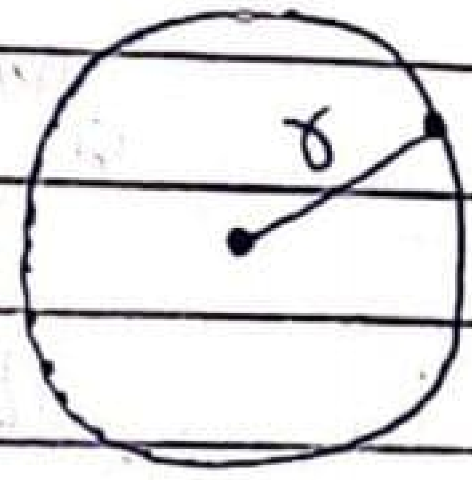
Chapter no :- 13

S and P Block Elements

Atomic Radius (Size):-

Distance between the nucleus and the outer most electron in an atom is called atomic radius-

Trend in Periodic Table:-



Down the group:-

Atomic radius increases down the group

Reason:-

$_{1}H = \underbrace{1s^2}_{K}$

$_{3}Li = \underbrace{1s^2}_{K}, \underbrace{2s^1}_{L}$

$_{11}Na :- \underbrace{1s^2}_{K}, \underbrace{2s^2, 2p^6}_{L}, \underbrace{3s^1}_{M}$

This is becauses down the group atomic number increases electrons are being added to a new shell - Therefore atomic radius increases down the group -

Along the Period:-

Atomic radius decreases

along the period -

Reason :-

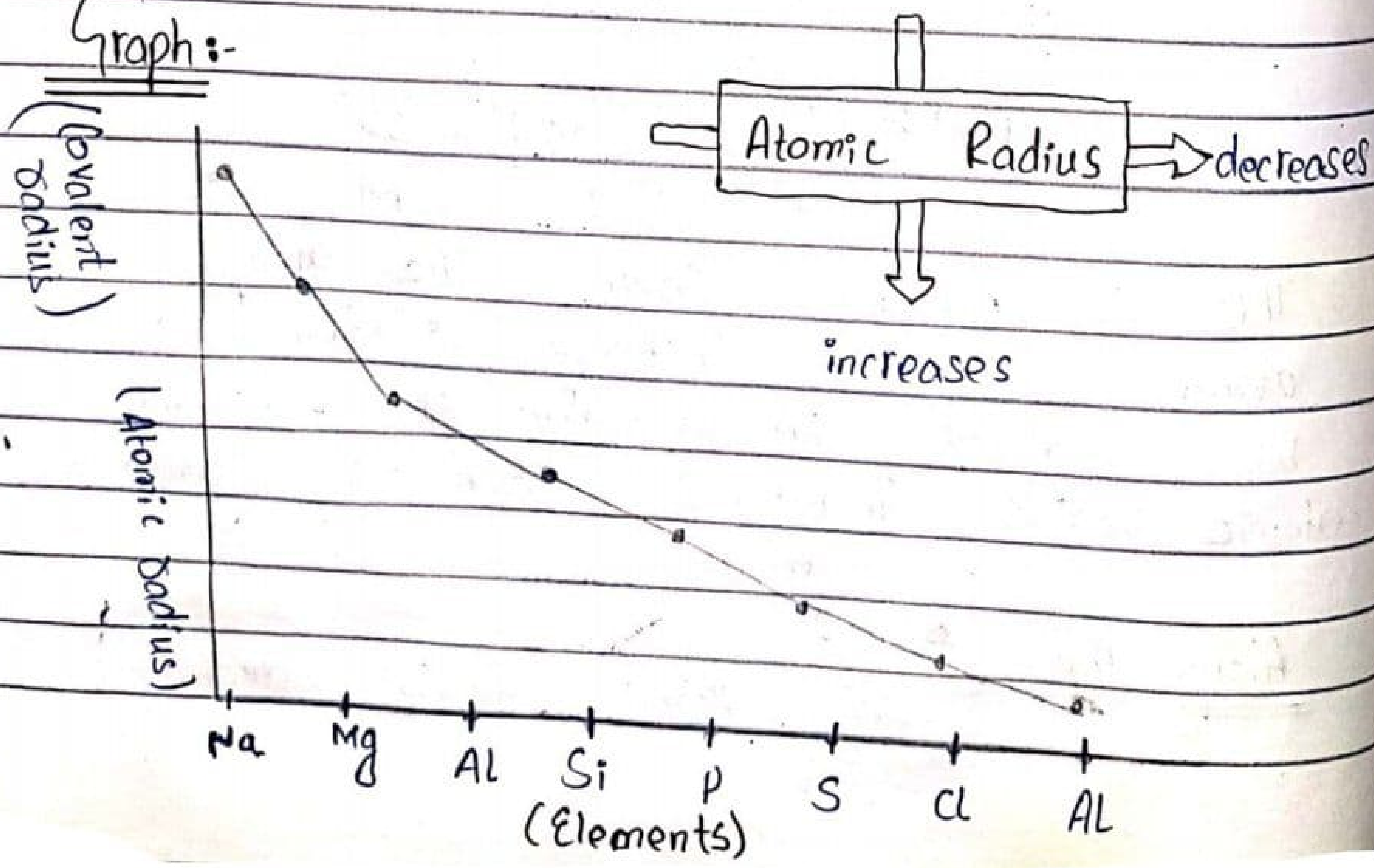
$_{11}Na = \underbrace{1s^2}_{K}, \underbrace{2s^2, 2p^6}_{L}, \underbrace{3s^1}_{M}$

$_{12}Mg = \underbrace{1s^2}_{K}, \underbrace{2s^2, 2p^6}_{L}, \underbrace{3s^2}_{M}$

$_{13}Al = \underbrace{1s^2}_{K}, \underbrace{2s^2, 2p^6}_{L}, \underbrace{3s^2, 3p^1}_{M}$

This is becauses along the period atomic number increases electrons are being added to a same shell neculear attraction increases as a result atomic radius decreases along the period -

Graph :-



Ionic radius :-

Distance between the nucleus and outer most electron in an ion is called ionic radius

TYPES :-

1. Radius of cation (+ve ion)
2. Radius of anion (-ve ion)

Radius of Cation :-

Radius of cation is always less then from their Parents

Example; $Na = 1.54 A^{\circ}$

$Na^{+} = 0.95 A^{\circ}$

Reason :-

This is becauses;

- Effective nuclear charge increases
- shielding effect decreases

Radius of anion :-

Radius of anion is always greater than from their Parents

Example; $Cl = 0.99 A^{\circ}$

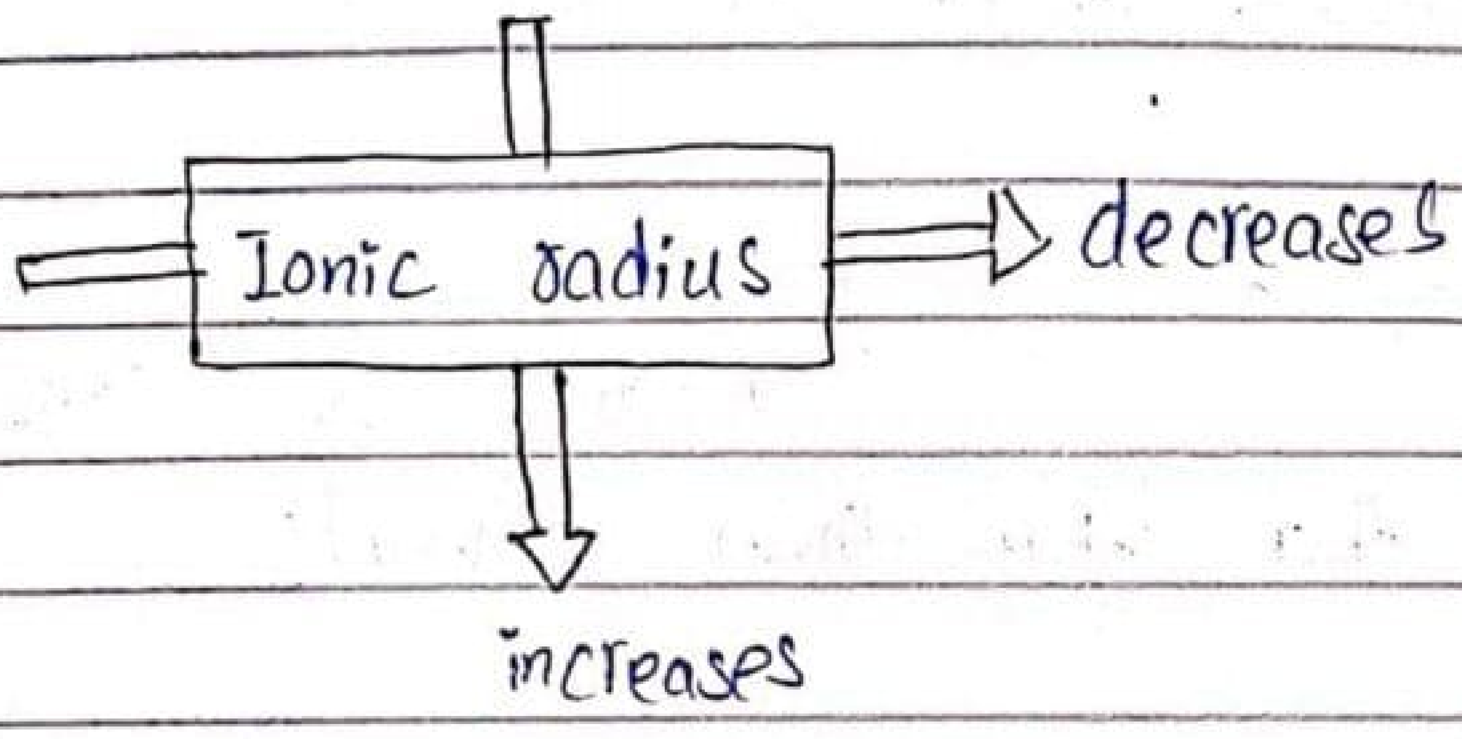
$Cl^{-} = 1.81 A^{\circ}$

Reason:-

This is because,

- Effective nuclear charge decreases
- Shielding effect increases

Trends in Periodic table:-



Ionization energy (I.E) & Ionization Potential I.P :-

Definition:-

Minimum amount of energy required to remove outer most electron from the gaseous atom is called ionization energy

Examples;

$X_{(g)} \longrightarrow X^{+}_{(g)} + e^{-}$ I.E = +ve

$Na_{(g)} \longrightarrow Na^{+}_{(g)} + e^{-}$ I.E = 496 kJ/mol

Trend in Periodic table :-

Down the group :-

Ionization energy decreases down the group

Reason :-

- Atomic Size increases -
- Distance between nucleus and outer most electron increases -
- Force of attraction between the nucleus and outer most electron decreases -
- Removal of electron is easy -

Along the Period :-

Ionization energy increases along the Period

Reason :-

- Atomic Size decreases
- Distance between the nucleus and outer most electron decreases
- Force of attraction between nucleus and outer most electron increases
- Removal of electron is difficult

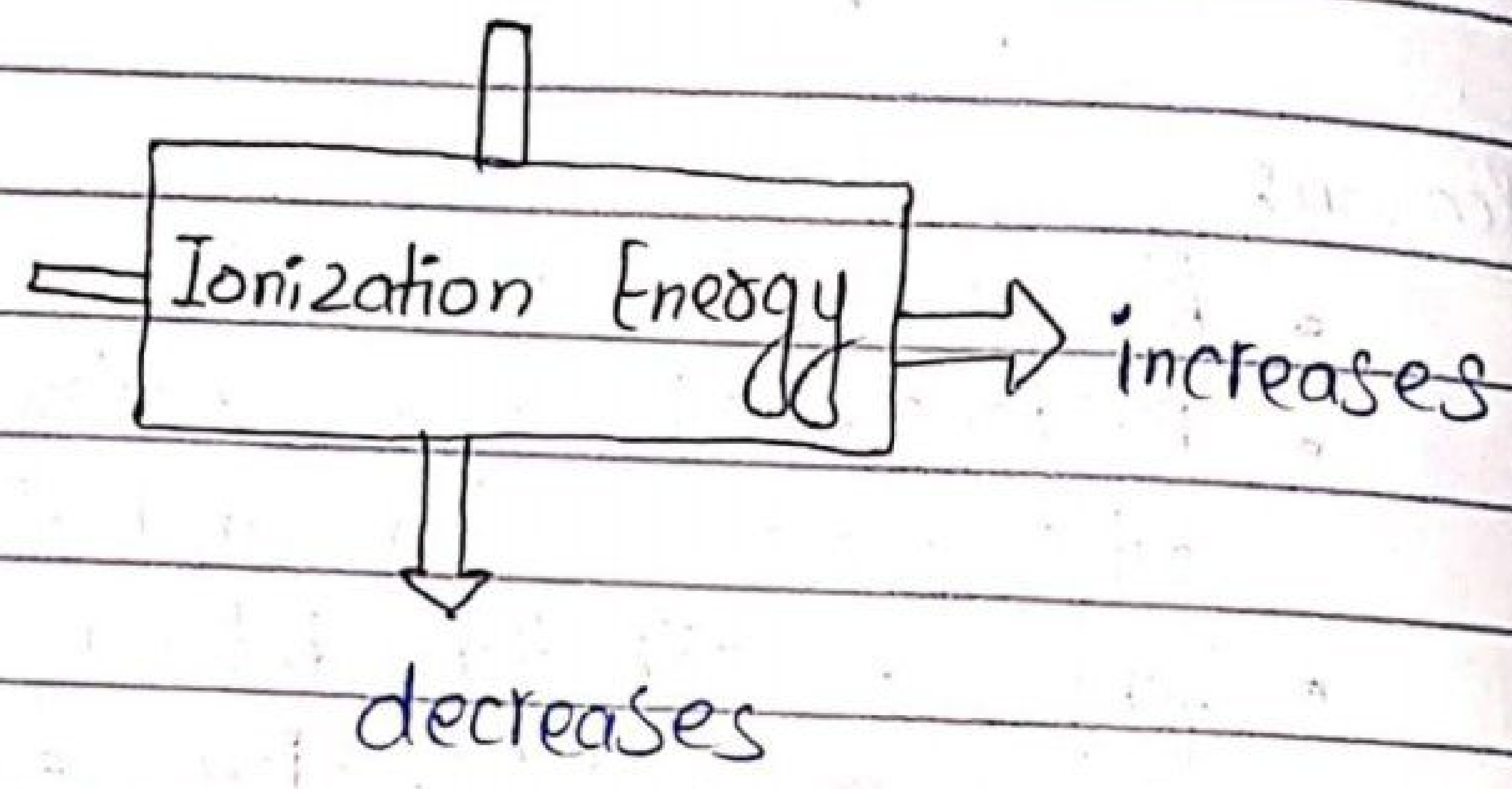
Factors :-

(1) • Atomic Size $\propto \frac{1}{I \cdot E}$

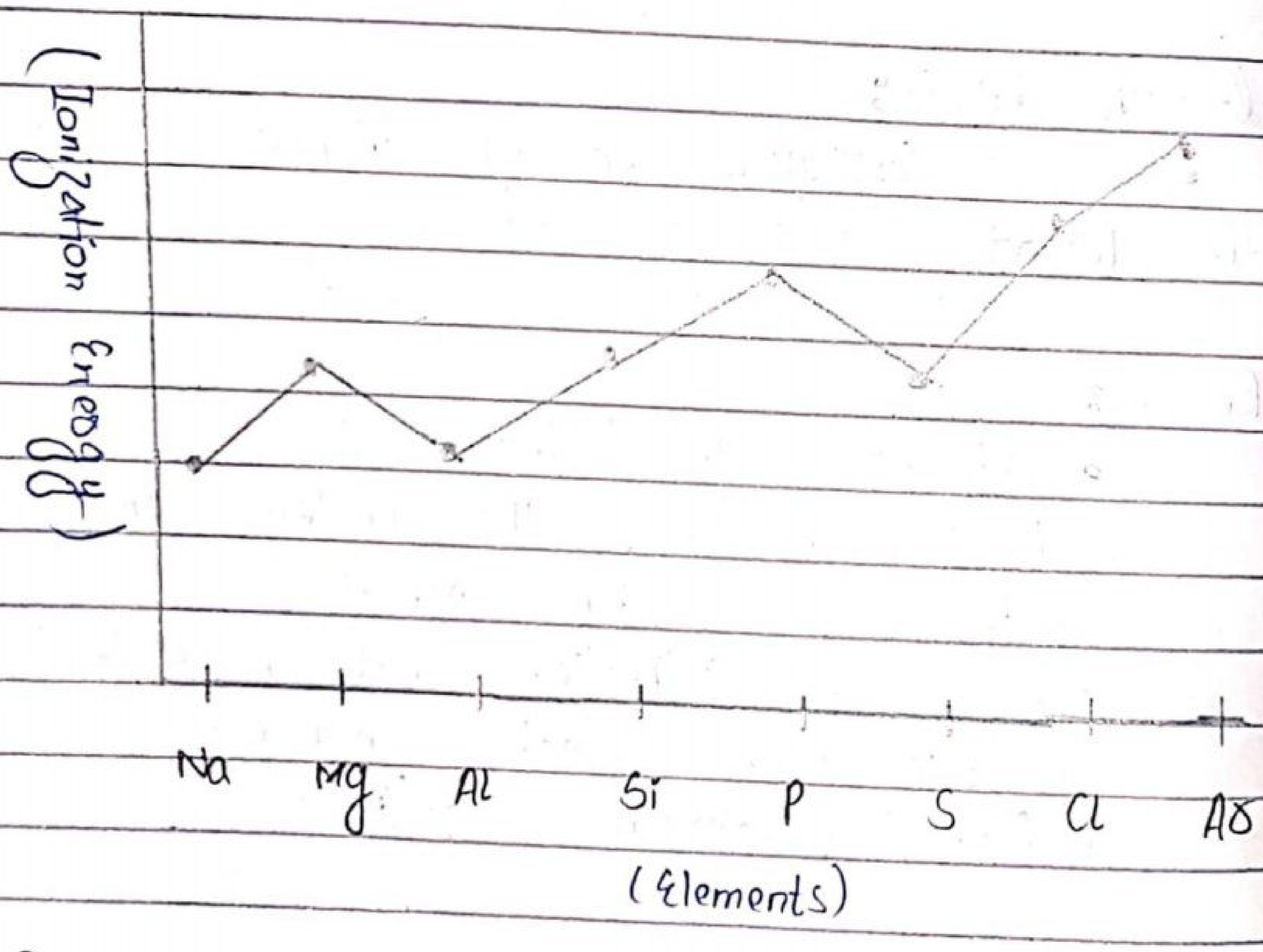
② Shielding & Screeing effect $\propto \frac{1}{I \cdot E}$

③ Nuclear charge $\propto$ I·E

④ Nature of orbitals $s > p > d > f$



Graph:-



Q#01 why Ionization energy of Mg is greater than Al although I·E increases along the period?

