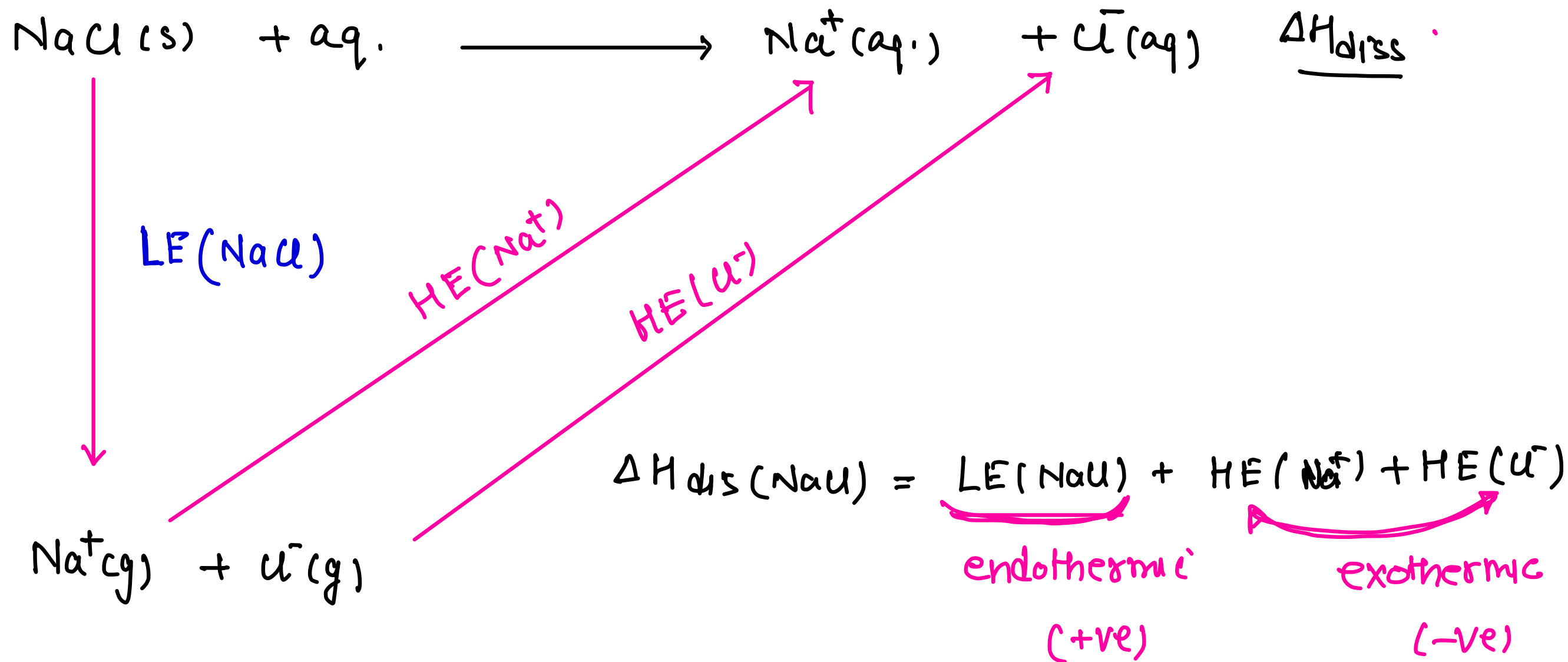


CHEMICAL BONDING

Note : if ΔH_{diss} . Lenthalpy of dissolution is -ve then salt will be soluble and breaks into ion.



CHEMICAL BONDING

47*. Is a data sufficiency problem in which it is to be decided on the basis of given statements whether the given question can be answered or not. (No matter whether the answer is yes or no)

If $\Delta H_{\text{solution}} < 0$ then compound acts as ionic in aqueous solution. Is $\text{AlCl}_3(\text{s})$ ionic in aqueous solution.

Statement 1 : L.E. of AlCl_3 is 5137 kJ/mol

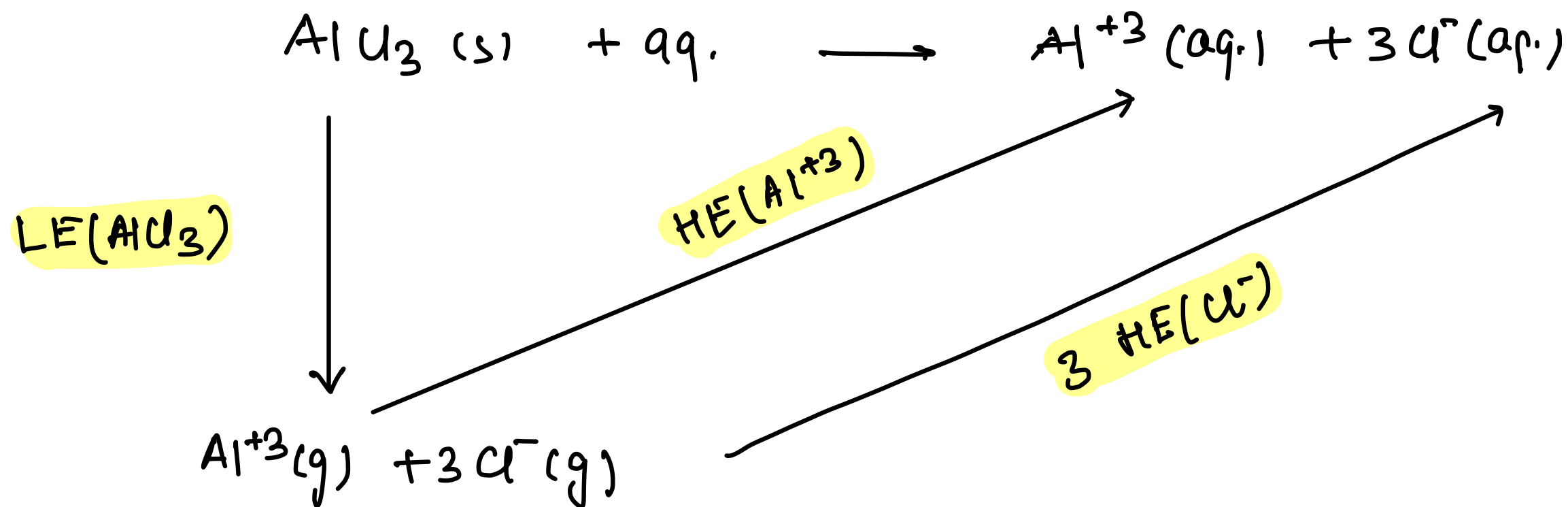
Statement 2 : ΔH_{HE} of Al^{+3} ion is $-4665 \text{ kJ/mol}^{-1}$ & ΔH_{HE} of Cl^- is -381 kJ/mol^{-1}

(A) Statments (A) alone is sufficient but statement (B) is not sufficient

(B) Statments (B) alone is sufficient but statement (A) is not sufficient

✓ (C) Both statement together are sufficient but neither statement alone is sufficient

(D) Statement (A) & (B) together are not sufficient



$$\begin{aligned} \Delta H_{\text{diss}} &= 5137 + (-4665) + 3(-381) \\ &= 5137 - 5808 = -671 \text{ kJ/mol} < 0 \end{aligned}$$

CHEMICAL BONDING

IONIC BOND/ELECTROVALENT BOND

- **Boiling point and melting point :-**

Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.

