Paper - CHEMISTRY OF S & P BLOCK ELEMENTS ....

TEACHER NAME - DR. OM PRAKASH YADAV

COURSE & SEMESTER - B.SC (Hon) GE. II SEM

Electron gain enthalpy. Electron affinity:

When an electron is added to an isolated gaseous atom some amount of energy released which is called an electron gain ~~entha~~ enthalpy or electron affinity.

$$M + e^- \longrightarrow M^- + \text{energy}$$

↓

EGE or EA

$$\Delta E = -ve$$

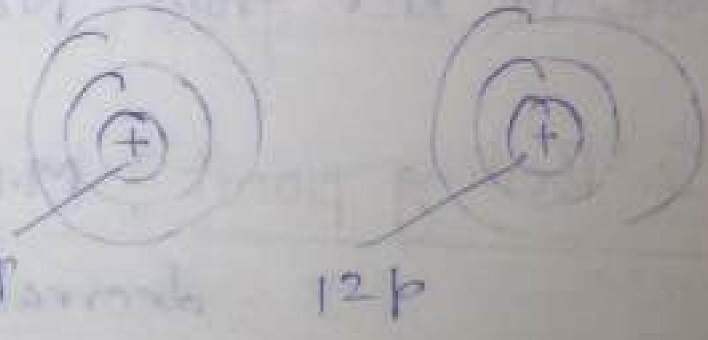
Electron affinity was positive quantity

Electron gain enthalpy = -ve value

(*) Electron gain enthalpy for alkali metal in respective period is smallest except Noble gas

(*) On ~~moo~~ moving down the group electron gain enthalpy decreases.

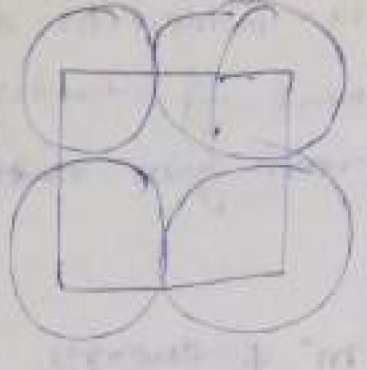
(*) Electronegativity:- Tendency to atract shaired pair of electron



Na Mg Al

0 - lattice unit

Density :

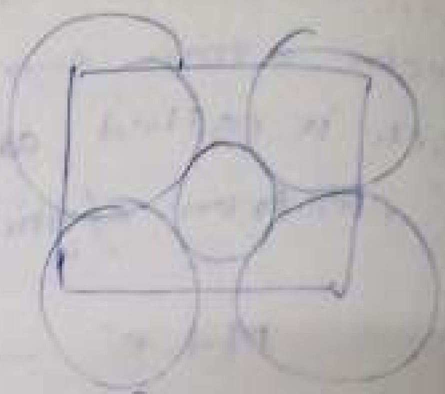


Atomic mass = ~~20~~ 22

22 × 4 = 88

(A)

less density



Atomic mass = 20

20 × 5 = 100

(B)

more density

Li Na K, Rb Cs

↓

Body centred cubic closed pack

Metallic radius	
Li	1.52Å
Na	1.86Å
K	2.27Å
Rb	2.48Å
Cs	2.65

(Na → K: large size) ⇒ down the group density increases but exceptionally density of K is smaller than that of Na because there is large increase in size from Na to K

$d = \frac{m}{V}$

Melting point & Boiling point :

M.P & B.P decreases down the group.

Chemical Properties :-

1. **Reaction with Oxygen :-** All alkali metals directly react with oxygen

Li → simple oxide

Na → peroxide

K, Rb, Cs → Superoxide

⇒ small cation stabilises with small anion.
Large cation stabilises with large anion.

Li^{+} (small) O^{-2} (small) → Li_2O

$\overset{+}{Na} - \overset{-}{O} - \overset{-}{O} - \overset{+}{Na}$ — Sod peroxide

⇒ On moving down the group stability of super oxide increase.

⇒ Potassium superoxide is used in the removal of CO_2 (or generation of O_2)

$4KO_2 + 2H_2O \longrightarrow 4KOH + 3O_2$

$4KOH + 2CO_2 \longrightarrow 2K_2CO_3 + 2H_2O$

$4KO_2 + 2CO_2 \longrightarrow 2K_2CO_3 + 3O_2$

⇒ Peroxides

$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2 \downarrow$

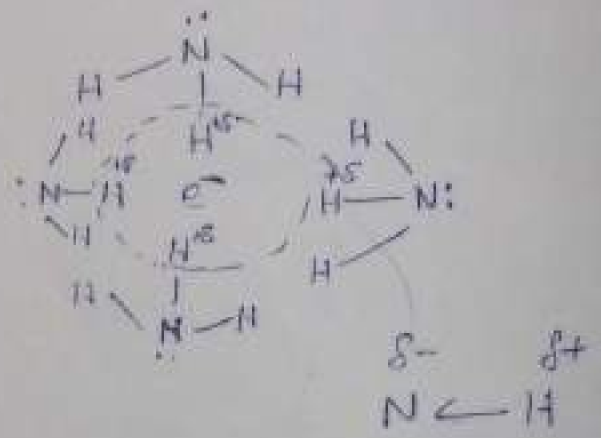
Solubility in Ammonia :-

$$M + NH_3 \longrightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

$[M(NH_3)_x]^+$ → Solvated cation (Ammoniated cation)

$[e(NH_3)_y]^-$ → Solvated electron (Ammoniated electron)

Ammoniated electron is present in the cavity formed by ammonia molecule



Dilute solution of alkali metal in ammonia is (i) blue due to the presence of ammoniated electron
(ii) paramagnetic
(iii) Strong reducing agent.

Ammoniated electron reduce aerial oxygen to superoxide to peroxide

$$O_2 \xrightarrow{e^-(am)} O_2^- \xrightarrow{e^-(am)} O_2^{2-}$$

superoxide → peroxide

Exception

$$Au + e^-(am) \rightarrow Au^{\ominus}$$

am → ammoniated

$K_2[\overset{+2}{Ni}(CN)_4] + 2K \xrightarrow{2e^- (am)} K_4[\text{Ni}$

$\overset{0}{Fe}(CO)_5 + 2Na \xrightarrow{e(am)} Na_2[\overset{-2}{Fe}(CO)_4] + CO$

Free ~~e~~ electron i.e Paramagnetic

⇒ if solution become concentrate electrons get paired ⟶ solⁿ ~~diag~~ diamagnetic

