

CHEMICAL BONDING

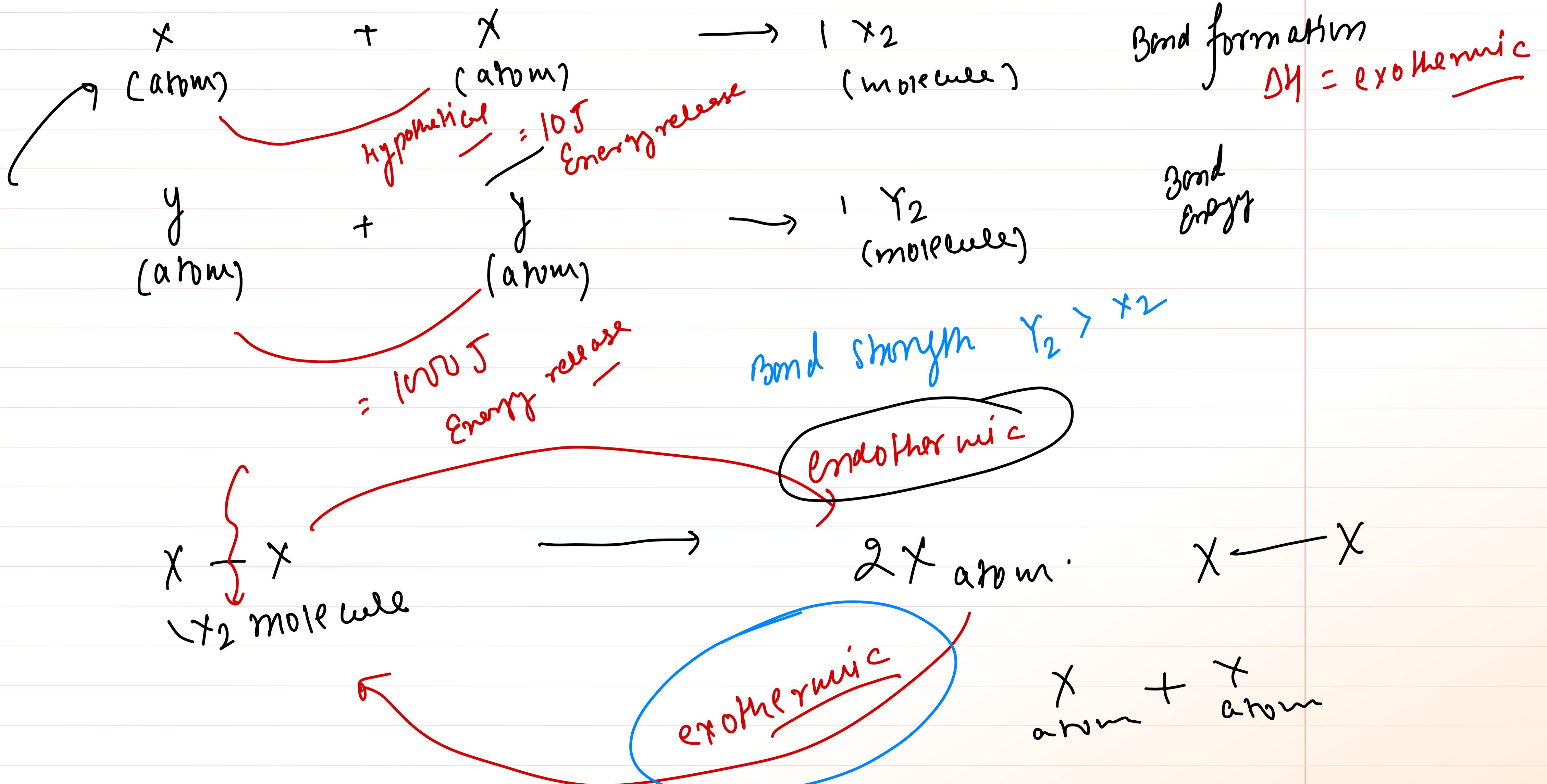
1.0 INTRODUCTION

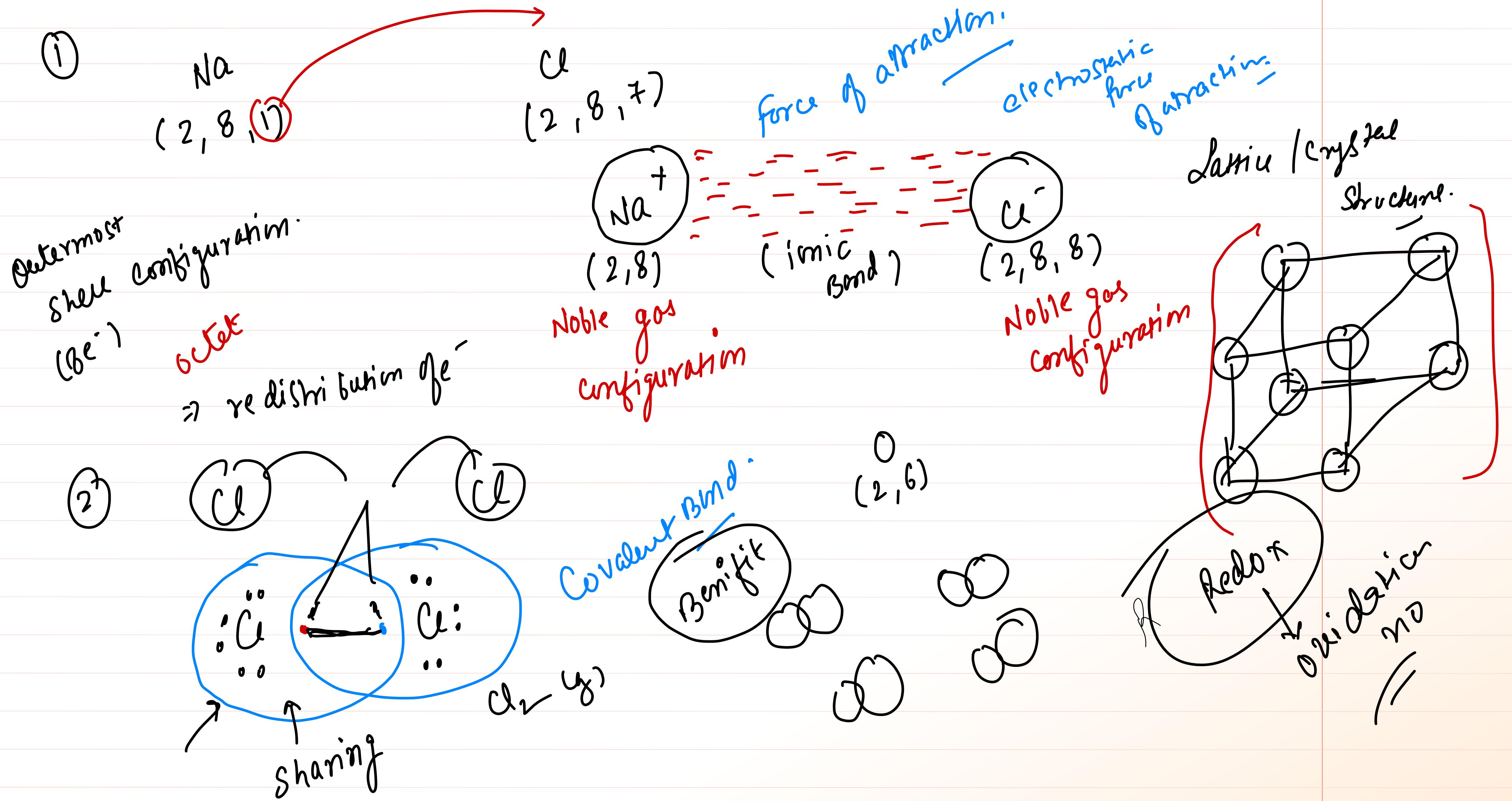
It is well known fact that except for inert gases, no other element exists as independent atoms under ordinary condition. Most of the elements exist as molecules which are cluster of atoms. How do atoms combine to form molecules and why do atoms form bonds? Such doubts will be discussed in this chapter.

1.1 Chemical Bond

SL AL

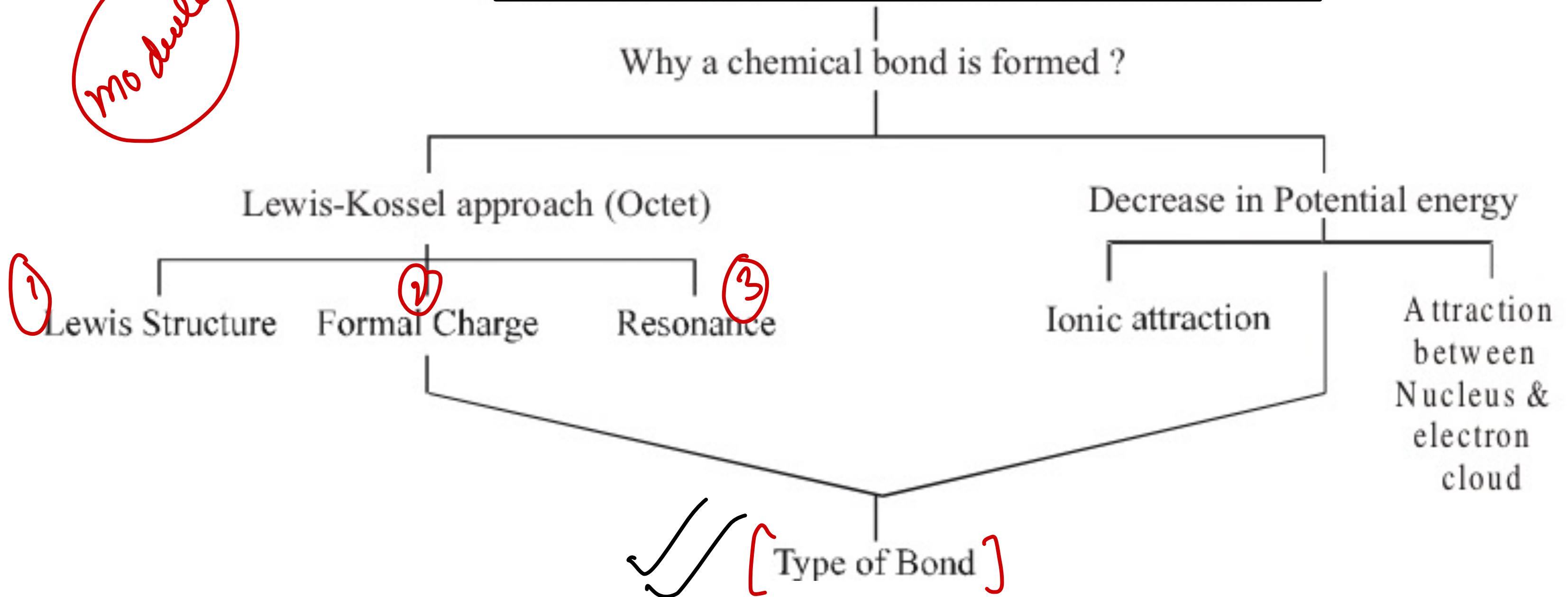
- (a) A force that acts between two or more atoms to hold them together as a stable molecule.
- (b) It is union of two or more atoms involving redistribution of e^- among them.
- (c) This process is accompanied by decrease in energy.
- (d) Decrease in energy \propto Strength of the bond.
- (e) A molecule will only be formed if it is more stable and has a lower energy, than the individual atoms.
Therefore molecules are more stable than atoms.





Module

FLOWCHART TO CHEMICAL BONDING

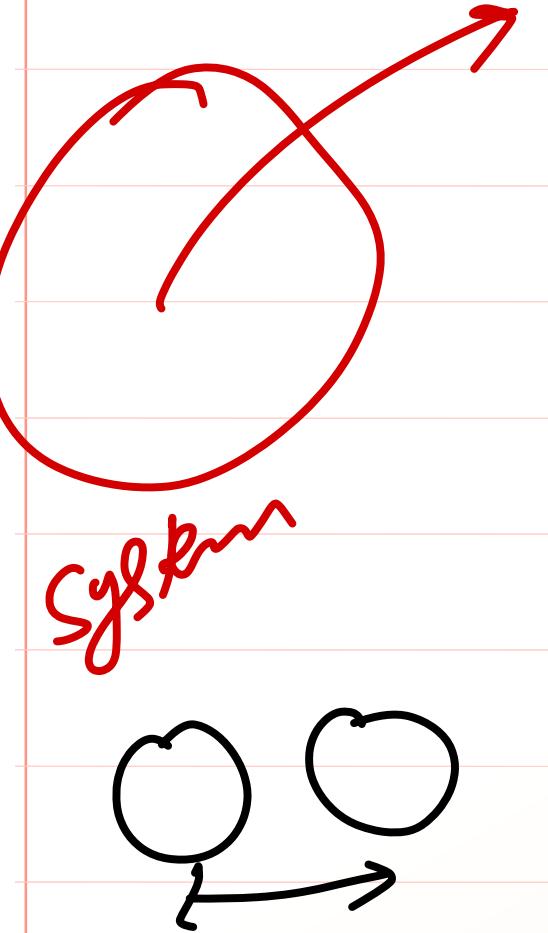
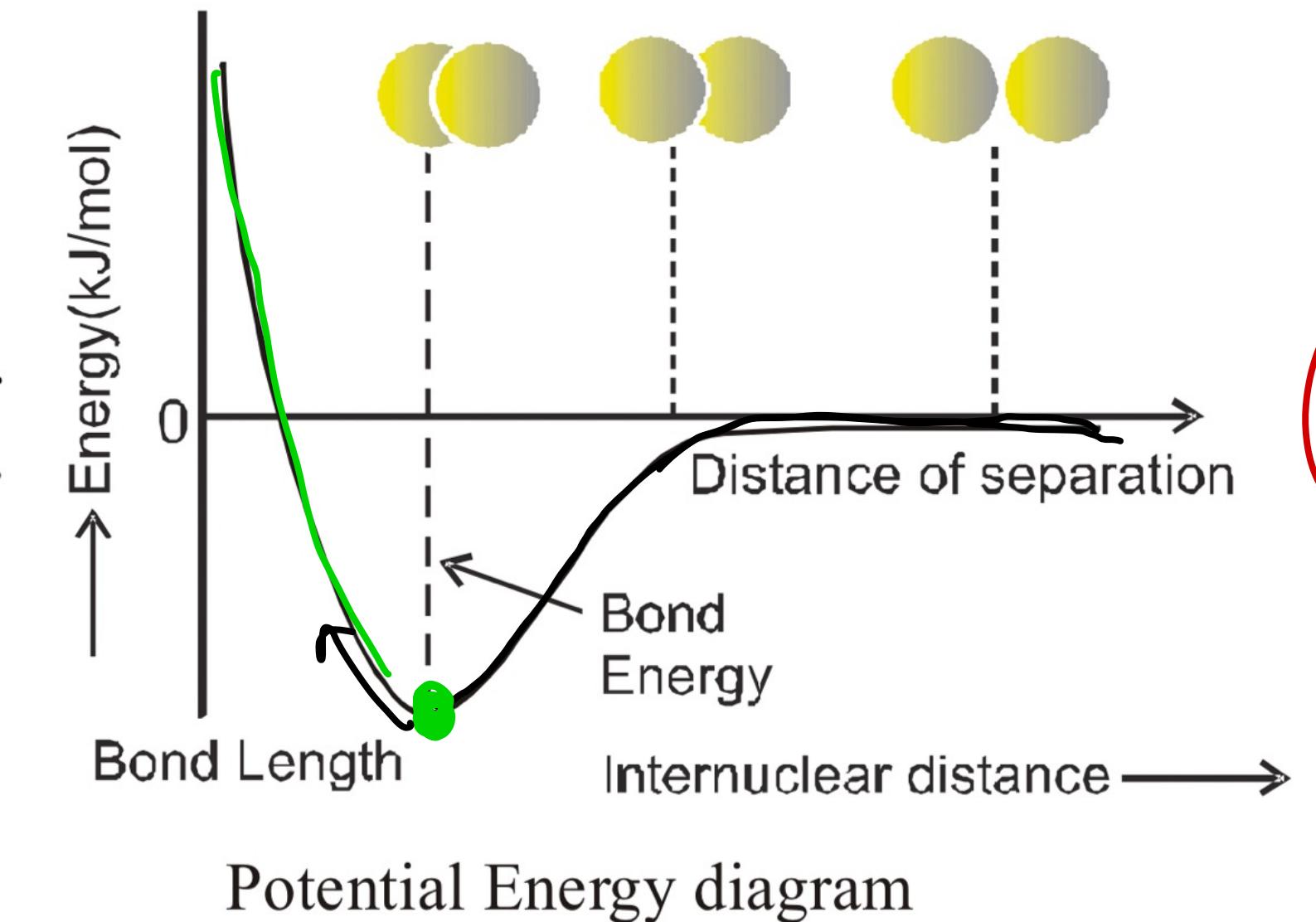
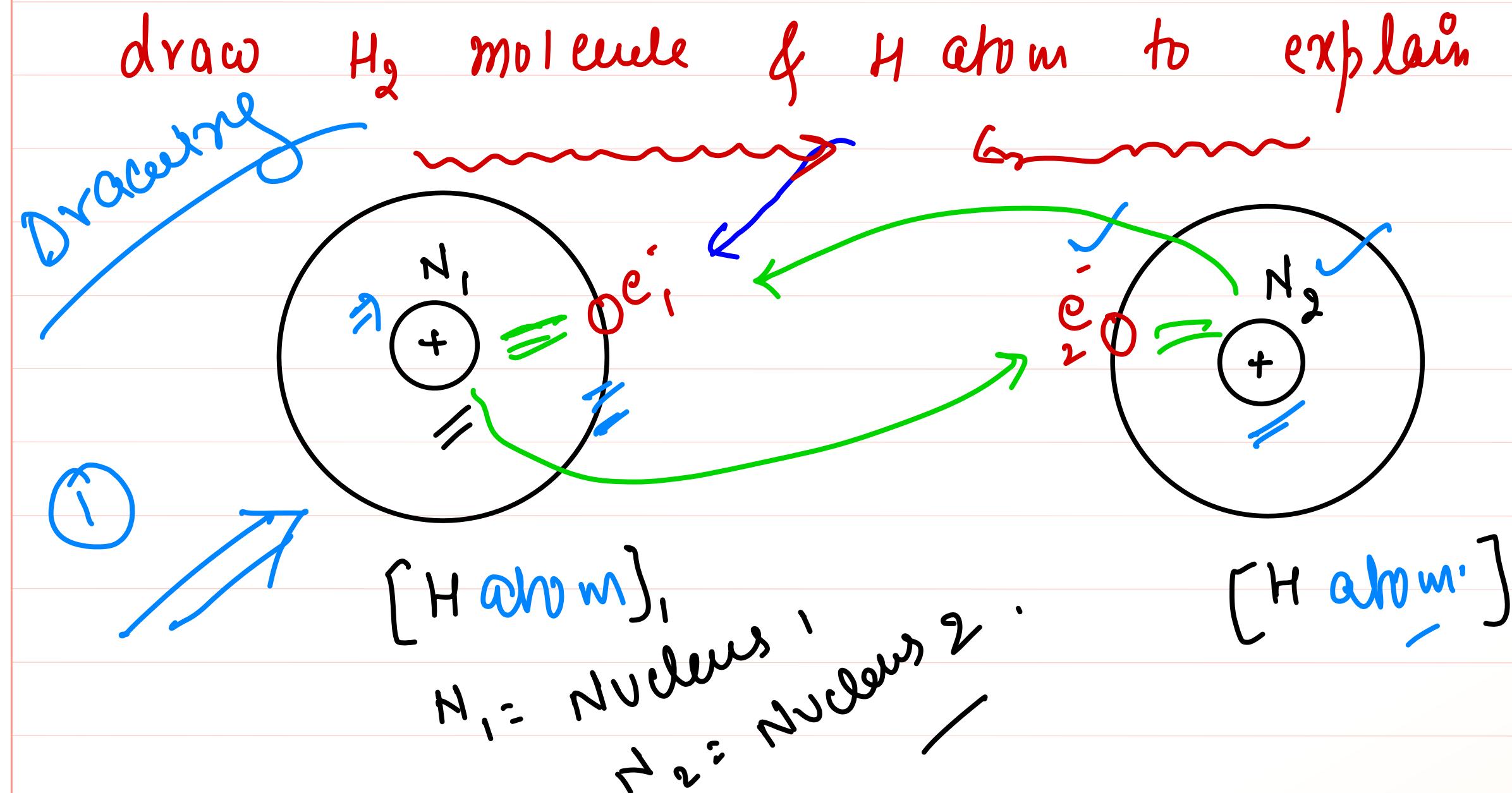


Cause of chemical combination

SL AL

Tendency to acquire minimum energy (decrease in P.E.)