- **Conductivity :-**

In solid state these are bad conductor of electricity due to absence of free mobile ion. In fused state or aqueous solution Due to presence of free ions they are Good conductor of electricity.

Conductivity order \longrightarrow [Solid state < fused state < Aqueous solution]

- **Solubility :-**

Generally more soluble in Polar solvents like water.

Less soluble in non polar solvents like benzene.

Ex. NaCl form a true solution in water but insoluble in CCl_4 .

CHEMICAL BONDING

LATTICE ENERGY

Definition :-

The amount of energy released when gaseous cation and anion are combined to form one mole of ionic compound solid is called lattice energy .

- It depends upon electrostatic force of attraction and affect the stability of compounds .
- **Factors affecting Lattice energy :-**

(1) $\text{L.E.} \propto Z^+, Z^-$ (Where Z^+, Z^- are charges of cation and anion respectively)

(2) $\text{L.E.} \propto \frac{1}{r^+ + r^-}$ (Where r^+ and r^- are the radius of cation and anion respectively)

CHEMICAL BONDING

Question

✓ Q.

Arrange the following in the correct order of lattice energy :

(1) Na_2O MgO Al_2O_3
_____→

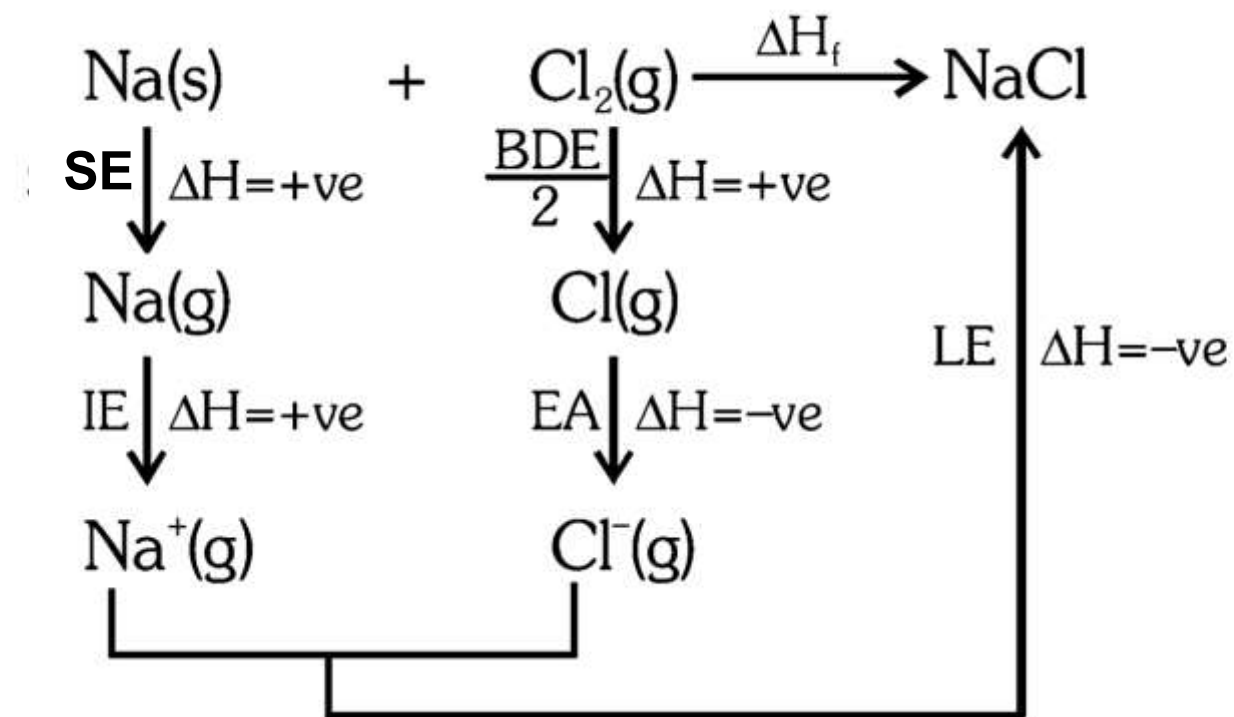
(2) AlF_3 Al_2O_3 AlN
_____→

(3) LiCl NaCl KCl RbCl CsCl
_____→

CHEMICAL BONDING

BORN HABER'S CYCLE

(Mechanism of ionic bond formation)



$$\Delta H_f = \underbrace{\text{SE} + \text{IE} + \frac{\text{BDE}}{2}}_{\text{Endo}(\Delta H = +ve)} + \underbrace{\Delta H_{eg} + \text{LE}}_{\text{Exo}(\Delta H = -ve)}$$

CHEMICAL BONDING

BORN HABER'S CYCLE

Favourable conditions for ionic bond formation :-

Low SBE
Low IE
Low BDE

} Absorbed energy

High ΔH_{eg}
High L.E.

} Released energy

Born Haber's Cycle:-

$$\underbrace{\text{SBE} + \text{IE} + \frac{1}{2} \text{BDE}}_{\text{(Endothermic process)}} > \underbrace{\Delta H_{eg} - \text{L.E.}}_{\text{(Exothermic process)}}$$

Case no. 1 :- If ΔH_f is more (–) ve then the compound is more stable .

Case no. 2 :- If ΔH_f is less (–) ve then the compound is less stable .

Case no. 3 :- If ΔH_f is (+) ve then the compound is unstable .

CHEMICAL BONDING

Question

Q. Heat of sublimation of Na = x J
Ionization energy of Na = y J
Bond dissociation energy of Cl_2 = a J
 e^- gain enthalpy of Cl = b J
Enthalpy of formation of NaCl = c J
Then what will be lattice energy of NaCl(s) = ?

Sol.

CHEMICAL BONDING

HYDRATION ENERGY

- Amount of energy released in the hydration of one mole of ionic crystal is known as **Hydration energy**.
- If this released amount of energy (HE) is greater than amount of energy required to break the bond (LE) , then substance is considered as soluble.

Dielectric constant :-

Capacity of a medium to minimize interionic attraction by neutralizing the charge of ions is known as dielectric constant.