↓

Colour ⟶ copper bronze

↓

because it form metal cluster

⇒ if a trace of any impurity over a dirty nail, metal amide and H_2 is gas is formed

$$M + NH_3 \longrightarrow MNH_2 + \frac{1}{2}H_2$$

Flame Colouration :-

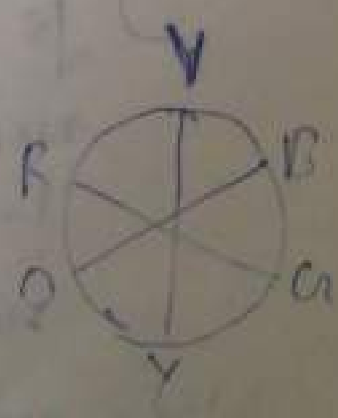
Li ⟶ Crimson red

Na ⟶ golden yellow

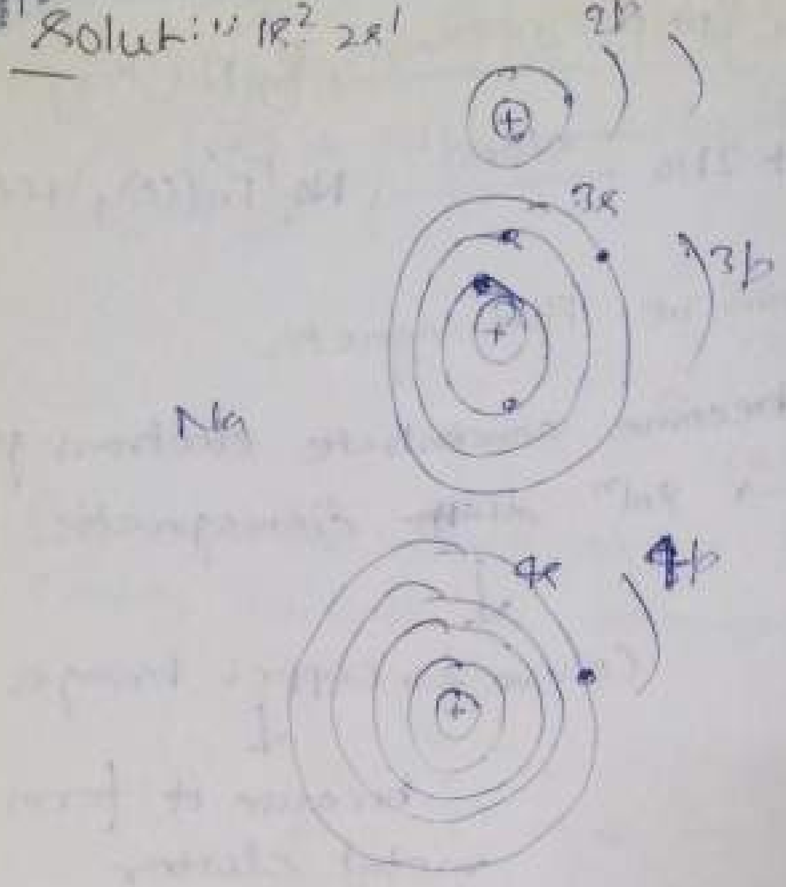
K ⟶ Violet

Rb, Cs ⟶ Violet

[Bunsen flame]



Solution: $1s^2 2s^1$



Halides: Alkali metal react directely with halogen to form halide

LiX, NaX, KX, RbX CsX   X = F, Cl, Br, I

Ex ⇒ LiCl, LiBr ⟶ dehumidifier

Lattice energy of halides ⟶ LiF, LiCl, LiBr, LiI

⊛ Lattice energy:

$Na(s) + \frac{1}{2}Cl_2 \xrightarrow{\Delta H} NaCl(s)$

$Na(s) \xrightarrow{S} Na(g) \xrightarrow{-e^-} Na^+$

$\frac{1}{2}Cl_2 \xrightarrow{D} Cl(g) \xrightarrow{e^- \text{ gain enthalpy}} Cl^-$

$Na^+ + Cl^- \xrightarrow{U_0} NaCl(s)$

When one mole of ionic crystal is form its constituent gaseous ion some amount of energy is released in this process this released energy is called lattic energy (U_0)

Or
Energy required to break one mole of io. crystal into its constituent gaseous ions is called lattice energy.

Born Lande equation :

$$U_0 = -\frac{NAZ_+Z_-e^2}{r_0}\left(1-\frac{1}{n}\right)$$

N = Avogadro number
A = Madulung constant depend only on the geometry of crystal
Z_+ and Z_- Charge on cation and anion respectively.
e^- = electronic charge
r_0 = Interionic distance
n = constant

$$U_0 \propto \frac{Z_+Z_-}{r_0}$$

LiF
LiCl
LiBr
LiI
lattice energy decrease ↓

* because internuclear distance increases.

LiCl
NaCl
KCl
RbCl
CsCl
Decreasing order of lattice energy

Solubility of Halides:-

Lattice energy > Hydration energy
↓
compound insoluble

~~HE > LE~~

| LE > HE | compound soluble

Na — Cl

$U_0 = 180$ Kcal

HE = 200 Kcal.

(*) Down the gp HE and lattice energy both decrease. But lattice energy decr more rapidaly than hydration energy. Thus solubility down the group increases.

$BeSO_4$
$MgSO_4$
$CaSO_4$
$SrSO_4$
$BaSO_4$ ↓ solubility decreases down the group

Insoluble [$SrSO_4$, $BaSO_4$]

| HE > LE |

⇒ Hydration energy decrease more rapidly than lattice energy

⇒ size increases
HE as well as lattice energy both increases.

⇒ MCO_3, $M_3(PO_4)_2$ solubility decrease, ~~the group~~ down the group.

BeF_2	$Be(OH)_2$	due to
MgF_2	$Mg(OH)_2$	LE > HE
CaF_2	$Ca(OH)_2$	
SrF_2	$Sr(OH)_2$	
BaF_2 ↓	$Ba(OH)_2$	

Solubility increase down the group.

* All Nitrate " soluble in water.

Alkaline earth metal:

$_4Be \rightarrow 2s^2$
$_{12}Mg \rightarrow 3s^2$
$_{20}Ca \rightarrow 4s^2$
$_{38}Sr \rightarrow 5s^2$
$_{56}Ba \rightarrow 6s^2$
$_{88}Ra \rightarrow 7s^2$

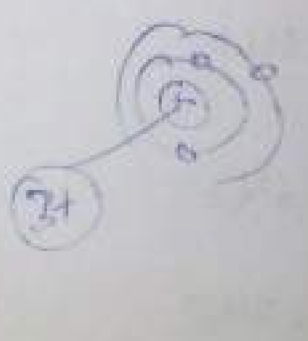
Ra → Radioactive

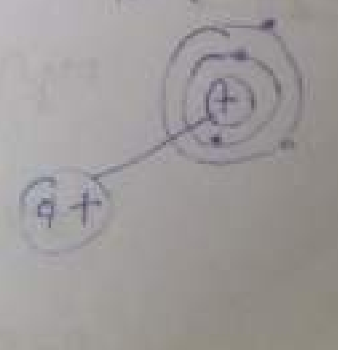
Nature of earth crust is alkaline (Basic) due to presence of oxides and hydroxides of gp 2 elements. so these elements are called alkaline earth metal

1) **Size:** size of alkaline earth metal is smaller than that of earth metal.