Ans :- $_{12}Mg$:- $1s^2, 2s^2, 2p^6, 3s^2$

$_{13}Al$:- $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

This is because in Mg outer most electron is S and it is fullfilled and also stable so it is difficult to remove electron. On the other hand in AL outer most electron is p and it is unstable so it is easy to remove electron. So that's why ionization energy of Mg is greater than AL.

Q#02:- why Ionization energy of Phosphorous is greater than Sulphur although I.E increases along the period.

Ans.. $_{15}P$:- $1s^2, 2s^2, 2p^6, 3s^2, 3p^3$

$_{16}S$:- $1s^2, 2s^2, 2p^6, 3s^2, 3p^4$

This is because outer most electron is p and it is half-filled and also stable. So it is difficult to remove electron. on the other hand in Sulphur outer most electron is p and it is partially filled and also unstable so it is easy to remove electron.

Electronegativity (E.N):-

Power of electron to attract Shared pair of electron toward it self is called electronegativity.

- It has no unit
- It is measured with the help of Pauling Scale.

Examples:-

F = 4.0 N
O = 3.5
N = 3.0
Cs = 0.7
Fr = 0.7

Trends in Periodic table:-

Down the group:-

Electronegativity decreases down the group

Reasons:-

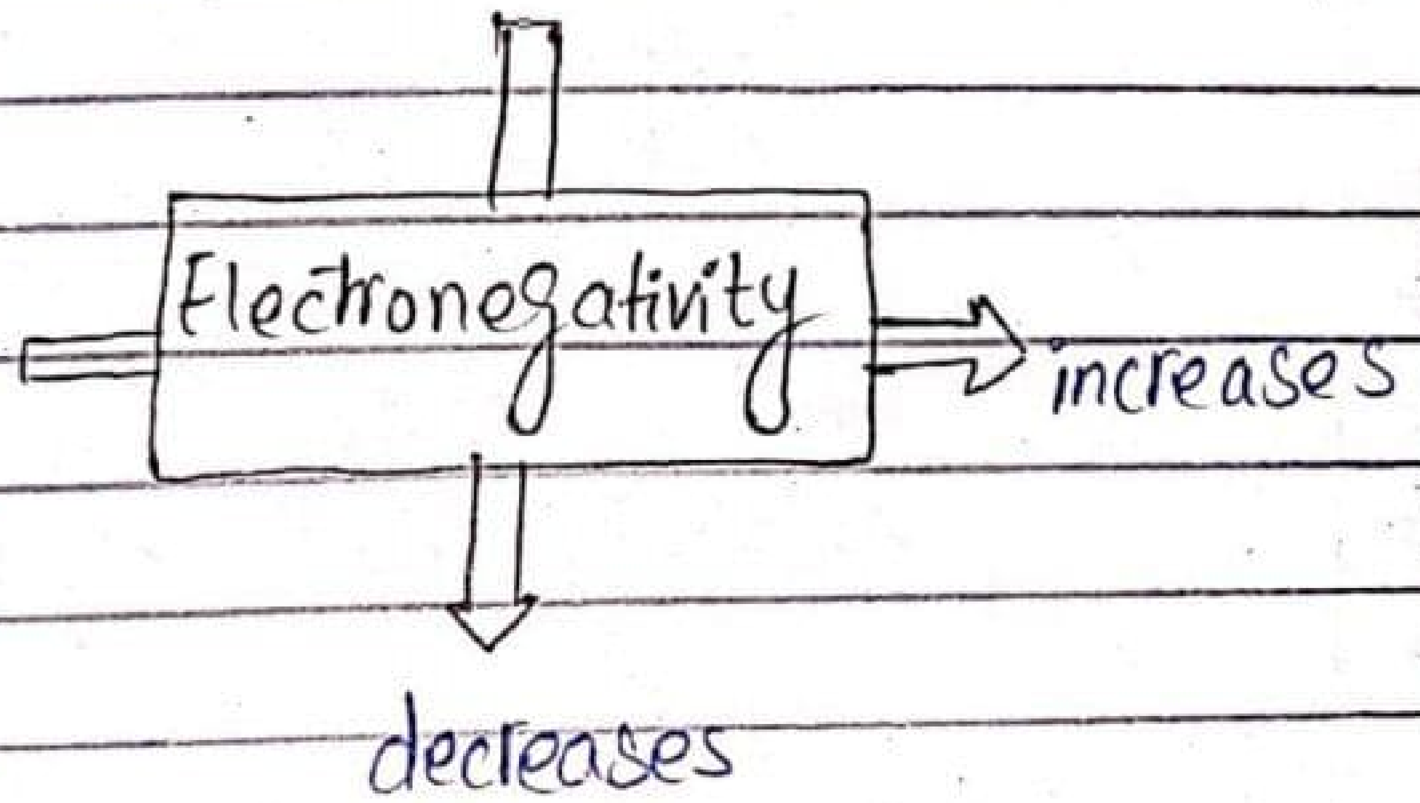
- Atomic Size increases
- Distance between nucleus and outer most electron increases
- Force of attraction between nucleus and outer most electron decreases.

Along the Period :-

Electronegativity increases along the Period.

Reason :-

- Atomic Size decreases along the Period.
- Distance between the nucleus and outer most electron decreases
- Force of attraction between the nucleus and outer most electron increases.



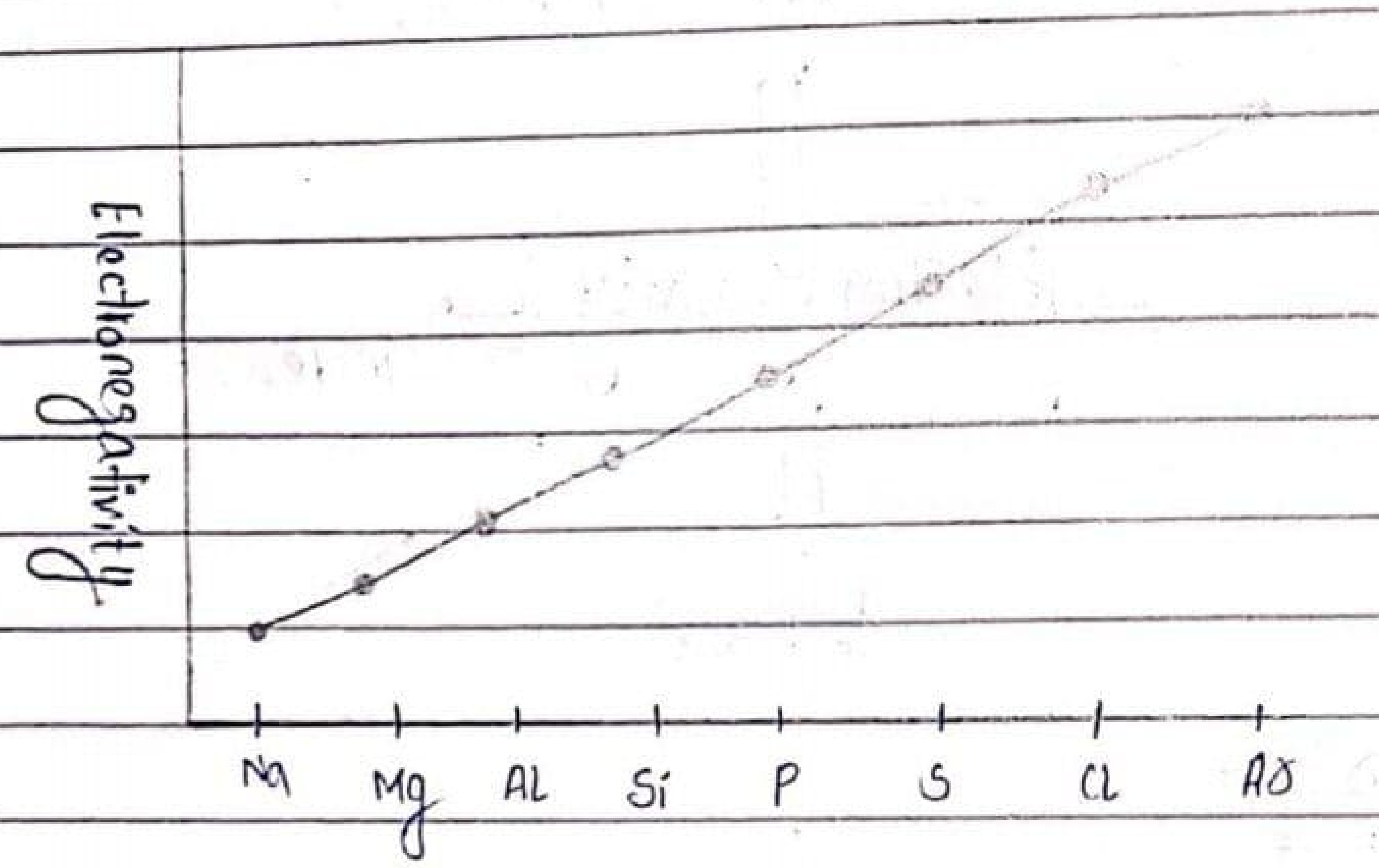
Factors :-

- Atomic Size $\propto 1/E.N$
- Shielding & Screening effect $\propto 1/E.N$
- Nuclear charge (proton number) $\propto E.N$

Q#03 why electro negativity cannot be assigned to Argon?

Ans- Electronegativity cannot be assigned to Argon. It is because electronegativity is the tendency of an atom to attrak a bonding pair of electron. Since argon does not form covalent bonds, electronegativity can not be assigned to it.

Graph:-



Electrical Conductivity or Electropositivity

- Ease of flow of electron is called electrical conductivity
- Metals can conduct electricity due to free electrons
- Electrolyte can conduct electricity due to

Free ions -

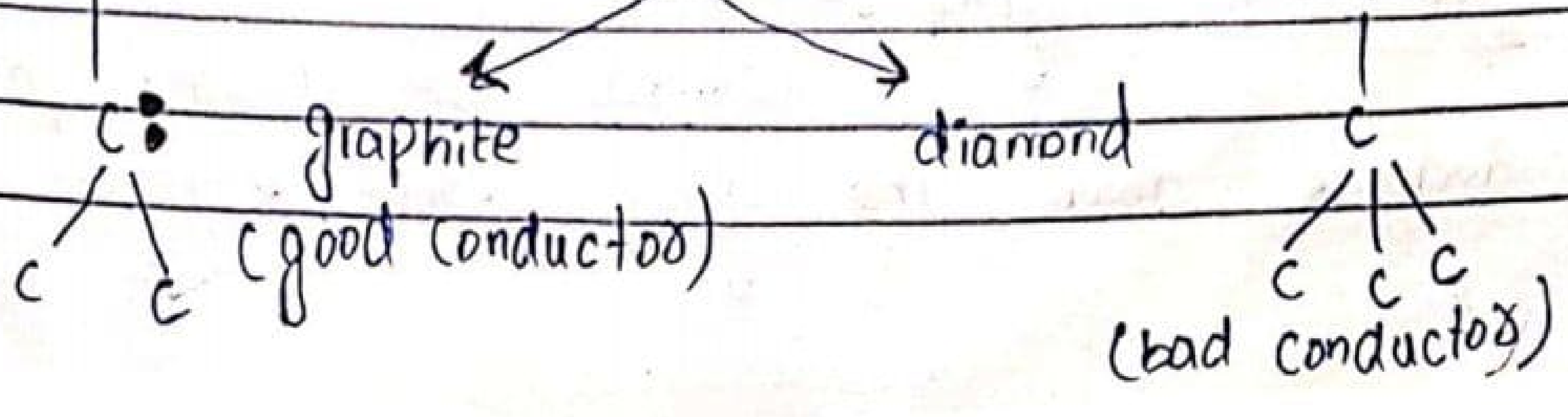
Electrical conductivity $\propto$ No of free electrons

Trends in Periodic table:-

1) Na, Mg, Al are good conductor of electricity
2) Electrical conductivity increases from Na to Al due to increase in free electron (delocalised electron).
3) Silicon is a Semi- Conductor
4) P, S, Cl and Ar are non-metals. they formed covalent Compound - They have no free electrons - They are non- conductor

IMPORTANT INFORMATION

1) IA & IIA ↓ increases
2) IVA ↓ increases
3) Carbon may be conductor or non conductor



4) Ag, Au, Cu are good conductor of electricity in all periodic table.

Melting & Boiling point:-

Melting point:-

Temperature at which there is an equilibrium between solid and liquid state is called melting point.

Boiling point:-

Temperature at which vapour pressure of liquid become equal to external pressure is called boiling point.

- M.P & B.P $\propto$ No of Bonding electrons
- M.P & B.P $\propto$ Intermolecular / vander waal forces
- Strength of forces can be discussed with the help of melting and Boiling point.

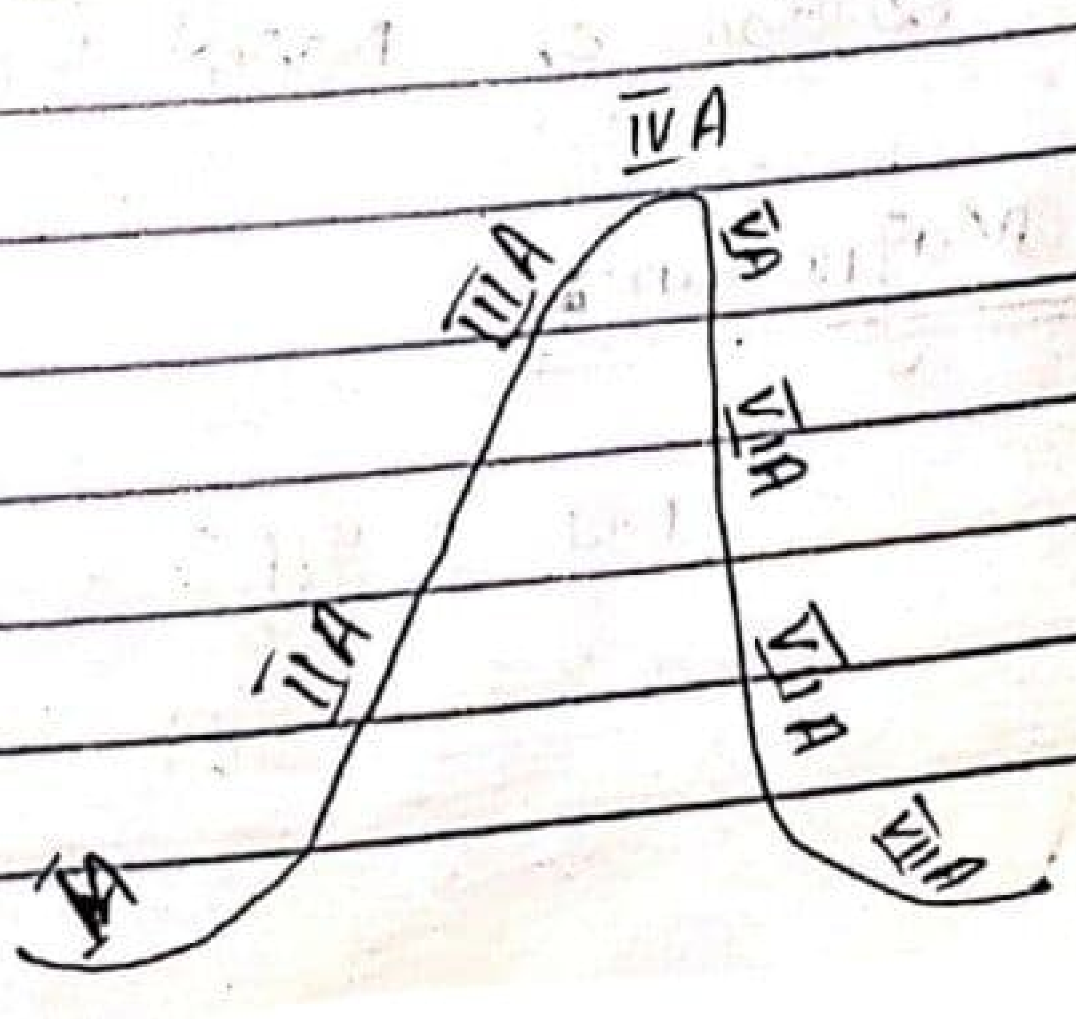
Trends in Periodic table:-

Down the group:-

Melting and Boiling point decreases down the group except halogen and noble gas.

Reason:-

- Atomic Size increases
- Distance between nucleus and outer most electron increases
- Force of attraction between nucleus and outer most electron decreases
- Therefore Melting and Boiling point decreases.
- In case of halogen and noble gas Melting and boiling point increases because halogen is di-atomic molecules and noble gas is mono-atomic molecules.
- Halogen and noble gas are non-polar molecules
- London Dispression force increases down the group.



Along the Period:-

Reason :-

- No of boinding electrons increases from IA to IV A group element and also due to gant Covalent Structure.
- From VA to VIIIA Melting and Boiling point decreases due to decrease in Size
- landon dispression force decrease from Phosphorus to Argon.

Reaction of 3rd Period Elements

(a) Reaction with water :-

Sodium :-

$$2Na + 2H_2O \text{ (Cold)} \longrightarrow 2NaOH + H_2$$

Reaction is highly exothermic Produce Solution of NaOH and evolved H_2 gas

Magnesium :-

$$Mg + 2H_2O \text{ (Cold)} \longrightarrow Mg(OH)_2 + H_2$$

$$Mg + H_2O \longrightarrow MgO + H_2$$
(Steam)

Magnesium as very slight reaction with cold water but give magnesium oxide (Mgo) with steam

Aluminium :-

$$2AL + 3H_2O \longrightarrow AL_2O_3 + 3H_2$$
(powder) (Steam)

AL_2O_3 is amphoteric in nature. Reaction is slow due to formation of oxide layer.

Silicon, Phosphorous & Sulphur :-

Silicon, phosphorous, and sulphur do not react with water because they do not dissolve in water.

Chlorine :-

$$2Cl_2 + 2H_2O \longrightarrow 2HCL + 2HOCL$$ (xing by 2)

$$2HOCL \longrightarrow 2HCL + 2O_2$$

$$2Cl_2 + 2H_2O \longrightarrow 4HCL + 2O_2$$

carbon dissolve in water to give a green Solution.

Argon :-

Argon do not react with water because noble gas can not react.

(b) Reaction with oxygen :-

Sodium :-

$$4Na + O_2 \longrightarrow 2Na_2O \text{ (Sodium oxide)}$$

$$4Na + 2O_2 \longrightarrow 2Na_2O_2 \text{ (sodium peroxide)}$$

Sodium burns in oxygen with an orange flame to produce mixture of oxides

Magnesium :-

$$2Mg + O_2 \longrightarrow 2MgO$$

Magnesium burn in Oxygen with white flame to produce white solid MgO

Aluminum :-

Aluminum does not react with oxygen at room temperature due to the formation of oxides layer.

Silicon:-

$$Si + O_2 \longrightarrow SiO_2 \text{ (Macro molecules)}$$

Si react with oxygen if heated strongly. Silicon dioxide is produced.

phosphorus :-

$$P_4 + 3O_2 \xrightarrow{\text{limited}} P_4O_6 \text{ phosphorus (III) oxide}$$

$$P_4 + 5O_2 \xrightarrow{\text{Excess}} P_4O_{10} \text{ Phosphorus (V) oxide}$$

proportions of these oxides depends up on amount of oxygen.