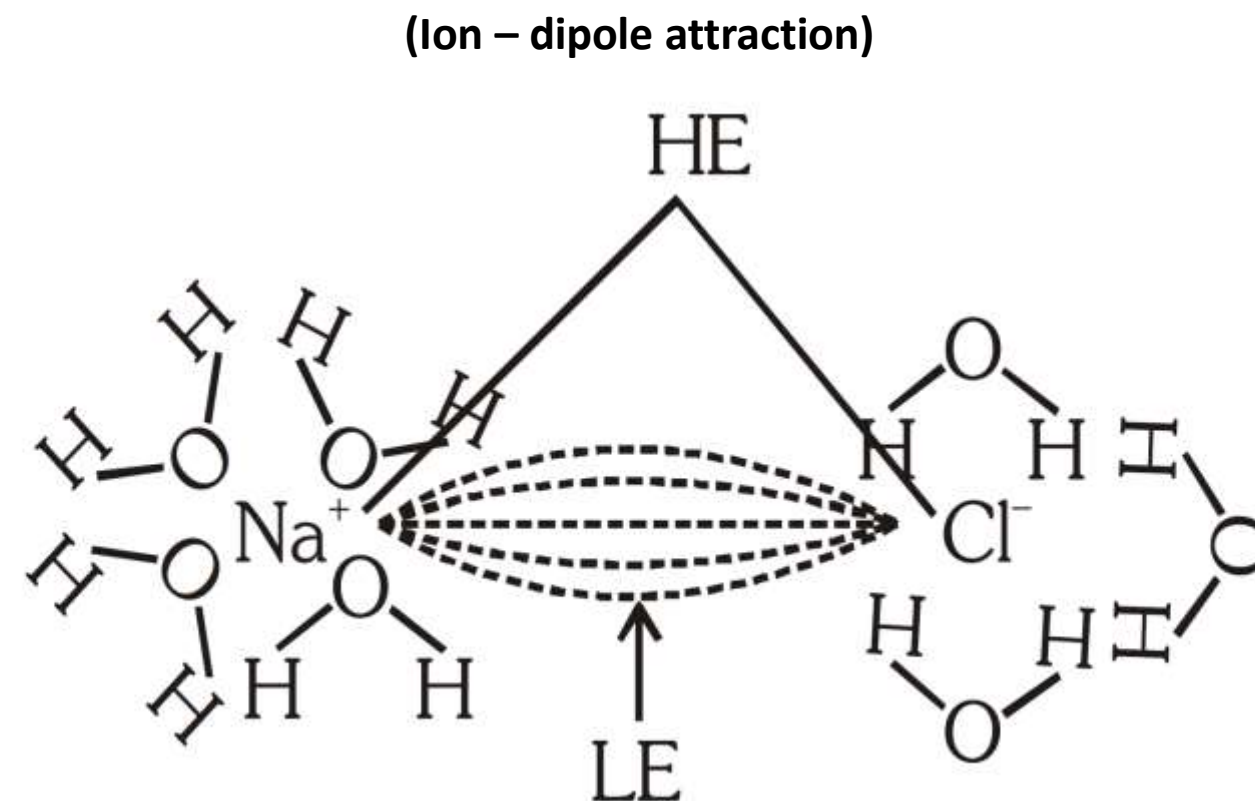
E.g.:-	HF	→	120
	H ₂ SO ₄	→	102
	H ₂ O	→	81
	D ₂ O	→	78

CHEMICAL BONDING

MECHANISM OF SOLVENCY

Solute :- NaCl (s)

Solvent :- H₂O



L.E. - lattice energy
H.E. - Hydration energy

Case no. 1 :- $HE > LE$ (then more soluble)

Case no. 2 :- $HE < LE$ (then sparingly soluble / insoluble)

CHEMICAL BONDING

HYDRATION ENERGY

Factors Affecting HE:-

(1) $HE \propto \text{charge } (Z^+ Z^-)$

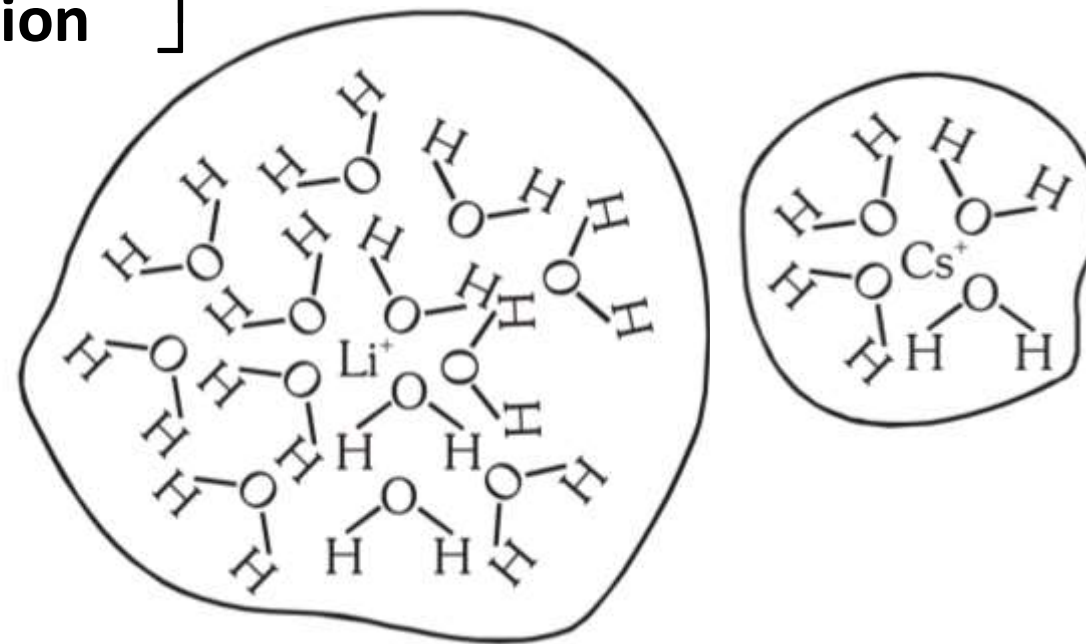
(2) $HE \propto \frac{1}{r^+} + \frac{1}{r^-}$

Hydration tendency :-

$$\left[\text{Hydration tendency} \propto \frac{\text{Charge on ion}}{\text{size of ion}} \right]$$

$\text{Li}^+ \quad \text{Na}^+ \quad \text{K}^+ \quad \text{Rb}^+ \quad \text{Cs}^+$

$r^+ (\uparrow) \text{ Hydration tendency } (\downarrow)$




CHEMICAL BONDING

HYDRATION ENERGY

E.g. :- (In Aqueous solution)

Li^+ Na^+ K^+ Rb^+ Cs^+

Ionic Radius (\uparrow) 

Hydrated radii (\downarrow)

Movement of ions (\uparrow)

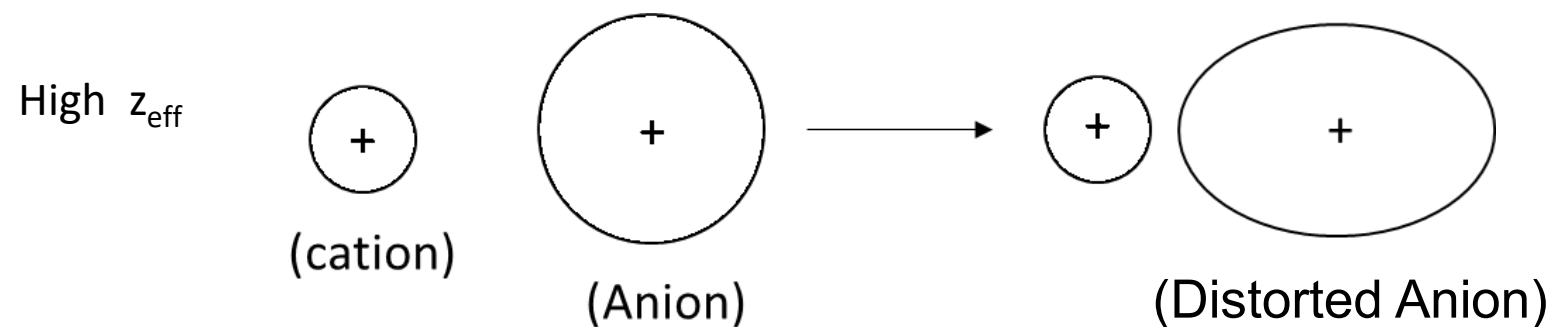
Ionic mobility (\uparrow)

Ionic conductivity (\uparrow)

CHEMICAL BONDING

POLARISATION (FAJAN'S RULE)

- Covalent character in an ionic compounds can be explained with the help of polarisation .
- Distortion in the e^- cloud of an anion due to the attraction of adjacent cation.
- Due to polarisation, covalent character are produced.