$_3Li$ $_4Be$

$_{11}Na$ $_{12}Mg$





alkali metal in the
respective period
⇒ down the gp decreases.

Electropositive and Mettalic Character :→

Less | Less

compare to alkalimetal.

Alkalimetals
↓
soft
↓
can cut with
the help of Knife

Cohessive energy

Alkali earth metal
↓
less soft
than alkalimetal

⊛ Electronegativity :

⊛ Electron affinity or electron gain enthalpy :

Na > Mg
$3s^1$ $3s^2$

⊛ Hydration energy :

NaCl	$MgCl_2 \cdot 6H_2O$
KCl	$CaCl_2 \cdot 6H_2O$
	$BaCl_2 \cdot 2H_2O$

Hydroxide :

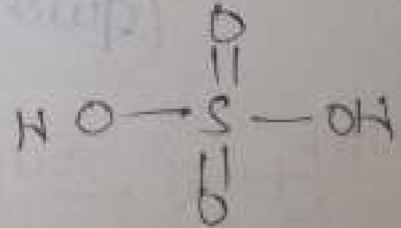
$Be(OH)_2$
$Mg(OH)_2$
$Ca(OH)_2$
$Sr(OH)_2$
$Ba(OH)_2$

↓ Basic character increases down the group

⇒ Hydroxide of metals : are basic

⇒ Hydroxides of non metal are oxy acids

$Ba(OH)_2$ $SO_2(OH)_2$



Sulphates :-

HE > LE

	HE		LE
Soluble in water	25?kcal	$BeSO_4$	15?kcal
	23?kcal	$MgSO_4$	-170
	200	$CaSO_4$	-160
Insoluble in water	150	$SrSO_4$	-155
	120	$BaSO_4$	-150

solubility decreases down the group

$$\text{(Fertilizer)} \leftarrow CaSO_4 \cdot 2H_2O \xrightarrow{150^\circ C} CaSO_4 \cdot \tfrac{1}{2}H_2O$$

Cal. sulphate dihydrate (Gypsum) — Plaster of paris

$$CaSO_4 \cdot \tfrac{1}{2}H_2O \xrightarrow{200^\circ C} CaSO_4$$

$$\uparrow SO_3 + CaO \xleftarrow{1100^\circ C} CaSO_4$$

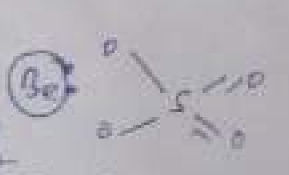
(quick lime)

⊛ Thermal Stability of sulphates :-

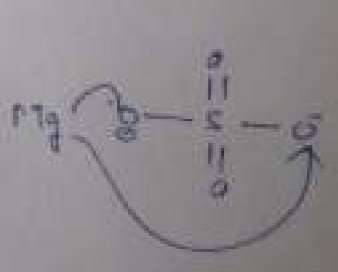
$BeSO_4$
$MgSO_4$
$CaSO_4$
$SrSO_4$
$BaSO_4$
↓

⊛ Thermal Stability down the gp increases because basicity down the gp increases

⊛ due to smaller it not bonded between both O of SO_4^{-2}



⊛ It is easily bonded due to larger size



* similarity thermal stability of carbonates incr. down the group

* Carbides :-

C ⟶ -ve oxidation state

* $\overset{+2}{Be_2C}$ and BeC_2

C^{4-} ; BeC_2 ⟶ $C_2 \Rightarrow \overset{\ominus}{C}\equiv\overset{\ominus}{C}$

* $2Be + C \xrightarrow{110^\circ c} Be_2C$

* $Be + CH\equiv CH \xrightarrow{heat} BeC_2 + H_2\uparrow$

Impt
* $BeC_2 + 2H_2O \longrightarrow Be(OH)_2 + CH\equiv CH$ ~~Ethylene~~ acetylene

Impt
* $Be_2C + 4H_2O \longrightarrow 2Be(OH)_4 + CH_4$

* MgC_2 and Mg_2C_3

by. K.K.Y

V.Impt
* $Mg + 2C \xrightarrow[\text{electric furnace}]{\Delta} \overset{+2\ 2-}{MgC_2} \longrightarrow \bar{C}\equiv\bar{C}$ or C_2^{-2}

* $2MgC_2 \xrightarrow{heat} Mg_2C_3 + C$; Mg_2C_3 ⟶ $\overset{\ominus}{C}=C=\overset{\ominus}{C}$ or C_3^{4-} or $^{-}C\equiv C-\overset{=}{C}$ or Allylide

* $Mg_2C_3 + H_2O \longrightarrow 2Mg(OH)_2 + CH_3-C\equiv CH$

Propyne

* Mg, Ca, Sr and Ba

$M + C \xrightarrow{heat} MC_2$

$MgC_2 \xrightarrow{\Delta} Mg_2C_3 + C$

CaC_2, SrC_2 ~~and~~ BaC_2

$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + HC\equiv CH$

Reaction of CaC_2 with N_2

$CaC_2 + N_2 \longrightarrow CaNCN +$
Calcium cynamide

$CaCN_2$
Ca^{2+} CN_2^{2-}

N → 5×2, C → 4, +2 =] 16

$[N=C=N]^{2-}$
Isoelectronic with CO_2

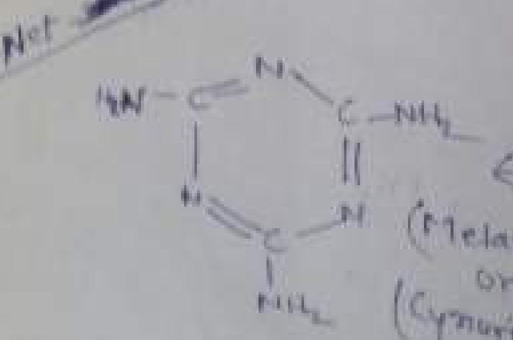
O=C=O (6, 4, 6) = 16 → Isoelectronic

O=C=O

React^n of $CaCN_2$ (Calcynamide) is better fertilizer than Urea but very expensive

- $CaNCN + 5H_2O \longrightarrow CaCO_3 + 2NH_4OH$
- $CaNCN + H_2SO_4 \longrightarrow CaSO_4 + H_2NCN$
- $CaNCN + CO_2 + H_2O \longrightarrow CaCO_3 + H_2NCN$
- $H_2NCN + H_2O \longrightarrow NH_2-CO-NH_2$ (Synthesis of urea)
- $H_2NCN + H_2S \longrightarrow NH_2CSNH_2$ Thiourea
- $H_2NCN + \xrightarrow{pH\ 7-9}$ $NCNC(NH_2)_2$ dicynamide → ~~Pyrolys~~ Pyrolysis

Note:

