambda = \frac{1}{\ldots}$

=) $\lambda = \frac{4}{R_H}$

$= \frac{4 \times 10^{-7}}{1.08}$

$= \frac{4}{108} \times 10^{-5}$

$\simeq 0.037 \times 10^{-5}$

$= 3.7 \times 10^{-7} m$

=) 370 nm

108
×8
864

(1) $\frac{1}{\lambda} = R_H (Z^2)\left(\frac{1}{9} - \frac{1}{n^2}\right)$

=) $\frac{1}{\lambda} = \frac{R_H}{9}$

=) $\lambda = \frac{9}{R_H}$

$= \frac{9 \times 10^{-7}}{1.08}$

$= \frac{9 \times 10^{-5}}{108}$

$= 0.08$

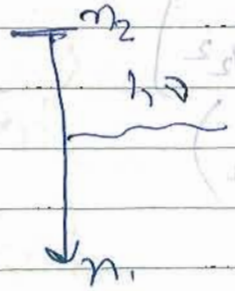
=) $\frac{1}{\lambda} = R_H \left(\frac{1}{9} - \frac{1}{16}\right)$

=) $\lambda = \frac{144}{7 R_H}$

$\simeq$ 1900 nm Ans.

Q. Which electronic transition in Li^{+2} will emit light of same λ as the 1st layman line in H atom

H $\rightarrow$ $\frac{1}{\lambda} = R_H \left(1 - \frac{1}{n_2}\right)$



$\Delta E = K(Z^2)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$= K\left(\frac{9}{n_1^2} - \frac{9}{n_2^2}\right)$ → This transition energy

is equal to $K(1)^2\left(\frac{1}{1} - \frac{1}{4}\right)$

Date

$\Rightarrow K\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = K(1)^2\left(\frac{1}{4} - \frac{1}{16}\right)$

$\Rightarrow n_1 = 3$
$n_2 = 6$ $\quad \left[\frac{1}{n_1^2} = \frac{1}{4}, \frac{1}{n_2^2} = \frac{1}{16}\right]$

Q. Determine the transitions occuring in He^+ which will emit light of same λ as given by 1st Pascal line in H atom

$\Delta E =$

$K(1)^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = K(1)^2\left(\frac{1}{9} - \frac{1}{16}\right)$

$\Rightarrow$

$n_1 = 6$
$n_2 = 8$

So, 8 to 6

Q. Determine the 1st 3 transitions occurring in He^+ which lies in the visible region of EM spectrum as well as they are also present in the emission spectrum of H atom.

(H) $\frac{1}{\lambda} = R_H\left(\frac{1}{4} - \frac{1}{n^2}\right)$

$He^+ \rightarrow \Delta E = KZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

TE in $He^+ \longrightarrow K\left(\frac{4}{n_1^2} - \frac{4}{n_2^2}\right)$

(H) atom

$\Delta E = R_H\left(\frac{1}{4} - \frac{1}{n^2}\right)$

Date

Now, For TE of He^+ to be in visible region,

$K^* \left(\frac{4}{n_1^2} - \frac{4}{n_2^2}\right) = K\left(\frac{1}{4} - \frac{1}{n^2}\right)$

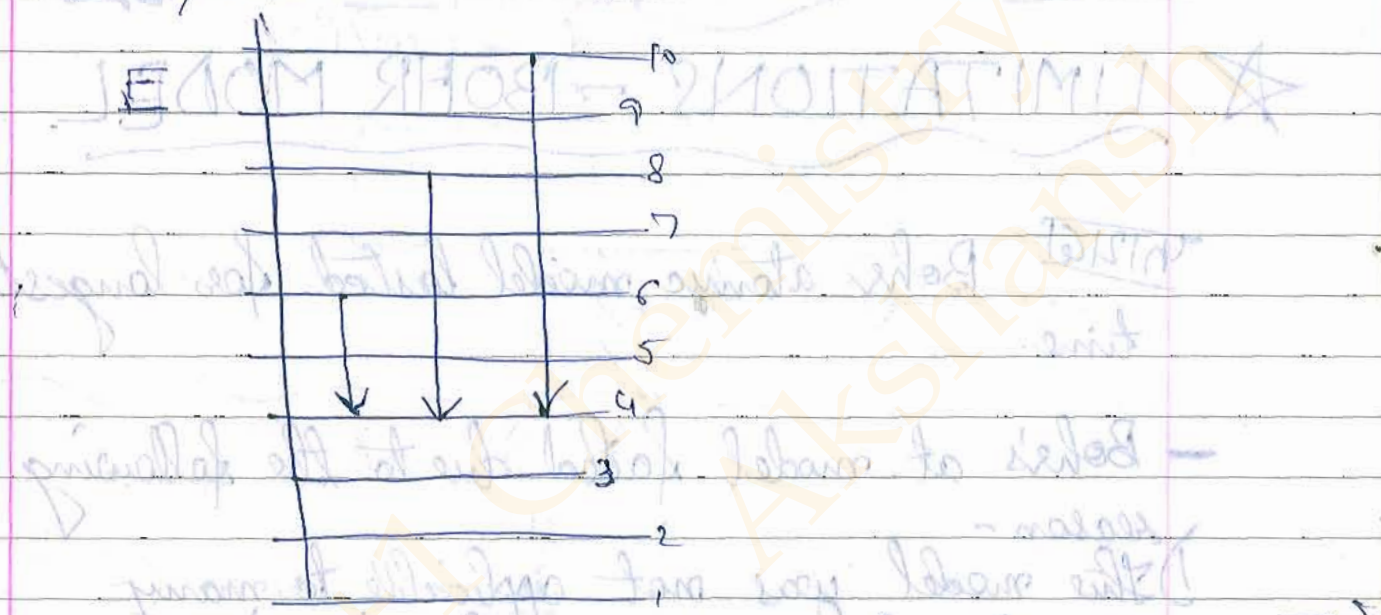
Taking

$n=3$
$n_1 = 4$
$n_2 = 6$

$n=4$
$n_1 = 4$
$n_2 = 8$

$n=5$
$n_1 = 4$
$n_2 = 10$

Q. Determine 1st 3 transitions occuring in He^+ which produces light in visible region of EM spectrum.



Limit of Balmer series for H-atom

$\frac{1}{\lambda} = R_H\left(\frac{1}{4} - \frac{1}{n^2}\right)$

$(n)_{max} \rightarrow \infty \Rightarrow \frac{1}{\lambda} = \frac{R_H}{4}$

$(n)_{min} \rightarrow 3 \Rightarrow \frac{1}{\lambda} = \frac{5R_H}{36}$

$\Rightarrow \lambda = \frac{4}{R_H} \longleftrightarrow \frac{36}{5R_H} = 7.2$

He^+ $(5 \to 4)$

$$\frac{1}{\lambda} = R_H(4)\left(\frac{1}{16} - \frac{1}{25}\right)$$

$$\Rightarrow \frac{1}{\lambda} = R_H\left(\frac{1}{4} - \frac{4}{25}\right)$$

$$= R_H\left(\frac{4}{4}\left(\frac{25-16}{25}\right)\right)$$

$$= R_H - \frac{9R_H}{100}$$

$$\Rightarrow \lambda = \frac{100}{9R_H} \longrightarrow \text{not in visible region.}$$

☆ LIMITATIONS - BOHR MODEL.

Note: Bohr atomic model lasted for longest time.

- Bohr's at. model failed due to the following reason -

1) This model was not applicable to many e^- system (having more than 1 e^-)
2) Bohr's at. model was unable to explain the elliptical orbit described by e^-, as predicted by SOMMERFIELD.
3) Bohr model was unable to explain the stark-effect (name of scientist)

Stark-effect : It is the effect produced by an atom in an electric field.

4) Bohr model was unable to explain the Zeeman-effect : The effect produced by atoms in magnetic field.

Date

de-Broglie wave-particle "Duality"

Acc. to de-Broglie, e⁻ in an atom has both the property of matter & wave.

— e⁻ as particle (having mass & momentum)
$E = mc^2$ (By Einstein)

— e⁻ as a wave : $E = h\nu = \frac{hc}{\lambda}$ (Planck's eqn.)

energy of e⁻ should be equal.

$\Rightarrow mc^2 = \frac{hc}{\lambda}$

$\Rightarrow mc = \frac{h}{\lambda}$

$\Rightarrow$ **p (momentum) $= \frac{h}{\lambda}$** → de-Broglie eqn.

$mvr = n\frac{h}{2\pi}$

$\Rightarrow mv = n\frac{h}{2\pi r}$

$\Rightarrow mv = p = \frac{nh}{2\pi r}$

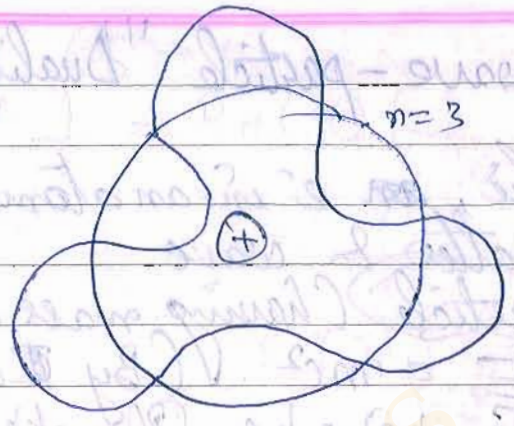
$\Rightarrow \frac{h}{\lambda} = n\frac{h}{2\pi r}$

$\Rightarrow \frac{1}{\lambda} = \frac{n}{2\pi r}$

$\Rightarrow$ **$n\lambda = 2\pi r$** → Bohr de-Broglie eqn

$2\pi r$ → circumference → integral multiple of λ

Date



☆ In any n^{th} Bohr orbit, no. of de-Broglie wave = orbit no.

Q ☆ Determine de-Broglie λ of e^- in the 3rd orbit of He^+

$3\lambda = 2\pi r$; $r = \frac{0.53 \times 10^{-10} \times n^2}{Z}$ m

$3\lambda = 2\pi \cdot \frac{9}{2} (0.53 \times 10^{-10}\ m)$

$\Rightarrow \lambda = \frac{22}{7} \times 3 \left(\frac{5.3}{10} \times 10^{-9}\ nm\right)$

$= \frac{66}{7} \left(\frac{5.3}{10}\right) nm$

$= 3498 \quad 499$

$= 53\ nm.$

$\lambda = 5.3\ \text{Å}.$

153
66.
318
318
3498

initially at rest.

e^- ↑ volt

$\frac{1}{2} mv^2 = eV$

$\frac{1}{2} mv^2 \times \frac{m}{m}$

$= \frac{m^2v^2}{2m} = \frac{p^2}{2m} \rightarrow K.E$

So, $\frac{p^2}{2m} = eV$

$\Rightarrow p^2 = \sqrt{2meV}$

$\lambda = \frac{h}{p} \Rightarrow \lambda = \frac{h}{\sqrt{2meV}}$

Q. Determine de-Broglie λ of e⁻ initially in rest, accelerated by Potential Diff of 500 V.

$h = 6.62 \times 10^{-34}$ Js

$m = 9 \times 10^{-28}$ g $= 9 \times 10^{-31}$ kg

$e = 1.6 \times 10^{-19}$ C

$\lambda = \frac{6.62 \times 10^{-34}}{\sqrt{2(9 \times 10^{-31})(1.6 \times 10^{-19})(500)}}$

$= \frac{6.62 \times 10^{-34}}{\sqrt{144 \times 10^{-48}}}$

$= \frac{6.62 \times 10^{-34}}{12 \times \sqrt{10^{-48}}}$

$= \frac{6.62 \times 10^{-34}}{12 \times 10^{-24}}$

$= 5.5 \times 10^{-11}$ m

$= 0.55$ pm.

$= 55$ Å

$= 550$ nm.

$\frac{6.6 \times 10^{-10}}{12}$

$= 0.55 \times 10^{-10}$ m

$= 55$ pm., 0.055 nm.

Date

Q. Determine the potential difference by which the e^- must be accelerated from rest in order to have same speed, as the speed of e^- in 2nd Bohr orbit of Li^{+2}.

$$V = 2.18 \times 10^6 \left(\frac{Z}{n}\right)$$

$$\Rightarrow V = 2.18 \times 10^6 \left(\frac{3}{2}\right)$$

$$\Rightarrow v = 3.27 \times 10^6 \text{ m/s}$$

$$mv = 9 \times 10^{-31} \times 3.27 \times 10^6$$

$$p = 29.43 \times 10^{-25}$$

$$\frac{h^2}{2m} = eV$$

$$\Rightarrow p = \sqrt{2meV} \quad \text{or} \quad \tfrac{1}{2}mv^2 = eV$$

$$\Rightarrow (29.43 \times 10^{-25})^2 = 2(9 \times 10^{-31} \times 1.6 \times 10^{-19} V)$$

$$\Rightarrow 99.136 \times 10^{-19} = 03.2 \times 10^{-19} \times V$$

$$\Rightarrow V = \frac{3.2}{100}$$

$$\Rightarrow V = 0.032 \text{ V}$$

$$9 \times 3.27 \times 9 \times 3.27 \times 10^{-30} = 3.2 \times 10^{-19} \times V$$

$$\Rightarrow V = 3.27 \times 9$$

$$\Rightarrow V = 29.4 \text{ V}$$

6 July 09

Date

☆ QUANTUM NUMBER

Quantum Nos. are the set of coordinates defined to specify an e⁻ in the atom.

Source.

Quantum nos. are mostly derived from Quantum Mechanical Model of atom.

- To define and describe an e⁻ completely, in an atom, 4 sets of Quantum nos. are required. They are called.

(A) Principal Quantum No. ('n')
(B) Subsidiary (Azimuthal or angular momentum) Q. No. ('l')
(C) Magnetic Q. No. ('m')
(D) Spin Q. No. ('s')

→ Derived from Quantum mechanical model.

(A) Principal Q. No. ('n')

- Principal Q. No. ('n') determines the size of orbit in which e⁻ revolve.

$n = 1, 2, 3, 4 ____ \infty$

- It determines the kinetic property of e⁻ → (KE, PE, speed, momentum can be determined) & any property related to E can be determined.

(B) Subsidiary Q. No. ('l')

- It determines the shape of orbitals in which e⁻ travel or stay in the atom.
- For a given value of n, the possible values of l are

n : 0, 1, 2, 3 ____ $(n-1)$

- Every value of 'l' correspond to a specific orbital. i.e

If $l = 0, 1, 2, 3, 4$

name : s, p, d, f, g

Date

• For a given value of 'l', the ~~an~~ vital angular momentum of an e⁻ 'L' = $\sqrt{l(l+1)}\,(B_M)$ Unit

(BM = Bohr Magneton)

electrical const^n.

$B_M = \frac{h}{4\pi\epsilon_0}$

(C) Magnetic Q. No. (m_l)

• It determines the orientations of orbitals in space.

m_l ; (-l) ——— (0) ——— (+l)

★ • All electrons with same value of 'l' but different value of 'm' have same energy.

eg: 3rd orbit

n = 3, l = 0, (1), 2

↓P

m_l = −1, 0, 1.

for same l (1) ; m_l = −1, 0, & +1 have same energy.

~~Orbitals with same value~~

★ • Electrons with similar value of 'l' but different value of m are DEGENERATE & the orbitals holding them are called DEGENERATE ORBITALS

• For any given 'l' the possible value of 'm' will be 2l+1 orientations (representation in 3D)

• For any given value of 'l', max. degeneracy of orbital is 2l+1

(D) Spin Q. No. (m_s)

★ When e⁻ revolve / move around nucleus simultaneously, it spins around its own axis

like earth in our Solar System. To specify the dirn of spin of e^-, 2 Q. Nos., known as Spin Q. No. were defined. They are -

$+\frac{1}{2}$ & $-\frac{1}{2}$

• $+\frac{1}{2}$ & $-\frac{1}{2}$, → value of spin Q. No., just represent the 2 opp. dirn of spinning of e^- on its axis.

$+\frac{1}{2}$ →	cw	a. cw
$-\frac{1}{2}$ →	a. cw	cw.

their dirn is not fixed, but opp. to each other

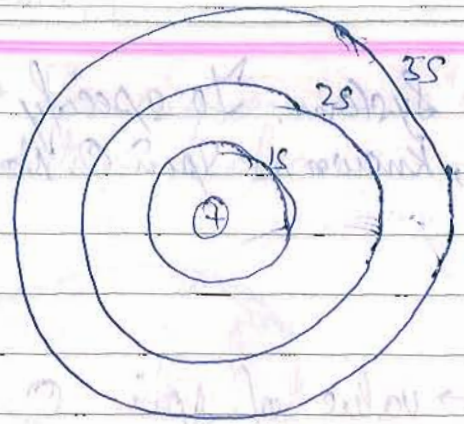
• Electrons spinning in opp. dirn have opp. magnetic properties - i.e. if e^- spinning in c.w dirn is attracted towards north pole of magnet, then essentially, electrons with opp. spin i.e., anti c.w, will be attracted towards south pole of magnet. However, $+\frac{1}{2}$ & $-\frac{1}{2}$ are not specific to pole of the magnets.

★ ORBITAL : It is an imaginary space in an atom where the probability of finding an e^- is max.

★ SHAPES OF ORBITALS

① S-orbital : S-orbital has spherically symmetrical shape.

• In s-orbital, e^- remains equidistant from the nucleus everytime.



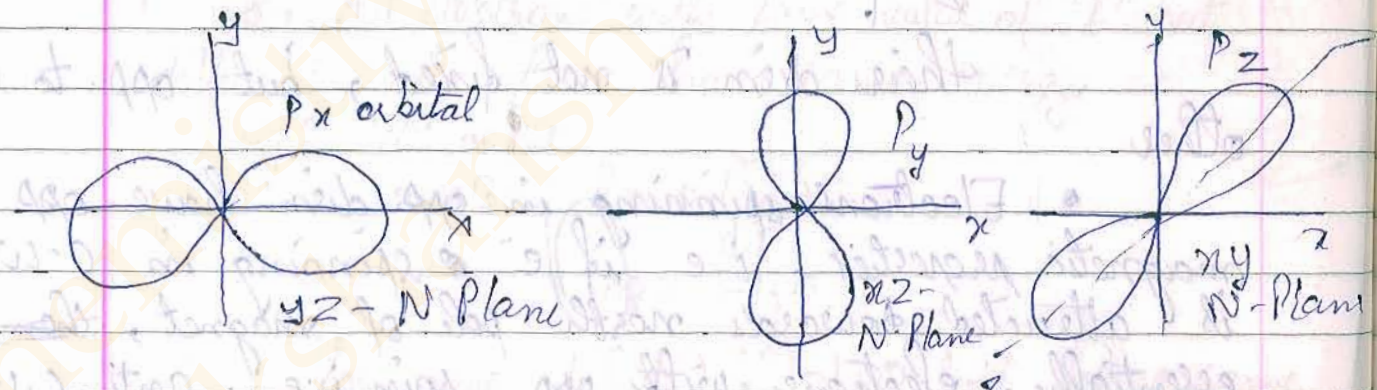
	l
n = 1	0
= 2	0, 1
= 3	0, 1, 2

(2) P-orbital : P-orbital has ~~dumbell~~ dumble like shape

lobe

p : l = 1

+1 , 0 , −1



✡ magnetic Quantum No. is not specific to any orbital. It only tells the no.

✡ ANGULAR NODE : It is an imaginary 2D plane passing through orbital on which probability of finding e⁻ is min. It is also known as NODAL PLANE.

All p-orbitals contain 1 Nodal plane ⊥ to the orientation of orbital.

S-orbital is devoid / free from any nodal plane.

(3) D-orbital : It has double dumble shape.

l = 2

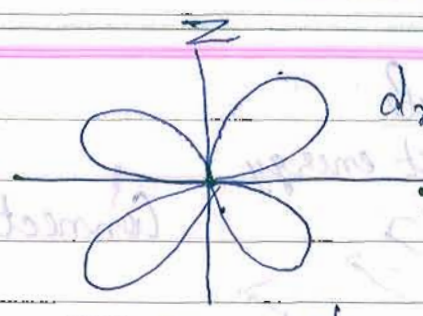
m = +2, +1, 0, −1, −2

★ The shape of car tube is TORUS

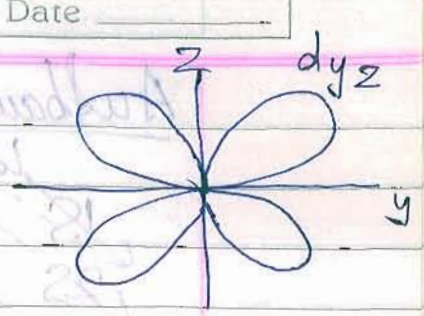
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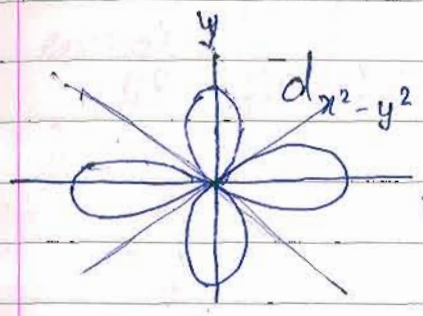
xz, yz N. Plane



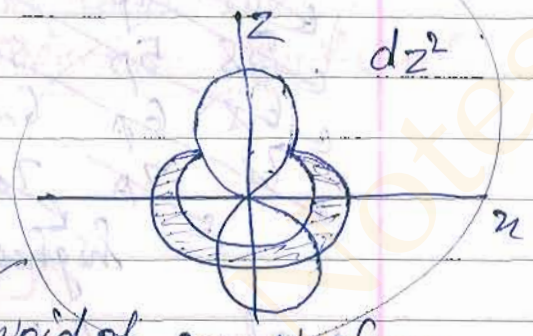
xy, zy N. plane



xy, zx N. plane



has 2 N-planes at an angle of 45° with coordinate axis



Devoid of any N-plance.

④ ~~s-orbital~~:

④ f-orbital $l = 3$

So, orientations = 7.

★ Shape of f-orbital & other higher orbitals are complicated, consist of several clumbles, sharing a common centre, i.e, nucleus. ~~After ka~~.

★ ELECTRONIC CONFIGURATIONS in Many Electron System:

↓

Arrangement of e^- in an atom.

Acc. to MODERN THEORY, Electronic configurations of an atom is based on the following rules —

Rule 1. Electrons are filled in ORBITALS in increasing order of their energy i.e. low energy at orbital is filled 1st, then, high Energy atomic orbital is occupied.

Energy of atomic orbitals is determined by

Aufbau Rule

lowest energy

1S

2S 2P

3S 3P 3d

4S 4p 4d 4f

5S 5p 5d 5f

6S 6p 6d 6f

7s 7p 7d

highest energy

Connect head ⊙ to tail ←⊙

— Writing Electronic Configuration of an atom (PEP) PAULI EXCLUSION PRINCIPLE is followed/obeyed

PEP rule

Acc. to PEP, no 2 electrons in an atom can have all 4 quantum nos. same/equal.

He (2e⁻)

denoted by half arrows

↑ (up half arrow)

↓ (down ")

1s

↑ ↓

n = 1

l = 0

m = 0

Li (3e⁻)

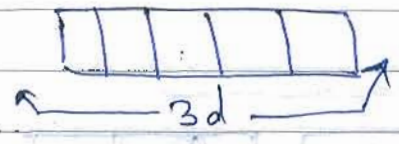
↑ ↓	↑

Date

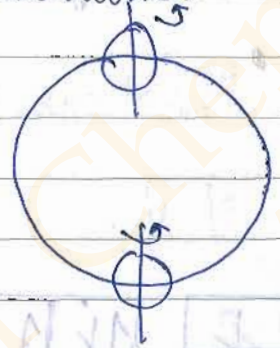
19 JULY

☆ During filling up of e⁻ in atomic orbital of same energy, direction of electronic spin HUNDS RULE OF Maximum Multiplicity is obeyed.

3d
n = 3
l = 2
m = +2, +1, 0, -1, -2



☆ When e⁻ spin in the same dirn, so, they would have resonance. They increase stability, ∴ multiplicity.



- In filling up of electrons in degenerate atomic orbitals, orbitals are 1st singly occupied with same dirn. of electronic spin.
- Once the degenerate atomic orbital is completely half filled, then pairing starts.

Electronic configuration → ORBITAL @ EC.

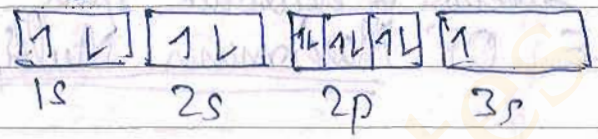
) Na (11) → (11e⁻)
$1s^2\ 2s^2\ 2p^6\ 3s^1$

Date

BOX DIAGRAM EC

Na (11) → (11e⁻)

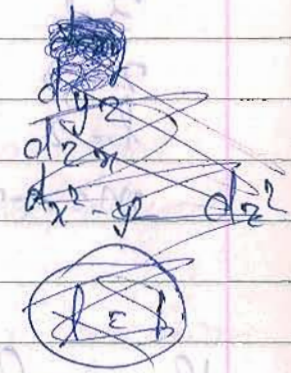
$1s^2$ $2s^2$ $2p^6$ $3s^1$



N (7)

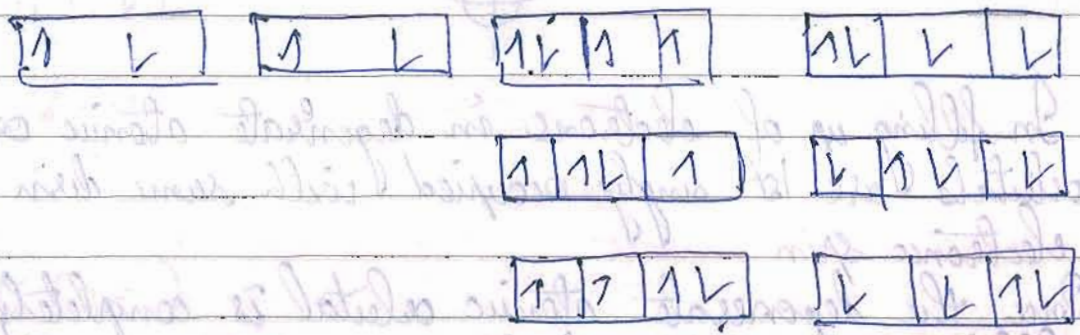








O (8)

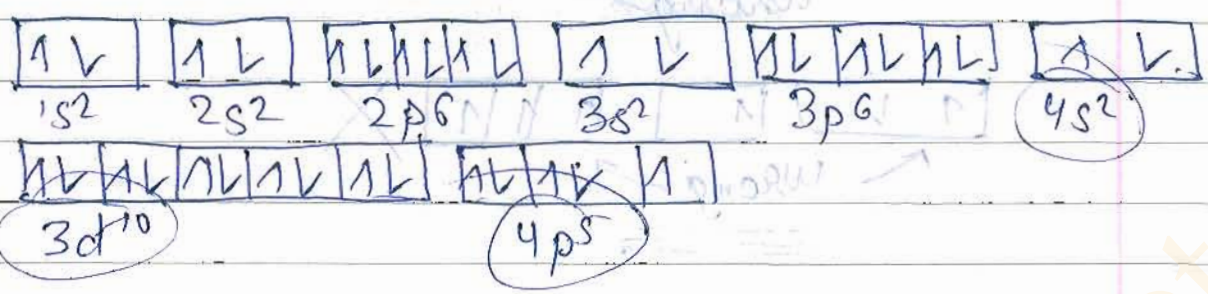


Here, 3 e⁻ are spinning.

Date

Br (35)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$



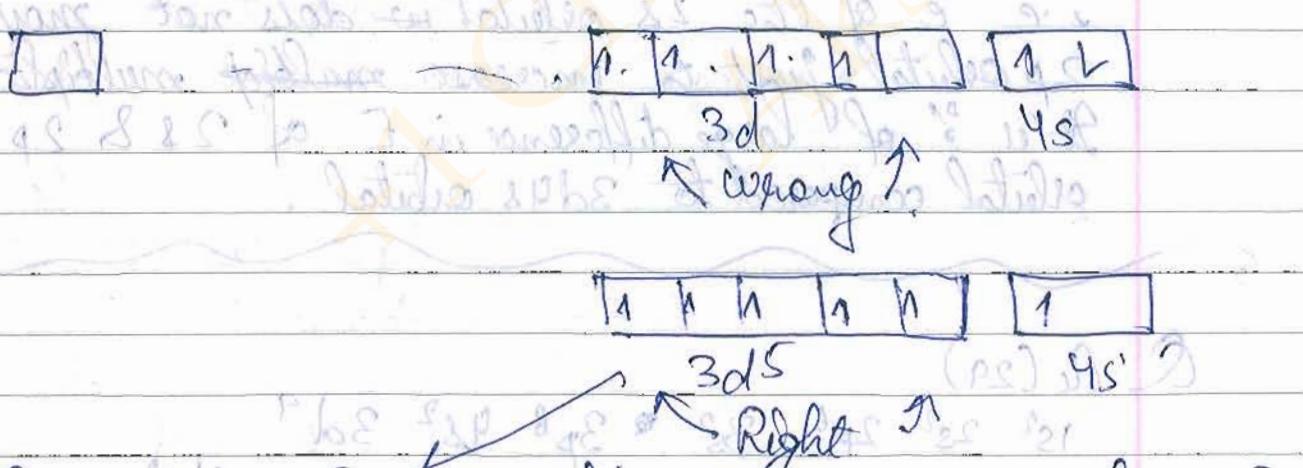
Written as: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$

~~Princi~~ Principal Quantum No. should be together

EXCEPTION IN E.C. (Electronic configuration)

Cr (24)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$



6e⁻ spinning in same dirn, there is no counter spin to cancel them. There is greater spin multiplicity.

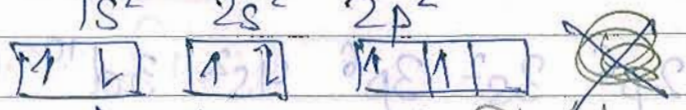
Due to greater stability of this EC, it is preferred over 1st. So, it is correct EC.

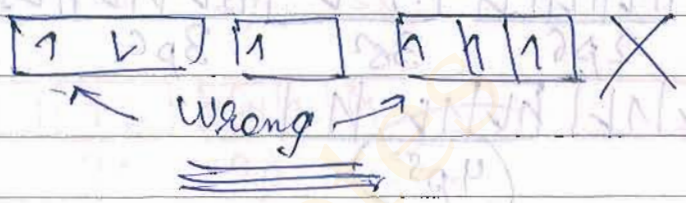
3d & 4s orbit are very close in Energy. ∴ e⁻ transfer from 4s to 3d does not de-stabilises

Date

C(6)

$1s^2$ $2s^2$ $2p^2$





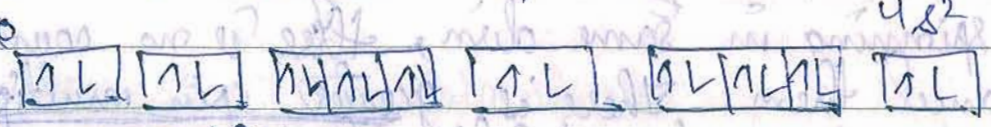
$1s^2\ 2s^2\ 2p^2$

* In case of Cr : the expected EC is $3d^4\ 4s^2$ However the experimentally determined EC for the same Cr is ⊙ $3d^5\ 4s^1$. This is preferred ∵ stability gain due to multiplicity is greater than the stability less due to e⁻ transfer from lower to high E orbital. This is possible only b/w adjacent s & d orbital.

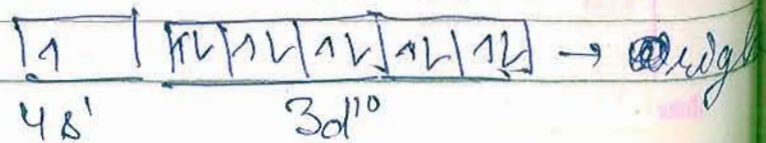
* In case of C (6) the experimentally determined EC is same as the theoretical EC of $2s^2\ 2p^2$ i.e. e⁻ of the 2s orbital do's not move to 2p orbital just to increase ~~multiplicity~~ multiplicity. It is ∵ of large difference in E of 2s & 2p orbital compared to 3d 4s orbital.

Q Cu (29)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$







Electronic motion is responsible for Magnetism in any substance

Date

Rule – Completely filled orbital is more stable than less than completely filled orbital.
- A completely half filled orbital is more stable than less than ½ filled orbital.

F(9)

$1s^2$ $2s^2$ $2p^5$

↑↓ ↑↓ ↑↓ ↑↓ ↑ ✓

↑ ↑↓ ↑ ↑ ↑↓ ✗

★ Spin-only Magnetic Moment (μ_s)

~~Motion of any~~

$\mu_s = \sqrt{n(n+2)}\ B_M$ → Bohr magneton

n → no. of unpaired e^-.

N

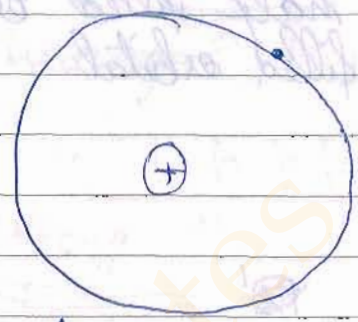
$1s^2\ 2s^2\ 2p^3$

Unpaired e^- → 3.

So, $\mu_s = \sqrt{15}$

Date

☆ HEISENBERG's UNCERTAINTY PRINCIPLE.



- You can't setup an experiment in which both posⁿ & its (c⁻) speed can be determined simultaneously
- Acc. to Heisenberg's Uncertainty Principle, both posⁿ of e⁻ & its 'p' cannot be determined accurately & simultaneously in a single expt.

If we want to measure distance of e⁻ from nucleus, accurately, we'll have to sacrifice the accuracy in measurement of 'p' & vice versa.

Qualitatively, if light of longer λ is used, K.E / 'p' / v of e⁻ can be measured accurately but, its posⁿ will be inaccurate.

If light of shorter / smaller λ is used, posⁿ of e⁻ can be measured accurately, but, 'p', will be inaccurate.

i.e: ∅ to measure posⁿ of e⁻ in an area.

Δx → uncertainty in posⁿ.

Δp → uncertainty of v.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

for calculations →

$$\Delta x \cdot \Delta p = \frac{h}{4\pi}$$

Q. Posn of an e⁻ in an atom can be measured in the range of 1nm. Determine the max. uncertainty which will be observed in measurement of v of e⁻ in the same exp.

$$\Delta v = \frac{6.625 \times 10^{-34} \times 7}{4 \times 9.1 \times 10^{-31} \times 22 \times 1 \times 10^{-9}}$$

$$= \frac{6.625 \times 10^{4} \times 7 \times 10}{91 \times 4 \times 22 \times 1000}$$

$$= \frac{46325}{8008} \times 10^{4}$$

$$= 5.8 \times 10^{4}\ m/s$$

$$\approx 6 \times 10^{4}\ ms^{-1}$$

46625 − 7 = 46375

91 | 364 | 728 | 4004 | 8008

4637 − 4004 = 6335 − 4004 = 2331.0

4004 | 20020

RO_2 RO R_2O R_2O_3

Date

Ch°

Periodic Table & Periodicity

★ PERIODICITY : It is the recurrence / ~~repetition~~ repetition of properties after a regular interval.

★ MENDELEEV P.T.

Mendeleev P.t is based on the observation that Periodicity is a fn of at. wt.

In Mende'leev P.T. 16 vertical columns known as groups & 7 horizontal rows called Periods.

22 July

Al(13) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

3rd orbit is the highest filled orbit.

~~$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$~~ ∴ it is called VALENCE SHELL.

★ ELEMENTS are classified into 4 blocks.

s, p, d, f — BLOCK elements

Block of an element is determined by the last filled orbital.

eg : Mg(12) → $3s^2$ so, S-block. elemt.

In ~~MED~~ MENDELEEV P.T., elemts were further classified into 2 groups — A group & B groups elemt.

Elements of s & p - block are collectively known as A GROUP elements.

Elements of d-block are known as B GROUP elements.

In M.P.T,

- No. of valence shell e⁻ determine groups no.
- No. of highest orbit filled (valence shell) determine period no.

Si (14)

$1s^2\ 2s^2\ 2p^6\ 3s^{\textcircled{2}}\ 3p^{\textcircled{2}}$ → 3rd period, IV A group

	IV A
3	Si

(X) (31)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3pd^{10}\ 4p^1$

Period → 4

Groups → III A

Fe, Co, Ni → TOGETHERLY CALLED AS FERRO ELECTRONS

Date

Sc (21)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$

$n=4$, so, valence shell = 3d 4s, no. of e^- V.S = 3. Grp → III

★ FOR D Orbital: Valence shell = (n-1)d ns

Fe (26)

$3d^6\ 4s^2 = 8$

Cu $3d^{10}\ 4s^1$ → I B

Zn (30) $3d^{10}\ 4s^2$ → II B.

Co (27) $3d^7\ 4s^2 = 9$

Ni (28) $3d^8\ 4s^2 = 10$

MENDELEEV P.T

	IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII	VIII B	IB	IIB	IIIA	IVA	VA	VIA	VIIA
1																
2																
3																
4			Sc					Fe	Co	Ni	Cu	Zn				
5																
6																
7																

Date

☆ long form of P.t → It is based on Moseley's findings.

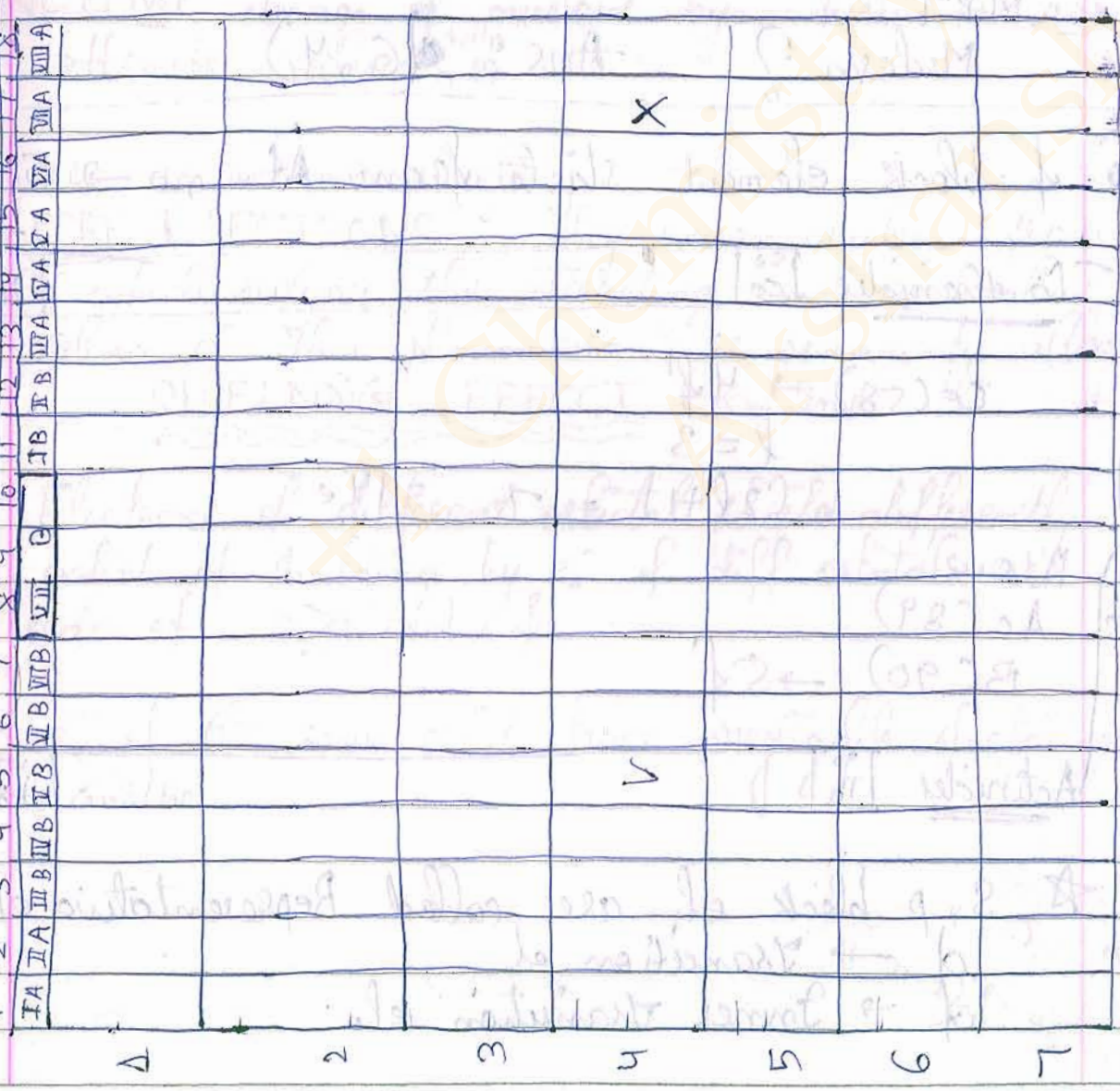
√ Acc to Mosley, Periodicity in the properties of elements is fn of at. no., rather at. wt.

- In modern P.t, there are 18 ~~groups~~ verticle columns called groups & 7 horizontal rows called Periods.
- Highest orbit no. determine the period no. & the no. of valence e⁻ determine the groups no.
- For s-block, & d-block element, no. of valence e⁻ will give groups no.

eg: Mg (12) → $3s^2$, 2 → G. 3 → P

√ (24) → $3d^5 4s^2$ 5 → G 4 → P

LONG FORM OF PERIODIC TABLE (MODERN P.T)



- For p-block elements, group no. will be = to no. of valence e⁻ + 10.

  G. No. = no. of V.e + 10

eg (X) (35)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

P → 4, G → 17

written as, (17, 4)

G P

(Q) (VII B, 4)

↓

MPT

Modern? Ans: (6, 4)

- f-block element starts from At. no → 58.

INNER-Transition ELEMENTS

Lanthanides [58 Ce] ... [71 Lu]

Ce(58) → 4f¹

l = 3

(2l+1) = 7 = 14e

Now,

Ac(89)

B(90) → 5f¹

Actinides [90 Th] ... [103 Lr]

☆ s, p block el. are called Representative el.

d → Transition el.

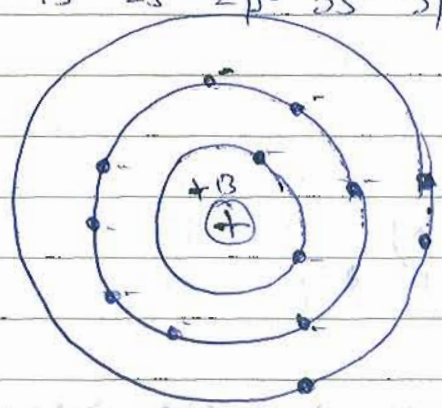
f → Inner Transition el.

Date

☆ PERIODIC PROPERTIES

~ Effective NUCLEAR CHARGE (ENC)

(13) Al → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$



INNER e^- are called CORE ELECTRONS

ENC is Net +ve charge on nucleus by which it actually attracts valence shell e^-.

- Core e^- act as shield.

~ CORE ELECTRONS : They screen nucleus from valence e^- which reduces the attracting power of nucleus for the valence e^-. This phenomenon is commonly called SHIELDING EFFECT (very Imp.)

~ Electrons of different orbital shield differently. The extent of shielding by e^- of diff orbitals are in the order of $s \geq p > d > f$ (max)

$l = 0, 1, 2, 3$

~ e^- of the same orbit have negligible shielding on another.

ns^{1-2}

$ns^2\ np^{1-6}$

$(n-1)d^{1-10}$

$(n-2)f^{1-14}$

ns^{0-2}

$(n-1)d^{1-2}$

ns^2

Date

PROPERTY 1

ATOMIC/IONIC SIZE

Atomic Size :

2nd period

4	5	6	7	8	9
Be	B	C	N	O	F
$1s^2 2s^2$	$2p^1$	$2p^2$	$2p^3$	$2p^4$	$2p^5$

PERIODIC TREND OF ATOMIC RADII

- Atomic Radii decreases as we move from left to right in a period. It is because of increase in effective nuclear charge as we ~~move~~ move from left to right in a period. The trend continue upto Group 17 only.
- Atomic Radii increases as we move from top to bottom in a groups.
- Variation in atomic radii is more rapid in a groups than in period.

IONIC RADIUS

K (Z=19) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1 \rightarrow K^+ + e^-$



Date

☆ CATIONS are always smaller in size than their own NEUTRAL atoms

Higher the valency of cation, smaller the size.

In case of variable valency of cation, higher the valency, smaller the size.

i.e

$Mn^{+2} > Mn^{+3} > Mn^{+4} > Mn^{+7}$

Cl (17) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

$\downarrow e^-$

$Cl^- \longrightarrow 3s^2\ 3p^6$

☆ ANIONS are always bigger in size than its own neutral atom (Due to decrease in ENC on addition of e^-)

---

① H^+ He^{+2} Li^{+3} Be^{+4}

I II III IV

No e^-s. So, size will depend on size of nucleus

So,

$Be > Li > He > H$.

---

same no. of e^-s

☆ ISO ELECTRONIC IONS HAVE COMPARABLE SIZE

K^+ (19) Cl^- (17) Ar (18) → 18 e^- $Na^+ < K^+ < Ar < Cl^- < Br^-$

Na^+ (11) Br^- (35)

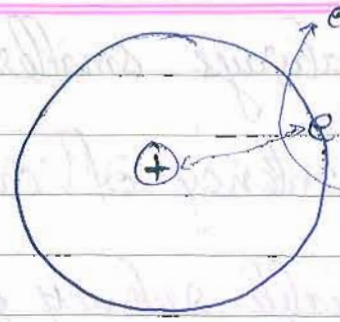
☆ IONIZATION ENERGY (IE)

It is the min. E req. to knock out the most loosely held e^- from the neutral gaseous atom / gaseous ion.

GROUND STATE of

☆ Closed shell configuration (i.e in case of Ne → $1s^2 2s^2 2p^6$ all e⁻s are fully filled).

Date



ENC ∝ IE (excluding exceptions)

ENC ∝ $Q_1 Q_2$

☆ PERIODIC TREND

IE increases as we move from left to right in a period due to increased ENC. Noble gas has the max. IE in its period.

IE decreases as we descend down in a group. due to increase in at. radii.

EXCEPTIONS

1

4	5
Be	$_5$B

$1s^2 2s^2$ $\quad$ $1s^2 2s^2 2p^1$

↑↓ ↑↓ $\quad$ ↑↓ ↑↓ ↑ | |

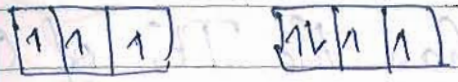
Acc. to periodic trend, B should have higher IE than Be. But the fact is opposite.

∴ of the reason that Be has completely filled 2s orbital which is stable & removing one e⁻ will cost more E. In case of B, e⁻ to be removed is in 2p orbital which is neither completely filled nor completely ½ filled. ∴ Removal of e⁻ will be RELATIVELY easier than Be. Hence, Be has higher IE than B.

THIS type of REVERSAL IN periodic TREND are OBSERVED ONLY B/W ADJACENT ELEMENTS OF A PERIOD.

Same is the case of Mg & Al. ∴ IE of Mg > Al.

$1s^2\ 2s^2\ 2p^3$ — N (7) — $2p^4$ — O (8) — IE: N > O



26 July

	13
	B
	Al
10 Tr. metals. Zn^{30}	Ga^{31}

Should be IE of Ga < IE of Al.

actually IE(Ga) > IE(Al)

Reason :

$Sc^{21} \longrightarrow Zn^{30}$.

$3d^1 4s^2$ $\quad$ $3d^{10} 4s^2$

Due to the 10 Transition elements, preceding Ga, increases ENC by 10 units. But gives very less shielding by the 10 e⁻ added in d orbital. The increased in ENC increases IE greatly., even greater than Al.

SUCCESSIVE IE OF AN ELEMENTS.

$A \xrightarrow{IE_1} A^+ + e^-$

$A^+ \xrightarrow{IE_2} A^{+2} + e^-$

$A^{+2} \longrightarrow A^{+3} + e^-$

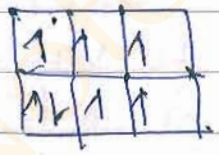
- Electrons are removed from atoms in succession.
- For any element, every next IE will be greater than previous 1 (without any exception)

Date

★ For any element $IE_1 < IE_2 < IE_3$ ——

(∵ With removal of e^-, ENC will increase
So, IE will increase —— this would go on)

Q 1st IE of N is greater than the IE_1 of O, But reverse is true for 2nd IE_2. Explain.

$N \rightarrow 1s^2\ 2s^2\ 2p^3$ 

$O \rightarrow 1s^2\ 2s^2\ 2p^4$

IE_1 of N > IE_1 of O ✓

Now, removing 1 e^-

$N^+ \rightarrow 2p^2$

$O^+ \rightarrow 2p^3$ → more stable (completely ½ filled)

removing e^- cost more E. So More IE.

So, IE_2 of O > IE_2 of N ✓

Q IE, of Na (11) is smaller than IE, of Mg (12)

$1s^2\ 2s^2\ p2p^6$

$3s^1\ \ 3s^2$

But, reverse is true for IE_2.

Compare their 3rd i.e

Na (11) → $3s^1$.

Mg (12) → $3s^2$ → ~~Fully filled. More IE.~~ ½

~~losing e^-~~

~~Mg~~ → IE, of Na < IE, of Mg

~~:.~~ Because of periodic trend.

losing $1e^-$

Na^+ (10 e) → $2s^2\ 2p^6$. (Closed shell confi) → Very sta

Mg^+ (11 e) → $2s^2\ 2p^6\ 3p^1$

So, IE_2 of Na > IE_2 of Mg

∵ Na^+ has got noble gas confi.

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$Na^{+1} \rightarrow 2s^2\ 2p^5 \rightarrow$ noble gas confi destroyed.
$Mg^{+2} \rightarrow 2s^2\ 2p^6 \rightarrow$ noble gas confi.

So, IE_3 of Mg > IE_3 of Na

ELECTRON AFFINITY

When an e^- is added to the valence shell, of a neutral gaseous atom, energy is released.

$$A(g) + e^- \longrightarrow A^- + \text{Energy (released)}$$

So, addition of an e^- is an EXOTHERMIC PROCESS.

Energy released = ΔH_{EA}

Read as: Electron gain Enthalpy (E released)

☆ When e^- gain es -ve sign for E indicates exothermic process.

eg: E = -190 kJ/mol.

So, exothermic process.

So, $|\Delta H_{EA}| = 190 \rightarrow$ E is released

☆ ΔH_{EA} the mod of the ΔH_{EA} is the E released when an e^- is added to the valence shell of a neutral gaseous atom.

eg $A(g) + e^- \longrightarrow A^-$ $\quad \Delta H_{EA} = -190$ KJ/mol

$B(g) + e^- \longrightarrow B^-$ $\quad \Delta H_{EA} = -70$ KJ/mol

(E_A)

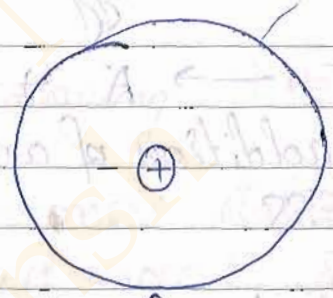
E^- affinity is greater in A. $E_A(A) > E_A(B)$

Date

☆ Electron Affinity is the E released when an e^- is added to the valence shell of a neutral gaseous atom.

Greater the e^- affinity of element, greater the amount of E will be released on add^n of e^-.

Imp



Election Affinity of an element depends on the ENC ~~More~~ Greater the ENC, greater will be E_A. i.e more E will be released on add^n of e^-.

PERIODIC TREND

- E_A increases from left to right in a period (Upto Group 17)
- E_A decreases from top to bottom in a group.

Exceptions of E_A

1) Noble gases have +ve ΔH_{EA} ($\Delta H_{EA} > 0$)

Reason: eg: Ne (10)

$1s^2\ 2s^2\ 2p^6 \rightarrow$

↑↓ ↑↓ ↑↓ ↑↓

If e^- is added in it, it would be destablise. So, e^- add^n is (endothermic)

Noble gases have closed shell confi. → highly stable.
Either add^n of e$^-$ or removal of e$^-$ destabilises the atoms. ∴ require E.

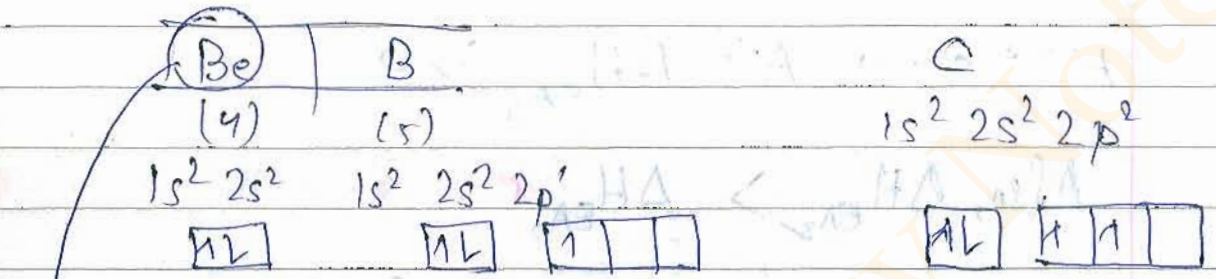
So, E_A in noble gases is +ve from He ⟶ Xe.

Comparing E_A in noble gases

E_A of He is max.

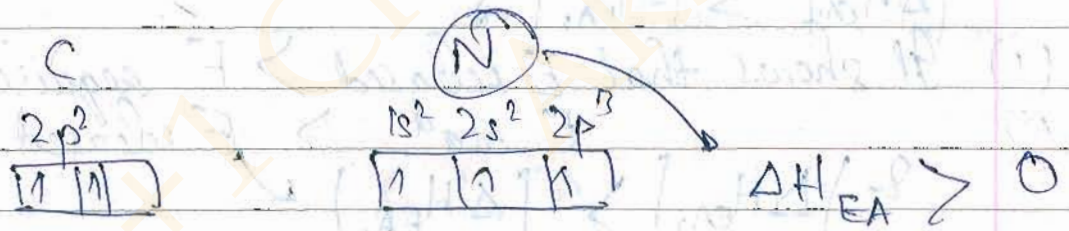
& most +ve H_{EA} is max ⟶ Xe.

2)



It has $\Delta H_{EA} > 0$.

This cond^n is true for all elements in this group.



All elements in the groups of N will also have $\Delta H_{EA} > 0$.

Be B C N

E_A : Be N B C order increasing.

ΔH_{EA} : N C B Be increasing order.

Date

☆ SUCCESSIVE E_A

$A^- + e^- \rightarrow A^{2-}$ Addn of 2nd & hegher e^- to a neutral atom is, ~~should be given always~~ gaseous always endothermic i.e for addn of e^- into valena shell of an anion work has to lee done to overcome the electrostatic repulsion b/w like charges.

Here, $\Delta H_{EA_2} > 0$

$A^{-2} + e \longrightarrow A^{-3}$ $\Delta H_{EA_3} > 0$

Also, $\Delta H_{EA_3} > \Delta H_{EA_2}$

• Adding more & more e^- will cost more & more E.

Q $A \rightarrow A^{2-}$ (i) ΔH = -120 KJ/mol.

(ii) ΔH = + 170 KJ/mol.

$|\Delta H_{EA_1}| > |\Delta H_{EA_2}|$

(i) It shows that E released > E required ~~for~~.

(ii) E reqd > E released.

& $|\Delta H_{EA_2}| > |\Delta H_{EA_1}|$

Q $O + 2e^- \longrightarrow O^{-2}$ ΔH = 740 KJ → ①

$e^- + O \longrightarrow O^-$ ΔH_{EA} = -170 KJ → ②

$O^- + e^- \longrightarrow O^{-2}$ ΔH = ?

① − ② = 740 + 170

= 910 KJ

$2p$ [↑↓|↑|↑] $+ e^- \rightarrow$ [↑↓|↑↓|↑] $\Delta H_{EA} = -170$ KJ

$\downarrow e^-$

[↑↓|↑↓|↑↓] $\Delta H_{EA} = 910$ KJ

EA_2 : O, N. N: $1s^2\ 2s^2\ 2p^3$ ✓ N^- [↑↓|↑|↑]

$1s^2\ 2s^2\ 2p^4$ O^- [↑↓|↑↓|↑]

N^{-2} [↑↓|↑↓|]

O^{-2} [↑↓|↑↓|↑↓] EA_2 of O > EA_2 of N.

Q. C → EA_2, EA_1

C – $1s^2\ 2s^2\ 2p^1$ EA_1(C) = $2p^3$ EA_2 (C) = $2p^4$

N – $1s^2\ 2s^2\ 2p^3$ (N) = $2p^4$ (N) = $2p^5$

EA_1 (C) > EA_1 (N) · EA_2 (N) > EA_2 (C)

EXCEPTION

(3) Acc. to periodic trend, F should have greater E_A than Cl. But, it is not the fact. In fact, Cl, has the max. E_A in P.T.

Reason:

F(9) $1s^2\ 2s^2\ 2p^5$ 

Cl(17) $3s^2\ 3p^5$ 

e^- density of F more than e^- density of Cl. So, it is compairitively difficult to pull the e^- inside than Cl. So, E_A of F < E_A of Cl.

☆ Electronegativity (E_N)

H ⋯ F

- Definition : E_N is the ability of an atom to attract the shared pair of e⁻s in a molecule or ion towards itself.

$\overset{\leftarrow}{\oplus}\ H \cdots F\ \overset{\oplus}{\rightarrow}$

$\overset{\delta+}{H} \cdots \overset{\delta-}{F}$ (supposed)

Periodic trend : E_N depends on ENC.

∴ E_N increases as we move from left to right in a period ~~it~~ (upto group 17) & it decreases on moving from top to bottom in a group.

→ F
↑ So, 'F' is the most electronegative element of P.T

- Pauling scale : Acc. to Pauling scale, E_N of any element is difference.

$X_A = X_A - X^\circ$ (Some known elements E_N)

(∵ He represented E_N by X)

- Assigned 0 value of E_N arbitarily to any element.
- Mulikan : Grave a simplified formula of $E_N = \frac{IE + EA}{2}$

☆ Covalent & Van der wall's radius :

At. radius is always measured in MOLECULE

eg : $O \rightarrow O_2$



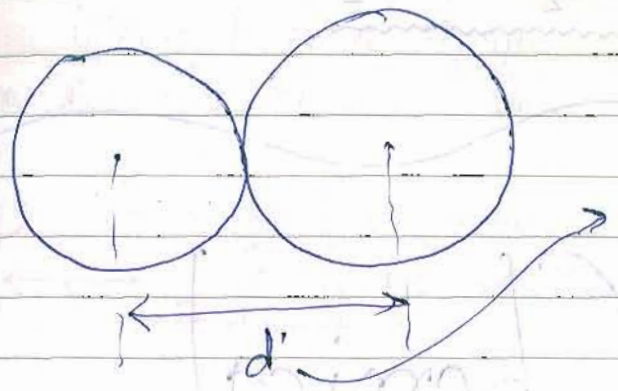
$\frac{d}{2}$ → COVALENT radius.

fig : 1

Date

Noble gases (atomic state only)

Fig: 2



- Covalent radius: It is ½ the inter nuclear distance of covalently bonded atoms (as shown in fig: 1 ↙) In covalent molecule, electron environments of 1 atom is shared partially by other decreasing inter-nuclear distance
- Van der Wall's radius: It is ½ of internuclear distance b/w adjacent atoms when they are just touching (as shown in Fig: 2 ↑).
- Comparison: Van der Walls radius is greater than Covalent radius (of same element)
- For noble gases, van der walls radius & covalent radius are same (∵ they don't form covalent compound)

- Metallic - Non-Metallic / Acid - Base Property
  - Metallic property ~~increases~~ decreases as we move from left to right in a period & it increases from top to bottom in a group.
    Eg, Cs is most metallic.
  - Metal oxides are all BASIC. Basic strength of oxide decreases from left to right & increases from top to bottom

Date

- Non-Metal oxides are acidic with exception of H_2O, CO, NO, N_2O, SiO_2.

+1 Chemistry Notes
Akshansh

30 July 09

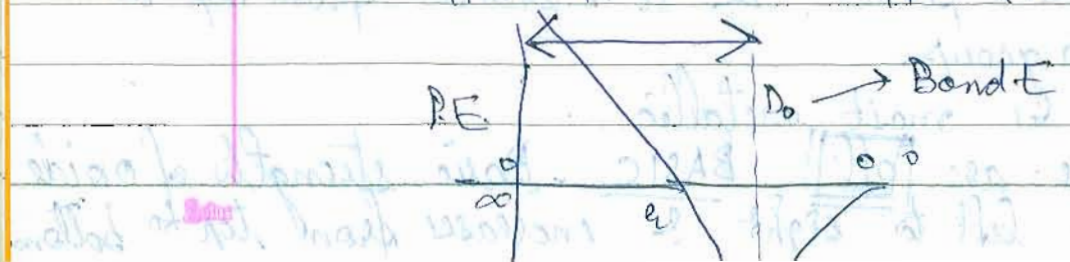
Ch- Chemical Bonding

☆ Why elements combines to form chemical bond?
Elements other than noble gases have unstable, open shell Electronic Config.(EC) In order to become stable, they tends to ~~do~~ acquire closed shell EC, which is achieved by interaction of valence shell of 1 element with valence shell of other elements. This interaction of valence shell electrons results in formation of chemical bond.
how E changes

☆ ENERGETICS OF BONDING (how E changes when e⁻ moves towards stability)

eg: H_2

H● ● H ⟶ H—H.

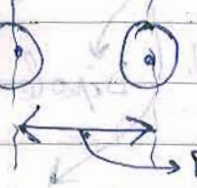


Date

As stability increases P.E. decreases.

(fig)

When P.E is at minima, then stability is max. showing chemical bond is formed.

- 

At P.E minima, distance b/w nucleus of covalently bonded atoms.

Bond length → Internuclear distance of the bonded atoms at P.E minima in P.E vs. inter nuclear distance (r) diagram.

This diagram is also called MORSE P.E DIAGRAM

- At P.E minima, there is max. attn b/w bonded atoms.

✱ After P.E. minima, P.E. increases sharply if the inter-nuclear distance is decreased further. It is because of the reason that, after this min. inter nuclear distance, valence shell & nuclei of bonded atoms comes very close. As and start repelling strongly if pushed further.

~ BOND ENERGY (D_0) (also called DISSOCIATION E)

The min. E required for separation of bonded atoms to infinitely apart.

OR

Bond E. is E released when 2 atoms, infinitely apart are brought to their internuclear distance.

Closed shell configuration is called OCTET

Date

☆ TYPES OF / CLASSIFICATION OF CHEMICAL BONDS

- Primary Bonds
  - Covalent Bonds.
    - Coordinate (dative) bonds. (subpart of Covalent bond)
  - Ionic bonds
  - Metallic bonds.
- Secondary Bonds
  - Hydrogen bond
  - Dipole-Dipole bond
  - Vanderwall's bond

PRIMARY BONDS

COVALENT BONDING

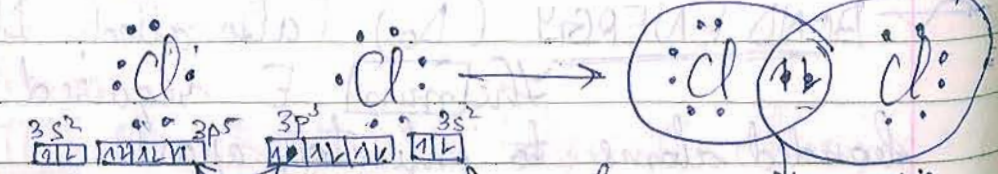
It arises due to sharing of e's b/w bonded atoms.

- In CHEMICAL BONDING,
  - Only valence shell e's are involved i.e core e's are not involved
- During sharing of e's for Covalent Bonding, it is the orbitals of the valence shell holding the e's being shared overlaps.

eg

$2Cl \longrightarrow Cl_2$





ONLY Covalent bond is represented by a line. :Cl—Cl:

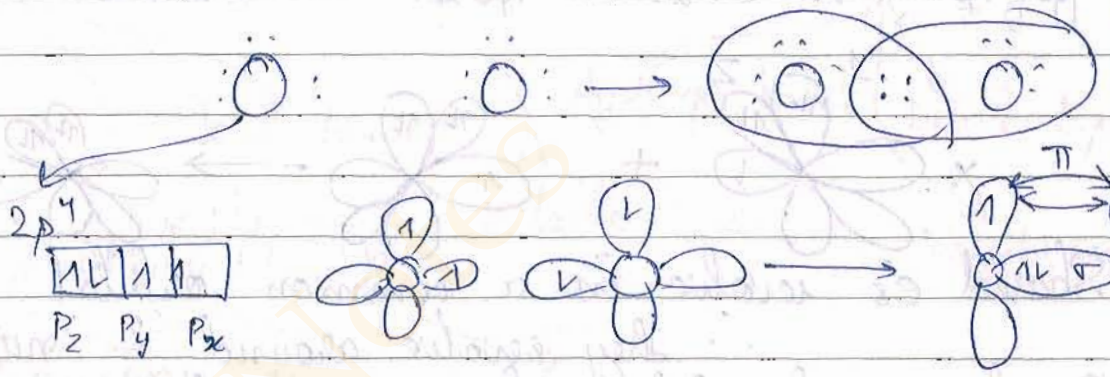
This type of structure is called LEWIS DOT STRUCTURE

- Only unpaired e⁻ (in valence shell) having opposite spin is involved in bonding.

Date

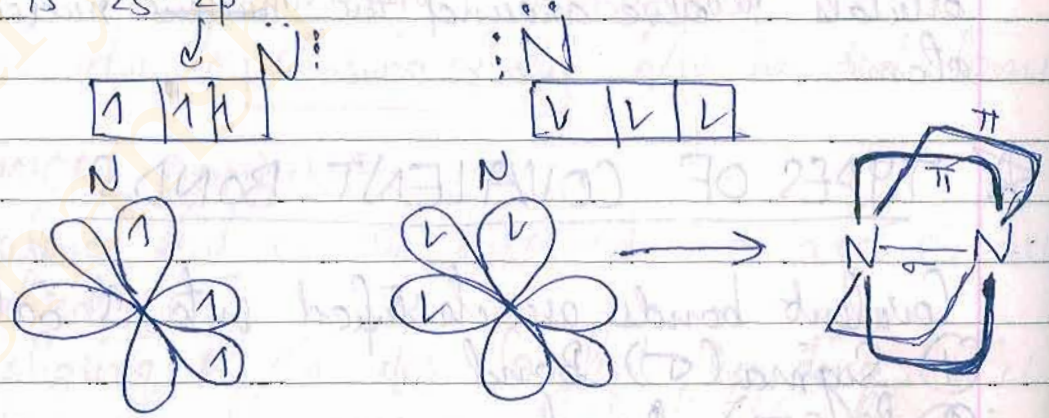
② Pi (π) bond : These bonds are formed by sidewise (lateral overlap) overlap of orbitals.

eg O_2



eg N_2

$1s^2\ 2s^2\ 2p^3$

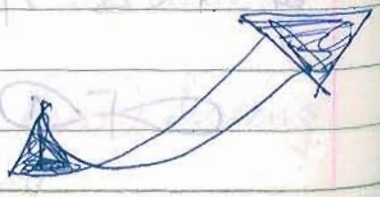


B/w the same atom, σ bond is always stronger than π bond.

Reason: ∵ In σ bonding greater area of orbitals are involved in overlapping ∴ forms stronger interaction.

While, in π bonding, due to lateral overlap, smaller area of orbitals are involved in overlaping, developing a weak interaction. ∴ forms a weak bond.

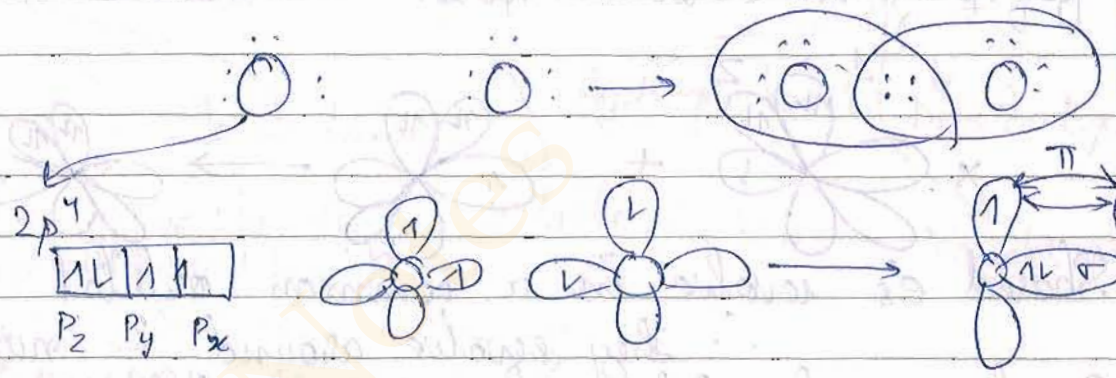
COORDINATE BOND



Date

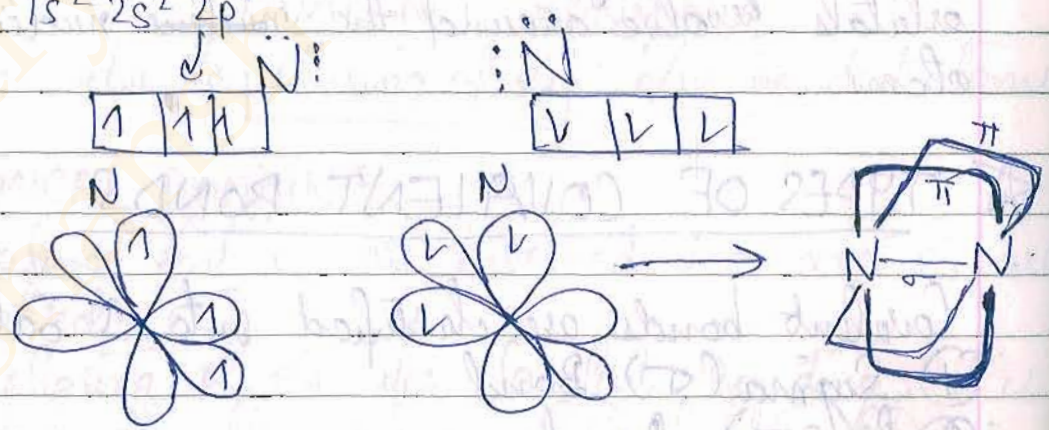
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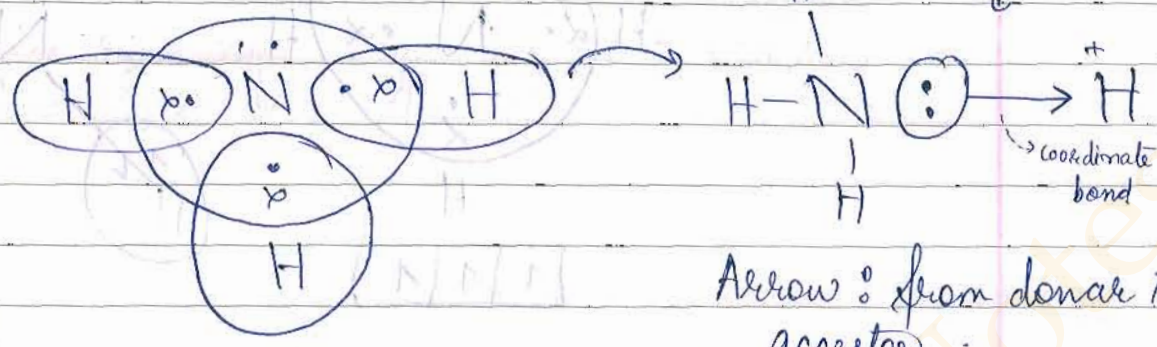
COORDINATE BOND

Date

NH_4^+

Source $NH_4^+ Cl^-$

$NH_3 + H^+$.



Arrow : from donar to acceptor.

* Coordinate Bond is formed by sharing of a pair of e's b/w bonded atoms in which both shared e's are contributed by a single atom :

Theory of Covalent Bonding

(1) VALENCE SHELL E⁻ PAIR REPULSION THEORY (VSEPR THEORY)
वेसपर

(2) MOLECULAR ORBITAL THEORY (MOT)

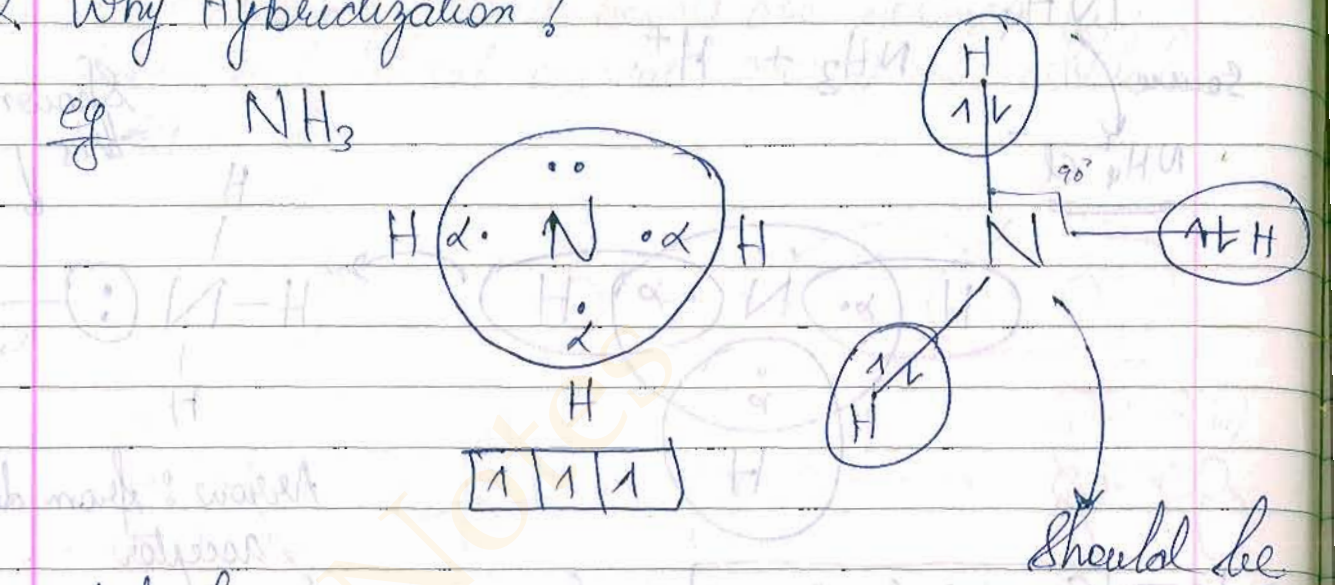
(1) VSEPR Theory : It is based on the theory of HYBRIDISATION (mixing up of atomic orbitals)

Acc to VSEPR theory, pure at. orbitals don't take part directly in chemical bonding. Before bonding, at. orbitals of valence shell hybridizes to produce hybrid orbitals.

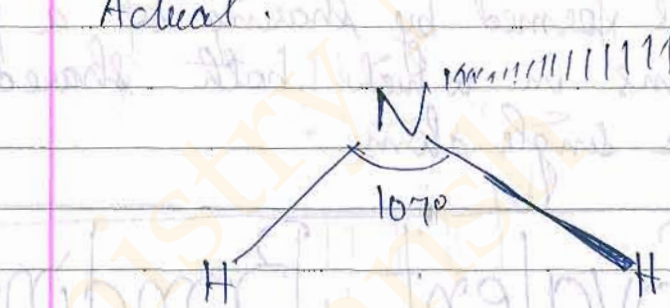
It is the hybrid orbitals which is involved in overlapping, forming covalent bonds.

Q. Why Hybridization ?

eg NH_3



Actual.



- This theory is req. because, if pure atomic orbital would be involved in bonding, there would be 90° angle b/w atoms. This is different from actual structure.

- **Hybridization** : 1) During Hybridization, at. orbitals of comparable E mixes up to give hybrid orbitals of equal E.

2) In the process of hybridization, the no. of hybrid orbitals produced are always equal to the no. of at. orbitals involved in Hybridization.

eg one S orbital + one P → 2 sp orbitals. name
sp + sp

eg one S + two P → 3 sp^2 orbital.
sp^2 sp^2 sp^2

1S + 3P → 4 sp^3 orbital

Date

Geometry of Hybrid Orbitals (HO$_s$)

Hybrid orbitals produced after hybridization project themselves in space in order to have max. distance b/w adjacent orbitals & min. repulsive force b/w them.

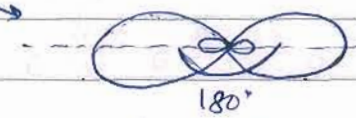
Representation



sp or sp^2

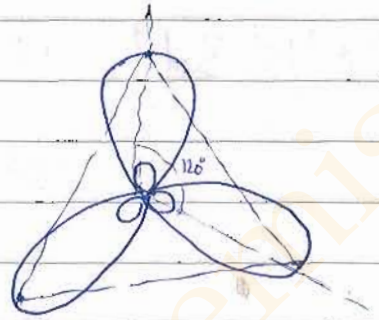
Geometry

sp (no = 2) →



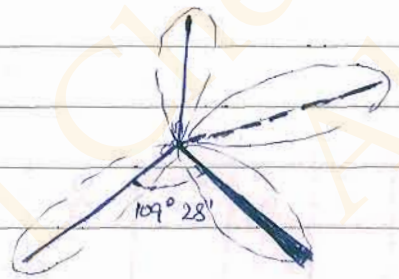
linear (linearly oriented in 3D)

sp^2 (No. = 3)



Triangular Planar (TP)

sp^3 (no. = 4)



Tetrahedral

Date

2 July

Chemical Bonding

... Continued

- Hybrid orbitals.

3) $S + 3p + 1d = sp^3d$ (name)

Projection in 3D



Trigonal bi pyramidal (TBP)

4) $1s + 3p + 2d = sp^3d^2$

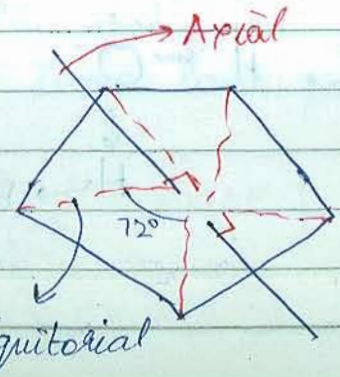


- All pts. are equivalent & equidistant from centre. All ∠s are of 90°.

Octahedral (has 8 faces)
Commonly known as → Square bi pyramidal.

5) $S + 3p + 3d = sp^3d^3$

- Pentagonal bi pyramidal



Date

Determination of Shape & Structure of covalent molecules & ions.

- Steps, needed to be followed for predicting molecular structure —

1. Determination of central atom.

Reason: Hybridisation at the central atom determine the overall shape of the molecule / ion.

uniqueness in property & no. also.

Rule 1: UNIQUE ATOM in the ~~molecul~~ molecule / ion becomes the central atom.

If more than 1 unique atoms are present largest (in size) unique atom becomes the Central Atom.

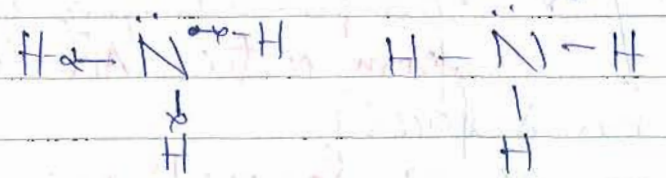
~~Rule 2~~.

2. Determination of e^- pairs (EP) at the central atom.

no. of non-bonded e^- pair in valence shell

EP (central atom) = no. of σ-bond + no. of lone pairs + no. of coordinate bonds if it occured alone.

✓ NH_3

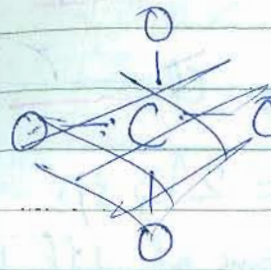


✓ H_2O



Date

✓ CO_2



$O :\ddot{O}: \rightleftharpoons C \overset{\pi}{\rightleftharpoons} \ddot{O}:$

EP = 2 + 0 = 2

✓ $COCl_2$

Cl

$Cl - C \rightleftharpoons \ddot{O}:$ EP = 3

2)

3) EP	HO (Hybrid orbital)	Geometry (Geo)	Bond Angle
2	sp	linear	180°
3	sp^2	Triangular planar	120°
4	sp^3	Tetrahedral	109° 28"
5	sp^3d	TBP	90°, 120°
6	sp^3d^2	Octa, SBP	90°
7	sp^3d^3	PBP	72°, 90°

4. • If there is no lone pair at the central atom, then geometry of Hybrid orbitals at the central atom will also be shape of the molecule.

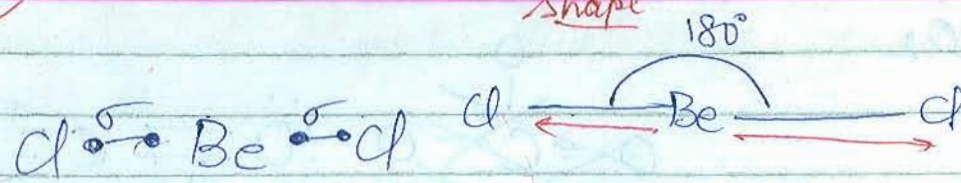
If central atom has some lone pairs, then,

Geo ≠ Shape

Geo − L.P = Shape

It has non-polar molecule. But, bond is polar.

- $BeCl_2$ → Shape



$EP = 2$, sp

☆ **DIPOLE MOMENT** — Separation of charge b/w atoms of diff E_N when they form bond.

Let $E_N(A) > E_N(B)$



e⁻ closer to A than B i.e e⁻s spend more time near more E_N atom.

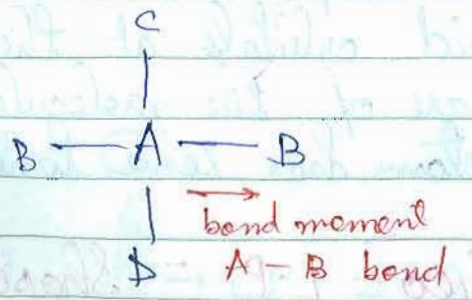
- Dipole in a molecule arises due to difference in E_N of the bonded atoms



- Dipole is a vector qty. whose dir^n is always +ve to -ve.
- Dipole moment, magnitude is measured by a qty. called DIPOLE MOMENT.

Magnitude of Dipole moment depends on E_N difference of bonded atoms. Greater the E_N difference higher will be dipole moment (denoted by μ)

$$\mu = qd$$



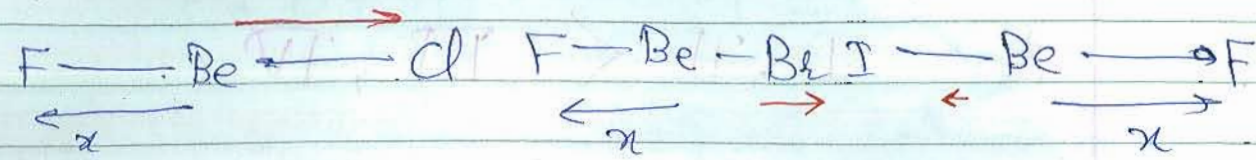
- Dipole moment of a molecule is the vector sum of individual bond moments.

Date

Family → BX_2

① $BeFCl$, $BeFBr$, $BeFI$

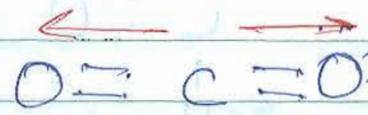
I , II , III



Max. polar → III

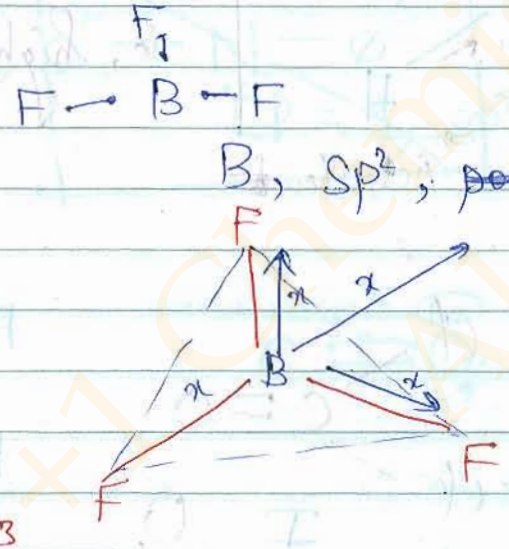
Min. → I

② CO_2



EP = 2 , sp , non-polar

③ BF_3

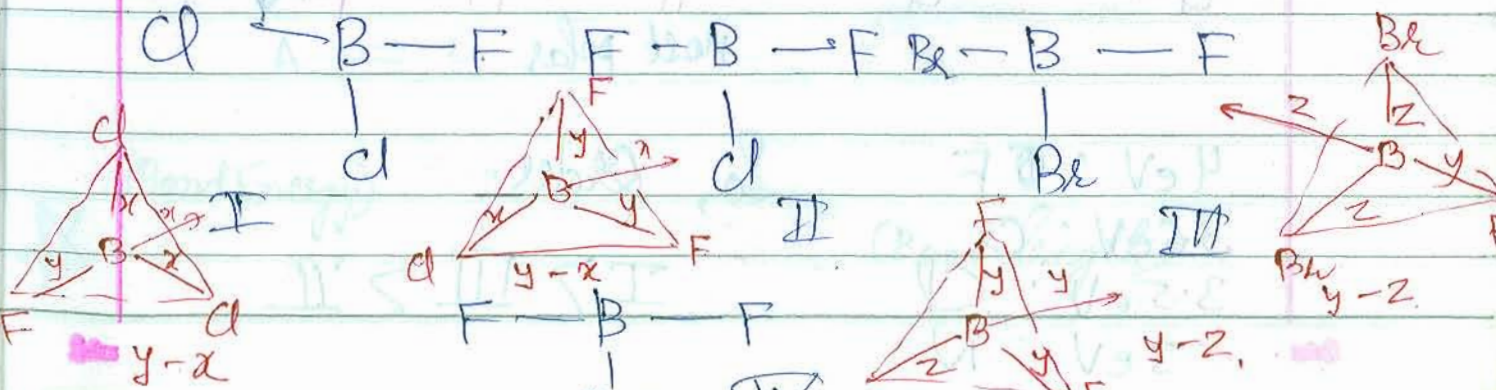


So, non-polar, resultant = 0.

Family → BX_3

④ $BFCl_2$, BF_2Cl , $BFBr_2$, BF_2Br

I , II , III , IV



Decreasing EN: (1st 4)

F > O > Cl > N

Date

So,

I = II & III = IV

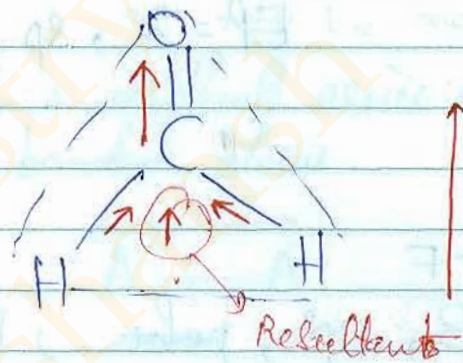
& I, II < III, IV

- H_2CO



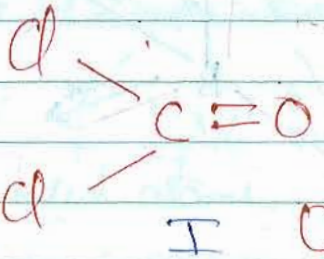


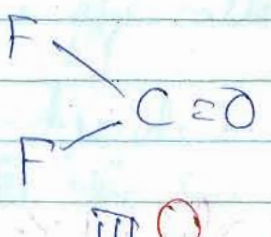
EP = 3, sp^2

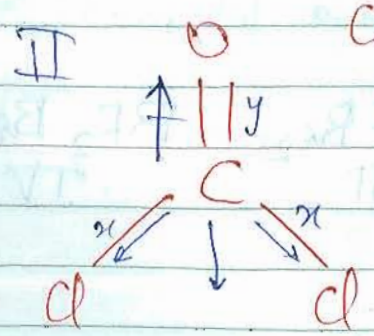


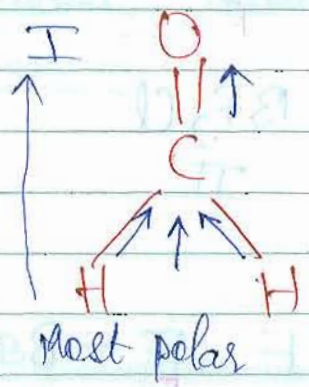
So, highly polar molecule.

- $COCl_2$

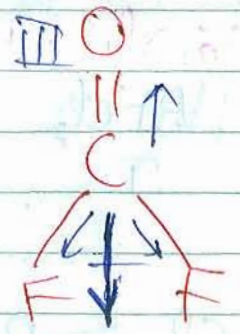








Most polar



4 eV : F

3.6 eV : O

3.5 eV : Cl

3 eV : N

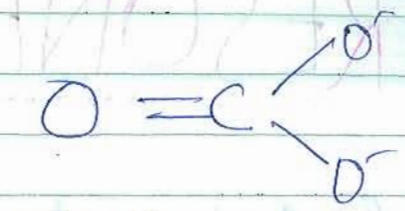
So, Order

I > III > II

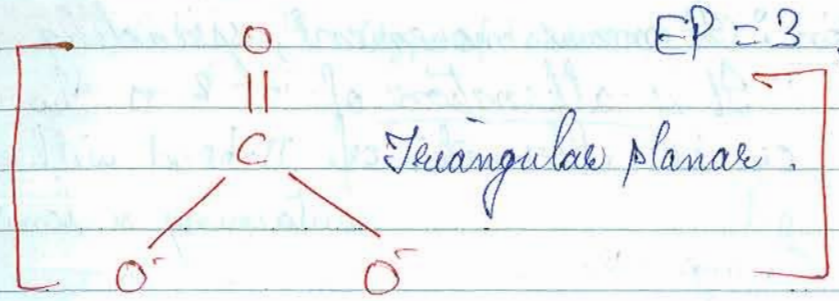
Date _____

- CO_3^{2-}

$C + O + 2O^- + 2e^-$

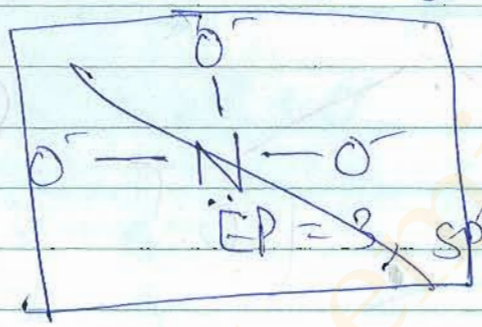


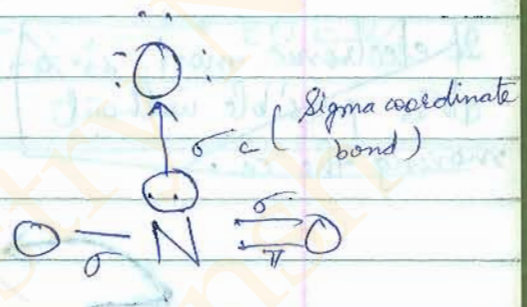
EP = 3, sp^2



- NO_3^-

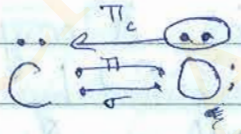
$N + 2O^{\bullet} + O^-$

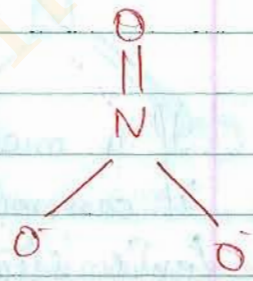




EP = 3, sp^2

- CO





- A — B

A = B

A ≡ B

} B/w like atoms, more the no. of bonds, stronger will be the bond i.e higher will be Bond E.

(Bond Energy) $BE \propto \frac{1}{BL}$ (Bond length)

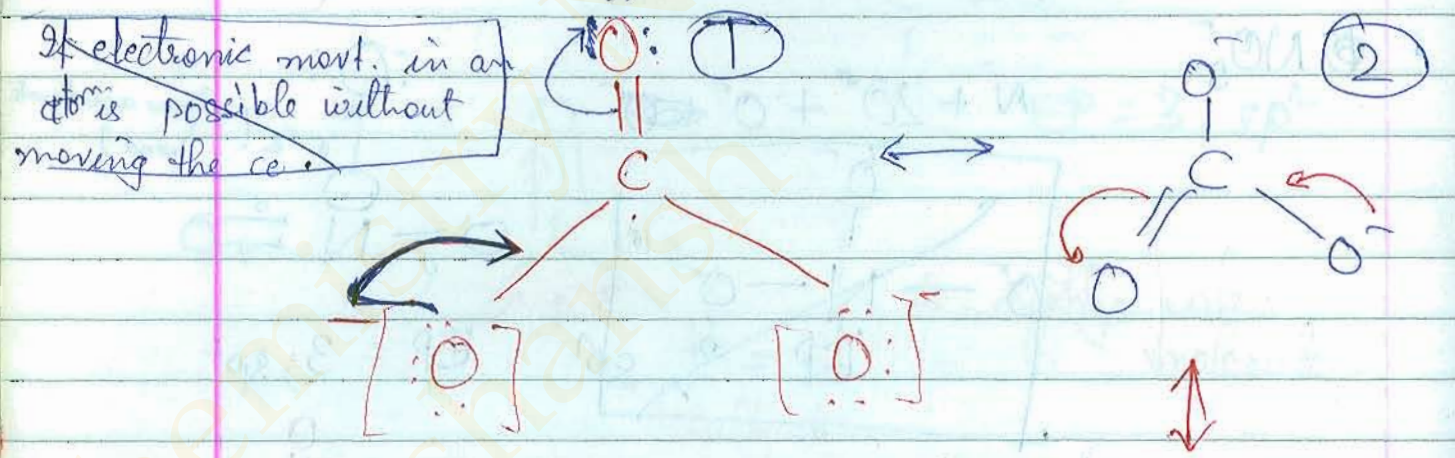
Date

☆ RESONANCE : It is a phenomena of delocalization of $\bar{e}$s in a conjugated molecule or ion.

- Delocalization : It means movement, spreading
- Conjugation : It is alternation of σ & π bonds (which allow movt. of $\bar{e}$) or is alternation of π-bond with an atom containing a lone pair.

many more — — — — —

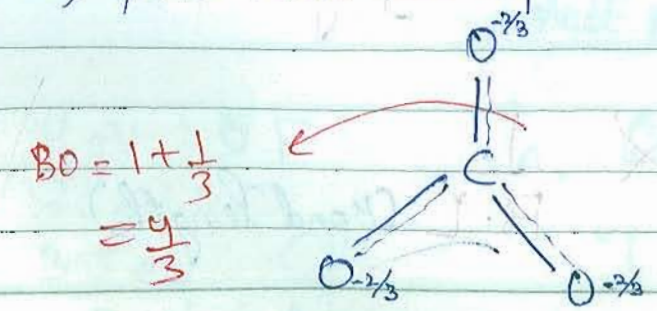
If electronic movt. in an atom is possible without moving the $\bar{e}$.



- If a molecule/ion is conjugated, it cannot be described by 1 single Lewis structure. The various structures arising due to movt. of $\bar{e}$s (delocalization) are known as RESONANCE Structure.

①, ②, ③ are resonance structures of CO_3^{2-}

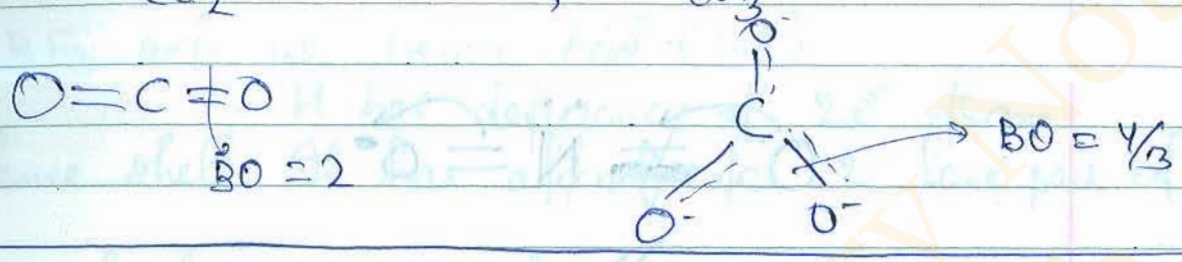
So, final structure of CO_3^{2-} is



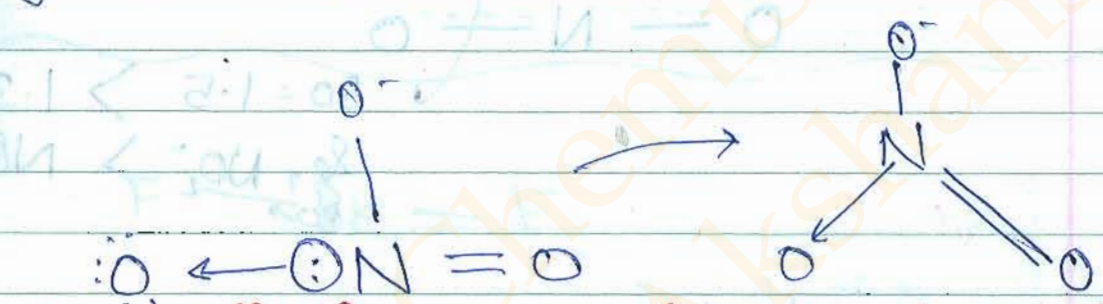
6 August 09

☆ BOND ORDER (types of bonds σ, π ...)
It represents the no. of bonds b/w the bonded atoms.
eg:

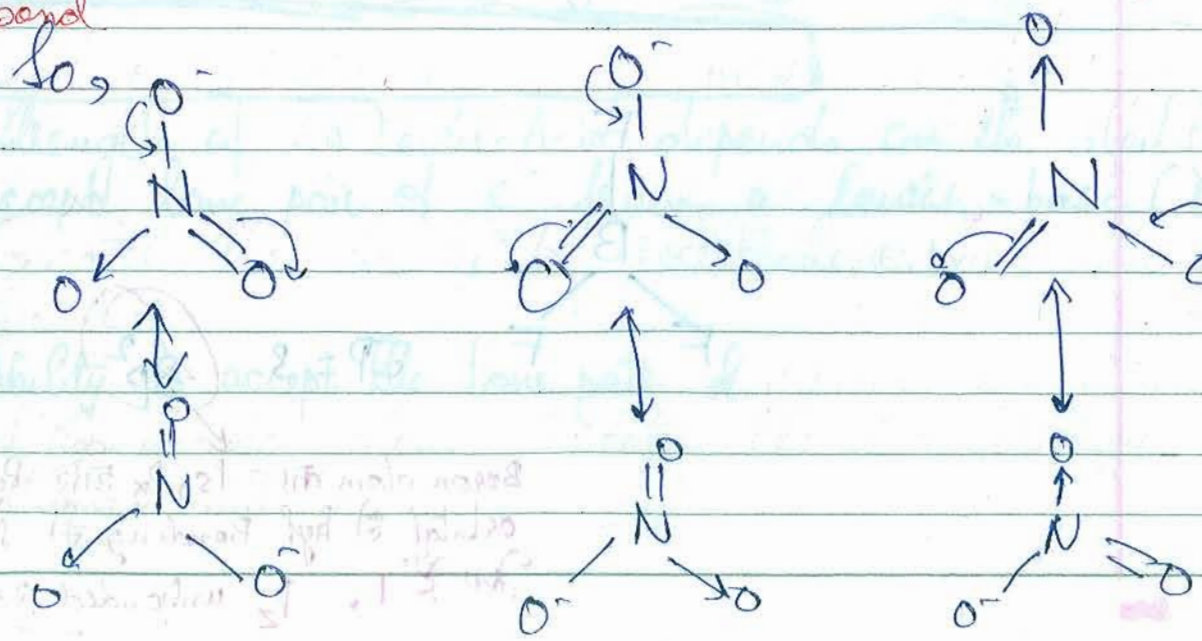
CO_2 , CO_3^{2-}

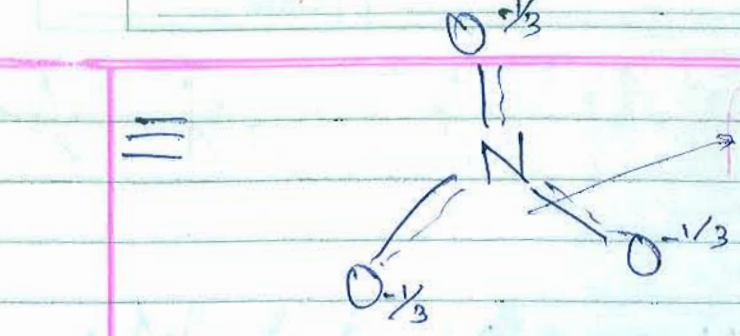


- $NO_3^- \longrightarrow N^+ + 2O^{\oplus} + O^-$

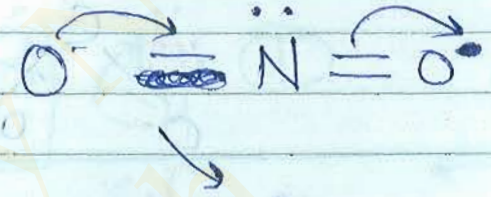


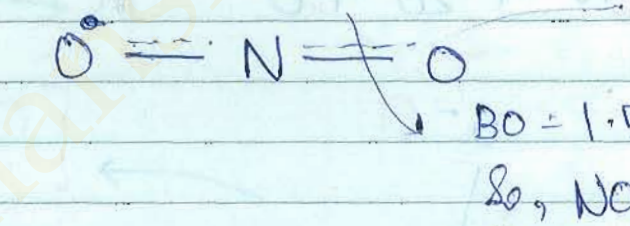
- In NO_3^-, all ~~them are eq~~ the O bonds are similar in properties ∴ here, the O in O_3 is indistinguishable i.e which is what ?, which O is ~~is~~ having which bond





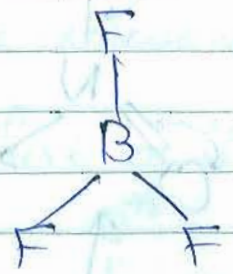
- $NO_2^- \rightarrow N + O^\circ + O^-$





☆ LEWIS-ACID

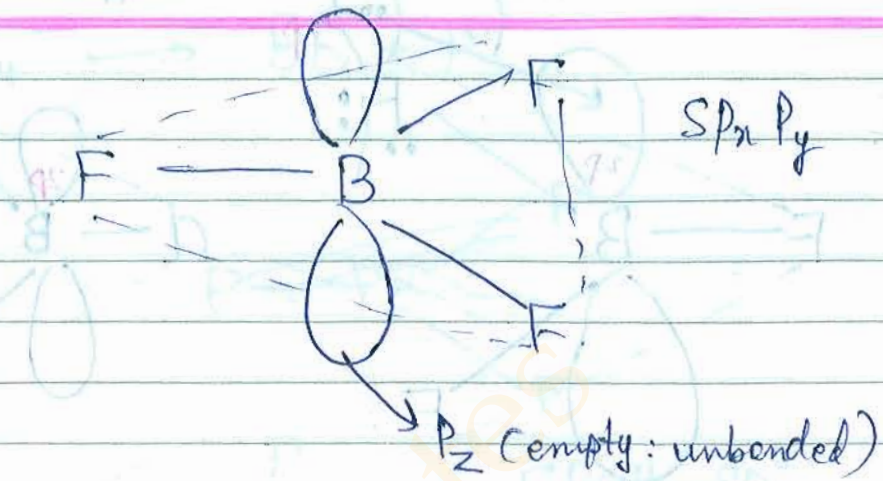
Lewis-acid are the species which can accept a L.P of e⁻ from a LEWIS BASE



EP = 3 sp^2

Boron atom का 1s, P_x और P_y orbital ही Bonding में Part लेता है, P_z unbonded रह जाता

Date



So, BF_3 acts as Lewis-Acid (L.A)
∵ it has deficiency of 2 e^- from valence shell. It has affinity for 2 lone pair of e^-.
So,
this situation is same for + BX_3.

F — Be — F

sp_x, EP → 2

- It is deficient of 4 e^-. So, it req. 2 EP. So, its a L.A. So, its a very strong L.A.

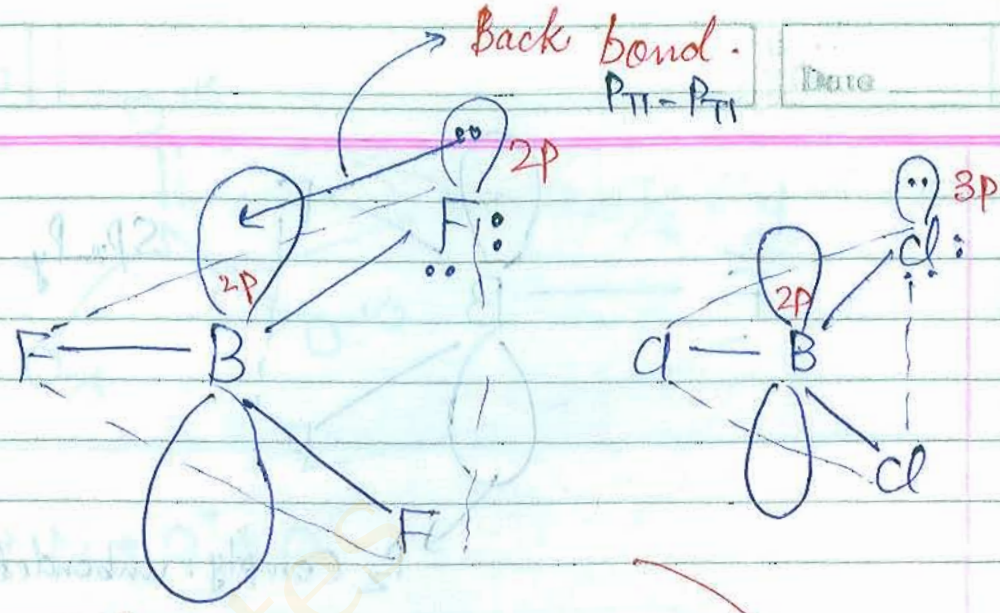
- **Relative Strength of lewis-Acid.**
- Strength of a lewis-Acid depends on its ability to accept lone pair of e^- from a lewis-base (L.B). Greater the ability to accept lone pair, stronger the L.A.
- Ability to accept the lone pair depends on e^- deficiency of the acceptor atom. Greater the e^- deficiency, stronger will be L.A.

33
O_3 -

which
BASE

Py
Part
RE 1121

Comparison.



☆ Back-Bonding

(i) $P_\pi - P_\pi$ Back-bond
(ii) $P_\pi - d_\pi$ Back-bond
(iii) $d_\pi - d_\pi$ Back-bond

2nd → orbital of acceptor.
1st: Orbital of donar

☆ EXTENT OF BACK-BONDING

Effective overlapping of orbital occur b/w orbitals of like E.

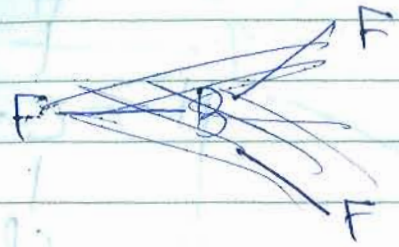
- On the basis of E_N, BF_3 should be stronger L-A than BCl_3.

But, the fact is opposite.

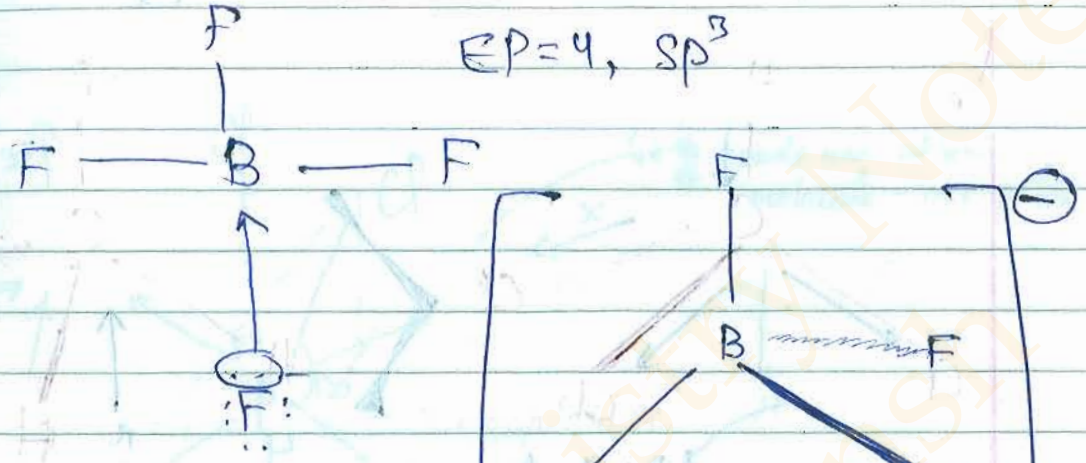
Reason: $P_\pi - P_\pi$ back bonding occur in BX_3. The extent of $P_\pi - P_\pi$ back bonding is max in BF_3 due to the like E orbitals involved in back bonding. This $P_\pi - P_\pi$ back bonding destroy the e⁻ deficiency in BF_3 & makes it weakest L-A among BX_3 (Boron tri-hallide)

Date

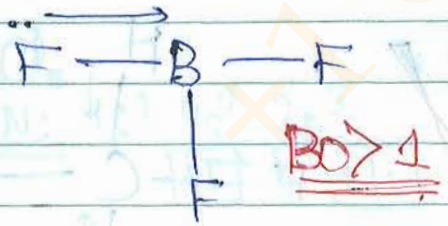
• $BF_4^- \longrightarrow BF_3 + F^-$



EP = 4, sp^3



Q. Which has stronger B-F bond? BF_3 or $NaBF_4$



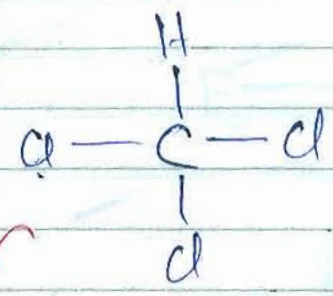
Ans: B-F bond is stronger in BF_3 than in BF_4^-

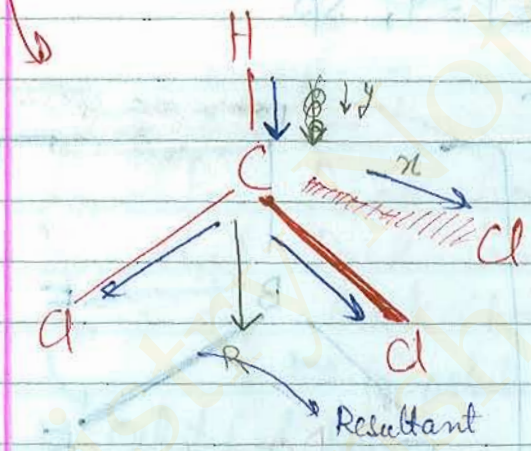
∵ in BF_3, due to $P_\pi - P_\pi$ back bonding, B-F bond acquire partial double bond character. while, in BF_4^-, B-F bond is pure, single, σ covalent bond with BO = 1, hence, weaker than B-F bonds in BF_3.

Hence, B.L (bond length) of BF_4^- is more than BF_3

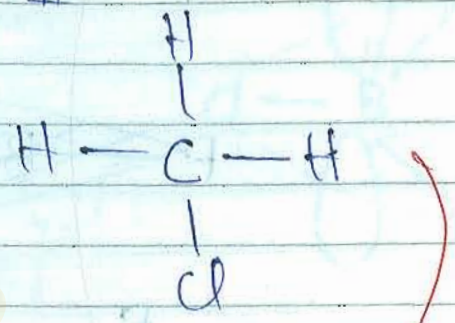
Date

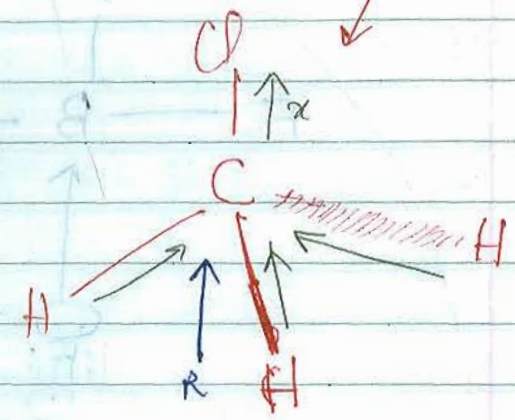
$CHCl_3$
I



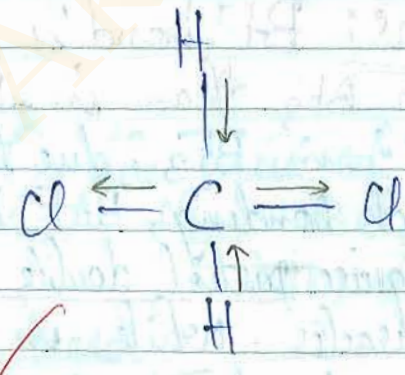


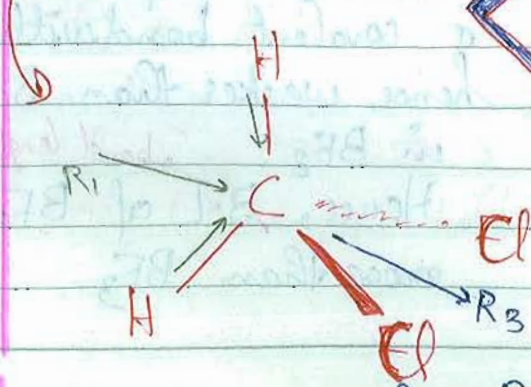
CH_3Cl
II



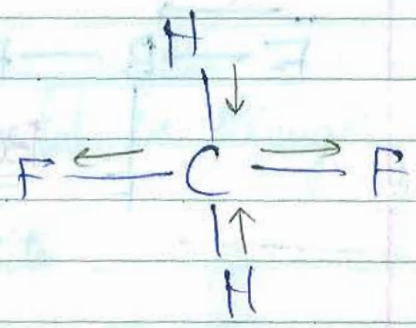


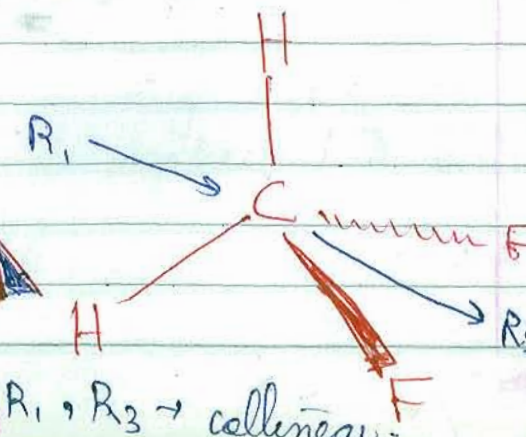
CH_2Cl_2
I





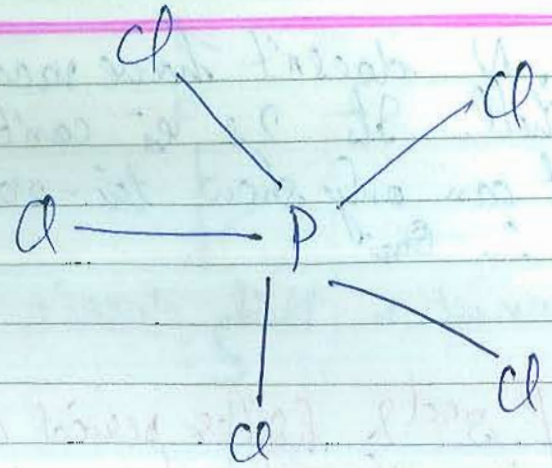
CH_2F_2
I



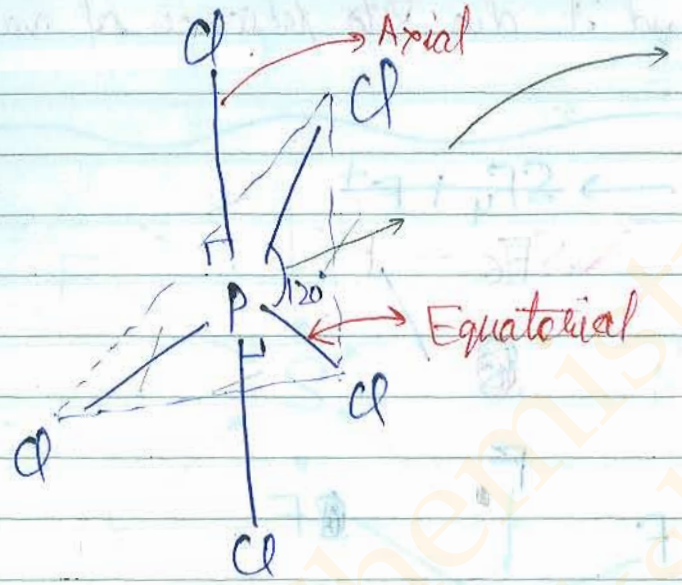


Date

- PCl_5.



$EP = 5$, sp^3d



- NCl_5

N: $1s^2\ 2s^2\ 2p^3$



$\rightarrow NCl_3$.

2nd

P: $3s^2\ 3p^3\ 3d^0$



3rd

Q. Why PCl_5 exist but NCl_5 doesn't, Why?

Ans. P has vacant 3d orbital in its valence shell. ∴ all the 5 valence e⁻ of P can be unpaired & can be made to take part in covalent bonding. So, in pentavalency.

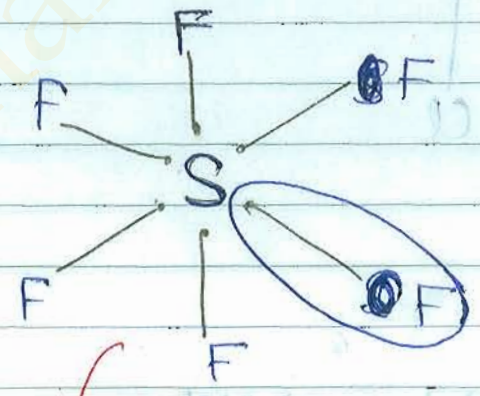
But, N doesn't have vacant d orbital in its valence shell. Its 2s e⁻ can't be unpaired. ∴ it can only show tri-valency, not pentavalency. ∴

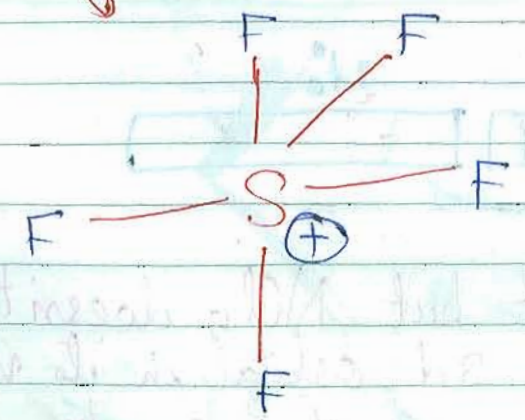
Only NCl_3 exist & NCl_5 doesn't

☆ Any element of 3rd & higher period can violate the octet rule i.e, they can expand their valence shell beyond it due to presence of vacant d orbital.

$SF_5^+ \longrightarrow SF_4 + F^+$

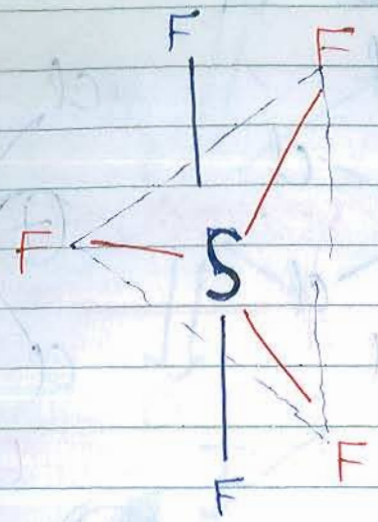
$SF_6 - F^-$



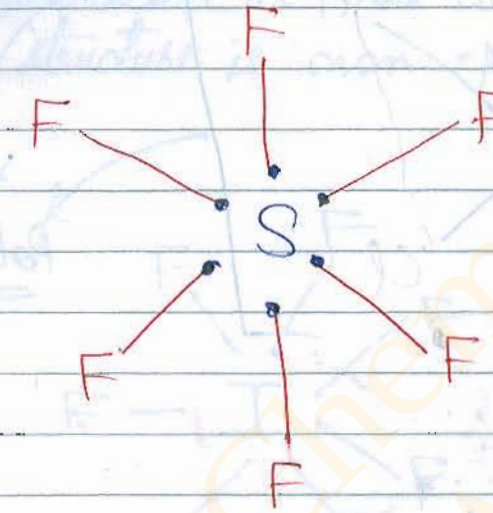


sp^3d.

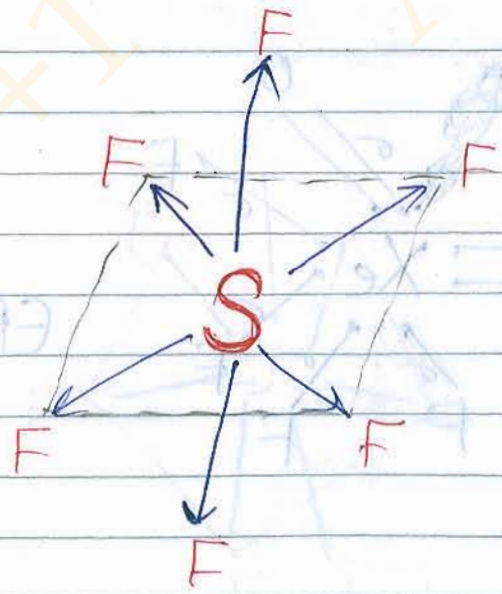
Date _____



- SF_6

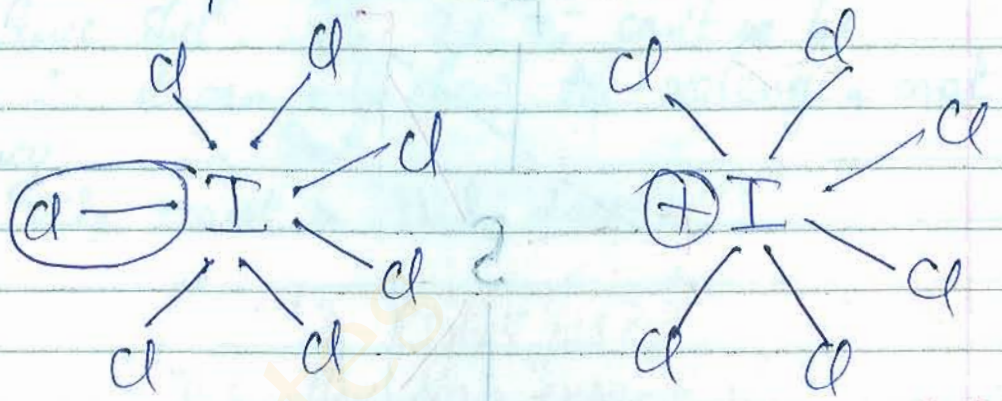


sp^3d^2, EP = 6.

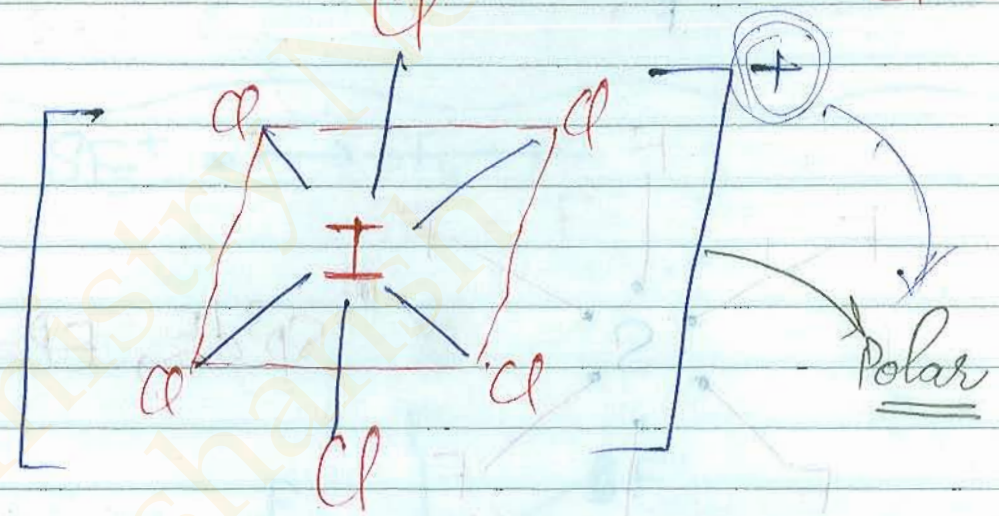


Date

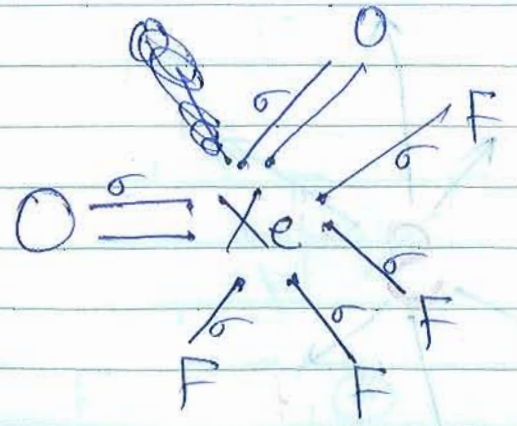
- $ICl_6^+ = ICl_7 - Cl^-$



$\in P = 6,\ sp^3d^2$

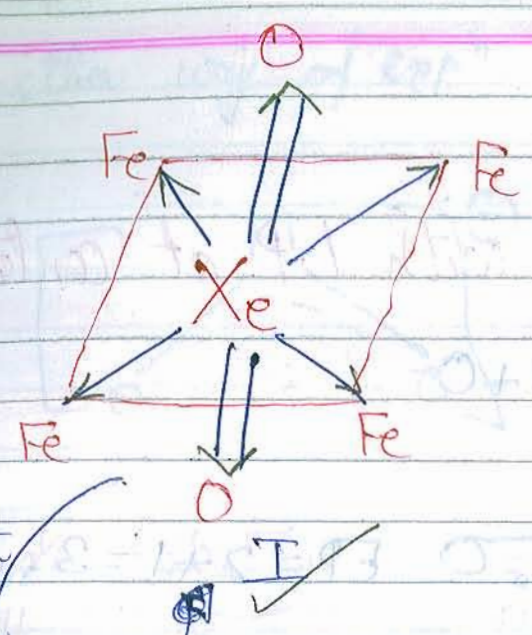


- XeO_2F_4



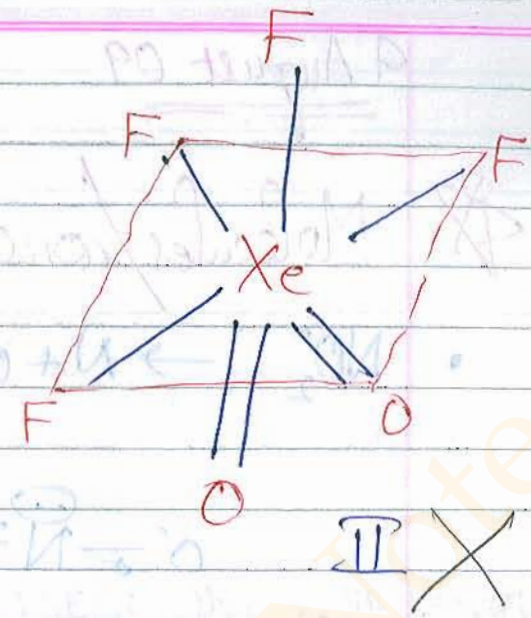
$\in P = 6,\ sp^3d^2$

Date



Correct

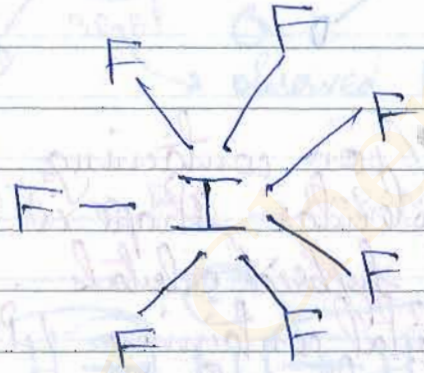
I ✓



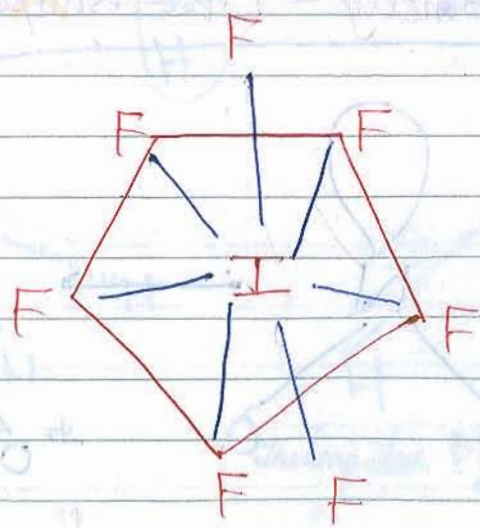
II ✗

Double bonds are at max. distance.
So its structure is non-polar.

• IF_7



EP = 7, sp^3d^3



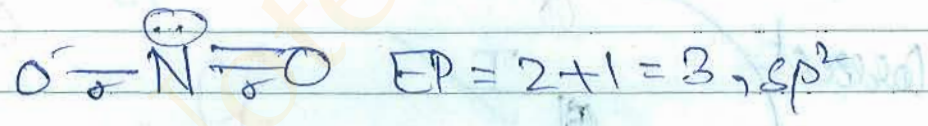
$\mu = 0$

Date

9 August 09

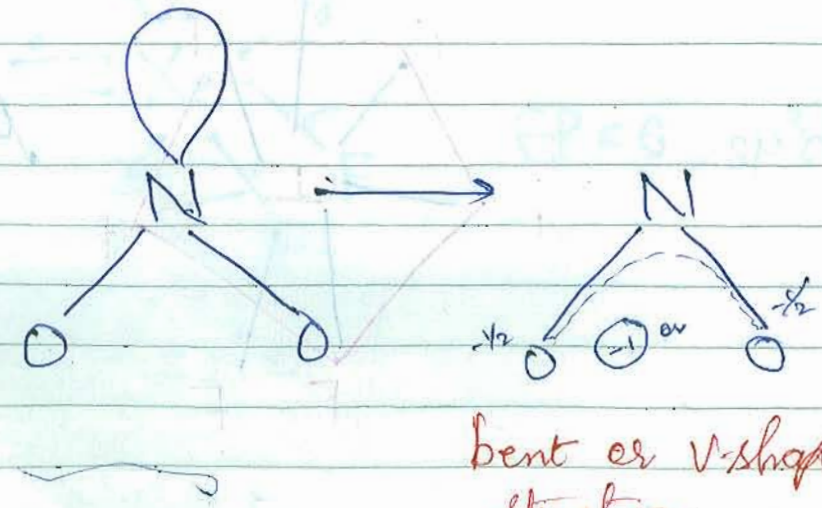
☆ Molecules/ions with L.P at central atom:

- NO_2^- → N + O + O⁻





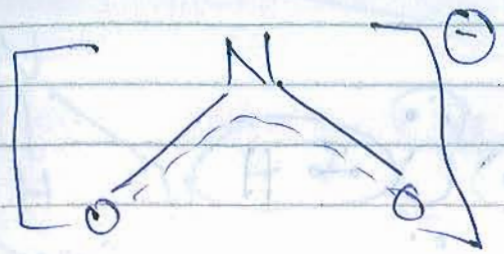
- In the molecule/ion containing L.P at central atom, molecular shape is determined from geometries of hybrid orbitals.
  Hybrid orbital containing L.P is not seen in the the molecular shape.
  So, **Geometry − L.P = Shape**



bent or V-shaped structure.

Date

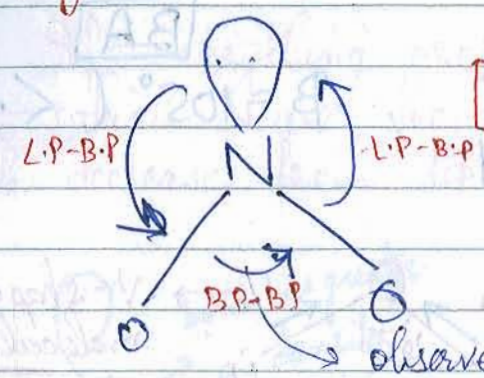
Or, another way of exp^{n}.



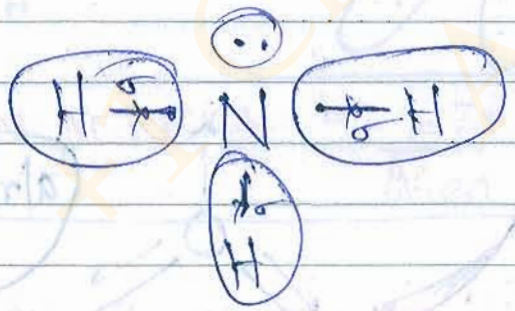
☆ Bond-angle distortion

By VSEPR Theory, this order of repulsion b/w e^{-}s is there.

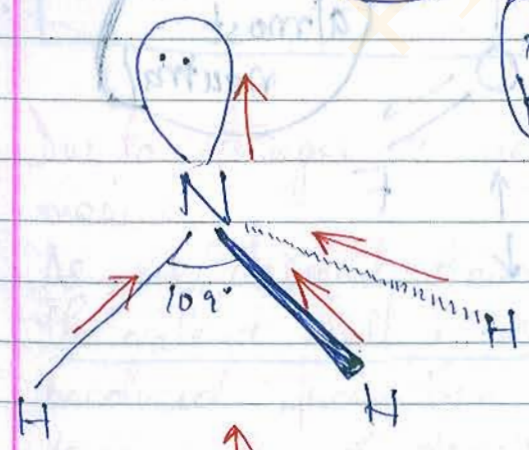
B·P − B·P < B·P − L·P < L·P − L·P



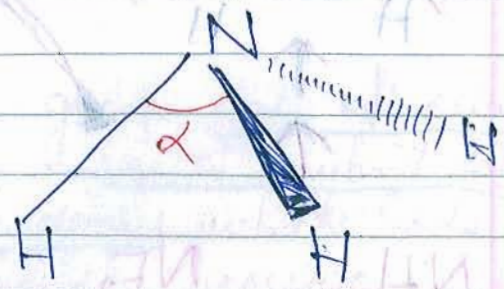
- NH_3 (107° → BA ; FOR NCERT WORK)



EP = 3+1 = 4, sp^3



Highly Polar molecule



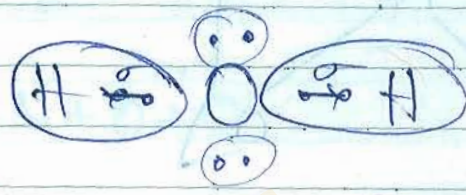
Triangular Pyramidal ~~sha~~ geometry.

α (BA) < 109°

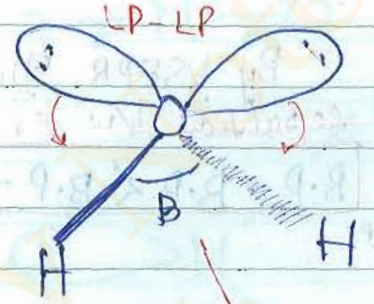
α = 107° (say)

Date

- H_2O

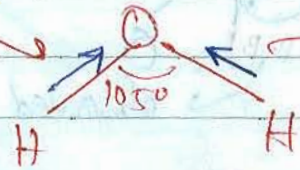


EP = 2+2 = 4, sp^3



BA

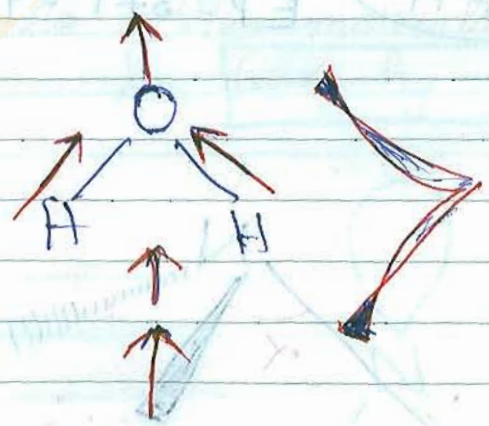
$\beta = 105°$ ($< \alpha$)

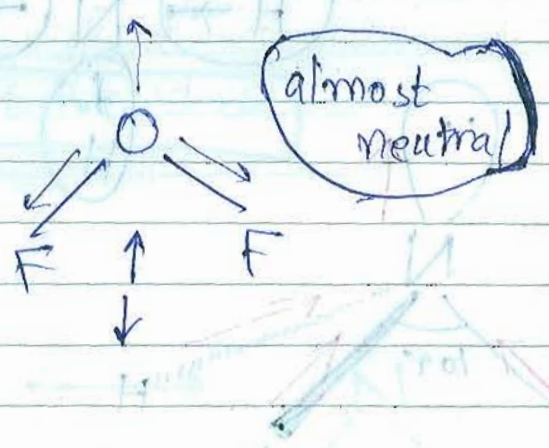


V-shape molecule

Polar molecule

Q. H_2O, OF_2
I II





Q. NH_3, NF_3

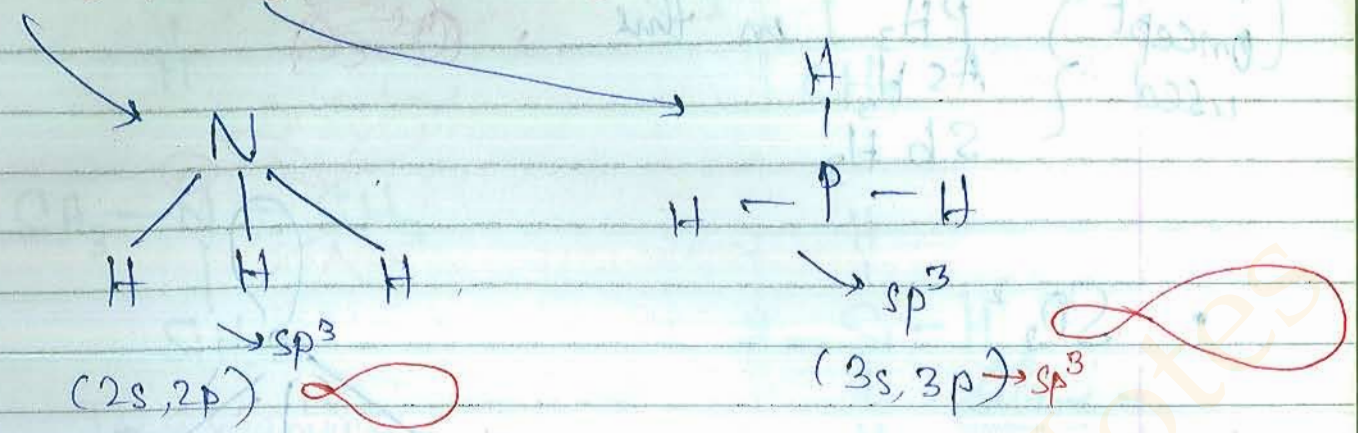




$COCl_2$ (PHOSGENE GAS): VERY POISONOUS GAS.

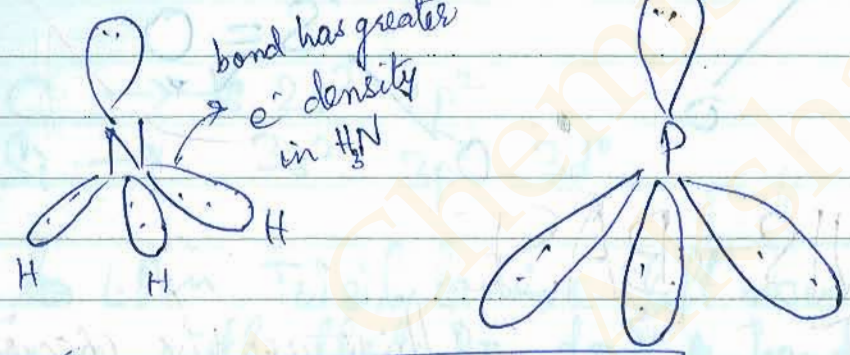
Date

Q NH_3, PH_3 (PHOSPHINE)



★ FACT:

If everything are same except the central atom - which are from a same group of P. Table, B. Angle decreases from top to bottom rapidly.



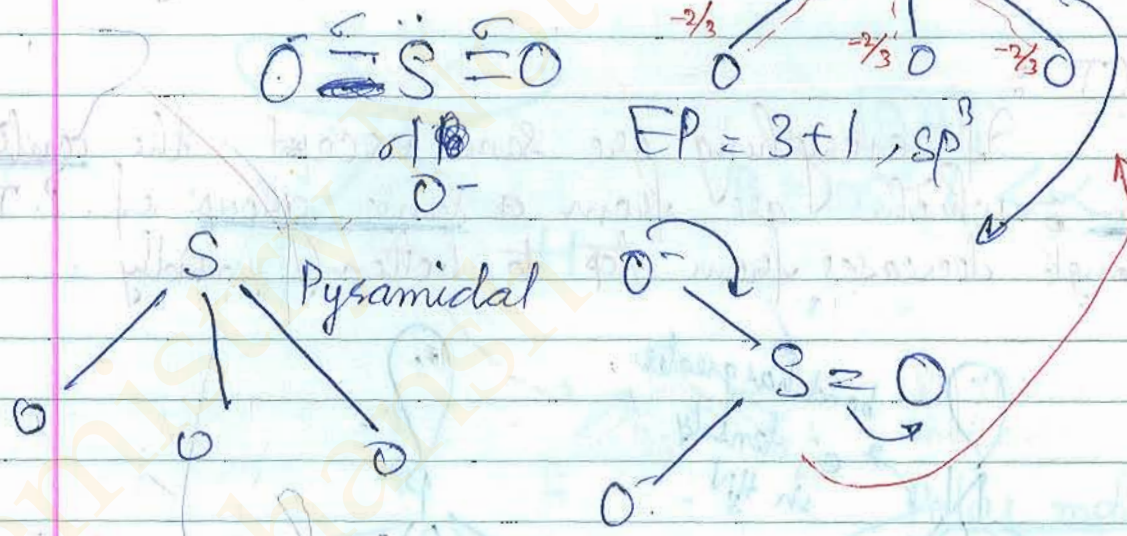
ELECTRON DENSITY = $\frac{e^-}{\text{Area}}$

- Due to stronger e^- density in NH_3, BP–BP repulsion is more.
- As we descend down in a group size of orbitals of the valence shell increases. ∴, Size of hybrid orbitals produced from them also increases which leads to decrease in e^- density of bond. Decrease in e^- density of bond, decreases BP-BP repulsion. So, L.P becomes more effective in compressing the bond. A greater reduction in BA is observed.

Concept used { NH_3, PH_3, AsH_3, SbH_3 } in this ,



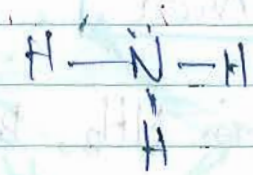
- SO_3^{2-}

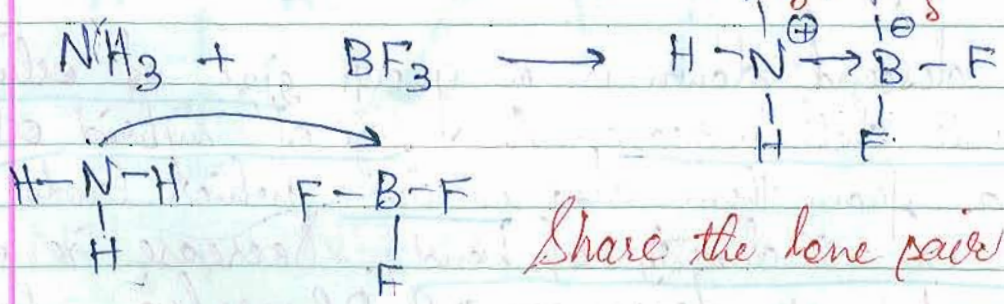


☆ LEWIS BASE

These are the species which can donate a lone pair of e^- to lewis Acid.

eg

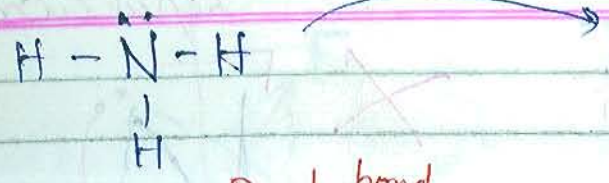


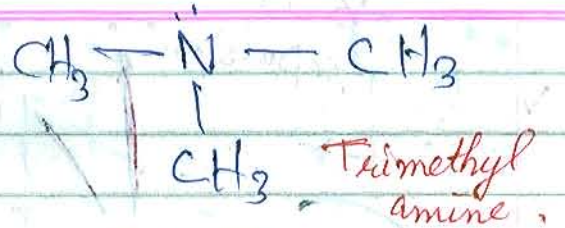


Share the lone pair

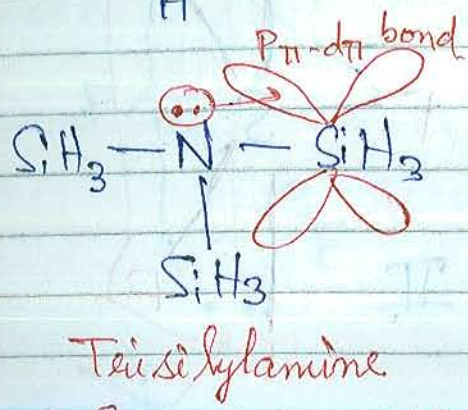
Q Tri methyl amine is pyramidal. Tri silylamine is planar in shape. Explain.

Date

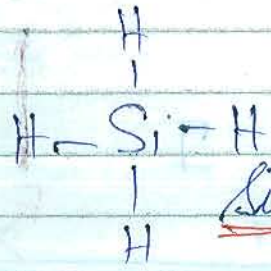




Trimethyl amine.

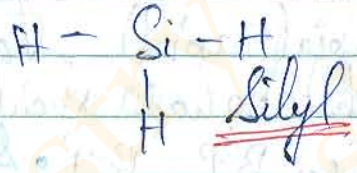


Trisilylamine



Silane.

So, sp^2 hybridization in Trisilylamine.



Silyl.

Ans

C → $2s^2$ $2p^2$

Si → $3s^2$ $3p^2$ $3d^0$

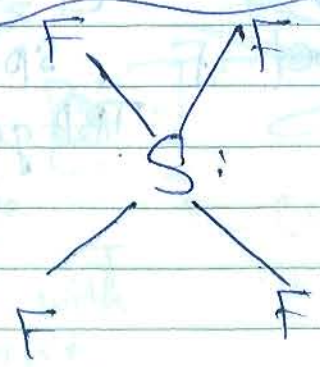
No L.P in Trisilylamine left now. because of resonance with the $P\pi$-$d\pi$ bonds. Also the hybridization is sp^2.

So, its shape will become planar.

But, in Trimethyl amine, 1 L.P is there. So, it can give. So, its a stronger Lewis Base than Trisilylamine.

which

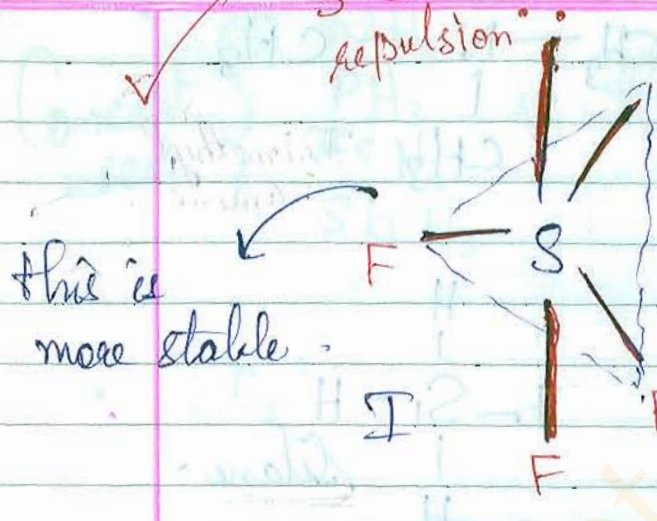
Q SF_4



EP = 4+1 = 5

sp^3d, TBP.

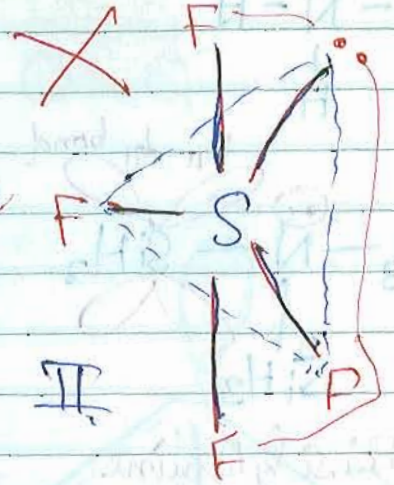
3 LP-BP repulsion ✓



this is more stable.

I

2 LP-BP repulsion ✗



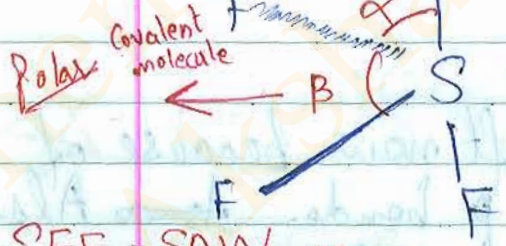
or

II

In TBP geometry, only apial-equitorial repulsion is significant; rest (equitorial-equi or apial-apial) are insignificant. Order of observation should be L.P-L.P, then L.P-B.P, then B.P-B.P. See 'LP-BP/. -- other repulsions. More repulsion, less stable → REJECT



I

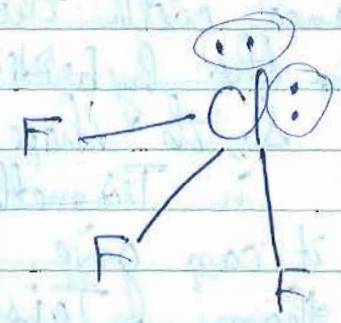


$\alpha < 90°$

$\beta < 120°$

SEE-SAW or (Distorted Tetrahedral)

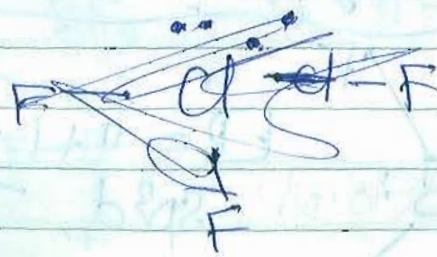
• ClF_3

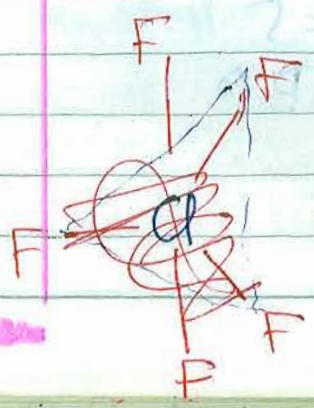


EP = 3+2

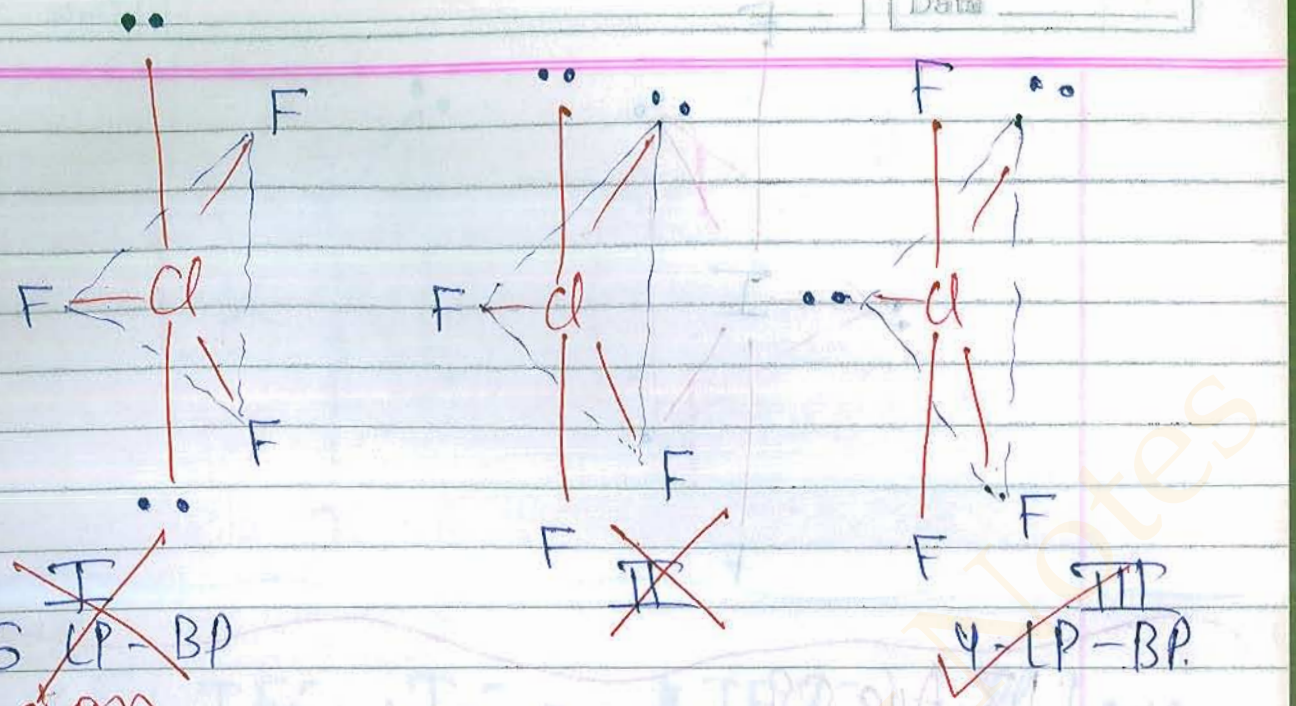
sp^3d

TBP geo.





Date

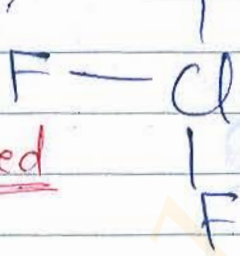


Conclusion

So, in TBP geo., L.P is more stable on equatorial pos^n.



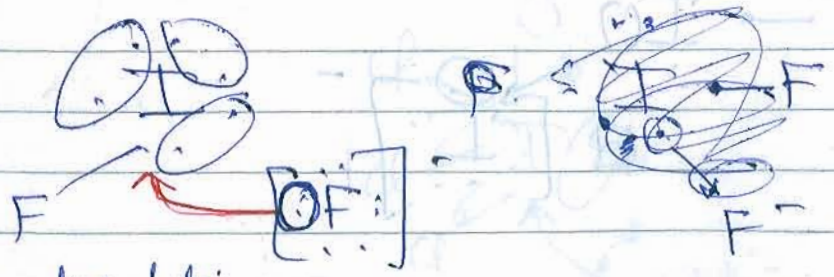
III



T-shaped

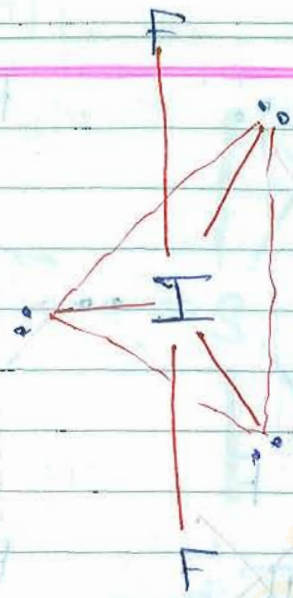
- $IF_2^- \rightarrow I + F + F^-$

$IF_3 \rightarrow IF_2^+ + F^-$



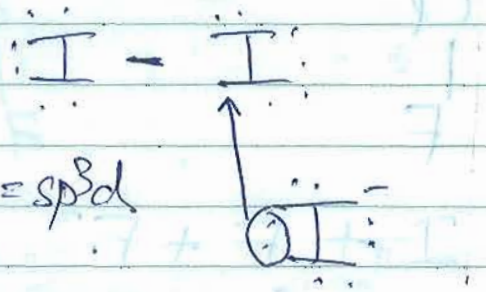
F makes dative bond with I. I doesn't make with F ∴ F can't violate octet rule.

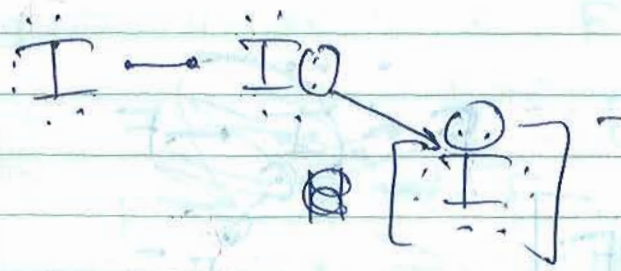




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☆ $I_3^- \rightarrow I_2 + I^-$



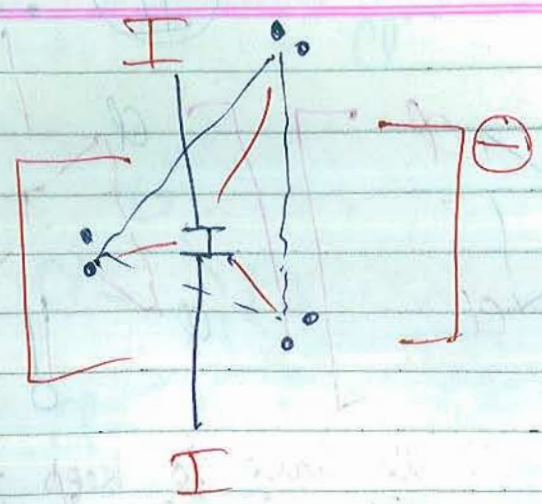


☆ ~~Electron with~~

☆ Dirn. of dative bond is always from high e⁻ density to low e⁻ density.