- For cation :- **Polarising power** term is used .
- For anion :- **Polarisability** term is used .

CHEMICAL BONDING

POLARISATION (FAJAN'S RULE)

Polarising power :-

It is the power of cation to attract electron cloud of an anion towards itself.

Factors affecting polarising power :-

$$\left[\text{Polarizing power} \propto \frac{\text{Charge of cation}(Z^+)}{\underbrace{\text{Size of cation}(r^+)}_{\text{Ionic potential}(\phi)}} \right]$$

$$[\text{Polarizing power} \propto \text{Ionic potential } (\phi)]$$

CHEMICAL BONDING

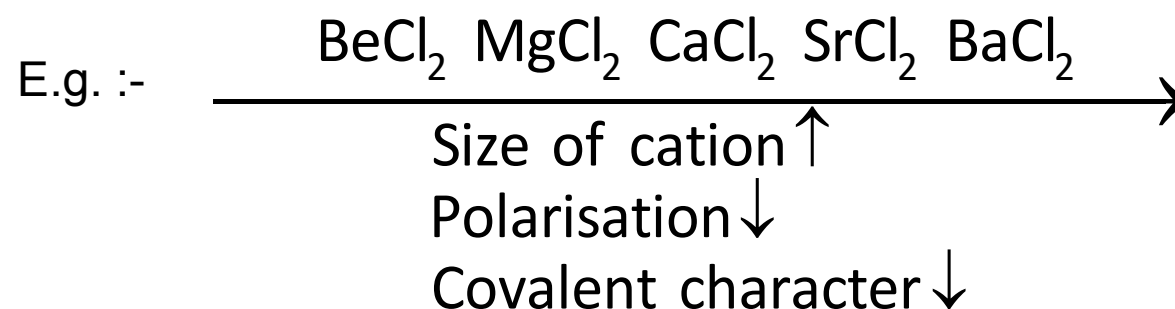
POLARISATION (FAJAN'S RULE)

- **Polarisability :-** It is the ability of an anion to get polarized by adjacent cation.

Factors affecting Polarizability :-

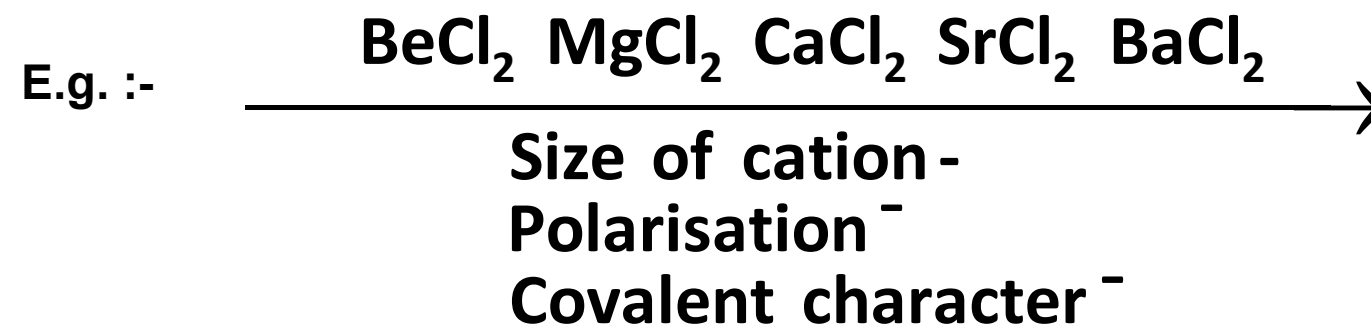
$$\left(\begin{array}{l} \text{Polarizability} \propto (-ve) \text{ Charge of anion} \\ \text{Polarizability} \propto \text{Size of anion} \end{array} \right)$$

- **Effective conditions of polarisation :-**
 - (1) Size of cation should be smaller.
 - (2) Size of anion should be large.
 - (3) Charge on cation/anion should be High .



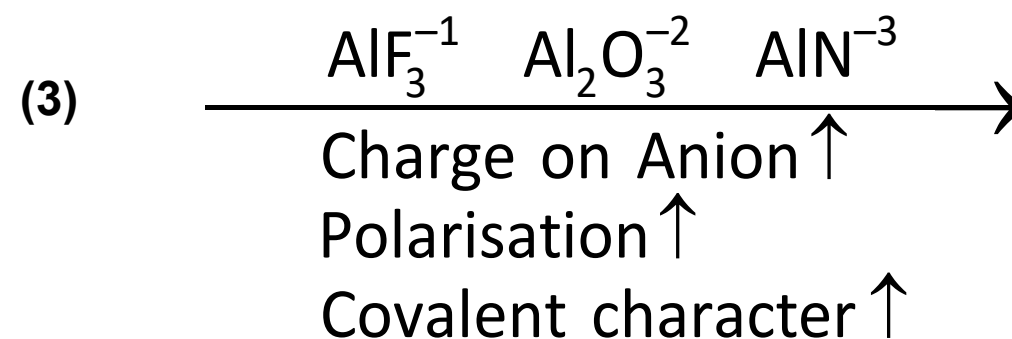
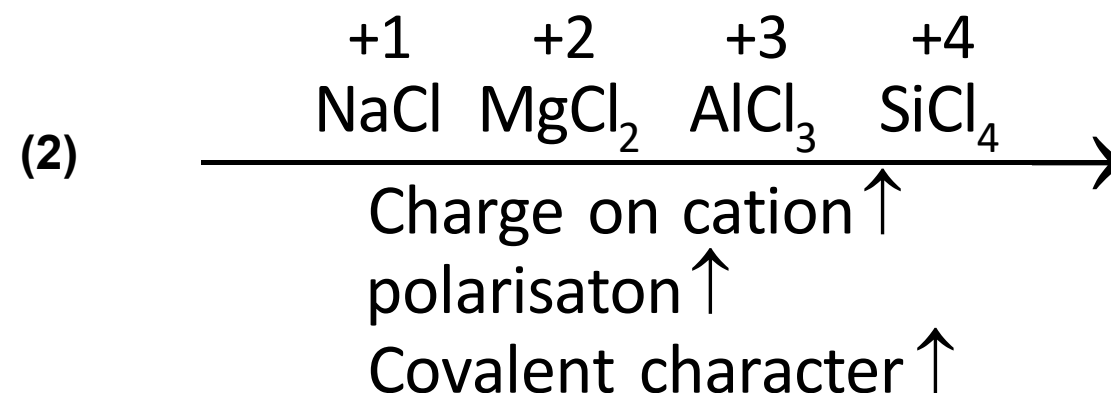
CHEMICAL BONDING

POLARISATION (FAJAN'S RULE)



CHEMICAL BONDING

POLARISATION (FAJAN'S RULE)



CHEMICAL BONDING

POLARISATION (FAJAN'S RULE)

Compare covalent character in the following sequences

Q. CrO Cr_2O_3 CrO_3

_____→

Q. $\begin{matrix} + & + & + & + & + \\ \text{LiCl} & \text{NaCl} & \text{KCl} & \text{RbCl} & \text{CsCl} \end{matrix}$

$\xrightarrow{\hspace{10em}}$

Q. PbF_2 PbCl_2 PbBr_2 PbI_2

_____→

CHEMICAL BONDING

POLARISATION (FAJAN'S RULE)