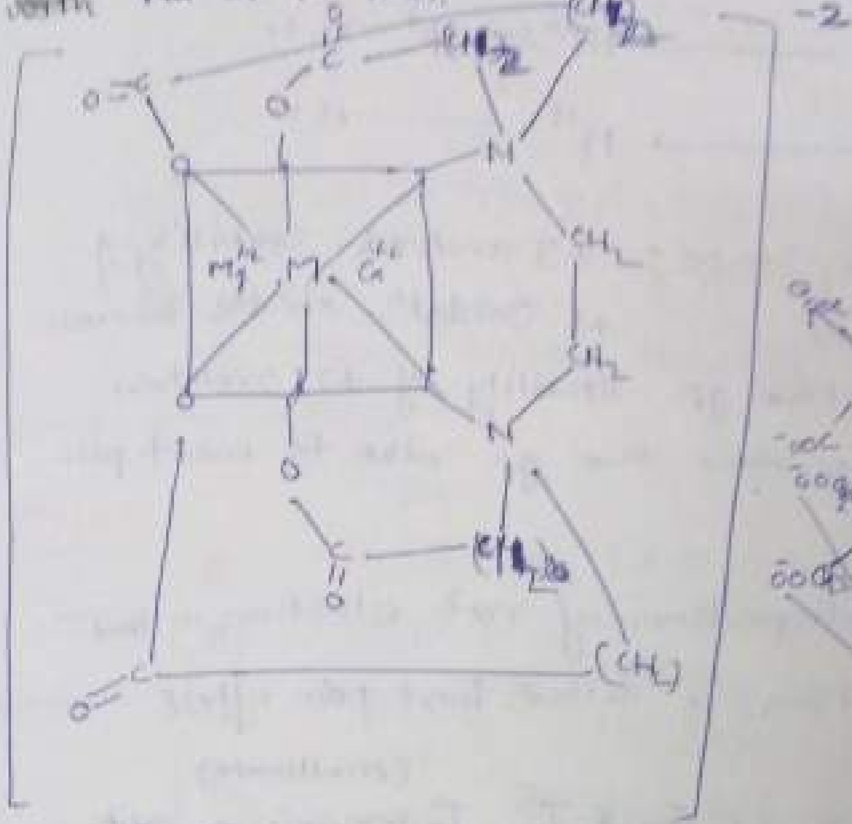


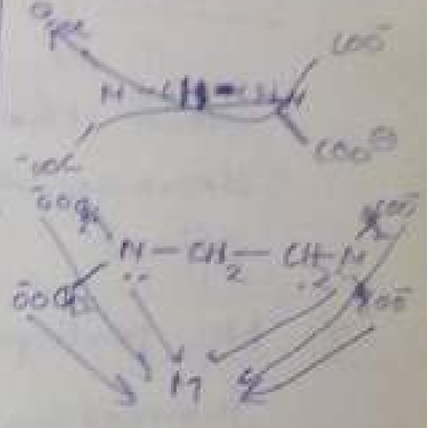
(Melamine) or (Cynuric amid)

* Complex formation:-
* Measurement of Hardness of water:-
* complexometric titration

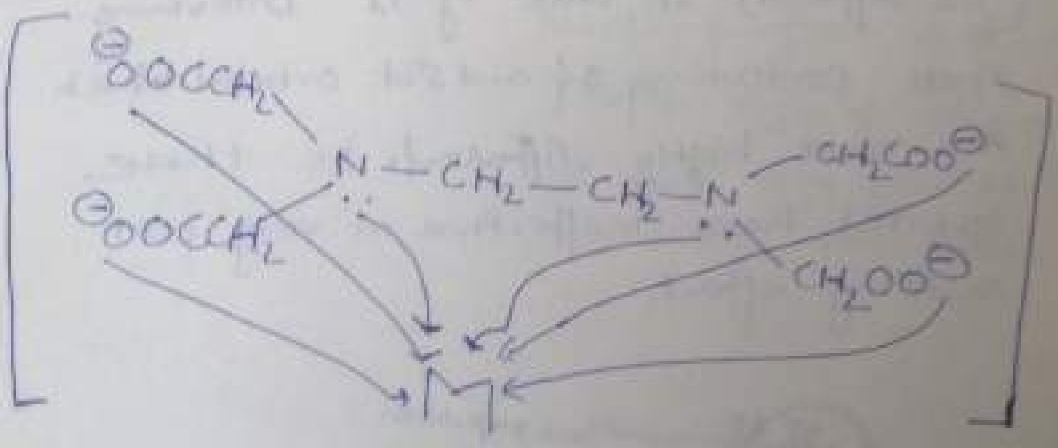
Hard Water V/s $EDTA^{4-}$
↓
Insoluble in water but soluble

with Na or K salt





* Because of Steric hindrance $[Mg(EDTA)]^{-2}$ is less stable



(EDTA Hexadentate ligand)

P- Block

* **Group 13 Element :-** General electronic configuration — ns^2np^1

Size			Ox. S
85pm	$_5B$ →	$2s^22p^1$	+3
143 pm	$_{13}Al$ →	$3s^23p^1$	+3
135 pm	$_{31}Ga$ →	$3d^{10}4s^24p^1$	+3, +1
167 pm	$_{49}In$ →	$4d^{10}5s^25p^1$	+3, +1
170pm	$_{81}Tl$ →	$4f^{14}$	+3, +1

Smaller size due poor shielding effect

Oxidation State :- +3 and +1 Stability of +1 Oxidatn state increases down the gp stability of +3 oxidation decreases down the gp due to inert pair effect

* No participation of ns^2 electron in bond formation is called. Inert pair effect

* In case of Ga & In Intervining (penultimate) orbit containing d-e which are large in size (i.e diffused). In Case of Tl Intevening shell containing 4f and 5d orbital which are more highly diffused. i.e there orbital have ineffective or very poor shilding effect.

* poor shilding of NH_2 of valence shell by interversing of d & f electron

(i) shiliding
(ii) interenergy e^- to unpaire NH_2 e^- is exceede the energy when they form the bond, then $2e^-$ remaine pair.

Tl^{+} Tl^{+3}

$Tl^{+3} + 2e^- \longrightarrow Tl^{+}$

* Tl^{+1} is more stable than Tl^{+3} due to inert pair effect

* **Size :-**

		Pm
Increase ↓	B	85
	Al	143
decrease ←	Ga	135
	In	167
Increase ← ↓	Tl	170

* S & p orbitals are present in intervining shell (strong shilding effect) increase size in large

* if d & f orbitals are present in the intewining shell, then due to poor shielding effect of d & f orbitals size of element increases very small & remain same as decrease

Ionization energy:-

B ⟶ 800

Al ⟶ 578

Ga ⟶ 579

In ⟶ 558

Tl ⟶ 589

Mettalic character:- Mettalic character increases from B to Al then decreases from Al to Ga to In + Tl

- B - Non-metal
- Mettalic charcter explain on the basis of standerd electrode potential.