☆ Odd e⁻ is not considered in Hybridization →

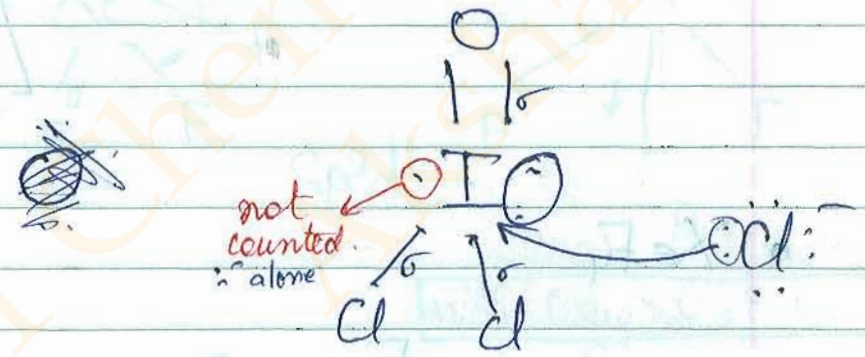
Date



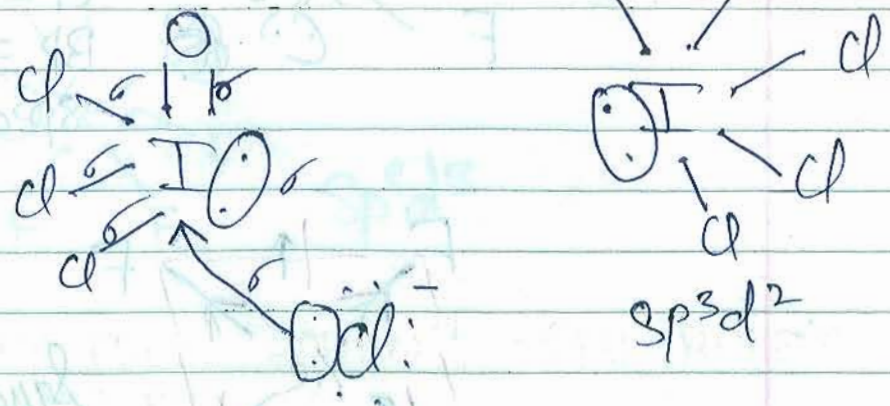
Imp:

☆ In $X_3^{\ominus}$ (IF_2^-, I_3^-, ---, $IFCl^-$) will have hybridization → linear & have 2 bond pair & 3 lone pair at central atom.

- $IOCl_3^- \rightarrow IOCl_2 + Cl^-$



- $IOCl_4^{\ominus} \rightarrow IOCl_3 + Cl^-$

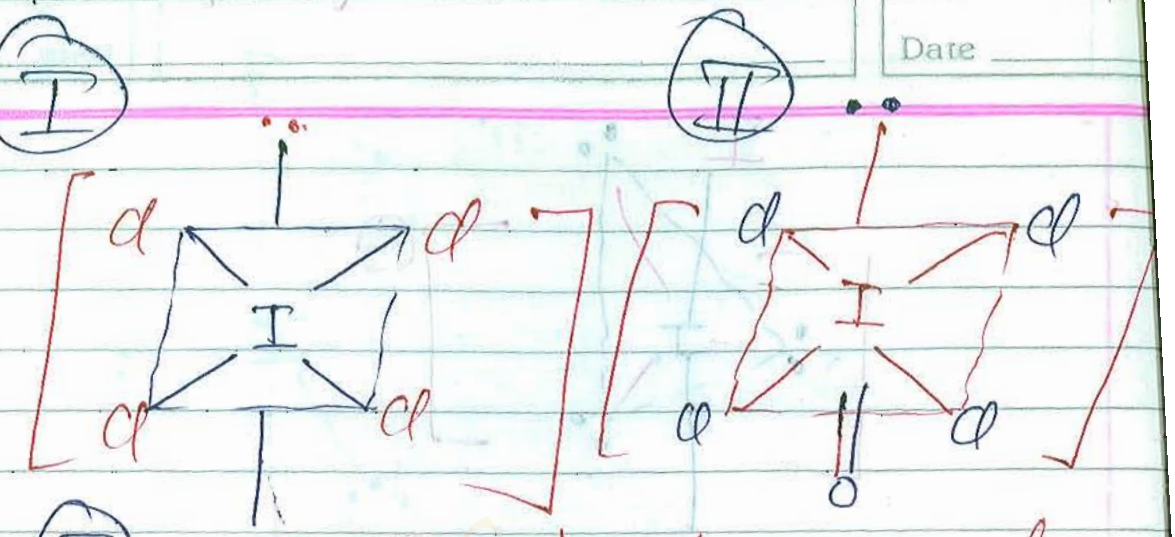


Hybridization : sp^3d^2

sp^3d^2

Date

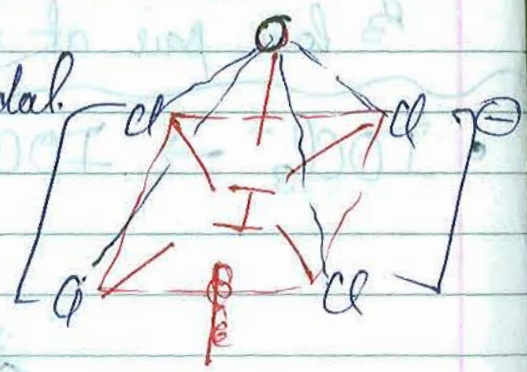
(I) (II)



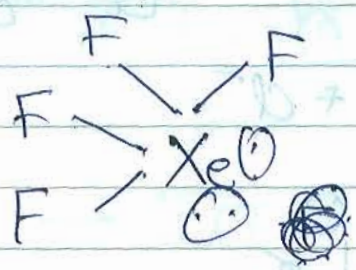
(I) O^- ∵ We have to keep -ve charge at the farthest possible place from the L.P.

(II) Double bond should be kept at more distance from L.P.

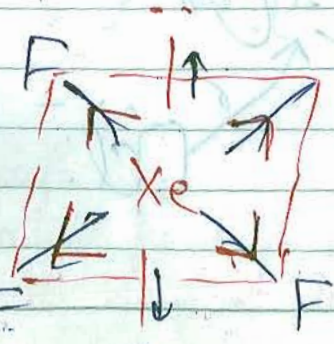
NAME : Square Pyramidal.



- XeF_4



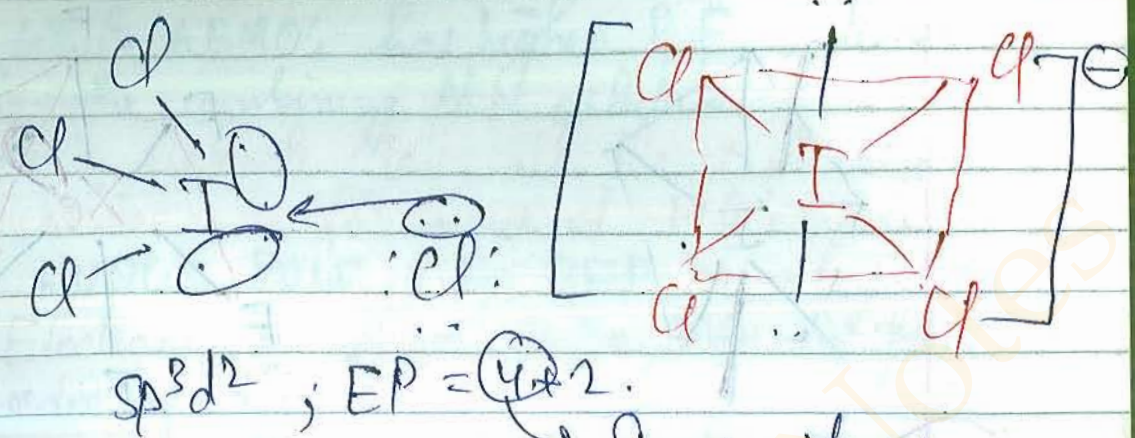
LP = 2
BP = 4
sp^3d^2.



Square planar.

Date

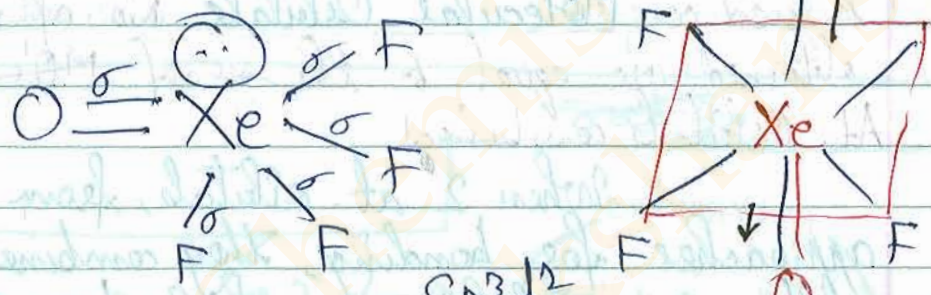
- $ICl_4^- \rightarrow ICl_3 + Cl^-$



sp^3d^2 ; EP = 4+2.

↳ Square planar.

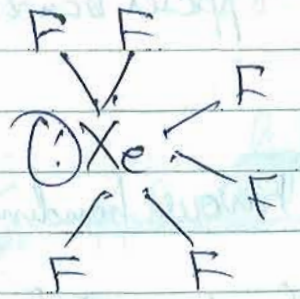
- $XeOF_4$



Sp^3d^2

Square Pyramidal with Oxygen at vertex

- XeF_6

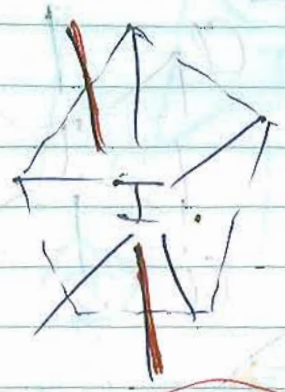


Sp^3d^3

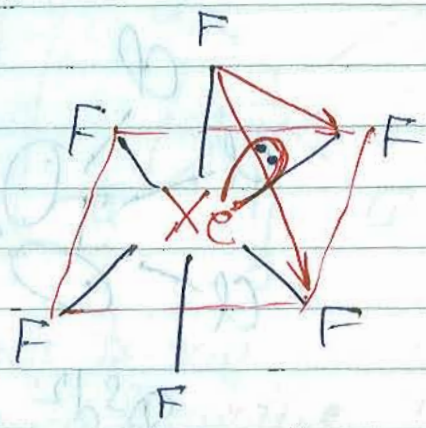
THIS MOLECULE DOESN'T OBEY RULES OF VSEPR THEORY.

↳ It is octahedral in shape with its L.P delocalized on the 8 faces of octahedral.

Should be →



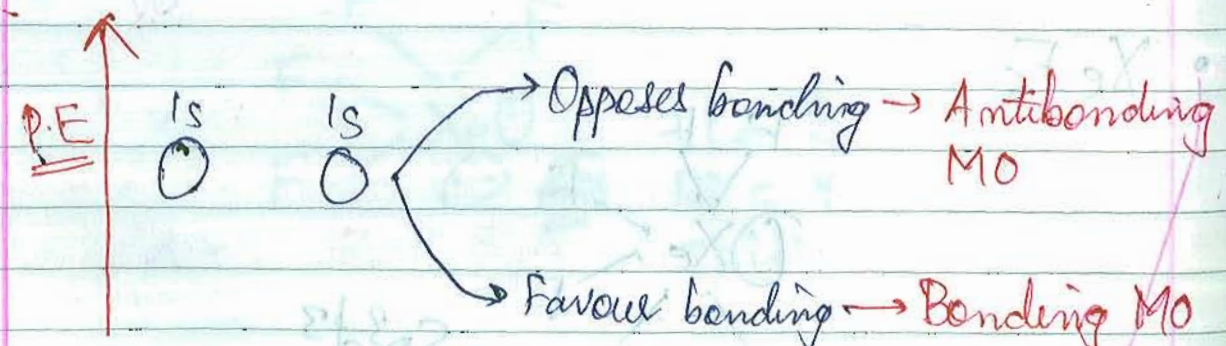
Actual →



MOT

- Acc. to MOT, pure atomic orbitals don't take part in chemical bonding. Before bonding, at. orbitals combines to produce Molecular Orbitals. No. of molecular orbitals obtained are equal to the no. of ~~MO's combined~~ At. Orbitals combined

When 2 at. orbitals, from diff. atoms approaches for bonding, they combines in 2 different orientations in which 1 combination favour bond formation while the other combination opposes bond formation.



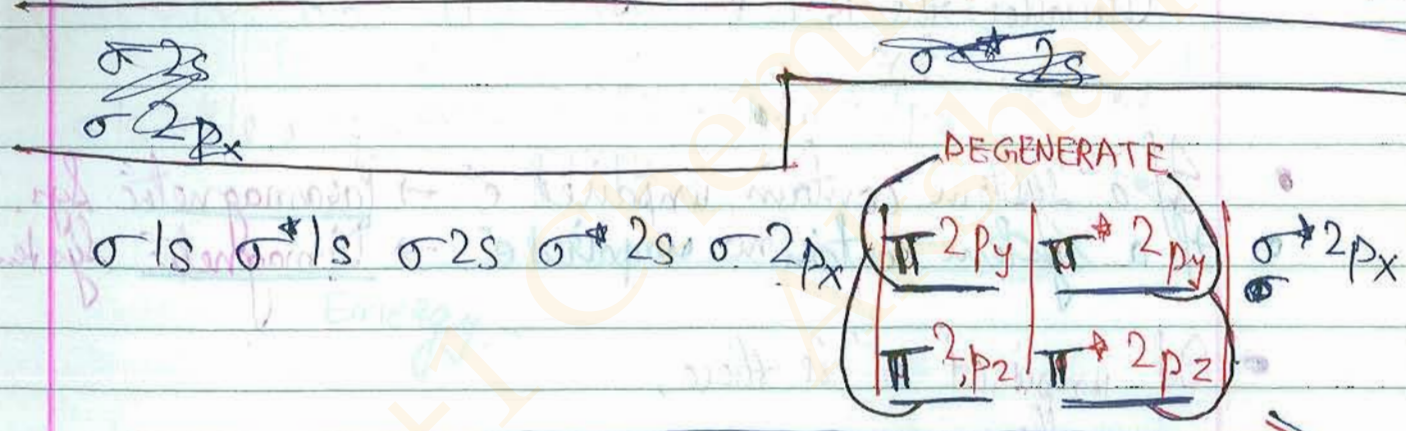
- Combination of at. orbitals, favouring bond formation leads to formation of Bonding MO (BMO) while the combination opposing bond formation leads to formation of Anti-bonding MO (ABMO)

• BMO has lower P.E, greater stability; than, Combining At. orbitals
While ABMO's has higher P.E., lower stability than the combining At. orbitals.
• For a molecule/ion, all the e's remain in molecular orbital. In filling up of MO's (with e's), both HUND'S RULE & P.E.P. are obeyed
• Electrons are filled in a MO in the increasing order of their E.

• Naming of MO's.

σ 1s. Read as 2 (Sigma 1s bonding)

σ^* 1s Read as 2 (Sigma 1s antibonding)



Note: This E order is applicable only to the molecules/ions lighter (i.e. heavier than oxygen) than oxygen (i.e. oxygen also) ~~is only applicable till NITROGEN.~~

• O_2 (16 e^-)

$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_x^2$ | $\pi 2p_y^2$ | $\pi^* 2p_y^1$ | $\pi 2p_z^2$ | $\pi^* 2p_z^1$ |

IMPORTANCE OF MOT

Date

(I) With the help of MOT, we can predict no. & nature of bonds.

(II) Bond E. or B.L. can be compared.

(III) Existence

(IV) Magnetic properties

To ans. any of (I), (II) or (III) :—

1) Determine $\boxed{\text{B.O} = \frac{\text{B.M.O(e}^-\text{)} - \text{ABMO(e}^-\text{)}}{2}}$

Oxygen: $\text{B.O} = \frac{10-6}{2} = 2.$ $\quad O \overset{\pi}{\underset{\sigma}{=}} O$

For comparison

- Higher the B.O, ~~higher~~ greater the B.E, smaller the B.L.

- If a system contain unpaired e^- → Paramagnetic Sys.
- If a system contain no unpaired e^- → Diamagnetic System
- If unpaired e^- is there, then $\boxed{\mu_s = \sqrt{n(n+2)}\ B_M}$

(1) O_2 KO_2 K_2O_2 O_2F_2

(I) (II) (III) (IV)

Arrange on the basis of O-O B.L.

Ans O_2 O_2^- O_2^{2-} O_2^{2+}

(I) (II) (III) (IV)

Date

(1) O_2 BO = 2

(2) O_2^- BO = $\frac{10-7}{2}$ = 1.5

] Paramagnetic

(3) O_2^{2-} BO = 1

(4) O_2^{2+} BO = 3

] Diamagnetic

BL = $O_2^{2+} < O_2 < O_2^- < O_2^{2-}$

TRICK : If an ion has odd no. of charge then it is surely paramagnetic (∵ pairing will be incomplete always.

★ FOR N_2 and LIGHTER MOLECULE

$\sigma 1s \; \sigma^* 1s \; \sigma 2s \; \sigma^* 2s \; \begin{vmatrix} \pi 2p_y \\ \pi 2p_z \end{vmatrix} \; \sigma 2p_x \; \sigma^* 2p_x \; \begin{vmatrix} \pi^* 2p_y \\ \pi^* 2p_z \end{vmatrix}$

Energy →

• B_2

$\sigma 1s^2 \; \sigma^* 1s^2 \; \sigma 2s^2 \; \sigma^* 2s^2 \; \begin{vmatrix} \pi 2p_y^{\uparrow} \\ \pi 2p_z^{\uparrow} \end{vmatrix}$

So, its paramagnetic.

★ Be_2 BO = $\frac{4-4}{2}$ = 0.

• To tell about existence of a molecule : Find its B.O. If '0', then, it will not exist as a molecule

Date

- H_2^+

$$BO = \frac{1-0}{2} = \frac{1}{2}$$



~~Bonds~~: TWO-CENTRE ONE e^- BOND (2c1e⁻)

- N_2 N_2^+ N_2^- N_2^{2+} N_2^{2-}
  1 2 3 4 5

$\frac{10-4}{2}$

$N_2 = \frac{4-3}{2} = \frac{1}{2}$	$N_2 = 3$
$N_2^+ = 1$	$N_2^+ = \frac{9-4}{2} = \frac{5}{2} = 2.5$
$N_2^- = 0$	$N_2^- = \frac{10-5}{2} = 2.5$
$N_2^{2+} = \frac{1}{2}$	$N_2^{2+} = \frac{8-4}{2} = 2$
$N_2^{2-} = \frac{1}{2}$	$N_2^{2-} = \frac{10-6}{2} = 2$

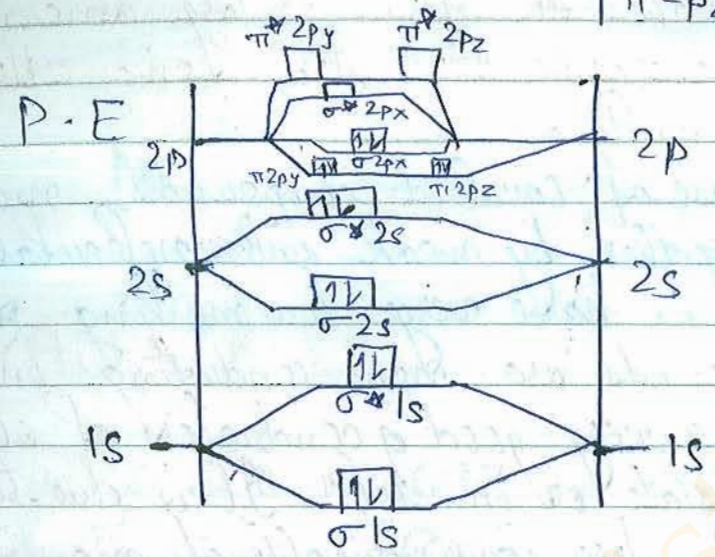
- Molecule/ion with more ~~ABE~~ Anti-Bonding e^- will be LESS STABLE. So, it will have lower B.E

$$N_2^{2-} < N_2^{2+} < N_2^- < N_2^+ < N_2$$

Date

MOLECULAR ORBITAL DIAGRAM

- N_2 (14) $\sigma 1s^2\ \sigma^* 1s^1\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_y^2 = \pi 2p_z^2\ \sigma 2p_x^2\ \sigma^* 2p_x^0\ \pi^* 2p_y^0 = \pi^* 2p_z^0$



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IONIC BONDING:

Ionic bond is formed by transfer of e^- b/w a highly electro +ve & highly electro -ve atom. After formation of an ionic bond, the valence shell of bonded atoms becomes independent with noble gas confi.

eg NaCl Na —e→ Cl

- The more electro +ve atom loses e^- due to smaller IE. While the more electro -ve atom accept e^- due to higher A_e.

Na —e→ Cl

Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$ → Na^+ (Ne) $2s^2\ 2p^6$

Cl: $3s^2\ 3p^5$ → Cl^- (Ar) $3s^2\ 3p^6$

PROPERTIES OF IONIC COMPOUNDS

1) IONIC Compounds have very high melting pt. compared to covalent compounds.

2) In ionic solids, ions are held together by strong electrostatic attn. ∴ large amount of E is req. to overcome this inter-ionic attn which is req. for melting.

In case of covalent compounds, molecules are held together by weak inter-molecular force of attn. ∴ have very low melting pts.

2) Ionic compounds are non-conducting in solid state but a very good conductors of electricity in molten state or in sol^n. It is due to existence of free ions capable of moving towards electrodes of opposite polarity in molten state or in sol^n.

3) Ionic solids are brittle, Breaks easily with sharp edge.

4) Ionic solids are all crystalline. Particles of the ionic solid have a regular shape & geo. & has a sharp melting pt. Covalent compounds in solid state are mostly amorphous & melts in a temp. range.

5) Solubility: Ionic compounds are more soluble in polar solvents of high dielectric constant. dielectric constant (measures polarity in salts → water is most polar)

% age IONIC CHARACTER =

$$= \frac{\text{Observed dipole moment}}{\text{Theoretical dipole moment}} \times 100$$

Date

☆ $\mu_{Theo} = qd$.

☆ If any compound has Ionic Character > 50% → Ionic Compound
< 50% → Covalent Comp.

IC : NaCl < KCl < RbCl

☆ FAJAN'S RULE

Fajan's rule measures the extent of covalency in predominantly ionic compound.

NaCl



Acc. to FAJAN'S RULE, in an ionic compound, cation polarizes some of the e⁻ density of anion, deform the spherical character of e⁻ density of anion & introduces some covalency into ionic compound. the extent of covalency depends on the polarizing power of cation & polarizability of anion (anion कितना willing है Polarize होने को)

Greater the polarizing power of cation, & higher the polarizability of anion, increases the extent of polarization. ∴ covalency.

Date

Li Cl ⊕ ⊖

Cs Cl ⊕ ⊖

★ +ve charge density = $\frac{q}{A(\text{area})}$

★ Smaller cation always have higher polarizing power due to greater +ve charge density.

Li F ⊕ ⊖

Li I ⊕ ⊖

★ larger the size of anion → greater will be polarizability.

Polarizability of anion depends on size.

★ RULE 1: Smaller the size of cation, or higher the charge on cation, greater the covalency.

If both charge & size of cations differ, charge is considered 1st.

$\overset{+1}{Na}\,Cl$

$\overset{+1}{K}\,Cl$

$\overset{+1}{Rb}\,Cl$

$\overset{+1}{Cs}\,Cl$

IC %

NaCl < KCl < RbCl < CsCl.

$^{+1}NaCl$
$^{+2}MgCl_2$
$^{+3}AlCl_3$
$^{+4}SiCl_4$

↓ covalency ↑ solubility ↑ IC ↑ Melting pt.

$NaCl$ KCl $MgCl_2$ $CaCl_2$ $AlCl_3$
I II III IV V

IC: II > I > IV > III > V

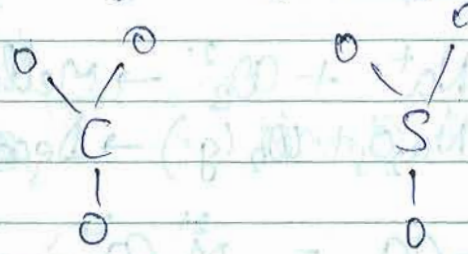
RULE 2:
larger the size of anion or higher the charge on anion, greater the covalency

eg NaF $NaCl$ $NaBr$ NaI
III I II IV

IC% III > I > II > IV

eg $CaCO_3$ $CaSO_3$ $CaSO_4$
I II III

Size: $CO_3^{2-} < SO_3^{2-} < SO_4^{2-}$



IC%: I > II > III

SUBRULE (APPLYING Rule 1 & Rule 2)

If both cation & anion differs, cations are always considered 1st (i.e polarizing power is more imp. than polarizability)

NaF KI LiBr CaF_2

I II III IV

% I.C. : II > I > III > IV

RULE 3: If cations have equal/same charge, comparable size, but one containing partially/completely filled d-orbitals while other without d e⁻s, then, the former will be a very large polarizing ion than latter (18e⁻ 18e⁻)

Very imp.

eg: $CaCl_2$ (Ca^{+2}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$) > $CuCl_2$ (Cu^{+2}: $\rightarrow 3d^{10}\ 4s^1$)

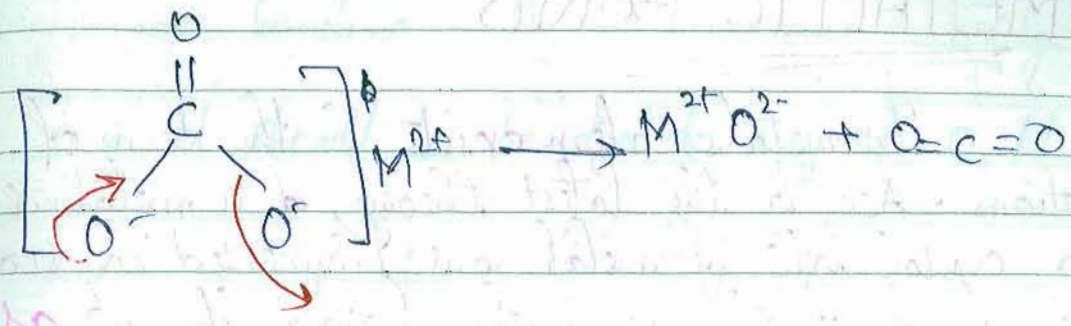
PP (polarizing power) $Cu^{+2} > Ca^{2+}$

THERMAL STABILITY OF SALTS

$Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{2-}$ → Melting

$\xrightarrow{\Delta} Na_2O + CO_2(g)$ → Decomposn

$CaCO_3$ $MgCO_3 = M^{2+}CO_3^{2-} \longrightarrow MO + CO_2$



☆ Greater the polarizing power of cation, greater will be easier will be the Thermal Decompos^{n} of salt. Thermally less stable will be the salt, will decompose at relatively lower temp.

Q. Na_2CO_3 (I) $CaCO_3$ (II) $MgCO_3$ (III) $Al_2(CO_3)_3$ (IV)

Find increasing order of decompos^{n} temp.

IV < III < II < I

Q. $NaHCO_3 \rightarrow Na_2CO_3$

$Mg(HCO_3)_2 \rightarrow MgO + CO_2 + H_2O$; Why?

$Mg(HCO_3)_2 \rightarrow MgCO_3 \rightarrow MgO$

Q. $NaNO_3 \xrightarrow{500°C} NaNO_2 + \frac{1}{2} O_2$

$NaNO_3 \xrightarrow{800°C} Na_2O + N_2 + O_2$

$NaNO_2 \xrightarrow{(500°C - 800°C)} Na_2O + N_2 + O_2$

Intermolecular bond : B/w molecules
Intra molecular bonds: Inside molecule

Date

METALLIC BOND

In metals, atom exist in the form of cations. Acc. to the latest theory, of a metal is a crystal latis of metal ions immersed in sea of e⁻s. Since e⁻s are -vely charged, it act as anions in the ionic solid. ∴ metallic bonds are like ionic bonds — very strong, giving rise very high melting pt. to the metals with exception of mercury & alkali metals.

Metals have very high electrical conductivity due to presence of free e⁻s.

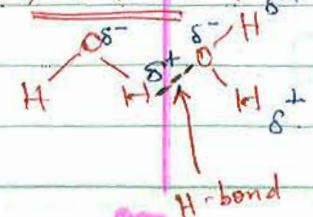
Metals are lustrous, ductile, malleable, due to presence of mobile e⁻s.

SECONDARY BONDS

Secondary bonds are the weak long range interaction b/w the molecules of covalent compound.

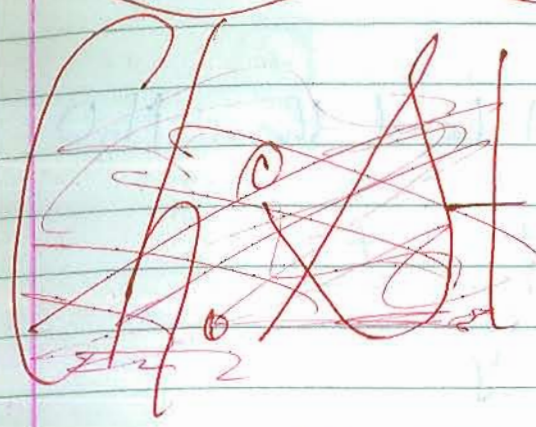
- Hydrogen Bond
- Dipole-Dipole attr"
- Vanderwall's force of attrn.

H-Bond: It arises when a hydrogen is bonded to one of the most electro -ve atom → F, N & O.

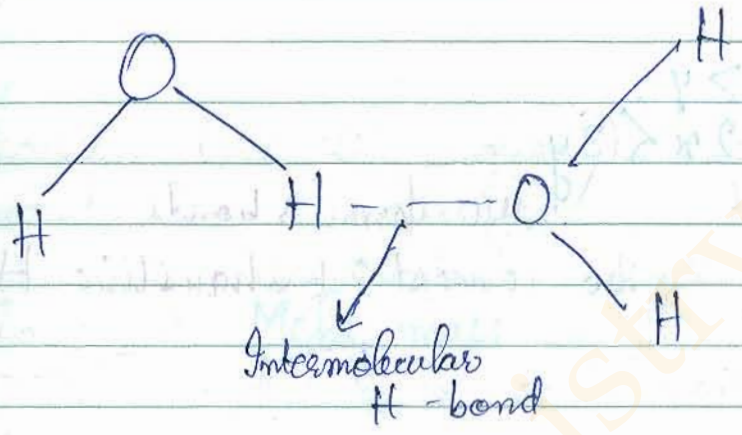


In Hydrogen bonding, H act as a bridge b/w 2 highly electro -ve atom → O, N or F
i.e H should be bonded to any of O, N or F

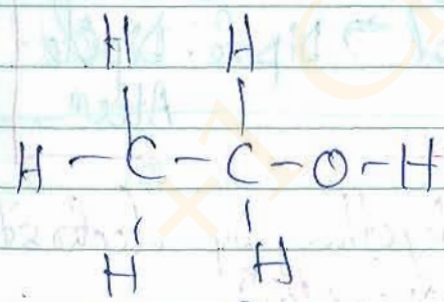
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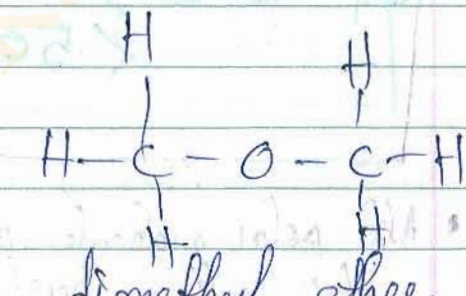
• Intermolecular force :



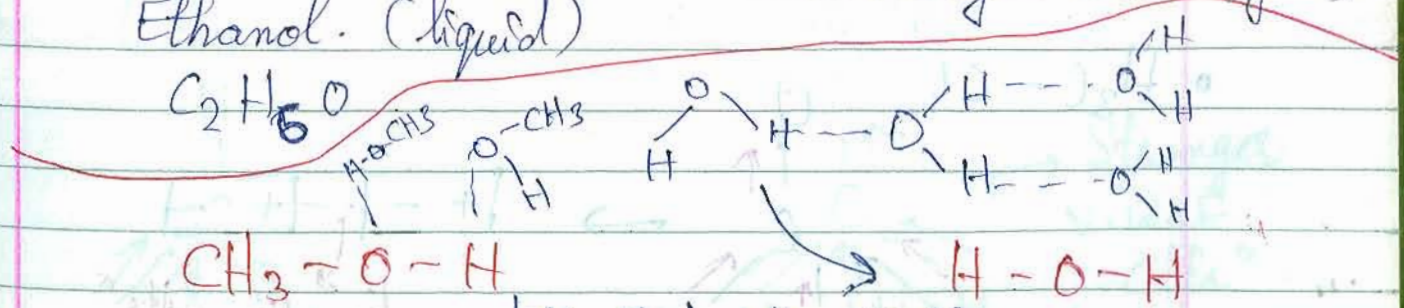
Q. H_2O has higher B.Pt. than H_2S ∵ water forms H-bond. H_2S doesn't



Ethanol. (liquid)
C_2H_6O



dimethyl ether (gas)



CH_3-O-H ← less Exhaustive more → $H-O-H$

Methanol B.pt. = 58°C

H-bonding

water B.Pt → 100°C

δ^+ δ^- → B.E = x.

H-F - - - H-F - - - H-F

|δ| of F > |δ| of O.

So, HF forms stronger H-bond than H_2O.

H

H-O-H - - - - O-H

→ B.E = y

So, x > y

But (2)x < (3)y

HF forms 2 bonds

H_2O forms 3 bonds.

So, concept : Exhaustive H-bonding

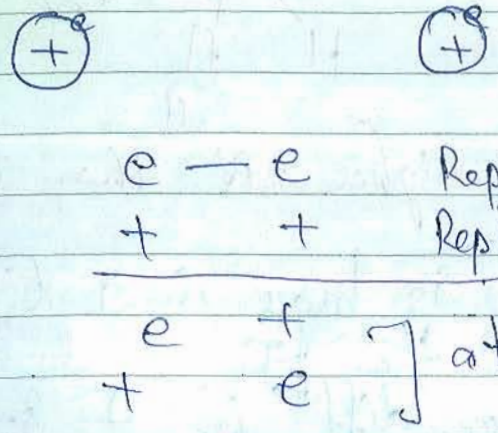
✡ DIPOLE-DIPOLE ATTR^n :—

✡ If B.E > 50 KJ/mol → H-bond
< 50 KJ/mol → Dipole-Dipole Attⁿ.

- All polar molecule are held together by electrostatic attⁿ called Dipole-~~Dipole~~ Dipole attⁿ.
- H_3C-Cl.



✡ VANDER WALL'S FORCE of Attⁿ.
(or DISPERSION FORCE or LONDON-FORCE)



Vander Wall's force of attⁿ arises due to weak interaction b/w the ~~odyar~~ e⁻s & nucleus of the adjacent atoms / molecules.

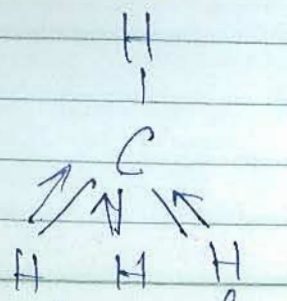
Vander Wall's force of attⁿ is directly proportional to Molar mass of the substance & this force also contribute to some extent the physical properties of substance.

It is a permanent molecular attⁿ present in all molecules. But, its the weakest.

H-bond >> Dip-dip Attⁿ > V.W.F Attⁿ.

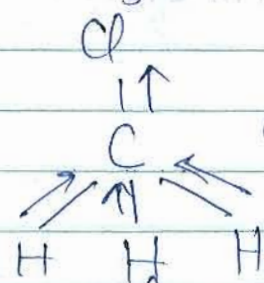
So, all noble gases are gases at room temp. ∵ it has V.W.F of attⁿ

⑥ CH_4



Non-polar

• CH_3Cl.

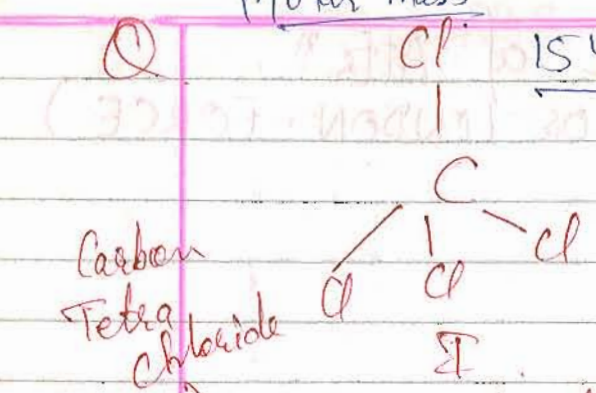


→ Stronger V.W.F attⁿ...

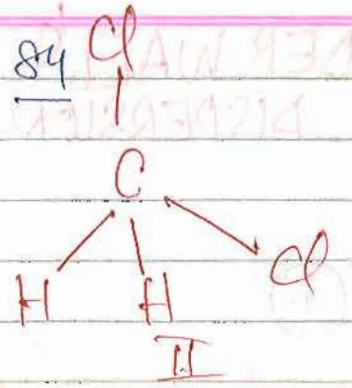
Polar.

Molar mass

Q



154



84

Carbon Tetra Chloride (CTC)

I

II

Given I has higher BPt. than II.

Why?

Ans Van der Waal's force is large in I (∵ of larger molar mass) than II.

Due to large diff^{ne} in I & II

So, it exceeds dip-dip - attr^{n}.

+1 Chemistry Notes
Akshansh

Ch: States of Matter

- GASEOUS STATE

2 Theories

Ideal Gas

Real Gas

- Pressure (P) = $\frac{F}{A}$ = Nm^{-2} = Pascal

$1\ N/m^{-2} = 1\ Pa$

- ↳ Types →

2. GAS

P

is

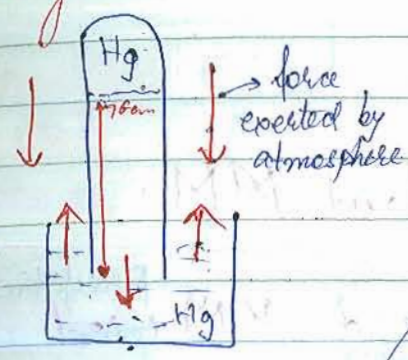
diff

2 ar

$\rho_{Hg} = 13.6\ g/cc$

Date

Atmospheric Pressure : Atmospheric Pressure (1 atm) is the pressure which support a mercury column of length 76 cm



1 atm ≡ 76 cm of Hg
≡ 760 mm of Hg
≡ 760 torr (by Torricelli name)

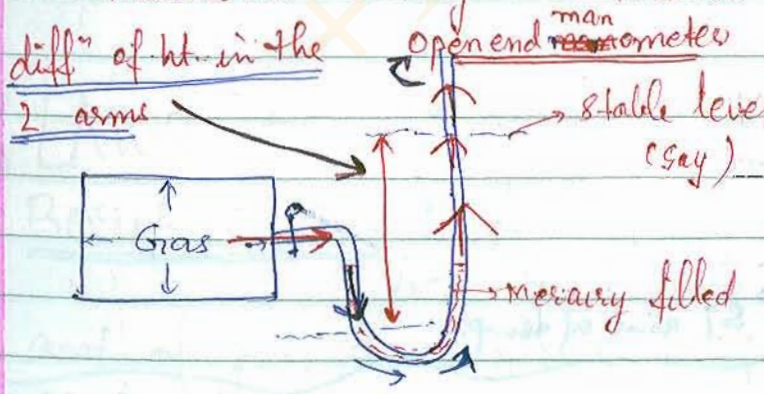
$P = h \rho g$

P → Pressure
h → Ht. of column.
ρ → density
g → accln due to gravity

$$1\ atm = 101325\ Pa = 10^5\ Nm^{-2} = 10^5\ Pa.$$

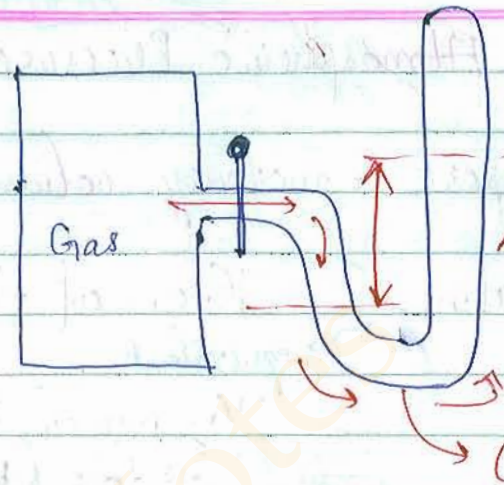
2. GAS PRESSURE

In a closed container, gas exerts uniform P on all sides on all sides of contained which is measured using an instrument called ~~Manometre~~ MANOMETER



Here

$P_{gas} = h + 76\ cm$



$P_{gas} = h$.

Closed End MM

- If $P_{gas} > 1$ atm → Open end MM preferred ~~used~~
- If $P_{gas} >$ or $<$ 1 atm → Closed end MM used

Why MERCURY USED for MM

- To make the MM compact.
- doesn't stick to ~~wo~~ glass.
- Its coefficient of thermal expansion (how it expands on heating) is very less.

Temperature:

~~Absol~~

Absolute scale → Kelvin temp
Relative scale → Celcius temp.

$°C + 273 = K$

SI unit of temp.

IDEAL GAS

The gas which obeys the eqn →

IDEAL GAS EQN

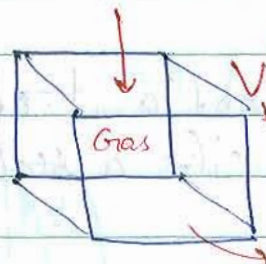
or

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

COMBINED GAS LAW

$PV = nRT$

P → Pressure
V → Volume of container.
n → mole
R → Universal gas constt. = 8.314 J K⁻¹ mol⁻¹ = 0.082 Lit atm K⁻¹ mol⁻¹ = 2 cal. K⁻¹ mol⁻¹
T → absolute temp.



n = Filled container mass − Empty container mass / Molar mass

- Ideal gas are the gases which obey Ideal gas eqn. If in the eqn → PV = nRT, 3 quantities (any), determined experimentally are used & 4th qty. is calculated to be equal to its actual value determined experimentally, then the gas is said to be an ideal gas.

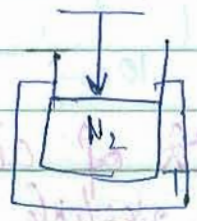
LAWS OF IDEAL GAS

- **BOYLE'S LAW:**

Acc. to Boyle's law, for a fixed amt. of gas, at a fixed temp., vol. is inversely :: to pressure.

$V \propto \frac{1}{P}$ (constt. n & T)

n → mole, T → temp.

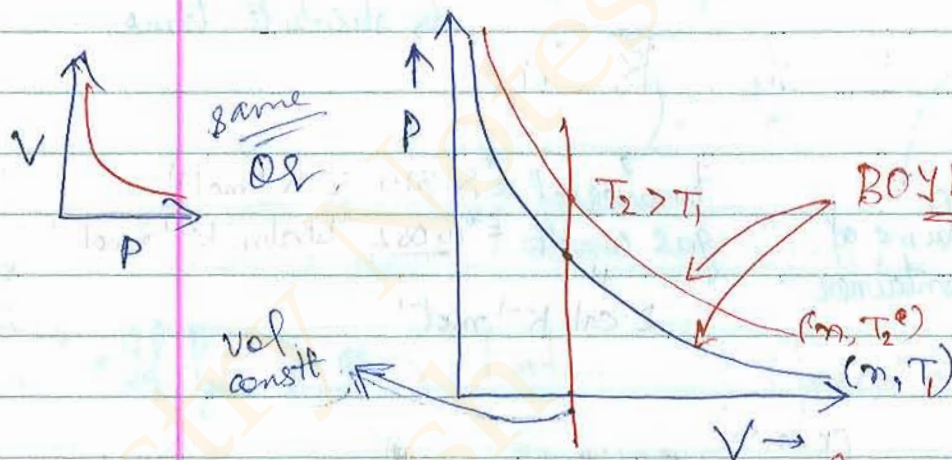


$xy = c$ } Coordinate Geo.

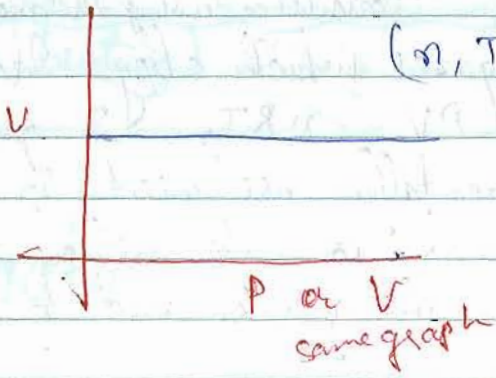
eqn. of Rectangular Hyperbola

$$V = \frac{K}{P}$$

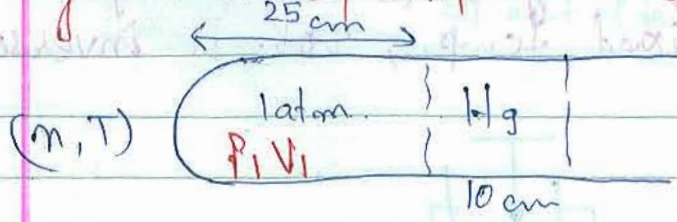
$$\Rightarrow \boxed{PV = K \; ; \; K = f(n, T)} \quad (K \text{ is a } f^n \text{ of } n$$



- At a constt. temp., for a fixed amt. of gas variation of V vs. P, describe a rectangular hyperbolic path.



Q. A 10 cm column of Hg traps a 25 cm air column at 1 atm in a long horizontal glass tube of uniform Bo bore (radius)



Determine length of air column if the

③ air held at an angle of 45° from vertical with open end up.

(1) (n, T)



$P_1V_1 = P_2V_2$ → $V = \pi r^2 l$

$P_1(\pi r^2 l_1) = P_2 \pi r^2 l_2$

$\Rightarrow P_1 l_1 = P_2 l_2$

$\Rightarrow 76 \times 25 = 86 \times l_2$ (76 + 10 mercury 10cm)

$\Rightarrow l_2 = \frac{76 \times 25}{86}$ 38 43

$\Rightarrow l_2 = 22$ cm

(2)

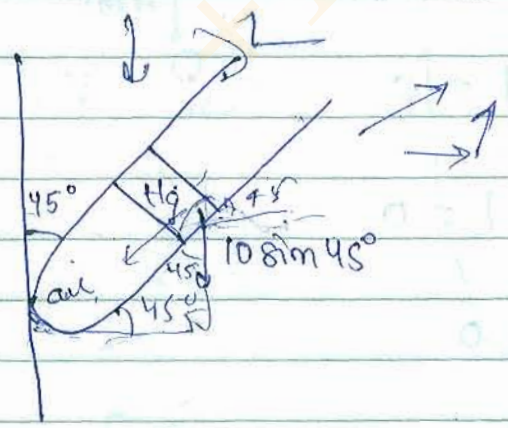


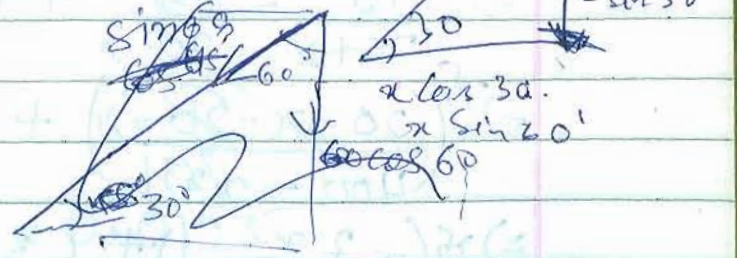
$76 = 10 + P_{gas}$

$\Rightarrow P_g = 66$ cm

$\Rightarrow P_1V_1 = P_3V_3$ (find all)

(3)

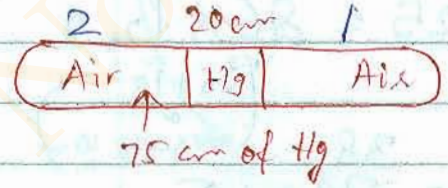




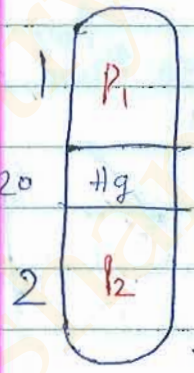
23/Aug/09

Date

Q. A 20 cm column of Hg is trapped at the centre of a 60 cm long uniform horizontally placed glass tube containing air on both sides at 75 cm of Hg and sealed at both ends. If glass tube is held vertical, determine, length of air column in the lower part of tube.



Ans.



$P_1 + 20 = P_2$

$75 \times 20 = P_1 (20 + x)$

$75 \times 20 = P_2 (20 - x)$

$\Rightarrow \frac{75 \times 20}{20 + x} + 20 = \frac{75 \times 20}{20 - x}$

$= 20 \left[\frac{75}{20 + x} + 1 \right] = \frac{75 \times 20}{20 - x}$

$\Rightarrow \frac{75}{20 + x} - \frac{75}{20 - x} + 1 = 0$

$\Rightarrow 75 \left(\frac{20 - x - 20 - x}{400 - x^2} \right) + 1 = 0$

$\Rightarrow 75 \left(\frac{-2x}{400 - x^2} \right) + 1 = 0$

$\Rightarrow \frac{2x}{400 - x^2} = \frac{1}{75}$

e) $400 - x^2 = 150x$

e) $x^2 + 150x - 400 = 0$

e) $x = \frac{-150 \pm \sqrt{22500 + 1600}}{2}$

$= \frac{-150 \pm \sqrt{23100}}{2}$

$= \frac{-150 \pm \sqrt{23100}}{2}$

$= \frac{-150 - 75 + 5(15.1)}{2}$

$= -75 + 75.5$

$\Rightarrow x = 0.5$ cm.

22500
1600
23100

15.1
1 | 23100
1
25 | 131
−125
301 | 600

400
200
100
50
25
5
1

23
69
25
301

2151
75
755

Q. A diver exhale an air bubble of vol. 1 cm^3 at the depth of 100 m in deep sea. Determine the vol. of air bubble as it reaches to the surface where it burst. Assume ρ of sea H_2O to be 1.25 g/cm^3. Assume temp. to be same at the surface and at depth of 100m

Ans:



$P_1 = h\rho g$

$= \frac{100 \times 1.25 \times 1000 \times 10}{10^5} = 12.5$ atm.

Total $P = 12.5 + 1$ atm.

$P_1 = \frac{100 \times 1.25 \times 10^3 \times 10}{10^5}$

$= \frac{125 \times 10}{10^5}$

$= \frac{1250}{10^5}$

$= 0.0125$

Now,

$P_1 V_1 = P_2 V_2$

$\Rightarrow (13.5)(1) = (1)(V_2)$

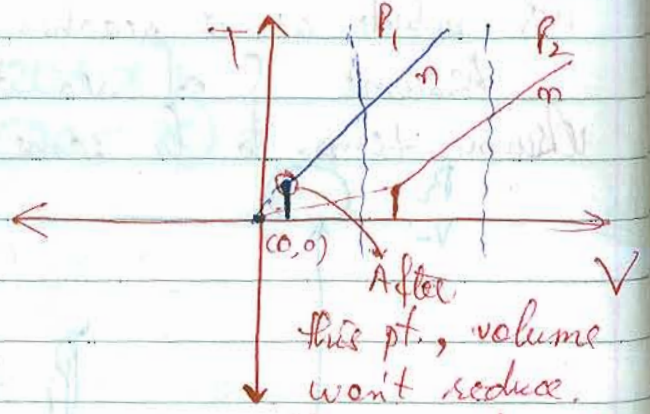
$\Rightarrow V_2 = 13.5 \text{ cm}^3$

☆ CHARLE'S LAW

↳ It consit pressure, for a fixed amt. of gas, V is directly $\propto$ to its absolute temp.
↳ temp. in K.

$V \propto T$ if P, n are constt.

$\Rightarrow V = kT$



Q. Heating an Ideal gas in a 1 Lit container at a constt. pressure, by 10°C, increases the vol. by 10%. Determine initial temp. of gas.
(fixed amt. of)

$\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$\Rightarrow \frac{1}{T_1} = \frac{1.1}{T_1 + 10}$

$\Rightarrow T(1.1) = T + 10$

$\Rightarrow (1.1)T - T = 10$

$\Rightarrow 0.1\,T = 10$

$\Rightarrow T = 100\,K.$

AVOGADRO'S HYPOTHESIS

At same temp. & P, equal volumes contain equal no. of molecules (moles) of gases.

i.e.

$\boxed{V \propto n,\ P, T \rightarrow \text{~~same~~ constt}}$.

$V \propto T \rightarrow$ Charle's law

$V \propto \frac{1}{P} \rightarrow$ Boyles law

$\boxed{V \propto \frac{nT}{P}}$ (combining all 3 laws)

$\Rightarrow V = \frac{RnT}{P}$

$\Rightarrow \boxed{PV = nRT}$

Q 4g of a mixture of He & CH_4 at 1 atm (P) & 300 K (T) occupies 10 L (V) vol. Determine mass %age of He in the mixture.

Let mass of He $\rightarrow x$.

So, $CH_4 \rightarrow 4 - x$.

$n = \frac{x}{4} \rightarrow (1)$ Also, $n' = \frac{4-x}{16}$

$PV = nRT$

$= (1)(10) = n\,(0.082)(300)$

$= \frac{10}{0.082 \times 300} = n$

$\frac{100}{82} = n$

So, $\frac{100}{82} = \frac{x}{4}$

$200 \times 100 = 82x$

$41 \quad 82$

$x = \frac{200}{41}$

$\frac{x}{4} \times 100 = \frac{200}{41 \times 4} \times 100^{25}$

$= \frac{5000}{41} \; 12$

10 Lit

4g

$xg \rightarrow He$

$(4-x)g \rightarrow CH_4$

$P = 1atm$

$T = 300\,K$

$\frac{x}{4} + \frac{4-x}{16} = \frac{1 \times 10}{0.082 \times 300}$

$\Rightarrow \frac{3x+4}{16} = \frac{10}{24.6} \rightarrow \frac{250}{10}$ $\quad \frac{6.4}{2.4}$

$\Rightarrow x = 0.8$

$He = \frac{0.8}{4} \times 100 = 25$

$= 20\%$.

Q. ρ of a mixture of H_2 & N_2 is 0.2 g/L at 1atm & 27°C. Determine mass % age of H in mixture.

$\rho = 0.2\,g/L$

let vol. = 1 L

$$\frac{x}{14} + \frac{0.2-x}{0.082\times 27} = \frac{1\times 10}{}$$

$\Rightarrow$ $\frac{14x - x + 0.2}{14} = \frac{1}{0.082\times 27}$

$\Rightarrow$ $\frac{13x + 0.2}{14000} = \frac{7000}{82\times 27}$

$\Rightarrow$ $13x + 0.2 = \frac{7000}{1107}$

$\Rightarrow$ $13x = 6.1$

$\Rightarrow$ $x = \frac{6.1}{13}$

H → $\frac{6.1}{13\times 0.2} \times 100 = 50$

$= \frac{3050}{13} = 23$

41
27
287
82×
1107
6
6642
1107
03
32
10

$\frac{3x+4}{16} = \frac{100}{250}$

2.4 6.4
= 6.0 2.0

$\frac{x}{2} + \frac{2-x}{28} = \frac{1\times 10}{0.082\times 300} = 0.4$

$\Rightarrow$ $x + \frac{2-x}{14} = 0.8$

$\Rightarrow$ $13x + 2 = 11.2$

$\Rightarrow$ $13x = 9.2$

$\Rightarrow$ $x = \frac{9.2}{13} = 0.7g$

So, $H = \frac{0.7}{2}\times 100$

$= 35\%$

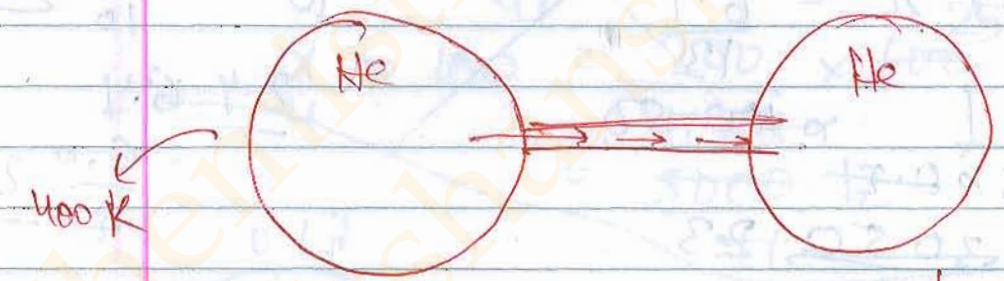
6.4
2.4 0.1
24

/4

Q. 2 flask of equal vol. containing 1 mol. of He gas in each flask are connected by a narrow tube of negligible vol; Initially present at same temp → 300 K & same pressure 1 atm.

One of the flask is heated to 400 K while other is maintained at const. temp. of 300 K

Determine mass of He gas remaining in the hot flask.



$n = 1 mol$
$T = 300 K$
$P = 1 atm$
V

$n = 1 mol$
$T = 300 K$
$P = 1 atm$
V

$P_1 = P_2$
$V_1 = V_2$

cold → $\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$ ← hot

$\Rightarrow n_1 T_1 = n_2 T_2$

$300 n_1 = 400 n_2$

$\Rightarrow 3 n_1 = 4 n_2$

$3 n_1 - 4 n_2 = 0$

$n_1 + n_2 = 2$

$\Rightarrow 4 n_1 + 4 n_2 = 8$

$3 n_1 - 4 n_2 = 0$

1 mol
e connected
el ;
300 K

400 K
ons H.

remaining

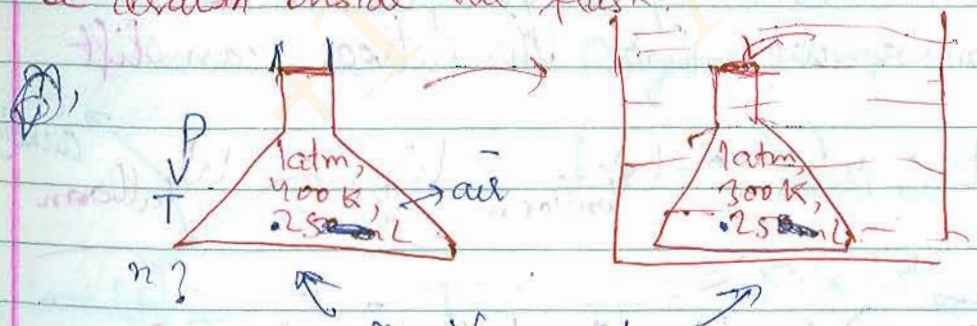
$\Rightarrow n_1 = 1.14\frac{8}{7}, \quad n_2 = \frac{6}{7}$

Also determine final pressure in the 2 flasks.

Ans - 1.1

H.W

Q. A 250 mL flask containing air at 1 atm is heated to 400 K & then sealed. The flask is then cooled to 300 K & immersed in a bucket full of H_2O at 300 K finally the seal of flask is opened. Determine the vol. of H_2O that will be drawn inside the flask.



$V \propto T$

$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$

$\Rightarrow \frac{250}{400} = \frac{V_2}{300}$

$\Rightarrow \frac{250}{4 \times 4} \times 3 = V_2$

$\Rightarrow V_2 = 187.5 \text{ mL}$

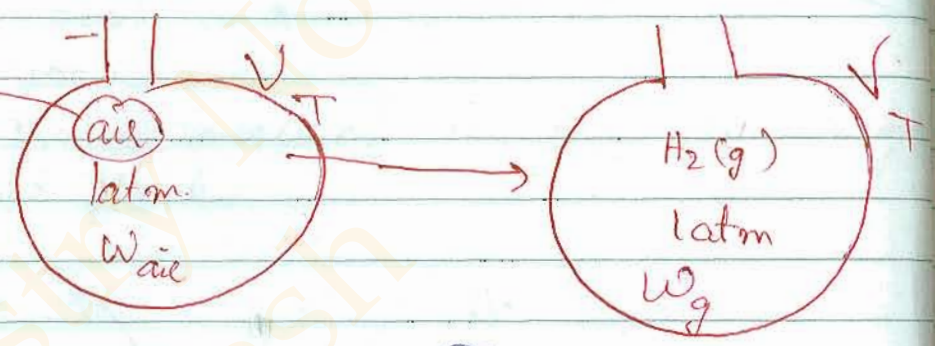
~~4 80~~ ×28 + ~~20~~ 1 ×16
~~100~~ ~~100~~ 5
5

Date

Vol. of H_2O = 250 - 187.5 ml
= 62.5 ml

✡ LIFTING CAPACITY OF A GAS FILLED BALLOON

80% N_2 & 20% O_2
= 28.8 g/mol
↳ avg. molar mass of air.



$W_{gas} = n \times M$
n → Same
M → Molar mass will be diff^t

$M \rightarrow air > H_2$

So, $Wt \rightarrow air > H_2$
$wt/V \rightarrow air > H_2$ (Vol. same)
So, density $air > H_2$

~~Payload~~ PAYLOAD of a gas filled ballon is the max. wt. that the balloon can lift

$P.L = W_{air} - W_{balloon} - W_{gas} - W_{balloon}$ (casing)

Q. Determine P.L of a He balloon of vol. 1000 L at 27°C & 1 atm. (Assume molar mass of air → 28.8)

GAS

$H_2(g)$
1 atm
W_g

V
T

e mass
be diff
ame)

balloon is
can lift
$W_{balloon}$
O (easily)

f vol.
me moles

air

$PV = nRT$

$n = \frac{PV}{RT} \rightarrow 24.6$

$\Rightarrow n = \frac{1000}{24.6}$

$Wt.\ air = \frac{28.8}{24.8} \times \frac{1000}{24.6}$

$= \frac{48}{41} \times 1000 = 1000\ g$

$Wt.\ gas = 28.8 \times 4$

$P.L = \frac{48}{41} \times 1000 - 28.8 \times 4$

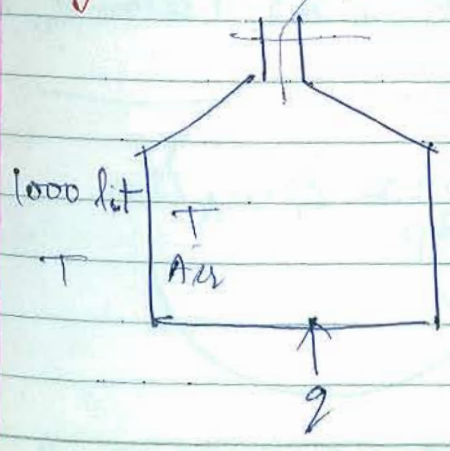
$= 1.17 \times 1000 - 115.2$

$= 1170 - 115.2$

70
−41
41
07
287

3288
04
1152

8. Determine the temp. diff. which must be created in a 1000 L, air filled steel cylinder in order to give a P.L of 1 kg. Mass of cylinder → 0, Original temp. = 300 K



$P.L = W_{cold\ air} - W_{hot\ air}$

$= M \times (n_{cold} - n_{hot})$

$1000 = \frac{MPV}{R}\left(\frac{1}{T_c} - \frac{1}{T_h}\right)$

$\Rightarrow 1000 = \frac{28.8(1)(1000)}{0.82}\left(\frac{1}{T_c} - \frac{1}{T_h}\right)$

So, find T_{hot}.

$$\Rightarrow \frac{0.082}{28.8} = \left(\frac{1}{300} - \frac{1}{T_h}\right)$$

$$\Rightarrow T_h = 1750$$

27/8/09

★ **STP - Volume** — 1 mol ideal gas, 0°C, 1.0 atm

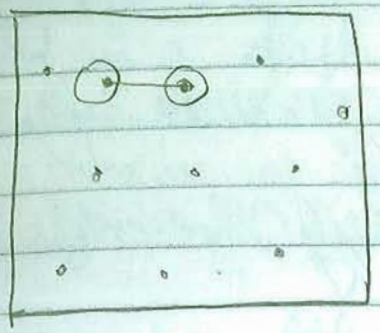
$$V_m = \frac{nRT}{P} = \frac{(1)(0.082)(273)}{1}$$

V_m → molar volume $= 22.4$ lit.

Std. Temp. & Pressure → 0°C & 1 atm, V_m = 22.4 lit

Q Determine, avg inter nuclear distance b/w the adjacent Ar atoms at STP

IIT-2001



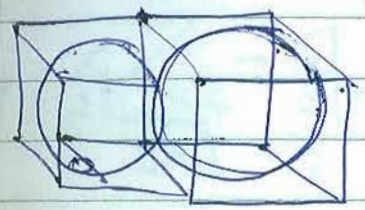
STP

6.023×10^{23} atoms will occupy $\rightarrow 22.4 \times 1000 cm^3$

1 atom will occupy $\rightarrow \frac{22.4 \times 10^3}{6 \times 10^{23}} cm^3$

$= 3.7 \times 10^{-20} cm^3$

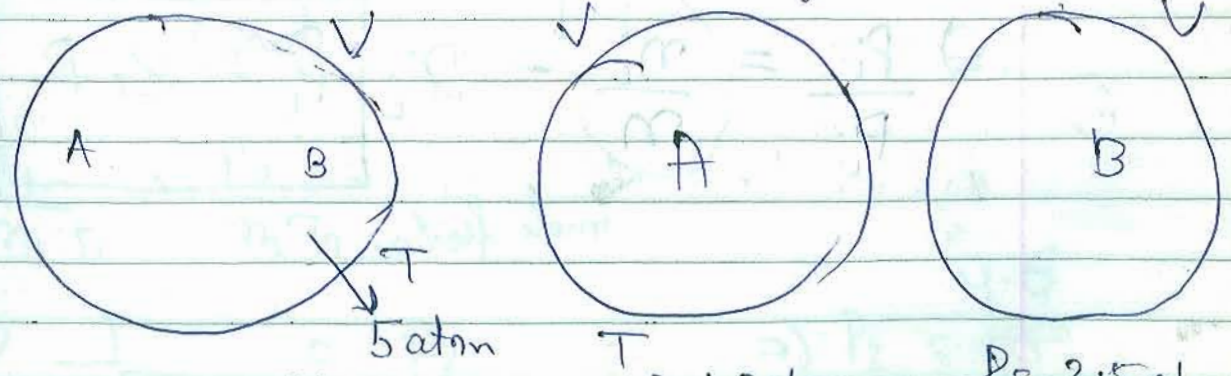
$= 37 \times 10^{-21} cm^3$



$l^3 = 37 \times 10^{-21}$

$= 3.5 \times 10 \times 10^{-\cdots}$

☆ Dalton's Law of Partial Pressure. (Very Imp)



A, B → non reacting gas

Date

Partial Pressure is the pressure exerted by a component of the gas mixture if that component occupy the entire volume alone at same temp.

Dalton's Law: Acc. to Dalton's law, in a non-reacting gaseous mixture, sum of the Partial Pressure of all components gives total P of gas.

$$P = P_A + P_B \quad : \quad \boxed{P = \sum_{i=1}^{n} P_i}$$

$$P_A = \frac{n_A RT}{V}, \quad P_B = \frac{n_B RT}{V} \quad : \quad \boxed{P_i \propto n_i}$$

$$P \propto n : n = \sum n_i$$

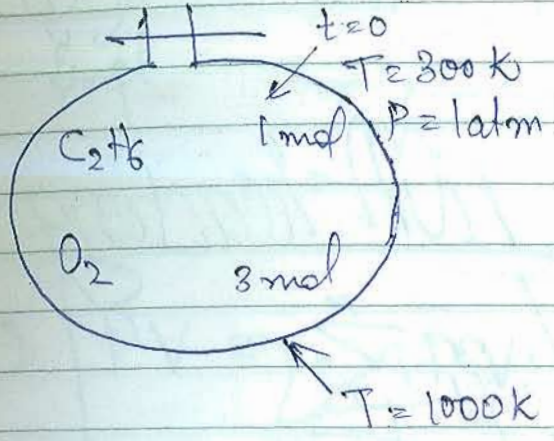
$$\Rightarrow \frac{P_i}{P} = \frac{n_i}{n} = x_i \quad \boxed{P_i = x_i P}$$

x_i → mole fraction

2. C_2H_6 (1 mol) is mixed with 3 moles of O_2 & sealed in a flask at 1 atm & 27°C (300 K) & finally heated to 727°C where the following rxn.

$$C_2H_6(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO(g) + 3H_2O(g)$$

occured completely. Determine partial pressure of each component at the end of rxn.



	$C_2H_6(g)$	+ $\frac{5}{2}O_2(g)$	⟶ $2CO(g)$	+ $3H_2O(g)$	n_i
n_i	1	3	0	0	4
t_∞	0	0.5	2	3	5.5

Initial → P = 1 atm, T = 300 K, 4 mol.

Final: P = ?, T = 1000 K, n = 5.5

$$\frac{P_1}{n_1 T_1} = \frac{P_2}{n_2 T_2}$$

$$\Rightarrow \frac{1}{(4)(300)} = \frac{P_2}{(5.5)(1000)} \Rightarrow P_2 = \frac{4.6}{12 \times 10}$$

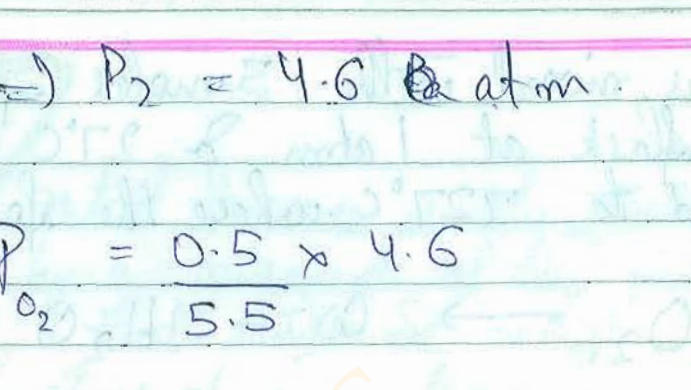
Date

$\therefore P_2 = 4.6$ atm

$P_{O_2} = \frac{0.5}{5.5} \times 4.6$

Solve ✗

Mixing of non-reacting ideal gases



Isothermal mixing of non-reacting ideal gases

$A: P_1V_1 = P_A^f (V_1 + V_2)$

$B: P_2V_2 = P_B^f (V_1 + V_2)$

$$P = P_A^f + P_B^f$$

$$= \frac{P_1 V_1}{V_1 + V_2} + \frac{P_2 V_2}{V_1 + V_2}$$

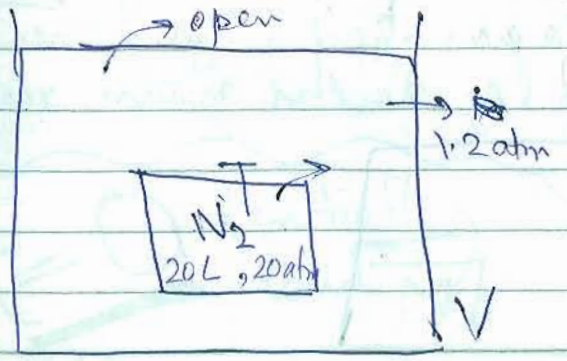
$$\Rightarrow P(V_1 + V_2) = P_1 V_1 + P_2 V_2$$

$$PV = P_1 V_1 + P_2 V_2$$

P, V: final; P_1: initial pressure of A; V_1: initial vol. of A

$$\Rightarrow PV = \sum_{i=1}^{n} P_i V_i \quad ; \quad \Delta T = 0$$

(1) A 20 L steel cylinder containing N_2 gas at 20 atm is placed in a big jar containing air at 1 atm ; but at same temp. & sealed finally. N_2 was allowed to leak out into the jar. The final P in the jar was found to be 1.2 atm. Determine vol. of jar



$PV = P_1 V_1 + P_2 V_2$

P: 1.2 atm; P_1: 20 atm, V_1: 20 L; P_2: 1 atm, V_2: V

$V = 20$

$V = 20$

Date

⇒ V = 1900 lit.

☆ EFFUSION of Gases

when gas comes out through a narrow opening from a container due to significant Δ diff.



Rate of Effusion

(instantaneous)

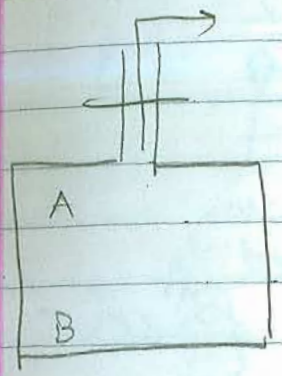
$$r = \left[-\frac{dm}{dt} \;\; -\frac{dV}{dt} \;\; -\frac{dn}{dt} \;\; -\frac{dP}{dt} \right]$$

☆ r (rate) of effusion of a gas from a container is inversely ∝ to sq. root of molar mass

$$r\,(\text{rate}) \propto \frac{1}{\sqrt{M}}$$

r (rate) $\propto$ P

So, $r \propto \frac{P}{\sqrt{M}}$



$r_A \propto \frac{P_A}{\sqrt{M_A}} \Rightarrow r_A = K \frac{P_A}{\sqrt{M_A}}$

$r_B \propto \frac{P_B}{\sqrt{M_B}} \Rightarrow r_B = K \frac{P_B}{\sqrt{M_B}}$

depends only on Temp. & geometry ~~with~~ ~~which~~ of pinhole with which gas comes out

$\frac{r_A}{r_B} = \frac{P_A}{P_B}\sqrt{\frac{M_B}{M_A}}$

(In relative rel^n, K is constt)

$= \frac{n_A}{n_B}\sqrt{\frac{M_{AB}}{M_{BA}}}$

$t = 0$ (initial Cond^n)

4 16

Date

Q. In what molar ratio He & CH_4 gas should be taken in a flask so that they start effusing at the same rate?

~~$n_1 = n_2$~~

$$\frac{r_{He}}{r_{CH_4}} = \frac{n_{He}}{n_{CH_4}}\sqrt{\frac{16}{4}} = 1$$

$$= \frac{n_1}{n_2}\,2 = 1$$

$$\Rightarrow n_{He} : n_{CH_4} = 2 : 2$$

42
16
58

Q. He, CH_4 & Heptane (C_7H_{16}) taken in molar ratio of 1:2:3 & allowed to effuse through a pin hole in the flask. Determine the molar ratio of the gases coming out initially.

$$\frac{r_{He}}{r_{CH_4}} : \frac{r_{He}}{r_{C_7H_{16}}} = \frac{n_{He}}{n_{CH_4}}\sqrt{\frac{M_{CH_4}}{M_{He}}} : \frac{n_{He}}{n_{C_7H_{16}}}\sqrt{\frac{M_{C_7H_{16}}}{M_{He}}}$$

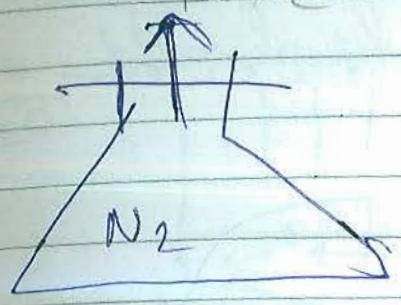
So, $r_{He} : r_{CH_4} : r_{C_7H_{16}} = \frac{n_1}{\sqrt{M_1}} : \frac{n_2}{\sqrt{M_2}} : \frac{n_3}{\sqrt{M_3}}$

$$= \frac{1}{2} : \frac{2}{4} : \frac{3}{10}$$

Date

Certain volume of N_2 gas takes 38 sec for effusion through a pin hole at 1 atm. while the same volume of an unknown gas of Xe & F takes 57 sec for effusion at 2 atm. Deduce formula of unknown gas given

Xe = 131



$$\ell = \frac{V}{t} = \frac{\ell_{N_2}}{\ell_{UK}} = \frac{t_{UK}}{t_{N_2}} = \frac{P_{N_2}}{P_{UK}} \sqrt{\frac{M_{UK}}{M_{N_2}}}$$

$$\Rightarrow \frac{38}{57} = \frac{1}{2} \sqrt{\frac{M_{UK}}{28}}$$

$$\Rightarrow \left(\frac{38 \times 2}{57}\right)^2 = \frac{M_{UK}}{28}$$

$$\Rightarrow \frac{38 \times 2 \times 2 \times 38 \times 28}{57 \times 57} = M_{UK}$$

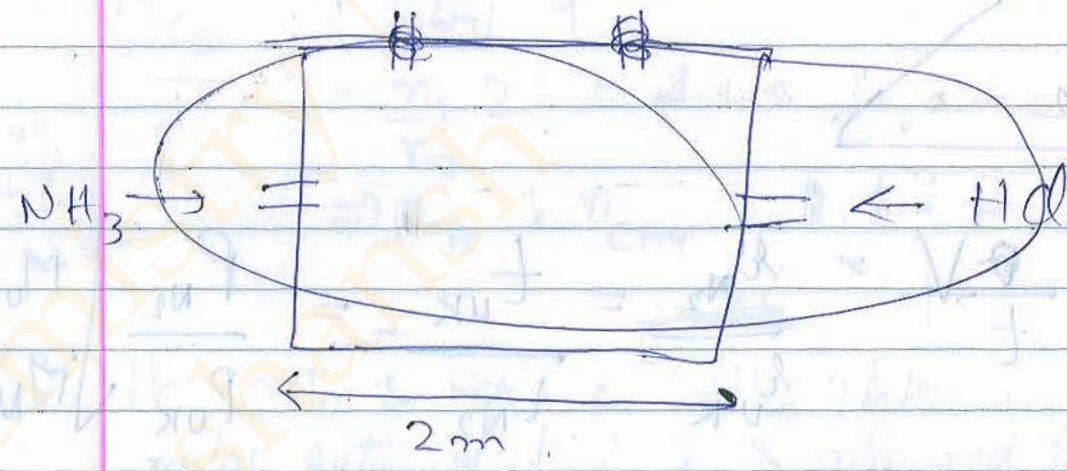
$$\Rightarrow M = 252 \quad (Xe, F_6)$$

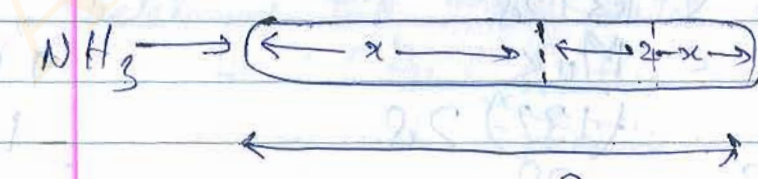
$$XeF_n = 131 + 19n = 252$$

$$\Rightarrow n = 6$$

$$\Rightarrow XeF_6$$

Q. NH_3 gas & HCl gas are injected simultaneously from 2 terminals of a 2m long uniform cylindrical glass tube. Assuming gases to be present at same T & P, and same geometry of inlet (opening), determine distance from NH_3 terminal at which 1st flash of white fume will be observed.





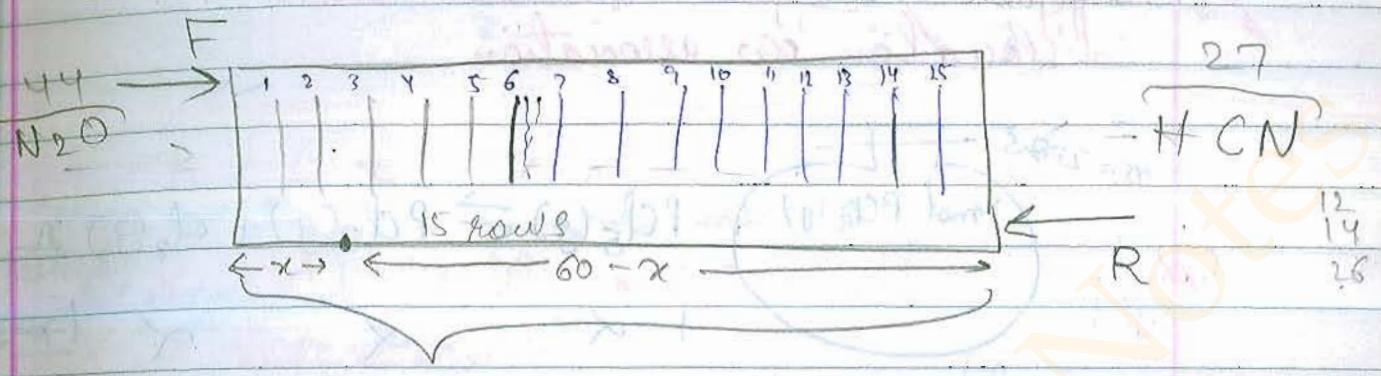
$$\frac{r_{NH_3}}{r_{HCl}} = \frac{x}{2-x} = \sqrt{\frac{36.5}{17}} \left(\frac{\frac{x}{t}}{\frac{2-x}{t}} \right)$$

t is same for both.

$$\Rightarrow \frac{x}{2-x} = \sqrt{\frac{36.5}{17}}$$

$$\Rightarrow \frac{x}{2-x} = 1.5 \quad x = \frac{3}{2.5} = \frac{36}{25}$$

Q. Cylinders of N_2O & HCN at equal temp & P are opened simultaneously at the front & rear door of 60 m long classroom. Seating rows are arranged uniformly after every 4 m. Determine Students of which row will die while laughing ?



$$\frac{N_2O}{HCN} = \frac{x}{60-x} = \frac{44}{27} \sqrt{\frac{27}{44}}$$

$$\Rightarrow \frac{x}{60-x} = \frac{7}{10}$$

$$\Rightarrow x = 24+$$

So, Ans. = 6th row.

Date

30 August 09

☆ Diffusion / Effusion associated with dissociation or association

$m = 208.5$

1 mol $PCl_5(g)$

$r\alpha \propto \frac{1}{\sqrt{M}}$

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\quad n$

$1 \to n$ $\quad x \quad x$

$1-\alpha \quad \alpha \quad \alpha \quad 1+\alpha$

$n \to 1+\alpha$ $\qquad \frac{W}{n} = M$

$\overline{M} / M_{avg} = \frac{208.5}{1+\alpha}$ $\qquad \therefore 1+(\alpha) > 1$ (+ve)

☆ α = degree of dissociation

It is the moles of reactant decomposed out of its 1 mole

$$\overline{M} = \frac{M_0}{1+\alpha}$$

$2Cl_2O_7(g) \rightleftharpoons 2Cl_2(g) + 7O_2(g)$ $\quad n$

$2\alpha \quad 7\alpha \quad 1+\frac{7}{2}\alpha$

$\overline{M} = \frac{183}{1+\frac{7}{2}\alpha}$

$$2NO_2 \rightleftharpoons N_2O_4$$

$1-\alpha$; $\frac{\alpha}{2}$; $\bar{M}$; $1-\frac{\alpha}{2}$

$$\bar{M} = \frac{M_0}{1-\frac{\alpha}{2}} \qquad 1-\frac{\alpha}{2} < 1$$

☆ In case of association

Molar mass of partically associated gaseous mix ($\bar{M}$) $>$ Molar mass of pure gas (M_0) ; rate of effusion: Less.

☆ In dissociation

$\bar{M}$ = avg. molar mass of dissociated gaseous mix $<$ M_0 ; rate of effusion: More

M_0 = Molar mass of pure gas

Q. Rate of effusion of a partially decomposed Cl_2O_7 gas is 2 times slower than rate of effusion of pure C_2H_6 gas under identical condⁿ.

Assume that the gas dissociates →

$$Cl_2O_7(g) \rightleftharpoons Cl_2(g) + \frac{7}{2}O_2(g)$$

$1-\alpha$; α ; $\frac{7}{2}\alpha$; $1-\frac{7}{2}\alpha$

Determine % age decomposition of Cl_2O_7

$$\bar{M} = \frac{183}{1+\frac{7}{2}\alpha}$$

Let r_A of Cl_2O_7 be r

$\therefore$ $C_2H_6 \rightarrow 2r$

$$\frac{r_{C_2H_6}}{r_{\text{Gmix}}} = 2 = \sqrt{\frac{M}{30}}$$

$$\Rightarrow 4 = \frac{M}{30}$$

$$\Rightarrow M = 120.$$

$$\Rightarrow \frac{183}{1+3.5\alpha} = 120$$

$$\Rightarrow 183 = 120 + 420.$$

$$\Rightarrow \frac{63}{42} = \alpha$$

$$= 0.15 = \alpha \quad \times 100$$

Ans → 15% dissociated.

Q. Rate of effusion of a partially ozonised sample of O_2 is 0.9 times the rate of effusion of pure O_2 gas. Determine mass %age of Ozone in the partially ozonized sample of O_2

$$\frac{r_{O_3}}{r_{O_2}} = 0.9 = \sqrt{\frac{32}{M}}$$

$$= 0.81 = \frac{32}{M}$$

$$\Rightarrow M = \frac{32 \times 100}{81}$$

$$3O_2 \rightleftharpoons 2O_3 \qquad n$$

$$1-\alpha \qquad \alpha \qquad 1-\frac{\alpha}{3} = \frac{3-\alpha}{3}$$

$$M = \frac{16}{\frac{3-\alpha}{3}}$$

$$\Rightarrow \frac{32}{81} \times 100 = \frac{16}{1-\frac{\alpha}{3}}$$

$$\Rightarrow 1-\frac{\alpha}{3} = \frac{81}{200}$$

$$\Rightarrow 1-\frac{81}{200} = \frac{\alpha}{3}$$

$$\Rightarrow 2-\frac{81}{100} = \alpha$$

$$\Rightarrow \frac{200-81}{100} = \alpha$$

$$\Rightarrow \alpha = 1.19$$

$$\Rightarrow \frac{32}{81} \times 100 = \frac{16 \times 3}{3-\alpha}$$

$$\Rightarrow 3-\alpha = \frac{3 \times 81}{200}$$

$$\Rightarrow 3 - \frac{3\alpha 81}{200} = \alpha$$

$$\Rightarrow 3\left(1-\frac{81}{200}\right) = \alpha$$

$$\Rightarrow 3\left(\frac{119}{200}\right) = \alpha$$

$$\Rightarrow \alpha = 0.57$$

$$\text{Mass \% of } O_3 = \frac{3}{3} \times 0.57 \times 48 \times 100$$

$$32$$

$$= 57\%$$

Kinetic Theory of Gases (KTG)

Kinetic Theory of gas is theoretical model of ideal gas.

KTG is based on certain assumptions known as postulates of Kinetic Theory.

Postulates

ASSUMPTIONS

1) Gas molecules are spherical - For a pure gas, all the molecules are identical in shape, size & mass.

2) Avg. distance b/w adjacent molecules of gas is very large in comparison to size of the molecule.



Acc to KTG molecules are treated as a point mass of negligible volume.

Based on this it is concluded that, molecular volume ($\frac{4}{3}\pi r^3 N$) is negligible in comparison to volume of gas (volume of container)

3) Molecules of ideal gas obey Newton's law

Gas molecules are in constant random motion & moves in a straight line path until it collides with other molecules or with the walls of the container.

molecule or with wall of container.

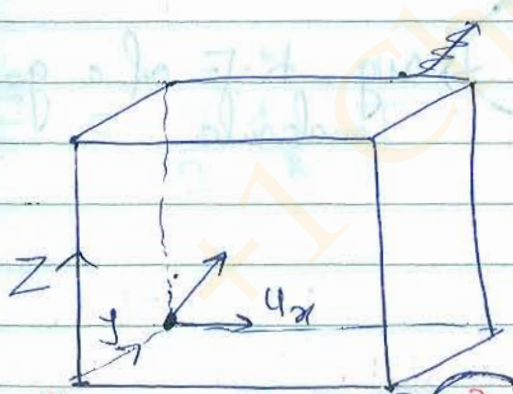
Collision of a gas molecules either with other molecule or with wall of container is perfectly elastic in nature i.e K.E & momentum ~~&~~ are conserved.

i) A gas molecule may have very high K.E. another gas molecule may have very low K.E. But, avg K.E is consth. at a consth. temp.

So,

Avg. K.E of gas depends ONLY on Temp.

ii) In a given sample of gas, there is always distribution of molecular speed in which some molecule move at ~~higher~~ slower speed, some at higher speed, but avg speed remains consth as long as temp. is consth.



$-u_x : \Delta u = -2u_x$

$$P = \left(\frac{1}{3}\frac{mN\bar{c}^2}{V}\right)$$

$$\Rightarrow PV = \frac{1}{3}(m)(N)(\bar{c}^2)$$

$\bar{c}^2$ → Read as → Mean of the sq. speed.

N → no. of molecules

m → mass of molecule. $\left(\frac{M}{A_0}\right)$

It is ~~known as~~ known as KINETIC GAS EQN.

MEAN OF SQ. SPEED

Date

c_1 c_2 c_3
c_4 c_5

$$\bar{C}^2 = \frac{C_1^2 + C_2^2 + C_3^2 + C_4^2 + C_5^2}{5}$$

$$= \frac{C_1^2 + \cdots\cdots + C_N^2}{N}$$

If N_1 ~~molecules~~ molecules are at speed C_1, N_2 at C_2 ——————

then

$$\bar{C}^2 = \frac{N_1 C_1^2 + N_2 C_2^2 + \cdots\cdots}{N_1 + N_2 + N_3 + \cdots\cdots}$$

$$= \frac{n_1 C_1^2 + n_2 C_2^2 + \cdots\cdots}{n_1 + n_2 + \cdots\cdots}$$

$$PV = \frac{1}{3} m N \bar{C}^2 = \frac{2}{3} N \left(\frac{1}{2} m \bar{C}^2\right)$$

$$\Rightarrow PV = \frac{2}{3} N \bar{E}$$ → avg. K.E of a gas molecule.

Boyle's law

At constt. temp., $\bar{E}$ is constt.
for a fixed amount, N is constt.

So, PV = constt.

So, this law is verified.

Charles law

At constt. P, for a fixed amt. (N → constt.)

$$V = \left(\frac{2N}{3P}\right) \bar{E}$$

$\Rightarrow V \propto$ temp. ($\because KE \propto$ Temp)

Avogadro law

At constt T, P

$\Rightarrow V = N$

So, ~~KE~~ Kinetic Gas eqn. ~~all~~ verifies all laws of ideal gas.

Hence, $\boxed{PV = \frac{2}{3} N\bar{E} = \frac{1}{3} mN\bar{C}^2 = nRT}$

IDEAL GAS EQN.

$\bar{E} = nRT \cdot \frac{3}{2N} = \frac{3}{2} \frac{RT}{N}(n)$

$= \frac{3}{2}\left(\frac{R}{N_A}\right)T \quad \left[\because \frac{N}{N_A} = n\right]$

$\Rightarrow \bar{E} = \frac{3}{2}\left(\frac{R}{N_A}\right)T \rightarrow$ Boltzmann's Eqn

$\left(\frac{R}{N_A}\right) \rightarrow K_B$ = Boltzmann's Constt.

$= 1.38 \times 10^{-23}$

K.E/mol $= \frac{3}{2}RT$

So, avg. K.E is independent of identity of gas. It depends only on temp.

(constt)

$\bar{E} = \bar{E}_{trans.} + \bar{E}_{rot.} + \bar{E}_{vib.}$ (ignored)

So, $\bar{E} = \bar{E}_{trans.}$

Every molecule has 3 types of motion →
Translational (straight line), rotational (ooooo)
vibrational (wwwww)

Now

$$PV = nRT = \frac{1}{3} mN\bar{c}^2$$

$$\bar{c}^2 = \frac{3nRT}{mN} = \frac{3RT}{mN_A} = \frac{3RT}{M}$$

$\sqrt{\bar{c}^2} = \sqrt{\frac{3RT}{M}} = u_{rms}$

↓ root mean sq. speed

$$E = \frac{3}{2} RT$$

$\lambda = \frac{h}{p}$

Q. Determine de-broglie wavelength of an e^- at 27°C, $e^-_m = 9.1 \times 10^{-31}$ kg

$$E_K = \frac{3}{2} KT$$

$$\Rightarrow E_K = \frac{3}{2}(8.31)(300)$$

$$\Rightarrow E_K = \frac{3}{2}(1.38) \times 10^{-23} \times 300$$

$$= 450 \times 1.38 \times 10^{-23}$$

$$= 62.1 \times 10^{-23}$$

$$= 6.21 \times 10^{-21}$$

$E = \frac{1}{2}mv^2 \times \frac{m}{m} = \frac{p^2}{2m}$

$\Rightarrow 6.21 \times 10^{-21} = \frac{p^2}{2m}$

$\Rightarrow \lambda = \frac{h}{p}$

$\Rightarrow \sqrt{2mE} = p.$

$\Rightarrow \lambda = \frac{h}{\sqrt{2mE}}$

$\Rightarrow \lambda = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 10^{-21} \times 6.21}}$

$\Rightarrow \lambda = \frac{6.626 \times 10^{-34}}{10.5 \times 10^{-26}} 10^{-8}$

$\Rightarrow \lambda = 6 \times 10^{-9} m = 6 nm.$

Q. U_{rms} of N_2 in air is 580 m/s. Determine U_{rms} of He present in the same air.

$\sqrt{(580)^2} = \sqrt{\frac{3(\cancel{8+580}) \times RT}{28}}$

$\Rightarrow (580)^2 = \frac{3}{28} \times RT$

$\frac{U_{rms}(He)}{U_{rms}(N)} = \sqrt{\frac{28}{4}} 7. \Rightarrow U_{rms} = 580\sqrt{7}$ m/s

3 Sept 09

Q. Determine U_{rms} of CH_4 gas at 300 K

$$U_{rms} = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3 \times 300 \times R}{16}}$$

$$= \sqrt{\frac{3 \times 300 \times 8.314}{7482 \; 3741}}$$

$$= \sqrt{46.7}$$

$$= 6.7$$

$$= \sqrt{\frac{3 \times 8.314 \times 300}{16 \times 10^{-3} \; kg \; mol^{-1}}}$$

$$= \sqrt{\frac{3 \times 8314 \times 300}{16}}$$

$$= \sqrt{\frac{74826 \times 100}{16}}$$

Q. Determine U_{rms} of N_2 gas at 10 atm, where its density is 2 g/L.

$V = 14\ l$

$p = 10\ atm$

$10 \times 14 = 1 \times R \times T$

$\Rightarrow 140 = RT$

Now, $v_{rms} = \sqrt{\frac{3 \times 140 \times 10^5}{28 \times 10^{-3}}}$

$= \sqrt{15000}$

$PV = nRT = \frac{W}{M} RT$

$PM = \frac{W}{V} RT$

$PM = \rho RT$

$\Rightarrow \frac{RT}{M} = \frac{P}{\rho}$

So, $v_{rms} = \sqrt{\frac{3P}{\rho}}$

$= \sqrt{\frac{3 \times 10^5 \times 1000}{2}} = \sqrt{15000}$

$= \sqrt{\frac{3 \times 10^5 \times 10^5}{2}}$

$= \sqrt{150 \times 100}$

$= 1220\ m/s$

$\rho = \frac{M}{V} \Rightarrow 2 = \frac{M}{V}$

$\Rightarrow V = \frac{M}{2}$

2245
05
1125
22
242
e2
484

3 | 15.00
-9
600

1243
e3
729

12.2
1 | 150.00
-1
22 050
-44
242 600

1500000

$x^{1/2} = \frac{1}{2}(x$

Date

Q. In a specific temp. range, rate of change of U_{rms} is 2 times rate of change of temp. for N_2 gas. Determine U_{rms} of N_2 in the temp. range

At $t_{rms} = S$

$$\frac{dS}{dt} = 2\frac{dT}{dt}$$

$$\Rightarrow \frac{d}{dt}\sqrt{\frac{RT3}{M}} = 2\frac{d}{dt}T$$

$$\Rightarrow \frac{dS}{dT} = 2 \quad , \quad S = \sqrt{\frac{3RT}{M}}$$

$$\Rightarrow \frac{dS}{dT} = \sqrt{\frac{3R}{M}} \times \frac{1}{2\sqrt{T}} \times \frac{\sqrt{\frac{3R}{M}}}{\sqrt{\frac{3R}{M}}}$$

$$= \frac{3R}{M} \times \frac{1}{2\sqrt{\frac{3RT}{M}}}$$

$$\Rightarrow \frac{dS}{dT} = \frac{3R}{2MS} = 2$$

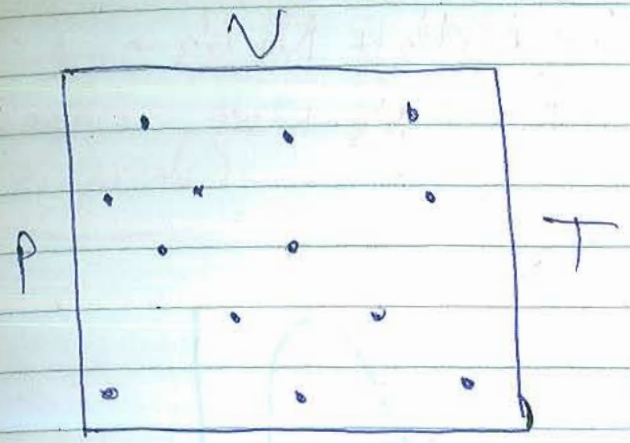
$$\Rightarrow S = \frac{3 \times R}{4 \times 28} = \frac{3 \times 8.314 \times 1000}{4 \times 28}$$

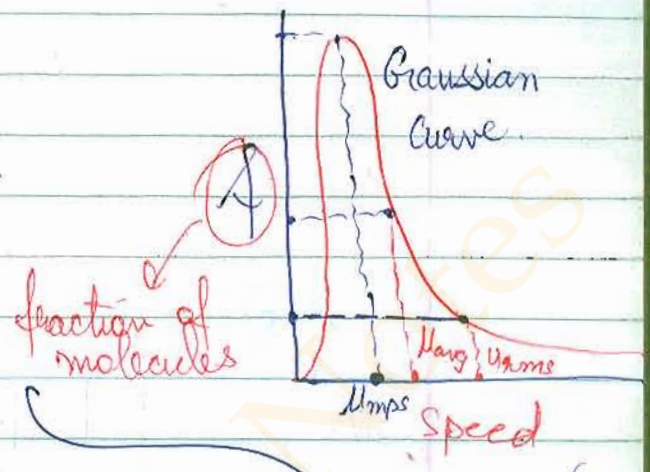
$$= \frac{3 \times 8314}{4 \times 28}$$

HW ☞ Find T also

MAXWELL-BOLTZMANN'S

Distribution of molecular speed





- जो दिख रहा है Graph से
- Molecules moving at very low speed as well as at very high speed are very less.
- Indicates what is the fraction of molecules moving at a particular speed.

2. For a given sample of gas, majority of the molecules moves in a specific range of speed.

MoSt PrObAbLe SpEeD (U_{mps})

वो Speed जिसपर Fraction (map) के molecules move कर रहे हों।

Most Probable Speed is the speed possessed by largest fraction of the molecules.

Formula of $U_{mps} = \sqrt{\frac{2RT}{M}}$

Date

☆ AVERAGE SPEED (U_{avg})

Avg. speed is the algebraic mean of the molecular speed.

$$U_{avg} = \frac{N_1U_1 + N_2U_2 + N_3U_3 + \dots}{N_1 + N_2 + N_3 + \dots}$$

$$\Rightarrow U_{avg} = \sqrt{\frac{8RT}{\pi M}}$$

So, SPEEDS

$$rms = \sqrt{\frac{3RT}{M}}$$

$$mps = \sqrt{\frac{2RT}{M}}$$

$$avg = \sqrt{\frac{8RT}{\pi M}}$$

Q. For a given gas, at a given temp., the increasing order of 3 types of speed is?

$\sqrt{3} > \sqrt{2}$; $\sqrt{\frac{8}{\pi}}$ $\frac{56}{22}$ $\frac{28}{11}$ 2.

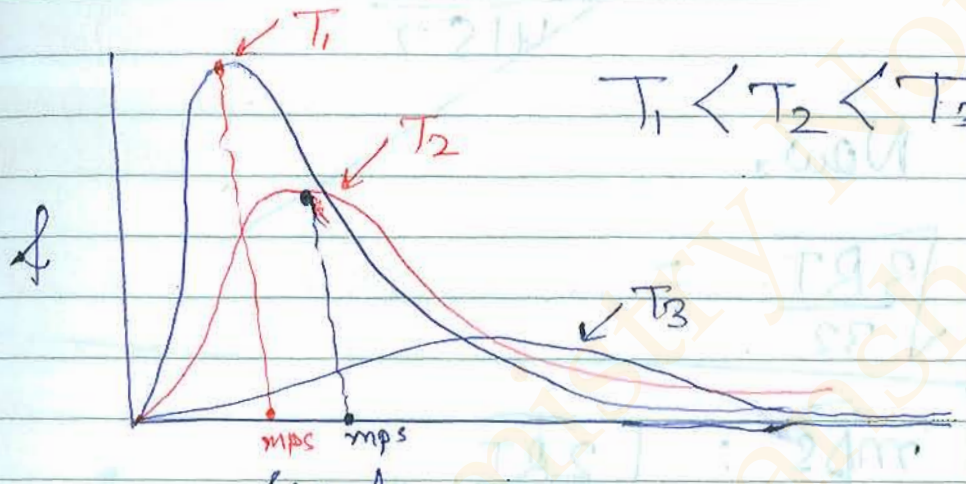
$\sqrt{3} > \sqrt{2.\dots} > \sqrt{2}$

So, rms > avg > mps.

Among 3 types of speeds,

Note: (1) mps is the speed possessed by greatest %age of molecules but has smallest value (among the 3 speeds)

(2) rms speed is the speed possessed by smallest fraction, but has largest value (among the 3 speeds)



1) As we increase the temp., Maxwell curve broaden (flatten).

2) Increasing temp. increases the value of speed, but decreases the fraction of molecules ~~having~~ ~~the~~ moving at a particular speed.

☆ At a constt. temp, heavier molecule will have less type of speeds.

As we decrease molar mass, type of speed increases.

Decreasing M, broader the Maxwell curve, i.e., distribution of molecular speed becomes more & more scattered.

Q. Determine ⅈms of O_2 in air if ⅈmps of He in the same air is 1600 m/s

$$1600\ m/s = \sqrt{\frac{2RT}{4}}$$

$$= 256 \times 10^4 = \frac{8.314}{2} \times T$$

$$\Rightarrow T = \frac{256 \times 10^4}{4157}$$

Now,

$$\sqrt{\frac{3RT}{32}} =$$

$$mps : \sqrt{\frac{2RT}{4}}$$

$$ⅈms : \sqrt{\frac{3RT}{32}}$$

$$\Rightarrow \frac{1600}{ⅈms} = \frac{\sqrt{1/2}}{\sqrt{3/32}} = \frac{4}{\sqrt{3}}$$

$$\Rightarrow ⅈms = \frac{400\sqrt{3}}{\sqrt{3}}$$

$$= 692\ m/s.$$

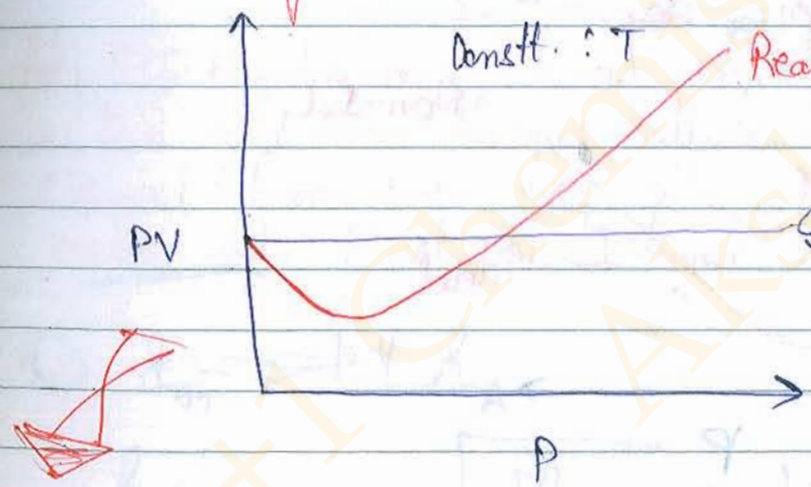
Imps of

Real Gas (non-ideal gas)

Gases which don't obey $PV = nRT$ eqn. of state, are known as REAL GAS or NON-IDEAL GAS.

Properties

* $PV = nRT$ is obeyed by a gas at a very narrow range of Temp. & P. In most of the cases, gases deviate from ideal behaviour.



2173 & 692

1) In lower P region, at a constt. temp, for a fixed amt., PV decreases on increasing P, attains a minima & then, increases with increasing P.

2) If PV observed is less than $PV_{(ideal)}$: Negative Deviation (-ve deviation) from Ideal behaviour.

3) If PV observed > PV ideal, then, it is known as +ve deviation.

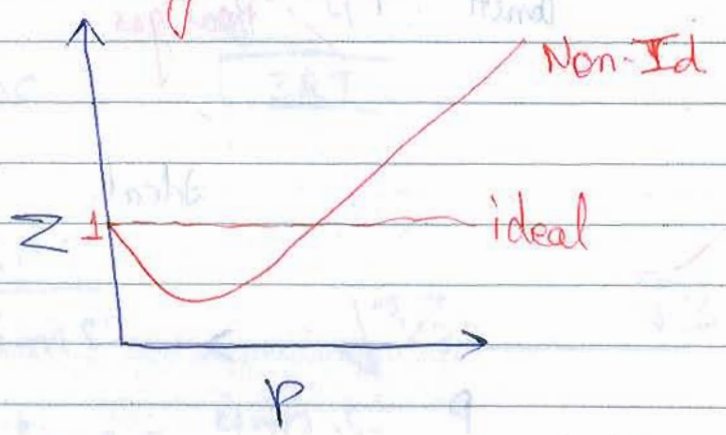
★ **Z : Compression factor**
or
Compressibility factor

It is the measure of deviation from ideal behaviour.

$$Z = \frac{V}{V_{ideal}} = \frac{V\,P}{nRT} = \frac{PV}{nRT}$$

$$\Rightarrow Z = \frac{PV}{nRT}$$

★ For ideal gas, Z = 1



At low P, Z decreases. After attaining a min. value, Z increases

★ Deviation is to be seen w.r.t ideal gas compressibility (1)

Q. At 300 K, 1 atm, Z for O_2 is 0.9. Determine mass of O_2 gas present in 100 L tank at 1 atm, 300 K.

$$0.9 = \frac{1(100)}{n \times 0.082 \times 300}$$

$$\Rightarrow n = \frac{10000}{9 \times 82 \times 3}$$

$$\Rightarrow n = \frac{10000}{2214} 4.5$$

$$\Rightarrow n = 4.5$$

$$\Rightarrow \frac{m}{32} = 4.5$$

$$\Rightarrow m = 144\ g.$$

Q. At 500 K, 1 atm, 1 of an non-ideal gas is 0.8 g/L & the gas effuses 1.4 times slower than pure O_2 gas. Determine Z & molar vol. (Vol. of 1 mol.)

$$\frac{r_{O_2}}{r_A} = \sqrt{\frac{M_A}{32}} = 1.4$$

$$\Rightarrow \frac{1}{\sqrt{2}} = \sqrt{\frac{M_A}{32}}$$

$$\Rightarrow \frac{1}{2} = \frac{M_A}{32} \Rightarrow M = 64$$

$V_m = \frac{64}{0.8} = 80$ lit.

$Z = \frac{PV_m}{RT}$

$= \frac{(1)(80)}{0.082 \times 500}$

$= \frac{8 \times 1000}{50 \times 8.} = 20$

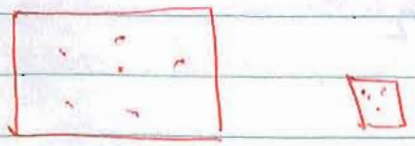
$\Rightarrow Z = 1.9$ approx.

6 Sept. 09

Reasons for Deviation from Ideal Behaviour.

Postulates of Kinetic Theory of gases are not always true for all gases in all range of temp & P.

Acc. to Kinetic Theory, vol. of a molecule is negligible in comparison to vol. of container, which is not always true.



$P_i V_i = nRT.$

Volume Correction for molecular vol.

✡ EXCLUDED VOLUME (CO-VOLUME) = b (per mol)

Effective space occupied by molecules per mole = Effective vol.

For 'n' mol., Ex. vol. = nb

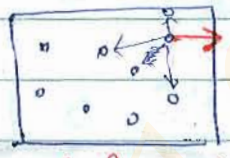
Kinetic theory of gas treat each molecule independent of one another.

i.e when a molecule travels, it is neither attracted nor repelled by other molecules.

✡ PRESSURE CORRECTION

Acc. to Kinetic Theory, ideal gas molecules are independent of one another.

i.e, that does not exist any inter molecular attn or repulsion, which is not always true. Gas molecules may exert attn / repulsion to the adjacent molecules.



• Let there be net attn

In case of inter molecular attn, the observed P, will be less than the expected Ideal P.

• Let there be net repl^n

In case of inter molecular repul^n, the observed P will be greater than P_{ideal}.

$Z = \frac{Real}{Ideal} = \frac{P}{P_{id}} = \frac{V}{V_{id}}$

In case of net attn : $P < P_{id}$

$\frac{P}{P_{id}} < 1 \Rightarrow Z < 1$

In case of net repul^n : $\frac{P}{P_i} > 1 \Rightarrow Z > 1$

Date

Attraction

$P_{id} = P + p$

p → pressure correction factor.

P → observed P

$p \propto (\rho)^2$

ρ → gas density

$p \propto \frac{n^2}{V^2}$

pressure correction factor.

$p = a\frac{n^2}{V^2}$

a → Constant of proportionality

Pa / mol

So,

$$P_{id}\, V_{id} = \left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

VANDERWALL'S EQN. OF STATE

a, b = Vanderwall's constant

b → min. vol. occupied by gas in solidified state.

$a = (\text{lit})^2 \text{ atm. mol}^{-2}$

$b = \text{lit mol}^{-1}$

7. Determine the ideal & real P exerted by 1 mol of $(CO_2\ g)$ at 300 K when confined in
(a) 24.6 l container
(b) 0.2 l "
(c) 0.05 l "

Given: $a = 3.6$ atm $l^2\ mol^{-2}$
$b = 0.4\ l.\ mol^{-1}$

Ans $n = 1$

$CO_2 \rightarrow 44$ $\quad T = 300\ K$, $R = 0.082$.

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$ → Vander wall gas P.

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

(a) $P_{id} = \frac{0.082 \times 300}{24.6} = 1$ atm.

$P_{real} = \frac{24.6}{24.6 - 0.04} - \frac{3.6}{}$

$= 1$ atm (approx)

(b) $P_{id} = \frac{24.6}{0.2} = 12.3$

$P = \frac{24.6}{24.6 = 0.2 - 0.04} - \frac{3.6}{0.04} \quad \frac{36 \times 100}{10}$

$153.75 \qquad = 90$

$= \frac{2460}{16} - 90$

$P = 63.75$ atm

(c) $P_{id} = \frac{24.6}{0.05} \times \frac{2460}{5}$ 492 atm.

$P = \frac{24.6}{0.05 - 0.04} - \frac{3.6}{25} \times 10^4$

$= 246 - \frac{36}{25} \times 10^4$

$= 2460 - \frac{36}{25} \times 10^3$

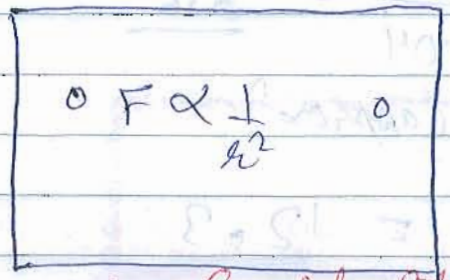
$\Rightarrow P = 2460 - \frac{1024}{25} \frac{36}{} \times 10^3$

$P = 1020$ atm

$2^{3}\cancel{4}\overset{1}{\cancel{6}}0$
-162
$\overline{2295}$
5
2460
-162^{4}
$\overline{836}$

☆ CRITERIA for Ideal Behaviour (Ideal behaviour)

1) $V \to \infty$



Gas approaches ideality

$V \propto T$ } So $T \to \infty$
$V \propto \frac{1}{P}$ } $P \to 0$

So, criteria for ideality is high temp & low pressure, ideal behaviour will be more.

If we lower temp & increase P, gas

For He(g), V_{molar} at 10 MPa ($\times 10^6$) & 300 K is 0.011 times its V_{molar} at 100 KPa ($\times 10^3$) at 300 K. Determine "b" assuming that there is negligible inter molecular atten

$P(V - nb) = nRT$, $P(V - b) = RT$ for 1 mol.

(1) $P_1 = \frac{nRT}{V - nb} = 0.011$

$P_2 = \frac{nRT}{V - nb}$

Let at 10^5 Pa, molar Vol. = V.

So $10^5 (V - b) = RT \rightarrow (1)$

$10^7 (0.011V - b) = RT \rightarrow (2)$

$\Rightarrow V - b = 100(0.011V - b)$

$\Rightarrow V - b = 1.1V - 100b$

$\Rightarrow 99b = 0.1V$

$\Rightarrow V = 990b$.

$\frac{10^5}{\approx 10^5} (989b) = RT \rightarrow 300$

1 atm.

$\Rightarrow b = \frac{RT}{989} = \frac{(\frac{10}{300} \times 0.082)}{990}$

$= \frac{0.82}{33}$ l/mol

= 0.024 lit mol⁻¹

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

modify

① If P is very low

$$\left(P + \frac{n^2 a}{V^2}\right)(V) = nRT$$

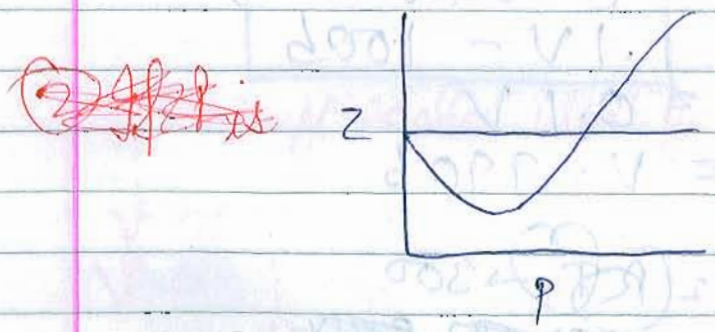
For 1 mol → $PV + \frac{a}{V} = RT$

∴ ÷ by RT ⇒ $\frac{PV}{RT} = 1 - \frac{a}{VRT}$

$$Z = 1 - \frac{a}{VRT}$$

$Z < 1$

* As we increase P, Z will decrease



② In High P. region, (For 1 mol)

$P(V - b) = RT$

$PV = RT + Pb$

Q. For a V.W. Gas, 500 K, Z = 0.85 ~~dm⁶ mol⁻²~~. Determine V_{molar} of gas in the given cond^n if, a = 2.5 atm l^2 mol^{-2} & the $V_{molecular}$ is negligible in comparision to vol. of container.

~~$P(V-b) = RT$~~

$$\Rightarrow Z = 1 - \frac{a}{VRT}$$

$$\Rightarrow 0.85 = 1 - \frac{2.5}{V \times 500 \times 0.082}$$

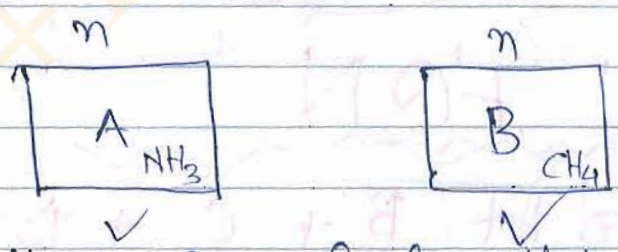
$$\Rightarrow V = 0.4\ lit.$$

★ a, b

a & b are characteristic constants for a gas.

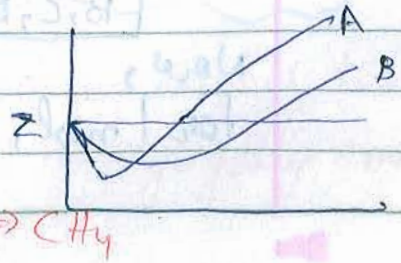
(i) a. (measures deviation in P)

$$P = \frac{n^2 a}{V^2}$$



NH_3 (inter molecular attr^n) > CH_4

Intermolecular attr^n $\propto$ a.



A → NH_3, B ⇒ CH_4

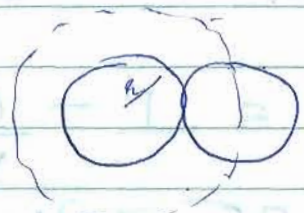
Date

(1) NH_3 H_2O CH_4 CO_2
I II III IV

Inc. order of a ?

$CH_4 < CO_2 < NH_3 < H_2O$

b : Excluded vol



Ex. vol. by a pair of molecule
$= \frac{4}{3}\pi(2r)^3$

Ex. vol. per molecule $= 4\left(\frac{4}{3}\pi r^3\right)$

So,
Excluded vol. per molecule = 4 times molecular

So, Ex. vol/mol $= 4\left(\frac{4}{3}\pi r^3\right) \times N_A = b$

So, b depends on r, radius of molecule/atom.

☆ VIRIAL EQN

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \dots$$

B, C, D → 1st, 2nd, 3rd Virial Coeff. ; V_m → molar V

Now,
For 1 mol, $P = \frac{RT}{} - \frac{a}{}$

× $\frac{V_m}{RT}$

2 → $\frac{PV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT}$

$= \frac{1}{\left(1 - \frac{b}{V_m}\right)} - \frac{a}{V_m RT}$

$= \left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a}{V_m RT}$

$\left[(1-x)^{-1} = 1 + x + x^2 + x^3 + \cdots\right]$

$= 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \frac{b^3}{V_m^3} + \cdots - \left(\frac{a}{V_m RT}\right)$

$= 1 + \frac{1}{V_m}\left(b - \frac{a}{RT}\right) + \frac{b^2}{V_m^2} + \cdots\cdots$

B C

here $V_m > b$ (always)
so, its a decreasing series. (~~Diverging series~~ converging series converging at 0)

So, $Z = 1 + \frac{1}{V_m}\left(b - \frac{a}{RT}\right)$

(Ignoring higher term (∵ its negligibly small)

Vanderwall cum Virial Eqn.

a pair of

molecular

b

de/atom.

→ molar Vol.

Date

☆ Condition for ideal behaviour.

For $z = 1$, $\left(b - \frac{a}{RT_B}\right) = 0$ → at a specific temp

$\Rightarrow$ $T_B = \frac{a}{Rb}$ → वो specific te... जिसपर non ideal ... ideal बन जाएगा

Boyle's Temp.

① T_B of a gas is 107 K & Z at 300 is 0.9

Determine a, b, considering n = 1 in V = 1 lit.

$z = 1 - \frac{a}{VRT}$, $z < 1$

$\Rightarrow 0.9 = 1 - \frac{a}{1 \times 0.082 \times 300}$ 82 / 03 / 246

$\Rightarrow -0.1 = -\frac{a}{0.082 \times 300}$

$\Rightarrow a = \frac{246}{1000} \times 1000 \times \frac{1}{10}$

$\Rightarrow \boxed{a = 2.46}$

Now.

$T_B = \frac{a}{Rb}$.

specific temp
ो specific temp.
442 non ideal gas
eal बन जाएगी।

Z at 300K

ing n=1

!

82
03
246

$\Rightarrow 107 = \frac{2.46}{0.082 \times b}$

$\Rightarrow b = \frac{2.46}{0.082 \times 107}$

$= \frac{2460}{8774} \; 0.28$

$\Rightarrow \boxed{b = 0.28}$

107
82
214
856
8774

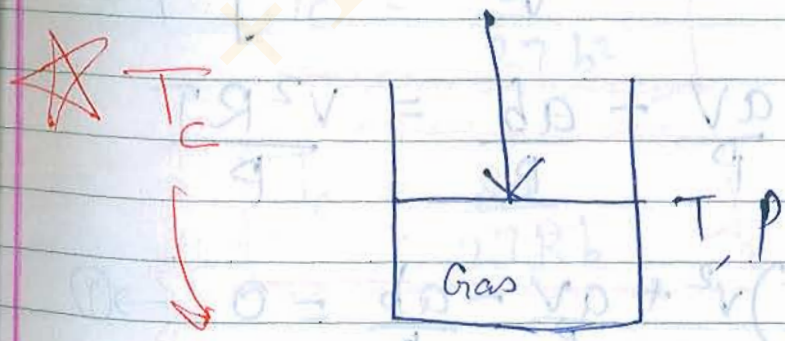
18774 | 18774 | 2
526 44 | 17548
8774 | 2460
70192 | 1954 | 20
8774
2

1246 00
17548
7052
705 20

10 Sept. 09

✡ CRITICAL CONSTANTS

- Critical temp. (T_c)
- Critical Pressure (P_c)
- Critical vol (V_c)



It is a temp above which a gas can't be liquified by applying any amt. of P

We can't observe liquid state of matter above T_c.

☆ Every gas has a characteristic T_c.

(lower limit of P)

☆ P_c: Critical P is the min. P. below which gas can't be liquified by decreasing temp. to any value.

☆ For liquification of gas →
P should be > P_c
T < T_c

☆ V_c: Critical vol is the vol. occupied by 1 mol of gas at its T_c & P_c.

→ Vander Wall eqn. for 1 mol.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

$$\Rightarrow \left[PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT\right] \frac{V^2}{P}$$

$$\Rightarrow V^3 - bV^2 + \frac{aV}{P} - \frac{ab}{P} = \frac{V^2RT}{P}$$

$$\Rightarrow V^2 - \left(b + \frac{RT}{P}\right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \quad \rightarrow (1)$$

↳ Vander wall eqn.

$$(V - V_c)^3 = 0$$

$$= V^3 - V_c^3 - 3V^2V_c + 3VV_c^2 = 0 \rightarrow (2)$$

Comparing Coeff.

$$V_c^3 = \frac{ab}{P_c} \rightarrow (A)$$

$$3V_c^2 = \frac{a}{P_c} \rightarrow (B)$$

$$3V_c = \frac{b + RT_c}{P_c} \rightarrow (C)$$

Div. (A) by (B)

$$\Rightarrow \frac{V_c}{3} = b$$

$$\Rightarrow \boxed{V_c = 3b}$$

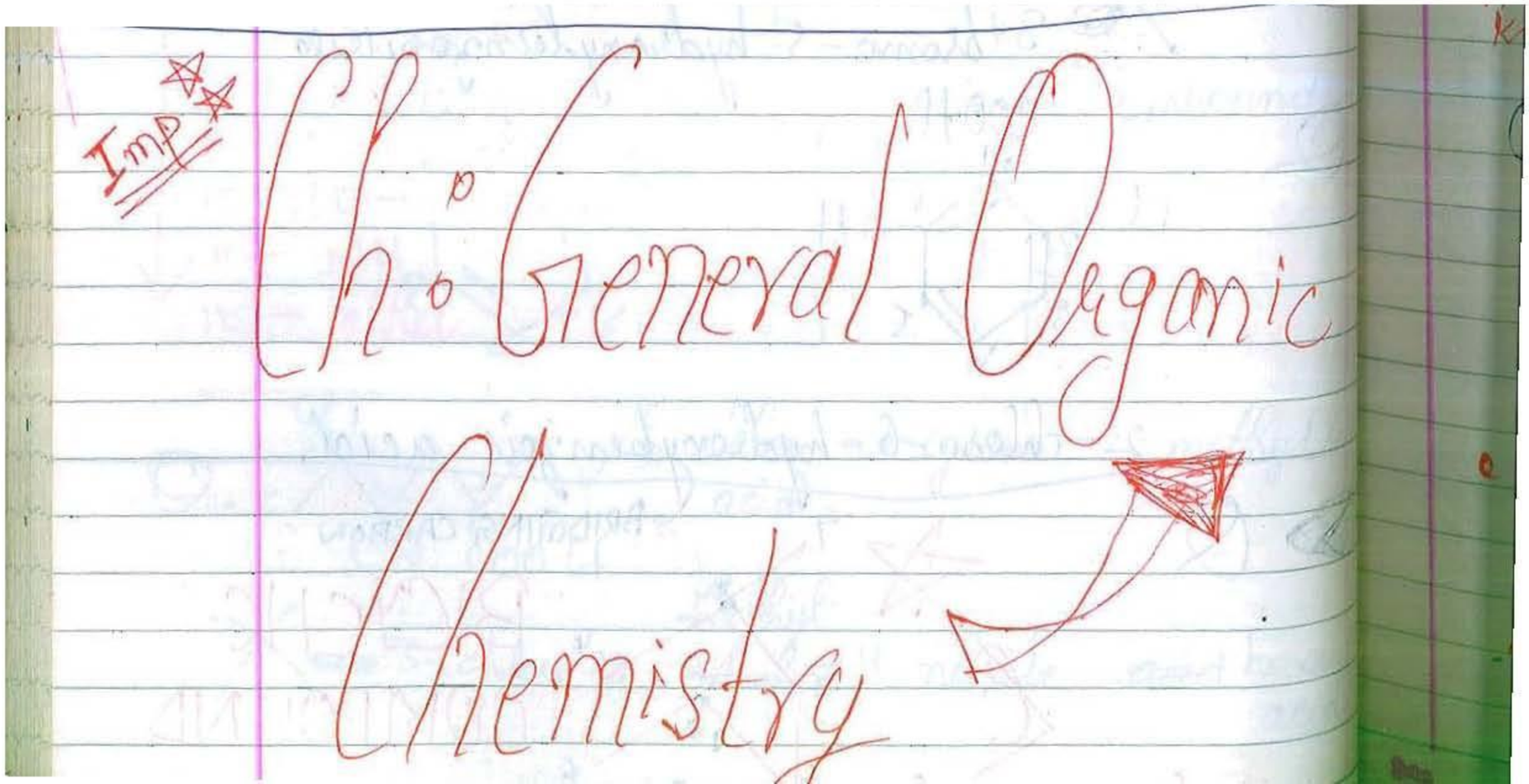
So,

$$\boxed{P_c = \frac{a}{27b^2}}$$

$$\boxed{T_c = \frac{8a}{27Rb}}$$

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{\cancel{a}}{\cancel{27b^2}} \times 3\cancel{b} \times \cancel{27Rb} \times \frac{1}{\cancel{R} \times 8\cancel{a} \times \cancel{b}} = \frac{3}{8}$$

+1 Chemistry Notes
Akshansh



ISOMERISM: Phenomena of exhibiting diff structural formula, differing in some of their physical, chemical or both properties; but having same chemical composition (i.e same molecular formula) showing

$C_4H_{10}O$

$CH_3-O-CH_2CH_2CH_3$





ISOMERISM

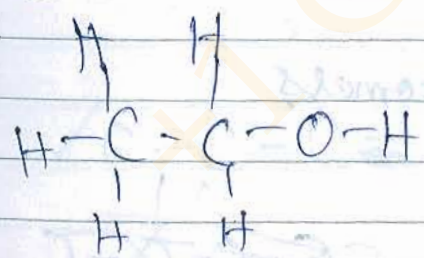
STRUCTURAL ISOMERISM (CONSTITUTIONAL)

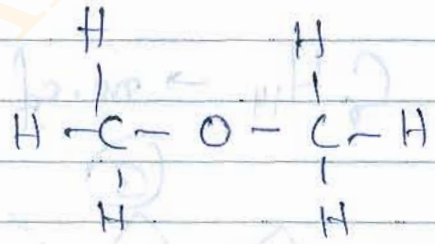
STEREO-ISOMERISM

Structural (Constitutional) Isomerism

Diff^t structures with same molecular formula are known as ISOMERS.

C_2H_6O





- Structural isomers have same molecular formula but diff^t bonding pattern. i.e atoms are differently connected (bonded). ∴ Structural isomers differ in their constitution.

Date

IUPAC naming of Organic Compounds

Naming Hydrocarbons

Compounds - Functional groups

NAMING HYDROCARBONS

unsubstituted

☆ Naming unbranched, ~~unsaturated~~, saturated Hydrocarbon.

Unsubstituted Hydrocarbon have a generic name called ALKANE

First 4 members are -

1) Methane
2) Ethane
3) Propane
4) Butane.

They originate their name from the source & now have been accepted as their official name.

Other higher members are named with ~~ner~~ numeric prefix as follows -

No. of carbon	IUPAC name
5)	Pentane
6)	Hexane
7)	Heptane
8)	

No. of carbon	IUPAC Name.
11	Undecane
12	Dodecane
13	Tri - - -
14	Tetra - - -
15	Penta - - -
16	Hexa - -
17	~~Nona~~ Hepta - - -
18	Octa - - -
19	Nona - -
20	Icosane

non cyclic (not having ring)

☆ Naming Branched Saturated Acyclic hydrocarbons

Rule 1: Selection of longest C chain.

The longest C chain will determine parent name & form suffix of the name.

☆ LOCANT: Group which substitute Hydrogen from the parent chain is known as locant. Also called - SUBSTITUENT.



↳ the one which substitutes H is locant.

eg:



4-dimethyl heptane

Date

Rule 2 : Numbering Rule.

The parent chain is numbered starting from 1 of its terminal. Numbering starts from a terminal giving lowest possible no. to the locant.

eg



4-ethyl-3-methyl heptane.

☆ R - Alkyl (C_nH_{2n+1})

Alk ane
yl

Rule 3 : Writing name of the compound:

1) Name of the locants are written 1st followed by parent name.
2) If more than 1 locants are present on the parent chain, their names are written in alphabetical order, irrespective of their pos^n
3) If similar locant is present more than once on the parent chain, their nos. are denoted as

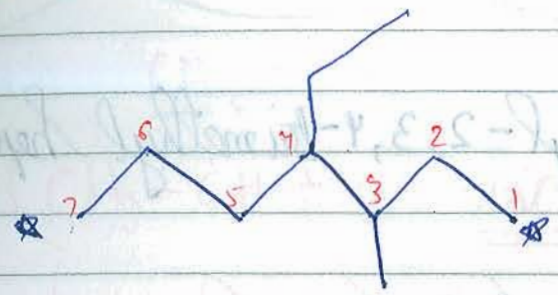
2 - di
3 - tri
4 - tetra
5 - penta
6 - [illegible]

when considers alphabetical order of locant, original name of locant are considered, not the initials of prefixes.

4) Positions of the locant is denoted by numerals (1, 2, 3 ——) before the name of locant.

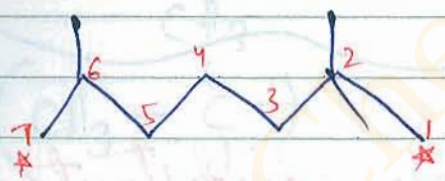
5) Nos. are always separated by comma.
Nos. & alphabet are always separated by hyphen (—)

eg



4-ethyl-3-methyl heptane

eg



2,2,6-trimethyl heptane.

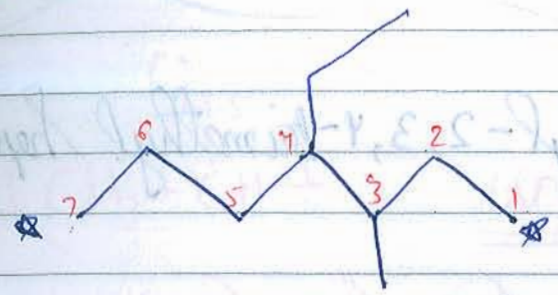
Rule 4: If more than 1 no. series exist simultaneously, lower no. coming at the 1st pt. of difference, will determine the correct no. series.

when considers alphabetical order of locant, original name of locant are considered, not the initials of prefixes.

4) Positions of the locant is denoted by numerals (1, 2, 3 ——) before the name of locant.

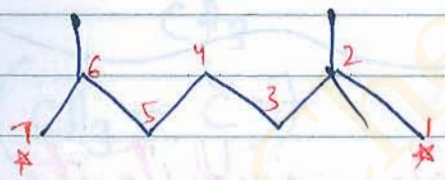
5) Nos. are always separated by comma.
Nos. & alphabet are always separated by hyphen (—)

eg



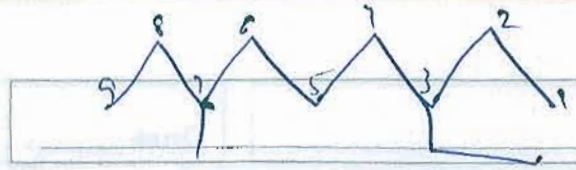
4-ethyl-3-methyl heptane

eg



2,2,6-trimethyl heptane.

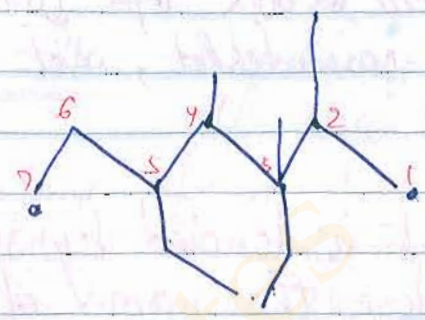
Rule 4: If more than 1 no. series exist simultaneously, lower no. coming at the 1st pt. of difference, will determine the correct no. series.



3-ethyl-7-methyl nonane

Date

Q.

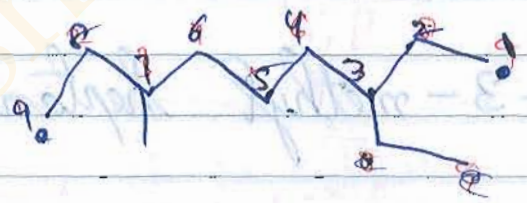


3,5-diethyl-2,3,4-trimethyl heptane

X 2-methyl-3-methyl-methyl-4-methyl-5 heptane.

✓ 3,5-diethyl-2,3,4-trimethyl heptane

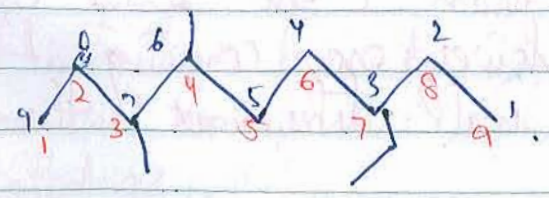
Q.



3-ethyl-7-methyl nonane ~~heptane~~.

Rule 5: If groups are equidistant from the terminal, numbering is done in alphabetical order

Q.



3-ethyl-6,7-methyl-nonane

Rule 4 X 3-ethyl-6,7-~~me~~dimethyl nonane 3,6

✓ 7-ethyl-3,4-dimethyl

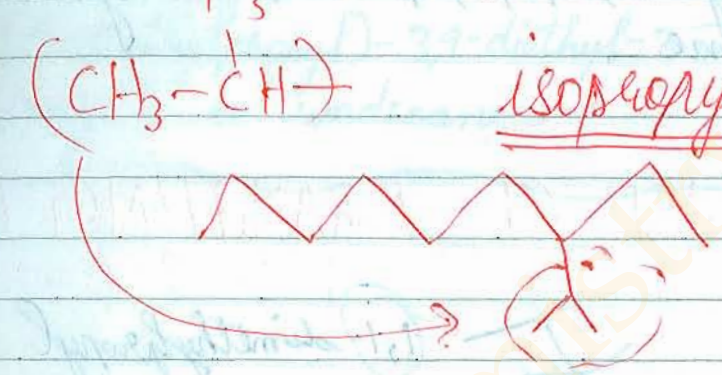


2,2-dimethyl 5-ethyl

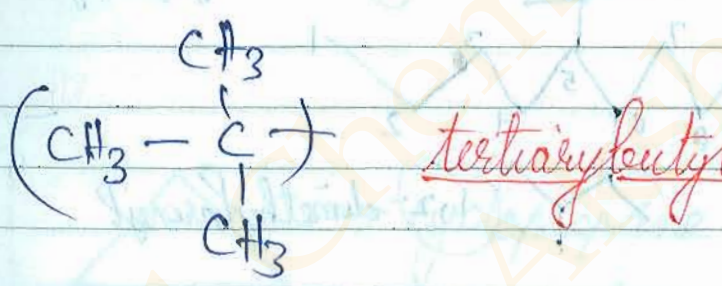
3-heptyl

Rule 6: If more than 1 longest chain exist, longest chain contain max. no. of locants will be the parent chain.



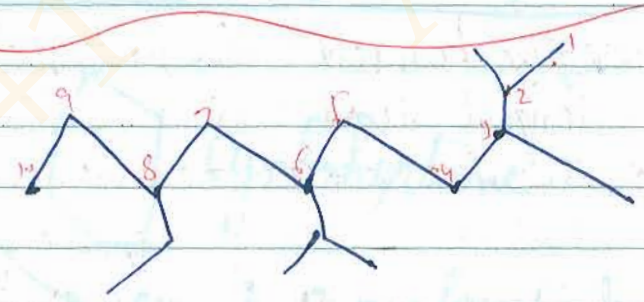


isopropyl



tertiarybutyl

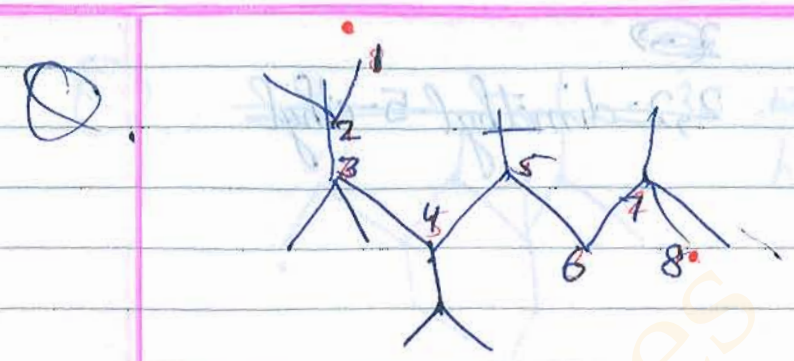




2-methyl

8-ethyl-6-isopropyl-2,3-dimethyl decane.

Q.



~~2,2-dio~~

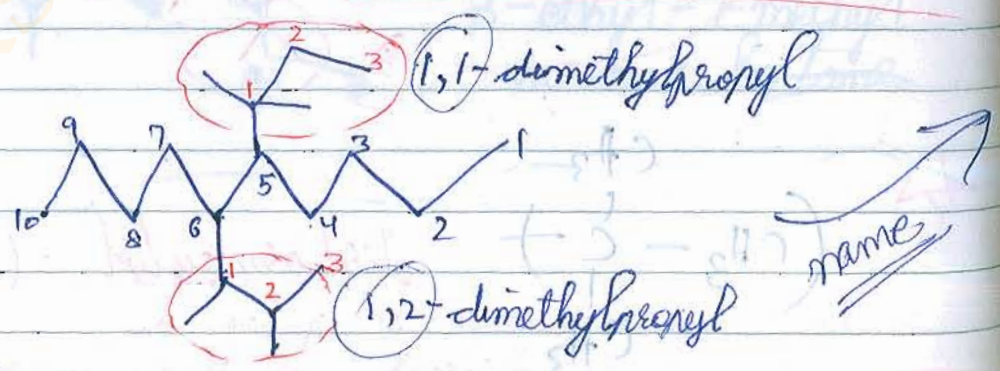
~~6-Ethyl-2,2,7,7-tetramethyl~~

~~2,2-d~~

~~2,5,3,3~~

4-isopropyl-2,2,3,3,7,7-hexamethyl-5-tertiaryl octane.

13/9/09 CASE OF BRANCHING IN BR



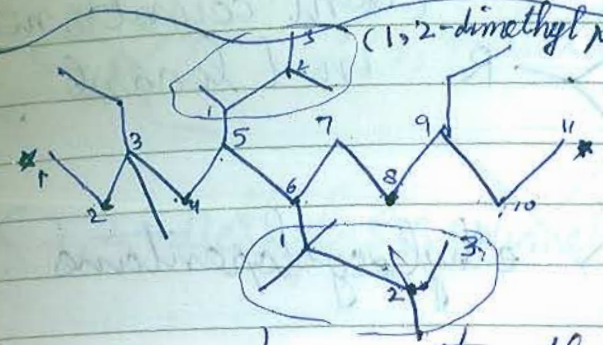
Number the ~~Name~~

☆ C atom directly bonded with parent chain.
Then the longest locant is numbered.

☆ Then find locant names → arrange in alphabetical order & use.

If names are same, then less no. will decide 1st locant.

5-(1,1-dimethylpropyl)-6-(1,2-dimethylpropyl) decane.



~~3,9-Btriethyl-3-m~~

5-(1,2-diethylpropyl)-3,9-diethyl-3-methyl-6-(1,1,2,2-tetramethylpropyl) undecane.

NAMING CYCLO-ALKANES (C_nH_{2n})

- Unsubstituted cycloalkanes



→ cyclopropane.



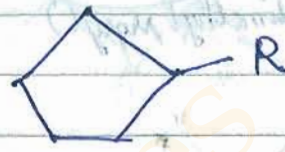
Cycloheptane.

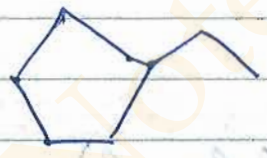
count C atoms & add 'cyclo' to saturated H. carbon name.

Date

☆ Substituted cycloalkane

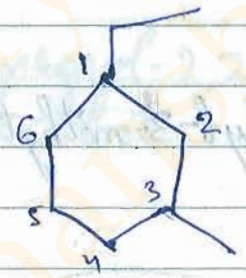
(Don't count no. in 1 locant)





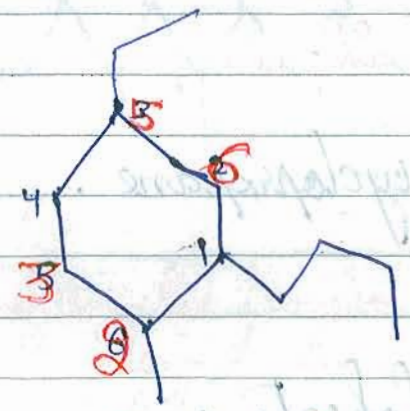
ethylcyclopentane.

* More than 1 locant. (no. will be expressed)



1-ethyl-3-methyl cyclohexane.

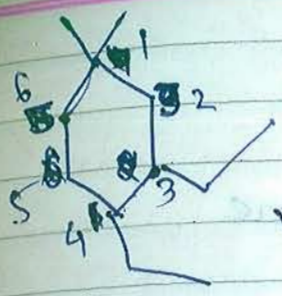
Q



1-butyl-~~3~~-ethyl-~~6~~-methyl cyclohexane.

~~1-butyl-2~~

Q.

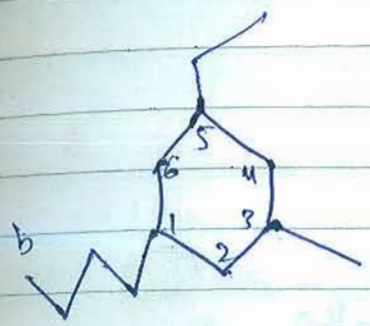


✗ 1,1-dimethyl-3,4-diethyl cyclohexane.

✓ 3,4-diethyl-1,1-dimethyl cyclohexane

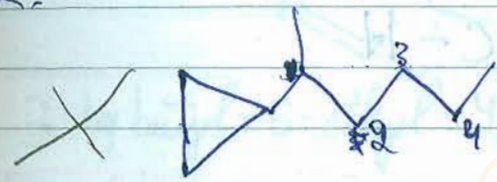
✗ 1,2-diethyl-5,5-dimethyl cyclohexane.

Q.

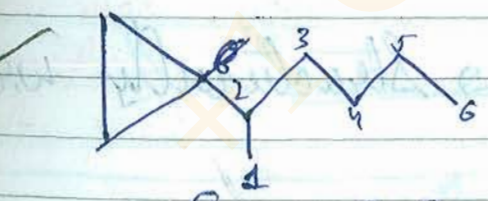


1-butyl-~~6~~-3-ethyl-~~5~~-5-methyl cyclo~~pentane~~ hexane.

Q.

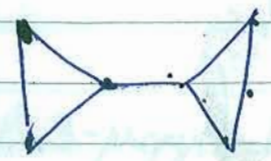


1-methyl-1-cyclopropyl ~~pentane~~



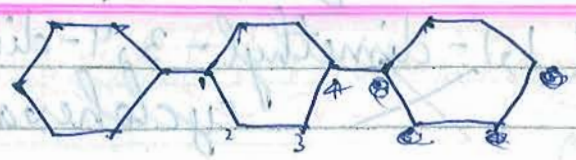
2-cyclopropyl hexane.

☆ If no. of carbon in straight chain of alkyl groups > no. of carbon in ring, then the straight chain will be parent chain. Also, the locant, ie. the ring will have radical name (yl.)

Q.  cyclopropyl cyclopropane.

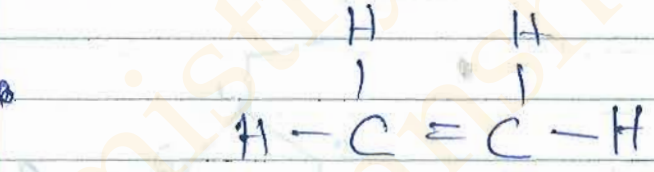
Date

Q.



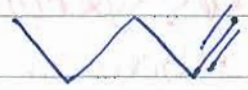
1,4-dicyclohexyl cyclohexane

UNSATURATED acyclic hydrocarbons :





- $CH_3-CH_2-CH_2-C\equiv C-H$



- C-C-C-C-C≡C-C



→ Structurally wrong



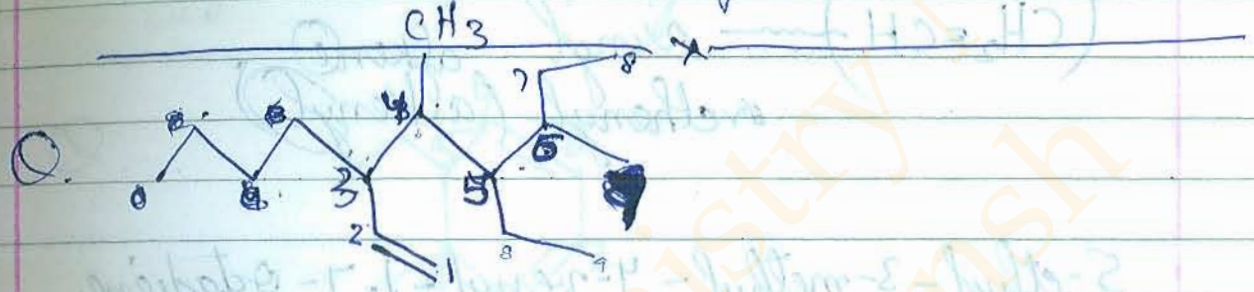
Alkene :→ Generic name = alkene

• Double-bond has preference over alkyl groups in numbering (Hindi → Preference Double Bond को देना है)



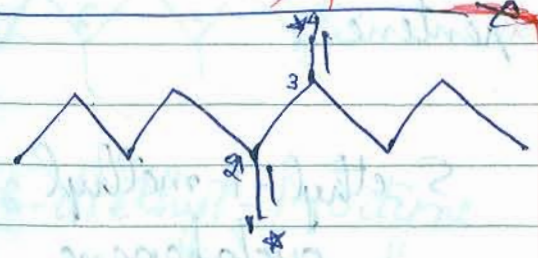
parent chain.

⊛ 6-ethyl-5-methyl-3-octene
oct-3-ene
gap



3-butyl-5-ethyl-4,6-dimethyl-1-octene

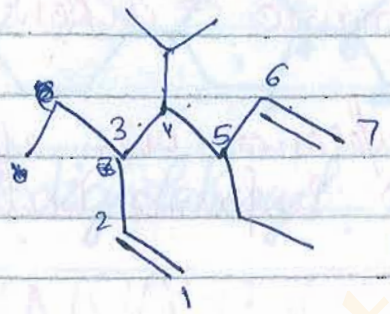
Rule : If the ~~parent chain~~ compound contain 2 or more double bonds, then the ~~parent~~ longest chain containing max. no. of double bonds will become the parent chain, for 2,3,4----double bonds, V



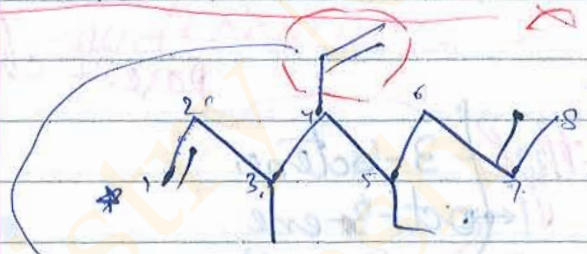
alk-adiene
atriene
atetraene
are used.

2-butyl-3-propyl-1,3-butadiene
~~butane~~
buta-1,3-adiene

Q.



3,5-diethyl-4-isopropyl-1,6-heptadiene



→ All double bonds can't be taken on a single chain.

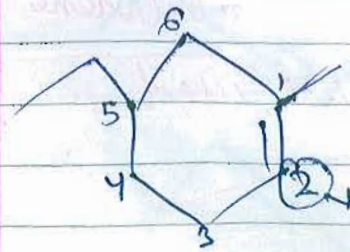
$(CH_2=CH)$— vinyl or ethenyl alkene (alkenyl)

5-ethyl-3-methyl-4-venyl-1,7-Octadiene
or
4-ethenyl-5-ethyl-3-methyl-1,7-octadiene

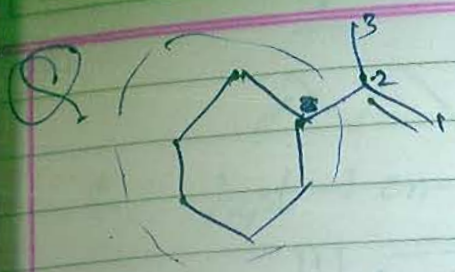
☆ Naming cyclo alkenes



cyclopentene



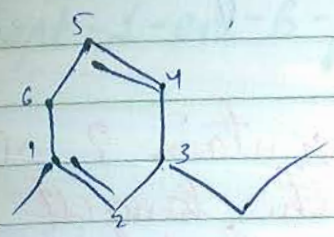
5-ethyl-1-methyl cyclohexene

Q. 

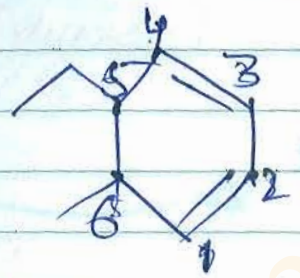
C-C=C → propene

C-C-C=C → 1-butene

2-cyclohexyl propane

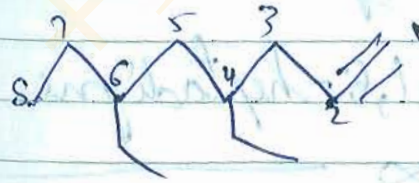
Q. 

3-ethyl-1-methyl-1,4-cyclo ~~hexene~~ hexadiene

Q. 

6-ethyl-6-methyl-1,3-cyclohexadiene

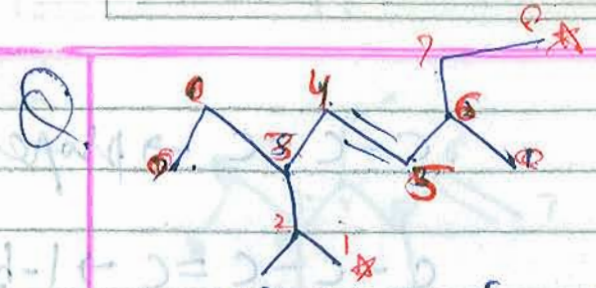
☆ NAMING ALKYNES



4,6-diethyl-1-octyne

☆ TRIPLE bond has preference over alkyl groups. i.e, it should get the lowest no.

Date

Q. 

✗ 2-ethyl-5-isopropyl-3-heptyne

✓ 3-ethyl-2,6-dimethyl-4-octyne

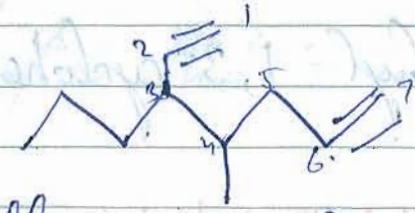
Rule: If the compound contain 2 or more triple bonds, then the longest chain with max. no. of triple bonds become the parent chain.

for 2, 3, 4 — — — triple bonds,

a diyne

a triyne

a tetrayne

Q. 

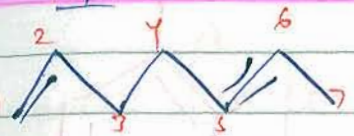
~~3-ethyl-4-methyl-heptadiyne~~

3propyl

4-methyl-3-propyl-1,6-heptadiyne.

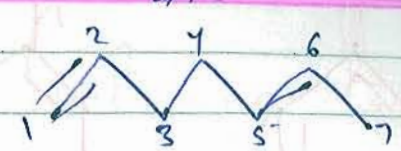
- Compound with both double & triple bond & Chain containing both double bond & triple bond will be the parent chain irrespective of their length.

I



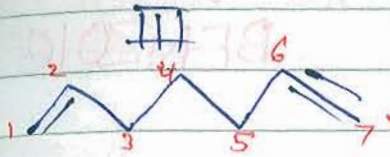
hept-1-en-5-yne

II



hept-5-en-1-yne.

III



hept-1-en-6-yne

→ both equidistant.

So, ene ✓
yne

• alphabetical preference

alk en yne (One double one triple)

ene ✗
ene ✓

alk ene diyne (1 double 2 triple)

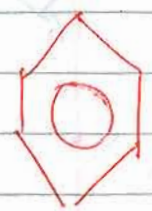
17/9/09

☆ Aromatic hydrocarbon- and derivatives of Benzene

Benzene







LEARN

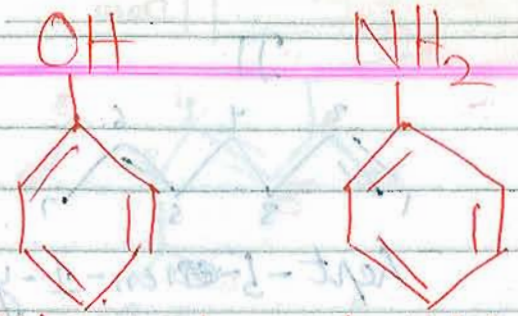


TOLUENE



STYRENE

Date



LEARN

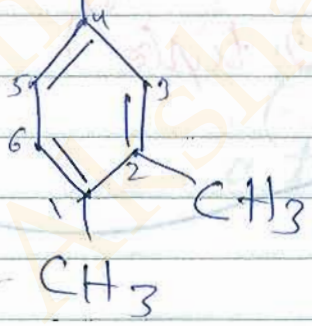
PHENOL ANILINE BENZOIC ACID



BENZONITRILE

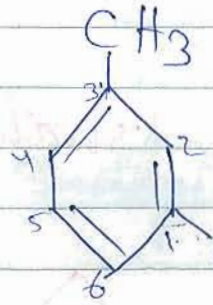
$C_6H_5 \rightarrow$ Phenyl

Q.



1,2,4-trimethyl benzene

Q.



1-ethenyl-3-methyl benzene

Or

1-methyl-3-vinyl benzene

Naming Compounds Containing Principal Functional Groups.

★ **Principal Functional Groups**: It is an atom or a group of atoms which determine, the predominant properties of compound. Compound containing principal functional group have a specific ending in their name known as suffix of that functional group.

Compound	Formula	Prefix	Suffix
1) Carboxylic Acid • Generic name → alkanoic acid	$-\overset{\overset{O}{\|\|}}{C}-OH$ ($-COOH$)	carboxy	-oic acid
2. Sulfonic acid • Generic name → alkanesulfonic acid	$-\overset{\overset{O}{\|\|}}{\underset{\underset{O}{\|\|}}{S}}-OH$ ($-SO_3H$)	~~sulpho~~ Sulfo	sulfonic acid
3. Aldehyde • Generic name: alkanal	$-\overset{\overset{O}{\|\|}}{C}-H$ ($-CHO$)	formyl (aldo)	-al

LEARN

Date

Compound	Formula	Prefix	Suffix	Genera
4) Ketone	$\overset{C}{\star}-\underset{\underset{O}{\parallel}}{C}-\overset{C}{\star}$	-oxo (keto)	-one (ओन)	alkanon
5) Alcohol	-OH	hydroxy	-ol	alkanol
6) Cyanide	$-C\equiv N$ (-CN)	cyano	-nitrile	alkanenitril
7) Ester	$-\underset{\underset{O}{\parallel}}{C}-O-R$ ($-COOR$) ($-CO_2R$)	—	-oate	alkyl alkan
~~8) Ester~~ ~~Anhydride~~				
8) Anhydride	$R-\underset{\underset{O}{\parallel}}{C}-O-\underset{\underset{O}{\parallel}}{C}-R$	—	-oic anhydride	alkanoic anhydride
9) Amide	$R-\underset{\underset{O}{\parallel}}{C}-NH_2$ ($-RCONH_2$)	—	-amide	alkanamide
10) Acid-chloride	$R-\overset{O}{\overset{\parallel}{C}}-Cl$ (RCOCl)	—	-oyl chloride	alkanoyl chloride
11) Amine	$R-NH_2$	amino	-amine	alkanamine
12) Ether	$R-\ddot{O}-R$	alkoxy	alkoxyalkane	alkoxyalka

Name
Pre Pre

[A] RU
If t
numbers
of the

[B] RU
If (2)
are pr
termina
chain le

CAR

Q.

Q.

6-cl

Q.

5
6

2,4-di

Genera
alkanon
alkanol
alkanenit
alkyl alka
alkanoic anhydride
alkanamide
alkanoyl chloride
alkanamine
alkoxyalka

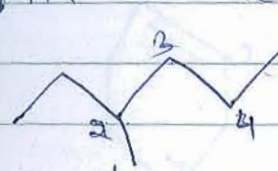
Naming Compounds containing only 1 type of Principal Functional Group.