- (a) When two atoms approaches to each other-
Nucleus of one atom attracts the electron of another atom.
- (b) Two nuclei and electron of both the atoms repels each other.
- (c) If net result is attraction, the total energy of the system (molecule) decreases and a chemical bond forms.
- (d) So Attraction \propto 1/energy \propto Stability.
- (e) Bond formation is an exothermic process.



forces

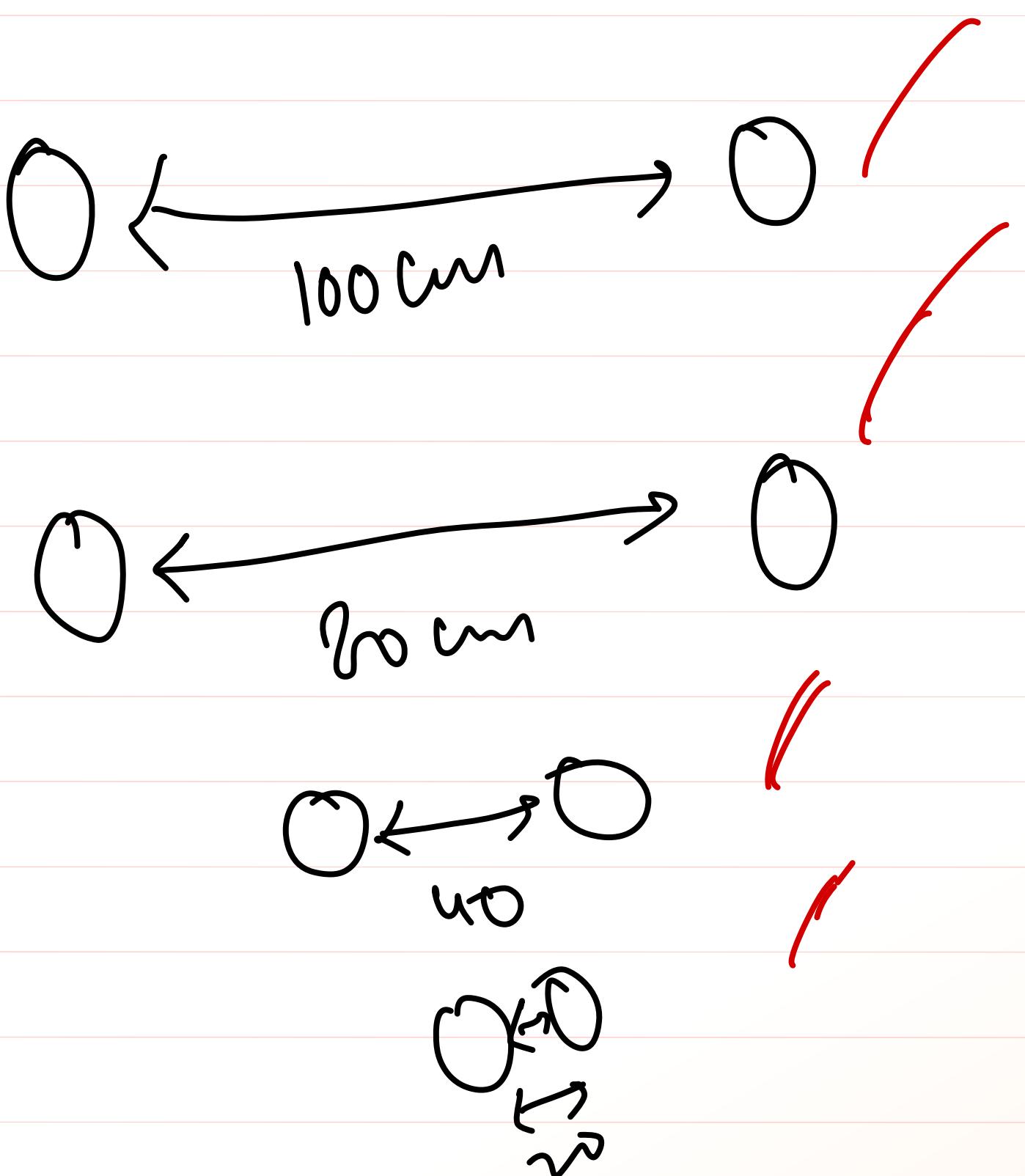
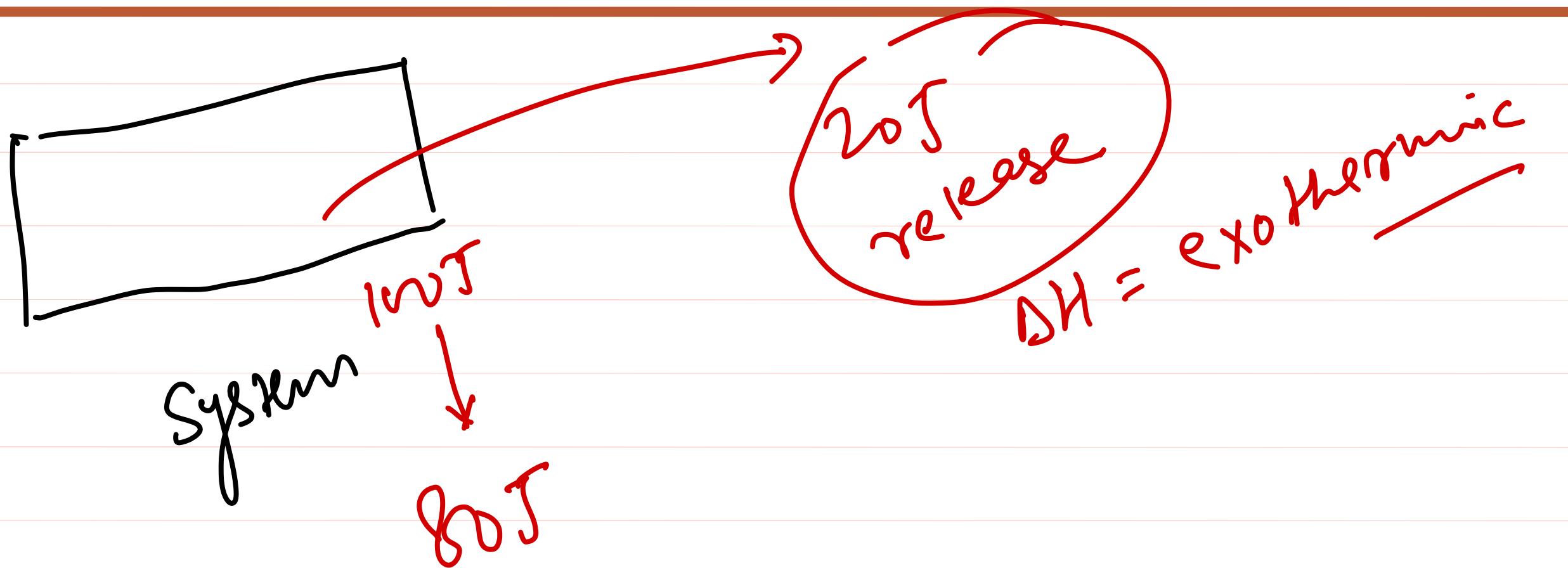
$N_1 - e_1$ - repulsion ✓

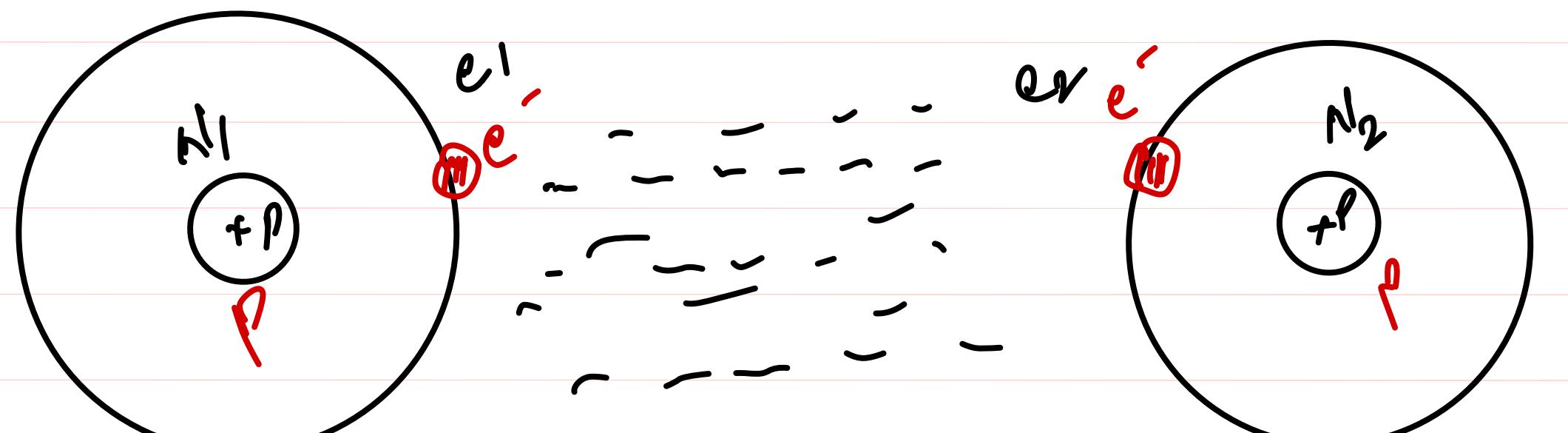
$(N_1 - e_1) - e_2$ - attraction ✓

$N_2 - e_2$ - attraction ✓

$N_2 - e_2 - e_1$ - attraction ✓

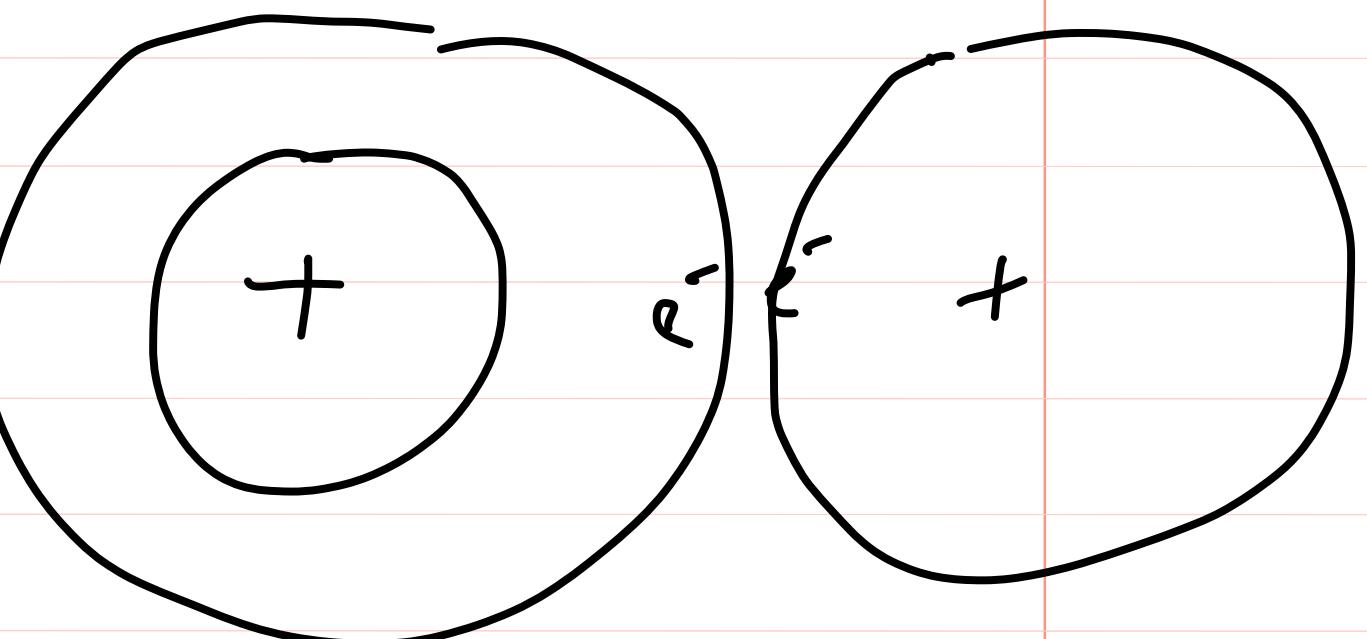
$(e_1 - e_2)$ - repulsion ✓



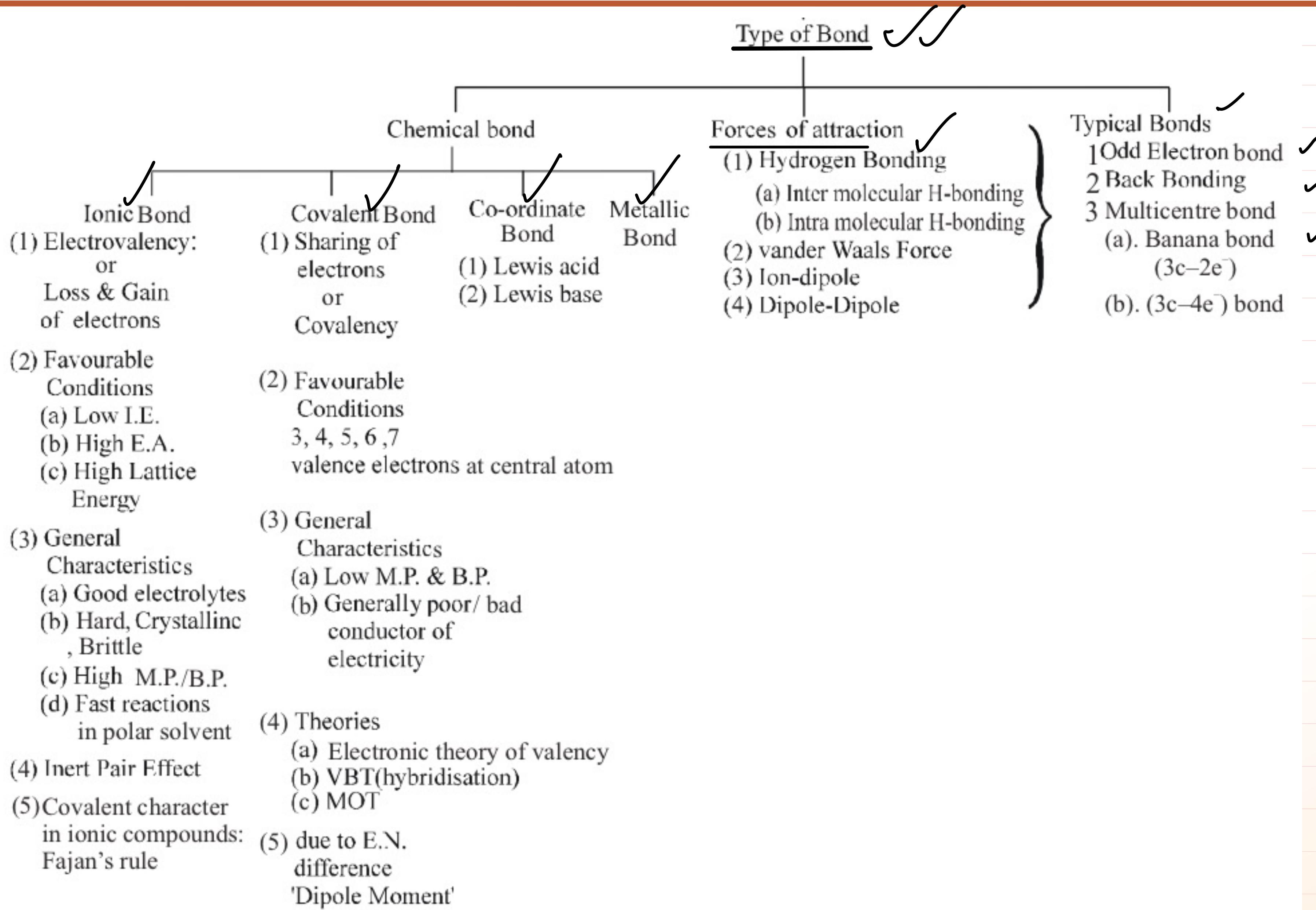


✓ H atom

H atom.



- $N_1 - e_1 \rightarrow$ attraction
- $N_1 - e_2 \rightarrow$ attraction
- $N_2 - e_2 \rightarrow$ attraction
- $N_2 - e_1 \rightarrow$ attraction
- $e_1 - e_2 \rightarrow$ repulsion
- $N_1 - N_2 \rightarrow$ repulsion.



Octet rule :

Theories'

"Tendency of atoms to have eight electrons in their outermost shell is known as Lewis octet rule". To achieve inert gas configuration atoms lose, gain or share electrons.

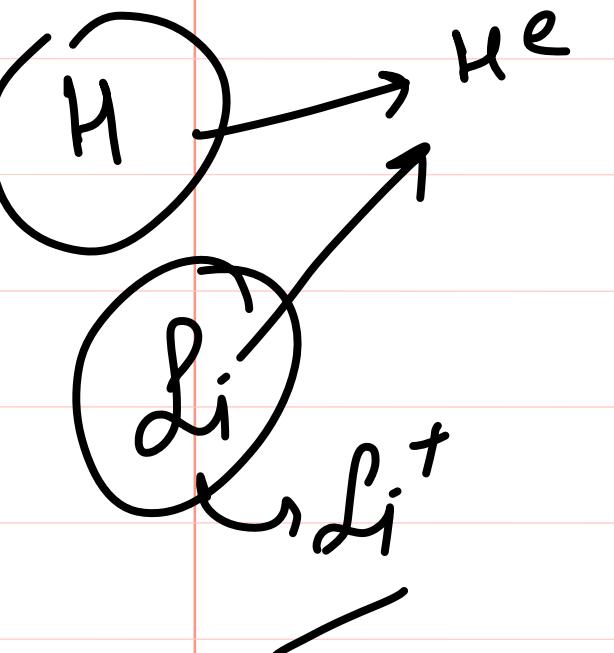
- (i) It has been observed that atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements.
- (ii) It means that these atoms must have a stable electronic configuration.
- (iii) These elements (noble gases) have 8 electrons ($ns^2 np^6$) except helium which has 2 electrons ($1s^2$) in their outer most shell.

Element	Ne	Ar	Kr	Xe	Rn
Outer most shell	<i>valence shell</i>				
configuration	$(2s^2 2p^6)$	$(3s^2 3p^6)$	$(4s^2 4p^6)$	$(5s^2 5p^6)$	$(6s^2 6p^6)$
(iv) It is therefore concluded that $ns^2 np^6$ configuration in the outer energy level constitutes a structure of maximum stability or minimum energy.					