	M^{3+}/M (in volt)
B	−0.87
Al	−1.66
Ga	−0.56
In	−0.36
Tl	+0.26

$M^{3+} + 3e^- \longrightarrow M \qquad E^\circ = -0.87V$

$\Delta G^\circ = -nEV = +ve$

$M \longrightarrow M^{3+} + 3e^-, \quad E^\circ = +0.87$

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

$= -3 \times 96500 \times .87$

Al > Ga > In > Tl

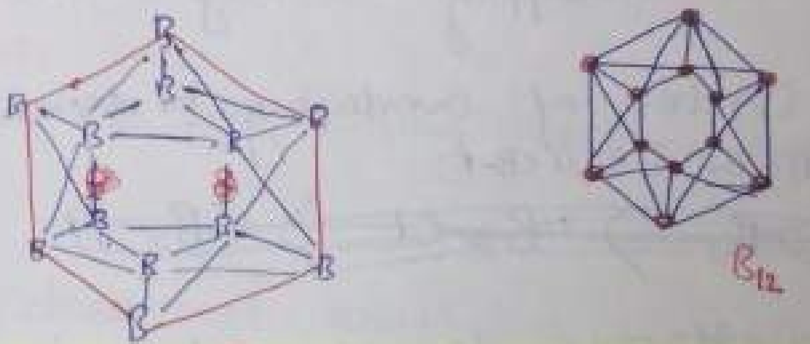
⟵ Mettalic charcter order

* 1 Faraday = Charde carried by one mole of electro

$$1 \text{ Faraday} = 6.023 \times 10^{23} \times 1.6 \times 10^{-19}$$
$$= 9500 \text{ Culamb}$$

Melting Point :-

* Boron has highest M.P because of its icosahedral structure.
* 20 faces & 12 Corners
* Each B-atom attached with five adjecent B-atom



* Boron exist B_{12}

Icosahedral of Boron

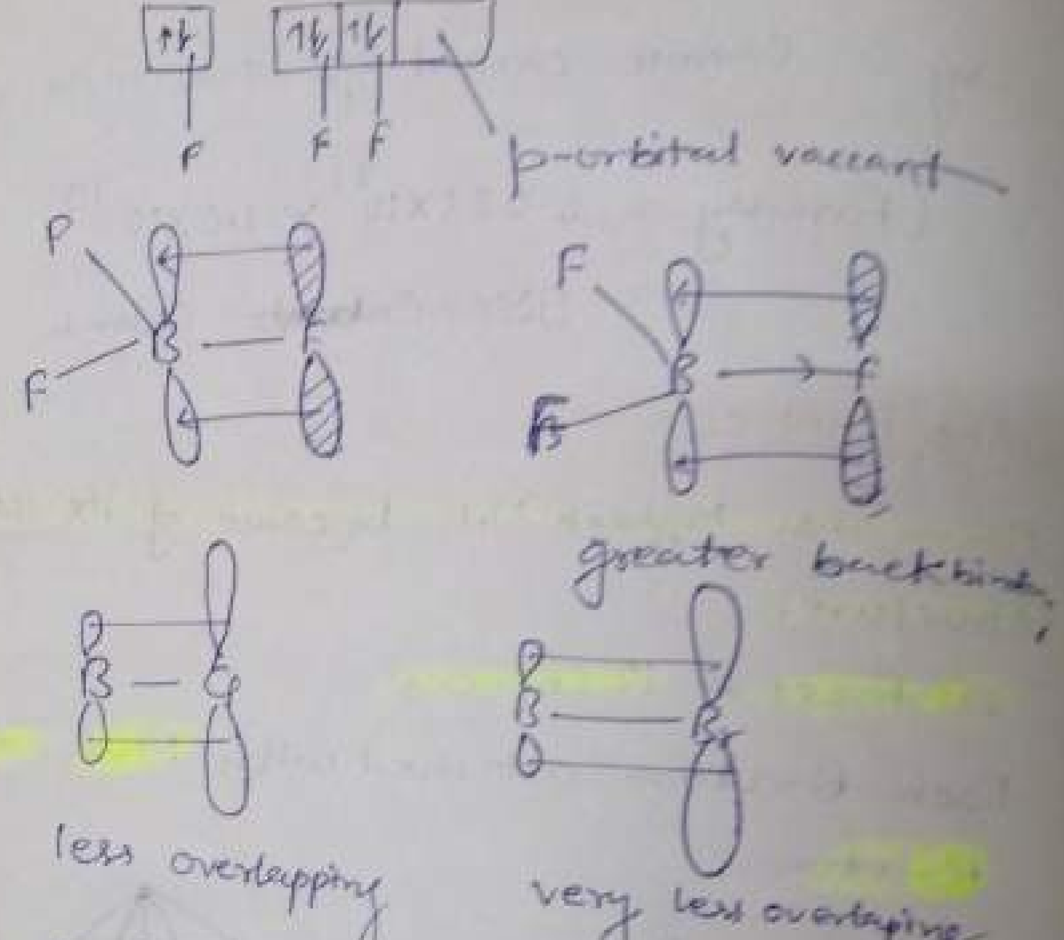
* Halides :- Halides are e⁻ dificient i.e lewis ~~base~~ acids

BX_3 AlX_3 GaX_3 InX_3 TlX_3

BF_3
BCl_3
BBr_3
BI_3

* Order of acidity
But in actual
$BF_3 < BCl_3 < BBr_3$
due pπ - pπ bonding

BF_3 — sp^2



⊛ Order of overlaping in decreasing order.

⊛ B–Br < B–Cl < B–F

~~B–Br > B–Cl > B–F~~

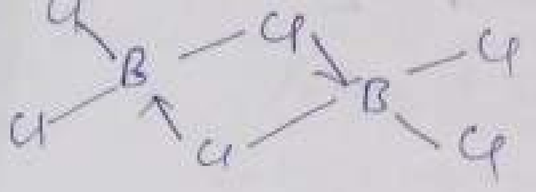
⊛ overlaping decrease due size increase F to Br.

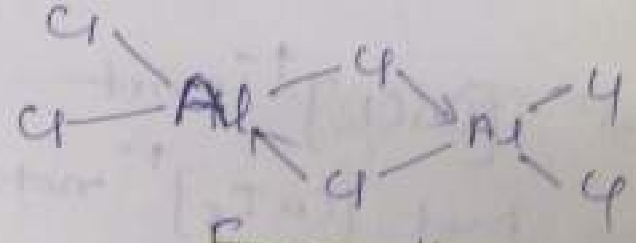
⊛ <u>Note</u> BI_3 is not exist

BCl_3 → Monomer

Al_2Cl_6 → dimer

(both) → Lewis acid





Form dimer.