Sulphur:-

$$S + O_2 \longrightarrow SO_2$$

Sulphur burn in oxygen with Pale blue flame produce Sulphur dioxide

Chlorine & Argon :-

Chlorine and Argon do not react with oxygen

⇒ However chlorine has two oxides Cl_2O, Cl_2O_7 which are obtained by indirect method.

(c) Reaction with chlorine :-

(1) Sodium :-

$$2Na + Cl_2 \longrightarrow 2NaCl$$

(white Solid)

- Sodium burn in Steam of chlorine with bright orange flame produce white Solid of NaCl

(2) Magnesium :-

$$Mg + Cl_2 \longrightarrow MgCl_2$$

(white Solid)

- Magnesium burn in Steam of Chlorine with white flame produce white Solid of $MgCl_2$ -

(3) Aluminium :-

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

(Pale Yellow Solid)

- when aluminium foil is heated with Steam of Chlorine pale yellow solid ($AlCl_3$) is Produced.

(4) Silicon :-

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

(Colourless liquid)

- when Silicon is heated with steam of Cl_2, $SiCl_4$ is produced.

(5). Phosphorous:-

$$P_4 + 6Cl_2 \xrightarrow{\text{limited}} 4PCl_3$$

(fuming colourless liquid)
↓
(Evaporates it self)

$$P_4 + 10Cl_2 \xrightarrow{\text{Excess}} 4PCl_5$$

(off-white solid)

- White phosphorous react with steam of Chlorine produce mixture of PCl_3 and PCl_5.

(6) Sulphur:-

$$2S + Cl_2 \longrightarrow S_2Cl_2$$

(orange evils smelling liquid)

- when Sulphur is heated with chlorine disulphur dichloride is produced.

(7) Chlorine and Argon:-

Chlorine and argon do not react with Chlorine.

1) Physical Properties of oxides of 3rd Period Element

Na_2O	MgO	Al_2O_3
⇓	⇓	⇓
Strongly basic oxides	Basic oxides	Amphoteric oxides
SiO_2	P_4O_{10} & P_4O_6	SO_3 & SO_2
⇓	⇓	⇓
weakly acidic oxides	Acidic oxides	Strongly acidic oxides

Cl_2O_7
Cl_2O
⇓
very Strongly acidic oxide

2) Structures of oxides

⇒ Na_2O, MgO, or Al_2O_3 = Metallic, giant, ionic oxide

⇒ SiO_2 = gaint Covalent oxide

⇒ P_4O_{10} & P_4O_6, SO_3 & SO_2, Cl_2O_7 & Cl_2O = Simple molecular oxide.

3) Melting & Boiling Point:-

⇒ Na_2O, MgO, Al_2O_3 and SiO_2 have giant structure therefore they have high melting and Boiling point.

⇒ Molecular oxides have low melting and boiling point because they have dipole dipole force or london dispression force.

4) <u>Electrical conductivity :-</u>

- Na_2O, MgO, Al_2O_3 are non-conductor of electricity in Solid form but they conduct electricity when they are present in molten form because they contain ions -

- Covalent oxide and molecular oxide are non- conductor of Electricity -

★ Long Question :- [F.B 2019]

Discuss Acid - Base behaviour of oxide of 3rd period Element?

Na_2O → Strongly basic oxides || MgO → Basic oxides || Al_2O_3 → Amphoteric oxides

SiO_2 → weakly acidic oxides || P_4O_{10} & P_4O_6 → acidic oxides || SO_3 & SO_2 → Strongly acidic oxide

Cl_2O_7 & Cl_2O → Very Strongly acidic oxide

(1) Sodium oxide (Na_2O) :-

Reaction with water

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Reaction with Acid

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

* Sodium is a metal, metal form basic oxide because when it is dissolve in water it form base. PH of NaOH is 14.

(2) Magnesium oxide (MgO) :-

Reaction with water :-

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

Reaction with Acid :-

$$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$$

* Magnesium is a metal, metal form basic oxide because when it is dissolve in water is form base. PH of $Mg(OH)_2$ is 9.

(3) Aluminium oxide (Al_2O_3) :-

Reaction with Acid :-

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

(hot Solution)

Reaction with Base :-

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$$

(Sodiumtetra hydroxo Aluminate (III))

* when aluminium oxide is reacted with acid

acid and base it behave as amphoteric oxide
Amphoteric oxide is insoluble in water -

4) Phosphorus oxide (P_4O_x)

Reaction with water:-

$$P_4O_{10} + H_2O \longrightarrow 4H_3PO_4$$

Reaction with base:-

$$H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$$

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

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

OR

$$P_4O_{10} + 12NaOH \longrightarrow 4Na_3PO_4 + 6H_2O$$

Phosphorus oxide react with NaOH Solution give Solution of Sodium phosphate -

5) Sulphur oxide (SO_x):-

Reaction with water:-

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Reaction with Base:-

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

$SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$

$SO_3 + CaO \longrightarrow CaSO_4$

Sulphur trioxide react with NaOH to give solution of Sodium sulphate -

Reaction with water :-

$SO_2 + H_2O \longrightarrow H_2SO_3$

(sulphurous acid)

Reaction with base :-

$H_2SO_3 + 2NaOH \longrightarrow Na_2SO_3 + 2H_2O$

$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$

$SO_2 + CaO \longrightarrow CaSO_3$

Sulphur dioxide react with Sodium hydroxide to give solution of Sodium sulphite -

6) Chlorine oxides (Cl_2O_x) :-

Reaction with water :-

$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$

(Perchloric acid)

Reaction with base:-

$$HClO_4 + NaOH \longrightarrow NaClO_4 + H_2O$$

(Sodium per Chloride)

$$Cl_2O_7 + 2NaOH \longrightarrow 2NaClO_4 + H_2O$$

Reaction with water:-

$$Cl_2O + H_2O \longrightarrow 2HClO$$

(Hypochlorous acid)

Reaction with Base:-

$$HClO + NaOH \longrightarrow NaClO + H_2O$$

$$Cl_2O + 2NaOH \longrightarrow 2NaClO + H_2O$$

* perchloric acid is very strong acid. Its pH is zero. Oxides of chlorine react with sodium hydroxide give a solution of sodium chlorate (I) (sodium hypochlorite).

Chlorides of 3rd Period Elements

1) Sodium Chloride = $NaCl$

2) Magnesium Chloride = $MgCl_2$

3) Aluminium chloride = $AlCl_3$

4) Silicon tetrachloride = $SiCl_4$

5) phosphorus chloride = PCl_5, PCl_3

6) Disulphur dichloride = S_2Cl_2

(1) Structures :-

i) Sodium chloride & Magnesium chloride are ionic Solid consist of giant ionic lattice.

ii) Aluminium chloride & phosphorus Pentachloride(V) (PCl_5) have ionic as well as covalent structure. They are converted from ionic to covalent when solid form is turned into liquid or gas (vapours) form.

iii) $SiCl_4$, S_2Cl_2 and PCl_3 are covalent compound (Sample covalent compound).

(2) Melting & Boiling point:-

i) NaCl & $MgCl_2$ are ionic Solid having high melting and Boiling Point because a large amount of heat which is needed to break the strong ionic attractions

2) $AlCl_3$ and PCl_5 have high melting and boiling point as compared to covalent Solid.

3) $SiCl_4$ & S_2Cl_2 and PCl_3 are covalent Solid having low melting and boiling point because they have weak Vander waal forces.

(3) Electrical Conductivity:-

i) NaCl & $MgCl_2$ are non-conductor of electricity in Solid form because they do not have free ions but they are good conductor of electricity in aqueous or molten form

Short question:-

2) $AlCl_3$ & PCl_5 are non-Conductor of electricity in Solid form but in molten form they are converted from ionic to covalent they do not conduct electricity.

(3) $SiCl_4$, PCl_3, S_2Cl_2 are non-conductor of electricity in Solid and molten form

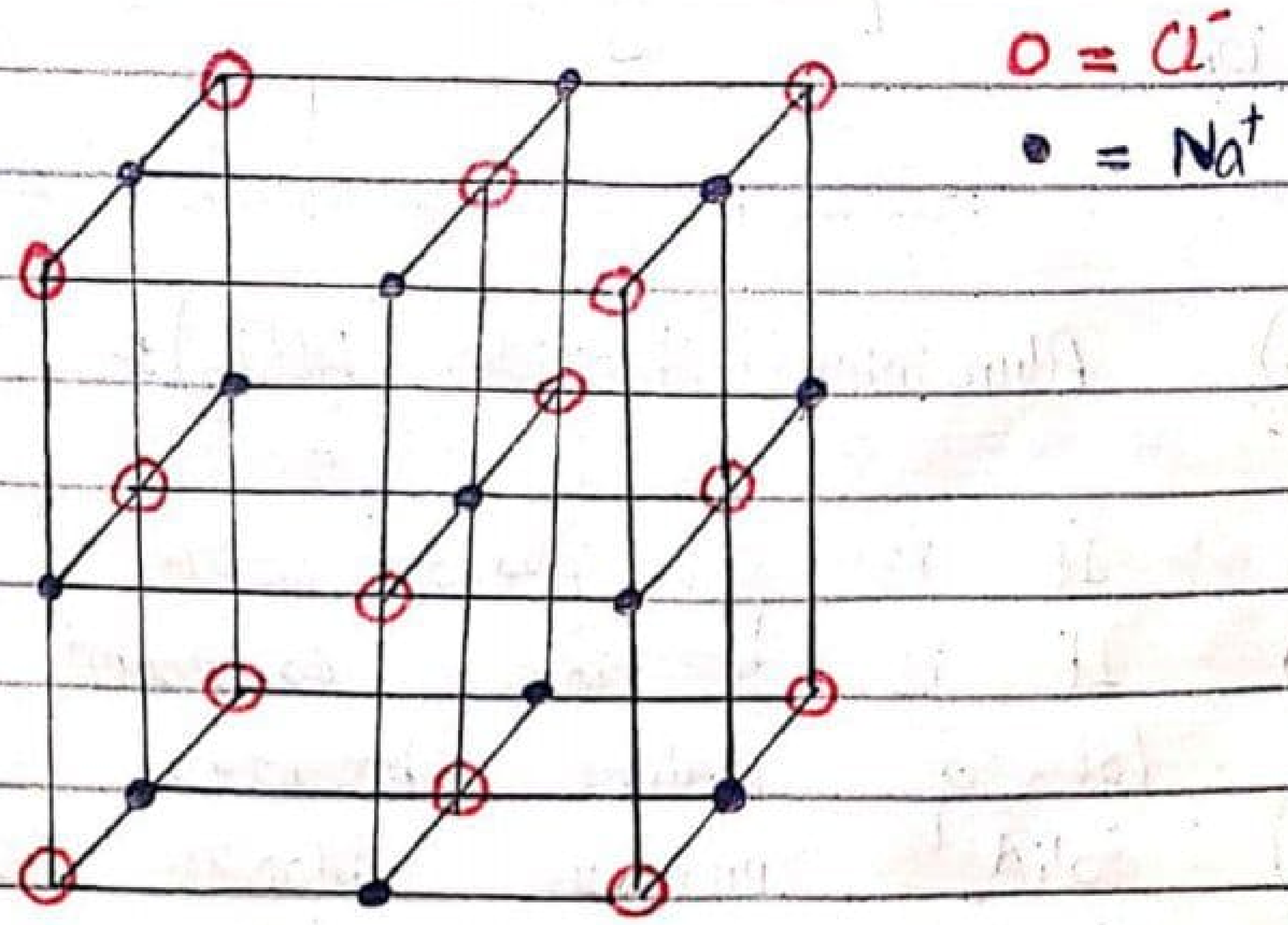
(4) Reaction of Chlorides with water

Sodium chloride and magnesium chloride dissolve in water and all other chloride react with water give different product.

★ **The individual Chlorides**

01 - Sodium chloride (NaCl)

1. It is ionic Solid.
2. It has high melting and boiling point.
3. It is non-conductor of electricity in Solid form because they do not have free electrons.
4. It is conductor of electricity in aqueous and molten form.
5. When it is dissolve in water it give neutral Solution



⇒ Crystal Lattice of NaCl

(02) Magnesium chloride ($MgCl_2$):-

i) It is a ionic Solid-

ii) It has high melting and boiling point because a large amount of energy is required to break their crystal lattic

iii) It is white Solid -

iv) Solid magnesium chloride is non- Conductor of electricity because ions are not free to move -

v) Molten magnesium chloride is conductor of electricity because it has free ions -

vi) when it is dissolve in water it form weak acidic Solution having pH "6"-

vii)

$$MgCl_2 + 6H_2O \longrightarrow [Mg(H_2O)_6]^{+2} + 2Cl^-$$

Hexaaqua magnesium (II) io

Magnesium chloride react with water give Hexaaqua magnesium (II) ion and chloride ion

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(03) Aluminium Chloride ($AlCl_3$):-

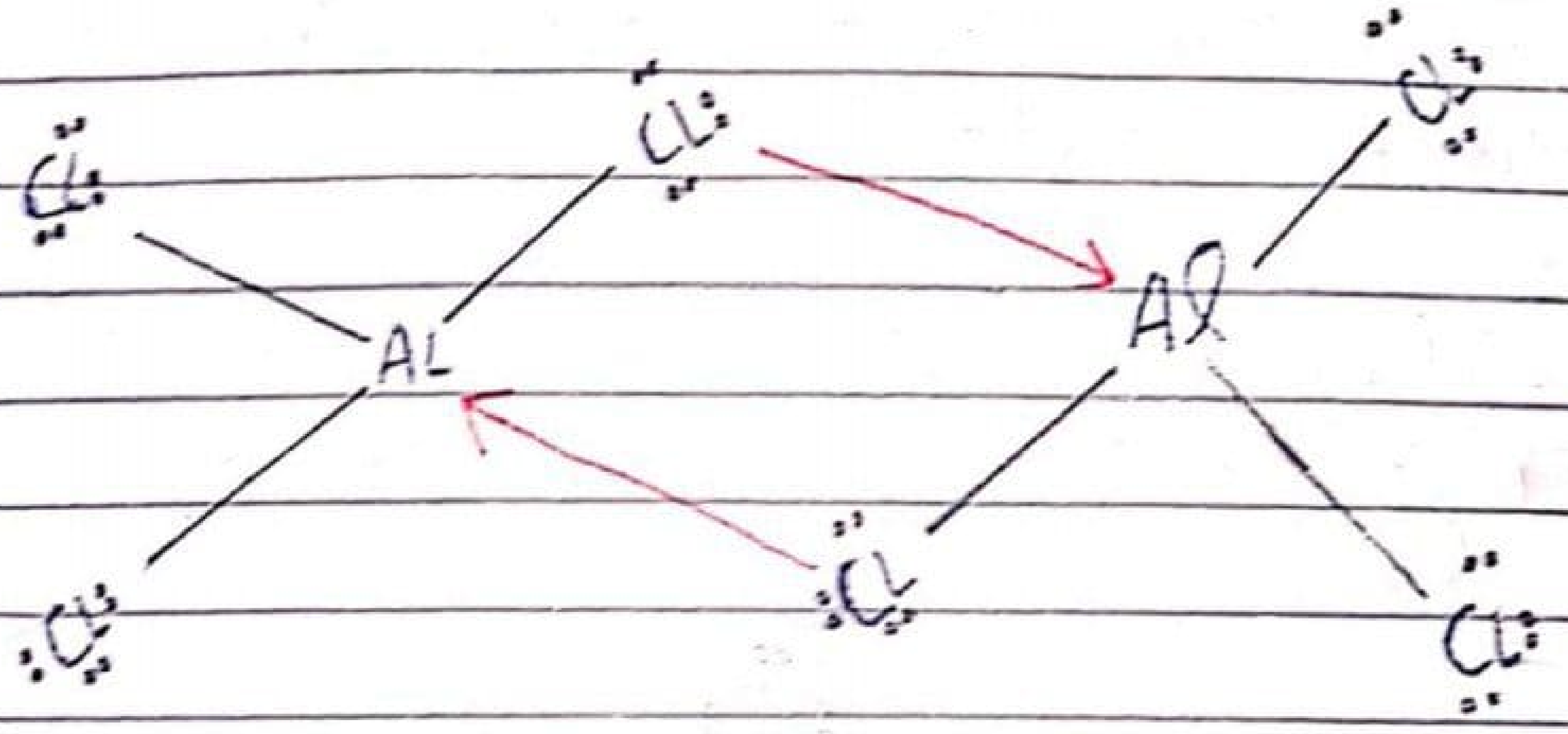
i) It is pale Yellow Solid-

ii) It is a ionic compound with a lot of covalent character-

iii) Solid aluminium chloride is non-conductor of electricity because ions are not free to mo

4) Molten aluminium Chloride is non-Conductor of electricity because in molten form it it converted from ionic to covalent therefore ions are not free to move.

$$2AlCl_3 \longrightarrow Al_2Cl_6$$



5) Aluminium Chloride violently react with water produce clouds of flumes of hydrogen chloride gas.

6)
$$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{+3} + 3Cl^-$$

Hexaaqua aluminium (III) ion

4) <u>Silicon Tetrachloride ($SiCl_4$):-</u>

i) It is a covalent Chloride.

ii) It is a colourless liquid at room temperature.

iii) There is not enough electronegativity difference between Silicon and chlorine to form ionic compound.