Order of polarizing power for some special type of cations :-

- Stability of Cations :-

Inert gas configuration > Pseudo inert gas configuration > Inert pair effect configuration

(8 e⁻)

(18 e⁻)

(18 + 2e⁻)

- Order of polarizing power of Cations :-

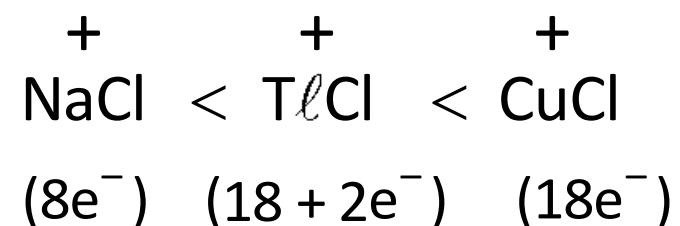
Pseudo inert gas configuration > Inert pair effect > Inert gas configuration

(18 e⁻)

(18 + 2e⁻)

(8 e⁻)

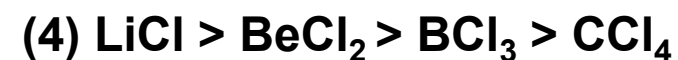
Example of cation . :-



CHEMICAL BONDING

POLARISATION (FAJAN'S RULE)

Q. Among LiCl , BeCl_2 , BCl_3 and CCl_4 , the covalent bond character follows the order :



CHEMICAL BONDING

POLARISATION (FAJAN'S RULE)

Q. Which one of the following show correct order of covalent character ?

(1) $\text{ZnO} < \text{ZnS}$

(2) $\text{ZnS} = \text{ZnO}$

(3) $\text{ZnS} < \text{ZnO}$

(4) None

CHEMICAL BONDING

(1)

Melting points

• Cation is from

S-Block

✓ $IC > 50\%$
all are ionic

$m.p \propto LE$

$(\text{ionic } mp) > (\text{covalent } mp)$

$IC < 50\%$

d-Block

$IC < 50\%$

$m.p \propto \frac{1}{\text{polarisation}}$

$IC \propto \frac{1}{\text{polarisation}}$

$\text{polarisation} \propto \frac{q_c}{r_c} + q_a r_a$

P-Block

Compound having ionic bond but $IC < 50\%$

determined as d-Block

if packing is good the LE will be very high.

CHEMICAL BONDING

Ex Compare the melting point of following
 (i) $\overset{+1}{\text{Na}}\overset{-1}{\text{Cl}} < \overset{+2}{\text{Mg}}\overset{-2}{\text{O}} < \overset{+3}{\text{Al}}\overset{-3}{\text{N}}$ $LE \propto \frac{1}{r_c r_a}$

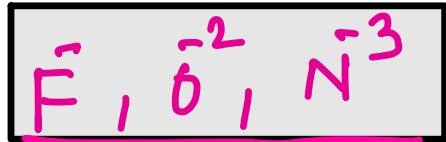
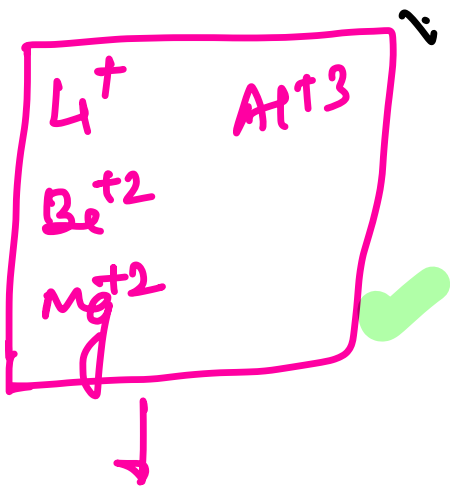
(ii) $\overset{+1}{\text{Na}}_2\overset{-2}{\text{O}} > \overset{+1}{\text{Na}}\overset{-1}{\text{Cl}}$ $LE \propto r_a$
 $\overset{+2}{\text{Fe}}\text{O} < \overset{+3}{\text{Fe}}_2\text{O}_3$ $LE \propto r_c$

(iii) $\overset{+2}{\text{Pb}}\text{Cl}_2 > \overset{+4}{\text{Pb}}\text{Cl}_4$ $\text{polarisation} \propto r_c$

(iv) $\overset{+1}{\text{Na}}_2\overset{-2}{\text{O}} > \overset{-1}{\text{Na}}_2\overset{-2}{\text{S}}$ $LE \propto \frac{1}{r_a + r_c}$

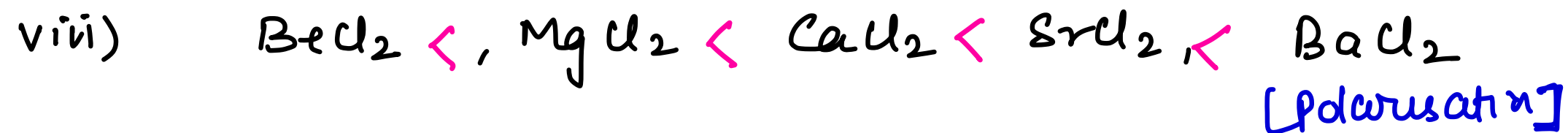
(v) $\overset{+1}{\text{Na}}\text{Cl} > \overset{+2}{\text{Mg}}\text{Cl}_2$ $IC < 50\%$
 polarisation

(vi) $\text{ZnCl}_2 < \text{CaCl}_2$ [pseudo inert gas]



ही 6-यादा
 ionic होते हैं!
 $IC > 50\%$

CHEMICAL BONDING

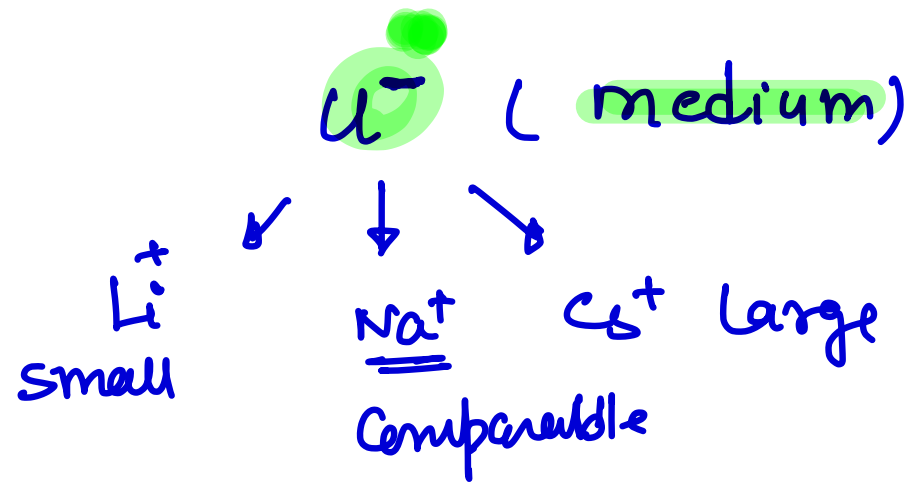


** For Chloride, bromide and Iodide of group (IIA) and Li melting point is determined by polarisation because their $I_c < 50\%$ for \rightarrow their $\begin{matrix} \text{- chloride} \\ \text{- iodide} \\ \text{- bromide} \end{matrix}$