[A] RULE:
If the principal functional group contain a 'C', numbering always starts from that 'C'; irrespective of the chain length.

[B] RULE:
If (2) similar principal functional group containing 'C' are present in the compound, they 2 become terminals of the parent chain, irrespective of chain length.

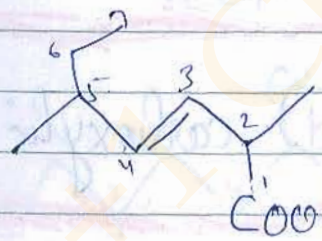
CARBOXYLIC ACID → GROUP

Q.



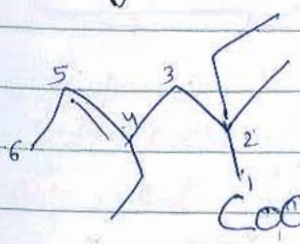
2-ethyl pentanoic acid

Q.



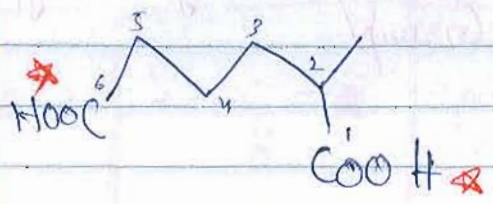
~~5-ethyl-3-~~ 2,5-dimethyl-3-heptenoic acid

Q.



2,4-diethyl-2-methyl-4-hexenoic acid

Q.



2-methylhexanedioic acid

Q.



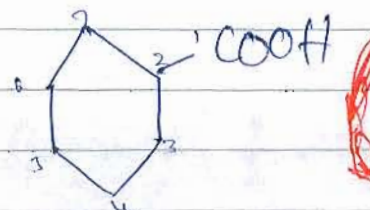
2-butyl-2-ethyl~~pentane~~propanedioic acid

Q.



cyclopropylethanoic acid

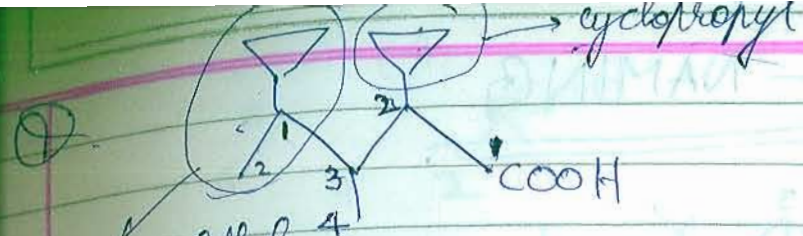
Q.



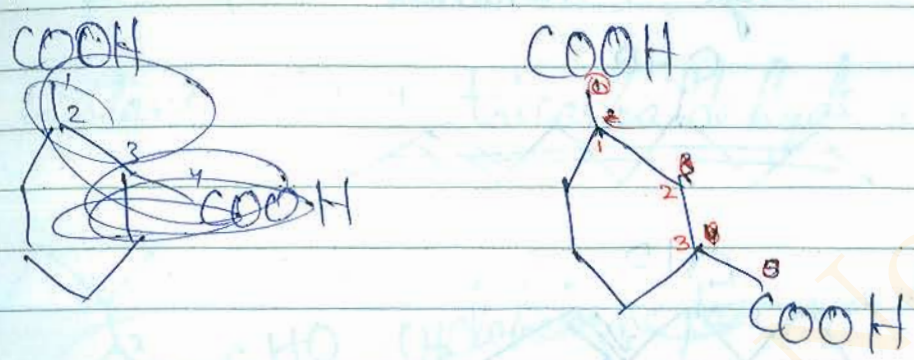
(-C(=O)-OH) carboxylic acid

~~heptacyclicic acid~~

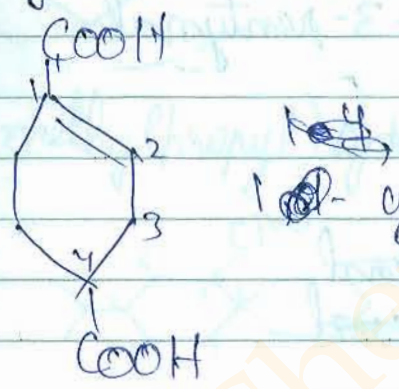
cyclohexanecarboxylic acid



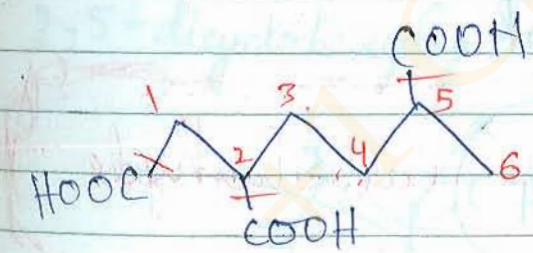
2-cyclopropyl-3-(1-cyclopropylethyl) butanedioic acid.



1,3-cyclohexanedicarboxylic acid.



1-cyclohexene-1,4-dicarboxylic acid.



1,2,5-hexanetricarboxylic acid.

Or

hexane-1,2,5-tricarboxylic acid

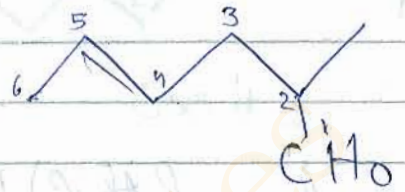
~~1,2,5 tricarboxylic~~

→ If more than 1 final grp. appears in a chain, cut that parts (as shown), name the compd. without these grps., at last, specify the pos^n of these final grps.

Rule: Position of final grp. not told if single is present.

Date

ALDEHYDE - NAMING

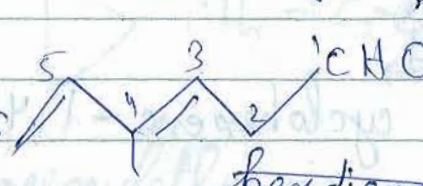


2-methyl-4-hexenal





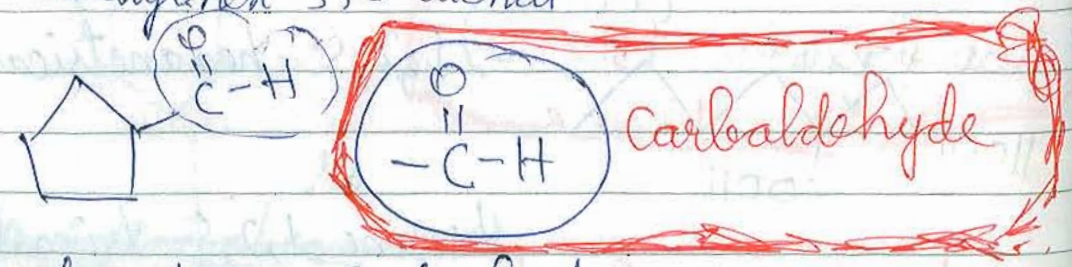
2-methyl-2-propyl-3-pentynal



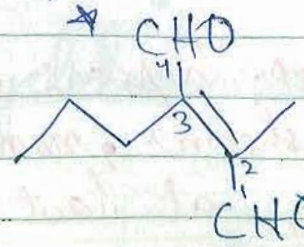
~~hexdienal~~

~~4-methyl-3,5-dihexenal~~

4-methylhex-3,5-dienal



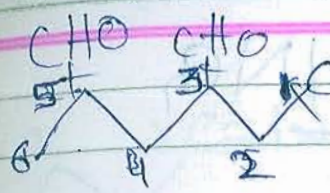
Cyclopentanecarbaldehyde.



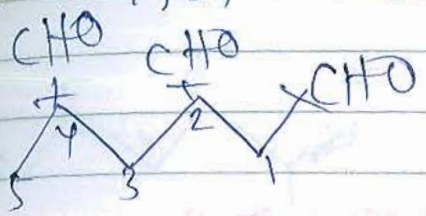
~~2-butyl-2-methyl-2-~~ ~~but~~ butena

2-methyl-2-

(i)

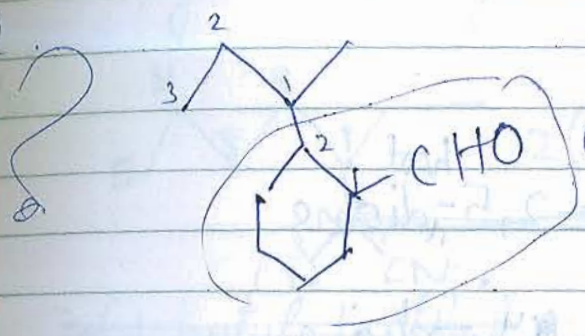


~~2,4,6~~ ~~1,3,5 - tricarbaldehyde hexane~~



pentane - 1, 2, 4 - tricarbaldehyde.

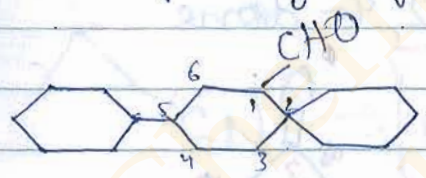
(ii)



cyclohexane ~~ed~~ carbaldehyde

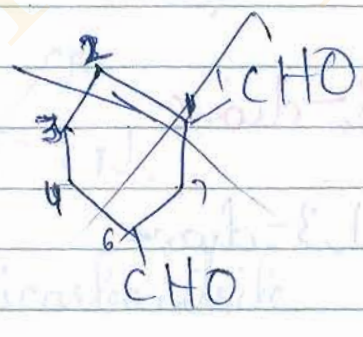
2 - (1 - methylpropyl) cyclohexanecarbaldehyde.

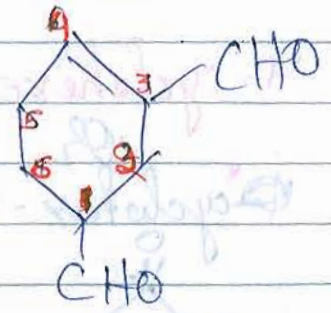
(iii)



2,5 - dicyclohexylcyclohexanecarbaldehyde

(iv)



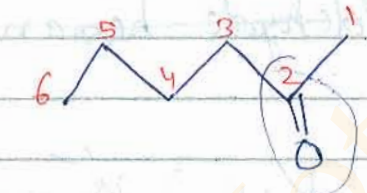


~~3~~ 3 - cyclohexene - 1, 3 - dicarbaldehyde

वो जिस terminal के पास है, Numbering उससे शुरू करनी है

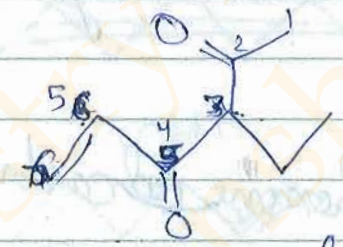
KETONE - NAMING

Q



2-hexanone / hexane-2-one

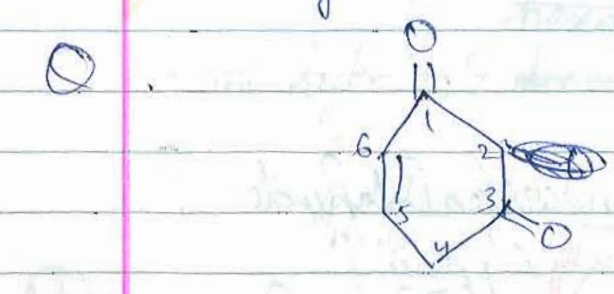
Q



~~4-ethyl-6-se~~ ~~heptene-2,5-dione~~ heptadione

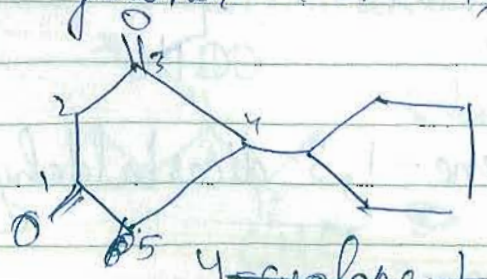
3-ethyl-5-hexene-2,4-dione
or
3-ethylhex-5-ene-2,4-dione

Q



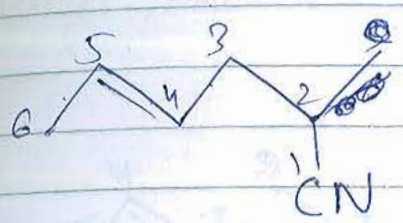
4-cyclohexene-1,3-dione
Or
cyclohex-4-ene-1,3-dione

Q

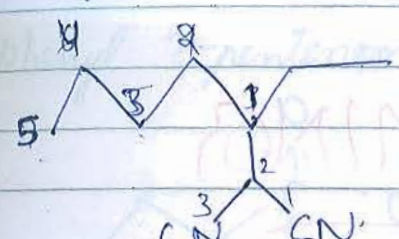




butanenitrile



~~2-butyl~~ 2-methyl-4-hexenenitrile

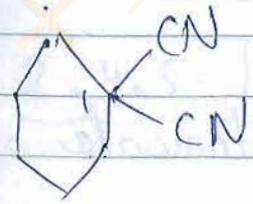


2(1-ethylpentyl)propanenitrile

~~2-(1-butyl-1-ethyl~~



cyclopropanecarbonitrile



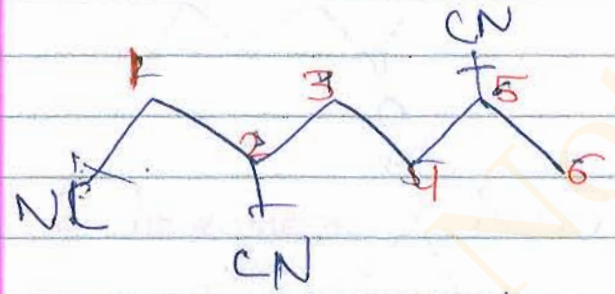
1cohexane-1, 1- dicarbonitrile

1cpentanedione
ne-1, 3-dione

Date

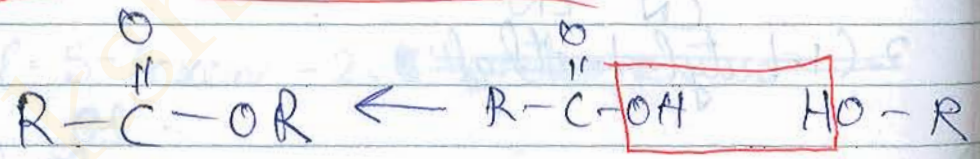
20/9/09

Q.



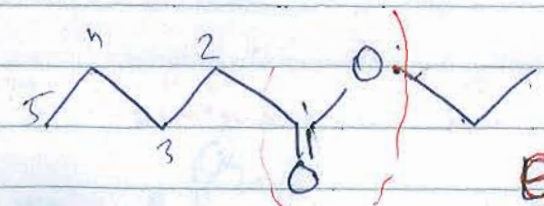
1,2,5-hexanetricarbonitrile.

ESTER NAMING



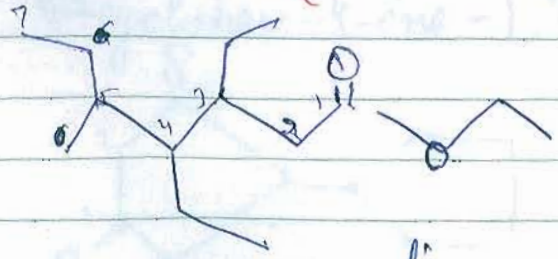
alkyl alkanoate → acid
alcohol

Q.



ethyl pentanoate.

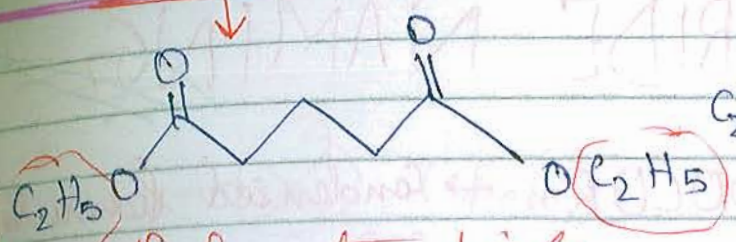
Q.



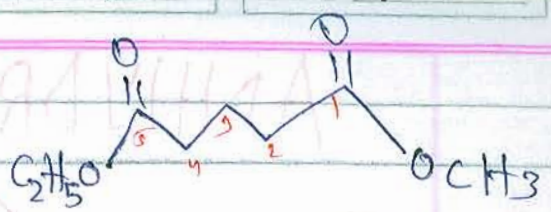
ethyl 3,4-diethyl-5-methyl hexa

SYMMETRIC ESTER

Q.



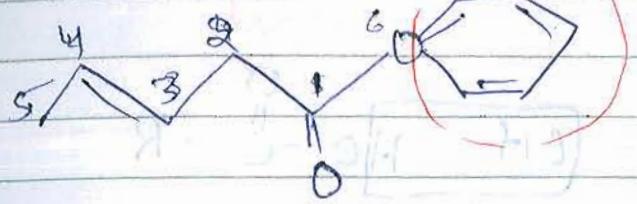
ethyl pentanedioate



ethylmethyl pentanedioate

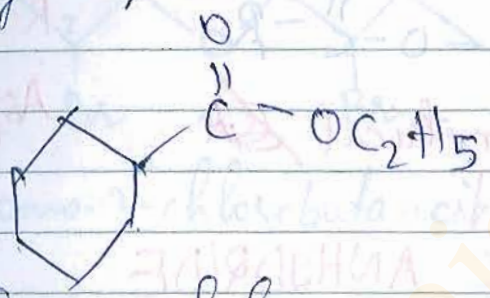
PHENYL

Q.



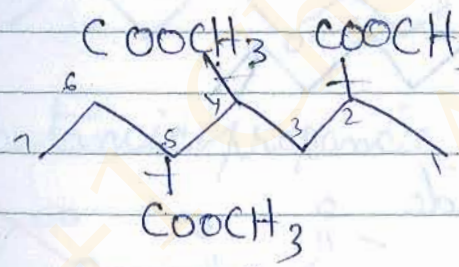
phenyl 3-pentenoate

Q.



ethyl cyclohexanecarboxylate

Q.



methyl 2,4,5-heptanetricarboxylate

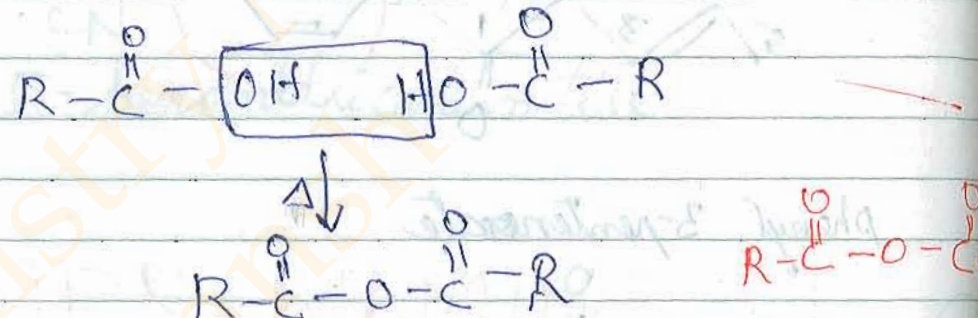
Q.

ANHYDRIDE NAMING

R-COOCOR → Condensed formula.



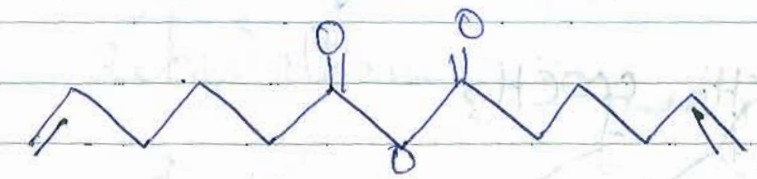
R-C(=O)-O-C(=O)-R → Structural.



Symmetrical → ALKANOIC ANHYDRIDE

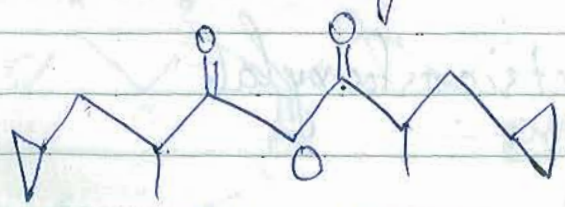
Asymmetrical → ALKANOIC ALKANOIC ANHY

Q.



5-hexenoic anhydride

Q.



~~4-cyclopropyl-2-methy~~

~~2-methyl & cyclopropanoic~~ ~~anhydri~~

3-cyclopropyl-2-methylpropanoic & anhydride.

NG7

formula.

eral.

R-C(=O)-O-C(=O)-

Asymmetrical

↓

KANOIC ANHY

opyl-2-methyl

oic

& anhydride.



(halo)

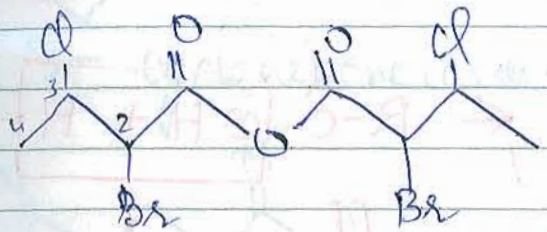
↳ halogen

-Cl Chloro

Bromo

Iodo ---.

Q.



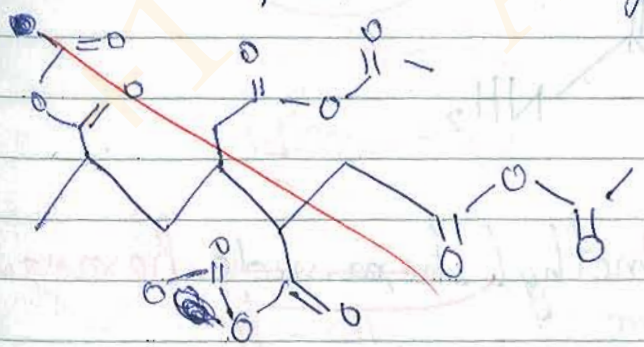
2-bromo-3-chlorobutanoic anhydride.

Q.

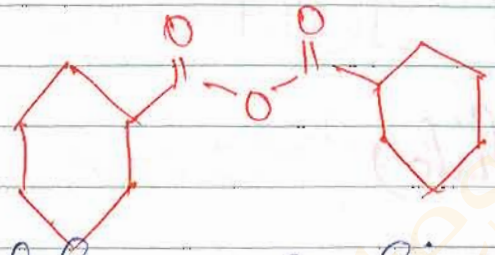


butanoic propanoic anhydride.

Q.

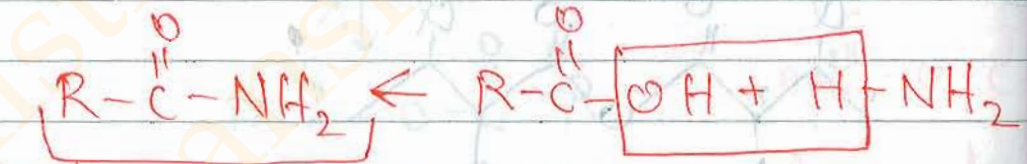


Date



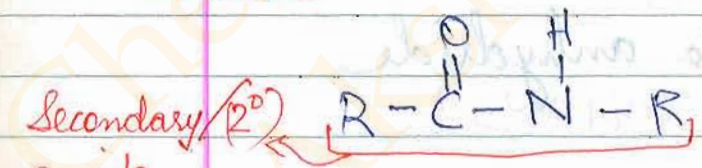
cyclohexanecarboxylic anhydride

AMIDE NAMING

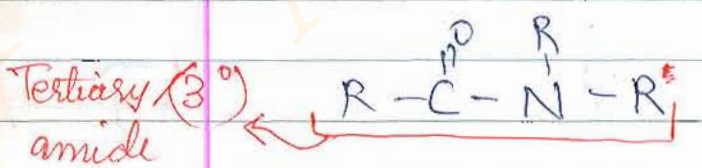


Primary amide (1° amide)

alkanamide

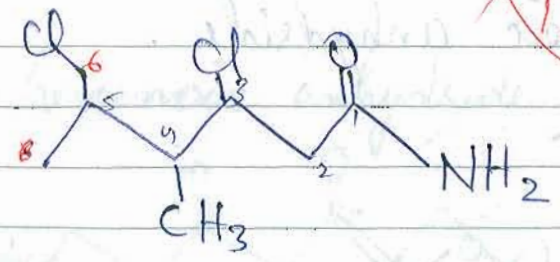


Secondary (2°) amide

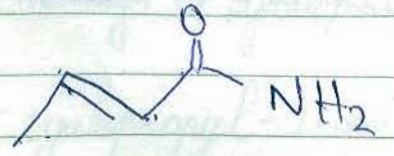


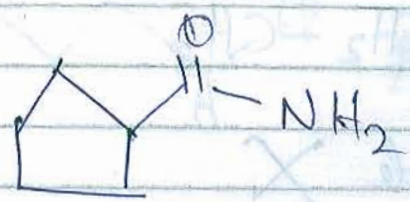
Tertiary (3°) amide

Primary

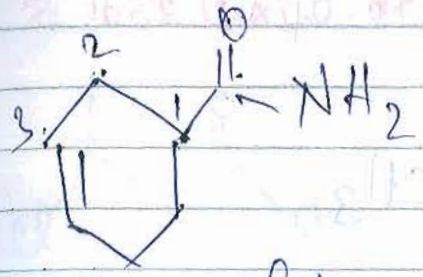


3,5-dichloro-4,5-dimethylhexanamide ~~hexamide~~

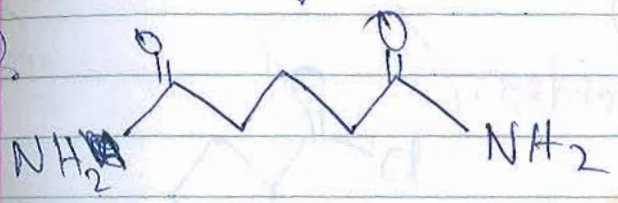




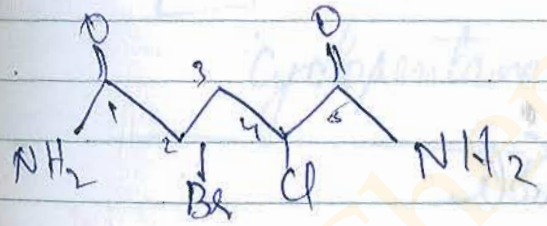
cyclopentanecarboxamide



3- cyclohexene carboxamide

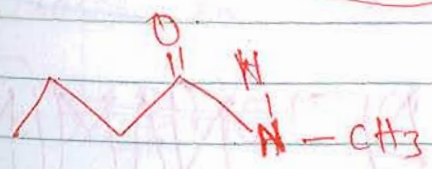


pentanediamide ~~amide~~



2-bromo-4-chloropentanediamide

Secondary



N-methylbutanamide

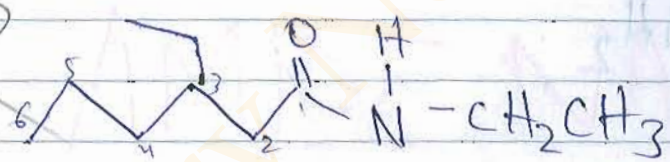
Date



N-propylmethanamide ✗

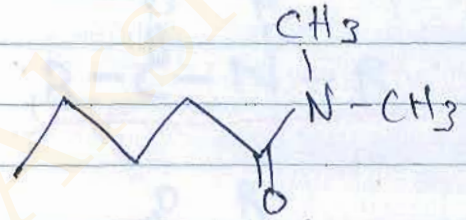
propylmethanamide (Pos^{n} single हो तो उसका No. fixed रहता है)

View

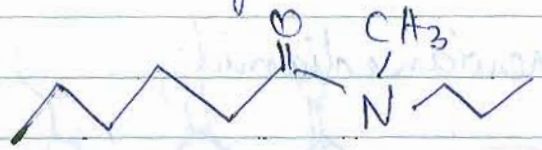


N,3-dimethylhexanamide

TERTIARY



N,N-dimethylpentanamide

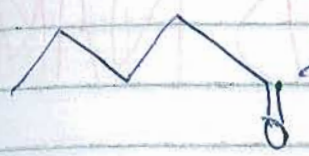


N-~~pro~~methyl-N-~~pro~~propylhexanamide

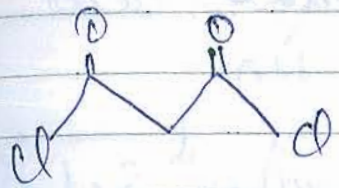
ACID-CHLORIDE NAMING



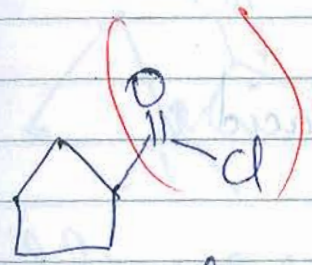
alkanoyl chlo

Q.  pentanoyl chloride

Q.  4-chloropentanoyl chloride

Q.  propanoyldichloride ✗

propandedioyl chloride ✓

Q.  carbamoyl chloride

cyclopentanecarbamoyl chloride

✗

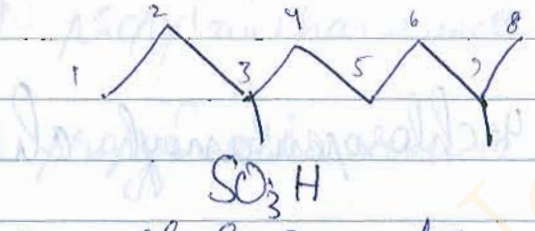
★ Naming compounds containing principal final group without C.

Sl⊙ Select the longest chain including PFG as the parent chain & no. it from a terminal closer to PFG.

~~SULPHONIC~~

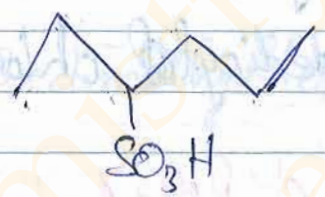
Date

SULFONIC ACID NAMING



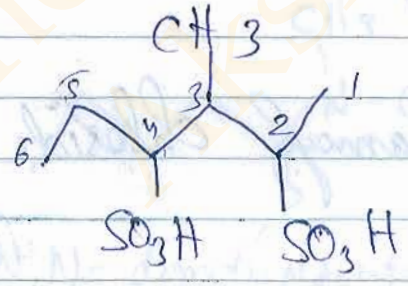
7-methyl-3-octanesulphonic acid

Q.



5-hexene-3-sulphonic acid

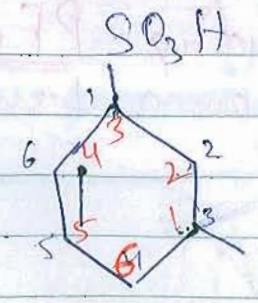
Q.

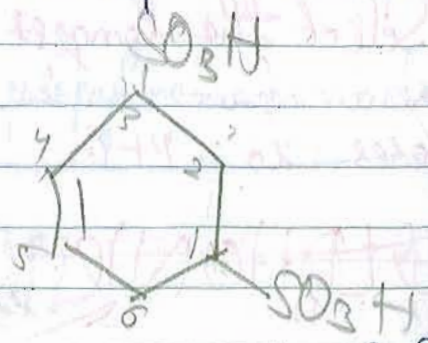


4-cyclohexene-1,3-disulphonic acid

3-methyl-2,4-~~disulphonic acid~~ hexanedisulphonic acid

Q



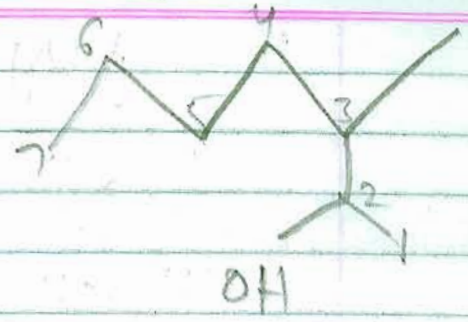


X ~~4~~ 5-~~hex~~cyclohexene-1,3-disulphonic a

Date

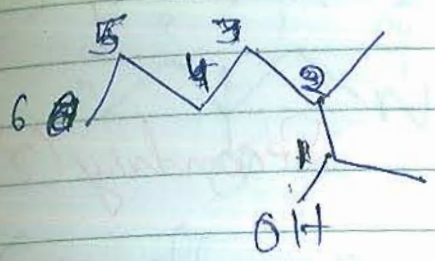
ALCOHOL NAMING

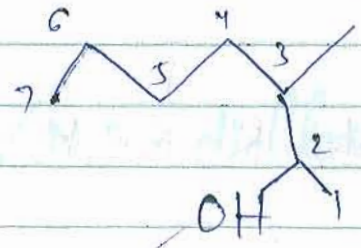
3-methyl-2-heptanol



alkanol —OH

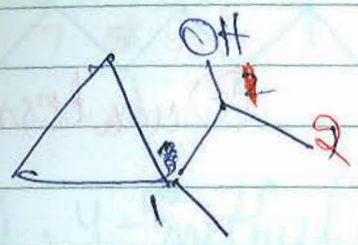
Q.





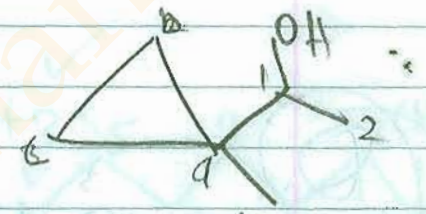
✗ 1,2-dimethylhexanol ✓ 3-methyl-2-heptanol

Q.



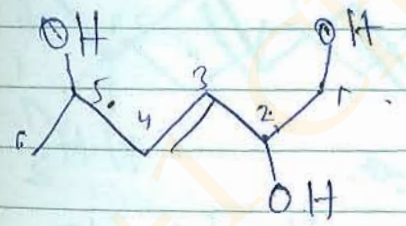
1-(1-methylcyclopropyl)ethanol

✗ 2,3-dimethylpropanol



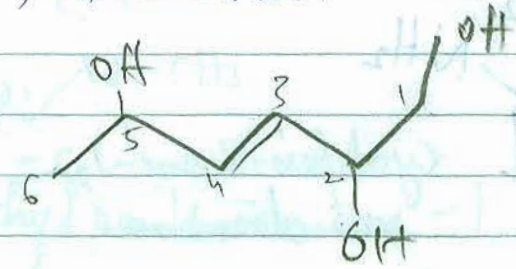
1-(1-methylcyclopropyl) ethanol

Q.



3-hexene-1,2,5-~~hexanol~~ triol

or hex-3-ene-1,2,5-triol.



3-hexene hex-3-ene-1,2,5-triol.

AMINE NAMING

$R-NH_2$

$CH_3CH_2-\underset{H}{N}-H$ — Primary (1°)

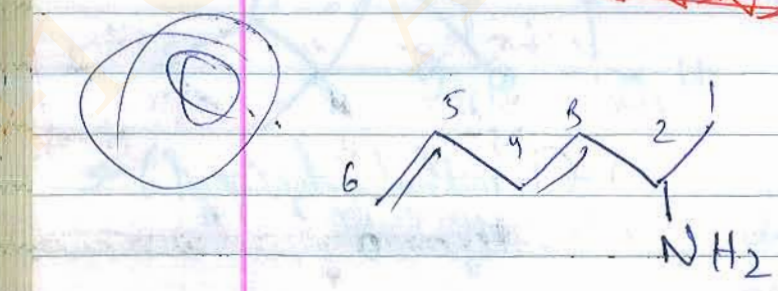
$R-\underset{R}{N}-H$ — Secondary (2°)

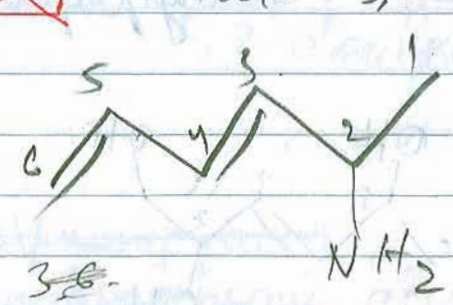
$R-\underset{R}{N}-R$ — Tertiary (3°)

$R-\overset{+}{\underset{R}{N}}-R$ (with R') — Quaternary.

alkanamine

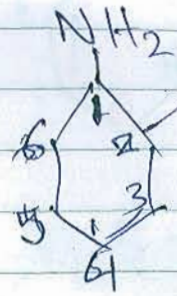
hex-3,5-dien-2-amine



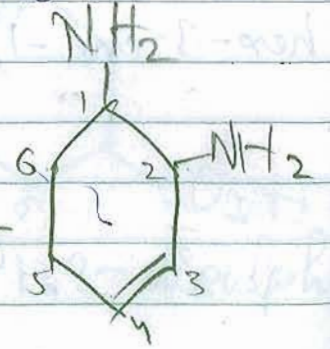


✗ 3,5-hexamine

3,5-hexadien-2-amine



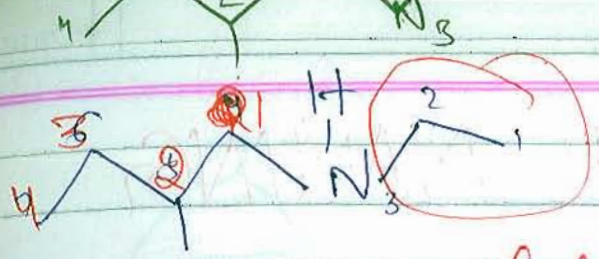
cyclohex-3-ene-1,2-diamine



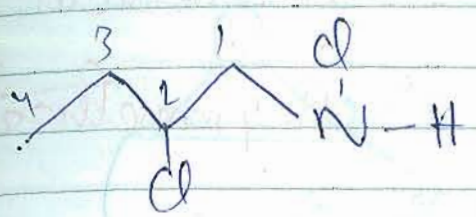
3-cyclohexene-1,2-diamine

Date

Date

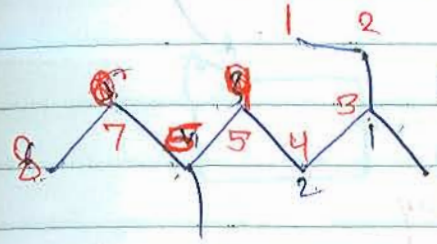


5-methyl N-ethyl-2-methylbutanamine



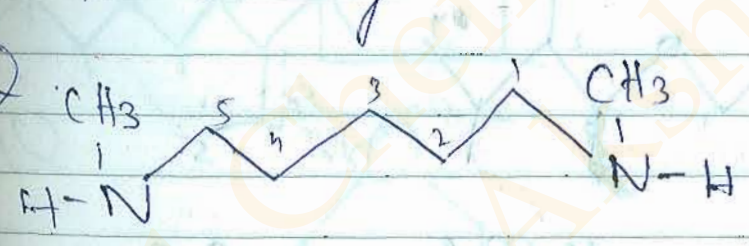
✓ N,2-dichlorobutanamine

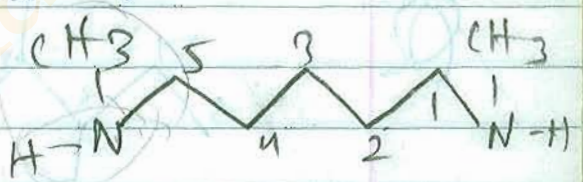
✗ N-chloro-2-chlorobutanamine



1-ethyl-N, 4-dimethylhexanamine ✗

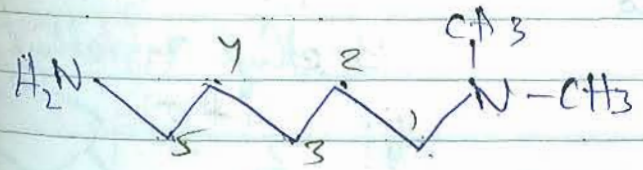
N, 6-dimethyl-3-octanamine ✓





N,N-dimethylpentanamine

✗ N, N'-pentanedi dimethyl-1, 5-pentanediamine



N, N-dimethylpentanamine-1, 5-pentanediamine

24/4/09 Date

ETHER NAMING

Prefix → (alkoxy) Parent → alkane

R – O – R Symmetrical

R – O – R' Asymmetrical

$CH_3-CH_2-O-CH_2-CH_3$

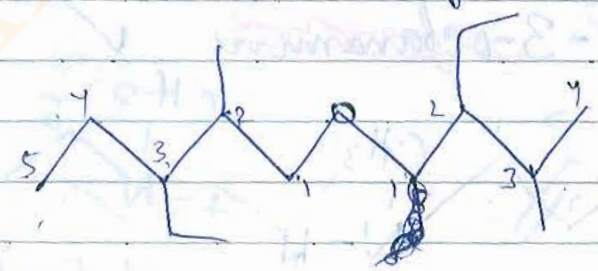
ethoxy ethane

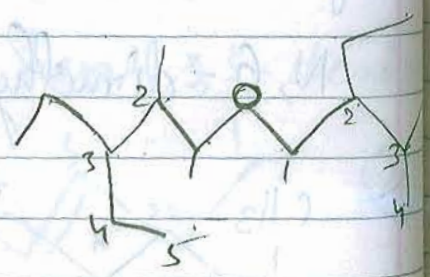
CH_3-CH_2 / O / CH_3

-alkane. (the longer alkyl chain) / alkoxy

methoxy ethane

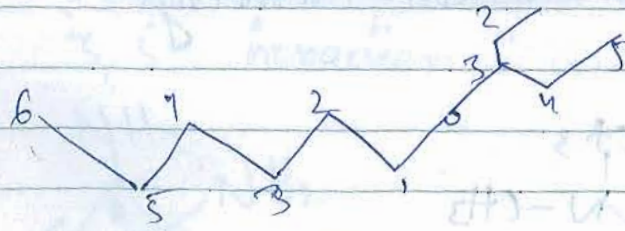
Q





Q 2-ethyl-3-methylbutoxy 3-ethyl-2-methyl

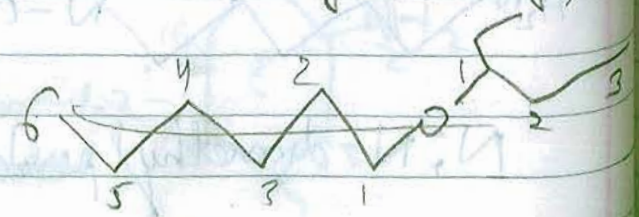
Q.



2-ethyl-3-methylbuto

3-ethyl-2-methylpen

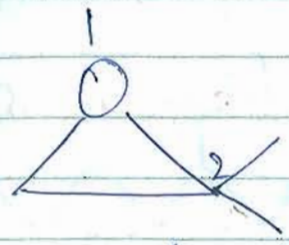
3-pentoxy hexane



3 membered cyclic ether

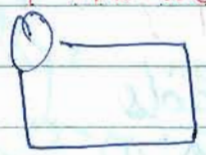


Oxirane → Oxygen giving no. 1 if locant is present



2,2-dimethyl oxirane

4 membered cyclic ether



Oxitane → Numbering starts from Oxygen

5 membered



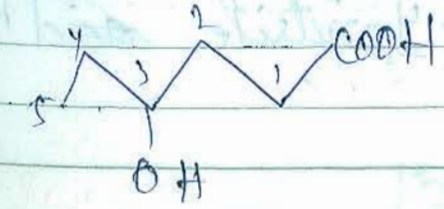
Oxipane

6 membered



Oxane

☆ Naming of compounds containing more than one ~~PFG~~ type of PFGs.



3-hydroxy ~~acid~~ pentanoic acid

Date

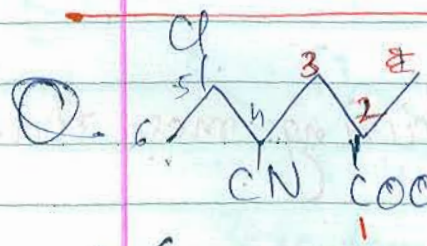
☆ If the compound contain more than 1 type of PFG, group with highest priority becomes ~~the Principle~~ determine suffix of the name & prefixes of the remaining PFGs are used.

Priority is assigned once it's no secondary priority is given.

PRIORITY TABLE:

Decreasing order of priority

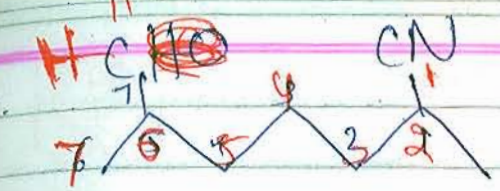
1	$-COOH$	Acids
2	$-SO_3H$	Acids
3	Anhydride	Acid derivatives
4	Ester	Acid derivatives
5	Acid chloride	Acid derivatives
6	Amide	Acid derivatives
7	$-CN$ (nitrile)	Acid derivatives
8	$-CHO$ (aldehide)	Neutral Compound
9	Ketones	Neutral Compound
10	$-OH$ (alcohol)	Neutral Compound
11	$-NH_2$	Base
12	ether	Base



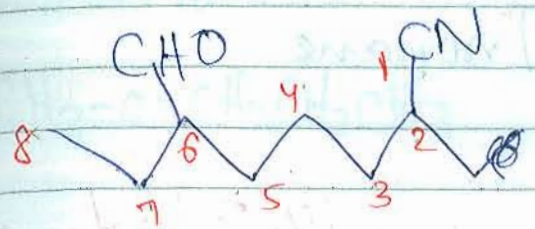
✓ 5-chloro-4-cyano-2-methylhexanoic acid.

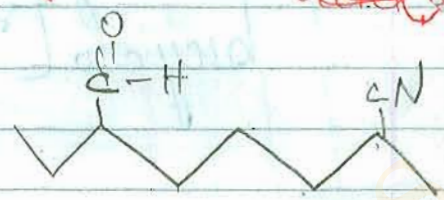
✗ ~~4~~ 5-chloro-2-~~methyl~~ methyl-4-nitrile ~~acid~~ hexanoic acid

showing
of exhibiting diff
la, differing
hysical,
ties; but
osition

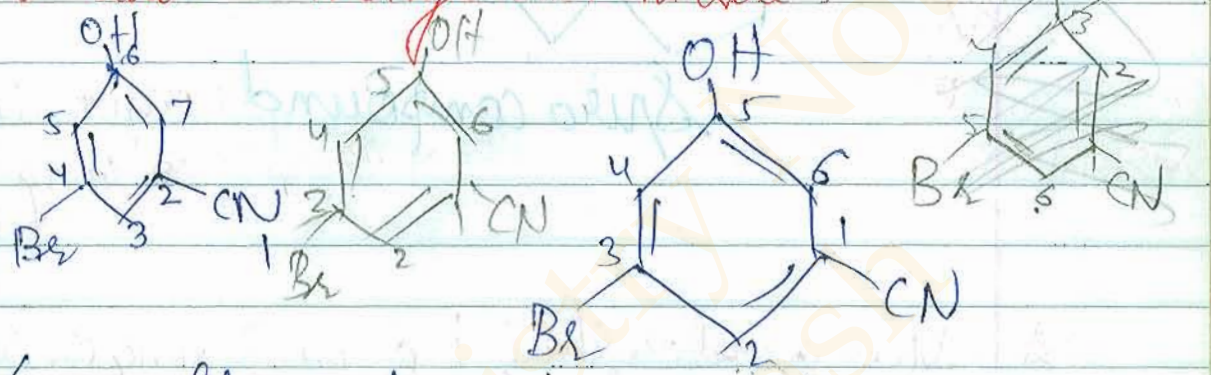


5-methanal 2,6-dimethyl-7-oxyo



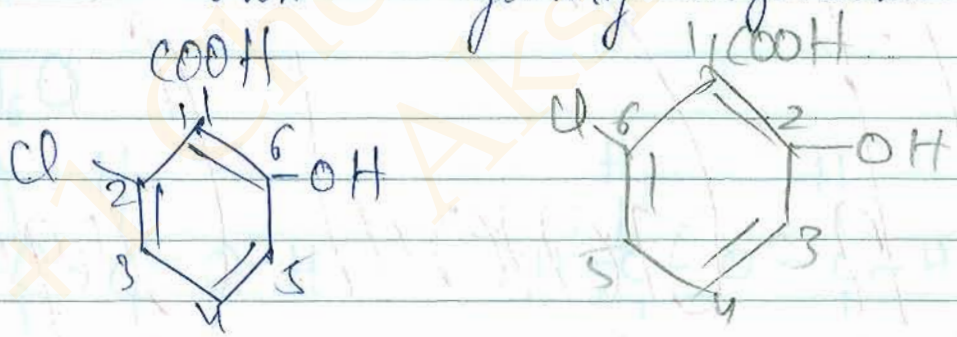


6-aldo-2-methyloctanenitrile

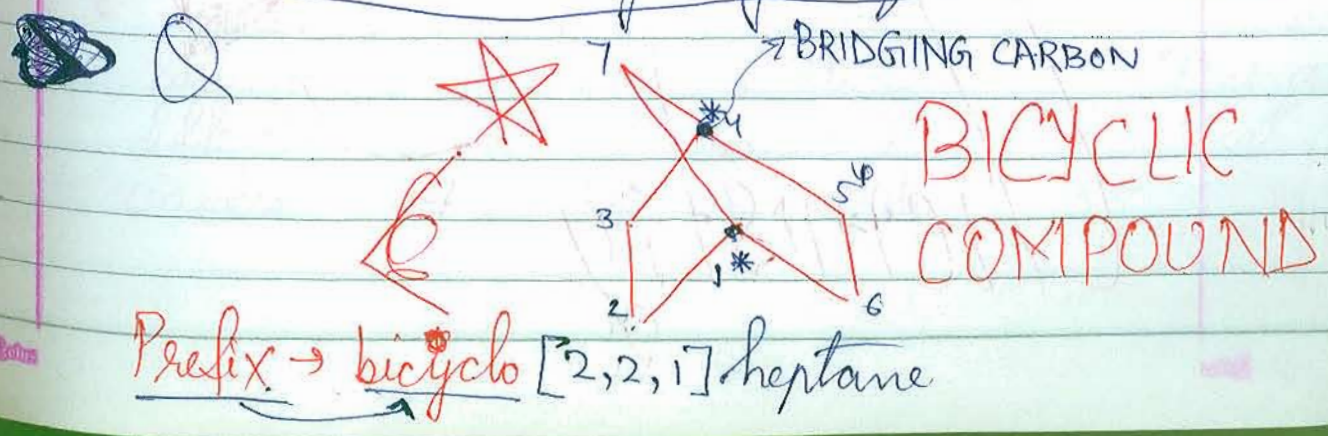


X 5-aldo-3-bromobenzonitrile

✓ 3-bromo-5-hydroxybenzonitrile



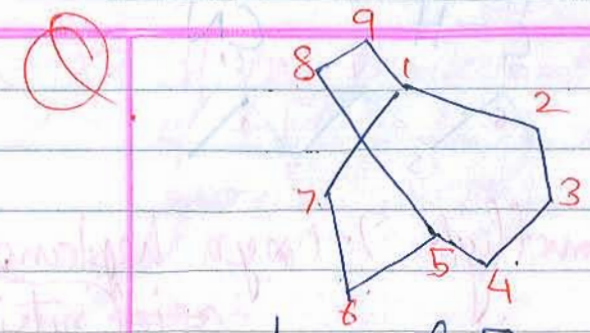
2-chloro-6-hydroxybenzoic acid



Prefix → bicyclo [2,2,1] heptane

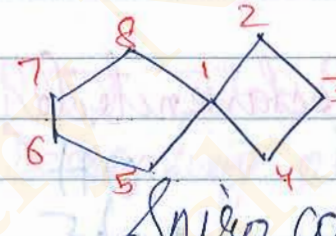
Date

Q



bicyclo [3,2,2] nonane

Q



Spiro [4,3] octane

Spiro compound (name smaller ring 1st)

☆ Spiro compd → share 1 C in 2 rings.
Bicyclo compd → share 2 C in 2 rings.

Date

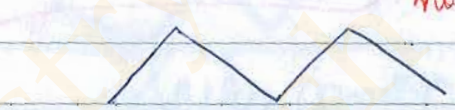
☆ TYPES OF STRUCTURAL ISOMERISM

① Chain - Isomerism

Isomers having same compos^{n}. but diff^{t} length of parent chain are known as Chain - isomers.

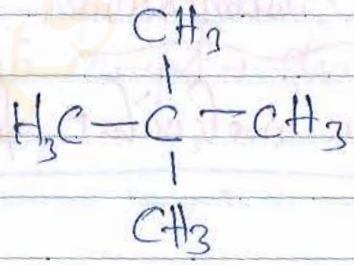
Chain isomers differ only in the length of parent chain.

Chain isomers:

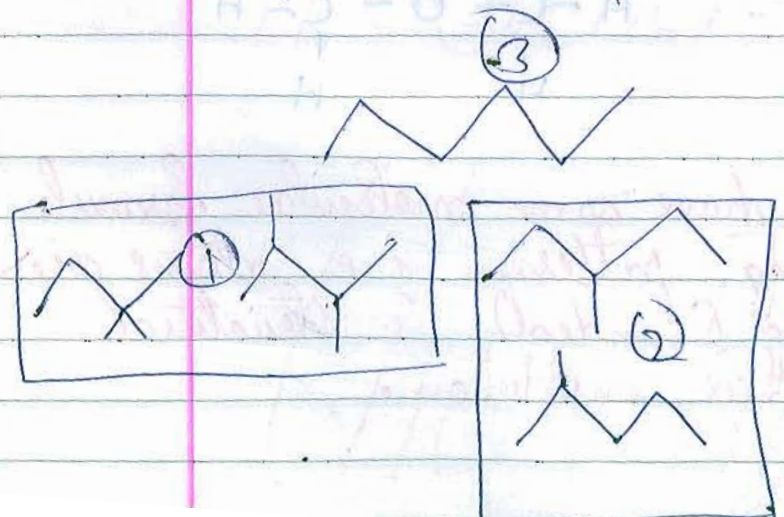
→  n-pentane (normal)

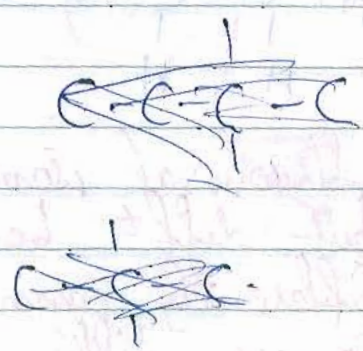
→  isopentane

Isomers:

→  neopentane

Q. C_6H_{14} → no. of chain isomers





Date

MERISM

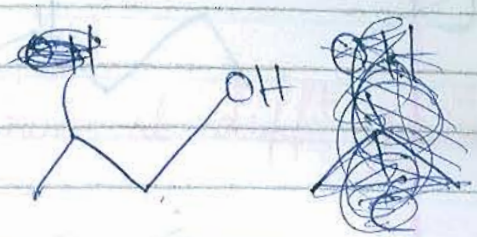
es^n but diff^t
on as)
n the length

ne

Date

Q. $C_4H_{10}O$





Q. (2) Functional-Isomerism

Same molecular formula but diff^t f^nal groups (PFG) gives f^nal Isomerism.

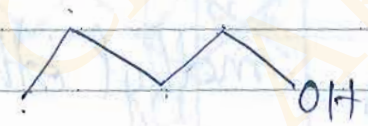
$C_2H_6O \rightarrow C_nH_{2n+2}O : n \geq 1$

CH_3CH_2OH - Alcohol

CH_3-O-CH_3 - Ether

☆ For $n \geq 1$, for every alcohol, there will be atleast 1 ether isomer

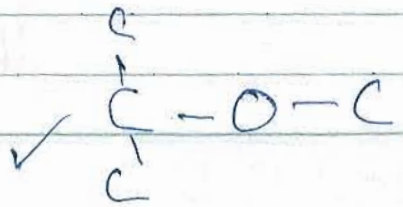
Q.



✓ C-C-C=O-C

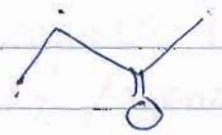
X 

✓ C-C-O-C-C

✓ 



C_4H_8O

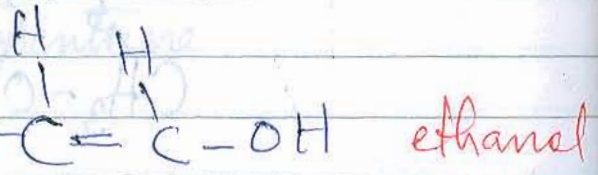


C_4H_8O

☆ Aldehyde & Ketones exhibit functional isomerism, for every ketone, ∃ atleast 1 aldehyde as functional isomer, reverse may'n't be true.

Q. $CH_3-\overset{O}{\overset{\|}{C}}-H$ ethanal





ethanal

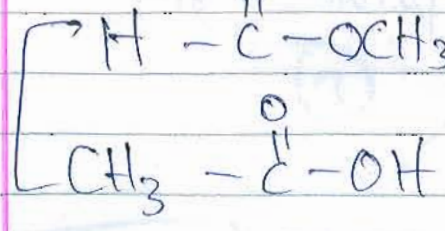
Q. $CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH$ propanoic acid

Acid

$CH_3-\overset{O}{\overset{\|}{C}}-OCH_3$ methyl ethanoate

Ester

Q.



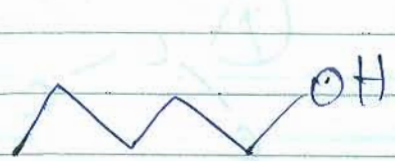
☆ For every ester we can always draw an acid as functional group. Reverse may'n't be true

Date

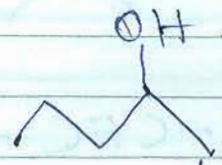
Date

(3) Positional Isomerism

Isomers with same PFG but at diff^{t} pos^{ns} of the parent chain ——— .



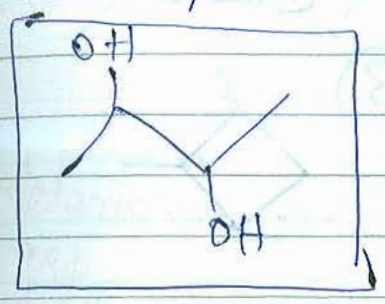
1-pentanol

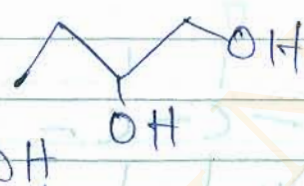


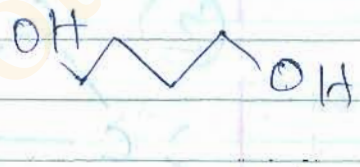
2-pentanol

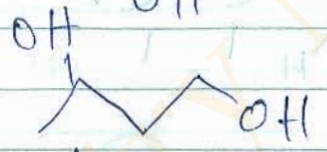


3-pentanol

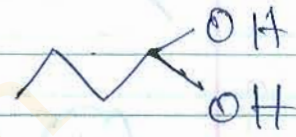




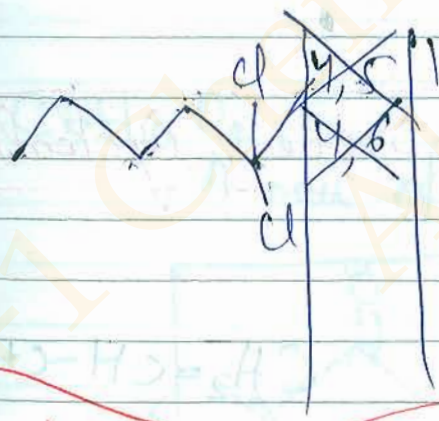




Butanediol



1,1 | 2,2 | 1,2 | 1,3 | 1,4

Q 

1,1 | 2,2 | 3,3 | 1,2 | 1,3 | 1,4 | 1,5 | 1,6 | 2,3 | 2,4 | 2,5 | 2,6 | 3,4 | 3,5 | 3,6

e 1|10|09

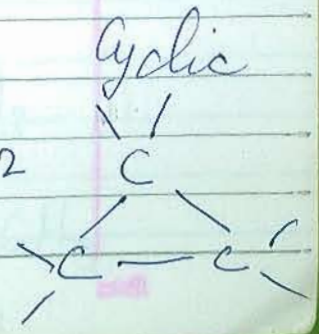
(4) Ring-chain Isomerism :—

C_nH_{2n}

$CH_3-CH=CH_2$

Acyclic

Cyclic



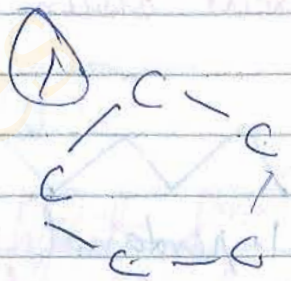
Alkene & cycloalkane

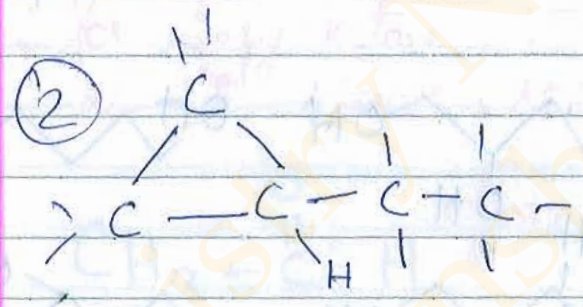
Date

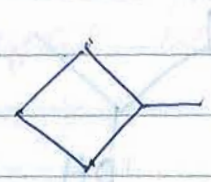
★ Pair of structural isomers in which one is acyclic while other is cyclic are called Ring-chain isomers.

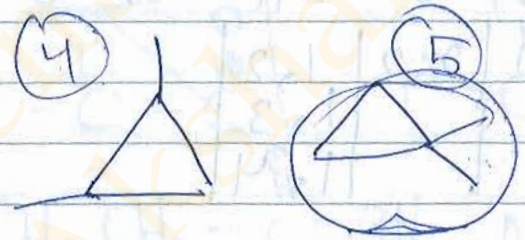
C_5H_{10}

$C-C-C=C-C$





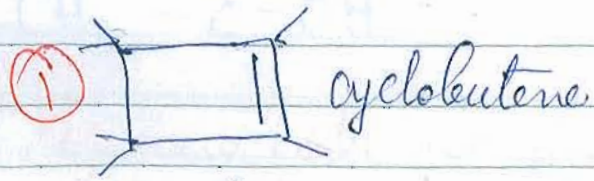




★ ⑨. | C_nH_{2n-2} | Alkyne & Diene & Cycloalkene | bic

C_4H_6

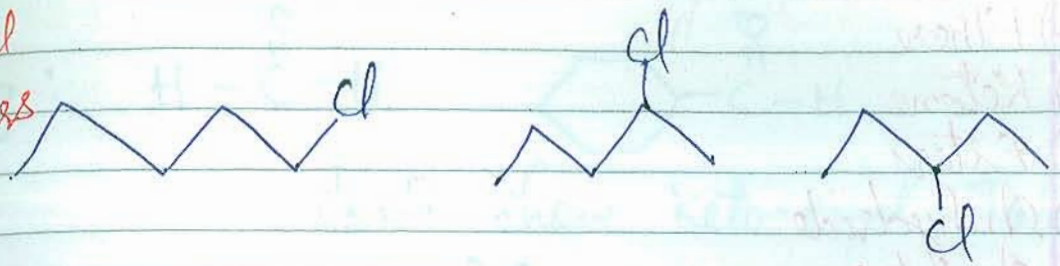
$CH_3-CH_2-C\equiv C-H$ $\quad$ $CH_2=CH-CH=CH_2$



cyclobutene

(5) Metamerism

Posnal Isomers



Metamers →



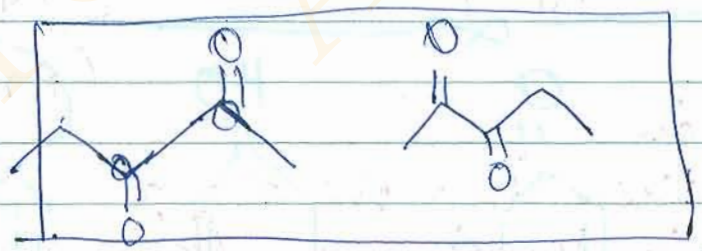
Metamerism arises due to diff^{t} pos^{ns} of the f^{nal} grp. in the parent chain (not on the parent chain). Metamerism is a special case of posnal isomerism - Isomers showing metamerism are called METAMERS.

All metamers are Pos^{nal} isomers

But, all Pos^{nal} isomers are not metamers.

Q. $C_5H_{10}O_2$

A pair of metameric esters.

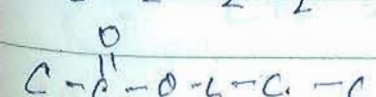


31
22



I $CH_3CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$

IV $CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$ × $CH_3-\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-OCH_3$

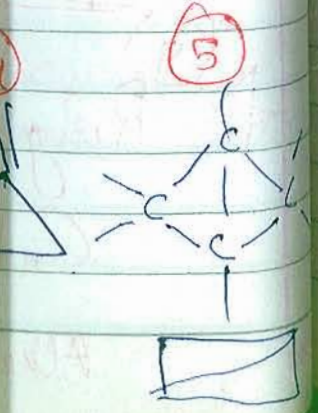
(V) 

II $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

III $H-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_2CH_3$

cloalkene Ibu

H-CH=CH$_2$



Groups which can show metamerism are →

1) Ether
2) Ketone
3) Esters
4) Anhydride
5) Amides
6) Amines.

Q. Can Pentene show isomerism?

Yes

Metamers

$C-C-C=C$ (I) $C-C=C-C$ (II)

6 Keto-Enol Tautomerism.

$CH_3-\overset{\overset{O}{\|}}{C}-H \underset{\text{Dynamic isomerism}}{\rightleftharpoons} CH_2=\overset{OH}{\overset{|}{C}}-H$

KETO ENOL

(ene-ol)

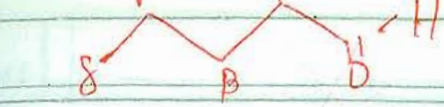
ene → double bond

ol → alcohol

together → enol

Imp.

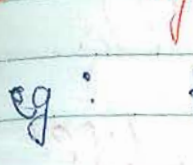
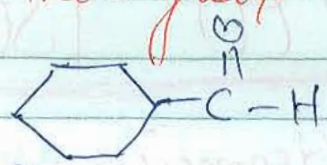
Definition:
Tautomerism is a phenomena of dynamic isomerism in which the 2 structural isomers remains in equi. Equi is dynamic in nature i.e, a rapid interconversion continue occuring. The pair of isomers showing Tautomerism are known as



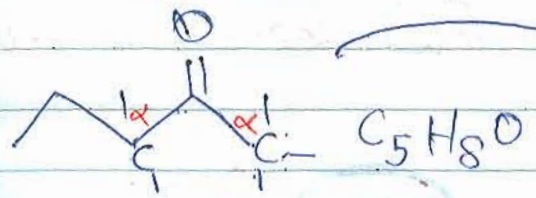
Date

Date

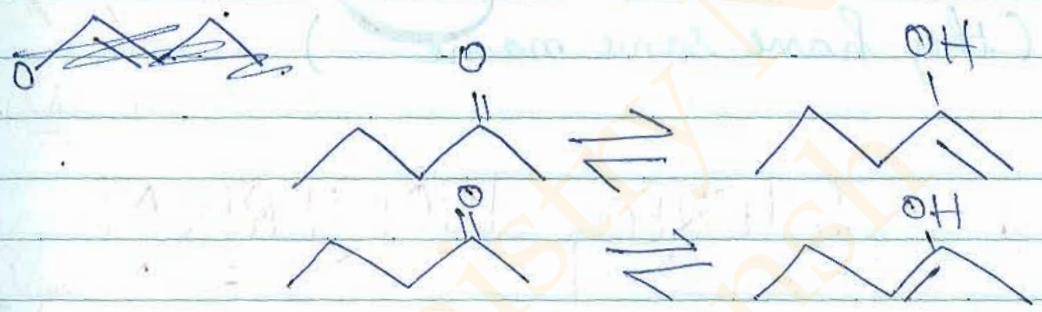
★ For keto enol Tautomerism there must be atleast 1 α hydrogen to the keto group.

eg:  

don't show keto-enol Tautomerism

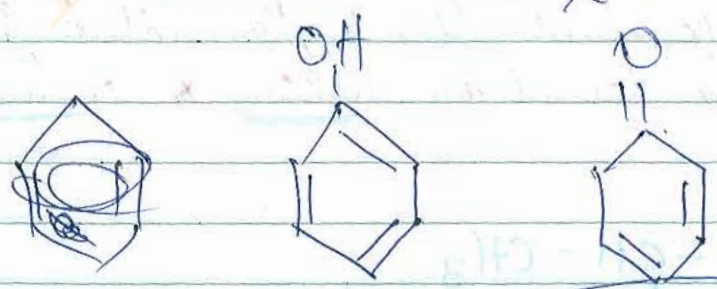


α-hydrogen → number : 5
type : 2



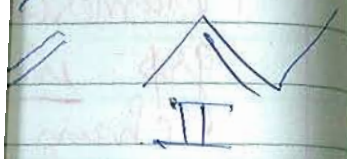
Imp:

Among keto-enol Tautomers, keto form, always predominate at equi due to its greater thermodynamic stability.



End of Structural Isomerism.

Metamers





NOL

ene (OL)

alcohol

double bond

together

enol

e known as

ness)

Important

Date

Stereo Isomerism.

Stereo Isomerism arises due to diff^{t} assay of atoms / groups in 3D space.

Isomers showing stereo Isomerism are known as Stereo Isomers.

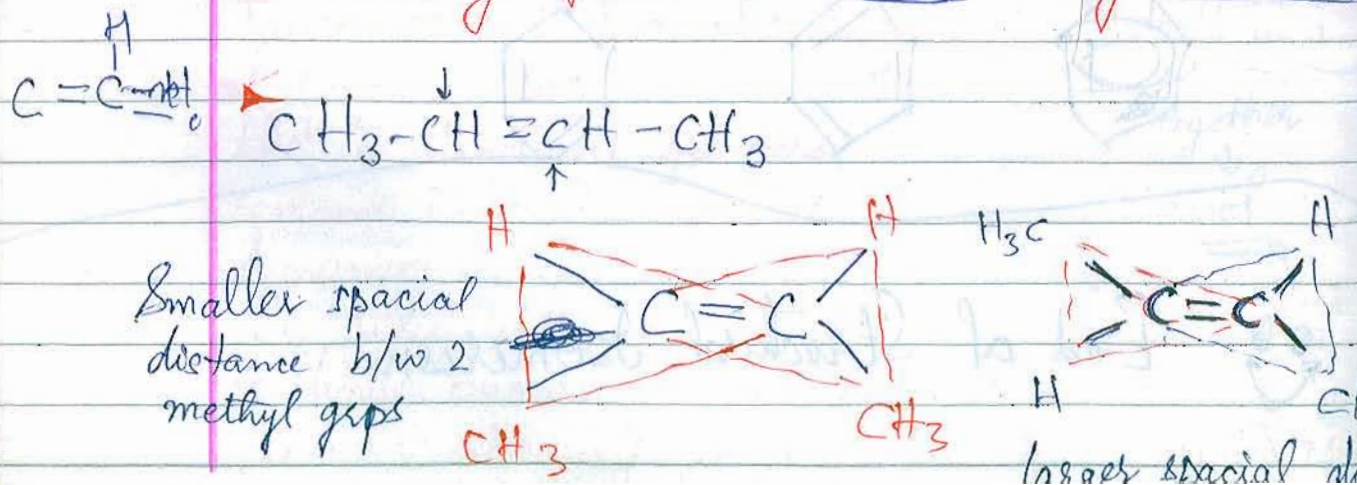
★ Stereo Isomers have (same) bonding pattern (they have same name)

1 STEREO ISOMERISM

★ Geometrical | Conformational | Optical ★ (Non superimposable on its mirror image)

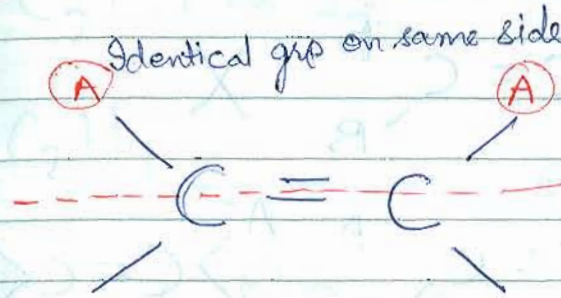
§ Geometrical Isomerism

Geometrical Isomerism arises due to restricted rotation of π bond grps. about a covalent bond. Restricted rotations are usually found in alkene & cycloalkane



GEOMETRICAL Isomerism

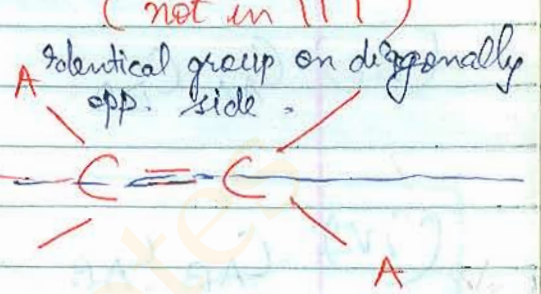
Cis-Trans Isomerism



Cis (same side)

'E' and "Z" (not in IIT)

All → 4 diff^t

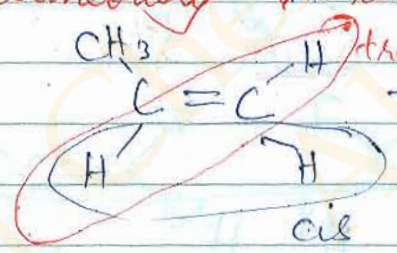


trans

☆ Criterion for Cis-trans Isomerism.

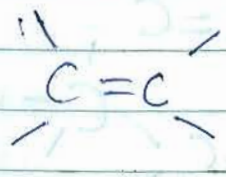
For a compd. to ~~exhibit~~ show cis-trans isomerism, following criterion must be satisfied.

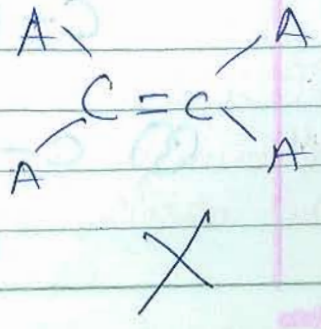
(1) cis & trans must exist independently, not simultaneously in the ~~&~~ same structure.

eg: 

→ It will not show cis-trans isomerism.

(2) cis & trans are diff^t isomers, cannot be interconverted by rotation.

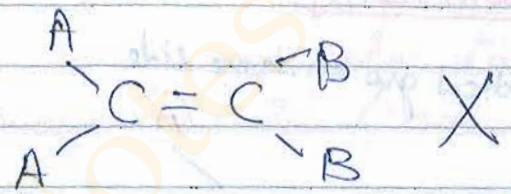
(i) 

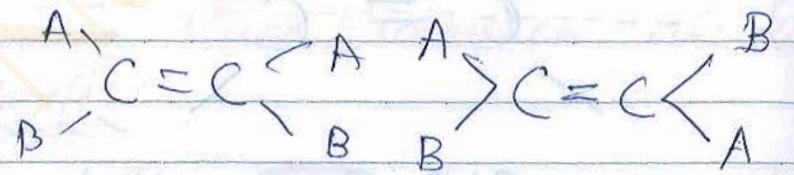
(1) $C_{AA}C_{AA}$ 

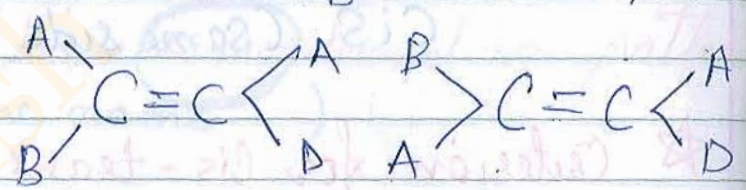
Date

(i) 

$C_{AA}\ C_{AB}$ 

(iii) $C_{AA}\ C_{BB}$ 

(iv) $C_{AB}\ C_{AB}$ 

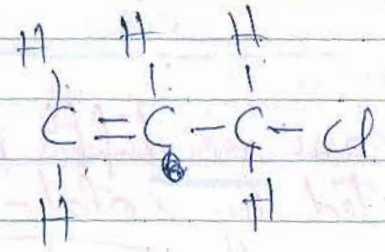
(v) $C_{AB}\ C_{AD}$ 

(vi) $C_{AB}\ C_{DE}$ 

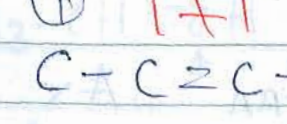
E & Z

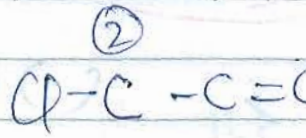
☆ An alkene with ~~same~~ 2 identical grp. on the same carbon don't show geometric isomerism.

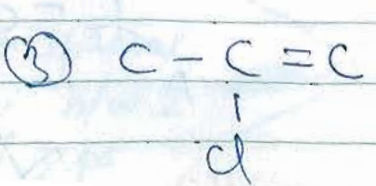
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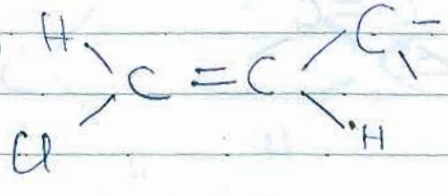
(1) C_3H_5Cl 

(1) 1+1



(2) 

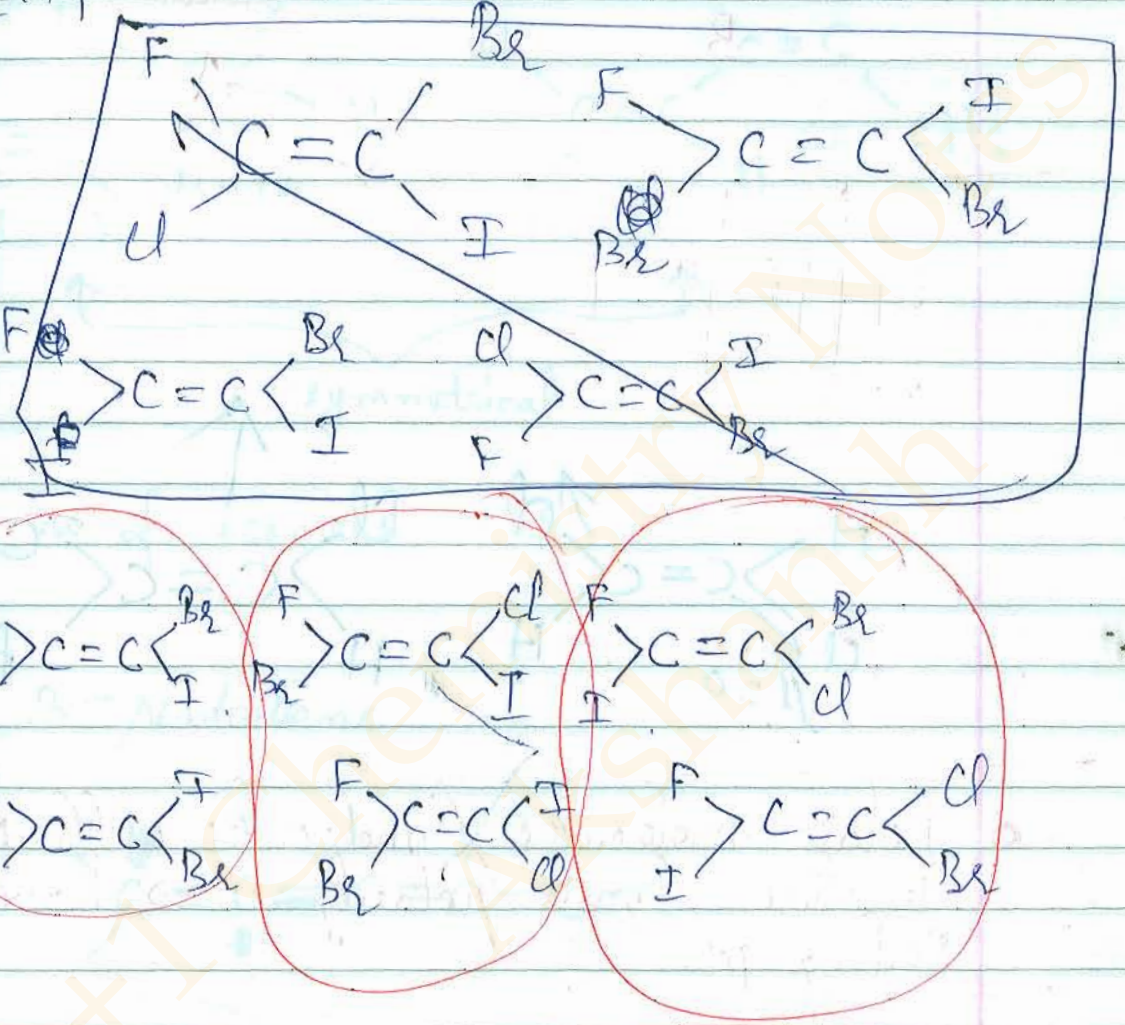
(3) 

(4) 



Q. $C_2FClBrI$.

C_2H_4

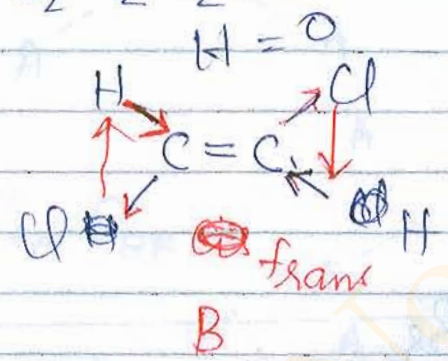


$C_2H_2Cl_2$

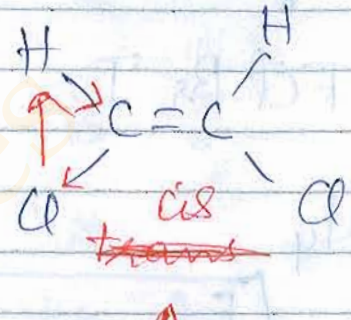
Q. An organic compd. has mol. formula $C_2H_2Cl_2$ & exist in 2 isomeric form A & B in which A is more polar than B; deduce structure of A & B considering them to be stereo isomers.

Date

$C_2H_2Cl_2$



B

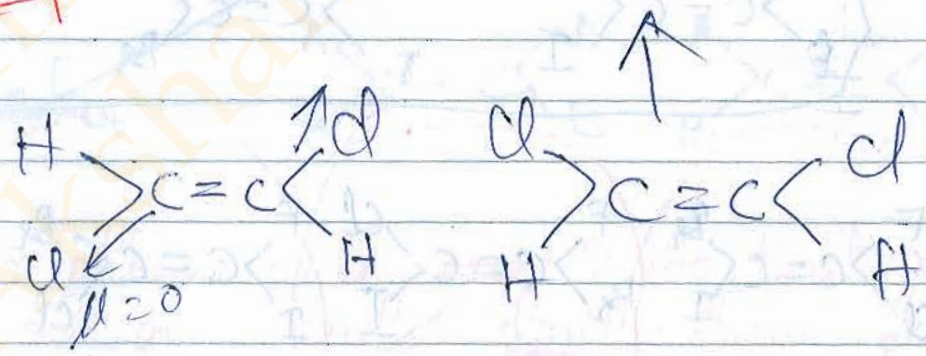


~~trans~~

A

X

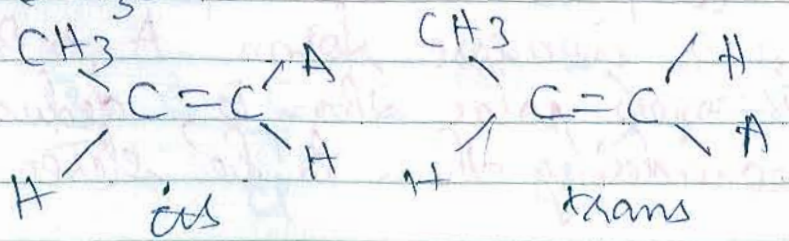
4/10/09

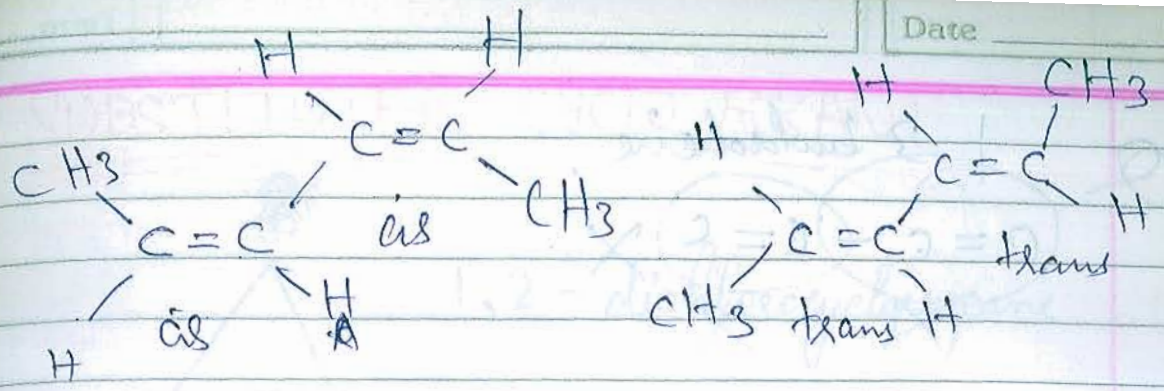


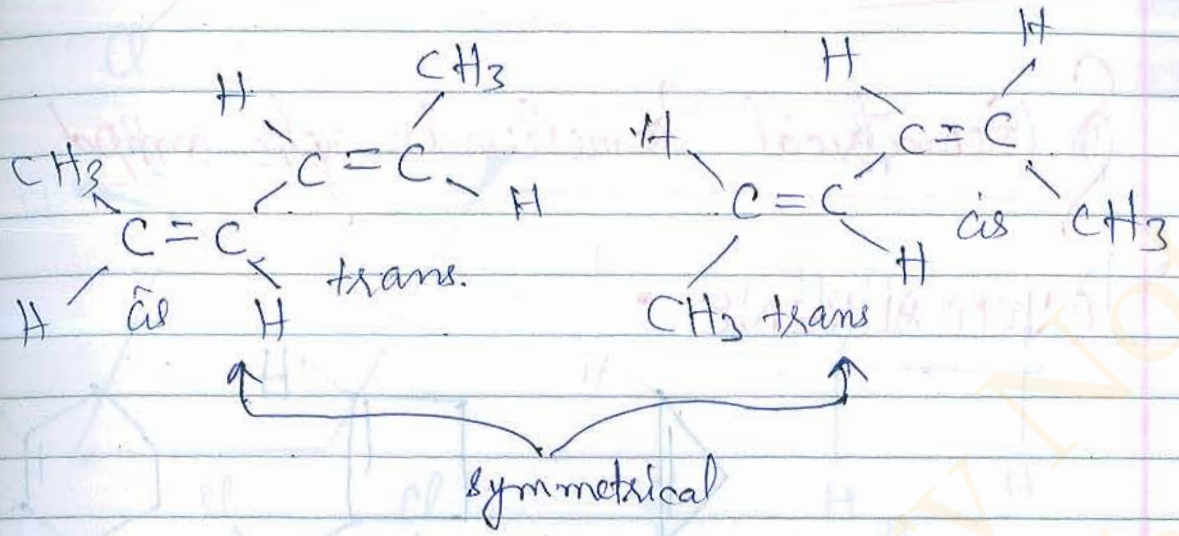
- Polar molecules / molecules with polar structure / more polarity ⟶ have greater Boiling pt.

$CH_3 - CH = CH - CH = CH - CH_3$ A

$CH_3C\ HC = CH$ A







So, no. of isomers = 3

Q. 1, 3 - pentadiene

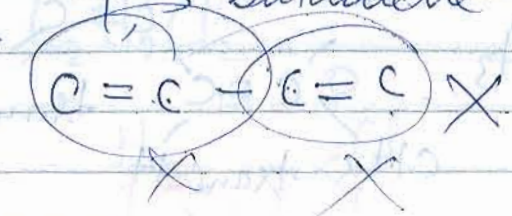


$CH_2=CH-CH=CH-CH_3$

A $-CH=CH-CH_3$

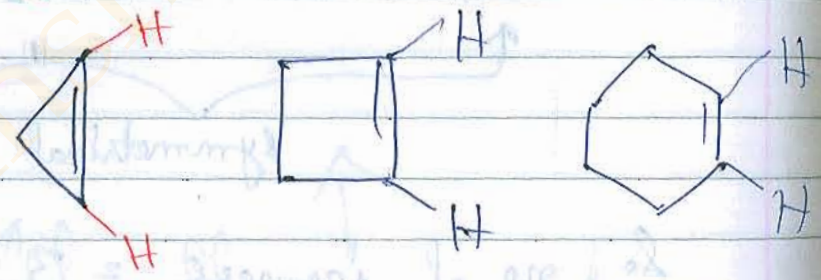
Date

Q 1,3 butadiene

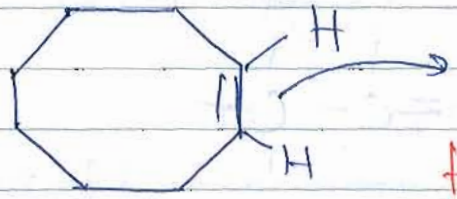


§ Geometrical Isomerism in cyclic compd.

(1) CYCLOALKENE :

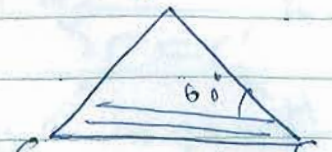


- Smaller ring exist mainly in cis isomerism ∴ their trans form will be highly strained & ~~hence~~ hence, it won't exist.

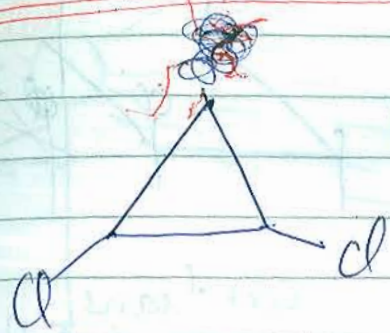


Smallest cycloalkene which exist in trans form practically:
cyclo Octene

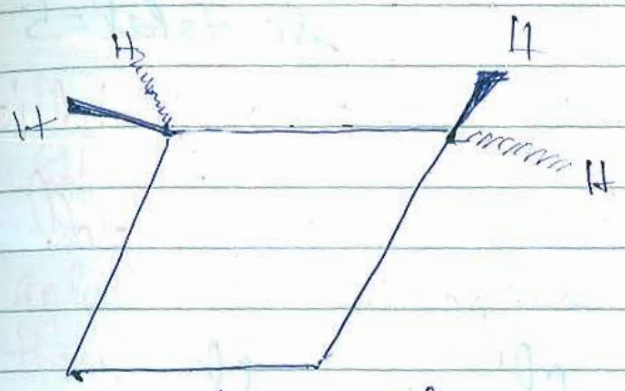
- All ring containing 8 or more C show cis - trans isomerism at double bond of the ring.



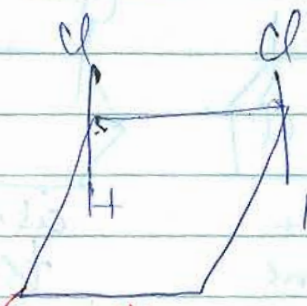
(2) SUBSTITUTED CYCLO ALKANE



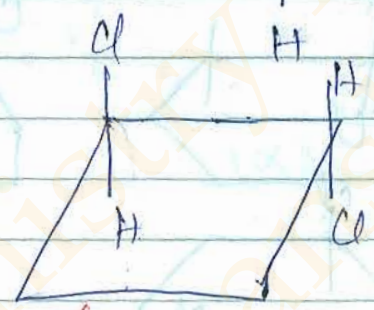
1,2 - dichlorocyclopropane







cis



trans

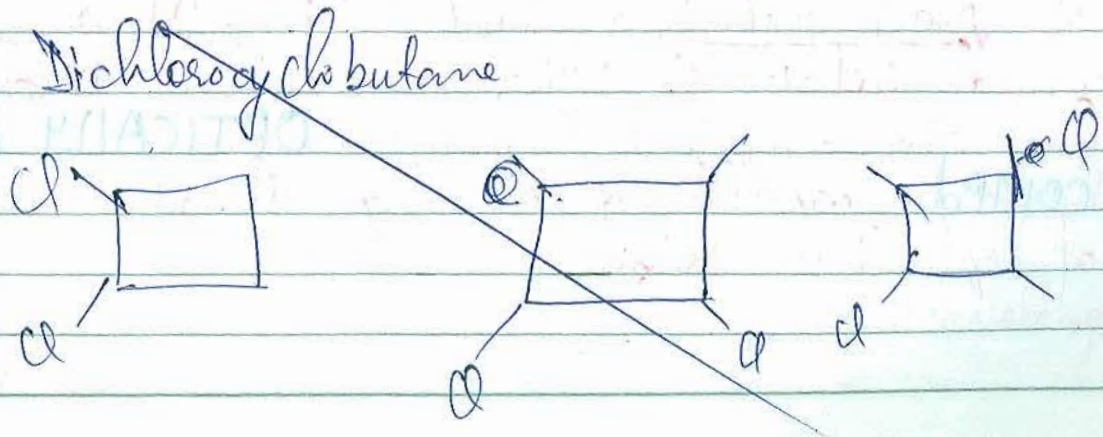
1,2 - dichlorocyclobutane

→ non-interconvertible by rotatⁿ

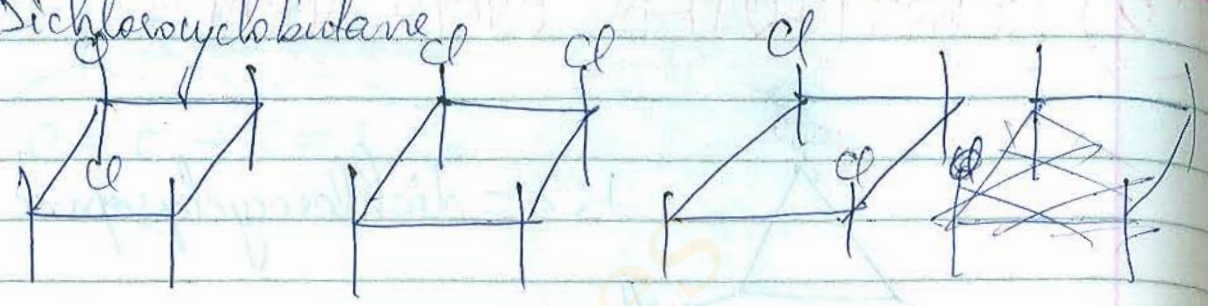
Cis → identical grps. on same side of plane

trans → identical grps. on opp. side of plane

① Dichlorocyclobutane



Q. Dichlorocyclobutane

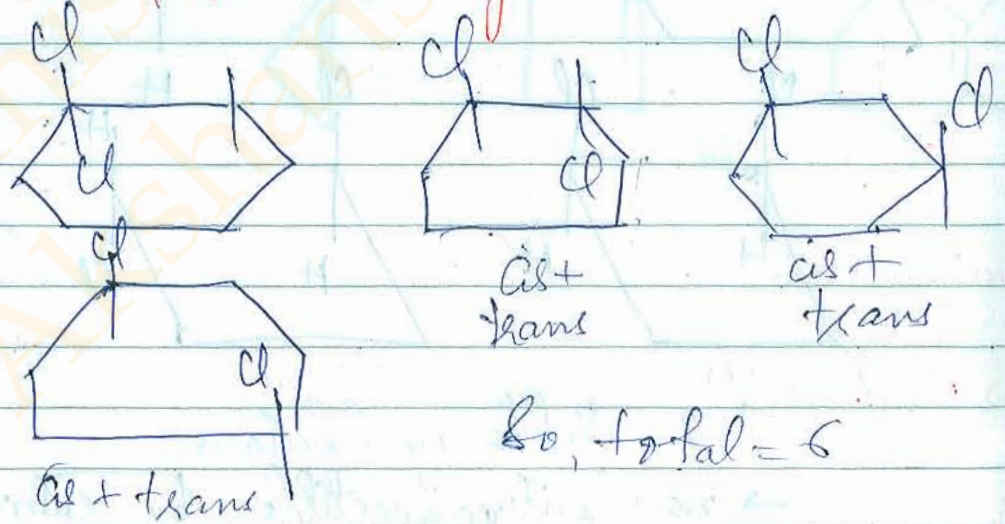


I cis + trans cis + trans

So, total = 5

Find all isomers excluding optical isomers

Q. How many geometric isomers are ~~total~~ possible for dichlorocyclohexane



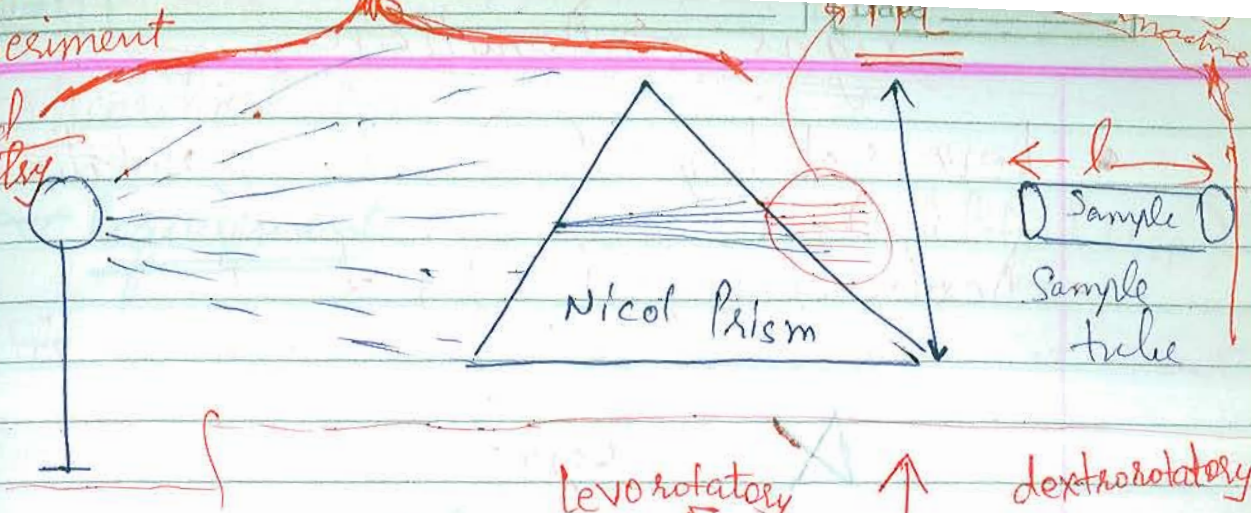
cis + trans cis + trans cis + trans

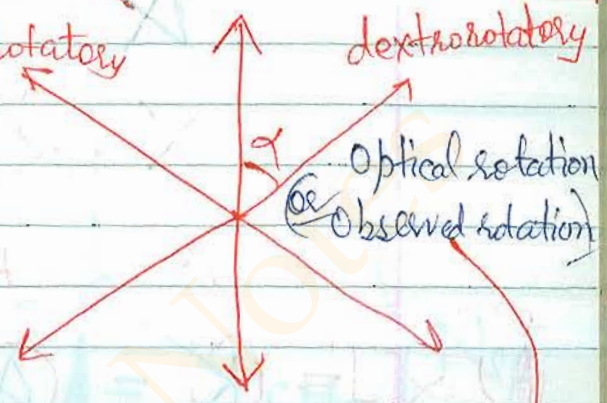
So, total = 6

OPTICAL ISOMERISM

Optical Isomerism is a phenomena of rotation of plain polarized light : PPL. If a compd. rotate the PPL, when passed through it, then the compd. is known as OPTICALLY ACTIVE COMPd. capable of showing the phenomena of optical isomerism.

its experiment is called Polarimetry





- Dextrorotatory: If optically active compd rotate PPL to the rt., then that isomer will be called dextrorotatory. If the PPL is rotated to the left, isomer is called LAVOROTATORY.

- Optical rotation (α) is the angle by which the PPL, is rotated from the normal plane of propagation.

☆ Factors affecting the magnitude of optical rotation

1) Concentration of the test (जितनी check करना चाहते हैं) Sol^{n}: Higher the concentration, greater will be magnitude of optical rotation.

2) length of sample tube

length (sample tube) ∝ magnitude.

3) (α) → Mod of optical rotation also depends on Temp. & wavelength of used light of source.

Date

Signs → Denotion

- Levo rotatory = (−) , l. (−) } notations.
- Dextrorotatory = (+) ; d }

$\alpha \propto$ Conc

$\alpha \propto l$

$\alpha \propto lc$

$\alpha = k\,lc$

$[\alpha]_\lambda^T = K = \frac{\alpha}{lc}$

- l → length of sample tube.
- K is the → observed rotation.
- c → concentration & density

Specific rotation : It is the observed rotation when the conc. is unity (1) & present in a sample tube of unit length.

here, $c = g/ml$, $l = dm$

Standard defin: Specific rotation is the optical rotation produced by sample of density → 1 g/ml when present in 1 dm long sample tube.

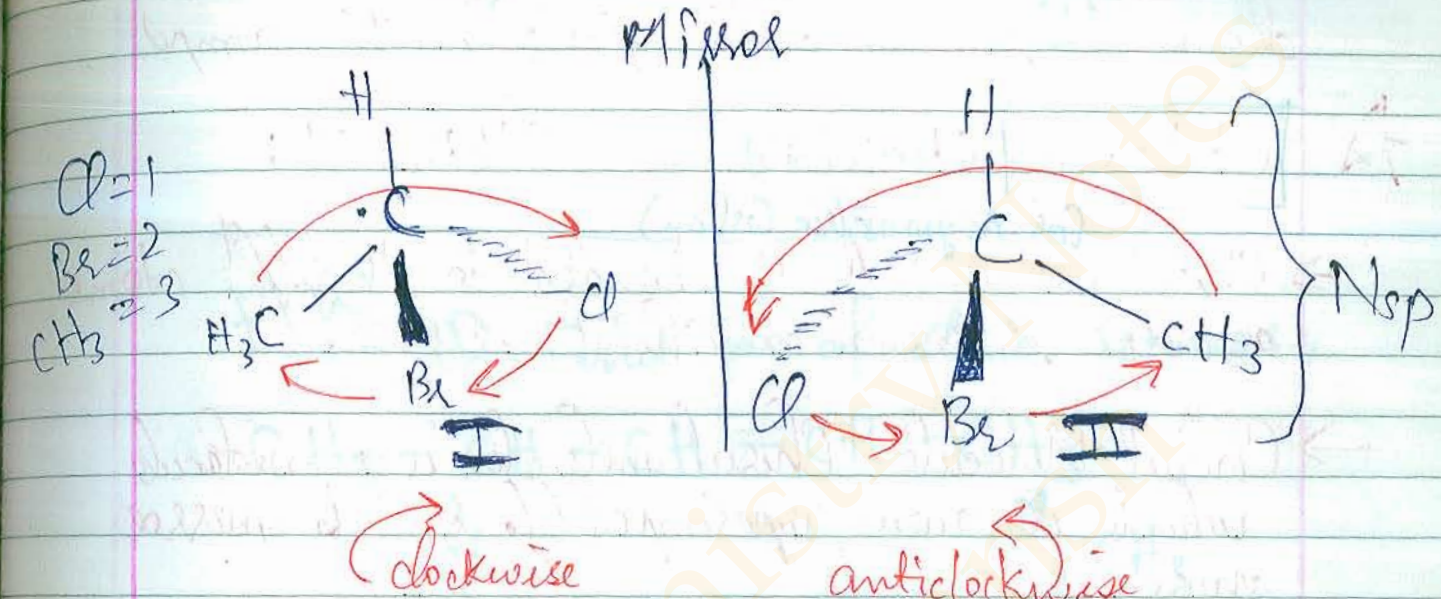
- Specific rotation has a fixed value for any compd. at a fixed T, λ of light.
- Specific rotation is a characteristic const. of an optically active compd. at a given temp. & for a given λ of light.

Solid line : (Out of plane)

Theoretical Part of Isomerism.

Requirement : Non-Superimposability (Nsp)

For a compd. to be optically active, it must be ~~non-Sp~~ Nsp on its mirror image.



I & II are optical isomers of (1-bromo-1-chloroethane)

ENANTIOMERS (a rel^n)

Enantiomers are the ~~optical~~ pair of optical isomers related by Nsp mirror-image relationship.

The enantiomerism is a rel^n b/w a pair of optical isomer.

Properties of Enantiomers.

i) Pair of enantiomers have same physical properties like Boiling pt., M.P., ρ, surface tension, viscocity are similar for pair of enantiomers.

3) Enantiomers have same magnitude of specific rotation, But, opposite sign. If one is levo - - other must be dextro.

4) Enantiomers have same chemical properties with optically inactive compds.
However, enantiomers differ in their chemical property with optically active compd.

☆ CHIRAL CARBON and CHIRALITY:
(or Asymmetric Carbon)

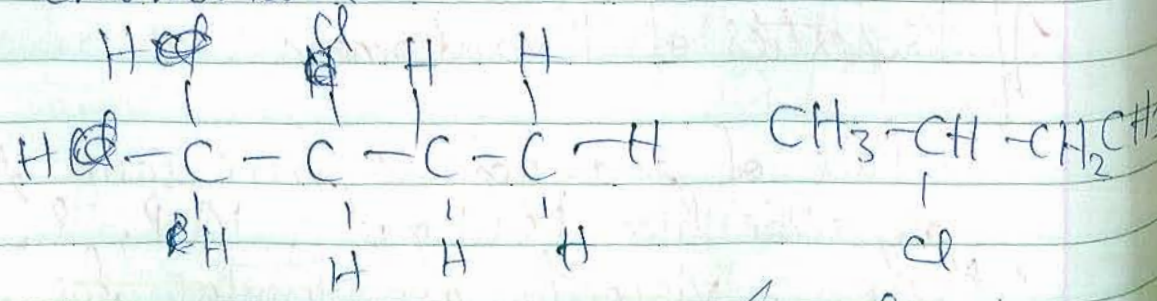
→ Chiral Carbon: A C bonded to 4 diff atoms or grps is known as Chiral carbon.

→ Chiral Molecule: Chiral molecule is a molecule which is non-superimposible on its mirror image.

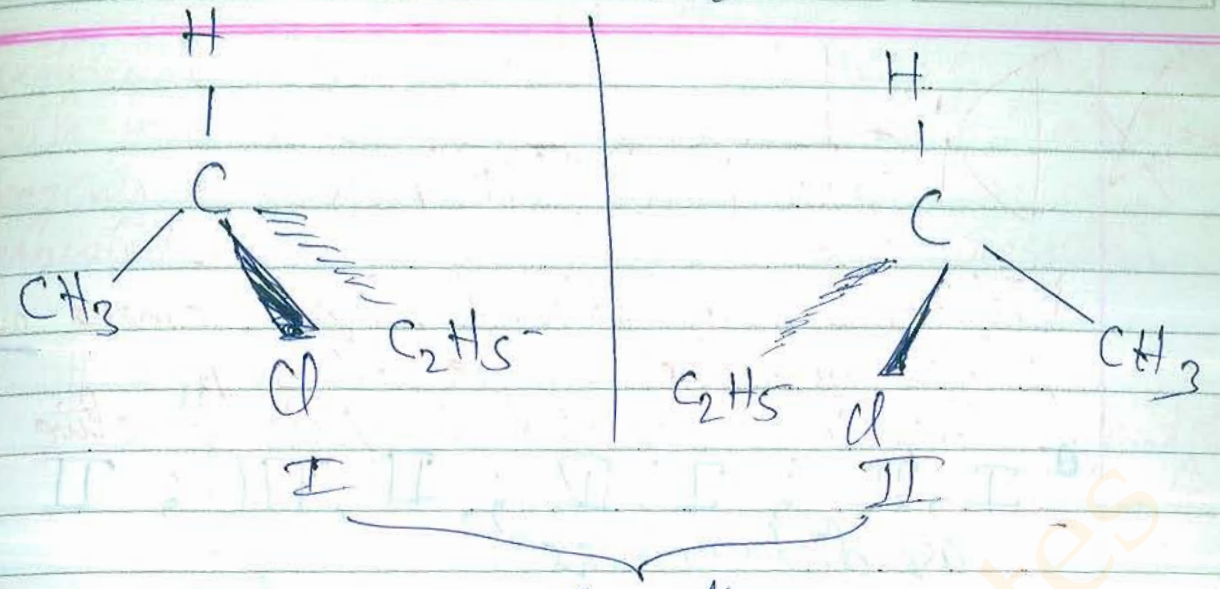
☆ जिस Compd. में एक ही Chiral C हो तो वो Compd. भी chiral होता।

☆ If a compd. contain 1 & only 1 chiral C then the compd. will also be chiral.

2-chlorobutane



Mirror



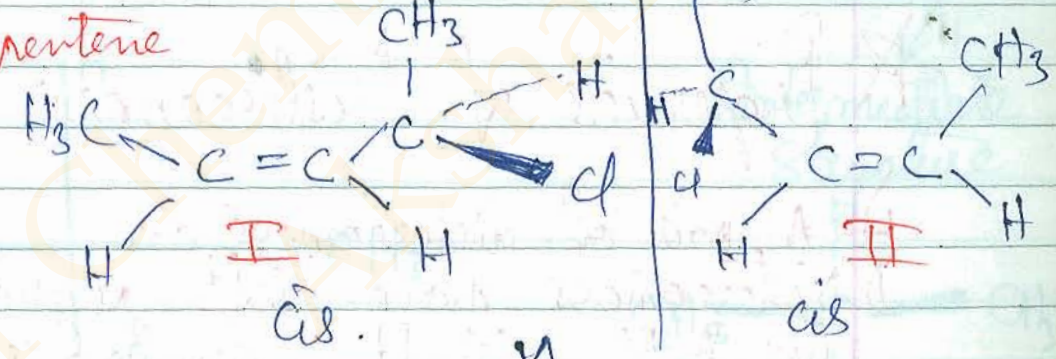
Enantiomers.

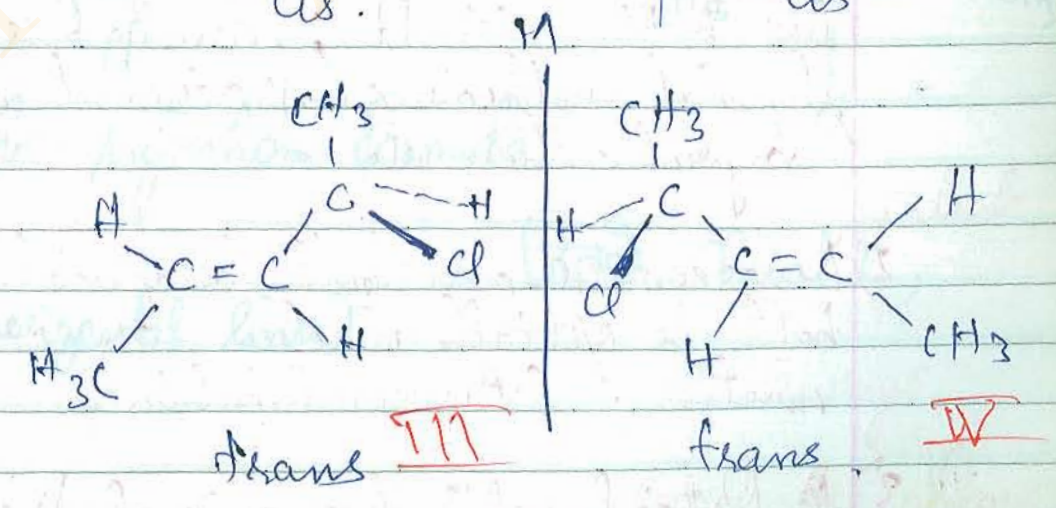
HW Q. Find no. of stereo isomers.

$CH_3 - CH - CH = CH - CH_3$

Cl

4-chloro-2-pentene





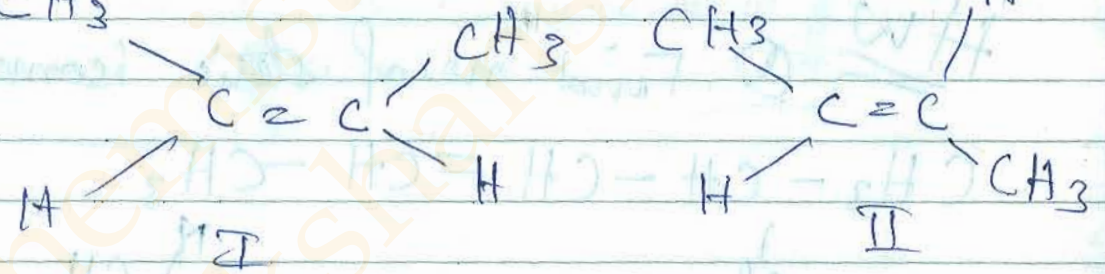
All 4 are stereo isomers of same compd.
I & II ; III & IV are enantiomers.

Date

☆ Distereomers.

Distereomers are pair of stereo isomers not related by mirror image rel^{n} ship.
They may/maynot be optically active.

Q I, II ; I, IV ; II, III ; II, IV are distereomers.



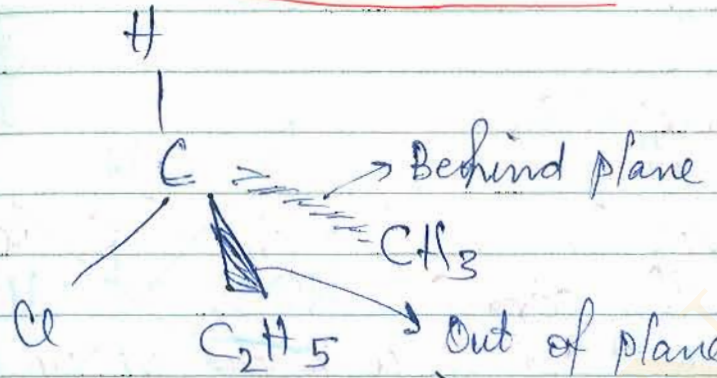
☆ Properties of Distereomers

1) ~~A pair of distereomers can~~
2) Distereomers have diff^{t} physical properties like B.Pt. ; M.Pt. ; can be separated by physical methods as fractional distillation, crystallization etc.

2) Distereomers can both be optically active, both be optically inactive, one active — one inactive. (Any combination)

3) Optical rot^{n} of a pair of Distereomers are

9. Diastereomers have diff^{t} ph chemical properties with both optically active & optically inactive reagents ∴ A pair of diastereomers can be separated by chemical method of separation.



3D representation of a molecule is done by a formula called ↓ SAW-HORSE PROJECTION

☆ FISCHER-PROJECTION

Fischer projection is a way of representing Saw-Horse projection in 2 D.

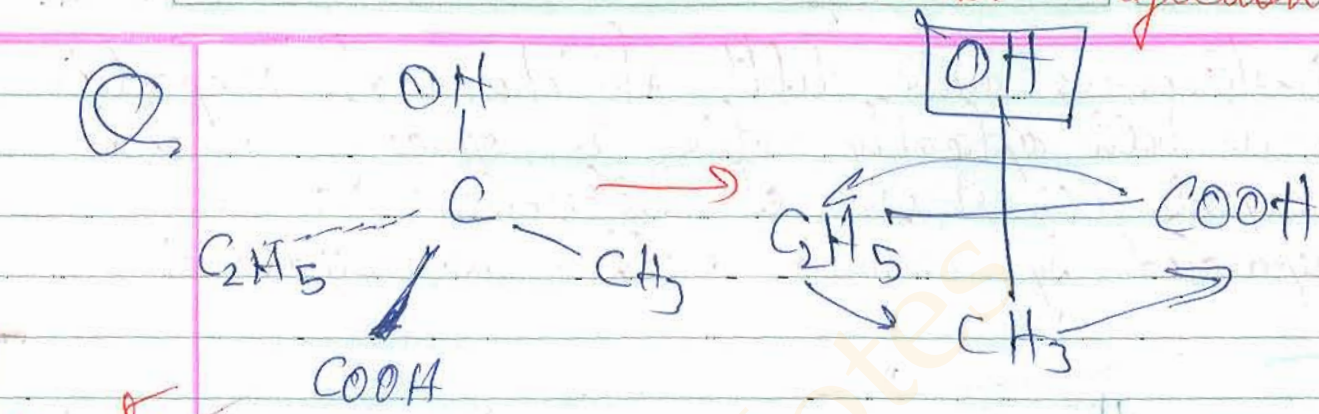


Intermediate Structure



1) In Fischer-projection formula, the pt. of intersection of horizontal & vertical line represent the Chiral C. (जितने Chiral C, उतने horizontal lines)
2) Groups directed towards viewer are always placed on horizontal line.
3) Groups directed away from viewer are always placed on vertical line.

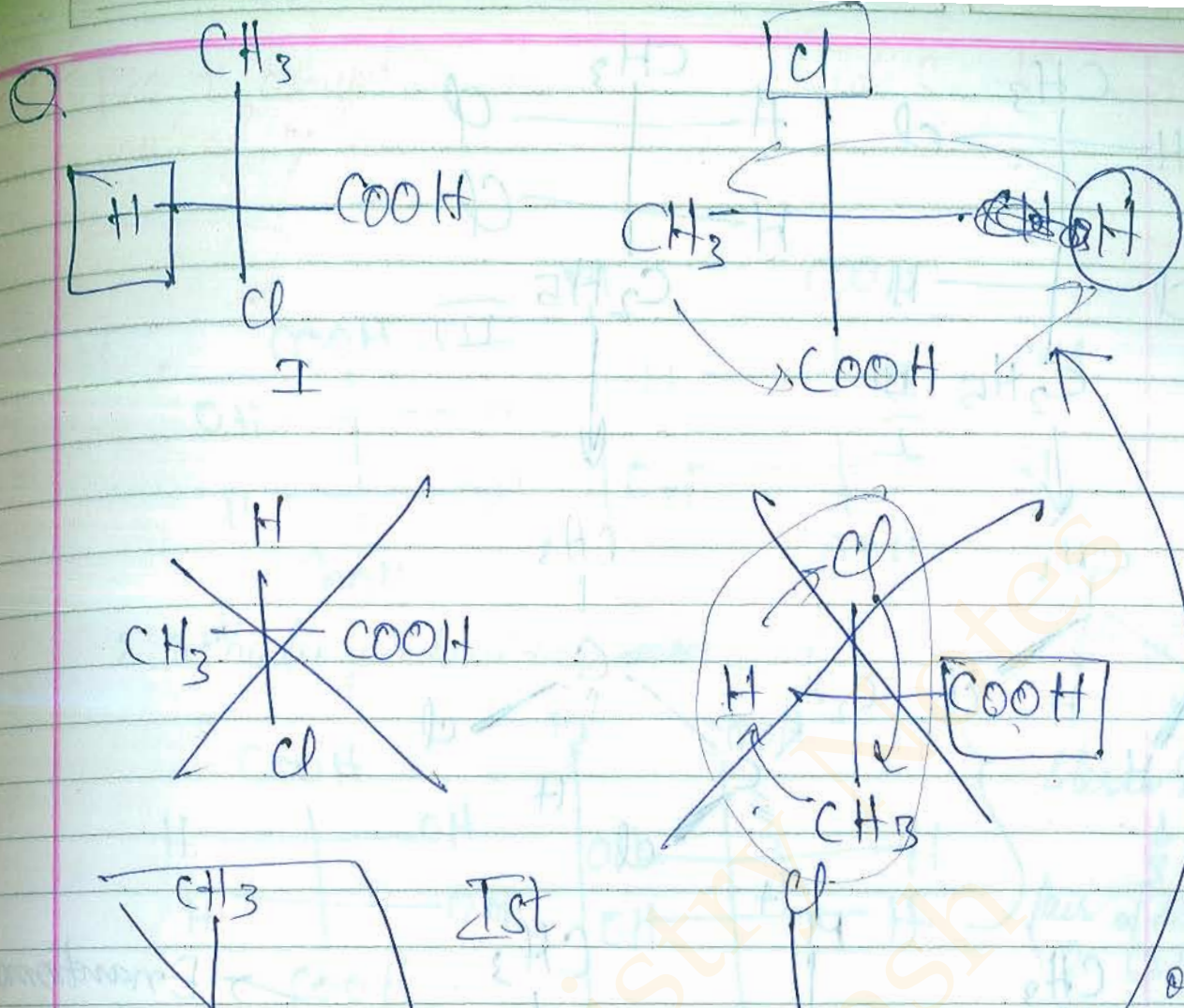
Fischer Projection



Property ☆

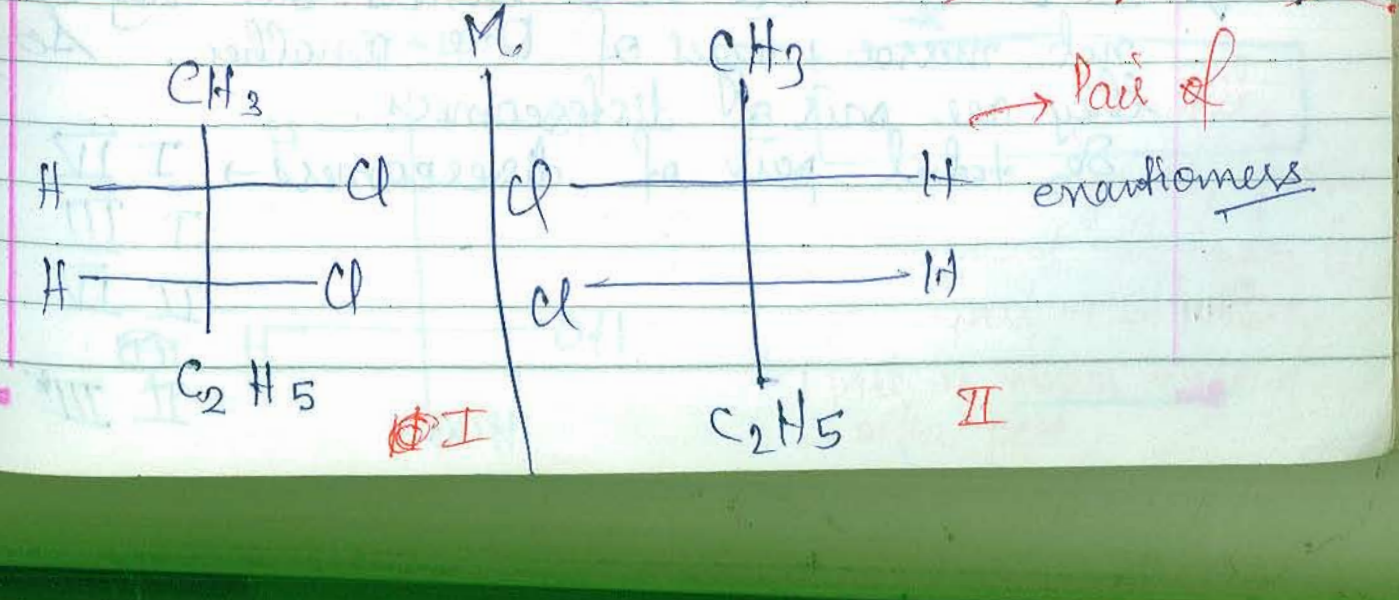
In fischer-projection,

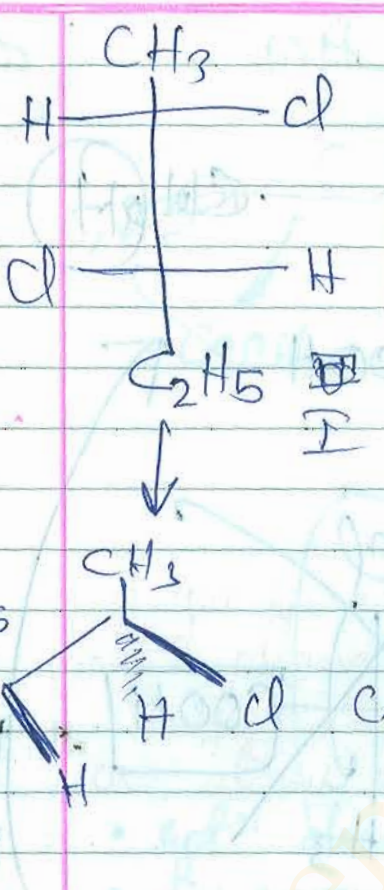
1) 3-group interchange at a chiral C does not change the config
Configuration → It is a ~~fixed~~ spatial arrangement of atoms or grps around a chiral carbon
- rotⁿ doesn't change config.
- fix anyone 3-group interchange should be there in a cyclic process.

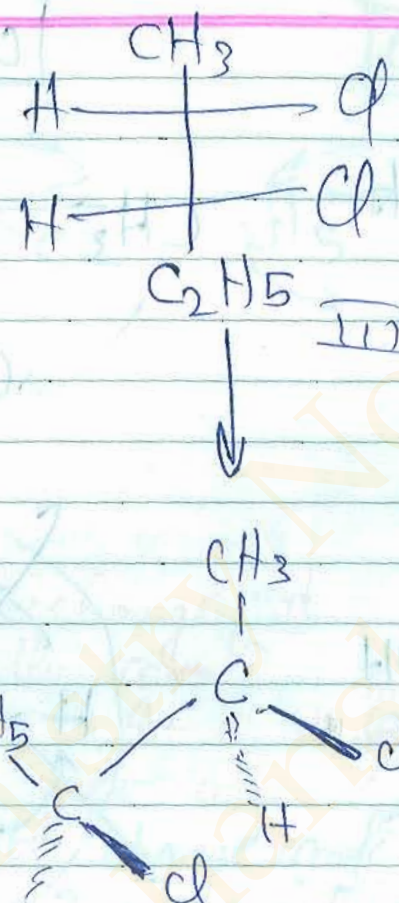


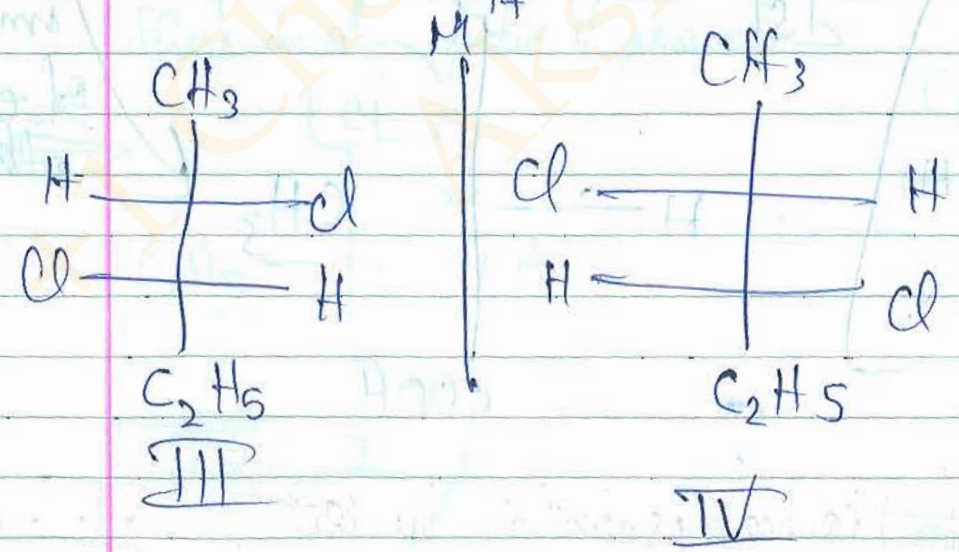
Q.

★ Rotⁿ of Fischer-projection by 180° in plane of paper doesn't change config.









→ Enantiomers
↓
III & IV

☆ I & III are stereo isomers but they are not mirror images of one-another. So, they are pair of diastereomers.

So, total pair of diastereomers → I IV
I III
II IV

☆ For a
no. of

OH

H

2,3 di hy

C

H —

H

☆ Phis
optica
its

☆ Conf
on its
as

→ Enantiomers
↓
III & IV

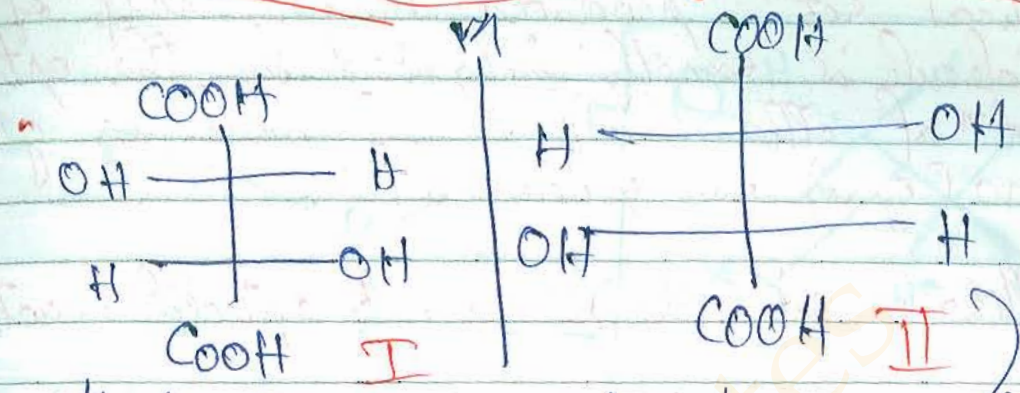
H

Cl

ss but they are
another. So,
s.

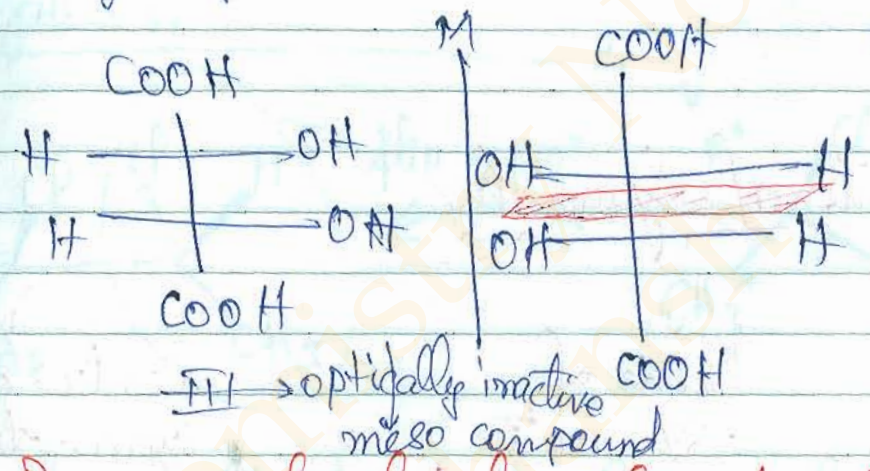
omers → I IV
I III
II IV
II III

☆ For a compd containing n chiral C, the max. no. of optical isomers will be 2^n.



2,3 dihydroxy butanedioic ~~acid~~ acid

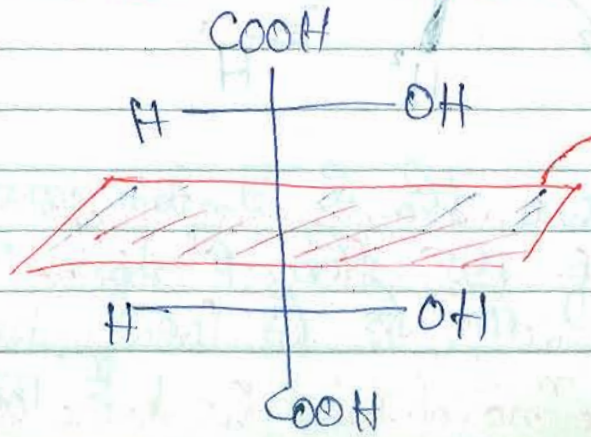
optical isomers
↓ (I, II)
2
Stereo Isomers
↓ (I, II, III)
3
Pair of diastereomers
2 (I III & II III)



III → optically inactive meso compound

☆ Presence of chiral carbon doesn't guarantee optical isomerism. (∵ its superimposible on its mirror img) - Its optical inactive.

☆ Compds. containing chiral C but superimposible on its mirror image (optically inactive) is known as MESO COMPDS.



☆ Plane of Symmetry (an imaginary plane which bisect the molecule in 2 part → in which 1 part is mirror image of other part)

☆ Meso compd. is optically inactive due to the presence of plane of symmetry. Meso compd. has internal Enantiomerism i.e., optical rot^{n}. produced by one-half of the molecule is exactly balanced by the optical rot^{n} of other half of the molecule giving no (zero) net optical rot^{n}.

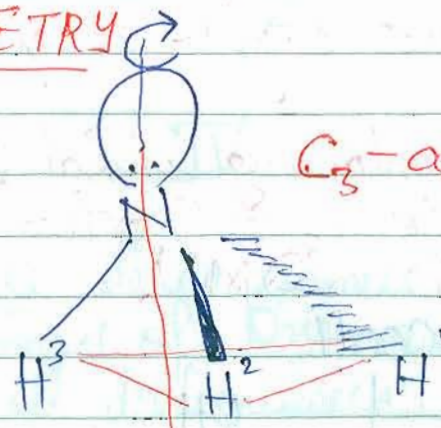
☆ Meso compd. has <u>permanent</u> optical inactivity.

11/10/09

☆ ## Elements of Symmetry

- Axis or Line of symmetry
- Plane of Symmetry
- Centre of symmetry (Inverson Pt. / Inversion center)

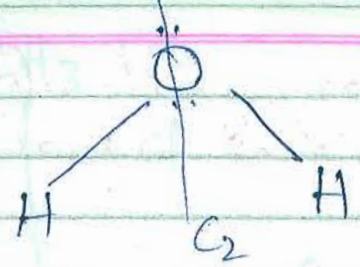
1) AXIS OF SYMMETRY



C_3 – axis of rot^{n} symmetry

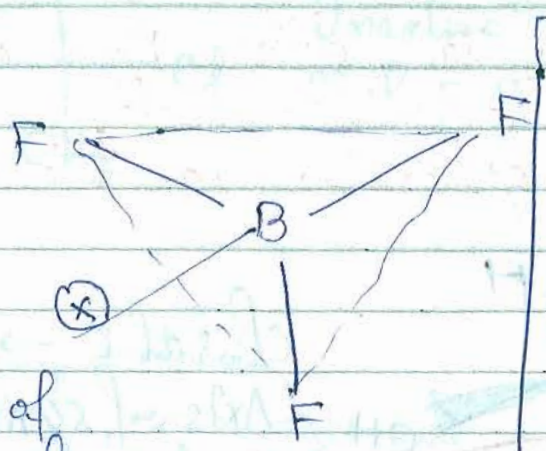
☆ Axis of symmetry is an imaginary axis abt. which, when the molecule is rotated in 3D by an angle of 360°, the similar structure is

H_2O

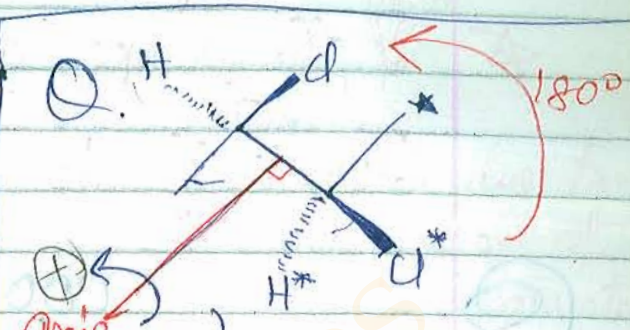


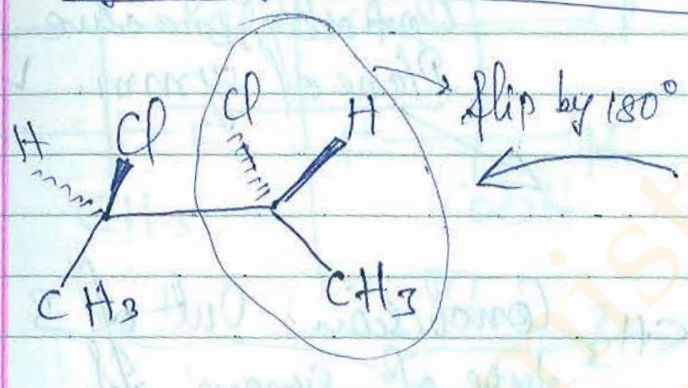
C_2 axis of rot. (symmetry)

BF_3

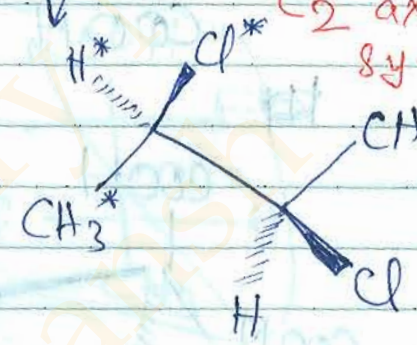


C_3 axis of symmetry





after rotn



Cl
H

C_2 axis of symmetry

Conclusion: It has axis of symmetry but not plane of symmetry. It is optically active.

★★ Axis of symmetry का Present होना Optical activity/inactivity पर Depend नहीं करता। ★ अगर Cmpd. में Plane of symmetry होता, तो ★ वो optically inactive होता है (Reverse is not true)

★ CENTRE OF SYMMETRY

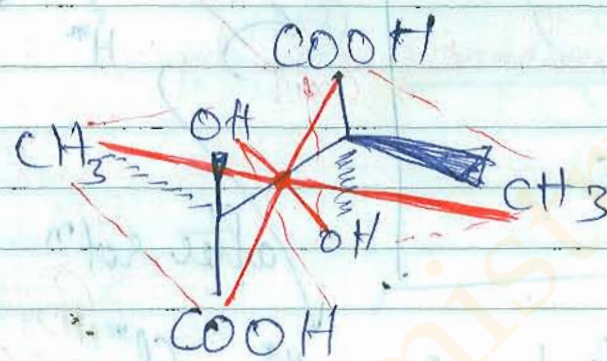
(अगर molecule में कोई centre exist करता हो, जिससे 180° angle पे कोई like grp (equal distance पे) exist करता हो, तो, वो centre, centre of symmetry होता है।

Date

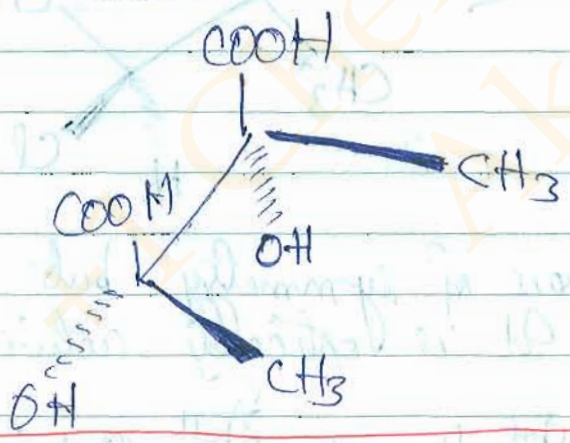
Definition: Its an imaginary pt. abt. which identical grps. are found at equal distance at an angle of 180°

* If the compd. contain either plane of symmetry / centre of symmetry; it would essentially be optically inactive.

Q.



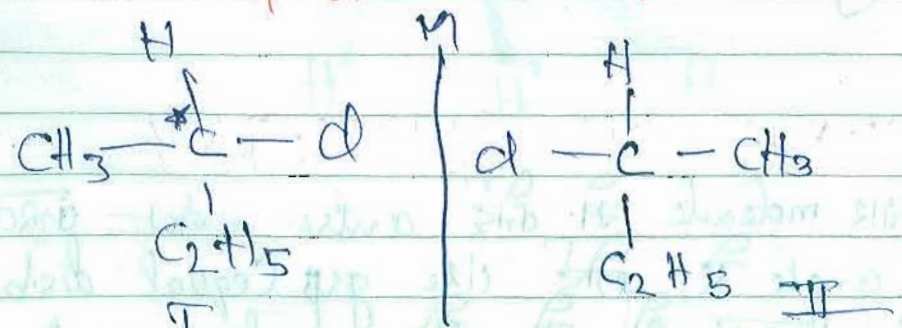
Chiral C → ✓
Axis of symm. ✗
Centre of symm ✓
Optically inactive.
Plane of symm. ✓

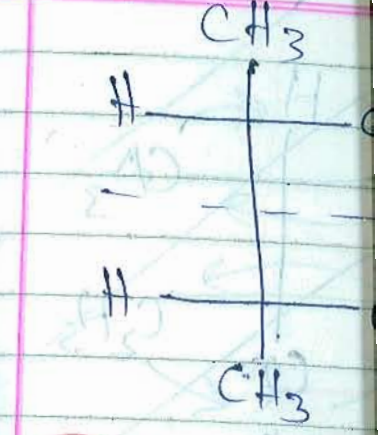


Conclusion: Out of 3 type of symm. If axis of symm. is present, nothing can be said about activity/inactivity

RACEMIC MIXTURE

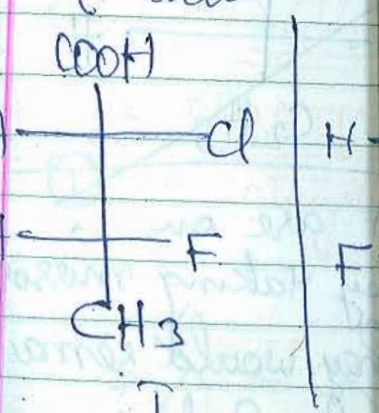
Racemic Mixture is a mixture containing equal amt. of enantiomers.





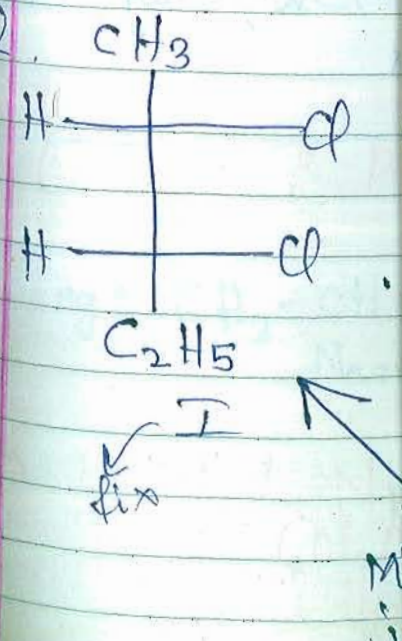
Q.

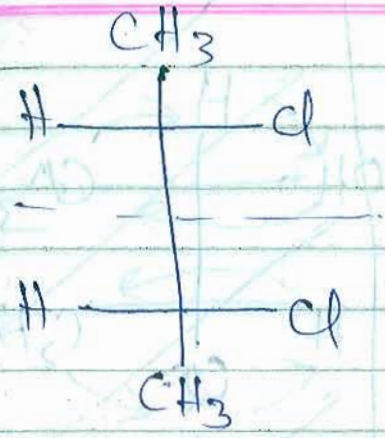
2-chloro-3-fluorobuta
acid



Positio

Q.

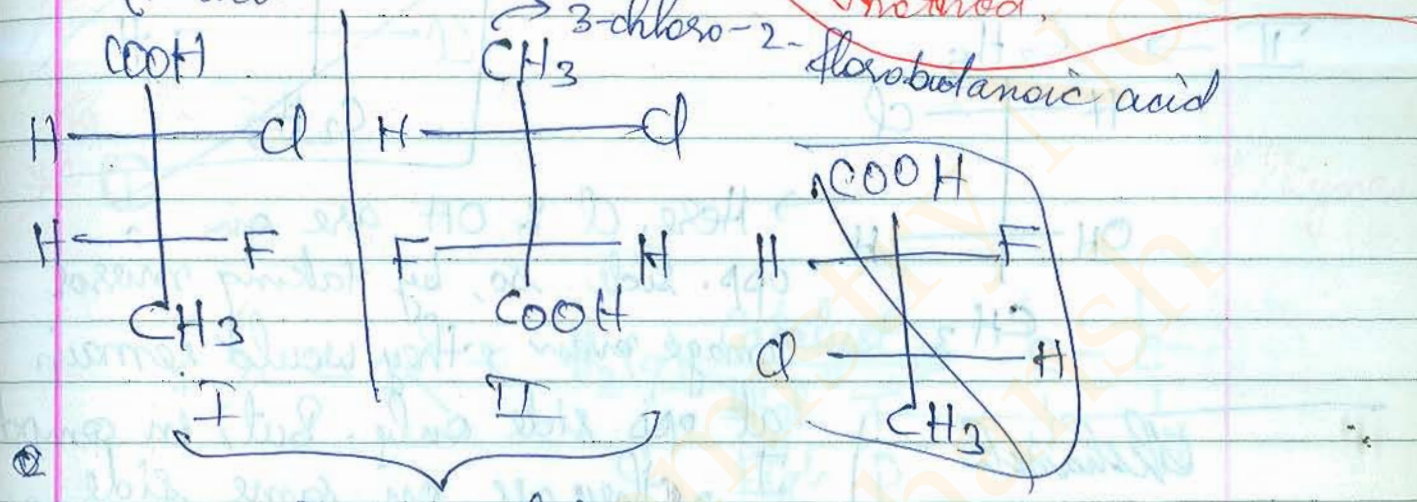




Inactive
O.R = 0

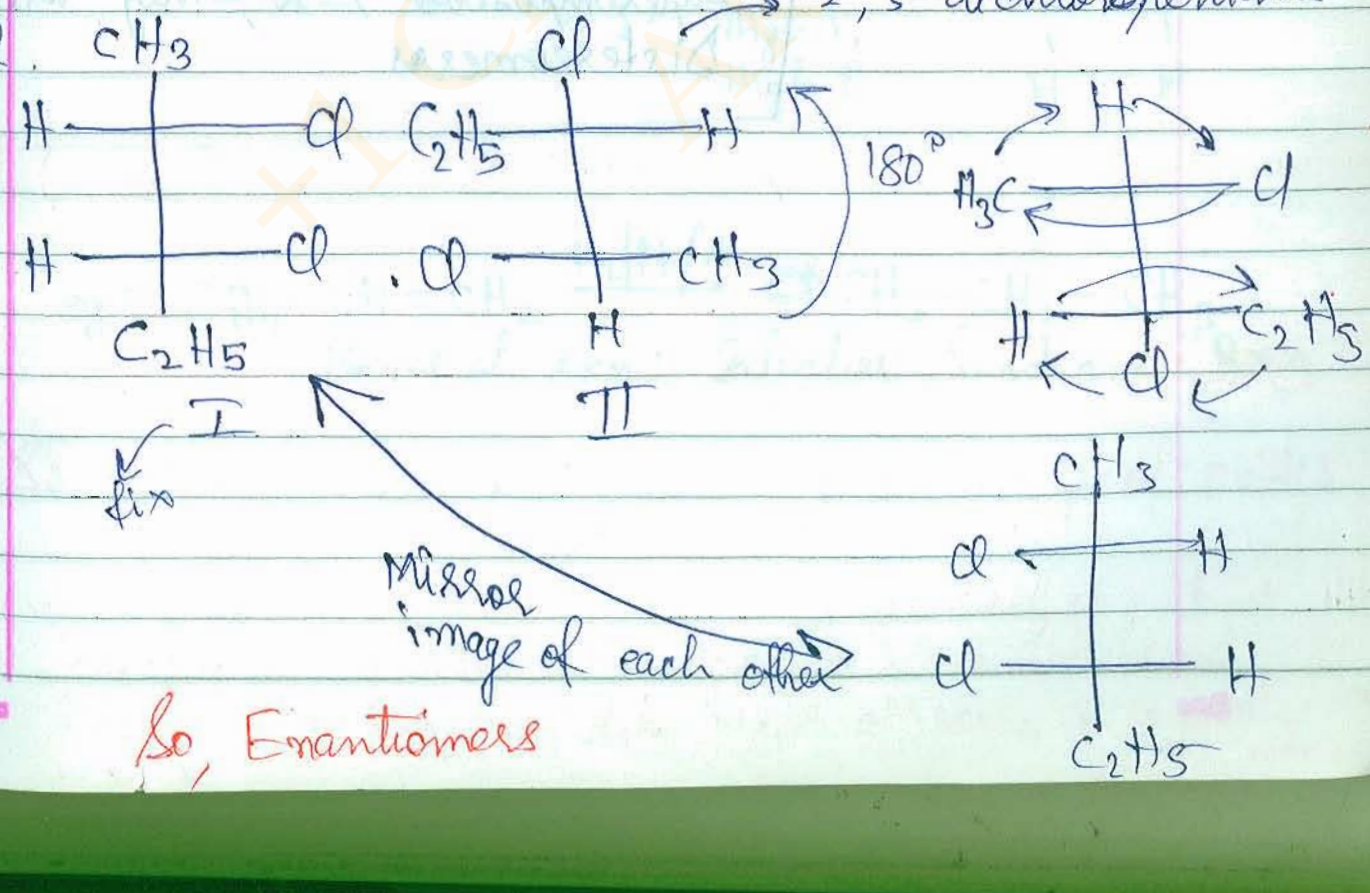
Racemic mixture has external compensation of optical rotⁿ; can be separated into enantiomers.
Meso-compd. is optically inactive due to internal compensation of OR., cannot be separated by physical/chemical method.

Q.

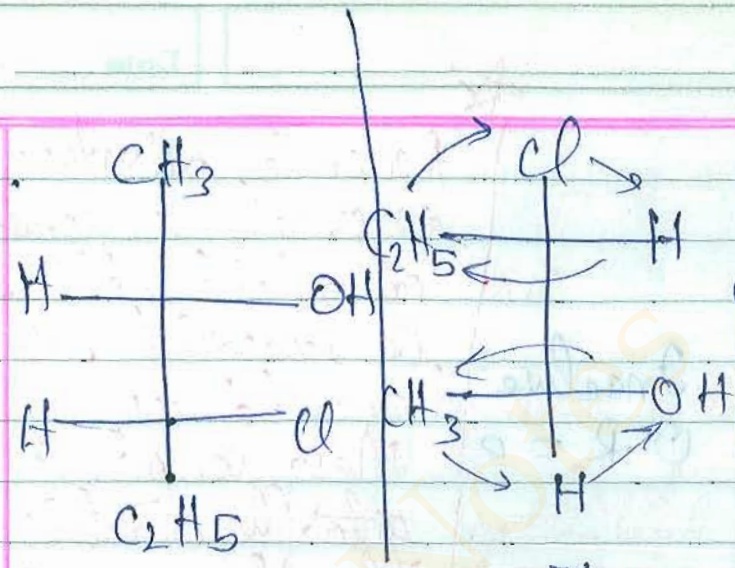


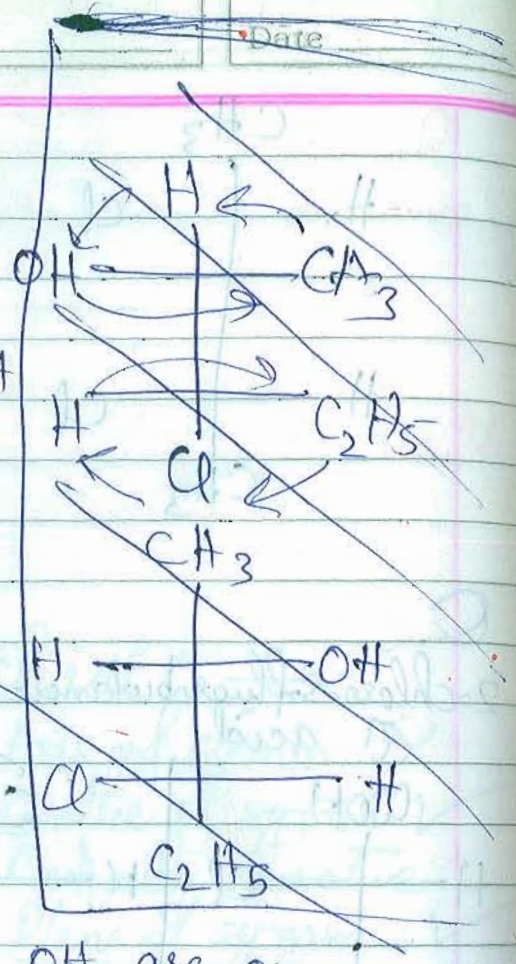
Positional isomers

Q. 2,3-dichloropentane



Q.







→ Here, Cl & OH are on opp. side. So, by taking mirror image even, they would remain at opp. side only. But, in compd. I, they are on same side. Since the 2 structures are non superimposible, so, they are Diastereomers

Akshansh

Ch. Hydrocarbons

☆ Alkanes

☆ PREPARATION ☆

1 ✳ (1) By Catalytic Hydrogenation of Alkenes & Alkynes

$$>C=C< + H_2(g) \xrightarrow[\text{High T, High P}]{\text{Catalyst}} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}-$$

$$-C\equiv C- + 2H_2(g) \xrightarrow[\text{High T, High P}]{\text{Cat.}} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}-$$

Catalyst : Pt or Ni or Pd.

eg: $CH_3-CH=CH_2 \xrightarrow{H_2/Pt/\Delta}$ (2) $CH_3-CH_2-CH_3$

Name of rxn: Sabatier Sandrans Rxn.

☆ RANEY Ni : Raney Ni is an alloy of oxides of Al (Al_2O_3) [$Al_2O_3 + Ni$].

With the use of Raney Ni as catalyst, it is capable of absorbing H-gas at normal room temp (i.e Rxn. can take place at room temp with this cata.)

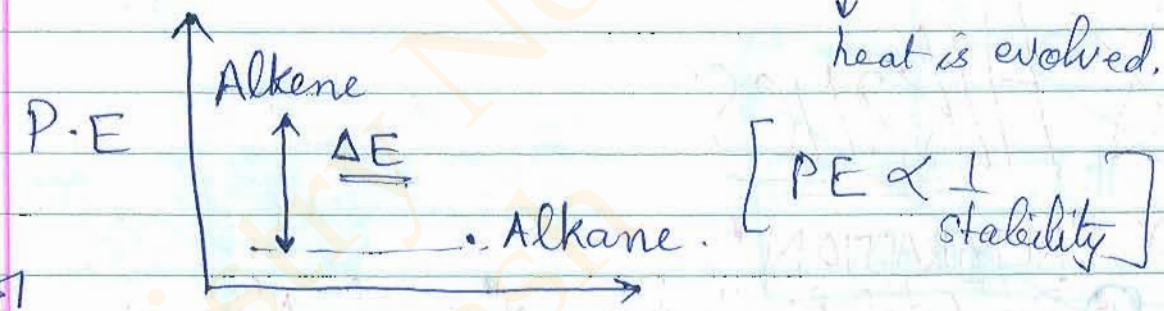
Diff. [Adsorb : अपने surface पर चिपका के रखना
[Absorb : अंदर तक ले जाना

Date

Hydrogenation occur at the surface of metal containing Adsorbed $H_2(g)$. Ni, Pt, Pd, have the property of adsorbing $H_2(g)$ but at higher temp., whereas, Raney Ni, adsorb H_2 at room temp.

$$CH_3-\overset{H}{C}=\overset{H}{C}-H + H-H \xrightarrow{Cat.} CH_3-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H \quad \Delta H < 0$$

↓ heat is evolved.



Reason why heat is evolved ?

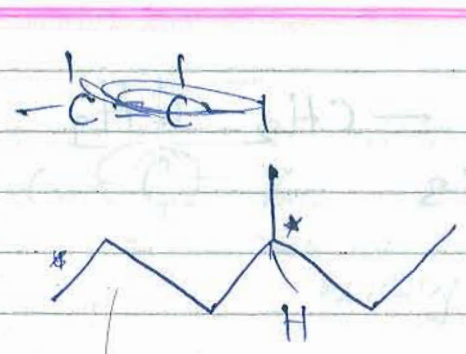
(1)

(2) Breaking bond require E, Formation of bond releases E. In above case, heat req^d to break double bond < heat released due to alkane formed. So, net → heat released.

Q. A hydrocarbon has exist in 6 isomeric form A to F. All, on hydrogenation, absorb 1 mole of H_2 to produce the same, smallest optically active hydrocarbon G. Identify A to G & label ~~lab~~ ~~level~~ the isomer b/w A to F which can show geometrical isomer & optical isomer. A to F are non-~~st~~ stereoisomers

Ans: We have to make smallest optically active compd. G.

$$CH_3-CH_2-CH_2-\overset{H}{\underset{}{C}}-CH_3 \quad \Big\} G.$$



A ① X ② B



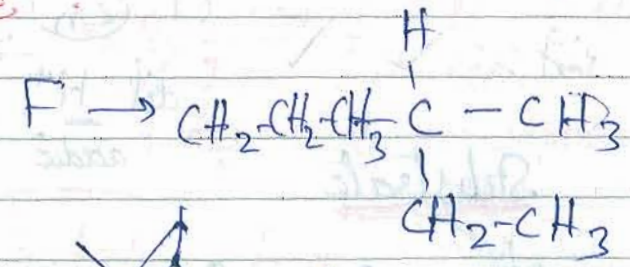
C ③ ④ D

E ⑤ X ⑥ F X

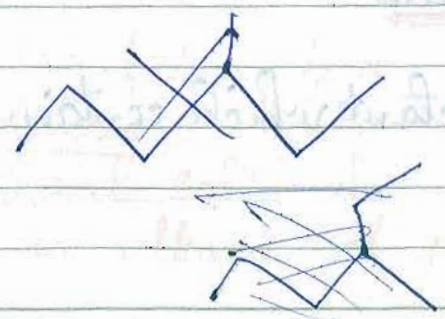
Geometric → B, C, D.

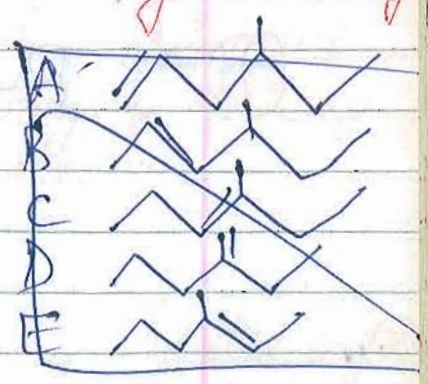
Optical : A, B, F

Q An alkene has 5 isomeric forms A to E. & all on hydrogenation, gives the same smallest optically active hydrocarbon F. Alkenes, A to E are constitutional isomers. Identify A to F. Also, label, them as optically active, geometrically active.