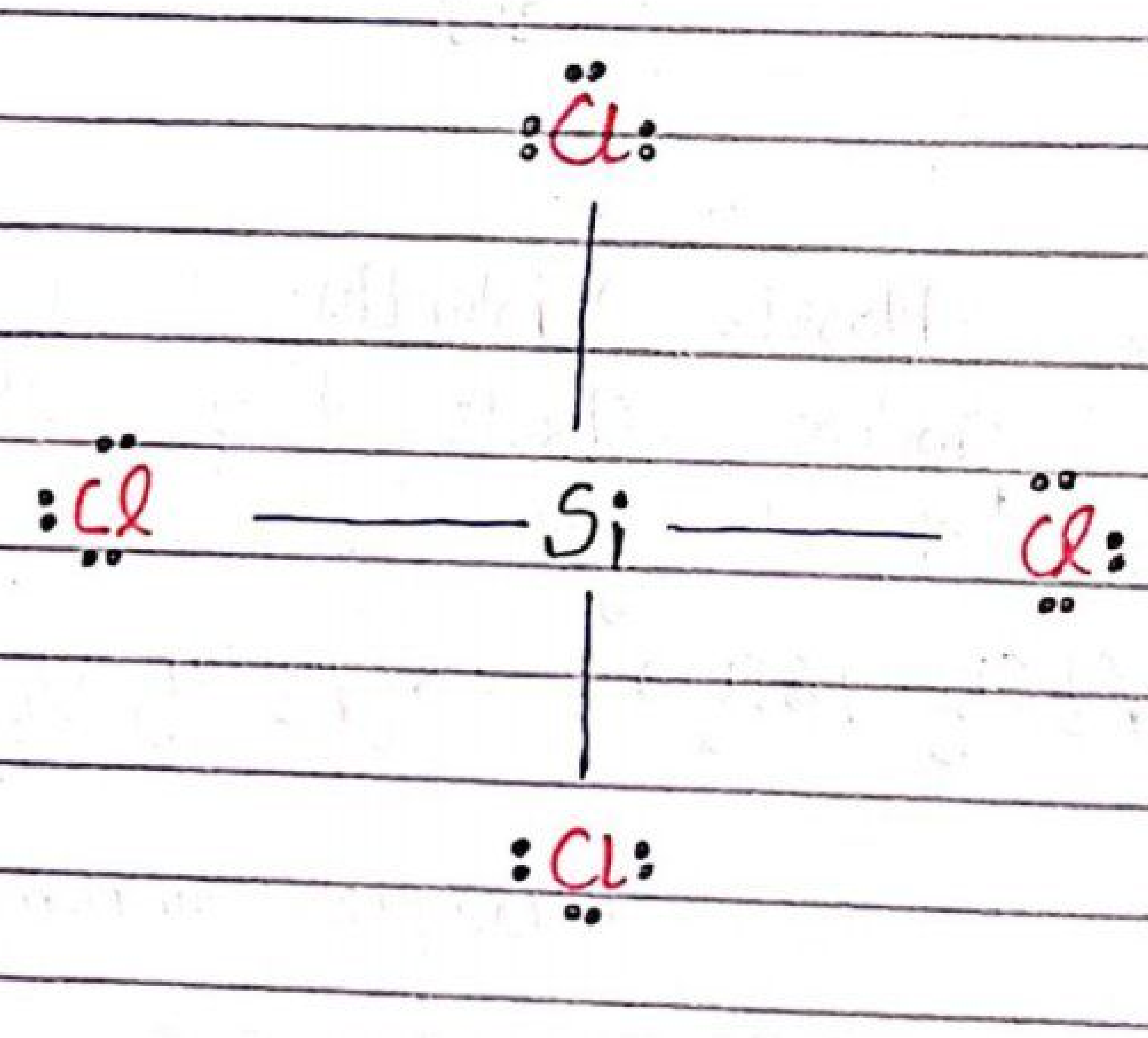
iv) It is non-conductor of electricity because it has no free ions.

v)

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

Silicon tetrachloride violently react with water produce silicon dioxide and flumes of hydrochloric acid.

vi) Solution of $SiCl_4$ with water is strongly acidic due to hydrochloric acid.



(05) phosphorus Chloride (PCl_x):-

i) There are two chlorides;

a) PCl_3

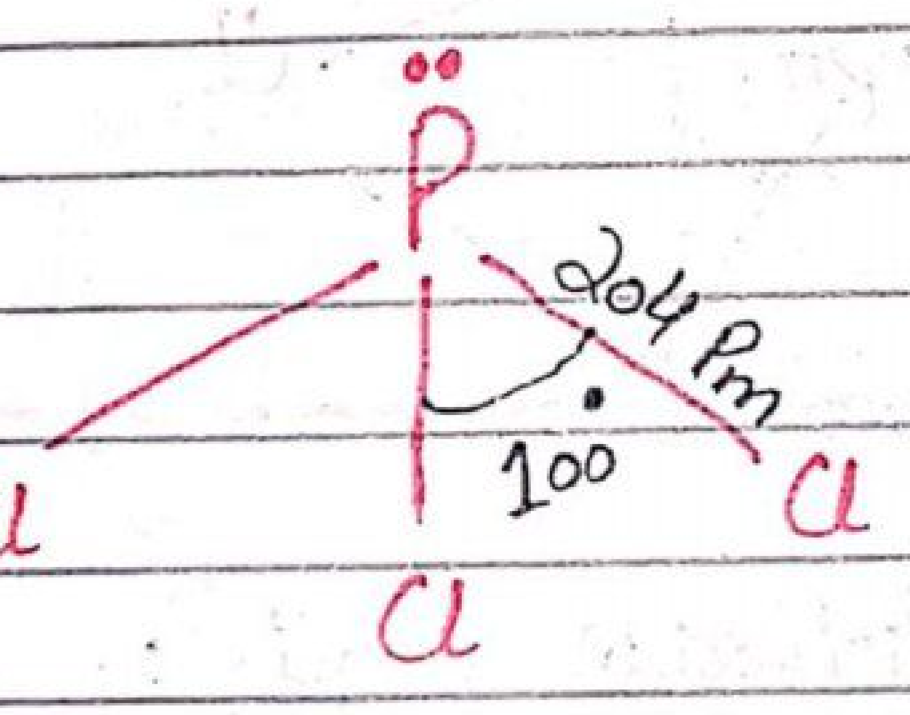
b) PCl_5

(a) Phosphorus (III) chloride (PCl_3):-

1) It is covalent chloride.
2) It is a fuming colourless liquid.
3) It is non-conductor of electricity because it has no free ions.
4) There are london dispersion forces and dipole-dipole forces between the molecules.
5) $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$

(Phosphorous acid)

PCl_3 react violently with water to produce phosphorous acid and fumes of hydrochloric acid



(b) Phosphorous (V) chloride (PCl_5):-

1) It is a off-white solid
2) when it is heated at high temperature it decompose in to;

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

3) When it is reacted with cold water it produce phosphorous oxychloride and HCl.

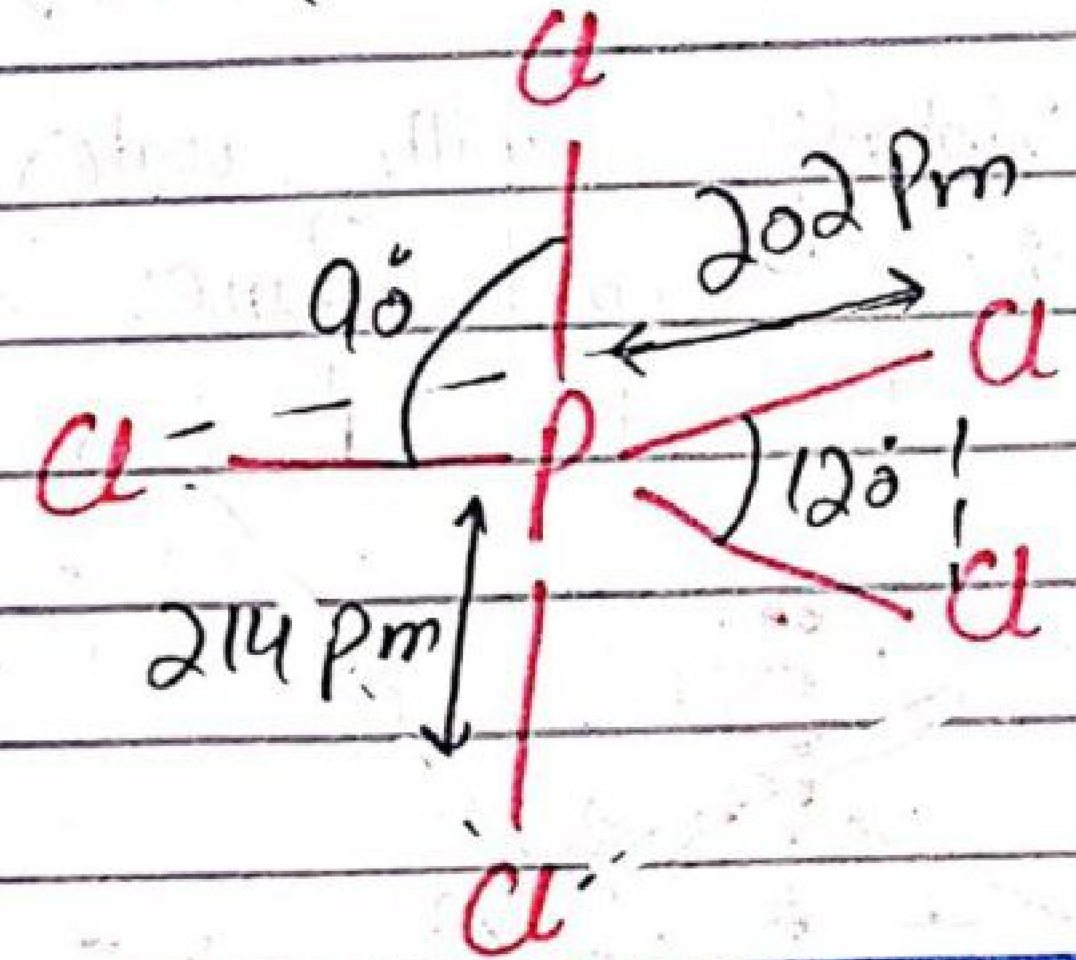
$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

(cold)

4) when it is reacted with boiling water it produce phosphoric acid

$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

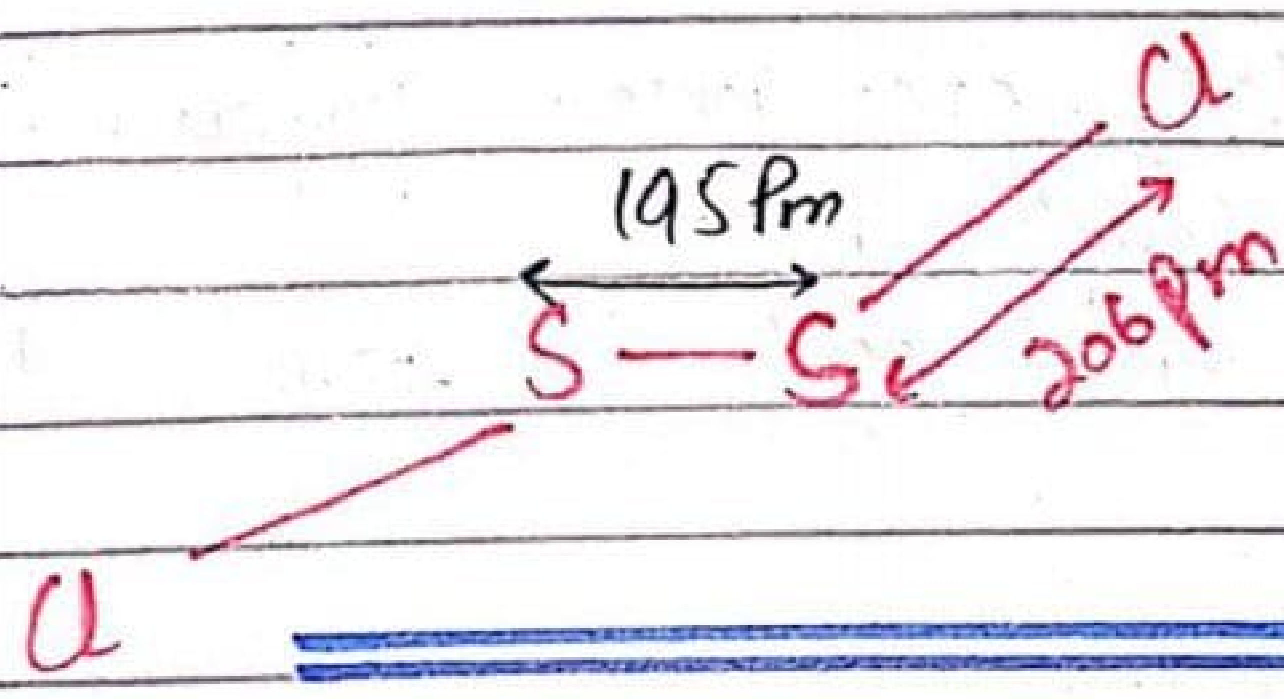
5) In Solid form it contain ions



(06) Disulphur dichloride (S_2Cl_2):-

1) It is a Covalent Chloride -
2) It is an orange evil smelling liquid -
3) There are landon dispersion and dipole - dipole forces between the molecules -
4) It produce by the reaction of chlorine with hot sulphur -
5) It react with water slowly produce hydrochloric acid, hydrogen Sulphide, Sulphur containing acids, Sulphur compound and anions

6) There are no ions in disulphur dichloride and no mobile electrons - so it never conduct electricity.



★ **Properties of the chloride of the elements in the third Period**

Formula of Chloride	NaCl	$MgCl_2$	Al_2Cl_6	$SiCl_4$	PCl_3 (PCl_5)	S_2Cl_2	Cl_2
State of chloride (at 25°C)	Solid	Solid	Solid	liquid	liquid	liquid	gas
b.pt of chloride/°C	1465	1418	423	57	74	136	-35
Conduction of Electricity by molten or liquid chloride	good	good	v. poor	nil	nil	nil	nil
Structure of Chloride	Giant Structure			Simple molecular Struct			
Enthalpy change of formation of chloride at 298 K / $KJ\,mol^{-1}$	-411	-642	-1408	-640	-320	-60	0
Enthalpy change of formation of chloride at 298 K per mole of Cl atoms	-411 / KJ	-321	-235	-160	-107	-30	0
Effect of adding chloride to water	Solid dissolves readily			Chloride reacts with H_2O, HCl fumes are produced			Some Cl_2 reacts with H_2O
pH of aqueous solution of chloride	7	6.5	3	2	2	2	2

Hydroxides of the Period 3 Elements:-

(1) Sodium hydroxide and Magnesium hydroxide:-

i) NaOH & $Mg(OH)_2$ are ionic compound.
ii) Both are sample base
iii) They react with acid to form salt

Reactions:-

$$NaOH + HCl \rightleftharpoons NaCl + H_2O$$

$$Mg(OH)_2 + 2HCl \rightleftharpoons MgCl_2 + 2H_2O$$

(colourless solution)

Q1- Prove that sodium hydroxide and magnesium hydroxide are base?

(2) Aluminium hydroxide:-

i) It is amphoteric
ii) It has acidic as well as basic properties

Q2 Prove that Aluminium hydroxide is amphoteric in nature?

Reactions:- (1) Reaction with acid:-

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

(02) Reaction with Base :-

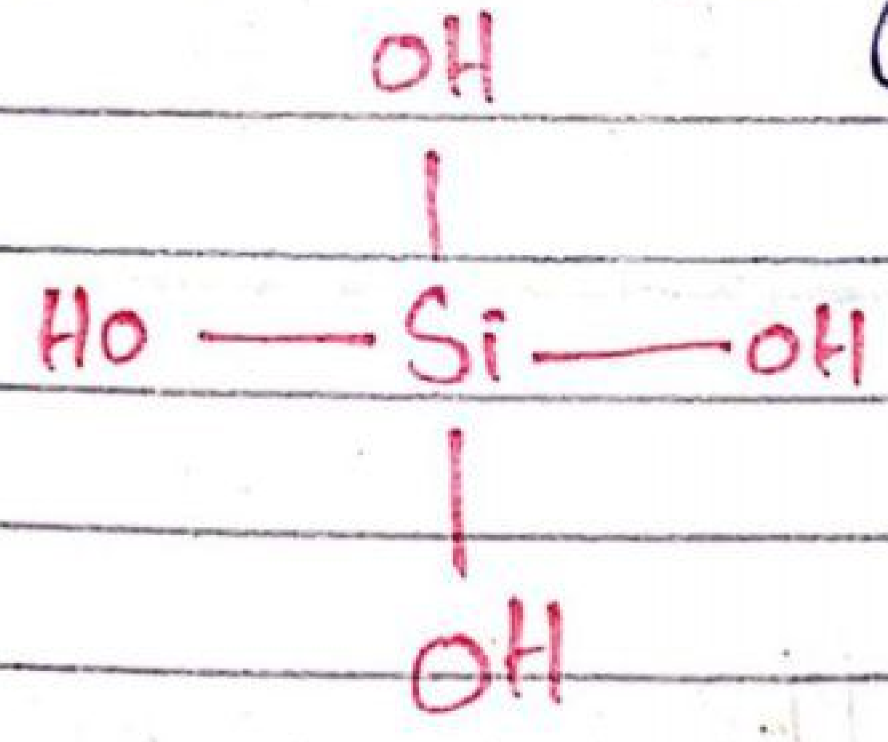
$$Al(OH)_3 + NaOH \longrightarrow NaAl(OH)_4$$

(Sodium tetrahydroxoalumin

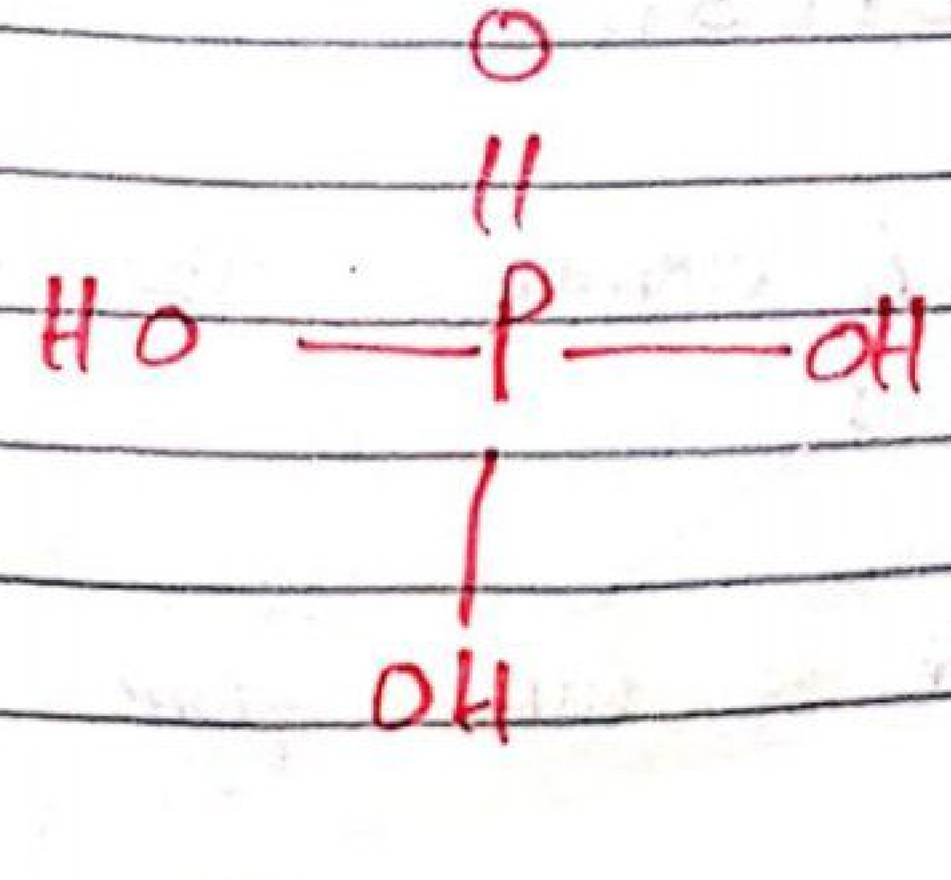
(03) Other hydroxide

i) Silicon, phosphorous, Sulphur and chlorine have (OH) group with other element which is covalently bonded - Therefore hydroxide of these element are acidic.