(*) Not form dimer due to smaller size of B atom and hence it is unable to accomodate electron from Halogenes

(*) $TlCl_3$ exist but strong oxidising agent

~~TlCl~~

TlI_3 does not exist

$$Tl^{+3} + 2e \longrightarrow Tl^{+} + e$$

$$2I^{-} \longrightarrow I_2 + 2e$$

I^{-} → strong ~~oxidising~~ reducing agent

Tl^{+3} → strong oxidising agent

$$Tl^{3+} + 2e \longrightarrow Tl^{+}$$

less stable → more stable

* FeI_3 does not exist
$FeCl_3$ exist

$$Fe^{3+} + e^- \longrightarrow Fe^{+2} \times 2$$
$$2I^- \longrightarrow I_2 + 2e$$
$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

* $[CuCl_6]^{4-}$ exist
but $[CuI_6]^{4-}$ not exist

$$2 \times [Cu^{+2} + e \longrightarrow Cu^{+}]$$
$$2I^- \longrightarrow I_2 + 2e$$

* SnI_4 does not exist

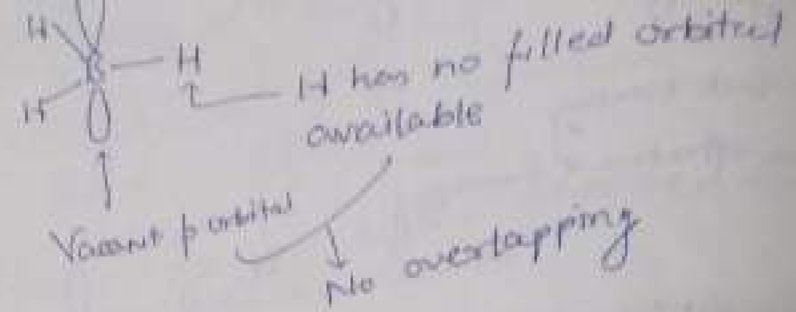
$$Sn^{4+} + 2e \longrightarrow Sn^{2+}$$
$$2I^- \longrightarrow I_2 + e$$

* due to ~~te~~ inert pair effect

* $F_2 > Cl_2 > Br_2 > I_2 \longrightarrow$ strong oxidising agent
* $F^- < Cl^- < Br^- < I^- \longrightarrow$ strong reducing agent

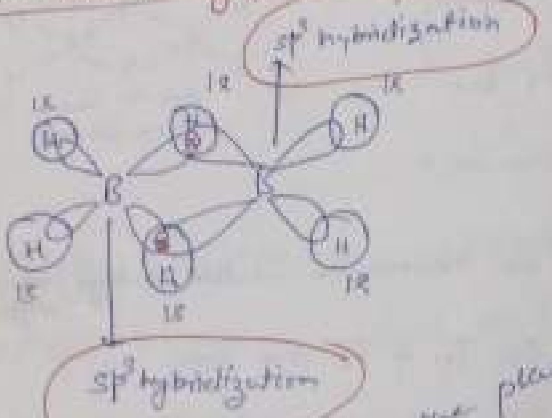
* dimer exist dimer/polymer
⇒ Hydrides of Boron called **Boranes**

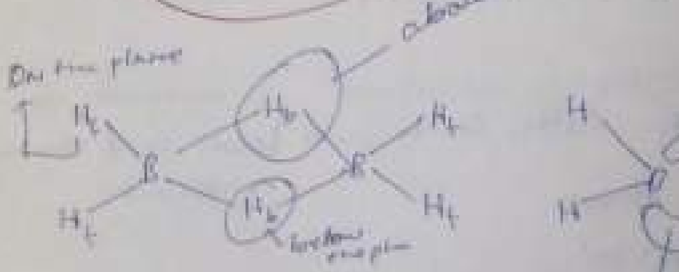
* **Diborane** :-

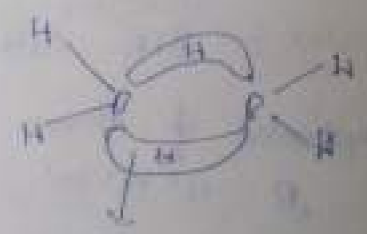


* Size of B is larger than H.
⇒ B — H σ bond is weak.

* **Structure of diborane** :-







H_t - Terminal Hydrogen
H_b = bridges Hydrogen

Banana bond

$B - H_b - B$

3C - 2E⁻ bond

$BH_t \rightarrow$ 3C - 2E bond

Physical properties

Properties:– Colourless, spontaneously react with and explodes with oxygen.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + 2165\ kJ$$

Chemical properties :–

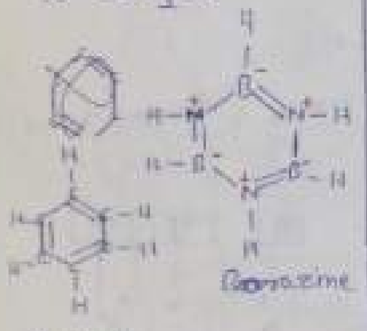
Rxn with Ammonia :–

$$B_2H_6 + NH_3 \xrightarrow[\text{low temp}^r]{\text{Excess } NH_3} B_2H_6 \cdot 2NH_3 \text{ adduct}$$

$\xrightarrow[\text{High temp}^r]{\text{excess } NH_3} (BN)_x$ Boron nitrile

$\xrightarrow[\text{High temp}^r]{2NH_3 : 1B_2H_6} B_3N_3H_6$ Borazine (Inorganic benzene)

Borazine is similar to benzene



Borazine is isoelectronic with benzene

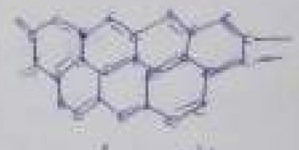
addition with HCl :–

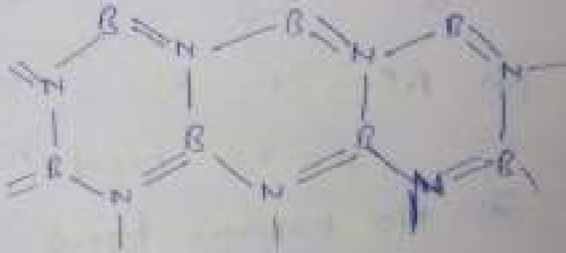
$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$

$B_2H_6 + 2LiH \longrightarrow 2Li[BH_4]$

$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$

Boron nitrile similar to graphite





(Boron nitrile)

Borazine :- ($B_3N_3H_6$)

Preparation :-

(i) By heating B_2H_6 and NH_3 in 1:2 ratio

$$2B_2H_6 + 6NH_3 \longrightarrow 3[B_2H_6 \cdot 2NH_3] \xrightarrow{200°C} B_3N_3H_6 + 12H_2$$

adduct → Borazine

Gate (ii) By heating BCl_3 with NH_4Cl ⟶

$$3NH_4Cl + 3BCl_3 \xrightarrow[\text{of } (C_6H_5Cl + Fe)]{140°C \text{ (In the presence}} Cl_3B_3N_3H_3$$