F → $CH_2-CH_2-CH_3-\underset{\displaystyle CH_2-CH_3}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-CH_3$





Date

F → $H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-CH_3$

F →



A →



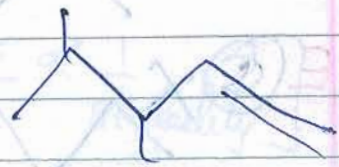
D →



B →



E →



C →

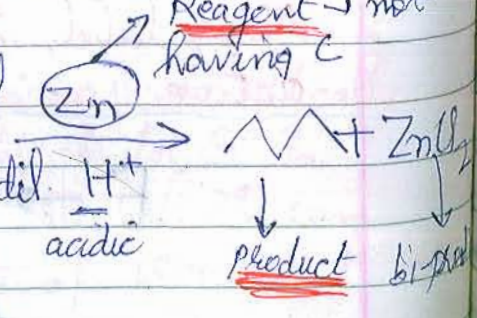


22 Oct 09

Preparation of Alkane → Methods

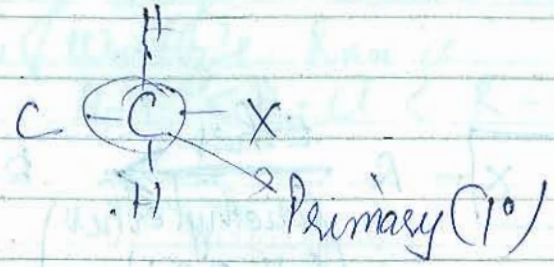
2 * Redⁿ of Alkyl Halides

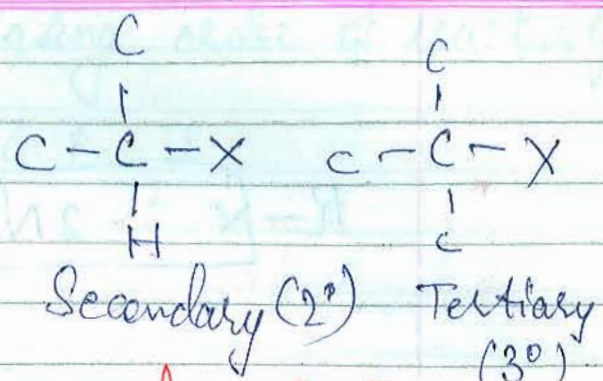
(1) R–X eg 



Substrate

The reactant which contain C.





* Zn reduces all the above compds. (Primary, Secondary & Tertiary)

- Reducing Agents (Most common)
  - $LiAlH_4$ → Lithium Aluminium Hydride
  - $NaBH_4$ → Sodium boro hydride

- $LiAlH_4$ & $NaBH_4$ are mild R.A.s. B/w $LiAlH_4$ & $NaBH_4$, $LiAlH_4$ is stronger R.A.

Points:
1) $LiAlH_4$ reduces 1° & 2° Alkyl hallides into corresponding alkanes. However, tertiary hallide, with $LiAlH_4$ gives alkene. (i.e not alkane)
2) $NaBH_4$, being a slightly weaker R.A, can't reduce the less reactive primary halides, but reduces secondary & tertiary halides into corresponding alkane.

---

3 * Wurtz's Rxn (W.R.)

Statement: When an alkyl hallide is heated with ethereal sol^n of alkali metal, coupling takes place & an alkane is produced.

Me → methyl Ph → phenyl

Et = ethyl → eg : Et_2O : diethyl ether

$$R-X \quad 2Na \quad X-R \xrightarrow[\text{(diethyl ether)}]{\text{Ether}} R-R+NaX$$

($C_2H_5OC_2H_5$, Et_2O → Same meaning)

eg:

$$CH_3CH_2Cl + Na \xrightarrow[\Delta]{Et_2O}$$

Solvent → Ether

metal used → Na (most commonly)
→ ∵ of greater abundance

Role of Et_2O in the above Rxn

or

Why not water is used?

* Solvent should always be inert toward reactant

Here, H_2O ~~will~~ is not used as a solvent

∵ $Na + H_2O \longrightarrow NaOH + H_2$

Ether is the most ~~not~~ inert organic compd.

So, Ether is used as a common solvent in most of the organic ~~rxns~~ syntheses.

Reactivity

R-F
R-Cl
R-Br
R-I

→ R-R

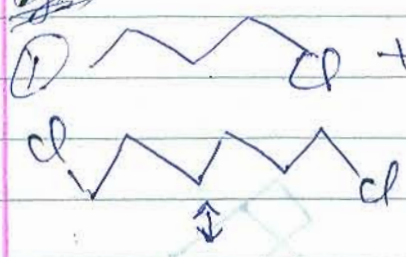
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• Among alkyl halides, increasing order of reactivity in Wurtz's Rxn is

$$R-F < R-Cl < R-Br < R-I$$

Reason: C–F bond is the strongest covalent bond in alkyl halide, most difficult to break, ∴, least reactive in Wurtz's Rxn.

Eg

① 

$$\xrightarrow[\Delta]{Et_2O} \text{(long chain)}$$

→ Intermolecular W.R

b/w 2 ~~cpds~~ molecules

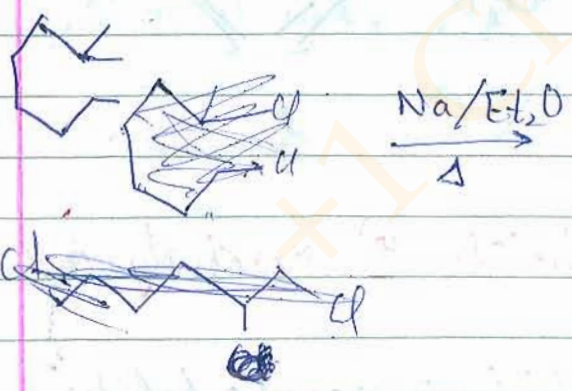
② 

$$\xrightarrow{Et_2O}$$



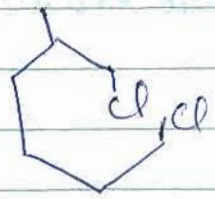
Intramolecular W.R

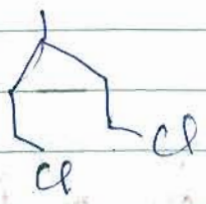
in 1 molecule

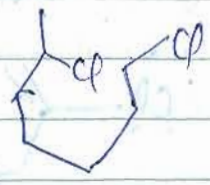


$$\xrightarrow[\Delta]{Na/Et_2O}$$



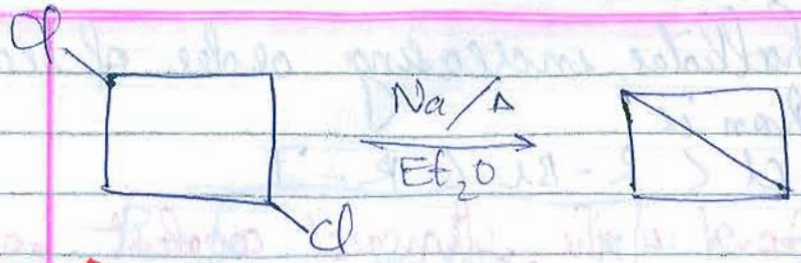
① 

② 

③ 

So, 3 diff^{t} type of di halides + Na → cyclohexane.

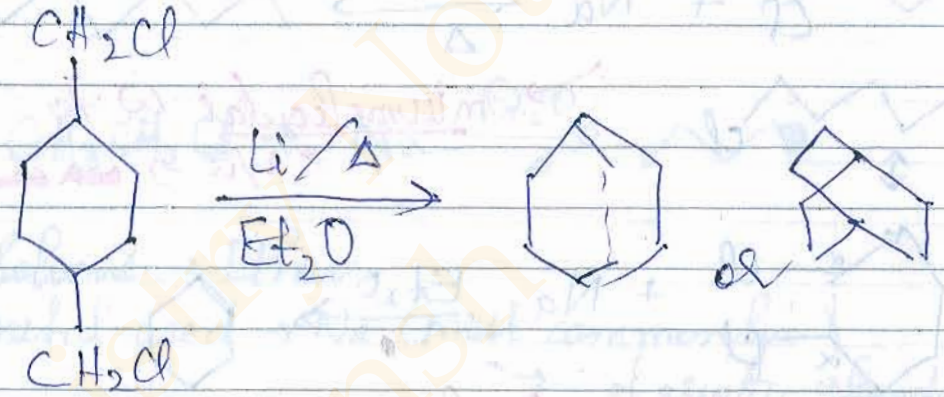
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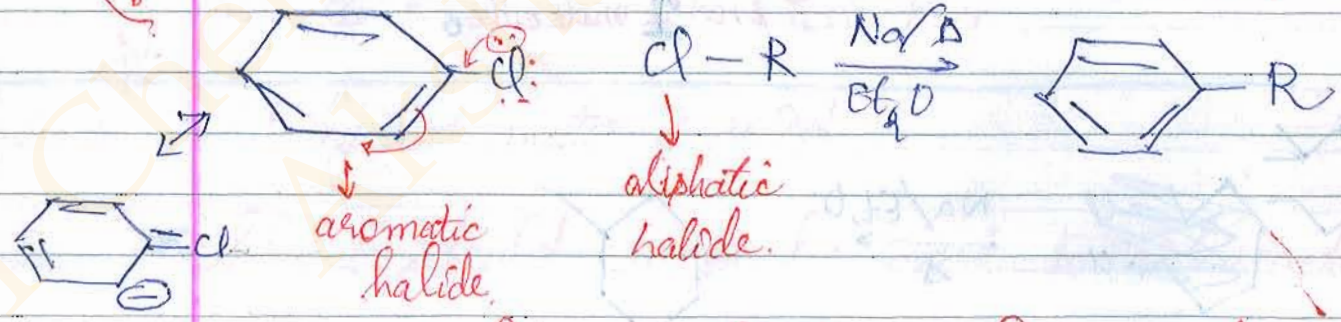
⑥ Basic दोनों

α - carbon वाले end में connect होती है.

eg

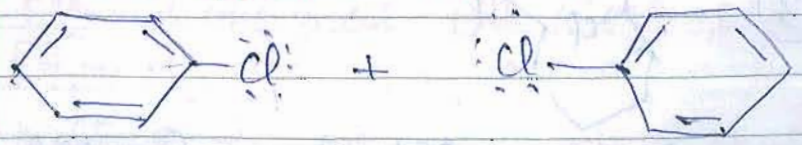


WURTZ's FITTIG's REACTION



So, W.R में aromatic halide की Reactivity कम होती है।

FITTIG's RXN (b/w 2 aromatic halides)



LIMITATIONS of W.R.

1. W.R can't be used for preparation of Methane

Date

e, the smallest alkane which can be obtained by W.R is ethane.

* 2. W.R is not suitable for preparation of unsymmetrical (odd no. of C) alkane.

मतलब → जब Product में कोई compd. में odd no. of C है, तब जिस alkyl grp. से वो बना है, वो दोनों अलग - अलग होंगे i.e

→ $R-X + X-R'$

eg: $CH_3CH_2Cl + CH_3CH_2CH_2Cl \xrightarrow[Et_2O]{Na/\Delta} CH_3CH_2CH_2CH_3 + CH_3CH_2CH_2CH_2CH_2CH_3 + CH_3CH_2CH_3CH_2CH_3$

all combinations will occur

→ जो similar molecule के join होने से बनेगा → Self coupling product

diff^t molecule के join होने से बनेगा → Cross - coupling product

in above case, ⌇ & ⌇⌇⌇ are self coupling products

& ⌇⌇ is cross - coupling product

moreover, all alkanes have similarity (very close) in their physical properties. So, its very difficult to separate them from the mixture.

→ self coupling products

4* KOLBE's RXN (KOLBE's Electrolytic Method Rxn.)

When aq. sol^n of Na or K salt of a carboxylic acid is electrolysed, alkanes are produced.

Free radical : Any species possessing odd no. of e⁻.

Date

$R-\overset{O}{\overset{\|}{C}}-OH$

$R-\overset{O}{\overset{\|}{C}}-ONa \xrightarrow{\text{Electrolysis}} R-R$

$CH_3CH_2CH_2COOK \xrightarrow{\text{Electrolysis}} CH_3CH_2CH_2CH_2CH_2CH_3$

Mechanism : To describe a rxn. on molecular level.

Mechanism :

1) $CH_3CH_2CH_2COOK + H_2O \rightarrow CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}O^- + K^+$

2) $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-\ddot{O}: \xrightarrow{\text{At anode}} CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\dot{O}: + e^-$

Carboxylate — Carboxy Free-radical

Here, carboxylate is oxidised (loss of e^-) into carboxy Free-radical at anode.

3) $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-\ddot{O}: \rightarrow CH_3-CH_2-\dot{C}H_2 + CO_2$

Alkyl free radical.

4) $CH_3CH_2-\dot{C}H_2 \rightleftharpoons \dot{C}H-CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_3$

This could also be possible (i.e carboxy free Radical would directly combine with Alkyl (F.R)

$CH_3CH_2-\dot{C}H \cdot \quad \cdot O-\overset{O}{\overset{\|}{C}}-R$

$\downarrow$

$CH_3CH_2CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$

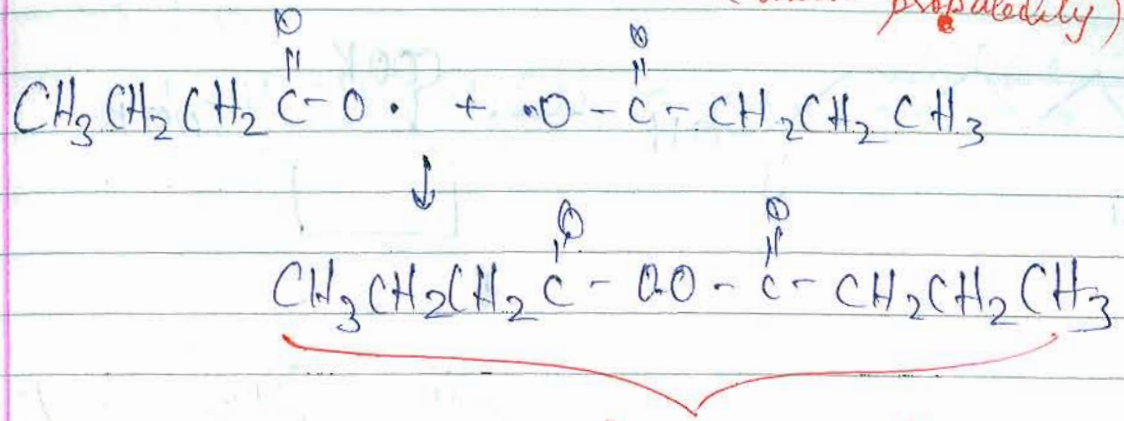
Propyl Butanoate.

* ESTER formed. (bi-product)

• Any compd. containing a O-O single bond is called PEROXY COMPd.

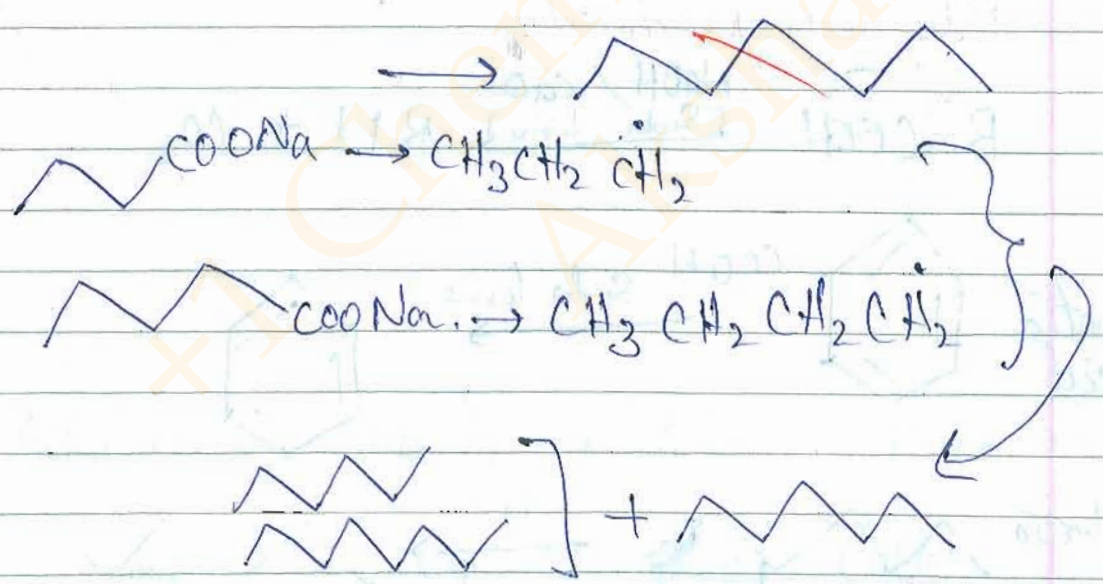
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1 more possibility → (Carboxy F.R & carboxy F.R combines) (comin. probability)



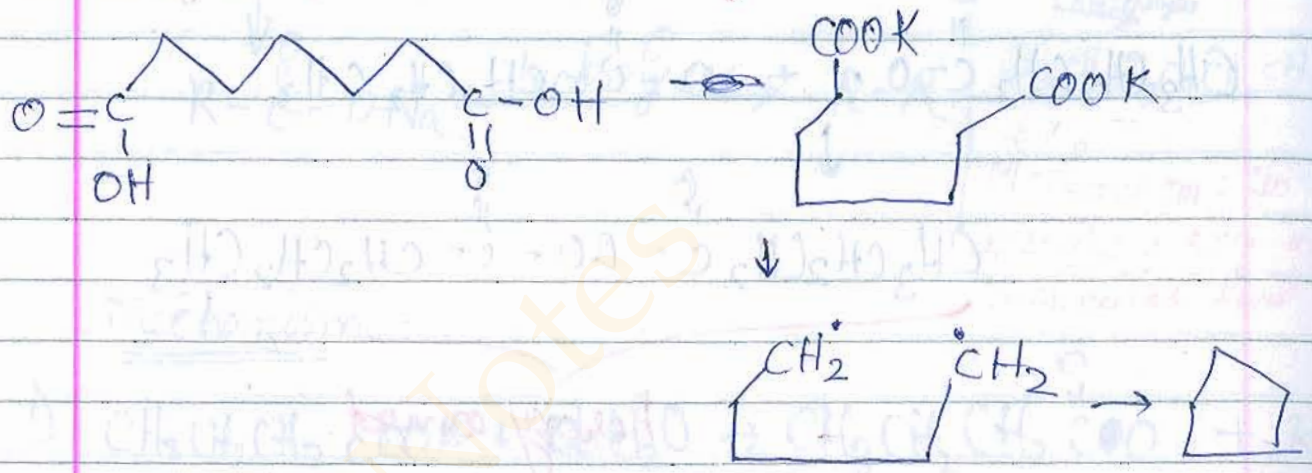
Peroxy compd.

• In Kolbe's Rxn → 3 products formed.
  1) Alkane → Product
  2) Ester → Bi Product
  3) Peroxy compd → Bi product



☆ like W.R, Kolbe's Method is not suitable for the preparation of unsymmetrical alkane. More than 1 type of salts will have to be electrolysed simultaneously. Under this condn, besides (cross-coupling, self-coupling products are also produced in comparable (~~comparatively less~~) amt.

Q. heptanedioic acid $\xrightarrow[\text{Electrolysed}]{KOH(aq)}$

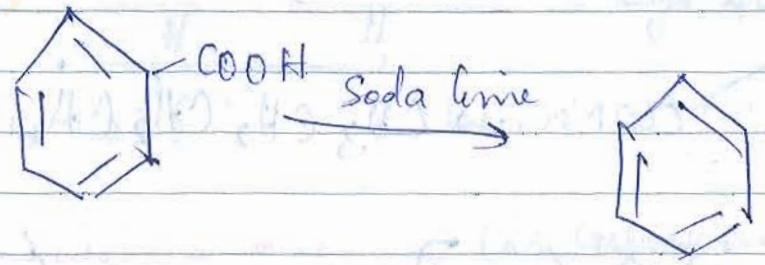


5A DECARBOXYLATION OF RCOOH

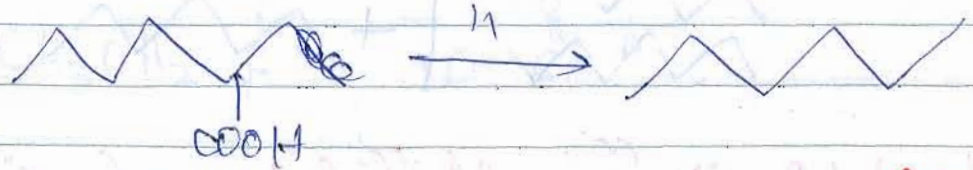
When a carboxylic acid is heated with $Ca(OH)_2$ (soda lime), decarboxylation (loss of CO_2) takes place & alkane is produced.

$$R\text{-}COOH \xrightarrow[\text{(Soda-lime)}]{NaOH/CaO} RH + CO_2$$

aromatic acid



aliphatic acid



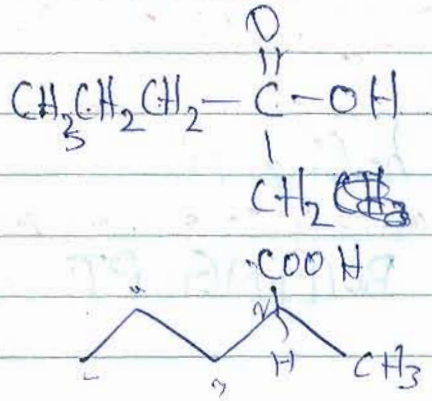
Q. A chiral acid ($C_6H_{12}O_2$) $\xrightarrow[\Delta]{NaOH/CaO}$ pentane

What is acid.

1) E_N of C & H are very close — almost same.
2) Physical properties of compd. depend on intermolecular attⁿ.

C_5H_{12}

$CH_3CH_2CH_2CH_2CH_2COOH \xrightarrow{\text{Soda lime}}$



: 25 | 10 | 09

✡ Properties of Alkanes

PHYSICAL

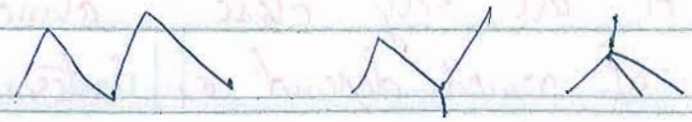
① Boiling pt:

Alkanes are highly volatile — Have Vanderwaal bond. So,

from $C_1 - C_4$ → gases (alkanes)
$C_5 - C_7$ → volatile liquids.
C_{18} - - - - → Solids.

Vanderwaal force of attⁿ depends on molar mass.

✡ Pts. 1) In general, alkanes have very low boiling & melting pt. compared to other organic compds.



Date

2) The only intermolecular force present in alkanes is Vanderwall force which depends on —
(a) Molar mass → Higher Molar M, greater Vanderwall ~~(b) Structure~~ force of attⁿ, higher will be boiling pᵗ.
(b) Structure : Among isomers, Vanderwall F.O.Attⁿ depends on Surface area of contact. Greater the S.A, higher will be Boiling pt. i.e branching decreases the boiling pt.
~~(c) Effective surface area — area of contact~~
NO EXCEPTIONS IN BOILING PT.

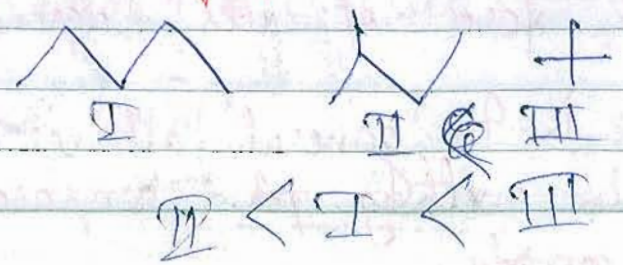
(2) Melting Pt.

Melting is a phenomena associated with solid state of matter. It also depends primarily on inter-molecular force of attⁿ. In general M.Pt. increases with Molar mass. (∵ Vanderwaall F.O. attⁿ increases) however, exception occur in the following cases →

1) Melting pts. of linear chain, unbranched alkane containing odd no. of Carbons is smaller than the adjacent homologues with even no. of C.

2) Among isomeric alkane, greater the symmetry, higher the melting pt.

eg



5, 4, 6, 8

4, 5, 6, 8

IV I II III

Date

q (2)

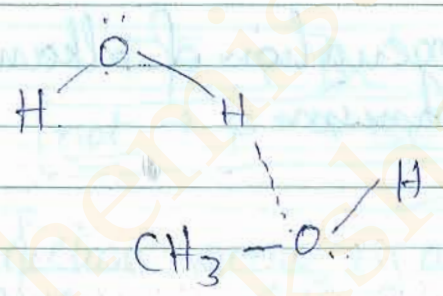
C_4H_{20} → most symmetrical structure.

(3) Density

Hydrocarbons are all lighter than H_2O; have Density < 1 g/cm³

Melting pt. depends on efficiency of packing (i.e how fast a molecule becomes in solid state)

(4) Solubility



Hydrocarbons are all insoluble in H_2O, but soluble in other hydrocarbons.

= Molecules of like nature dissolve in one another. (i.e polar–polar, non polar–non-polar etc)

☆ Reactivity of organic compd. depends on the fnal grp. present in that compd.

☆ Chemical reactivity of organic compd depends on nature of fnal grp. present in that compd. Alkanes are one of them – least reactive organic compd. due to absence of any fnal grp. It reacts only under drastic condn (extreme condn)

Chemical Rxns

** 1) HALOGENATION

Alkane, on treatment with halogen in presence of light or heat, undergo halogenation to give alkyl halides.

$$R-H + X_2 \xrightarrow[\text{or heat } (\Delta)]{\text{light } (h\nu)} R-X + HX$$

(X_2 = F_2, Cl_2, Br_2, I_2)

1) Halogenation of alkane follow free radical mechanism.

Ex.

* Electrophile : Electrophiles are e^- deficient species which require e^- in order to become stable. Electrophile can be a neutral ~~(BF_3)~~ or a +vely charge (H^+) species. Some common electrophiles are H^+, Cl^+, BCl_3, $BeCl_2$. ALL LEWIS ACID ARE ELECTROPHILES

TYPES OF BOND - FISSION

(1) Homolytic Bond fission

(2) Heterolytic

(1)

A bond fission in which shared pair of e^-s are distributed equally after bond fission.

then the type of fission is known as homolytic bond fission. Homolytic bond fission always produces a pair of free radicals. (So in homolytic bond fission, paramagnetic species(2) are produced)

It is in homonuclear (b/w same molecules) & heteronuclear (b/w 2 diff^t molecules).

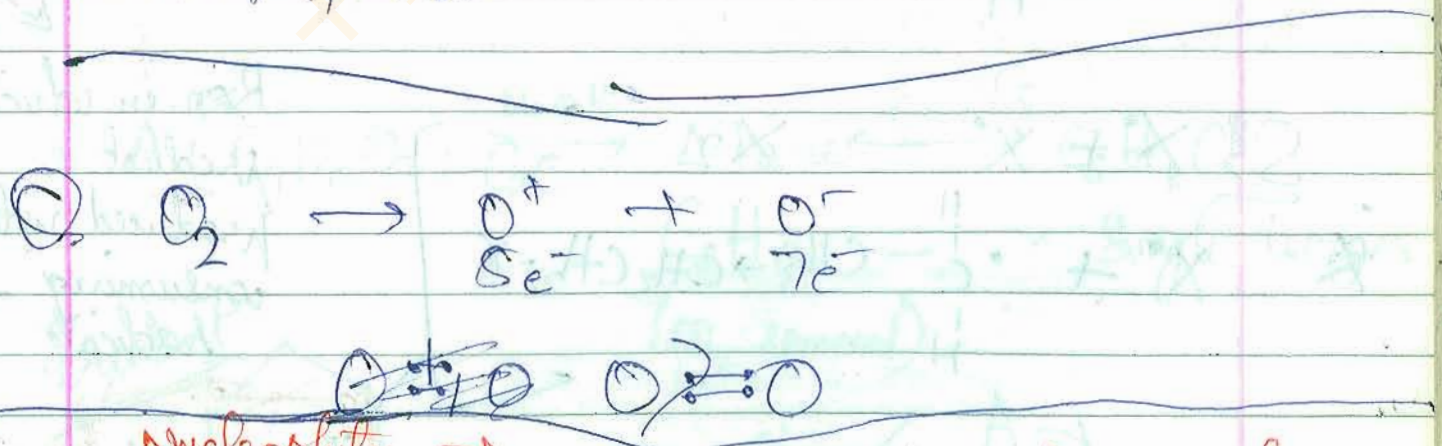
(2) If shared pair of e$^-$s goes only with 1 atom after bond fission, then the type of fission is called heterolytic bond fission.

$A \overset{\cdot}{-}\!\!\!/\; A \longrightarrow A^- + A^+$

$F \overset{\cdot}{-}\!\!\!/\; Br \longrightarrow F^- + Br^+$

not $\rightarrow F^+ + Br^-$

If heterolytic fission occur in a ~~heterolytic~~ heteronuclear diatomic molecule, shared pair of e$^-$s goes with the more electro -ve atom after bond fission



Nucleophiles →

~~Electrophile~~ They are e$^-$ rich species which can share some of its valence e$^-$s with an electrophile without losing its own stability. Nucleophile can be a neutral or a -vely charged species

eg: NH_3, $H_2\ddot{O}$:, $:PCl_3$ (neutral)

(-ve) → HO^-, Cl^-, Br^-, NO^-, NO_3^-, SO_4^{-2}, S^{2-}

Date

Halogenation – A free radical MECHANISM

All free-radical rxns. are chain rxns. & include 3 imp. steps: 1) Initiation 2) Propagation 3) Termination

S1 $X-X + h\nu \longrightarrow 2X^{\bullet}$

Initiation → Rxn in which radical is produced effectively.

S2 $CH_3-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-H + X^{\bullet} \rightarrow CH_3-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}^{\bullet} + HX$

Alkyl free radical

$CH_3-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}^{\bullet} + X-X \rightarrow CH_3-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-X + X^{\bullet}$

Propagation → Rxn in which product is produced without consuming radical

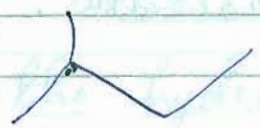
S3 $X^{\bullet} + X^{\bullet} \rightarrow X_2$

$X^{\bullet} + \cdot\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-CH_3 \rightarrow CH_3CH_2-X$

Termination → Rxn in which Radicals are consumed effectively

Termination: In halogenation rxn., the steps in which radicals are consumed effectively are called termination.

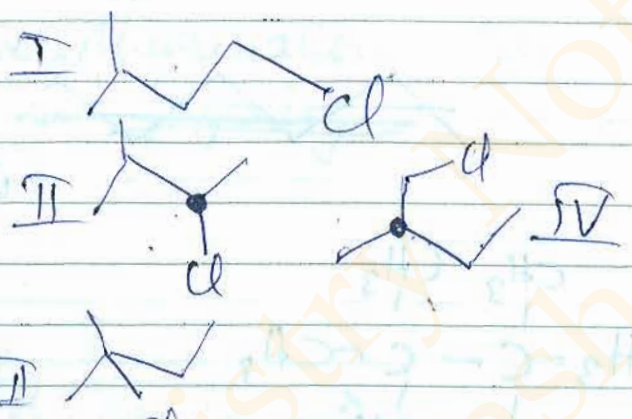
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Q.  + Cl_2 $\xrightarrow{h\nu}$ (A) how many mono-chlorobutanes (only structural iso)

(B) — " — (including stereo isomers)

$CH_3CH_2CH_3$

(A) ④4



(B)

(B) 6. (only optical isomerism)

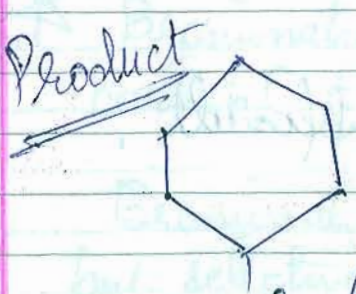
Q. An organic compd. A, has molecular formula $C_7H_{12}O_2$ which on heating with soda lime gives an alkane, which on treatment with Cl in presence of sunlight gives $C_6H_{11}Cl$ as single isomer. What is structure of A?

$A(C_7H_{12}O_2) \xrightarrow[CaO]{NaOH}$ Alkane $\xrightarrow{Cl_2/h\nu}$ $C_6H_{11}Cl$

C_6H_{12} Single isomer

(CO_2 removed)

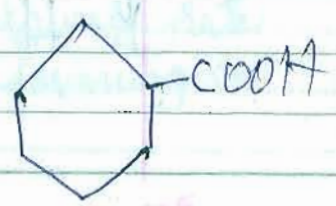
Product



Cl (Single product)

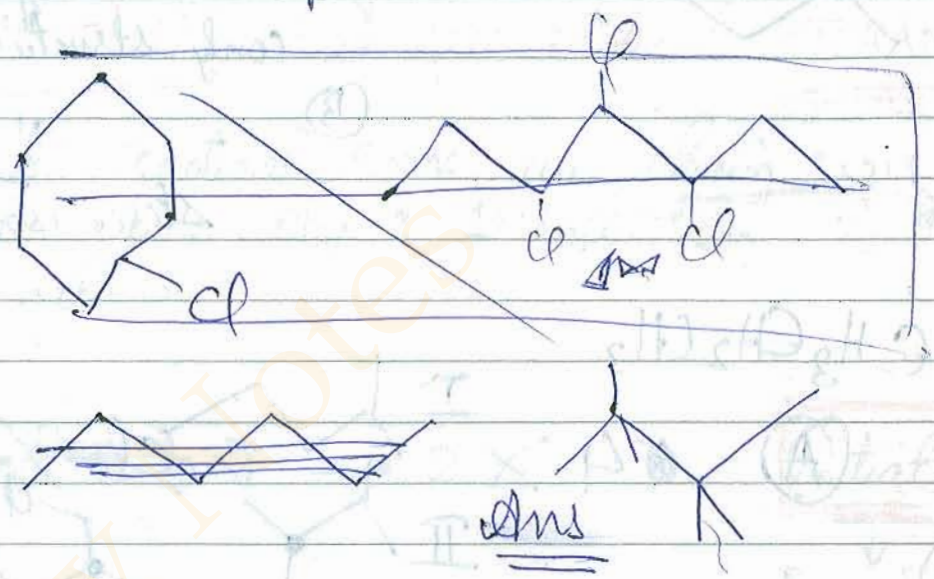


A →

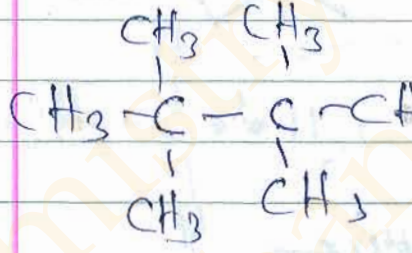


Date

Q. $C_8H_{18} \xrightarrow[h\nu]{Cl_2}$ Single monochloroalkane.



Ans



So, no. of isomers in a molecule relates with its structure.

☆ Reactivity of diff^t halogens

Reactivity of halogens towards free radical halogenation decreases from top to bottom.

~~Chlor~~ ~~Chloromethane~~

Fluorination → easiest

Iodination → most difficult.

$R-H + F_2$ / Cl_2 / Br_2 / I_2 ↑ reactivity.

Date

① **Fluorination** → Freacts violently with alkane even at room temp. & all the hydrogens are replaced by F together.

eg

$CH_4 + 2F_2 \longrightarrow CF_4 + 4HF$

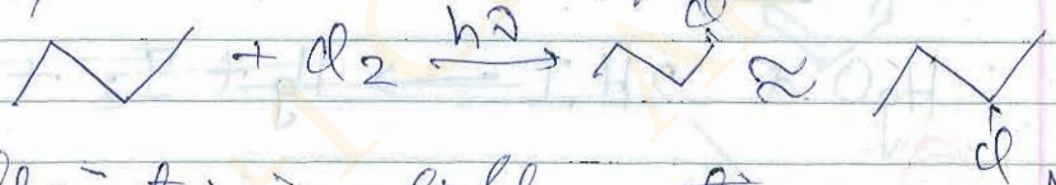
$C_2H_6 + 3F_2 \longrightarrow C_2F_6 + 6HF$

Due to exhaustive fluorination, direct fluorination is never used for preparing → ~~ex.~~ monofluoro alkane

~~Fluorination &~~

② Chlorination / Bromination :

Cl is more reactive than Br ∴ Chlorination occur at all C with comparable ease giving all possible isomers in comparable amts.



Chlorination is a highly reactive process but very less selective process. Amt. of all isomers formed would be comparable.

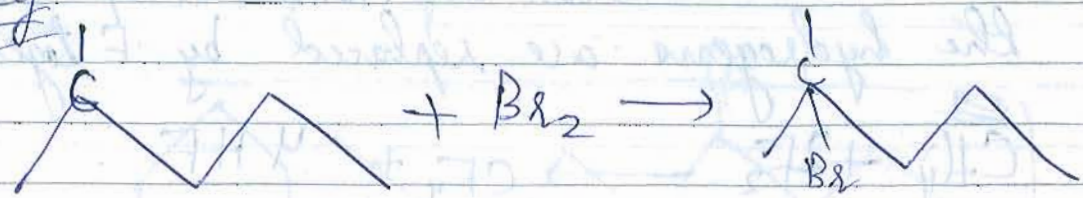
(of alkane)

✡ Bromination occur selectively at highest degree carbon (∵ higher degree C is most reactive)

Bromination of alkane occur at slower rate but selectively at highest degree C forming a single product as major product.

Date

So,
eg.



☆ Iodination

$R-H + I_2 \longrightarrow R-I + HI$

(HI → highest reducing agent.)

~~Hydrogenation~~

Iodination, if occured would revert back with same product due to presence of HI which would reduce it to R-H again.

Iodination possible by using catalyst → HgO

$HgO + 2HI \longrightarrow Hg + I_2 + H_2O$

29/10/09 JUST FOR NCERT

Reaction Rxns. of Alkanes.

☆ Oxidation of Hydrocarbon

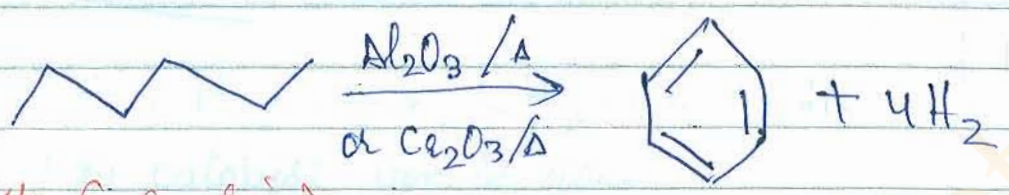
{Combustion} $C_nH_{2n+2} + \frac{(3n+1)}{2}O_2 \longrightarrow nCO_2 + (n+1)H_2O$

Some Rxns.

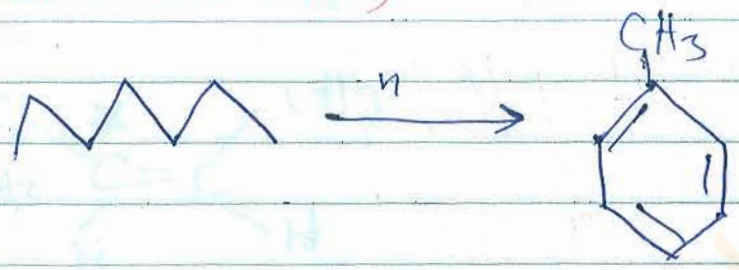
Date

* $R-H \xrightarrow[O_2/\Delta]{CuO} R-OH$ (alcohol) $+ Cu$.

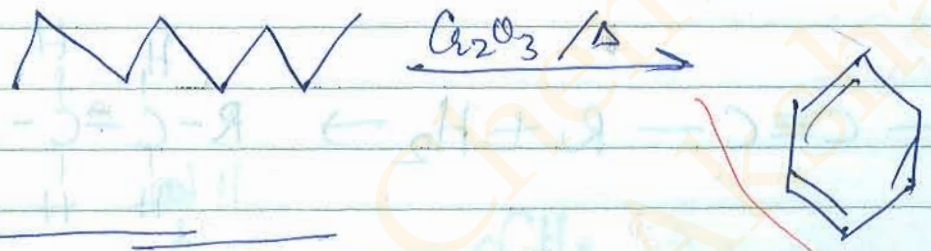
* AROMATIZATION



(atleast 6 C chain)

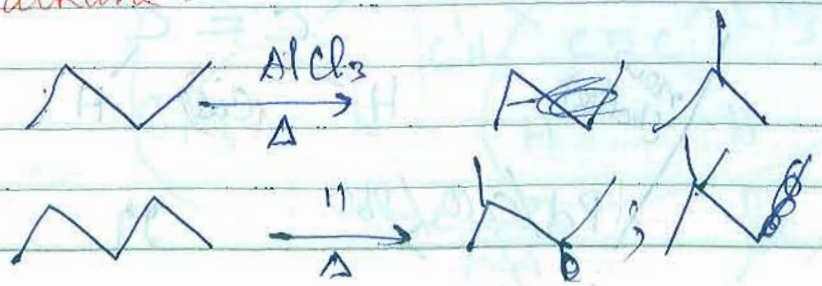


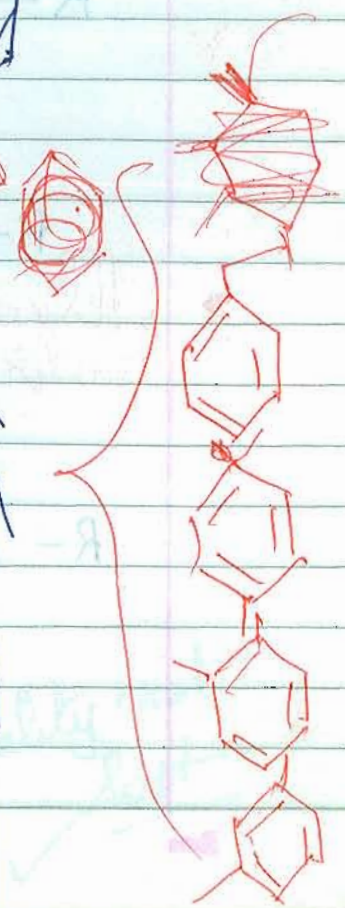
बराबर Benzene होते हैं.
Additional C → Locant बनेंगे.



* Isomerization

When linear chain alkane is heated with a lewis acid catalyst, it isomerises into a branched chain alkane.





Date

Alkene

C_nH_{2n}

☆ PREPARATION

1. By Controlled / Partial Hydrogenation of Alkyne, alkene is produced.

$$R-C\equiv C-R + 2H_2 \rightarrow R-\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}-R$$

$$R-C\equiv C-R \longrightarrow R-CH=CH-R$$

- Alkyne can be successfully hydrogenated only partially by proper choice of catalyst.

$R-C\equiv C-R$ → old: $Pd/C/H_2$ → Palladium metal supported over activated charcoal + H_2

$R-C\equiv C-R$ → new (better): $Pd/CaCO_3/PbO$ → Lindlar's Catalyst

$$\underset{H}{\overset{R}{C}}=\underset{H}{\overset{R}{C}}$$ (Cis)

or all alkali metals, alkali earth metals

$$R-C\equiv C-R \xrightarrow[\text{liq } NH_3]{Na} \underset{\text{trans}}{\text{R, H alkene}}$$

Q. $CH_3-C\equiv CH \longrightarrow CH_3-CH=CH_2$

Any catalyst can be used

$H_3C-C\equiv C-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\ast}{C}=C(CH_3)(H)$

(A) $H_2/Ni/\Delta$

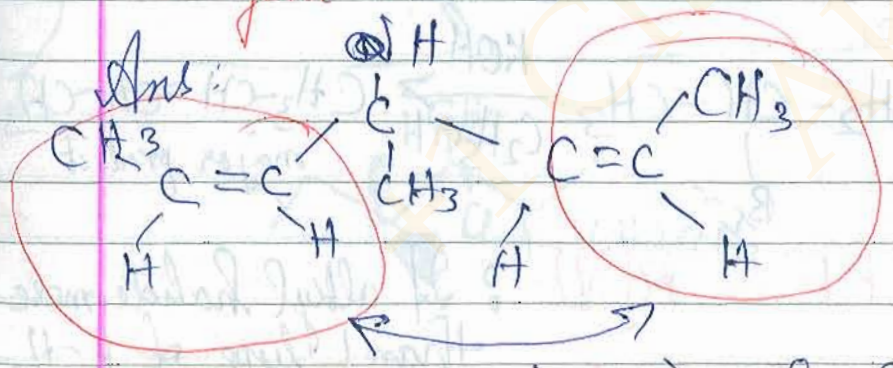
(B) $Na/liq.\ NH_3$

(C) $Pd/CaCO_3/PbO$

(D) All of above

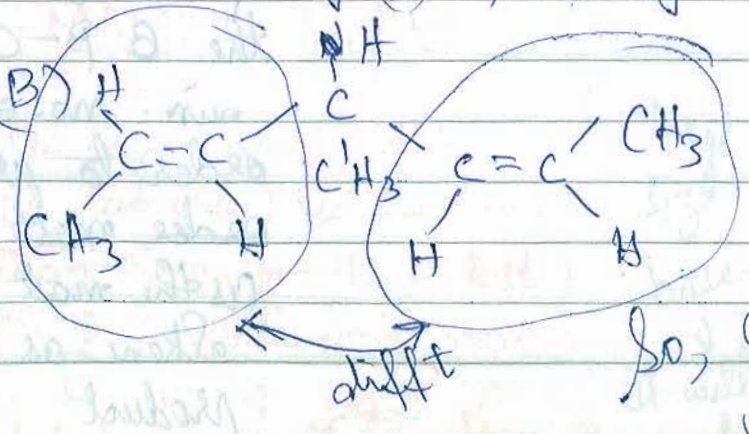
Q. The following hydrocarbon will give an optically active product with which of the following reagent.

Ans:



using (C), chirality lost.

In (B)



diff t

So, chirality not lost

(B) ✓

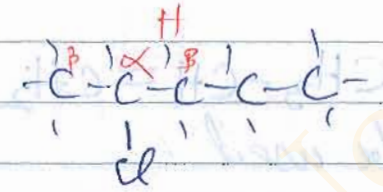
• जिस C पर final grp. हो उसे α-C कहते हैं।

• Teflon → poly Tetra fluoro ethylene

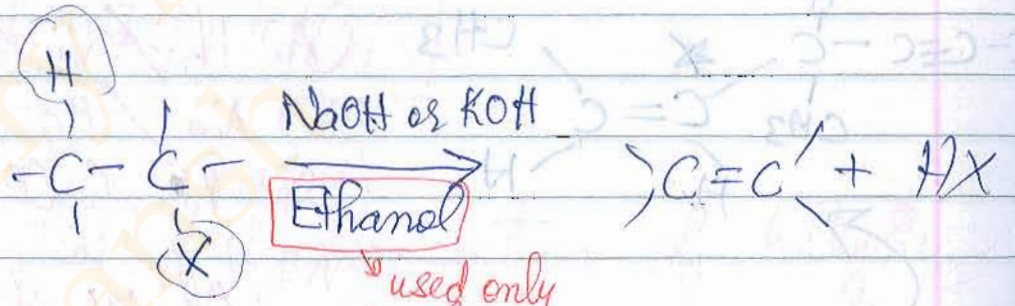
Date

☆ (2) By Dehydrohalogenation of Alkyl halides

$R-X$



An alkyl halide containing 1 β H, when treated with alcoholic soln of strong base (usually NaOH or KOH), Dehydrohalogenation takes place to produce alkene.



{X → Cl, Br, I ; not F}

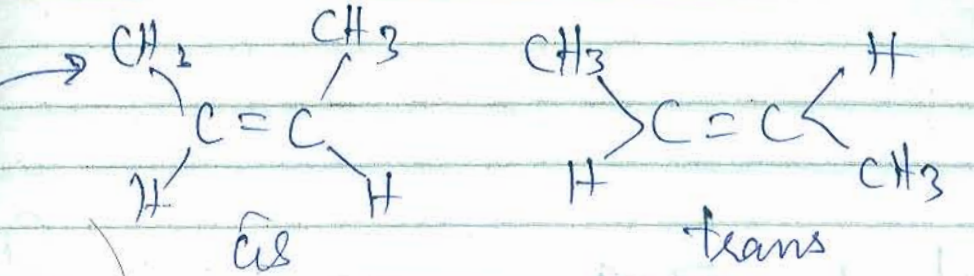
Elimination Rxn.

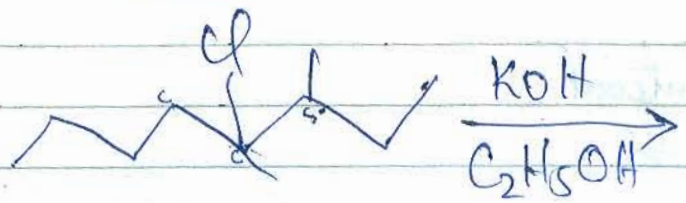
$CH_3-CH_2-\underset{Br}{CH}-CH_3 \xrightarrow[C_2H_5OH]{KOH} CH_3-CH=CH-CH_3$ major product

Poor become Poorer → SYTZEFF'S RULE OF ELIMINATION: If alkyl halide more than 1 type of β-H, β-H is lost from the 6 β-C containing min. no. of H_2 in order to produce ~~order~~ most substituted as the most stable alkene as major product

☆ C-I bond is very strong, inert.

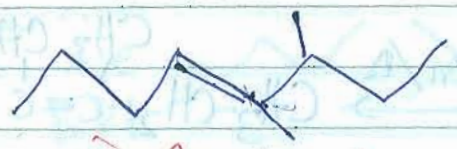
Date



Q. 

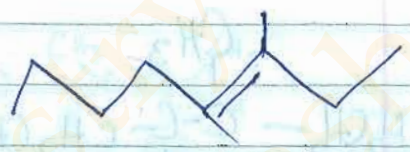
~~$C_4H_9-CH_3$~~

Tell total isomers.

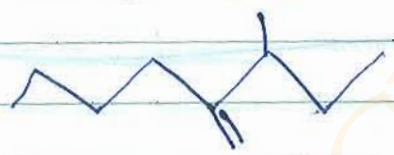
① 

~~cis & trans~~

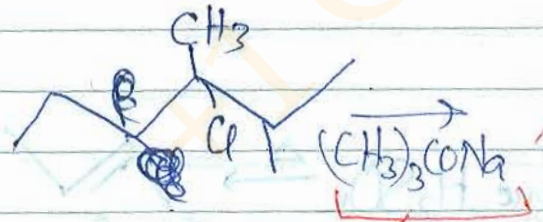
E-Z

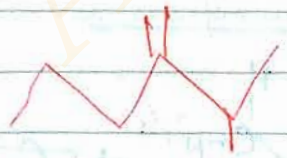
② 

cis & trans
major

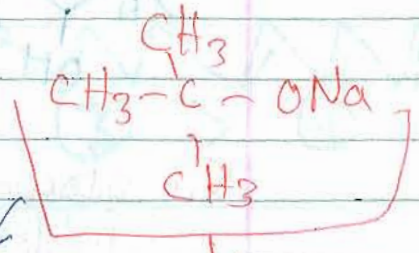
③ 

So, total → 5





ROH → RO^- (alkoxide)



HOLFMANN'S RULE

If large sized base (Na/K Tertiary butoxide) is used in elimination Rxn, β-H is lost from the β-C containing max. no. of H giving least substituted, least stable alkene as major product

large size base

Sodium Tertiary butoxide

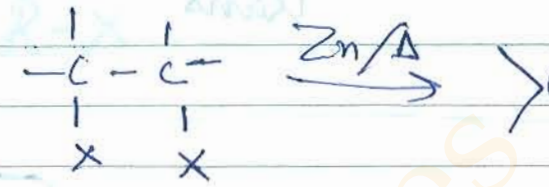
It will take H from β → C containing max^ H

अगर Identical final grp. adjacent identical C पर हों,
तब ० उसे Vicinal कहते हैं

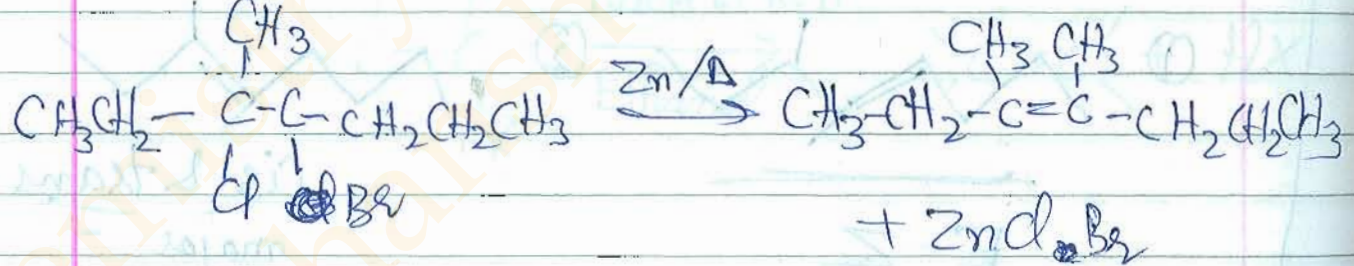
Date

(3) Dehalogenation of Vicinal dihalides

OH
Cl

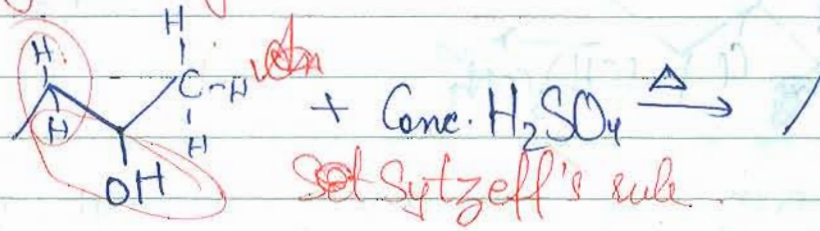


Identical
अगर ~~Identical~~ final grp. को एक ही C पर रख दें तो → Geminal कहते हैं।





(4) By Dehydration of Alcohols



Saytzeff's rule.

(absorbs H_2O)
dehydrating agent

An alcohol on heating with conc. H_2SO_4 loses a molecule of H_2O to produce alkene.

Date

✡ PROPERTIES

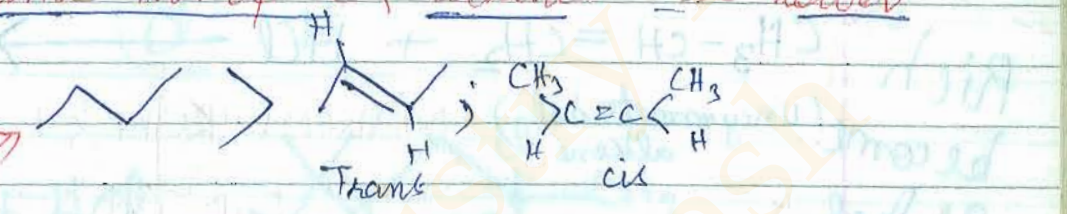
(1) Physical

(depends on intermolecular force)

§1. Like alkane, alkenes are also highly volatile substance. B.Pts. of alkane & alkene containing equal no. of Cs are very close due to comparable molar mass & vanderwaal force of attⁿ. B/w alkane & alkene containing same no. of C, alkenes have lower B.Pt

i.e

B.Pt →



If an alkene has geometrical isomers, cis isomer has lower B.Pt. than its trans (∵ of S.A)

Among alkenes B.Pt. increases with molar mass. If (diff⁺ no. of double bonds are present in a hydrocarbon of same chain length (same no. of C), increasing the no. of double bonds, more the no. of double bond, smaller will be B.Pt.

i.e

B.Pt → (1) > (2) > (3) > (4)

§2 Melting Pt: With same no of C, alkenes have smaller melting pt. than alkane.

Reactions of Alkene

(1) Addition Rxn.

$$-\overset{|}{C}=\overset{|}{C}- + AB \longrightarrow -\overset{|}{\underset{A}{C}}-\overset{|}{\underset{B}{C}}-$$

(A) Addition of HX (HCl, HBr, HI, HF)

$CH_3-CH=CH_2 + \overset{+}{H}\overset{-}{Cl} \longrightarrow CH_3-\underset{(Cl)}{CH}-\underset{(H)}{CH_2}$

(unsymmetrical alkene) MARCONIKOFF's Rule (MK's Rule) ~~VE's~~

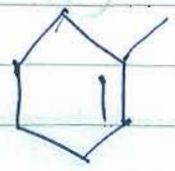
Rich become Richer

Acc to MK's Rule, +ve part of the addendum (जो add होता है) is added to the C bearing more H's.

Q. Which of the following on addition of HCl will produce pair of stereo isomers.

(1) $CH_3-CH=\overset{CH_3}{\overset{|}{C}}-CH_3$

(2) $CH_3-CH=\overset{H}{\overset{|}{C}}-CH_2CH_3$

(3) 

(4) 

✱✱ R-O-O-R → Organic Peroxide.

Date

(1) $CH_3-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_3 + HCl$

$\rightarrow CH_3-\underset{\displaystyle H}{\overset{\displaystyle |}{CH}}-\underset{\displaystyle Cl}{\overset{\displaystyle |}{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}}}-CH_3$

(2) $CH_3-CH=\underset{\displaystyle H}{\overset{\displaystyle |}{C}}-CH_2CH_3 + HCl \longrightarrow$

$CH_3-\underset{\displaystyle Cl}{\overset{\displaystyle |}{\underset{\displaystyle H}{\overset{\displaystyle |}{CH}}}}-\underset{\displaystyle H}{\overset{\displaystyle |}{\underset{\displaystyle H}{\overset{\displaystyle |}{C}}}}-CH_2CH_3$ ~~$CH_3CH_2-CH-C_2H_5$~~

(3) $+ HCl \rightarrow$

move stepwise on both side of cycloalkane, if identical grps. are found on 2 sides of ring, then that C is non chiral.

(4)

1 Nov. 2009

(B) ✱ Addition of HBr in presence of Peroxide.

(Kharash Effect)

$R-CH=CH_2$ (unsymmetrical) $+ HBr \xrightarrow[H_2O_2]{ROOR \text{ or}} RCH_2CH_2Br$ [By Anti-Markonikoff's Rule]

Occurs only with H-Br.

Common inert, non-aqueous organic solvents (instead of H_2O) →
Ether, ~~Ethene~~, CCl_4 (Carbon tetra chloride)

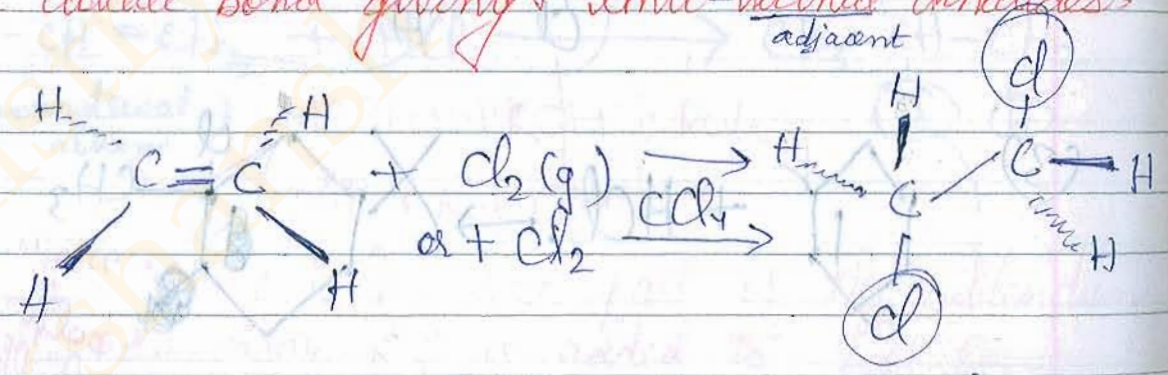
Date

☆ In anti-Markonikoff addⁿ or Kharash Effect

→ Observed only with H-Br (not with HI, HF or HCl)

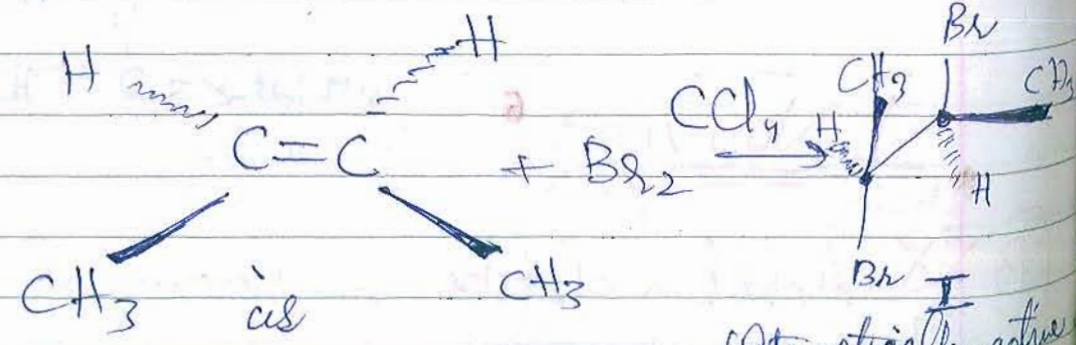
(C) Addition of Halogen (X_2)

(I) Dry addⁿ of X_2:
In dry condⁿ, halogen is added to the C-C double bond giving Anti-vicinal (adjacent) dihalides.

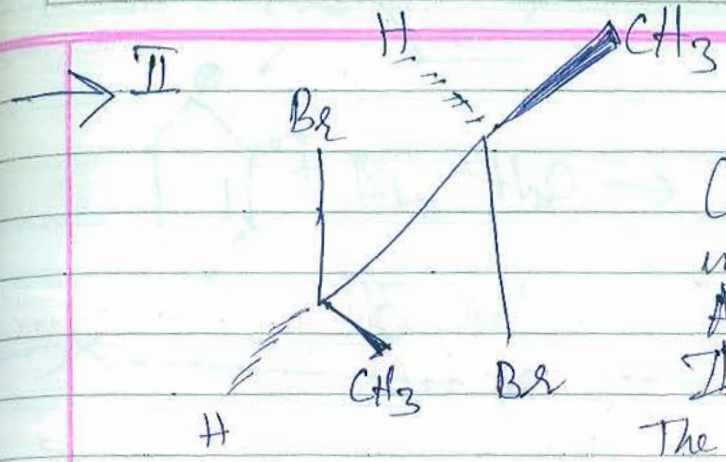


* i.e, one from above the plane & 1 from below the plane, → X_2 would be added.

eg

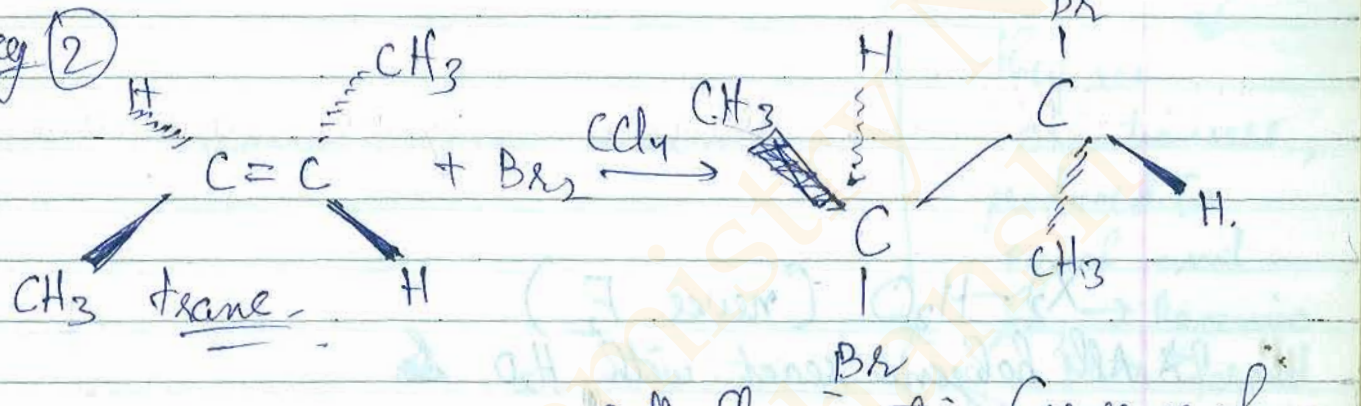


(Its optically active ∵ it doesn't have centre & plane of symmetry)



Clearly, I & II are mirror image of each other. Also, I is optically active. So, II will be enantiomer of I. The probability of formation of I & II is same. So, this is a RACEMIC MIXTURE formed.

eg (2)

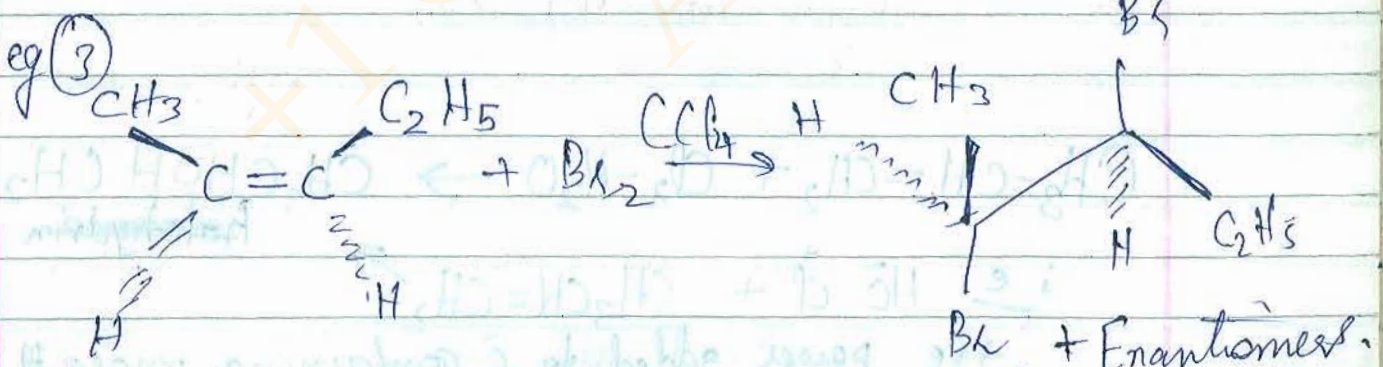


trans.

Optically inactive (presence of Centre of sym)

So, its a meso compd.

eg (3)



+ Enantiomers.

* It a Racemic Mixture formed.

Its trans. part will also be a Racemic Mix.

☆ Compd containing both hydroxy & halogen are called halohydrin

Date

Summarising

If alkene is stereomeric & can show cis-trans isomerism, cis-symmetrical will give Racemic Mixture, trans-symm. will give Meso product.
Unsymmetrical cis/trans always give Racemic Mixture.

II Addition of Halogen in aqueous medium.

$X_2 - H_2O$ (never F_2)

☆ All halogens react with H_2O.

$$X_2 + H_2O \longrightarrow \underset{HO^- \mid X^+}{HOX} + HX(g)\uparrow$$

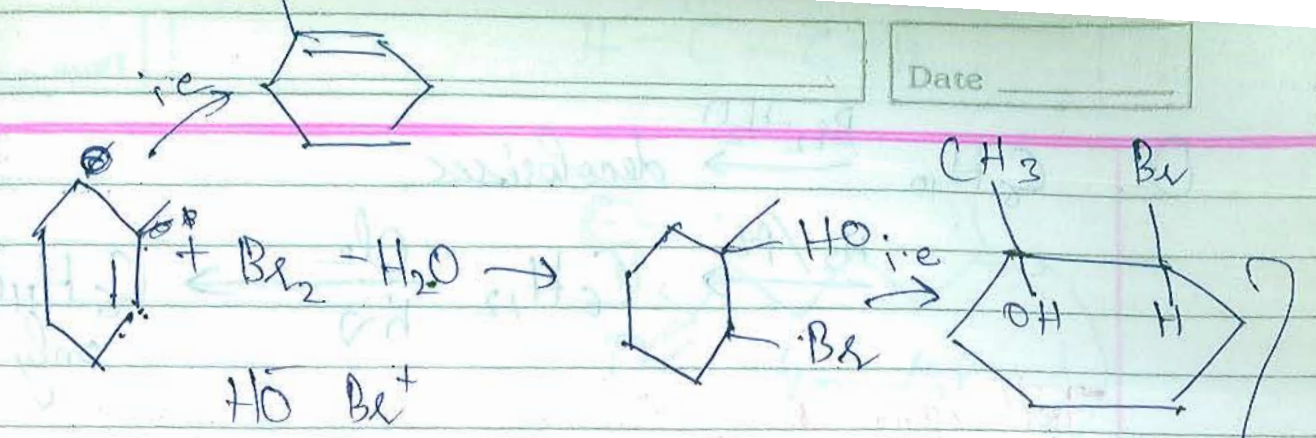
• All HX are gas at Room Temp.

$$CH_3-CH=CH_2 + Cl_2-H_2O \longrightarrow CH_3\underset{\text{Halohydrin}}{\underset{|}{C}H(OH)}-CH_2Cl$$

i.e $HO\overset{+}{Cl} + CH_3CH=CH_2$

+ve power added to C containing more H_2, By MK's rule.

∴ Alkene, on treatment with aq. soln of Halogen give anti-halohydrin acc. to MK's rule.



☆ Bromine is deep brown liquid at room temp.

When Br dissolved in H_2O, then Br doesn't react 100% to form $HO^- Br^+$.

Some amt. of Br would be left unreacted, thus, making the soln brown.

- Visible changes → colour change, ppt, gas evolved.

They are enantiomers, produced in equal amt. So, → Racemic Mix. formed.

☆ BROMINE Water Test

Br in aq. soln is brown in color due to dissolved Br. Br water when added to a compd containing C-C π bond (alkene & alkyne), brown color of soln disappear due to rxn. on Br, on double bond forming colourless Dibromide (Br_2) or Bromohydrine (BrOH).

If a compd. decolorises Br H_2O → It contains C-C π bond.

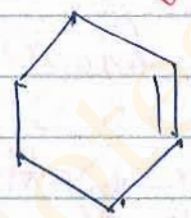
C_6H_{10}

Date

Q. $C_6H_{10} \xrightarrow{Br_2\text{-}H_2O}$ decolorises.

$\xrightarrow{H_2/Pt} C_6H_{12} \xrightarrow[h\nu]{Cl_2} C_6H_{11}Cl$ only isomer.

Tell name of starting compd.

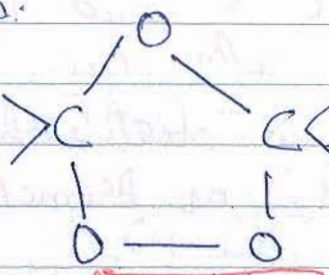
Ans →  → Starting compd. cyclohexene

(D) Ozonolysis Rxn.

When an alkene, is treated with ozone, an unstable intermediate OZONIDE is formed. Ozonide, on further workup with Zn (pwde) in aq. medium undergo red^n to produce aldehydes or ketones or both. Depending upon nature of alkene.

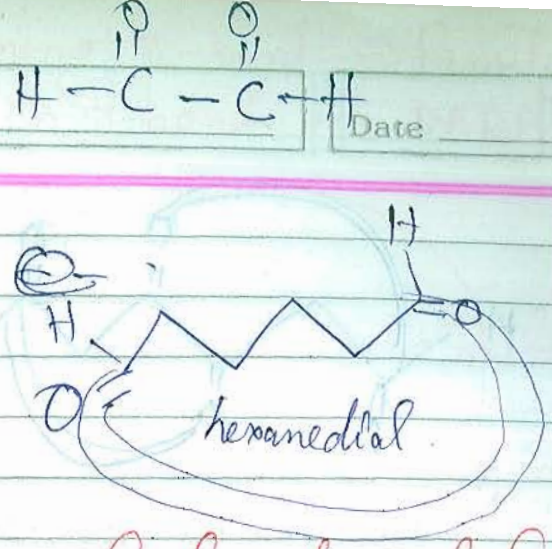
This Rxn is known as Reductive Ozonolysis.

********* very Imp. Rxn.

$>C=C< + O_3 \longrightarrow$  $\xrightarrow[H_2O]{Zn} >C=O + O=C< + ZnO$

Ozonide

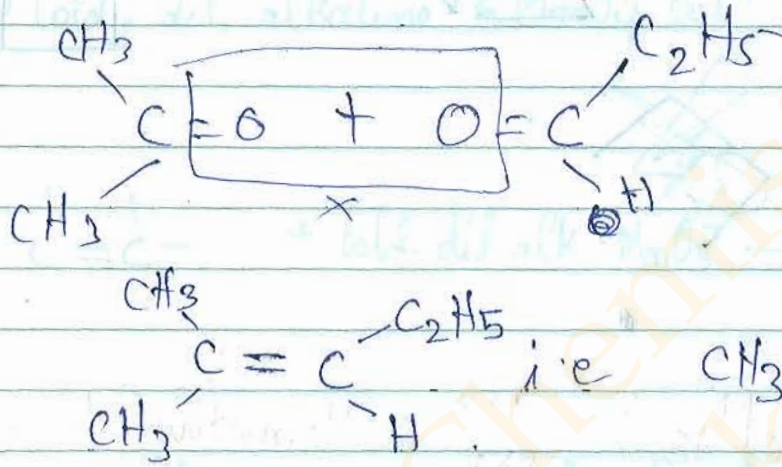
Q. An alkene of 6-C on ozonolysis, followed by $Zn\text{-}H_2O$ gives hexane dial. What's alkene.



Q. An alkene A has molecular formula, C_6H_{12},

$A\ (C_6H_{12}) \xrightarrow{O_3} \xrightarrow{Zn-H_2O}$ Propanone + an aldehyde.

A → structure ?



$$CH_3-C(CH_3)=CH-CH_2-CH_3$$

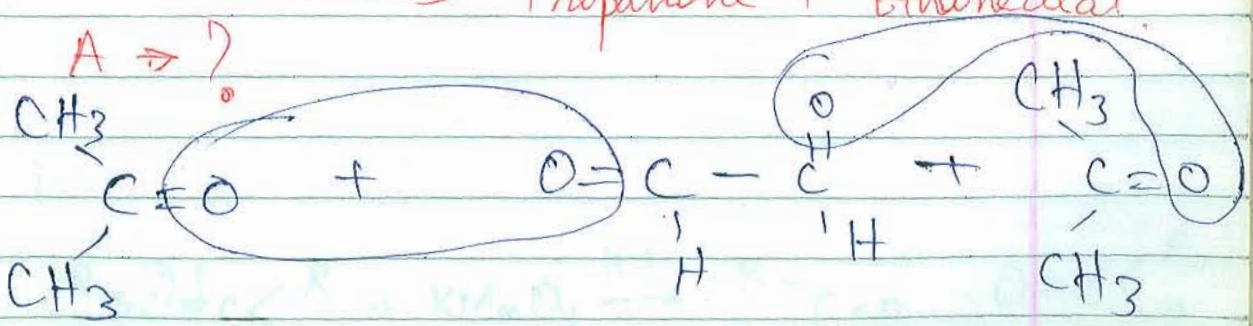
Q.

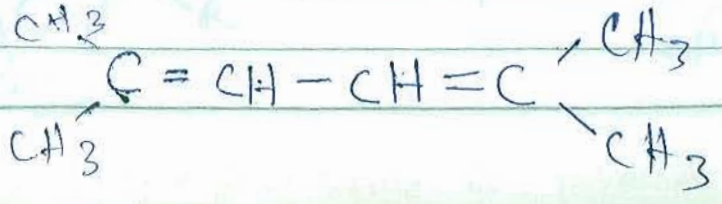
$A\ (C_8H_{14}) \xrightarrow{H_2/Pt} C_8H_{18}$

$\downarrow O_3$

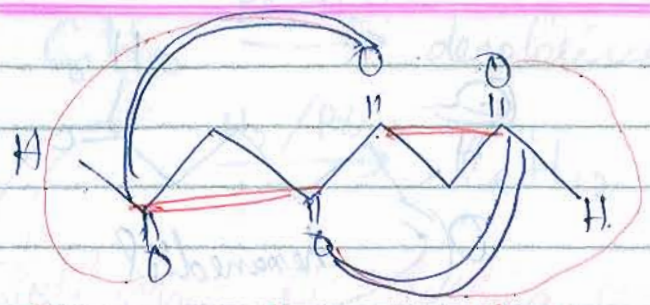
$\xrightarrow{Zn-H_2O}$ Propanone + Ethanedial

A → ?

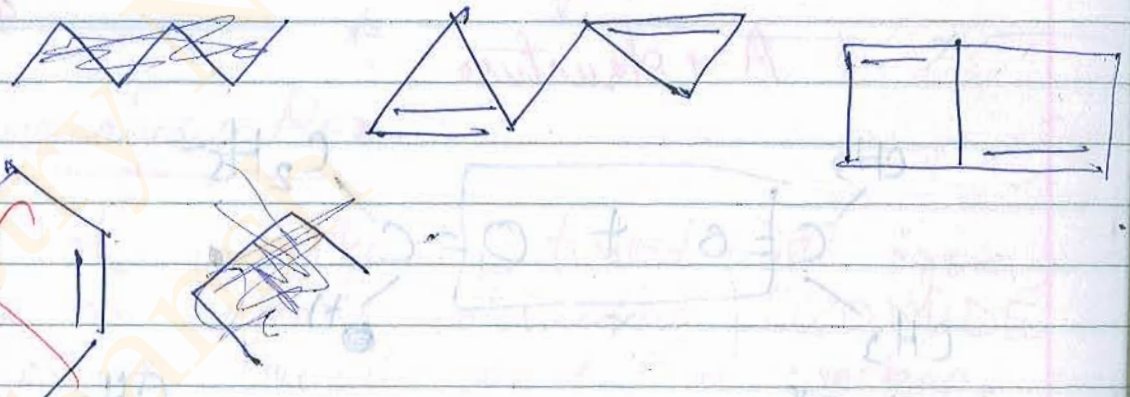


A :— 

2,5-dimethylhex-3,4-diene



Propose atleast 2 hydrocarbon structures containing 6 C only which give above on ozonolysis (Reductive).



Q. A ($C_{10}H_{18}$) $\xrightarrow[Ni]{H_2}$ 4-methyl-1-isopropyl cyclohexane

Also A, on ozonolysis followed by Zn Hydrolysis gives methanal + $CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2C$ $=O$

Find A ?

HW

called → OLEFINS. No π-bonds → PARAFFIN

(E) Rxn with $KMnO_4$

- $KMnO_4$ in alkaline medium act as a mild (weak) O.A (Oxidising agent).
  Whereas, in acidic medium, it act as a strong O.A.

$$KMnO_4 \longrightarrow K^+ + MnO_4^-$$

(MnO_4^-: Purple color) → Mn^{2+}

(MnO_4^-) → $MnO_2\downarrow_{(s)}$

(1) Cold, dil. alkaline $KMnO_4$ soln : BAYER'S REAGENT

$$-\overset{|}{C}=\overset{|}{C}- + \text{cold. dil alk. } MnO_4^- \longrightarrow -\overset{|}{C}(OH)-\overset{|}{C}(OH)- + MnO_2\downarrow$$

Vicinal diol

* Presence of π-bond can be detected using Bayer's Reagent
  ↓
  BAYER'S TEST

If a compd. decolorises purple color of Bayer's Reagent, it indicate presence of double / triple bond in compd.

So, OLEFINS decolorises Bayer's Reagent.

(I) With acidic $KMnO_4$

$$R\text{-}\overset{H}{C}=C\langle_{R}^{R} + KMnO_4 \xrightarrow{H^+} R\text{-}\underset{OH}{C}=O + O=C\langle_{R}^{R}$$

H → acid

If any H is present on C, then, carboxylic acid would be formed.

(F) With dilute H_2SO_4 $\left[HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{-}{O}\right]H^+$

eg: $CH_3-CH=CH_2 + \underset{[Cold]}{dil.\ H_2SO_4} \longrightarrow CH_3-\overset{\overset{H}{\oplus}}{CH}-CH_2$

$CH_3-\underset{\underset{O-SO_3H}{|}}{CH}-CH_2 \xrightarrow{\Delta}$ By MK's rule

$CH_3-CH=CH_2$ (alkene)

★ ~~Prep~~ Separation of alkene from mixture of alkane & alkene.

5/11/09

ALKYNES

C_nH_{2n-2}

TYPES

$R-C\equiv C-H$ (triple bond at end of chain) → TERMINAL ALKYNE

$R-C\equiv C-R$ (triple bond in b/w chain) → INTERNAL ALKYNE

$R-C\equiv C-R$ — Symmetrical alkyne

$R-C\equiv C-R'$ — Unsymmetrical alkyne

Date

H_2O (excess) → (slow heating) i.e Refluxing

$CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{H}{|}}{CH_2}$ (hydration) (acc. to MK's rule)

(alcohol)

☆ PREPARATION OF ALKYNES

(1) From Calcium carbide (CaC_2)

Calcium carbide, on hydrolysis gives ethyne (acetylene).

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + \underset{\text{acetylene}}{H-C\equiv C-H}\ (g)$$

Application of acetylene → welding, ripening.

(2) From geminal or vicinal dihalides :-

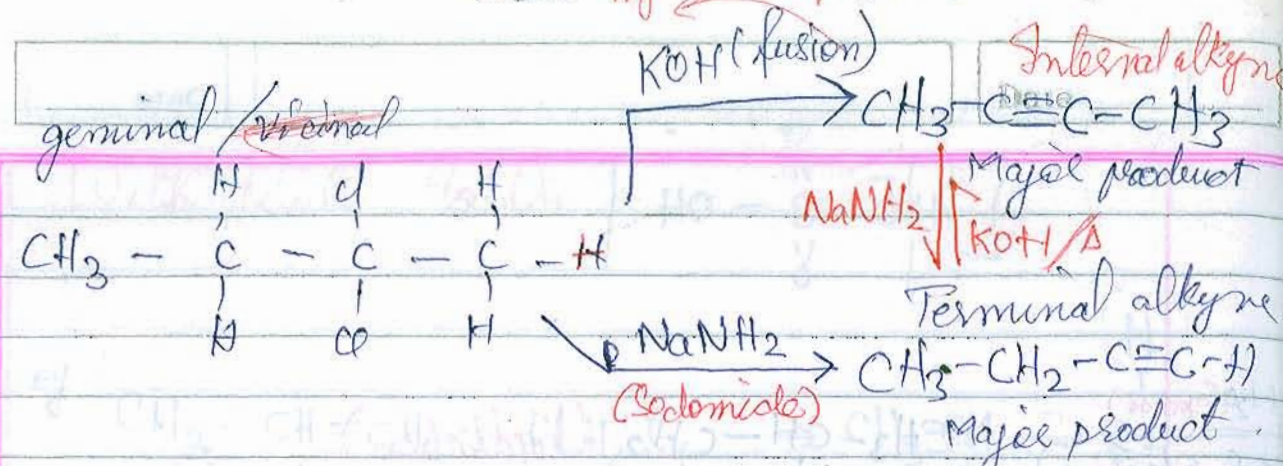
(Same C ✱ ✱) (adjacent C ✱ ✱)

geminal: $-\overset{Cl}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-$ ⟶ Double Dehydro halogenation

vicinal: $-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$ ⟶

$-C\equiv C-$

means high heating (200°C ----->)



Q. 8.

☆ (8) fusion of either geminal / vicinal dihalide gives internal alkyne as the major product.

☆ If geminal / vicinal dihalide is treated with aq. sol^n of sodamide, terminal alkyne is produced as the major product.

☆ KOH के साथ fuse करेंगे → Internal alkyne
$NaNH_2$ के साथ treat करेंगे → Terminal alkyne.

Q. (a) $CH_3CH_2CH_2CH=CH_2$ → $CH_3CH_2CH_2-C\equiv CH$ (1)

$\xrightarrow{Cl_2/CCl_4}$ $CH_3CH_2C\equiv C-CH_3$ (2)

(b) $CH_3CH_2CH_2CHClCH_2Cl$

KOH / Δ, fusion → gives (2)

$NaNH_2$ (aq) → gives (1)

Q. $C_3H_8 \longrightarrow C_3H_4$

$-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}- \longrightarrow -\overset{|}{C}-C\equiv C-$

Chlorination

Dehydro halogenation elimination

$CH_3CH_2CH_3 \xrightarrow{Cl_2/\Delta \text{ or } Cl_2/h\nu}$ $CH_3CH_2-CH_2Cl$ + $CH_3CH(Cl)-CH_3$ $\xrightarrow{alc.\ KOH}$ $CH_3CH=CH_2$

$CH_3CH=CH_2 \xrightarrow[\text{halogenation}]{Cl_2/CCl_4}$ $CH_3-CH(Cl)-CH_2(Cl)$

Double dehydro elimination: $\xrightarrow{KOH\ (\Delta) \text{ or } NaNH_2\ (aq.)}$ $CH_3-C\equiv CH$.

8(3) From vicinal tetrahalide

$$R-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-R \xrightarrow{2Zn/\Delta} R-C\equiv C-R + 2ZnCl_2$$

Double Dehalogenation

8(4) From ~~vicinal~~ Geminal trihalides

$$R-C(Cl)_3 \xrightarrow{Ag\ Ag} C-R \longrightarrow R-C\equiv C-R + 6AgCl$$

✡ PROPERTIES OF ALKYNE

(A) With the same no. of C, alkynes have lower melting pt. as well as boiling pt. than alkene or alkane.

Date

- Among alkynes, both B.Pt. & M.Pt. increases with molal masses.

Most IMP.

Chemical Properties

(1) **ACIDITY**: Terminal alkynes are slightly acidic.

$R-C\equiv C-H$

Internal alkyne not acidic (∵ H not present at terminal)

(a) $R-C\equiv C-H + Na \xrightarrow{\Delta} R-C\equiv C^-Na^+ + \frac{1}{2}H_2\uparrow$

(R-C≡C-H plays role of acid; Na (base) plays role)

$+ NaOH(aq.) \longrightarrow$ No rxn.

$R-C\equiv C-R + Na \xrightarrow{\Delta}$ No rxn.

☆ This Na metal can be used to differentiate terminal & internal alkyne.

Terminal alkyne, on heating with Na metal gives effervescence of $H_2(g)$.

No effervescence is observed with internal alkyne.

☆ $R-C\equiv C-H$ is weakly acidic. So, it requires a very strong base, stronger than OH^- (water).

These bases are → NaH (Sodium hydride), $NaNH_2$ (Sodamide), Na (metal)

All these bases can be used for distinguishing internal & terminal alkyne.

$R-C\equiv C-H + NaH \rightarrow R-C\equiv C^-Na^+ + H_2\uparrow$

$+ NaNH_2 \rightarrow R-C\equiv C^-Na^+ + NH_3(g)\uparrow$

(ppt.)

Dehydrohalogenation → removal of halogen

Date

(b) (2) Preparation of higher alkyne from acetylene

$$H-C\equiv C-H + Na \xrightarrow{\Delta} \underset{Na^+}{H-C\equiv C^-} + \tfrac{1}{2}H_2\uparrow$$

(only alkyne having 2 acidic H)

a nucleophile displaces another halide nucleophile

$$H-C\equiv C^- Na^+ + H_3C-Cl \longrightarrow H-C\equiv C-CH_3 + Cl^-$$

Na^+ dropped as no role in rxn

i.e

$$H-C\equiv C\boxed{Na + Cl}R \longrightarrow H-C\equiv C-R + NaCl$$

Imp — Imp.

called as

- Nucleophilic substitution rxn. ✱✱
- Chain-extension Rxn.

Generalization

$$R-C\equiv C-H + Na/\Delta \longrightarrow R-C\equiv C^- Na^+ \xrightarrow{Cl-R'} R-C\equiv C-R'$$

$$H-C\equiv C-H + Na/\Delta \xrightarrow{\text{excess}} {}^-C\equiv C^- \xrightarrow{R-Cl} R-C\equiv C-R$$

$$\xrightarrow{Cl-R}$$

$$H-C\equiv C-H \xrightarrow{Na/\Delta} \xrightarrow{CH_3Cl} CH_3-C\equiv C-H \xrightarrow{Na/\Delta} \xrightarrow{CH_3CH_2Cl} CH_3-C\equiv C-CH_2CH_3$$

Date

(3) Reaction with Tollen's Reagent & Fachling Solution

TOLLEN'S REAGENT

It is an ammonical soln of $AgNO_3$ used for a test known as Silver Mirror Test

- Terminal alkyne gives Silver mirror test with Tollen's Reagent, can be used for both distinction & separation of terminal alkyne from internal alkyne.

$$\underset{\text{Colourless}}{R-C\equiv C-H} + AgNO_3 \xrightarrow{NH_3(aq)} R-C\equiv C-Ag\downarrow$$

(Silver salt of alkyne (insoluble))

(H → acidic H)

Distinction → Silver ppt formed → a mirror type of thing is formed.

★ $R-C\equiv C-R + AgNO_3 \xrightarrow{NH_3(aq)}$ No rxn

Distinction

$$\left.\begin{matrix} R-C\equiv C-H \\ R-C\equiv C-R \end{matrix}\right] + AgNO_3 \xrightarrow[(aq.)]{NH_3} \underset{ppt}{R-C\equiv C-Ag}\downarrow + \underset{(sol^n)}{R-C\equiv C-R}$$

Separation

$$R-C\equiv C-Ag + dil.\ HCl \longrightarrow R-C\equiv C-H + AgCl\downarrow$$

★ Ag (salt) brings complete ppt also. others don't

Date

Fehling's Solution

It is an ammonical soln of Cu^{2+} – tartarate (Cyric tartarate) → Cyric ion

- Terminal alkyne on treatment with Fehling's soln gives deep red colored ppt. of cyprous salt of terminal alkyne.

$$R-C\equiv C-H + Cu^{2+} \xrightarrow[(aq.)]{NH_3} R-C\equiv C^-Cu^+ \downarrow$$

Red colored ppt.

This can also be used for separation of terminal alkyne from internal alkyne.

- It is a good rxn. to differentiate b/w terminal & internal alkyne ∵ along with ppt., color also appear. So, its better as compared to others.

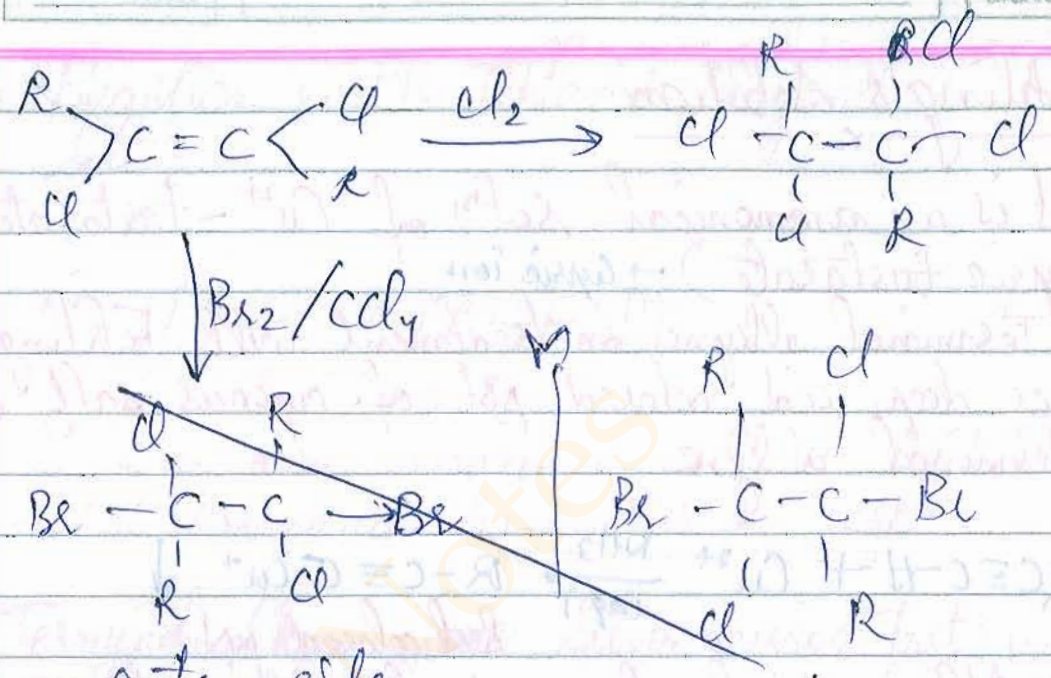
(4) Addition of Halogen

(a) If halogen is added in dry cond^n, first, dihalide is formed which on further rxn. with excess of Halogen gives tetrahalide.

$$R-C\equiv C-R + Cl_2/CCl_4 \longrightarrow \underset{Cl}{\overset{R}{\diagdown}}C=C\underset{R}{\overset{Cl}{\diagup}}$$

1 : 1 ratio → trans dihalide is only produced. (trans only (∵ + comes from anti-side))

If Cl (excess) → rxn will continue.



(It has centre of symm.)

So, its a meso compd.

⑤ Hydrogenation

Like alkene, alkyne undergo catalytic hydrogenation in presence of Ni/Pt at high temp. Hydrogenation occur in uncontrolled manner giving alkane as the end product.

$$R-C\equiv C-H + H_2 \xrightarrow[\Delta]{Ni/Pt} R-CH_2CH_3$$

Q. An organic compd. A with molecular formula C_6H_8 is optically active & gives effervescence with Na metal. A on treatment with H_2/Pt gives optically inactive C_6H_{14}. Identify A.

A (C_6H_8) is o·A $\xrightarrow{3H_2}$ C_6H_{14}

Date



$CH_2=CH-\overset{*}{C}(CH_3)-C\equiv C-H$ → on hydrogenation gives an optically inactive compd. ∵ the compd will become symmetric about C with *.

12/11/09

✱6) HYDRATION OF ALKYNES

Q $R-C\equiv C-H + H^+/OH^- \longrightarrow$

$R-C(OH)=C-H$ unstable → tautomerises to keto form → $R-C(=O)-CH_2-H$

During hydration Rxn, H_2O is added at C-C triple bond acc. to Markonikoff's rule.

$R-C(=O)-CH_3$ Ketone

$CH_3CH_2CH_2-C\equiv C-CH_3 + H^+/OH^- \longrightarrow$

$CH_3CH_2CH_2-C(OH)=C-CH_3$ + $CH_3CH_2CH_2-C(H)=C(OH)-CH_3$

H & OH can be added in any orientation.



Oxymercuration Rxn. of alkyne → name of the rxn. discussed before.

→ Oxymeracuration - demercuration of alkyne.

$R-C\equiv C-H + HgSO_4/H_2SO_4 \longrightarrow R-\underset{\underset{O}{\|}}{C}-CH_3$ Ketone

$H-C\equiv C-H + HgSO_4/H_2SO_4 \longrightarrow H-C(OH)=C-H$

$H-C(H)=C(OH)-H \longrightarrow H-C(H)(H)-C(=O)-H$ ethanal

only 1 alkyne will give aldehyde → otherwise mainly Ketone

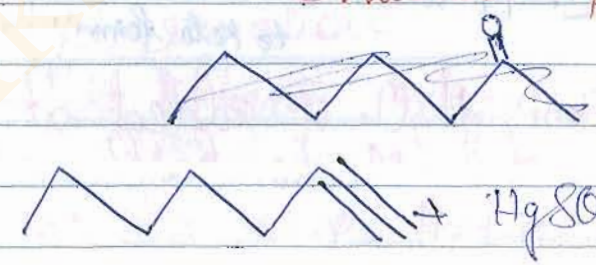
Q. $A \rightarrow C(C_7H_{12}) \xrightarrow[Pt]{H_2} C_7H_{16}$

$\downarrow HgSO_4/(H_2SO_4\ aq.)$

$B(C_7H_{14}O)$

Single Isomer

Structure of A.



$A \rightarrow C_5H_{11}-C\equiv C-H$

A is optically active

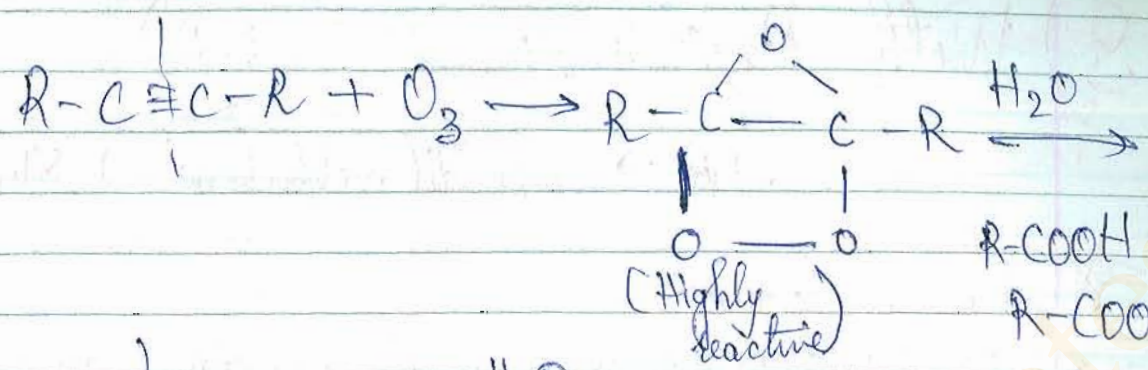
$CH_3CH_2CH_2-C(CH_3)(H)-C\equiv C-H$ ✓

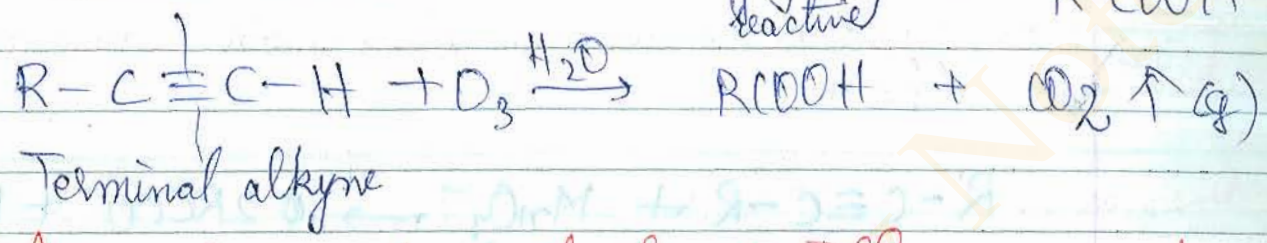
or

$CH_3CH_2-C^*(CH_3)(H)-CH_2-C\equiv C-H$

Date

7) Ozonolysis





☆ An organic compd. on treatment with ozone produces a compd. that turns lime water ~~alke~~ milky. So, the starting organic compd. will be Terminal alkyne as shown above.

—— × ——

Q. $C_{10}H_{14} + H_2/Pt \longrightarrow C_{10}H_{22}$

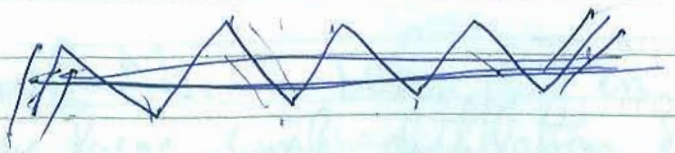
$\downarrow O_3/H_2O$

$2C_4H_8O_2 + H_2C_2O_4$ oxalic acid

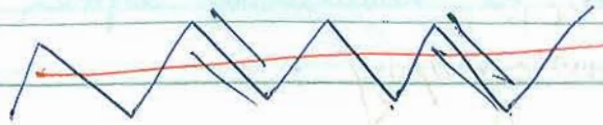
Structure of starting hydrocarbon?

→ $CH_3CH_2CH_2-C\equiv$

$2(CH_3CH_2CH_2COOH) + \underset{\underset{COOH}{|}}{CDOH} \longrightarrow \equiv C-C\equiv$



~~2,6-dec~~



dec-2,6-yne

Starting compd. →

Date

$CH_3CH_2CH_2-C\equiv C-C\equiv C-CH_2CH_2CH_3$

8) With Bayer's Reagent (BR)

BR → cold, dil, alkaline, $KMnO_4$

☆ Alkyne decolorises purple color of BR. So, BR can't be used to distinguish b/w alkene & alkyne.

$$R-C\equiv C-R + MnO_4^- \longrightarrow 2RCOO^- + MnO_2$$

(BR)

Since medium is alkaline, so, $RCOOH$ formed would be neutralised to its salt to form $RCOO^-$.

$$R-C\equiv C-H + \text{[illegible]} \longrightarrow RCOO^- + CO_2\uparrow$$

Only for NCERT

SEPARATION Techniques

1. Sublimation
2. Crystallization
3. Distillation
4. Extraction
5. Chromatography

Date

(1) Sublimation method of purification/separation is used when one of the component is volatile, sublime on simple heating, while the other is stable to heat. When the mixture is heated, the more volatile substance sublimes leaving behind residue of the stable component.

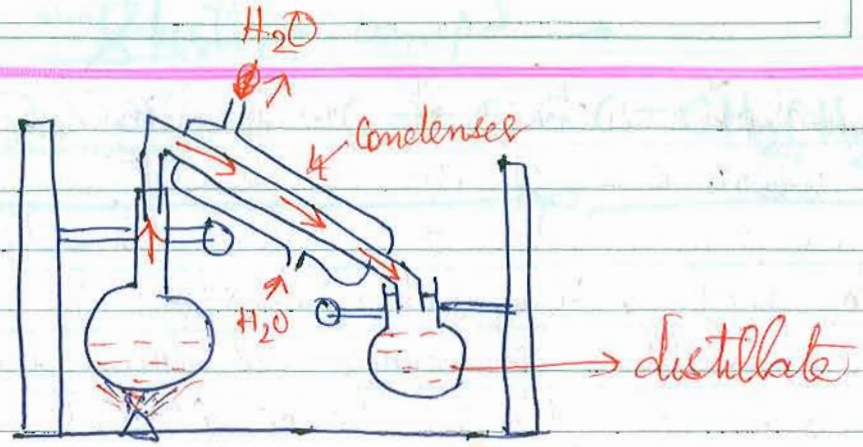
(2) Crystallization method of separation depends on the diff in solubility of the diff components of the mixture in a solvent. In this method, the mixture is dissolved in a suitable solvent, initially at higher temp. where both component of mixture are freely soluble. Now the resulting sol^n is cooled gradually. The less soluble solute crystallizes out 1st at higher temp; separated & dried. Further cooling of sol^n brings about crystallization of the more soluble component & so on ---- Hence, separation is done.

(3) Distillation method of separation is used for separation of liquids. For distillation method to work properly, liquids to be separated must have significant diff in their B.Pt. Distillation is further classified into 3 main categories

(a) Simple Dis. (b) Fractional (c) Distillation under Reduced Pressure.

(a) Simple Dis.: When diff in B.Pt. of liquids is very large, simple distillation is used for their separation.

Date



(b) Fractional: This technique is used for distillation of liquids whose B.Pt. are very close.

In fractional distillation method, a Fractional column is used; when heated vapours of both component of the mixture ~~rises~~ rises in the fractionating column. However, vapours of more volatile component rises faster than the other one. As the vapour pass through fractional column, they collide with glass beeds & condense back. The fast moving more volatile component condenses slowly; while slow moving, less volatile component condenses at faster rate. As a result, vapour becomes richer in more volatile component as they ~~ascend~~ rise in the fractionating column. At the top of fractionating ~~colum~~ column, vapour contain predominantly the more volatile component which is passed through condenser & collected in another flask.

(c) Distillation under Reduced Pressure.

Organic compds decomposes on heating.

Distillation under R.P. is used for separation of organic compds which decomposes before its B.Pt.

Reducing P. lowers the B.Pt. & can prevent decompos^{n} during distilation.

④ Extraction: In extraction method the mixture is 1st dissolved in a solvent to produce the stock sol^{n}. A portion of stock sol^{n} is taken in a separating funnel & a 2nd solvent is added which is immiscible with the 1st solvent; produces 2 separate layers. One of the component of the mixture has greater solubility in 1 solvent while the other has greater solubility in 2nd solvent. After stirring the sol^{n} for sometime, components of the mixture are distributed completely into 2 solvents acc. to their ~~sol~~ solubility. ~~Hence, separation is done.~~ Now separate layers are collected & individual components are removed from the sol^{n} by crystallization / distillation.

⑤ Chromatography:

Detection of elements C, H, O, N, X, S

① C & H (CuO Test): Organic compd. is heated with CuO where CO_2 & H_2O are produced if C & H are present.

$$C \& H + CuO \longrightarrow \underset{\text{product}}{CO_2 + H_2O}$$

The ~~product~~ gas is passed through glass tube containing ($\underbrace{CaCl_2}_{\text{absorbs moisture}}$) & then through lime soln.

Weight gain in $CaCl_2$ tube → H present, otherwise absent. If lime water turns milky → confirms C in starting compd.

(2) N, Cl, S → (LASSAIGNE'S TEST)

In lassaigne's test, the organic compd. is fused with Na metal & finally dissolved in H_2O where N is converted into CN^- (cyanide) Cl & S into Cl^- & S^{2-}. Each ion is then tested independently

★ Test of CN^-

PRUSSIAN BLUE TEST

$$CN^- + FeSO_4 \xrightarrow{\text{conc } H_2SO_4} [Fe(CN)_6]^{4-}$$

H_2SO_4 also produces some amt. of Fe^{3+}

$$Fe^{3+} + Fe(CN)_6^{4-} \longrightarrow Fe_4[Fe(CN)_6]_3$$

P.B (blue)

★ Test of S^{2-}

Pb-acetate TEST

$$S^{2-} + Pb(CH_3COO)_2 \longrightarrow PbS\downarrow$$

black

★ Test of Cl^-

$AgNO_3$ TEST

$$Cl^- + Ag^+ \longrightarrow AgCl\downarrow$$

white ppt. (soluble in excess NH_4)

NITROPRUSIDE TEST

→ Test of S^{2-}

$Na_2[Fe(CN)_5NO]$ → Sodium Nitroprusside.

It forms Yellow color soln in H_2O.

$$[Fe(CN)_5NO]^{-2} + S^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$$

Yellow → to → Violet

Sulphide

C, N, S → SCN^-

Thiocynate

$$SCN^- + FeCl_3(aq.) \rightarrow Fe(SCN)_3$$

blood-red color

If all other tests come -ve, we have to test for SCN^-.

15/11/09

Date

Ch: Energetics

☆ System & Surroundings

System: It is that part of universe on which we focus our attention for observing a thermodynamic change.

eg: A chemical rxn occuring in a flask is considered to be a sys.

Surrounding: It is remaining part of universe other than system

☆ For practical purpose, surrounding is the immediate vicinity of sys. which is influenced practically by change occuring in sys.

System

q → energy m → matter	OPEN	CLOSED	ISOLATED
	$\Delta q \neq 0$ $\Delta m \neq 0$	$\Delta q \neq 0$ $\Delta m = 0$	$\Delta q = 0$ $\Delta m = 0$

Open Sys: It is one which can exchange both matter and energy with surrounding

eg: A rxn. occuring in open test tube or open flask

Date

Closed System: It is a sys. which can exchange only energy with surrounding but cannot exchange matter. For closed sys, $\Delta m = 0$, $\Delta q \neq 0$.
eg: A rxn occuring in sealed flask

Isolated system: An isolated sys. is a sys. in which neither matter nor energy is exchanged with the surrounding. For an isolated sys, $\Delta q = 0$, $\Delta m = 0$

✱ THERMODYNAMIC PROCESSES

1) **Isothermal Process ($\Delta T = 0$):** It occurs at constt temp. In an isothermal process, temp. of sys remains constt throughout the change.

2) **Isobaric process ($\Delta P = 0$):** Pressure of the sys. is constt. eg: a chemical rxn in an open container.

3) **Isochoric process ($\Delta V = 0$):** Volume is constt. before & after.

4) **Adiabatic Process ($\Delta q_{sys.} = 0$):** Heat is constant.

✱ **State function:** It is a thermodynamic parameter, change in which doesn't depend on the path followed. For a given initial & final stage of sys, change in state f^n is constt. irrespective of path.

Date

Thermochemistry is a branch of thermodynamics in which we study change in E during a chemical rxn.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H = -890\ KJ/mol.$

☆ Enthalpy : H is the heat content of the sys. At const P, it is a state fn.

☆ Standard molar enthalpy of formation (ΔH_f°)

Standard molar enthalpy of formation is the enthalpy change when 1 mole of the ~~sys~~ substance is produced from constituent elements in their standard state (In thermochemistry standard state is state of 1 atm & 25°C)

$C + 2H_2 \rightarrow CH_4 \quad \Delta H_f^\circ = -83\ KJ/mol.$

$C(gr) + 2H_2(g) \rightarrow CH_4(g) \quad \Delta H_f = -83\ KJ/mol.$

$C_6H_{12}O_6(s) \rightarrow -1300\ KJ/mol.$

$6C(gr) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6 \quad \Delta H_f^\circ = -1300\ KJ/mol.$

☆ Standard Enthalpy of formation of an element is zero.

☆ Standard Molar Enthalpy of Combustion (ΔH_c°)

(ΔH_{comb}° or ΔH_c°)

It is the heat evolved when 1 mole of substance in its standard state is oxidised completely.

$Fe(s) + O_2(g) \rightarrow Fe_2O_3(s)$

☆ Standard Enthalpy of Rxn. (ΔH_R°)

$\Delta H_R^\circ = \sum \Delta H_f^\circ (Product) - \sum \Delta H_f^\circ (Reactants)$

Date

$$\Rightarrow \Delta H_R^\circ = \sum H_c^\circ (\text{Reactant}) - \sum \Delta H_c^\circ (\text{Product})$$
$$= \sum H_f^\circ (\text{Product}) - \sum \Delta H_f^\circ (\text{Reactant})$$

H_R° is the net heat change of a given rxn in the standard state. It is determined using either ΔH_f° or ΔH_c°.

✱ HESS'S LAW

Acc. to Hess's Law
1) If a ~~thermodyn~~ thermochemical eqn is multiplied by a factor, then ΔH is also multiplied.
2) If eqⁿ is reversed, sign of ΔH changes.
3) The thermochemical eqns. can be added, subtracted algebraically.

✱ It is because of state fⁿ property of H.

Q. Determine standard molar enthalpy of formation of ethanol.
$\Delta H_c^\circ = C_2H_5OH = -1368$, $\Delta H_c^\circ C(g) = -394$
$\Delta H_f^\circ\ H_2O(l) = -285$ KJ/mol.

Ans→ $\frac{1}{2}O_2 + 2C + 3H_2 \rightarrow C_2H_5OH$

$C_2H_5OH(g) + O_2 \rightarrow 2CO_2 + 3H_2O \quad -1368$

$C(s) + O_2 \longrightarrow CO_2 \quad -394 \times 2$

$H_2 + O_2 \rightarrow H_2O \quad -285 \times 3$

-855
788
1643
$1368 \nearrow -275$

Ans: -275 KJ/mol.

Given: $\Delta H_c^\circ\ CH_4(g) = -890\ KJ/mol$ $\Delta H_c^\circ\ C(g) = -395\ KJ/mol$

$\Delta H_c^\circ\ (C_2H_6) = -1560\ KJ/mol$ $\Delta H_f^\circ\ C_3H_8(g) = -104\ KJ/mol$

$\Delta H_c^\circ\ H_2(g) = -285\ KJ/mol$

Q. Determine enthalpy change for the following rxn. Find ΔH_r°

$C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$

What is the need of ΔH_c° C

$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O$ -890

$C_2H_6 + O_2 \rightarrow 2CO_2 + 3H_2O$ $+1560$

$2H_2 + O_2 \longrightarrow 2H_2O$ $+285\ ]\frac{1}{2}$

$C(g) + O_2(g) \rightarrow CO_2$ -395

$3C + 4H_2 \longrightarrow C_3H_8$ $+104$

$C_3H_8 \rightarrow 3C + 4H_2$ 104

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $-285\ ]\times 5$

$2CO_2 + 3H_2O \rightarrow C_2H_6 + O_2$ 1560

$6CO_2 + 2H_2O \rightarrow CH_4 + O_2$ 890

$3C(g) + O_2 \rightarrow 3CO_2$ -3×395

-56

Q. $\Delta H_c^\circ\ C_6H_{12}O_6 = -2800\ KJ/mol$. If only 25% E is available for muscular work & 100 KJ E is consumed in 1 km walk, what max. distance a person can walk after consuming 120g glucose.

$1\ mol \rightarrow -2800\ KJ$

$\frac{120}{180} = \frac{2}{3} \times \frac{1}{42} \rightarrow 2800 \times 6 = -16800$

$\frac{2}{3} \times 2800 \times \frac{1}{42}$

$100 \rightarrow 1$

$\frac{2800}{6} \rightarrow \frac{1}{700} \times \frac{2800}{6}$

4.67

Ans = 4.67 km

Date

19/11/09

Q. Standard molar enthalpy of combustion of Diborane (B_2H_6) is -2020 KJ/mol.

$\Delta H_f^\circ (H_2O) = -285$ KJ/mol.

$\Delta H_c^\circ (B)(c) = -632$ KJ/mol

Determine ~~Hand~~ $\Delta H_f^\circ (B_2H_6)$

~~$B_2H_6 + O_2 \longrightarrow$~~

Reqd rxn

$2B_{(s)} + 3H_2 \rightarrow B_2H_6$.

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$, $= +2020$

$3H_2 + \frac{3}{2}O_2 \rightarrow 3H_2O$ $\quad (-3)(285)$

$2B + 3O_2 \rightarrow B_2O_3$ $\quad 2(-632)$

$2020 - 3(285) - 1264$

$= -99$ KJ.

Date 22.4

Q. A methane burner using gas @ 5 l/he in laboratory is to be replaced by butane burner. What should be the rate of supply of gas in order to have same energy calorific value.

(a) Given :- $\Delta H_c^\circ (CH_4) = -890\ KJ\ mol^{-1}$

$\Delta H_c^\circ\ C_4H_{10} = -2800\ KJ\ mol^{-1}$

$V \propto n$

In 5 lit → 5(C) (const) moles of $CH_4(g)$ will be there.

From 1 mol CH_4 → 890 KJ.

5 mole → 890 × 5 KJ

2800 KJ → 1 mol

(890 × 5) KJ → $\frac{890 \times 5}{2800}$ mol.

Volume = $\frac{890 \times 5}{2800}$ l = 1.6 lit/he.

56

(b) For optimum calorific (fuel value) value, ~~hydrogen to oxygen ratio~~ The vol. of O_2 must be 3 times its theoretical requirement - what should be rate of supply of O_2 gas in butane burner in the previous question.

$C_4H_{10} + \frac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O$

5

Q 1 — $\frac{13}{2}$

$1.6 \rightarrow \left(\frac{13}{2}\right)\left(\frac{16}{10}\right) \times 3$

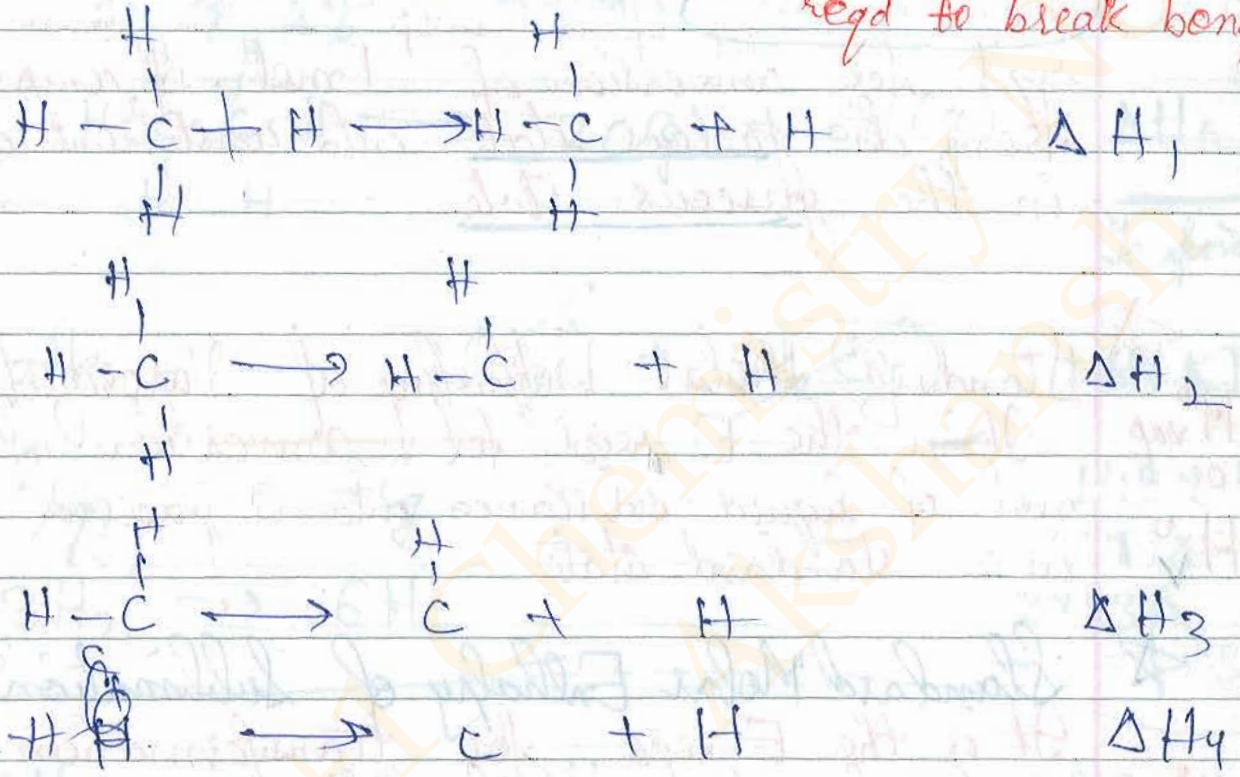
$\frac{8}{10}$

$\frac{39}{8}$

31.2

Min rate of Supply of O_2 = 31.2 Lit /~~mol~~ he Ans

✡ BOND ENTHALPY (always +ve → E would always be reqd to break bond)



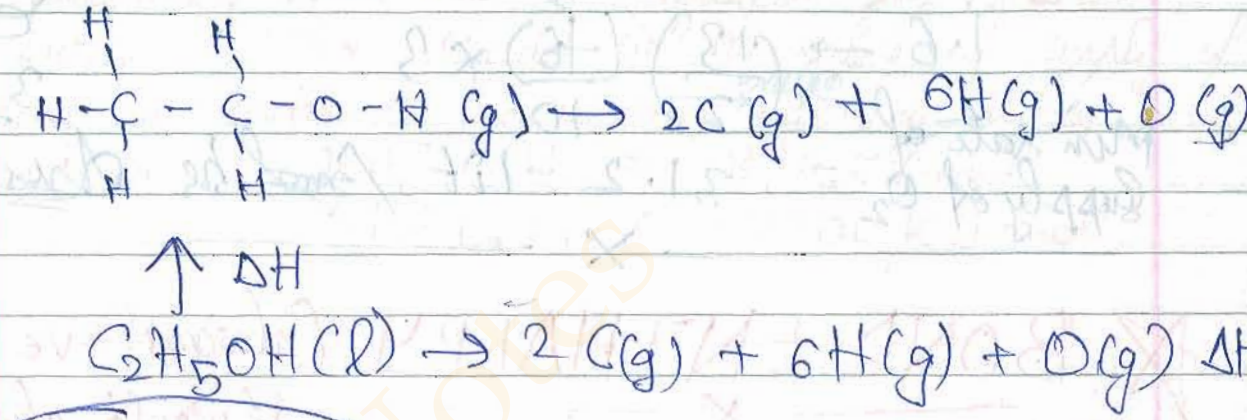
✡ Bond Dissociation Enthalpy (ΔH_{DE})

BDE is the E reqd to break a specific bond in a compd (per mole of compd.).

✡ Avg. BDE: It is the $\overset{avg}{E}$ reqd. to break like bonds in a compd.

Date

★ Bond Enthalpy of a compound (BE)



Bond Enthalpy of a compd. is the total E. reqd. for conversion of 1 mol. of compd. from its gaseous state into constituent atoms in the gaseous state.

★ **Standard Molar Enthalpy of Vaporization (ΔH°_{vap} or ΔH°_V)**
It is the E reqd. for conversion of 1 mol of liquid substance into a gaseous state in a standard state.

★ **Standard Molar Enthalpy of Sublimation (ΔH°_{sub})**
It is the E reqd. for transformation of 1 mol. of solid directly into gaseous state under standard state.

★ ~~Fusion~~ ΔH°_{fusion} (Std. mol. enthalpy of fusion)
It is the E reqd. for transformation of 1 mol of solid into liqd. in std. state.

★★ $\Delta H^\circ_{sub} = \Delta H^\circ_{fusion} + \Delta H^\circ_{vap}$

717
2
1434

2826
2490
336

415
6
2490

Q. Determine C-C BE from given info →

$\Delta H_f^\circ\ C_2H_6(g) = -84\ KJ\ mol^{-1}$

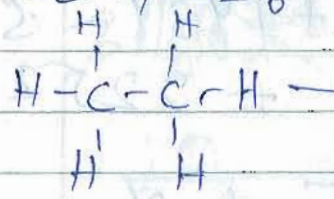
$\Delta H_{sub}^\circ\ C(gr) = 717\ KJ\ mol^{-1}$

$DE(H_2) = 436\ KJ\ mol^{-1}$

Avg Bond Energy ← $\overline{BE}(C-H) = 415\ KJ\ mol^{-1}$

★ Total BE of C_2H_6 = 6 times C-H BE + C-C BE

Reqd. Rxn



$\rightarrow 2C(g) + 6H(g)$ $\quad \Delta H = ?$

To find.

$C_2H_6 \rightarrow 2C(gr) + 3H_2(g) + 84\ KJ$

$2C(gr) \rightarrow 2C(g)$ $\quad$ 1434 KJ (717×2)

$3H_2 \rightarrow 6H$ $\quad$ 3×436 = 1308 KJ

Add

$C_2H_6 \rightarrow 2C(g) + 6H$ $\quad$ 2826 KJ

II

$6\times415 + BE(C-C)$

Now

$2826 = 6(415) + BE(C-C)$

$\Rightarrow BE(C-C) = 336\ KJ.$

Q. Given $\Delta H_f^\circ\ C_2H_4(g) = 54\ KJ\ mol^{-1}$

Determine C=C BE. Use data from previous question → $DE(H_2)$, $\Delta H_{sub}^\circ(C(gr))$, $\overline{BE}(C-H)$

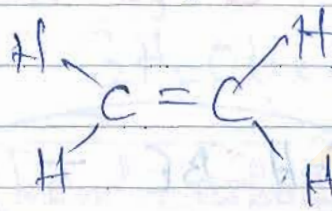
Date

436 ×2
872

~~$2C_{(g)} + 4H_{(g)} \rightarrow C_2H_{4(g)}$~~

$2H_2 \rightarrow 4H_{(g)}$ $+872$ KJ

$2C_{gr} \rightarrow 2C_g$ $+1434$ KJ



$\rightarrow 2C_g + 4H_g$ -54 KJ

Add → $872 + 1434 - 54$

$= 2252$ KJ

Now

$2252 = 4 \times 415 + x$

$\Rightarrow x = 592$ KJ

Q. Determine Std. ~~ME~~ ΔH_f $C_2H_5OH \rightarrow$

Given:

BE

C-H = 415 KJ/mol.

C-C = 348 KJ/mol

C-O = 352 KJ/mol

O-H = 463 KJ/mol

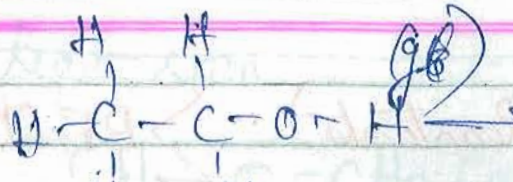
O=O = 500 KJ/mol.

$C_{gr} \rightarrow C_g$ = 717 KJ/mol.

$H_2 \rightarrow 2H$: 436 KJ/mol.

$\Delta H_f (C_2H_5OH) = 35$ KJ/mol.

Date



Total BE = 2075 + - -

= 3238 KJ

$2C_{(g)} + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH_{(l)}$

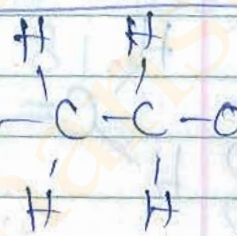
$-3238\ KJ$

$2C_{(g)} \rightarrow 2C_{(g)}$ $\quad -1454\ KJ$

$3H_2(g) \rightarrow 6H_{(g)}$ $\quad -2616\ KJ$

$\frac{1}{2}O_2 \rightarrow O$ $\quad +250\ KJ$

2
415
05
2075
348
352
463
3238

$2C_{(g)} + 6H_{(g)} + O_{(g)} \rightarrow$ 

$-3238\ KJ$

$2C_{(g)} \rightarrow 2C_{(g)}$ $\quad 1454\ KJ$

$3H_2(g) \rightarrow 6H$ $\quad 1308\ KJ$

$\frac{1}{2}O_2 \rightarrow O(g)$ $\quad 250\ KJ$

$C_2H_5OH(g) \rightarrow C_2H_5OH(l)$ $\quad -35\ KJ$

Ans = 1454
1308
250
2992

3238
+35
2 3 2 7 3
−2992
281

Ans = −281 KJ

ΔH_R° = $\sum$ BE$_{in}$ − BE$_{out}$ Date

//

$$\Delta H_R^\circ = \sum BE(\text{Reactants}) - \sum BE(\text{Products})$$

→ Keep in mind that all compds are in gaseous state

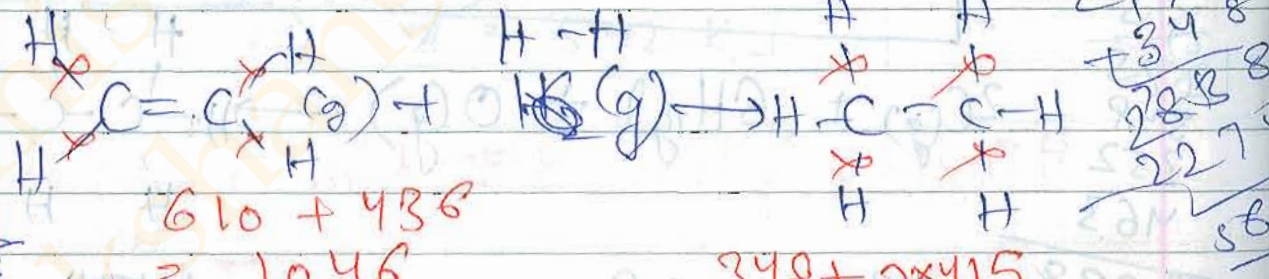
Q. Determine enthalpy of hydrogenation of C_2H_4. Given →

C−C = 348 KJ/mol

C=C = 610 KJ/mol

BE(H_2) = 436 KJ/mol

BE(C−H) = 415 KJ/mol



ΔH_R° = −2838 + 2706

= −132 Ans.

$\Delta H_R^\circ = \sum BE(\text{Reactant}) - \sum BE(\text{Product})$

= 1046 − 1178

= −132 KJ Ans

Q. Determine std. state enthalpy of isomerisation of dimethylether (g) → RT into C_2H_5OH

Given: C−H = 415 KJ/mol

C−C = 348 KJ/mol

C−O = 352 KJ/mol

O−H = 463 KJ/mol

$\Delta H_v^\circ (C_2H_5OH)(l)$ = 35 KJ/mol

1830
352
463
1645

415
02
830

Date

Reqd. rxn.

$CH_3-O-CH_3(g) \longrightarrow CH_3CH_2OH(l)$ $\Delta H = ?$

352
02
704

1645
704
941

$704 - (830+352+463)$
$= 704 - 1645 = -941$

Ethanol $C_2H_5OH(l) \longrightarrow C_2H_5OH(g)$ 35 KJ

C-H
C-O
(415+352)
767

C-C
O-H
(348+463)
811

415
352
767

$767 - 811$
$\Delta H_f^\circ = -44$ KJ

$C_2H_5OH(g) \longrightarrow C_2H_5OH(l) = -35$ KJ

Ans $= -44 - 35 = -79$ KJ

—×—

Q. Std $\Delta H_v^\circ (H_2O) = 41$ KJ/mol
$\Delta H_v^\circ (H_2O_2) = 98$ KJ/mol
$\Delta H_f^\circ (H_2O) = -285$ KJ/mol
$\Delta H_f^\circ (H_2O_2) = -122$ KJ/mol.

Determine:
O-O Single B.E in H_2O_2
peroxide if O=O = 500 KJ/mol.

$2H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g/l)$ -285 KJ

$2H + O_2 \rightarrow H_2O_2(l)$ -122 KJ

$H_2O(l) \rightarrow H_2O(g)$ 41 KJ

$H_2O_2(l) \rightarrow H_2O_2(g)$ 78 KJ

$H-O-O-H(g) \rightarrow H-O-H(g) + \frac{1}{2}O=O(g)$

$O-O$ $\quad$ $\frac{1}{2}O=O$

x

$x - 250 = \Delta H$ (in gaseous state)

In std. state

$H-O-O-H(l) \rightarrow H-O-H(l) + \frac{1}{2}O=O(g)$

Product - Reactant

$= -285 - (-122) = -163$ KJ

$H-O-O-H(g) \rightarrow H-O-O-H(l)$ -78

$H_2O(l) \rightarrow H-O-H(g)$ $+41$

-37

Add.

Eqn →

$H-O-O-H(g) \rightarrow H-O-H(g) + \frac{1}{2}O=O(g)$

$\Delta H = -200$ KJ

Date

Now,

$x - 250 = -200$

i.e $BE(O-O) - 250 = -200$

$\Rightarrow BE(O-O) = 50\ KJ$

HW → 11T → 96

Q Determine C-C & C-H from following info →

$\Delta H_c^\circ\ C_2H_6 = -1560\ KJ\ mol^{-1}$

$\Delta H_c^\circ\ C_3H_8 = -2215\ KJ/mol$

$C_{gr} \rightarrow C_g = 717\ KJ/mol$

$H_2 \rightarrow 2H \rightarrow 436\ KJ/mol$

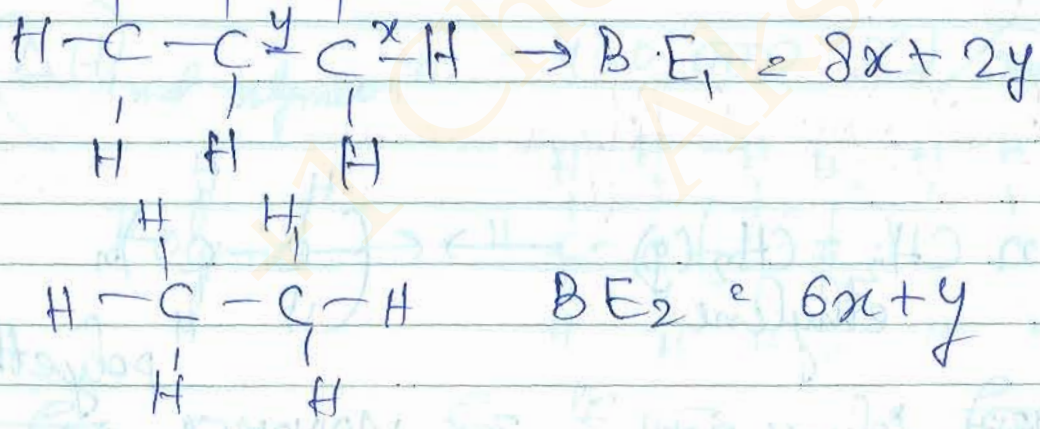
$\Delta H_f^\circ\ CO_2 = -394\ KJ/mol$

$\Delta H_f^\circ\ H_2O = -285\ KJ/mol$

① $C_2H_6 \rightarrow 2C + 6H \quad \Delta H_1 = ?$

$C_3H_8(g) \rightarrow 3C(g) + 8H(g) \quad \Delta H_2 = ?$

$BE_1 = ?$



$BE_2 = 6x + y$

$C_3H_8 + O_2 \rightarrow 3CO_2 + 4H_2O \quad -2215$

$3CO_2 \rightarrow 3C_{gr} + O_2 \quad +3(394)$

$4H_2O \rightarrow 4H_2 + O_2 \quad +4(285)$

$3C_{gr} \rightarrow 3C_{(g)} \quad 3\times(717)$

$4H_2 \rightarrow 8H \quad 4(436)$

Similarly, find BE_2.

H.W

22/11/09

✱ Enthalpy of Polymerisation

$$n\,CH_2=CH_2\,(g) \longrightarrow \left(-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\right)_n$$

ethylene → monomer

polyethylene → polymer

$\Delta H < 0$

✱ जिससे Polymer बनता है, उसे MONOMER कहते हैं। वो चीज़ Monomer के कई unit combine करके बनता है, उसे Polymer कहते हैं।

✱ The above polymerisation is called OLEFINIC POLYMERISATION. It is always exothermic.

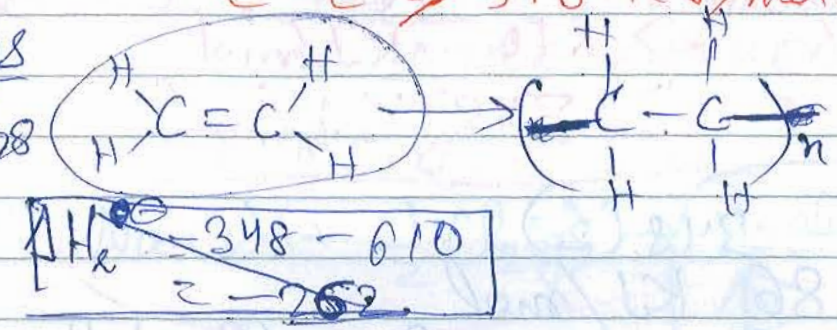
Q. Determine enthalpy of polymerisation per mole of
(i) ethylene.
(ii) polyethylene : If molar mass of polymer is
M = 140,000 g/mol

Given: C=C ⇒ 610 KJ/mol
C-C ⇒ 348 KJ/mol.

5 8 10
- 3 4 8
2 5 2

3 4 8
e 2
6 9 6

Ans



ΔH_r = 348 - 610
= -262

(a) ΔH_r = 610 - 348(2)
= -86

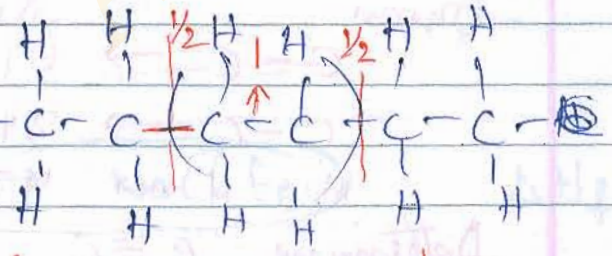
(b) $\frac{140,000\ g}{28}$ = 5000 moles.

8 6
x 5 0 0 0
4 3 0

ΔH = (-86)(5000) KJ/mol

$(\Delta H)_{1\ mol\ polymer}$ = -430,000 KJ/mol.

Polymer →



Bond conservation → 2 bonds (C≡C) gives 2 bonds of C-C in product as shown above.

Date

C=C → 1
C-C → 2
C-C → 4

Q. $n\,CH_2=\underset{\underset{CH_3}{|}}{C}-CH=CH_2 \longrightarrow \frac{1}{2}\left(CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2\right)\frac{1}{2}$

Isoprene — Natural rubber.

Determine enthalpy of polymerisation per mole of isoprene

C=C ⇒ 610 KJ/mol
C-C ⇒ 348 KJ/mol

Ans $\Delta H = 610 - 348(2)$
$\Delta H = -86$ KJ/mol.
(Calculation is same as the problem before)

Q. $H-C\equiv C-H + H_2 \longrightarrow CH_2=CH_2 \longrightarrow \Delta H_1$

$CH_2=CH_2 \longrightarrow \left(CH_2-CH_2\right)_n \longrightarrow \Delta H_2 = -86$

If 1 mole of acetylene is hydrogenated partially into ethene, & polymerised finally, to polyethylene a total of 226 KJ heat is evolved.

Given
C=C → 610 KJ/mol
C-C → 348 "
H-H → 436 "
C-H → 415 KJ/mol

Determine C≡C BE.

$436 + 2(415) + (610) - x = \Delta H_1$

226
86
140

Here
$\Delta H_1 + \Delta H_2 = -226$
$\Rightarrow \Delta H_1 - 86 = -226$
$\Rightarrow \Delta H_1 = -140$

O_2 830 + 610

$2(415) + 610 + 436 - x = -140$ ~~876~~

$-140 = x + 436 - (610 + 2 \times 415)$

$\Rightarrow x = 862$ KJ

✡ LATTICE ENERGY (U_o)

= LATICE ENTHALPY

Its defined only for ionic compds → salts at RT.

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s) \rightarrow \Delta H_f^\circ$

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ ← Lattice E

✡ Ionic bond will always be formed in this process & U_o° will always be -ve.

→ Lattice E is the heat evolved when 1 mole of an ionic compd (salt) in its std. state (always solid) is formed from constituent ions in their gaseous state.

$Na(s) + \frac{1}{2}Cl(g) \longrightarrow NaCl(s)$ $\quad \Delta H_f^\circ$

Sublime ↓ ΔH_{sub}° $\quad$ $\frac{BE}{2}$ ↓

$Na(g)$ $\quad$ $Cl(g)$

IE_1 ↓ $\quad$ ↓ E_A

$Na^+(g) + Cl^-(g)$ → $U_o (\Delta H_{lattice}^\circ)$

Born-Haber cycle

Here $\Delta H_f^\circ = \Delta H_{sub}^\circ + IE + \frac{BE}{2} + E_A + U_o$

(By property of State fn)

All strong acids, strong bases & strong salts are strong electrolyte

① Determine U_o of NaCl. Given →

$\Delta H^\circ_{sub} = 160$ KJ/mol

IE = 560 KJ/mol

E_A = −350 KJ/mol

BE_{Cl} = 360 KJ/mol ~~≥ BE ≥ 180~~ KJ/mol

ΔH_f° NaCl(s) = −180 KJ/mol

$-180 = 160 + 560 - 350 + U_o + 180$

$-360 + 350 - 720 = U_o$

$\Rightarrow U_o = -730$ KJ/mol Ans

---

② Determine U_o of CaC_2 (Calcium Carbide)

Given:—

$Ca(s) \longrightarrow Ca(g)$ 186 KJ/mol

Ca : $IE_1 = 600$ KJ/mol

$IE_2 = 1150$ KJ/mol

$C_{(gr)} \rightarrow C_g$ → 717 KJ/mol

$BE\ (C_2)(g) = 614$ KJ/mol

EA_1 of $C_2 = -315$ KJ/mol

EA_2 of $C_2 = 415$ KJ/mol

$\Delta' H_f^\circ$ $CaC_2 = -236$ KJ/mol

1150 + 600 = 1750

315 + 415 = 730

$Ca(s) + 2C_{(gr)} \longrightarrow CaC_2(s)$

$Ca(s) \xrightarrow{186} Ca(g)$

$2C_{(gr)} \xrightarrow{1434} 2C(g)$

$Ca(g) \xrightarrow{1750\ IE_1, IE_2} Ca^{2+}(g)$

$2C(g) \xrightarrow{614} C(g) \longrightarrow C^{2-}(g)$

$+ 100 - 730$

Date

186
1750
1434
3370
1344
2026
-236

614
+720
1344

186
21750
715
+614
3267
-730
2537

6
3470
-614
2856
-236
2092

2537
-730
1807

2537
+236
2773

$\Rightarrow U_0 = 730 - 236$

$\Rightarrow U_0 = -1807$ KJ/mol.

$= -2773 - 3092$

So,

$186 + 1750 + 1434 + 100 - 614 + U_0 = -236.$

$U_0 = -3092$ KJ

☆ Std. Enthalpy of Neutralisation

↔ Std. Enthalpy of Neutralisation is the heat evolved when 1 g equivalent of an acid / a base is neutralised completely

(Its value is always -ve (∵ Neutralization is always exothermic)

(a) $NaOH + HCl \longrightarrow NaCl + H_2O \quad \Delta H = -57$ KJ/mol

$Na^+ + OH^- + H^+ + Cl^- \longrightarrow Na^+ + Cl^- + H_2O$

$H^+ + OH^- \rightarrow H_2O \quad \Delta H = -57$ KJ/mol.

(b) $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$

$2H^+ + SO_4^{2-} + 2K^+ + 2OH^- \rightarrow 2K^+ + SO_4^{2-} + 2H_2O$

$\Rightarrow 2H^+ + 2OH^- \rightarrow 2H_2O \quad \Delta H = -114$ KJ/mol

☆ Equilibrium is a state of disorder, randomness.

eg:

Date

☆ For strong acid & strong base, enthalpy of Neutralization per equivalent of either acid or base is constt. & it is = −57 KJ (approx.)

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

~~$CH_3COO^- + H^+ + OH^- \Longrightarrow H_2O + CH_3COO^-$~~

$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O$

Nett ⇒

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Adding gives Nett

$CH_3COOH \rightarrow CH_3COO^- + H^+$ $\quad \Delta H > 0$

$H^+ + OH^- \rightarrow H_2O$ $\quad -57$ KJ

☆ When a weak acid reacts with strong base, value of enthalpy of ~~ionization~~ neutralization is less than −57 KJ because some energy is reqd. to ionize the weak acid as shown above.

☆ $Q = m S \Delta T$ → Temp.

Q = Heat, m = mass, S = Specific heat (constt. for any condn)

HCl	NaOH
0.1	0.1

If vol. increase is same in both acid & base containers, then, Temp. would be constt. (see above eqn)

Spontaneity

Date

* SPONTANEOUS PROCESS: A thermodynamic process having potential of occuring on its own i.e without help of any external source of E are known as Spontaneous Thermodynamic processes.

* CRITERION for Spontaneity:

& Entropy (S): Entropy is the measure of randomness (disorderness) of a ~~substance~~ sys. Greater the randomness, higher entropy of sys.

* Entropy is a state fn ∴ ΔS is independent of path. It is measured quantitatively by eqn

$$\Delta S = \frac{q_{reversible}}{T} = \frac{q_{rev}}{T}$$

Imp A non-equilibrium sys approaches spontaneously towards equi. As sys approaches towards equi., it becomes more & more random. ∴ entropy of sys. increases as it approaches to equi.

i.e Sys → equi → (entropy)$_{max}$.

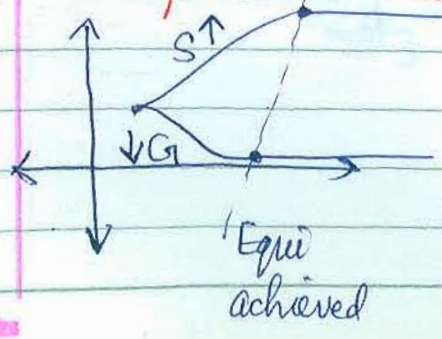
* A spontaneous process is one which leads to increase in entropy.

* ΔG: An expn that relates ΔH & ΔS i.e

↓ Gibb's Free Energy Change

** $\Delta G = \Delta H - T\Delta S$

& For a process to be spontaneous, ΔG must be -ve.



At equi → S → max
G → min.

CRITERION FOR SPONTANEITY

① ΔH -ve, ΔS +ve.
The process will always be spontaneous ∵ ΔG would always be -ve ∀ T

② $\Delta H > 0$; $\Delta S < 0 \longrightarrow \Delta G > 0 \quad \forall T$

③ $\Delta H > 0$; $\Delta S > 0 \longrightarrow$ For $\Delta G < 0$; $T\Delta S > \Delta H$

The process will be spontaneous at very high temp. as then, $\Delta G < 0$.

④ $\Delta H < 0$; $\Delta S < 0$: $T\Delta S < \Delta H$ for $\Delta G < 0$

So, the process will be spontaneous at low temp.

☆ Spontaneity & equi. constt

Gibbs's free Energy change $\Delta G = -RT \ln K$

(R: Gas constt., T: Temp, K: Equi. constt)

for ΔG to be -ve, $K < 1$.

End of Energetics

26/Nov./09 Date

(N.C.E.R.T.) Chemical Equilibrium

☆ IRreversible Chemical Reaction:
These are those chemical rxn. which go upto completion exhausting the limiting reactant in finite length of time.

☆ Reversible Chemical Rxns.
These are those rxns. which proceed in both dirns. Reversible chemical rxn. never complete.
No. component vanishes in finite time.
But, Reversible chemical rxn. attain a state of Chemical Equi.

eg: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (forward →, backward ←)

☆ CHEMICAL EQUILIBRIUM.
It is a state in a reversible rxn. at which both forward & backward rate of rxn. become equal.
i.e Rate of forward rxn (R_f) = Rate of backward rxn. (R_b) at equi.
From above example $-\frac{d[H_2]}{dt} = \frac{d[H_2]}{dt}$

$-\frac{d[H_2]}{dt}$: rate of disappearance of any component (H_2)
$\frac{d[H_2]}{dt}$: rate of appearance of any component

☆ At chemical equi., components of equi stop changing their amt.

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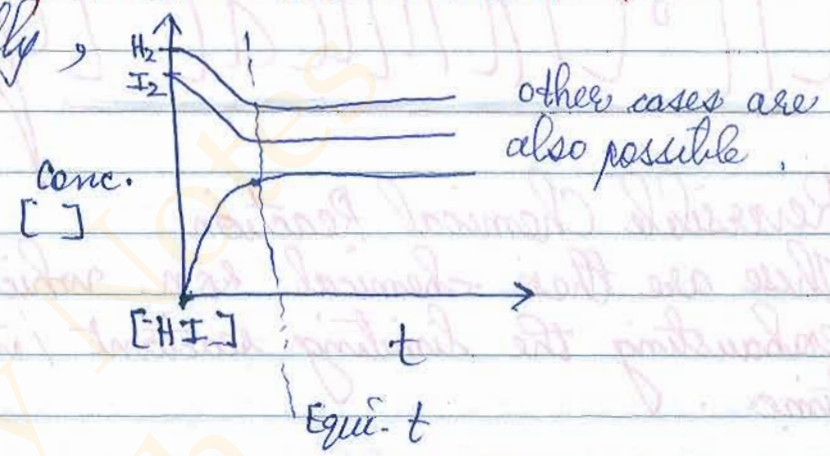
☆ Chemical equi. is dynamic in nature.

DYNAMIC EQUI.

At state of chemical equi; rxn doesn't stop occuring. However, species stop changing their amt.

∴ Rate ~~for~~ forward = rate backward.

Diagramatically,



☆ Equi. Composition

LAW OF MASS-ACTION (Guldberg Wagge's law)

Rxn. in Soln → $aA \rightleftharpoons bB$.

Acc. to law of mass-action, rate of chemical rxn. is directly proportional to active masses of reacting species raised to the power stoichiometric coeff.

☆ Active mass: For soln, active mass is the molarity of solute in the soln & for gaseous sys., active mass is partial pressure of reactant & product. For solids & pure liquid, active mass is always 1 C ∴ their conc. remains constt during rxn.)

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Sol^{n} → $aA + bB \underset{R_b}{\overset{R_f}{\rightleftharpoons}} cC + dD$

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

$R_f = k_f [A]^a [B]^b$

k_f, k_b → rate consttⁿ for forward & backward rxn.

$R_b \propto [C]^c [D]^d$

$R_b = k_b [C]^c [D]^d$

At. equi. $R_f = R_b$.

$\Rightarrow \frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_c$ = Equilibrium consttⁿ in term of conc

* K_c will have a fixed value in any ⊕ rxn. and would depend only on temp.

K_c is characteristic consttⁿ of a given reversible rxn. It doesn't depend on P, V, ~~&~~ catalyst, m, n etc.

Gas → $aA + bB \underset{R_b}{\overset{R_f}{\rightleftharpoons}} cC + dD$

$R_f = k_f P_A^a P_B^b$

$R_b = k_b P_C^c P_D^d$

At equi $R_f = R_b$

$\Rightarrow \frac{k_f}{k_b} = \frac{P_C^c P_D^d}{P_A^a P_B^b} = K_p$

* K_p has all properties similar to that of K_c i.e. it depends only on temp.

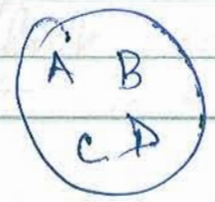
K_p = Equi. consttⁿ in terms of P

---

* $PV = nRT$

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

$\frac{n}{V}$ → conc.



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So, $P_i = C_i RT$ ← conc. of that component

Partial Pressure of a component

So, now,

$$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \, P_B^b} = \frac{\{[C]RT\}^c \{[D]RT\}^d}{\{[A]RT\}^a \{[B]RT\}^b}$$

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

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

$$\Rightarrow \boxed{K_p = K_c \cdot (RT)^{\Delta n}}$$

$$\boxed{; \Delta n = \sum(n \text{ of Product}) - \sum n \text{ reactant}}$$

—x—

PROPERTIES OF EQUI CONSTTs. (K_p & K_c).

1) $aA \rightleftharpoons bB$.

$$K_c = \frac{[B]^b}{[A]^a}$$

$2aA \rightleftharpoons 2bB$.

$$K_c' = \frac{[B]^{2b}}{[A]^{2a}} = (K_c)^2$$

Conclude → If we multiply an equi by a constt factor, the factor goes into exponent of equi. constt (see above to understand).

Date

127 + 273 = 400

2) $A + B \rightleftharpoons P$ $\quad K_{c_1} = \frac{[P]}{[A][B]}$

$P \rightleftharpoons Q + R$ $\quad K_{c_2} = \frac{[Q][R]}{[P]}$

Add

$A + B \rightleftharpoons Q + R$ $\quad K_{c_3} = \frac{[Q][R]}{[A][B]} = K_{c_1} \times K_{c_2}$

more than 1 equi. rxns. are added

Conclude → If equilibrias are ~~multiplied, equi consts of~~ to obtain a new equi, then its equi. consts will be products of individual equi. consts of rxns. being added.

3) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\quad K_c = 4 = K_p = K$

$2HI \rightleftharpoons H_2(g) + I_2(g)$ $\quad K_c' = \frac{1}{4}$

Conclude → If a rxn. is reversed, equi. consts. will be reciprocal of initial equi. consts.

EQUILIBRIUM

① $\Delta n = 0$

$K_c = K_p = K$ (dimensionless)

② $\Delta n \neq 0$

eg: $PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g)$

Here, $n = 1$

① • $\Delta n = 0$

Q. For K_c for formation of $HI(g)$ from $H_2(g)$ & $I_2(g)$ at 127°C is 2.5. If 1 mol. of H_2 is mixed with 2 mol. of I_2 in a flask, sealed, & heated to 127°C (400K); determine the amt. of $HI(g)$ formed at equi.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K = 2.0$, 400 K

	H_2	I_2	HI
Initial n	1	2	0
At equi n	$1-x$	$2-x$	$2x$

$K = \frac{n_{product}}{n_{reactant}}$

So, $K = 2.0 = \frac{(2x)^2}{(1-x)(2-x)}$

$\Rightarrow 2 = \frac{4x^2}{2 - 3x + x^2}$

$\Rightarrow 4x^2 = 4 - 6x + 2x^2$

$\Rightarrow 2x^2 + 6x - 4 = 0$

$\Rightarrow x^2 + 3x - 2 = 0$

$\Rightarrow (x+3)(x-1) = 0$

$\Rightarrow x = 1$

$x = \frac{-3 \pm \sqrt{9+8}}{2}$

$= \frac{-3+\sqrt{17}}{2}, \left(\frac{-3-\sqrt{17}}{2}\right)$ ✗ -ve reject

$\Rightarrow x = 0.55$

4.1
4 | 17
-16
81 | 100
4.1
3

Q. CO (g) & steam (H_2O) (g) are mixed in equimolar amt. in a flask & heated to 1000K where following equi is established.

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

At equi, the flask was found to contain 20% CO_2 by mole. Determine K for given equi.

$\frac{80}{5} = 16$ $\quad 2-2x = \frac{x}{5} + y \Rightarrow y = 2 - 2x - \frac{x}{5}$

Date $= 10 - \frac{10x}{5} - x$

$= 10 - \frac{11x}{5}$

	$CO(g)$	$+ H_2O(g)$	$\rightleftharpoons CO_2(g)$	$+ H_2(g)$
n	1	1	0	
equi n	$1-x$	$1-x$	$\frac{x}{5}$	$\frac{10-11x}{5}$
OR	$50-20 = 30$	$50-20 = 30$	20	20

$$K = \frac{(20)^2}{(30)^2} = \frac{4}{9}$$

20%

Q. In the previous Q., if equi. mixture contain 20% of $H_2O(g)$ & 25% $(O_2(g)$, determine K.

	$CO + H_2O \rightleftharpoons$	$CO_2 +$	H_2
	60		
50 70	50	25	30
30	20%		25%

$$K = \frac{(25)^2}{(30)(20)} = \frac{25}{24}.$$

29/11/09

Q. H_2 & I_2 combine to produce $HI(g)$ & at 450°C, equi consth for following rxn.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K = 4.$$

If 1 mole of H_2 is mixed with 3 moles of $HI(g)$, in a flask, & heated to 450°C, determine moles of I_2 produced at equi.

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial n	1 mol				3 mol
At equi.	$1+x$		x		$3-2x$

$K = 4$

$K = \frac{[HI]^2}{[H_2][I_2]}$

So, $K = 4 = \frac{[HI]^{3-2x}}{[H_2]^{1+x}[I_2]^{x}}$

$\Rightarrow K = 4 = \frac{(3-2x)^2}{(1+x)(x)} \Rightarrow 4x + 4x^2 = 9 + 4x^2 - 12x$

$\Rightarrow 16x = 9$

$\Rightarrow x = \frac{9}{16}$

So, $HI \rightarrow 3 - \frac{9}{16} = \frac{30}{16}$.

$H_2 \rightarrow \frac{25}{16}$, $I \rightarrow \frac{9}{16}$

Q. 1 mol of H_2 is mixed with 3 mol. of I_2 & sealed in a flask where following equi. is established.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

At equi. the flask was found to contain x mole of $HI(g)$. 2 mole of $H_2(g)$ is added further at equi. & a further x mole of $HI(g)$ is produced before equi was re-established. Determine x & K (equi. const^t).

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial n	1		3		
equi. n	$1-\frac{x}{2}$		$3-\frac{x}{2}$		x

$K = \frac{(x)^2}{(3-\frac{x}{2})(1-\frac{x}{2})}$ → (1)

Date

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Init. 1 3 2x.

equi. $3-x$ $3-x$ $2x$.

$$K = \frac{(2x)^2}{(3-x)^2} = \frac{x^2}{\left(3-\frac{x}{2}\right)\left(1-\frac{x}{2}\right)}$$

$$\Rightarrow \frac{4}{(3-x)^2} = \frac{4}{(6-x)(2-x)}$$

$$\Rightarrow 12 - 8x + x^2 = 9 + x^2 - 6x$$

$$\Rightarrow 3 = 2x$$

$$\Rightarrow x = \frac{3}{2}.$$

Now,

$$K = \frac{\left(\frac{3}{2}\right)^2}{\left(3-\frac{3}{2}\right)^2} = \frac{\frac{9}{4}}{\left(\frac{3}{2}\right)^2}$$

$$= \frac{9}{4} \times \frac{4}{9}$$

$$\Rightarrow K = 1 \quad \text{Ans} = 1$$

Q. A 1L flask containing 1 mol. of $A_2(g)$ is connected to a 2L flask containing $B_2(g)$ at same temp. & P where following equi. is established.

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g) \quad ; \quad K = 10.$$

Determine mole of $AB(g)$ produced at equi.

$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

$1-\frac{x}{2}$ $2-\frac{x}{2}$ $2x$

$$10 = \frac{x^2}{\left(1-\frac{x}{2}\right)\left(2-\frac{x}{2}\right)}$$

$\Rightarrow 10\left(1-\frac{x}{2}\right)\left(2-\frac{x}{2}\right) = x^2$

$\Rightarrow 10\left(2 - 3\frac{x}{2} + \frac{x^2}{4}\right) = x^2$

$\Rightarrow \frac{5}{10}\left(\frac{8 - 6x + x^2}{4\ 2}\right) = x^2$

$\Rightarrow 40 - 30x + 5x^2 = 2x^2$

$\Rightarrow 3x^2 - 30x + 40 = 0$

$\Rightarrow x = \frac{30 \pm \sqrt{900 - 4(120)}}{6}$

$= \frac{30 \pm \sqrt{420}}{6}$

$= \frac{30 + 60}{6}$

$= \frac{90}{6}$

900
−480

60.
6 | 420
−36
120 60

$10 = \frac{4x^2}{(1-x)(2-x)}$

$\Rightarrow 20 - 30x + 10x^2 = 4x^2$

$\Rightarrow 6x^2 - 30x + 20 = 0$

$\Rightarrow 3x^2 - 15x + 10 = 0$

$\Rightarrow x = \frac{15 \pm \sqrt{225 - 120}}{6}$

$= \frac{15 \pm \sqrt{105}}{6}$

225
120
105
30
10 | 105.
100
6 | 15

4. — not possible.

$= \frac{25}{6}\ \frac{5}{6}\ 0.8$

$x = 0.8$

$2x = 1.6$

Date

Reaction Quotient (Q)

$K = 5$

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Initial: 2 2 2 taken

2 possibilities

- Equi → some amt. no change
- non-equi. →
  - Forward rxn
  - Backward rxn.

* Q determines in which way rxn will occur.

replace

$$K = \frac{[HI]^2}{[I_2][H_2]} = Q = \frac{4}{4} = 1 \neq K.$$

* For a non-equi. sys, Q approaches spontaneously towards K.

Q is law of mass-action at non-equi. pt.:

§ If $Q < K$; Q will increase → So, num ↑ & den. ↓. So, rxn. is forward

§ If $Q > K$; Q will decrease → So num ↓ & den. ↑. So, rxn. is backward.

~~So, If $Q < K$.~~

eg $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$3+x \quad 2+x \quad 16-2x$

$Q = \frac{256}{6} > 5$

$K = \frac{(16-2x)^2}{(3+x)(2+x)}$

So, rxn. is backward rxn.