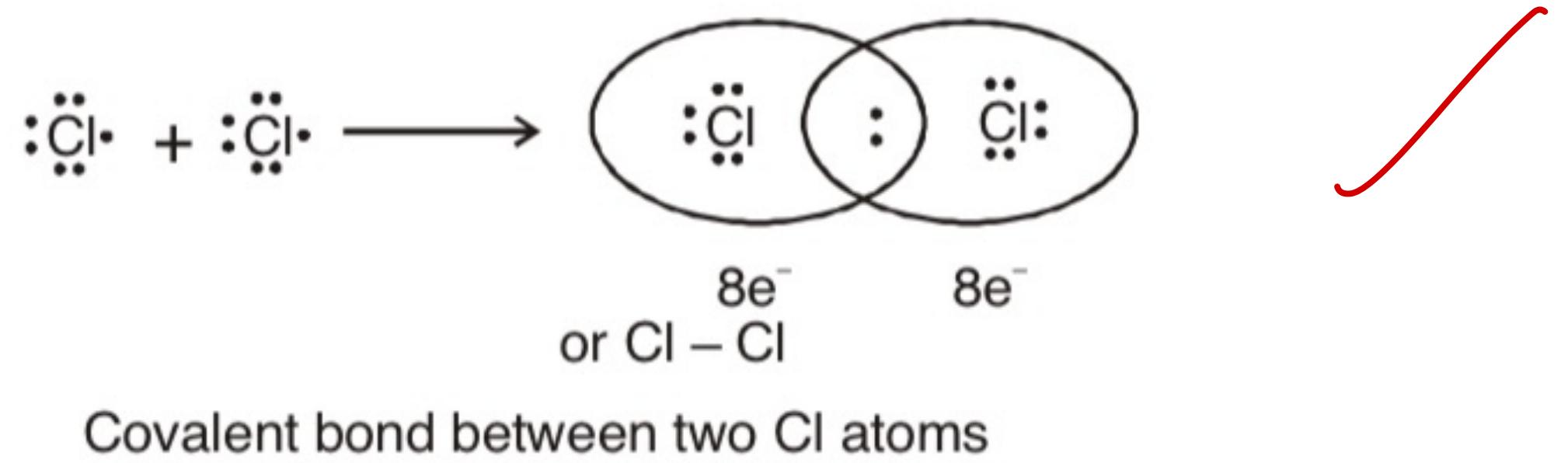
Outermost shell *Levi's* *Valence shell (B.E.)*

Noble gas *fulfilled configuration* *stable* *Reactivity*

nearest
no
one

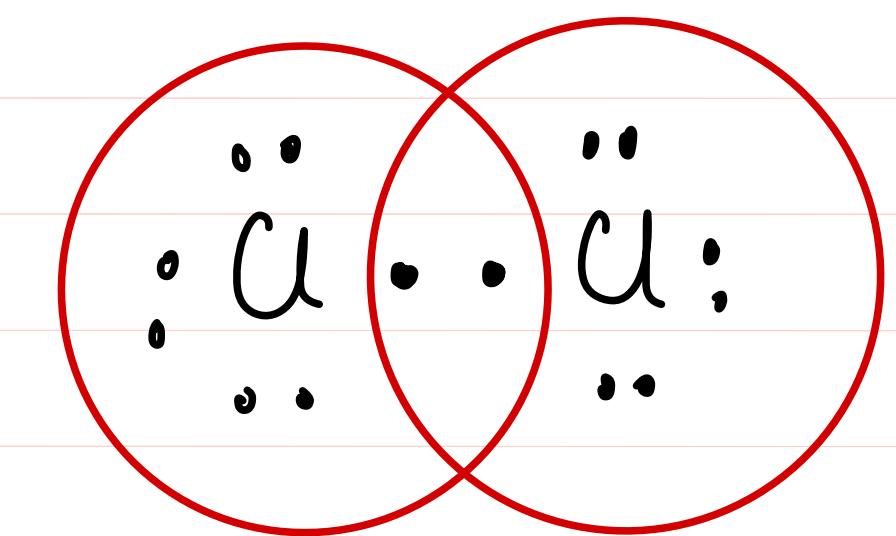
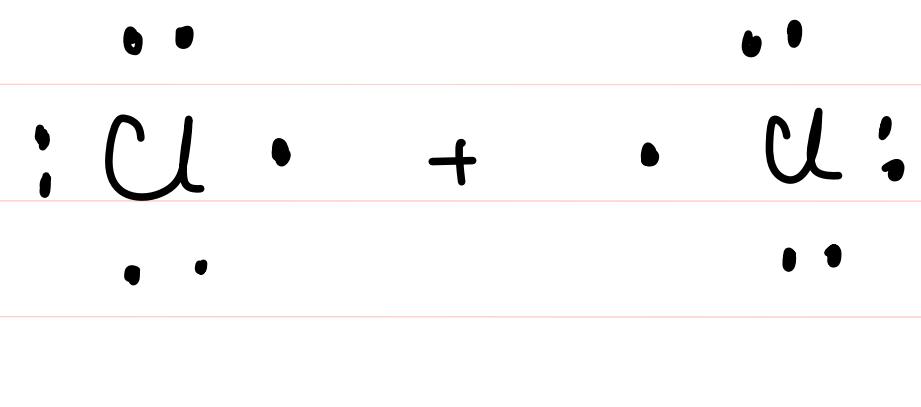


The **Octet rule** can be understood by considering the formation of the chlorine molecule, Cl_2 . The Cl atom with electronic configuration, $[\text{Ne}]^{10} 3s^2 3p^5$, is one electron short of the argon configuration. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both



Figure

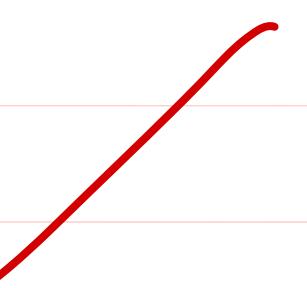
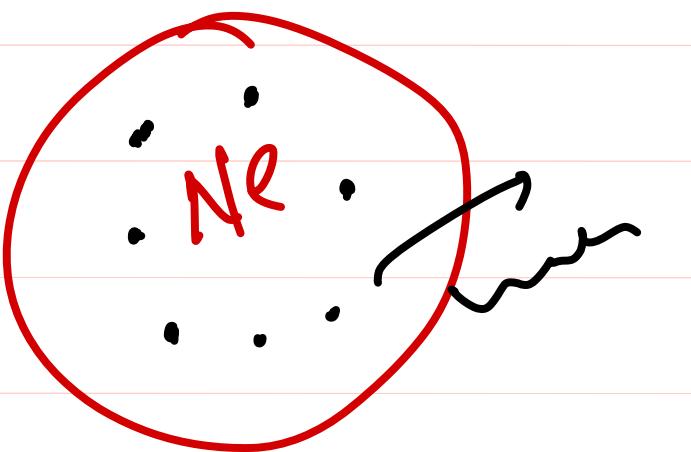
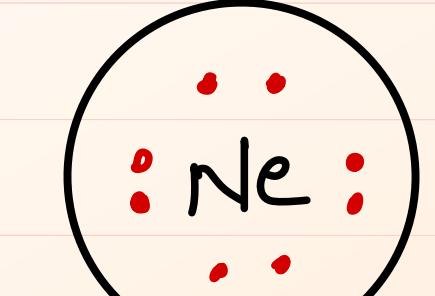
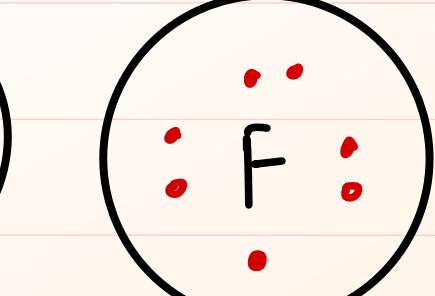
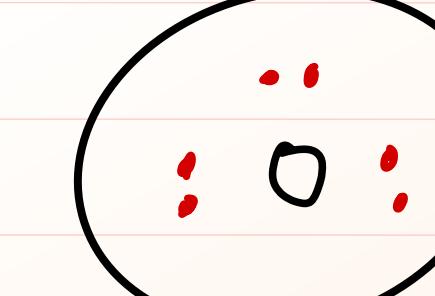
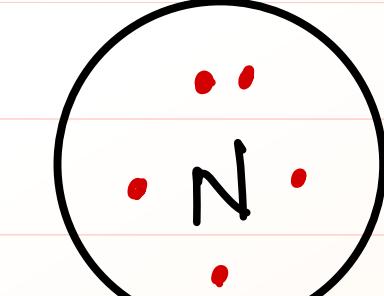
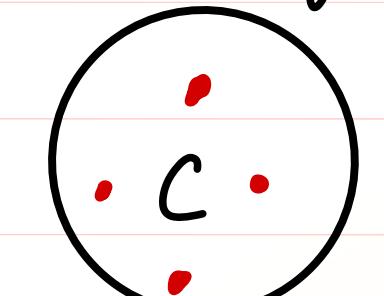
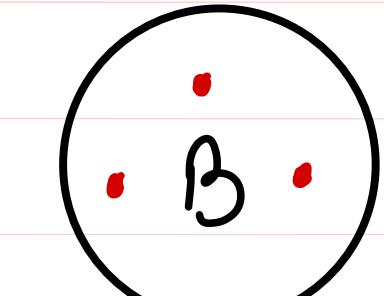
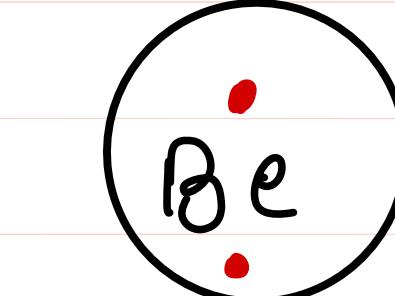
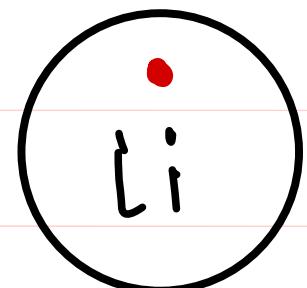
chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon). The dots represent electrons. Such structures are referred to as Lewis dot structures.



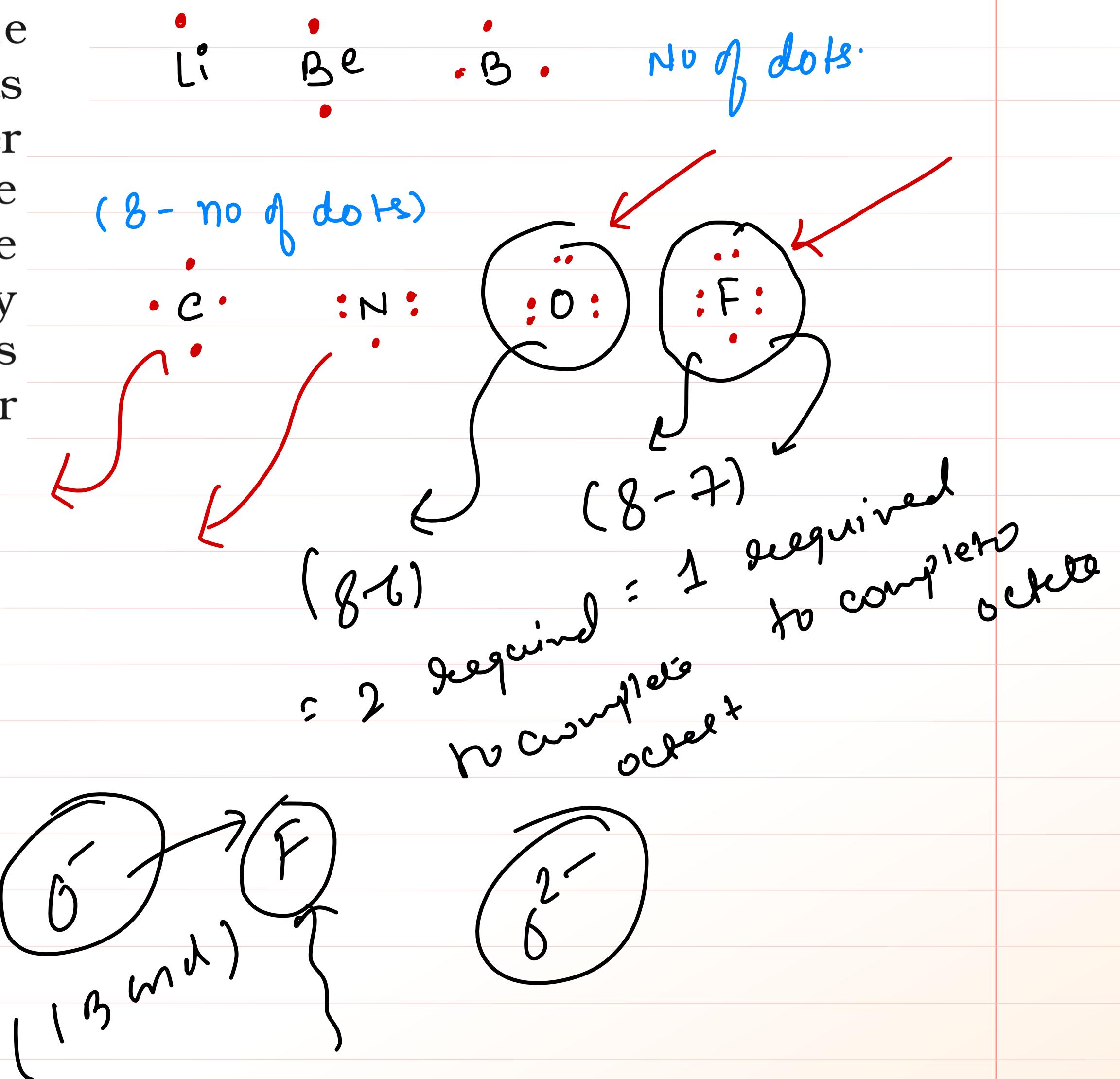
Lewis Symbols: In the formation of a molecule, only the outer shell electrons takes part in chemical combination and they are known as valence electrons. The inner shell electrons are well protected and are generally not involved in combination process. Lewis introduced simple notation to represent valence electrons in an atom. These notation are called Lewis symbol.

for example the Lewis symbols for the element of second period

Notation:



Significance of Lewis Symbols : The number of dots around the symbol represents the number of valence electrons. This number of valence electrons helps to calculate the common or **group valence** of the element. The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons.



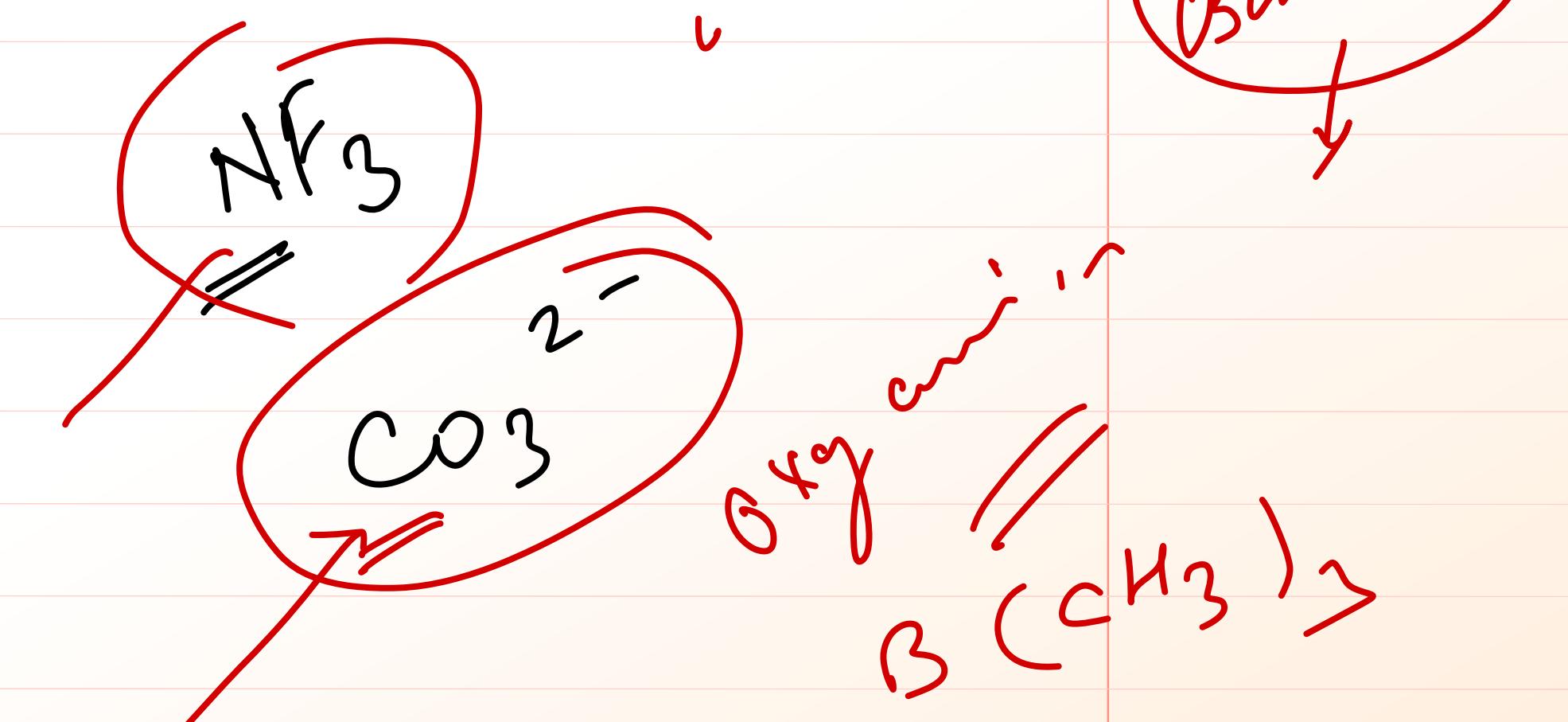
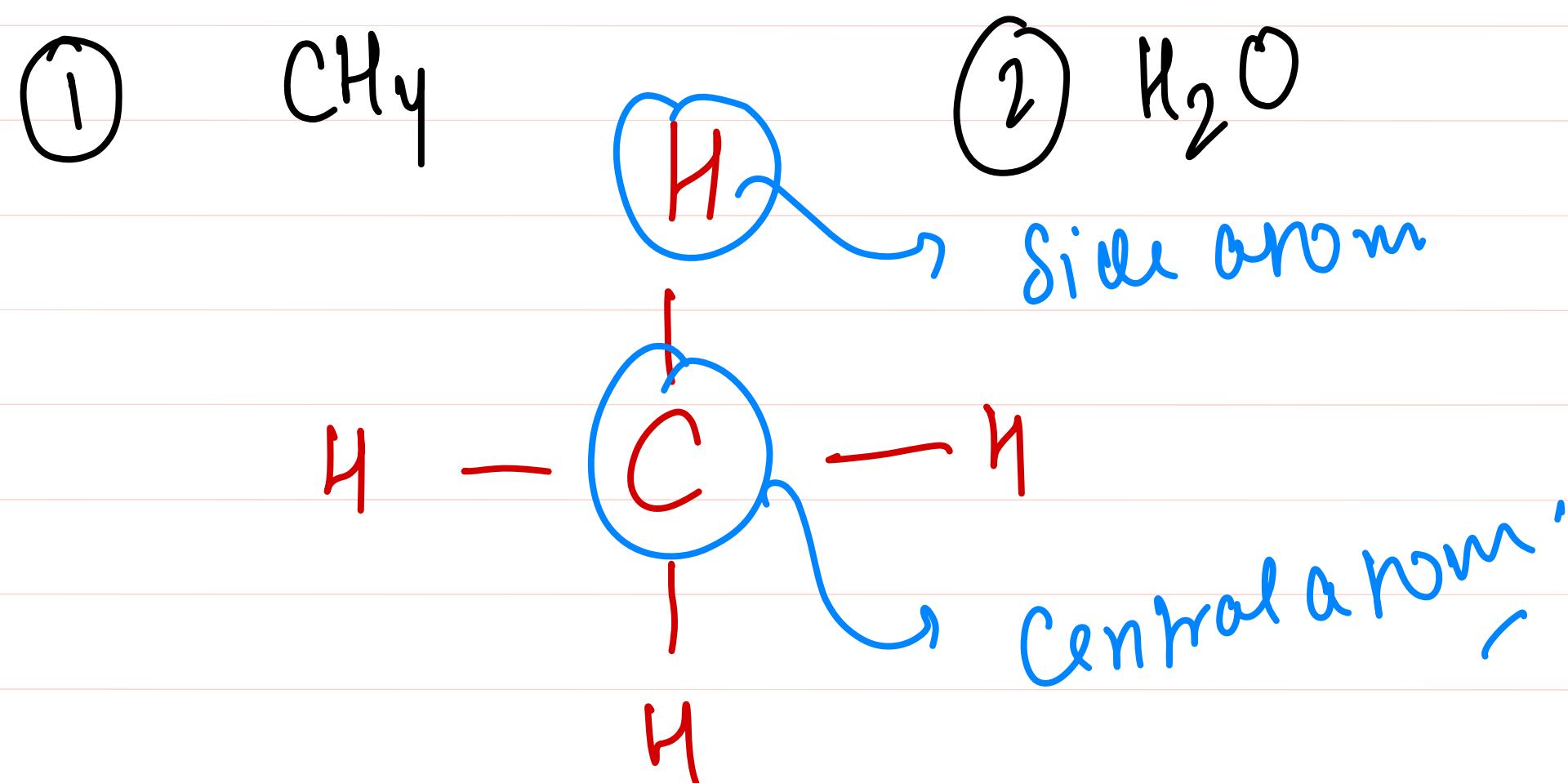
To write the Lewis dot structure following steps are to be followed :

- The total number of electrons are obtained by adding the valence electrons of combining atoms.
- For Anions, we need to add one electron for each negative charge.
- For cations, we need to subtract one electron for each positive charge.
- After then the central atom is decided.