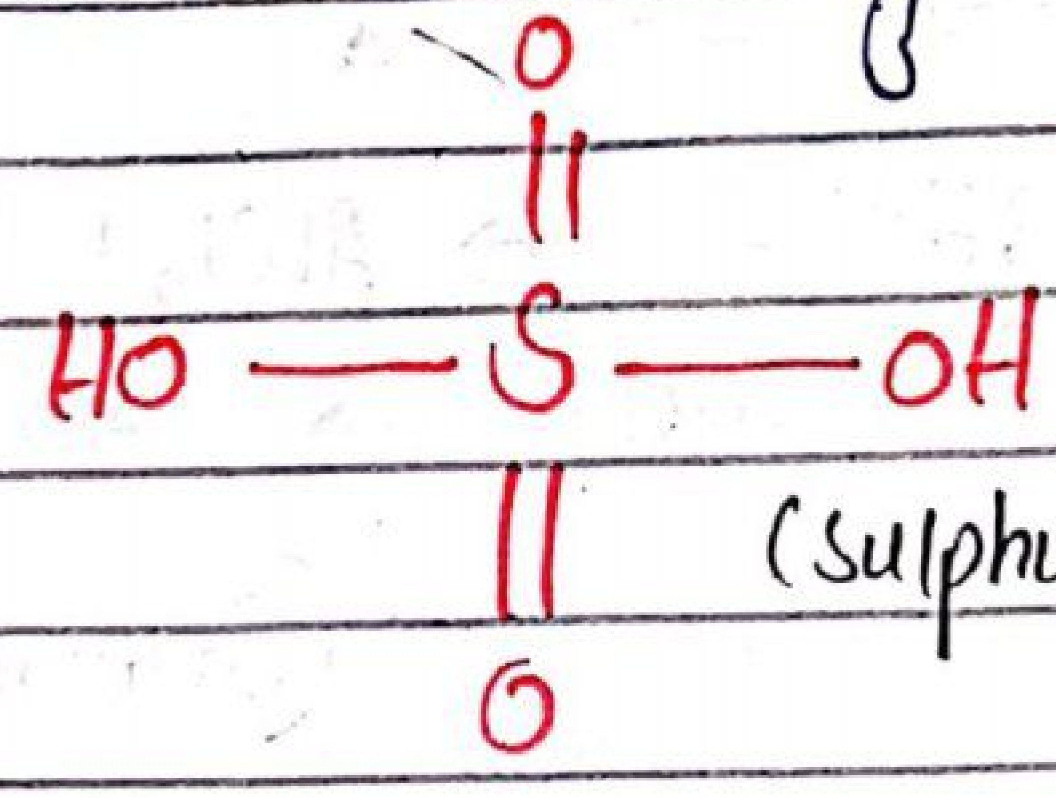
ii) orthosilicic acid is very weak acid -



(iii) phosphorous acid is a weak acid but stronger acid as compared to Ethanoic acid (CH_3COOH) -

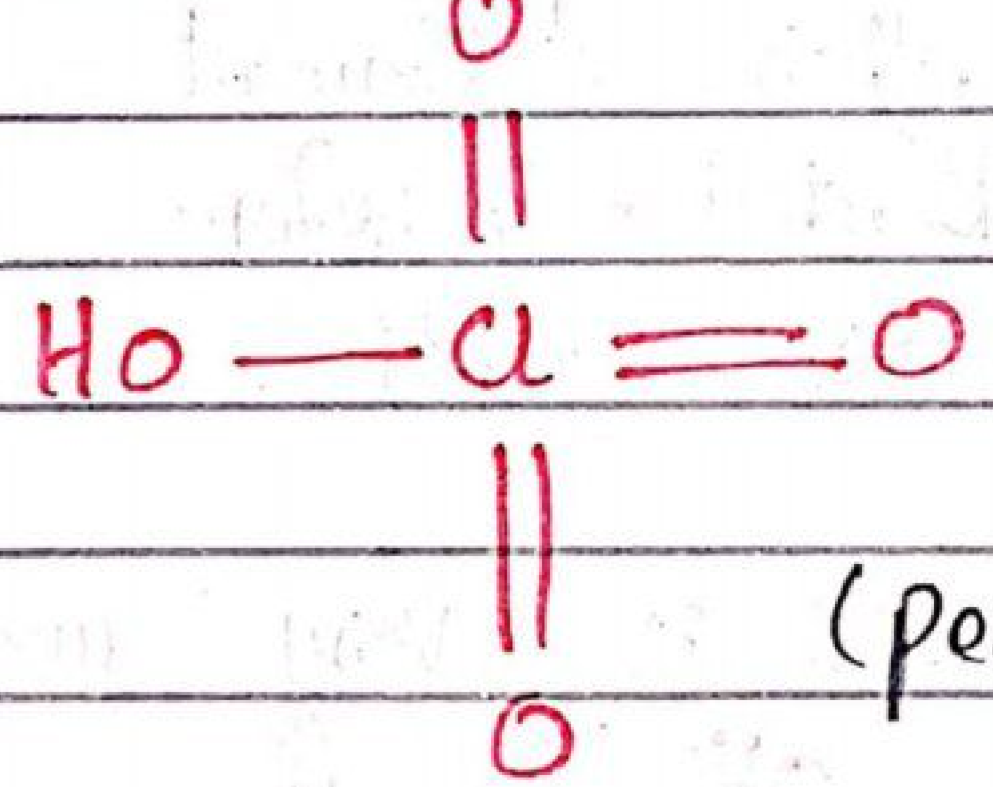


(iv) Sulphuric acid is a very strong acid.



(sulphuric acid)

(v) Perchloric acid is a very strong acid as compared to Sulphuric acid



(perchloric acid)

Atomic and Physical trends of 1A

IA group elements = Alkali Metal ↳ except hydrogen
⇓
(Li, Na, K, Rb, Cs, Fr)

Q- why group 1A elements are called alkali metal ?

Ans- Name alkali came from Arabic

mean Ashes - Arab use this term for these metal because ashes of plants are mainly composed of Na and K. Alkalic metal include (Li, Na, K, Rb, Cs, Fr).

01) Atomic radius:-

Distance between the nucleus and outermost electron in an atom is called atomic radius.

★ Down the group:- Atomic radius increases from Li to Cs in 1A group.

Reason:-

i) Atomic number increases.
ii) Electrons are being added to new shell.
iii) These for atomic radius increases from lithium to Caesium.

02) Ionization energy:-

OR

Ionization potential (I.E):-

Amount of energy required to remove outer most electron from the gaseous atom is called ionization energy.

Example; $Na_{(g)} \longrightarrow Na^{+} + e^{-}$ $I.E = 496\ kJ/mol$

Note:-

Alkali metals have low ionization energy as compared to other group element-

Down the group:-

Ionization energy decreases from Lithum to Caesium in IA group

Reason:-

This is because down the group

i) Atomic Size increases
ii) Distance between the nucleus and outer most electron increases
iii) Force of attraction between the nucleus and outer most electron decreases-
iv) Removal of electron become easy-

Note:-

Second ionization Energies of alkali metal are very high because after lossing one electron they gain noble gass electronic configuation and become Stable than removal of second electron is diffciult-

3) Trend in Electronegativity (E.N)

i) Alkali metals have Low electronegativity as compared to other group element-

i) Electronegativity decreases from lithum to Caesium -
ii) Due to decrease in force of attraction b/w electrons in nucleus -

(4) Melting & Boiling Point:-

i) Alkali metals have very low melting and boiling point -
ii) Melting and Boiling point decreases from lithum to Caesium -
iii) Due to less number of binding electrons

(5) Trends in Density:-

i) Alkali metals have low densities -
ii) Same piece of Lithum, Sodium, Potassium float over water
iii) Density increases with increase in atomic number -
iv) Density of alkali metal increases from lithum to Caesium -
v) Potassium is lighter than Sodium due to unsual increase in atomic Size of potassium -

(6) Trends in Reactivity with water:-

i) Reaction of alkali metal with water are very fast -

ii) Small piece of lithum, Sodium, potassium, float on water -

iii) They react vigorously with water produce metal hydroxide and hydrogen gas -

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2 \quad \Delta H = -ve$$

iv) These reaction are highly exothermic -

v) Reactivity of alkali metal increases from top to buttom -

vi) Potassium and other alkali metal have very fast reaction - They react with water (ice) even at -100°C -

Reaction with oxygen:-

Alkali metals are highly reactive they react with oxygen or air get tarnished due to formation of oxides on the surface of metal - Therefore alkali metals are stored in kerosene or paraffin oil -

i) Lithum react with oxygen form normal oxide

$$4Li + O_2 \longrightarrow 2Li_2O$$

(lithium normal oxide)

ii) Sodium react with oxygen form sodium peroxide -

$$2Na + O_2 \longrightarrow Na_2O_2$$

(Sodium Peroxide)

i) All other alkali metal react with oxygen form Superoxide -

$$K + O_2 \longrightarrow KO_2$$

(Potassium Superoxide)

* only lithum form normal oxide by direct reaction of lithum with oxygen - All other alkali metal form normal oxides by indirect method -

(i) $2Na_2O_2 + 4Na \longrightarrow 4Na_2O$

(ii) $2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$

(iii) $2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$

Properties :-

(i) Normal oxide react with water produce hydroxide by Proton transfer lose proton -

$$O^{-2} + \overset{+3}{H}-\overset{-3}{OH} \rightleftharpoons OH^{-} + OH^{-}$$

Proton gain

(ii) peroxide (O_2^{-2}) and superoxide (O_2^{-1}) react with water produce hydrogen peroxide and oxygen -

$$2O_2^{-2} + 2H_2O \longrightarrow 2H_2O_2 + O_2$$

Reaction of oxides with water and Dilute Acid

1) Sample oxide (Normal oxide) (M_2O)

a) Reaction with water:-

(i) $Li_2O + H_2O \longrightarrow 2LiOH$

(ii) $M_2O + H_2O \longrightarrow 2MOH$

★ Normal oxide react with water produce hydroxide

b) Reaction with dilute acid :-

(i) $Li_2O + 2HCl \longrightarrow 2LiCl + H_2O$

(ii) $M_2O + 2HCl \longrightarrow 2MCl + H_2O$

★ Normal oxide react with dilute acid give Salt and water

② Peroxides (M_2O_2) :-

a) Reaction with H_2O :-

★ Peroxide react with water produce hydrogen peroxide and hydroxide

(i) $Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

(ii) $M_2O_2 + 2H_2O \longrightarrow 2MOH + H_2O_2$

b) Reaction with dilute acid :-

★ Peroxide react with dilute acid produce salt and hydrogen peroxide - Reaction take place in ice cold water if temperature of the reaction increases hydrogen peroxide decompose into water and oxygen -

$$Na_2O_2 + 2HCl \longrightarrow 2NaCl + H_2O_2$$

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

3) Superoxide (MO_2):-

a) Reaction with water:-

★ Superoxide react with water produce hydroxide, hydrogen peroxide and oxygen.

(i) $2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$

(ii) $2MO_2 + 2H_2O \longrightarrow 2MOH + H_2O_2 + O_2$

b) Reaction with dilute acid:-

★ Superoxide react with dilute acid produce salt, hydrogen peroxide and O_2 if temperature of the reaction increases hydrogen peroxide decompose into water and oxygen.

(i) $2KO_2 + 2HCl \longrightarrow 2KCl + H_2O_2 + O_2$

(ii) $2MO_2 + 2HCl \longrightarrow 2MCl + H_2O_2 + O_2$

if temperature raise then,

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

* Reaction of the Elements with Chlorine :-

(i) Alkali metals react with halogen (chlorine) produce metal halide (metal chloride) -

Example:-

(i) $Na + Cl_2 \longrightarrow 2NaCl$

(ii) $2Li + Cl_2 \longrightarrow 2LiCl$

ii) Lithum, Sodium react slowly with Chlorine at room temperature to produce lithum chloride and Sodium chloride -

ii) Potassium, Rbadium, Caesium Vigorously with all halogen to produce their corresponding metal halide -

Effect of heat on Nitrates, Carbonates and hydrogen Carbonates :-

) All alkali metal nitrate decompose into their corresponding nitrite and oxygen on heating except lithum nitrite ($LiNO_3$) -

Examples:-

(i) $2NaNO_3 \longrightarrow 2NaNO_2 + O_2$

(ii) $2KNO_3 \longrightarrow 2KNO_2 + O_2$

(iii) $4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$

(ii) All alkali metal carbonate are stable on heating except lithum carbonate their stability increases down the group due to increase in electropositive character.

Examples:-

(i) $Li_2CO_3 \longrightarrow Li_2O + CO_2$

(iii) All alkali metal bicarbonate are stable on heating their stability increases down the group due to increase in electro positive character.

Flame Test:-

Flaming test are used to identify the presence of a relatively small number of metal ions in a compound.

Procedure for flame test:-

(i) Take a platinum or nichrome (a nickel

chromium alloy wire).
(ii) Clean it by dipping into a concentrated hydrochloric acid (HCl)
(iii) Then hold it in a hot Bunsen flame.
(iv) Repeat until the wire does not produce any colour in the flame.

★ Different colours shown by different Elements

Elements	Flame colour	Elements	Flame colour
Li	Red (Crimson)	Ca	orange Red
Na	golden Yellow	Sr	red
K	Violet	Ba	pale green
Rb	(redish-violet)	Cu	blue-green (often with white flashes)
Cs	Blue	Pb	greyish-white

Q7. why different colours are imparted by the atoms of the group 1 metals to the flame?

Ans- Outer electrons (i.e ns^1 electron) of atom of alkali metals is loosely held with the nucleus and hence it can be easily excited to a higher energy levels even by a small amount of heat energy (e.g by heating the metals or their salts into Bunsen burner). During the excitation process the electron absorbs some energy and when this excited electron comes back to its original position, it gives out absorbed energy in the form of lights in visible region of the electromagnetic Spectrum and hence the colour is imparted by the atoms to the flame. Since the amount of energy absorbed during the excitation process is different in different atoms different colour are imparted by the atoms to the flame.

The Colour:-

* Different colour shown by different elements are given below -

Elements	Flame Colour	Elements	Flame Colour
Li	Red (crimson)	Ca	orange-Red
Na	golden Yellow	Sr	red
K	Violet	Ba	pale green
Rb	Redish-Violet	Cu	blue-green (often with white flashes)
Cs	Blue	Pb	greyish-white

Group 2 Elements (Alkaline Earth Metals)

Atomic and Physical properties

01) Trends in Atomic Radius :-

Definition :-
Distance between the nucleus and outer most electron in an atom is called atomic radius

Down the Group :-
Atomic radius increases down the group from Be to Ra (group IIA Elements)

Reason :-

(i) Atomic number increases
(ii) Electrons are being added to a new shell.
(iii) Therefore atomic radius increases down the group.

02) Trends in First Ionization :-

Definition :-
Amount of energy required to remove outer most electron from the gaseous atom is called ionization energy.

Down the Group :-

The first and Second ionization energies of Group IIA Elements decrease down the group.

Reason :-

(i) Atomic number increases
(ii) Distance between the nucleus and outer most electron increases.
(iii) Force of attraction between the nucleus and outer most electron decreases
(iv) Removal of electron become easy.

(03) Trends in Electronegativity :-

(i) Alkaline Earth Metals have low electronegativity
(ii) Electronegativity decreases from Be to Ba
(iii) Due to increase in atomic radii
(iv) Decrease in force of attraction between the nucleus and outer most electron.

(04) Trends in melting and Boiling point :-

(i) IIA group element have high melting and boiling point as compared to I-A group element this is because melting and boiling point depend up on binding of electrons -

(ii) II A group element use two electron for binding purpose and IA group element use one electron for binding purpose.

(iii) There is no regular trend present in II-A group element for melting and boiling point however melting point decreases from top to bottom except mg -

(05) Trends in reactivity with water :-

Reactivity of alkaline Earth metal with water increases down the group.

★ Berylium (Be) :-

Berylium has no reaction with water or steam even at red hot.

★ Magnesium (Mg) :-

Magnesium has very slight reaction with water

(i) $Mg + 2H_2O \text{ (cold)} \longrightarrow Mg(OH)_2 + H_2$

(ii) $Mg + H_2O \text{ (steam)} \longrightarrow MgO + H_2$

★ Calcium (Ca), Stantium (Sr), Berium (Ba) :-

Ca, Sr and Ba react with cold water produce hydroxide and hydrogen gas those hydroxide are Soluble in water. Reaction is highly exothermic

(i) $Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$

(ii) $M + 2H_2O \longrightarrow M(OH)_2 + H_2$

Reaction with oxygen & Nitrogen :-

(a) Formation of Sample oxide :- (Normal oxide)

Preparation :-

(i) II-A group element react with oxygen form normal oxide at high temperature

$$2Ca + O_2 \longrightarrow 2CaO$$

(ii) By heating Carbonate of II-A group element normal oxide are obtain.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Properties :-

(i) These oxides are Stable due to high

crystal lattice.

(i) They are white crystalline Solid.

(iii) BeO, MgO are quite insoluble all other oxides of this group are Soluble in water and form strong base.

(iv) BeO is amphoteric in nature.

★ Reaction with Acid:-

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$

★ Reaction with Base:-

$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$$

(Sodium beryllates)

(v) Other oxide of this group is basic

(vi) BeO is **covalent** other oxide of this group is **ionic**.

(vii) BeO is **hard** other oxides of this group is **soft**.

(b) Peroxides:-

Preparation:-

Normal oxide of Ca, Sr and Ba react with oxygen at high temperature for peroxide.

$$2BaO + O_2 \longrightarrow 2BaO_2$$

Properties :-

(i) They are ionic Oxide -
(ii) They are white crystalline Solid -

(iii) $$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

- Peroxide react with acid form Salt and hydrogen peroxide -

Reaction of Group 2 Element with Nitrogen -

01) An alkaline earth metal react with nitrogen form nitrades having general formula (M_3N_2).

$$Ca + N_2 \longrightarrow Ca_3N_2$$

(Calcium nitride)

02) These nitrides dissolve in water produce their hydroxide and ammonia gas -

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$$

3) Be_3N_2 is volatile while other nitride of this group are non-volatile -

Solubility of hydroxides, Sulphates and Carbonates :-

Solubility of hydroxide :-

01) Solubility of alkaline Earth metal hydroxide increases down the group -

02) $Be(OH)_2$ is insoluble in water -

03) $Mg(OH)_2$ is slightly soluble in water at room temperature form solution having pH 9 - Suspension of $mg(OH)_2$ is called milk of magnesium - It is used for acidity of stomach -

04) $Ca(OH)_2$ Solution is called lime water It is more soluble - Its solubility is 1 gram of $Ca(OH)_2$ is dissolve in one litre at room temperature

05) $Sr(OH)_2$ & $Ba(OH)_2$ are more

06) Soluble in H_2O having concentration of Solution 0·1 of molar at room-temperature.

Solubility of Sulphates

01) Solubility of alkalin earth metal Sulphate decreases down the group

02) $BeSO_4$ & $MgSO_4$ are fairly soluble in water.

03) Calcium Sulphate is sufficient soluble in water.

04) $SrSO_4$ and $BaSO_4$ are in Soluble in water.

Solubility of the Carbonates:-

01) Solubility of alkaline earth Carbonate decreases down the group.

02) They are all Soluble in water.

03) They are Soluble in water containing CO_2 due to formation of their bi Carbonates.