Date

8 If Q = K, the sys. would be in equi.

9. Q. 0.6 mol of each CO & H_2O are mixed with another mixture containing 1 mol of CO_2 & H_2 at 1000 K in a closed flask where the following equi. is established

$$CO(g) + H_2O(v) \underset{K=4}{\rightleftharpoons} CO_2(g) + H_2(g)$$

(i) determine the moles of components at equi.
(ii) determine the moles of CO_2 which is req'd to be added to the original mixture so that moles of others doesn't changes.

	$CO(g)$	+ $H_2O(v)$	$\underset{K=4}{\rightleftharpoons}$	$CO_2(g)$	+ $H_2(g)$
Initial	0.6 − x	0.6 − x		1 + x	1 + x

$$Q = \frac{1}{(0.6)(0.6)}$$

$$= \frac{1}{0.36} = \frac{100}{36} = 2.9$$

$Q = 2.88 < K$.

So, rxn. is forward.

$$4 = \frac{(1+x)^2}{(0.6-x)^2}$$

$$\Rightarrow \frac{1+x}{0.6-x} = 2$$

$$\Rightarrow 1+x = 1.2 - 2x$$

$$\Rightarrow 3x = 0.2$$

$$\Rightarrow x = \frac{2}{30} = \frac{1}{15} \approx 0.066$$

Date

$\Rightarrow x = 0.067$

$0.6 - 0.067 = 0.533$

So, $CO \rightarrow 0.6 - 0.067 = 0.533$

$H_2O = 0.533$

Now, $K = \frac{(1+x)1}{(0.6)(0.6)}$

$\Rightarrow 4 = \frac{1+x}{0.36}$

$\Rightarrow x = 0.44$

Tendency of particles to escape from liqd (or solid)

☆ Vapour Pressure (VP) of Volatile Solid



If solid non-volatile → vacuum remains

If volatile → It will liberate some molecule in vapour phase.
Also, after some time solid ⇌ gas

The pressure exerted by gas at this instt. is called VP $= K_p \left(= \frac{PV}{1}\right)$

Defⁿ: VP of a volatile solid is equi P exerted by the molecules in the vapour phase in equi. with solid at a given Temp. VP is independent of amt(n) of solid as well as V of container.
It is characteristic of a substance.

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Q. VP of $I_2(s)$ is 0.1 atm at 27°C. 12.7 g of solid I_2 is placed in an evacuated 10L flask sealed & maintained at 27°C. equi. consett (K) for $H_2(g)$, $I_2(g)$

for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 27°C = 4.
Determine min. no. of moles of $H_2(g)$ ~~req~~ req^d to be added in order to just remove all ~~$I_2(g)$~~ I_2 from solid state. ($I = 127$, $I_2 = 254$)

$$H_2(g) + I_2(g) \underset{K=4}{\rightleftharpoons} 2HI(g)$$

$H_2(g)$ + $I_2(g)$ ⇌ $2HI(g)$

0.01 + 0.04 mol ⇌ 0.02

1L

$I_2(s)$

0.05 mol → 0.01 left

10 L, 27°C

$n_{I_2(g)} = \frac{PV}{RT} = \frac{0.1 \times 10}{24.6} \approx 0.04$

Here, some I_2 must have gone in vapour state

We want to dissociate the left 0.01 mol $I_2(s)$ in solid state.

If H_2 taken 0.101 mol, it cancels with 0.01 mol of $I_2(s)$. But at that Pt. $Q = \frac{(0.02)^2}{(0.04)(0)}$ which is ∞. Then ~~Q~~ $Q > K$, i.e rxn will be backward, making $I_2(s)$ again. So, $H_2(g)$ should have more than 0.01 moles so that $H_2 + I_2 \rightleftharpoons 2HI$ is also achieved & 0.01 $I_2(s)$ is also vaporised.

So, moles of $H_2 > 0.01$.

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Now, $K = \frac{(0.02)^2}{(0.04)\,x}$

$\Rightarrow 4 = \frac{(0.02)^2}{(0.04)\,x}$.

$\Rightarrow 0.16x = 0.0004$

$\Rightarrow 16x = \frac{4}{100}$

$\Rightarrow 4x = \frac{1}{100}$

$\Rightarrow x = \frac{1}{400}$.

$\Rightarrow x = 0.0025$.

So, now, moles of H_2 should be $0.0025 + 0.01$ so that $I_2(s)$ is vaporised & equi. is also achieved.

Hence, H_2 moles $= 0.0035$ Ans

$\Delta n \neq 0$

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$	n_T
mol	$1-\alpha$		α		α	$1+\alpha$
n_i	$\frac{1-\alpha}{1+\alpha}$		$\frac{\alpha}{1+\alpha}$		$\frac{\alpha}{1+\alpha}$	

If equi. $P = P$

then $P_i = \left(\frac{1-\alpha}{1+\alpha}\right)P \quad \left(\frac{\alpha}{1+\alpha}\right)P \quad \left(\frac{\alpha}{1+\alpha}\right)P$

$K_p = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}}$

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$\Rightarrow K_p = \frac{\left(\frac{\alpha}{1+\alpha}\right)^2 P^2}{\left(\frac{1-\alpha}{1+\alpha}\right) P} = \frac{\alpha^2 P}{1+\alpha} \times \frac{1+\alpha}{(1-\alpha)} = \frac{\alpha^2 P}{1-\alpha^2}$

$\Rightarrow \boxed{K_p = \frac{\alpha^2 P}{1-\alpha^2}}$ → for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

↓ for any no. of moles

α : amt. decomposed out of 1 mole.

★ α : Degree of dissociation :— Defined as the ~~mole~~ moles of reactant decomposed out of its 1 mol.

★ Initial P → denotion → P_0
Final/equi. P → → P

$K_p = \frac{\alpha^2 P}{1-\alpha^2}$

$\Rightarrow \frac{1-\alpha^2}{\alpha^2} = \frac{P}{K_p}$

$\Rightarrow \frac{1}{\alpha^2} - 1 = \frac{P}{K_p}$

$\Rightarrow \frac{1}{\alpha^2} = \frac{P+K_p}{K_p}$

$\Rightarrow \sqrt{\frac{K_p}{P+K_p}} = \alpha$

Q. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
K_p, P. derive α as a fn of K_p & P.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$
$1-\alpha$ 2α

$K_p = \left(\frac{1-\alpha}{1+\alpha}\right) P \left(\frac{2\alpha}{1+\alpha}\right) P$

$K_p = \frac{[(2\alpha)P]^2}{(1-\alpha)(1+\alpha)}$

$\Rightarrow K_p = \frac{4\alpha^2 P}{1-\alpha^2} \Rightarrow \frac{4P}{K_p} = \frac{1-\alpha^2}{\alpha^2}$

$$\Rightarrow \frac{1}{\alpha^2} - 1 = \frac{4P}{K_p}$$

$$\Rightarrow \frac{1}{\alpha^2} = \frac{4P + K_p}{K_p}$$

$$\Rightarrow \alpha = \sqrt{\frac{K_p}{4P + K_p}}$$ Ans.

Q $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ n_T $K_p = 2.5$ atm

$1-\alpha$ $\quad 2\alpha \quad 1+\alpha$ $P_{N_2O_4}$ at equi $= 0.5$ atm.

$\left(\frac{1-\alpha}{1+\alpha}\right)P \quad \left(\frac{2\alpha}{1+\alpha}\right)P$

Determine (a) P_{NO_2} at equi (b) α.

$$\left(\frac{1-\alpha}{1+\alpha}\right)2.5 = 0.5$$

$$\Rightarrow \frac{1-\alpha}{1+\alpha} = \frac{1}{5}$$

$$\Rightarrow 5 - 5\alpha = 1 + \alpha$$

$$\Rightarrow 4 = 6\alpha$$

(b) $\Rightarrow \alpha = \frac{2}{3}$.

$$K_p = \left[\left(\frac{2\alpha}{1+\alpha}\right)(2.5)\right]^2 \cdot \left(\frac{1-\alpha}{1+\alpha}\right)2.5$$

$$= \frac{4\alpha^2(2.5)}{(1+\alpha)(1-\alpha)}$$

$$2.5 = \frac{4\alpha^2(2.5)}{1-\alpha^2}$$

$$\Rightarrow 1 - \alpha^2 = 4\alpha^2$$

$$\Rightarrow \alpha^2 + 4\alpha^2 - 1 = 0$$

$$\Rightarrow \alpha = \frac{-4 \pm \sqrt{16+4}}{2}$$

$$= \frac{-4 + \sqrt{20}}{2}$$

$$= -4 +$$

n_T

$3-2\alpha$

$1+\alpha$

$$\left(\frac{2\alpha}{1+\alpha}\right)2.5 = P_{NO_2}$$

$$\Rightarrow \left(\frac{\frac{4}{3}}{1+\frac{2}{3}}\right)2.5 = P_{NO_2}$$

$$\Rightarrow \left(\frac{4}{5}\right)(2.5) = P_{NO_2}$$

$$\Rightarrow \frac{4(5)}{10} = P_{NO_2}$$

$$\Rightarrow P_{NO_2} = 2.$$

Here,

$$K_p = 2.5 = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 (2.5)^2}{0.5}$$

$$\Rightarrow P_{NO_2}^2 = (1.25)(0.5)$$

$$\Rightarrow P_{NO_2} = \sqrt{1.25} = 1.12 \text{ atm.}$$

Now

$$\left(\frac{1-\alpha}{1+\alpha}\right)P = 0.5 \quad \& \quad \left(\frac{2\alpha}{1+\alpha}\right)P = \sqrt{1.25} = 1.12$$

Find α & P

Or

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\quad V, T \rightarrow$ constt

0.5 atm $\quad$ 1.12 atm. $\quad n \propto P$

Initially $\quad 0.5 + \left(\frac{1.12}{2}\right)$ $\quad$ 0

$= 0.5 + 0.56$

$= 1.06$

1.06 atm $\longrightarrow$ 0.56 atm

1 atm $\rightarrow \frac{0.56}{1.06} = \alpha$

$= \frac{56}{106} \quad \frac{28}{53} \quad 0.5$

$\Rightarrow \alpha = 0.5$

1 S 3 e 4 2 P

10/12/09

Q. $PCl_5(g)$ is taken in an evacuated flask at 2 atm & sealed where it decomposed partially acc. to following rxn.

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

The equi mixture was found to be effusing

$PCl_5(g) \rightarrow$ 208 | Date

2·25 times slower ~~than~~ than pure $O_2(g)$ under identical cond^n of P & T. Determine K_p for decompos^n rxn

Ans Let rate of effusion of original mixture be r_i
After equi. state $r_f = 2.25\, r_i$

Now, $\frac{r_{O_2}}{r_{mix}} = \sqrt{\frac{M_f}{M_i}} = \frac{1}{2.25} = \sqrt{\frac{M_f}{208}}$

$\Rightarrow \frac{1}{5.0625} = \frac{M_f}{208}$

$\Rightarrow M_f = \frac{208}{5.0625}$

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ — n_{Total}

$1-\alpha$ — α — α — $1+\alpha$

$x_i = \frac{1-\alpha}{1+\alpha} P$ — $\frac{\alpha}{1+\alpha} P$ — $\frac{\alpha}{1+\alpha} P$

$K_p = \frac{\left(\frac{\alpha}{1+\alpha}\right) P \left(\frac{\alpha}{1+\alpha}\right) P}{\left(\frac{1-\alpha}{1+\alpha}\right) P} = \frac{\alpha^2 P}{1-\alpha^2} = K_p$

$P_{equi} = (1+\alpha) P_0$ $\left(\because \frac{P_1}{P_2} = \frac{n_1}{n_2} \rightarrow \frac{P_0}{P} = \frac{1}{1+\alpha}\right)$

Now $K_p = \frac{\alpha^2 P_0}{1-\alpha}$

Now $M = \frac{M_0}{1+\alpha}$

$\Rightarrow \frac{r_{O_2}}{r_{mix}} = 2.25 = \sqrt{\frac{208}{\frac{1+\alpha}{2}(32)}}$

$\Rightarrow 5.06 = \frac{13}{2(1+\alpha)}$

$\Rightarrow \alpha = 0.3$

So, $K_p = \frac{(0.3)^2 \times 2}{1 - 0.3}$

$= \frac{0.09 \times 2}{0.7}$

$= \frac{18}{70}$ ~~2.~~

$\Rightarrow K_p = 0.3$ atm.

Q 2 moles of $N_2(g)$ mixed with 3 moles of pure $PCl_5(g)$ is taken in a 100 L flask sealed & heated to 227°C; where following equi. is established.

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

At equi, total P inside flask was found to be 2.55 atm. Assuming $N_2(g)$ to be inert, determine α & K_p for the rxn.

$K_p = \frac{\alpha^2 P}{1 - \alpha^2}$ $\quad P = 2.55$ atm

$273 + 227 = 500$

$2 \rightarrow N_2$
$3 \rightarrow PCl_5$

$2.25 = \frac{2}{5} \cdot P_{N_2}$ $\qquad 2.25 = \frac{3}{5} \cdot P_{PCl_5}$

$\Rightarrow P_{N_2} = \frac{22.5}{2} = 11.25$

$P(100) = 2(0.082)(500)$

$\Rightarrow (P_{N_2})_0 = .82$ atm

$\frac{P_1}{P_{PCl_5}} = \frac{n_1}{n_{PCl_5}} = \frac{0.82}{P_{N_2}} = \frac{2}{3}$

$\Rightarrow P_{PCl_5} = \frac{3}{2} \times 0.82 \quad 0.41 \times 3$

$\Rightarrow \boxed{P_{PCl_5} = 1.23 \text{ atm.}}$

1.23 / 0.82 / 0.41 — 2.55 − .82 = 0.53

At equi. Partial P. of $PCl_5 + PCl_3 + Cl_2$ =

$1.23 - 0.82 = 0.41$

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$1.23 - p$ (Assumed that till equi, its pressure (p) is reduced.) 0.73 atm. Left

p p

$1.23 + p = 2.55 - 0.82$

$\Rightarrow p = 0.5$

$$K_p = \frac{(0.5)(0.5)}{(0.73)} = \frac{25}{73} \; 0.34$$

$\Rightarrow K_p = 0.34$ atm.

$\alpha = \frac{p}{1.23} = \frac{0.5}{1.23}$

23 + 27 = 340

73 / 23 / 219 / 173 / 64 / 252

Q. $F_2(g)$ & $PF_3(g)$ at 0.5 atm each are mixed in a flask, sealed & heated to 127°C. At (340K) 127°C, K_p for

$PF_5(g) \rightleftharpoons PF_3(g) + F_2(g) \quad K_p = 0.25$ atm

Determine mole fraction of PF_5 present in the flask at equi.

Date

$PF_5(g) \rightleftharpoons PF_3(g) + F_2(g)$ $K_p = 0.25$ atm

$\Rightarrow$ None, $\frac{2\alpha}{2}$ $\frac{1-\alpha}{2}$ $\frac{1-\alpha}{2}$ 2

$2 - 2\alpha + 2\alpha$

$\frac{(1-\alpha)^2}{4} \times \frac{2}{2\alpha} = 0.25$

42

$\Rightarrow \frac{(1-\alpha)^2}{4\alpha} = 0.25$

$\Rightarrow \frac{1+\alpha^2-2\alpha}{4\alpha} = 0.25$

$\Rightarrow 1+\alpha^2-2\alpha = \alpha$

$\Rightarrow 1+\alpha^2-3\alpha = 0$

$\Rightarrow \alpha^2-3\alpha+1 = 0$

$\Rightarrow \alpha = \frac{3 \pm \sqrt{9-4}}{2}$

$= \frac{3 \pm \sqrt{5}}{2}$

$= \frac{3-2.2}{2}$

$\Rightarrow \alpha = \frac{0.8}{2} = 0.4.$

2
2 | 5.0000
-4
4 | 100

Or

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ $K_p = 4$

	$PCl_3(g)$	$Cl_2(g)$	$PCl_5(g)$
n_i	0.5	0.5	0
n_{equi}	0.5-p	0.5-p	p

Now

$K_p = 4 = \frac{p}{(0.5-p)^2}$

$\Rightarrow 1 + 4p^2 - 4p = p$

$\Rightarrow 4p^2 - 5p + 1 = 0$

$\Rightarrow p = \frac{5 \pm \sqrt{25-16}}{8}$

$\Rightarrow p = \frac{5 \pm 3}{8}, 1, \frac{1}{4}$

1 → reject ($\because p \leq 0.5$)

$\Rightarrow p = 0.25$ atm.

$P_{equi} = 1 - p = 0.75$ atm.

Now, $P_i = x_i P$

$\Rightarrow x_i = \frac{0.25}{0.75} = \frac{1}{3} = 0.33$

☆ ~~Homogeneous equi~~

☆ Chemical Equi → Homogeneous equi

→ Heterogeneous equi

1) Homogeneous → Reversible sys. in which all components are in same phase is known as homogeneous sys. & equi. is called homogeneous equi

2) Heterogeneous :- Reversible sys in which more than 1 phase are involved are known as heterogeneous sys & equi. is called heterogeneous equi.

eg

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\quad K_p = P_{CO_2}$ (1)

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

Date 27/3/27

(53.5) (300K)

Q. VP of $NH_4Cl(s)$ at 27°C is 0.25 atm. If 50g of $NH_4Cl(s)$ is sealed in a 5L evacuated flask, at 27°C, determine mass of solid salt remaining in the flask. Also determine K_p.

14
4
+35.5
53.5

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

$VR = p^2 = 0.5$

$\Rightarrow p = \frac{1}{\sqrt{2}}$

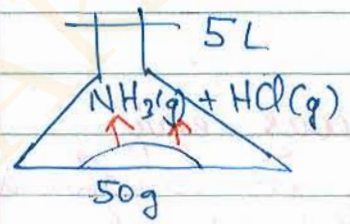
$\Rightarrow p = \frac{1}{1.4}$

$\Rightarrow p = 0.07$ atm.

14
6
84

$2p = 0.5 \Rightarrow p = 0.25$ atm.

$K_p = (0.25)^2 = 0.0625$ atm^2.



$n(NH_3) = \frac{(0.25)(5)}{24.6}$

$= \frac{1.25}{24.6}$

$= \frac{125}{246} \times 10^{-1}$

$n(NH_3) = 0.05$ mol

$n = \frac{(0.5)(5)}{24.6}$

$= \frac{0.25\ 5}{246 \times 10}$

$= \frac{5}{49 \times 10^2}$

$= 0.001$

mol. NH_4Cl initial $= \frac{50}{53.5}$

$m(NH_4Cl)_{left} = \left(\frac{50}{53.5} - 0.05\right) 53.5$

$= 47.5$ g.

H.W

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Q. In previous question, if flask initially contain $NH_3(g)$ at 1 atm, then, what would be equi Partial P of NH_3 after decompos^n ~~of~~ equi of NH_4Cl is established

✡ Le Chatelier's Principle

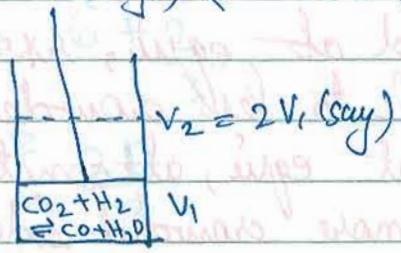
If a change is made at equi; sys readjust itself by changing equi. compos^n in order to ignore (→ nullify, undo) the change made at equi.

① Effect of P/V (or)

$\Delta n = 0$ or $\Delta n \neq 0$

(a) $\Delta n \neq 0$

$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(v)$



$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]}$$

At V_2:

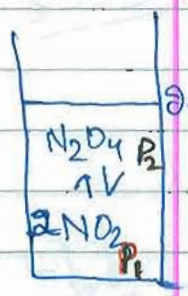
$$Q_c = \frac{[CO]/2\ [H_2O]/2}{[CO_2]/2\ [H_2]/2}$$

$\Rightarrow Q_c = K_c$

☆ If $\Delta n = 0$, equi amnt
Changing P or V, moles of reactant or product won't change in a closed sys.

(b)(2) $\Delta n \neq 0$

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta n = 1$



$K_p = \frac{(P_1)^2}{P_2}$ $V_1 \rightarrow V_1/2$: $N_2O_4 \rightarrow 2P_2$, $NO_2 \rightarrow 2P_1$ $Q_p = \frac{(2P_1)^2}{2P_2} = 2\frac{P_1^2}{P_2}$

~~$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$~~ ~~$\Delta n = -1$~~

~~$\Delta n = -1$~~

So, backward dirn on increasing P.

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ $\Delta n = -1$

$K_p = P_{PCl_5} / P_{PCl_3} \cdot P_{Cl_2}$

Let $V_1 \rightarrow V_2 = V_1/2$

$Q_p = \frac{K_p}{2} < K_p \rightarrow$ Foward dirn. ⟶

☆ If P is increased at equi, rxn proceed from more crowded side to less crowded side.
Increasing P at equi, at constt n, T drive (rxn) from more crowded side to less crowded side & vice versa.

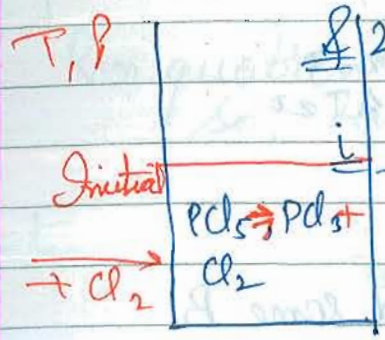
Imp

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Q. 2 moles of each PCl_5, PCl_3 & Cl_2 are taken at equi in a flask. Now, some $Cl_2(g)$ is added at constt T, P till vol. is doubled. Determine moles of $Cl_2(g)$ added.



$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\Delta n \neq 0$

$\frac{2}{V}$ $\quad \frac{2}{V}$ $\quad \frac{2}{V}$ $\quad K_c$

Forward → (∵ m is variable)

So,

$\frac{2+y}{2V}$ $\quad \frac{2-y}{2V}$ $\quad \frac{2+x-y}{2V}$ $\quad \frac{x}{V}$

$\frac{(2P_1)^2}{2P_2}$ $\quad \frac{2P_1^2}{P_2} = K_p$ $\quad = 1$

This rxn will move in backward dirn.

∵ Q > K.

$n_{Total} = 6 + x - y = 12$ → V → 2V

$\Rightarrow x - y = 6 \rightarrow (1)$ So, n → 2n

⇒ 6 → 12

y = moles of Cl reacting

$K_c = \frac{8(2-y)}{2 \times V^2} \times \frac{2x}{2+y}$

$= \frac{8(2-y)}{2(2+y)} = \frac{2x(2-y)}{x(2+y)} = \frac{2}{x}$

$\Rightarrow y = \frac{2}{3}$ $\quad \Rightarrow \frac{2-y}{2+y} = \frac{1}{2}$

$\Rightarrow x = 6 + \frac{2}{3}$

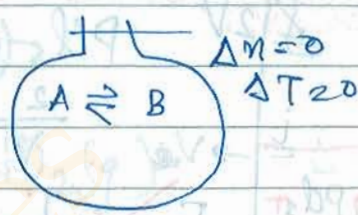
$\Rightarrow x = \frac{20}{3}$

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☆ Effect of add^n/removal of reactants/products.

$A \rightleftharpoons B$



$K_c = \frac{[B]}{[A]}$

(1) Add some A : ($\Delta V \geq 0$)

$Q_c = \frac{[B]}{[A]}$

(2) Add some B

Add A → Forward rxn.
Add B → Backward rxn.

☆ If reactant or product is added at equi, rxn proceed in a ~~de~~ dirn. opp. to the side where add^n is done.

Q. Equi. constt for decompos^n of $N_2O_4 \rightleftharpoons 2NO_2$ is 0.6 mol/L. 2 moles of each N_2O_4 & NO_2 are taken in an evacuated 2L flask & allowed to attain equi. If 1 mol of NO_2 is further added at equi, determine the moles of N_2O_4 which must be added so that the equi. moles of N_2O_4 ~~are~~ doesn't change.

$N_2O_4 \rightleftharpoons 2NO_2$; $K_c = 0.6$ mol/L



$0.6 = \frac{[NO_2]^2}{[N_2O_4]}$

Date

i)

$$N_2O_4 \rightleftharpoons 2NO_2$$

n		
V = 2L		
[ ]	1 M	1 M

Rxn quotient = 1 > K_c

So, rxn. will be ~~forward~~ backward.

t = t	$1+x$	$1-2x$	$2-1$
			$1 \rightarrow \frac{1}{2}$
			$x \rightarrow \frac{x}{2}$
			So, $2x \rightarrow x$

$$K_c = \frac{(1-2x)^2}{(1+x)}$$

$$\Rightarrow 0.6 + 0.6x = 1 + 4x^2 - 4x$$

$$\Rightarrow 4x^2 - 4.4x + 0.4 = 0$$

$$\Rightarrow x^2 - 1.1x + 0.1 = 0$$

$$\Rightarrow x = \frac{1.1 \pm \sqrt{1.21 - 0.4}}{2}$$

$$= 1.1 \pm \sqrt{\quad}$$

$$\Rightarrow 4x^2 - 4.6x + 0.4 = 0$$

$$\Rightarrow x = \frac{4.6 \pm \sqrt{\quad}}{\quad}$$

$$\Rightarrow 40x^2 - 46x + 4 = 0$$

$$\Rightarrow x = \frac{46 \pm \sqrt{2116 - 640}}{80}$$

$$= \frac{46 \pm \sqrt{1476}}{80}$$

$$= \frac{46 + 38}{80}$$

$$= \frac{84}{80} \quad 1. \quad = 0.1$$

$$\Rightarrow \boxed{x = 0.1}$$

1.21
− 0.40
0.

46
46
1276
1184
216
40
1
216
640
1476

At equi.

~~Mol.~~

$$N_2O_4 \rightleftharpoons 2NO_2$$

Equi. 1.1 M $0.8\,M + 0.5\left(\frac{1}{2}M\right)$

$1.1 + x$ $= 1.3$

So, Rxn backward.

let x mole/L of N_2O_4 is added

Now $0.6 = \frac{(1.3)^2}{1.1+x}$

$\Rightarrow .66 + 0.6x = 1.69$

$\Rightarrow 0.6x = 1.03$

$\Rightarrow x = \frac{10}{6}\frac{5}{3} 1.6$

$\Rightarrow x = 1.67$

Ans = $(1.7 \times 2) + 3.4$ M

Removal

$$A + B \rightleftharpoons AB \qquad K_c = \frac{[AB]}{[A][B]}$$

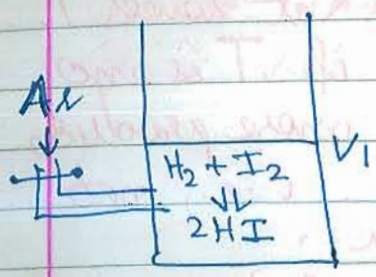
☆ If reactant / product is removed at equi, Rxn proceed to the side from where removal is done

(i.e non-reacting in mixture)

☆ Effect of adding inert gas at equi.

① $\Delta n = 0$ ② $\Delta n \neq 0$

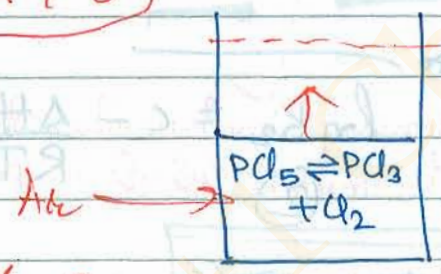
① $\Delta n = 0$ ∴ Adding inert gas, equi. doesn't gets disturbed (T, V → constt). Conc. remains same.



$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Finally → In case of $\Delta n = 0$, there will be no effect on the MOLES of either reactant/product on add^n of inert gas at equi; either at constt → V or at constt → P.

② $\Delta n \neq 0$



$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

☆ If $\Delta V = 0$, inert gas add^n mole change नहीं होगा, → $\Delta n = 0$ or $\Delta n \neq 0$.

+ Ar(g)
$\Delta V = 0$
$\Delta T = 0$

no

☆ Effect on moles of reactants/products

Case (i) Ar(g) is added at T, P → constt.

V ↑
P ↓ So, rxn → less crowded to more crowded.

So, moles of more crowded compds. ↑.

Date

☆ Effect of T → apply samely for $\Delta n = 0$ & $\Delta n \neq 0$

$A \rightleftharpoons B$ $\quad \Delta H > 0$ (Endo) → favoured at high T

or $\Delta H < 0$ (Exo) → non favoured at high T

☆ Endothermic rxn is favoured at high T while exothermic rxn is favoured at lower T.

∴ in case of endothermic rxn, if T is inc. maintaining other things constt, more products will be present at new equi. i.e, net rxn will occur in forward diren.

Reverse will be true for exothermic rxn.

$$\ln K = C - \frac{\Delta H}{RT}$$

K → equi constt; C → constt of integration; ΔH → enthalpy of rxn; R → universal gas constt.

Van't Hoff's eqn.

$$\ln K_1 = C - \frac{\Delta H}{RT_1} \quad (1) \qquad ; \qquad \ln K_2 = C - \frac{\Delta H}{RT_2} \quad (2)$$

$$\Rightarrow \ln \frac{K_2}{K_1} = \frac{2\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 \times T_2}\right)$$

(1) $\Delta H > 0$

$T_2 > T_1$; $K_2 > K_1$

In case of endo rxn, if T ↑, K ↑

$A \rightleftharpoons B$.

$K_2 = \frac{[B]}{[A]}$; rxn → forward.

X A 2

Date

EFFECT OF ~~CAL~~ CATALYST

Catalyst neither changes compos^n nor pos^n. (K)
Catalyst neither affect equi. compos^n, nor equi. constt. It just increases rate of rxn. However, it increases rate of both forward & backward rxn by the same factor which just reduces the time reqd to attain equi.

ured at
high T
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er T.
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rxn.

Chemistry Notes
Akshansh

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1. Hydrogen

* Most abundant elemt of UNIVERSE ; 90%
ICBM → Inter Continental Ballistic Missile

POSITION OF H in P.T :-

* H has some similarities with elemts. of both grp I & grp 17. ~~elemts~~ ∴ it can be placed in either of these 2 grps. On that ground, its pos" in P.T is not fixed.

* ISOTOPES OF HYDROGEN → $[{}_1H^1]$, $[{}_1H^2$ or ${}_1D^2]$, $[{}_1H^3$ or ${}_1T^3]$

A → Mass no. (no. of neutrons + protons)

Z → Atomic no. (No. of Proton)

Date

☆ It has no neutron.
$_1H^1$ → has 99.9987 %. rest % age existence is of $_1H^2$ & $_1H^3$.

$_1T^3$ is the only radioactive isotope of H. Other 2 are stable.
approx → $10^{18}\ H \xrightarrow{\beta^-} {}_1T$

☆ PREPARATION OF H: At RT, H exist as diatomic gaseous molecule. ($H_2 \rightarrow g$)

Industrial method of Preparation:

(1) By the action of Zn on dil soln of HCl.

$$Zn + \underset{\text{(acid)}}{2HCl} \longrightarrow ZnCl_2 + H_2(g)\uparrow$$

(2) By action of Zn metal on conc. soln of alkali (NaOH)

$$\underset{\text{(base)}}{2NaOH} + Zn \longrightarrow \underset{\text{Sodium Zincate}}{Na_2ZnO_2} + H_2(g)$$

(3) Passing steam over Fe gives $H_2(g)$.

$$3Fe(s) + 4H_2O(g) \xrightarrow{\Delta} Fe_3O_4(s) + 4H_2(g)\uparrow$$

Date

Laboratory Method :- In laboratory $H_2(g)$ is produced in pure form by electrolysis of ~~H_2O~~ doubly distilled H_2O in presence of trace (small) amt. of either strong acid / strong base.

① $H_2O \rightleftharpoons H^+ + HO^-$

$H^+ + e^- \rightarrow \frac{1}{2}H_2(g)$ (At cathode) → Red^n

② By action of steam over either Hydrocarbon or C.

$C_nH_{2n+2} + nH_2O(v) \longrightarrow \underbrace{nCO_2 + (2n+1)H_2}_{\text{water gas}}$

$C(gr) + H_2O(v) \longrightarrow CO + H_2(g)$

☆ PROPERTIES :

1. H is colourless, odourless, tasteless, lightest gas at RT.
2. It has least solubility in H_2O.

RXNS:

i) Rxn with non-metals

H combines directly with Halogens, S, & O on heating to produce their hydrides.

$H_2 + X_2 \xrightarrow{\Delta} 2HX$; $H_2 + \frac{1}{2}O_2 \xrightarrow{\Delta} H_2O$

$3H_2 + N_2 \rightleftharpoons 2NH_3$

2) Rxn. with metals
H combines with some highly electro +ve metals of gp 1 & gp 2 forming metal hydrides. H_2 on heating with Na, K, Ca forms NaH, KH, CaH_2.

$$H_2 + Na \xrightarrow{\Delta} NaH$$
$$+ K \xrightarrow{\Delta} KH$$
$$+ Ca \xrightarrow{\Delta} CaH_2$$

★ H doesn't react with either acids or base in aq. soln

{USES} 1. Rocket fuel :- It is used for hydrogenation of unsaturated organic compd.
2) As most efficient rocket fuel.
3) Industrial fuel.

★ HYDRIDES (Class of compds) : Hydrides are all those compds. formed from 2 elemts. in which 1 is H.

① Ionic/Saline (Salt like hydride)
② Molecular/Covalent
③ Metallic (Non-Stoichiometric) (Interstitial)

① Ionic hydrides : Ionic hydrides are the compd formed b/w gp 1, gp 2 metals, Al & Zn, with H. Compounds are ionic in nature & conduct electricity in aqueous soln. Their aqueous soln is strongly basic in nature.

Ionic

Date

eg: LiH, CaH_2, AlH_3, ZnH_2.

* They are conductive in their aqueous soln.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2\uparrow$$

(2) Molecular hydrides are the binary compds. formed b/w H & non-metals.

- Molecular hydrides are all covalent in nature & ∴ have lower B. Pt. & melting Pt. than ionic hydrides.
- They are non conducting in aqueous soln.
- They are either neutral or acidic in aqueous soln.

eg: CH_4, H_2O, BH_3, HCl.
(Neutral: CH_4, H_2O, BH_3; Acidic: HCl)

① e^- deficient hydride
They are the hydrides in which atleast 1 atom has deficiency of e^-s. i.e octet of atleast 1 atom is incomplete.
eg: ~~BH_3~~, B_2H_6, BeH_2

② e^- precise hydride
Hydrides in which all the atoms have exactly closed shell confi. are known as e^- precise hydride. In this type of hydride, no non-bonded e^-s are present in valence shell of any of the atom.
eg: all hydrocarbons.

③ e^- rich hydride
Hydrides in which there is 1 or more lone pair of e^-s present in valence shell of 1 or more atom. eg: H_2O, NH_3, HCl.

Date

(3) Metallic hydrides :

→ Stoichiometric of compds → In which elemts are present in simple whole no ratio as known as stoichiometric compds.
eg: $NaCl$, $CaCl_2$, CH_4.

→ Non-Stoichiometric compds → In which elemts are not present in simple whole no. ratio are known as non-stoichiometric compds.
eg: $Na_{19}Cl_{20} \rightarrow NaCl_{\frac{20}{19}}$ (just an eg. → not actually true)

→ Non Stoichiometric hydrides are formed by heavy metals - transition metals, inner-trans" metals & some heavy metals of p-block.
Hydrides of this category are always non-stoichiometric. eg: $LaH_{2.8}$ ($La_{10}H_{28}$), $TiH_{1.85}$



★ H_2O_2 Hydrogen Peroxide :

PREPARATION :

M1
By action of (dil.) soln of H_2SO_4 over grp 1 / grp 2 metal peroxide.
Na_2O_2, CaO_2, K_2O_2
+
H_2SO_4 ↓
Na_2SO_4 + H_2O_2 ; $CaSO_4$ + H_2O_2 ; K_2SO_4 + H_2O_2
Distilling the soln just above B.Pt. of H_2O_2 enable separation of H_2O_2 from rxn mixture.

M2
On large scale, H_2O_2 is produced in industry by electrolysis of (conc.) soln of H_2SO_4.
$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$
conc.
At anode : oxidn
$2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$
(Per Sulphuric acid)
$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$

* When H_2SO_4 is conc. then it ionises partially → H^+ + HSO_4^-

M1

BaO_2 is preferred over others ∵ $BaSO_4$ (ppt) formed.

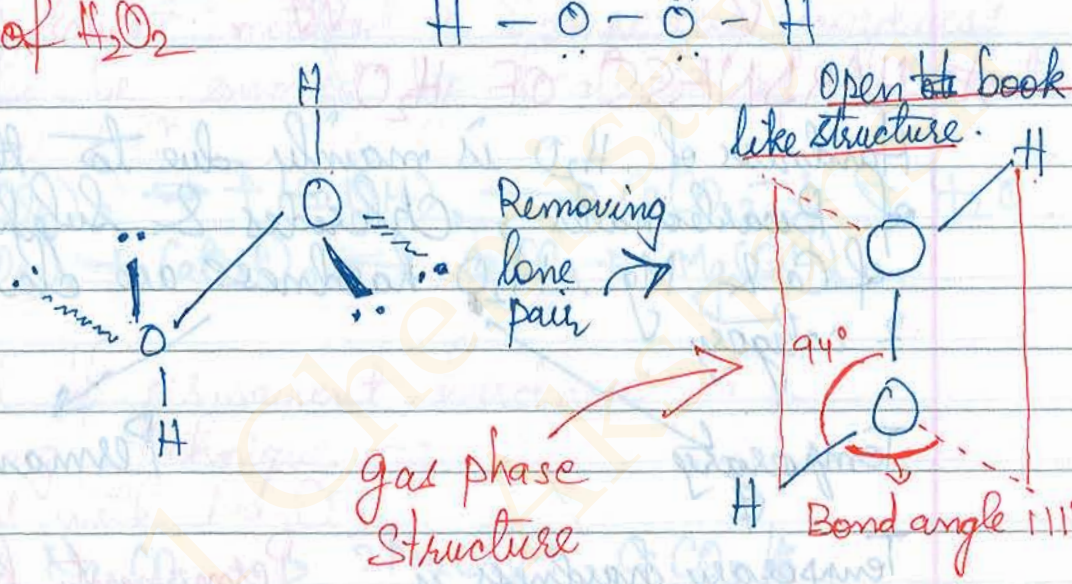
$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

M2

In this process, in electrolytic sol^n → concentration of H_2SO_4 remains same. It plays role of catalyst.

* Uses of H_2O_2 → • Bleaching agent (most common), • ~~Photography (developing)~~, ~~in~~ • Used for developing photographic film, • Used as an analytic reagent in laboratory for redox titration.

* Structure of H_2O_2



* In solid state, inter planar angle decreases to ≈ 96° due to intermolecular H bonding b/w adjacent molecules.

* H_2O_2 is highly soluble in H_2O (∵ it can form H-bond) due to its ability to form intermolecular H-bond

• H_2O_2 is unstable compd; it decomposes on either heating or in presence of light into $H_2O + \frac{1}{2}O_2$.

$$H_2O_2 \xrightarrow[\text{or } h\nu]{\Delta} H_2O + \frac{1}{2}O_2$$

(Sunlight can decompose H_2O_2). Due to that, H_2O_2 always comes in Black bottle.

① Temporary hardness can be removed ✓ by boiling H_2O. Bicarbonates are removed as follows →

$$Ca(HCO_3)_2 \xrightarrow{\Delta} \underset{\text{Filtered off}}{CaCO_3\downarrow} + CO_2 + H_2O.$$

$$Mg(HCO_3)_2 \xrightarrow{+H_2O,\ \Delta} Mg(OH)_2 + 2CO_2 + H_2O$$

Mg comes out in the form of $Mg(OH)_2$ due to a relatively lower solubility of $Mg(OH)_2$ than $MgCO_3$.

② Lime treatment method → Temporary hardness can also be removed by treatment of H_2O with CaO (lime) sol^n.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O.$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 + Mg(OH)_2.$$

☆ Removal of permanent hardness :
Following technique →

① Treatment with Na_2CO_3.

$$CaCl_2 + Na_2CO_3 \longrightarrow 2NaCl\downarrow + CaCO_3$$

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4\downarrow$$

$$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3 + 2NaCl\downarrow$$

$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4.$$

② Softening by ion-exchange method (Commercial Method)
In ion-exchange method, the hard H_2O is passed through an Ion exchanger, the commonly used ion exchanger is ALUMINA (Al_2O_3) supported over C. Another one contain $NaAlSiO_4$ (Sodium Alumino Silicate). When H_2O is passed through these exchangers, Ca^{2+}, Mg^{2+} ions are exchanged with Na^+ (mainly) present in exchanger & purification is done.

Date

D_2O (HEAVY WATER)

D_2O is prepared by electrolysis of ultra-pure H_2O using very high voltage.

It is used ~~to absorb neutrons~~ as a moderator in nuclear rxn. ∴ Fission can be nuclear fission; Nuclear fission can be controlled for power generation.

Chemistry
Akshansh

Ch. S-block

GROUP ONE-A

Li
Na
K
Rb
Cs

Metals of grp I are obtained by Electrolytic Reduction Method from their salts (Usually Chloride salts).

☆ Alkali metals can't be obtained by chemical red^{n} method from their salts. It is due to the reason that alkali metals are themselves R.A. ∴ obtained only by Electrolytic Red^{n}

$NaCl(l) \rightarrow Na^+ + Cl^-$

(l) = melted

$H_2O + NaCl(aq) \rightarrow H^+, OH^-$
Na^+, Cl^-

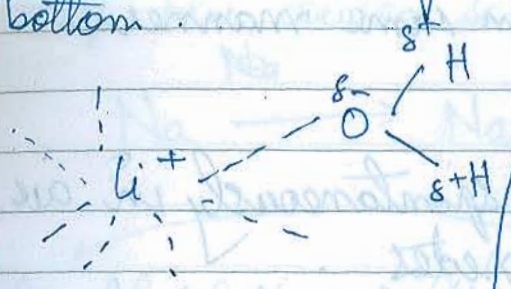
ρ ∝ M.Pt in metals

Date

★ Electrolysis is carried out in molten state of salt — not of their aq. sol^n ∵ in aq. sol^n H^+ is reduced in preference to Na^+ (alkali ion)

PROPERTIES:

1) IE: Alkali metals have smallest IE in its period.
2) Alkali metals have high hydration E. Among alkali metal, Hydration E decreases from top to bottom.



Hydration Energy (ΔH_{hyd}) → Hydration is a process of solvation in which H_2O molecules develop a weak electrostatic attⁿ with metal ion. It is always an exothermic process. E released per mole of metal ion in the process of hydration is called Hydration Enthalpy

★ Li^+ has highest ΔH_{hyd} due to its max. polarising power in its grp.

3) B.Pt & M.Pt: B.Pt of metals increases from top to bottom. M.Pt also increases from top to bottom with an ~~ex~~ exception → Na has higher M.Pt than K. In general, metals are soft at RT, can be cut from knife. ~~All alkali~~
4) Li, Na, K floats over H_2O due to their ρ < 1 g/cc Rb & Cs have ρ slighly > 1 g/cm^3

Reason for lower ρ or M.Pt of alkali metals → Alkali metals have very large size (in period) ∴ in solid state produces large void space due to which metals have low ρ. ρ parallels M.Pt, so, alkali metals have low M.Pt.



Date

CHEMICAL RXNS

1) With H_2O.

Li is stable in cold H_2O. Other metals react with H_2O at RT & reactivity increases from top to bottom.

$Na + H_2O \rightarrow NaOH + \frac{1}{2}H_2\uparrow$

$M + H_2O \rightarrow MOH + \frac{1}{2}H_2\uparrow$

} Li doesn't react with cold H_2O.

★ Li reacts with hot H_2O in same manner.

2) With O_2

Imp ★ All Alkali metal react spontaneously in air forming diff type of oxides.

Reactivity ~~de~~ increases from top to bottom.

- $2Li + \frac{1}{2}O_2 \rightarrow Li_2O$
- $4Na + \frac{3}{2}O_2 \rightarrow \underline{Na_2O} + \underline{Na_2O_2}$ Sodium peroxide
- $3K + 2O_2 \rightarrow K_2O_2 + \underline{KO_2}$ (super oxide) Mainly (major)

Rb, Cs only form superoxide.

★ All oxides are strongly basic in aq. soln

3) With halogens

Alkali metal combines with F & O_2 spontaneously at RT; Br, I reacts on heating forming Metal halides

$M + \frac{1}{2}X_2 \rightarrow MX$

4) With Acid

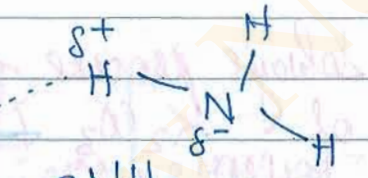
Alkali metal reacts with acid sol^n forming their salt & $H_2(g)$ is evolved.

Imp ✱ ↓ PROPERTY → BOTH OF GRP 1 & GRP 2.

✱ Alkali metal in (liq.) NH_3 → compressed $NH_3(g)$

Alkali metal when dissolved in $NH_3(l)$ forms a deep blue colored sol^n.

$$Na \longrightarrow Na^+ + e^-$$



i.e eNH_3

solvated electron.

It absorb in visible range of electromagnetic radiation. ~~Blue colorate~~ Alkali & Alkaline earth metals produces a deep blue colored sol^n in $NH_3(l)$. Blue coloration is due to presence of solvated (or ammoniated) e^- which absorb in visible region.

When sol^n is heated, free neutral metal is recovered back (only alkali metals) ~~recover~~ which establishes presence of solvated e^- in the sol^n.

13/12/09

✱ $Na_2CO_3 \cdot 10H_2O$ (Washing Soda)

SOLVAY'S PROCESS : In Solvay's process, brine sol^n is treated with $CaCO_3$ where following rxn takes place →

$$CaCO_3 + 2NaCl \longrightarrow Na_2CO_3 + CaCl_2.$$

Steps (SODA-AMMONIA PROCESS)

$$CO_2 + H_2O + NH_3(g) \longrightarrow NH_4HCO_3 \text{ (ammonium bicarbonate)}$$

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3\downarrow + NH_4Cl$$

crystallises out

$NaHCO_3$ ~~Solubility~~ < NH_4Cl solubility.

Date

* $NaHCO_3$ being less soluble than NH_4Cl. separates out from soln by process of fractional crystallization.

$$NH_4Cl\ NaHCO_3 \xrightarrow{\approx 150^\circ C} \underbrace{Na_2CO_3}_{\text{anhydrous}} + H_2O + CO_2$$

highly hydroscopic and absorbs moisture

$$Na_2CO_3 + 10H_2O \rightarrow Na_2CO_3 \cdot 10H_2O.$$

stable.

* Solvay's process can't be used for preparation of K_2CO_3 (∵ ~~solubility of $KHCO_3$ is~~ as $KHCO_3$ (∵ greater solubility of $KHCO_3$ compared to $NaHCO_3$; from the soln, $KHCO_3$ & NH_4Cl crystallises at same T. ∴ they can't be separated by fractional crystallization

* USES

1. Na_2CO_3 is used in softening of H_2O.
2. Glass industry (for hardening glass).
3. Paper industry (whitening of paper).
4. Cement industry., paint industry (for removing old paint).
5. Soap Industry (long chain fatty acid Na salt).
6. $NaHCO_3$ also called baking soda is used for Baking process

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

$$\underbrace{\begin{matrix} COOK \\ | \\ CH(OH) \\ | \\ CH(OH) \\ | \\ COOH \end{matrix}}_{\text{Potassium bitartarate or Potassium Hydrogen tartarate}} + NaHCO_3 \xrightarrow{\Delta}$$

Date

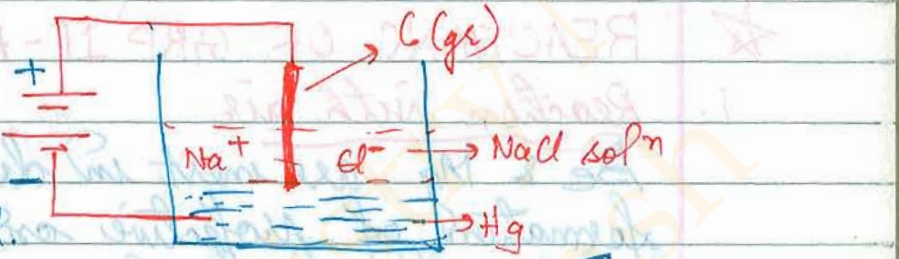
COOK
|
CH(OH) + H_2O + (CO_2 ⟵ Baking)
|
CH(OH)
|
COONa

Sodium Potassium Tartarate.

Castner Process.

✡ NaOH

It is prepared on large scale by electrolysis of brine sol^n in a special type of electrolytic cell called Castner-Kellner Cell. So, this process is also called



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

Anode → C (gr) rod.

Cathode → Hg plays role.

$Na^+ + e \rightarrow Na$ —dissolve in Hg→ Na(Hg) Amalgum.

$Na(Hg) \xrightarrow[\text{boil}]{H_2O} Na + H_2O \rightarrow NaOH + \frac{1}{2}H_2 \uparrow$

USES

- NaOH is used in glass & soap industry. It is highly hydroscopic & a very common laboratory reagent.

GROUP TWO - A

Be, Mg, Ca, Sr, Ba

Elements of grp 2 are all highly electro +ve & have several similarities with grp 1 metals.

~~Pt. of Difference~~

✡ Pt. of Difference b/w grp 1 & grp 2 metals.

1) Elements of grp 2 are harder & denser than elements of grp 1 (due to size)

2. Ions of grp 2 metal has higher hydration E than ions of grp 1 metal. (∵ of charge → polarising power)
3. Elements of group 2 associate more H_2O molecules when present in compd. (∵ of more polarising power of grp 2 metals)
4. Be & Mg forms some covalent compd; but no covalent compd. exist for grp 1 metals.
eg: $BeCl_2$ → covalent.

☆ REACTIONS OF GRP II-A METALS.

1. Reaction with air

Be & Mg are inert in dry/moist air due to formation of protective oxides on their surface. Other elents of this grp. forms normal oxide on heating in dry air & hydroxide in moist air.

$Ca + O_2 \rightarrow CaO$ $\quad CaO + H_2O \rightarrow Ca(OH)_2$

$Ba + O_2 \rightarrow BaO \xrightarrow{H_2O} Ba(OH)_2$.

2. With halogens

All ~~ements~~ elents of this grp combine with halogen on heating forming halides, F reacts at RT.

$Ba + Cl_2 \xrightarrow{\Delta} BaCl_2$

3. ~~Std~~ Sol^n in $NH_3(l)$

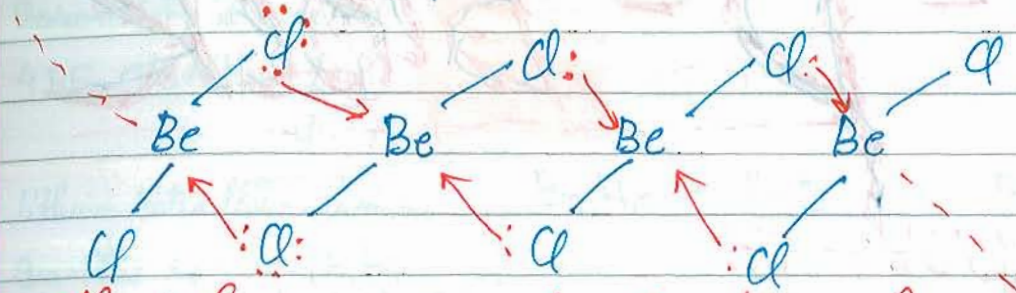
All elents of grp 2 form deep blue sol^n in $NH_3(l)$ due to presence of solvated e^- like alkali metal. However, on heating NH_3 sol^n, metal amide is obtained.

$Ca + NH_3(l) \rightarrow Ca^{2+} + e^-(NH_3) \xrightarrow{\Delta} Ca(NH_2)$
blue
$+ H_2$

Date

→ Gas at RT.

* **Be** : $BeCl_2$ → Covalent
e⁻ deficient



When compressed, ↑ type of polymerisation occurs (due to incomplete octet of Be).

* CaO (कली चूना) (Quick lime).

Preparation

It is prepared on large scale by thermal decompos^n of limestone ($CaCO_3$).

$CaCO_3(s) \xrightarrow{\Delta} CaO + CO_2\uparrow$.

PROPERTY

It is strongly basic & reacts with H_2O exothermically.

$CaO + H_2O \longrightarrow \underset{\text{Slaked lime}}{\underset{\text{(बुझा चूना)}}{Ca(OH)_2}}$ $\quad \Delta H < 0$

Uses :→ Cement Industry (Quick setting → takes H_2O).

POP : $CaSO_4 \cdot 2H_2O \xrightarrow[\Delta]{393\,K} CaSO_4 \cdot \frac{1}{2}H_2O + \frac{3}{2}H_2O$

Gypsum $\qquad$ POP

If heated above 393 K, $CaSO_4$ → dead burnt plaster or cement is formed.

Imp ★ Flame Colouration : Flame test : Used for detection of Ca, Sr, Ba. Ca → Brick red color to flame
Sr → Crimson red
Ba → Apple-green

Date

13 - P - Block

GROUP - 13

Very Imp. **Boron (B)**

Imp

Diborane
B_2H_6

① By action of conc. sol^n of phosphoric acid (H_3PO_4) over Mg_3B_2 (Magnesium Boride)

$Mg_3B_2 + H_3PO_4 \xrightarrow{\text{conc}}$

$Mg_3(PO_4)_2\downarrow + B_2H_6$

ppt.

② By red^n of Boric anhydride with Al (metal) in stream of $H_2(g)$

$B_2O_3 + H_2 \xrightarrow{Al} Al_2O_3 +$ B_2H_6

Boric anhydride

③ By red^n of Boron halides (usually BF_3) with either ~~NaBH4~~ or $LiAlH_4$ NaH

Continued

Boric acid
H_3BO_3

Preparation

① By action of dil. HCl on borax ($Na_2B_4O_7$)

$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow$

Borax

$4H_3BO_3 + 2NaCl$

② By passing $SO_2(g)$ through aq. sol^n of Colemanite ($Ca_2B_6O_{11}$)

$Ca_2B_6O_{11} + 2SO_2 + 9H_2O \rightarrow$

$2CaSO_3\downarrow + 6H_3BO_3$

Boric acid → One of strongest disinfectant. (put ✱ on carrom)

Borax
$Na_2B_4O_7 \cdot 10H_2O$

Preparation

① By action of Na_2CO_3 with aq. boric acid.

$4H_3BO_3 + Na_2CO_3 \rightarrow$

$Na_2B_4O_7 + CO_2 + 6H_2O$

② Adding Na_2CO_3 to aq. sol^n of colemanite ($Ca_2B_6O_{11}$)

$Ca_2B_6O_{11} + Na_2CO_3 \rightarrow$

$CaCO_3 + Na_2B_4O_7$

$+ NaBO_2$

(Sodium metaborate)

$Na_2B_4O_7$ when crystallised from its sol^n, it comes out as decahydrate.

DIBORANE

Date

Diborane

- $2BF_3 + 6NaH \rightarrow B_2H_6 + 6NaF$

  ↓

  Boron BF_3 is reduced

- $4BF_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3Li[AlF_4]$

  Lithium Tetrafloro aluminii.

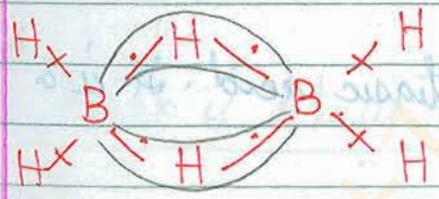
  In this rxn → $LiAlH_4$ reduces Boron hydride → BF_3.

PROPERTIES

- B_2H_6 is gas at RT., it has strong reducing property & it has very high heat of combustion.

→ common rocket fuel

& STRUCTURE



- 4 terminal B-H bond that are pure, single σ covalent bond.
- It has 2 internal 3-centered-2-e⁻ (3c2e) bond. Also called B-H-B bridge bond (also called Banana bond)
- It is called e⁻ deficient molecule.
- Hybridisation of B → sp^2.
- It has H-B-H plane ⊥ to B-H-B plane

Chemical Properties →

(1) Hydrolysis →

B_2H_6 hydrolyses spontaneously at RT to give $H_2(g)$

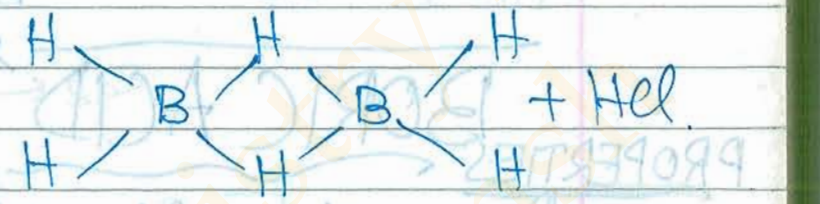
$$B_2H_6 + H_2O \rightarrow B(OH)_3 + H_2\uparrow$$

↓

H_3BO_3

Orthoboric acid.

(2) with HCl



$$\rightarrow B_2H_5Cl + H_2$$

If excess HCl (excess), then $B_2H_2Cl_4$. (all terminal H substituted) $+ 4H_2$.

(3) Very Imp — Reaction with NH_3.

3 rxns

- $B_2H_6 + NH_3$ (excess) $\xrightarrow[\text{low temp}]{\text{RT gas}}$ $B_2H_6 \cdot 2NH_3$

  Adduct

  Addition Product

$$+ NH_3 \text{ (excess)} \xrightarrow[\text{High P}]{\text{High T}} (BN)_x$$

Boron Nitride.

↳ M.Pt → greater than 1000°C.

Used for making nosel of rocket.

☆ F, Cl are very strong O.A. Oxidising property decre from top to bottom.

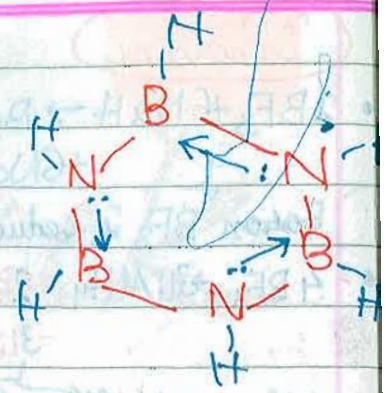
Date

Most Imp

$B_2H_6 + NH_3 \xrightarrow{\Delta} B_3N_3H_6$

1 : 2

Borazine
ob
Borazole
or
Inorganic
Benzene



(4) Reaction with Halogens

$B_2H_6 + F_2 \longrightarrow BF_3 + HF$

$+ Cl_2 \longrightarrow BCl_3 + HCl.$

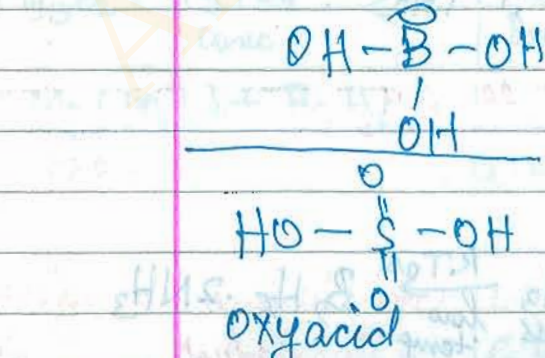
x

BORIC ACID

PROPERTIES

- Boric acid is white crystalline powd. at RT
- It is strong disinfectant & used as an antiseptic

STRUCTURE



$OH-\overset{OH}{\underset{|}{B}}-OH$ → It is not a tribasic acid. It is a monobasic acid

$HO-\overset{O}{\overset{\|}{S}}-OH$ (O)

Oxyacid

☆ Boric acid is a weak monobasic Lewis acid. Due to very weak nature of acid, it is not completely neutralised with bases like NaOH, KOH. Rather, equi is established
∴ Boric cannot be estimated by neutralisation titration in laboratory

Date

BORAX

USES

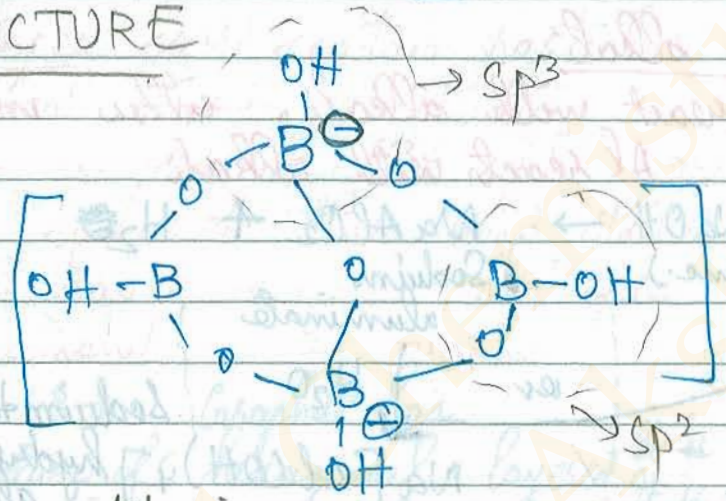
1) Borax is used for making superior ~~grade~~ grade glass. (Quality → Temp. withstand)

Imp. Borax on strong heating loses 8 molecules of water of crystallisation → This means that it is 8 water molecules of 1 type & 2 H_2O molecules of other type.

$$Na_2B_4O_7 \cdot 10H_2O \longrightarrow [Na_2B_4O_7 \cdot 2H_2O] - 8H_2O$$

$$[Na_2B_4O_5(OH)_4] \cdot 8H_2O$$

STRUCTURE



Borax is dibasic.

☆ General Properties (only for NCERT) of gp 13

D. Rxn. with O_2

B is inert to dry O_2 at RT.

$$B + O_2 \longrightarrow \text{no rxn}$$

$$+ O_2 \xrightarrow[\text{very strong heating}]{\Delta\Delta} B_2O_3.$$

$$2Al + \frac{3}{2}O_2 \xrightarrow{RT} Al_2O_3$$

F is strongest O.A.

Date

2) Rxn. with acid

B is not affected by common acids (HCl, H_2SO_4 & HNO_3) at RT. However, Al reacts with HCl, H_2SO_4 & RT forming $AlCl_3$, $Al_2(SO_4)_3$ liberating $H_2(g)$

$$Al + HCl \xrightarrow{RT} AlCl_3 + H_2\uparrow$$

$$+ H_2SO_4 \xrightarrow{RT} Al_2(SO_4)_3 + H_2\uparrow$$

Al is inert with HNO_3 ∴ Reason → HNO_3 is strong OA. It oxidises Al to Al_2O_3 forming protective hard layer ~~which~~ on the surface & prevent further rxn. of metal.

3) Rxn. with alkali

B doesn't react with alkali, either in cold or in hot. Al reacts with alkali.

$$Al + NaOH \xrightarrow{(conc.)} \underset{\text{Sodium aluminate}}{NaAlO_2} + H_2\uparrow$$

$$Al \xrightarrow{NaOH\ (dil.)\ \text{or}\ H_2O} \underset{\text{Sodium tetra hydroxo-aluminate}}{Na[Al(OH)_4]}$$

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^{\ominus} + Na^{\oplus} \rightarrow Na[Al(OH)_4]$$

4. Rxn. with halogens:

$$B + \underset{\text{Highly reactive}}{\frac{3}{2}F_2} \xrightarrow{RT} BF_3$$

$$B + \frac{3}{2}Cl_2 \xrightarrow{\Delta} BCl_3$$

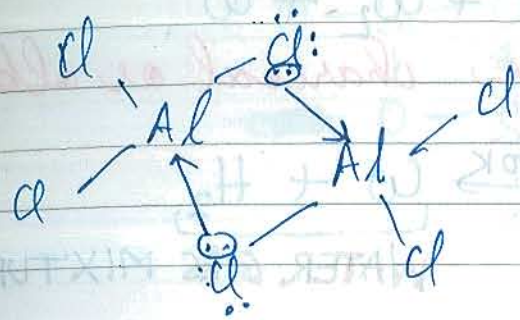
$$Al + \tfrac{1}{2}F_2 \xrightarrow{RT} AlF_3$$

$$Al + \tfrac{1}{2}Cl_2 \xrightarrow{\Delta} AlCl_3$$

dimer → reactant ⅔ single unit ⅔ बनते हैं,
two

Date

☆ In solid & liq. state $AlCl_3$ exists are dimer → $(AlCl_3)_2$ i.e Al_2Cl_6 in order to complete its valency.



Thus, ~~AlCl~~ $AlCl_3$ acts as a strong Lewis Acid in gaseous state.

GROUP - 14

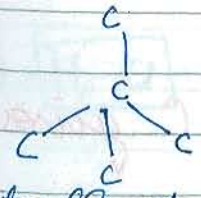
C, Si

Allotropes contain particles of same chemical constitution which maybe an atom or molecule but diff^t array in the crystal lattice of their solid state.

C has 3 common allotropes —

1) Diamond

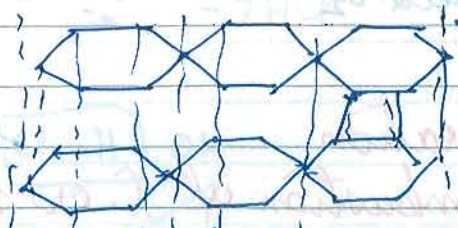
Diamond has 3-D network structure of C in which each C is tetrahedrally bonded to the 4C, which extend infinitely in 3D.



Due to this structural reason, it is the hardest material present in nature. It has max refractive index. Its chemically inert.

2) Graphite

Graphite has hexagonal layered array of C atoms with large inter-planar distance.



Due to its layered structure it has got some of unusual characteristic like, its soft, good conductor of both heat & electricity

3) Buckminsterfullerene or Fullerene

It is the 3rd allotrope of C.
It is not a natural allotrope-
It is prepare synthetically (1986)
It was prepared by Smalley.

In nano tech., nano tubes are made of Fullerene.

CO

Preparation

(1) By thermal decompos^n of FeC_2O_4 (ferrous oxalate)

$$Fe_2C_2O_4 \xrightarrow{\Delta} FeO + CO_2 + CO$$

(2) By passing steam over charcoal or alkane hydrocarbon (alkane).

$$C(s) + H_2O(v) \xrightarrow{+1000K} \underbrace{CO + H_2}_{\text{WATER GAS MIXTURE}}$$

$$CH_4(s) + H_2O(v) \xrightarrow{\text{High T}} CO + H_2(g)$$

(3) By heating C(g) in air above 1200 °C.

$$C + O_2(air) \xrightarrow{1200°C} CO + N_2 \rightarrow \text{PRODUCER GAS}$$

(∵ CO_2 decomposes at around 900K. So, we keep 1200°C for safety)

(used for production of NH_3 ⇒ Haber's Process)

PROPERTIES OF CO

1) Neutral :- CO is neutral oxide.
2) Its a poisonous gas.
3) Its a very strong RA.

eg : $CO + \frac{1}{2}O_2 \rightarrow CO_2$ (reduced O_2)

CO_2

Preparation

1) Combustion of C or hydro C gives CO_2.

PROPERTY

1) CO_2 is acidic in nature. It has very low solubility in H_2O at RT & P. However, it dissolves in H_2O significantly, but at very high P.

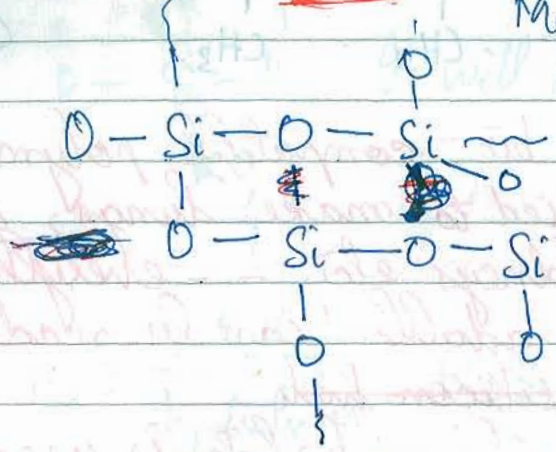
Date

Si

Silica — SiO_2

O=Si=O

Melting pt (> 3000°C)



3D network structure.

No independent existence of SiO_2.

SILICONES Silicones are organo silicon polymers in which individual units are linked together by Si — O — Si linkage.

Silicones are prepared by hydrolysis of organosilicon halides, which is obtained by alkylation of $SiCl_4$.

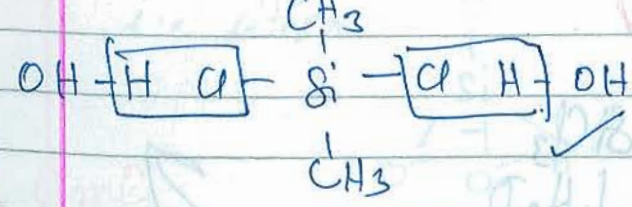
$$SiCl_4 + 2RMgCl \longrightarrow \underbrace{R_2SiCl_2}_{\text{monomer}} + 2MgCl_2$$

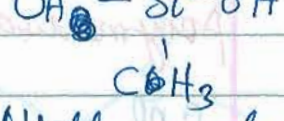
Grignard's reagent (Alkyl Magnesium Halide)

$$R_2SiCl_2 + 2CH_3MgCl \longrightarrow (CH_3)_2SiCl_2$$

dimethyl silicon chloride

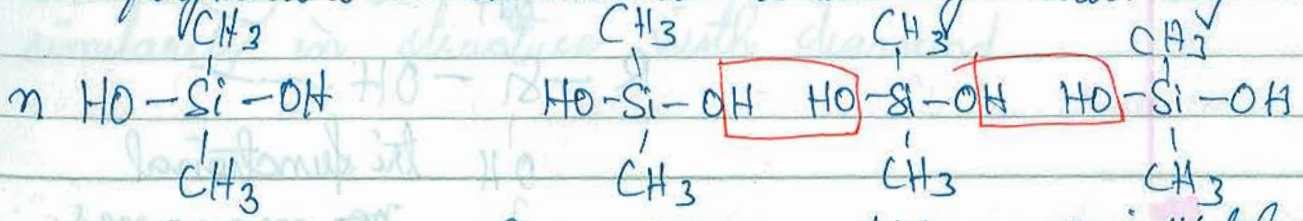
$$(CH_3)_2SiCl_2 + H_2O \xrightarrow[-2HCl]{} Si(CH_3)_2(OH)_2$$





Highly reactive.

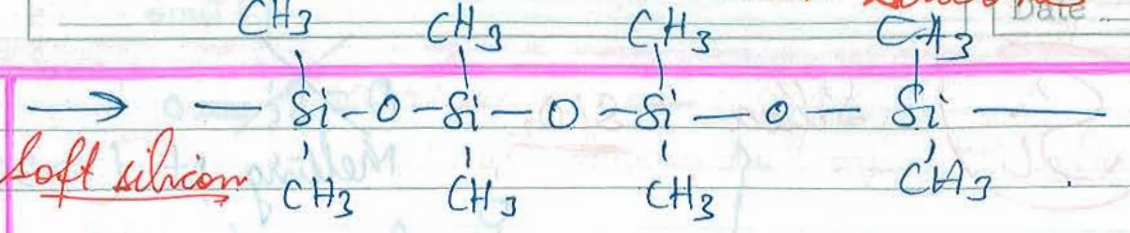
This polymerises on its own due to its high reactivity.



Q. Prepare H_2 and it converts spirits!

~~Dihg~~

Lineal chain Silicone



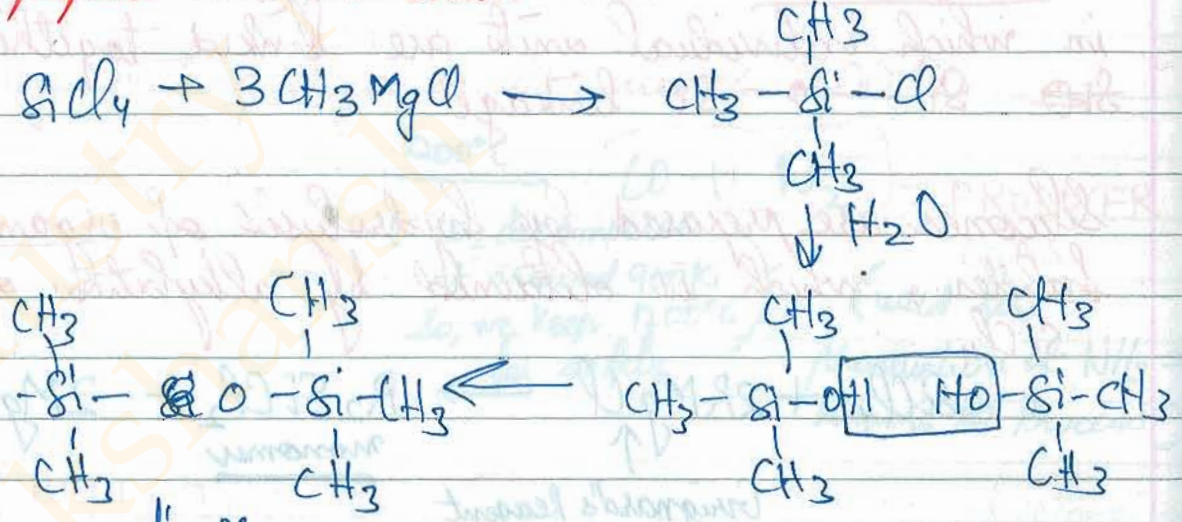
Soft silicon

☆ Silicones are bio-compatible polymer → ~~lungs~~ It is used to make lungs, heart, bones, kidneys etc. -- everything.

☆ ~~It~~ Is biodegradable (can be made so)

☆ ~~So, dihalide silicon hal~~

☆ So, dialkyl silicon halide is used to prepare lineal chain silicone.

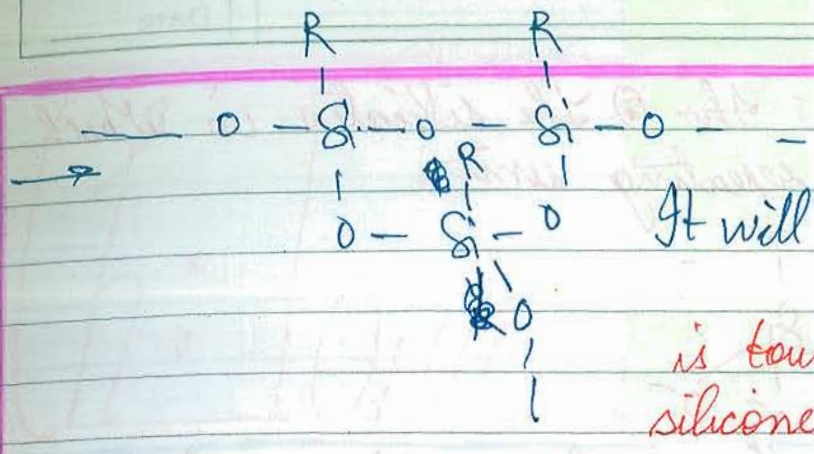


dimer

☆ dimeric silicones are liq. at RT at are used as lubricants.

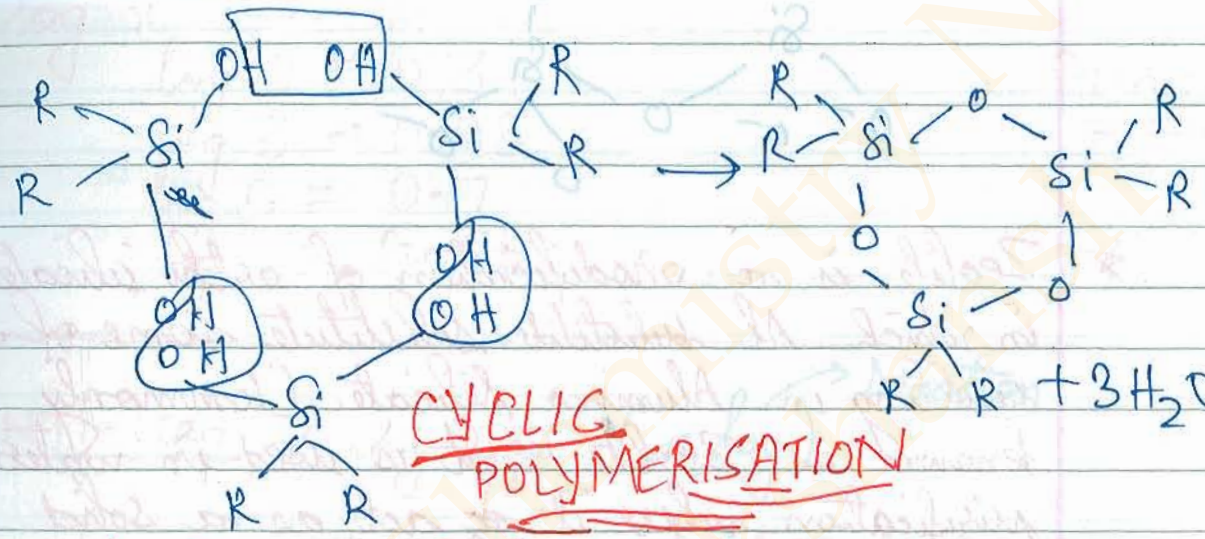
☆ Trialkyl silicon halide is used to stop the polymerisation of lineal chain silicone. ~~because~~ It is added after sometime when polymerisation is started.

tri functional monomer



It will be a CROSS LINKED SILICONE which is tougher than linear chain silicone.

$$R_2SiCl_2 + H_2O \xrightarrow[\text{hydrolysis}]{\text{controlled}} R_2Si(OH)_2$$

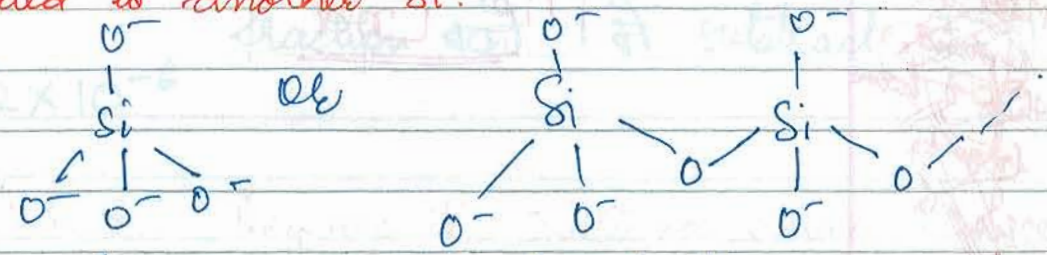


CYCLIC POLYMERISATION

* 6 member is most stable in cycle product

SILICATES : They are 3-D network of polymers in which silicon is tetrahedrally bonded to $4O_2$ which either bear -ve charge or further bonded to another Si.

i.e either



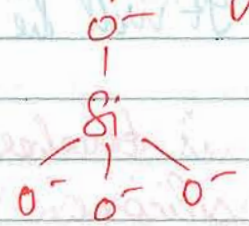
mp.

Silicates are all very hard material due to its similarity in structure with diamond.

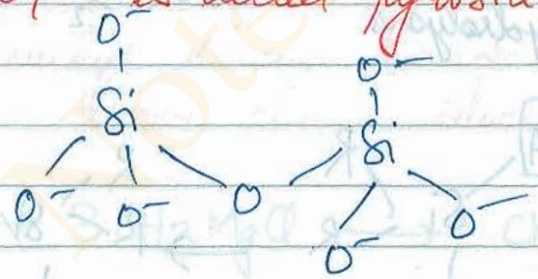
Silicates are of 2 types → 1) Orthosilicates

Date

(1) Orthosilicate : ~~The~~ ⊛ The silicates in which SiO_4^{4-} is the repeating unit.



(2) Pyrosilicate : The repeating unit is $Si_2O_7^{6-}$ is called pyrosilicate



* Zeolite is a modification of ortho silicate in which Al ~~substitute~~ substitute some of Si resulting in Alumino Silicate (commonly known as Zeolite). It is used in water purification where it ~~act~~ act as a solid support for Ion-exchange ~~to~~ resin.

The End



Ch: Ionic Equilibrium

* $\ln_e x = 2.303 \log_{10} x$

* $\log x$: $x = 2$

$\log 2 = 0.3$

$\log 3 = 0.48$

$\log 5 = 0.7$

$\log 7 = 0.85$

Approx

---

* ANTI-LOG of any qty (a log) → Denotion

eg: $\log x = 2.1 = 0.7 \times 3 = 3 \log 5 = \log 125$.

$\log x = 5.3 \quad x = 2 \times 10^5$

$5 + 0.3$

$\log x = -5.7$ — -ve qty का log कैसे लेते है ?

$= \bar{6}.3$ (Z से 1 add करना fraction को 1 से subtract करना)

$= 2 \times 10^{-6}$

19/12/09

* ELECTROLYTES : They are the substance which produce ions when dissolved in soln. They are of 2 type :

Strong electrolyte ↓

They are the electrolytes which is completely ionised in soln

eg: All strong acids → HX (excluding HF), $HClO_4$, HIO_4, H_2SO_4, HNO_3

All strong base (oxides & hydroxides of grp. 1 & grp 2 metals) & all salts

Weak Electrolytes

Date

☆ Weak electrolytes – They are the substance which are partially ionised in soln. After ionisation to some extent, equi is established b/w weak electrolyte & its ions.

eg: All weak acids are weak electrolyte — HF, all carboxylic acid (RCOOH), HCN, HNO_2, H_2SO_3, $H_2C_2O_4$, H_2CO_3 - - - - -; All weak base are weak electrolytes eg:- @ NH_3 & $R\text{-}NH_2$ (amines) are weak @ base.

☆ CONCEPT OF pH.

★ $pH = -\log_{10}[H^+]$ → concentration of H^+ ion → molar conc. i.e MOLARITY

eg: $[H^+] = 2\times10^{-4}$

$\Rightarrow -\log[H^+] = -\log(2\times10^{-4}) = 4 - \log 2 = 3$

★ $pOH = -\log[OH^-]$

$p = -\log$ s.t $pK = -\log K$.

a type of fn producing -ve log. of some qty.

@ At 25°C, pH of acid(soln) < 7.

pH of base(soln) > 7 (only at 25°C)

Imp → At 25°C, for a soln, $pH + pOH = 14$ (constt. at any T)

At other T, $pH + pOH$ = constt, but not 14.

14 → only at 26°C.

Date

☆ For a neutral sol^n ; pH = pOH = 7 at 25°C.
= const^t at any T.

A neutral sol^n refers to a ~~sol~~ sol^n which doesn't change color of ~~a~~ moistened litmus paper.

☆ pH of sol^n of strong acid & strong base

• [I] → $[H^+]$ or $[OH^-] \geq 10^{-6}$ M

eg $H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$
1 2

molarity C 2C

$pH = -\log [2C]$

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

$[2C] = 3 - 0.3$
$= 2.7$

Q. Determine pH of a sol^n which is twice as basic as pure water at 25°C.

$[OH^-] = 10^{-7}$ M in water at 25°C.

In given sol^n $[OH^-] = 2 \times 10^{-7}$
$= 7 - 0.3$

pOH $= 6.7$

$pH = 14 - 6.7 = 7.3$.

Q 0.5 g of an impure sample of Na_2O is dissolved in a 100 mL, 0.12 M HCl sol^n at 25°C. pH of final sol^n was found to be 1.7. Determine purity of original sample assuming impurity to be neutral.

$Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$

$\frac{0.5 \times 10}{62 \times 5}$ $\frac{5}{62}$ 0.12 $\frac{10}{62}$

$= \frac{5}{62}$

Ans

HCl 0.12 M
100 mL

Na_2O (strong base)

CONCEPT

• Final soln ka pH = 1.2.
⇒ soln is acidic now also
Hence, base i.e Na_2O has reacted completely & HCl is still left.
So, Na_2O is limiting reagent

$$Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$$

M = 62
E = 31 ~~mole~~ mass of Na_2O = 0.31 g

$$\frac{0.31}{0.5} \times 100 = 62\%$$

Now
$pH = -\log[H^+] = 1.7$.
$\log[H^+] = -1.7 = \bar{2}.3$
$= 2 \times 10^{-2}$
$\Rightarrow [H^+] = 0.02$ M
meq. of HCl (initial) = 12.
meq of HCl (final) = 2
10 meq. HCl used.
⇒ 10 meq. Na_2O must have been there.

Q Determine pH of soln obtained by mixing 100 mL HCl soln of pH = 1 with 400 mL HCl soln of pH = 2.

$pH = -\log[H^+] = 1$
$\Rightarrow \log[H^+] = \bar{1}$
One $= 10^{-1}$ M
two $= 10^{-2}$ M.

$\frac{14}{500} = \frac{28}{1000}$ mmol

$pH = -\log(28 \times 10^{-3})$

$= -\log 28 + 3$

$= -0.85 - 0.6 + 3$

$= 1.55$

1 85
+6
1.45

23.00
−1.45
1.55

Q. What V of NaOH soln of pH = 10 should be added to a 100 mL HCl soln of pH = 1 in order to increase its pH to 1.7.

$M_{NaOH} = 10^{-1}$ e , mmol = 10

$M_{HCl} = 10^{-1}$

$-\log 10 \cdot pH = -\log [OH^-] = 10$

$= \log [OH^-] = -10 = 10^{-10}$

$M_{NaOH} = 10^{-10}$

mmol of NaOH $= (V \times 10^{-10})$

$mmol_{final} (10 + V \times 10^{-10})$.

$pH = -\log [H^+] < 1.7$

$= 2.3$

$= 2 \times 10^{-2}$.

$10 + V \times 10^{-10} = 2 \times 10^{-2} \times V$.

$\Rightarrow 10 = 2 \times 10^{-2} V - V \times 10^{-4}$

$= V \times 10^{-4} (2 \times 10^{-2} - 10^{-4})$

$\Rightarrow V = \frac{10}{(2 \times 10^{-2}) - 10^{-4}}$

$N_2O_5 + 2H_2O \rightarrow 2HNO_3$

Date

Ans 100 mL pH = 1 0.1 M H^+ = 10 mmol H^+

NaOH (10^{-4} M) → x mL added.

= 10^{-4} x mmol.

= $(10 - 10^{-4}x)$ mmol H^+

Final pH = 1.7 = $-\log[H^+] = 2 \times 10^{-2}$

$\Rightarrow \left(\frac{10 - 10^{-4}x}{100 + x}\right)$ M $H^+ = 2 \times 10^{-2}$

$\Rightarrow x = \frac{20000}{201} \approx 400$.

Q. 100 M HCl, pH = ?

2 M HCl, pH = $-\log 2 = -0.3 <$ pH

☆ HCl H_2SO_4 HNO_3

18 M 36 M 24 M.

They have a limit of conc. due to a limit of solubility in H_2O.

Imp eg 80g NaOH / 1L H_2O.

$\Rightarrow$ 2M NaOH.

$\Rightarrow$ pOH = −0.3

pH = 14.3.

So, 0–14 is not the range of pH.

If conc. > 1M, we are out of range of pH → 0–14.

Q. pH = ?, 10^{-9} M HCl at 25°C

Imp:

Theory of Ionization of Water.

weak electrolyte

* Water itself act at a weak electrolyte. It ionises in soln a ley following ⇔ eqn →

Endothermic $\Delta H > 0$

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

At constt T,

$$K_c \times [H_2O] = [H^+][OH^-]$$

K_w = 10^{-14} at 25°C ← Ionic product of H_2O.

* ~~At constt T~~

* Molarity of pure liquid depends only on T

* In ultrapure water $[H^+] = [OH^-] = 10^{-7}$ M. 25°C

* On inc. T, pH $[H_2O]$ will decrease.
∴ K_w will increase on inc. T.
So, $[H^+]$ ↑ & $[OH^-]$ ↑
Now, $pH = \log\left[\frac{1}{[H^+]}\right]$ ← inverse rel^n. So, $[H^+]$ ↑ So, pH ↓.

$$HCl \rightleftharpoons H^+ + Cl^-$$
$$10^{-2}$$

* H^+ or OH^- from solute < 10^{-7} M, ionisation of H_2O will have to be considered.

Date

☆ COMMON ION EFFECT (CIE)

CIE is suppression of ionisation of a weak electrolyte on add^n of a strong electrolyte having an ion common in them.

$$H_2O \underset{\Delta H > 0}{\rightleftharpoons} H^+ + OH^-$$

assuming x mol/L water is ionised back

$$\underset{-x}{} \qquad \underset{x+c}{} \qquad \underset{x}{}$$

$$HCl \longrightarrow H^+ + Cl^-$$

$$\underset{c}{} \qquad \underset{x+c}{} \qquad \underset{c}{}$$

$$K_w = [H^+][OH^-]$$

$$= (x+c)(x)$$

$$\Rightarrow \boxed{x^2 + cx - K_w = 0}$$

10^{-7}

Find x. So, conc. H^+ ion $= x + c$.

So, $pH = -\log(x+c)$.

ALITER

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$HCl \longrightarrow H^+ + Cl^-$$

PRINCIPLE OF ELECTRONEUTRALITY.

Charge remains balanced.

$$[H^+] = [OH^-] + [Cl^-]$$

$$\Rightarrow \boxed{[H^+] = \frac{K_w}{[H^+]} + c} \quad **$$

$\therefore K_w = [H^+][OH^-]$

$\Rightarrow [H^+]^2 - c[H^+] - K_w = 0$

→ applicable everywhere.

Q Determine pH of 10^{-7} M HCl (soln).

$x^2 + 10^{-7}x -$

$H_2O \rightleftharpoons H^+ + OH^-$

$-x \qquad x+c \qquad x$

$HCl \rightarrow H^+ + Cl^-$

$\not{c} \qquad c \qquad c$

$K_w = (x+c)x$

$\Rightarrow x^2 + 10^{-7}x - 10^{-14} = 0$

$\Rightarrow x = \dfrac{-10^{-7} + \sqrt{10^{-14} + 4\times10^{-14}}}{2}$

$= \dfrac{-10^{-7} + 2\sqrt{10^{-14}}}{2}$

$\Rightarrow \dfrac{10^{-7}}{2}\left(\sqrt{5}-1\right) \times 10^{-7} < 10^{-7}$

$[H^+] = 1.6 \times 10^{-7}$

$pH = 7 - \log 1.6 = 6.8.$

SOLUTION OF WEAK ACID/BASE 24/12/09

1) Weak Monobasic acids

CH_3COOH
HCN
HNO_2
HF

$HA \rightleftharpoons H^+ + A^-$

General eqtn

Date

$HA \rightleftharpoons H^+ + A^-$

$C - C\alpha \quad C\alpha \quad C\alpha$

$K_c = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{C\alpha^2}{1-\alpha} = K_a$ (ioniz^n const)

all equi conc.

α → degree of ionisation : It is the moles of electrolyte ionised out of its 1 mol.

So, For strong electrolyte $\alpha = 1$

" weak " $\alpha < 1$

$K_a = \dfrac{C\alpha^2}{1-\alpha}$ → Ionization constt. of an acid

It is K_c for weak electrolyte.

Working ✗ Let us assume that α is very small as compared to 1.

$\Rightarrow 1 - \alpha \simeq 1$

So, $K_a = C\alpha^2$

$\Rightarrow \alpha = \sqrt{\dfrac{K_a}{C}}$ at $\alpha \ll\ll 1$ → OSTWALD'S DILUTION LAW

∵ at a particular temp, K_a = constt. So, by formula if $C \downarrow, \alpha \uparrow$ & hence, with dil^n, dissociation ↑

Acc. to Ostwald's law, for a weak electrolyte at a given T, degree of ionisation (α) increases with dilution (i.e decreasing conc. 'C')

So, $\lim_{C \to 0} \alpha = 1$ → case of infinite dilution

at infinite dilution, strong & weak electrolyte behave samely ∵ $\alpha = 1$.

Date

☆

Q. From ostwald's law, If α concs less than 0.1, then $1-\alpha \approx 1$

Then, $K_a = [H^+]^2 / c$ → $[H^+][H^-]$

$\alpha < 0.1$ → $c(1-\alpha) \approx c(1)$.

$\Rightarrow [H^+] = \sqrt{K_a c}$ → Master eqⁿ.

★ If $\alpha > 0.1$, then solve quadratic → $K_a = \frac{c\alpha^2}{1-\alpha}$

α ✓

———— × ————

Q. Determine pH of (a) 0.1 M HF solⁿ. (b) 0.001 M HF solⁿ. $K_a = 5\times10^{-4}$ at 25°C

$\frac{5\times10^{-4}}{0.1}$

$= \sqrt{5\times10^{-3}}$

$= \frac{1}{10}\left(\sqrt{\frac{1}{2}}\right)$ ∵ $\alpha = 1$

$[H^+] = \sqrt{5\times10^{-5}}$

$= \frac{1}{100}\sqrt{\frac{1}{2}}$ $= \frac{1}{100}\sqrt{0.5}$

$= 0.07 \times 10^{-2}$ $= 7\times10^{-3}$

$= 7\times10^{-4}$

$= 4 - 0.85$ $= 3 - 0.85$

$= 3.15$ $= 2.15$

(b) $\alpha = \sqrt{\frac{5\times10^{-4}}{10^{-3}}} = 0.7 > 0.1$

So, solve

$5\times10^{-4} = \frac{0.1\alpha^2}{1-\alpha}$

$\Rightarrow 5 - 5\alpha\times10^{-4}$

$\Rightarrow 5\times10^{-4} - 5\alpha\times10^{-4} = 0.1\alpha^2$

$\Rightarrow 2\alpha^2 + \alpha - 1 = 0$

$\Rightarrow \alpha = 0.5$

$[H^+] = C\alpha$

$= 5 \times 10^{-4}$

$pH = 4 - \log 5 = 3.3$

Q* Sulphuric acid is a dibasic acid in which its 1st ionisation is complete. But 2nd ionisation never completes. K_a for 2nd ionisation (Ka_2) is 10^{-2} at 25°C. Determine pH of 0.01 M H_2SO_4 sol^n at 25°C considering partial 2nd ionisation.

(1)

$H_2SO_4 \longrightarrow H^+ + HSO_4^-$

0.01 M: 0.01 0.01

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ $\quad K_a = 10^{-2}$

$M = \frac{n}{V}$

$0.01 - x \quad x \quad x$

$+0.01$

$K_C = \frac{(x+0.01)\,x}{(0.01-x)}$

$\Rightarrow 10^{-2} = \frac{x^2 + 0.01x}{0.01 - x}$

$= 10^{-4} - 10^{-2}x - 10^{-2}x = x^2$

$\Rightarrow x^2 + 2 \times 10^{-2} x - 10^{-4} = 0$

Ans = 1.85

2 x 7 | Date = 1 | 0.85 + 0.3 = 1.15

x12

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$

$0.01(1-\alpha)$ $\quad 0.01\alpha + 0.01 \quad 0.01\alpha$

$K_a = 10^{-2} = \dfrac{(0.01\alpha + 0.01)(0.01\alpha)}{(0.01)(1-\alpha)}$

$\Rightarrow 10^{-2} = \dfrac{0.01\alpha(1+\alpha)\,0.01}{0.01(1-\alpha)}$

$\Rightarrow 1-\alpha = \alpha + \alpha^2$

$\Rightarrow \alpha^2 + 2\alpha - 1 = 0$

$\Rightarrow \alpha = \dfrac{-2 \pm \sqrt{4+4}}{2}$

$= -1 \pm \sqrt{2}$

$\Rightarrow \alpha = 0.4$

$\Rightarrow H^+ = 0.01 \times 0.4 + 0.01$

$= 14 \times 10^{-3}$.

$\Rightarrow pH = 3 - \log 14$.

$= 1.85$.

Q) 1 ml 0.1 M HCl sol^n is added to a 100 ml 0.1 M sol^n of a weak monobasic acid whose $K_a = 2 \times 10^{-3}$ at 25°C. Determine pH of resulting sol^n ignoring V change due to add^n of HCl.

HCl → $H^+ + Cl^-$

$(0.1)(1) = M(100)$

$\Rightarrow M_{HCl} = 10^{-3}$ now.

HCl → H^+ + Cl^-

10^{-3} M $\quad 10^{-3} \quad 10^{-3}$

HA $\rightleftharpoons$ H^+ + A^- $\quad K_a = 2 \times 10^{-3}$.

$0.1(1-\alpha) \quad 0.1\alpha + 10^{-3} \quad 0.1\alpha$

$$2\times10^{-3} = \frac{(0.1)\alpha(0.1\alpha+10^{-3})}{(0.1)(1-\alpha)}$$

$\Rightarrow 2\times10^{-3} - (2\times10^{-3})\alpha = 0.1\alpha^2 + 10^{-3}\alpha.$

$\Rightarrow 0.1\alpha^2 + 3\times(10^{-3})\alpha - 2\times10^{-3} = 0.$

$\Rightarrow \alpha^2 + 3\times10^{-2}\alpha - 2\times10^{-2} = 0$

$\Rightarrow 100\alpha^2 + 3\alpha - 2 = 0$

$\Rightarrow \alpha = \frac{-3 \pm \sqrt{9+800}}{200}$

$= \frac{-3 \pm 20\sqrt{2}}{200}$

$= \frac{-3 + 20\sqrt{2}}{200}$

1.4
e^2
28

$= \frac{25}{200} \quad \frac{1}{8}$

$= \frac{1}{8}.$

$H^+ = (0.1)\frac{1}{8} + 10^{-3}$

$= 0.012 \times 10^{-3}$

$= \frac{12}{1000} + \frac{1}{1000}$

$= 13\times10^{-3}$

$= 3 - \log 13$

$\Rightarrow 2\times10^{-3} = 0.1\alpha^2 + 10^{-3}\alpha$

$\Rightarrow 2 = 100\alpha^2 + \alpha.$

$\Rightarrow 100\alpha^2 + \alpha - 2 = 0$

$\Rightarrow \alpha = \frac{-1 \pm \sqrt{1+800}}{200}$

$= \frac{-1 \pm \sqrt{801}}{200}. \quad = \frac{-1 \pm 20\sqrt{2}}{200}.$

$= \frac{27}{200} = 0.13$ ~~$= 13 \times 10^{-2}$~~ $\simeq 1 \times 10^{-1}$

$\Rightarrow$

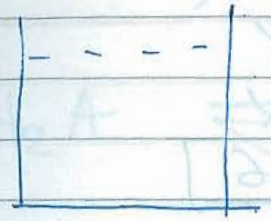
$H^+ = 0.1 \times 0.1 + 10^{-3}$

$= 11 \times 10^{-3}$

$pH = 3 - \log 11 \simeq 2$ ✓

Q To what V 0.5 M, 1L CH_3COOH soln must be diluted in order to double its pH. $K_a = 2 \times 10^{-5}$.

JEE



$\xrightarrow{H_2O}$

$c = 0.5$

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

$\downarrow H_2O$

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

Let C be new conc.

Initial pH =

10×10^{-6}

$= 10^{-3}$

$\alpha = \sqrt{\frac{2 \times 10^{-5}}{0.5}}$

$= \frac{2}{5} \times 10^{-6} < 0.1$

$\Rightarrow$ ~~$2 \times 10^{-5} = 0.5 \alpha^2$~~

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

$= 10^{-3}\sqrt{10}$

$=$

pH initial $= +\frac{1}{2}(5) = (2.5)$

$\Rightarrow$ Reqd pH $= 5$.

C = 0.5

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

$\downarrow H_2O$

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

c (say)

$\Rightarrow c(1-\alpha)$ $\quad c\alpha$ $\quad c\alpha$

$c\alpha = 10^{-5}$ ($\because$ pH final = 5)

$K_A = 2\times10^{-5} = \frac{c\alpha^2}{1-\alpha}$

$= 2\times10^{-5} = \frac{c\alpha \cdot \alpha}{1-\alpha}$

$\Rightarrow 2(1-\alpha) = \alpha$

$\Rightarrow 2 - 2\alpha = \alpha$

$\Rightarrow \boxed{\alpha = 0.6}$

$c\alpha = 10^{-5}$

$\Rightarrow c = \frac{10^{-5}}{0.6}$

Initial c after dilⁿ. $(C) = 1.5\times10^{-5}$

Now

$M_1V_1 = M_2V_2$

$\Rightarrow (0.5)(1) = (1.5\times10^{-5})V_2$

$\Rightarrow V_2 = \frac{0.5\times10^5}{1.5}$

$= 0.3\times10^5$

$\Rightarrow V_2 = 3\times10^4$ L

2) Weak - Dibasic Acid

- H_2CO_3
- H_2S.
- COOH / COOH
- H_2SO_3

H_2A.

their value would be sum of conc. of H^+ ions from both

Steps → General

$H_2A \rightleftharpoons H^+ + HA^-$ $\quad K_{a_1} = \frac{[H^+][HA^-]}{[H_2A]}$

c − x $\quad$ x + y $\quad$ x − y

$HA^- \rightleftharpoons H^+ + A^{2-}$ $\quad K_{a_2} = \frac{[H^+][A^{2-}]}{[HA^-]}$

x − y $\quad$ y + x $\quad$ y

In sol^n $[H^+] = x + y$ $\quad x >>> y$

$\Rightarrow x + y$ or $x - y$

$\Rightarrow x$

ALWAYS, for DIBASIC ACID.

$K_{a_1} >>> K_{a_2}$ - - - - - -

K_{a_1} $H_2A \rightleftharpoons H^+ + HA^-$

K_{a_2} $HA^- \rightleftharpoons H^+ + A^{2-}$

Now, $K_{a_2} = \frac{[H^+][A^{2-}]}{[HA^-]}$

If α is small, they are same.

2nd ionisation is contributing towards $[H^+]$ very small. So, its value can be neglected out of total $[H^+]$ while calculation

Hence, $K_{a_1} = \frac{[H^+][HA^-]}{[H_2A]} = \frac{[H^+]^2}{[H_2A]_{sc}} \Rightarrow [H^+] = \sqrt{K_{a_1} \cdot c}$

Q. Determine pH of 0.01 M CO_2 sol^n & $K_{a_1} = 4 \times 10^{-7}$, $K_{a_2} = 5 \times 10^{-11}$. Also, determine c of CO_3^{2-} in sol^n.

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $\quad K_{a_1} = 4 \times 10^{-7}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $\quad K_{a_2} = 5 \times 10^{-11}$

$pH = \sqrt{4 \times 10^{-9}} = 2 \times 10^{-4.5}$

$= \frac{1}{2}(9 - 0.6) = 4.2$

$$K_{a_1} = \frac{[H^+]^2}{C} \quad \Big| \; 1-\alpha \approx 1$$

$$[H^+] = \sqrt{K_{a_1} C} \Rightarrow 4.2 = pH$$

$$K_{a_2} = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]}$$

Taking 2nd Ionization is negligible, we can say that H^+ & HCO_3^- are in equimolar amt. i.e their conc will be same.

$$\text{So, } K_{a_2} = \frac{\cancel{[H^+]}\,[CO_3^{2-}]}{\cancel{[HCO_3^-]}}$$

$$\Rightarrow [CO_3^{2-}] = 5 \times 10^{-11}$$

★ Solubility of gas in H_2O (HENERY'S LAW)

Acc. to Henery's law, solubility of gas in H_2O is directly proportional to gas P.

i.e

$$(\text{mol } L^{-1})\, S \propto P_g$$

$$\Rightarrow S = k_H P$$

k_H = Henery's constt.
= mol $L^{-1} atm^{-1}$

★ In case of a mixture of gases (A, B → say), to find solubility of A, we should know Partial P of A.

JEE

Q. Conc of SO_2 in atmosphere over a town on a particular day was found to be 20 ppm. $K_{H_{SO_2}} = 10^{-4}$ at 25°C

Q. pH of an aqueous soln of CH_3NH_2 prepared by dissolving 1 mL of CH_3NH_2 in H_2O & making V to 50 mL was found to be 11.65 at RT[25°C]. If K_b of CH_3NH_2 is 2×10^{-4}, determine ρ of ⊜ in .

CH_3NH_2 11.65

$p(OH) = 2.35$

$= \bar{3}.07$

$= 5.8\times10^{-3}$

14.00
−11.65
2.35

pH = 11.65

pOH = 2.35 = −log [OH⁻]

⇒ log [OH⁻] = −2.35

= $\bar{3}$.65

[OH⁻] = 5×10^{-3}

$K_b = \frac{c\alpha^2}{1-\alpha}$

⇒ $2\times10^{-4} = \frac{5\times10^{-3}\times\alpha}{1-\alpha}$

⇒ $1-\alpha = \frac{5\alpha\times10^{1}5}{2}$

⇒ $1-\alpha = 25\alpha$

⇒ $1 = 26\alpha$

⇒ $\alpha = \frac{1}{26} = 0.04$

⇒ $\alpha = 0.04$ ✓

Determine pH of rain water occured on that day if $K_H (SO_2) = 1.5\ L^{-1} mol\ atm^{-1}$

7 Jan 10

✡ WEAK- BASE

$$NH_3(g) + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

(Weak base)

$$c(1-\alpha) \qquad c\alpha \qquad c\alpha$$

If α is very small

$1-\alpha \simeq 1$

$\Rightarrow \alpha = \sqrt{\frac{K_b}{c}}$ ✡✡

K_b

$$K_c = \frac{[OH^-][NH_4^+]}{[NH_4OH]} = \frac{c\alpha^2}{1-\alpha}$$

→ Dissociation constt. of base (basic ionisation constt.)

If $1-\alpha \simeq 1$; $K_b = [OH^-]^2 / c$

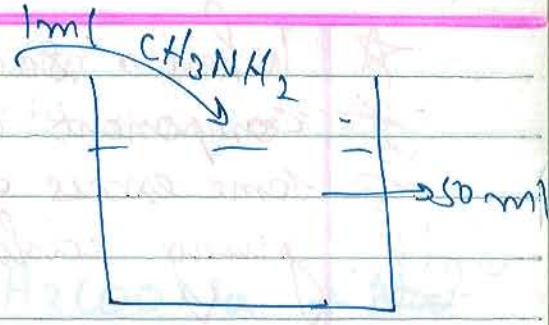
$\Rightarrow [OH^-] = \sqrt{K_b c}$ ✡✡

$C\alpha = 5 \times 10^{-3}$

$\Rightarrow C = \frac{5 \times 10^{-3}}{4 \times 10^{-2}}$

$= \frac{1.25}{10}$

$C = 0.125$



Now, n of amine $= 0.125 \times 50$

$= 6.25$ mmoles

mass $= 6.25 \times 31$

$= 193.75$

$= 0.1937$

$= 0.194$ g

$\rho = \frac{0.2}{1} \approx 0.2$ g/ml.

625
31
625
1875
19375

SALT - SOLUTION

Imp:

Category

(1) Strong Acid + Strong Base = Neutral : doesn't hydrolyse

~~(2) St. Base~~

eg : NaCl, Na_2SO_4, KNO_3, $CaBr_2$

(2) St. Base + Wk. acid = Basic

CH_3COONa, NaF, NaCN, CaF_2

(3) St. Acid + Wk. base = Acidic

NH_4Cl, CH_3NH_3Cl.

(methanamine chloride)

(4) Wk acid + wk. base = Find K_a & K_b of all compds.

If $K_a > K_b$ → acidic

$K_b > K_a$ → basic,

eg : CH_3COONH_4, NH_4NO_2

So, it can be acidic / basic.

Date

☆ When a salt is dissolved in H_2O, weaker component of the salt hydrolyses producing some excess of either H^+ ion or OH^- ion giving acidic / basic nature to the soln.

Category (2)

Imp.

$CH_3COO^{\ominus}Na \longrightarrow$ (base)

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$c(1-\alpha)$ $\quad$ $c(\alpha)$ $\quad$ $c(\alpha)$

K_h = Hydrolysis const.

reason why basic nature in this category.

$$K_h = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} \times \frac{[H^+]}{[H^+]} \rightarrow \frac{x}{x}\left\{\frac{H^+}{H^+}\right\}$$

III

$[H^+][OH^-] \rightarrow K_w = 10^{-14}$.

$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \rightarrow K_a = \frac{c\alpha^2}{1-\alpha}$.

☆ $K_H = K_w / K_a$ (acetic acid.) $= \frac{K_w}{K_a} = \frac{c\alpha^2}{1-\alpha}$

$K_a \cdot K_b = K_w$ for conj. acid base pairs

If $1-\alpha \approx 1$

$\Rightarrow \alpha = \sqrt{\frac{K_H}{c}}$

If $\alpha < 0.1$, then $K_h = \frac{[OH^-]^2}{c}$

$\Rightarrow [OH^-] = \sqrt{K_h \cdot c}$.

Date

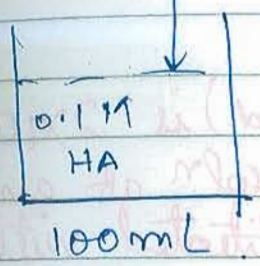
0·1 M CH_3COOH is being neutralised by adding 0·1 M NaOH sol^n. Determine pH at end pt. if Ka of CH_3COOH is 2×10^{-5}.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

0·1 M. 0·1 M 0·1 mol

·1 mol ·1 mol

0·1 M NaOH



At end pt.,

$[CH_3COO^-] = 0.05\ M = C$

(∵ V becomes double)

$\left(\frac{0.1}{2}\right)$

$K_h = 5 \times 10^{-10}$

$[OH^-] = \sqrt{K_h \cdot c}$

$= \sqrt{25 \times 10^{-12}}$

$= 5 \times 10^{-6}$

$\Rightarrow pOH = 6 - \log 5$

$= 5.3$

$pH = 8 + \log 5$

$= 8.7$

Q. pH of 0·05 M CaF_2 sol^n is if $K_a(HF) = 5 \times 10^{-4}$

$K_h = \frac{10^{-14}}{5 \times 10^{-4}}$

$= \frac{10 \times 10^{-14+11}}{5}$

$K_h = \frac{2 \times 10^{-11}}{}$

$[OH^-] = \sqrt{100 \times 10^{-13}}$

$= 10 \times 10^{-7}$

$= 10^{-6}$.

$pOH =$

$CaCl_2 + 2HF \rightarrow CaF_2 + 2HCl$

0·05

$CaCl_2 + HF \rightarrow CaF_2$

0.1 — 0.05

Date

$[F^-] = 0.1\ M$.

$K_h = 2 \times 10^{-11}$

$[OH^-] = \sqrt{2 \times 10^{-12}}$

$=$

$pOH = \frac{1}{2}(12 - \log 2)$

$= 5.85$.

$pH = 8.15$.

Fluorous. HO Chlorous

Q K_a of HOI (Hypo Iodous acid) is 2×10^{-12} at 25°C. Determine pH of soln at end pt if 1 M HOI soln is titrated with 0.25 M NaOH soln.

Na(OI)

$HOI + NaOH \rightarrow$

1 M — 0.25 M

4V — V

$OI^- + H_2O \rightleftharpoons HOI + OH^-$

5V

$K_h = \frac{10^{-14}}{2 \times 10^{-12}} = 5 \times 10^{-3}$

$\alpha = \frac{5 \times 10^{-3}}{2 \times 10^{-1}}$

$= \sqrt{25 \times 10^{-2}}$

$= 0.15 > 0.1$

So, not negligible.

$V + 4V = 5V(M)$

$\Rightarrow 5V$

$4V + 0.25V = 5VM$

$\Rightarrow 4 + \frac{1}{4} = 5M$

At end pt $[NaOI] = 0.2\ M$.

Now

$5 \times 10^{-3} = \frac{C\alpha^2}{1-\alpha} \approx (2 \times 10^{-1})\alpha^2$

NaOH
0.25M
$0.25 N \times 1 V = 1 V$

Date

$\Rightarrow 5 \times 10^{-3} = \frac{(2 \times 10^{-1})\alpha^2}{1-\alpha}$

$\Rightarrow 40\alpha^2 + \alpha - 1 = 0$

$\Rightarrow \alpha = \frac{-1 \pm \sqrt{1+160}}{2 \times 40}$

$= \frac{-1 \pm \sqrt{161}}{80}$

$= \frac{11.8}{80}$

$\alpha = .14$

$C\alpha = [OH^-]$

$[OH^-] = 0.028$

$= 28 \times 10^{-3}$

$= 4 \times 7 \times 10^{-3}$

$= 3 - \log 28$

$= 1.55$

$= -\log(28 \times 10^{-3})$

$= -(3)(\log 4 \times 7)$

$= 3 + (2\log 2 + \log 7)$

$= 3 + (0.6 + 0.85)$

pOH

Category 3 : St. acid Wk. base → $K_h = (K_a \text{ of ammonium ion}) = \frac{K_w}{K_b}$ (K_b of ammonia)

(In conj. base pairs)

NH_4Cl

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$ (acidic property)

$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+]} \times \frac{[OH^-]}{[OH^-]}$

$= \frac{K_w}{[NH_4^+][OH^-]} = \frac{K_w}{K_b \text{ of } NH_3}$

$[NH_4OH]$

$\frac{C\alpha^2}{1-\alpha}$ If $1-\alpha = 1$ then $K_h = [H^+]^2$

DENOTION

Base → BOH Acid → HA.

Date

$$\Rightarrow [H^+] = \sqrt{K_h \cdot C}.$$

Q. 25 ml of $\frac{2}{15}$ M weak ~~acid~~ base whose $K_b = 10^{-12}$ is $\frac{1}{5}$ titrated against $\frac{2}{15}$ M HCl soln. Determine conc. of H^+ at end pt. JEE 08

$BOH + HCl \rightarrow BCl + H_2O$

$K_b = 10^{-12}$

$K_h = 10^{-2}$

mmol = $2.5 \times \frac{2}{5}$

= 1 mmol of weak base.

So, 1 mmol HCl reqd

$MV = 1$

$\Rightarrow V = \frac{15}{2} = 7.5$ ml.

6.86

Salt → 1 mmol, V = 10 ml.

Conc = 0.1

$BOH + H_2O \rightleftharpoons$

$\alpha = \sqrt{\frac{10^{-12}}{0.1}}$ $[B^+] = 0.1$ M.

$= [H^+] = \sqrt{10^{-3}} = 0.032$

$\alpha = \sqrt{\frac{10^{-2}}{0.1}} > 0.1$

So, α is not negligible

DENOTION

Base → BOH Acid → HA.

Date

$$\Rightarrow [H^+] = \sqrt{K_h \cdot C}.$$

Q. 25 ml of $\frac{2}{5}$ M weak ~~acid~~ base whose $K_b = 10^{-12}$ is titrated against $\frac{2}{15}$ M HCl soln. Determine conc. of H^+ at end

JEE 08

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So, α is not negligible

$K_h = \frac{C\alpha^2}{1-\alpha} = 10^{-2}$

$\Rightarrow \frac{0.1\alpha^2}{1-\alpha} = 10^{-2} = \frac{1}{10}$

$\Rightarrow 10\alpha^2 + \alpha - 1 = 0$

$\Rightarrow \alpha = \frac{-1 \pm \sqrt{1+40}}{20}$

$\Rightarrow \alpha = 0.27$

$\Rightarrow C\alpha = [H^+]$

$= 0.027$ ✓ Ans

Q. 0.3 H_2SO_4 soln is being titrated using $\frac{0.3}{3}$ M aq NH_3 soln i.e NH_4OH.

K_b $NH_3 = 2 \times 10^{-5}$

pH at end pt = ?

$H_2SO_4 + NH_4OH \longrightarrow (NH_4)_2SO_4 + H_2O$

$NH_3 + H_2O \rightleftharpoons NH_4OH + H^+$

$K_b = 2 \times 10^{-5}$

At end pt

$[(NH_4)_2SO_4] = 0.1$ M

$K_h = \frac{10^{-14}}{2 \times 10^{-5}} = \frac{10}{10 \times 2} \times 10^{-14-5}$

$K_h = 5 \times 10^{-10}$

$\Rightarrow [NH_4^+] = 0.2$

$[H^+] = 10^{-5}$ $(\sqrt{K_h \cdot C})$

So, pH = 5 ✓

HNO_2

Date

Category 4 Weak acid Weak base

1 : 1

CH_3COONH_4 (c)

$\downarrow$

$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

$c(1-\alpha)$ $c(1-\alpha)$ $c\alpha$ $c\alpha$

c

$K_h = \dfrac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \cdot \dfrac{[H^+][OH^-]}{[H^+][OH^-]}$

$K_h = \dfrac{K_w}{K_a \cdot K_b}$

K_a K_b

$\dfrac{[CH_3COOH]^2}{[CH_3COO^-]^2}$ or $\left[\dfrac{\text{base}}{\text{base}^+}\right]$

$= \dfrac{c^2\alpha^2}{c^2(1-\alpha)^2}$

$\alpha \to 0$,

Considering independent ioniz^n of any one:

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

$K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Put in (1)

$\Rightarrow K_h = \dfrac{[H^+]^2}{K_a^2}$

$\Rightarrow \dfrac{K_w}{K_a K_b} = \dfrac{[H^+]^2}{K_a^2}$

$\Rightarrow [H^+] = \sqrt{\dfrac{K_w \cdot K_a}{K_b}}$

for a given salt of WK. acid & WK. base, pH will be independent of conc at a given temp.

$$\Rightarrow -\log[H^+] = -\frac{1}{2}\log\left[\frac{K_w \cdot K_a}{K_b}\right]$$

$$= -\frac{1}{2}\left(\log K_w + \log K_a - \log K_b\right)$$

$$\Rightarrow pH = \frac{1}{2}\left(pK_w + pK_a - pK_b\right)$$

($pK_w \to 14$)

At 25°C

$$\Rightarrow pH = 7 + \frac{1}{2}\left(pK_a - pK_b\right)$$

Imp.

If $K_a > K_b$

$pK_a < pK_b \Rightarrow pH < 7$

So, salt will be acidic.

$\Rightarrow K_a < K_b$, $pH > 7$.

So, salt will be basic.

10 Jan 2010

☆ BUFFER SOLUTION

☆ Conjugate acid-base pair

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

Acid — Conjugate BASE of CH_3COOH

$NH_3 + H^+ \rightleftharpoons NH_4^+$

base — Conjugate acid

Acid $\xrightarrow[H^+]{\text{remove}}$ conjugate base

Imp: base + H^+ ion $\xrightarrow{\text{gives}}$ conjugate acid

☆ Conjugate pair differ by just 1 H ion.

eg:

H_2CO_3 — CO_3^{2-} ✗ its not

↘ HCO_3^- ✓ its a conjugate base of H_2CO_3

Also, HCO_3^- is conjugate acid of CO_3^{2-}.

Buffer Sol^n: Its a sol^n which resist any significant change in pH of sol^n ($[H_3O^+]$ ion conc.) on add^n of small amt. of either strong acid or strong base.

pH is almost constt.

BUFFER COMPOS^n

(A) Acidic Buffer

It is a mixture of a weak acid + salt of its conjugate base

eg: $CH_3COOH + CH_3COO^-(Na^+)$

Na^+ from strong base (∵ it should not be hydrolysable)

eg 2 → $HF/CaF_2 \rightarrow HF/F^-$

eg 3 → $H_3PO_4 + NaH_2PO_4$.

eg 4 → HNO_2/KNO_2

pH < 7

(B) Basic Buffer.

It is a mixture of weak base + salt of its conjugate acid.

eg: $NH_3/NH_4^+Cl^-$

Cl^- must be from strong acid.

2) $NH_3/(NH_4)_2SO_4$

3) $CH_3NH_2/CH_3NH_3^+NO_2^-$

pH > 7

☆ pH of buffer sol^n

Case-(1) acidic

☆ Salts are all strong electrolyte i.e they ionise 100% in soln

Considering CH_3COOH / CH_3COONa.

CH_3COONa → CH_3COO^- + Na^+

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$

$\Rightarrow -\log[H^+] = -\log K_a - \log \frac{[CH_3COOH]}{[CH_3COO^-]}$

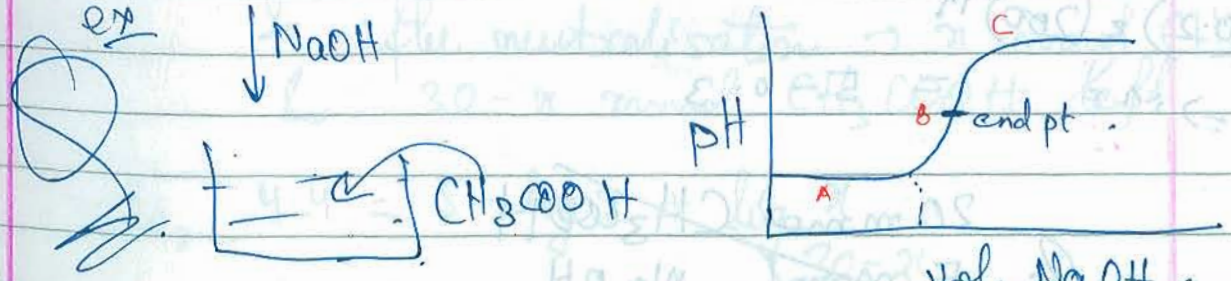
$\Rightarrow pH = pK_a + \log \frac{[Acid]}{[salt]}$ → HENDERSON'S EQN.

or $pH = pK_a + \log \frac{[Salt]}{[Acid]}$

COMMON ION EFFECT :

CH_3COOH + $NaOH$ → $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

ex



region A → buffer existence

" B → end pt

" C → exceeded end pt.

Case ② basic $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$K_b = \frac{[OH^-][NH_4^+]}{[NH_4OH]}$

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

initial c of base

$[OH^-] = \frac{K_b [NH_4OH]}{[NH_4^+]}$

$[NH_4^+]$ of salt

$\Rightarrow pOH = pK_b + \log \frac{[salt]}{[base]}$

Or $pOH = pK_b - \log \frac{[salt]}{[base]} \frac{[base]}{[salt]}$

Q. Determine pH of sol^n obtained by mixing 100 mL 0.2 M CH_3COOH sol^n with 100 mL 0.05 M NaOH

$K_a(CH_3COOH) = 2 \times 10^{-5}$ at 25°C

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$NaOH \longrightarrow Na^+ + OH^-$

$pH = p[2 \times 10^{-5}] + \log \frac{(0.2)}{(0.2)}$

$(100)(0.2) = (200) M$

$\Rightarrow M = \quad = 5 - 0.3$

20 mmol CH_3COOH

5 mmol NaOH

15 mmol CH_3COOH

5 mmol CH_3COONa

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$= (5 - 0.3) + \log \frac{5}{15}.$$

$$= 4.7 + (-0.5)$$

$$= 4.2 \checkmark$$

Q. 0.5 g of a sample containing NaOH & some neutral impurity when dissolved in 100 mL of 0.3 M CH_3COOH at 25°C, pH of resulting soln is found to be 4.4. Determine %age purity of original sample.

K_a CH_3COOH → 2×10^{-5}.

CH_3COOH → 30 mmol.

$$4.4 = 4.7 + \log \left\{ \frac{Salt}{Acid} \right\}$$

$$\Rightarrow -0.3 = \log \frac{[Salt]}{[Acid]}$$

$$= \log \frac{[Salt]}{30}.$$

$$\Rightarrow 5.5 = \log [Salt].$$

Let NaOH → x mmol.

So, after neutralisation → x mmol CH_3COONa
& 30 − x mmol CH_3COOH left.

So, $4.4 = 5 - \log 2 + \log \frac{x}{30-x}$.

$$\Rightarrow -0.3 = \log \frac{x}{30-x}.$$

$$\Rightarrow 2 = \frac{30-x}{x} \Rightarrow 2x = 30 - x$$

$\Rightarrow x = 10$ mmol NaOH

3×10.

$= 4.8 + 1$

$= 5.8$

10 mmol NaOH $\longrightarrow \frac{10}{1000} \times 40 = 0.4\,g$

$\frac{0.4}{0.5} \times 100^{20}$

$= 80\%$

Q. What V of 2M HCl should be added to 100ml 0.5 M ~~$(H_3$~~ CH_3COONa sol^n in order to obtain a buffer sol^n of pH = 5; 2×10^{-5} = K_a acetic acid,

HCl
2M

CH_3COONa
0.5 M
100 ml
= 50 mmol

$CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$
L.R. x mmol.

~~$HCl \rightleftharpoons H^+ + Cl^-$~~
$(50-x)$ mmol x mmol

$5 = 4.7 + \log\left(\frac{50-x}{x}\right)$

$= 4.7 +$

$\Rightarrow 0.3 = \log\left(\frac{50-x}{x}\right)$

$\Rightarrow 2 = \frac{50-x}{x}$

$\Rightarrow 2x = 50 - x$

$\Rightarrow x = 16.6$ mmol, $= 2\times V$

$\Rightarrow V = 8.3$ ml

Ans

Q. ~~Determine mass~~

Q. Determine pH of ~~aq~~ soln obtained by mixing equal V of 0.5 M NH_3 (soln) & $(NH_4)_2SO_4$ soln.

K_b NH_3 = 2×10^{-5} at 25° C. 1 M

$$pH = 4.7 + \log \frac{0.5}{0.5}$$

NH_4OH 0.5 — x M — 4.7 — Na_2SO_4

14.0 − 4.5 = 9.5

pOH = 9.3

9

0.5 M NH_4OH + 0.5 M $(NH_4)_2SO_4$

↓

0.25 M NH_4OH 0.25 M $(NH_4)_2SO_4$

↓

0.5 M NH_4^+

$$pOH = 5 - \log 2 + \log \frac{0.5}{0.25}$$

⇒ pOH = 5

⇒ pH = 9 ✓

Q. Determine mass of CH_3COONa & V of 4 M HCl soln req^d for preparing 250 mL of a buffer soln of pH = 5 in which conc. of CH_3COO^- = 0.5 M

Na = 23. $K_a = 2 \times 10^{-5}$.

$CH_3COONa + HCl \rightarrow CH_3COOH + NaOH$

$\frac{x}{82}$ mol 4V 4V

132
24
23
+3
82

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

4V 0.5 M (CH_3COONa)

Q 125 mmol salt is left unreacted in buffer soln.

$5 = 4.7 + \log\left(\frac{\text{Salt}}{\text{acid}}\right)$

250×0.5

$= 4.7 + \log\left(\frac{125}{y}\right)$

y → conc. of acid.

$\Rightarrow y = 62.5$

Now, $y = \frac{x}{82}$

$\Rightarrow$

So, 62.5 mmol of HCl used.

$\Rightarrow \frac{62.5}{4}$ mL 15.6

$\Rightarrow$ 15.6 mL of HCl

125 + 62.5 mmol originally
= 187.5 mmol

Now, mass of $CH_3COONa \simeq 15$ g

$= 15.05$ g

6) 187.5
82
3050
1520
1505
15.05

BUFFER ACTION

100 mL CH_3COONa + CH_3COOH (2×10^{-5})
0.5 M 1 M

$$pH = 5 - \log 2 + \frac{0.5}{1}$$

$$pH = 4.4$$

(a) 1 mL 0.1 M HCl is added.

$$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl.$$
50 mmol 0.1 mmol 0.1 mmol
(diluted)

So, new mmol of $CH_3COONa \rightarrow 49.9$
in $CH_3COOH \rightarrow 0.6$

$$pH = 4.7 + \log \frac{49.9}{100.1} \simeq 4.4$$

(b) 1 mL 0.1 M NaOH added

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$
0.1 M 0.1 M

So, $\log \frac{50.1}{49.9} \simeq 4.4$

BUFFER ACTION

A buffer soln contain both weak acid & weak base (i.e. or basic salt). When small amt of strong acid/base is added, it is neutralised by buffer & maintained almost constt pH of soln.

Date

☆ Solubility & Solubility Product of (Sparingly soluble) salt

Solubility is negligible ← small

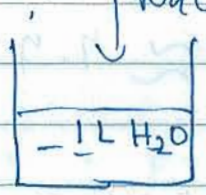


+ NaCl 58 g at 25°C

100 ml H_2O → $AgCl_{(s)}$ → 10^{-5} g dissolved.

☆ Sparingly soluble : If a solute has a very small solubility i.e. in the range ~~of~~ smaller than 10^{-3} g per 100 ml, we call solute to be sparingly soluble & doesn't make any diff. in stoichiometric calculⁿ.
Majority of salts are sparingly soluble.
• Nitrate & NH_4 salts are highly soluble.

☆ Solubility : 1 L saturated solⁿ बनाने के लिए जितना salt चाहिए । पूरा-पूरा
Molar Solubility : Min. no. of moles of a salt reqᵈ to produce 1 L of its saturated solⁿ.



At saturation pt.

$NaCl_{(s)} \rightleftharpoons Na^+_{(aq.)} + Cl^-_{(aq.)}$

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq.)} + Cl^-_{(aq.)}$
S S S

Saturated solⁿ : rate of disolⁿ = rate of pptⁿ

$K_c = [Ag^+][Cl^-]$

Date

☆ Solubility & Solubility Product of Sparingly soluble salt

Solubility is negligible ← {Sparingly soluble} salt

small

+ NaCl 58 g at 25°C

100 ml

H_2O . $\xrightarrow{AgCl(s)}$ 10^{-5} g dissolved .

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NaCl

1 L H_2O

At saturation pt.

$NaCl(s) \rightleftharpoons Na^+(aq.) + Cl^-(aq.)$

$AgCl_{(s)} \rightleftharpoons Ag^+(aq.) + Cl^-(aq.)$
S S S

Saturated solⁿ : rate of dissolⁿ = rate of pptⁿ

$K_c = [Ag^+][Cl^-]$

If S is molar solubility

So, $K_c = S^2$.

$= K_{sp} = S^2$ (here)

K_{sp} → solubility product ∴ It is K_c of saturated soln.

Now

$PbCl_2(s) \longrightarrow Pb^{2+} + 2Cl^-$

$-S \qquad\quad S \qquad 2S$

$K_c = S(2S)^2$

$= 4S^3$

i.e $K_{sp} = 4S^3$

$A_pB_q \longrightarrow pA + qB$

$\quad\quad pS \quad qS$.

$= [pA]\,[pS]^p\,[qS]^q$

$K_{sp} = p^p q^q (S^{p+q})$

---

14 Jan 2010

Q. 100 ml 0.05 M $PbNO_3$ soln is mixed with another 100 ml 0.1 M NaCl soln at 25°C. If K_{sp} of $PbCl_2 = 4 \times 10^{-6}$ at 25°C, determine mass of $PbCl_2$ ppted. out. (Pb = 204), Cl → 35.5

$Pb(NO_3)_2 + NaCl \rightleftharpoons PbCl +$.

$Pb(NO_3)_2 + 2NaCl \rightarrow PbCl_2 \downarrow + 2NaNO_3$

100 ml 100 mL
0.05 M 0.1 M
5 mmol 10 mmol

$PbCl_{2(s)} \rightleftharpoons Pb^{2+} + 2Cl^-$
$-S$ S $2S$

$K_{sp} = 4S^3 = 4 \times 10^{-6}$
$\Rightarrow S = 10^{-2}$ M.

mmol of $PbCl_2$ in soln :- $10^{-2} \times 200 = 2$ mmol.

204
+71
1275
c2
550

mass = $\frac{3 \times 275}{1000} = 0.825$ g

Q $Mg(OH)_2$ is a sparingly soluble compd in water. A saturated soln prepared by dissolving pure $Mg(OH)_{2(s)}$ in pure H_2O has pH = 10.48 at 25°C. Determine solubility product of NaOH

1.35
0.02
3.52
14.00 =

pH = 10.48 pOH = 3.52
$[H^+] = 3 \times 10^{-11}$ $= -\log[OH^-]$
$\Rightarrow \log[OH^-] = 3 \times 10^{-4}$

$Mg(OH)_2 + H_2O \rightleftharpoons Mg^{2+} + 2OH^-$
S S $2S$

$2S = 3 \times 10^{-4}$

$K_{sp} = S$
$= 1.5 \times 10^{-4} (3 \times 10^{-4})^2$
$= 1.35 \times 10^{-11}$

Date

☆ Condns for ppt^n.

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

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

$$Q_{IP} = [Ag^+][Cl^-]$$

Q_{IP} → Ionic product of salt

(1) $Q_{IP} < K_{sp}$ → Rxn is forward. Hence, sol^n is unsaturated, more salt can be dissolved, no ppt^n occurs.

(2) $Q_{IP} > K_{sp}$ → backward rxn. ppt^n will occur. Some ions will combine to form ppt. in order to restore the ..... limit.

Q Equal V of 3×10^{-5} M $AgNO_3$ sol^n & mixed with 2×10^{-5} M $BaCl_2$ sol^M. K_{sp} ($AgCl_{(s)}$) → 2×10^{-10}
Determine, whether ppt form / not.

$$2\,AgNO_3 + BaCl_2 \longrightarrow 2AgCl + Ba(NO_3)_2$$

3×10^{-5} M 2×10^{-5} M 3×10^{-5}

$[Ag^+] = 1.5 \times 10^{-5}$ M, $[Cl^-] = \frac{2 \times 2 \times 10^{-5}}{2} = 2 \times 10^{-5}$

$Q_{IP} = 3 \times 10^{-10}$ $\geq K_{sp}$.

So, rxn backward, ppt formed.

Q. 10 mL 2×10^{-4} M $BaCl_2$ sol^n is mixed with 20 mL 10^{-4} M Na_2SO_4 sol^n → diluted to 50 mL. K_{sp} of $BaSO_4$ is 10^{-10} at 25°C. Determine (a) whether ppt forms/not (b) If ppt^n occur, determine V of water req^d to be added to just prevent ppt^n of $BaSO_4$.

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 \downarrow + 2NaCl.$$

2×10^{-4} $\quad$ 10^{-4}

2×10^{-3} mmol

$[Ba^{+}] = 1\times10^{-4}$

$[SO_4] = 2\times10^{-4}$

$Q_{IP} = \frac{2\times10^{-7}}{10^{-4}}$

(a) $[Ba^{+}] = \frac{2}{5}\times10^{-4} = 4\times10^{-5}$

$[SO_4^{2-}] = \frac{10^{-4}\times(2\cancel{0})}{5\cancel{0}} = 4\times10^{-5}$.

$\Rightarrow Q_{IP} = 16\times10^{-10} > K_{sp}$

ppt ↓

(b) $[Ba^{2+}]$ — 50 mL

$S = 10^{-5}M = [Ba^{2+}]$

$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$K_{sp} = S^2$

$\Rightarrow S = \sqrt{K_{sp}} = 10^{-5}$

$(4\times10^{-5})\,50 = 10^{-5}\,V$.

$\Rightarrow V = 200$.

So, V to be added = 150 mL.

✡ SOLUBILITY & COMMON ION EFFECT

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

$-S' \quad S' \quad S'$

$+ NaCl \rightarrow Na^+ + Cl^-$

$C \quad C \quad C+S'$

$K_{sp} = [Ag^+][Cl^-]$

$\Rightarrow K_{sp} = (S')(S'+C)$

Generally $S' \ll\ll C$

$\Rightarrow K_{sp} \simeq S'C$.

Ag+ a-

Q K_{sp} of AgCl = 2×10^{-10} M. Determine molar solubility of AgCl in 0.01 M $CaCl_2$ soln. Also Determine the factor by which solubility has decreased, compared to solubility in pure water.

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

$-S' \quad S' \quad S'$

$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^-$

$0.01 \quad 0.01 \quad 0.02$

$2\times10^{-10} = S'(0.02)$

$\Rightarrow 10^{-8} = S'$

$\sqrt{2\times10^{-5}}$

$S = 1.414\times10^{-5}$

$$\frac{S'}{S} = \frac{10^{-8}}{1.4\times10^{-5}} = \frac{10^{-3}}{\sqrt{2}} \quad \text{Ans}$$

$$\Rightarrow \frac{S}{S'} = 1414$$

Q. A soln is 0.01 M in both Cl^- & Br^-. K_{sp} for AgCl = 2×10^{-10}, AgBr → 3×10^{-13}. If $AgNO_3$ soln is added from burette, determine the min. conc of

(a) $[Ag^+]_{min}$ where ppt. formation starts

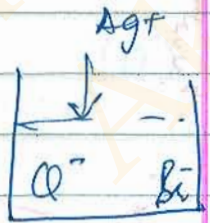
(b) Determine $[Ag^+]$ where 2nd ppt start forming.

(c) Determine ~~on~~ conc of ~~2nd~~ 1st anion when 2nd anion starts precipitating

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

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

0.01 M



$$AgBr \rightleftharpoons Ag^+ + Br^-$$

0.01 M

$[Ag^+]$ reqd for ppt^n of AgBr =

$$\frac{3\times10^{-13}}{0.01} = 3\times10^{-11}\ M$$

$[Ag^+]$ reqd for ppt^n of AgCl

$= 2\times10^{-8}$ M $\left(\frac{K_{sp}}{[Cl^-]}\right)$

So, (a) 3×10^{-11} of AgBr starts 1st to conc. is attained 1st.

(b) K_{sp} AgBr $= 3 \times 10^{-13} = [Ag^+][Br^-]$

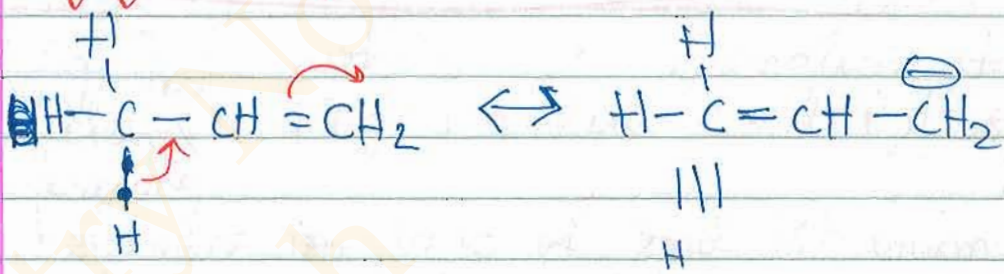
$\Rightarrow \frac{3 \times 10^{-13}}{2 \times 10^{-8}} = [Br^-]$

$\Rightarrow 1.5 \times 10^{-5} = [Br^-]$

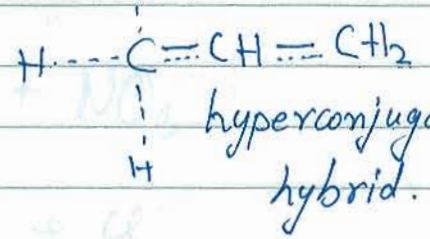
Date

☆ Hyperconjugation:

It is delocalisation of σ e⁻s in a conjugated sys.



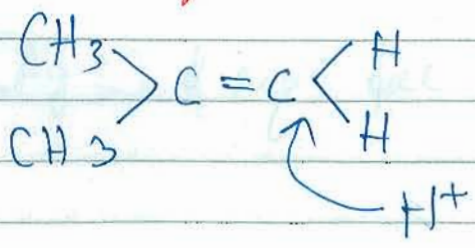
So, sp^3–p orbitals are involved in hyperconjugation.



hyperconjugation hybrid.

☆ Electromeric Effect.

It is a temporary effect observed during the attack of electrophile or nucleophile in a chemical rxn.



Date

Ionic Revision

Q 0.5g of an impure sample of Al_2O_3, when dissolved in 500ml HCl sol^n pH of sol^n ↑ from 1 to 1.3 at 25°C. Determine mass %age of Al_2O_3 in the sample

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$\frac{25}{6}$ mmol 25

$pH_{initial} = 1 \Rightarrow [H] = 10^{-1} = [HCl]_{initial}$

$\Rightarrow 500 \times 10^{-1} = 50$ mmol of $HCl_{initial}$

$pH_{final} = 1.3 \Rightarrow [H^+] = 5 \times 10^{-2}$

$\Rightarrow [H^+] = 0.05M$

$\Rightarrow [HCl]_{final} = 25$ mmol

$\Rightarrow$ 25 mmol must have reacted

$\Rightarrow$ mmol $\rightarrow Al_2O_3 = \frac{25}{6}$

$$\text{mass} = \frac{25}{6} \times 10^{-3} \times 102$$

$$= \frac{0.425}{0.5} \text{ g}$$

$$\text{mass \%age} = \frac{0.425}{0.5} \times 100 = 85\%$$

Q pH of 10^{-7} M NaOH sol^n at 25° C

If $[H^+]$ or $[OH^-]$ from strong acid or strong base $> 10^{-6}$ M, then only, contrib^n from H_2O can be ignored.

Date

✱ Ioniz^{n} of H_2O

$H_2O \rightleftharpoons H^+ + OH^-$ $\quad K_c = \frac{[H^+][OH^-]}{1} = K_w = 10^{-14}$ at 25°C

$\Delta H > 0$

$K_w = [OH^-]^2 = [H^+]^2$ } only in pure water always

$\Rightarrow [H^+] = [OH^-] = 10^{-7}$

$\Rightarrow$ pure water :- $pH = pOH = 7$ at 25°C

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.3R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

↳ can be used to find (K_w) at a new Temp (T_2) (K_2 ✓) (K_1 here)

$H_2O \rightleftharpoons H^+ + OH^-$

$NaOH \longrightarrow Na^+ + OH^-$

$c \qquad c \qquad c + x$

$\Rightarrow 10^{-14} = (x)(x+c)$

x ✓

$[OH^-] = 10^{-7} + \frac{10^{-14}}{[OH^-]}$

$\Rightarrow [OH^-] \approx \left(\frac{\sqrt{5}+1}{2}\right) \times 10^{-7}$

Principle of electroneutrality

$[OH^-] = [Na^+] + [H^+]$

(net +ve charge = net -ve charge

⇕

+ve conc. = -ve conc.

(∵ no. 2 same))

$\Rightarrow$ ✱ $[OH^-] = c + \frac{K_w}{[OH^-]}$ → $[H^+]$

Ily. $[H^+] = c + \frac{K_w}{[H^+]}$ → OH^-

$\Delta G = RT \ln K$

$\Rightarrow \frac{\Delta G}{RT_1} = \log K_1$ $\quad \Rightarrow \log K_2 = \frac{\Delta G}{2.3 RT_2}$

$\Rightarrow \log(K_2) = \frac{\Delta G}{2.3}\left(\frac{T_2 - T_1}{RT_1 T_2}\right)$ $\quad \Rightarrow \log K_2 - \log K_1 = \frac{\Delta G}{2.3}\left[\frac{1}{RT_1} - \frac{1}{RT_2}\right]$

Date

Q Determine pH of a 0.01 M soln of H_2SO_4 assuming its 1st ioniz^n to be complete, but, ioniz^n const^t for 2nd ioniz^n $= 10^{-2}$ at 25°C.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$
$$0.01 \qquad 0.01 \qquad 0.01$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$
$$0.01 - c \qquad 0.01 + c \qquad c$$

$$K_{a_2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 10^{-2}$$

$$K_{a_1} = [H^+][HSO_4^-]$$

$$\Rightarrow 10^{-2} = \frac{(c)(c+0.01)}{0.01-c}$$

$$\Rightarrow 10^{-4} - 10^{-2}c = c^2 + 0.01c$$

$$\Rightarrow c^2 + 0.02c - 10^{-4} = 0$$

$$\Rightarrow 10^4 c^2 + 200c - 1 = 0$$

$$\Rightarrow c = \frac{-200 \pm \sqrt{40000 + 4}}{2}$$

$$c \simeq 0.004$$

$$\Rightarrow [H^+] = 0.014 \text{ M}$$

Q K_a (HCOOH) $= 2 \times 10^{-4}$ at 25°C

To what vol. a 1 L, 0.5^M HCOOH soln must be diluted in order to double its pH at 25°C

$$HCOOH \longrightarrow H^+ + HCOO^-$$
$$0.5 - x \qquad x \qquad x$$

$$\frac{x^2}{0.5-x} = 2 \times 10^{-4}$$

$$\Rightarrow x^2 = 10^{-4} - (2 \times 10^{-4})x$$

$$\Rightarrow x^2 + (2 \times 10^{-4})x - 10^{-4} = 0$$

$\Rightarrow x^2 \times 10^4 + 2x - 1 = 0$

$\Rightarrow x = \frac{-2 \pm \sqrt{4 + 4\times10^4}}{2}$

$= -1 \pm \sqrt{1+10^4}$

$\Rightarrow x = \frac{-101}{10^4}$ or $\frac{99}{10^4}$

$\Rightarrow x = 99\times10^{-4}\ M \approx 10^{-2}\ M$

$\Rightarrow pH = 2$.

$H_2O \rightleftharpoons H^+ + OH^-$

$pH_{final} = 4 \Rightarrow [H^+] = 10^{-4}$

M2

HCOOH
1L
0.01M 0.5M

Initially $\rightarrow \sqrt{\frac{K_a}{C}} = \sqrt{0.02} < 0.1$

So, α is negligible

$\Rightarrow [H^+] = \sqrt{2\times10^{-4}\times0.5}$

$= 10^{-2}$

$\Rightarrow pH = 2$.

$HCOOH \rightleftharpoons H^+ + HCOO^-$

$C(1-\alpha)$ $C\alpha$ $C\alpha$

$\approx 10^{-4}$ ($\because pH = 4$)

conc. after dil^n initially

$\Rightarrow K_a = \frac{C\alpha^2}{1-\alpha} = (C)\frac{\alpha}{1-\alpha}$

$\Rightarrow K_a = 2\times10^{-4} = 10^{-4}\left(\frac{\alpha}{1-\alpha}\right)$

$\Rightarrow \alpha = 2/3$

$\Rightarrow C\alpha = 10^{-4} \Rightarrow C = \frac{3}{2}\times10^{-4}$. M

$M_1V_1 = M_2V_2$

$\Rightarrow (0.5)(1) = \left(\frac{3}{2}\times10^{-4}\right)V$.

$\Rightarrow \frac{1}{3}\times10^4 \Rightarrow = Vol$.

JEE modified

$[CO_2]$ in atm over Chd is 100 ppm. Henry's constt of CO_2 is 0.33 mole L^{-1} atm^{-1}. If

$K_{a_1}[CO_2] = 2\times10^{-7}$

$K_{a_2}[CO_2] = 3\times10^{-11}$ at 25°C ↔ no use

Determine pH of rain water in that city.

Solubility (S) = $\left(\frac{1}{3}\right)(100\times10^{-6})$

$S = \frac{10^{-4}}{3}$

$2\times10^{-7} = \frac{C\alpha^2}{1-\alpha}$, $[H^+] = \sqrt{3\times10^{-11}\times C}$

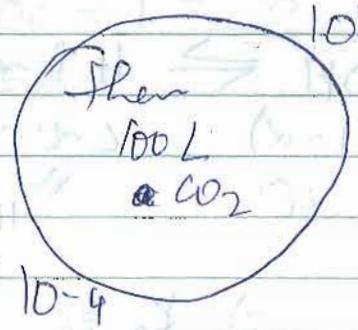
$\Rightarrow 2\times10^{-7} = \frac{10^{-4}}{3}\times\frac{\alpha^2}{1-\alpha}$

$\Rightarrow 6\times10^{-7}(1-\alpha) = 10^{-4}\alpha^2$

$\Rightarrow 10^{-4}\alpha^2 + 6\times10^{-7}\alpha - 6\times10^{-7} = 0$

$\Rightarrow 1000\alpha^2 + 6\alpha - 6 = 0$.

1000 ppm (V/V)



Vol. fr^n of $CO_2 = \frac{100}{10^6} = 10^{-4}$

P, T → same

$\Rightarrow V \propto n \Rightarrow$ Vol fr^n = Mole fr^n. $= 10^{-4}$

$\Rightarrow P_{CO_2} = (10^{-4})(1) = 10^{-4}$ atm.

$\Rightarrow S = \frac{10^{-4}}{3}$ molar

$\Rightarrow [H^+] = \sqrt{\frac{K_{a_1}S}{}} = \sqrt{\frac{2\times10^{-3}}{3}} = 0.6\times10^{-3}$

$= \frac{\sqrt{6}}{10^3}$

$\Rightarrow pH = 5.59 \approx 5.6$

$\sqrt{0.06} = 0.2$

$\frac{\sqrt{6}}{10} =$

$2\overline{)6.00}$

-4

200

$2 \times 10^{-12} = [OH^-]$

$\Rightarrow [OH^-] = 5 \times 10^{-3}$ M

Q 50 mL methanamine CH_3NH_2 is dissolved in H_2O & diluted to .5L pH of resultant soln was found to be 11.3 at 25°C. $K_b = 2 \times 10^{-4}$ at 25°C

What is ρ_b of methanamine

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\underset{C(1-\alpha)}{CH_3NH_2} \rightleftharpoons \underset{C\alpha}{X^+} + \underset{C\alpha}{OH^-}$$

methanamine

$$\frac{[X^-][H^+]}{[X]} = 2 \times 10^{-4}$$

$\Rightarrow [OH^-] = \sqrt{K_b \cdot C}$

$\Rightarrow 2 \times 10^{-12} = \frac{4 \times 10^{-14} \cdot 2}{2 \times 10^{-4}} C$

$\Rightarrow C = 2 \times 10^{-10}$ M $= \frac{m}{29 \times 50 \times 10^{-3}}$

$\Rightarrow$ m ✓

$\{5 \times 10^{-3}\} = \sqrt{K_b C}$

$\Rightarrow \frac{25 \times 10^{-6}}{2 \times 10^{-4}} = C$

$\Rightarrow 12.5 \times 10^{-2} = C$

$\Rightarrow 0.125\ M = C$

$n_{base} = (0.125) \times 5$ L.

$= 0.625$ Mole

$\Rightarrow$ mass $= 0.625 \times 31$

$\Rightarrow \rho = \frac{125}{0.625 \times 31}$ ~~$\times 10^{-5}$~~

$\rho = \frac{3875 \times 10^5}{10^3}$

≈ 0.4 g/m2

125
031
125
375×
3875

Q. ~~0.1 M~~ 0.3 M $Ca(OH)_2$ sol^n is titrated by 0.3 M HF sol^n. $K_a(HF) = 5 \times 10^{-4}$ at 25°C Determine pH of sol^n at end pt.

$HF \rightleftharpoons H^+ + F^-$

$K_a = \frac{[H^+][F^-]}{[HF]}$

$pH_{(HF)} = 2$

$pH_{Ca(OH)_2} = 2$

$[H^+] = \sqrt{0.3 \times 5 \times 10^{-4}}$ $\quad \alpha = \sqrt{\frac{5 \times 10^{-4}}{0.3}}$

$[H^+] = \sqrt{15 \times 10^{-5}}$

$Ca(OH)_2 + 2HF \rightarrow CaF_2 + 2H_2O$.

1 2

V 2V

At endpt:- Vol $= 3V$

$[CaF_2] = \frac{0.3M}{3} = 0.1$

$\Rightarrow [F^-] = 0.2$

$K_h = 2\times10^{-11}\left(\frac{K_w}{K_a}\right)$

$\Rightarrow [OH^-] = \sqrt{2\times10^{-11}\times C} = 2\times10^{-6}$

$\Rightarrow pOH = 5.7$

$\Rightarrow pH = 8.3$

Q. 10 mL of a weak [monoacidic base] = 0.1 M $K_b = 10^{-12}$ at 25°C. & $K_h = 10^{-2}$ is mixed with 30 mL, $\frac{1}{30}$ M HCl soln. Determine pH of resulting soln.

$[H^+] = \sqrt{K_h \cdot C}$

$= \sqrt{10^{-2}\times10^{-1}}$

$= \sqrt{10^{-3}}$

$= \frac{\sqrt{10}}{100}$

$[H^+] = \frac{1}{10\sqrt{10}} \simeq \frac{1}{30}$ M

3.1

$3\overline{)10.00}$

-9

$\overline{100}$

61

$HCl \longrightarrow H^+ + Cl^-$

$\frac{1}{30}$ M $\times 30$

At end pt $:= 1$ mmol. of salt

$\alpha \rightarrow$ negligible. Vol = 40 ml,

$\Rightarrow [B^+] = \frac{1}{40} = 0.025$ M

$[H^+] = \frac{1}{60} = 0.016$

$= 0.016$

$K_h = 10^{-2}$

$\Rightarrow \alpha = \sqrt{\frac{10^{-2}}{0.025}} > 0.1$

$\Rightarrow 10^{-2} = 2.5\times10^{-2}\times\frac{\alpha^2}{1-\alpha}$

$\Rightarrow 5\alpha^2 + 2\alpha - 2 = 0$

$\Rightarrow \alpha = \frac{-2 \pm \sqrt{44}}{10} \simeq 0.45$

$\sqrt{44}$

6.6^2

$6\overline{)44.00}$

36

800

126

16×10^{-3}

$= 4(0.3)$

$= 1.2$

$= 2 - 0.2$

$= 1.8$

$= 0.45$

$10^{-2} = \frac{0.1\alpha^2}{1-\alpha}$

$\Rightarrow 1-\alpha = 10\alpha^2$

$\Rightarrow 10\alpha^2 + \alpha - 1 = 0$

$\Rightarrow \alpha = \frac{-1 \pm \sqrt{1+40}}{2}$

$= \frac{-1 \pm 6.3}{2}$

$\alpha = \frac{5.3}{2}, 2.065$

$\Rightarrow [H^+] = (0.45)(0.025)(\alpha)$

pH ✓

Q. Determine pH of 0.01 M Na_2CO_3 sol^n giving $Ka_1 = 2\times10^{-7}$, $Ka_2 = 4\times10^{-11}$] 25°C

$NaOH$, H_2CO_3

0.01 M $-\alpha$

$Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$

$2(0.01)(\alpha)$ $(0.01)(\alpha)$

$Ka_1 = 2\times10^{-7} = \frac{[H_2CO_3][NaOH]^2}{[Na_2CO_3]}$

$(0.01)(1-\alpha)$

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$Ka_2 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4\times10^{-11}$

$\Rightarrow 2\times10^{-7} = \frac{(0.01)^2(\alpha)^2\times2}{0.01-\alpha}$

2017 1.4. Date

MA2

$$CO_3^{2-} + H_2O \overset{K_{h1}}{\rightleftharpoons} HCO_3^- + OH^-$$

$$HCO_3^- + H_2O \overset{K_{h2}}{\rightleftharpoons} H_2CO_3 + OH^-$$

$$K_{h_1} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} \times \frac{[H^+]}{[H^+]} = \left\{ \frac{K_w}{\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}} \right\}$$

$$K_{h_2} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} \times \frac{[H^+]}{[H^+]}$$

$\rightarrow K_{a_2}$

$$K_{h_2} = \frac{K_w}{K_{a_1}}$$

$$\Rightarrow K_h = \frac{K_w}{K_{a_2}} = 2.5 \times 10^{-4}$$

$K_{h_1} \gg K_{h_2}$ → Ignored.

$$\Rightarrow [OH^-] = \sqrt{K_{h_1} c}$$

$$= \sqrt{2.5 \times 10^{-4} \times 0.01}$$

$$= \sqrt{2.5} \times 10^{-3} M$$

$$\Rightarrow [OH^-] = 1.5 \times 10^{-3} M$$

pOH ✓

Date 7/6/1

Ch:- Extraction of metals

PROCESS
- → Carbon Redⁿ method (Fe & Sn)
- → Electrolytic redⁿ method (Mg & Al)
- → Self redⁿ method (Cu & Pb)
- → Cyanide process (Ag & Au)

<1> EXTRACTION of (Fe) (Carbon Redⁿ method)

Method is applicable for metals which exists as oxide & are not very electro pe

Fe

→ Ores :-

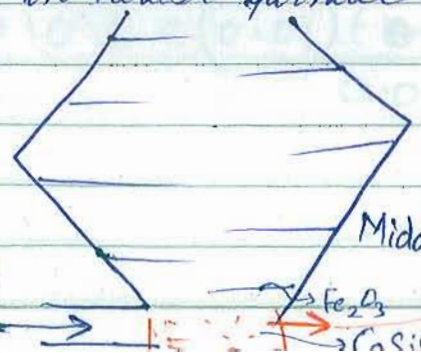
Haematite (Fe_2O_3)
Magnetite (Fe_3O_4)
Iron pyrite (FeS_2) (fool's Gold)
Limonite ($Fe_2O_3 \cdot 3H_2O$)
Siphatic ($FeCO_3$)
Copper pyrite ($CuFeS_2$) : an ore of Cu containing Fe

C is used as a RA for redⁿ of metal oxides.

☆ EXTRACTION FROM OXIDE ORE

The oxide ore is 1st calcined to remove volatile impurity & then roasted to oxidise FeO (if present) into Fe_2O_3.

The purified Fe_2O_3 is mixed with $CaCO_3$ & coke & heated in blast furnace.



At bottom :
$C + O_2 \longrightarrow CO$. ΔH
CO rises up after form
Middle: $CO + Fe_2O_3 \longrightarrow Fe + O_2$

At bottom :- $CaCO_3$ (flux) $\xrightarrow{\text{absorbs heat liberated in previous rxns}}$ $CaO + CO + \frac{1}{2}O_2$ $\Delta H > 0$

$CaO + SiO_2$ (main impurity present in ore (infusible)) $\longrightarrow$ $CaSiO_3$ (molten at temp. of blast furnace) fusible.

($\rho_{CaSiO_3} < \rho_{Fe}$)

* Classific^n of Fe (on the basis of C %age) → obtained from blast furnace
  - ✓ Cast Iron (2.5–4.5 % C (by wt)). : most impure form of Fe
  - ✓ Wrought Iron (< 0.25 % C (by wt)). : purest form of Fe
  - ✓ Steel (b/w 0.25 – 2.5 % C (by wt.)).

• Chemical Reactions of Iron

✓ Rxns with air :-

Iron doesn't react with dry air at RT. However, in presence of moisture iron gets rusted in air.

$Fe + H_2O + O_{2(g)} \longrightarrow Fe(OH)_3 \cdot Fe_2O_3 \cdot n H_2O$

cathode, Anode

ferric hydroxide, hydrated ferric oxide (RUST)

↳ Prevention from rusting : not used, preferred

↳ Cathodic protection (with Mg or Zn)

↳ i.e replaced cathode (Fe) with more electro +ve el^t.

Cathodic prot^n :- $Zn + O_2 \longrightarrow ZnO$.

$ZnO + CO_2 \longrightarrow ZnCO_3$ (atmosphere; hard film → physical protection)

Galvaniz^n.

• With Mg, physical protection is not there, so, its not used.

✓ Rxns with water

Fe doesn't react with water (at RT) ∴ Air also reqd for rusting.