✓ To decide, Central atom, following steps are followed :

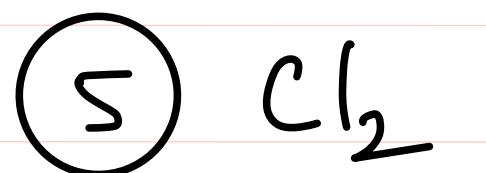
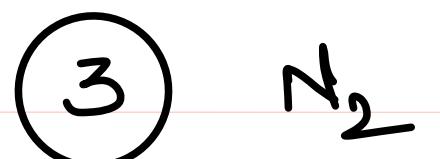
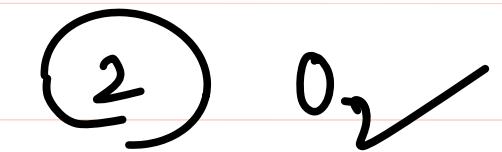
- In general the **least electronegative atom** occupies the central position in the molecule/ion. For example in the NF_3 and CO_3^{2-} , nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.
- Generally the atom which is/are less in number acts as central atom.
- Generally central atom is the atom which can form maximum number of bonds(which is generally equal to the number of electrons present in the valence shell of the atom).
- Atom of highest atomic number or largest atom generally acts as central atom.

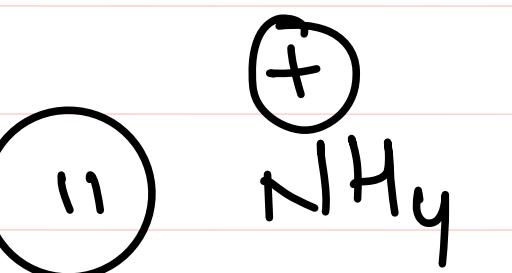
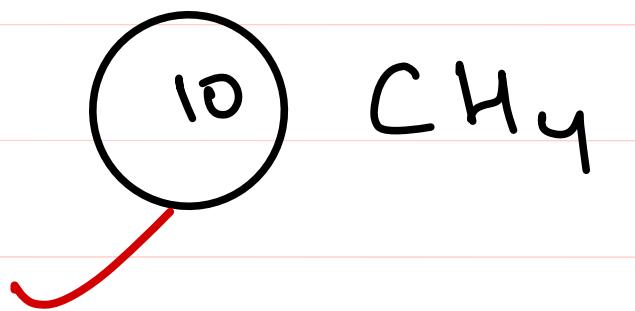
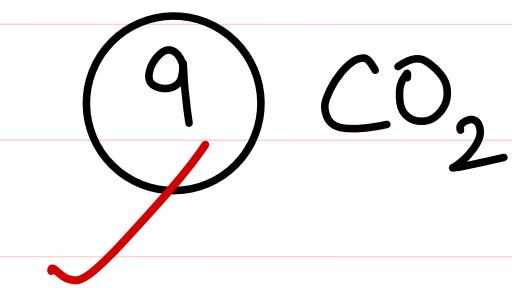
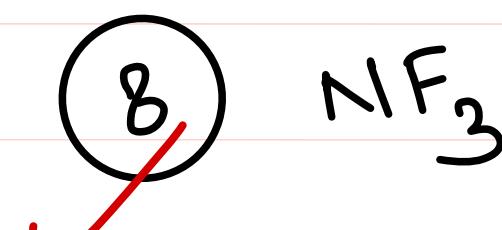
Hydrogen



Some examples:-

Draw Lewis dot structure for :-





(12) CO

(13) CO_3^{2-} (14) NO_3^- (15) NO_2^+

NOTE: * 2nd period element can accomodate maximum of
Be in outermost shell.

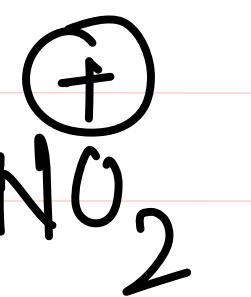
$$n=2(2s\ 2p)$$

* 2nd period element cannot expand their octet due to absence of 2d orbital.

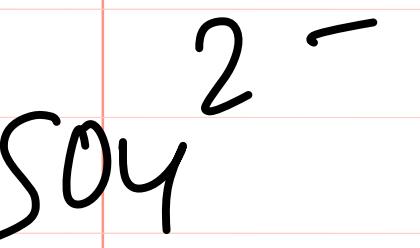
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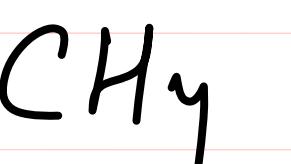
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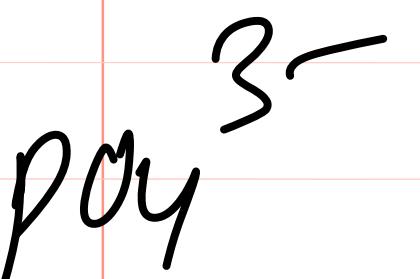
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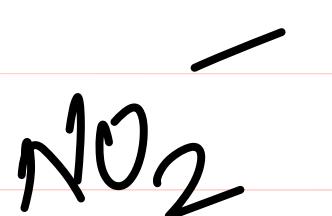
(17)



(24)



(18)



(22)



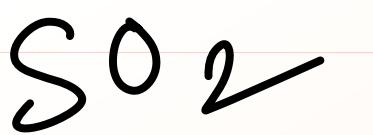
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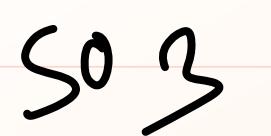
(20)



(21)

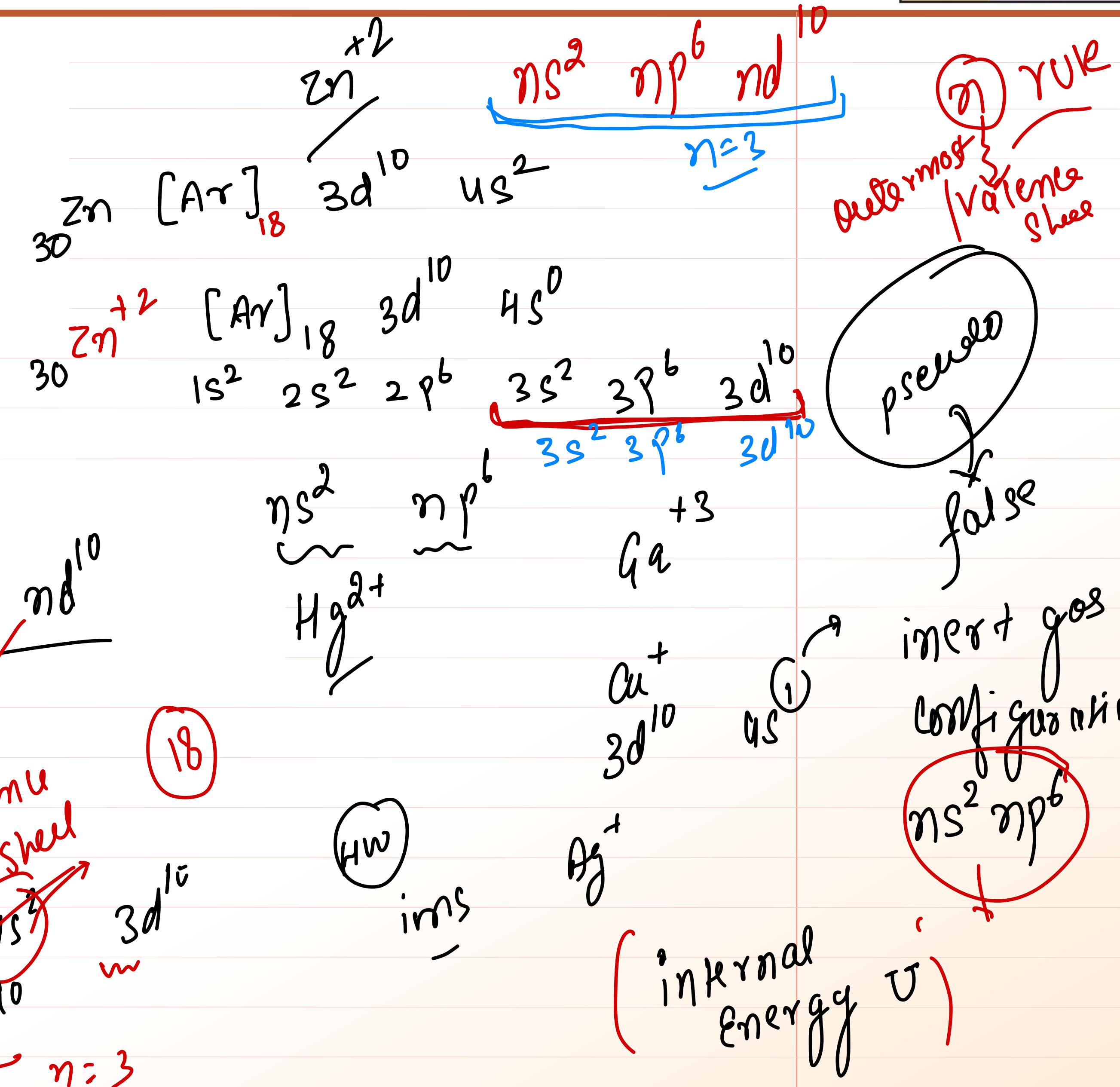
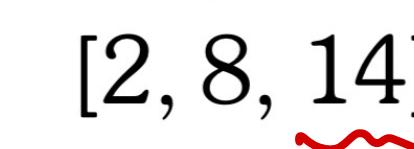
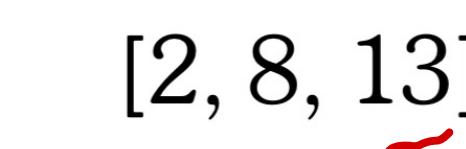
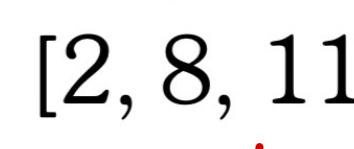
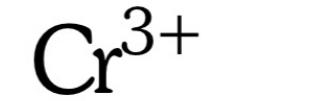


(22)



Exceptions of octet rule

(i) Transition metal ions



29
Cu

$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$

$4s^1$

11th group
12th group

13th group

29
 Cu^+

$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$

$3s^2$ $3p^6$ $3d^{10}$

pseudo inert gas configuration:

Z^n
Cd

$Ar^{40}Ne^{18}F^3$
RR-Si₆

learn:

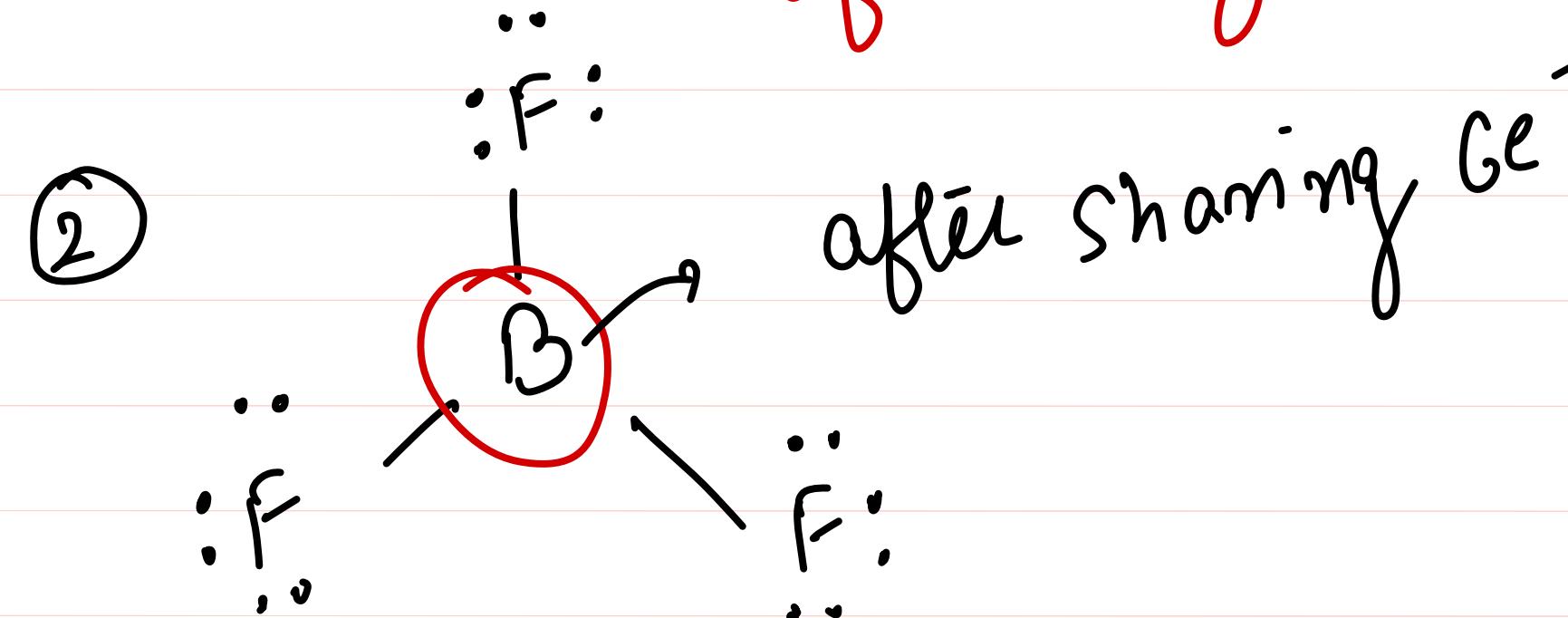
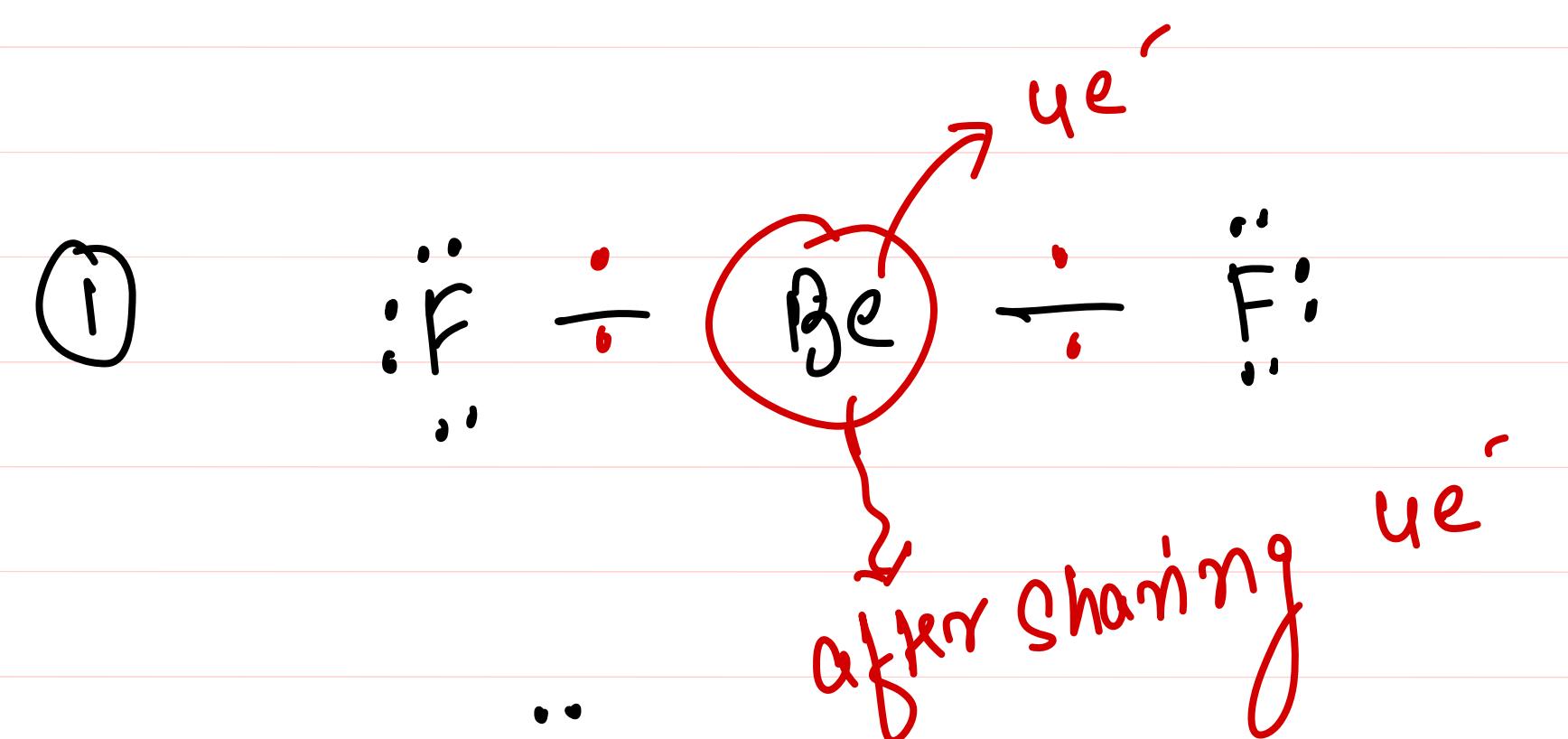
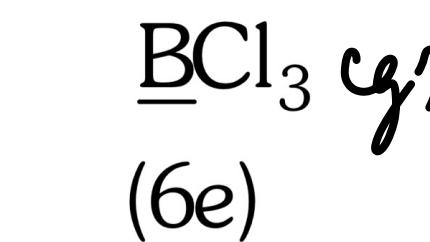
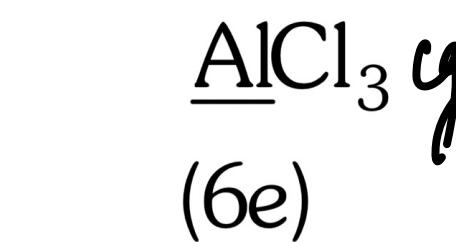
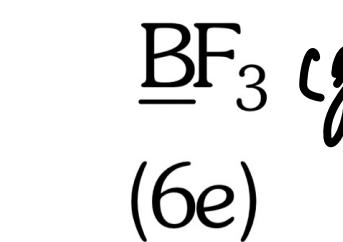
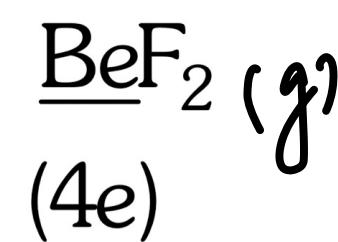
30