$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_{2\,(aq)}$

Important Steps for Solubility :-

(01) Hydration Energy $\propto$ Solubility

Hydration Energy $\propto$ charge density

$$\text{charge density} = \frac{\text{Charge}}{\text{Size OR Volume}}$$

(02) Lattic energy $\propto \frac{1}{\text{Solubility}}$

→ Cation / Anion $\propto 1/\text{Size}$

(03) hydration energy > lattic energy then Compound is Soluble -

---

Q- why Solubility of Carbonates and Sulphate of 2 group element decreases from top to buttom?

Ans - Carbonate and Sulphate anion are balky anion. Therefore hydration energy over come lattice energy. From top to bottom in II group Size is increasing due to this Charge density is decreasing due to this hydration energy is decreasing therefore Solubility is decreasing

Hydration Energy ∝ Solubility

(Long Question) ⟷

Thermal Stability of the Carbonates and Nitrates

01) Effect of heat on the Group 2 Elements Carbonates:-

1) All alkaline Earth metal Carbonate decompose on heating into their oxide and Carbon dioxide.

01) $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

02) $SrCO_3 \xrightarrow{\Delta} SrO + CO_2$

2) Stability of these Carbonate on heating increases down the group -

01) $BeCO_3 \xrightarrow{25^\circ C} BeO + CO_2$

02) $MgCO_3 \xrightarrow{540^\circ C} MgO + CO_2$

03) $CaCO_3 \xrightarrow{900^\circ C} CaO + CO_2$

04) $SrCO_3 \xrightarrow{1290^\circ C} SrO + CO_2$

05) $BaCO_3 \xrightarrow{1360^\circ C} BaO + CO_2$

3) Reason:-

This is because down the group the size of resulting oxide increases, lattic energy of resulting oxide decreases - Resulting oxide become unstable therfore original carbonates become stable -

02) Effect of heat on the Group 2 Nitrates :-

01) All alkaline Earth metal nitrate decompose into their oxide, nitrogen dioxide and oxygen

01) $2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$

02) $2Ca(NO_3)_2 \xrightarrow{\Delta} 2CaO + 4NO_2 + O_2$

03) $2Ba(NO_3)_2 \longrightarrow 2BaO + 4NO_2 + O_2$

02) These nitrate white crystalline Solid and produce form like oxide also also white crystalline Solid and NO_2 is a reddish brown gas oxygen is a colour less gas

03) Their thermal stability increases down the group.

Q- why lithum Carbonates and nitrate is unstable while other group element Carbonate and nitrate is stable.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$

⇒ lattic energy $\propto$ stability

⇒ lattic energy $\propto$ 1/Size

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How Beryllium is differ from other members of its Group?

Beryllium is differ from its family members due to following reason.

- Small Size
- high Electronegativity

1) Hardness:-

Beryllium is the hardest of all the elements of its group.

2) Melting & boiling point:-

The melting and boiling points of beryllium are the highest among their family member.

3) Formation of covalent Compound:-

Beryllium has the tendency to form covalent compound while other family member of Beryllium form ionic compound. when they react with other elements the electronegativity difference is not so large and the bond is therefore covalent.

4) Reaction with water:-

Beryllium does not react with water even at high temperature. All other alkaline earth metal react with water evolved hydrogen gas -

(i) $Mg + H_2O \longrightarrow MgO + H_2$

• 5). Reaction with hydrogen:-

Beryllium does not react with hydrogen directly to from Beryllium hydride - It is prepared by indired method - All other alkaline earth metal react directly with hydrogen from hydride - BeH_2 and MgH_2 are covalent all other hydride of this group are ionic -

• 6) Reaction with Alkalis:-

Beryllium react with alkali evolve hydrogen gas other alkaline earth metal do not react with alkalis-

(i) $Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$

• 7) Behaviour of oxides and hydroxide :-

The oxides and hydroxide of beryllium are amphoteric, All other element oxide and hydroxide are basic -

(i) $BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$

(ii) $BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$

8) **Behaviour of Carbides:-** Beryllium Carbide react with water evolve methane gas - Other alkaline earth metal Carbide react with water evolved ethyne gas (acetylene).

(i) $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$

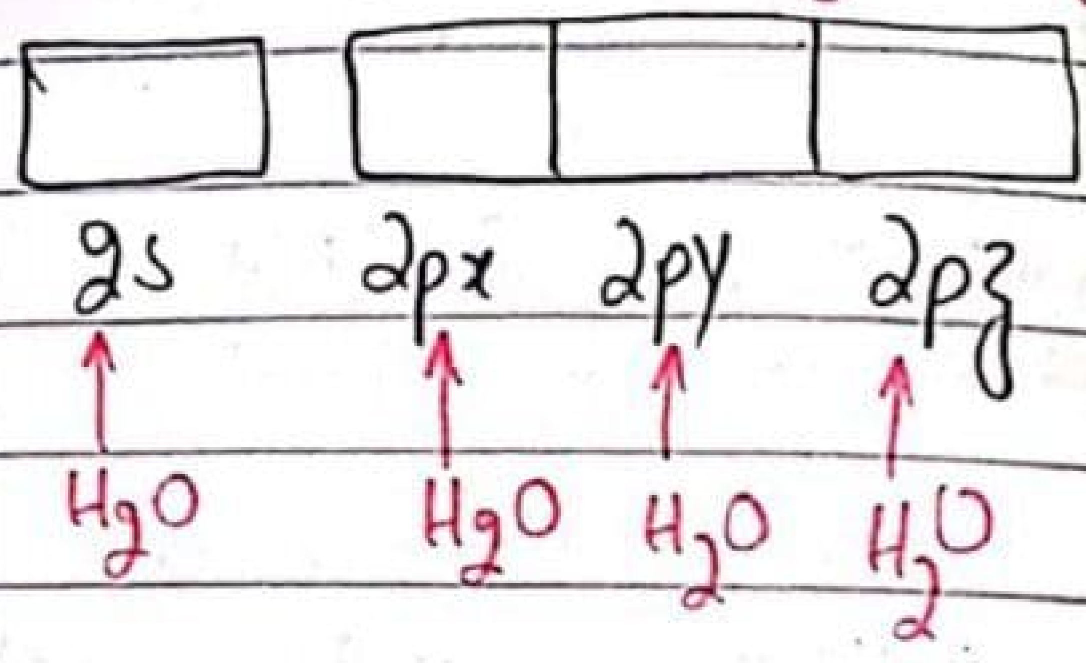
(ii) $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

9) **Behaviour of Nitrides:-** Be_3N_2 is Volatile while other nitrides of other alkaline earth metals are non-Volatile -

10) **Numbers of Molecules of water of crystalisation:-** Beryllium Salt can not have more then four water of crystalization due to absence of d-orbital. All other element of this group can form more than four water of crystallization due to the presence of d-orbital

$_4Be = 1s^2, 2s^2, 2p_x, 2p_y, 2p_z$

$Be^{+2} = 1s^2, 2s^0, 2p_x, 2p_y, 2p_z$



11) Formation of complex compound :-

Beryllium form stable complex condound like $[BeF_3]^{-1}$ / $[BeF_4]^{-2}$ other alkaline earth metal form fex complexes.

Group 4-Elements (Carbon Family)

* Group 4 Element includes
  C, Si, Ge, Sn, Pb

Melting and Boiling points :-

01) Melting and boiling point decreases down the group in 4A group element this decreases in not regular.

02) Carbon and Silicon have high melting and boiling point due to formation of gaint covalent molecules.

03) Melting point of Sn is less than Pb due to distorted 12-co-ordinated structure rather then pure one.

Trends from non-metals to metal in IVA group Element:-

01) Metallic character increases down the group in IVA group elements.

02) Carbon and Silicon are non-metal however Silicon has some metalloid properties

03) Ge is metalloid that is metal as well as non-metal.

04) Sn and Pb are metals.

C, Si	Ge	Sn, Pb
Non-metals	Metalloid	Metals

Oxidation State:-

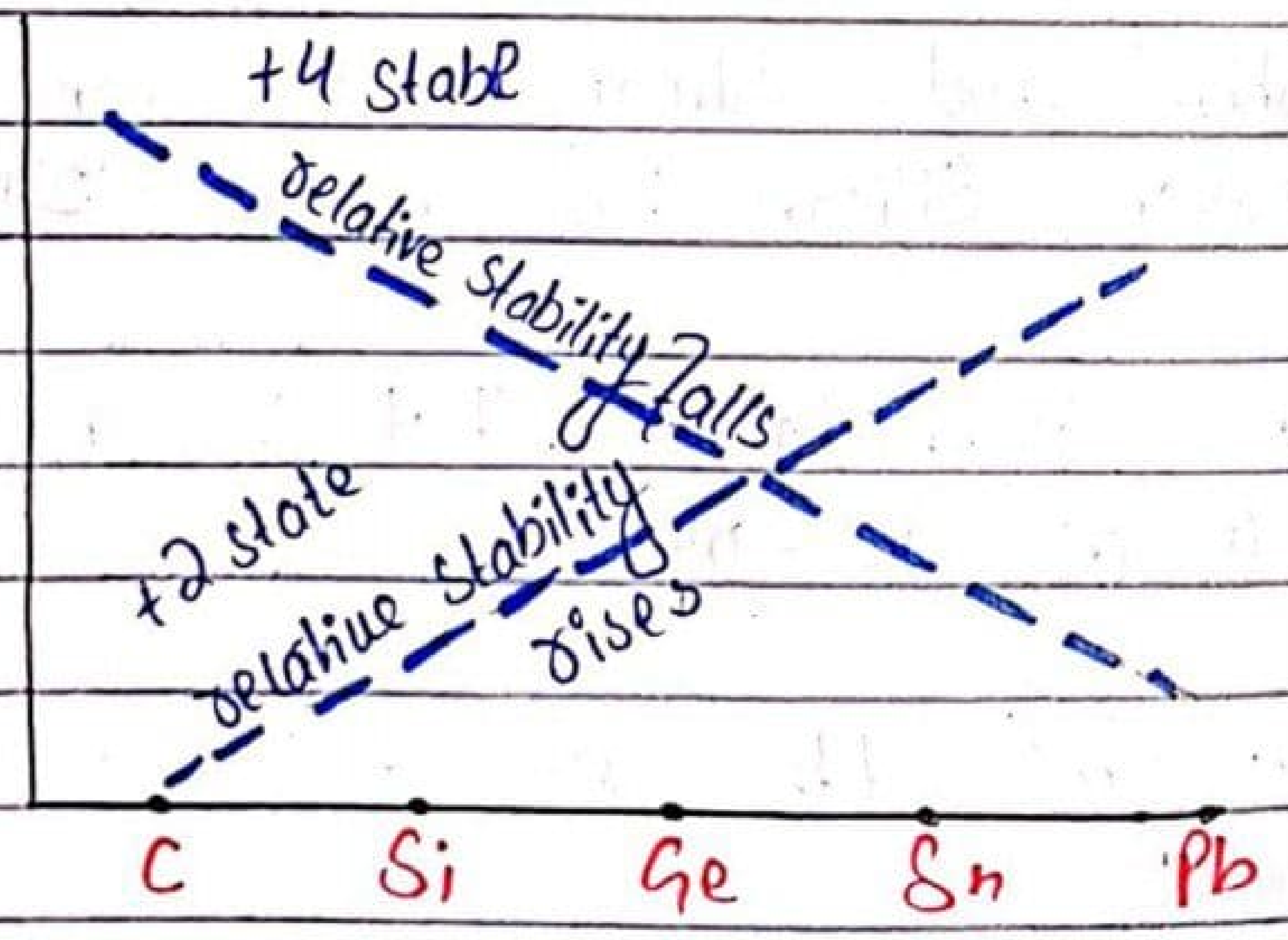
★ Apparent charge on an atom which may be positive or negative on a substance is called oxidation state -

01) Carbon and silicon shows +4 oxidation state -

02) All other element of this group shows +2 oxidation state -

03) Relative stability of two oxidation state is different for different elements -

04) Stability of +2 oxidation state increases down the group -



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Inert pair effect and Positive oxidation states:-

Inert Pair effect:-

Pair of electron which do not take part in a chemical reaction is called inert pair and this effect is called inert pair effect.

- Carbon and Silicon commonly show +4 oxidation state.
- Germanium commonly shows both +2 and +4 oxidation state
- Tin and lead commonly shows +2 oxidation state.

- The general valence shell electronic configuration of group 4 elements is ns^2np^2.

- When two np^2 electrons are lost from ns^2np^2 configuration, the element show +2 oxidation states.

- The two electron in ns^2 are not lost in the formation of M^{+2} cations.
- The stability of +2 oxidation state increases from i.e Ge^{+2} to Pb^{+2} i.e $Ge^{+2} < Sn^{+2} < Pb^{2+}$

- When the four ns^2np^2 electrons are lost, the element show +4 oxidation state i.e M^{+4} cation are formed.
- The stability of +4 oxidation state decreases down the group i.e $Ge^{+4} > Sn^{+4} > Pb^{+4}$

(01) Ge^{+2} compound ⟶ $Ge^{+4} + 2e^-$

- less stable
- Reducing agent

- more Stable
- oxidising agent

The compound Ge^{2+} acts as a strong reducing agent.

(02) Sn^{+2} Compound ⟶ $Sn^{+4} + 2e^-$

- less stable
- Reducing agent

- more stable
- oxidising agent

The compound Sn^{+2} acts as a strong reducing agent.

(03) $Pb^{+4} + 2e^-$ Compound ⟶ Pb^{+2}

- less stable
- oxidising agent

- more stable
- Reducing agent

The compound Pb^{+4} acts as a strong oxidising agent.

Thus the order of stability of M^{2+} and M^{4+} cation of Ge, Sn and Pb is

$Ge^{2+} < Ge^{4+}$, $Sn^{2+} < Sn^{4+}$, $Pb^{2+} > Pb^{+4}$

Negative Oxidation State :-

The electronegativity of these elements are low, they do not have tendency to form negative ion.

However Carbon form C^{4-} and C_2^{2-} ions in certain compounds.

Examples:-

- $Be_4^{2+}C_2^{4-}$ or Be_2C (Be^{2+} and C^{-4} ions)
- $Al_4^{2+}C_3^{4-}$ (Al^{3+} and C^{4-} ions) etc.

Nature of M^{2+} and M^{+4} Compounds :-

The nature of M^{2+} and M^{4+} compound can be predicted by Fajan's Rule.

Fajan's Rule :-

The smaller the cation the greater is the amount of covalent character in the compounds.

Since for an element M^{4+} ion is smaller than M^{+2} ions. Therefore M^{4+} ions are covalent while M^{+2} ions are ions.