However, iron decomposes steam {$H_2O(v)$}

$3Fe + 4H_2O(v) \xrightarrow{\Delta} Fe_3O_4 + 4H_2$

In metallurgy, if conc. H_2SO_4 comes, ferm^n of SO_2 is necessary.

conc. HNO_3 ⇓ NO_2 always

OCHA. In steam engines, surface of iron is coated with graphite (inert to steam) so that Fe doesn't corrode with steam.

$$Fe + H_2O(v) \xrightarrow{\Delta} Fe_3O_4 + H_2$$

✓ With acids

→ with HCl / H_2SO_4 in dil cond^n

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2(g)$$
$$+ H_2SO_4 \longrightarrow FeSO_4 + H_2(g)$$

With conc. H_2SO_4

$$Fe + 2H_2SO_4 \longrightarrow FeSO_4 + SO_2 + 2H_2O$$
(conc.)

→ With dil. HNO_3

$$Fe + \overset{+5}{H}NO_3 \longrightarrow Fe(NO_3)_2 + NH_4NO_3$$
(dil.)

→ With conc. HNO_3

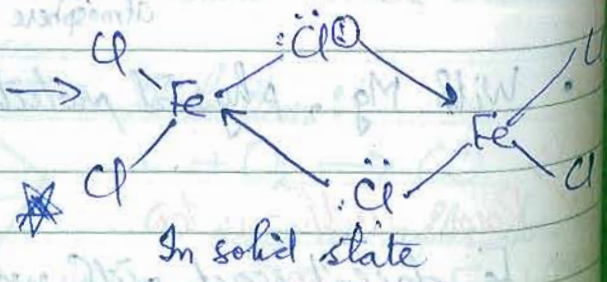
$$Fe + HNO_3 \longrightarrow \overset{+3}{Fe}(NO_3)_2 + NO_2$$
(conc.)

highest oxid^n state ∵ conc. HNO_3 is strong

✓ With halogens

$$Fe + F_2 \xrightarrow{RT} FeF_3$$
$$+ Cl_2 \longrightarrow FeCl_3$$
$$+ Br_2 \longrightarrow FeBr_2 + FeBr_3$$ (not very stable) : with difficulty
$$+ I_2 \xrightarrow{\Delta} FeI_2$$

$FeCl_3$

$Cl - \overset{Cl}{\underset{|}{Fe}} - Cl\ (g) \longrightarrow$ 

• LA

In solid state

Date 12/1/2011

✓ With O_2

$$Fe + O_2 \xrightarrow[\text{Dry}]{\Delta} Fe_3O_4 \xrightarrow{\text{Strong heating}} Fe_2O_3.$$

$(FeO \cdot Fe_2O_3)$

---

(2) Extraction of Sn

Sn ore : Cassiterite (tin-stone) — (contains SnO_2)

$$C + \tfrac{1}{2}O_2 \longrightarrow CO.$$

$$2CO + SnO_2 \longrightarrow 2CO_2 + Sn$$

- extraction of tin is done in same way as iron.

✱ properties

- Action of air : It is less electro +ve than Fe. ∴ it doesn't rust. Its not attacked by dry or moist air at RT. On high heating, Sn →

$$Sn + O_2\,(air) \xrightarrow{\Delta} SnO_2.$$

- Action of H_2O : It is not attacked by cold/hot water.
- Action of acid :

(1) Sn doesn't react with dil. HCl or dil. H_2SO_4 at RT.

(2) In presence of O_2, Sn react with conc. HCl & H_2SO_4 →

$$Sn + 2HCl\,(\text{Conc}) + \tfrac{1}{2}O_2 \longrightarrow SnCl_2 + H_2O$$

$$\begin{cases} Sn + H_2SO_4\,(\text{conc}) + \frac{1}{2}O_2 \longrightarrow SnSO_4 + H_2O. \\ Sn + H_2SO_4\,(\text{conc}) \xrightarrow{HOT} SnO_2 + SO_2 + H_2O. \end{cases}$$

(3) With Nitric acid

$$Sn + HNO_3\,(\text{dil}) \longrightarrow Sn(NO_3)_2 + NH_4NO_3$$

Stannous

Sn :- amphoteric

$Sn + HNO_3 \text{ (conc)} \longrightarrow H_2SnO_3 + NO_2 \uparrow$ (formed only in strong oxidising cond^n)

Meta stannic acid

- With alkali

$Sn + NaOH(conc) \longrightarrow Na_2SnO_2 + H_2 \uparrow$ (formed in mild oxidising cond^n)

Sodium stannite

- With $Cl_2(g)$

$Sn + Cl_2(g) \xrightarrow{\Delta} SnCl_4$ (Sn^{+4})

(∵ ~~Cl_2 case~~ X_2 are all OA)

~~But $I_2(g)$ is~~

But $\rightarrow Sn + I_2(g) \xrightarrow{\Delta} SnI_2$

(3) Extraction of Cu & Pb : SELF-REDUCTION METHOD

↓

Applied generally for extraction of metal from their sulphide ores.

§ COPPER

Basic copper carbonate

✓ Malachite $CuCO_3 \cdot Cu(OH)_2$

Imp. ores :-

✓ Copper glance → Cu_2S

✓ Copper pyrite → $CuFeS_2$ [extraction of Cu preferred over that of Fe, here → cost

✓ Cuprite → Cu_2O

✓ Extraction from pyrite

S1) Purified pyrite ore is 1st roasted ~~in presence of~~

$CuFeS_2 + O_2 \xrightarrow{\Delta} Cu_2S + FeS + SO_2 \uparrow$ + FeO (minor)

S2) Smelting : Roasted ore is mixed with coke & SiO_2 & heated in blast of hot air.

$FeS + O_2 \longrightarrow FeO + SO_2 \uparrow$

infusible material

Self Red" method ⇒ Preferable ∴ when → extraction of metal from Sulphide ore.

$FeO + SiO_2 \longrightarrow FeSiO_3$

FeO — infusible; SiO_2 — silica, Flux; $FeSiO_3$ — fusible slag

(a rxn in which silica is flux. & $FeSiO_3$ is slag)

S3) $Cu_2S + O_2 \xrightarrow{\Delta} Cu_2O + SO_2$

~~excess~~ Limiting Reagent

Now, More Cu_2S is added & heated in absence of O_2, where :-

SELF REDUCTION: $Cu_2S + 2Cu_2O \xrightarrow{\Delta\Delta} 6Cu + SO_2 \uparrow$

(rough surface; SO_2; Cu)

BLISTER Copper

also called as BESSMERIZATION

- Properties

1. Action of air :- DRY air has no effect on Cu at RT. In presence of moisture & CO_2 (from air) a green depos^n of basic copper carbonate is formed on the surface

$CuCO_3 \cdot Cu(OH)_2$

i.e $Cu + H_2O + CO_2 \longrightarrow CuCO_3 \cdot Cu(OH)_2$

green :- Malachite green.

2. With O_2

$Cu + O_2$ (dry) $\xrightarrow{RT} \times$

$Cu + O_2$ (dry) $\xrightarrow{\Delta,\ \approx 1000^\circ C} CuO \xrightarrow{T > 1000^\circ C} Cu_2O$

CuO — black (black copper oxide); Cu_2O — red (red copper oxide)

i.e : An element on heating → Black & then, high heating → red

⇓

Cu.

3. With acid

(a) with (dil) HCl, $H_2SO_4 \longrightarrow \times$ (Cu less electro +ve than H_2)

(b) BUT

$Cu + H_2SO_4$ (conc or DIL) $\xrightarrow{BOIL} CuSO_4 + H_2O + SO_2 \uparrow$

$CuSO_4 \rightarrow [Cu(H_2O)_6]^{2+} + SO_4^{2-}$

Blue

(c) With HNO_3

Cu or Pb + HNO_3 (dil) $\longrightarrow$ $Cu(NO_3)_2$ or $Pb(NO_3)_2$ + NO

Cu or Pb + HNO_3 (conc) $\longrightarrow$ $Cu(NO_3)_2$ or $Pb(NO_3)_2$ + NO_2

Thermally unstable (Hafan's rule)

So, $Cu(NO_3)_2 \xrightarrow{\Delta} \underset{\text{black}}{CuO} + NO_2$

ie Cu + HNO_3 (dil or conc) $\xrightarrow{\text{boil}}$ $\underset{\text{black}}{CuO}$ + ——

(d) With halogens

$Cu + F_2 \longrightarrow CuF_2$

$+ Cl_2 \xrightarrow{\Delta} CuCl_2$

$+ Br_2 \xrightarrow{\Delta} CuBr_2$

$+ I_2 \xrightarrow{\Delta} CuI$

(e) With alkali

Cu + alkali $\longrightarrow$ ✗

★ Cu_2O

- preparation

① $Cu + O_2 \xrightarrow{>1100^\circ C} Cu_2O$ (red)

(remember → $Cu + O_2 \xrightarrow{<1000^\circ C} \underset{\text{(black)}}{CuO}$)

② Cu^{2+} —tartarate (NH_3) + Glucose (or aldehyde) $\longrightarrow Cu_2O$

Fehling sol^n

- properties :-

disproportionate ★ $Cu_2O + HCl \longrightarrow \overset{+2}{Cu}Cl_2 + \overset{0}{Cu} + H_2O$

$+ H_2SO_4 \longrightarrow \overset{+2}{Cu}SO_4 + \overset{0}{Cu} + H_2O$

★ CuO

- preparation

① $Cu + O_2 \xrightarrow{T<1000^\circ C} CuO$ (black)

(2) $Cu(NO_3)_2 \xrightarrow{\Delta} CuO + NO_2 \uparrow$ (brown)
(simple, not high)

Why, $Cu(SO_4)_2 \xrightarrow{\Delta} CuO + SO_3 \uparrow$

* **BLUE-VITRIOL : $CuSO_4 \cdot 5H_2O$**

• Preparation :-

(1) $Cu + H_2SO_4 \xrightarrow{\text{boil}} CuSO_4 \xrightarrow[\text{Crystallizn}]{\text{cool}} CuSO_4 \cdot 5H_2O$
(dil → H_2O source)
Blue, solid (transperent) at RT.

✓ $CuSO_4 \cdot 5H_2O(s) + \text{In open air} \rightleftharpoons CuSO_4 \cdot 3H_2O + 2H_2O(v)$
(blue) (decomposes to lower extent)

✓ $CuSO_4 \cdot 3H_2O(s) + \text{"} \rightleftharpoons CuSO_4 \cdot H_2O + H_2O(v)$
(light blue)

✓ $CuSO_4 \cdot H_2O(s) + \text{"} \rightleftharpoons CuSO_4 + H_2O(v)$
(colorless)

* VP of $CuSO_4 \cdot 5H_2O$ is more than partial VP of water vapour in air. So, when left for long time, ~~$CuSO_4$~~ it converts to $CuSO_4 \cdot 3H_2O$ (~~Le Chatelier~~). due to motion of $H_2O(v)$ towards air (Le Chatelier). So, inspite of small equi constant, rxn proceeds to completion. This does NOT happen with other hydrides (lower)

§ **LEAD**

• Lead ore → Galena (PbS)

• Preparation :-

(1) Purified PbS is heated in limited supply of O_2 where PbO is formed

$PbS + O_2 \xrightarrow{\Delta} PbO + SO_2$
(Limiting Reagent)

* More PbS is added & heated in absence of O_2 (roasting)

Self Redn : $PbS + PbO \xrightarrow{\Delta} 3Pb + SO_2 \uparrow$
(high density → Blistering effect not observed)

Cu_2O

Date

• CARBON RED^{n} method of Lead

$$PbS + O_2 \xrightarrow[\text{excess}]{\text{Roasting}\ \Delta} PbO + SO_2$$

$$PbO + CO \xrightarrow{\Delta} Pb + CO_2$$

$\uparrow\Delta$ C

• Properties

(a) Action of air :-

$$Pb + \text{air} \xrightarrow{RT} \text{no reaction}$$

(dry or wet)

$$Pb + O_2 \xrightarrow{\Delta} PbO \xrightarrow{\Delta\Delta} Pb_3O_4$$

PbO: White Lead (a strengthening material)

Pb_3O_4: Red Lead (used as a pigment in metallic paints (Vermillion → सिंदूर) (carcinogenic))

(b) With acid :-

↳ with HCl, H_2SO_4

$$Pb + \underset{\text{dil or conc}}{HCl \text{ or } H_2SO_4} \xrightarrow{RT} \text{no reaction}$$

$$Pb + 2HCl + \tfrac{1}{2}O_2 \xrightarrow{\Delta} PbCl_2 + H_2O$$

conc. ; $PbCl_2$: white ppt.

$PbCl_2 \xrightarrow[\text{excess}]{Cl^-} [PbCl_4]^{2-}$ (redissolves)

$$Pb + H_2SO_4 \xrightarrow{\Delta} PbSO_4 + SO_2 + H_2O$$

conc. ; $PbSO_4$: highly insoluble (covers surface of Lead) ⇒ Rxn immediately stops

↳ with HNO_3

$$Pb + \underset{\text{dil}}{HNO_3} \longrightarrow Pb(NO_3)_2 + NO$$

$$Pb + \underset{\text{conc}}{HNO_3} \longrightarrow Pb(NO_3)_2 + NO_2$$

↳ with CH_3COOH

$$Pb + CH_3COOH + O_2 \longrightarrow Pb(CH_3COO)_2(aq) + H_2O$$

(an essential component of ...)

$Pb(CH_3COO)_2$: H_2O soluble

Crystalline substance + anything/something ⟶ M.Pt lowers.

Date

Extraction of Al & Mg

(C-redⁿ method ⟶ ✗ ∵ C can't reduce Al, Mg ∵ of electro +vity)

• ALUMINIUM ELECTROLYTIC METHOD

(Aluminium ore → (Bauxite → $Al_2O_3 \cdot 2H_2O$; Alumina))

S1) $Al_2O_3 \cdot 2H_2O \xrightarrow[\text{Calcinⁿ}]{\Delta} Al_2O_3$ anhyd. (Corrundum)

• Al_2O_3 → direct electrolysis ⟶ ✗

↳ ∵ (1) It has very high M.Pt (> 2100°C)
(2) It is bad conductor of electricity

So,

S2) $Al_2O_3 + Na_3AlF_6 + CaF_2$ ⟶ Electrolysed in Graphite furnace.

Cryolite, Fluorspar

both mixes with Al_2O_3
↳ lowers M.Pt
↳ Ionises completely & ↑ conductivity

react with O_2 to give CO_2

Cathode :- $Al^{3+} + 3e^- \longrightarrow Al$

Anode :- $2O^{2-} \longrightarrow O_2 + 4e^-$

• Properties

(1) Action of air

$Al + Air \longrightarrow \underset{\text{protecting layer}}{Al_2O_3} + \underset{\text{(further oxidⁿ)}}{O_2} \longrightarrow$ ✗

(2) Action of H_2O

$Al + \underset{\text{cold}}{H_2O} \longrightarrow$ ✗

$Al + \underset{\text{Steam}}{H_2O(v)} \xrightarrow{\Delta} Al_2O_3 + H_2 \uparrow$

Date

(3) Action of acid

$Al + HCl \longrightarrow AlCl_3 + H_2$

$+ H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2$

$+ \underset{(dil)}{HNO_3} \longrightarrow Al(NO_3)_3 + NO$

$Al + \underset{(conc.)}{HNO_3} \longrightarrow Al(NO_3)_3 + NO_2$

$Al + \underset{(conc.)}{HNO_3} \longrightarrow Al_2O_3 + NO_2\uparrow$

Al_2O_3 covers layer of Al ⇒ Rxn stops

(4) With alkali

$Al + NaOH \longrightarrow NaAlO_2 + H_2$

Sodium aluminate

* (5) With Fe_2O_3 "THERMITE WELDING"

$Fe_2O_3 + Al \xrightarrow{\text{Electric spark}} Fe + Al_2O_3 \quad \Delta H << 0$

3 : 1 (RA)

Fe melted

for Fe

Thermite

⇒ Also called: GOLDSMITH THERMITE PROCESS

(6) With halogens

$Al + Cl_2 \xrightarrow{\Delta\Delta} AlCl_3$ (+3 → only possible oxid^n state)

(X_2) (AlX_3)

(7) With N_2

$Al + N_2 \xrightarrow{\Delta} AlN$

Covalency ↑ ⇒ M.pt ↑

Date

Date

* $AlCl_3$ (a salt) → of $Al(OH)_3 + HCl$

• preparation

(1) $Al + HCl \longrightarrow AlCl_3 + H_2$ } hydrated

(2) $Al_2O_3 + HCl \longrightarrow AlCl_3 + H_2O$ }

(3) $Al + Cl_2 \xrightarrow{\Delta} AlCl_3$ (anhyd.)

• properties

1. Structure related :-

Al^{3+} → very high polarising power

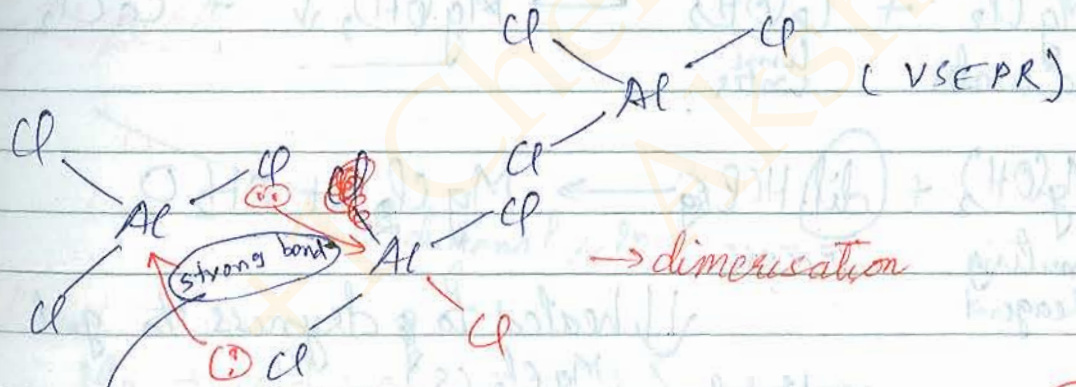
↓↓

covalent compd.

⇒ • $AlCl_3(s)$ ~~ha~~ ⇒ Ionic ⇒ NaCl type unit cell.

• $AlCl_3(s) \xrightarrow{\Delta} AlCl_3$ (molten)

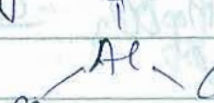
covalent behaviour.



⇒ CN of Al in molten $AlCl_3$ → (4)

⇒ In vapour phase, at lower temp. (just enough to vapourise) ~~ha~~ exists as dimer (CN = 4)

In vapour phase, at high temp, exists as monomer (CN = 3)



2. ~~Alcl~~ $AlCl_3$ soluble in both polar & non polar solvents. (large covalent character)

ΔH<<D

on stops

ss

Solubility :- $Mg(OH)_2 << Ca(OH)_2$

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(3) $AlCl_3 + H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^{\ominus}$

highly soluble
(∵ Hydr^n energy is much larger than lattice energy)

☆ Magnesium

By electrolytic method :-

- Source → $MgCl_2$ (sea water) → mainly
  Ores :- ✓ Carnalite ($KCl \cdot MgCl_2 \cdot 6H_2O$)
  ✓ Dolomite ($MgCO_3 \cdot CaCO_3$)

→ Magnesium from sea water :- DAW PROCESS

$MgCl_2$ (sea water) + $Ca(OH)_2$ (lime water) $\longrightarrow Mg(OH)_2 \downarrow + CaCl_2$

$Mg(OH)_2$ (Limiting Reagent) + dil. HCl (excess) $\longrightarrow MgCl_2 + 2H_2O$

↓ heated to dryness to get $MgCl_2(s)$

$MgCl_2(s)$ —(Melted & electrolysed)→ $Mg^{2+} + 2e^- \longrightarrow Mg$ Cathode

$2Cl^- \longrightarrow 2e^- + Cl_2(g)$ Anode

→ From Dolomite (Natural brine process)

$CaCO_3 \cdot MgCO_3$ (purified) —Calcination→ $CaO \cdot MgO + CO_2$

$CaO \cdot MgO + HCl$ (dil.) $\longrightarrow CaCl_2 \cdot MgCl_2 + H_2O$

* For gap 2 metals → $M(OH)_2$, MF_2 ⇒ Solubility ↑ down the gap.
in all other cases → MCO_3, MSO_4, ... ⇒ Solubility ↓ down the gap
* For solubility :- Hydⁿ energy >> lattice energy.
* Both hydⁿ & lattice energy ↓ down the gap.
For $M(OH)_2$, MF_2 ⇒ lattice energy decreases more rapidly than hydⁿ energy down the gap. So, solubility ↑ down the gap. Heve Reverse happens for MCO_3, MSO_4.

PERIODIC CLASSIFICⁿ

Now, through the solⁿ, more calcined ore is added & $CO_2(g)$ is passed resulting in sptⁿ of $CaCO_3$ leaving $MgCl_2$ in solⁿ.

$$MgCl_2 \cdot CaCl_2 + CaO \cdot MgO \xrightarrow{+2CO_2} 2CaCO_3 \downarrow + 2MgCl_2(aq)$$

$$MgCl_2(aq) \xrightarrow{\text{heat to dryness}} MgCl_2(s) \xrightarrow{\text{electrolysis}} Mg \text{ (at cathode)} + Cl_2 \text{ (anode)}$$

- Properties

Li, Be, Mg → diagonal relⁿ

→ Reaction with water

Mg + cold water ⟶ X

Mg + Steam ($H_2O(v)$) ⟶ $MgO + H_2\uparrow$

→ With air

$Mg + \text{dry air} \xrightarrow{RT}$ X

$Mg + \text{dry air} \xrightarrow{\Delta} MgO + Mg_3N_2$
burns ($N_2 + O_2$)

* Hence, ignition of Mg continues burning even in nitrogen atmosphere only (Mg_3N_2).

All elemts of grp. 1 & grp 2 + Liq. NH_3 (not aq) ⟶ Blue soln

Date

⇒ Solution of Mg in liq. (NH_3)

$$Mg + NH_3(l) \longrightarrow e(NH_3) + Mg^{2+}(NH_3)$$

solvated electron (emission spectrum in visible region of EM spectrum)

hence, sol^n of Mg in liq. NH_3 act as a strong RA ⟶ : it gives solvated $\bar{e}$ as it can reduce other compds - Same is true for other metals of grp 1 & grp 2

* Sol^n of Mg in liq^d NH_3 is para magnetic.

Imp ✱ When ⟶ sol^n is evaporated, metal is not recovered Rather,

$$Mg^{2+}(NH_3) \longrightarrow \underset{\text{Metal amide}}{Mg(NH_2)_2} + H_2\uparrow$$

* Chlorophyll contains Mg

✱ Extraction of Ag & Au : CYANIDE PROCESS

valid: when compds of metals are insoluble in most of the solvents

Ag

Ore :- Argentite (Ag_2S) — black

very strong ligand

$$Ag_2S + 4KCN(aq) \xrightarrow[\text{CONC}]{\text{Leaching}} 2K[Ag(CN)_2] + K_2S$$

Imp

$$2K[Ag(CN)_2] + Zn \xrightarrow{\text{Displacement rxn}} K_2[Zn(CN)_4] + 2Ag$$

most suited for effective rxn (electro positivity)

Mg → 2nd option.

Na → X → fire catches

H_2S ⇒ Sulphasyl hydrogen ⇒ hydrogen sulphide.

Date

properties.

1) Action of air

$Ag + air \xrightarrow{RT} X$

- $Ag + air \xrightarrow{\text{left for long time}}$ Blackening of silver.
  (having H_2S) (due to form^n of $Ag_2S\downarrow\downarrow\downarrow$)
  (black)

removal of black stain of silver

$Ag_2S + Na_2S_2O_3\,(aq) \longrightarrow Na_3[Ag(S_2O_3)_2]\,(aq)$
hypo sol^n

2) With acids:-

Ag + HCl (dil) or (conc) $\longrightarrow X$
(lower in electrochemical series below H)

$2Ag + \frac{1}{2}(O_2) + 2HCl\,(conc.) \longrightarrow 2AgCl\,(s) + H_2O$
(white layer of AgCl on surface of Ag)

If Cl^- in excess

$2AgCl\,(s) \xrightarrow[(excess)]{Cl^-} [AgCl_2]^-$

✓ $Ag + H_2SO_4\,(dil.) \longrightarrow X$

$+ H_2SO_4\,(conc.) \xrightarrow[\text{necessary}]{\Delta} Ag_2O\downarrow + SO_2$
(yellow)
(not Ag_2S, it decomposes to Ag_2O)

leads to yellowing color on surface of Ag due to Ag_2O (yellow)

✓ $Ag + (dil)\,HNO_3 \rightarrow AgNO_3 + NO\uparrow$
(just as with Cu)

$Ag + (conc)\,HNO_3 \longrightarrow AgNO_3 + NO_2\uparrow$

All salts of heavy metals (excluding nitrate salts) are all sparingly soluble whose solubility can be compared using Fajans Rule

(3) With halogens (all)

$$Ag + X_2 \xrightarrow{\Delta} AgX$$

AgBr

Fajans Rule — solubility in water:

$$AgF > AgCl > AgBr > AgI$$

✓ $AgNO_3 + NaBr \longrightarrow AgBr$

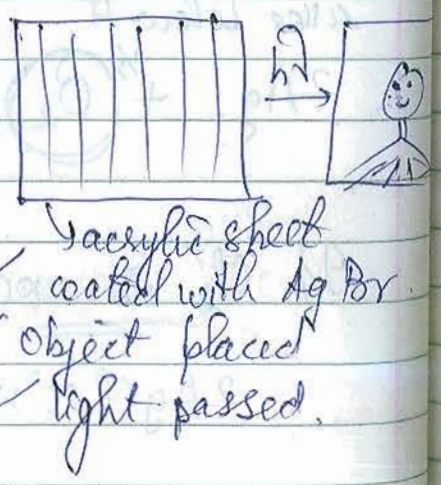
✓ $Ag + Br \xrightarrow{\Delta} AgBr$

properties :-

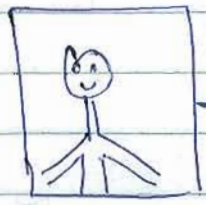
AgBr : used in photographic films

(∵ AgBr is light sensitive)

$$AgBr + h\nu \longrightarrow Ag + Br_2\uparrow$$



✓ acrylic sheet coated with AgBr
✓ object placed
✓ light passed.



$Na_2S_2O_3$ (aq)

$AgBr + Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O$

unreacted AgBr comes in soln

negativ
form

✓ Ag :- highEST electrical conductivity

✓ 2nd highest thermal conductivity (after Au)

Date

Au

✓ noble metal, inert ⇒ FREE STATE in nature.

Ore: Azurite (Au in free state is present in it)
(Africa)

extraction

Azurite + KCN (conc) —leaching→ $K[Au(CN)_2]$ —+Zn (Displacement rxn)→ Au + $K_2[Zn(CN)_4]$

*properties :-

most malleable, most ductile, most thermally conducting, 2nd highest ↓ electrical conductivity (after Ag)

Au + dry or moist air ⟶ ✗

$Au + O_2 \xrightarrow{\Delta}$ ✗ (not oxidised)

Au + dil. or conc. HCl (or), H_2SO_4 (or), HNO_3 ⟶ ✗

Au + base or halogens ⟶ ✗

Au + AQUA ~~REGIA~~ REGIA ⟶ dissolves

⇓

HNO_3 (conc.) + HCl (conc.)
1 : 3

$(HNO_3 + 3HCl \longrightarrow \underset{\text{nitrosyl chloride}}{NOCl} + 2H_2O + 2Cl\uparrow) \times 3$

$Au + 3Cl + HCl \xrightarrow{\text{dissolves}} HAuCl_4 \times 2$
(hydrochloroauric acid)

net rxn $3HNO_3 + 11HCl + 2Au \longrightarrow 3NOCl + 6H_2O + 2HAuCl_4$

end of metallurgy

Date

Group - 13

Boron

Ores :- Borax ($Na_2B_4O_7 \cdot 10H_2O$)
Colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$)

(1) By red^n of B_2O_3 → (Borax or colemanite + acid → B_2O_3 → anhydride of the

$$B_2O_3 + Al \xrightarrow{\Delta} B + Al_2O_3$$

(2) Thermal decompos^n of BI_3 (water insoluble) → ($B_2O_3 + HI \rightarrow BI_3 + H$

$$BI_3 \xrightarrow{\Delta} B + \frac{3}{2}I_2$$

(3) Thermal decompos^n of hydrides

$$B_2H_6 \xrightarrow{\Delta} 2B + 3H_2 \uparrow$$

Properties

✓ Boron in solid state → B_{12} (Icosahedral structure)
↓ as ~~hard as~~ diamond stru

B → hard, less reactive, not attacked by common reagents.

✓ $B + N_2 \xrightarrow[\text{high T, P}]{\Delta\Delta} (BN)_x$
Boron nitride
(polymer → graphite like structu

$(BN)_x$ → ✓ M.Pt ≈ 10,000 °C
- ✓ Properties resemble that of graphite.
- ✓ has graphite like layered str. giving it electrical conductivity.



• preparation

(i) By treatment of Mg-boride with conc. H_3PO_4

$$Mg_3B_2 + 2H_3PO_4 \text{ (conc.)} \longrightarrow Mg_3(PO_4)_2 + B_2H_6$$

(ii) By red^n of Boric anhydride (B_2O_3) with Al in presence of $H_2(g)$

$$B_2O_3 + H_2(g) + Al \longrightarrow Al_2O_3 + B_2H_6$$

(iii) By red^n of Boric halides (usually BF_3) with $LiAlH_4$ (or ~~NaBH$_4$~~ NaH) (or $NaBH_4$)

$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3Li[AlF_4]$$

lithium tetrafluoro aluminate.

$$+ NaBH_4 \longrightarrow B_2H_6 + Na[BF_4]$$

(iv) By red^n of boron halides with gp 1 or gp 2 metal hydrides

$$2BF_3 + 6NaH \longrightarrow B_2H_6 + 2NaF$$

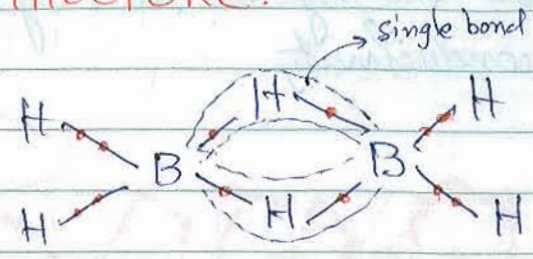
(v) By red^n of Boron halides with NaI

$$BCl_3 + NaI(aq) \xrightarrow{+H_2O} B_2H_6 + NaCl + I_2$$

Date

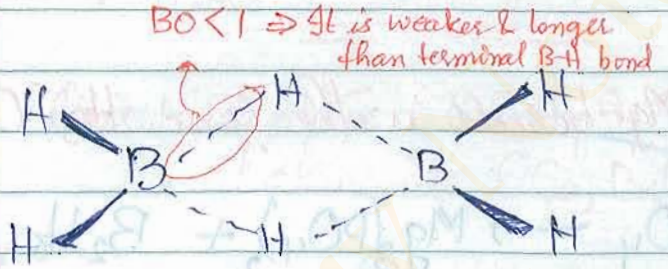
* properties

(1) STRUCTURE :-



✓ 4 B-H terminal bonds which are normal σ bonds

✓ 2 B-H-B bridged bonds also known as 3-centre-2-electron bond & its just one bond.



✓ H-B-H ⊥ B-H-B

✓ Individual bridged B-H bond is weaker & longer than terminal B-H bond

✓ Combined BO & hence BE of bridged > terminal so, terminal gets replaced in rxns

✓ H-B-H plane ⊥ B-H-B plane

(2) With H_2O

$$B_2H_6 + H_2O \longrightarrow H_3BO_3 + H_2\uparrow$$

(3) With HCl, (S_N rxn)

$$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2\uparrow$$

$$+ \underset{\text{excess}}{HCl} \longrightarrow B_2H_2Cl_4 + 4H_2\uparrow$$

(4) With $Cl_2(g)$

$$B_2H_6 + 6Cl_2(g) \xrightarrow{\text{oxidn}} 2BCl_3 + 6HCl$$

(5) With NH_3 & $R-NH_2$ (amines) :—

(a) At RT

$$B_2H_6 + NH_3(g) \longrightarrow B_2H_6 \cdot 2NH_3$$

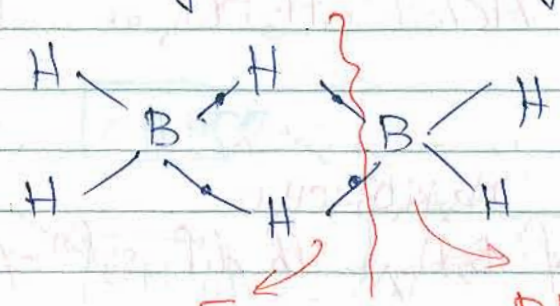
$$\text{or } NH_3(aq)$$

(each NH_3 provides 1 LP to)

* Inorganic benzene (or) Borazine (or) Borazole
* fuel value : per gm of fuel → energy released

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* But NH_3 brings about cleavage of B_2H_6 as :-



BH_4^- octet complete

BH_2^+ requires 2 LP

Hence, $B_2H_6 \cdot 2NH_3 \equiv [BH_4]^{\ominus}[BH_2(NH_3)_2]^{\oplus}$

Ily, $RNH_2 \longrightarrow [BH_4][BH_2(RNH_2)_2]$

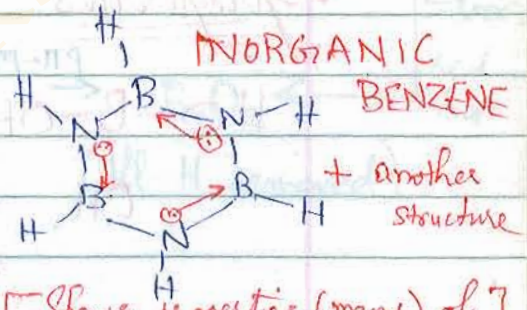
But R_3N (3° amine) → Symmetric cleavage (to avoid overcrowding) → $2BH_3(NR_3)$

* $B_2H_6 + NH_3$ (excess) $\xrightarrow{\text{high T, P}}$ $(BN)_x$ formed as earlier also.

** $B_2H_6 + NH_3$ (1 : 2) $\xrightarrow{\text{high T, P}}$ $B_3N_3H_6$

BORAZINE

BORAZOLE



INORGANIC BENZENE + another structure

Shows properties (many) of benzene.
like benzene, it undergoes FCA, FCA_c, - ——— -

* Here, INDIVIAL BONDS ARE POLAR (unlike C_6H_6)

(6) With O_2

$B_2H_6 + O_2 \longrightarrow B_2O_3 + H_2O$ $\quad \Delta H < 0$

Its fuel value is very high. So, it releases more energy than hydrocarbons. Hence, its used for short range rockets.

~~oxo~~ oxy acid : An acid having acidic H with OH.

e.g. : $H_2SO_4 \rightarrow HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$: oxy acid.

Date

★ Orthoboric Acid H_3BO_3 or $B(OH)_3$

expected • preparation

Borax → $Na_2B_4O_7 \cdot 10H_2O$

1) By treatment of ~~B_2H_6~~ with dil soln of HCl (dil) & dil. H_2SO_4

$5H_2O + Na_2B_4O_7\,(aq) + 2HCl\,(aq) \longrightarrow 2NaCl + 4H_3BO_3$

$+ H_2SO_4(aq) \longrightarrow Na_2SO_4 + H_3BO_3$

2) By passing $SO_2(g)$ through aq. solution of COLEMANITE ($Ca_2B_6O_{11} \cdot 5H_2O$)

$9H_2O + Ca_2B_6O_{11} + 2SO_2\,(aq) \longrightarrow 2CaSO_3\downarrow + 6H_3BO_3$

is

• properties

$HO-\overset{\overset{p\pi-p\pi}{\leftarrow}}{B}-OH$; LA (NOT oxy acid)
|
OH

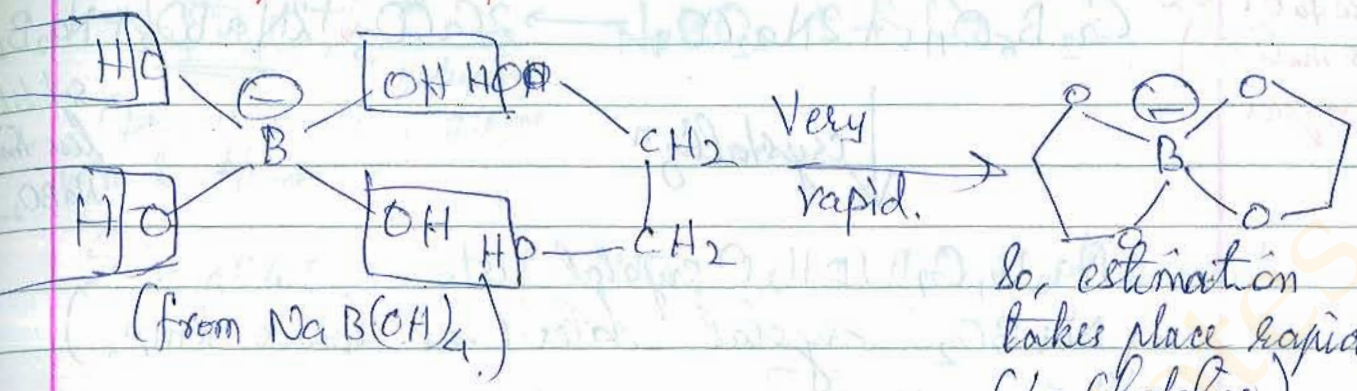
★★ Its mono basic (not tribasic) (∵ it can accept only 1 LP)
∴ Its e^- accepting efficiency is very less making it a weak acid (due to $p\pi-p\pi$ back bonding)

⇒ ★ Boric acid is a very weak, monobasic, LA

• $B(OH)_3 + NaOH \rightleftharpoons Na^{\oplus}B(OH)_4^{\ominus}$

It cannot be estimated by titration with strong base (∵ neutralisn is significant if rxn occurs quantitatively & Boric acid doesn't react effectively. Rxn

- Boric acid can be estimated by titration with NaOH (only) in the presence of SYN-VICINAL DIOL



So, estimation takes place rapidly (Le Chatelier)

* Cis st. is reqd in cyclic so that from both places, removal of water is able

- Boric acid is disinfectant : used in cassom, billiards, ---
  Boric acid is used as an antiseptic and disinfectant.
- Action of Heat

$H_3BO_3 \xrightarrow[\text{low temp}]{\approx 100^\circ C,\ \Delta} H_2B_4O_7$ (tetra boric acid) $\xrightarrow[\Delta]{170-180^\circ C} HBO_2$ (Meta boric acid) $\xrightarrow{\approx 300^\circ C,\ \text{red hot}} B_2O_3$ (all H removed)

✱ BORAX ($Na_2B_4O_7 \cdot 10H_2O$)

(CN → Tincle (सुहागा)) → used to melt gold at RT itself.

- Preparation

1. By treatment of Boric acid with sodium carbonate in aq. solution

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7(aq) + CO_2\uparrow + 6H_2O$$

Date

2. By treatment of sodium carbonate with Colamenite

(useful for multiple ans-ques)

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3\downarrow + 2NaBO_2 + Na_2B_4O_7$$

Solubility less than $NaBO_2$

↓ crystalliz^n

$Na_2B_4O_7 \cdot 10H_2O$ crystal 1st

$NaBO_2$ crystal later (at lower temp^s)

- properties

✓ Basic salt (Boric acid (WA) + NaOH (SB))

✓ Structure :-

$$Na_2B_4O_7 \cdot 10H_2O \longrightarrow Na_2[B_4O_5(OH)_4] \cdot 8H_2O$$

Structural formula

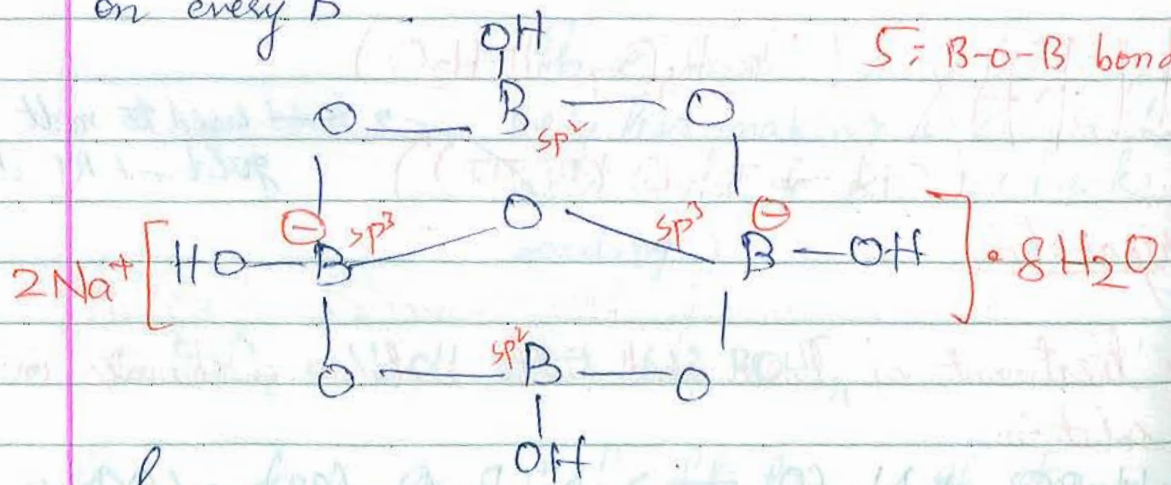
(It has 2 diff^t types of H_2O molecules

2 → covalent

8 → water of crystalliz^n

Keep 4 B on 4 corners of tetrahedron and make peripherical B–O–B bonds (2 on sides) and one bridge B–O–B bond. Now, keep one OH on every B.

5 ; B–O–B bond.



So, Borax on simple heating (not high) gives

Date

Thermal property

$$Na_2B_4O_7 \xrightarrow{\Delta} NaBO_2 + B_2O_3$$

(Put on Pt wire & flame) Reducing flame.

In qualitative, eg. if $Co(NO_3)_2$, $Co(BO_2)_2$ is formed.

Borax bead test.

- Co or Cu → Blue.
- Fe or Cr → Green
- Ni → Reddish Brown
- Zn → colorless (white)
- Mg → Pink

- Borax: It is used in water treatment as an ION EXCHANGER.

GROUP - 14

✱ OXIDES of CARBON (CO & CO_2)

Si, Silicones, Silicates

CO

✱ preparation

1) By treatment of methanoic acid with (conc.) H_2SO_4 (strong dehydrating agent)

$$H-\underset{\underset{O}{\|}}{C}-OH + H_2SO_4 \xrightarrow{\Delta} CO + H_2O$$

conc.

2) By thermal decompos^n of oxalic acid

$$H_2C_2O_4 \xrightarrow{\Delta} H_2O + \underbrace{CO + CO_2}$$

both oxides formed
(can come in multiple ans.)

3) By red^n of gp 1 or gp 2 metal carbonates with Zn or C (charcoal or coke)

$CaCO_3 \xrightarrow{\Delta} (CaO + CO_2) + Zn \rightarrow CaO + ZnO + CO$

$CaCO_3 + Zn \xrightarrow{\Delta} CaO + ZnO + CO$

$CaCO_3 + C \xrightarrow{\Delta} CaO + 2CO$

4) It is also formed at bottom of blast furnace

5) $H_2O(v) + C \longrightarrow H_2 + CO$: water gas reaction

- **Properties**
- CO is a neutral non metallic oxide (not ~~basic~~ acidic)
- CO → gas at RT.
- Is highly combustible (CO_2 form^n)
- Burns with blue flame

$$CO + \frac{1}{2}O_2(g) \xrightarrow{\Delta} CO_2 \uparrow$$

excess — blue flame

- Poisonous gas (∵ very strong ligand and haemoglobin (pentavalent) keeping one place for O_2 to make it hexavalent. But, if CO, its much stronger ligand than O_2 & so O_2 supply stops ∴ it forms bond with (Fe) of haemoglobin)
- CO is used as a strong RA in metallurgy.

Date

CO_2

• preparation

1. Hydrocarbon or carbon + O_2 (excess) —(for complete combustion)→ $CO_2 + H_2O$ (with hydrocarbon)

(∵ efficiency of O_2 is less so, its supply is reqd more)

2. Decompos^n of metal carbonate

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

3. $CO + \frac{1}{2}O_2 \longrightarrow CO_2$

• properties

• CO_2 is a weakly acidic oxide.
• Very low solubility in H_2O at RT.
• Turns like water milky ($Ca(OH)_2(aq) + CO_2 \longrightarrow CaCO_3\downarrow$ milky)

$Ca(HCO_3)_2$ ← CO_2 excess.

turbidity vanishes

Si

The most abundant element of earth crust found in the form of Silica and silicates.

• preparation (i.e extraction of Si from silica (SiO_2))

$SiO_2 + C \xrightarrow{\text{Electric arc}} Si + CO$

(SiO_2 excess; C - red^n method; Electric arc for heating (≈2200°C & not possible in blast furnace); Si — Industrial grade (Si) (not that pure))

∵ Si produced combines with coke significantly forming SiC. If SiO_2 excess, it further reacts with SiC → $2SiC + SiO_2 \longrightarrow Si + 2CO$

(2) Prepar^n of pure Si

not very suitable for semiconductor based Si (if impurity is Fe major ∵ Fe too reacts with Zn in similar manner)

$$Si + Cl_2 \xrightarrow{\Delta} SiCl_4\,(g) \longrightarrow \text{Condensed in separate containers}$$

(in prepar^n 1) — (volatile liq at RT) — (due to heating)

$$SiCl_4\,(g) \xrightarrow{Zn} ZnCl_2 + Si$$

pure

(3) $SiCl_4 + H_2\,(g) \longrightarrow SiHCl_3(g) + HCl$

$SiCl_4$: just like alone; H_2: calculated amt; $SiHCl_3$: trichlorosilane

($FeCl_3$ doesn't react ~~like this~~)

$$SiHCl_3 + Zn \longrightarrow Si + ZnCl_2 + HCl$$

pure (semiconductor grade)

(4) By thermal decompos^n of SiI_4 (s) at RT

$$SiI_4(s) \xrightarrow{\Delta} Si + 2I_2(g)$$

(B also produced by thermal decompos^n of I_2)

* Properties

Si is almost inert in air, water, acid & base due to presence of inert layer of SiO_2 on surface.

* $SiCl_4$ > CCl_4

($SiCl_4$: vacant d-orbital; H_2O: poor $Nu^\ominus$, attacks d-orbital of Si and thus, it is hydrolysed making it soluble)

(CCl_4: not soluble in H_2O)

Date

☆ $SiCl_4$ has greater solubility in $NaCl + H_2O$ than H_2O alone.

Reason.

$$SiCl_4 + 2NaCl \longrightarrow Na_2SiCl_6$$

→ Stronger $Nu^{\ominus}$ than H_2O, so possibility of complex form^{n} more probable.

☆ SILICONES :

expected

They are polymers of organo silicon oxide and obtained by hydrolysis of organo silicon halides

$$R-\underset{\underset{Cl}{|}}{\overset{Cl}{|}}{Si}-Cl \quad \left(\text{or } R-\underset{Cl}{\overset{Cl}{|}}{Si}-R \text{ or } R-\underset{R}{\overset{Cl}{|}}{Si}-R\right)$$

- Preparation of organo silicon halides

Organo Si halides are formed by treatment of $SiCl_4$ with calculated amt. of $RMgX$ → Cl or Br.

$$SiCl_4 + RMgCl \xrightarrow{1:1} RSiCl_3 + MgCl_2$$

$$1 : 1$$

$$1 : 2 \longrightarrow R_2SiCl_2 + 2MgCl_2$$

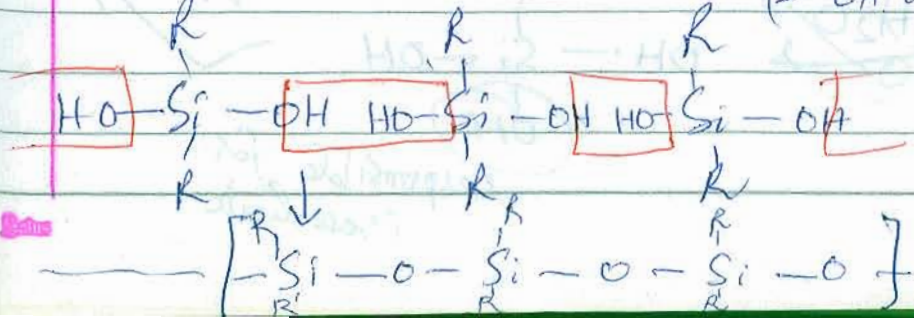
$$1 : 3 \longrightarrow R_3SiCl_2 + 3MgCl_2$$

- Types of Silicones

▷ Linear chain silicones :- Obtained by hydrolysis of dialkyl Si halide.

$$R-\underset{\underset{Cl}{|}}{\overset{Cl}{|}}{Si}-R + H_2O \xrightarrow[\text{excess}]{} R-\underset{\underset{OH}{|}}{\overset{OH}{|}}{Si}-R + (2HCl)$$

(2 OH unstable at one C or Si)



☆ Properties of any polymer depends on molar mass

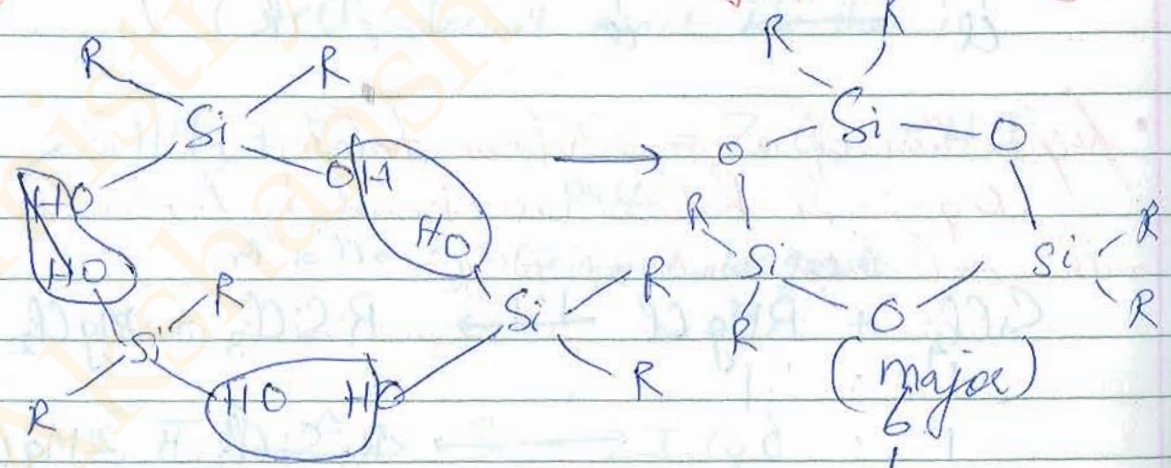
Date

- for linear chain silicones used as a lubricant
- The previous rxn, it proceeds infinitely. To control molar mass, R_3SiCl is used -

$$R_3SiCl \xrightarrow{H_2O} R-\underset{\displaystyle R'}{\overset{\displaystyle R}{\underset{|}{\overset{|}{Si}}}}-OH$$

blocks terminal
CHAIN TERMINATOR

- If organo silicon halide is subjected to limited amt. of H_2O, cyclic silicones are produced with 6-membered ring predominating.

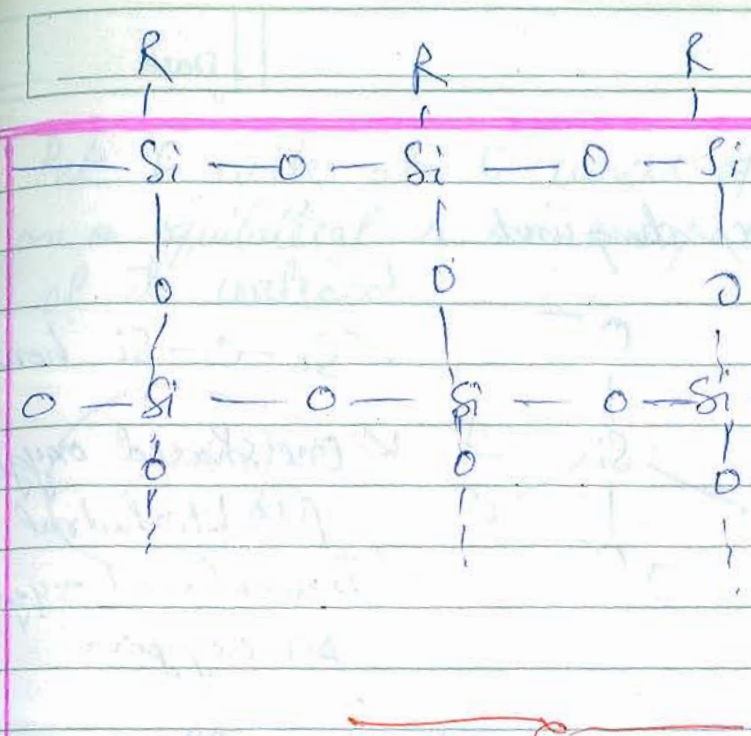


2) Cross linked Silicones

Obtained by hydrolysis of mono alkyl Si halides.

$$Cl-\underset{\displaystyle Cl}{\overset{\displaystyle R}{\underset{|}{\overset{|}{Si}}}}-Cl \xrightarrow{H_2O} OH-\underset{\displaystyle OH}{\overset{\displaystyle R}{\underset{|}{\overset{|}{Si}}}}-OH$$

responsible for cross link.



Solid (RT)

- Bio compatible
Blood clotting doesn't take place on it. So, used in surgery → intricate implant devices.

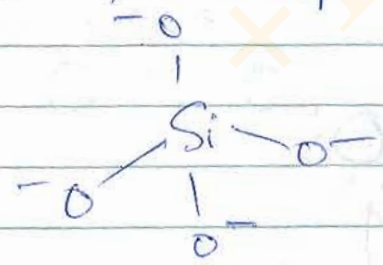
✱ SILICATES:

They are 3D polymes of Si, O, and some active metals.
Classified into 5 categories :-

1. Ortho silicates
2. Pyro silicates
3. Cyclic silicates
4. Chain silicates
5. 3D-network silicates

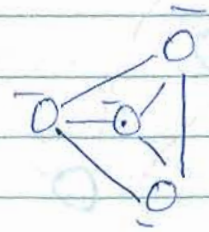
(1) Orthosilicates

Consist of SiO_4^{4-} Repeating unit (can come as Ca_2SiO_4, $NaAlSiO_4$, ...)



no oxygen i.e shared with Si. All are independent.

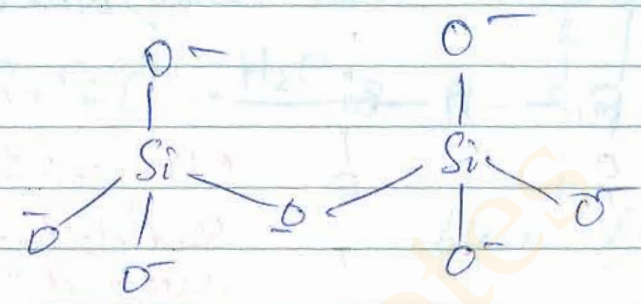
Topological structure →



Date

(2) Pyro silicates :-

$Si_2O_7^{6-}$ repeating unit



✓ Si-O-Si bond

✓ one shared oxygen per tetrahedral

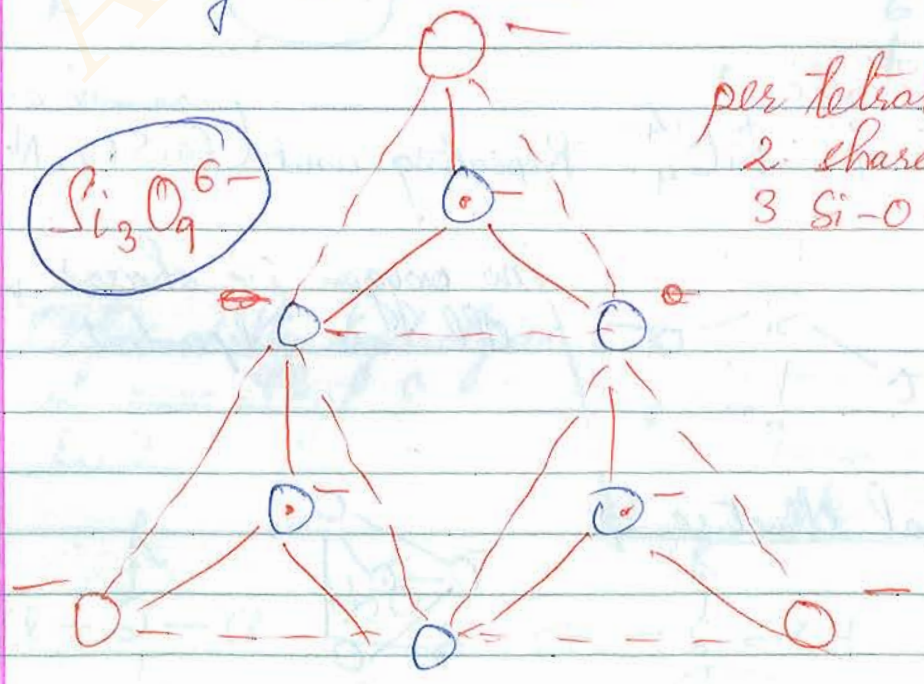
✓ 3 unshared oxygen per oxygen

(3) Cyclic silicates

Based on a general formula → $(SiO_3)_n^{2n-}$

2 common :- $Si_3O_9^{6-}$, $Si_6O_{18}^{12-}$

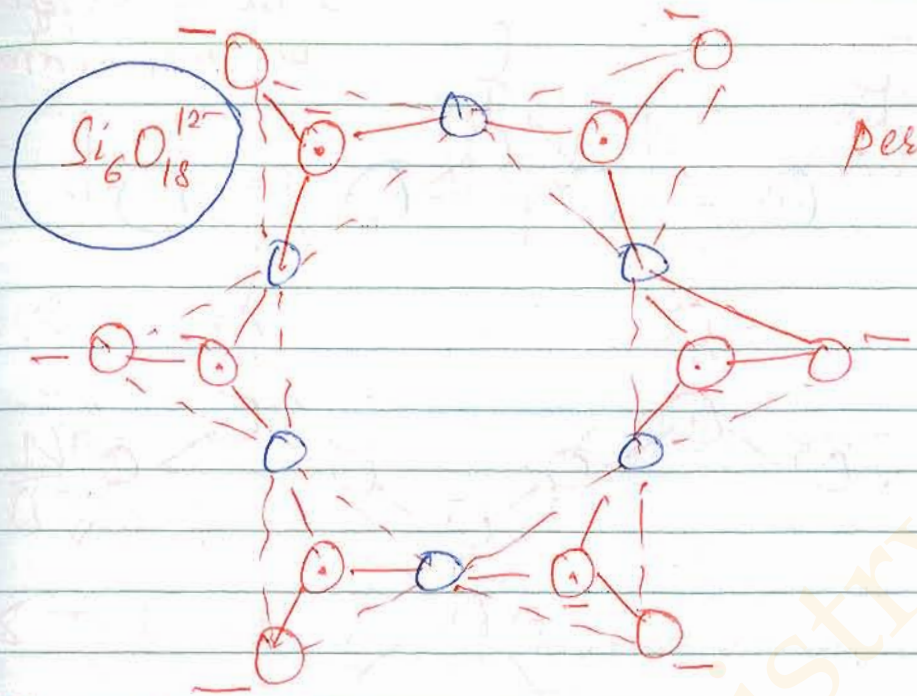
Put 6 circles at 6 corners of hexagon & take every alt., make an equilateral △ s.t the one left becomes centroid. Keep Si on centroid. Then, make tetrahedron on Si. Put charge on vertices & centroid.



per tetrahedral
2 shared, 2 unshared
3 Si-O-Si bond.

Date _____

Put 6 circles at 6 corners of hexagon and make an equilateral Δ on every side. Keep a Si at its centroid.



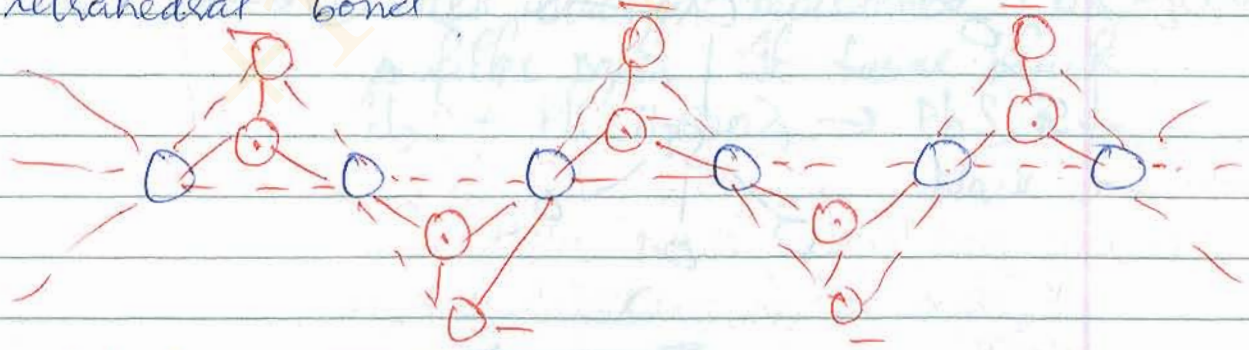
per tetrahedral, 2 shared Oxygen

(4) Chain silicates

2 common :- (1) PYROXENE

Make Δ on alt. side, and its extended.

Put a Si ⊙ at centre of every Δ & make tetrahedral bond



per tetrahedral, 2 shared oxygen.

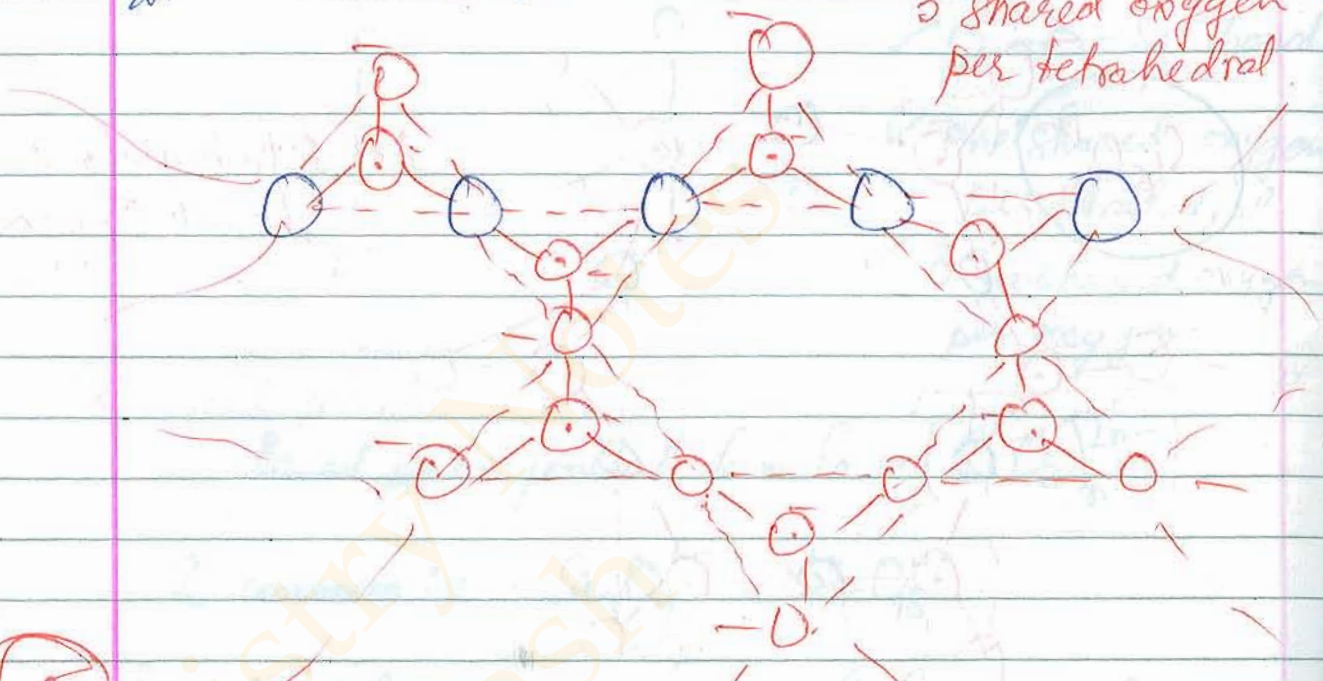
single chain silicate.

Date

(2) AMPHIBOLE (double chain silicate)

Make ~~mirror~~ mirror image of pyroxene and stick to it.

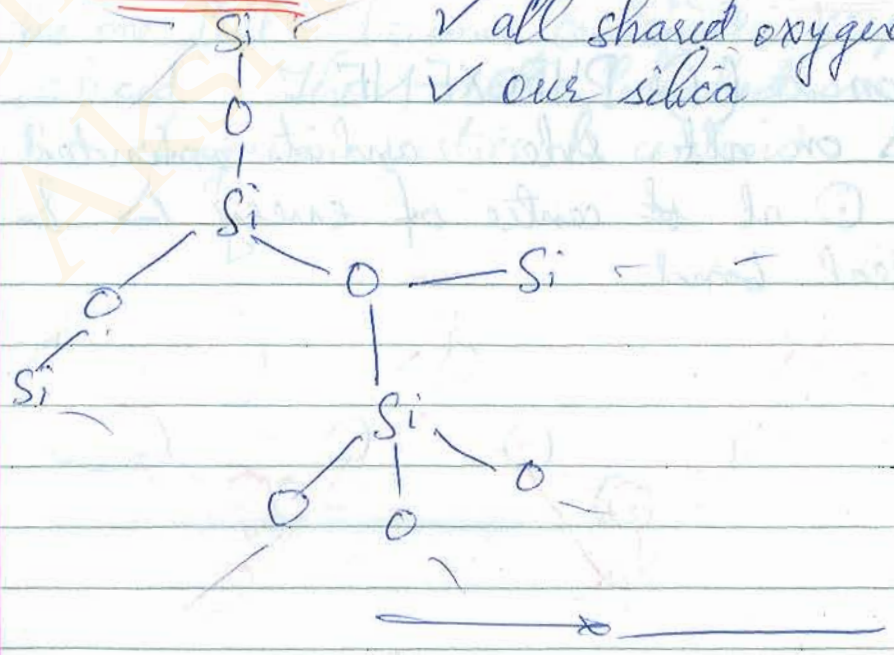
3 shared oxygen per tetrahedral



(5)

(3) 3D - silicate

∴ ✓ emperical formula (SiO_2)
✓ all shared oxygen
✓ our silica



* Qualitative Inorganic Analysis, by Vogel → World Reference.

Date 28/1/11

Qualitative Inorganic Analysis.

✡ Tests of ANIONS

S^{2-}
SO_4^{2-}
NO_3^-
Cl^-, Br^-, I^-

✡ Test of S^{2-} (Remember all surely)

(1) S^{2-} + (dil. H_2SO_4 or dil. HCl.) → $H_2S(g)\uparrow$ + $2Cl^-$ or SO_4^{2-}
SB. SA WA WB

Nao. H_2S (g) is tested.

① Pungent repelling odour.

② Pass through moistened $Pb(CH_3COO)_2$ filter paper. It turns black.
$H_2S + Pb(CH_3COO)_2 \rightarrow PbS\downarrow$ + ...
black

③ Hold $Cd(CH_3COO)_2$ (moistened with filter paper. It turns yellow.
$H_2S + Cd(CH_3COO)_2 \rightarrow CdS\downarrow$
yellow

(2) $AgNO_3$ test

$S^{2-} + AgNO_3 \rightarrow Ag_2S\downarrow + NO_3^-$
black ppt.

→ Black ppt. is insoluble in dil. HNO_3, on treatment with boiling sol^n of conc. HNO_3, it turns white (∵ It oxidises from S^{2-} to SO_4^{2-} by conc. HNO_3 in boiling cond^n as OA)

$Ag_2S \xrightarrow[\Delta]{\text{conc. } HNO_3} Ag_2SO_4$ (White)

Illy, Silver foil test :- If thin Ag foil is brought in contact of the test sol^n, black stain (of Ag_2S) is seen.

$Ag + S^{2-} \longrightarrow Ag_2S$

black stain (not whole black → ∵ Ag is very less reactive)

Imp ⟨3⟩ Methylene blue test (organic dye)

Fe^{3+} + N,N-dimethylp-phenylene diamine (reagent) + S^{2-} (Test sol^n) →

Also a test of Fe^{3+} ion

Fe^{2+} + (Methylene blue)

Blue (water soluble dye)

Expected ⟨4⟩ Nitroprusside test

$2Na^+[Fe(CN)_5NO]^{2-} + S^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$

Sodium nitroprusside (Colorless) — Transient purple

⟨5⟩ $2N_3^- + (\text{aq. Iodine} \Rightarrow I^{3-}) \xrightarrow{+S^{2-}\text{ decompos}^n\text{ of iodine ONLY in presence of } S^{2-}} 3N_2\uparrow + 3I^-$

N_3^- = Azide ion

∵ more soluble salt is converted less soluble salt

Date

☆ Tests of SO_4^{2-}

① $BaCl_2$ test

$$BaCl_2 + SO_4^{2-} \longrightarrow \underset{\text{white ppt.}}{BaSO_4\downarrow} + 2Cl^-$$

- Insoluble in dil. or conc. HCl or H_2SO_4 confirms SO_4^{2-}

② $Na_2CO_3 + BaSO_4 \xrightarrow{\Delta} Na_2S + BaO\downarrow + SO_2\uparrow$

($BaSO_4$: filtered and extracted; Na_2S: goes in soln)

$+ CO_2\uparrow$

Then used in test of S^{2-}

② Mercuric nitrate test ($Hg(NO_3)_2$)

$$SO_4^{2-} + \text{dil. } H_2SO_4\ HCl + Hg^{2+} \longrightarrow \underset{\text{Basic mercuric sulphate}}{HgO\cdot HgSO_4}$$

Yellow ppt.

↑ also a test of Hg^{2+}.

- Can detect even ppm order SO_4^{2-}

③ $Pb(CH_3COO)_2$ test

$$SO_4^{2-} + Pb(CH_3COO)_2\ (aq.) \longrightarrow \underset{\text{white ppt}}{PbSO_4\downarrow}$$

(except Yellow PbI_2, PbS, all $Pb(\ )$ are white; SO_4 just coming of white ppt doesn't count.)

$PbCrO_4\downarrow$ (Yellow, ppt exchange) $\xleftarrow{Na_2CrO_4}$

$Na_2[Pb(OH)_4]$ ← OH^- (excess)

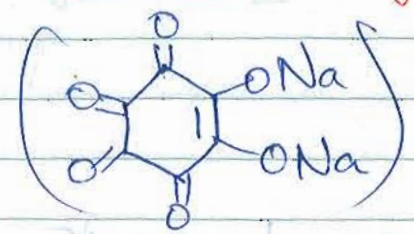
Sodium tetrahydroxo plumbate(II)

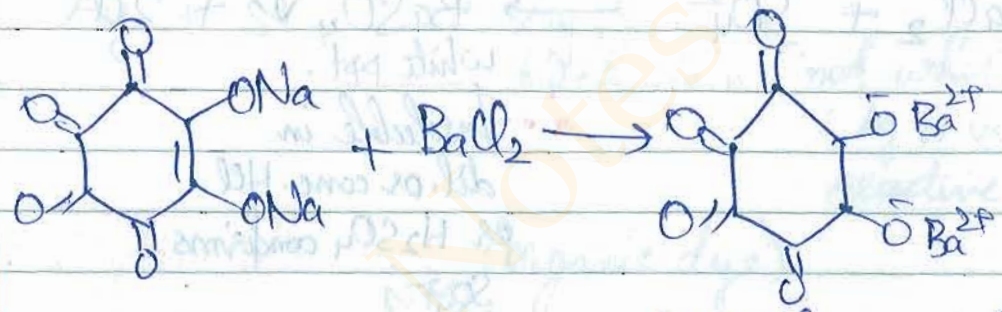
ppt dissolves

∵ more soluble salt is converted to less soluble salt

organic dye

(4) Sodium (Rhodizonate test



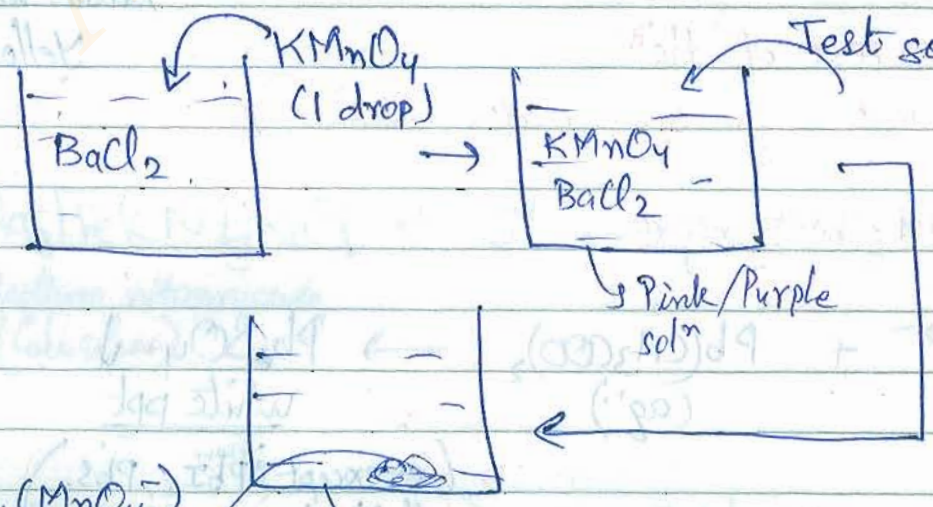


Ba^{2+}-rhodizonate
Reddish brown ppt.

+ Test soln (containing SO_4^{2-})

Ba^{2+}-rhodizonate ~~dot~~ decolorises to produce white ppt. ($BaSO_4$) confirming SO_4^{2-}.

(5) Permanganate test



ppt. of $BaSO_4$ (purple in color due to adsorption of $KMnO_4$ on $BaSO_4$)

strong OA

Date

✡ Test of NO_3^-

(1) Treatment with conc. H_2SO_4

✡ $NO_3^- + \text{conc. } H_2SO_4 \xrightarrow{\text{boil}} NO_2\uparrow + O_2\uparrow + SO_4^{2-}$

deep brown fumes

(2) Copper chips test

$NO_3^- + Cu + H_2SO_4 \xrightarrow{\Delta} NO_2\uparrow + CuSO_4(aq.)$

brown — blue sol^{n}

(3) BROWN-RING TEST.

(can't differentiate b/w NO_2^- & NO_3^-)

$FeSO_4$ (excess) + NO_3^- + conc. $H_2SO_4 \xrightarrow[\text{rxn at junction}]{\text{Redox}} Fe^{3+} + NO$ (strong ligand)

Freshly prepared (otherwise old, $Fe^{2+} \rightarrow Fe^{3+}$ by atmospheric O_2 which is orangish yellow)

→ so that $Fe^{2+} + NO \longrightarrow \underset{\text{actually existent}}{[Fe(NO)]^{2+}} \equiv \underset{\text{✡ more appropriate}}{[Fe(H_2O)_5NO]^{2+}}$

Formed at junction.

✡ Brown colored liq^{d}

Forms brown ring at junction.

(4)

NO_3^- + Al + OH^- (conc.) $\xrightarrow{\text{very slow}} NH_3\uparrow + NaAlO_2$

(or NO_2^-) + Zn + OH^- (conc.) $\xrightarrow{\text{slow}} NH_3\uparrow + ✡\ Na_2ZnO_2$

Now, confirm^{n} of NH_3 is reqd.

$NH_3(g)$ →
- Pleasant odour
- A glass rod moistened in dil. HCl when brought near test tube, white cloudiness is developed on glass rod (NH_4Cl formed)
- Nessler's Reagent ($K_2[HgI_4]$) → brown ppt confirms NH_3.

To increase efficiency of previous test

DEVARDA ALLOY

	Al	Zn	Cu	mixture
% by wt	45	5	50	

(To remember → 45+5 = 50 remember order)

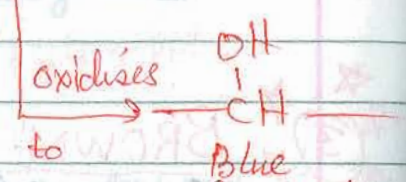
✓ NO_3^- + Devarda alloy ⟶ $NH_3\uparrow$ efficiently.

(5) Blue-ring test

NO_3^- + conc. H_2SO_4 + CH_3-N(CH3)-C6H4-CH_2-C6H4-$N(CH_3)-CH_3$

(methylene grp.; Tetrabase (dye))

oxidises to Blue colored ring at junction.



☆ Test of Cl^-

① With conc. H_2SO_4

$NaCl + H_2SO_4 \xrightarrow{\Delta} HCl\uparrow + Na_2SO_4$

(eye irritating)

conc. litmus test (or) + NH_4OH (glass rod moistened with NH_3)

NH_4Cl (white dourdiness)

☆ (2) Silver nitrate test

$Cl^- + AgNO_3 \longrightarrow AgCl\downarrow$ white ppt. (but can be any other salt of Ag)

(Also a test of Ag^+)

$\downarrow$ aq. NH_3

salt dissolves forming Tollens Reagent

$Ag(NH_3)_2^+$

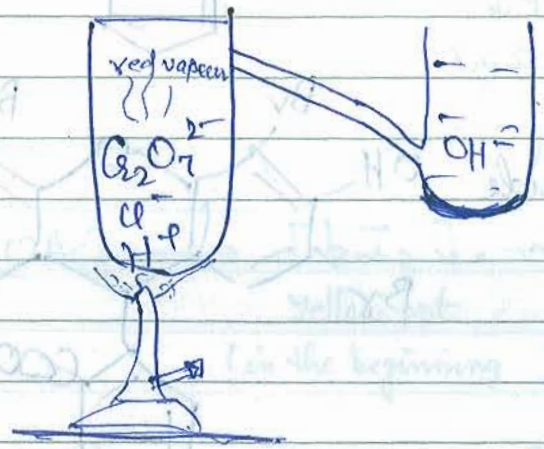
Date

③ Chromyl chloride test

$K_2Cr_2O_7(s) + Cl^- + .conc.H_2SO_4 \xrightarrow{\Delta} CrO_2Cl_2$

$\approx$ 3 : 1

(exactly applicable only for NaCl)



CrO_2Cl_2
red vapour
$\downarrow OH^-$
CrO_4^{2-}
Yellow
$OH^- \uparrow$ | $\downarrow$ Acidific^n H^+
$Cr_2O_7^{2-}$
Orange colour^n

④ $Pb(NO_3)_2$ test

$Pb(NO_3)_2 + Cl^- \longrightarrow PbCl_2 \downarrow$ white ppt (can conform both Cl^-, Pb^{2+})

$PbCl_2 \xrightarrow[water]{+hot}$ $PbCl_2$ dissolves (ONLY salt that dissolves in hot water. ($\because PbCl_2 \rightarrow \Delta H > 0$ of dissolution))

✡ Test of $Br^\ominus$

① With conc. H_2SO_4

undergoes redox rxn, unlike Cl^-, due to comparitively more Reducing power of Br^-

$Br^- + conc.H_2SO_4 \xrightarrow{\Delta} Br_2 \uparrow + SO_2$

Brown vapours

② Manganese dioxide test

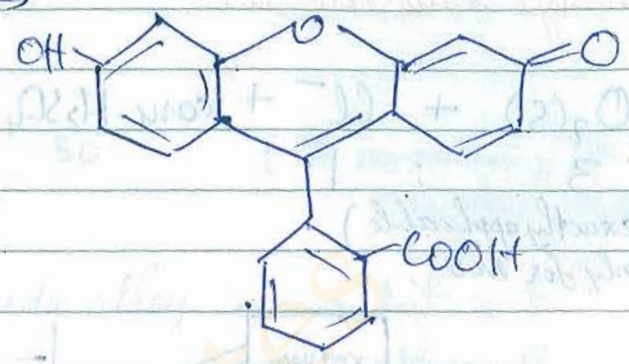
$Br^- + MnO_2 \xrightarrow{boil} Br_2(v) + Mn^{2+}$

③ Exclusive test of Br^- only :-

Bromide sol^n changes color of Yellow Fluorescein to Red Eosin (dyes)

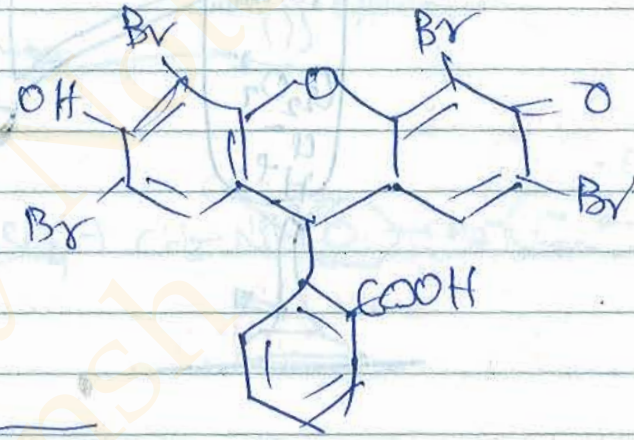
Date

- Fluorescein →



F
~~Fluorescein~~

- Eosin → tetra bromide of Fluoresin.



④ Chlorine water test

$Cl_2 + H_2O$ (colorless. (Chlorinated water)) + Test sol^n having Br^- → $Br_2 + Cl^-$

Brown color. ($Br_2 - H_2O$ formed)

⇓

decolorise olefins.

✱ Test of $I^\ominus$

① conc. H_2SO_4 test

$$I^- + \text{conc. } H_2SO_4 \xrightarrow{\Delta} I_2 + SO_2 \uparrow$$

(I_2 comes out as dark brown ppt. due to very less solubility. Color of sol^n is yellow ∵ of some dissolved Iodine) ⇒ confirms I^-

Date

(2) Action with strong OA

I^- + H_2O_2 → I_2 + Starch → Deep blue
RA OA. (some in soln → yellow
more as (ppt) → black)
↓ + NaI
$NaIO_3$
color goes off.

(3) $Pb(OAc)_2$ test → for Pb^{2+} & I^-

$I^- + Pb(OAc)_2 \longrightarrow PbI_2\downarrow + I^- \xrightarrow{\text{redissolve}} PbI_4^{2-}$
yellow ppt. (in the beginning) excess. tetraiodoplumbate (II)

(4) $CuSO_4$ test (i.e basically Cu^{2+} ion)

$I^- + Cu^{2+} \longrightarrow CuI + I_2$
RA white yellow (dominant initially)

~~CuI formed further reacts with I_2 to form white ppt. of CuI~~

$Na_2S_2O_3$ (dissolves I_2)

$I^- + S_4O_6^{2-} + CuI\downarrow$
white
(visible now)

Date 2/2/11

CATIONS

As per JEE based on → Increasing order of solubility.

Grp 1	Grp 2	Grp 3	Grp 4	Grp 5
Ag^+	Cu^{2+}	Al^{3+}	Ca^{2+}	Mg^{2+}
Pb^{2+} → mainly here	Bi^{3+}	Fe^{3+}	Ba^{2+}	
	Hg^{2+}	Cr^{3+}		
		Mn^{2+}		
	Pb^{2+}	Zn^{2+}		
Reagents				
Cl^- (HCl, $NaCl$) ⇓ Cl^- salts.	H_2S (g) in acidic medium.	$H_2S/NH_3 - NH_4Cl$.	Na_2CO_3	Not fixed.

★ Pb^{2+} is not completely ppt ed in grp 1 & ∴ $PbCl_2$ solubility is rel. higher.
But, PbS (grp 2) has less solubility.
So, it precipitates very nicely in grp 2.
Hence Pb^{2+} is present in both grps

Grp 1

Silver

1 ✓ White ppt with HCl, soluble in excess of NH_3 sol^m. Ag^+ confirmed.

2 ✓ In weakly basic medium, yellow ppt of Ag_2O is obtained. Ppt is insoluble in excess of NaOH, but soluble in excess NH_3

2/2/15

Date

3 ✓ With I^-, yellow ppt., insoluble in excess of I^-.

4 ✓ With N_2H_4 (hydrazine), grey colored Ag metal is obtained.

5 ✓ With CN^-, forms a white ppt, in excess, forms a complex.

Lead

2 ✓ Pb^{2+} —$NH_3(aq.)$→ $Pb(OH)_2\downarrow$ white

Pb^{2+} —$NaOH(aq)$→ $Pb(OH)_2\downarrow$ white

$Pb(OH)_2$ —NaOH (excess)→ $[Pb(OH)_4]^{2-}$ • $Pb(OH)_2$ dissolves.

$Pb(OH)_2$ —NH_3 (excess)→ doesn't dissolve (∵ It doesn't form complex with NH_3)

3 ✓ Pb^{2+} —SO_4^{2-}→ $PbSO_4\downarrow$ white —OH^- or acetate→ becomes soluble.

with $OH^- \longrightarrow Pb(OH)_4^{2-}$

with $CH_3COO^- \longrightarrow Pb(OAc)_4^{2-}$

4 ✓ Pb^{2+} —(i) H_2O_2→ $PbO_2\downarrow$ black ppt —$[(CH_3)_2NPh]_2CH_2$ i.e tetrabase→ Blue colored soln (due to oxidn of tetrabase)

5 ✓ Pb^{2+} —Na_2CO_3→ A basic mixed ppt is obtained.

That is Basic lead Carbonate.

$Pb(OH)_2$ + $PbCO_3$ — both white.

—+NaOH→ become soluble forming $Pb(OH)_4^{2-}$

Date

6. ✓ Pb^{2+} $\xrightarrow{CN^-}$ $Pb(CN)_2$ ↓ white ppt

↓ excess

insoluble

* Ag^+ & Pb^{2+} * $\xrightarrow[\text{excess}]{CN^-}$ dissolves ⇒ Ag^+

↘ insoluble ⇒ Pb^{2+}

Group 2

Mercury

1 ✓ Hg^{2+} $\xrightarrow{H_2S / H^+}$ HgS(c) ↓ black $\xrightarrow[\text{excess}]{S^{2-}}$ becomes soluble in the form of $[HgS_2]^{2-}$ (otherwise K_{sp} of Hg^{2+} is 10^{-54} range)

2 ✓ Hg^{2+} $\xrightarrow[\text{of salt, treated with } NH_3]{\text{Nitrate sol}^n}$ $HgO.Hg(NH_2)NO_3$ Mercuric amido nitrate $\xrightarrow[\text{excess}]{NH_3}$ insoluble

3 ✓ Hg^{2+} $\xrightarrow[(NaI/KI)]{I^-}$ HgI_2 ↓ red ppt. $\xrightarrow[I^-]{\text{excess}}$ $[HgI_4]^{2-}$ dissolves to give colorless sol^n of Nessler's Reagent

Date

4 ✓ Cobalt Thiocyanide test

$Hg^{2+} + Co(SCN)_2(aq) \longrightarrow Co[Hg(SCN)_4] \downarrow$

blue

Cobalt tetrathiocyanido mercurate(II)

5 ✓ Diphenyl carbazide test (organic dye) or DPC test

Hg^{2+} + DPC ⟶ violet ppt. of complex of Hg^{2+} formed

6 ✓ Stannous Chloride test

$Hg^{2+} \xrightarrow[\text{reduces } Hg^{2+}]{SnCl_2} HgCl_2 \xrightarrow[\text{excess}]{SnCl_2} Hg$

$HgCl_2$ white ppt

Hg black ppt finally.

Copper

1 ✓ $Cu^{2+} + H_2S \longrightarrow CuS \downarrow$

black

(But, metal sulphides are generally black. & the step after this is more imp.)

$CuS \xrightarrow[RT]{\text{conc. } HNO_3} Cu^{2+} + S$

(CuS dissolves & Cu^{2+} comes in soln & S^{2-} is oxidised to elemental sulphur. This is a colloidal soln white in color due to formn of S sol.)

$Cu^{2+} + SO_4^{2-} \xleftarrow{\text{on boiling}}$

Blue colored soln

Date

4 ✓ Cobalt Thiocyanide test

$Hg^{2+} + Co(SCN)_2(aq) \longrightarrow Co[Hg(SCN)_4] \downarrow$

blue

Cobalt tetrathiocyanido mercurate(II)

5 ✓ Diphenyl carbazide test (organic dye) or DPC test

Hg^{2+} + DPC ⟶ violet ppt. of complex of Hg^{2+} formed

6 ✓ Stannous Chloride test

$Hg^{2+} \xrightarrow[\text{reduces } Hg^{2+}]{SnCl_2} HgCl_2$ (white ppt) $\xrightarrow[\text{excess}]{SnCl_2}$ Hg (black ppt finally)

Copper

1 ✓ $Cu^{2+} + H_2S \longrightarrow CuS \downarrow$ (black)

(But, metal sulphides are generally black. & the step after this is more imp.)

$CuS \xrightarrow[RT]{\text{conc. } HNO_3} Cu^{2+} + S$

(CuS dissolves & Cu^{2+} comes in soln & S^{2-} is oxidised to elemental sulphur. (This is a colloidal soln white in color due to formn of S sol.))

$Cu^{2+} + SO_4^{2-} \xleftarrow{\text{on boiling}}$ (blue colored soln)

Date

2 ✓ $Cu^{2+} + CN^- \longrightarrow Cu(CN)_2 \downarrow \xrightarrow[\text{excess}]{CN^-} CuCN +$

yellow — white.

$(CN)_2(g) \uparrow$

cyanogen gas (highly poisonous)

3 ✓ $Cu^{2+} + SCN^- \longrightarrow Cu(SCN)_2 \downarrow$

black ppt

left for some time or $SO_2(g)$

$CuSCN + (SCN)_2(g)$

cute — thiocyanogen gas

4 ✓ $Cu^{2+} + NaOH \longrightarrow Cu(OH)_2 \downarrow \xrightarrow{\Delta} CuO$

blue — black

5 ✓ Organic dye → Oxime of salicyaldehyde

Salicyladoxime forms green colored water insoluble ppt. with Cu^{2+} which is sq. planar complex.

6 ✓ $Cu^{2+} + I^- \longrightarrow CuI \downarrow + I_2$

White — can be tested (starch soln → blue)

Bismuth

1 ✓ ✱ Black ppt. with $I^- \longrightarrow$ always Bi

Its a unique property

With excess I^-, it gives orange color.

Date

Grp III

Fe^{3+}, Al^{3+}, Cr^{3+} | Mn^{2+}, Zn^{2+}

$H_2S/NH_3/NH_4Cl$

reddish brown — white — green

$Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$

(sparingly soluble hydroxides)

For Fe^{3+}, Al^{3+}, Cr^{3+}, ~~Sol~~ Ksp of their hydroxides are lesser than sulphides. So, sulphides are ppt-ed.

pink — white

MnS, ZnS

For Mn^{2+} & Zn^{2+}, their sulphides are less soluble than hydroxides. So, their sulphides are precipitated.

** They can be identified by their color of grp 3 so known.

Iron (Fe^{3+})

1 ✓ $Fe^{3+} \xrightarrow{NH_4Cl/NH_3/H_2S \text{ or } NH_3(aq) \text{ or } NaOH(aq})$ $Fe(OH)_3 \downarrow$ (brown) $\xrightarrow[\text{excess.}]{OH^-}$ Insoluble (Al^{3+} & Cr^{3+} dissolve in excess OH^-)

2 ✓ $Fe^{3+} + NH_4SCN(aq) \longrightarrow Fe(SCN)(aq)$

(remains suspended in soln making a sol of red color) deep red soln (not ppt)

Date

Prussian blue test

3 ✓ $Fe^{3+} + K_4[Fe(CN)_6] \longrightarrow Fe_4[FeCCN)_6]_3$

Prussian blue ppt

Aluminium

1 ✓ $Al^{3+} + OH^- \longrightarrow Al(OH)_3 \xrightarrow{NaOH\ excess} Na[Al(OH)_4]$ dissolves

Lake Test NH_3 (aq) $\longrightarrow Al(OH)_3$

Voluminous white ppt. → Lake test.

~~To identify $Al(OH)_3$,~~

2 ✓ Red Lake test :- Aluminon dye (doesn't contain Al), when dissolved in H_2O, has colorless sol^n.

↓ + (Test sol^n containing Al^{3+} having Alkali or NH_3 ↓ $Al(OH)_3$)

The white ppt. of $Al(OH)_3$ gets covered with red color of Aluminon dye on its surface due to adsorption of Aluminon.

Red lake test also comes with Alizarin dye.

Date

Chromium

1 ✓ $Cr^{3+} + NH_3 + OH^- \longrightarrow Cr(OH)_3\downarrow$ (green)

$Cr(OH)_3 \xrightarrow{OH^-}$ dissolves $Cr(OH)_4^-$

$Cr(OH)_3 \xrightarrow{NH_3 \text{ excess.}}$ insoluble

2 ✓ $Cr^{3+} \xrightarrow[OH^-/\Delta.]{H_2O_2} CrO_4^{2-}$ (yellow)

$CrO_4^{2-} \xrightarrow{BaCl_2} BaCrO_4$ (yellow) $\xrightarrow{OH^-}$ insoluble

$CrO_4^{2-} \xrightarrow{Pb(OH)_2} PbCrO_4$ (yellow) $\xrightarrow{OH^-}$ soluble.

(∵ CrO_4^{2-} is yellow)

Manganese

Date 4/2/11

Ch: Wave Mechanical Treatment of e_s^-

* Heisenberg's uncertainty principle was the major reason for the breakthrough in Quantum Mechanical model of an atom.
* e_s^- motion was compared to that of standing wave & amplitude of this wave is given by 2nd order DE. (Differential eq^n)

Let Ψ : amplitude of wave.

Then

$$\frac{\partial^2 \Psi}{\partial x^2} = +\frac{1}{c^2}\frac{\partial^2 \Psi}{\partial t^2} \longrightarrow (A)$$

} 2nd ord. DE with consett coeff

⇓

- It has infinite sol^{ns}
- It has been considered as a 1D wave (along x-axis only)

Solving and showing 1 sol^n out of ∞ →

$$\Psi = A \sin\left(\frac{2\pi x}{\lambda} - 2\pi\nu t\right)$$

$$\Psi_1 = \text{or } A \sin 2\pi\left(\frac{x}{\lambda} - \nu t\right) \longrightarrow (1) \longrightarrow$$

$$\Psi_2 = A \sin 2\pi\left(\frac{x}{\lambda} + \nu t\right) \longrightarrow (2) \longleftarrow$$

$$\Psi = \Psi_1 + \Psi_2 = \left\{2A \sin 2\pi\left(\frac{x}{\lambda}\right)\right\}\left\{\cos(2\pi\nu t)\right\}$$

$f(x)$ only — $f(t)$ only.

$$\Psi = \Psi_{(x)} \cdot \Psi_{(t)}$$

$\Rightarrow \psi = \psi_{(x)} \cdot \psi_{(t)}$

$\Rightarrow \dfrac{\partial^2 \psi}{\partial x^2} = \cos(2\pi \nu t) \dfrac{\partial^2 \psi_{(x)}}{\partial x^2} \longrightarrow (B)$

$\dfrac{\partial^2 \psi}{\partial t^2} = -4\pi^2 \nu^2 \cos 2\pi \nu t \; \psi_{(x)} \longrightarrow (C)$

$\Rightarrow \dfrac{\partial^2 \psi_{(x)}}{\partial x^2} = \dfrac{-1}{c^2} (4\pi^2 \nu^2) \psi_{(x)}$ $\left[\because \dfrac{\partial^2 \psi}{\partial x^2} = \dfrac{-1}{c^2} \dfrac{\partial^2 \psi}{\partial t^2}\right]$ ($\nu \to \frac{c}{\lambda}$)

$\Rightarrow \dfrac{\partial^2 \psi_{(x)}}{\partial x^2} = -\left(\dfrac{2\pi}{\lambda}\right)^2 \psi_{(x)}$ ($\lambda \to \frac{h}{mv}$)

$= -\dfrac{4\pi^2}{h^2} (m^2 v^2) \psi_{(x)}$

If E (Total E of e^-) $= \frac{1}{2} m v^2 + V$ (PE)

$\Rightarrow m^2 v^2 = 2(E - V)m$

$\Rightarrow \dfrac{\partial^2 \psi_{(x)}}{\partial x^2} + \dfrac{8m(E-V)\pi^2}{h^2} \psi_{(x)} = 0$

$\Rightarrow \boxed{\dfrac{\partial^2 \psi_{(x)}}{\partial x^2} + \dfrac{8\pi^2 m}{h^2} (E - V) \psi_{(x)} = 0}$

↳ SCHRÖDINGER EQN FOR 1D WAVE

- For 3D WAVE, eqn $\longrightarrow$

$$\star \left\{ \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \right\}$$

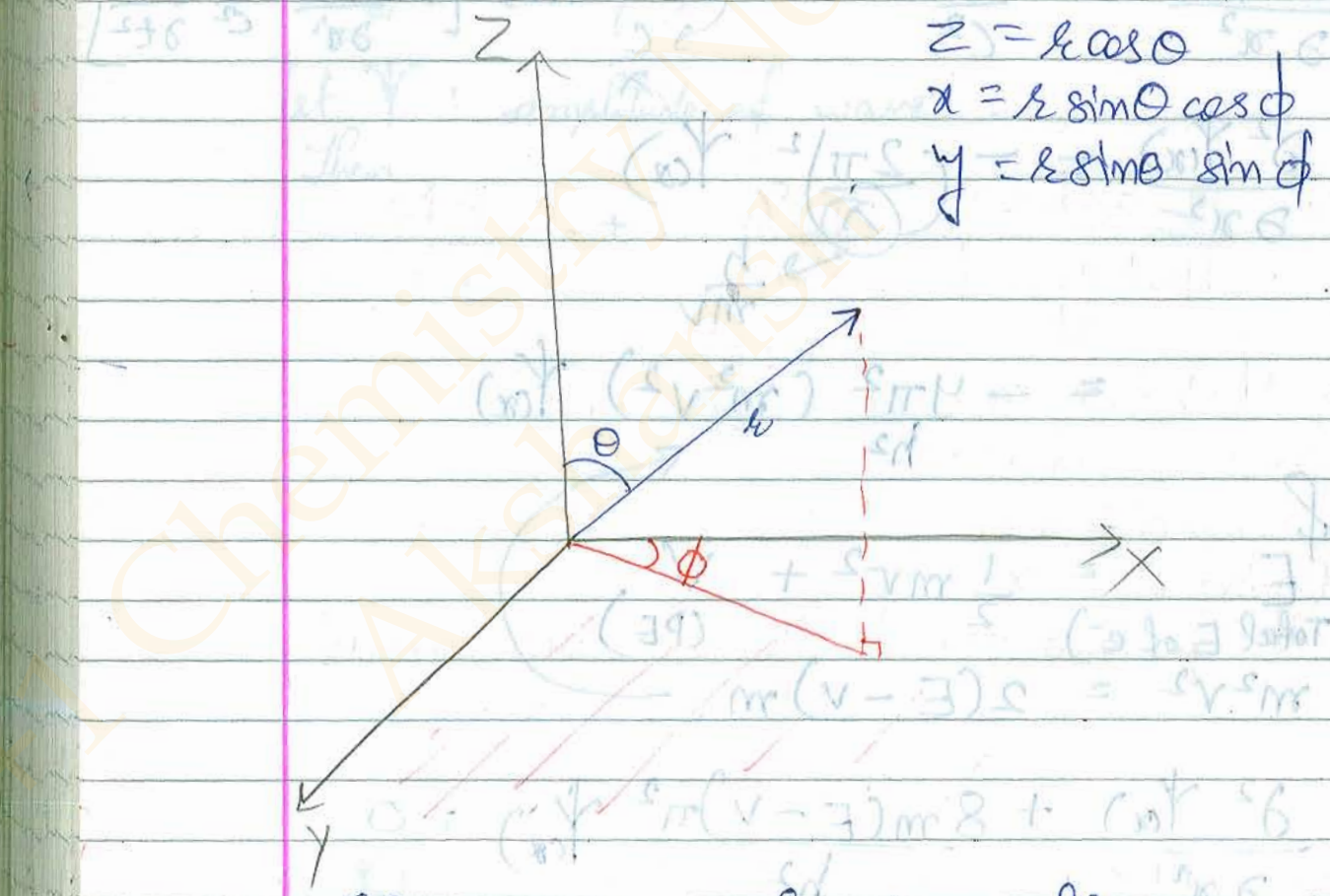
↳ Schrödinger Equation.

Date

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

$$\nabla = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \longrightarrow (D)$$

∇ A mathematical operator called as HAMILTONIAN



$z = r\cos\theta$
$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$

Solving eq^n (D) for ψ after converting into spherical coordinates, we get.

Radial part — Angular part

$$\psi = R_{n,l}\left(\Theta_{l,m}\,\Phi_m\right) = R_{n,l} \cdot Y_{l,m}$$

Radial part — Angular part

n : principal Q no.
l : subsidiary Q. no.
m : magnetic Q. no.

Date

* Note :- Spin Q. no. came after Quantum mechanics. Quantum mechanics is based on just 3 Q. Nos.

* Wave eqⁿ containing both radial and angular part is called Normalised wave function

amplitude of e⁻ in 1s orbital

✓ $\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{a_0}}$ → distance of e⁻ from nucleus

$a_0 = 0.53$ Å.

✓ 1s has only radial part, no angular part (no dumbell) (∵ S orbital wave fⁿ → no angular)

✓ $\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$

✓ $\psi_{2pz} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{5/2} r\cos\theta\, e^{-r/2a_0}$

$\left(\psi_{2px} = " \quad " \quad r\sin\theta\cos\phi \quad "\right)$

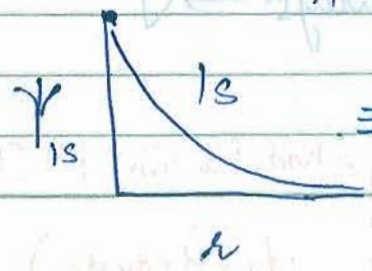
$\left(\psi_{2py} = " \quad " \quad r\sin\theta\sin\phi \quad "\right)$

ψ = wave fⁿ → represents amplitude of standing wave

Nodal Point of ψ : Nodal point of ψ is the pt at which ψ vanishes to zero. For a given orbital, the no. of nodal points are $(n - l - 1)$

✓ For 1s orbital, no. of nodal pt = 0

$n = 1, \; l = 0, \; 1 - 0 - 1 = 0$



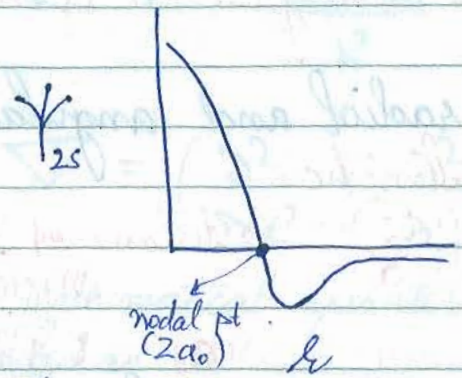
$\equiv y = \alpha e^{-\beta x}$

$y = \psi_{1s}$; $\alpha = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2}$; $\beta = \frac{1}{a_0}$

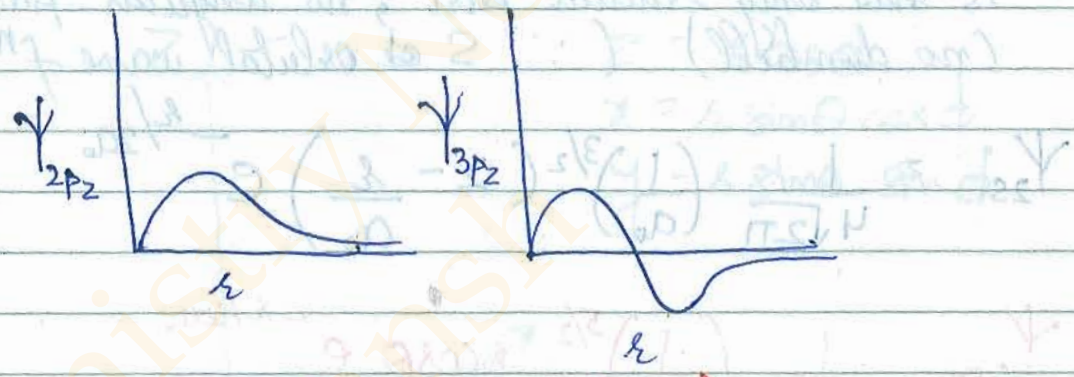
* Only for wave fn :- wave fn always changes its sign at nodal pt.

Date

✓ For 2s orbital, no. of nodal pts = 1.



✓



* PROBABILITY DENSITY :- (P.D)

It is the probability of an e⁻ at a pt, at a distance r, at a given instant.

$P.D = \Psi^2$, for real

$= \Psi \cdot \Psi^*$, for complex.

(complex conjugates of each other)

$\Psi^2_{1s} = \frac{1}{\pi a_0^3} e^{-\frac{2r}{a_0}}$ ⇒ for 1s, $(P.D)_{max}$ is at nucleus

* PROBABILITY (P)

It is the total probability of finding an e⁻ at a distance r. It is always :→

$P = (P.D) \times (SA)$

For (s) ~~For s~~ → $P = (\Psi)^2 \times 4\pi r^2$ = Radial distribⁿ fⁿ (RDF)

(For others, $P = \Psi^2 d\tau$; $d\tau = dx\,dy\,dz$)

Date

~~For~~

$P_{1s} = \psi_{1s}^2 (4\pi r^2)$

$P_{1s} = \frac{4r^2}{a_0^3} e^{\frac{-2r}{a_0}}$, P_{1s} at $r=0$ $= 0$.

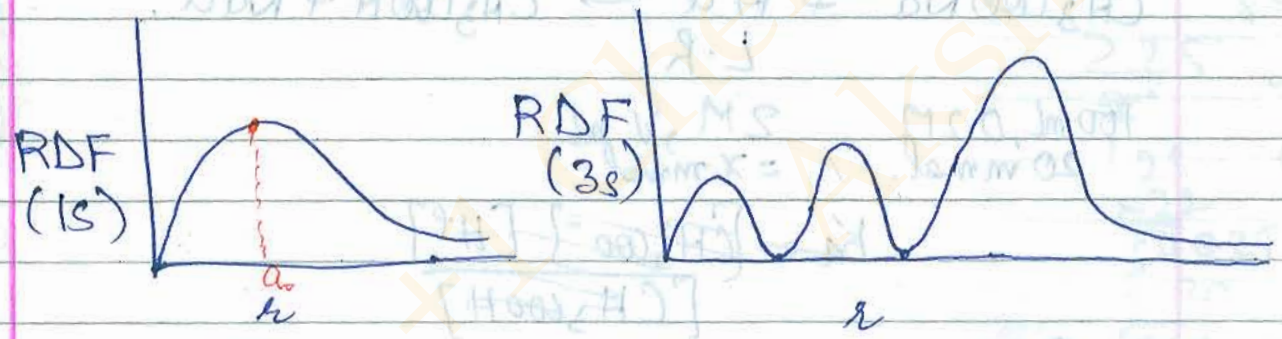
$\Rightarrow$ ~~PD at~~

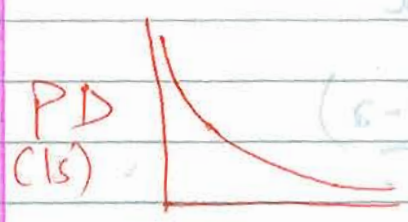
** For every s orbital,
at $r=0$ (nucleus) P.D = max
P = min

$\because$ size of nucleus is very small and for ~~very~~ zero time, e^- arrived to nucleus

** PD & P of P:

* Nodal pt. of the ~~a~~ RDF and PD are the pts. where both have their minima (ψ^2 & P^2).
No. of nodal pts. will be $(n-l-1)$





$\therefore \frac{d}{dr}(P_{1s}) = 0$.

value of r = maxima value
$= a_0$ (solve & get)

P of finding an e^- from a_0 to ∞.

$P = \int_{a_0}^{\infty} \frac{4r^2}{a_0^3} e^{\frac{-2r}{a_0}} dr$

Date

Buffer Solution

(i) Acidic Buffer :- WA + Salt of conj. Base.
$CH_3COOH + CH_3COONa$.

(ii) Basic Buffer :- WB + Salt of conj. acid
$CH_3NH_2 + CH_3NH_3Cl$.

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Q. What vol. of a 2 M HCl soln will be req^d to be added to a 100 ml 0.2 M CH_3COONa soln in order to lower its pH to 5.
$K_a(CH_3COOH) = 2\times10^{-5}$.

$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$.
L.R.

100 ml, 0.2 M — 2 M, V ml
20 mmol — $= x$ mmol

$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

@ $20-x$ — -0 — x

$2\times10^{-5} = 10^{-5}\,\frac{(20-x)}{x}$

$\Rightarrow 2x + x = 20$.

$\Rightarrow x = \frac{20}{3} = M\times V$

$\Rightarrow V = \frac{10}{3}$ ml.

Q $K_a(HIO_3) = 0.2$ at 25°C. If a 50 mL, 0.1 M HIO_3 soln is mixed with 50 mL, 0.05 M NaOH soln, what is pH of resulting soln.

$$HIO_3 + NaOH \longrightarrow NaIO_3 + H_2O$$

5 mmol 2.5 mmol

2.5 0 2.5 2.5

Ka value is large.

So, $HIO_3 \rightleftharpoons H^+ + IO_3^-$

$2.5\ mmol - x \quad x \quad x + 2.5\ mmol$

$NaIO_3 \rightarrow Na^+ + IO_3^-$

$2.5\ mmol \quad 2.5\ mmol + x$

$$K_a = [H^+]\left(\frac{[IO_3^-]}{[HIO_3]}\right) = \frac{\left(\frac{x}{100}\right)(2.5+x)}{(2.5-x)} = 0.2$$

$\Rightarrow 2.5x + x^2 = 50 - 20x$

$\Rightarrow x^2 + 22.5x - 50 = 0$

$\Rightarrow x = \frac{-22.5 \pm \sqrt{\quad}}{2}$

$\Rightarrow x \approx 2$

$\Rightarrow [H^+] = \frac{2}{100} = 2 \times 10^{-2}$

$\Rightarrow pH = 4 - \log 2$

1.7

Date

Q. To a 100 mL, 0.1M soln of H_2SO_4, 100 mL, 0.3M NH_3 soln is added. Determine pH of resulting soln. $K_b(NH_3) = 2\times10^{-5}$ at 25°C.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

30 mmol, 10 mmol, 10

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

10 mmol − x, 2x, x

$$2\times10^{-5} = (2x)\,[OH^-]\;\frac{20}{10}$$

$1 \rightarrow 2$

$10 \rightarrow \frac{2}{10}\times10$

$\Rightarrow pOH = 5$

$pH = 9$

Q. 20 ml of a soln of weak monobasic acid is mixed with 30 ml of NaOH soln. pH of resulting soln is found to be 4.3. To the resulting soln, 20 ml of same NaOH was further added. pH of final soln was found to be 5. Determine

(i) Ka

(ii)

$$MA \rightarrow M^+ + A^-$$

$$NaOH \rightarrow Na^+ + OH^-$$

20 → y

30 → 1.5y

NaOH + to MA

20 ml, 20 ml

conc. $[H^+] = 5\times10^{-5}$

5×10^{-5} NaOH → $Na^+ + OH^-$

20 ml → y mmol, says

$$HA + OH^- \longrightarrow A^- + H_2O$$

x mmol − y, y mol, y

x − (y + 1.5y), 2.5y

$$K_a = \frac{[H^+]\,y}{\quad};\quad K_a = [H^+]\,(2.5y)$$

$$K_a = \frac{(5\times10^{-5})\,y}{x-y} \;;\; \frac{(2\times10^{-5})\,(2.5y)}{x-2.5y} = K_a$$

$$x - 2.5y = 2.5x - 2.5y$$

$$\frac{50y}{x-y} = \frac{2.5y}{x-2.5y}$$

$$\frac{20y}{x-y} = \frac{5}{x-2.5y}$$

$$\Rightarrow 4x - y = 5x - 5y$$

$$\Rightarrow x = 4y$$

$$K_a = \frac{(5\times10^{-5})\,(8y)}{3y}$$

$$K_a = 1.6\times10^{-5}$$

(ii) What vol. of same NaOH would be reqd to be added furthur to reach end point.

$x = 4y$

$20 \rightarrow y$

$30 \rightarrow 1.5y$

$+ \qquad +$

$30 \rightarrow 1.5y$

$(x) = 4y$ ⇒ add another 30 mL

Date 11.2.11

Solubility & Solubility product

Q. $K_{sp}(PbCl_2) = 4\times10^{-6}$ at 25°C Determine whether any ppt. form^n will take place or not if equal vol. of 10^{-2} M $Pb(NO_3)_2$ & 2×10^{-2} M $CaCl_2$ is mixed.

$$\underset{10^{-2}}{Pb(NO_3)_2} + \underset{2\times10^{-2}}{CaCl_2} \longrightarrow PbCl_2 + Ca(NO_3)_2$$

$$\underset{10^{-2}}{Pb^{2+}} + \underset{2\times10^{-2}}{2Cl^-} \longrightarrow PbCl_2$$

$$Q_{sp} = [PbCl_2]$$

$Pb(NO_3)_2$	$CaCl_2$	$\frac{1}{2}\times10^{-2}$
		2×10^{-2}
V	V	2V

$$Q_{sp} = [Pb^{2+}][Cl^-]^2$$

$$= \tfrac{1}{2}\times10^{-2}\times 4\times10^{-4}$$

$$= 2\times10^{-6} < K_{sp}$$

No ppt

Q. A sol^n is 0.05 M in each Cl^- & I^-. K_{sp} of AgCl & AgI are 2×10^{-10} & 5×10^{-15} resp. Solid $AgNO_3$ is added gradually to above sol^n.
(a) Determine the min. conc. of Ag^+ in sol^n req^d to start ppt^n.
(b) Determine conc. range of Ag^+ in the sol^n in which only less soluble halide will be ppted.

(c) Determine conc. of the 1st halide ion when 2nd start precipitating.

$$AgNO_3 \longrightarrow \underset{x}{Ag^+} + NO_3^-$$

$$Ag^+ + Cl^- + I^- \longrightarrow AgCl + AgI$$

$$Ag^+ + I^- \longrightarrow AgI$$

(a) $5 \times 10^{-15} = [Ag^+][I^-]$

$\Rightarrow [Ag^+] = \dfrac{5 \times 10^{-15}}{5 \times 10^{-2}}$

$= 10^{-13}$ M

(b) $10^{-13} - 4 \times 10^{-9}$

$\dfrac{[AgCl]}{[Cl^-]} \dfrac{2 \times 10^{-10}}{5 \times 10^{-2}} = 0.4 \times 10^{-8}$ or 4×10^{-9} M

(c) $5 \times 10^{-15} = [Ag^+][I^-]$

$= (4 \times 10^{-9})(I^-)$

$\Rightarrow I^- = \dfrac{5}{4} \times 10^{-6}$ M

Q. K_{sp} of AgCl is 2×10^{-10} & for $Ag_2CrO_4 = 2 \times 10^{-12}$ A sol^n of Cl^- is being analysed by ppt^n titr^n against a std. AgII sol^n & end pt$^.$ is detected by appearance of orange ppt. of Ag_2CrO_4. Determine min. conc. of indicator in the sol^m so that end pt. can be detected.

$[Ag^+]$ at end $M = \sqrt{2 \times 10^{-10}}$ $(\because K_{sp} = S^2)$

~~$\sqrt{2 \times 10^{-10}}$~~

$$[CrO_4^{2-}][Ag^+]^2 = 2 \times 10^{-12}$$

$$\Rightarrow [CrO_4^{2-}] = \frac{2 \times 10^{-12}}{2 \times 10^{-10}}$$

$$= 10^{-2} M$$

Q. Determine conc. of Ag^+ in a sol^n obtained by mixing equal volumes of 0.1M each $AgNO_3$ & $CaCl_2$ sol^n

$K_{sp}(AgCl) = 2 \times 10^{-10}$

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$

0.1 − x → 0.1

Conc. halved on mixing: 0.05

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$$

0.05 → 0.1

$$AgCl \longrightarrow Ag^+ + Cl^-$$

$$2 \times 10^{-10} = [Ag^+][Cl^-]$$

$$2AgNO_3 + CaCl_2 \longrightarrow 2AgCl \downarrow + Ca(NO_3)_2$$

0.05 → 0 ; 0.05 → 0.025 M

$$\Rightarrow [Cl^-] = 0.05 \text{ M}$$

$$\left(\frac{K_{sp}}{[Cl^-]}\right) \frac{2 \times 10^{-10}}{5 \times 10^{-2}} = [Ag^+]$$

$$[Ag^+] = 0.4 \times 10^{-8} = 4 \times 10^{-9} \text{ M}$$

Date

Q. K_{sp} of $AgBr = 10^{-12}$
$AgSCN = 5 \times 10^{-13}$ } 25°C

If excess of solid AgBr and solid AgSCN is added simultaneously, to a beaker full of H_2O, determine, conc. of Ag^+, Br^-, SCN^- in soln.

$$\underset{x}{AgBr} \longrightarrow \underset{x+y}{Ag^+} + \underset{x}{Br^-}$$

$$\underset{y}{AgSCN} \longrightarrow \underset{x+y}{Ag^+} + \underset{y}{SCN^-}$$

$$10^{-12} = (x+y)(x)$$

$$5 \times 10^{-13} = (x+y)(y)$$

$$\Rightarrow \frac{(5 \times 10^{-13})}{y}(x) = 10^{-12}$$

$$\Rightarrow x^2 + xy = 10^{-12} \quad \& \quad xy + y^2 = 5 \times 10^{-13}$$

$$x^2 + xy - 10^{-12} = 0$$

$$\Rightarrow x = -y \pm \sqrt{\quad}$$

$$\frac{x}{y} = 2 \Rightarrow x = 2y$$

$$\Rightarrow 5 \times 10^{-13} = 3y^2$$

$$\Rightarrow \frac{50}{3} \times 10^{-13}$$

$$= 4 \times 10^{-7} = y$$

$$x = 8 \times 10^{-7}$$

$$x + y = 12 \times 10^{-7}$$

Date

8. K_{sp} $CaF_2 = 4 \times 10^{-9}$ M Large diff. ⇒ more soluble salt becomes source of common ion
$BaF_2 = 3.2 \times 10^{-5}$ M

Determine conc. of both Ca^{2+} & Ba^{2+} if a sol^n is prepared by dissolving excess of solid CaF_2 & BaF_2 in H_2O.

$CaF_2 \longrightarrow Ca^{2+} + 2F^-$

$x \qquad x \qquad 2x+2y$

$BaF_2 \longrightarrow Ba^{2+} + 2F^-$

$y \qquad y \qquad 2y+2x$

$4 \times 10^{-9} = 2^2 (x+y)^2 x$

$3.2 \times 10^{-5} = 2^2 (x+y)^2 y$ or $3.2 \times 10^{-5} = 4S^3$

$\Rightarrow S = 2 \times 10^{-2}$ M

$= [Ba^{2+}]$

$[F^-] = 2S = 4 \times 10^{-2}$ M

For CaF_2

$4 \times 10^{-9} = [Ca^{2+}][4 \times 10^{-2}]^2$

$\frac{10^{-5}}{4} = Ca^{2+}$

$= 0.25 \times 10^{-5}$ M

$\Rightarrow \frac{40}{28} \times 10^{-4} = \frac{x}{y}$

$\Rightarrow \frac{10}{7} \times 10^{-4} = \frac{x}{y}$

$\Rightarrow x = \left(\frac{10}{7} \times 10^{-4}\right) y$

$\Rightarrow 4 \times 10^{-9} = 2\left(\frac{10}{7} \times 10^{-4}\right) y \left(y + \frac{10}{7} \times 10^{-4} y\right)$

$\Rightarrow 4 \times 10^{-5} = \frac{20}{7} y \left(y + \frac{10}{7} \times 10^{-4} y\right)$

$4 \times 10^{-5} = \left(\frac{20}{7} + \frac{10}{7} \times 10^{-4}\right) y^2$

K_f = form^n constt
K_d = dissociation constt

$K_f = \frac{1}{K_d}$ ☆

Effect of complex form^n on solubility

$AgCl(s) + 2NH_3 \xrightleftharpoons{K} Ag(NH_3)_2^+ + Cl^-$

ppt (Sparingly soluble salt) — complexing agent (dissolving) — complex form^n

We would be given: $K_{sp}(AgCl) = 2\times10^{-8}$.

$K_c = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} \times \frac{[Ag^+]}{[Ag^+]} = \{Ag(NH_3)_2^+\} = 10^8$ form^n constt

$Ag^+ + 2(NH_3) \rightleftharpoons Ag(NH_3)_2^+$

$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$

$\Rightarrow K_c = K_f \times K_{sp}$

$= K_{sp} \times \frac{1}{K_d}$

Q) Determine molar solubility of AgCl in 0.01 M
(a) NH_3 soln, given K_{sp} (AgCl), K_f [$Ag(NH_3)_2^+$]
(b) Also find $[Ag^+]$ in final soln

$K_{sp}(AgCl) = 2\times10^{-80}$
$K_f(Ag(NH_3)_2^+) = 10^8$

$AgCl$	$+ 2NH_3$	$\rightarrow Ag(NH_3)_2^+$	$+ Cl^-$
~~S~~	0.01 M	0.01 + S	S
$-x$	$0.01-2x$	x	x

$K_c = 2 \left[(2\times10^{-8}) \times (10^8)\right] = \frac{(0.01+S)(S)}{(0.01)^2}$

$\Rightarrow 2\times10^{-4} = 10^{-2}\times S + S^2$

$\Rightarrow S^2 + S\times10^{-2} - 2\times10^{-4} = 0$

$$s^2 + 5\times10^{-2} - 2\times10^{-4} = 0$$

$$(10^4)s^2 + 100s - 2 = 0$$

$$\Rightarrow s = \frac{-100 \pm \sqrt{10^4 + 8(10^4)}}{2\times10^4}$$

$$= \frac{-100 \pm 3\times10^2}{2\times10^4}$$

$$= \frac{2\times100}{2\times10^4}$$

$$s = 10^{-2}$$

$$k = 2\times10^{-2} = \left\{\frac{x}{0.01-2x}\right\}$$

$$\Rightarrow 0.14 = \frac{x}{0.01-2x}$$

$$\Rightarrow 14\times10^{-4} - 0.28x = x$$

$$\Rightarrow 1.28x = 14\times10^{-4}$$

$$\Rightarrow x = \frac{14}{128}\times10^{-2}$$

$$= \frac{7}{64}\times10^{-2}$$

$$x = 1.09\times10^{-3}$$

(b) $2\times10^{-10} = [Ag^+](1.1\times10^{-3})$

Date

Q Determine

Ag_2CrO_4 K_{sp}

$Ag(NH_3)_2^+$ K_f

$$Ag_2CrO_4 + 4NH_3 \rightleftharpoons 2Ag(NH_3)_2^+ + CrO_4^{2-}$$

$$K_c = \frac{[Ag(NH_3)_2^+]^2 \overbrace{[CrO_4^{2-}] \times [Ag^+]^2}^{K_{sp}}}{[NH_3]^4 [Ag_2CrO_4] \quad [Ag^+]^2}$$

$$K_{sp} = [Ag^+]^2 [CrO_4^{2-}] \Rightarrow K_c = K_{sp} \times (K_f)^2$$

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

Q $K_{sp}\ (Zn(OH)_2) = 2 \times 10^{-17}$

$K_f\ Zn(OH)_4^{2-} = 10^{15}$

Determine the min. conc. of NaOH reqd to dissolve 0.1 mole of solid $Zn(OH)_2$ in a 2L soln

$$K_{sp} = [Zn^{2+}][OH^-]^2$$

$$K_f = \frac{[Zn(OH)_4^{2-}]}{[Zn^{2+}][OH^-]^4}$$

$$Zn(OH)_2 + 2OH^- \longrightarrow 2Na^+ + Zn(OH)_4^{2-}$$

1 mole, 2L $\quad x - (0.05)2 \quad\quad 0.05$

$0.05 = \frac{1}{20}$ M

$$K_c = \frac{[Na^+]^2[Zn(OH)_4^{2-}]}{[NaOH]^2[Zn(OH)_2]} \times \frac{[Zn^{2+}][OH^-]^2}{[Zn^{2+}][OH^-]^2}$$

$K_c = K_{sp} \times K_f$

$= 2\times10^{-2} = \frac{0.05}{(C-0.1)^2}$

$\Rightarrow (C-0.1)^2 = \frac{5\times10^{-2}}{2\times10^{-2}}$

$(C-0.1)^2 = \frac{2.5}{10}$

$\Rightarrow (C-0.1) = \frac{5}{3}1.6$

$C \approx 1.7\ M$

Effect of strong acid or base

$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$

SB + WA

On addⁿ of nitric acid

$2H^+ + 2F^- \rightleftharpoons 2HF \quad \therefore K = \frac{1}{K_a^2}$

K_a very small
$\Rightarrow K$ is very large
So, F^- goes & solubility goes on ↑ (le Chatelier's)

★ Add

$\Rightarrow BaF_2(s) + 2H^+ \rightleftharpoons Ba^{2+} + 2HF$

$K = \frac{[Ba^{2+}]}{} \frac{K_{sp}}{K_a^2}$

Date

Q Determine molar solubility of AgCN in 0.1M HNO_3 sol^n

$K_{sp}(AgCN) = 2\times10^{-12}$

$K_a(HCN) = 5\times10^{-10}$

$AgCN \rightleftharpoons Ag^+ + CN^-$ K_{sp}

~~$HCN \rightleftharpoons H^+ + CN^-$~~

$HNO_3 \rightarrow H^+ + NO_3^-$

0.1

$H^+ + CN^- \rightleftharpoons HCN$ $\frac{1}{K_a}$

0.1

$AgCN + H^+ \rightleftharpoons Ag^+ + HCN$

S 0.1−S S S

$K = \frac{K_{sp}}{K_a} = \frac{2\times10^{-12}}{5\times10^{-10}} = 0.4\times10^{-2}$

$= 4\times10^{-3}$

$\frac{S^2}{0.1-S} = 4\times10^{-3}$

$\Rightarrow S^2 + 4\times10^{-3}S - 4\times10^{-4} = 0$

$\Rightarrow (10^4)S^2 + 40S - 4 = 0$

$\Rightarrow S = \frac{-40 \pm \sqrt{1600 + 16\times10^4}}{2\times10^4}$

$= \frac{-40 \pm 4\times100\sqrt{1+100}}{2\times10^4}$

$= \frac{360}{2\times10^4} = \frac{18}{1000} = 1.8\times10^{-2}$

$\Rightarrow S = 0.018$

Date

Theory of Indicators

Indicator indicate the end pt by change in color of soln.

At end pt, indicator changes its form predominantly from ionised to unionised or vice versa.

Indicators are weak organic acids or weak organic base.

$$H(In) \rightleftharpoons H^+ + In^-$$

(Indicator)

(HA) colorless — pink/gray

$$HCl \longrightarrow H^+ + Cl^-$$

$$(K_{In}) = \frac{[H^+][In^-]}{[HIn]}$$

Constt.

$$\therefore [H^+] = K_{In} \frac{[HIn]}{[In^-]}$$

$$pH = pK_{In} + \log \frac{[In^-]}{[HIn]}$$

Till $[HIn] \geq 10[In^-]$

$$pH_1 = pK_{In} + \log \frac{1}{10} \quad \left[\text{when } \frac{In^-}{[HIn]} = \frac{1}{10}\right]$$

$$= pK_{In} - 1$$

When $[HIn] \geq 10 [H^+In]$

$pH_2 = pK_{In} + 1$ (when solved on equality)

hence, the indicator chosen is ~~not~~ suitable iff, it changes its color b/w pH_1 & pH_2
i.e end pt. is b/w pH_1 & pH_2

Hence, pH range $= pK_{In} \pm 1$

Date 16/2/11

Ch - Alkynes

- Preparation :-

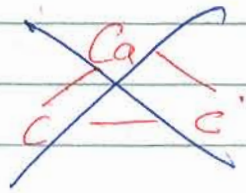
(1) Hydrolysis of carbides

Industrial CaC_2 (acetylyde) $+ H_2O \longrightarrow H-C\equiv C-H + Ca(OH)_2$

acetylene

(Higher alkynes produced by further rxn on acetylene)

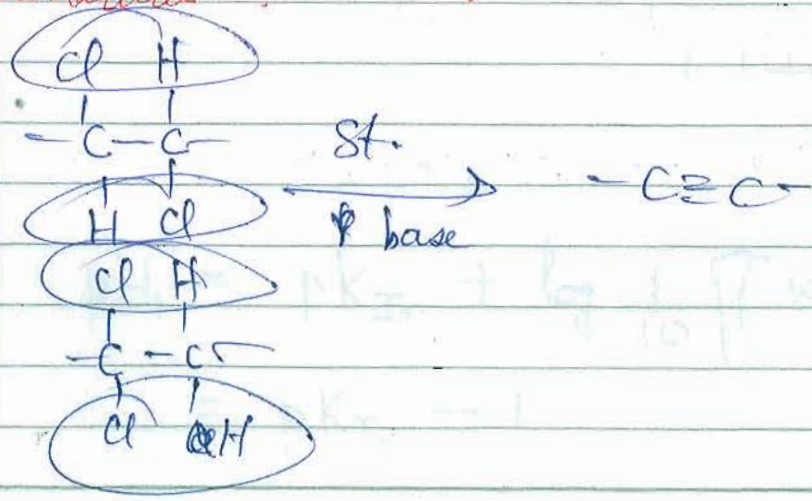
Structure of $CaC_2 \rightarrow Ca^{2+}[C\equiv C]^{2-}$

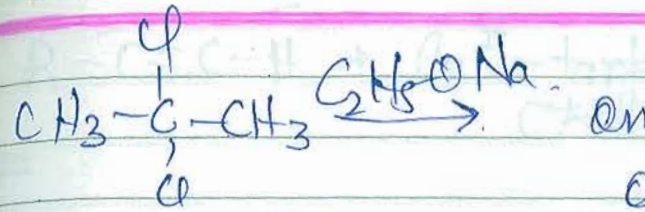


Magnesium carbide or Propynide or Mg_2C_3.

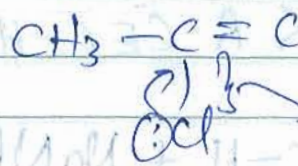
$Mg_2C_3 + H_2O \longrightarrow CH_3-C\equiv C-H + Mg(OH)_2$

(2) Double dehydrohalogen" of geminal & vicinal dihalides



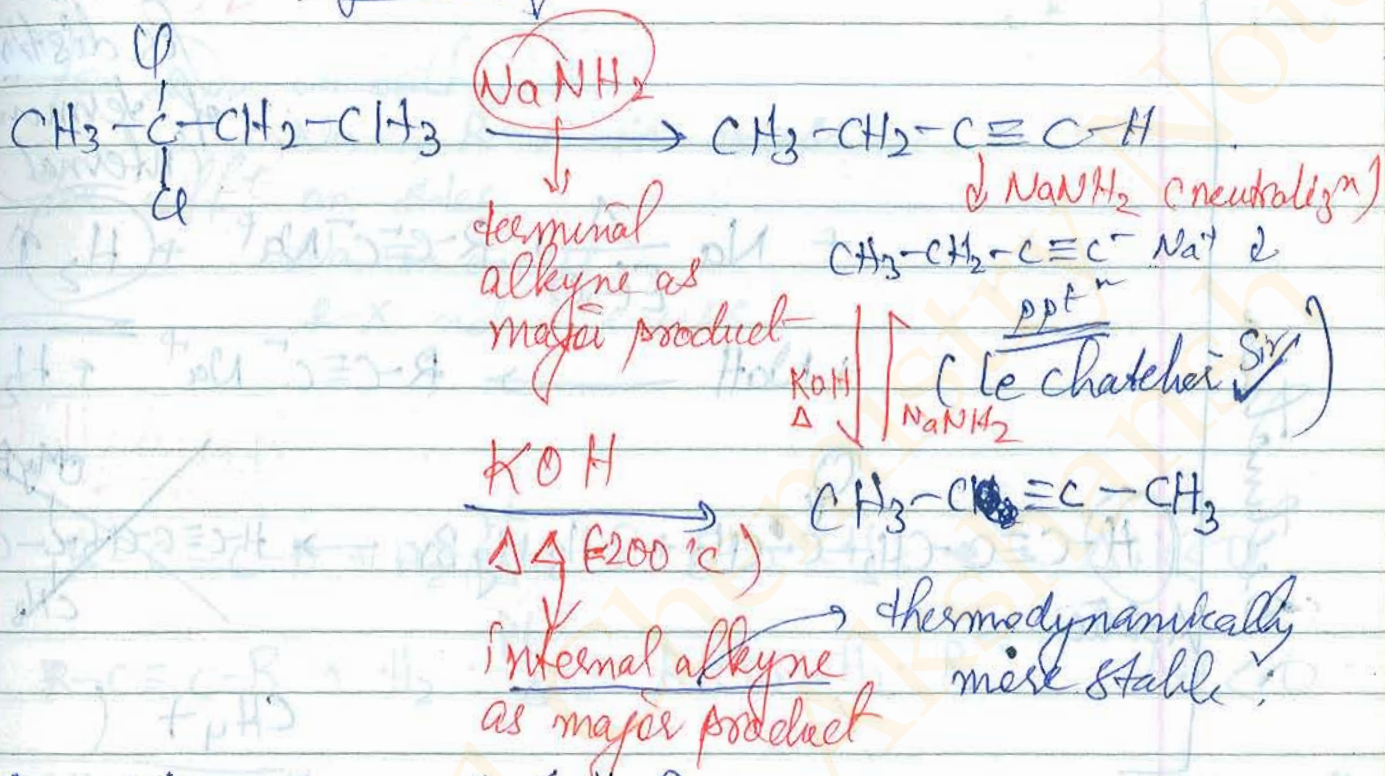


Only single dehydrohalogen^{n} occurs.



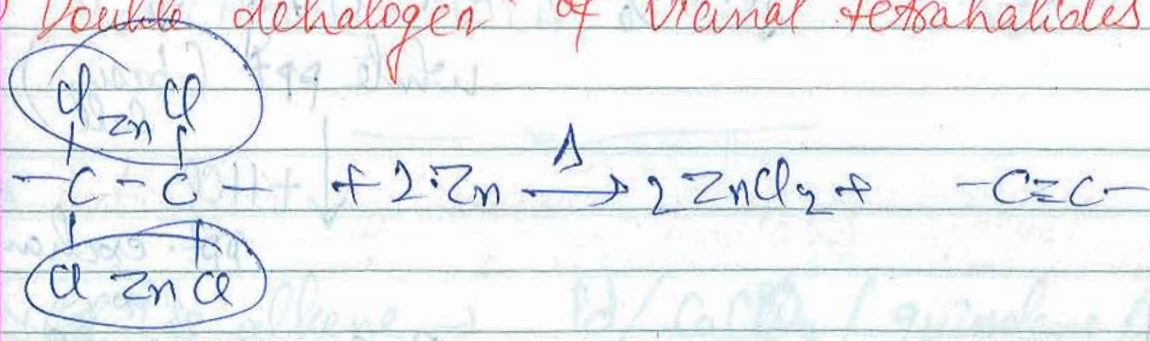
Partial (=) bond.

For double dehydrohalogen^{n} :—



Acidity : $NH_3 < R-C\equiv CH < H_2O$

(3) Double dehalogen^{n} of vicinal tetrahalides.



More stable → less heat of hydrogen^{n} (ΔH)

Date

REACTIONS

(1) ACIDITY

Acidity $NH_3 < R-C\equiv C-H < R-OH < H_2O$

Distinction

$R-C\equiv C-H + NaNH_2 \longrightarrow R-C\equiv C^{-}Na^{+} + NH_3\uparrow$

(can be used for distinction of terminal & internal)

$+ Na \xrightarrow[Et_2O]{\Delta} R-C\equiv C^{-}Na^{+} + H_2\uparrow$

$+ NaH \longrightarrow R-C\equiv C^{-}Na^{+} + H_2\uparrow$

Acidic H $H-C\equiv C-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3MgBr \longrightarrow H-C\equiv C-CH_2-\underset{CH_3}{\overset{OMgBr}{\overset{|}{\underset{|}{C}}}}-CH_3$

$CH_4 +$ ( )

Separation

$R-C\equiv C-H + Ag(NH_3)_2^{+} \rightarrow R-C\equiv C^{-}Ag^{+}\downarrow$

white ppt (basic salt)

$\downarrow + HCl$

ppt. exchange ion

$R-C\equiv C-H + AgCl\downarrow$,

Separ^{n} ✓

Internal alkyne remains in sol^{n}.

Heterogeneous

Cu^{+1} → All compds having this give red colored sol^{n} / ppt.

Why

$R-C\equiv C-H + Cu^{2+}\text{-tartarate}(NH_3) \rightarrow R-C\equiv C\,Cu\downarrow$ red ppt.

(2) Chain extension rxn

$H-C\equiv C-H \xrightarrow{+Na} H-C\equiv C^{-}Na^{+} \xrightarrow[S_N2]{R-X} H-C\equiv C-R + NaX$

for same on both side.
Na, R-X in excess.
For diff^{t} on sides
Na in excess
R-X not in excess.

(3) Hydrogen^{n}

$R-C\equiv C-H + H_2 \xrightarrow[\Delta]{Pt} R-CH_2-CH_3$ $\Delta H<0$

$R-C\equiv C-R + H_2 \xrightarrow[\Delta]{Pt} R-CH_2-CH_2-R$ $\Delta H<0$

$CH_3-C\equiv C-H + 2H_2 \longrightarrow CH_3-CH_2-CH_3$ $\Delta H<0$

$CH_2=CH-CH_2-CH=CH_2 + 2H_2 \longrightarrow$  $\Delta H<<0$

2 = bond

• Controlled hydrogen^{n}

Heterogeneous catalysis

Cis alkene → Pd/$CaCO_3$ / quinoline or xylene (Lindlar's catalyst: PbO or $Pb(CH_3COO)_2$)

Pd/$BaSO_4$ / PbO or $Pb(CH_3COO)_2$ quinoline or xylene (Rosenmund catalyst)

Trans alkene → Na/$NH_3(l)$ or Na/C_2H_5OH (dry)

or any grp 1 element

Na / NH_3(aq)

Date

* PbO or $Pb(CH_3COO)_2$ or Quinoline / Xylene

catalytic poisons

(∵ they form complexes with the alkene formed)

↓

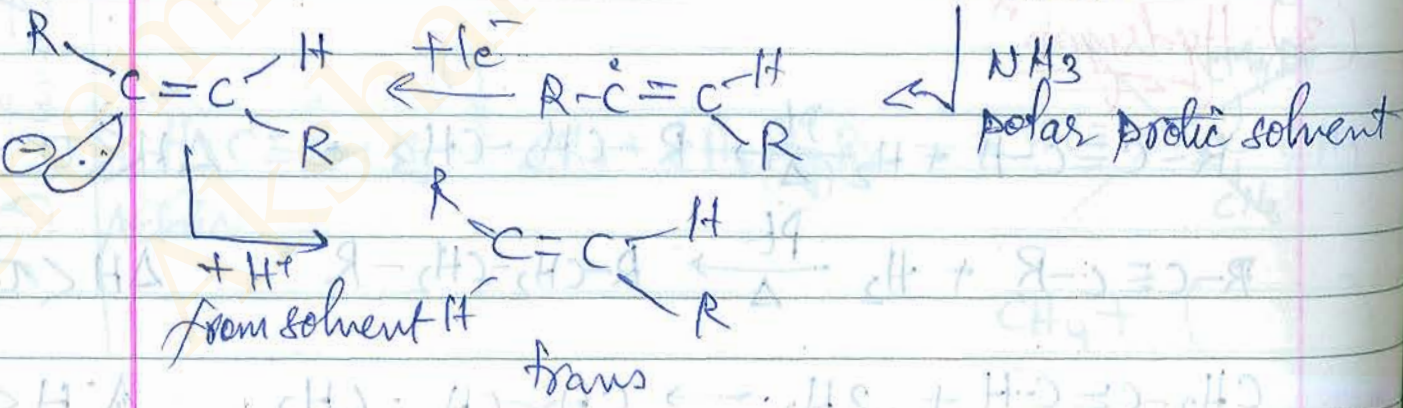
further hydrogenⁿ prevented.

In trans hydrolysis

$Na \rightarrow Na^+ + 1e^-$

$R-C\equiv C-R + 1e^- \rightarrow R-\dot{C}=\ddot{C}-R$

Radical anion

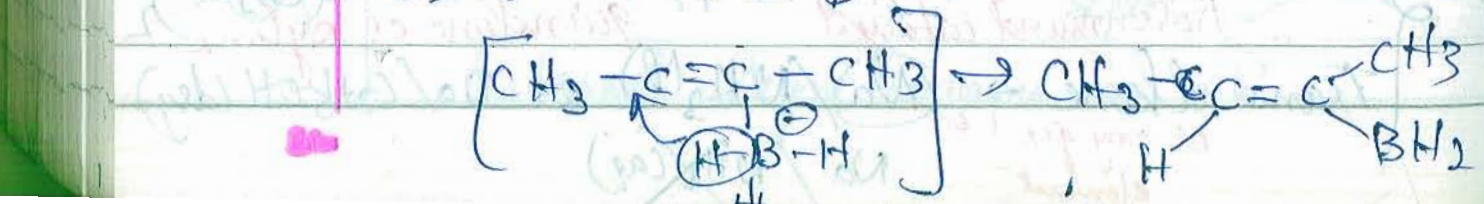


∴ RI :- Radical anion, free radical, carbanion.

For Rosenmund catalyst

$CH_3-C\equiv C-CH_3 + Pd/BaSO_4\ BH_3 \xrightarrow{B_2H_6}$

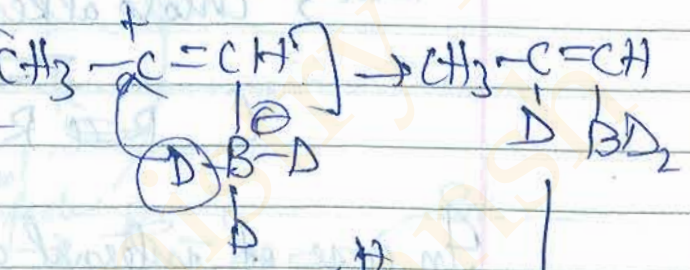
$B_2H_6 \rightleftharpoons 2BH_3$





★ Very Very Imp. (only possible with B_2H_6 / BH_3)
Hydroboration is of great importance in putting deuterium or tritium to the alkene in S2.

eg:- BD_3 in place of BH_3 gives D.
& RCOOD gives D.

i.e $CH_3-C\equiv C-H + BD_3 \rightarrow$ 



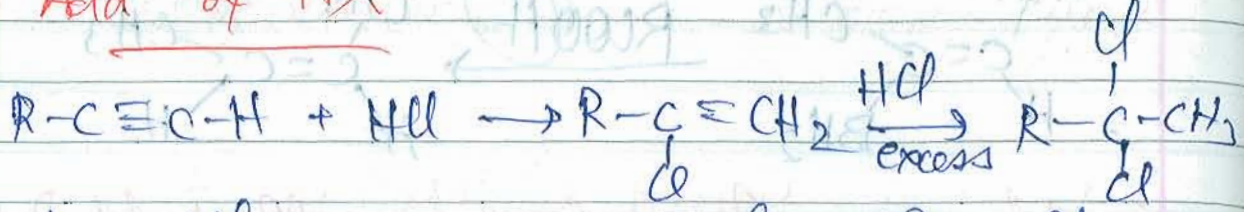
(4) Electrophilic addⁿ rxn

$R-C\equiv C-H + E^{+} \rightarrow R-\overset{+}{C}=CHE$
Vinyl carbocation

$R-CH=CH_2 + E^{+} \rightarrow R-\overset{+}{C}H-CH_2E$
Alkyl carbocation.

Stability :- Vinyl < Alkyl carbocation
So, alkynes, although having more -ve charge undergoes by E^{+} attack slowly as compared to alkene.

(5) Add^n of HX



Now, Alkenes are more reactive than alkynes, so addⁿ of HCl reaction should be now on alkene. But, this is false.

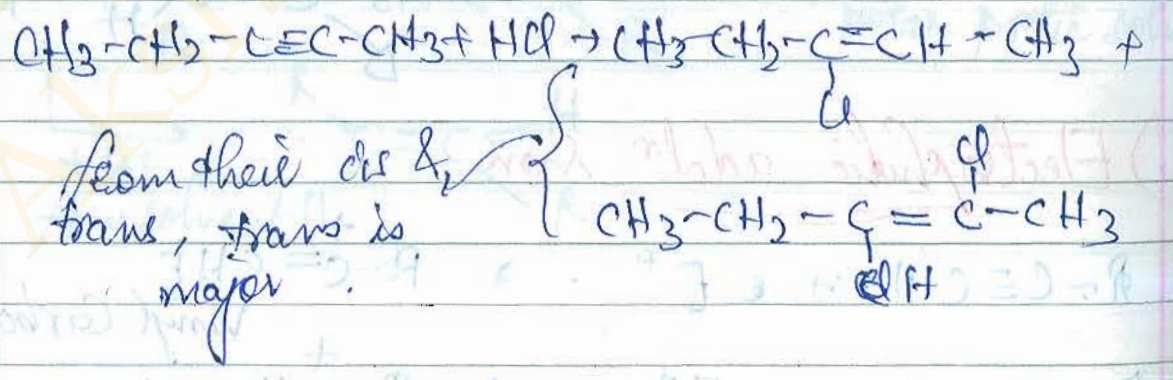
∵ Reactivity of alkene > alkyne

∵ R^+ > vinyl carbocation in stability

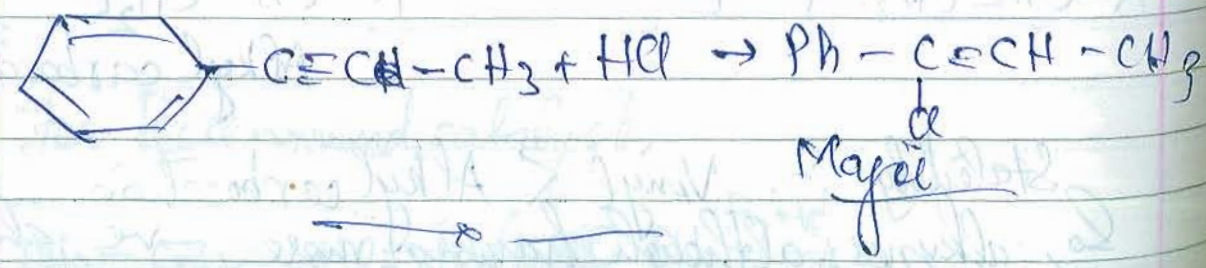
But, Chloro alkene < alkyne.

($R-\overset{+}{C}-R$ is less stable than vinyl even

In case of internal alkyne.



from their cis & trans, trans is major.



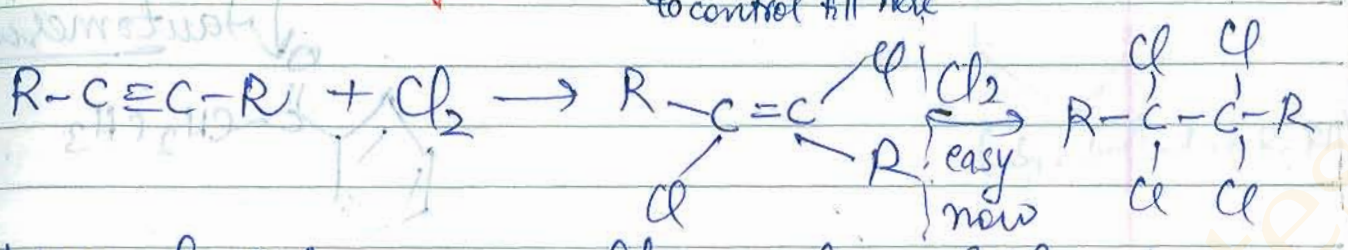
Major



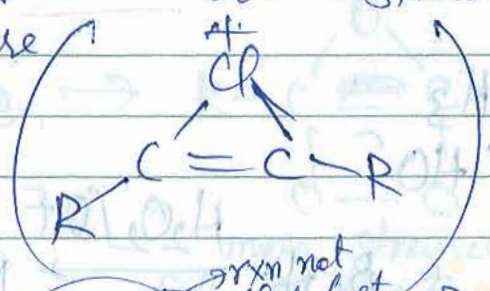


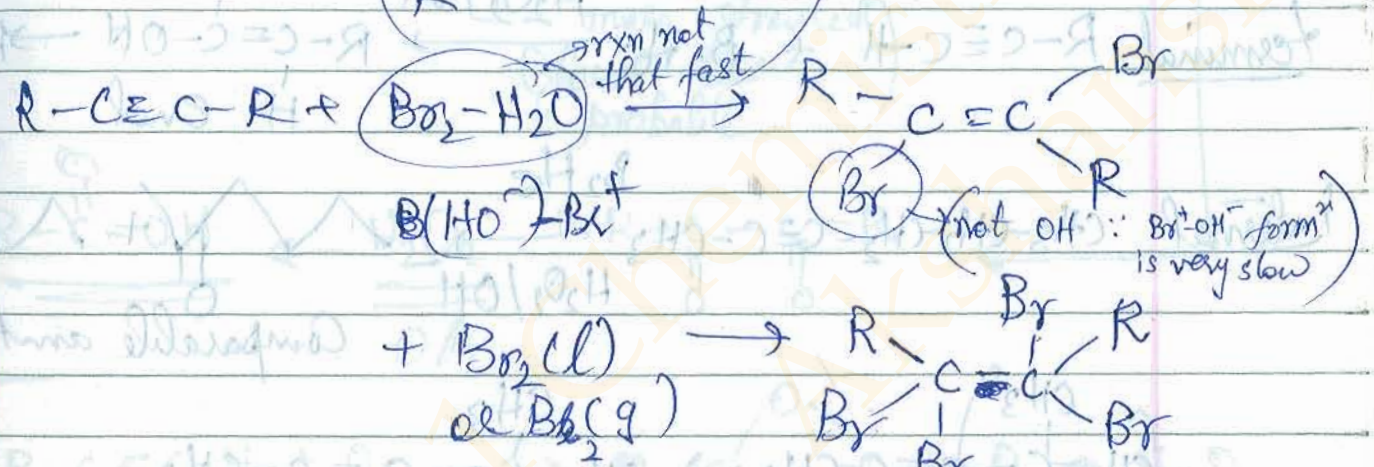
(6) Addⁿ of Halogens

difficult to control all here

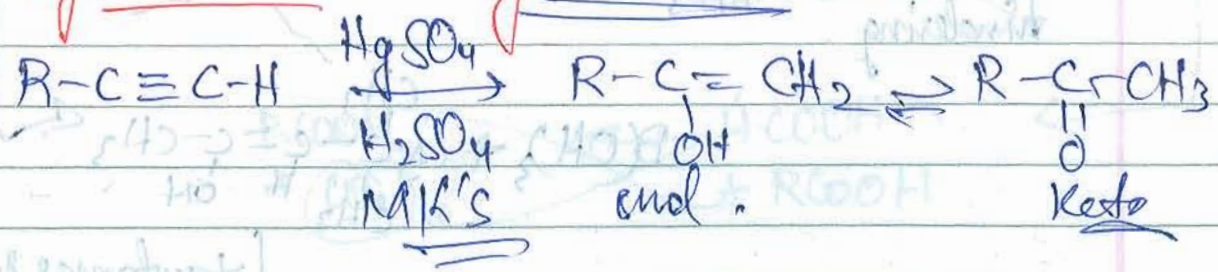


Addⁿ of halogen on alkyne less stable than alkene ∴ more strained cyclic chloronium ion formed here

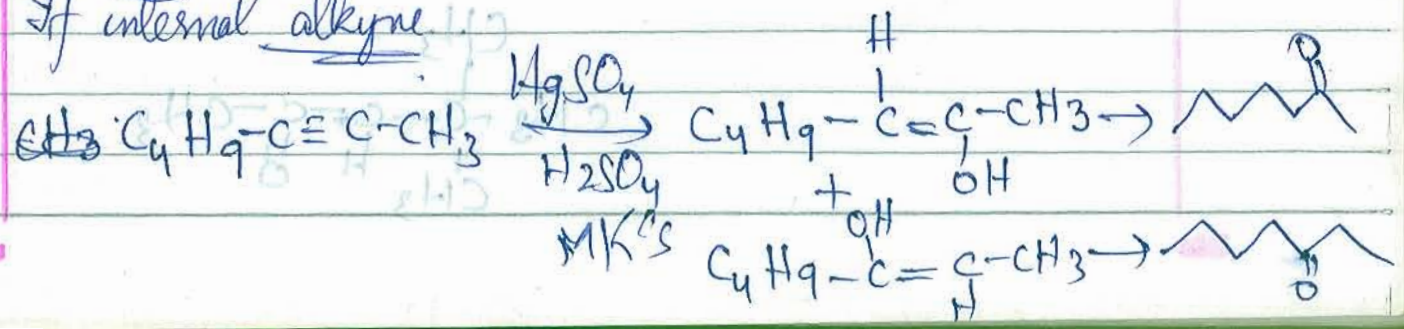




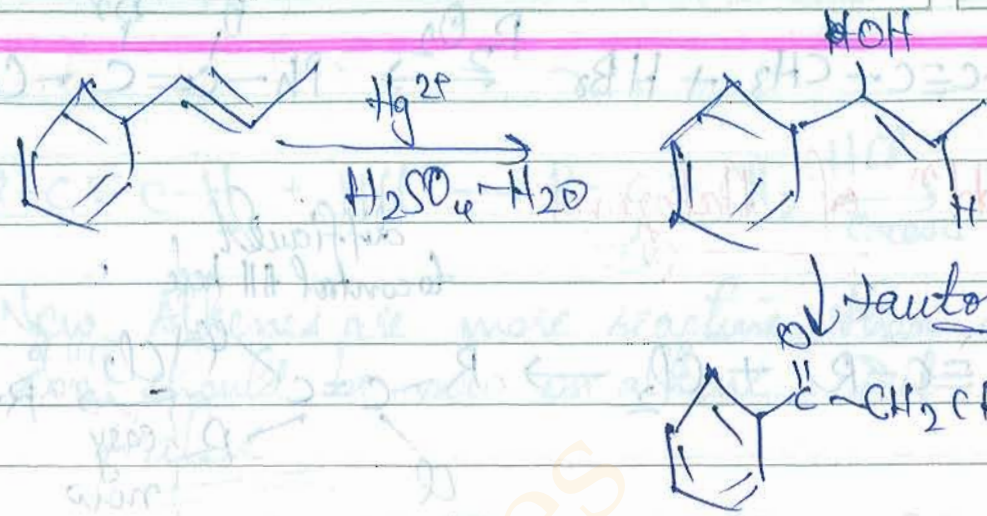
(7) Hydeⁿ son – Oxymercuⁿ – demercuⁿ



If internal alkyne



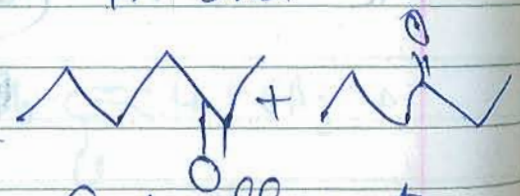
Date

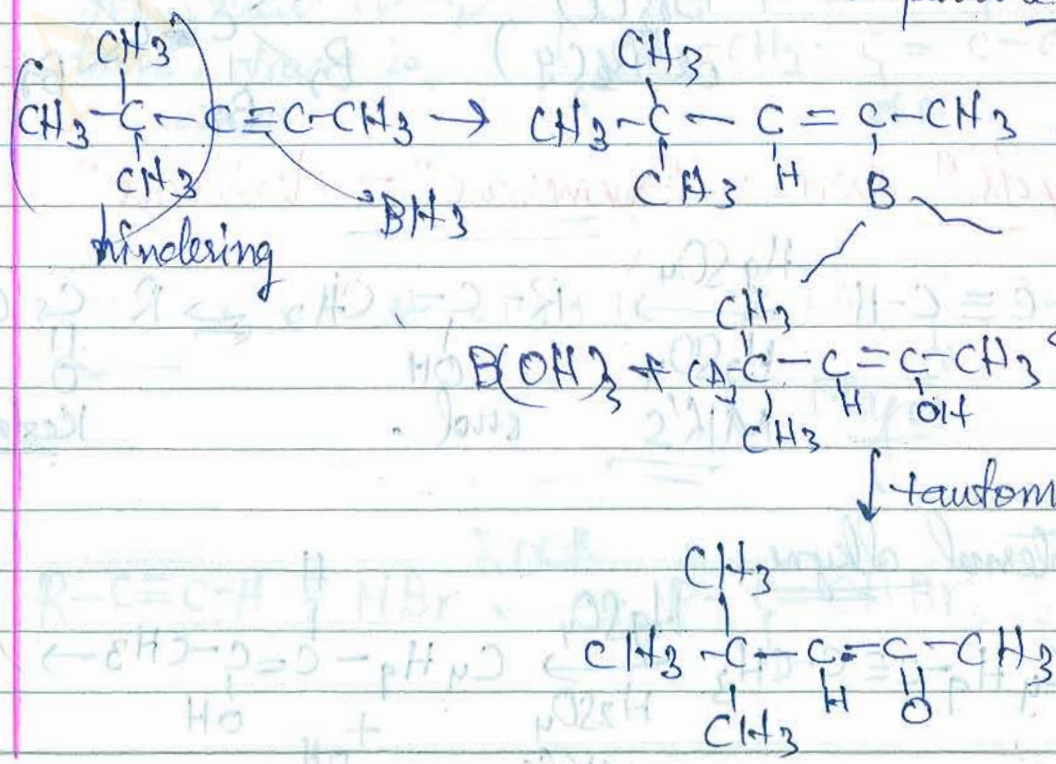


✡ HBO Anti MK's add^n

(i) B_2H_6 / BH_3
(ii) H_2O_2 / HO^-

Terminal $R-C\equiv C-H + B_2H_6 \xrightarrow{H_2O_2/OH^-} R-\underset{H}{\overset{H}{C}}=\underset{H}{C}-OH \longrightarrow R-CH_2-\overset{O}{\overset{\|}{C}}-H$ enol

Internal $CH_3-CH_2-CH_2-C\equiv C-CH_3 \xrightarrow[H_2O_2/OH^-]{B_2H_6}$  Comparable amt



Date

For selectivity of rxn ⇒ Reagent → heavy grps.