CHEMICAL BONDING

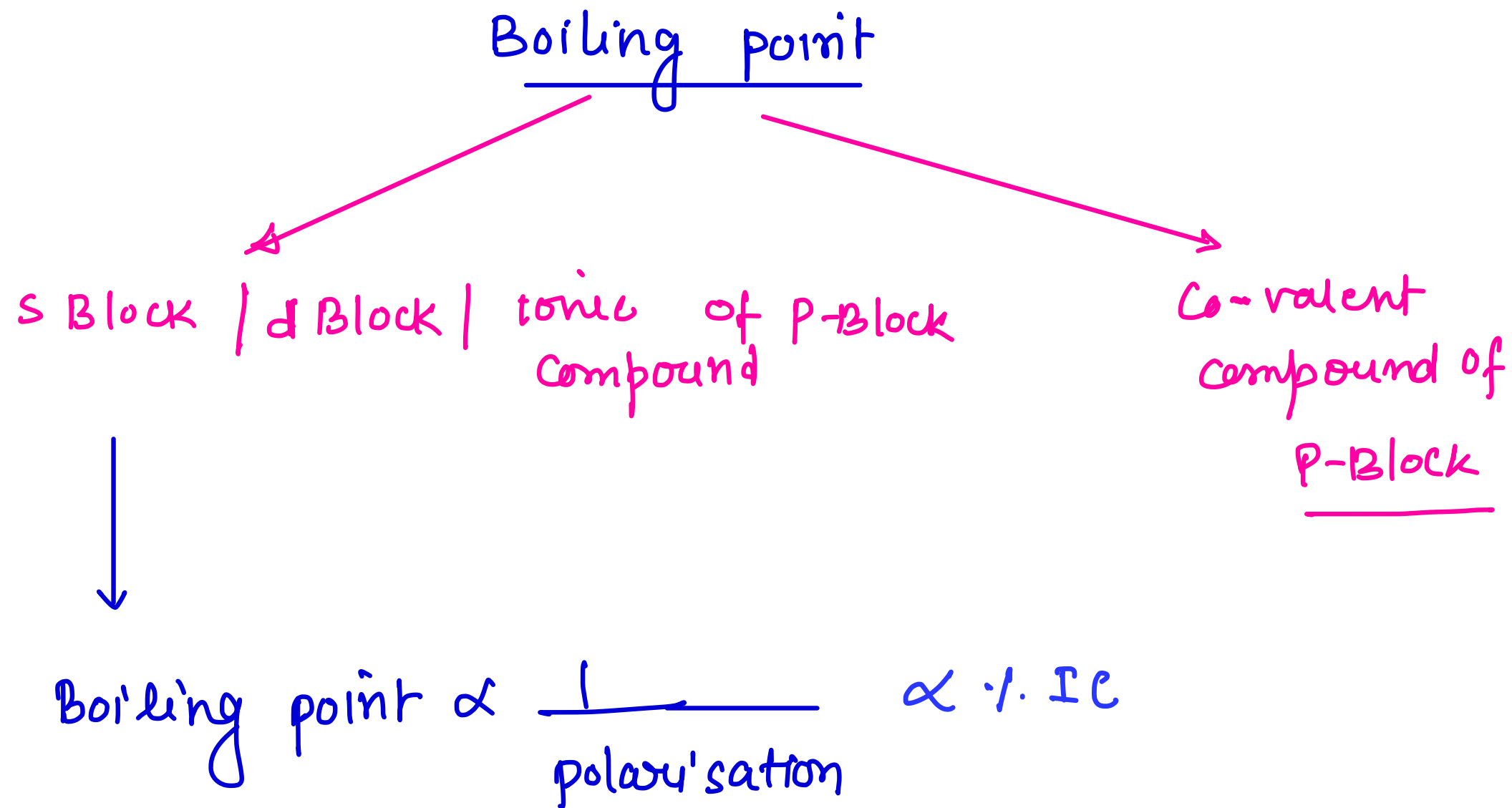
$\rightarrow \Delta EN$
 $\rightarrow \uparrow E$
 \rightarrow packing

Exception :



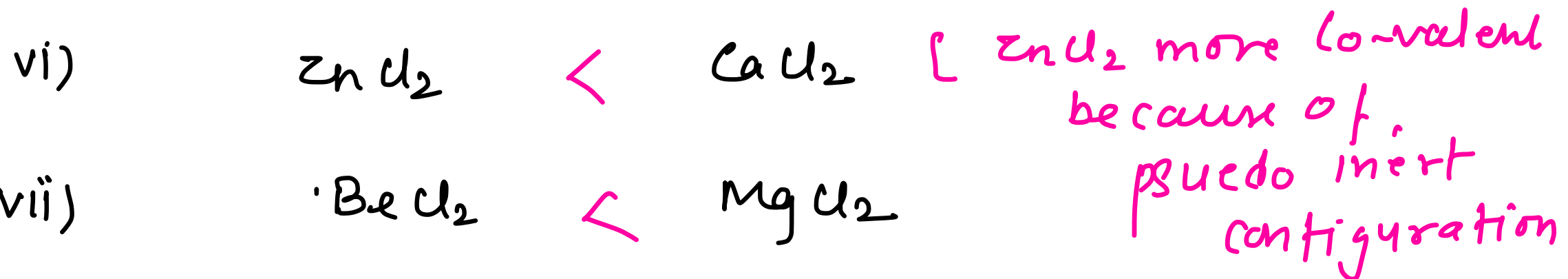
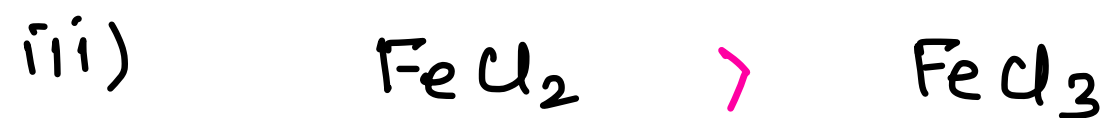
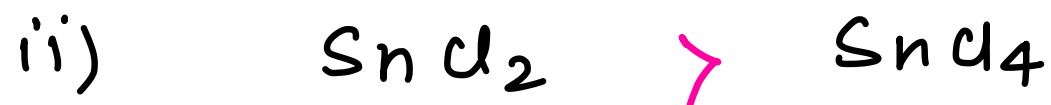
- $NaU > KU > RbU > CsU > \underline{LiU}$
- $MgO > CaO > BeO > SrO > BaO$
- $\underline{NaF} > KF > LiF > RbF > CsF$
- $KI > NaF > RbI > CsI > \underline{LiI}$

CHEMICAL BONDING



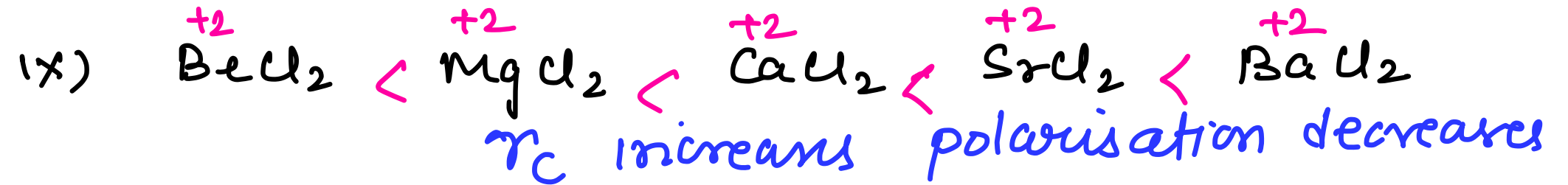
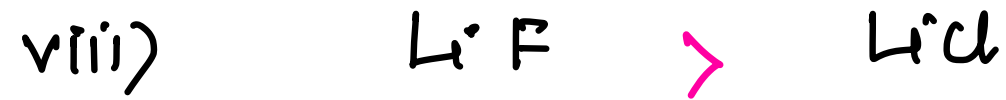
CHEMICAL BONDING

Ex. Compare Boiling point of following.