24
Cr
 $3d^5 4s^1$

29
Cu
 $3d^{10} 4s^1$

η_0 of exchanges exchange energy:

(iii) Contraction of octet (incomplete octet)



: Cl - I :

Octet complete

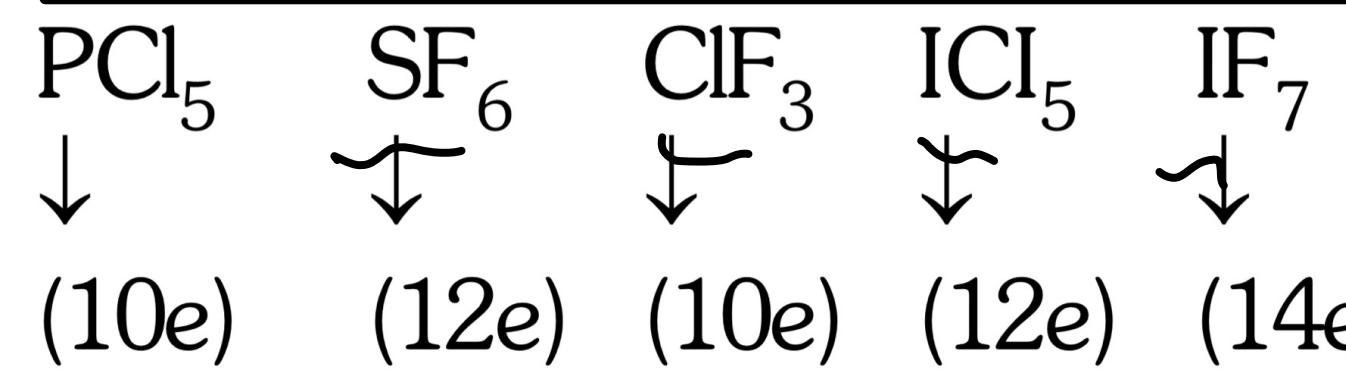
Be $1s^2 2s^2$

less than 8e⁻

Octet (Contraction of octet)

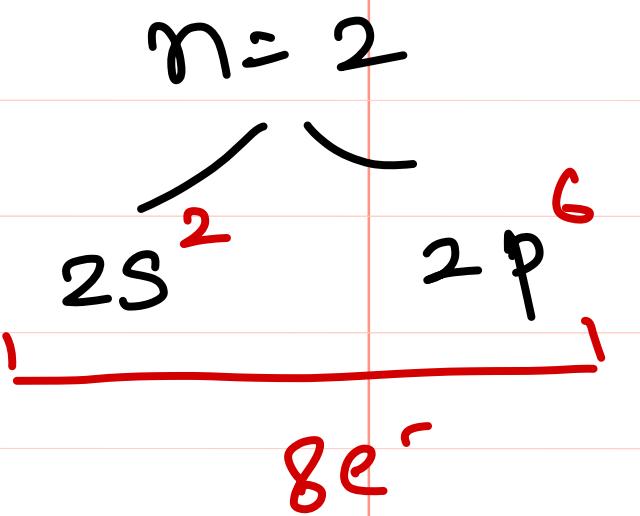
Hypervalent species

(iv) Expansion of Octet (due to empty d-orbitals)

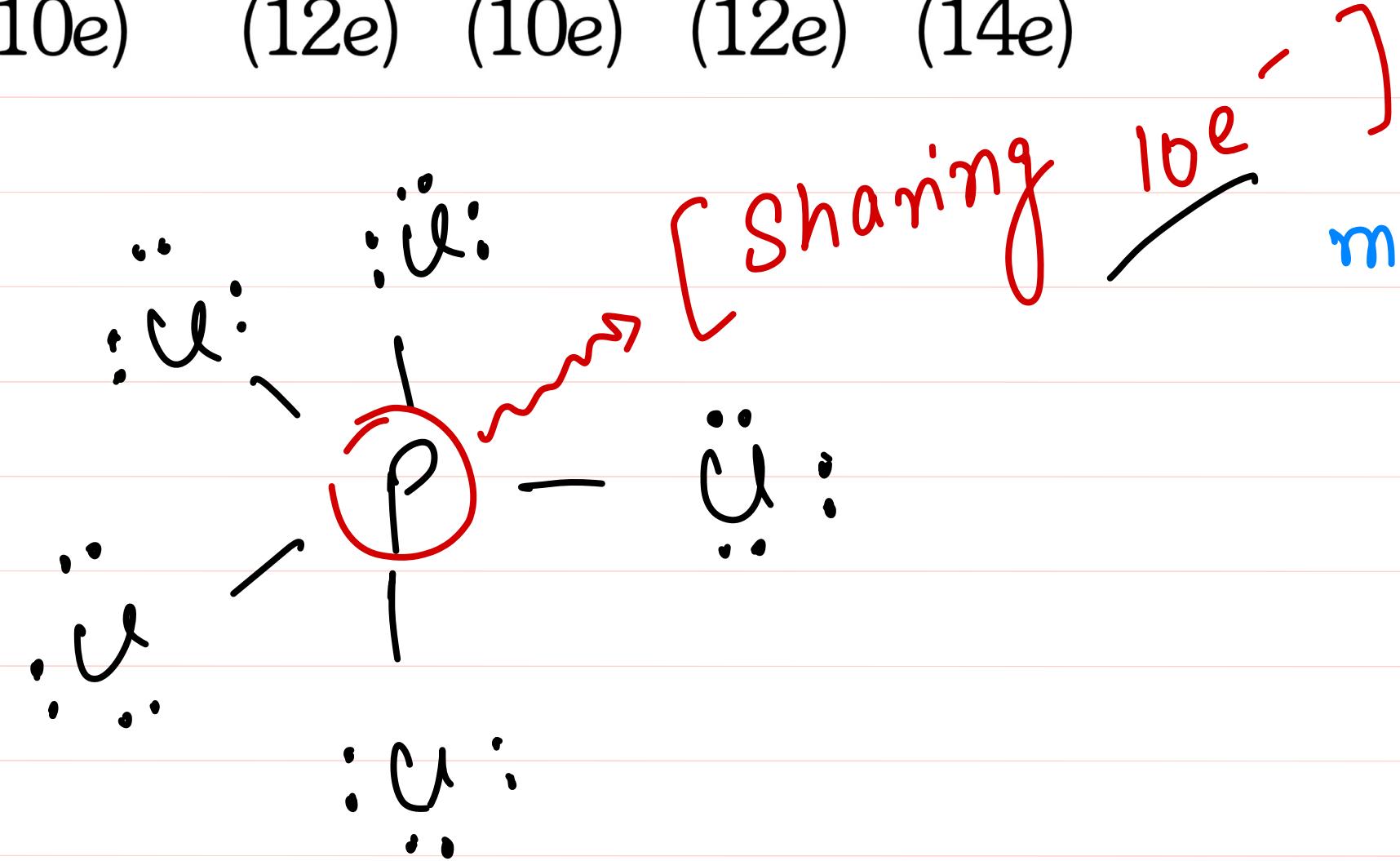


or Hyper valent Compound

2nd period

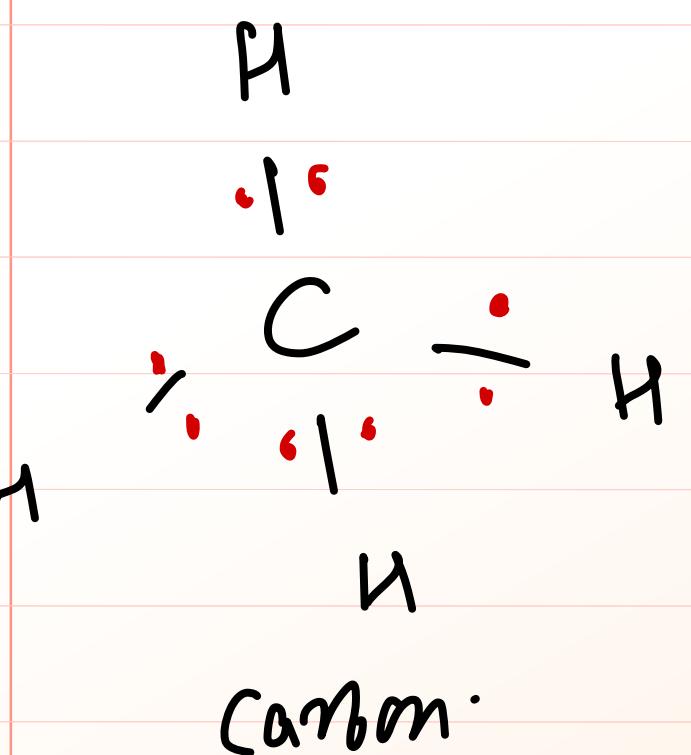
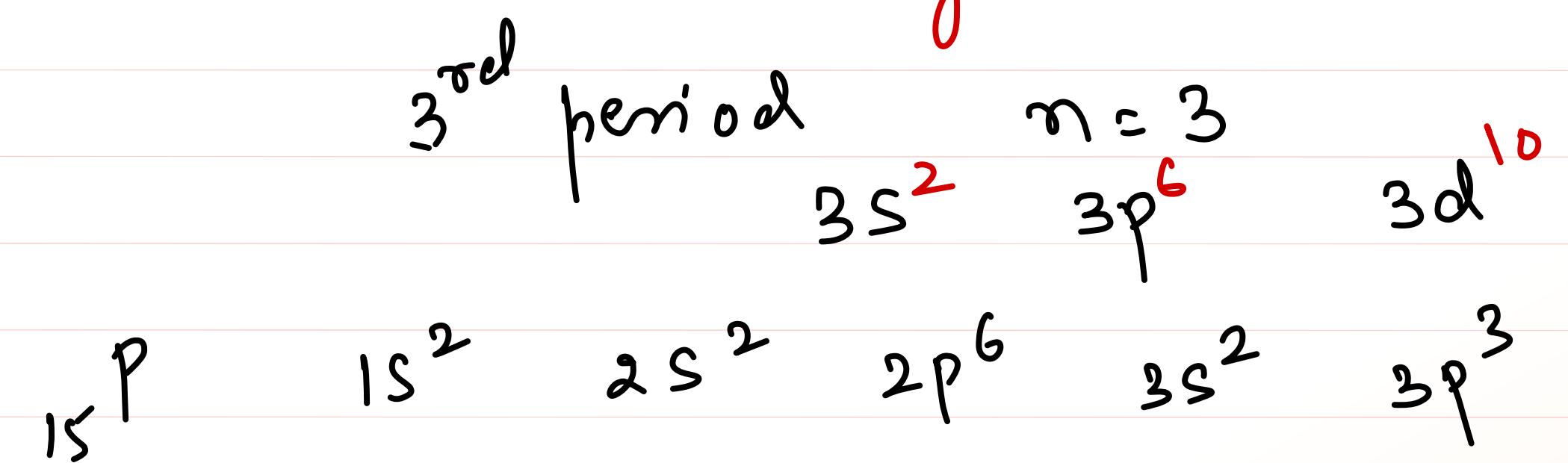


2d



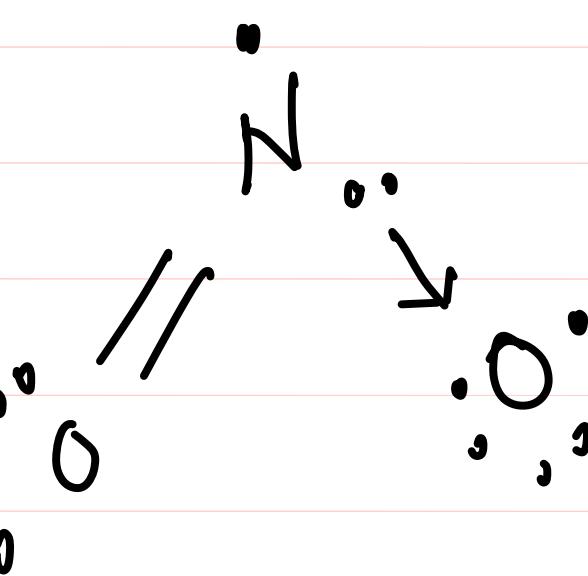
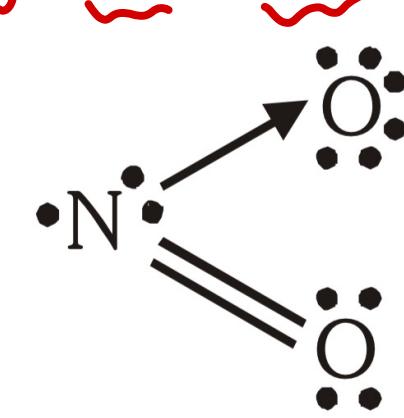
expansion of octet
Hyper valent species.

3rd period



2d

(v) **Odd electron species**

Ex. NO, NO₂, ClO₂ etc.


①



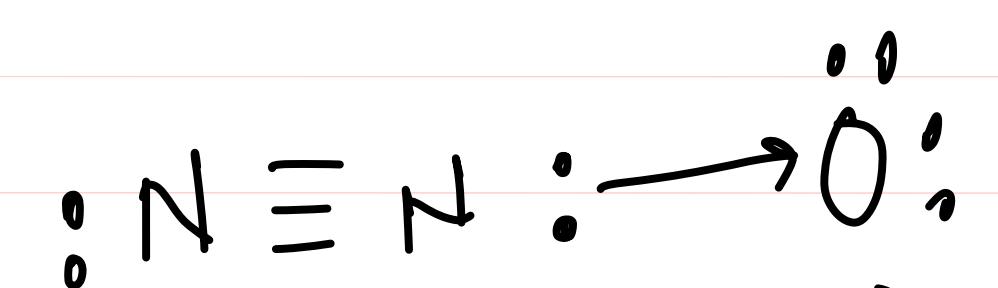
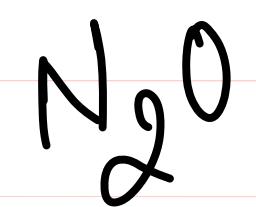
after scanning

 He'

module



octet



NO



Species

odd e⁻ Species

Species

Valence bond theory

oxidation number

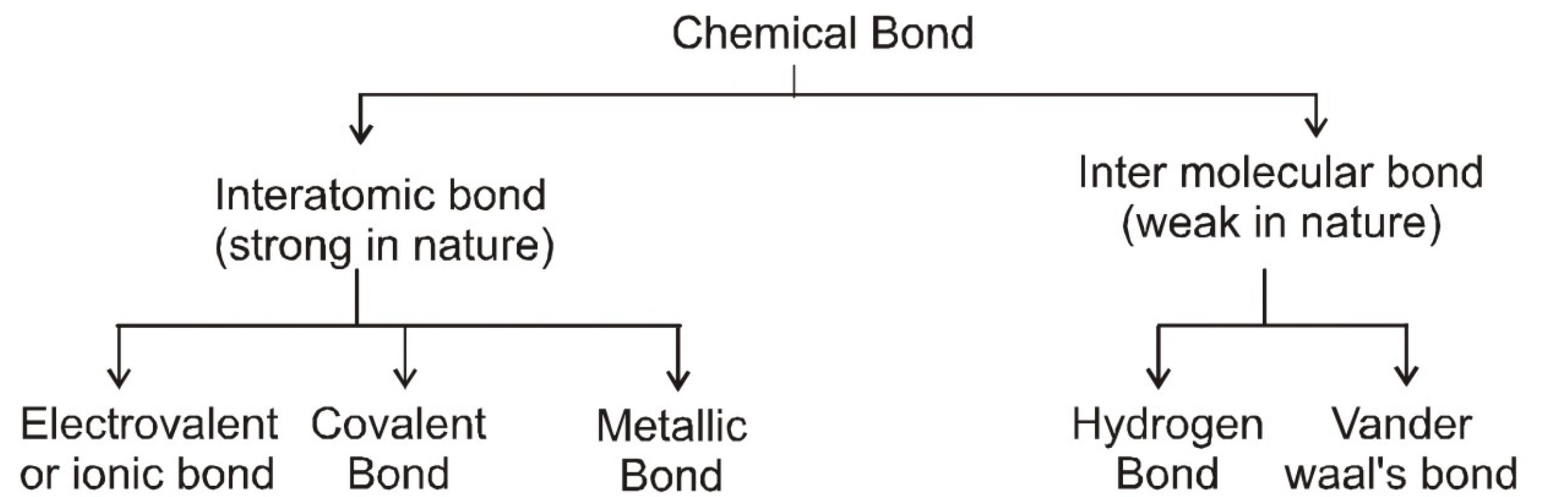
Redox

(vi) **Compounds of Noble gases**

Noble gases which have already completed their octets (or douplet in case of He.) should not form compounds. However, their compounds like XeF_2 , XeF_6 & KrF_2 etc., have been actually prepared.

CLASSIFICATION OF CHEMICAL BONDS :

On the basis of electronic valency theory and structure, chemical bonds can be classified as follows.



Bond

Ionic, Covalent & Co-ordinate

200 kJ

Hydrogen bonding

10 – 40 kJ

{

Vander-waal's

2 – 10 kJ

Bond Energy per mole

ELECTROVALENT OR IONIC BOND :

The chemical bond formed between two or more atoms as a result of complete transfer of one or more electrons from one atom to another is called ionic or electrovalent bond.

Electrovalent bond is not possible between similar atoms. This type of bonding requires two atoms of different nature. One atom should have the tendency to loose electrons i.e. electropositive in nature and the other atom should have the tendency to accept electrons i.e. electronegative in nature.

Electropositive atom loses electrons (group IA to IIIA)

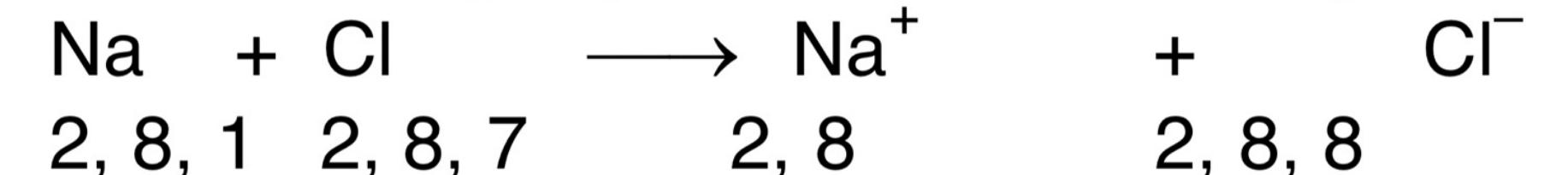
Electronegative atom gains electron (group IVA to VII A)

Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.

Total number of electron lost or gained is called electrovalency.