B, B, B trichloroborazine

$$Cl_3B_3N_3H_3 + 6LiBH_4 \longrightarrow 2B_3N_3H_6 + 6LiCl + 3B_2H_6$$

(iii) By heating NH_4Cl with $Li(BH_4)$ ⟶

$$3NH_4Cl + 3LiBH_4 \xrightarrow{220°C} B_3N_3H_6 + 2LiCl + 9H_2$$

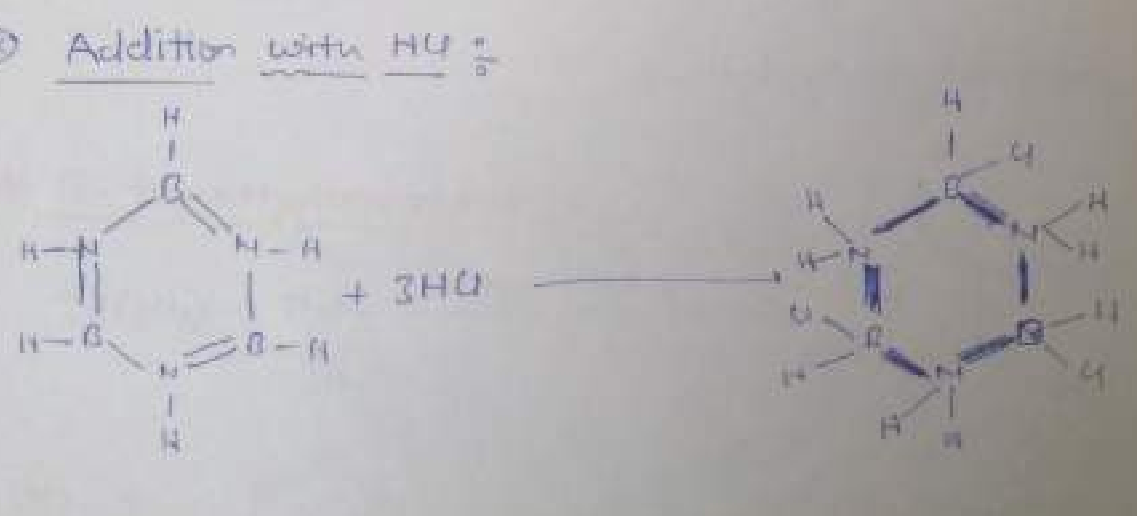
Gate 2014 Q.-18 The reaction of NH_4Cl

(b) (b)-(iv)

Chemical properties :-

Addition reaction : It only gives addition reaction and benzene only gives substitution reaction

Addition with HCl :



Carbon Family

General electronic configuration (Covalent Radius) Å I.P.

$_6C$	→ $2s^2 2p^2$	0.77	large decrease	1086
Si	→ $3s^2 3p^2$	1.17	small decrease	786
Ge	→ $3d^{10} 4s^2 4p^2$	1.22	large decrease	760
Sn	→ $4d^{10} 5s^2 5p^2$	1.44	small	709
$_{82}Pb$	→ $4f^{14} d^{10} 6s^2 6p^2$	1.47		716

Increase (C–Ge); small increase (Ge–Sn)

Ionization energy (KJ) mole :—

Oxidation state :- (+4)

oxidⁿ state of carbon

- Be_2C → −4
- Al_4C_3 → −4
- CaC_2 → +2
- Mg_2C_3 → −4
- CH_4 → +4
- CCl_4 → −4
- CH_2Cl_2 → 0
- CH_3Cl → +2

- C → +4
- Si → +4
- Ge → +4, +2
- Sn → +4, +2
- Pb → +4, +2

Stability of +2 oxidation state

Ge < Sn < Pb

- Pb^{+2} → strong reducing agent
- Pb^{+4} → strong oxidising agent

$Pb^{+2} < Pb^{+4}$ } stability order
$Sn^{+2} > Sn^{+4}$

* Down the gp +2 oxid^n state is more stable

* **Catenation** :- The ~~infinity~~ ability of atom to join with one another is called catenation.

C — C — C — C

this due to high bond energy

Catenation power of carbon is highest in periodic table due to small small high electronegativity & high I.P.

* Bond energy KJ mol⁻¹

C — C	→ 355
Si — Si	→ 297
Ge — Ge	→ 260
Sn — Sn	→ 240
Pb — Pb	→ 81

Increasing order of catenetation power

C >> Si > Ge ≃ Sn > Pb

* **M.P** :-

left to right in periodic table gp 14 element M.P increase

M.P of gp 14 element is higher than 13 element in the respective period because no of bond is more in gp of elements.

divalent carbides.

① Salt like carbides :- Ionic bond b/w electropositive ~~atom~~ element and carbon atom

Example :- Carbides of alkaline earth m… and gp 13 elements

For example – $\overset{2+\,2-}{BeC_2}$, $\overset{2+\,4-}{Be_2C}$, $\overset{2+\,2-}{CaC_2}$, $\overset{2+\,4-}{Mg_2C_3}$.

$\overset{3+\,4-}{Al_4C_3}$

Al carbides hydrolysed to give hydrocarbon

$BeC_2 + H_2O \longrightarrow Be(OH)_2 + CH\equiv CH$

Interstitial Carbide → Form by transition element like Cr, Fe, Sc e.t.c and Carbon

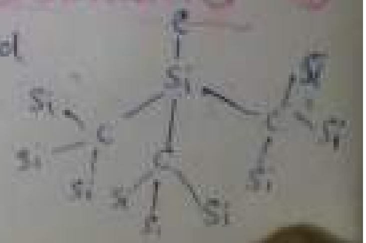
Steel :-

Iron + carbon

or Voids or Hole

Covalent carbides :- Electropositive non metal (B, Si) forms covalent carbide

exple :- SiC, B_4C
↓
Hard like dimond
Structure similar to dimond



Nitrogen family

		EC	Covalent radius (pm)	IE (kJ mol⁻¹)
Non Metal	$_7N$	$2s^2 2p^3$	70	1402
Non Metal	$_{15}P$	$3s^2 3p^3$	110	1012
Metalloid	$_{33}As$	$3d^{10} 4s^2 4p^3$	120	947
Metalloid	$_{51}Sb$	$4d^{10} 5s^2 5p^3$	140	834
Metal	$_{83}Bi$	$4f^{14} 5d^{10} 6s^2 6p^3$	150	703

Oxidation state

(I) Oxidation state of N →

$NH_3 \longrightarrow -3$
$N_2H_4 \longrightarrow -2$
$NH_2OH \longrightarrow -1$
$N_2 \longrightarrow 0$
$N_2O \longrightarrow +1$
$NO \longrightarrow +2$
$N_2O_3 \longrightarrow +3$
$NO_2 \longrightarrow +4$
$N_2O_5 \longrightarrow +5$

Nitrides
$Li_3N \rightarrow -3$
$Ca_3N_2 \rightarrow -3$

(II) Oxidation state of phosphorous:

$Ca_3P_2 \longrightarrow -3$
$P_4 \longrightarrow 0$
$PCl_3 \longrightarrow +3$
$PCl_5 \longrightarrow +5$
$PH_3 \longrightarrow -3$

$\overset{+3}{BiCl_3}$ $\overset{+5}{BiCl_5}$

Bi_2S_3 Bi_2S_5

P ⟶ PCl_3 and PCl_5

N - only NCl_3 not NCl_5 because no vacant d-orbital

Metallic character

⊛ Catenation :- Phosphorous has maximum catenation power in this gp.