CHEMICAL BONDING

$$\phi = \frac{q_c}{r_c} + \frac{q_a}{r_a}$$



CHEMICAL BONDING

Electrical Conductance

← Molten state / Gaseous state

Conductance $\propto \frac{1}{\text{Radius}}$
OR
mobility

→ Aqueous state

Conductance $\propto \frac{1}{\text{hydrated Rad.}}$
OR
mobility

CHEMICAL BONDING

CHEMICAL BONDING

APPLICATION OF FAJAN'S RULE

SOLUBILITY :-

LIKE DISSOLVES LIKE

- Ionic compounds are soluble in polar solvents like H_2O .
- Polar Covalent compounds are soluble in polar organic solvents like acetone, ether
- Non polar compounds are more soluble in non polar solvents like benzene, CCl_4 .

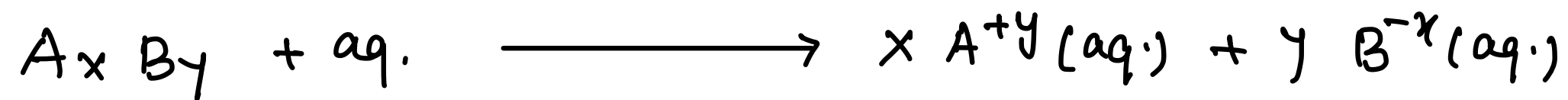
Ex. Select the true statements ?

T (i) NaCl will more dissolve than LiCl in H_2O

F (ii) LiCl will more dissolve than NaCl in H_2O

T (iii) LiCl will more dissolved than NaCl in benzene

CHEMICAL BONDING



$$\Delta H_{drss} = \underbrace{LE(A_x B_y)}_{(+ve)} + x \underbrace{HE(A^{+y}) + y (HE(B^{-x}))}_{(-ve)}$$

if $\Delta H_{diss} < 0$, salt will be more soluble.

Factor affecting solubility

- (i) If Lattice energy increases solubility decreases
- ii) If hydration increases solubility increases.

CHEMICAL BONDING



(i) LE energy decreases $LE \propto \frac{q_c q_a}{r_c + r_a}$

(ii) HE energy decrease $HE \propto \left(\frac{q_c}{r_c} \right) + \left(\frac{q_a}{r_a} \right)$

✓ from statement (i) on going down the group LE decrease
solubility increase



✗ from statement (ii) on going down the group HE
decreases so solubility decreases



CHEMICAL BONDING

- if common ion is large (Anion)

$$LE \propto K \frac{q_c q_a}{r_c + r_a}$$

$$r_a \gg r_c$$

$$LE \propto K \frac{q_c q_a}{r_a}$$

{ Lattice energy remains almost constant

$$HE \propto \frac{q_c}{r_c} + \frac{q_a}{r_a}$$

we can't neglect any term

✓

⇒

$$\text{Solubility} \propto HE$$

CHEMICAL BONDING

(ii) Common ion (Anion) is small

$$LE = \frac{K q_c q_a}{r_c + r_a}$$

$$LE = \frac{K q_c q_a}{r_c}$$

↪ direct relation

• Solubility $\propto \frac{1}{LE}$

$$HE \propto \frac{q_c}{r_c} + \frac{q_a}{r_a}$$

$\underbrace{\hspace{10em}}$
 $r_c \approx r_a$

$$HE \propto \frac{q_c + q_a}{r_a}$$

HE ÷ remains
constant:

CHEMICAL BONDING

Cation is from

Solubility

S-Block

Common ion

Small

$$\text{Solubility} \propto \frac{1}{LE}$$

Common ion
Large

$$\text{Solubility} \propto HE$$

d-Block | P-Block

$$\text{Solubility} \propto I \cdot IC$$

$$\approx \text{Solubility} \propto \frac{1}{\text{polarisation}}$$

CHEMICAL BONDING

SOLUBILITY

(A) Solubility of ionic compounds of s-block:

(i) Solubility \propto Hydration energy

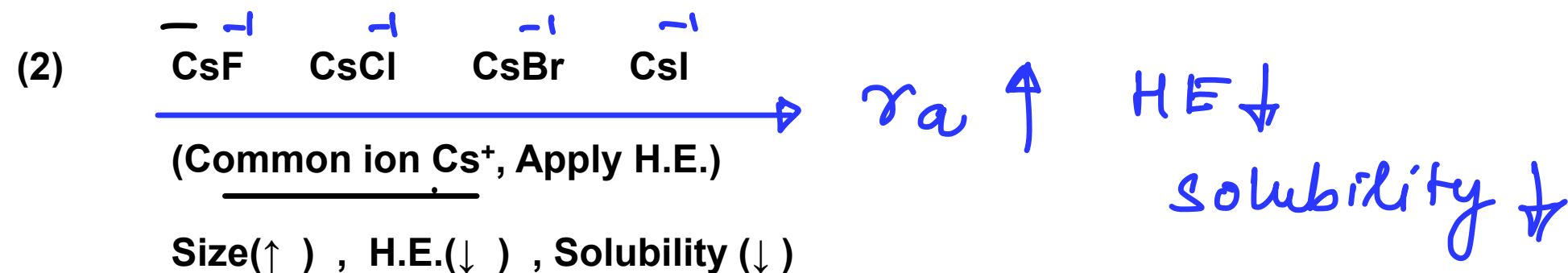
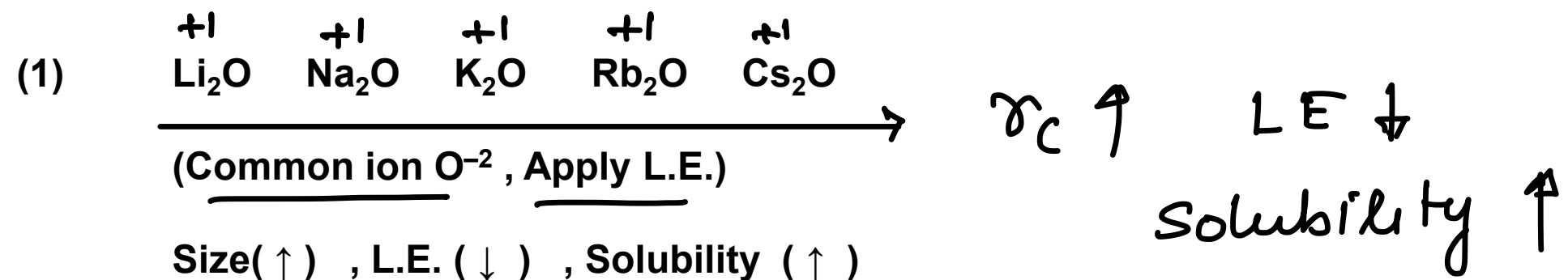
(ii) Solubility $\propto \frac{1}{\text{Lattice energy}}$

- ****** If common ion is smaller than apply L.E.
(F⁻, O⁻², OH⁻, Li⁺, Mg⁺², Be⁺² etc.)
- If common ion is larger than apply H.E.
(CO₃⁻², SO₄⁻², NO₃⁻, ClO₄⁻, HCO₃⁻, Cs⁺ etc.)
C₂O₄²⁻, ClO₃⁻, S₂O₃⁻²,

CHEMICAL BONDING

SOLUBILITY

Q. Compare Solubility in following :-



CHEMICAL BONDING

SOLUBILITY



(Common ion OH^- , Apply L.E.)