Example :

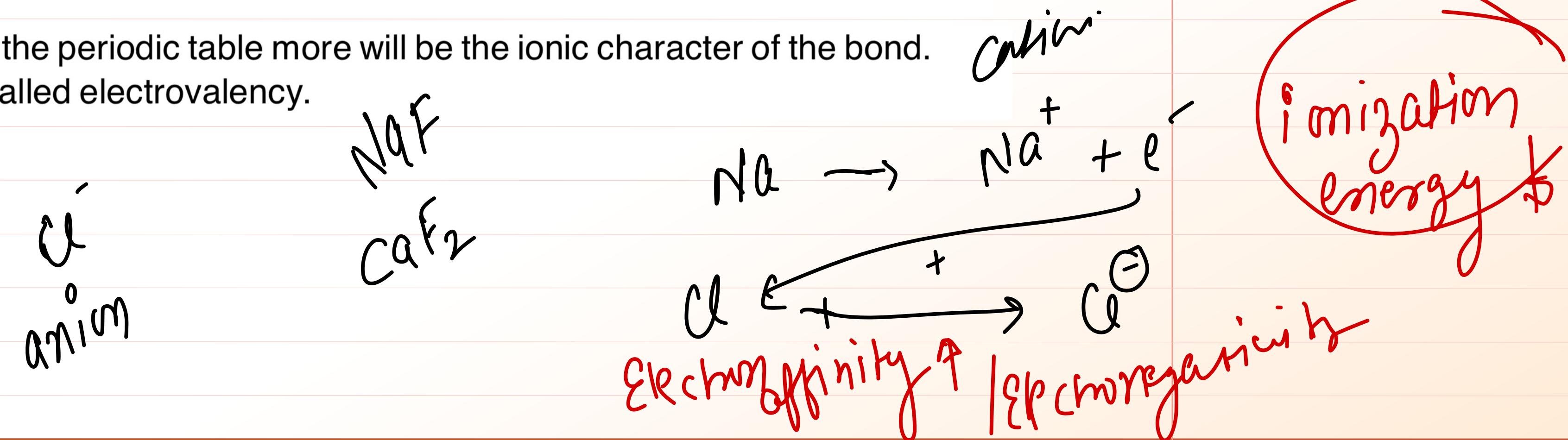
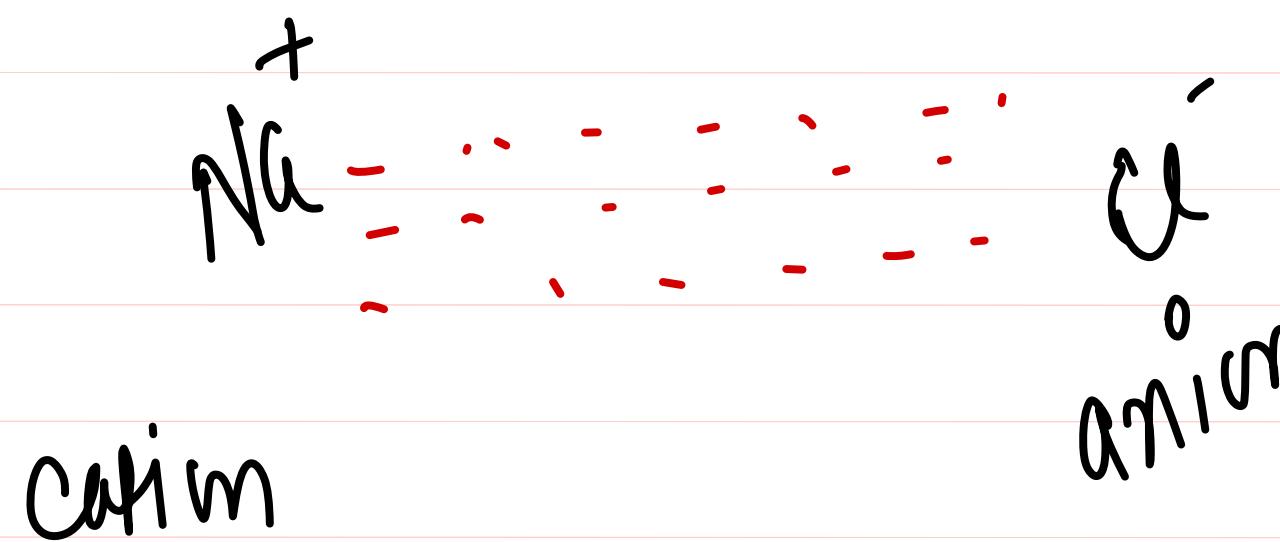
IA and VII A group elements form strong ionic compound.



(Ne configuration) (Ar configuration)

More the distance between two elements in the periodic table more will be the ionic character of the bond.

Total number of electrons lost or gained is called electrovalency.



ionic Bond

(+) \rightarrow favourable
and

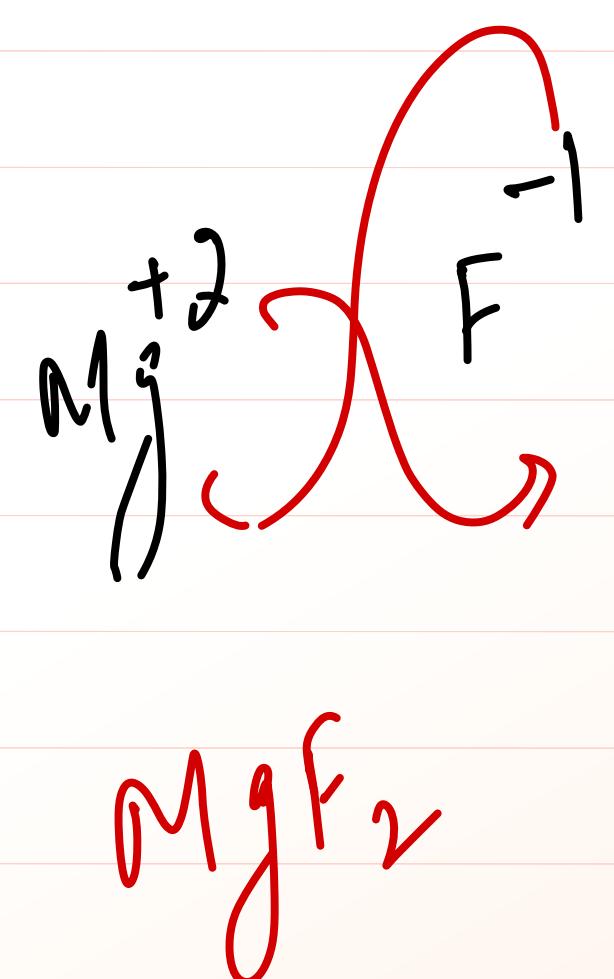
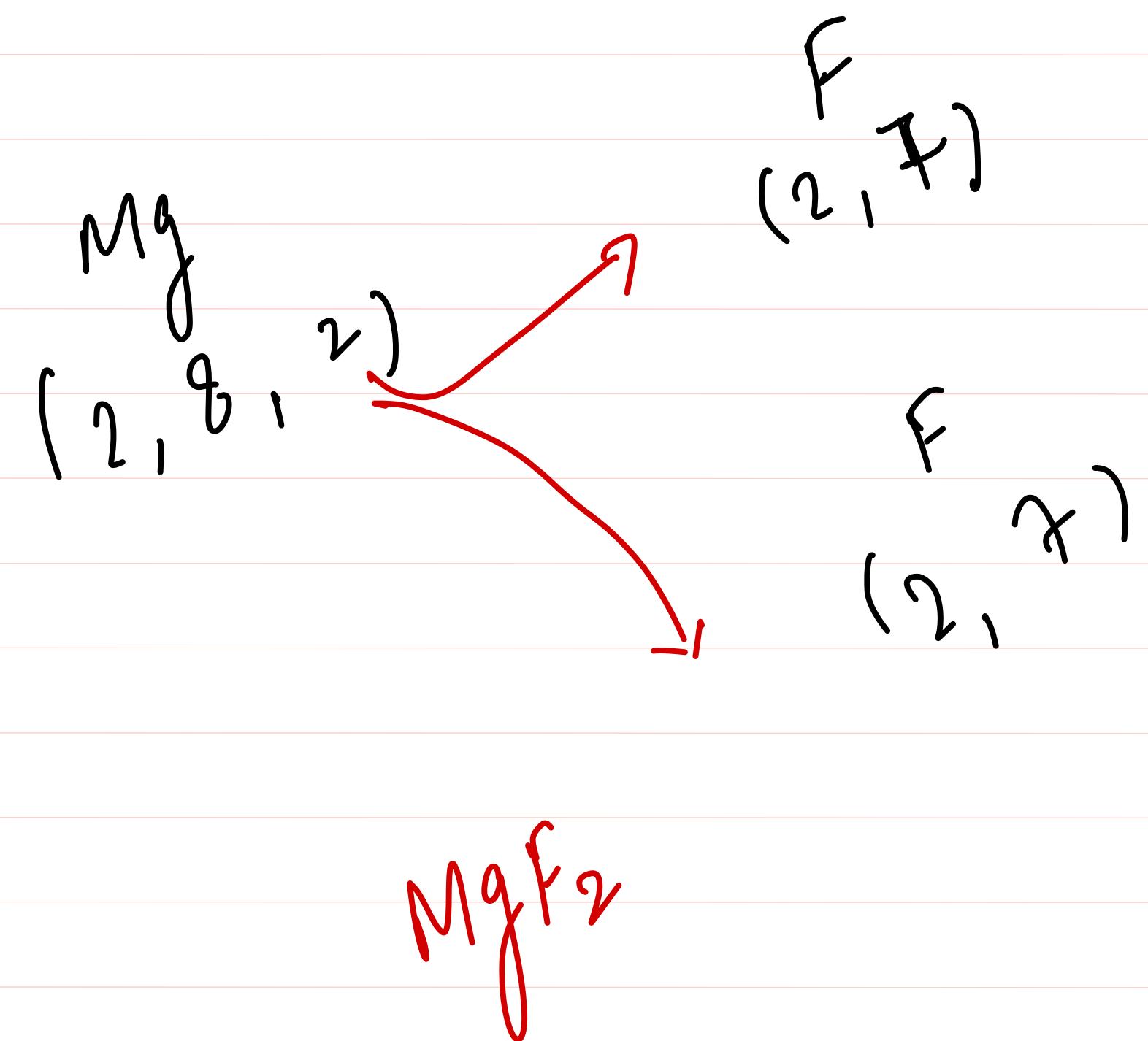
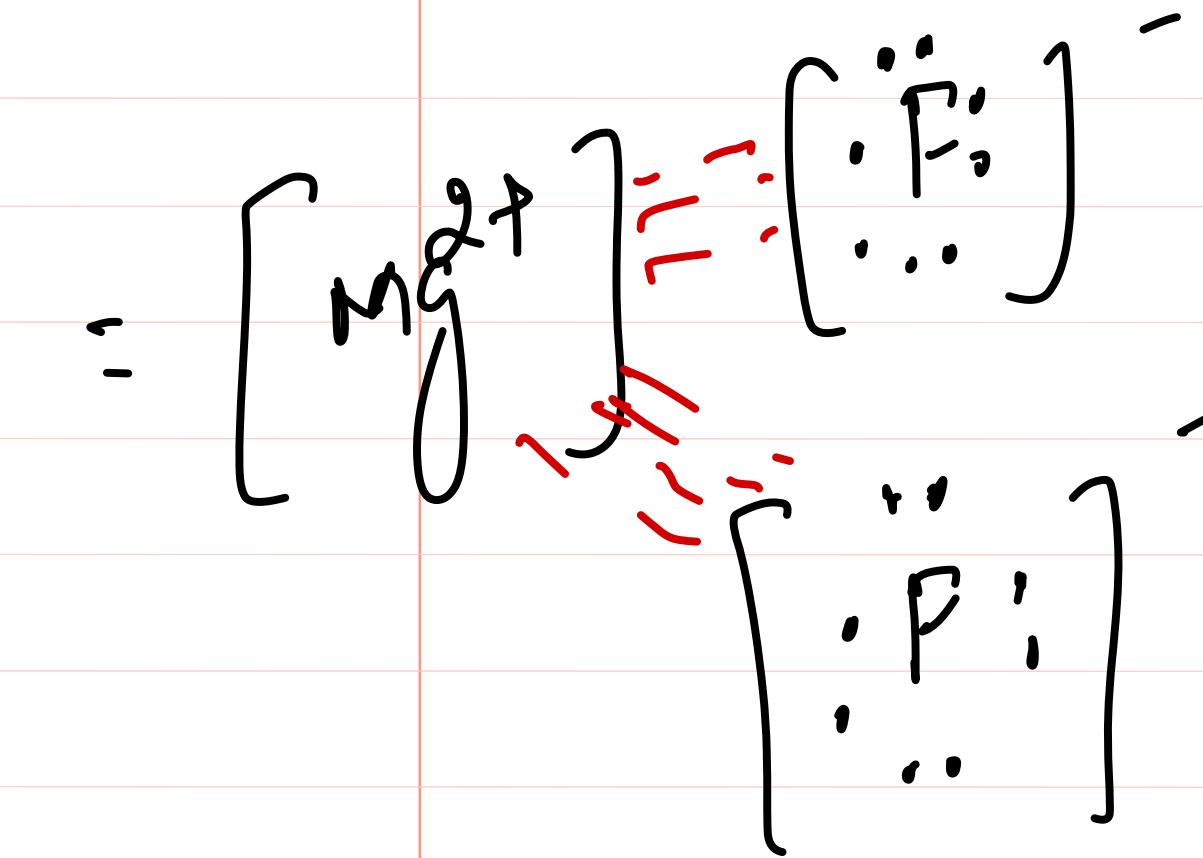
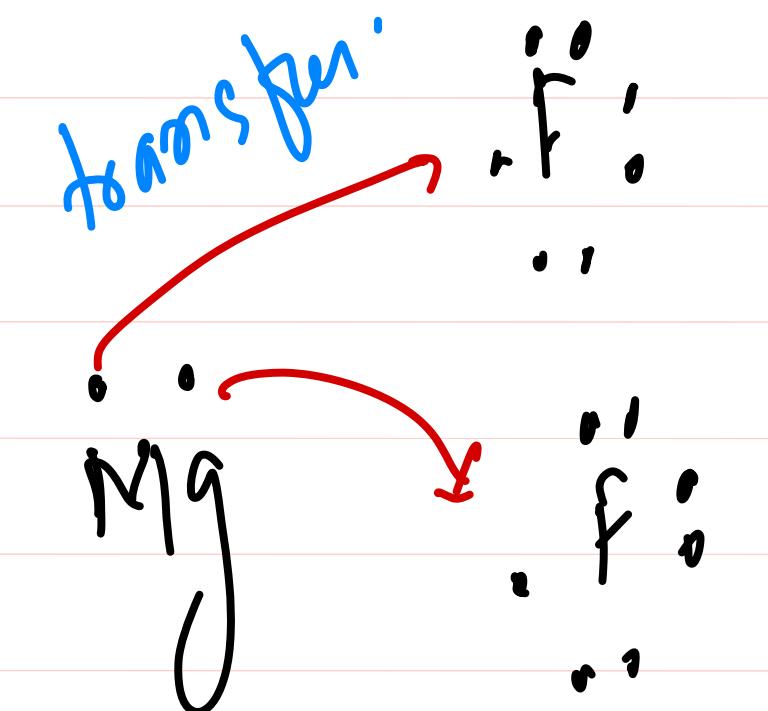
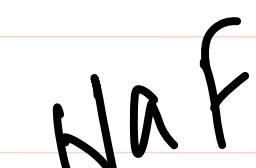
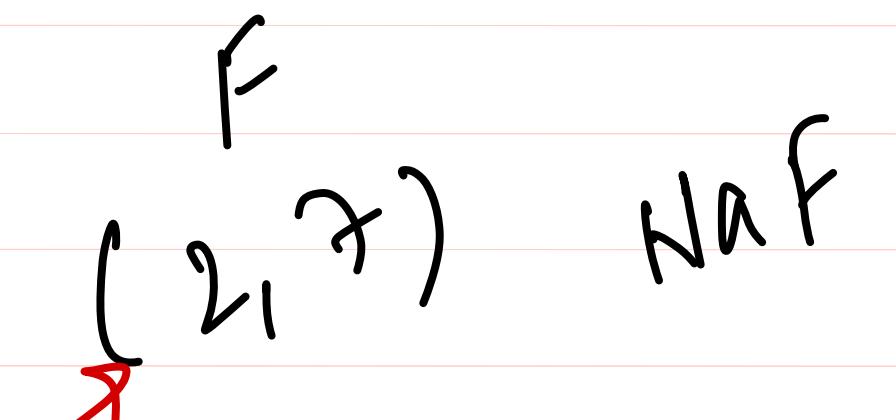
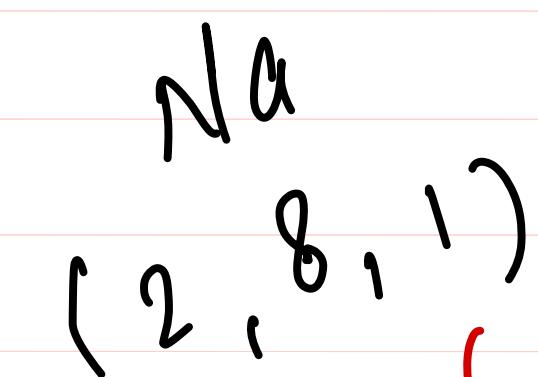
(1) Element
(metal)

IE ↓

(2) Element
(non-metal)

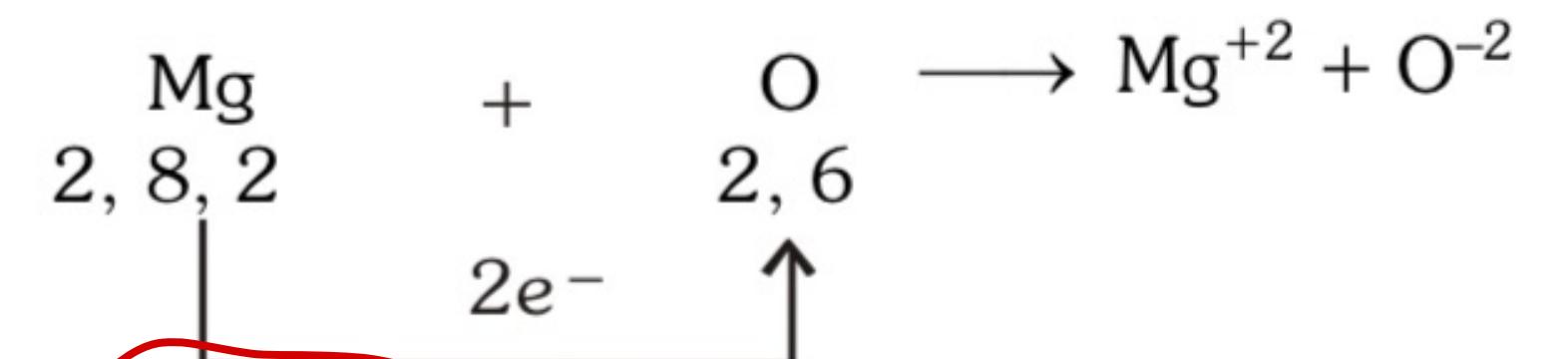
EA ↑

Language
of
chemistry



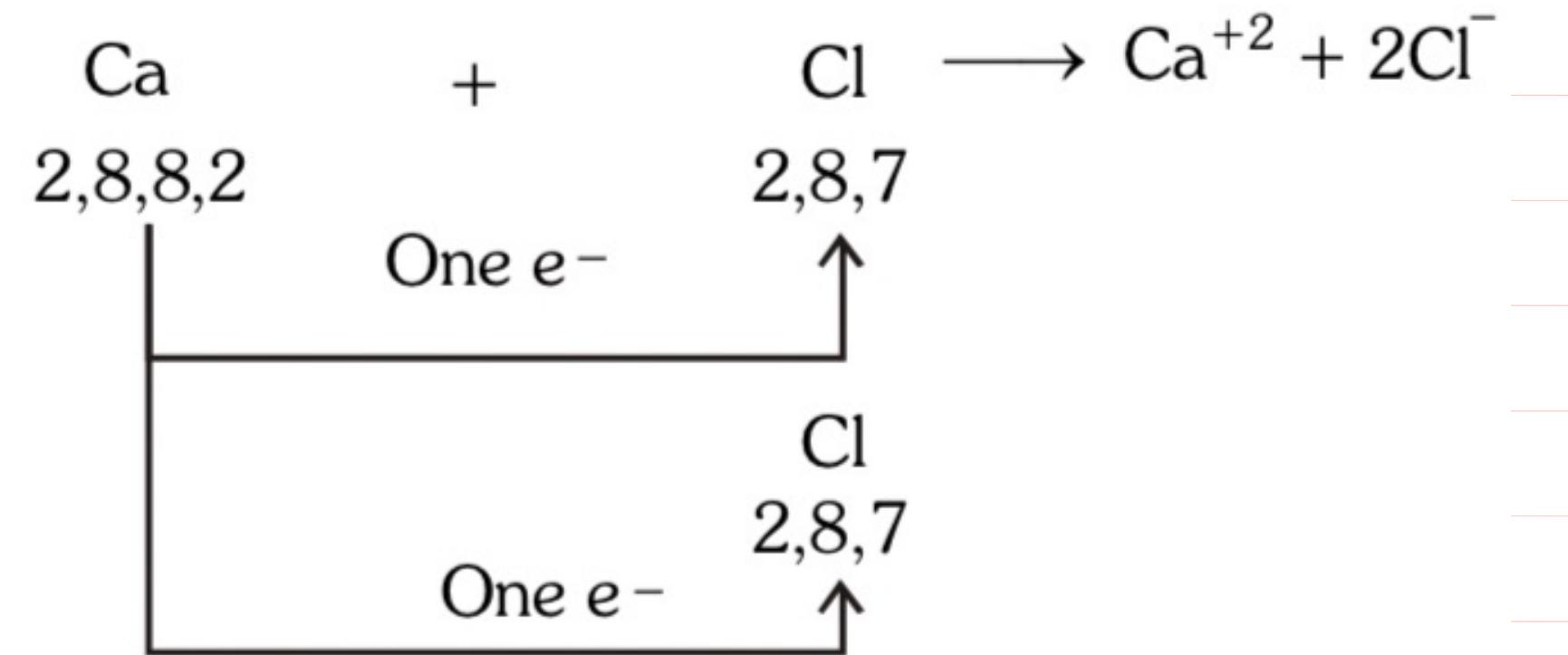
Ex. :