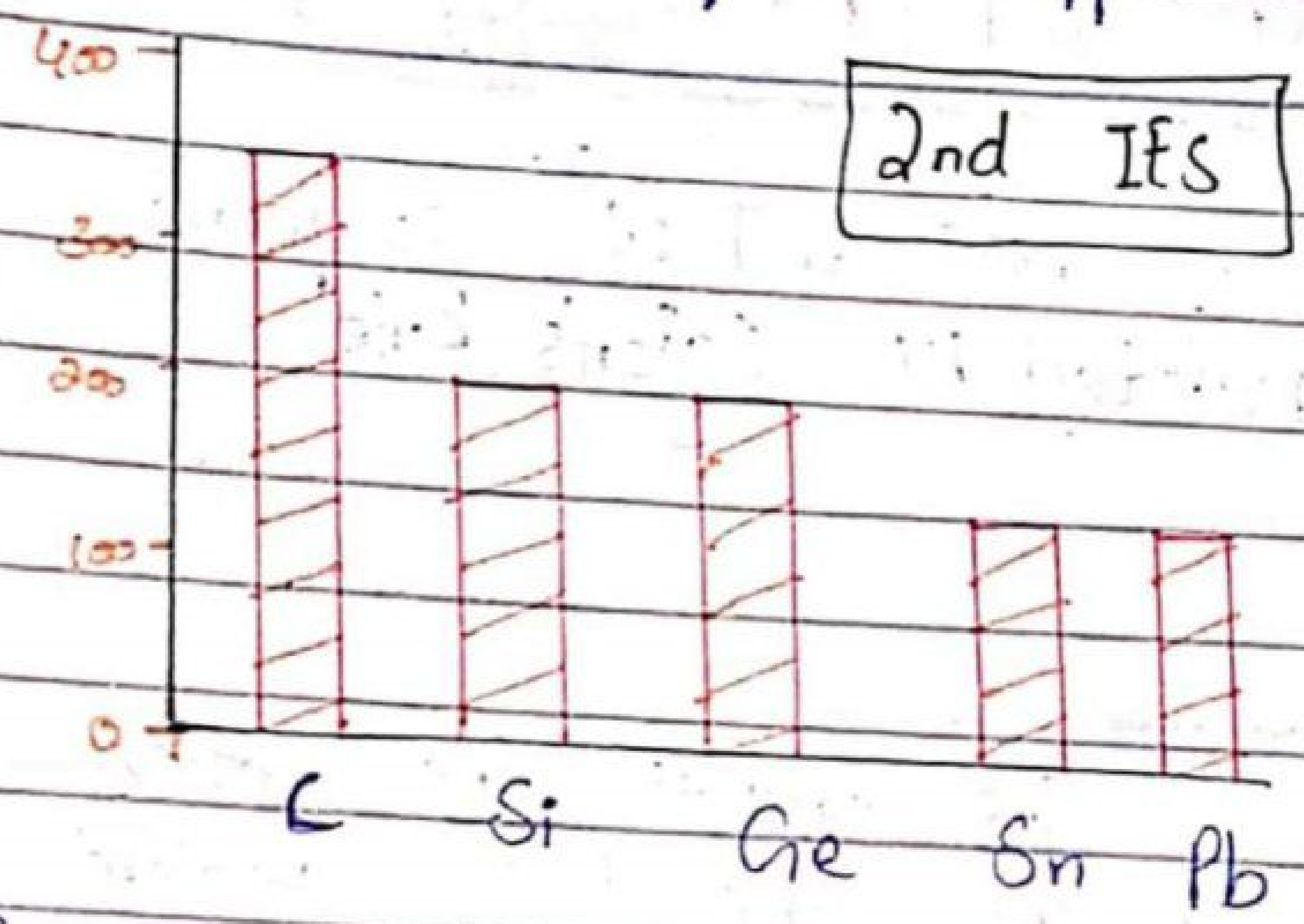
Sn^{+4} / Pb^{+4} ⇒ Covalent

Sn^{+2} / Pb^{+2} ⇒ ionic

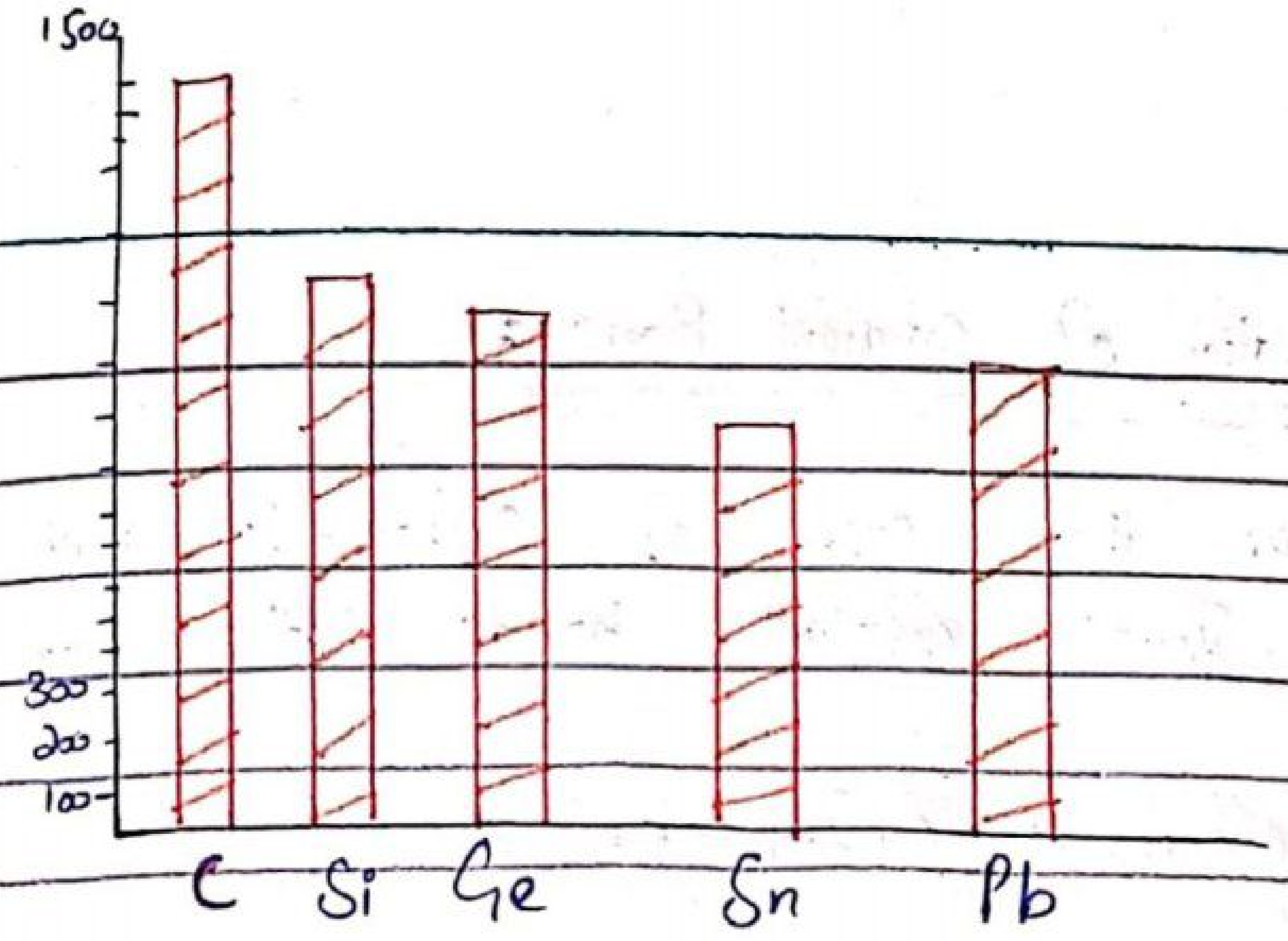
Q2. Discuss inert pair effect in the;

a) Formation of ionic bond:-

- If the group 4 form +2 ions, they will lose the p^2 electrons leaving the s^2 pairs unused.
- e.g; to form lead (II) ion; lead will lose the two 6p electrons but the 6s electrons will left unchanged which is the "inert pair".
- Generally ionization energies decreases down the group. However in group 4 this does not quite happen.



- Generally ionization energy needed to form the +2 ions as shown in figure in $kJ\ mol^{-1}$. The figure shows there is a slight increase between tin and lead. It shows that it is slightly more difficult to remove the p-electrons from lead then from tin.



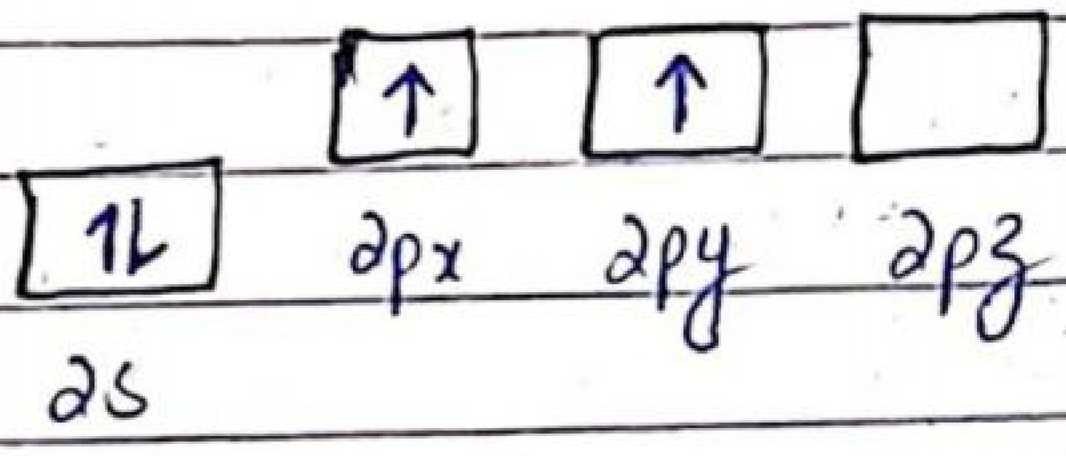
- The total ionization energy needed to form the +4 ions are shown in figure in $kJ\ mol^{-1}$. The difference between tin and lead is more prominent. The relatively large increase between tin and lead must be because the $6s^2$ pair is significantly more difficult to remove in lead then the corresponding $5s^2$ pair in tin. It can be explained by Theory of Relativity.

- In case of lead, the relative contraction makes it more difficult to remove the 6s electrons then expected. The energy releasing in other process like enthalpy and hydration enthalpy are not enough to compensate for this extra energy. It means for lead it is not energetically favourable to form 4+ ions.

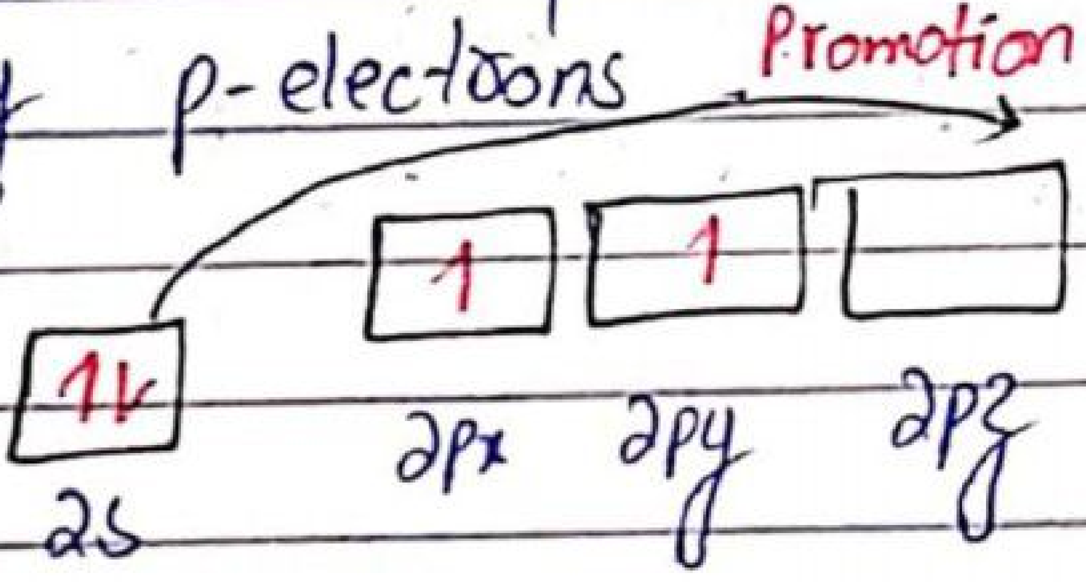
(b) Formation of Covalent Bonds:-

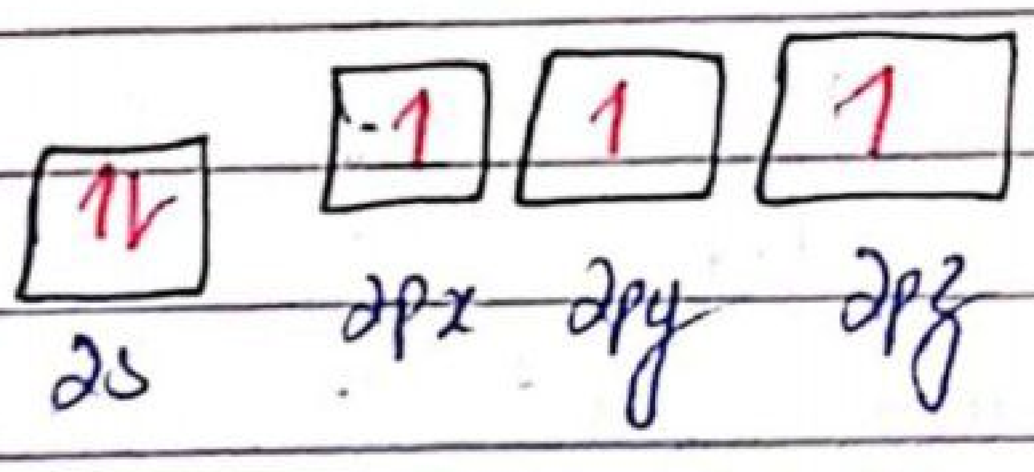
- Consider the case of Carbon - It normally form four covalent bonds rather than two.

- It electronic configuration is



- There are only two unpaired electrons.
- Before carbon form bonds, through it normally promotes one of the s-electrons to the empty p-electrons





- Thus there becomes 4 unpaired electrons - These undergo hybridization to form 4 covalent Bonds.

- The energy for promotion of s-electron is supplied because the Carbon can then form twice as many covalent Bonds - Each covalent bond formation releases energy which is more than needed for excitation.

- The lead cannot do this. This is because bond energies decreases down the Group due to increasing size. The bonding pair goes away from the two nuclei and better screened from them.

Example:-

- The energy released when two extra Pb-X bonds are formed may no longer be enough to compensate for the extra energy needed to promote a 6s electron into the empty 6p orbital.

- This because even more difficult, if the energy gap between the 6s and 6p orbital was increased by the relativistic concentration of the 6s orbital.

Chemical properties of the Elements of Group 4 Elements:-

The chlorides of Carbon, Silicon and lead

Structures and stability:-

Structures:-

Carbon, Silicon and lead Tetrachlorides:-

- These all have the formula MCl_4
- They are all simple covalent molecules with a typical tetrahedral shape.
- All of them are liquids at room temperature. However at room temperature lead (IV) chloride tend to decompose to give lead (II) chloride and chlorine gas.

Lead (II) chloride, $PbCl_2$

- It is a white solid.
- Its melting point is 501°C.
- It is very slightly in cold water, but more soluble in hot water.
- It is mainly ionic in character.

STABILITY

- The most stable oxidation state shown by Group 4 elements is +4.
- This oxidation state is shown by Carbon and Silicon in CCl_4 and $SiCl_4$. Those These therefore have no tendency to split up to give dichlorides.
- However the relative stability of the +4 oxidation state decreases down the Group while stability of +2 oxidation state increases.
- lead (IV) chloride decomposes at room temperature to give more stable lead (II) chloride and chlorine gas.

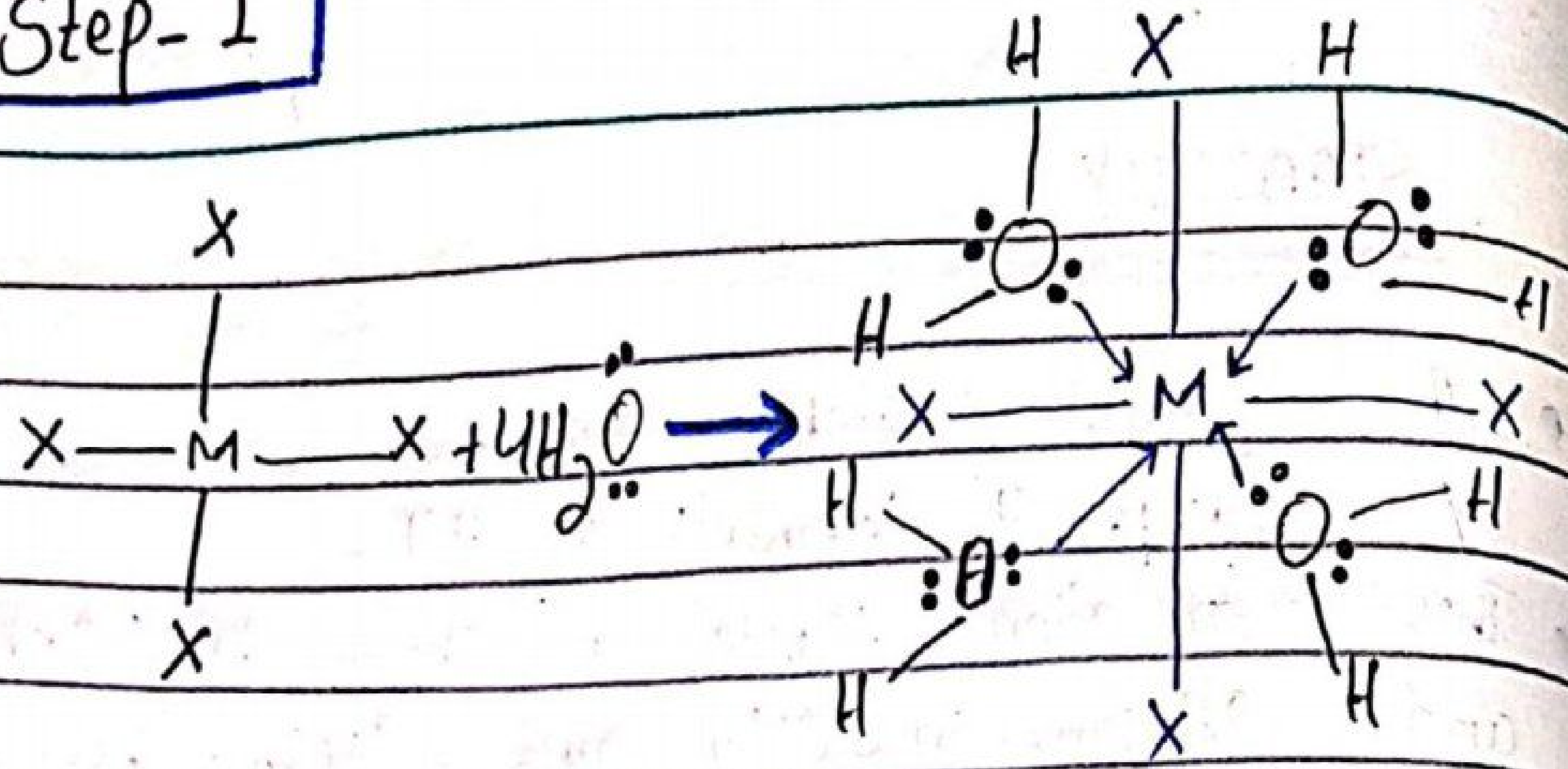
Easy reduction of lead from +4 to +2

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

Reaction with water:- (Hydrolysis of tetrahalides) :-

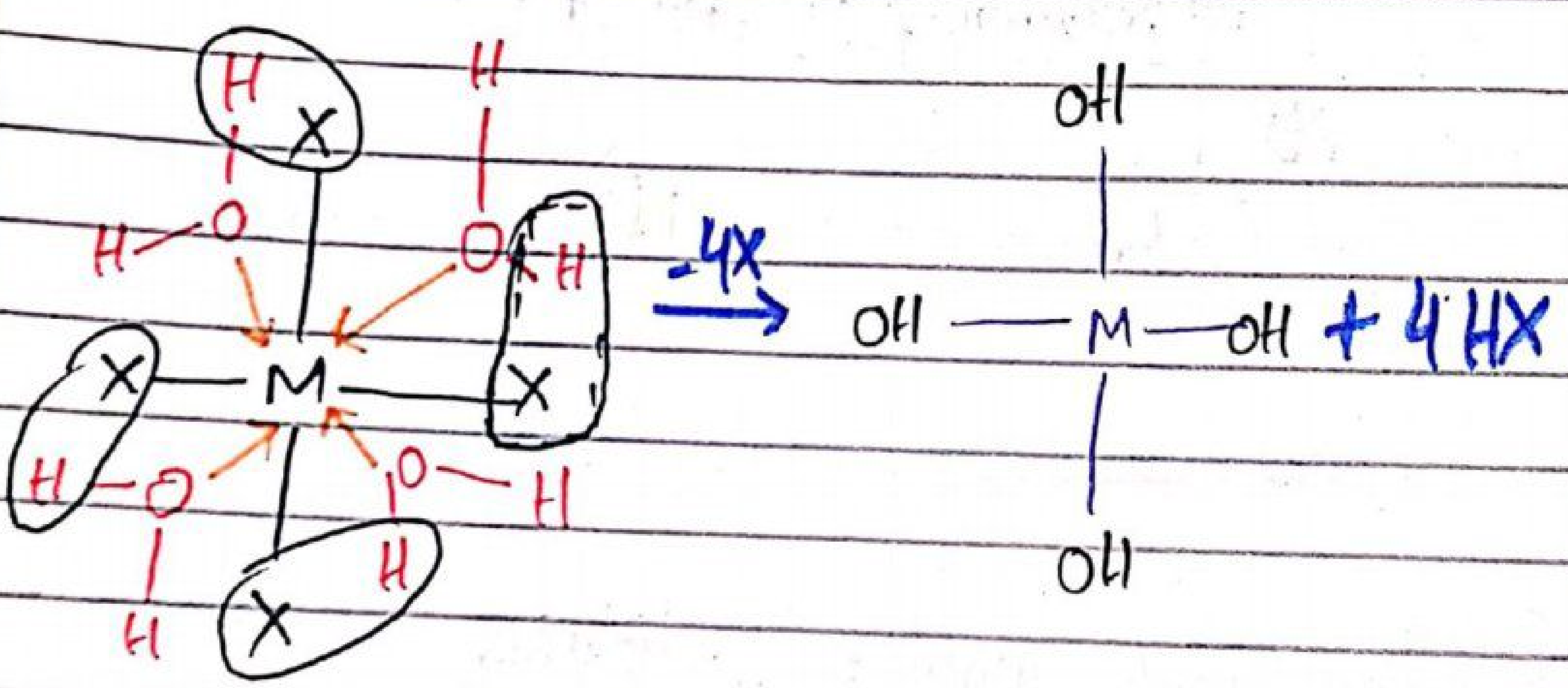
Actually the hydrolysis of tetra halides takes place through the following two steps -

Step- I



- In this step oxygen atom of H_2O which acts as a donor attacks the Central atoms of the halide to form a coordinate bond with it and thus produces and unstable intermediate compound ($MX_4 \cdot H_2O$)

Step-II



- In this step four HX molecules are eliminated from this unstable intermediate Compound and hydroxide of the Central element is formed. Thus X atoms of MX_4 molecules are replaced by OH^- ions.