Dicyclo borane →



(Symbolised as R_2BH)

(8) Ozonolysis

$$R-C\equiv C-R + O_3 \rightarrow R-C(-O-O-)C-R + H_2O$$

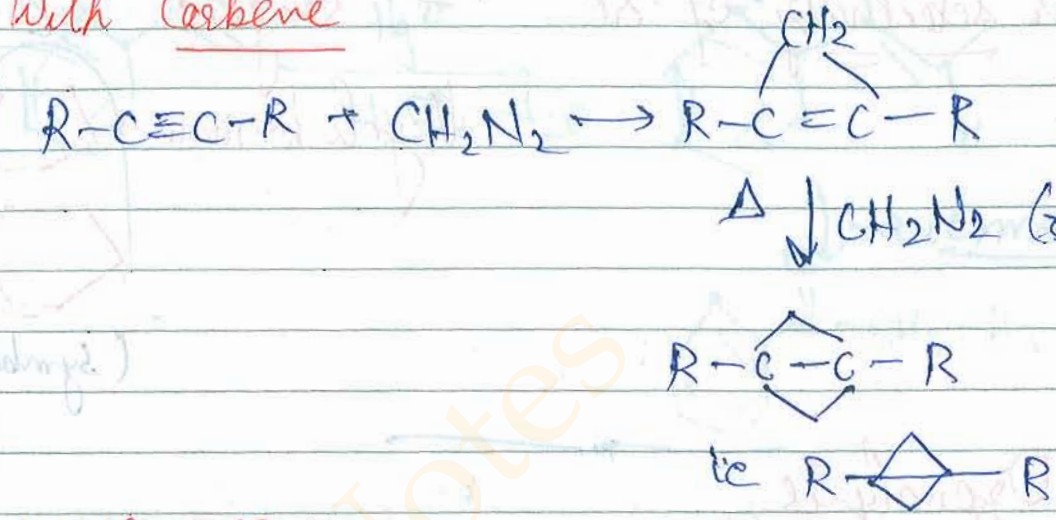
more strained (formⁿ less probable)

$$2\,R-\overset{\overset{O}{\|}}{C}-OH \xleftarrow{H_2O_2/OA} R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R$$

$$R-C\equiv C-H + O_3 \rightarrow R-C(-O-O-)C-R + H_2O$$

$$RCOOH + CO_2 \leftarrow HCOOH + RCOOH$$

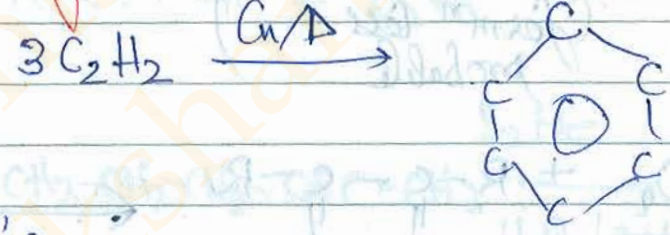
(9) With Carbene

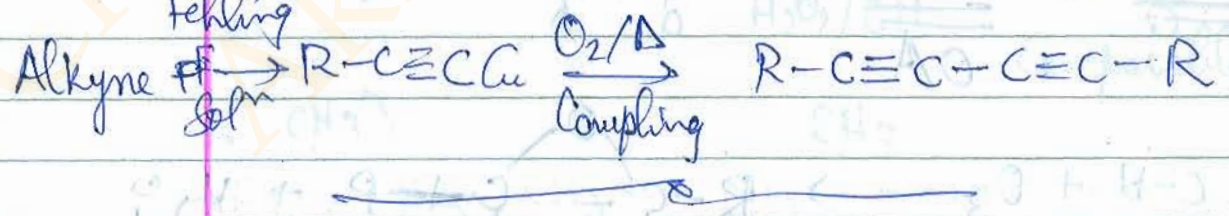


(10) With RCO_3H

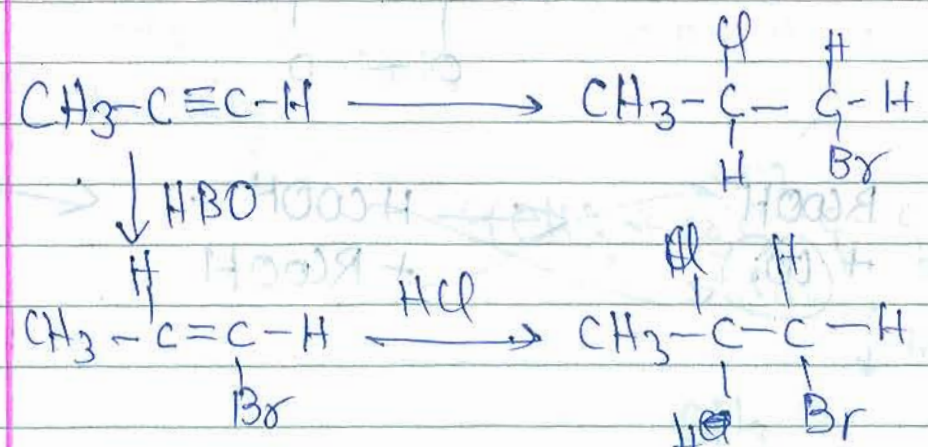


(11) Polymerisn





Q



Racemic

Date

(8) $CH_3-CH=CH_2 \longrightarrow CH_3-C\equiv C-CH_2-C_2H_5$

I Dehydrogen^n $CH_3-C\equiv CH \xrightarrow{Na/\Delta}$ $CH_3-C\equiv C^- Na^+$

HBr/ROOR $\longrightarrow CH_3CH_2CH_2Br$ (X)

I $\xrightarrow{Br_2}$ $CH_3-\underset{Br}{CH}-CH_2Br \xrightarrow[2NaNH_2]{} CH_3-C\equiv C^- Na^+$

$\downarrow X$

Product

Date

COORDIN^{n} COMPDS.

STEREO ISOMERISM

CN=2 MA_2, MAB : no stereo isomerism

Linear eg: $Ag(CN)_2^-$, $Ag(CN)(SCN)^-$

CN=4

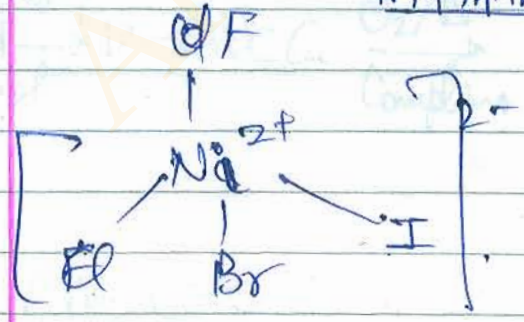
tetrahedral  no geometrical.

optical (All 4 ligands deff^{t}) only then

eg: $Na_2[^{28}NiFBrClI]^{2-}$.

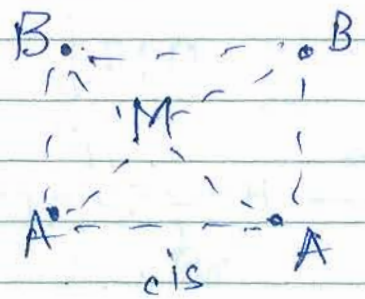
d^8, weak ligand → Tetrahedral.



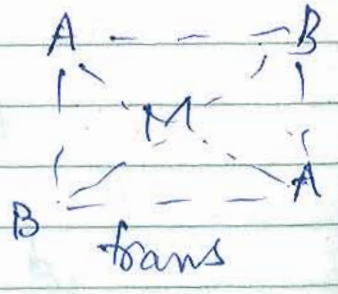


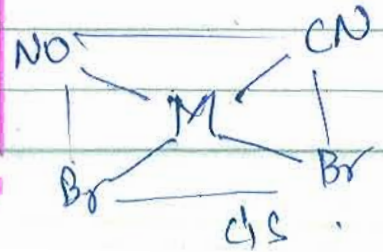
CN=4

Sq. planar

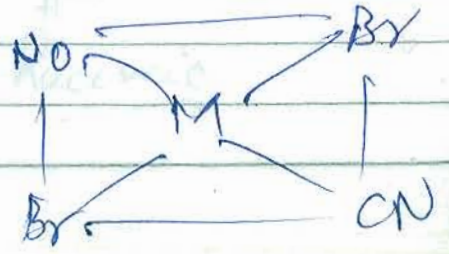


$M_{A_2B_2}$

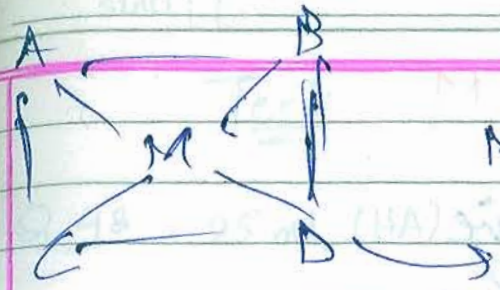




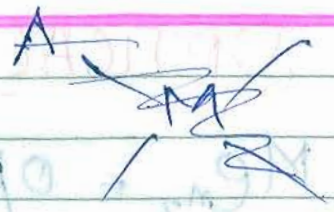
M_{A_2BC}



Date

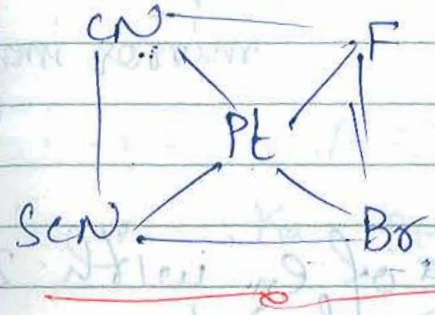


M_{ABCD}



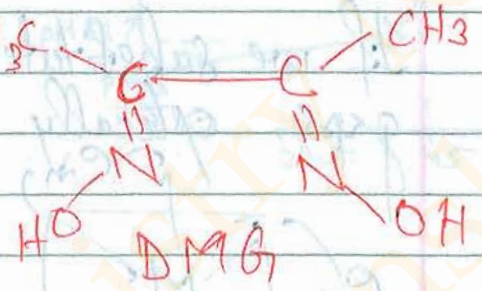
E-Z

Q. $[Pt(CN)(SCN)BrF]^{2-}$

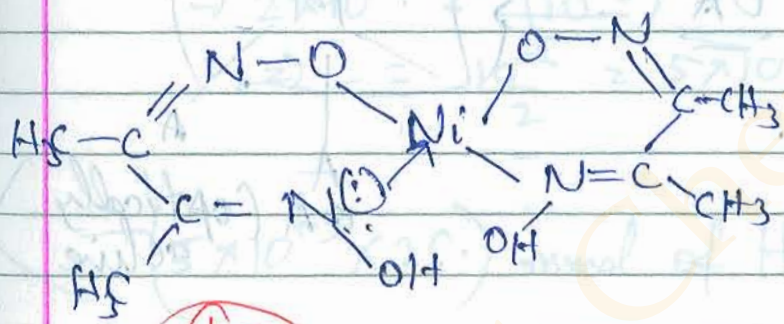


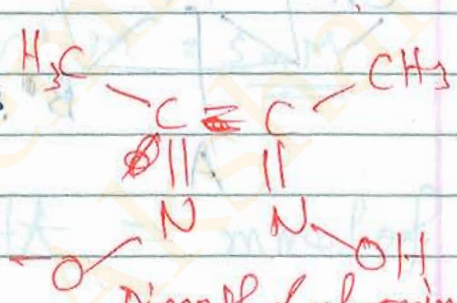
no. of geometrical isomers = 2+(1)

Complex $[Ni(DMG)_2]$ →



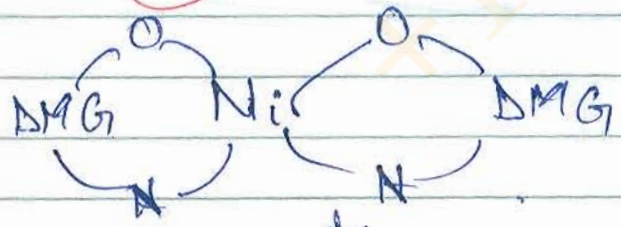
DMG

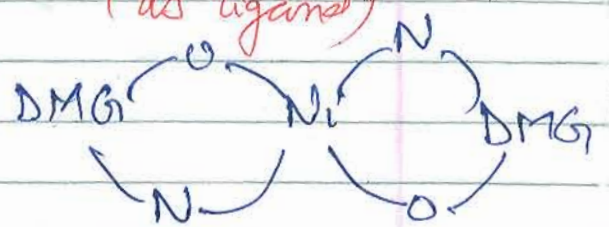




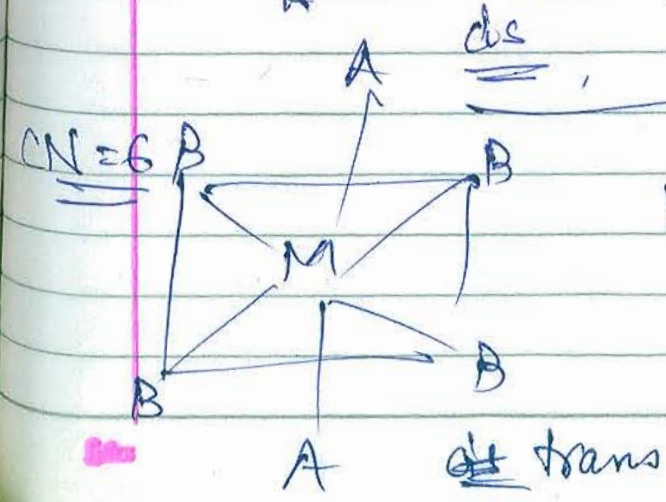
Dimethyl glyoximate (as ligand)

(i.e)





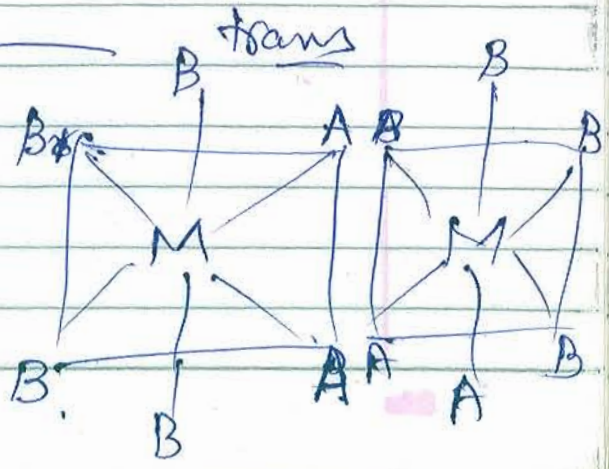
CN = 6



cis

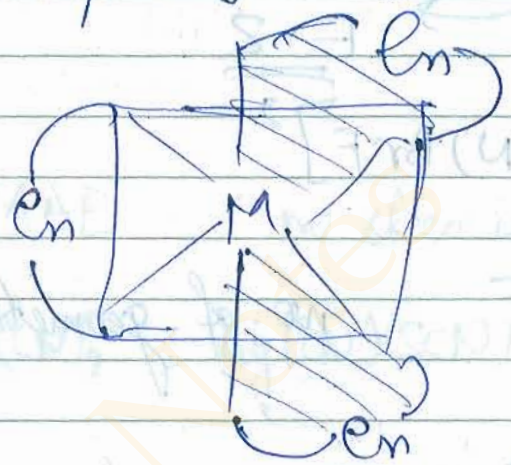
trans

$M_{A_2B_4}$



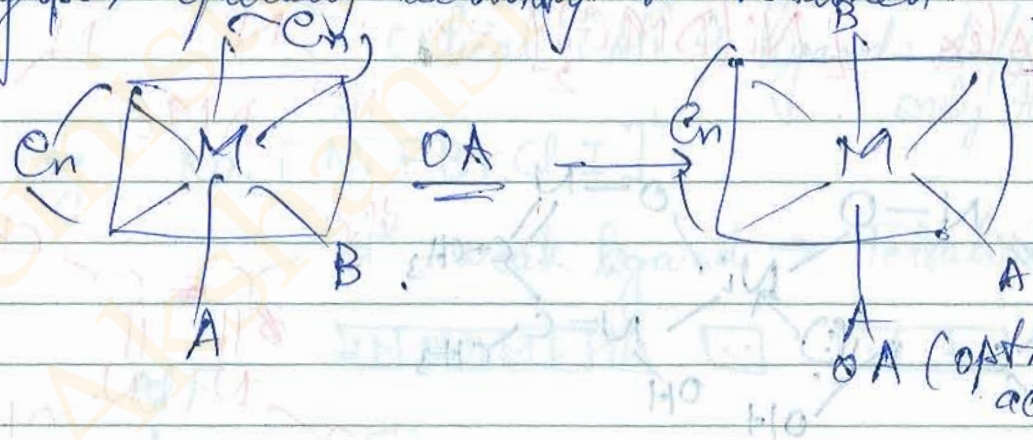
OPTICAL ISOMERISM

$MCen_3$ = Optically active



→ Nsp on mirror image

If we substitute one gsp of en with 2 gsps, optically activity is retained



Test

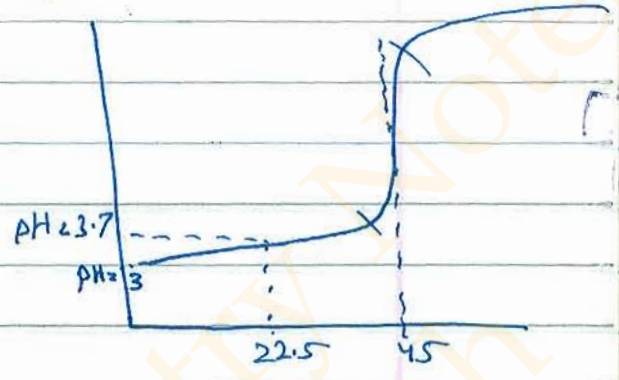
Q.48 25 mL (HA)

$$HA + NaOH \longrightarrow A^- + H_2O + Na^+$$

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

$\longrightarrow K_a = \frac{[H^+][A^-]}{[HA]}$

The sol^n would be buffer at every pt (Acidic buffer).



i : t = 0 $\quad HA \rightleftharpoons H^+ + A^-$

$K_a = \frac{[H^+]^2}{c}$

$pK_a = 3.7 \Rightarrow K_a = 2 \times 10^{-4}$

$\Rightarrow 2 \times 10^{-4} = (10^{-3})^2$

$\Rightarrow c = \frac{10^{-2}}{2} = 5 \times 10^{-3}\ M = 5\ mM$

$(5 \times 10^{-3} \times 25)$ mmol of HA = mmol of NaOH req^d.

classmate
Date 31·1·2010
Page

Ch: Reaction Mechanism

(A) Electronic Displacement

(B) Reactive Intermediates

(A) ✱ Electronic Displacement describe the movt. of e^-s during a chemical rxn.

- (i) Inductive Effect (Induction)
- (ii) Resonance Effect (Mesomeric effect)
- (iii) Hyperconjugation (No-bond resonance)
- (iv) Electromeric effect.

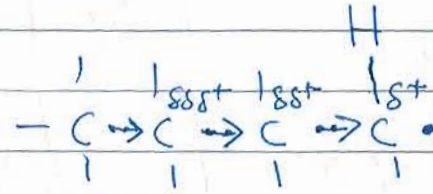
× ×

✱ ORDER TO REMEMBER

Imp. ORDER OF ACIDITIY

$RH < R-CH=CH_2 < NH_3 < R-C\equiv C-H < R-OH < H_2O$
$< Phenol < RCOOH < RSO_3$.

i ✡ INDUCTIVE EFFECT (INDUCTION) (I-EFFECT



~ Inductive effect is polarisation of shared pair of e⁻s towards more electro-ve atom.

~ C-H bond doesn't take part in I-effect
(∵ H → very small → strong bond ; nucleus close)

+I effect
It is the effect in which e⁻s are pushed towards C.

-I effect
It is the effect in which e⁻s are taken away from C.

✡ +I effect giving groups

R− , $-O^-$ (oxide group) , $-COO^-$, $-SO_3^-$
(i) (ii) (iii) (iv)

→ Among alkyl group, larger the size of alkyl group, greater, +I effect.
→ Branching increases the e⁻ donating power of alkyl gp.

✡ -I effect producing gps (common only)

$-\overset{+}{N}H_3$, $-NO_2$, $-CN$, $-COOH$, $-F$, $-Cl$, --

strongest

there are many others

decreasing order

☆ General Rules

- Inductive effect is a very weak effect & it becomes practically insignificant after 3 σ bond from source.

- Magnitude of inductive effect depends on
  (i) E_N of atom / grp. → greater E_N, higher I-effect.
  (ii) distance from source → greater distance from source, smaller effect

If E_N & distance are to be compared, distance is considered 1st.

- I-effect is additive in nature & the combined effect of 2 grp is always greater than the effect produced by any 1 grp.

- I-effect is a permanent effect because it depends on permanent property of atom i.e. E_N.

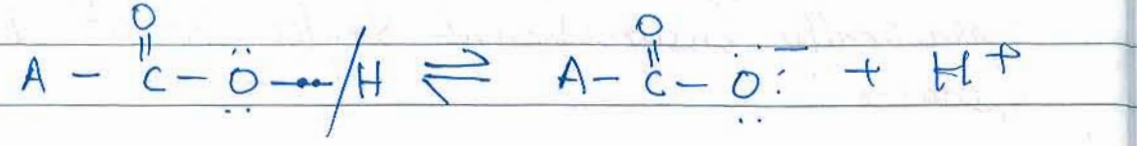
☆ APPLICATIONS

(i) ACID-BASE STRENGTH & I-EFFECT

(a) ACID STRENGTH

Under IDENTICAL CONDⁿ of conc. & T, a stronger acid is one which will produce greater H^+ ions.

Theory of Ionisation

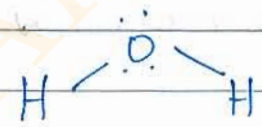


GENERAL

- If A is an e^- withdrawing grp., it facilitate the ionisation of acid & ∴ increases acid strength.
- If A is e^- donating grp., it retard the ionisation process & ∴ decreases acid strength.

- If A is -I producing grp., it will increase acid strength. If it is +I effect giving grp, it will decrease acid strength.

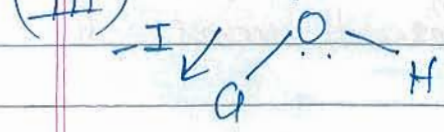
H_2O $\qquad$ $R-OH$.

(I) 

(II) 

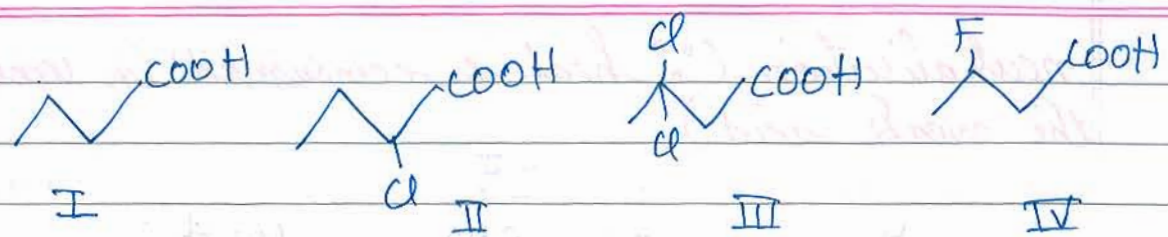
So, alcohols are weaker acidic than H_2O.

Exception CH_3OH is stronger acidic than H_2O (slightly)

(III) 

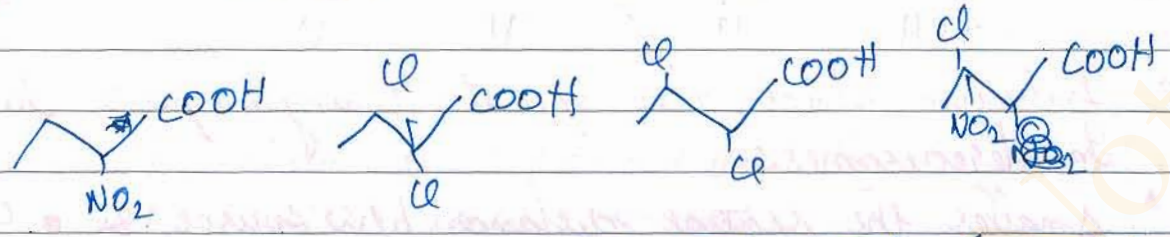
Acid Strength

III > I > II.

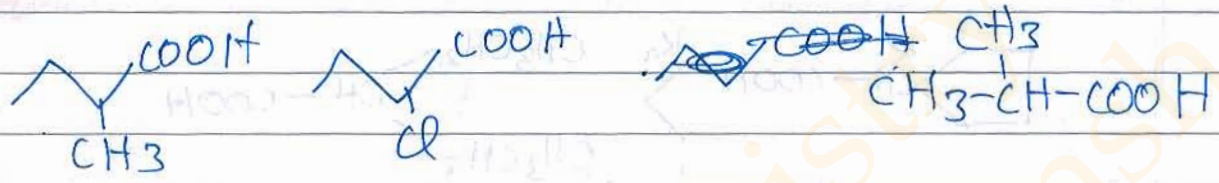
Q. 

I II III IV

Acid : I < IV < III < II

Q. 

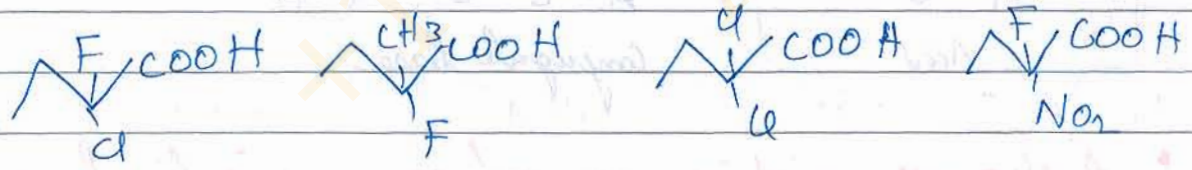
~~IV < IV < III < II~~ IV < III < I < II

Q. 

$CH_2CH-COOH$. ⇒ Inc. order of pKa value.

acid : I < III < II < IV

pKa : I > III > II > IV

Q 

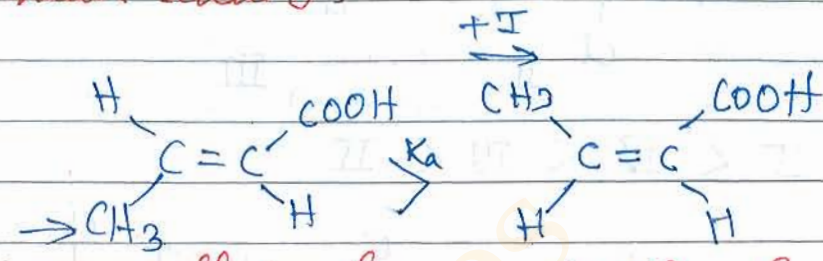
Consider equimolar soln, T is same.
inc. order of pH value.

Strength : IV > I > III > II

pH : IV < I < III < II

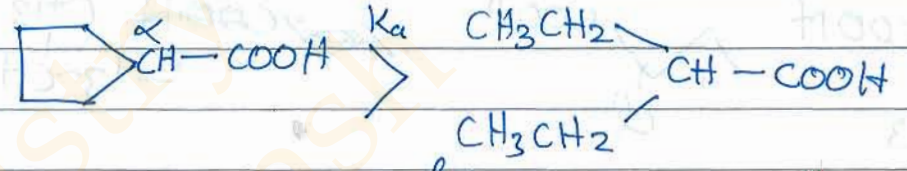
- Stronger the acid, more will be the heat (modulus) evolved during neutralisation.
- Weaker the acid, lesser heat will be evolved during

neutralisation (∵ heat is consumed in ionising the weak acid).



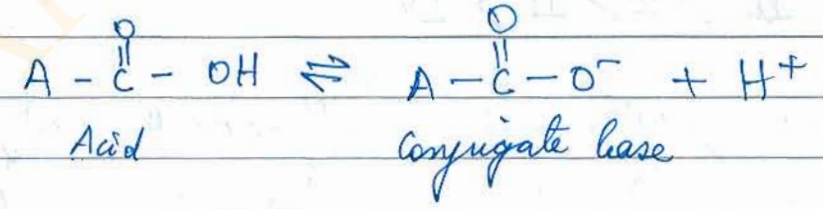
☆ Inductive effect also operate through space. Its imp. in stereoisomers,

- Smaller the spatial distance b/w source & • COOH, greater the effect (donating / withdrawing)



- Cycloalkyl grp has ~~greater~~ weaker strength of acid than acyclic alkyl grp.

Cond^ns : α carbon of same degree. and everything remains same.



- A stronger acid is one whose conjugate base is more stable. More stable conjugate base, more H⁺ is produces, hence, strength is high.

- -I effect producing grp. (if attached to conjugate base) increases the stability of conjugate base, thus, increasing acid steength

+I effect grp decreases stability of conjugate base, thus decreasing acid strength.

(b) BASIC STRENGTH

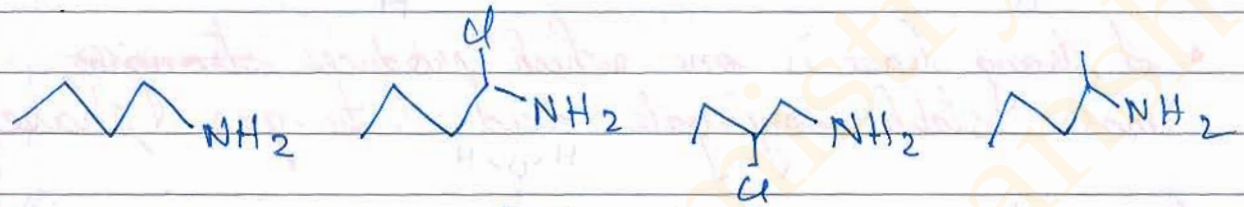
Base $A-\ddot{N}H_2$
Lewis base

• **Strength of Lewis base**

It depends on its ability to donate lone pair of e⁻s. which ultimately depends on e⁻ density on donar atom (N, here).

• $\bar{e}$ donating grp. bonded to donar atom increases e⁻ density & ∴ basic strength.

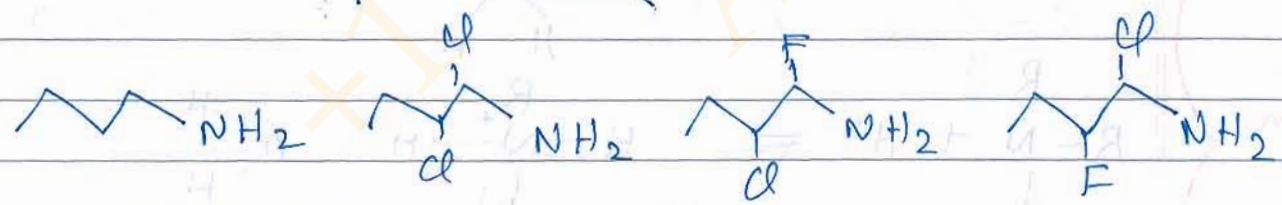
• e⁻ withdrawing grp decreases e⁻ density on donar atom & ∴ decreases basic strength.

Q. 

Basic : II < III < I < IV

Q. 

II < I < III < IV

Q. 

equimolar conc, same T, inc. order of pH of their sol^n

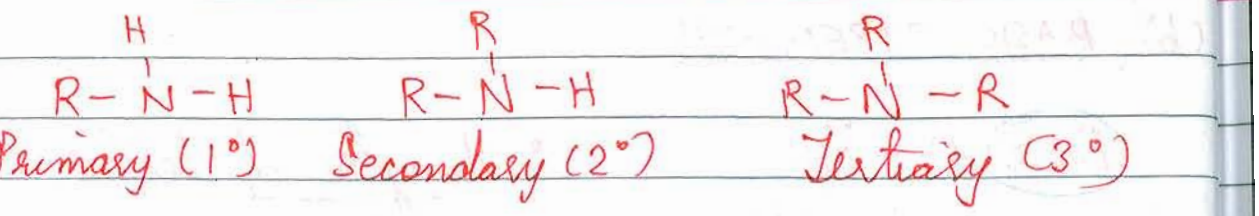
Basic : III < IV < II < I

pH : "

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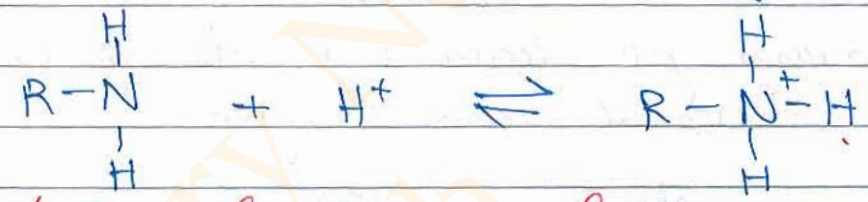
Primary (1°) Secondary (2°) Tertiary (3°)

$NH_3 < 1° < 2° < 3°$: (In gas phase)

In aq. soln

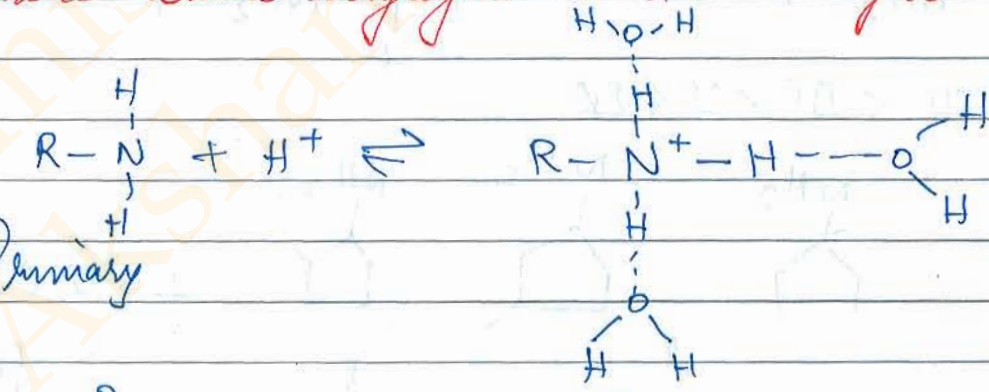
$NH_3 < 3° < 1° < 2°$ } SAT rule

Secondary > Primary > Tertiary



• A strong base is one which produces ~~strong~~ more stable conjugate acid. (In gas phase)

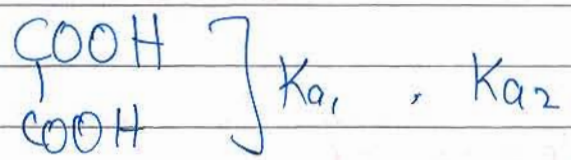
In aq. soln

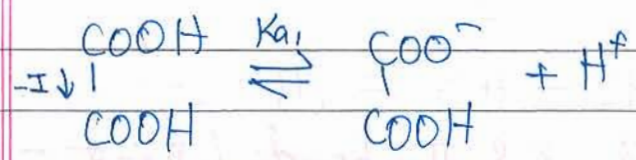


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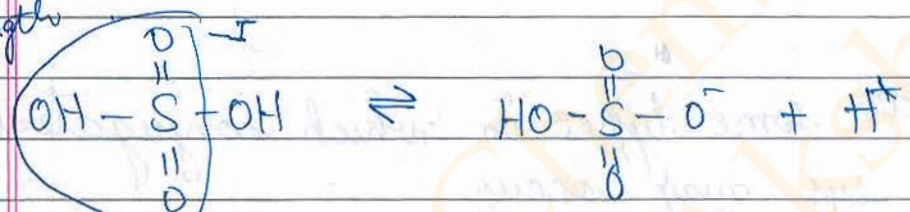
—— X ——

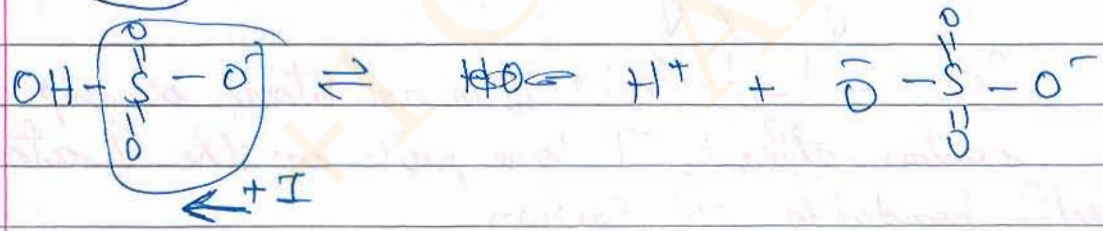






e⁻ donating decreases acid strength





——— X ———

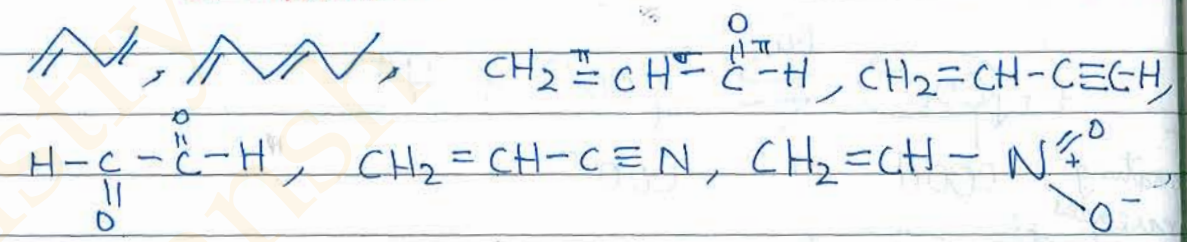
* Resonance is just a theoretical concept.

* **Resonance Effect** (R-effect) : Resonance effect is delocalisation of e⁻s in a conjugated sys. Resonance decreases P.E. of sys (molecule or ions) & ∴ increases stability.

* Law of electrostatics : If we bring like species together, P.E ↑, stability ↓.

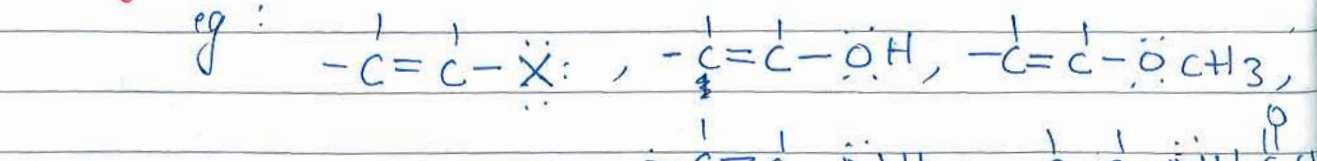
* **Conjugated System**

① Alternate σ & π bonds (π − σ − π bond)

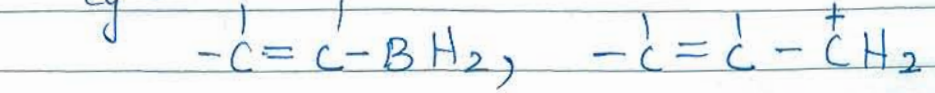
eg: 

 are some types in which conjugated sys. may occur.

② $-\overset{|}{C}=\overset{|}{C}-Z$ → it is an atom or grp which contain atleast 1 lone pair on the atom directly bonded to sp^2 carbon.

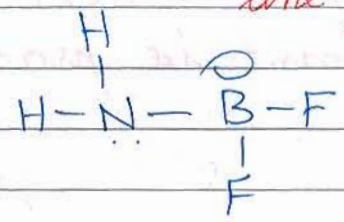
eg: 

③ $-\overset{|}{C}=\overset{|}{C}-Z$ → its an atom or grp. which contain deficiency of atleast 1 lone pair of e^- & is directly bonded to sp^2 carbon.

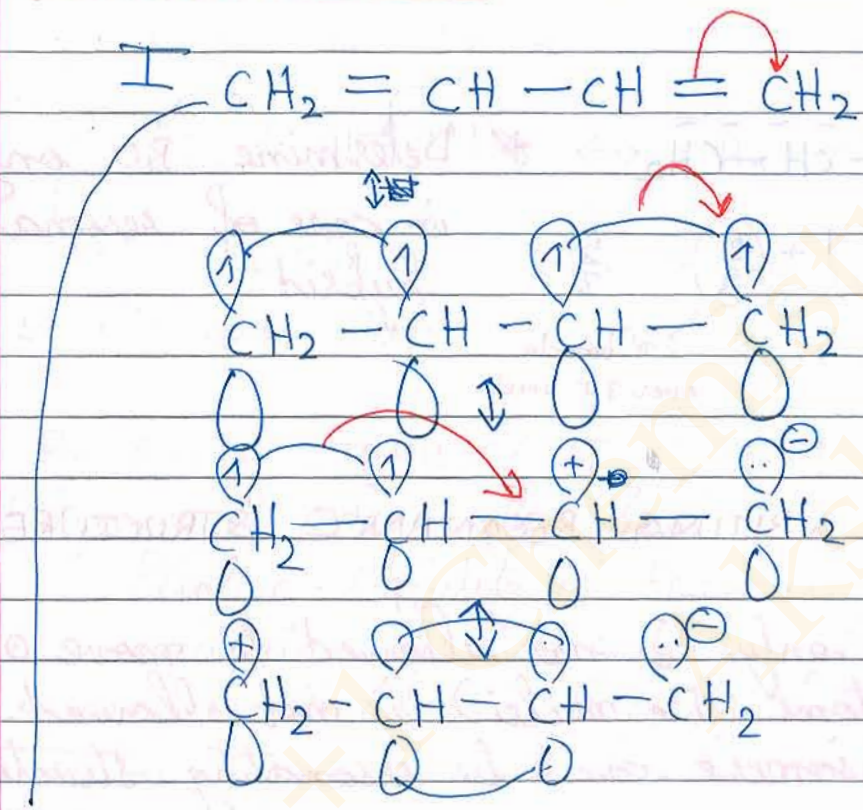
eg: 

(4) $\ddot{X}-Y$ (bond in which one has lone pair & other has deficiency of line pair)

eg:



✱ DELOCALISATION



I $CH_2=CH-CH=CH_2$

$CH_2-CH-CH-CH_2$

$CH_2-CH-CH-CH_2$

$CH_2-CH-CH-CH_2$

II $CH_2=CH-CH-CH_2$

III $CH_2-CH=CH-CH_2$

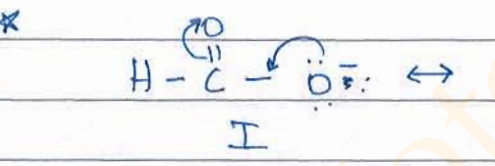
$\rightleftharpoons$ $CH_2-CH-CH-CH_2$ (Resonance hybrid)

Imp pts.

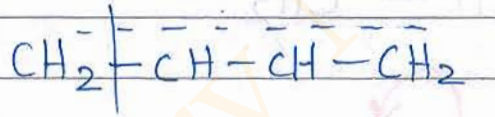
1) ✱ Various temporary array arising due to delocalisation of e⁻s are known as Resonance Structure or Resonating Structure or Canonical Structure.

* Large sized grps. attached to any chain are called BULKY GRPS.

2) * Various resonance structures of a conjugated sys have either equal or almost equal PE & thus, stability. ∴ Resonance structures of a conjugated sys can't be practically separated.



They are EQUIVALENT Resonance structures.



* Determine BO only in case of resonance hybrid.

$BO = 1 + \frac{2}{3} = \frac{5}{3}$

$\frac{2}{3}$ → 2π bonds over 3σ bonds

* $BO \propto \frac{BE}{BL}$

$BE \propto \frac{1}{BL}$

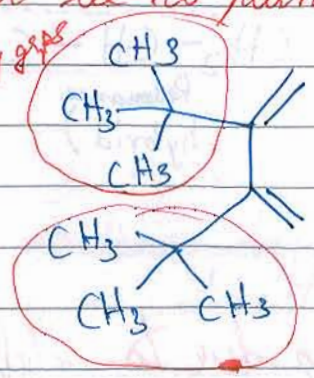
* RULES FOR WRITING RESONANCE STRUCTURES.

1) In resonance, only e^-s are allowed to move ONLY. Movt. of atoms (i.e nuclei) is not allowed. So, positional isomers can't be resonating structures.

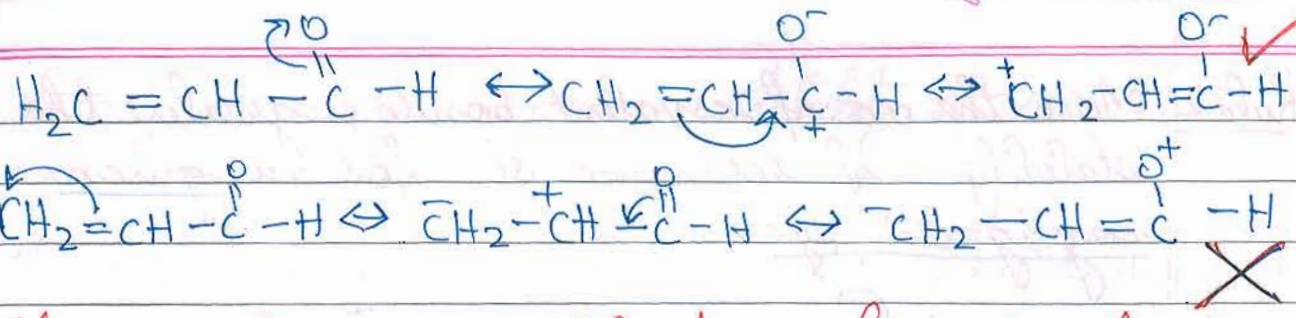
2) For resonance, all atoms involved in resonance must be co-planar.

bulky grps

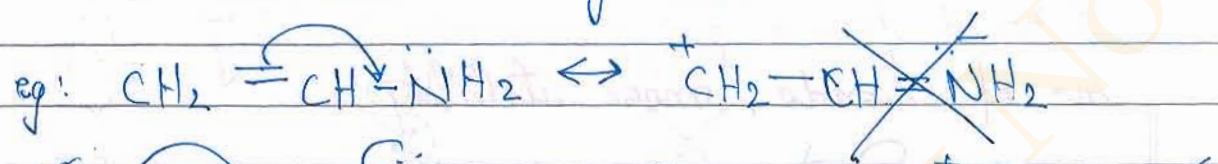
eg

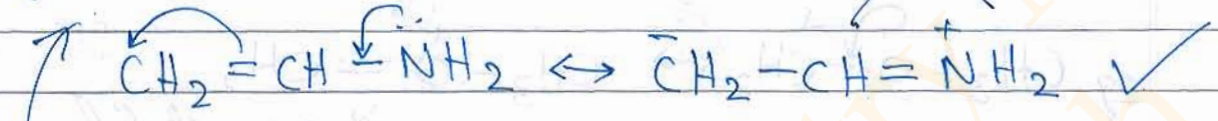


These bulky grps will become unstable and change their plane. So, they wont show resonance.

eg 

3) If more than 1 possible dirns of movt. of e^-s are available, e^-s prefer to move towards more electro -ve atom. eg: The above shows this.

eg: 



only 1 possible dirn. So, e^- may not necessarily move towards more electro -ve atom as seen.

☆ RELATIVE STABILITY OF RESONANCE STRUCTURES.

(Sequence of rules matters here)

Relative stability of Resonance ~~stru~~ structure of a conjugated sys depends on the PE of various resonance structures. Greater stability of resonance structure, greater will be its contribution to resonance hybrid.

The most stable resonance structure contributes the most to resonance hybrid & determine predominant properties of molecule/ion.

Rule 1 A neutral species is always more stable than the charged one.



↳ most stable.

Rule 2 More the no. of covalent bonds, greater the stability of resonance st. for a given conjugated sys.

eg $CH_3-\overset{+}{C}=\ddot{O} \leftrightarrow CH_3-C\equiv\overset{+}{O}$

II I

II is more stable.

* Bond formation increases stability. More the no. of bonds, more stability.

eg $CH_3-\ddot{O}-\overset{+}{C}H_2 \leftrightarrow CH_3-\overset{+}{\ddot{O}}=CH_2$

more stable.

Rule 3 For a given conjugated sys, if resonance st. has complete octet of all atoms, it will be most stable & will contribute the most to the resonance hybrid. (Supplement to rule 2)

eg: above 2.

Rule 4 For a conjugated sys, a resonance st. with -ve charge on electro -ve atom or +ve charge on electro +ve atom has greater stability than other with -ve charge on electro +ve or +ve charge on electro -ve.

eg $CH=CH-\ddot{O}^- \leftrightarrow \bar{C}H_2-CH=O$

I II

I is more stable.

$^-O-C\equiv\ddot{N}$ (OCN) $\leftrightarrow$ $O=C=\ddot{N}^{\ominus}$

I (Cyanate ion) II

I is more stable ∵ O is more electro -ve than N.

Rule 5 Separ^n of charge decreases stability of resonance structure.

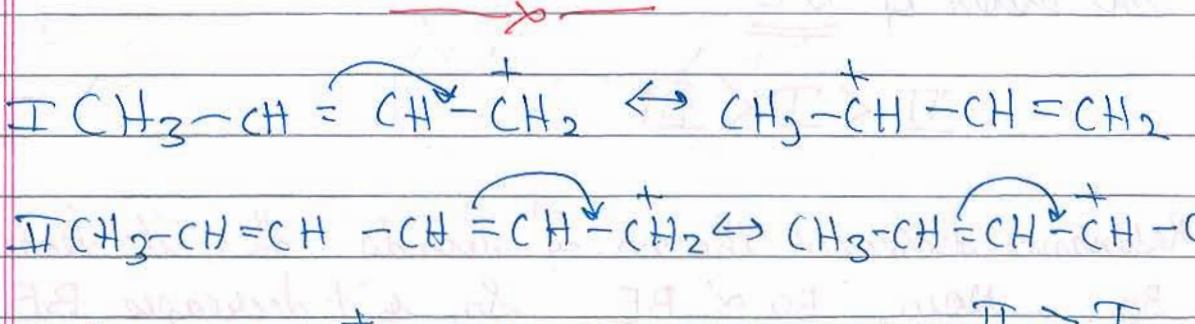
eg:

$$CH_2=CH-CH=CH_2 \leftrightarrow CH_2=CH-\overset{\oplus}{C}H-\overset{\ominus}{C}H_2 \leftrightarrow \overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{C}H_2$$

I II III

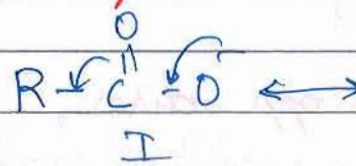
Stability I > II > III

eg



I > II > III

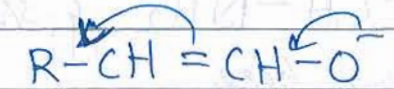
Rule 6 A sys. with more equivalent resonance structures has greater stability than the other with less no. of equivalent resonance structures. It is used to compare 2 diffl. sys.



1st sys



1st sys > 2nd sys.

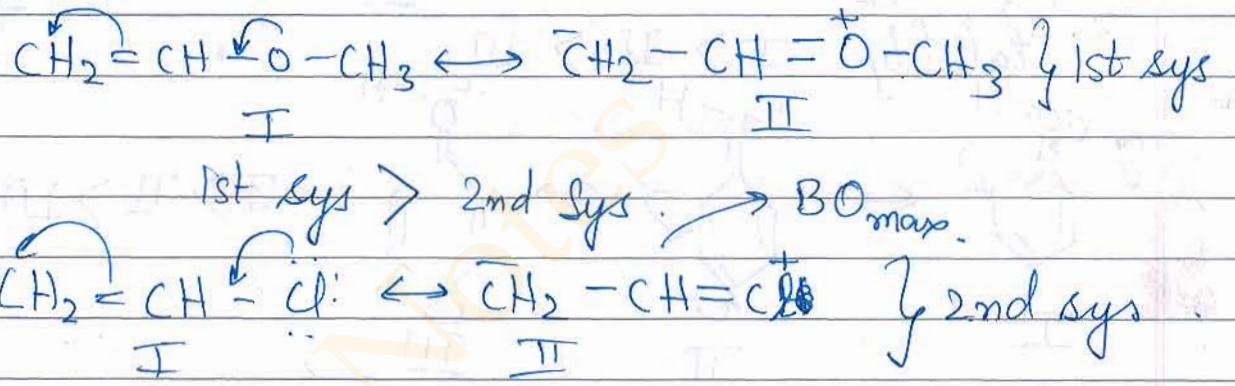


2nd sys.

II > I

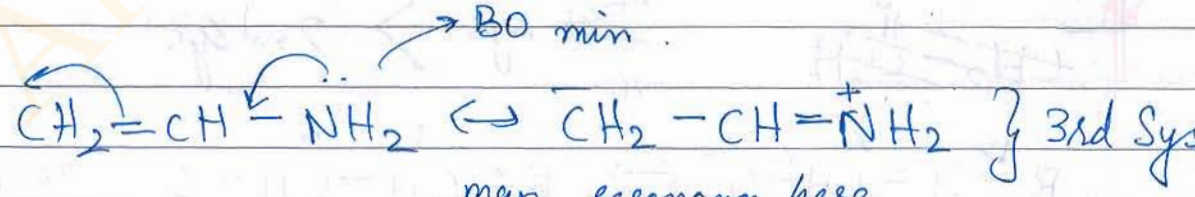
Rule 7: More the no. of resonance st., greater stability. Above eg. shows this. It is also for more than 2 sys.

Rule 8 (i) Extent of delocalisation depends on E_N of donar atom. Higher the E_N, smaller will be the extent of delocalisation.



(ii) Delocalisation is preferred b/w orbitals of like E. Greater the diff. in E of ~~obt~~ orbitals involved in delocalisation, smaller will be the extent of delocalisation.

(iii) If above 2 factors operate in opp. dirn, E diff. of orbitals is considered first.



2,3,1

* Inc. order of BL

1>3>2

II < I < III

* Resonance decreases the no. of bonds. So, it decreases BO. Now, BO ∝ BE. So, it decreases BE & thus increase BL. This can be used in comparing systems.

* Resonance effect is much stronger than I- effect.
(∵ In resonance, complete delocalisation of e^-_s takes place, while in I-effect, only partial delocalisation of only strongly bonded σ e^-_s takes place)

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* RESONANCE EFFECT & ACID-STRENGTH

$$R-OH \rightleftharpoons \underset{\text{ALKOXIDE}}{R-O^-} + H^+$$

$$R-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons \underset{\text{CARBOXYLATE}}{R-\overset{O}{\overset{\|}{C}}-O^-} + H^+$$

$$R-\overset{O}{\overset{\|}{C}}-O^- \leftrightarrow R-\overset{O^-}{\overset{|}{C}}=O$$

- Conjugate base of alcohol is called ALKOXIDE
- Any carboxylic acid is stronger acid than aliphatic alcohol (∵ carboxylic acid has resonance stabilised conjugate base).

- $R-OH < H_2O < RCOOH < RSO_3H$

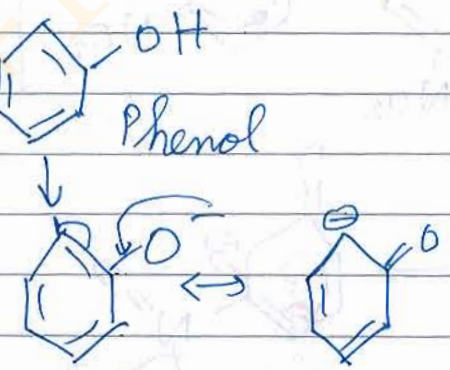
$$R-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-OH \rightleftharpoons R-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-O^- + H^+$$

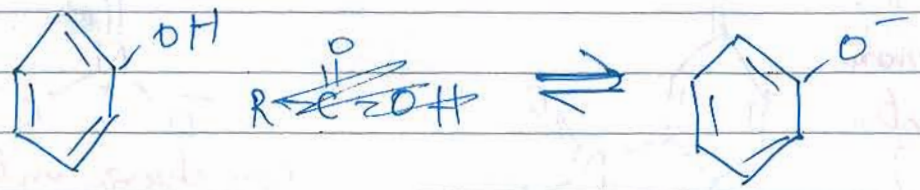
$$R-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}=O \leftrightarrow R-\overset{O}{\overset{\|}{\underset{O^-}{\underset{|}{S}}}}=O$$

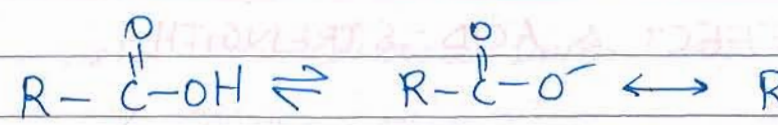
* Alkane sulphonic acid is stronger acid than carboxylic acid.

$$R-OH \quad < \quad \text{Phenol}$$

$$R-O^- \quad < \quad \text{PHENOXIDE}$$





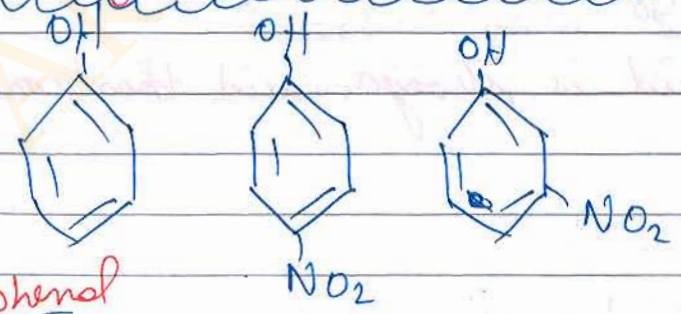


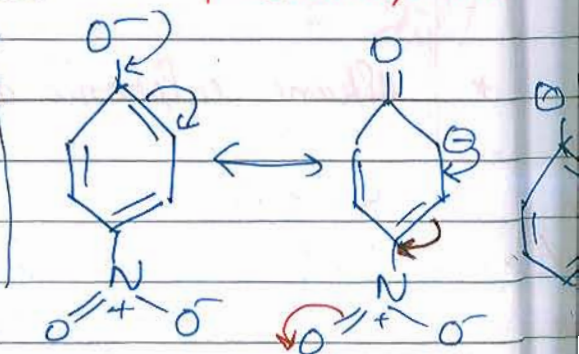
1) ✱ Carboxylate has both equivalent resonant structures than phenoxide.
2) ✱ In carboxylate -ve charge is only on Electro -ve atom while in phenoxide, -ve charge is on electro +ve & -ve atom.
Hence, from above 2, $R-COO^-$ is stronger than ~~or~~ aromatic alcohol.

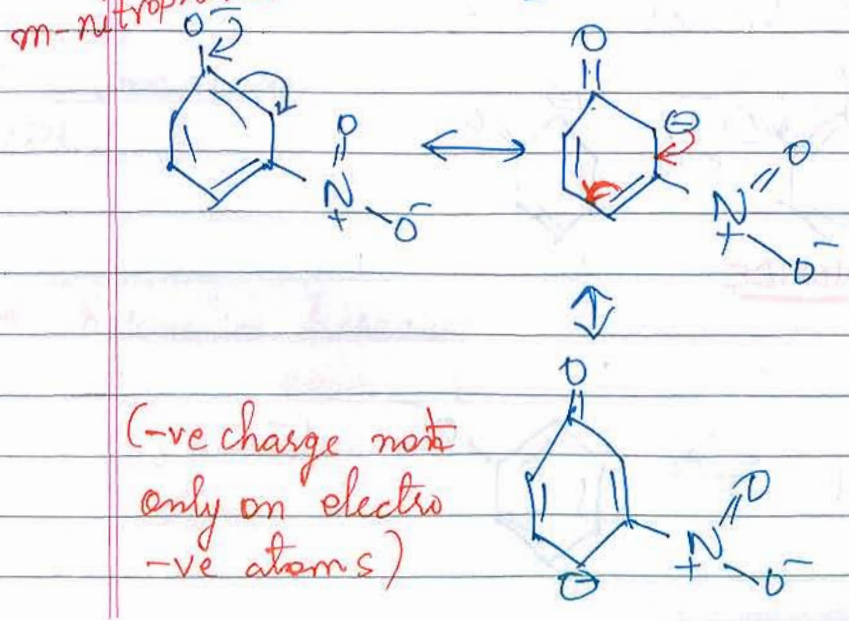
ORDER OF STABILITY

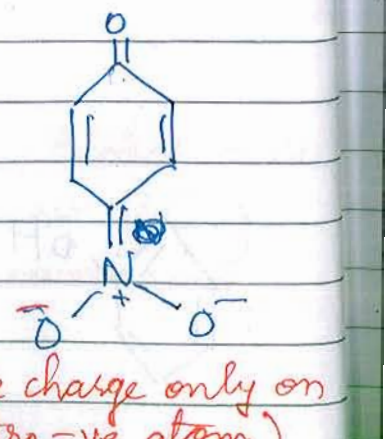
$R-OH < H_2O < \underset{\text{(aromatic)}}{R-OH} < R-COOH < R-SO_3H$
(aliphatic)

✱ Acidity of substituted phenols.









☆ Conjugate base of p-nitrophenol is more stable than conjugate base of m-nitrophenol. (See fig → -ve charge on electro -ve/+ve atom).

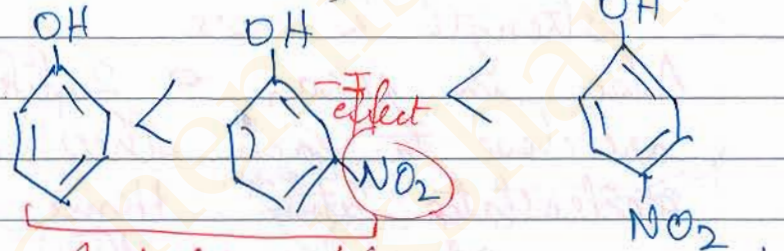
☆ Nitro grp. from para posⁿ exert e⁻ withdrawing -R effect, thus stabilises it. But, meta posⁿ can't exert -R effect because it is not in conjugⁿ with the -ve charge of conjugate base.

☆ Nitro grp. from from para posⁿ is in direct resonance with hydroxy grp from para posⁿ.

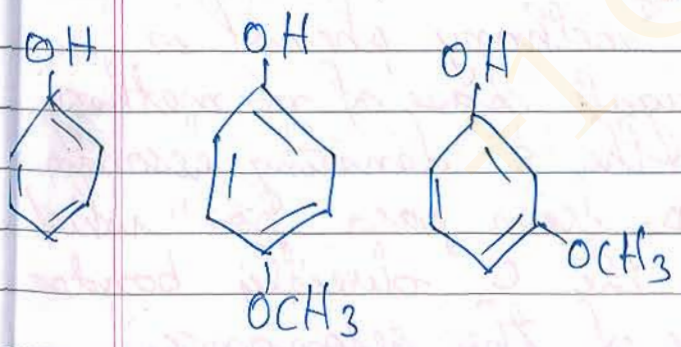
So, from above discussion,

R-OH

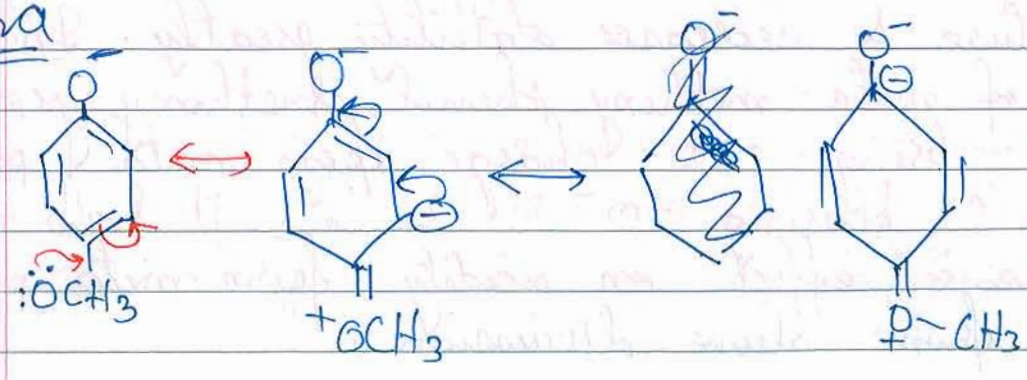
Stability :



Induction explains this.

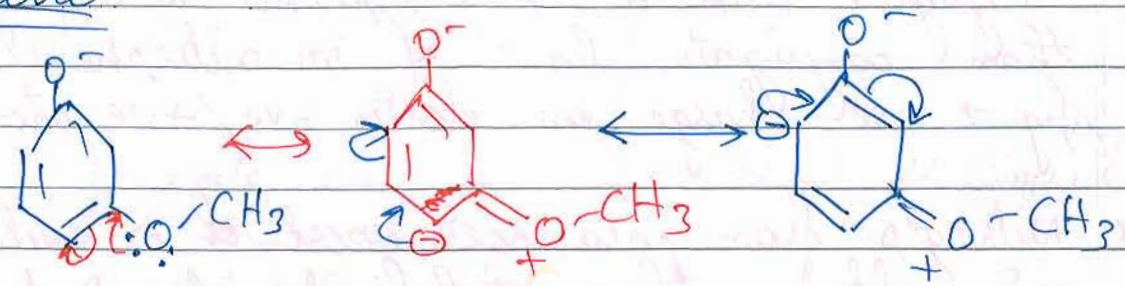


para



MeO : Methoxy

meta



Comparing meta & para methoxy

distance b/w +ve & −ve charge.

In para, distance is more, so, strength is less.

In meta, distance is less, strength is more.

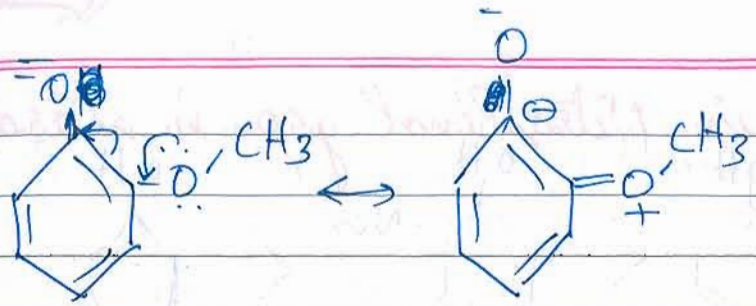
Also, in para, 2 like charges (−ve) are close to each other. So, increase in electrostatic repulsion. Hence, stability decreases.

~~Moreover, methoxy~~

Conjugate base of p-methoxy phenol is less stable than conjugate base of m-methoxy phenol. It is due to the e^- donating resonance effect of methoxy grp. from para posⁿ which bring −ve charge on the C directly bonded to (−O⁻) in one of the resonance structure & decreases stability greatly. In case of meta-methoxy phenol, methoxy grp doesn't bring −ve charge from meta posⁿ of on C-bearing O^-. & ∴ it has no resonance effect on acidity from meta posⁿ.

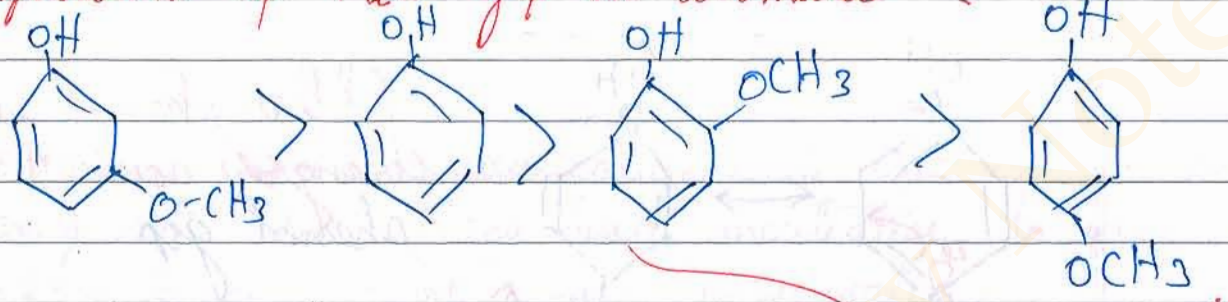
So, from above discussion,

pMeO < phenol < meta

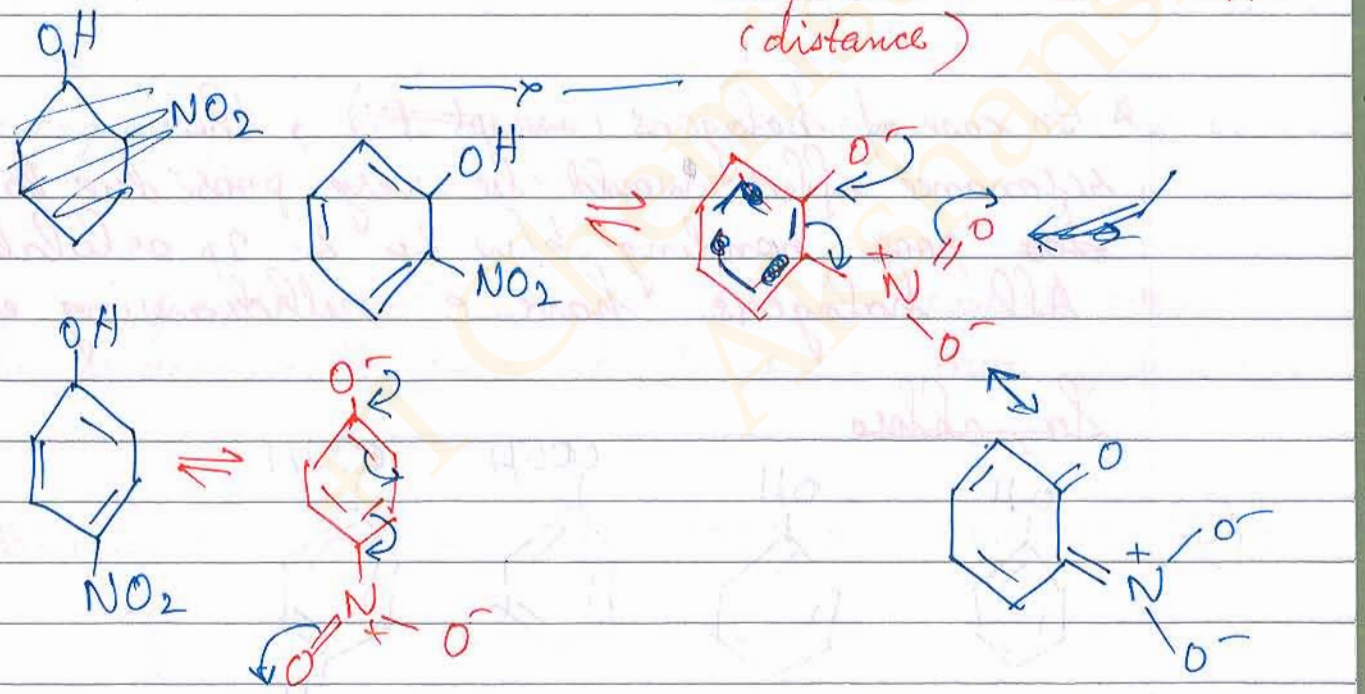


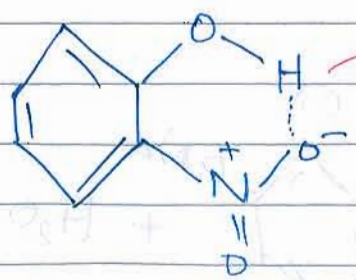
→ Destabilising nature.

- Comparison of M_eO grp in aromatic -



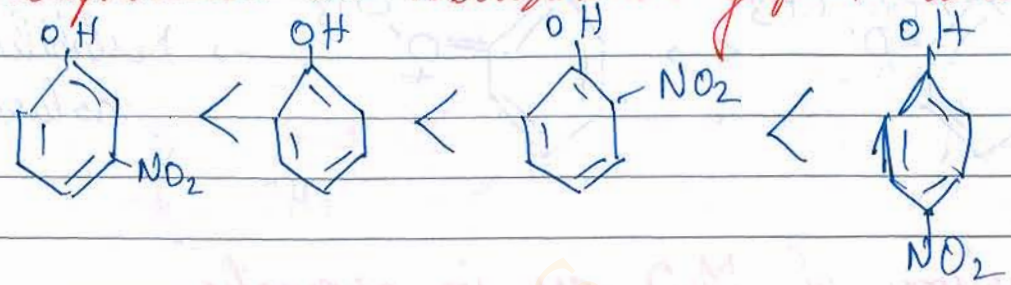
Comparison due to I-effect (distance)

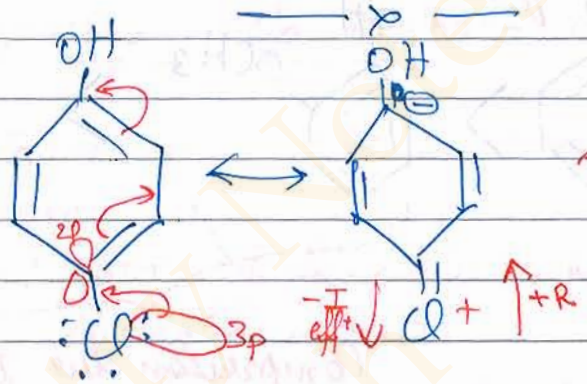




→ 6 membered ring is formed due to H-bonding (intra molecular). It retards removal of H^+. So, it would be slightly weaker acid than para NO_2. but stronger than meta NO_2.

- Comparision in Nitrophenol grp. in aromatic.



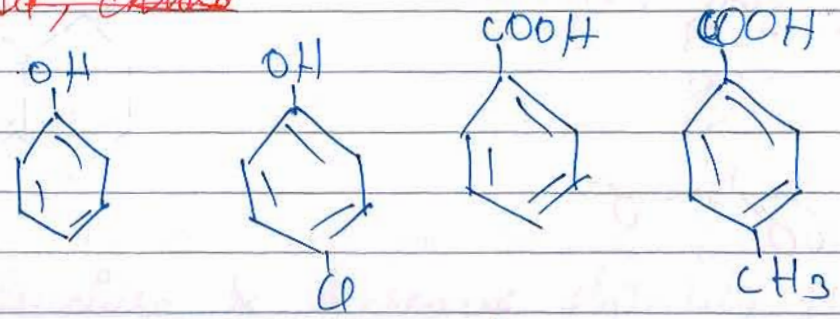


Chloro phenol is stronger acid than phenol grp.

* In case of halogens ~~(except F)~~, the resonance effect would be very poor due to ~~the~~ poor bonding b/w 2p & 3p orbitals. All halogens have e^- withdrawing effect.

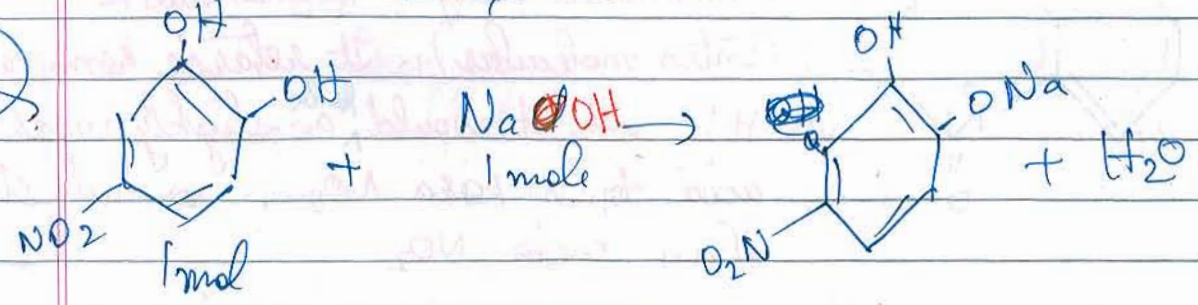
~~Eg, chloro~~

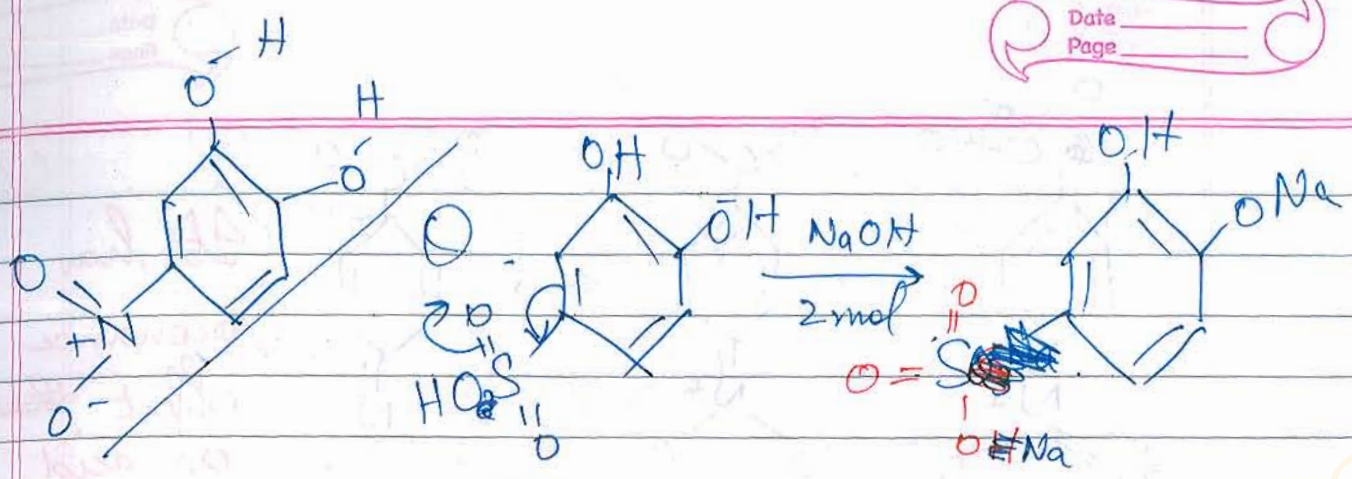
Q.



I < II < IV < III

Q.





✱ FEASIBILITY OF A NEUTRALIZATION RXN.

- Spontaneous rxn. (neutralisation) is one in which strong acid & strong base neutralise to give weak acid & weak base (conjugates).

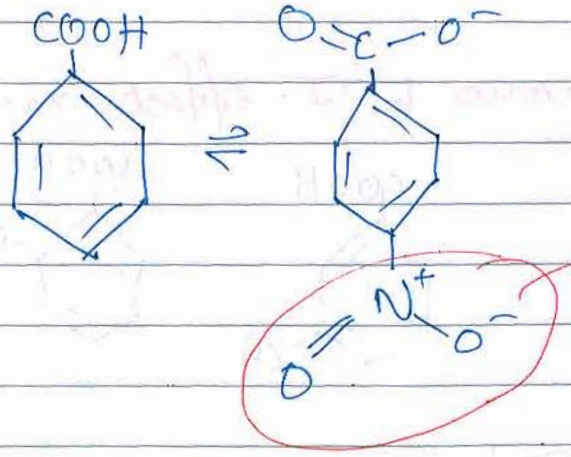
Q. $CH_3CH_2ONa + CH_3COOH \rightleftharpoons CH_3CH_2OH + CH_3COONa$

B_2	$Acid_1$	$Acid_2$	B_1
strong base	strong acid	weak acid	weak base.

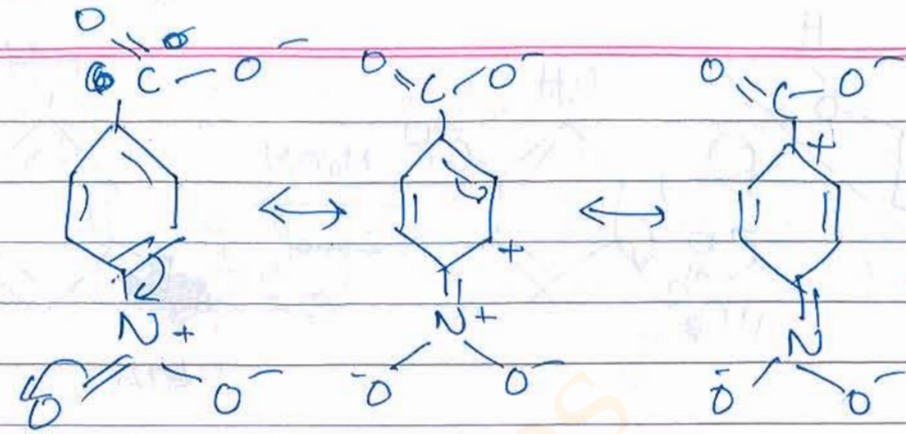
This rxn. is spontaneous.

- In a spontaneous rxn, $K_c > 1$ ∴ products would be predominantly produced. Reverse in non-spontaneous.

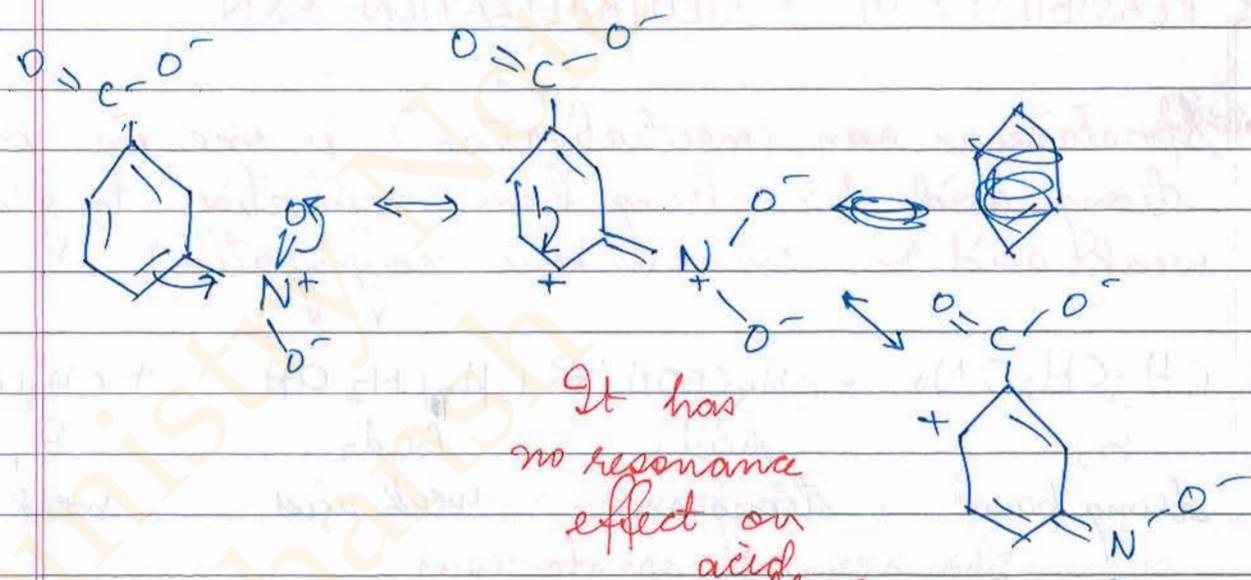
✱ BENZOIC ACID & SUBSTITUTED BENZOIC ACID



→ If it brings +ve charge on C-bearing $-COO^-$, increases acid & strength. & vice versa.

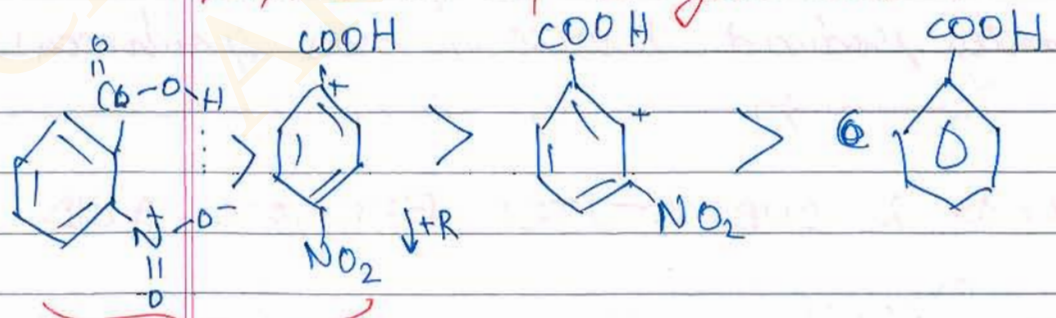


It has resonance effect ~~than~~ on acid.



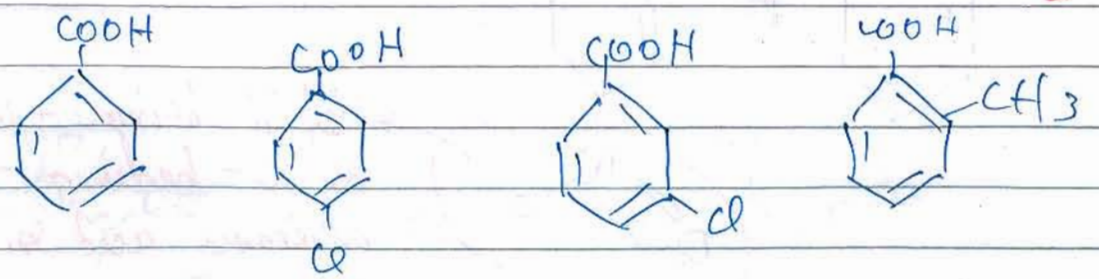
It has no resonance effect on acid attached.

* Sa. order of Benzoic acid.

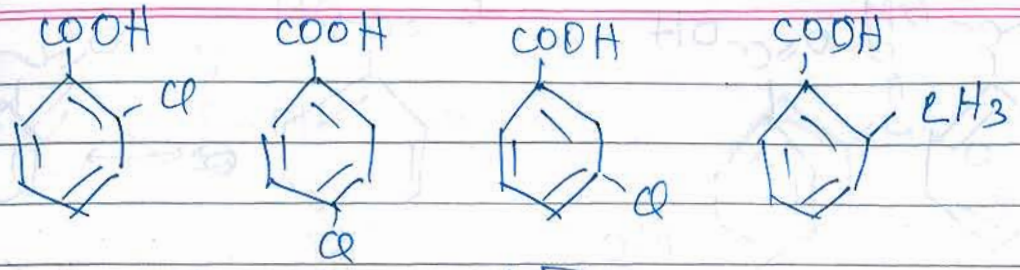


Ortho is max. (∵ Resonance & I-effect max)

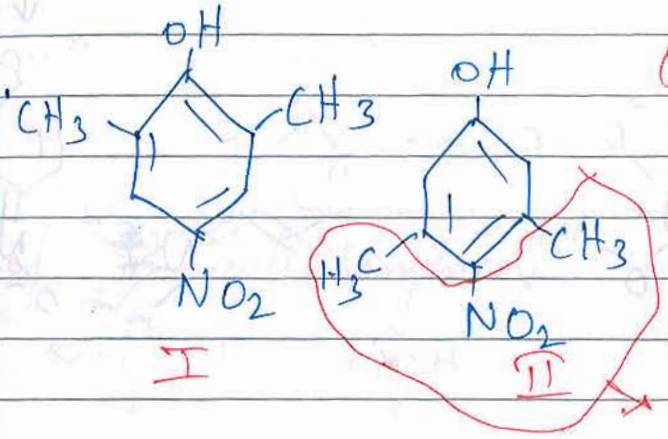
Q.



IV < I < II < III



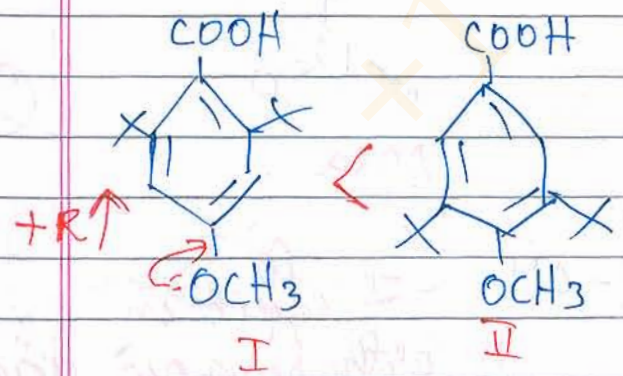
✓ IV < II < I < III .



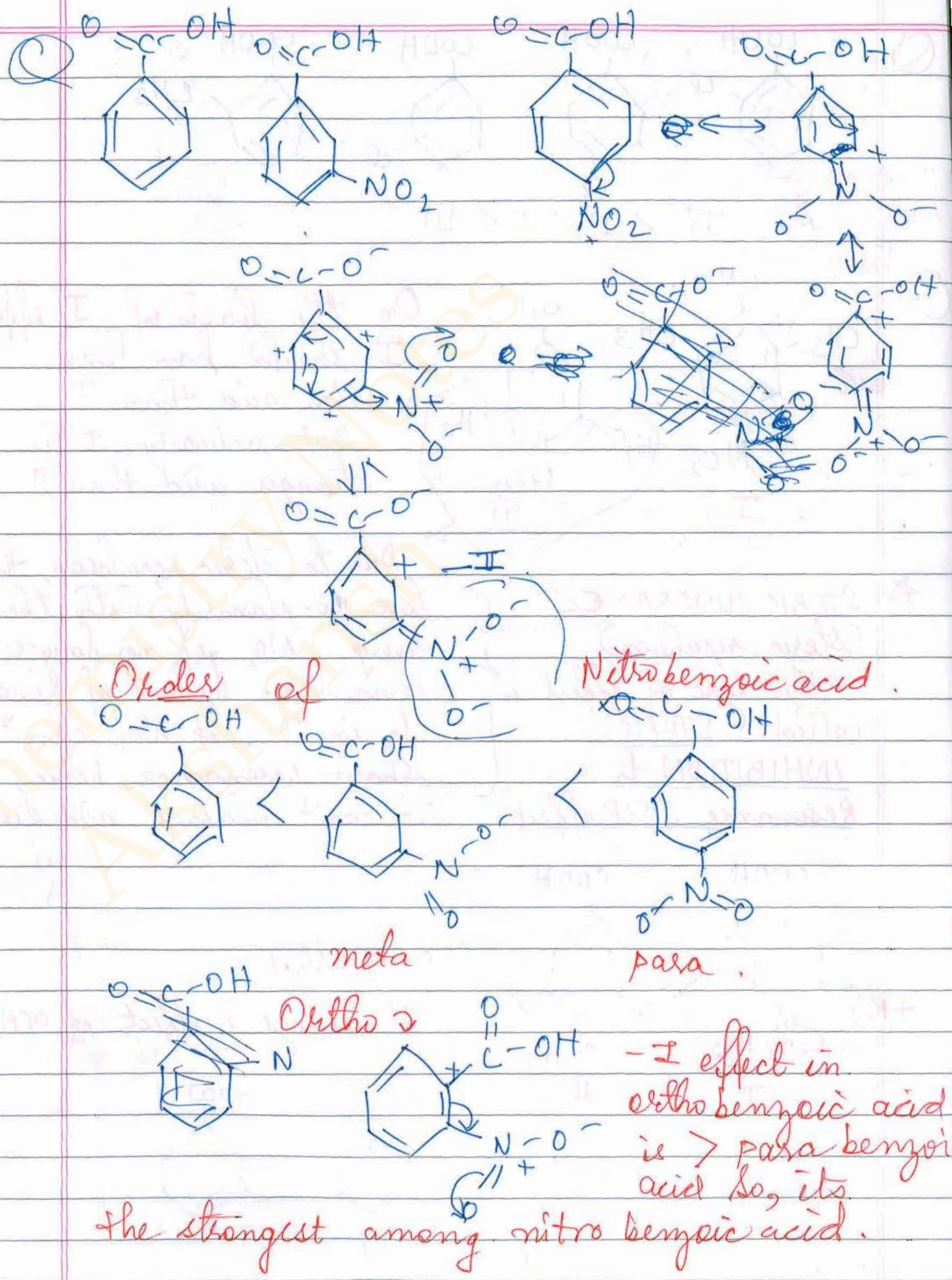
On the basis of I-effect, I should have been weaker acid than II
But actually I is stronger acid than II

Due to steric repulsion, they lose co-planarity with the ring. NO_2 grp. no longer remains in plane of ring. So, in II, NO_2 can't show resonance, hence, it can't increase acid strength.

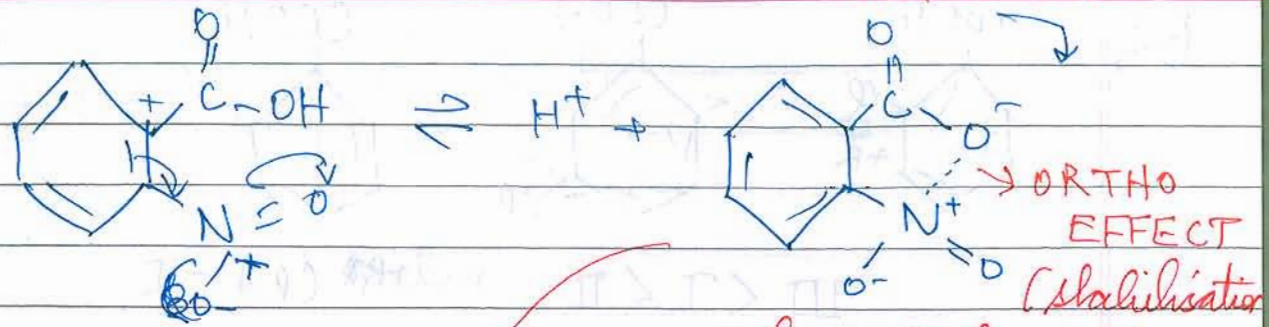
★ STERIC HINDRANCE (Steric repulsion)
This type of effect is called STERIC INHIBITION to Resonance (SIR effect)



(SIR effect)
↓ it destroys R-effect of OCH_3.


Order of
Nitrobenzoic acid.
meta
para.
Ortho >
-I effect in ortho benzoic acid is > para benzoic acid so, its the strongest among nitro benzoic acid.

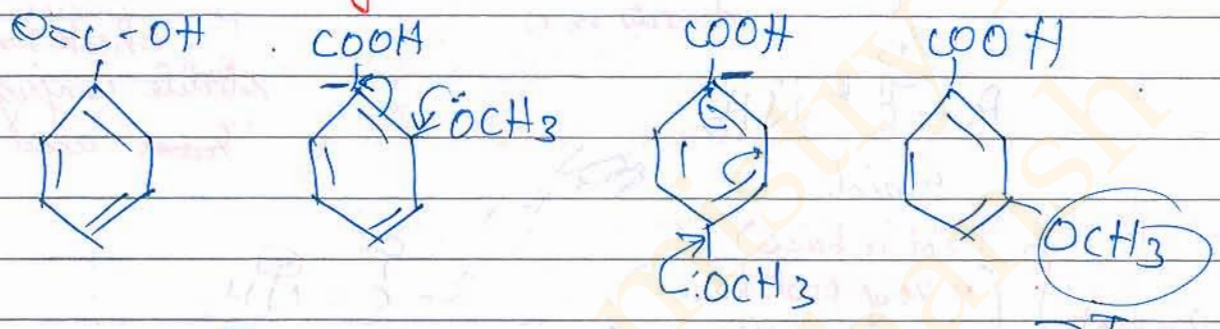
BIG REASON



→ ORTHO EFFECT (stabilisation of conjugate acid on lease from ortho posn)

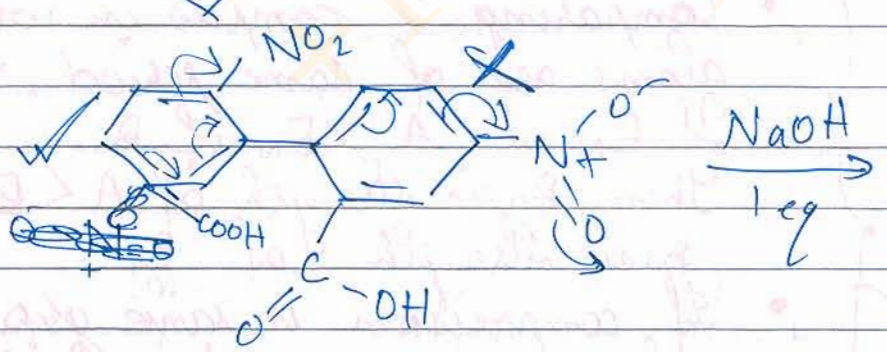
5 membered ring is formed. So, ortho gp. becomes the most stable of all nitrobenzenes.

Q.

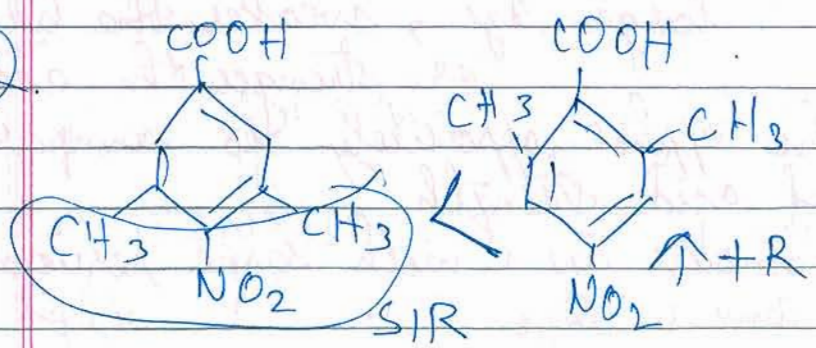


II < II < I < IV

Q.



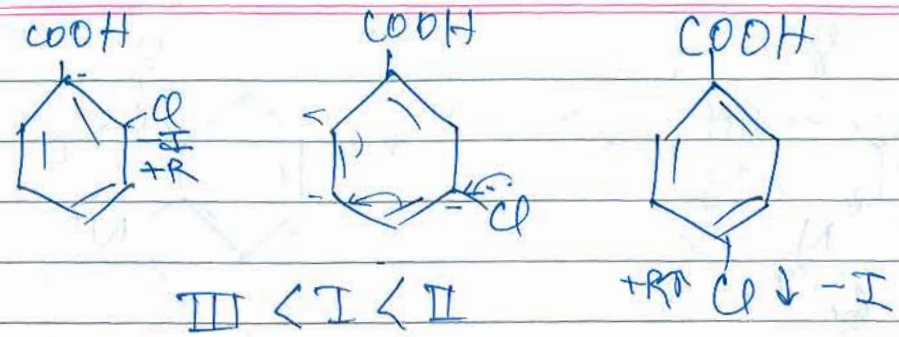
Q.



SIR

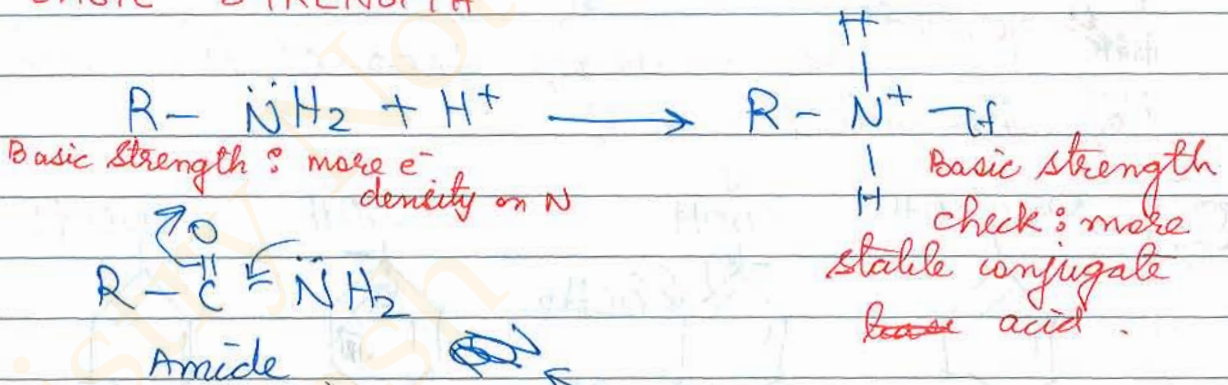
* In Cl, F... I-effect is stronger than R-effect.

Q.



III < I < II

* BASIC STRENGTH



I $R-\ddot{O}-H$

II $R-\ddot{N}(H)-H$

Basic II > I

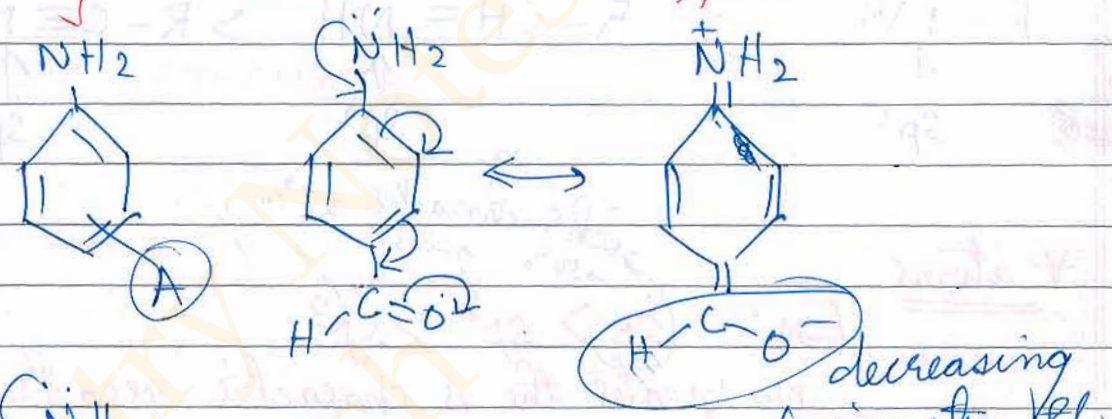
- Comparing 2 compds in which atoms are of same period, then, If E_N of A > E_N of B. Then, Basic strength of A < Basic strength of B.
- If comparison in same grp, larger size, weaker the base or stronger the acid.

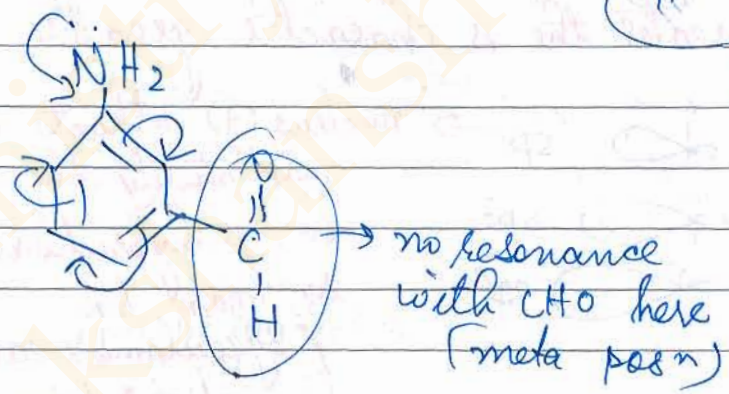
This applies oppositely to comparison of acid strength.

* In nutshell, compare E_N with same periods. & compare size " " grps.

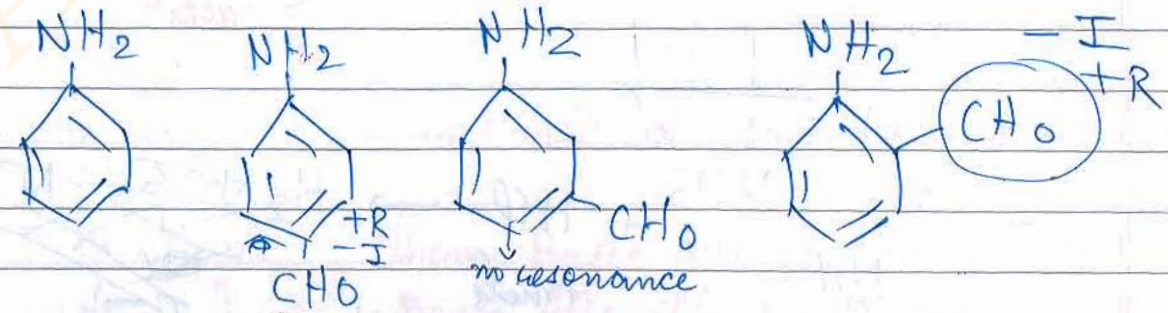
sys. because of 3 equivalent ⇌ structures. while if H^+ is attached to sp^2 g/p, no resonating st. is formed.

★ So hybridisation concept is used after seeing Resonance & I-effects.



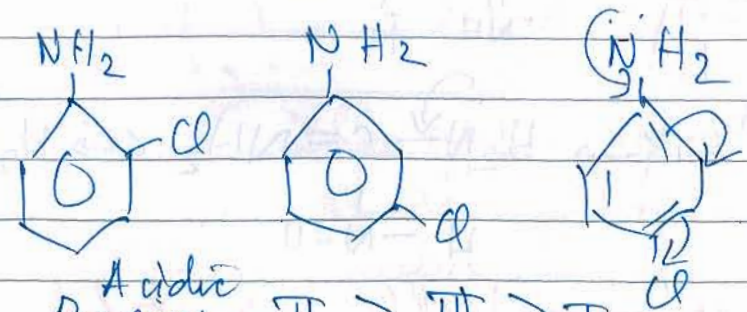


Q.



Basic : I > III > II > IV

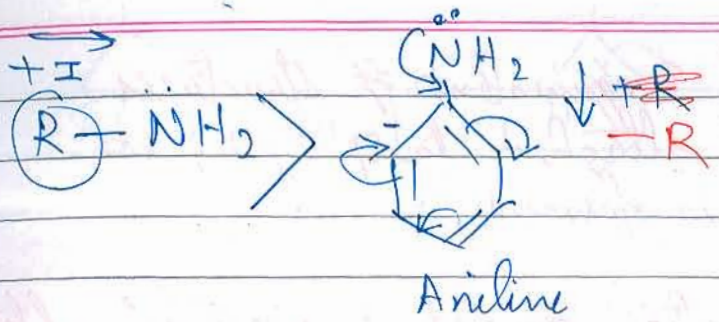
Q



Acidic ~~Basic~~ : II > III > I

Basic : II < I < III ~~II < III < I~~

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Date
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Q. 

Aniline

Q. AMINE IMINE NITRILE/CYANIDE

$R-\ddot{N}H_2 > R-CH=\ddot{N}H > R-C\equiv\ddot{N}$

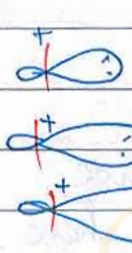
sp^3 sp^2 sp

s-character 25% 33.3% 50%

* ∀ atoms

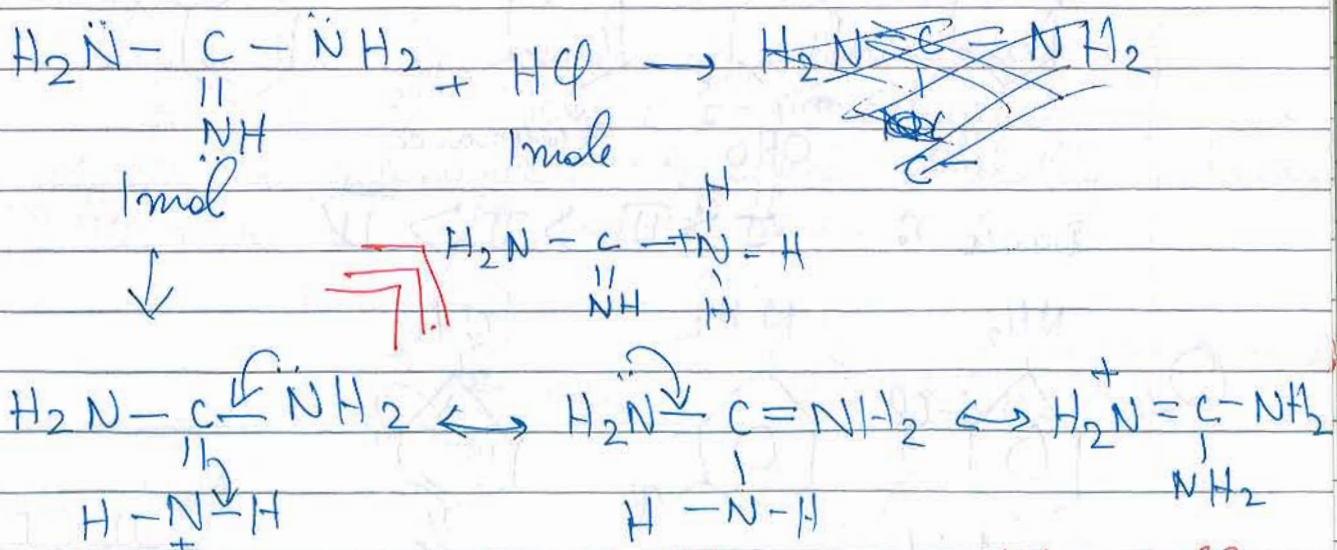
EN : $sp > sp^2 > sp^3$

or greater the s-character, greater the EN

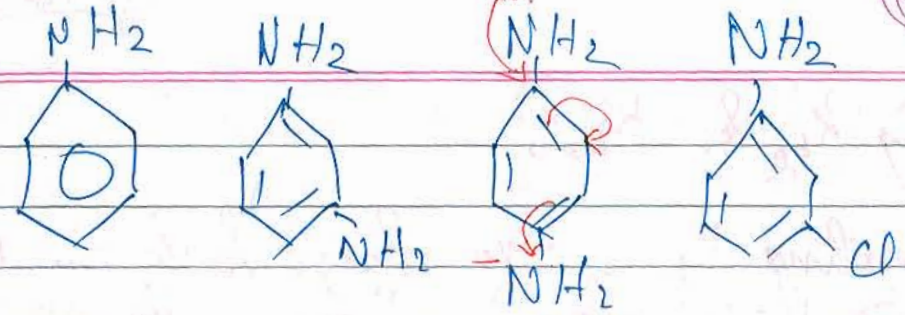


→ nucleus (+) attracts with max. ability, the e^-s (−) in sp hybridisation. So, max. EN

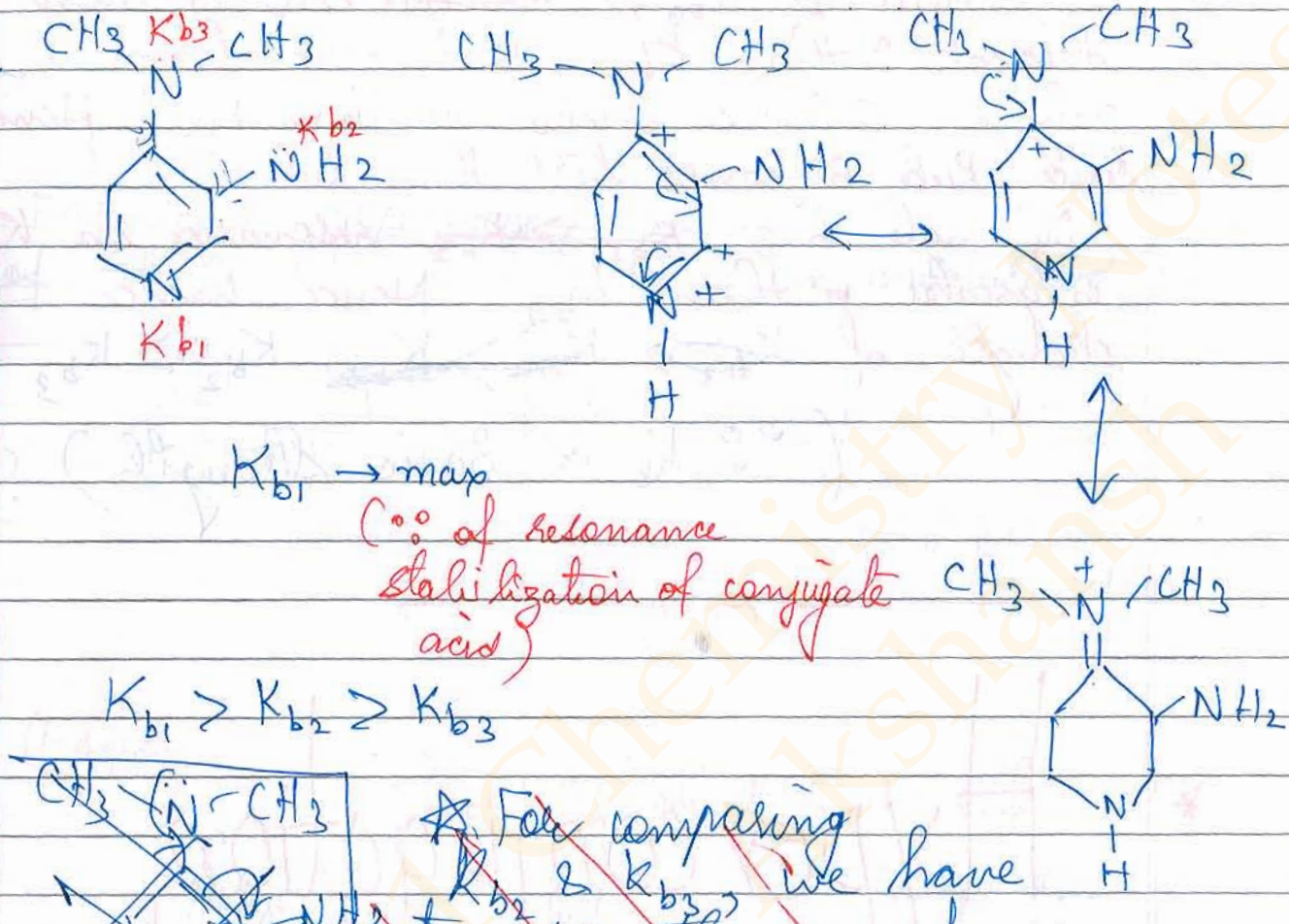
(By coulomb's law Electrostatic attⁿ ∝ $\frac{1}{(\text{Distance})^2}$)



Adding H^+ on sp gives highly conjugated & stable

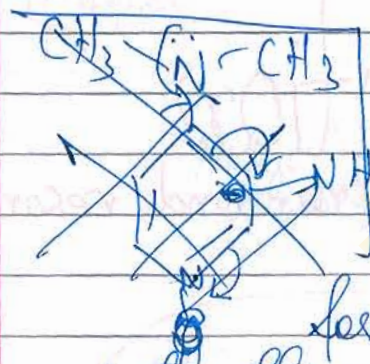


III > II > I > IV Basic : III > I > IV > II

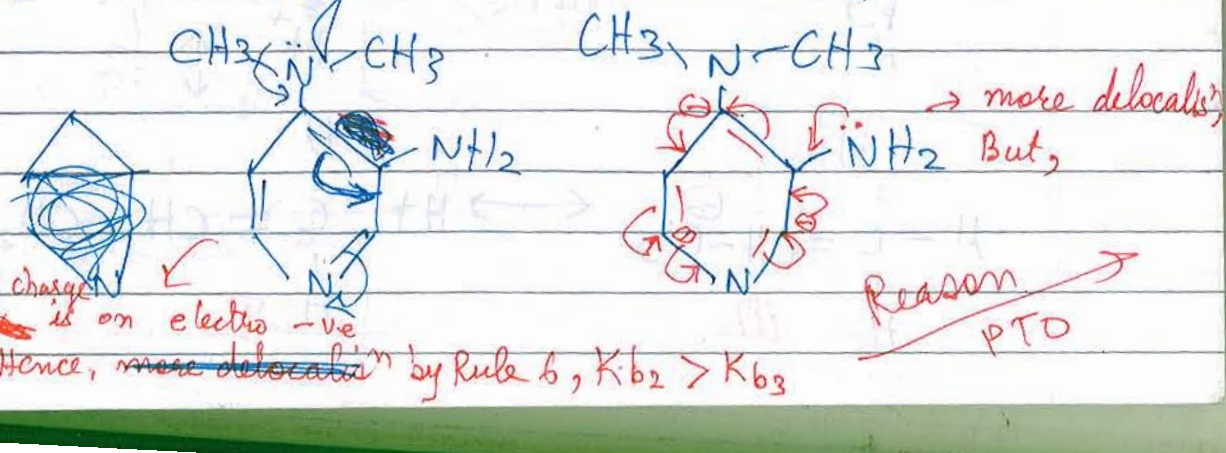


K_{b1} → max (∵ of resonance stabilization of conjugate acid)

$K_{b1} > K_{b2} > K_{b3}$



For comparing K_{b2} & K_{b3}, we have to see the no. of resonance st. that can be formed. More the delocalisation of e⁻, greater the resonance (+R-effect) stability. Hence, the basic strength would decrease.



→ more delocalisn, But,

-ve charge here is on electro -ve atom. Hence, ~~more delocalisn~~ by Rule 6, $K_{b2} > K_{b3}$

Reason PTO

• Comparing K_{b_2} & K_{b_3},

In resonating K_{b_3}, -ve charge lasts on N (an electro (-ve) atom). Hence, its st. would be more stable.

Now, in K_{b_2}, ~~-ve chas~~ there is more delocalis^n than K_{b_3}. But, -ve charge is only on C (less electro -ve than N)! Hence, Since Rule 6 comes first than Rule 7, So,

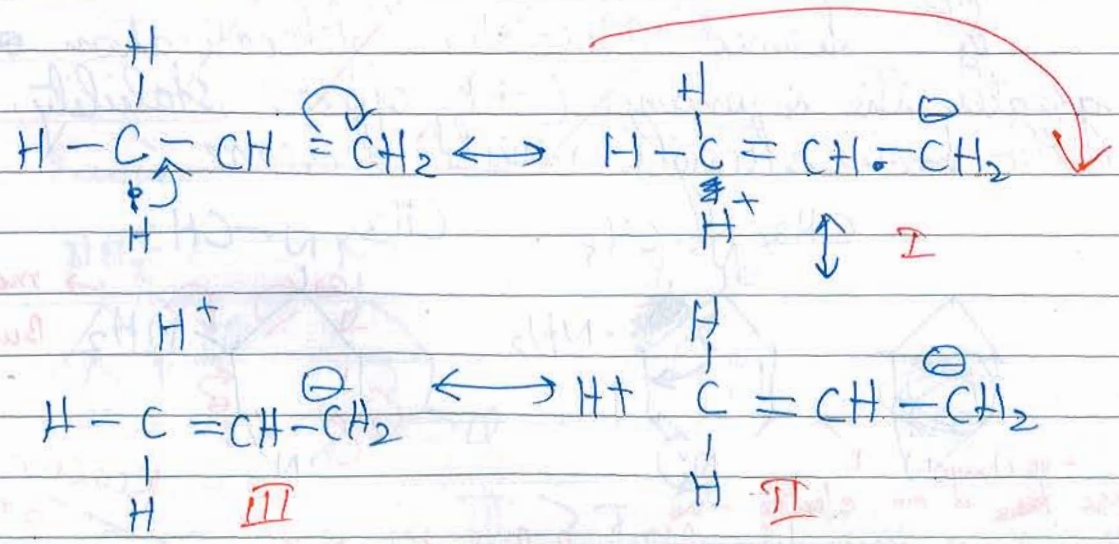
By rule 6 ~~$K_{b_2} \rightarrow K_{b_2}$~~. Resonance in K_{b_3} is greater than K_{b_2}. Hence, basic strength of ~~K_{b_2}~~ ~~K_{b_2}~~ ~~K_{b_3}~~ $K_{b_2} > K_{b_3}$

($\because K_b \propto$ Basic Strength)

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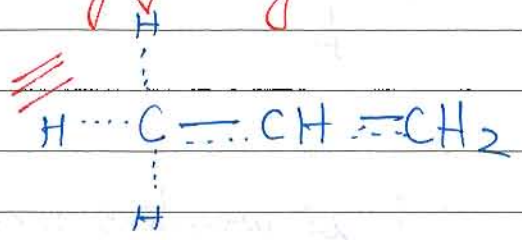
* # Hyperconjugation

(no-bond resonance)



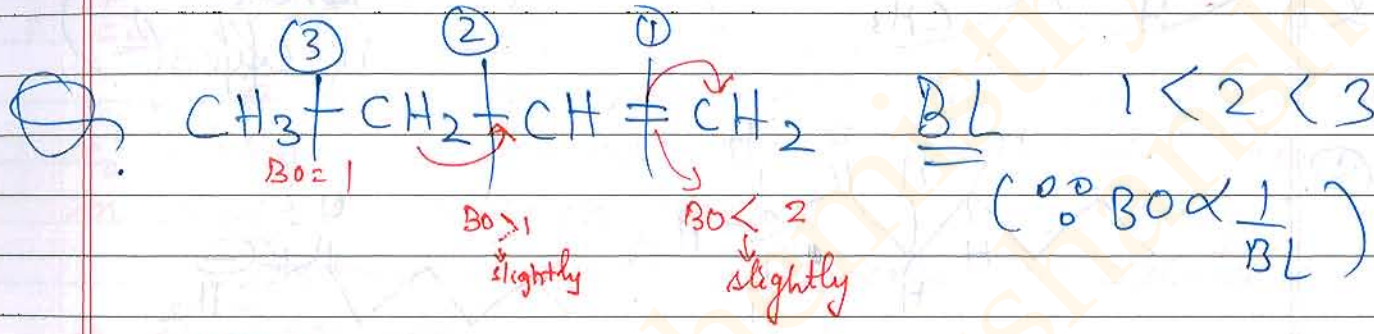
I, II & III are hyperconjugating structures.

Hyperconjugation hybrid



BO ∝ 1/BL

Define Hyperconjugation: Hyperconjugation is delocalisation of σ e⁻s of C–H bond, α to an unsaturated C.



BL: 1 < 2 < 3

(∵ BO ∝ 1/BL)

• Effects

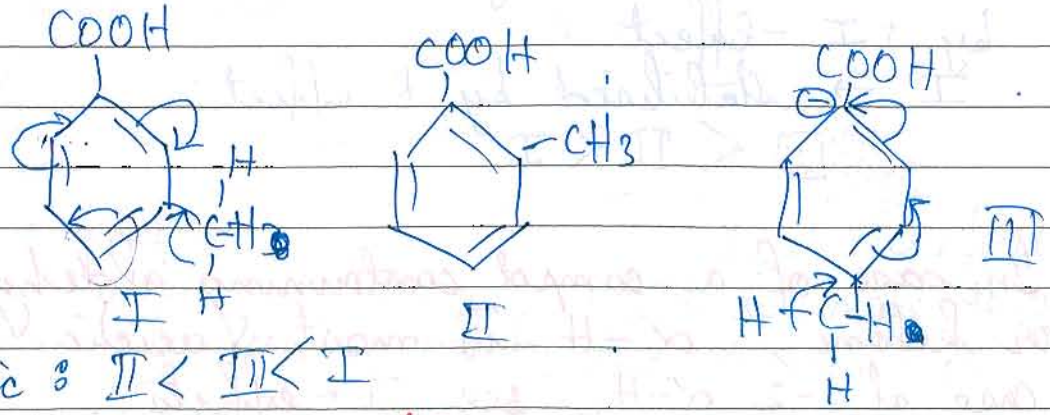
I-effect < H-effect < R-effect.

I-effect: partial delocalisation

H-effect: full delocalisation

R-effect: stronger than H-effect

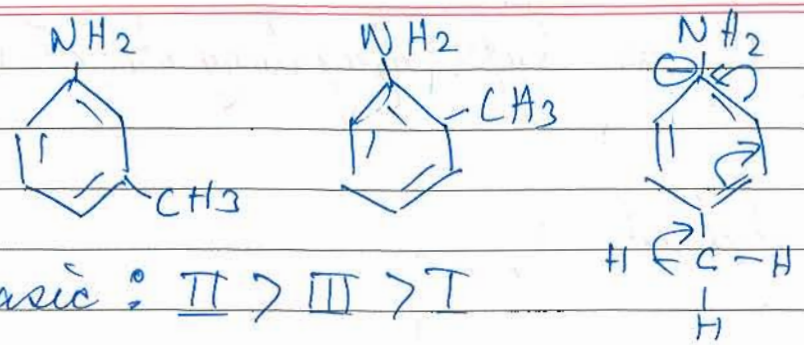
Q.



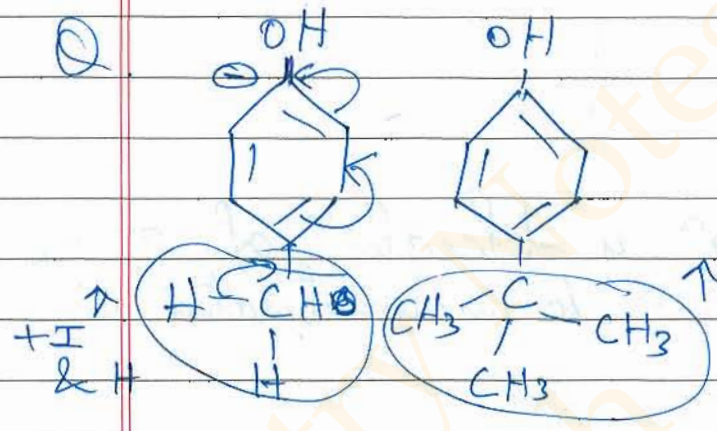
Acidic: II < III < I

• On the basis of I-effect III is strongest acid.
But, I is strongest acid due to H-effect

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Q. 

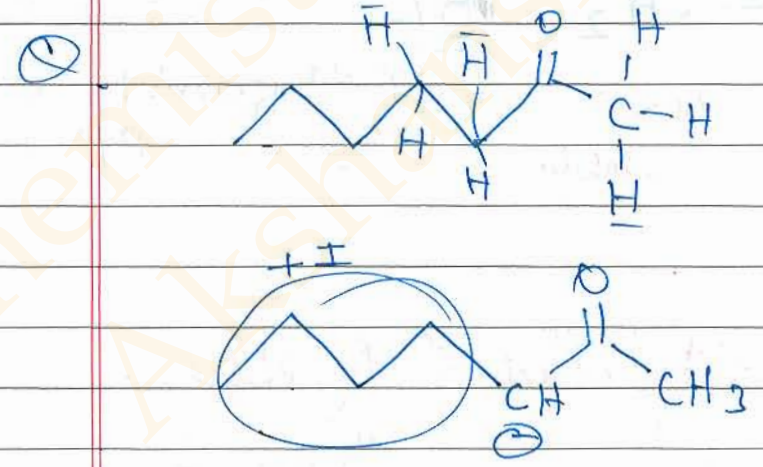
Basic : II > III > I

Q. 

I is weaker acid than II

I < II

(∵ I shows H-effect)

Q. 

III → no H-effect, least acidic.

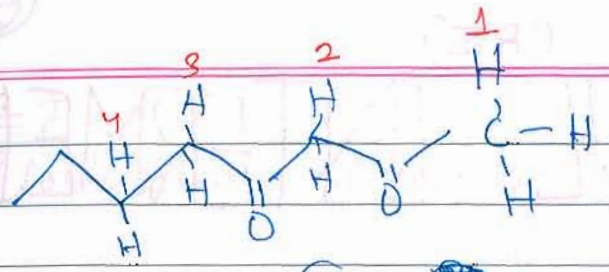
II → stabilised by R-effect, destabilised by +I -effect.

I → stabilised by R-effect.

III < II < I

- In case of a compd containing aldehyde & or ketone, α-H is most acidic. In case of 1-2 α-H, see I-effects.

Q.



(2) > I > 3 > (4) → No H-effect.

(2) → Resonance from 2 sides

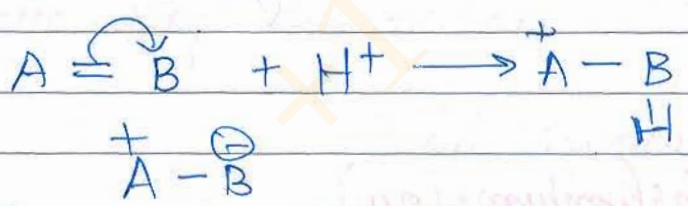
3 → destabilised by +I effect

ELECTROMERIC SHIFT

Its a temporary effect involving displacement of e^- during a chemical rxn. It is neither observed in reactant, nor in product.

Electromeric shift determines the orientation of a chemical rxn.

Electromeric shift occur in a direction which favour the chemical rxn.



Electromeric shift

+E effect

It is the effect in which e^- move away from an atom. Atom or grp. which donate e^- during electromeric shift produces +E effect.

-E effect

It is the effect in which e^- move towards an atom. An atom or a grp. which accept e^- by electromeric shift produces -E effect.

(RI)

REACTIVE INTERMEDIATE

* Reactive Intermediates are the species produced during a chemical rxn in the intermediate steps. Nature of reactive intermediate determines the nature of product in a chemical rxn.

* PROPERTIES of Reactive Intermediates

1) They are highly unstable species having a lifetime of approx. 10^{-15} sec.

2) Reactive Intermediate can't be isolated & preserved in a chemical rxn.

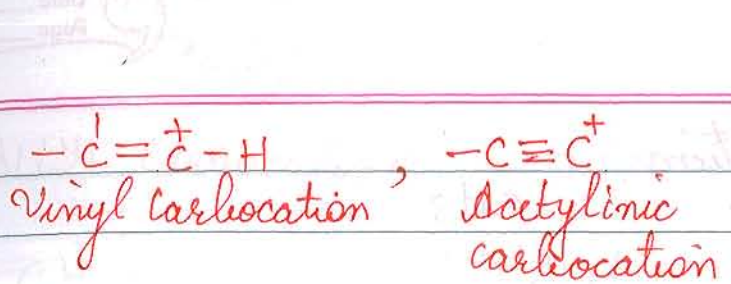
3) Stability of a reactive intermediate determine the rel. amts. of diff^{t} products in a chem. rxn. More stable the reactive intermediate, the corresponding product is major product.

* TYPES of R.I.

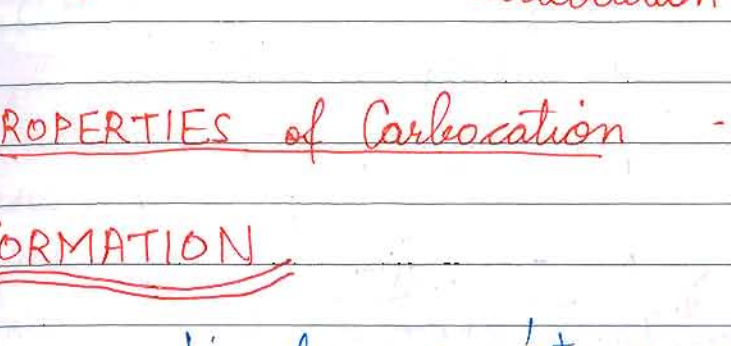
**** (1) CARBOCATION (Carbonium ion)
*** (2) CARBANION
** (3) FREE RADICAL (Radical)
* (4) CARBENE

(1) CARBOCATION : It is the reactive intermediate in which 1 of the C possesses +ve charge.

eg : 
methyl carbocation, ; R^+ Alkyl carbocation



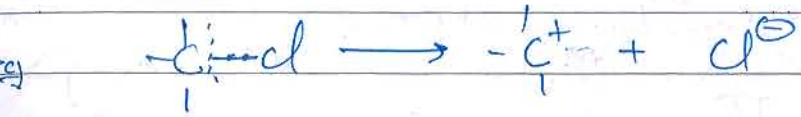
Vinyl carbocation



Acetylinic carbocation.

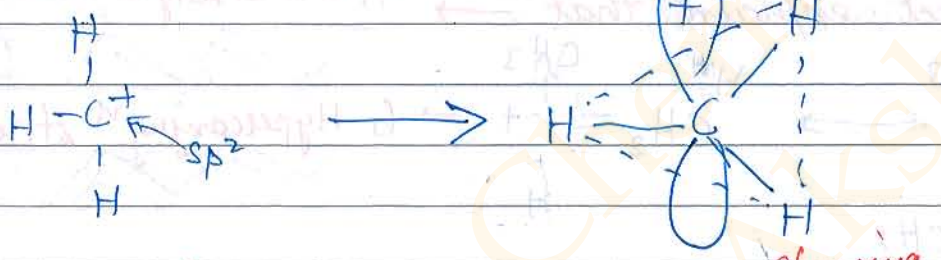
- PROPERTIES of Carbocation.

☆ FORMATION

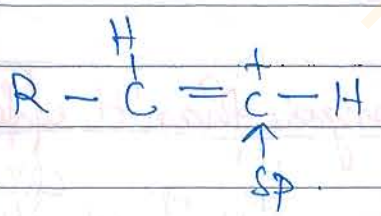


(i) A carbocation is formed by heterolytic fission of a covalent bond to a C atom in a molecule.

(a) ~~ALKYL Carbocation~~



(2) Carbo Alkyl carbocation will be a planar structure. showing



Vinyl carbocation has linear structure.

(3) RELATIVE Stability of carbocation -

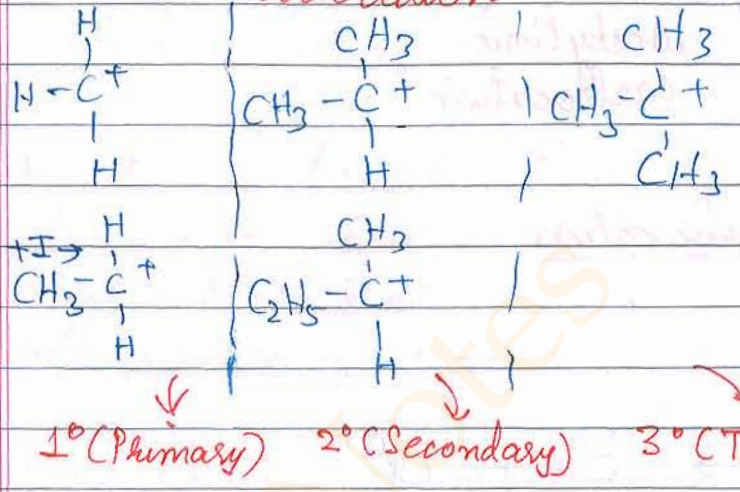


Carbocation is an e⁻ deficient reactive RI.

(i) An e⁻ donating atom/grp stabilises carbocation, lowers its PE.

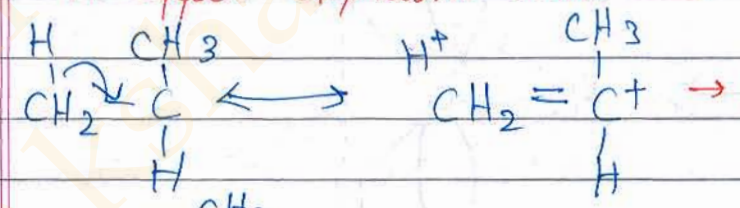
(ii) An electron withdrawing grp. destabilises carbocation, increases its PE.

(a) ALKYL carbocation

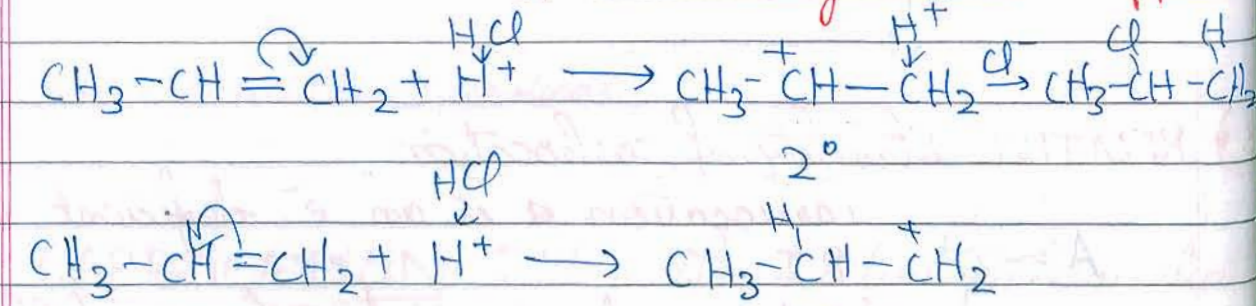


Carbocation Stability: $CH_3^+ < 1° < 2° < 3°$ (I-effect)

- If comparison is among carbocations of same grp, I-effect can't explain stability. H-effect explains that → (∵ H-effect is stronger than I-effect)



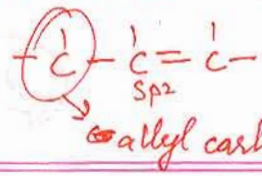
- NOTE: 2 times I-effect is stronger than H-effect.



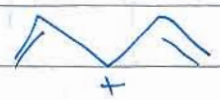
2° more stable than 1°.

So, I is major product than II.

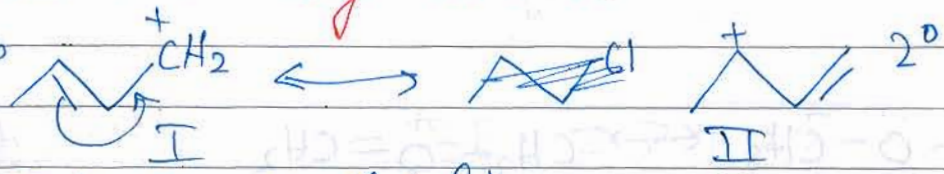
Allyl : α to double bond



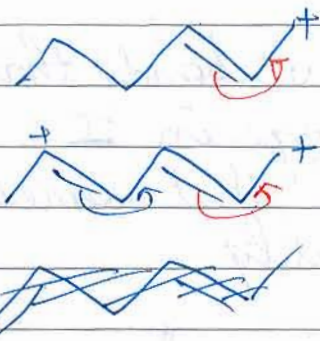
b) ALLYL carbocation $\left(-\overset{1}{C}=\overset{1}{C}-\overset{+}{\underset{1}{C}}-\right)$

eg $CH_2=CH-\overset{+}{C}H_2$, 

An allyl carbocation is always more stable than an alkyl carbocation due to resonance stability present in allyl carbocation.



II > I : Stability.
2° 1°

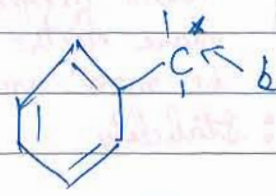


II > I : Stability.
∵ II has more no. of Resonance st.

(c) BENZYL carbocation.

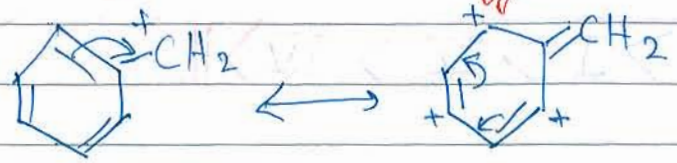


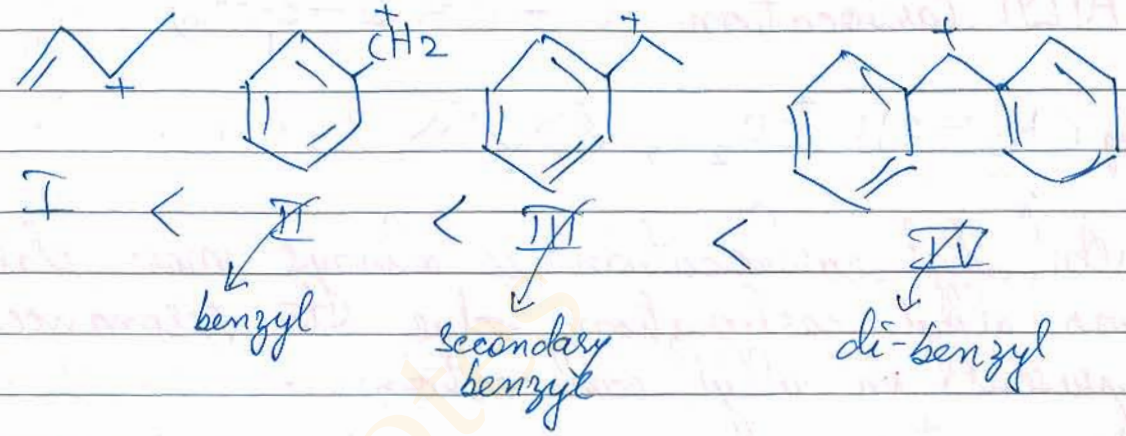
C_6H_5 : Phenyl
Phenylic C.



Benzyl.

A benzyl carbocation is more stable than an alkyl or allyl carbocation due to greater resonance stability in the benzyl carbocation.





(d)

$CH_3-\underset{I}{\ddot{O}}-\overset{+}{C}H_3 \longleftrightarrow CH_3-\overset{+}{O}=CH_2$

$CH_2=CH-\underset{II}{\overset{+}{C}H}-CH_3 \longleftrightarrow CH_2-CH=CH-CH_3$

In I, there are more no. of σ bonds than II. & Now, O has +ve charge in I. But extra bonds is the rule that comes before, so, I > II : stability.

$CH_3-\ddot{N}H-\overset{+}{C}H_2 \longleftrightarrow CH_3-\overset{+}{N}H=\overset{\ominus}{C}H_2$

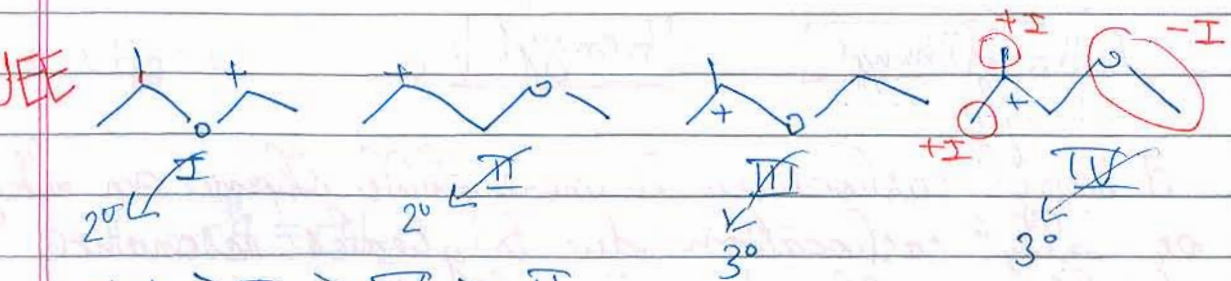
III

III > I > II

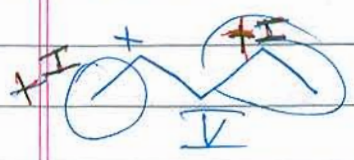
By rule 6, +ve charge on electro -ve atom decreases stability. Since O is more electro -ve than N, so, O^+ would be more unstable than N^+.

Hence III > I : Stability.

JEE



III > I > IV > II



III > I > V > IV > II

• If a carbocation is stabilised by resonance effect in which no. of covalent bond increases, the stability gain will be greater than any other effect.

———×———×———

(e)

$R-\overset{+}{C}H_2$ (I) > $R-CH=\overset{+}{C}H$ (II) > $R-C\equiv\overset{+}{C}$ (III) : Stability.

$R-CH_2 \overset{x}{-} H$ (sp³)

$R-CH=CH \overset{y}{-} H$ (sp²)

$R-C\equiv C \overset{z}{\equiv} H$ (sp)

BE : z > y > x

So, PE ″

So, stability III < II < I.

~~R-Cl~~ $R-C\equiv C \overset{z}{\equiv} H$

sp → requires max. E than above 2 to break H. Hence, PE max than above two. So, stability least than above 2.

———×———

* FATE OF CARBOCATION

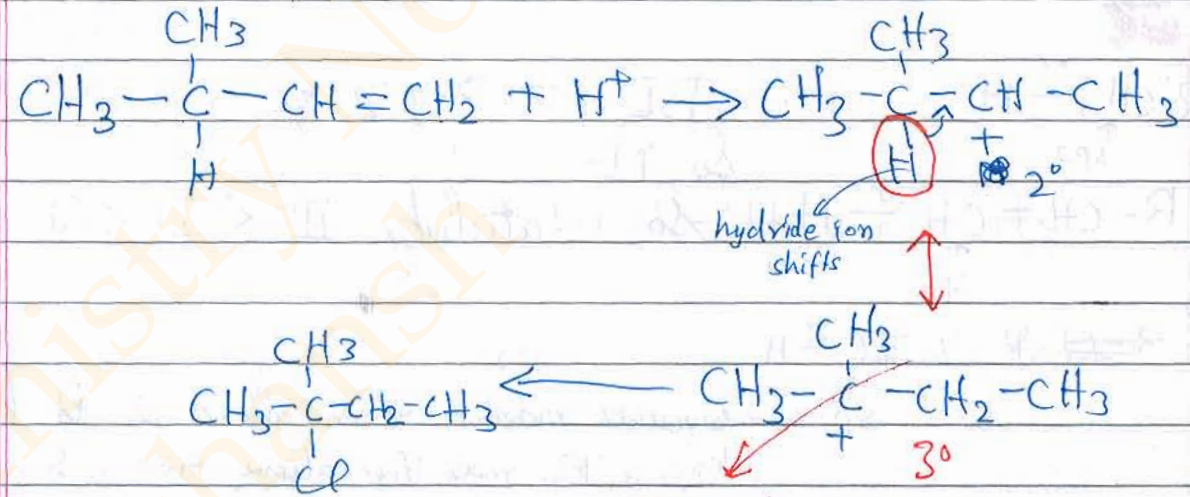
A carbocation produced in a chemical rxn has characteristic of rearrangement into more stable carbocation, provided the structure of carbocation allow this. ~~The rx~~

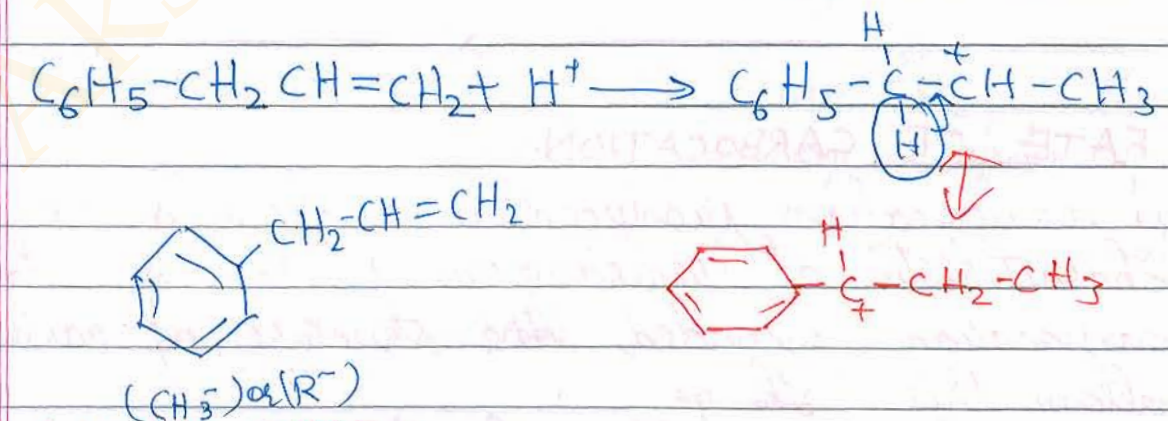
The most stable carbocation produced after reassay gives the major product by forming a covalent bond with -ve part (nucleophile) of reagent.

Rearrangements : (must occur from α-posⁿ)

(A) Hydride shift
(B) Alkyl shift
(C) Ring expansion

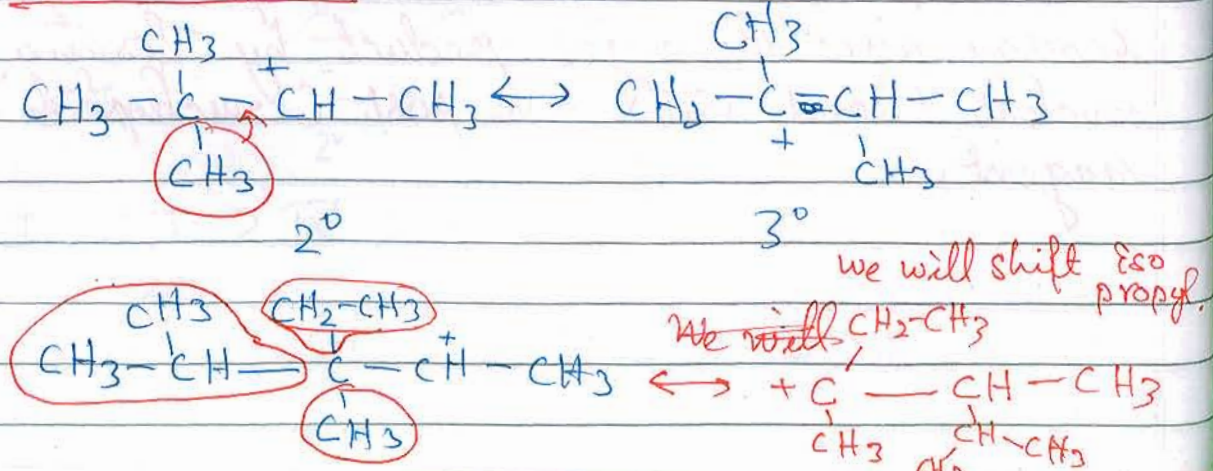
(A) HYDRIDE (H^-) SHIFT



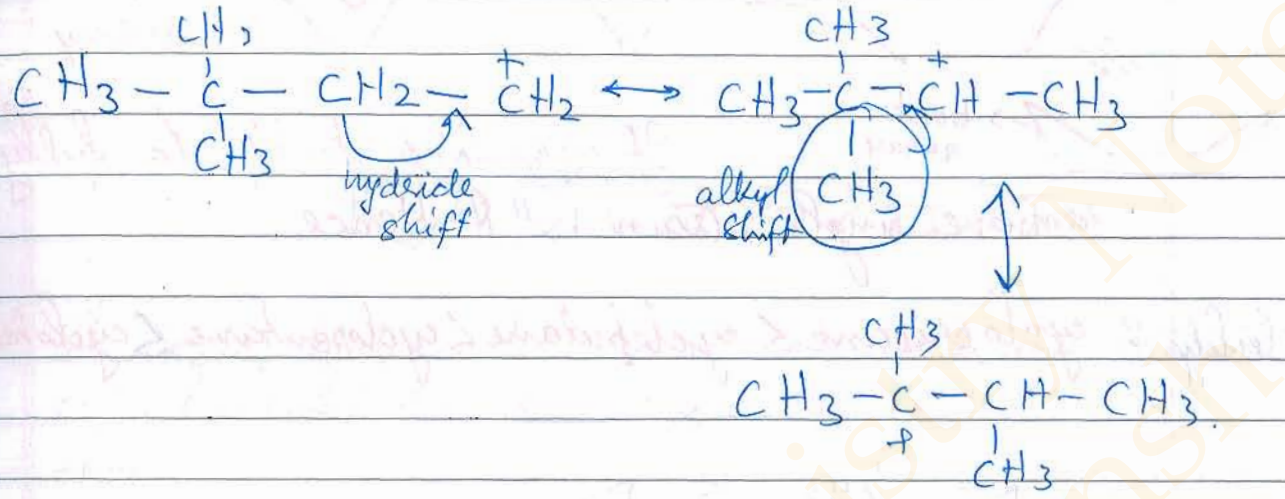


(CH3⁻) or (R⁻)

(B) ALKYL SHIFT

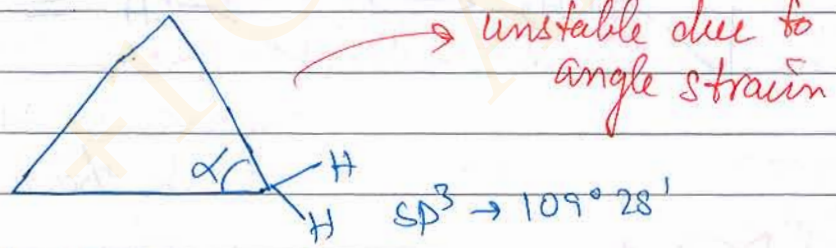


In ↙ among methyl, ethyl & isopropyl, we will shift isopropyl since it has less no. of α-H. ∴ the resulting carbocation should have max. no. of α-H for more no. of hyperconjugⁿ st.

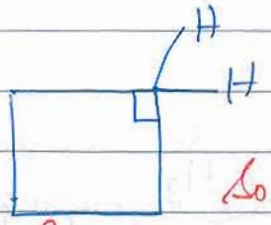


(c) Rearrangemt. by RING EXPANSION.

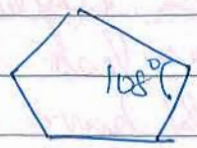
- Ring Strain & Stability



angle α should have been 109° 28', but, the Δ is equilateral. So, its angle is 60°. Hence it has ANGLE strain (strain due to angle)



Here also, its 90° instead of 109° 28'. So, it too has angle stain but less than cyclopropane. Hence, its more stable than

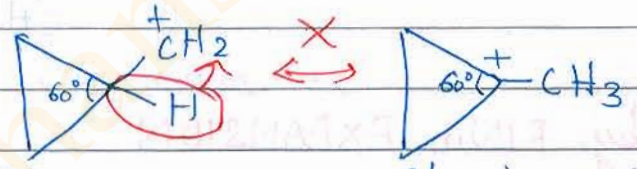


In this angle strain is almost negligible.

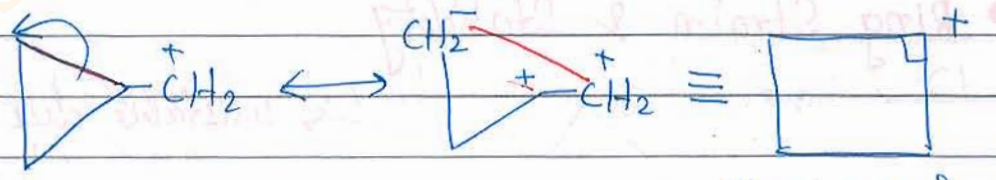


It arranges itself to fully remove angle strain. Hence

Stability : cyclopropane < cyclobutane < cyclopentane < cyclohexane

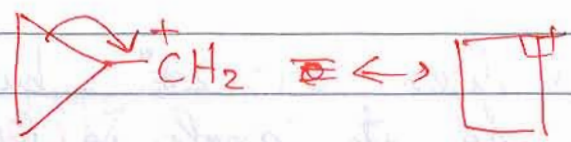


Strain = 49° Strain = 60°

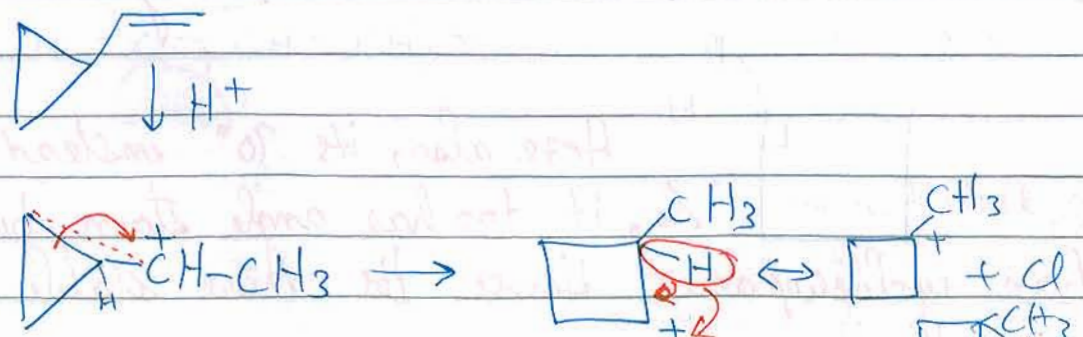


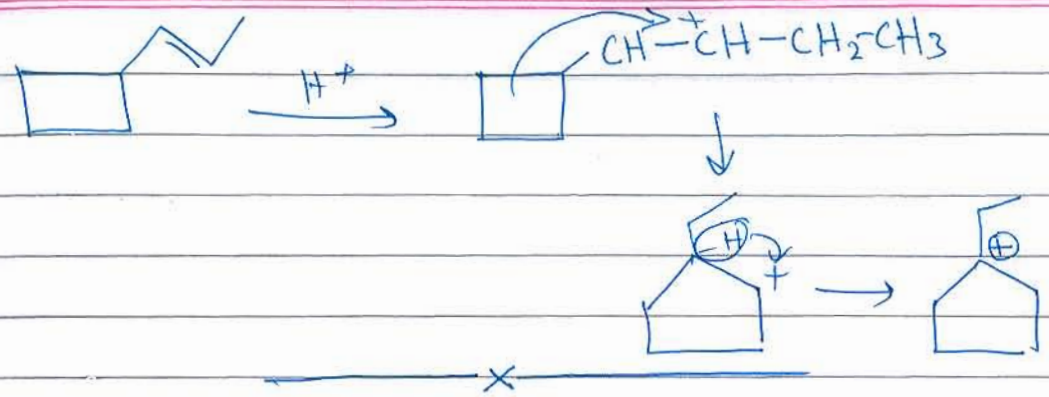
Strain = 30°.

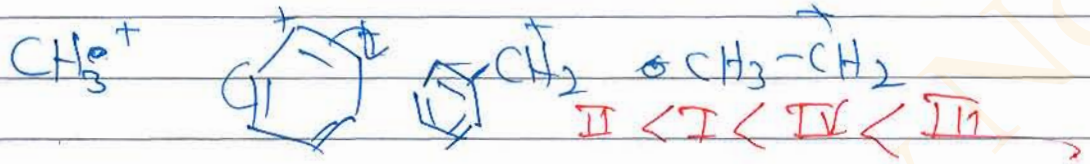
So, strain has decreased.



Q.







* A cyclic hydrocarbon can not have any carbon sp hybridised unless it is more than 8 C chains.

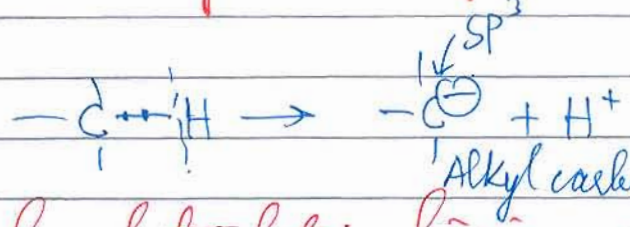
This is the reason why cycloalkyne exists or occurs only after cyclooctane.

(2) CARBANIONS

They are the reactive intermediates in which 1 C possesses –ve charge.