(i)



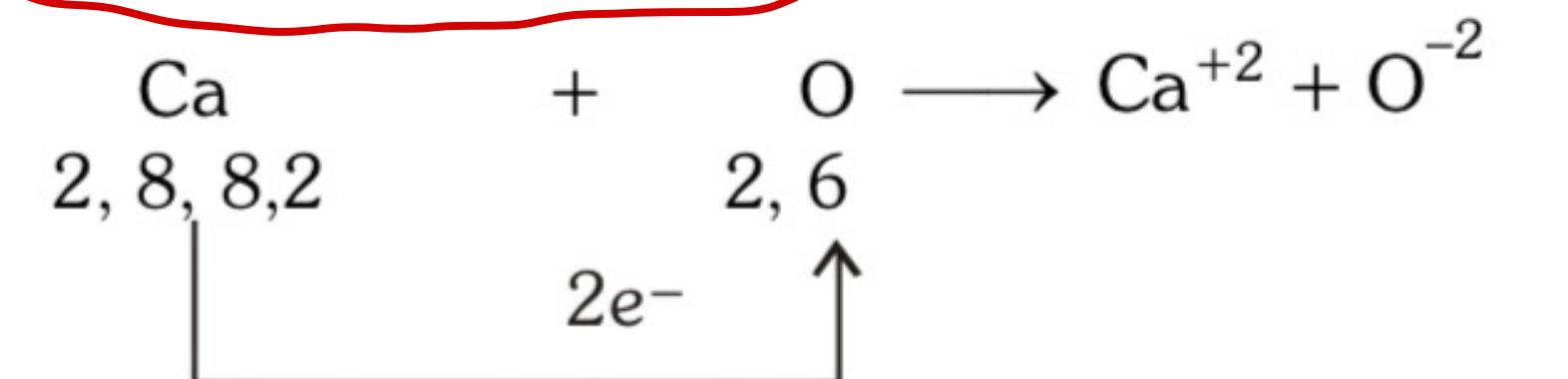
electrovalency of Mg = 2
electrovalency of O = 2

(ii)



electrovalency of Ca = 2
electrovalency of Cl = 1

(iii)



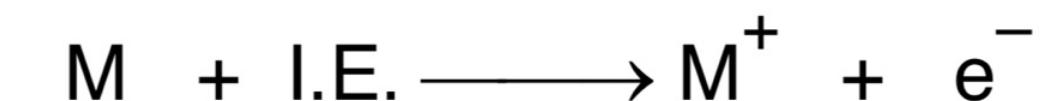
electrovalency of Ca = 2
electrovalency of O = 2

Factors favouring formation of Ionic bonds :



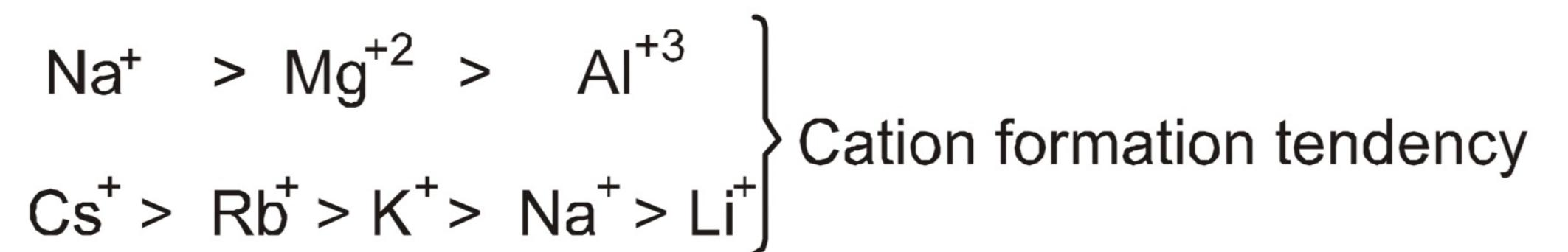
(A) Ionisation energy (IE) :

Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form positive ion or cation is called ionization energy [energy is absorbed so it is an endothermic process]



Less ionisation energy \Rightarrow Greater tendency to form cation.

Example :

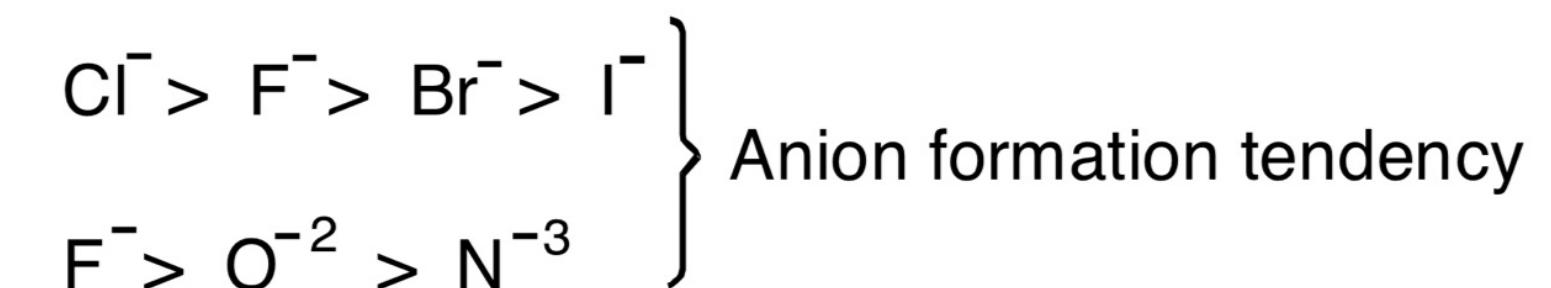


(B) Electron affinity :

Amount of energy released when an electron is added to an isolated gaseous atom to form negative ion or anion is called electron affinity [energy is released so it is an exothermic process]



High electron affinity \Rightarrow Greater tendency to form anions



I m P

(Q) An electrovalent bond or ionic bond is formed between :-

- (A) Two electronegative atoms
- (B) Two metals
- (C) Electropositive and electronegative atoms
- (D) Two electropositive atoms

(Q) Most favourable conditions for electrovalent bonding are :-

- (A) Low ionisation potential of one atom and high electron affinity of the other atom
- (B) High electron affinity and high ionisation potential of both the atoms
- (C) Low electron affinity and low ionisation potential of both the atoms
- (D) High ionisation potential of one atom and low electron affinity of the other atom

The electronegativity of cesium is 0.7 and that of fluorine is 4.0. The bond formed between the two is
 (A) Covalent (B) Electrovalent/ionic (C) Coordinate (D) Metallic

CSF

CS

Electrovalent bond or ionic bond is formed by :-

- (A) Sharing of electrons (B) Donation of electrons (C) Transfer of electrons (D) None of these

CS

Element X is strongly electropositive and Y is strongly electronegative. Both are univalent. The compound formed would be :

- (A) $X^+ Y^-$ (B) $X - Y$

- (C) $X^- Y^+$

- (D) $X \rightarrow Y$

Covalent coordinate

Element A has 3 electrons in the outermost orbit and element B has 6 electrons in the outermost orbit. The formula of the compound formed between A and B would be :-

- (A) A_2B_3

- (B) A_2B_6

- (C) A_2B

- (D) A_3B_2

Compound of a metal 'M' is M_2O_3 , The formula of its nitride will be:-

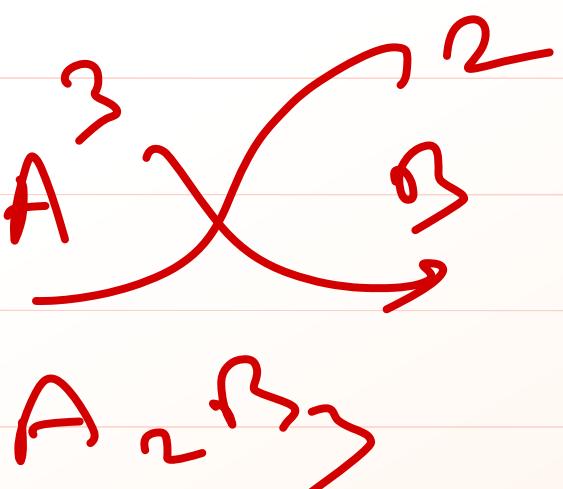
- (A) M_3N

- (B) MN

- (C) M_3N_2

- (D) M_2N_3

Bonding 1



Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.

Force of attraction is equal in all direction so ionic bond is non-directional.

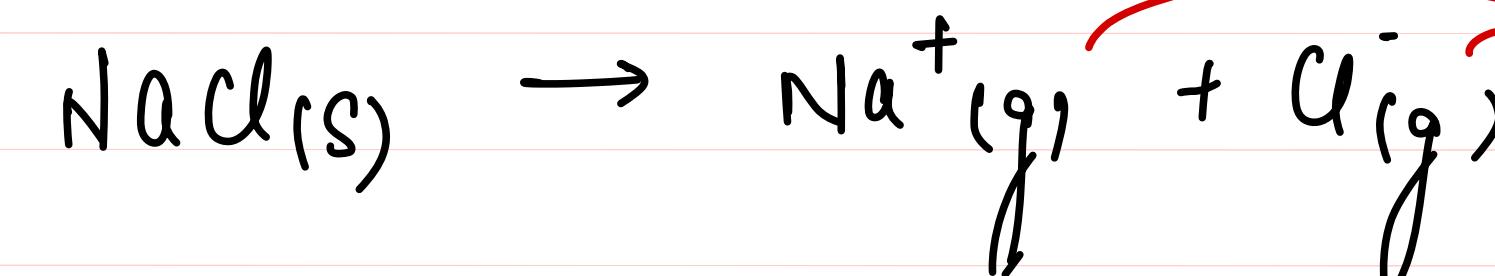
A definite three dimensional structure called crystal lattice is formed .

Energy released during the formation of one mole crystal lattice is called lattice energy.

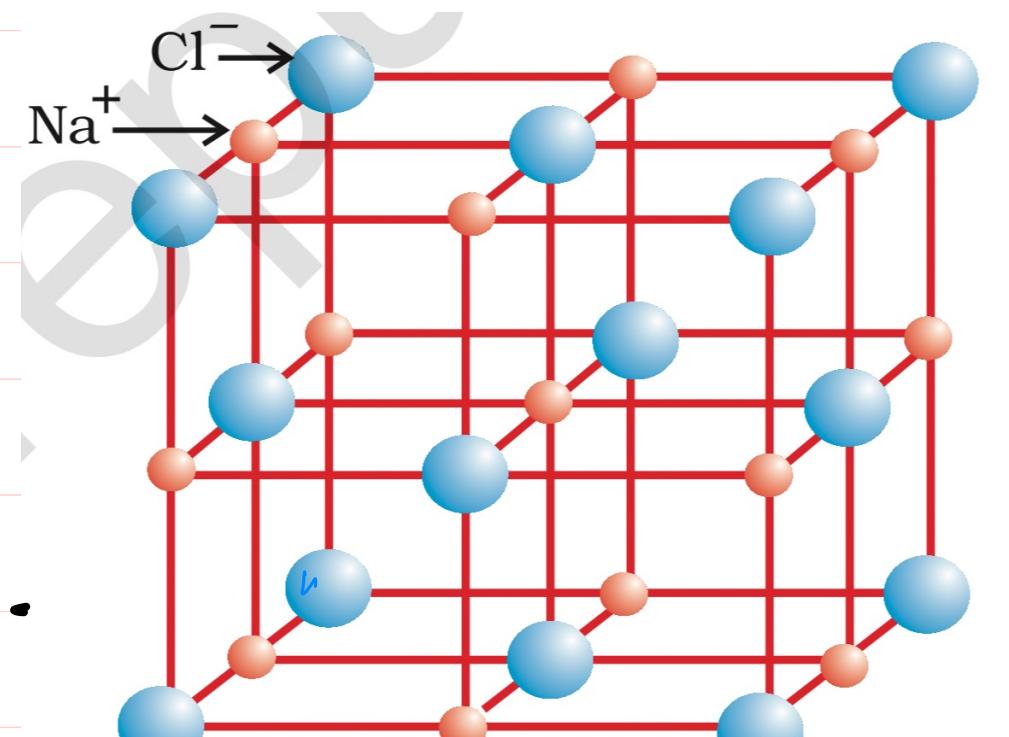
Lattice Enthalpy

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

For example : The L.E of NaCl is 788 kJ/mol.



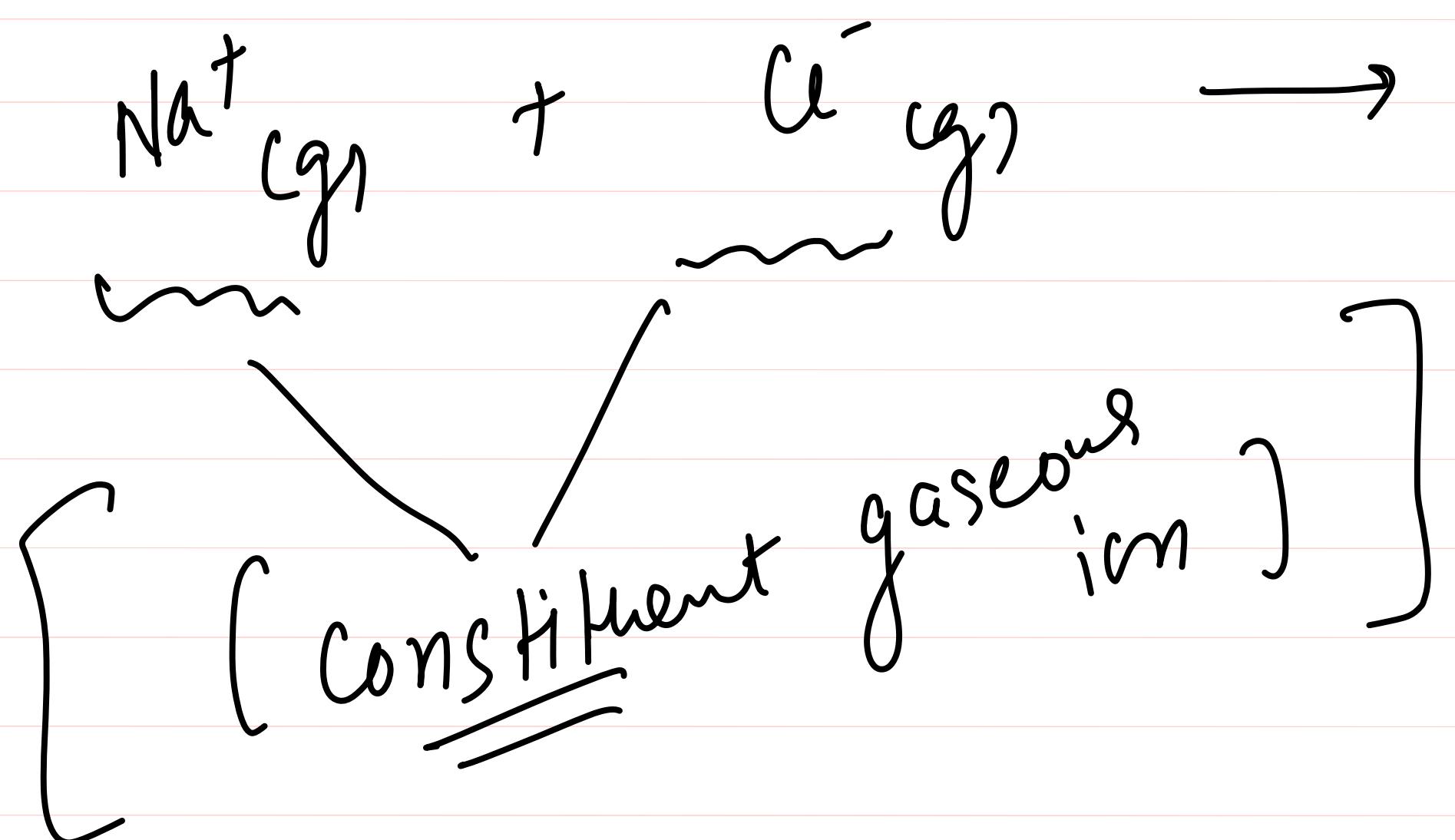
Separate to infinite distance
~ energy required



(Q) How to calculate lattice energy?