Tetrahalides of C are not hydrolyzed while those of Si, Ge, Sn get readily hydrolysed.

- The C-atom being a member of 2nd period of the periodic table, has no d-orbitals in its valence shell. Thus it is unstable to accomondate the lone pair denoted by the donor oxygen atom of H_2O molecule to form an unstable intermediate compounds. Hence the tetrahalides of C are not hydroyzed.

- On the other hand Si, Ge and Sn have vacant d-orbitals. These can accept the lone pair and thus this tetrahalides get readily hydrolysed.

- Ease of hydrolysis of tetrahalides by H_2O decreases from Si to Sn due to increase in the metallic character of the central atom. Thus GeX_4 and SnX_4 tetrahalides are less readily hydrolysed then SiX_4 tetrahalides.

- However empty orbitals are always present with any atom. They can be utilized only if sufficient energy is provided for the reaction to occur e.g CCl_4

undergoes hydrolysis when Superheated Steam is used.

$$CCl_4 + H_2O \text{ (superheated steam)} \rightarrow COCl_2 + 2HCl$$

Phosgene

- Hydrolysis of tetrahalides of Pb follows essentially the same pattern. It is a compound of Pb. Some decomposition of $PbCl_4$ to $PbCl_2$ takes places

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

- $PbCl_4$ is hydrolysed by H_2O as follows

$$PbCl_4 + 2H_2O \longrightarrow PbO_2 + 4HCl$$

- The tetrahalides of Si, Ge, Sn and Pb react will halide ions and form the hexahalo complex ions like $[SiF_6]^{2-}$, $[GeX_6]^{2-}$

e.g.;

$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

- The tetrahalides of C are exception. They do not form such complex ions.

Oxides:-

- The element of group IVA forms three types of oxides

- Monoxides (MO type)
- Dioxides (MO_2 type)
- Other oxides (C_3O_2, Pb_3O_4, Pb_2O, Pb_2O_3 etc)

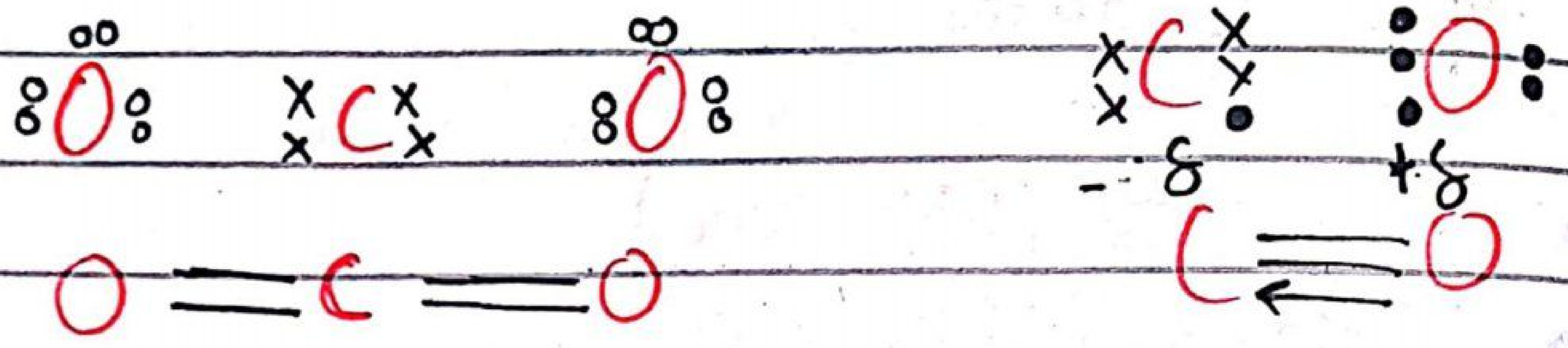
- Carbon dioxide is a gas whereas Silicon dioxide is a hard high-melting solid.

- The other dioxides in Group 4 are also Solids. This is due to the difference in Structure between carbon dioxide and the dioxides of the rest of the Group.

The Structure of Carbon dioxide:-

- It is a triatomic molecule.
- The dipole moment of carbon dioxide is zero. Therefore it is a linear molecule.
- It has two double bonds between carbon and oxygen atoms.
- Carbon is sp-hybridized and oxygen is sp^2-hybridized.
- The solid CO_2 has face centered cubic structure.
- The bond length between carbon and oxygen atoms are 115 pm.
- Both carbon and oxygen atoms have

complete their octet so it is stable molecule -



Carbon dioxide

Carbon monoxide

The Structure of Silicon dioxide:-

- It is a macromolecular compound in which Silicon and oxygen atoms are linked together covalently in tetrahedral basic unit -

- In crystobalite these units are joined as in diamond while in quartz and tridymite they are arranged spirally around an axis -

- Due to this structure Silicon dioxide is a non-volite and hard unlike Carbon dioxide -

Similarity between Structure of Silicon dioxide and carbon dioxide -

⇒ Triatomic molecules of Silicon dioxide and Carbon dioxide, Carbon and Silicon are Similar in having

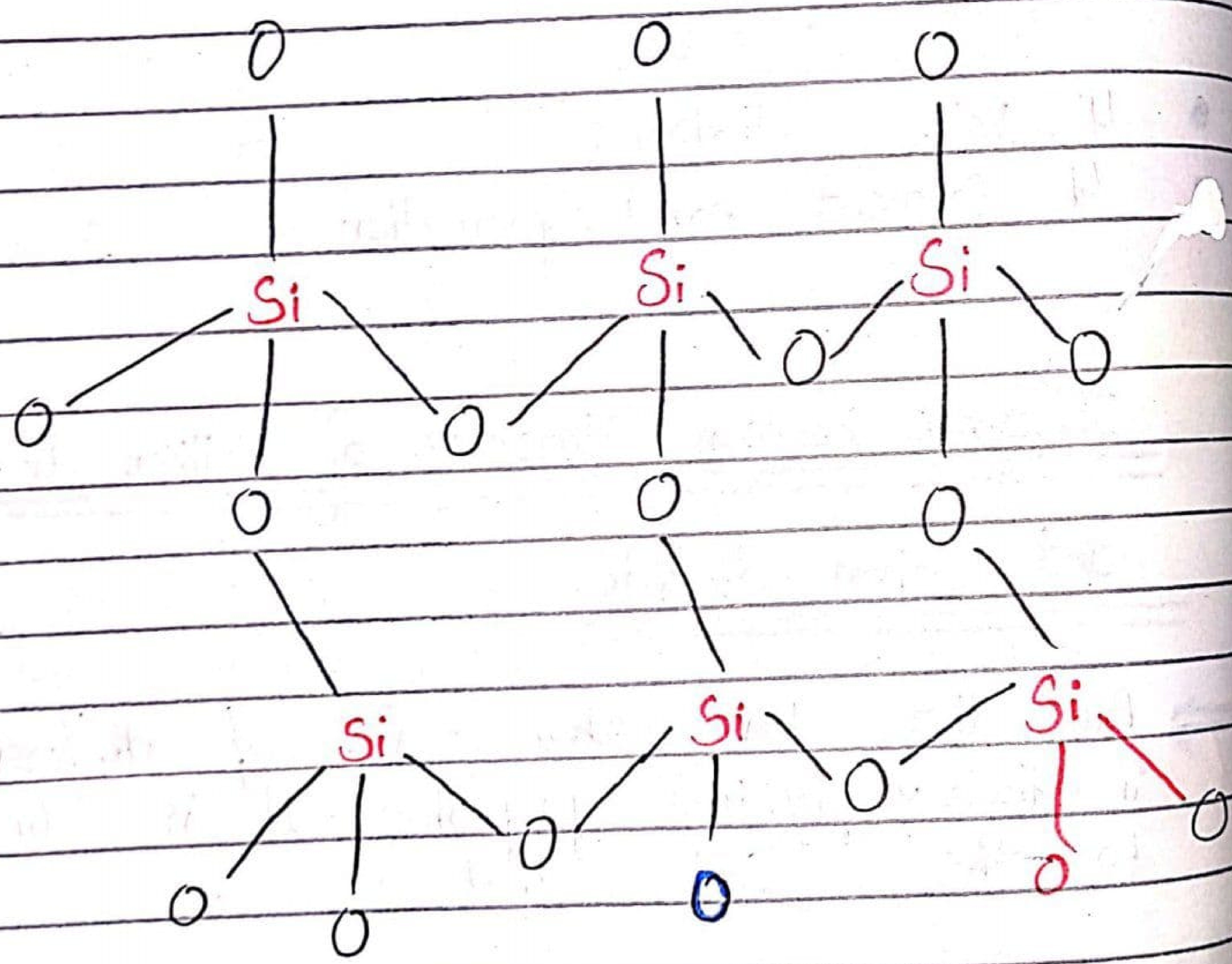
- 4 Valence electrons
- 4 Covalent bond formation.

Difference between Structure of Silicon dioxide and Carbon dioxide

⇒ But they have show a lot of difference in their physical properties - It is due to the fact that -

- Silicon atoms are much larger is size then Carbon atoms
- Silicon form only Single bond with oxygen while Carbon forms double bonds.
- Carbon form a linear molecules of CO_2 with two oxygen atoms - while Silicon atom is bound to four oxygen atoms in a tetrahedral Structure while result in the formation of Silicon

dioxide crystal. The simplest formula for silica is SiO_2. However the whole crystal of silica can be considered as one molecule.



Acid-Base Behaviour of the Group 4 oxides:-

Acitity of oxides of group '4' element decreases down the group i.e
oxides of Carbon are acidic at the top
oxides of Pb are amphoteric at bottom

Carbon and Silicon oxides:-

Carbon Monoxide:-

Carbon monoxide is consider as neutral oxides actually it is very sligltly acidic oxide. It does not dissolve in water. It react with hard Concentrated solution of Sodium hydroxide to produe Sodium methanote

$$CO + NaOH \longrightarrow HCOONa$$

(Sodium methanote)

Carbon and Silicon dioxides:-

These are both weakly acidic.

(02) Reaction with water:-

Carbon dioxide dissolve

in water form weak Carbonic acid

(01) $CO_2 + H_2O \longrightarrow H_2CO_3$

(02) $H_2CO_3 \rightleftharpoons H^+ + H^{-1}CO_3$

Silicon dioxide does not dissolve in water due to giant covalent structure.

(02) Reaction with Base:-

Carbon dioxide reacts with Sodium hydroxide in the cold to give either sodium Carbonate or Sodium hydrogen carbonate Solution depending upon the reaction proportions.

(01) $2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

(02) $NaOH + CO_2 \longrightarrow NaHCO_3$

Silicon dioxide also react with Sodium hydroxide Solution, but only if it is hot and Concentrated. Sodium Silicate Solution is formed.

(03) $2NaOH + SiO_2 \xrightarrow{heat} Na_2SiO_3 + H_2O$

Calcium oxide react with Silicon dioxide to produce a liquid slag, Calcium Silicate.

(04) $CaO + SiO_2 \longrightarrow CaSiO_3$ (liquid Slag)

Germanium, Tin and lead oxides:-

(01) **The Monoxides:-** All of these oxides are amphoteric.

The Basic Nature of the oxides:- These oxides all react with acids to form Salts

For Example; They all react with concentrated hydrochloric acid.

$$XO + 2HCl_{(cons)} \longrightarrow XCl_2 + H_2O$$

where X = Ge, Sn, Pb

However lead (II) oxide reacts will dilute HCl form an insoluble layer of lead (II) chloride over the lead (II) oxide and stops the reaction as

$$PbO + 2HCl \longrightarrow PbCl_2 + H_2O$$
(dil)

But when we use conc. HCl insolubility disappears and $PbCl_4^{-2}$ complex is formed which is soluble in water.

$$PbCl_2 + 2Cl^- \longrightarrow [PbCl_4]^{2-}$$
(cons)

The Acidic Nature of the oxides :-

All of those oxides also react with bases like Sodium hydroxide Solution.

$$XO + 2OH^- \longrightarrow XO_2^{2-} + H_2O$$

where $X = Sn, Ge, Pb$

(02) The Dioxides:-

These dioxides are amphoteric

The Basic Nature of the Dioxides:-

Thes dioxides react with concentrated hydrochloric acid first to give compounds of the type XCl_4.

$$XO_2 + 4HCl \longrightarrow XCl_4 + 2H_2O$$

These will react with excess chloride ions in the hydrochloric acid to give complexes such as XCl_6^{2-}

$$XCl_4 + Cl^- \xrightarrow{Excess} [XCl_6]^{-2}$$

However in case of $PbCl_4$ reaction take place in ice - cold hydrochloric acid because $PbCl_4$ decompose in to $PbCl_2$ and Cl_2.

The Acidic Nature of the Dioxides:-

The dioxides will react with hot concentrated Sodium hydroxide solution to give Solution of the form $[X(OH)_6]^{2-}$.

$$XO_2 + 2OH^-_{(conc)(aq)} + 2H_2O \longrightarrow [X[OH]_6]^{2-}$$

Some Sources suggest that the lead (IV) oxide needs molten Sodium hydroxide. In that case, the equation is different-

$$PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$$

Group 7-Elements :- (Halogens) :-

Trends in Atomic Radius

- Atomic radius increases down the group from F to I due to increase in no of shell.

Trends in Electronegativity:-

- Halogens have high value of electronegativity. Electronegativity decreases from F to I in group 7 element

Trends in Electron Affinity:-

- Electron Affinity (E.A) decreases from top to buttom in 7- group element
- chlorine has the highest electron affinity.
- The lower value of Electron affinity for F is due to its small size and repulsion between the electron added and electron already present (i.e compact 2p-orbital of F atom).

Trends in Melting & Boiling Point:-

- The melting and boiling points of the halogens regularly increases from F to I
- It is because, halogens exists as molecules. So, with increase in size down the group the attractive forces between molecules becomes stronger.
- F_2 and Cl_2 are gases at ordinary temperature Br_2 is a heavy liquid while I_2 is a solid.

Bond Enthalpies (Bond energies or bond strength):-

- Bond enthalpy is the heat needed to break one mole of a covalent bond to produce individual atoms starting from the original substance in the gas state and ending with gaseous atoms.
- For chlorine Cl_2 it is the heat energy needed to carry out this change per mole of bond.

$$Cl-Cl \longrightarrow 2Cl$$

- For bromine, the reaction is from gaseous bromine molecules to form gaseous Br atoms.

$$\underset{\text{Gas}}{Br-Br} \longrightarrow 2Br$$

Bond Enthalpy In the Halogens X_2:-

The bond enthalpies of the Cl-Cl, Br-Br and I-I bonds decreases down the group due to increase in atomic size except the F-F bond.

F-F bond has very low dissociation energy:-

(I) The F-F bond length is very small than other X-X bond lengths. So the F atoms in F_2 molecule repeal each other and thus the dissociation of F_2 molecules into F atoms becomes easy.

(II) X-X bond in Cl_2, Br_2 and I_2 molecules is stronger than F-F bond in F_2 molecules. It is due to the possibility of the formation of multiple bonds in X-X bonds with d-orbital - F-atom does not have d-orbital in its Valence Shell.

The bond enthalpies of HX decreases down the group :-

- It is because as the halogen atom gets bigger, the bonding pairs gets more and more distant from the nucleus.
- The attraction is less, the bond gets weaker. So the bond enthalpies of HX decreases down the group. The order is:

HI < HBr < HCl < HF

Strength of Halogens as oxidizing Agents:

$F_2 > Cl_2 > Br_2 > I_2$

Facts :-

- A Substance that has a tendency to accept one or more electrons is said to show oxidizing Property.

- The halogens due to high electron affinity values have a great tendency to accept electron and hence as a strong oxidizing agent.

- The oxidizing property of a halogen molecule, X_2 is represented by,

$$\frac{1}{2}X_2 + e^- + aq \longrightarrow X^- + \text{energy}$$

- During the reaction energy is released. This energy is made up from different energies like that of fusion, vaporisation etc.

- The value of energy decreases from F_2 to I_2. Thus the oxidizing power of halogen also decreases in the same direction. Order of oxidizing power is

$$F_2 > Cl_2 > Br_2 > I_2$$ (weakest oxidizing agent)

- Since F_2 is the strongest oxidizing agent in the series it will oxidize other halide ions to halogens in solution or when dry i.e F_2 displaces other halogens from their corresponding halides.

$$F_2 + 2X^- \longrightarrow 2F^- \times X_2$$

(01) $Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$

(02) $Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

- Similarly Cl_2 will displace Br^- and I^- ins from their Solution and Br_2 will displace I^- ions from their Solutions.

The Acidity of the hydrogen halides:-

- All the halogens acids in the gaseous states are esentially covalent.

However in aqueous Solution they ionise to give solvated proton (H_3O^+) and hence acts as acid.

$$H_2O + HX \longrightarrow H_3O^+ + X^-$$

- HCl ionise only slightly while HCl, HBr, and HI ionise completely. Hence HF is the weakest acid and strength of these acids increases from HF to HI.

- The order of acidity is

HF (weakest acid) < HCl < HBr < HI (Strongest Acid)

- The order is due to following reason

The weakest acidic nature of HF is due to fact that the dissociation energy of H-F bond in HF molecule is the highest. Hence this molecule has least tendency to splits up into H^+ and F^- ions in aqueous solution.

Halide ions as Reducing Agents

Trends in reducing strength ability of Halide ions

The redox reaction b/w Halide ion and Concentrated Sulphuric acid:-

Flouride and chloride ion can not reduce sulphuric acid

with Bromide

- Bromide ion is a strong reducing agents to reduce the Concentrated sulphuric acid. In this process the bromide ions are oxidised to bromine.

$$2Br^- \longrightarrow Br_2 + 2e^-$$

- The bromide ions reduce the Sulphuric acid to Sulphur dioxide gas -

- This is a decrease of oxidation state of the sulphur from +6 in the Sulphur from +6 in the sulphuric acid to +4 in the Sulphur dioxide -

$$H_2SO_4 + 2H^- + 2e^- \longrightarrow SO_2 + 2H_2O$$

- Combine these two half - equation to give the overall ionic equation for the reaction

$$H_2SO_4 + 2H^- + 2Br^- \longrightarrow Br_2 + SO_2 + 2H_2O$$

With iodide ions :-

- Iodide ions are stronger reducing agent than bromide ions -

- They are oxidized to iodine by the concentrated sulphuric acid -

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

- The reduction of the sulphuric acid is more complicated than before - The iodide are powerful enough reducing agent to reduce it -

- The most important of this mixture of reduction products is probably the hydrogen sulphide - the half equation for its formation is

$$HgSO_4 + 8H^+ + 8e^- \longrightarrow HgS + 4Hg_2O$$

- Combining these last two half - equation gives

$$HgSO_4 + 8H^+ + 8I^- \longrightarrow 4I_2 + HgS + 4Hg_2O$$

Explanation of halide:-

- Halide ions are reducing agent - Reducing agent ability halide ion increased down the group i.e iodide is the stronger reducing agent - Bigger the halide ion distance b/w the nucleus and outer most electron is large removal electron is easy it can easily be oxidized - Therefore it behave as strong reducing agent.