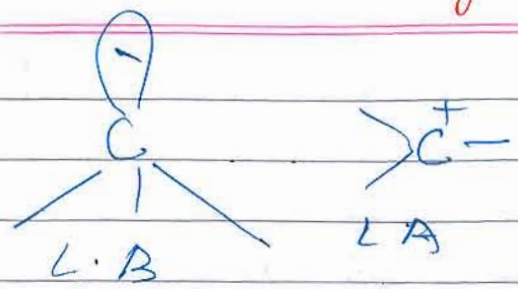
eg: $-\overset{\ominus}{\underset{|}{C}}-$ alkyl $-\underset{|}{C}=\underset{|}{C}^{\ominus}$ vinyl $-C\equiv C^{\ominus}$ acetylinic.

* FORMⁿ.



- Formed by heterolytic fission of covalent bond to a given C atom in a molecule.
- Carbanions have pyramidal st.
  Carbocations " planar "

- Carbanion is the strongest base (when comparing other bases)
- Carbocations are the strongest acid.

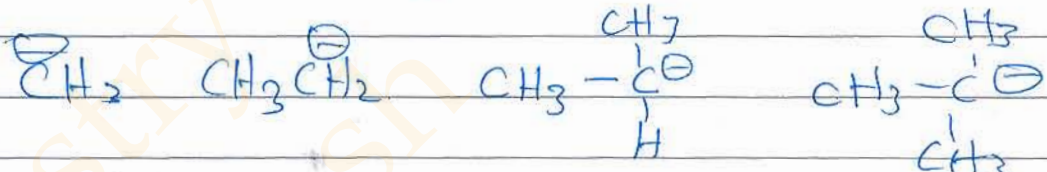


* Rel. Stability.



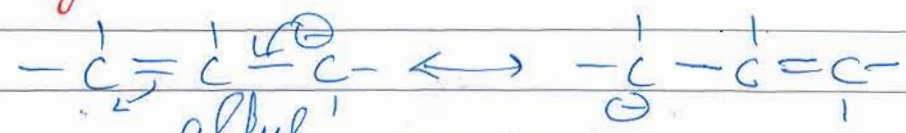
- If @ A is an e⁻ withdrawing grp, it stabilises carbanion.
- If its e⁻ donating grp, it destabilises carbanion.

* Rel Stability: Methyl carbanion (Me^-) > 1° > 2° > 3°

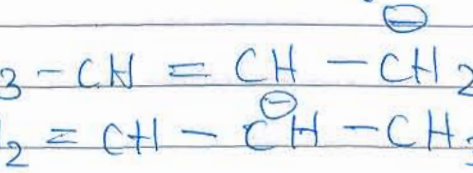


- The most stable carbanion is least reactive. Hence, it would be a weak base. Hence 3° carbocation is most reactive, very basic.

- Allyl carbanions are more stable than alkyl $C^\ominus$



allyl
Stabilised by resonance

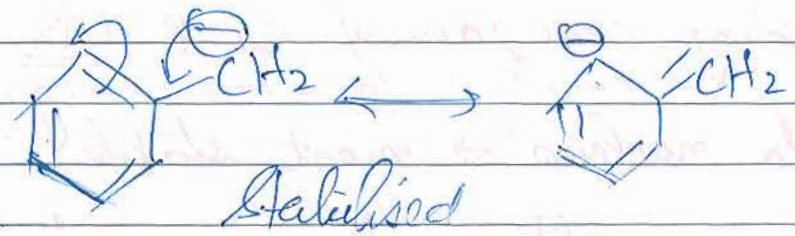
Q 
They are resonance st. of each other.

Stability:

IV < II < I < III

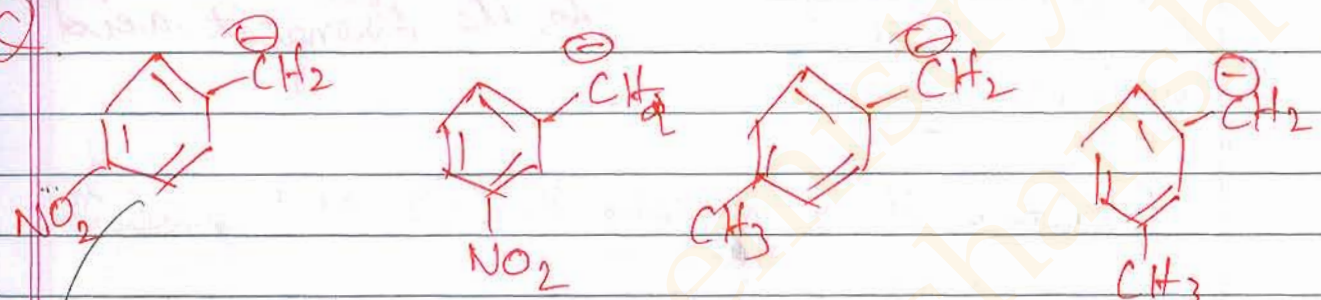
- BENZL CARBANION is more stable than allyl or alkyl carbanion.





Stabilised

Q.



I > II > IV > III

* Its conj. acid will be the most stable the strongest because its conj. base is most stable.

Q. $CH_3Li + CH_3CH_3 \rightleftharpoons CH_4 + CH_3CH_2Li \quad K_c = ?$

WB WA SA SB

weak base — This rxn will move in backward rxn. Hence, $K_c < 1$.

* A stable carbanion will be a weak base.

$SA + SB \rightarrow WA + WB$

classmate
Date
Page

Q. $CH_3-\overset{\ominus}{C}H_2 \quad < \quad CH_2=\overset{\ominus}{C}H \quad < \quad H-C\equiv\overset{\ominus}{C}$

I (sp^3) II (sp^2) III (sp)

E_N : $sp > sp^2 > sp^3$ (∵ -ve charge on electro -ve atom is most stable. So, sp hybridised orbital will be more capable of holding lone pair of e⁻s & OR in sp, size is small, so, -ve charge is closest to nucleus → most stable)

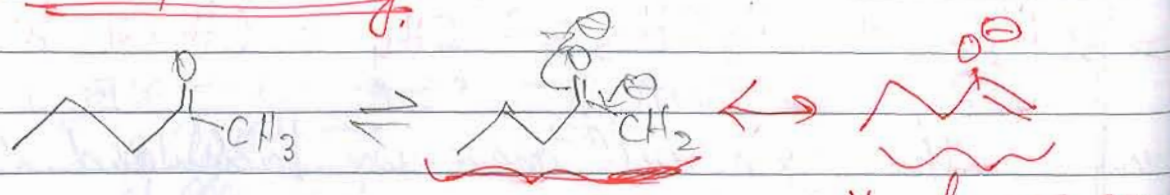
* $R-C\equiv C-H$ → Its conj. base is most stable. So, its strongest acid.
$R-CH=CH-H$
$R-CH_2-H$

$R-C\equiv C-H + Na \rightleftharpoons R-C\equiv C^- Na^+ + H-H_2\uparrow$

acidic hydrogen.

to, it will be used often • A weak acid (base) has a strong conj. base (acid) & vice versa.

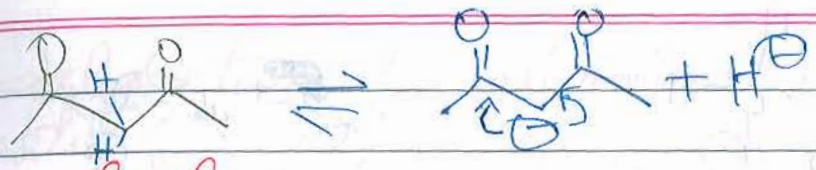
• α-H of carbonyl



-ve charge on Electro -ve atom

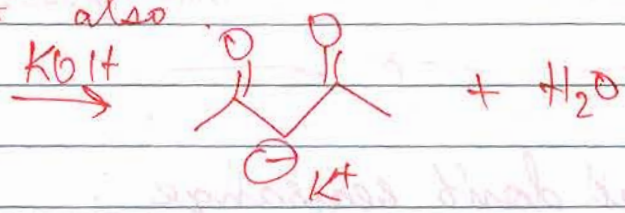
can be used • A carbanion which has C=O on its α-posⁿ, it would be most stable (∵ in its resonan st. has -ve charge • on electro -ve atom)

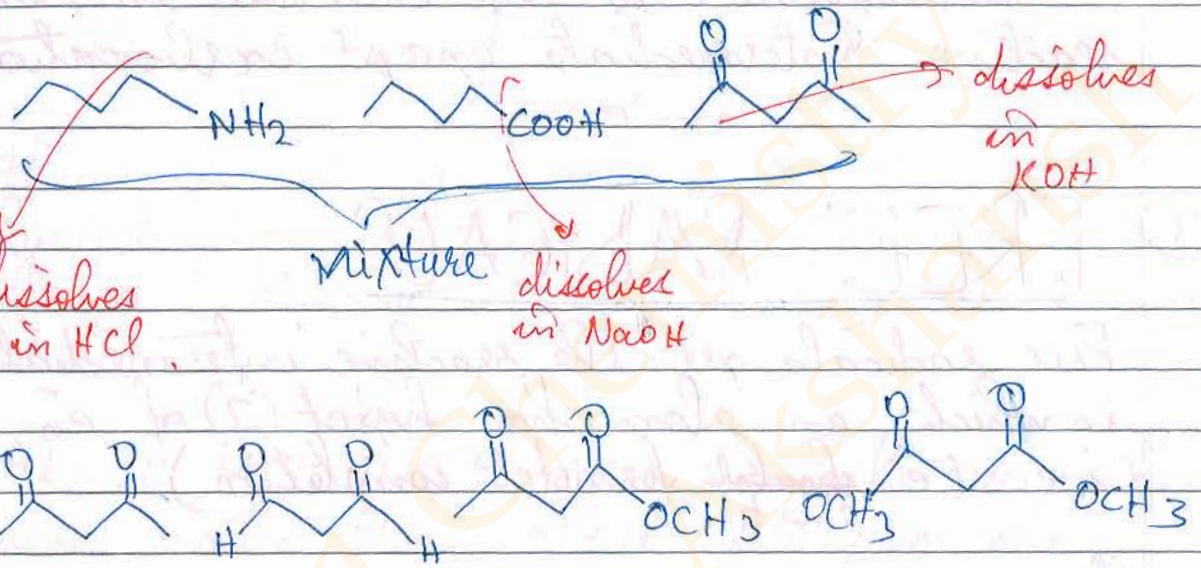
$-OCH_3 \rightarrow -I$ effect



1,3 dicarbonyl

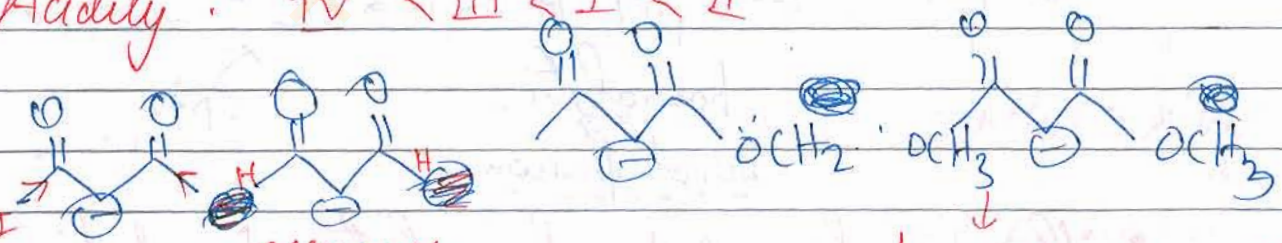
↳ Its acidity is stronger than H_2O (both side resonance stabilised). So, it reacts with KOH also.





Q.

Acidity : IV < III < I < II



+I

resonance opposed

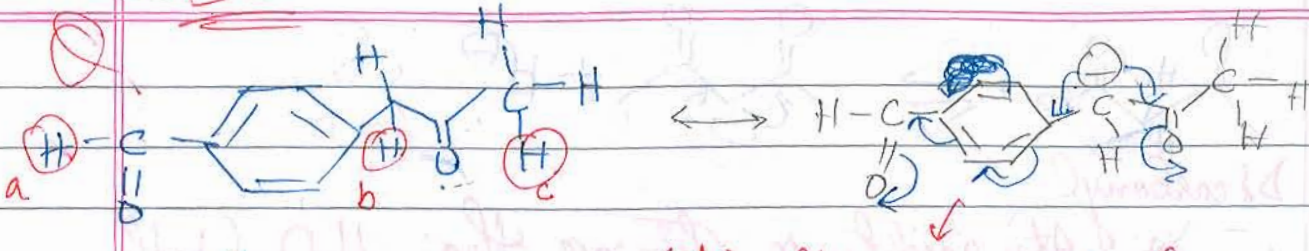
resonance not opposed. So its conj. acid will be most stable.

here resonance will be destabilised by resonance by ö which would prevent delocalisn.

* Thermal fission or Photochemical fissions are homolytic.

JEE

Q



Rel acidity:
a < c < b

✓(b) It can resonate from both sides

---

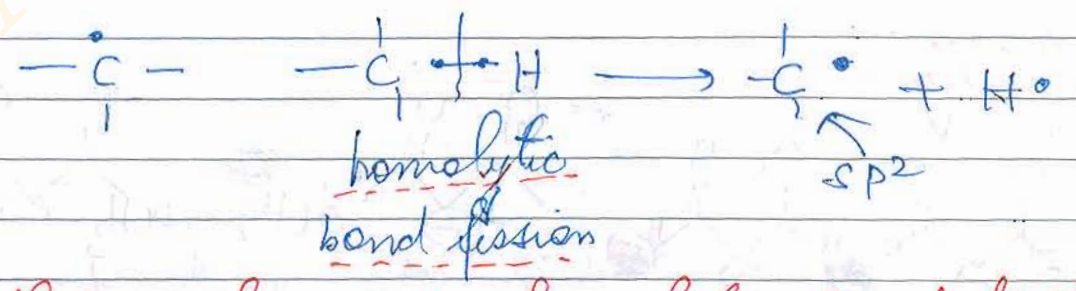
* Carbanions don't rearrange.
Rearrangement is not observed in any reactive intermediate except carbocations.

---

(3) FREE RADICALS

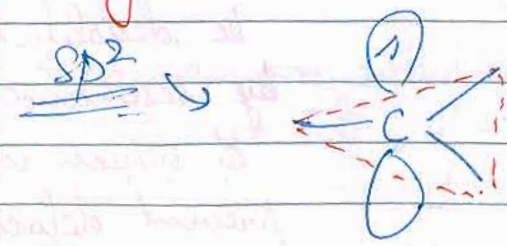
Free radicals are the reactive intermediate in which an atom has heptet (7) of e⁻s (i.e 1 e⁻ ~~should~~ short for octet completion)

eg



homolytic bond fission

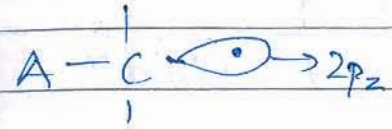
- They are formed by homolytic bond fission.



This free radical (e⁻) is in 2p orbital of C. (not in 2s orbital)

- It is an electrophile, but not a Lewis Acid.
- Free radicals are paramagnetic. whereas,

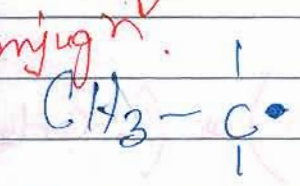
carbocations & carbanions are both diamagnetic.

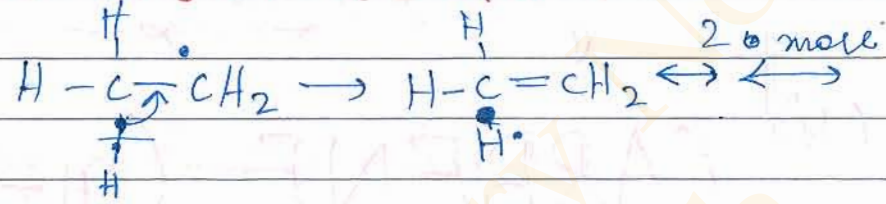


- If A is e⁻ donating grp, free radical is stabilised.
- A is e⁻ withdrawing, destabilised.

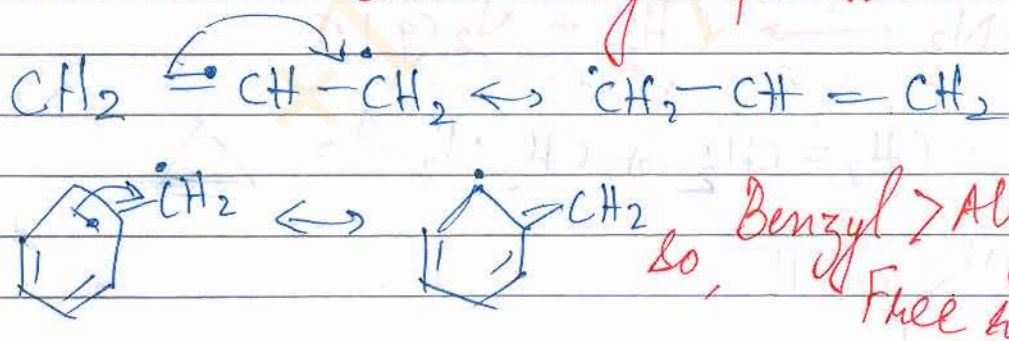
Stability order : $\dot{C}H_3 < 1^\circ < 2^\circ < 3^\circ$.

Hyperconjugation





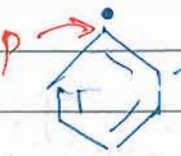
- If degree of free radicals ⊕ are same, hyperconjugation determine rel. stability, i.e more the no. of α-H (to sp^2 C) more is stability.
- ALLYL & BENZL Free radicals are rel. more stable than alkyl free radicals.



So, Benzyl > Allyl > Alkyl Free radicals.

- Free radicals don't rearrange.

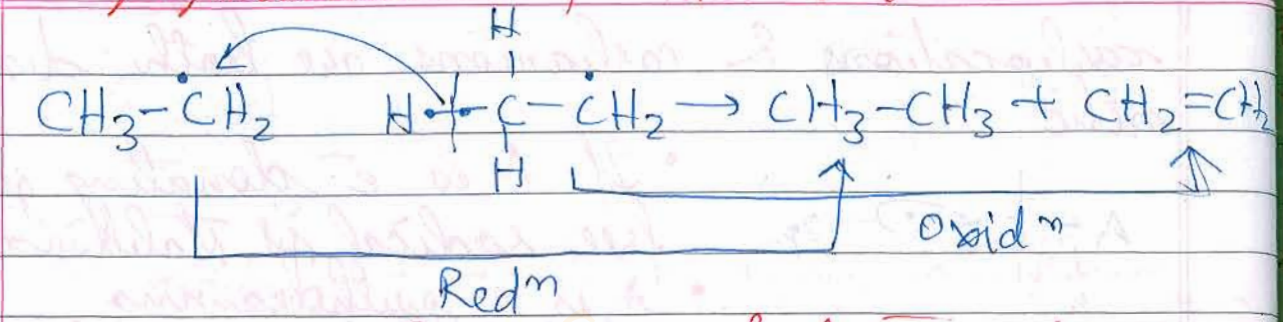
Q. $CH_3-\dot{C}H_2 > CH_2=\dot{C}H > CH\equiv\dot{C}$ Stability.



It is least stable. It can't exist. So, PHENYL FREE RADICAL DOESN'T exists.

IV

• Disproportionation of F. Radical.



* Free radical has property of disproportionⁿ. If produced in a chem. rxn, part of it undergo disproportionⁿ.

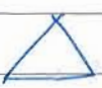
(4) CARBENE ($H-\overset{H}{\underset{}{C}}:$) or ($:CH_2$)

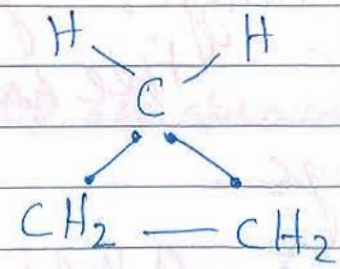
Or (methylene)

☆ PREPARⁿ

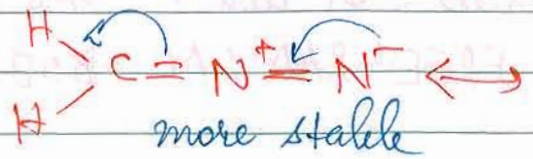
① By thermal decomposⁿ of DIAZOMETHANE. → (CH_2N_2)

$CH_2N_2 \xrightarrow{\Delta} CH_2: + N_2(g)\uparrow$

eg: $CH_2=CH_2 + CH_2N_2 \xrightarrow{\Delta}$ 



CARBENE 'in resonance



(2) By action of Zn (metal) over Diiodomethane (CH_2I_2)

$$Zn + CH_2I_2 \longrightarrow ZnI_2 + :CH_2$$

(3) By thermal decompos of KETENE ($H_2C=C=O$)

Keto + ene

$$H_2C=C=O \xrightarrow{\Delta} CO + :CH_2$$

(4) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{O}{||}}{S}}=CH_2$ (methylene dimethyl sulphoxide)

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{O}{||}}{S}}=CH_2 \longrightarrow CH_3-\overset{\overset{O}{||}}{S}-CH_3 + :CH_2$$

DMSO — Carbene.

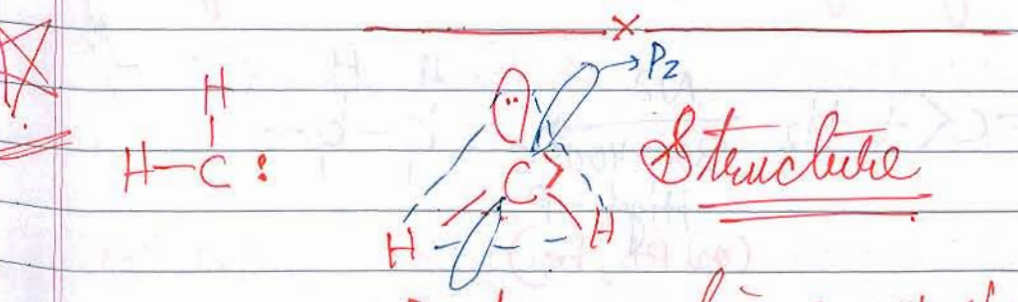
(5) CHX_3 (Haloform): Derivative of $:CH_2$ is produced.

eg: $CHCl_3$ → chloroform, $CHBr_3$ → bromoform - - .
(not CHF_3 → floroform)

$$CHCl_3 / CHBr_3 + KOH \longrightarrow :CX_2$$

(strong base) ($:CCl_2$ or $:CBr_2$)

(dichloro carbene — dibromo carbene)

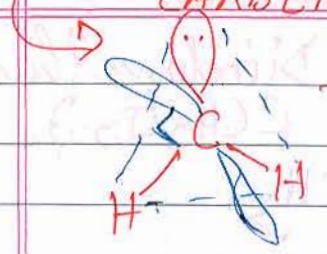


Structure

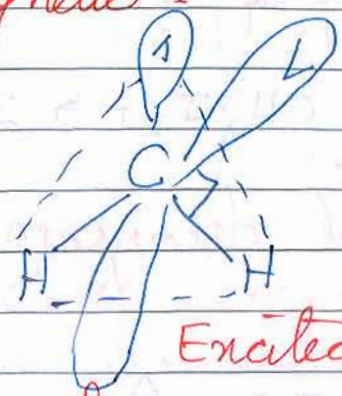
Bent, non linear, V-shaped.

- Carbene is a very strong electrophile & lewis acid. (See structure)

GROUND STATE CARBENE



Dimagnetic



(SINGLET carbene)

Excited carbene (Paramagnetic) (TRIPLET) carbene

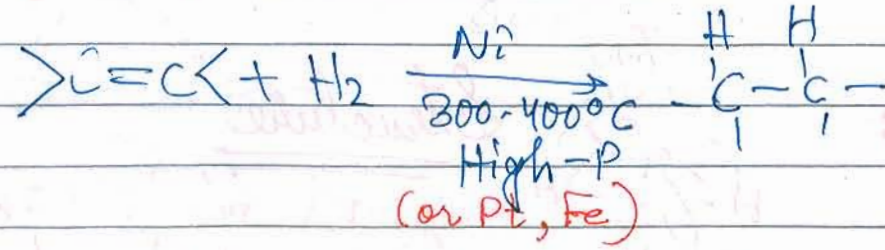
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h. Hydrocarbon

ALKANE

PREPARATION

1. Catalytic hydrogen^{n} of unsaturated hydroC



* Ni, Pt or Fe have affinity for H_2 (g) at high P. So, they are used.

Raney Ni

$Ni/Al + NaOH_{(aq)} \longrightarrow NaAlO_2 + H_2\uparrow$

$+ Ni\downarrow$
ppt. (Pwdr)

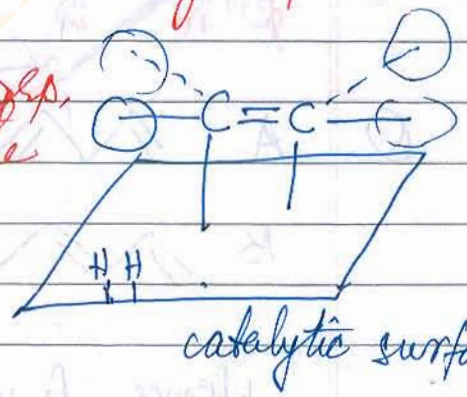
Ni (pwdr) has now increased SA. so, efficiency is improved.
Raney Ni reacts at RT :: Amt. of H_2 adsorbed per unit wt. of Ni becomes more.

Mechanism : ADSORPTION MECHANISM.

Reactivity of alkene depends on ease of adsorption.

- Easier the absorption, greater the reactivity.
- Ease of adsorption depends on size of alkyl gp present on sp^2 C.
- Smaller the size of alkyl gp, easier the adsorption, greater the reactivity.

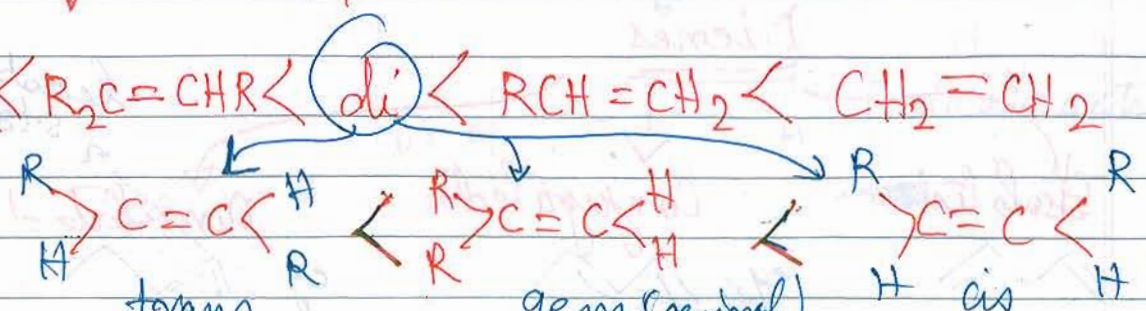
eg :- Ethene is most reactive alkene in this rxn.



Trend for compds having same no. of π-bonds

Reactivity order

$C=CR_2 < R_2C=CHR < (di) < RCH=CH_2 < CH_2=CH_2$



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~~Saturated~~

Saturated
S. table

Unsaturated
Unstable

PE ↓ ← PE ↑ (∵ stability ∝ $\frac{1}{PE}$)

E released.

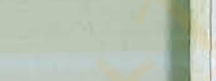
So, Unsaturated to saturated (Exotherm

(A) $-C\equiv C- + 2H_2 \rightarrow$

(B) $-\overset{|}{C}=\overset{|}{C}- + H_2 \rightarrow$

(C) $-C=C-\underset{|}{C}-C=C- + 2H_2 \rightarrow$

★ Heat evolved in hydrogen^n of alkyne <
" " " " " of diene.

Q. A  less stable. So, PE ↑

B  more stable (resonance)
PE less.

Hence, A will liberate more heat on hydrogen^n.

Dienes

Isolated — eg: 

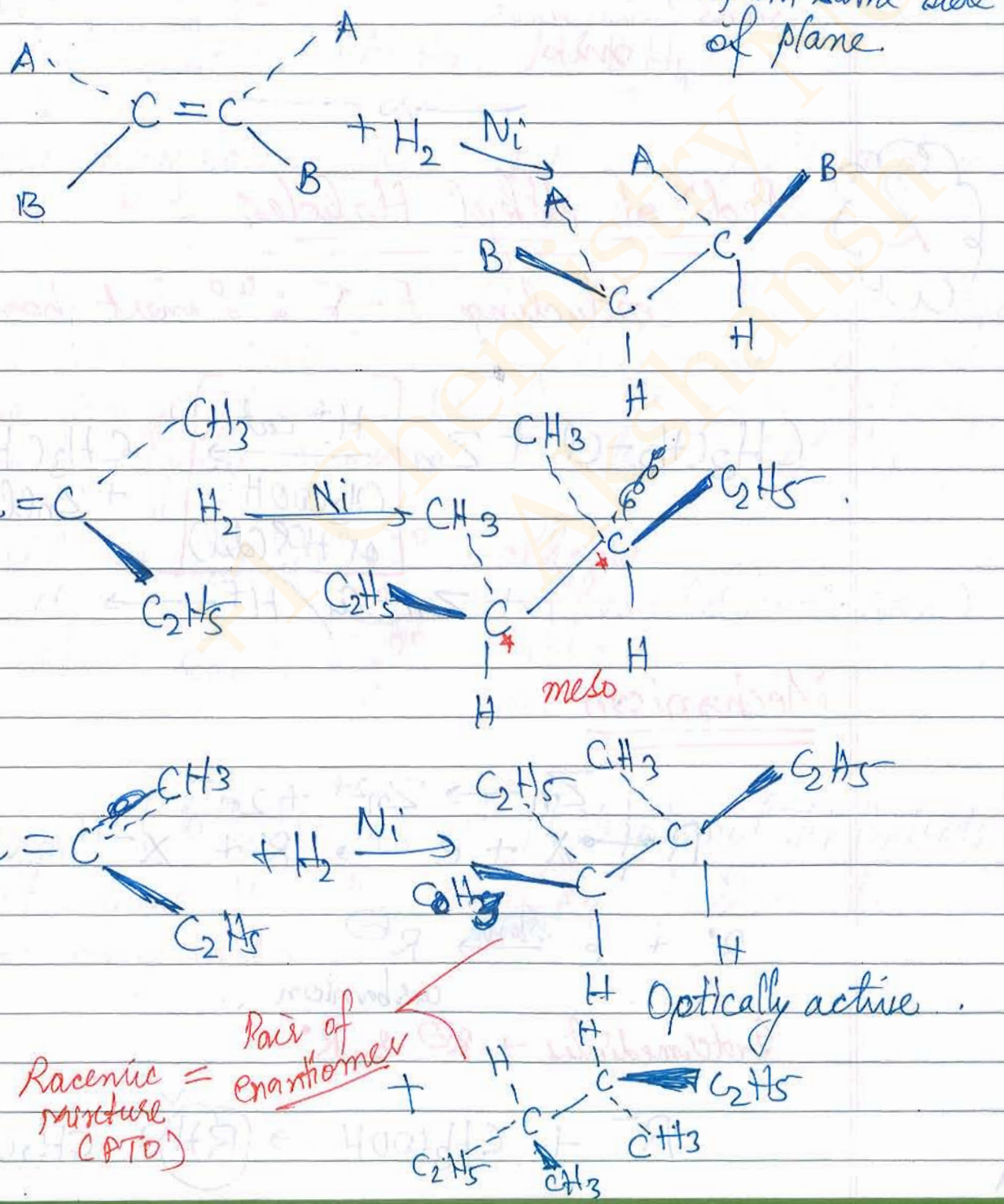
Conjugated — eg: 

Cumulated (least stable) — eg 

- Cumulated < Isolated < Conjugated : Stability
- " > " > " : PE ↓
- " > " > " : Heat evolved on hydrogenⁿ

★ Catalytic hydrogenⁿ occur with SYN-ORIENTⁿ.

↳ from same side of plane



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* The before drawn enantiomers have equa probability of forming hydrogen". So, they will be forming a RACEMIC MIXTURE.

* Symmetrical

cis → meso
trans → racemic mix.

Unsymmetrical

cis & trans } racemic mixture.

—∞—

2 Red^n of Alkyl Halides -

(excluding R–F : $\sigma\sigma$ most bond)

$$CH_3CH_2-Cl + Zn \xrightarrow[CH_3COOH \text{ or } HCl(dil)]{H^+ \text{ cat.}} CH_3CH_3 + ZnCl_2$$

$$+ Zn-Cu/H^+ \longrightarrow$$

Mechanism

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

$$R\text{–}X + e \longrightarrow R^\bullet + X^-$$

$$R^\bullet + e \xrightarrow{\text{slow}} R^\ominus$$

carbanion.

Intermediates → $R^\ominus$ & $R^\bullet$

$$R^- + CH_3COOH \longrightarrow (RH) + CH_3COO^-.$$

* In a multi step rxn, the slowest step determines the major product.

- Carbanion for^{n} (intermediate) is the slowest step, so, we have to see the ~~stabl~~ stability of carbanions ($1^0 > 2^0 > 3^0$) in the compds. Greater stability, more is major product.

- Reducing agent: Most common — $LiAlH_4$ (LAH), $NaBH_4$ (NBH).

They are moderately strong RA — can't reduce olefins. But, reduces Alkyl halides to alkanes

Important
- Ni, Pt are used to reduce alkenes & alkynes
- But $LiAlH_4$ & $NaBH_4$ can't reduce them. So, Ni & Pt are stronger (strongest) RA than $LiAlH_4$ & $NaBH_4$.
- $NaBH_4$ is slightly weaker RA than $LiAlH_4$.

- $LiAlH_4$ → reduces $1^0, 2^0$ → alkane
  3^0 → alkene (elimin^{n} rxn)
- $NaBH_4$ → reduces $2^0, 3^0$ → alkane
  1^0 → doesn't react.

- Ph_3SnH ($(C_6H_5)_3SnH$) (Triphenyl Tin Hydride)
  → It reduces 1^0, 2^0, 3^0 alkyl halides to corresponding alkanes.

(ether)

• ~~$C_2H_5OC_2H_5$~~ is most inert organic compd. Its a solvent.

(RMgX)

3 BY HYDROLYSIS OF GRIGNARD REAGENT.

$$RX + Mg \xrightarrow[(C_2H_5OC_2H_5)]{\text{dry ether}} RMgX$$

(Et_2O)

$$\overset{-1}{R}\overset{+2}{Mg}\overset{-1}{X} + H_2O \longrightarrow RH + Mg(OH)X$$

* RMgX is used for replacing H with D (or T)

$CH_4 \longrightarrow CH_3D$

$Cl_2/h\nu$ ↓ ; ↑ D_2O (heavy water)

$CH_3Cl \xrightarrow[\text{ether}]{Mg} CH_3MgCl \xrightarrow{T_2O} CH_3T$

4 DECARBOXYLⁿ OF CARBOXYLIC ACID

Carboxylic acid on heating with soda lime ($NaOH + CaO$) gives R-H.

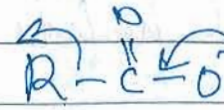
$$R\text{-}COOH + NaOH/CaO \xrightarrow{\Delta} R\text{-}H + CO_2\uparrow$$

• Neutralisⁿ rxn is fastest rxn.

*Mechanism

$$R\text{-}COOH + OH^- \longrightarrow \underset{\text{carboxylate}}{RCOO^-} + H_2O$$





$$R\text{-}C(=O)\text{-}O^- \longrightarrow \underset{\text{carbanion.}}{R^{\ominus}} + O=C=O$$

* Decarboxylⁿ involves formⁿ of carbanion. Carbanion stability determines the rate of rxn.



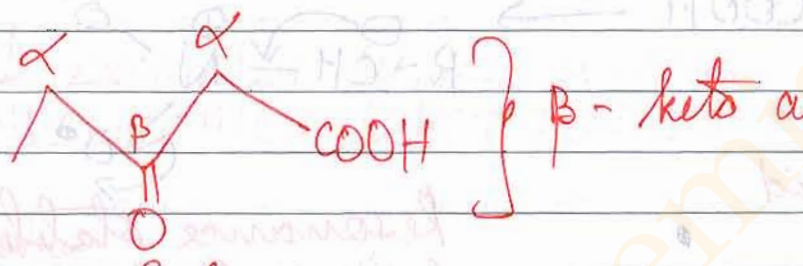
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eg : $R-\underset{R}{\overset{R}{C}}-COOH \longrightarrow R-\underset{R}{\overset{R}{C}}-\ominus$ least stable carbanion.

So most difficult will be decarboxylation.

eg CH_3CH_2COOH $\quad$ $CH_3-\underset{CH_3}{CH}-COOH$ $\quad$ $Cl-CH_2CH_2COOH$ ($-I\leftarrow$)

reactivity II < I < III (make carbanion)

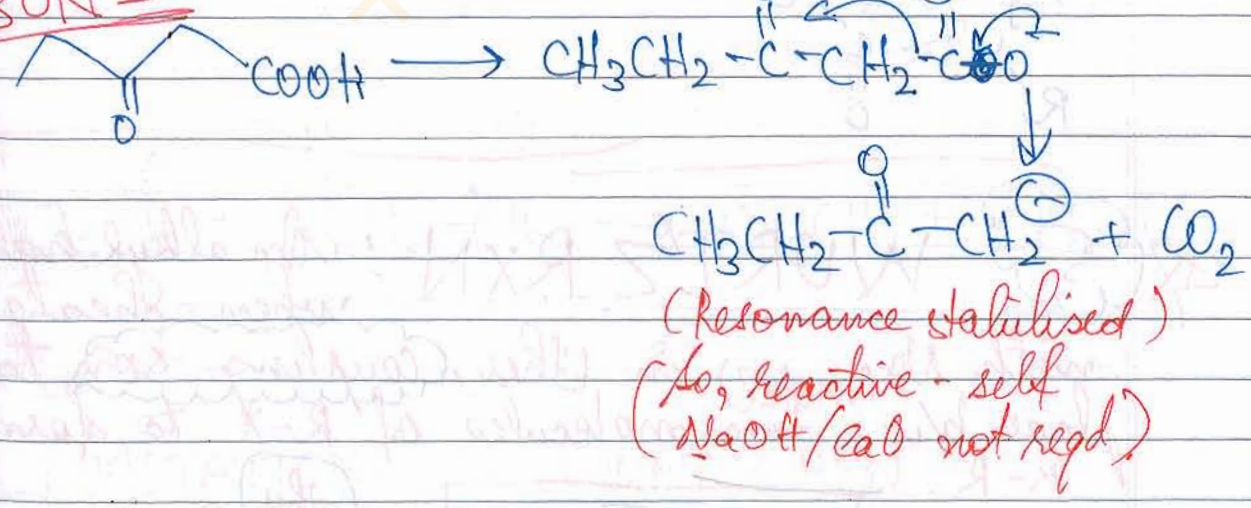


β-keto acid

* β-keto acid decarboxylate (lose CO_2) on simple heating — no NaOH/CaO catalyst reqd

* β-keto acid decarboxylate easily ~~is very reactive~~ by itself.

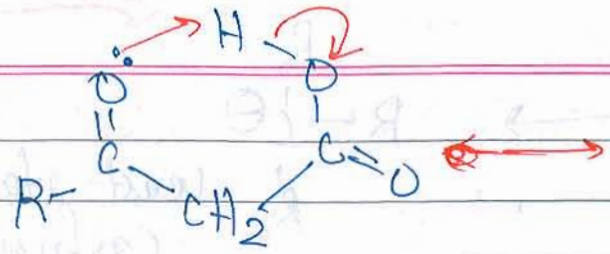
REASON 1

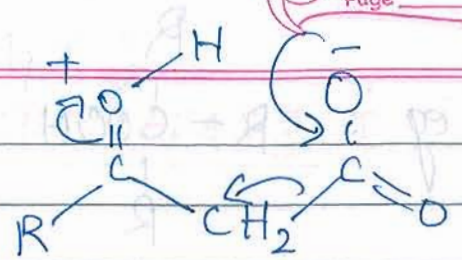


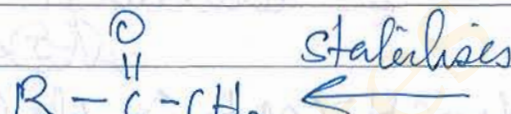
(Resonance stabilised)

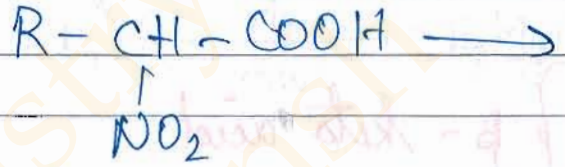
(So, reactive - self NaOH/CaO not reqd.)

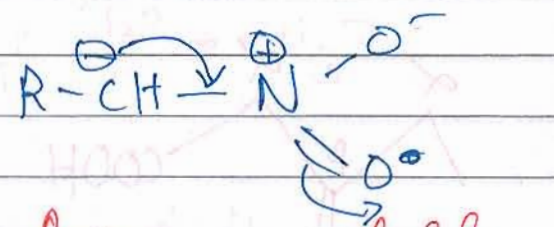
REASON 2



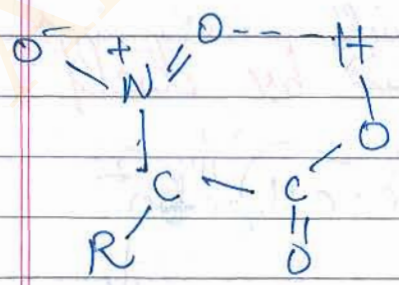




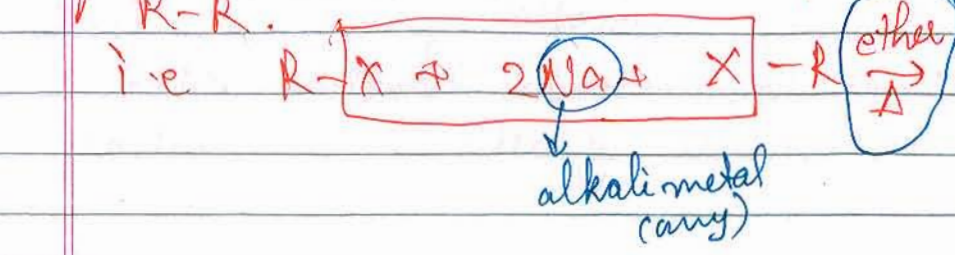




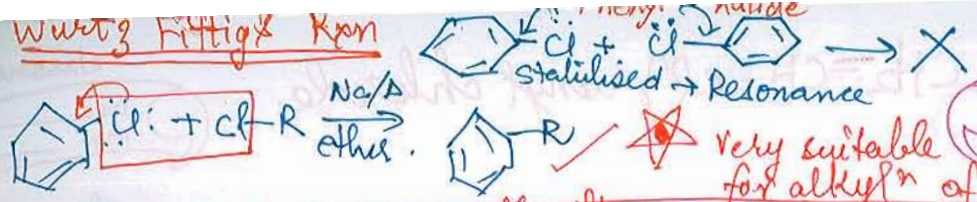
Resonance stabilised.
So, only heating decarboxylⁿ takes place.
NaOH/CaO not reqᵈ.



WURTZ RXN : An alkyl halide when heated with Na (metal) in Ether, coupling rxn takes place b/w two molecules of R–X to form R–R.

i.e 

Wurtz Fittig Rxn



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Mechanism

$$Na \longrightarrow Na^+ + e^-$$

$$e^- + R\text{-}Cl \longrightarrow R^\bullet + Cl^\ominus$$

$$R^\bullet + {}^\bullet R \longrightarrow R\text{-}R$$

or $R^\bullet + e^- \longrightarrow R^\ominus$



$$R^- + R\text{-}Cl \xrightarrow{\text{slow}} R\text{-}R + Cl^\ominus$$

1 nucleophile replaces another - so, its also called NUCLEOPHILIC SUBSTITUTION RXN.

Conceptual

Q. $CH_3CH_2Cl \xrightarrow[\Delta \text{ Ether}]{Na} CH_3CH_2CH_2CH_3$ +

$(CH_2=CH_2 + CH_3-CH_3)$

due to disproportionⁿ of free radical.

$$CH_3CH_2^\bullet + {}^\bullet CH_2\text{-}CH_2 \longrightarrow CH_3CH_3 + CH_2=CH_2$$

31·3·10

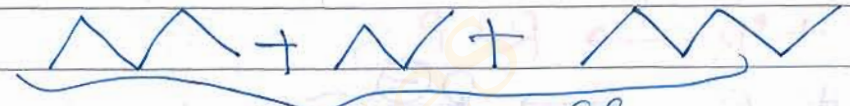
LIMITATIONS OF WURTZ RXN.

1. Methane can't be prepared.
2. Alkane containing odd no. of C can't be conveniently prepared.

$CH_2=CH-Cl$ Vinyl chloride

(3) 3 compds are formed instead of 1 → 2 by self-coupling & 1 by cross coupling.

eg: $CH_3CH_2Cl + CH_3CH_2CH_2Cl \longrightarrow$



all comparable products formed.

(Close physical properties. So, their separn is very difficult)

(4) It is also not capable when we want to produce & separate more than 1 R–R.

(5) Vinyl halide fail in Wurtz Rxn:

$CH_2=CH-\ddot{Cl}: \quad Cl-CH=CH_2 \xrightarrow[\text{Ether}]{Na/\Delta}$ ✗

Resonance, acquires partial double bond character.
So, coupling doesn't occur.

---

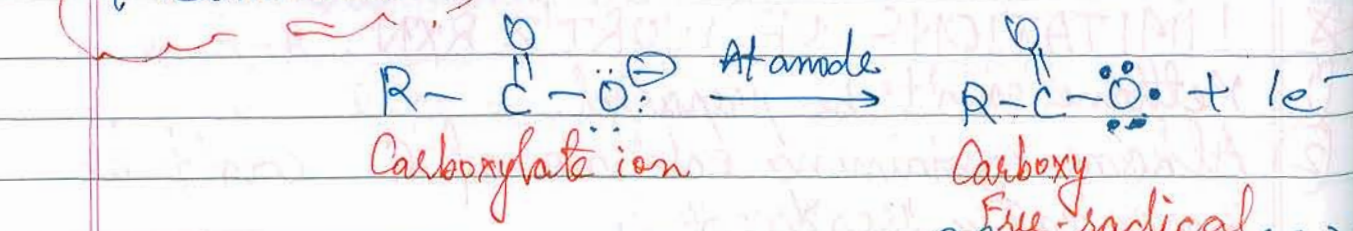
* (6) KOLBE'S ELECTROLYTIC METHOD.

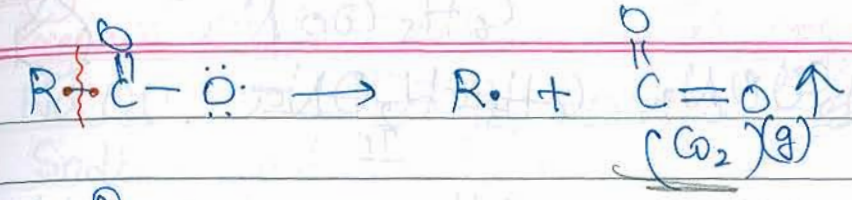
When Na/K salt of carboxylic acid, in aq soln is electrolysed, alkane is produced liberating $CO_2(g)$

i.e.

$R-COONa_{(aq)} \xrightarrow{\text{Electrolysis}} R-R + CO_2\uparrow$

Mechanism





$R-\overset{O}{\overset{\|}{C}}-\ddot{O}\cdot \longrightarrow R\cdot + \underset{(CO_2)(g)}{O=C=O}\uparrow$

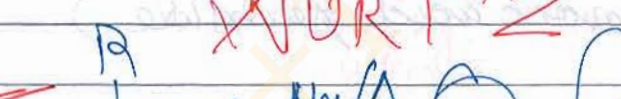
$R-\overset{O}{\overset{\|}{C}}-\ddot{O}\cdot$ is unstable because O (electro -ve atom) has deficiency of $1e^-$ (to complete octet).

$R\cdot\text{-----}\cdot R \longrightarrow (R-R)$

- Kolbe's Rxn :

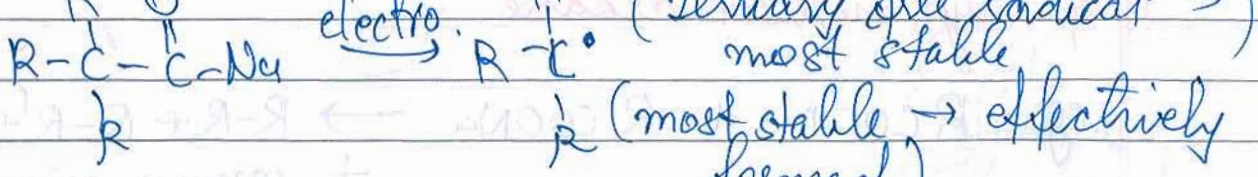
1) In this rxn, 1 C of the salt is decreased per molecule in product alkane (due to $\uparrow$ of CO_2)
2) It involves coupling of 2 alkyl radical in the final step of rxn. ∴ ethane is the smallest alkane which can be prepared (∵ no CH_4 that can be prepared)
3) In Wurtz rxn, final product is formed from carbanion, but, in Kolbe's Rxn → it is from free radical.

WURTZ



$R-\underset{R}{\overset{R}{C}}-Cl \xrightarrow{Na/\Delta} (X)$ $\left(R-\underset{R}{\overset{R}{C}}\ominus \cdot \rightarrow \text{very unstable. Can't be formed}\right)$

KOLBE'S



$R-\underset{R}{\overset{R}{C}}-\overset{O}{\overset{\|}{C}}-Na \xrightarrow{\text{electro}} R-\underset{R}{\overset{R}{C}}\cdot$ (Tertiary free radical → most stable)

(most stable → effectively formed)

(least)

(1°)

Q. CH_3CH_2COONa (I) C_6H_5COONa (II) $C_6H_5CH_2ONa$ (~~$C_6H_5CH_2ONa$~~)

$C_6H_5CH_2COONa$ (III) (Resonance) (most)

$CH_3CH_2\underset{\underset{CH_3}{|}}{CH}COONa$ (IV) (2°)

Reactivity : III > IV > I > II

Electro

$CH_3CH_2COONa_{(aq)}$

$CH_3CH_2-\overset{\overset{O}{\|}}{C}-\ddot{O}:^{\ominus} \longrightarrow CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\ddot{O}\cdot + e^{\ominus}$

$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O\cdot \longrightarrow CH_3CH_2^{\cdot} + CO_2\uparrow$

Minor : $CH_3CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$

① ethyl propanoate (ester)

② $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

Organic Peroxy ~~compd~~.

(Propanoic acid peroxide)

③ $CH_3\dot{C}H_2 \longrightarrow CH_2=CH_2 + CH_3CH_3$

decarboxyl^n disproportion^n

Limit^n of Kolbe's ↓ not suitable for unsymm. alkane.

→ Kolbe rxn is not suitable for prepar^n of unsymmetrical alkane.

eg: $RCOONa + R'COONa \longrightarrow R-R + R-R' + R'-R$ + many minors.

sp (180° never possible 6 mem

Q. Prepar of alkene ~~fro~~ in Kolbe's rxn.

$NaOOC-CH_2-CH_2-COONa \xrightarrow{electro}$

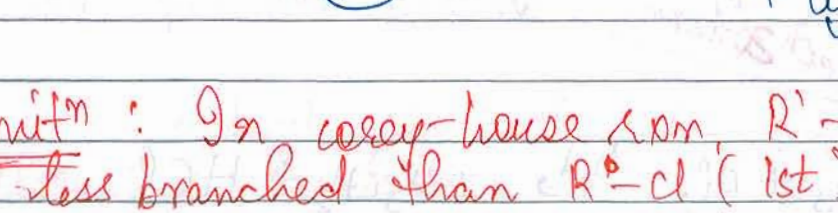
Sodium Butyl dioate ion.

$^{\cdot}O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O^{\cdot} + 2e^-$

vicinal diacid salt

$CH_2=CH_2 \leftarrow CH_2^{\cdot}-{}^{\cdot}CH_2 \leftarrow -2CO_2$

Q.



(7) COREY-HOUSE RXN. (can be used for preparing unsymmetrical alkane).

① $R-Cl + Li \xrightarrow[\text{Step 1}]{\Delta} R-Li$ (+ LiCl biproduct)

$R-Li \xrightarrow{CuCl} R_2CuLi \xrightarrow[\text{step (2)}]{R'-Cl}$

(Dialkyl lithium cuprate)

$R-CuLi + R'-Cl \longrightarrow R-R'$ Unsymmetrical

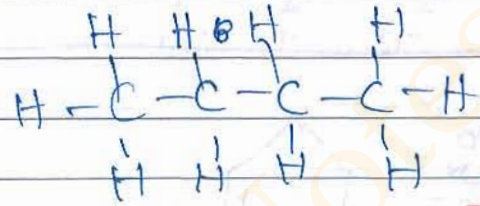
$+ CuR + LiCl$ Biproduct.

★ Limitn: In corey-house rxn, $R'-Cl$ (2nd) should be less branched than $R-Cl$ (1st).

• It is the most suitable & efficient method.

☆ Properties

CHEMICAL PROPERTIES



- Alkane is relatively less reactive in most of the chemical rxn compared to other class of organic compds ∵ of lack of reactive fonal grps. However, under drastic rxn cond'n, it reacts & the common known rxns are —

1) Halogen^{n}.
2) Nitr$_{n}$
3) Sulphon^{n}
4) Oxid^{n}

(1) HALOGENATION

$$R\text{-}H + X_2 \xrightarrow{h\nu} R\text{-}X + HX$$

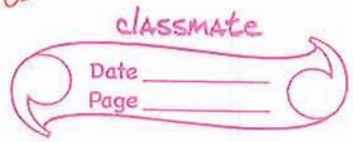
Alkane when treated with halogens in presence of light / heat, it undergo free-radical halogen^{n} to give alkyl halide.

General Mechanism

$$CH_3CH_3 + Cl_2 \xrightarrow{h\nu} CH_3CH_2 + HCl.$$

Mechanism: Halogen^{n} rxn is an eg. of free-radical chain rxn. ↪

* Whenever E → heat / light is given to a compd, always homolytic bond fission takes place.



$Cl-Cl \xrightarrow[h\nu]{\text{homolytic bond fission}} 2Cl^{\bullet}$ } INITIATION

$CH_3-CH_2-H + Cl^{\bullet} \rightarrow CH_3CH_2^{\bullet} + HCl$

alkyl free radical

OPA ATION

product is produced ($Cl^{\bullet}$)

$CH_3-CH_2-H + Cl^{\bullet} \rightarrow CH_3-CH_2Cl + H^{\bullet}$

This rxn didn't take place ∵ always a stronger bond fission is preferred.

H–Cl bond is stronger than C–Cl bond

$CH_3-CH_2^{\bullet} + Cl-Cl \rightarrow CH_3CH_2Cl + Cl^{\bullet}$ ✓

TERMINATION

$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$

$Cl^{\bullet} + {}^{\bullet}CH_2CH_3 \rightarrow CH_3CH_2Cl$ } free radical is consumed effectively.

Q. In free radical chlorin^{n}

butane $CH_2CH_3^{\bullet} + {}^{\bullet}CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3$

butane

butylchloride $CH_3CH_2CH_2CH_3 \rightarrow$ Chlorin^{n} $\rightarrow CH_3CH_2CH_2CH_2Cl$.

alkene $CH_3CH_2^{\bullet} \xrightarrow{\text{disproportion}^{n}} CH_2=CH_2$

Q. In free radical chlorin^{n} of ethane, some 1,1-dichloroethane & 1,2-dichloroethane is formed

A: By further chlorin^{n} of chloro ethane.

* Thus, infinite products are formed in chlorin^{n} of alkanes.

☆ Monochlorin^{n} : (how to reduce ∞ products)

Using excess of R_2, chances of di & tri - -> poly chlorin^{n} are reduce

$CH_3CH_3 + Cl_2 \xrightarrow{h\nu} CH_3CH_2Cl + HCl$

excess.

Increase probability of chlorin^{n} of alkane

CH_3CH_3 (excess) $+ Cl^{\bullet} \longrightarrow$ more chances.

$CH_3CH_2Cl + Cl^{\bullet} \longrightarrow$ less chances

INDIVIDUAL Rxn.

☆ (Fluorin^{n}) → Very reactive. Displaces all H with F.

mono fluoro not possible

$CH_3-CH_3 + 6F_2 \rightarrow CF_3-CF_3 + 6HF$

☆ (Chlorin^{n}) $CH_3-CH_2-CH_3 + Cl_2 \xrightarrow{h\nu}$

comparable $\begin{cases} CH_3CH_2CH_2Cl \\ + CH_3-\underset{Cl}{CH}-CH_3 \end{cases}$

$CH_3-\overset{(H)}{\underset{}{CH}}-\underset{(H)}{CH_2} + Cl^{\bullet} \longrightarrow CH_3\dot{C}H_2-CH_2 + CH_3CH_2\dot{C}H + CH_3$

I II

$Cl^{\bullet}$ is very ~~radical~~ reactive that it abstract H from various posn with equal ease in comparable amt. So, all products in comparable amt.

- So, Chlorin^{n} is very reactive process, but, less selective.

wavelength $\lambda \propto \frac{1}{E}$ $\left(\because E = \frac{hc}{\lambda}\right)$ speed of light

Planck's const.

* **Bromination**: Bromination require greater E than chlorination. It occurs at higher T / higher E / shorter λ

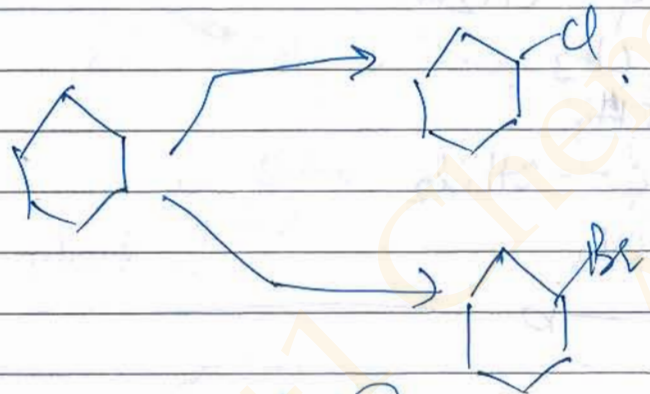
$CH_3-CH_2-CH_3 + Br^{\bullet} \longrightarrow CH_3-\dot{C}H-CH_3 + HBr$

→ less reactive but highly selective process.

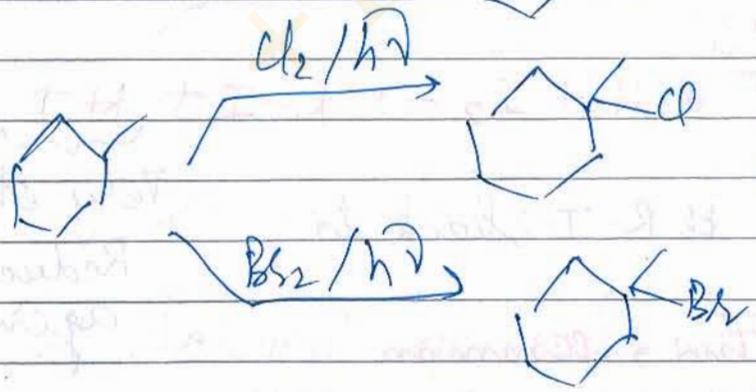
$CH_3-\underset{Br}{CH}-CH_3$

$CH_3CH_2CH_3 \xrightarrow{Cl_2/h\nu} CH_3CH_2CH_2Cl + CH_3-\underset{Cl}{CH}-CH_3$

$CH_3CH_2CH_3 \xrightarrow{Br_2/h\nu} CH_3-\underset{Br}{CH}-CH_3$.

Q. 

Purity of product will be same here.

Q. 

Purity of product will be more in Bromination.

Q. A hydrocarbon (alkane → 72) $\xrightarrow[Cl_2]{h\nu}$ Single monochloro isomer.

C_5H_{12}

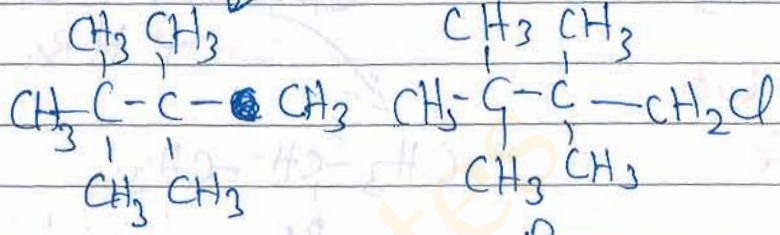


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$ neo-pentane

Q. $C_8H_{18} \xrightarrow{Cl_2/h\nu} C_8H_{17}Cl \xrightarrow{Cl/h\nu} C_8H_{16}Cl_2$

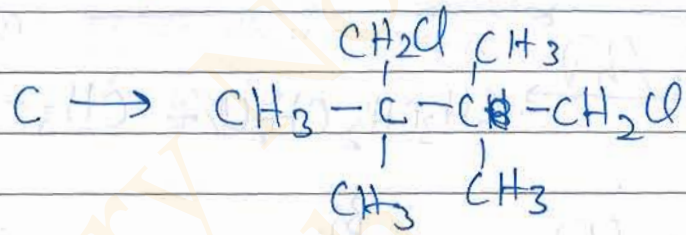
A — single isomer — B — C, D, E — 3 isomers.

A:

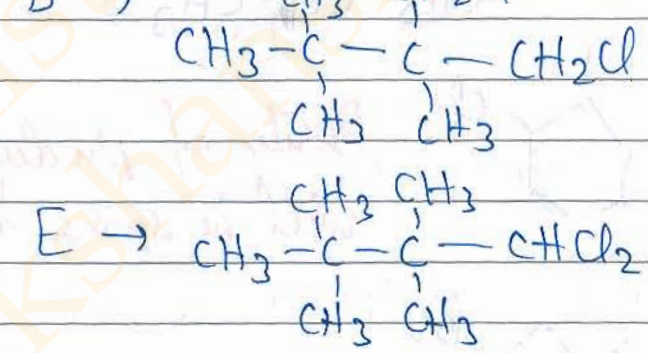


B:

C ⟶



D ⟶



E ⟶

★ IODENATION

$$R\text{-}H + I_2 \rightarrow R\text{-}I + \underbrace{HI}_{\text{Very strong Reducing agent}}$$

HI reduces R-I back to R-H

To prevent this, common OA is put.

i.t

$$2HI + HgO \rightarrow Hg + H_2O + I_2$$

e 3 benefits of adding HgO or dil. HNO_3.

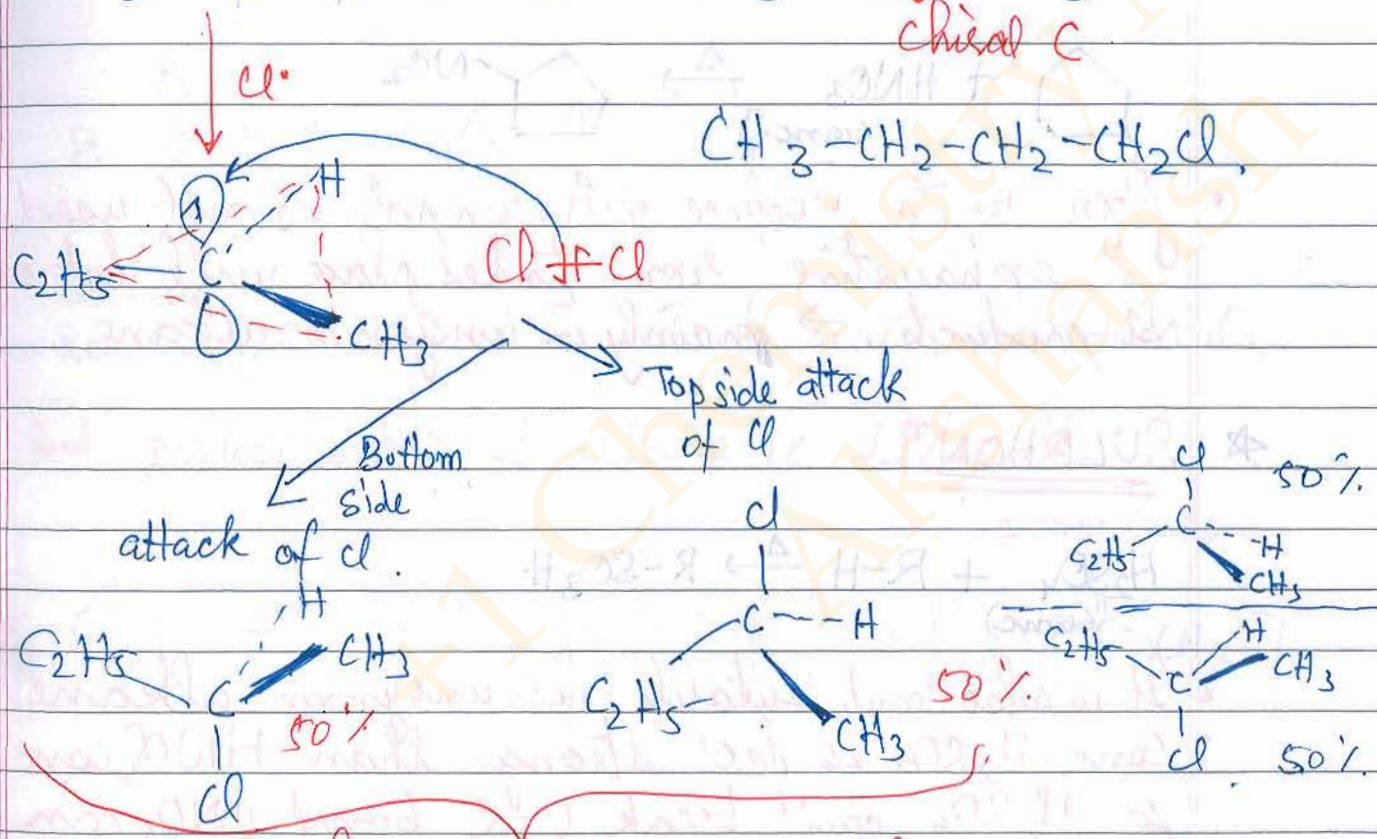
1) It helps rxn to take place.

2) It increases rate of forward rxn by consuming HI in its reactant → le-Chatelier Principle.
3) It increases rate by giving more I_2 in reactant of Iodenation → le-Chatelier Principle.

☆ STEREOCHEMISTRY OF HALOGEN:

$CH_3-CH_2-CH_2CH_3 + Cl_2 \longrightarrow CH_3-CH_2-\underset{\text{Chiral C}}{\overset{Cl}{\underset{\bullet}{C}}}H-CH_3 +$

$CH_3-CH_2-CH_2-CH_2Cl$.



Pair of Enantiomers → Racemic Mixture.

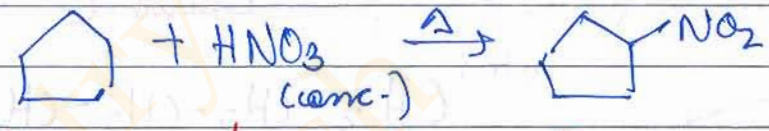
So, if halogen generates a chiral C, then, racemic mixture of product is formed.

classmate
Date 2.4.10
Page

✡ NITRATION OF ALKANE (free-radical rxn)

$CH_4 + HNO_3$ (conc) $\xrightarrow{\Delta}$ $CH_3-NO_2 + H_2O$.
nitro methane
(nitro alkane)

$CH_3-CH_3 + HNO_3$ (conc) $\xrightarrow{\Delta}$ $CH_3CH_2NO_2 + CH_2(NO_2)-CH_2(NO_2) + CH_3NO_2$
a lot of bi-products.

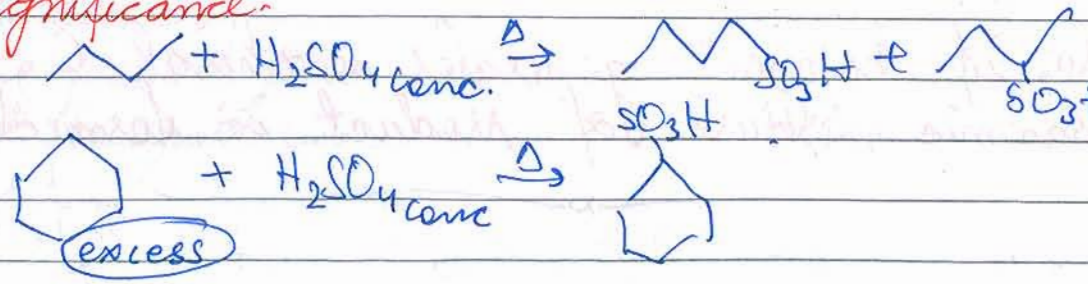


- Rxn to produce nitro compds is not used. Bcz exhaustive rxn takes place with lot of bi-products. → mainly in unsymm. alkane.

✡ SULPHONⁿ

H_2SO_4 (conc) $+ R-H \xrightarrow{\Delta} R-SO_3H$.

- It is also not suitable for unsymm. alkane.
- Conc. H_2SO_4 is less strong than HNO_3 conc. So H_2SO_4 can't break C=C bond. (HNO_3 can). So, H_2SO_4 has comparitively more practical significance.



✱ OXIDⁿ of Alkane.

$$\underset{-4}{CH_3}-H + [O] \longrightarrow \underset{-2}{CH_3}-OH \xrightarrow{[O]} H-\overset{\overset{O}{\|}}{\underset{O}{C}}-H \xrightarrow{[O]} \underset{+4}{CO_2} + H_2O \xleftarrow{[O]} H-\overset{\overset{O}{\|}}{\underset{+2}{C}}-OH$$

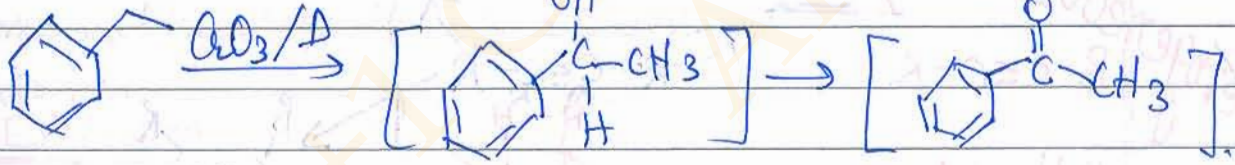
✱ Oxidⁿ of alkanes follows free-radical mechanism.

- $R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}-H + KMnO_4 \xrightarrow{H^+} R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}-OH$

  OA

  Tertiary-H
  Reactivity ↑. So, it is able to react with $KMnO_4$.

✱ But, partial oxidⁿ of alkane is difficult.

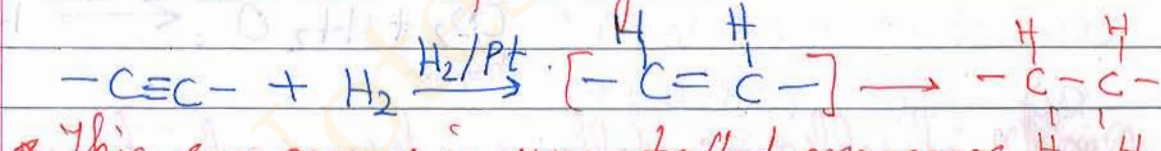
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— ∞ —

ALKENES

PREPAR^{n}

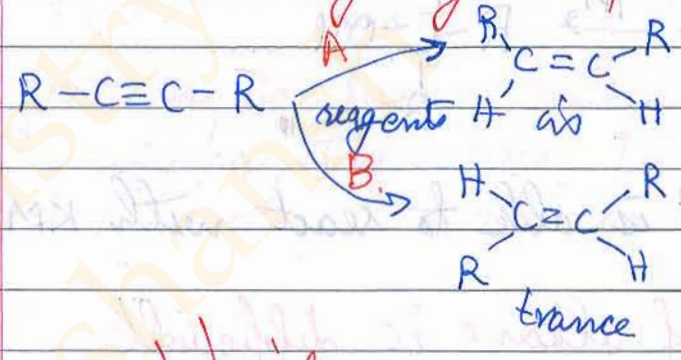
(1) Controlled red^{n} of alkyne



$-C\equiv C- + H_2 \xrightarrow{H_2/Pt} [-C(H)=C(H)-] \longrightarrow -C(H)(H)-C(H)(H)-$

* This rxn occuss in uncontrolled manner

To control hydrogen^{n} of alkyne,



CIS-HYDROGEN^{n}

A: Lindlar's Catalyst

Pd / $CaCO_3$ / PbO [or $PbCCl_4$]

or

Pd / $BaSO_4$ / quinoline / x

TRANS-HYDROGEN^{n}

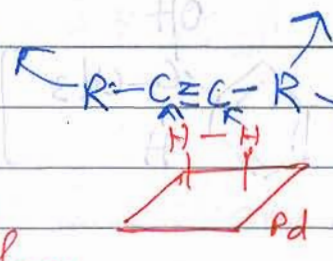
B. Na / NH_3 (l)

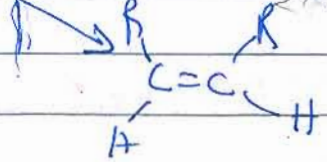
or

C_2H_5OH (x)

Heterogeneous catalysis

CIS

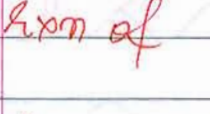




exn b/w diff. phases in syn orientn.

When it passes through the surface of Pd, H attacks on the same side giving cis

$CaCO_3$ & PbO are used to avoid ~~for~~ further

Exn of  formed.

i.e $CaCO_3$ plays role of INHIBITOR (CATALYTIC PO

Trans

Now

$R-C\equiv C-R + \underset{\text{or Li or K}}{Na}/liq\ NH_3$

Mechanism.

homogeneous catalysis.

$Na \rightarrow Na^+ + 1e^-$

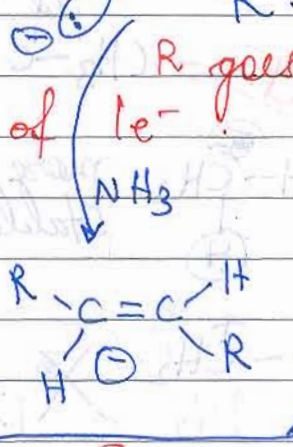
$R-C\equiv C-R + e^- \rightarrow R-\dot{C}=\overset{\ominus}{\underset{\cdot\cdot}{C}}-R$

Radical anion.

So, $Na/NH_3(l)$ hydrogenⁿ of alkyne gives radical anion as RI.



R goes at max. distance from bulky grp on addⁿ of $1e^-$.



- $NH_3(l)$ is used to provide H^+ without reacting. Also provides medium.
- C_2H_5OH (anhyd) can also be used instead of $NH_3(l)$ in trans hydrogenⁿ of alkyne.

(2) DEHYDRⁿ

$CH_2-CH_2 \xrightarrow[H_2SO_4]{conc.} CH_2=CH_2 + H_2O$

(OH, H)

hydro

(3) DEHALOGENⁿ. :—

$CH_2-CH_2 \xrightarrow{alk.\ KOH} CH_2=CH_2 + HCl$

(Cl, H)

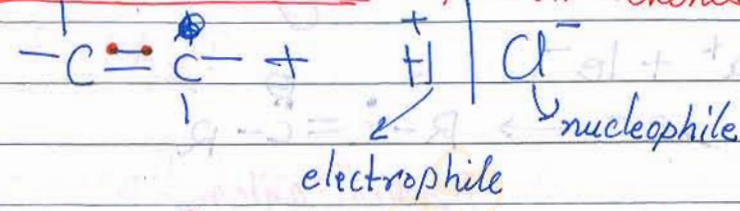
(4) Double dehalogenⁿ

$CH_2-CH_2 \xrightarrow{Zn/\Delta} CH_2=CH_2 + ZnCl_2$

Vicinal (Cl, Zn Cl)

☆ RXNS of Alkene

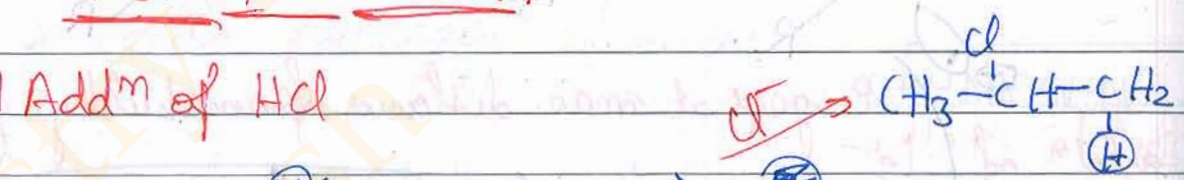
⟨1⟩ ADDITION RXN :- Always electrophilic addⁿ rxn take place in alkenes (∵ initiated by alke



- alkenes have ~~weak~~ π-bond (weak), so, e⁻s are loose — can be easily attacked by electrophile

Electrophilic Addⁿ

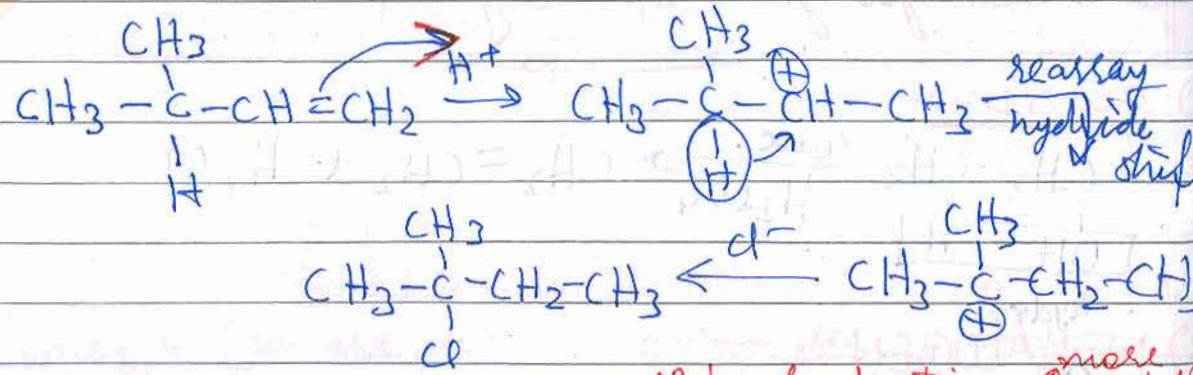
[1] Addⁿ of HCl

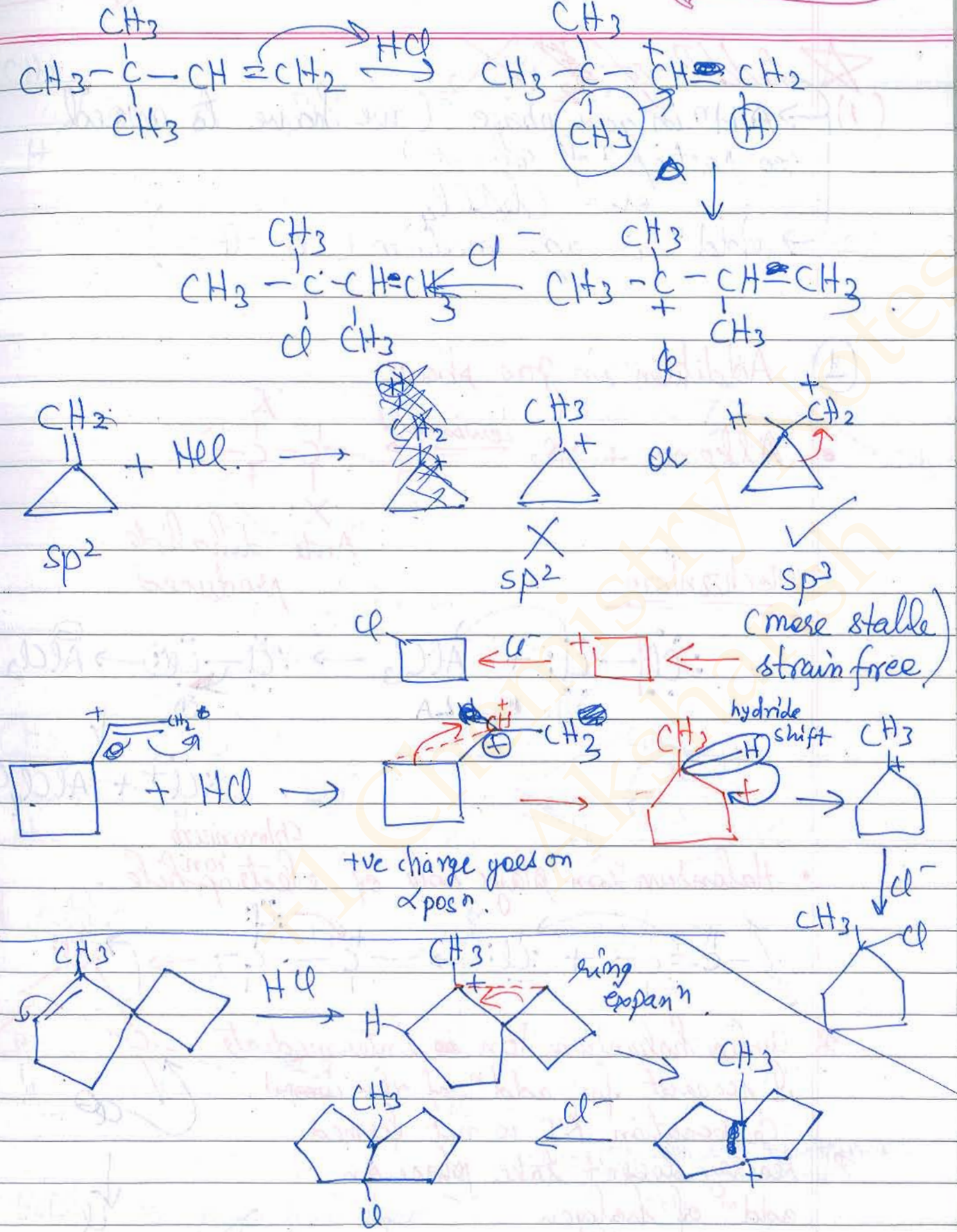


- $CH_3-CH=CH_2 \longrightarrow CH_3-\overset{+}{C}H-CH_2$ (H) — more stable, majo

H^+

$CH_3-CH=CH_2 \longrightarrow CH_3-CH-\overset{+}{C}H_2$ (H) ✗





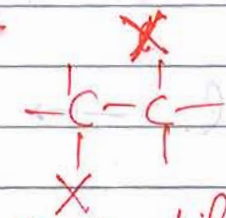
- Properties of HCl, HBr, HI, ——(HX) is same. So, do the above for all in the same way.

☆ Most common Lewis Acids :
$AlCl_3$, $FeCl_3$, BF_3

☆ Addⁿ of X_2

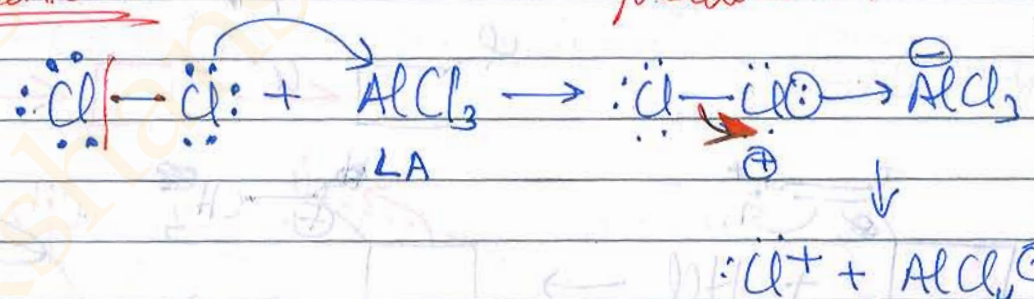
(1) → Addⁿ in gas phase. (we have to avoid participⁿ of solvent)
ex. Cl_2/CCl_4
(2) → Addⁿ in aq. medium ($Cl_2 - H_2O$)

(1) Addition in gas phase

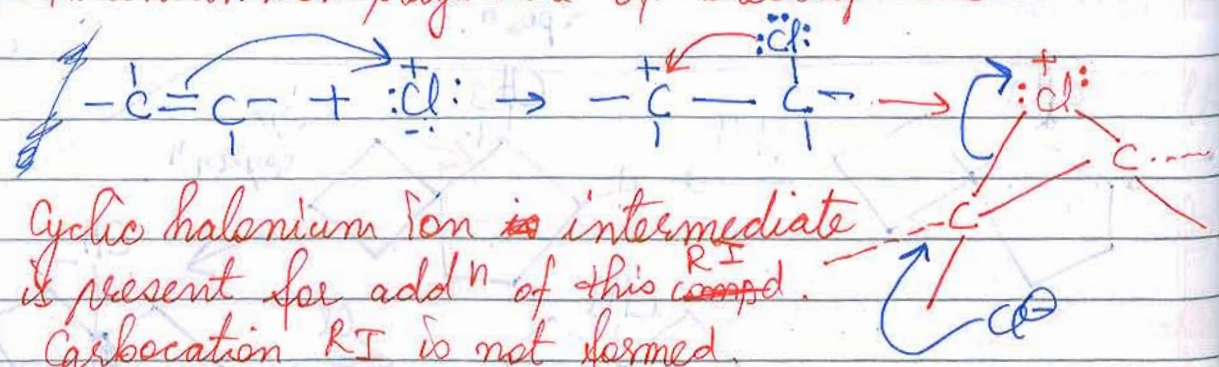
- Alkene + X_2 $\xrightarrow{\text{Lewis Acid}}$ 

Anti-dihalide produced.

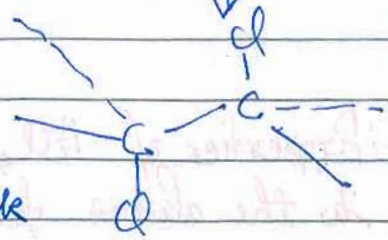
Mechanism



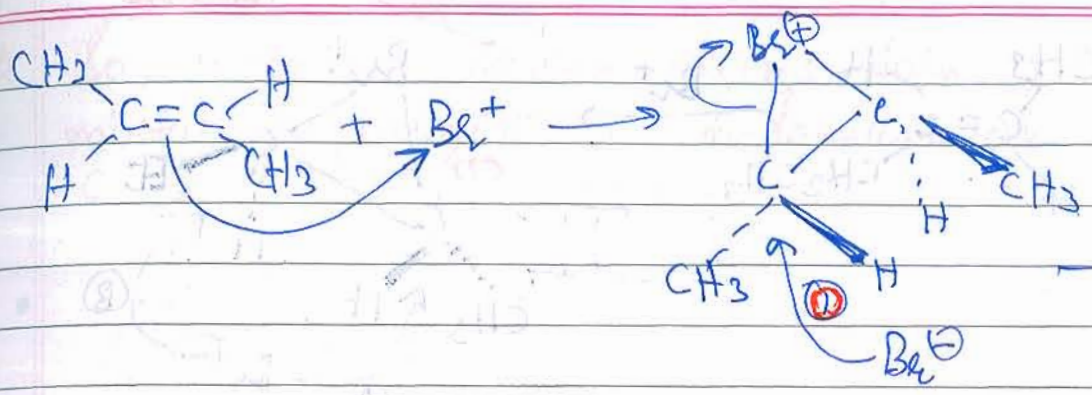
- Halonium ion plays role of electrophile.

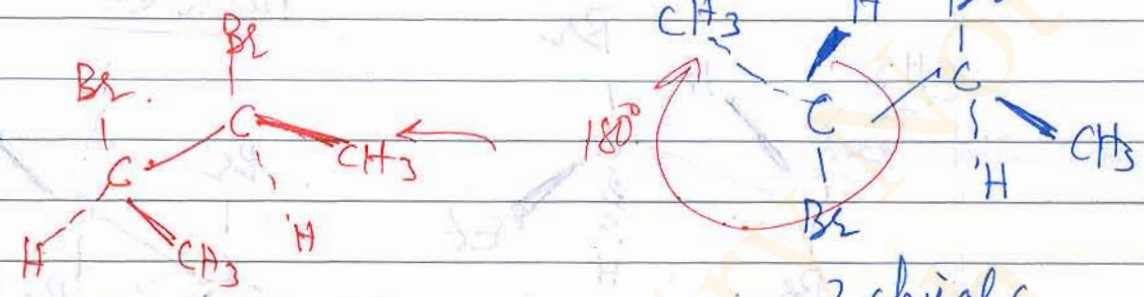


☆ Cyclic halonium ion is intermediate is present for addⁿ of this cmpd. Carbocation RI is not formed.
☆ Rearrangement doesn't take place on addⁿ of halogen

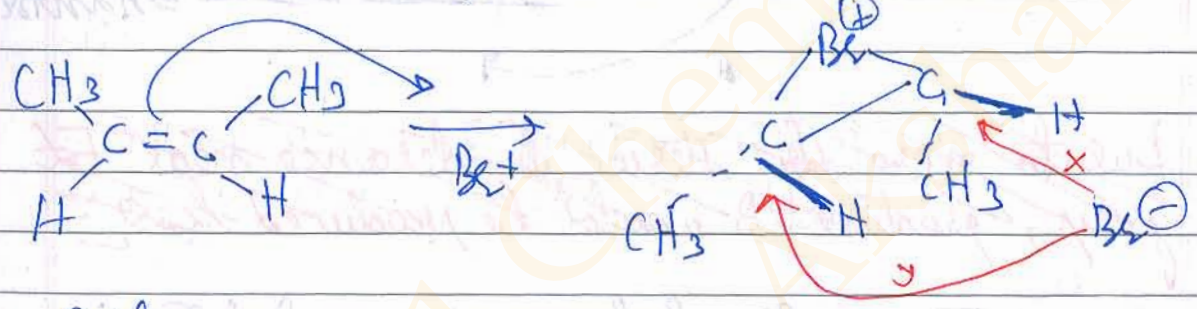


nucleophile attacks from back side on cyclic halonium ion.

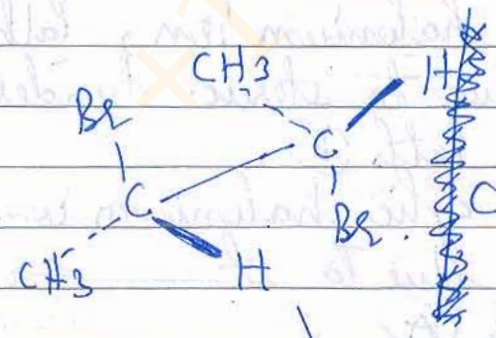




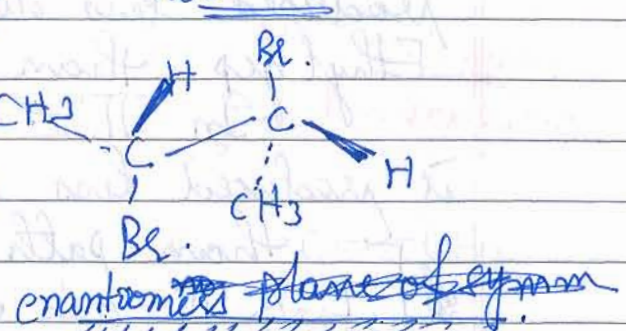
Plane of symm.
(Meso).



Path X

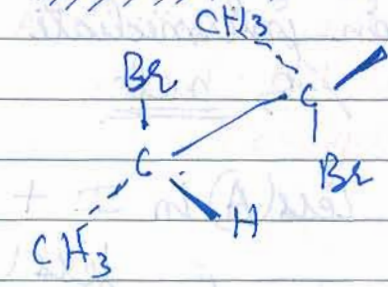


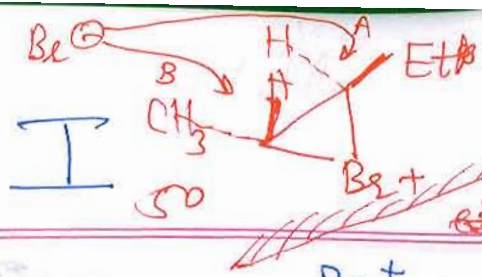
Path Y



Both C of cyclic halonium ion are equal. They form racemic mixture.

enantiomers ~~plane of symm~~.

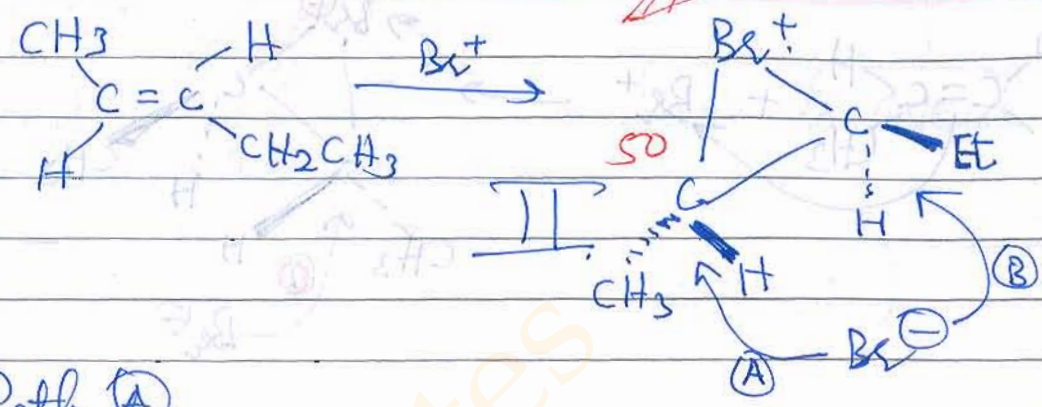




I

50

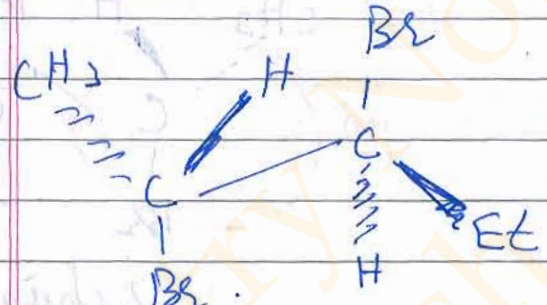
100, say



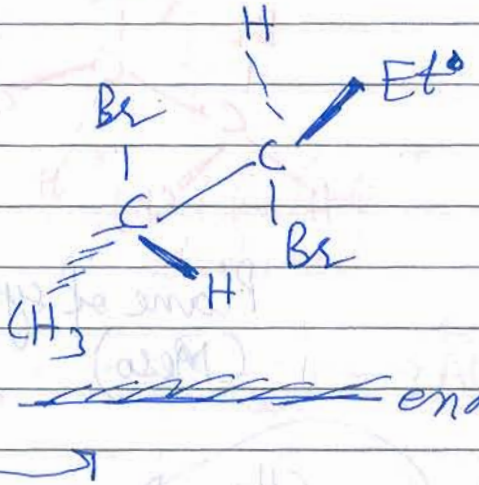
II

50

Path (A)



Path (B)



enantiom

- Due to more steric hinderance near Et group, product B would be produced less

In I → cyclic halonium ion, Path (A) is produced less due to steric hinderance of Ethyl grp. than Path (B).

In II → cylic halonium ion, Path (B) is produced less due to st——— than path (A)

[I & II are formed ∵ cyclic halonium ion intermediate is chiral.]

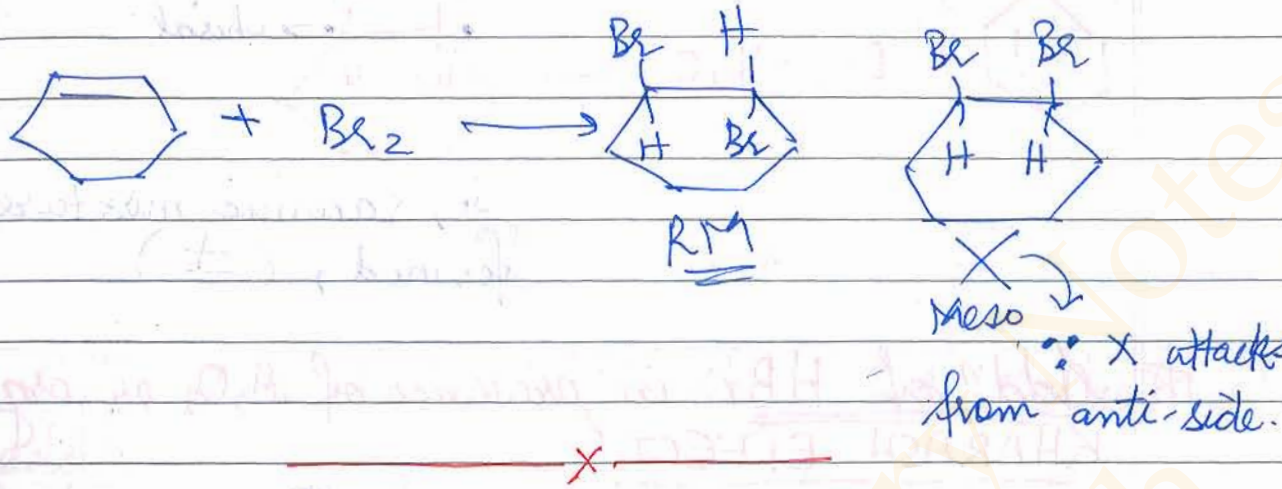
So, net

less(A) in I + More(A) in II =
less(B) in II + More (B) in I

So, Racemic mixture.

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☆ So, unsymm. alkene always form racemic mixture in halogen^{n} : halonium ion has chiral C so it has 2 isomers.



☆ Addn of X_2 in aqueous medium

Cl_2, Br_2, when put in H_2O, react with water 1st -

$$Cl_2 + H_2O \rightarrow \overset{-}{H}O\overset{+}{Cl} + HCl \uparrow$$
$$Br_2 + H_2O \rightarrow \overset{-}{H}O\overset{+}{Br} + HBr \uparrow$$

$CH_3CH=CH_2 + Cl_2-H_2O \rightarrow CH_3-\overset{OH^{\ominus}}{\underset{\uparrow}{CH}}-\overset{Cl^{+}}{\underset{\circlearrowright}{CH_2}}$

$\uparrow Cl^{+}$ (i.e HOCl)
Electrophilic

MK's rule
Nucleophilic

$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2$

ANTI VICINAL CHLORO HYDRIN
(General → Anti Vicinal halohydrin)

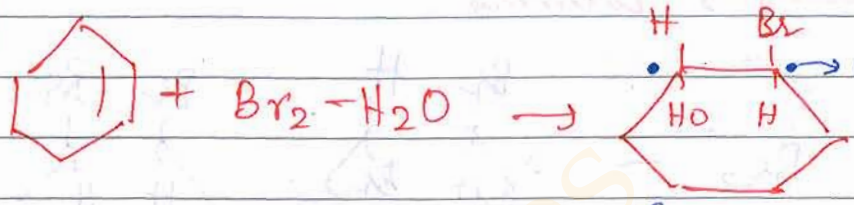
(Brown color due to presence of Br_2^{*})

$+ Br_2-H_2O$
$\uparrow V$
$HBr + HOBr$

When more product is formed, By le-chatelier principle, rxn shifts in forward rxn → decolorising Brown

$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Br^{*}}{\underset{|}{CH_2}}$

- I_2 is not soluble in H_2O & doesn't react.

- 

So, racemic mixture is formed, (±)

★ Addⁿ of HBr in presence of H_2O_2 or org. peroxi
KHARASH EFFECT.

$$CH_3-CH=CH_2 + HBr \xrightarrow[(O-O)]{H_2O_2} CH_3-\underset{(H)}{CH}-\underset{(Br)}{CH_2}$$

Anti-Markonikoff's addⁿ

- Anti-Markonikoff addⁿ doesn't take place with HF, HCl or HI. (only HBr)

So,

$$CH_3-CH=CH_2 + HCl \xrightarrow{H_2O_2} CH_3-\underset{(Cl)}{CH}-\underset{(H)}{CH_2}$$

plays no role. So, MK's rule is followed.

★ Mechanism

- Peroxide (any) when heated undergo ~~hetero~~ homolytic bond fission.

$$H-O\overset{\Delta}{\underset{\text{initiation}}{\}}}O-H \longrightarrow 2OH^{\bullet}$$

$$HO^{\bullet} + HBr \longrightarrow H-O-H + Br^{\bullet}$$

$(H \overset{\bullet}{+} Br)$

(H_2O is formed ∵ stronger bond is formed in a reaction → H-O bond is stronger than Br-O bond)

$\Delta H_1 < 0$ propagⁿ

$Br^{\cdot} + CH_2=CH-CH_3 \longrightarrow Br-CH_2-\overset{\cdot}{C}H-CH_3$ (2°)

($CH_2-\underset{Br}{CH}-CH_3$ not formed ∵ 1°)

$\Delta H_2 < 0$

$Br-CH_2-\overset{\cdot}{C}H-CH_3 + H\overset{\cdot}{-}Br \rightarrow Br-CH_2-\underset{H}{CH}-CH_3 + Br^{\cdot}$

(Here also $H^{\cdot}$ goes $\overset{\cdot}{C}-H$ bond stronger than C-Br)

- Why HF, HCl & HI don't show Anti-Markonikoff addⁿ.

Both propagⁿ steps in addⁿ of HBr are < 0. So, $\Delta G_1 < 0$ ($\because \Delta G = \Delta H - T\Delta S$). So, Anti-Markon — addⁿ becomes Spontaneous.

→ In case of HCl, $\Delta H_1 < 0$ & $\Delta H_2 > 0$.

$\Delta H_1 + \Delta H_2$ gives $\Delta H > 0$, So, ΔG_1 makes non-spontaneous.

→ In case of HI, $\Delta H_1 > 0$ & $\Delta H_2 < 0$

$\Delta H_1 + \Delta H_2$ gives $\Delta H > 0$ → non-spontaneous.

→ In case of HF

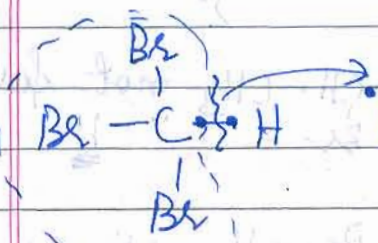
→ In case of HF $\quad \overset{\delta+}{H}-\overset{\delta-}{F}$

bond is very strong (small size of H & F, & dipole created).

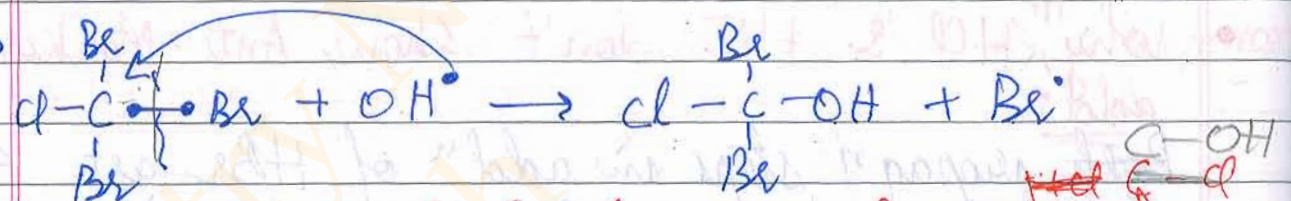
So, $HO^{\cdot}$ can't break this bond. Hence Anti-Markon — addⁿ doesn't take place with H-F.

✡ Some cases of Anti-Markonikoff

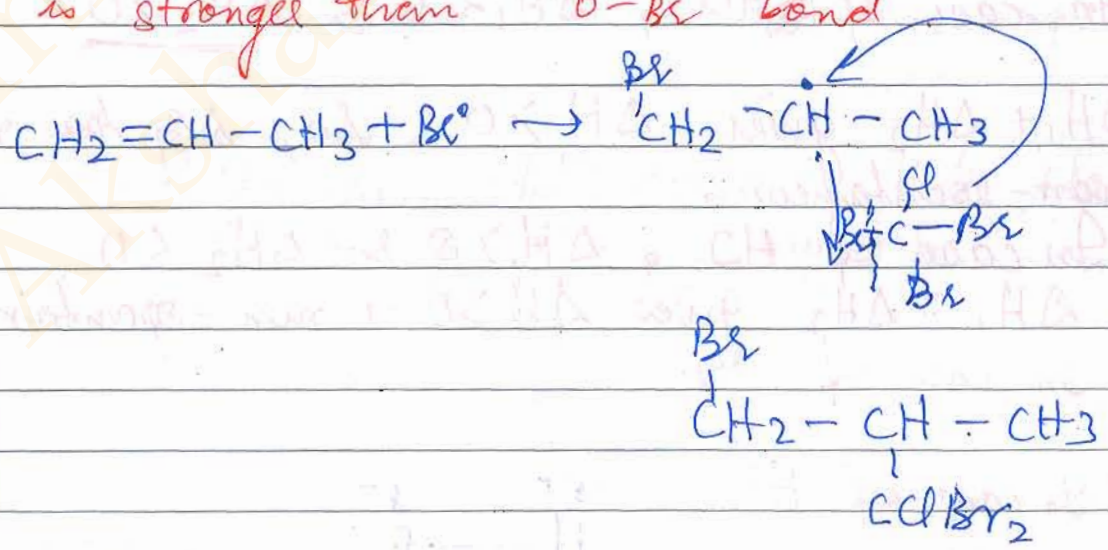
1) $CBr_3H + CH_3-CH=CH_2 \xrightarrow{H_2O_2} CH_3-CH(CBr_3)-CH_2$



↳ Plays role of $Br^\bullet$ Hence, Anti-Markoni --- addn of CBr_3 takes place.

2) 

C-Br breaks (∵ its weaker than ~~H-Cl~~ C-Cl)
$HO^\bullet$ reacts with $CBr_2Cl^\bullet$ ∴ C-O bond is stronger than O-Br bond



✡ HYDRⁿ of ALKENE

$-\dot{C}=\dot{C}- + H^+|OH^- \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$ (alcohol)

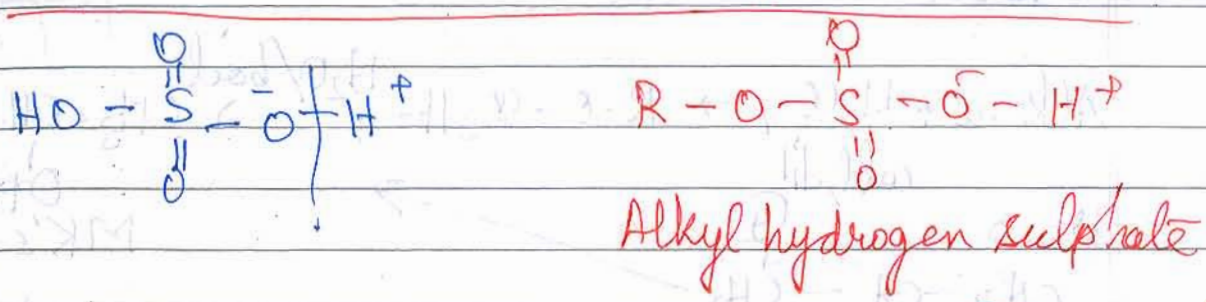
(c') ✡ ACID-CATALYSED HYDRⁿ

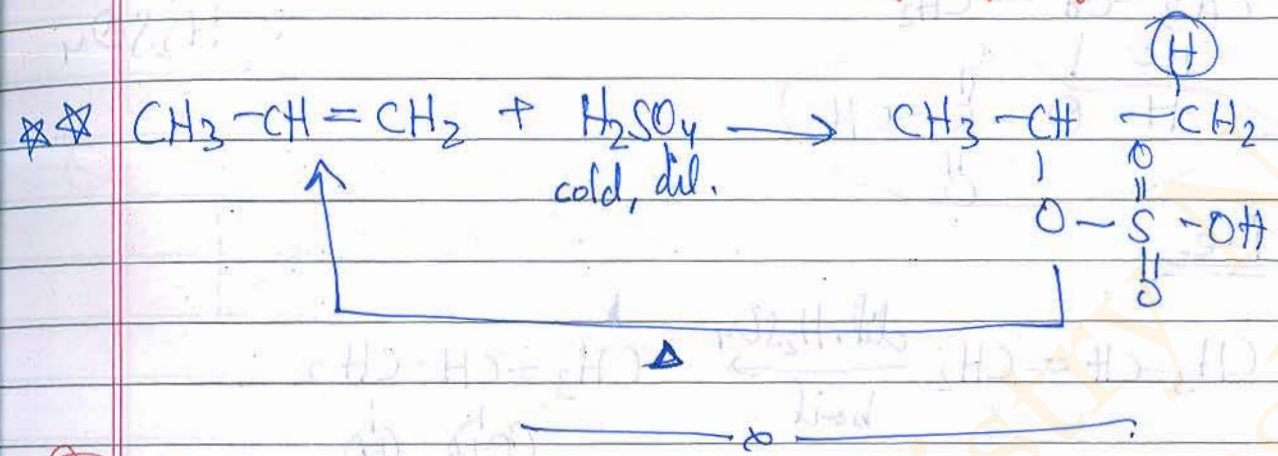
✡✡ $CH_3-CH=CH_2 + H_2SO_4 \xrightarrow[\text{cold, dil}]{(H^+ HSO_4^-)} CH_3-CH(OSO_3H)-CH_2(H)$

MK rule

dil H_2SO_4 → hydⁿ (जल आया)

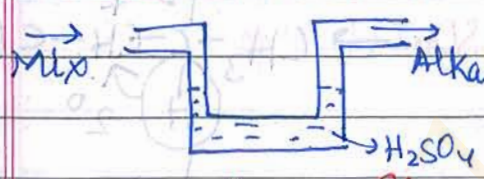
conc. H_2SO_4 → dehydⁿ (जल गया)
water gone





Q. R–H, Alkene — gaseous mixture — how to separate?

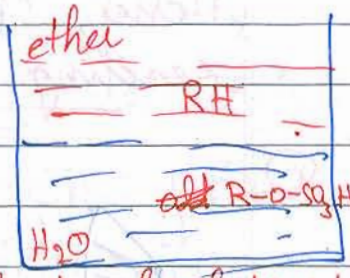
Alkene + R–H + H_2SO_4 (cold, dil.) → alkene reacts & retained, gas comes out is alkane.



Now, trap alkane in flask & heat the rest. Alkene is again formed (see above rxn). Hence, alkane & alkene are separated.

If alkane, alkene are liq.

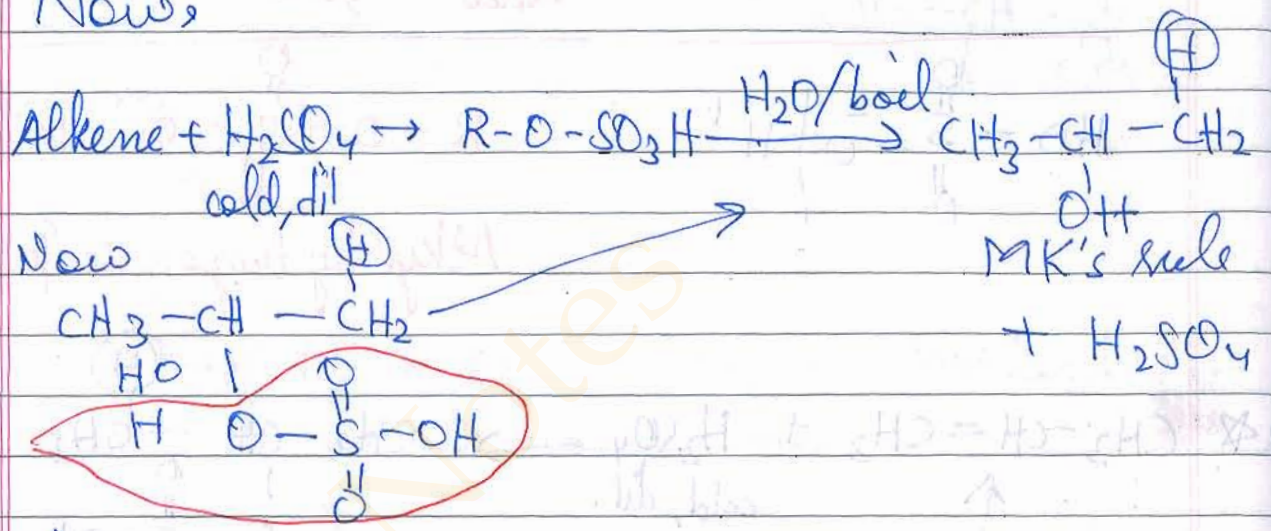
R–H, Alkene (liq) ⇌ Ether → Add H_2O + H_2SO_4



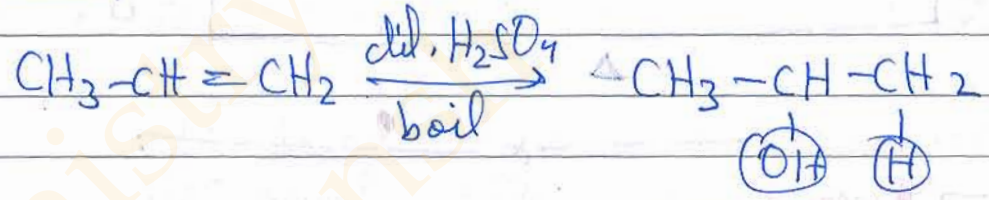
Separate by fractional distillⁿ

• alkene + H_2SO_4 (cold, dil) → $ROSO_3H$ (more H_2O soluble)

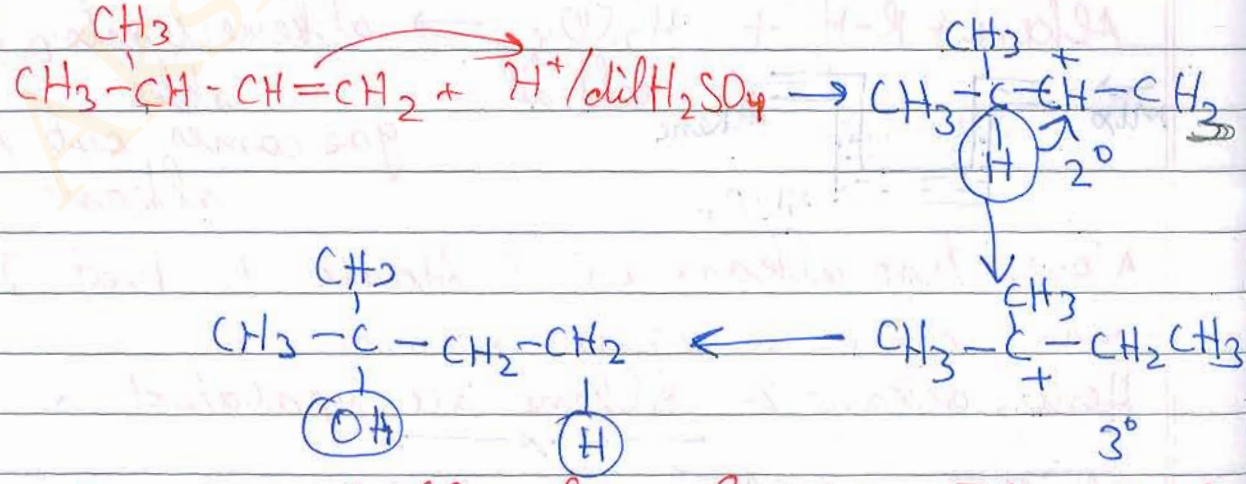
Now,



i.e.

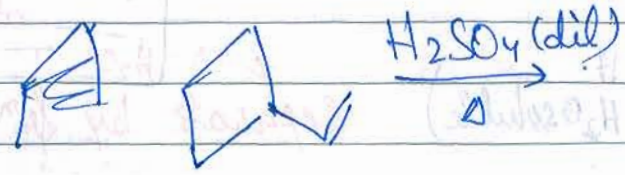


Mechanism

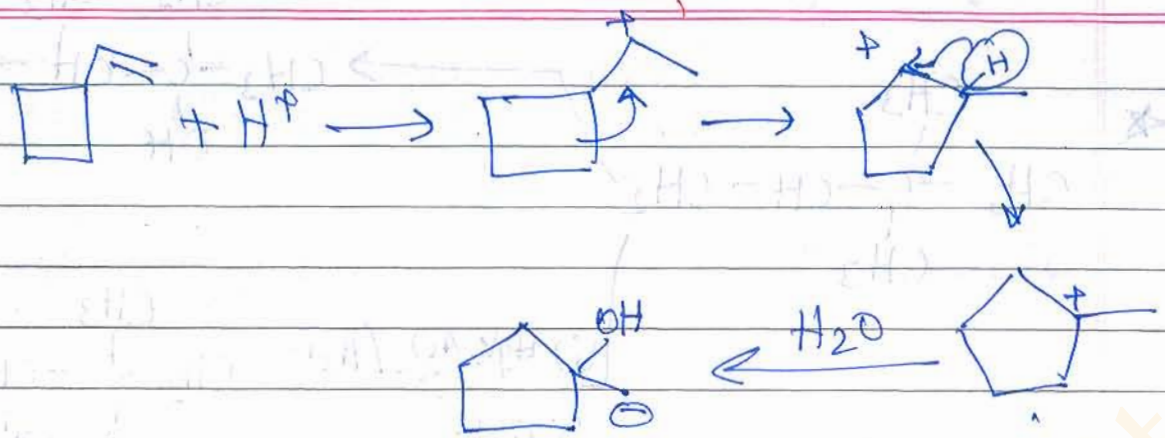


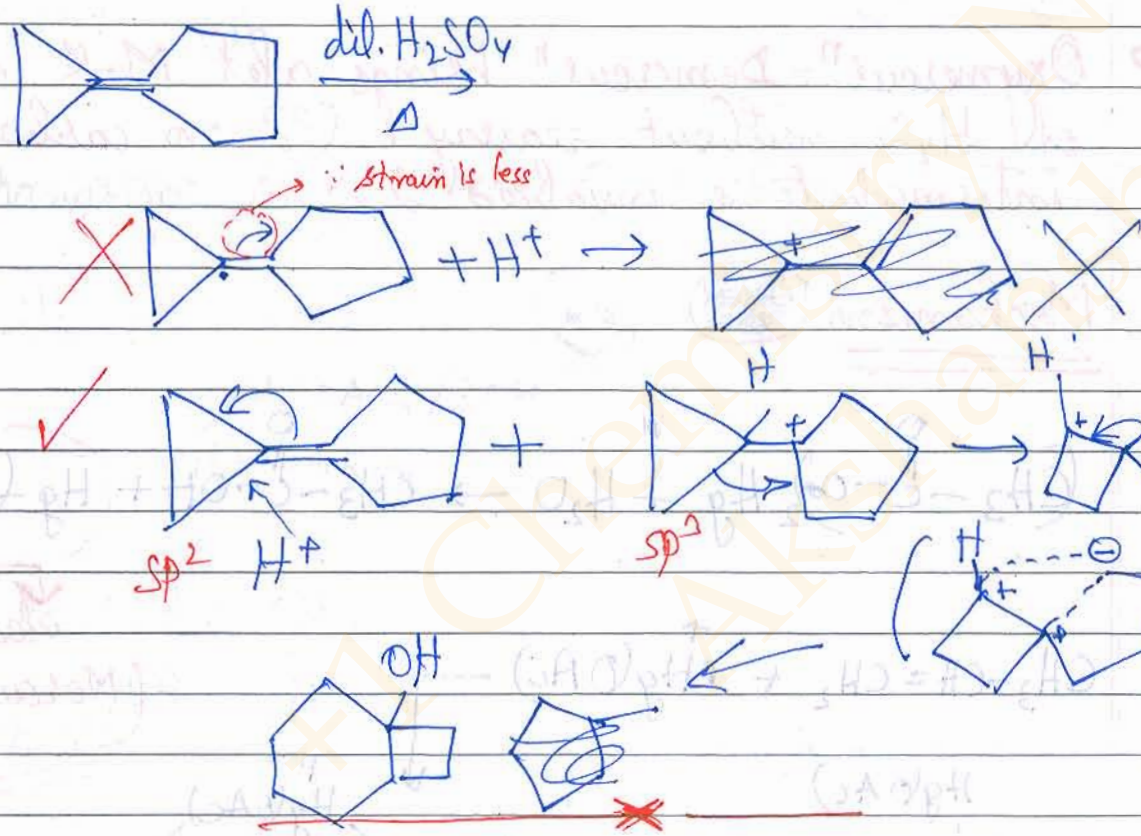
- Rxn proceeds through carbocation intermediate. Hence, H & OH can shift from their usual reacting posn.

(c)



Ac → acetyl grp ($CH_3-\overset{O}{\overset{\|}{C}}-$)





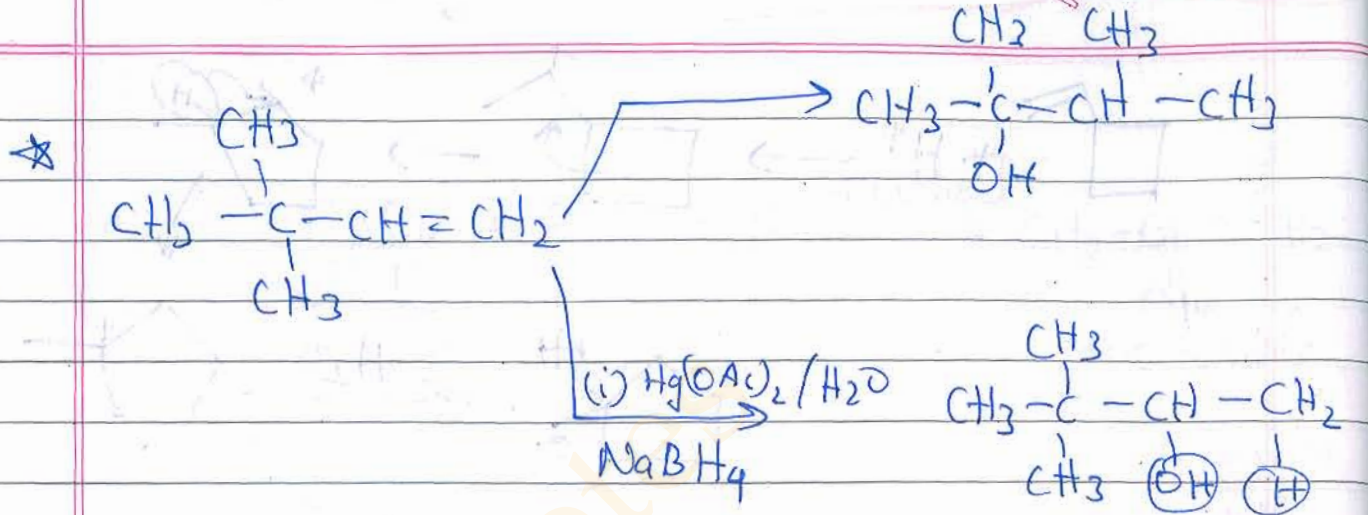
(ii) Hydⁿ of Alkene using $Hg(OAc)_2$ grp

OXYMERCURⁿ - DEMERCURⁿ RXN

$Hg(O-\overset{O}{\overset{\|}{C}}-CH_3)_2$ (Mercuric acetate)

$CH_3-CH=CH_2 \xrightarrow[H_2O]{Hg(OAc)_2} \xrightarrow{NaBH_4} CH_3-\underset{OH}{CH}-\underset{H}{CH_2}$

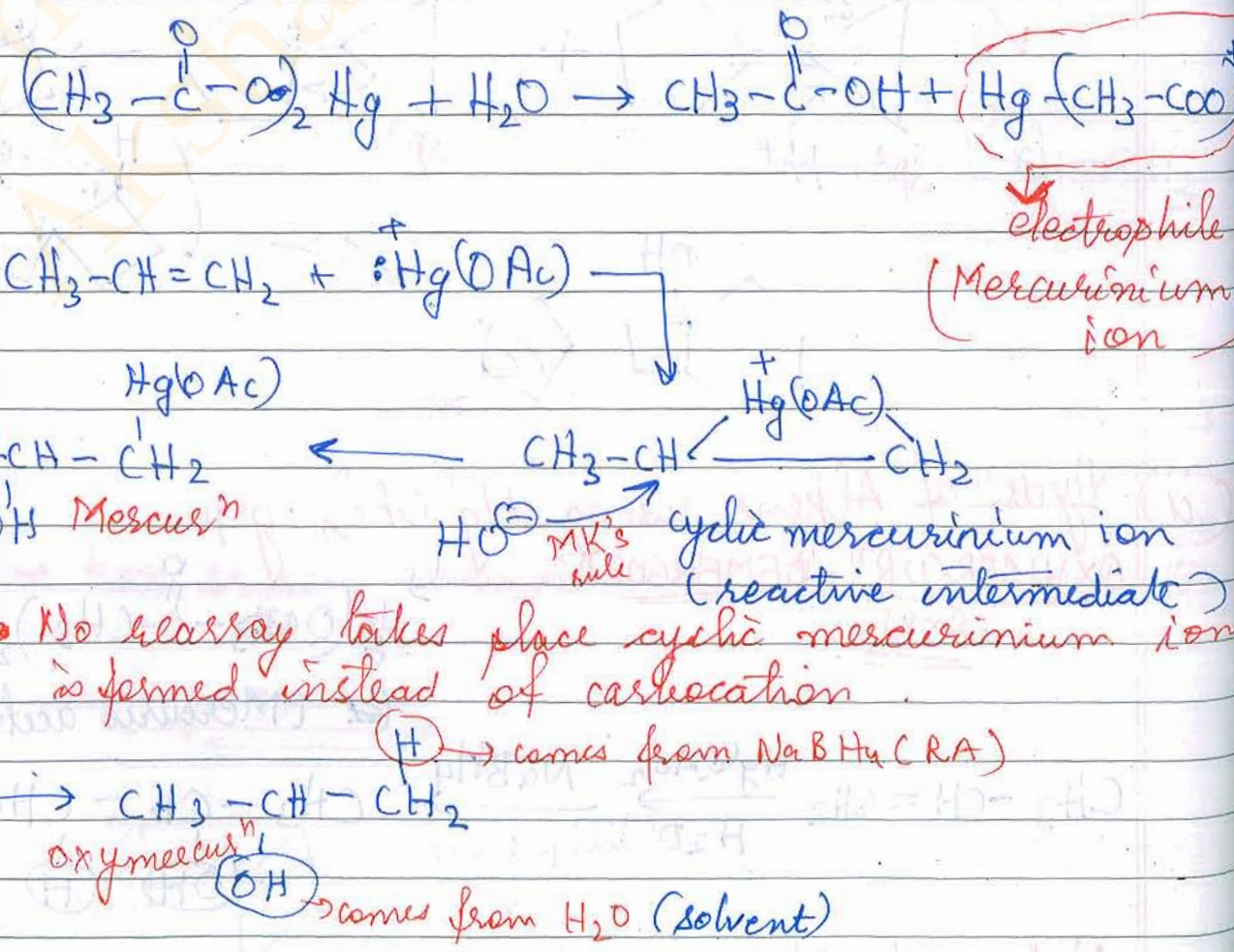
Note: Advantage: No rearrangement takes place



- Oxymercuⁿ - Demercuⁿ brings abt M.K. addⁿ of H_2O without rearrangement. (∵ no carbocation intermediate is involved)

Mechanism





- No rearrangement takes place cyclic mercurinium ion is formed instead of carbocation.

H → comes from $NaBH_4$ (RA)

- Change coming by Changing source.

$CH_3-CH=CH_2$

(i) $Hg(OAc)_2/H_2O$
(ii) $NaBD_4$.

$CH_3-CH(OH)-CH_2(D)$

(i) $Hg(OAc)_2/D_2O$
(ii) $NaBH_4$

$CH_3-CH(OD)-CH_2(H)$

- ~~Changing~~ ALKOXY MERCURⁿ ~~Rxn~~ demercusⁿ Rxn

$CH_3-CH=CH_2$

(i) $Hg(OAc)_2/ROH$.
(ii) $NaBH_4$

$CH_3-CH(OR)-CH_2(H)$

ether.

(iii) HYDROBORⁿ OXIDⁿ (HBO)

$CH_3-CH=CH_2 + B_2H_6 \xrightarrow[H_2O_2]{OH^- \text{ alkali}} CH_3-CH(H)-CH_2(OH)$

diborane

Anti MK's rule of addⁿ.

- Here also, rearray doesn't take place.

Mechanism

$B_2H_6 \rightleftharpoons 2\,H_2B-H$ (LA, electrophile)

$CH_3-CH=CH_2 + H_2B-H \rightarrow [CH_3-\overset{\oplus}{C}H-CH_2 \;\; H-\overset{\ominus}{B}H_3]$

$CH_3-CH_2-CH_2-BH_2 \rightleftharpoons R-BH_2$ (say)

$CH_2=CH-CH_3$ ← R_2BH ← $H-B(-H)-CH_2-CH=CH_3$

R_3B (intermediate)

$3CH_3-CH=CH_2 + BH_3 \rightarrow R-B(-R)-R$ (Trialkyl borane, intermediate)

$R_3B \xrightarrow{H_2O_2} 3R-OH + B(OH)_3$ (BORIC ACID)

At nett: $CH_3-CH_2-CH_2$ (H comes from B_2H_6, OH comes from solvent) — Anti MK addⁿ.

$CH_3-CH=CH_2 \xrightarrow{B_2H_6} (CH_3-CH-CH_2)_3B \xrightarrow[HO^-]{H_2O_2} CH_3-CH(H)-CH_2(OH)$

$CH_3-CH_2-CH_2 + B(RCOO)_3$ ← $RCOOH$

Hydrogenⁿ of double bond takes place.

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- B_2H_6 enables hydrogenⁿ of alkene (controlled & selective).

- $CH_3-CH=CH_2$ $\xrightarrow{B_2D_6}$ $(CH_3-\underset{D}{CH}-CH_2)_3B$ $\xrightarrow{RCOOH}$ $CH_3-\underset{D}{CH}-\underset{OH}{CH_2}$ + B(OO)

$(CH_3-\underset{D}{CH}-CH_2)_3B$ $\xrightarrow{H_2O_2/OH^-}$ $CH_3-\underset{D}{CH}-\underset{OH}{CH_2}$ Anti MK rule

✱ OXIDⁿ of ALKENE

(1) OZONOLYSIS ✱✱

$R_2C=C(R')H + O_3 \rightarrow$ R-C(-O-O-O-)-C(R')-H $\rightarrow$ OZONIDE

MOLOZONIDE (very unstable rearranges itself)

OZONIDE (not very very reactive → can be separated)

$R_2C=O + O=C(R')H + ZnO$ ← Zn/H_2O — Zinc Hydrolysis (only this) Reductive ozonolysis (full form name)

Ketone + aldehyde (other combinⁿs can also occur)

Alsotes

$R_2C=O + O=C(R')H +$ (DMSO) ← CH_3-S-CH_3 (DMS) dimethyl sulphide (mild RA)

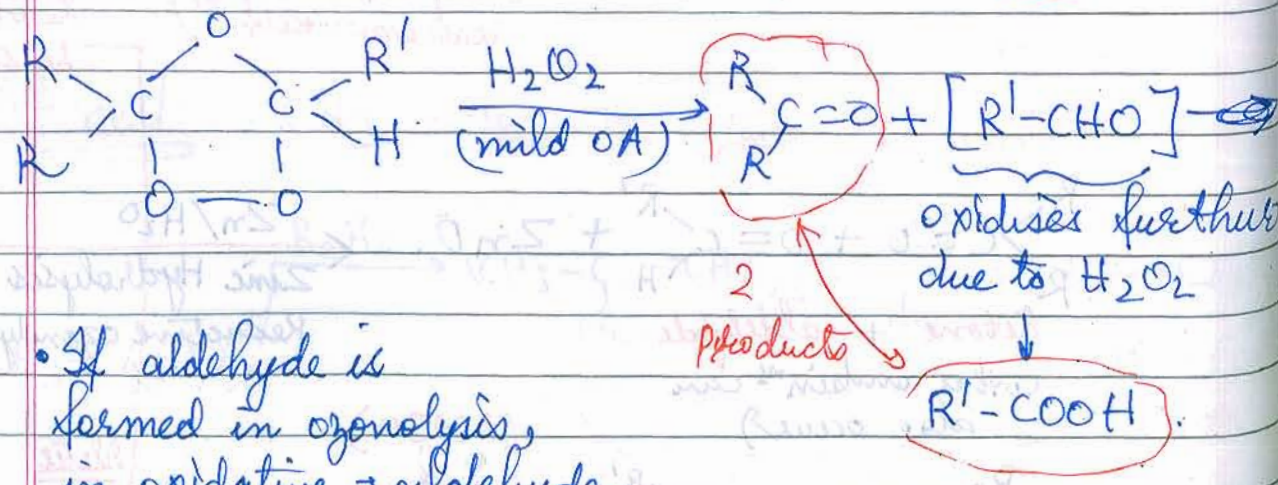
$CH_3-S(=O)-CH_3$ dimethyl sulphoxide

CONCEPTUAL QUESTION

☆ Redⁿ with DMS (dimethyl sulphoxide) is prefered over Zn/H_2O. Why?

Reason 1. With DMS homogeneous catalysis is there (DMS → liqd & ozonide → liqd).
But in Zn/H_2O, heterogeneous catalysis is there. (Zn/H_2O → metal(s) & ozonide → liqd).
Redⁿ with DMS is favourable i.e redⁿ with Zn occur heterogeneously & ∴ less effective
Reason 2. Homogeneous redⁿ occur with DMS & ∴ more effective.
Reason 2. DMS is a mild RA → reduces ozonide. But do not reduces the product aldehydes & ketones.
Zn/H_2O is a strong RA. → reduces a major portion of product aldehydes & ketones further into corresponding alcohols.
Reason 3. With DMS, the bi-product DMSO is also an organic compd as well as highly inert → mixes with the solvent, but, don't interfere into rxn. (Whereas, Zn does).

☆☆ • OXIDATIVE OZONOLYSIS OF OZONIDE



• If aldehyde is formed in ozonolysis, in oxidative → aldehyde will convert to carboxylic acid.

If alkene is terminal

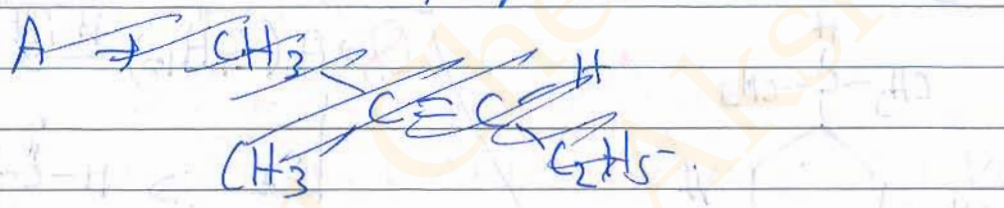
$$R-CH=CH_2 + O_3 \xrightarrow{H_2O_2} R-COOH + H-\overset{\overset{O}{\|}}{C}-OH$$

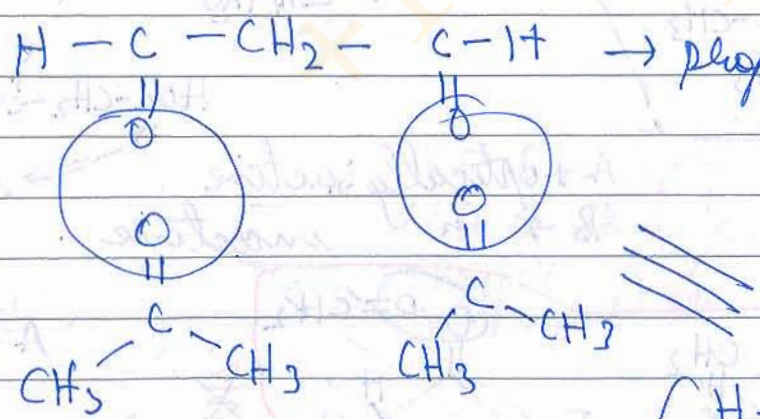
} oxidises to CO_2 & H_2O.

Q. $A\ (C_9H_{16}) \xrightarrow[\text{High T, P.}]{H_2/Pt} C_9H_{20}$

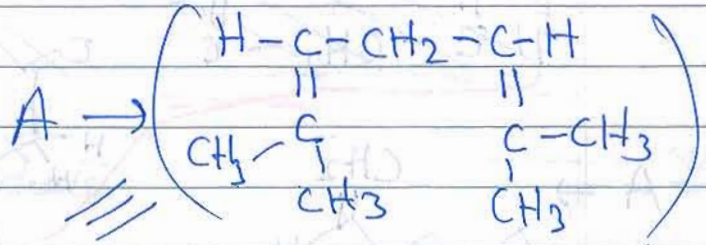
$A \xrightarrow[Zn-H_2O.]{O_3}$ Propanone + Propanedial.

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}=O$ Propanone.





Propane dial.



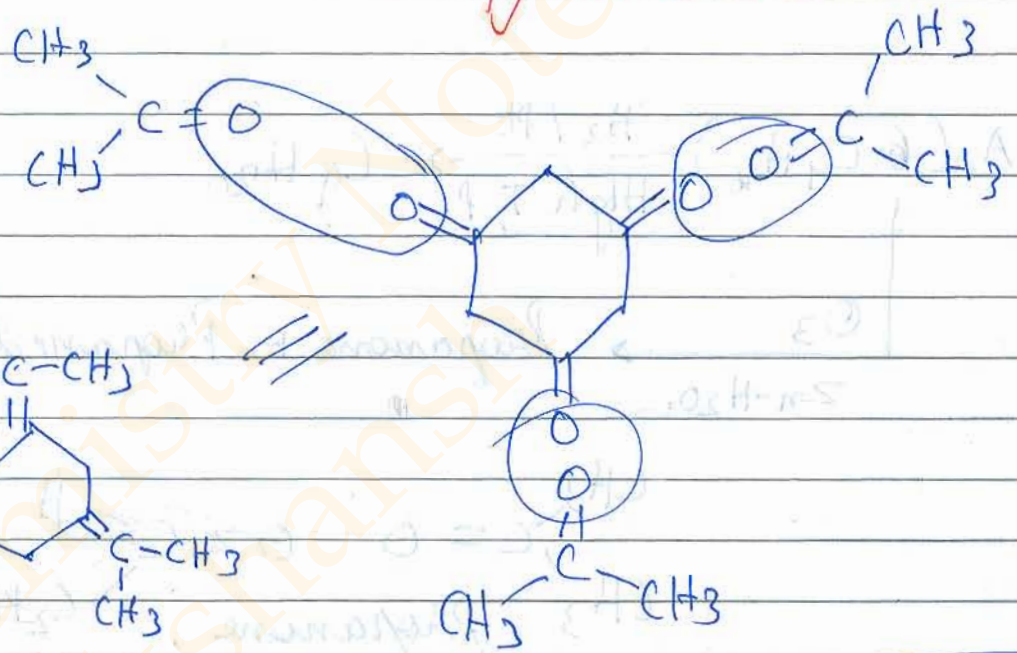
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}=CH-CH_2-CH=\underset{CH_3}{\overset{CH_3}{C}}$

Q. $A(C_{15}H_{24}) \xrightarrow{H_2/Pt} B(C_{15}H_{30})$

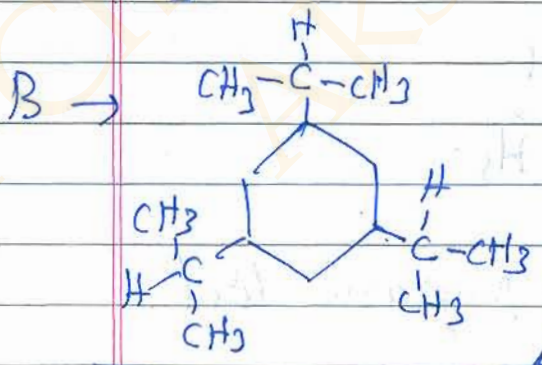
$A \xrightarrow[Zn/H_2O]{O_3}$ Propanone + Cyclohexane trione

B is optically inactive.

Identify A & B.

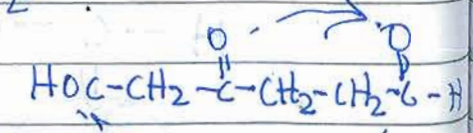


A →



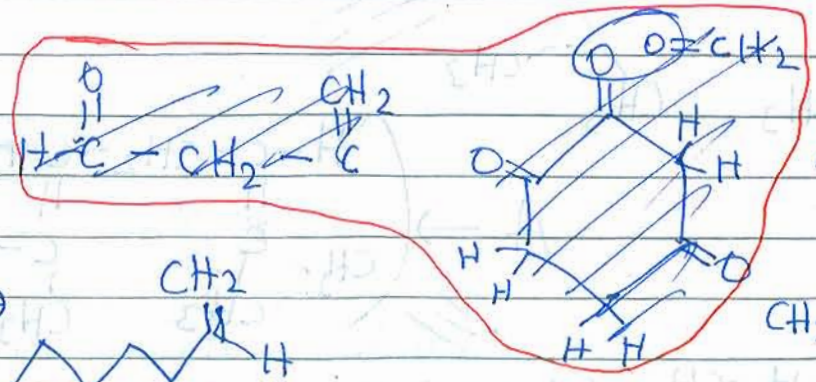
B →

Q. $A(C_7H_{10}) \xrightarrow{H_2/Pt} B(C_7H_{14})$

$A \xrightarrow[+Zn/H_2O]{O_3}$  + 

A → optically inactive

B → " inactive.



A →

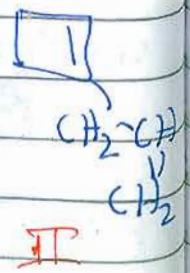


II

A →



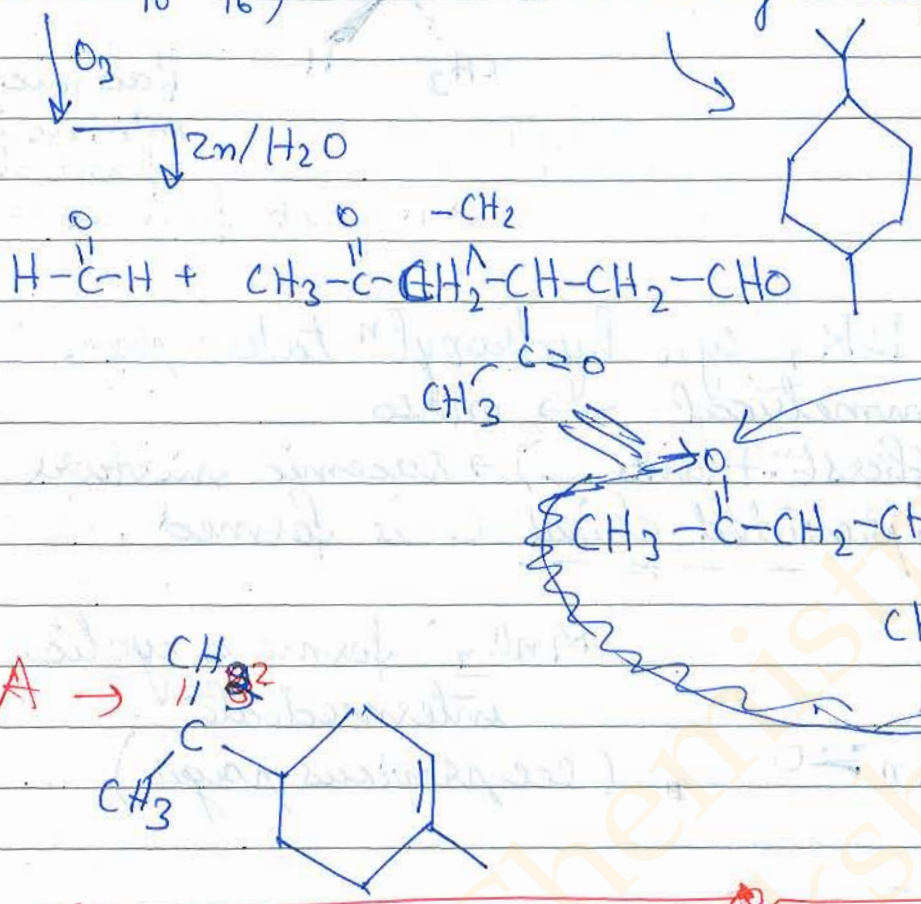
I



II

3 answers of A are possible by combining 2 C=O in permutn

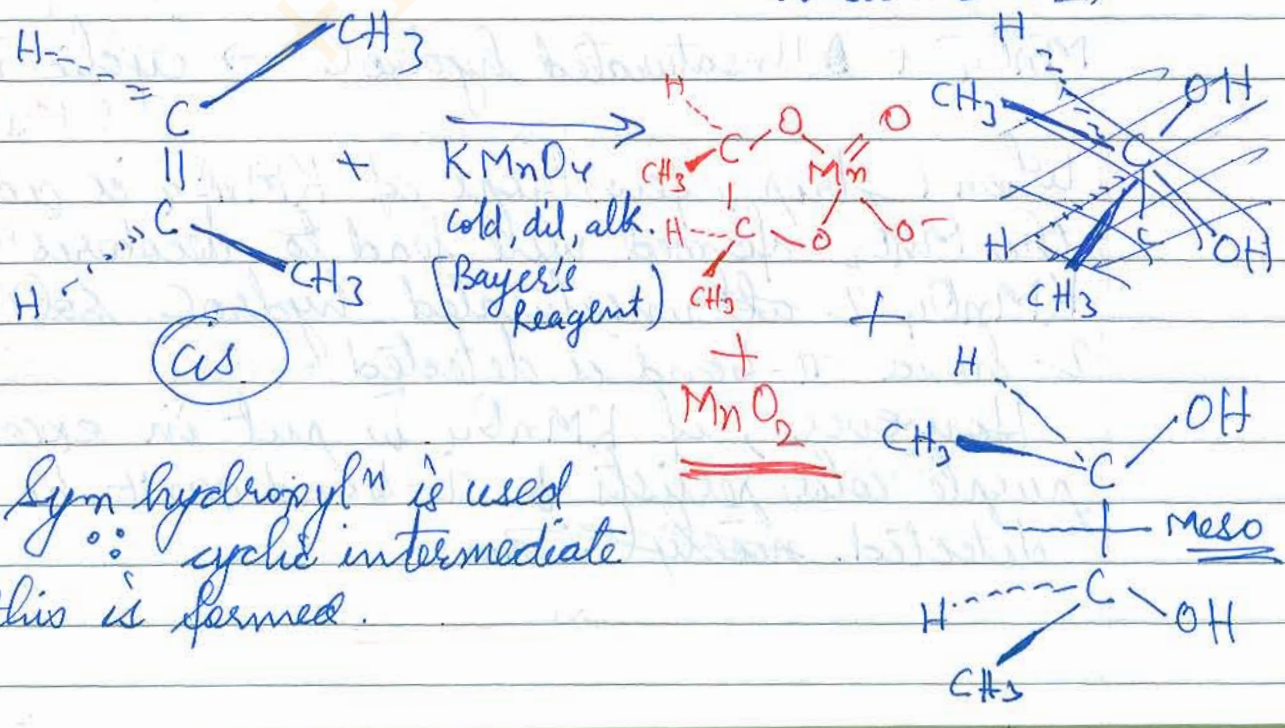
Q. A ($C_{10}H_{16}$) $\xrightarrow{H_2/Pt}$ 4-methyl-1-isopropyl cyclohexane



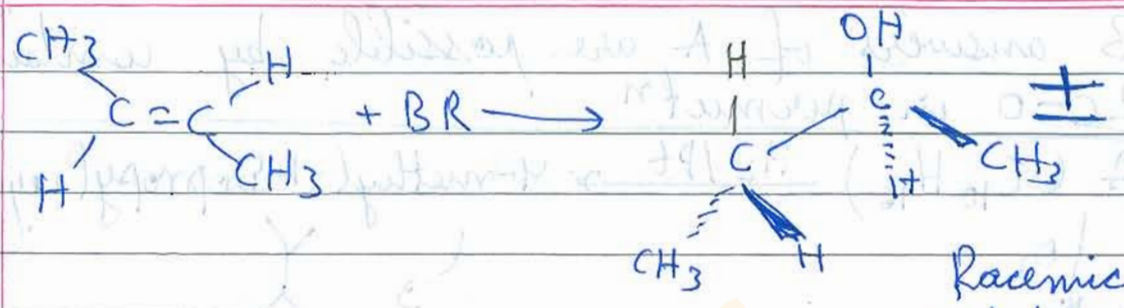
• BASIC-MEDIUM

✡ OXIDⁿ WITH PERMANGANATE ($KMnO_4$)

(basic medium)



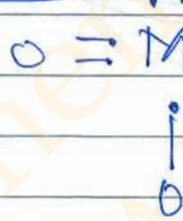
- Syn hydroxylⁿ is used ∵ cyclic intermediate this is formed.



Racemic mixture is formed (OH react from up & down)

With BR, syn hydroxyl^{n} takes place
as symmetrical → meso
rest others (--+ same --) → racemic mixture
• provided chiral C is formed.

MnO_4^-



MnO_4^- forms a cyclic intermediate.
(see previous page)

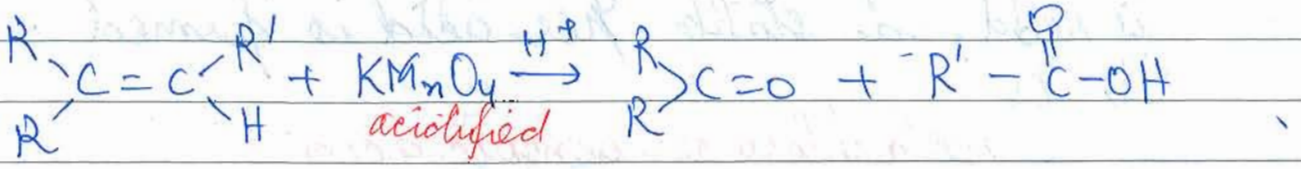
Rxn of MnO_4^- for π-bond detection

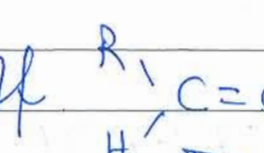
MnO_4^- + Unsaturated hydroC → cyclic intermediate + MnO_2

When 1 drop / few drops of $KMnO_4$ is added, the MnO_2 formed will lead to decolorisn of $KMnO_4$ & unsaturated hydroC soln & hence π-bond is detected.

However, if $KMnO_4$ is put in excess, purple color persists & π-bond can't be detected. ~~mostly~~ so

✱ $KMnO_4$ in ACIDIC MEDIUM.

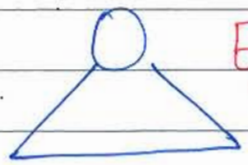


- If  + $KMnO_4 \xrightarrow{H^+}$ $R-\overset{O}{\overset{\|}{C}}-OH + CO_2\uparrow$

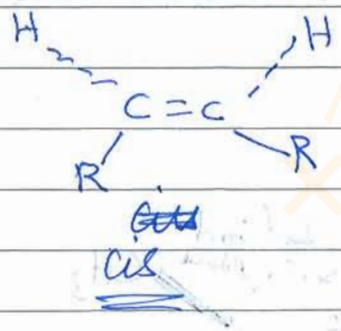
↓ lime water milky. So,

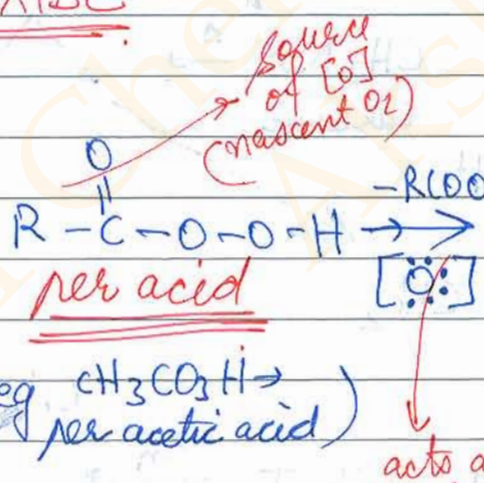
Imp- Detect terminal/internal alkene } we can detect terminal alkene. If it was internal alkene, CO_2 couldn't be produced.

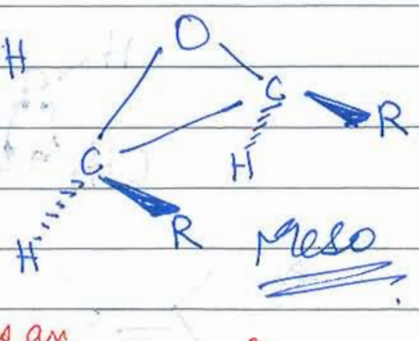
✱ EPOXIDⁿ of ALKENE



EPOXIDE





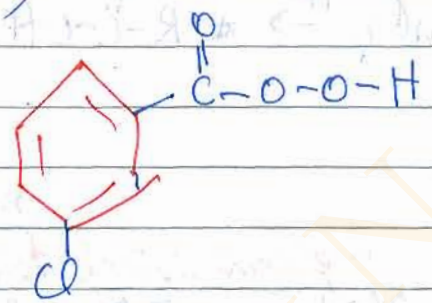


✱ trans/unsymmetrical → Racemic mixture.

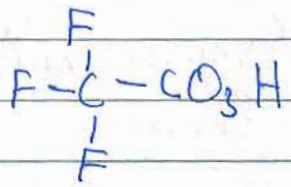
cis → meso compd

* Peroxy compd is very unstable. So, since it is reqd, a stable per acid is formed. It is

(1) meta chloro per benzoic acid (MCPBA)



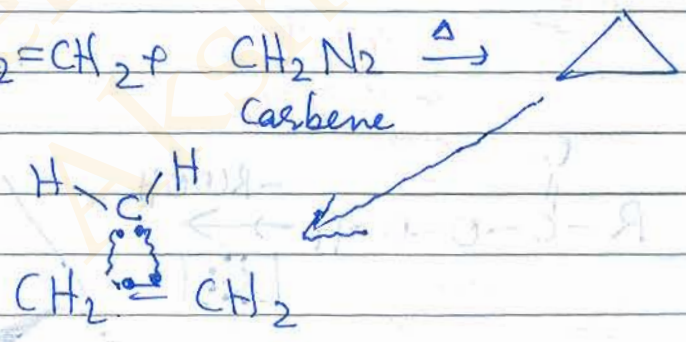
(2) TFPAA (Trifluoro per acetic acid)

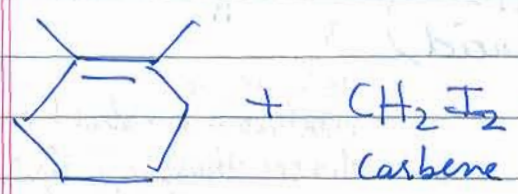


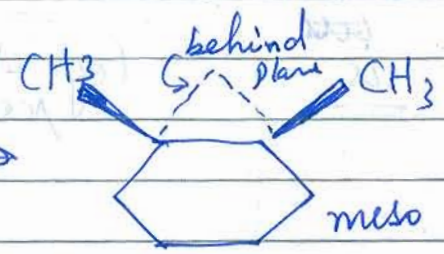
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* Rxn with Carbene

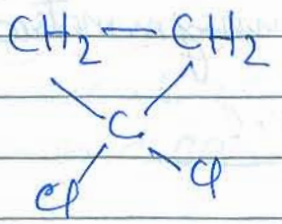
* $CH_2=CH_2 + CH_2N_2 \xrightarrow{\Delta}$



*  + CH_2I_2 (Carbene) $\xrightarrow{Zn}$

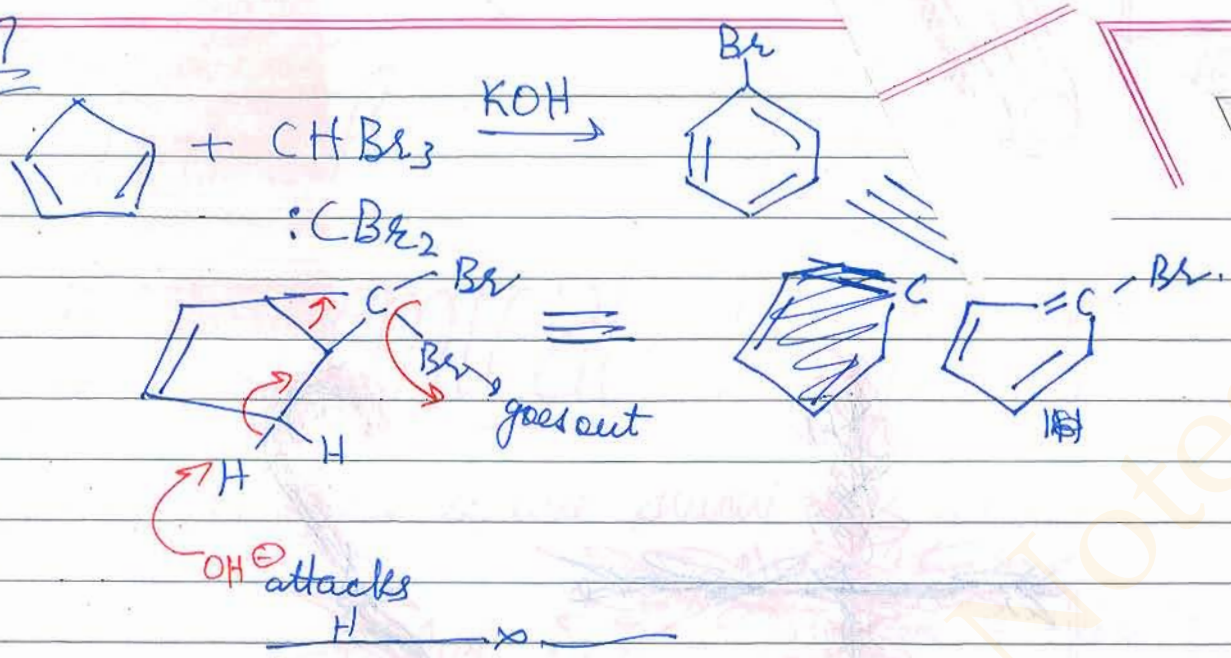


* $CH_2=CH_2 + CHCl_3 \xrightarrow{OH^-}$ $:CCl_2$



classmate
Date 14.4.10
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Q. 97



+1 Chemistry Notes
Akshansh