Size(\uparrow) , L.E. (\downarrow) , Solubility (\uparrow)



(Common ion SO_4^{2-} , Apply H.E.)

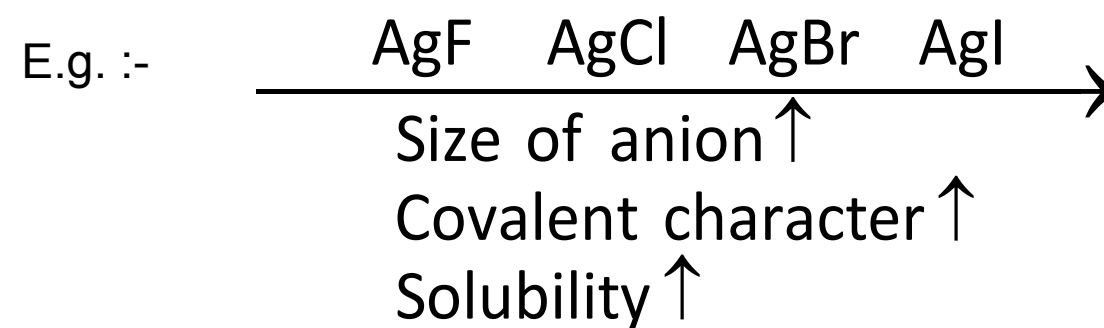
Size(\uparrow) , H.E. (\downarrow) , Solubility (\downarrow)

CHEMICAL BONDING

SOLUBILITY

(B) Solubility of ionic compounds of p and d block:

$$\text{Solubility} \propto \frac{1}{\text{Covalent character}}$$




CHEMICAL BONDING

SOLUBILITY


Q. Compare solubility in following sequence.

(i) PbF_2 PbCl_2 PbBr_2 PbI_2

Size of anion (↑) 

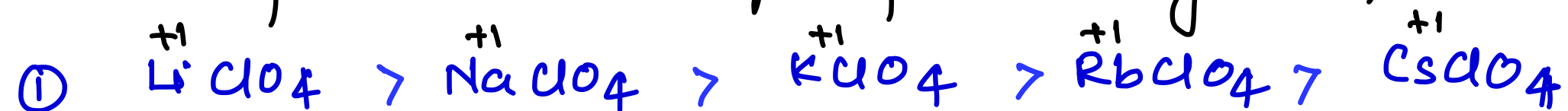
Covalent character (↑)

Solubility (↓)

(ii)	SnCl_2	SnCl_4
		
	Charge of cation (\uparrow)	
	Covalent character (\uparrow)	
	Solubility (\downarrow)	

CHEMICAL BONDING

Ex. Compare solubility of following compounds.



ClO_4^- large common Anion. Solubility \propto HE

$\text{HE}(\text{cation}) \propto \frac{q_c}{r_c}$, $r_c \uparrow$ HE \downarrow solubility \downarrow



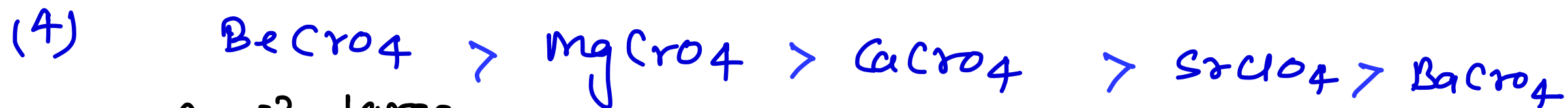
NO_3^- large common Anion. Solubility \propto HE

$\text{HE}(\text{cation}) \propto \frac{q_c}{r_c}$, $r_c \uparrow$ HE \downarrow solubility \downarrow



$\text{S}_2\text{O}_3^{2-}$ large common Anion. Solubility \propto HE

$\text{HE}(\text{cation}) \propto \frac{q_c}{r_c}$, $r_c \uparrow$ HE \downarrow solubility \downarrow



CrO_4^{2-} large common Anion. Solubility \propto HE

$\text{HE}(\text{cation}) \propto \frac{q_c}{r_c}$, $r_c \uparrow$ HE \downarrow solubility \downarrow

CHEMICAL BONDING



Br^- large common Anion. Solubility \propto HE

$$\text{HE}(\text{cation}) \propto \frac{q_c}{r_c}, \quad r_c \uparrow \quad \text{HE} \downarrow \quad \text{solubility} \uparrow$$



SO_3^{2-} large common Anion. Solubility \propto HE

$$\text{HE}(\text{cation}) \propto \frac{q_c}{r_c}, \quad r_c \uparrow \quad \text{HE} \downarrow \quad \text{solubility} \uparrow$$



Rb^+ large common. Cation. Solubility \propto HE

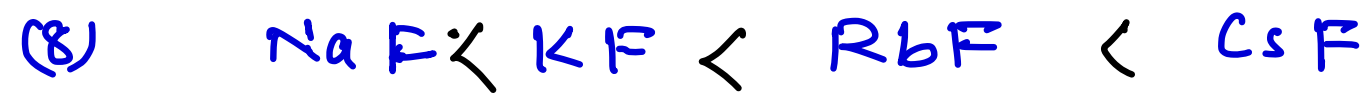
$$\text{HE}(\text{anion}) \propto \frac{q_a}{r_a}, \quad r_a \uparrow \quad \text{HE} \downarrow \quad \text{solubility} \uparrow$$



Cs^+ large common Cation. Solubility \propto HE

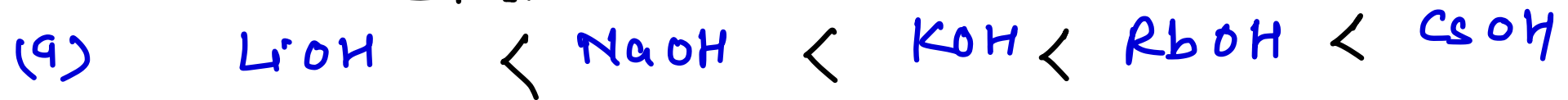
$$\text{HE}(\text{anion}) \propto \frac{q_a}{r_a}, \quad r_a \uparrow \quad \text{HE} \downarrow \quad \text{solubility} \uparrow$$

CHEMICAL BONDING



F^- is common Anion is smaller solubility $\propto \frac{1}{LE}$

$$LE \propto \frac{q_c q_a}{r_c + r_a}, \quad r_c \uparrow \quad LE \downarrow \quad \text{Solubility} \uparrow$$



OH^- is common Anion is smaller solubility $\propto \frac{1}{LE}$

$$LE \propto \frac{q_c q_a}{r_c + r_a}, \quad r_c \uparrow \quad LE \downarrow \quad \text{Solubility} \uparrow$$

CHEMICAL BONDING

SOLUBILITY

Exceptional Order of solubility :

(1) In IIA Fluorides BeF_2 is highly soluble due to its high H.E.



(2) In IA CO_3^{2-} , HCO_3^- solubility increases on moving down the group.



** compounds of Be do not form lattice so $\text{LE} = 0$, only hydration energy is there.