N ⟶ N_2

P ⟶ P_4

⊛ N—N bond dissociation energy smaller than P—P bond dissociation energy.

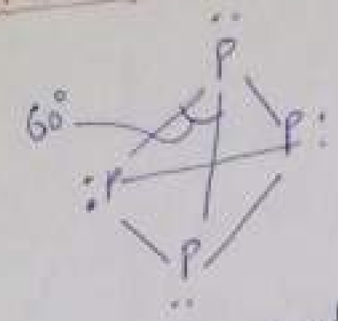
C—C	N—N	P—P	As—As
347	159	213	197
($KJ mole^{-1}$)	($KJ mole^{-1}$)	($KJ mol^{-1}$)	($KJ mole^{-1}$)

⊛ Allotropes :- Except N and Bi all element of this group so allotropy

Allotropes of Phosphorous :-

(i) White phosphorous
(ii) Red phosphorous
(iii) Metallic or α-Back phosphorous
(iv) β- Black (or black phosphorous)
(v) Scarlet phosphosphorous
(vi) Violet phosphosphorous

White phosphorous :-



Tetrahedral Structure

Properties :- (i) On exposure to light it turns to yellow so it is also called as yellow phosphorous

(ii) soft waxy, can be cut with knife

(iii) Various P_4 unit are held together by weak vanderwall force so M.P (317K) and B.P (553K) are low.

(iv) Action of air :-

spontaneously catches fire in air and give greenish glow

$$P_4 + 5O_2 \longrightarrow P_4O_{11} + P_4O_6$$

The above is called — Chemuloscence

Net :-

- It is kept in water became insoluble in water.
- soluble in organic solvent (C_6H_6)
- It is stable upto 1070K but at higher tempreture it decomposes to P_2

- **Reaction with Halogen :-** It also catches fire in the Environment of Cl_2 and form PCl_3 & PCl_5

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

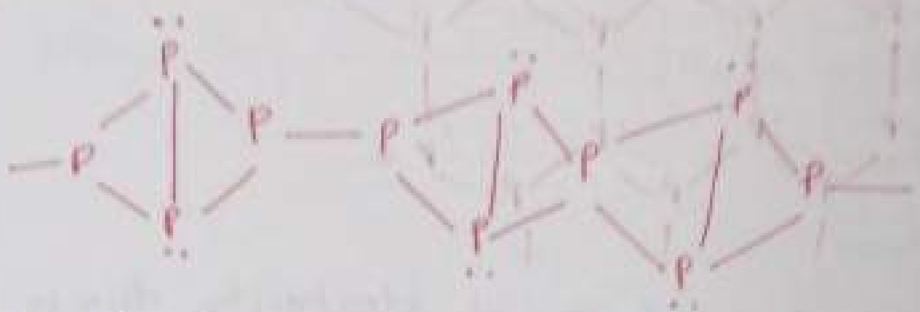
$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

(vi) Reaction with Sulphur :-

$$8P_4 + 3S_8 \xrightarrow{\text{Violently}} 8P_4S_3$$

(vii) Red Phosphorous :-

$$\underset{\text{White phosphorous}}{P_4(s)} \xrightarrow[\text{CO}_2 \text{ or coal gas}]{540-570} \underset{\text{Red phosphorous}}{P_4(s)}$$



⇒ Red phosphorous exist as P_4 tetrahedral but these joined together covalent bonds to give Polymeric structure

(*) Properties :- (i) Due to polymeric structure M.P is high. (883K)

(ii) Hard

(iii) Non poisonous

(iv) Insoluble in water

(v) Relatively more stable at room temperature than white phosphorous.

(vi) Ignition tempt^r of White phosphorous = 303K

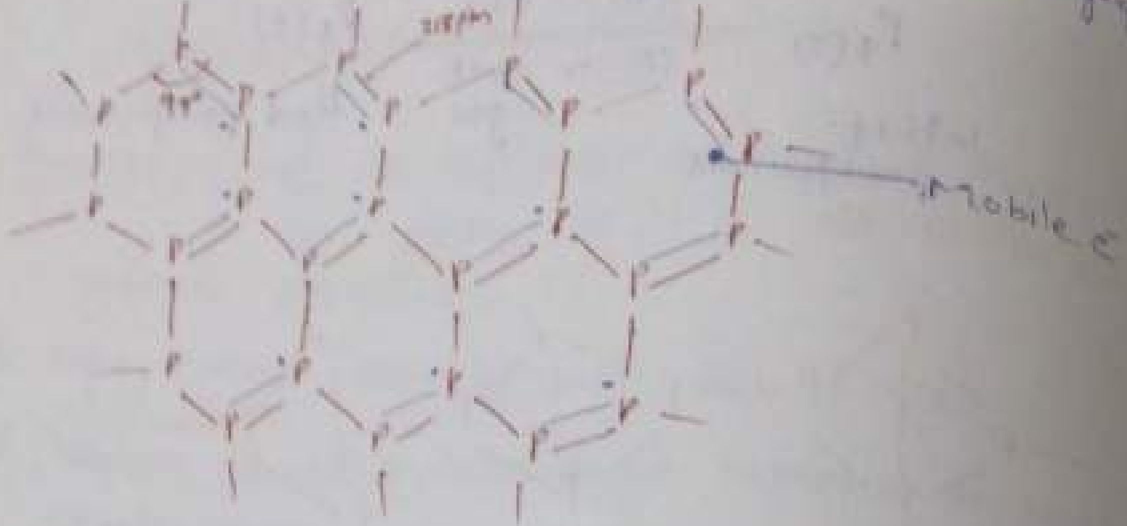
" " " Red " = 543K

17/8/14

β- Black phosphorous

White phosphorous $\xrightarrow[4000-12000\ atm]{470\ K}$ β- Black phosp...

β- Black phosphorous ⟶ larged Structure (similar to grap...



Note: good conducter of electricity due to pres... of mobile electron.

- Most stable allotrep of phosphorous due... vander wall force.

Properties:-
→ Polymerised form
→ mp → 860K
→ good conducter of electricity
→ Thermodynamically most stable
it does not burn in air upto 670K.