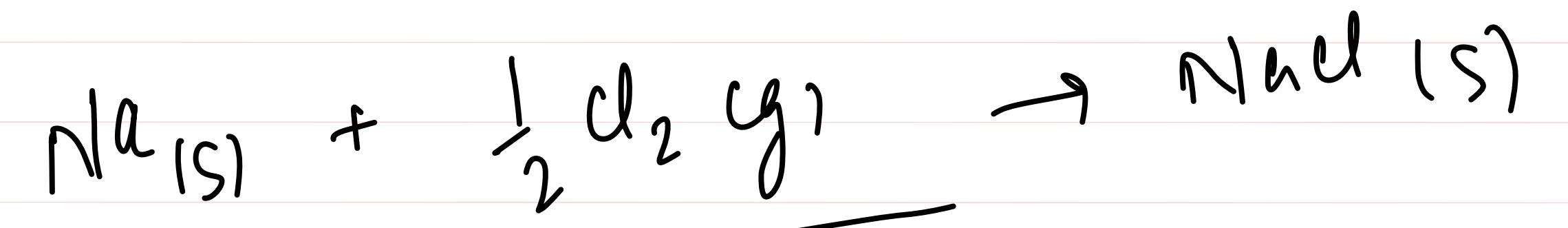
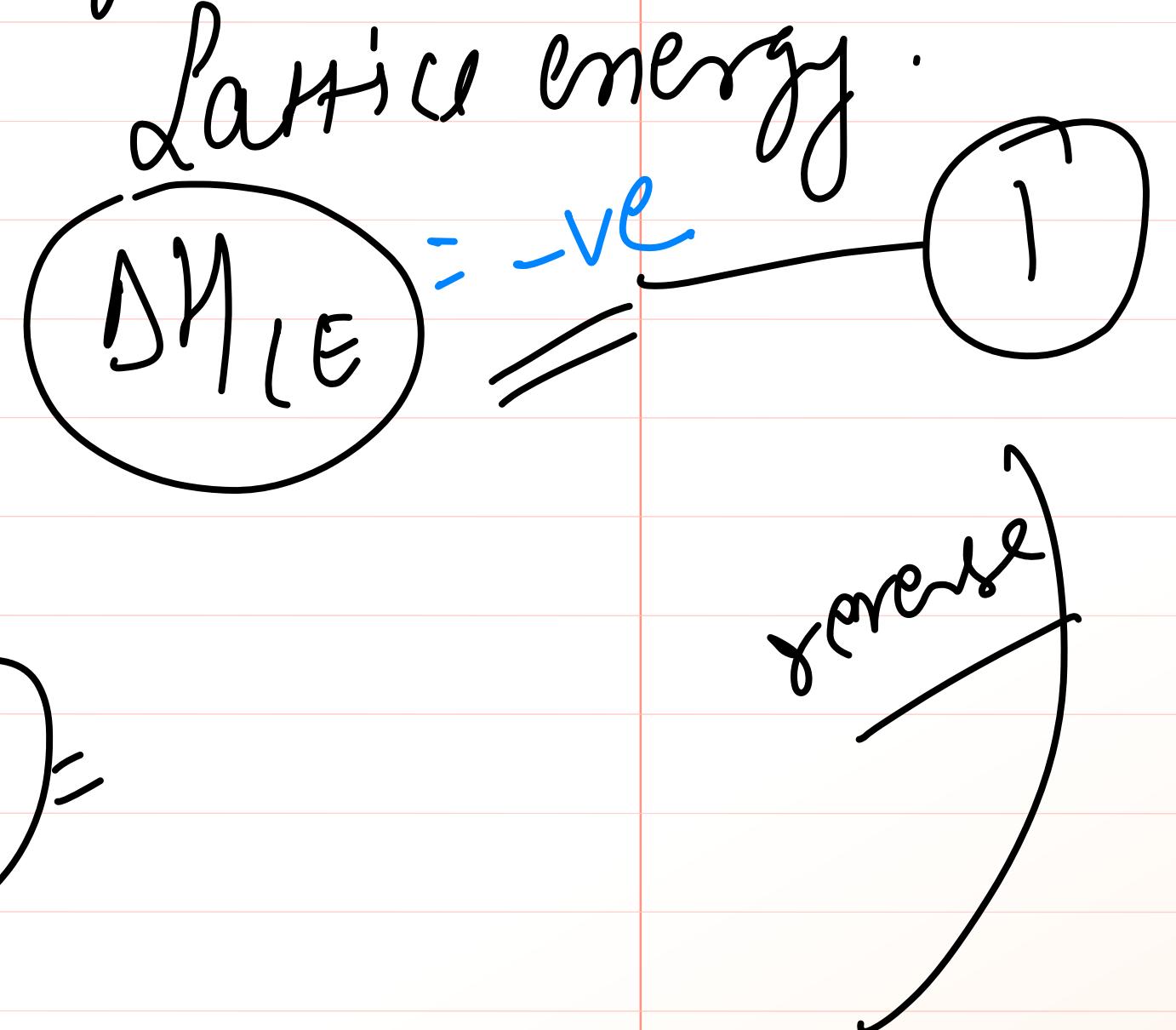
Ans:) Born Haber cycle (BHC)

Bond formation;

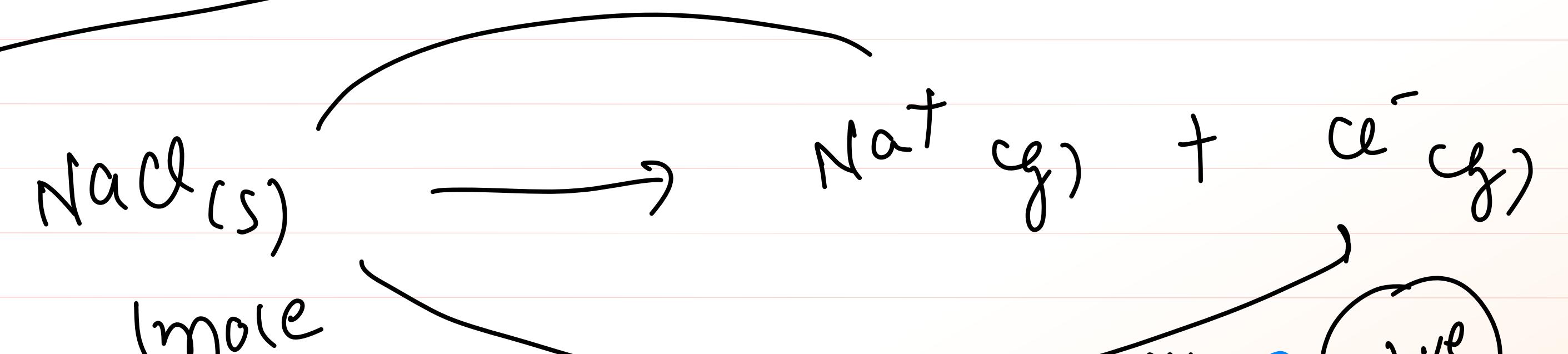


NaCl (s)
(mole)

Crystal lattice.



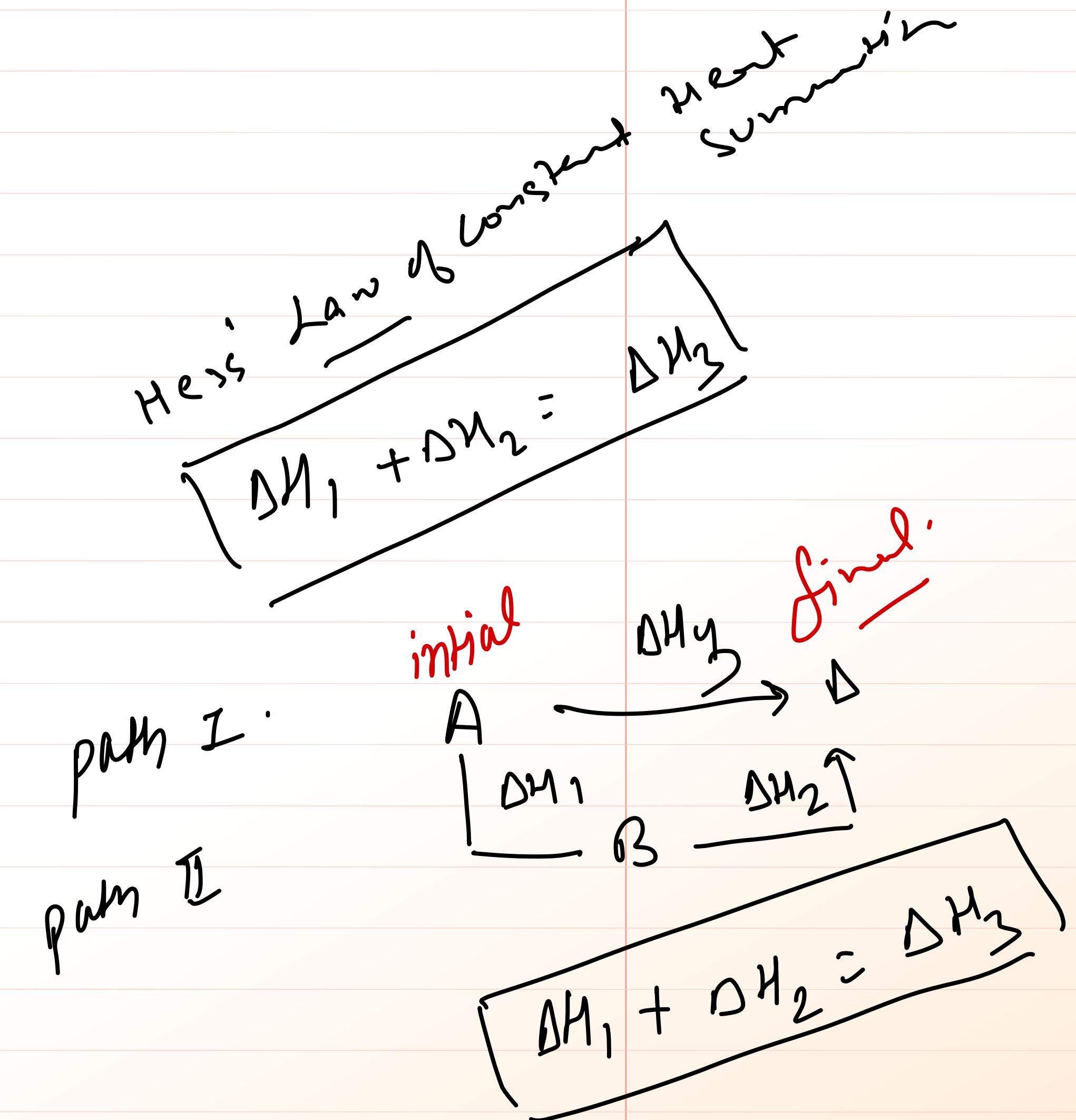
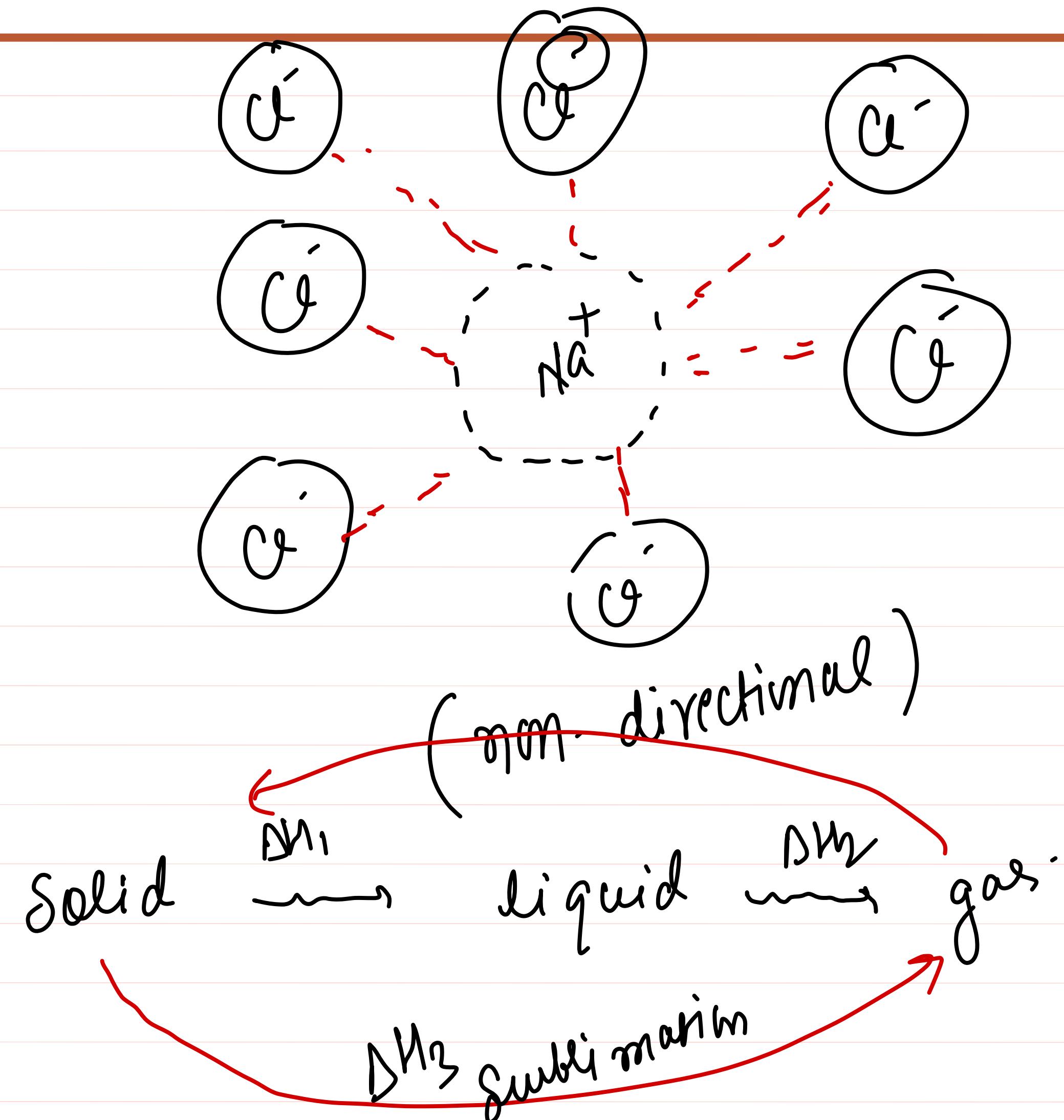
ΔH =



ΔH_{v.E} = +ve

Lattice energy.

2



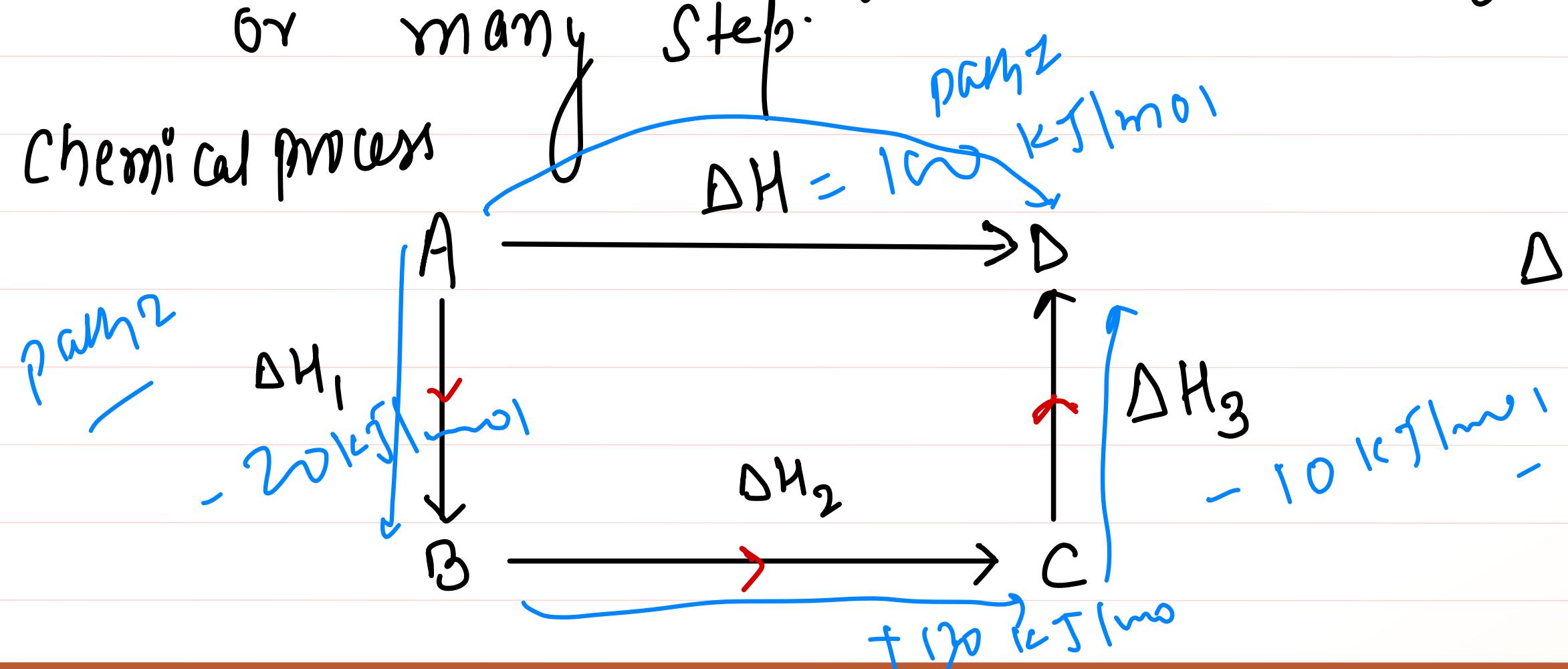
Determination of lattice Energy

[Born Haber cycle] indirect method

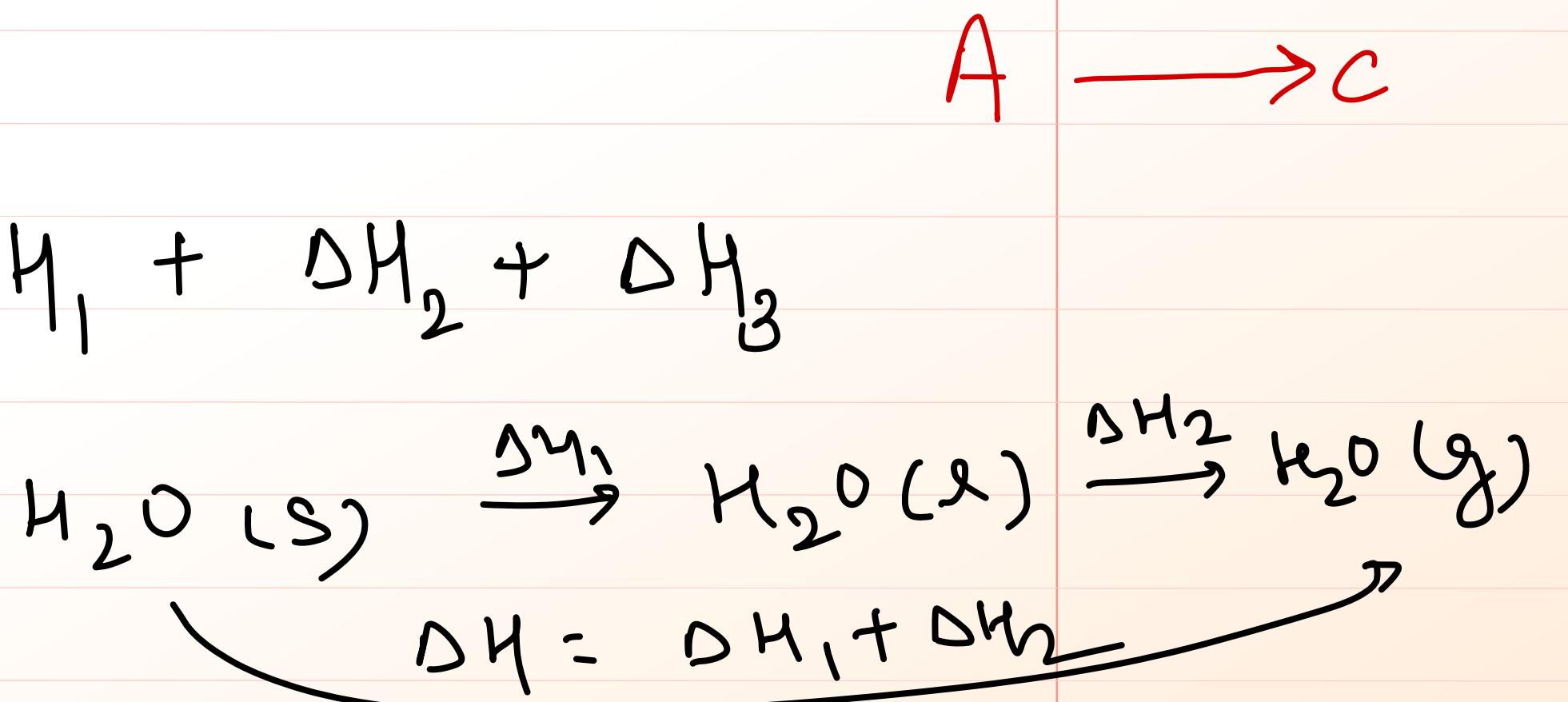
- * it inter relates the various energies involved during the formation of ionic compound.
- * it is thermochemical cycle based on Hess's law of Constant Heat Summation

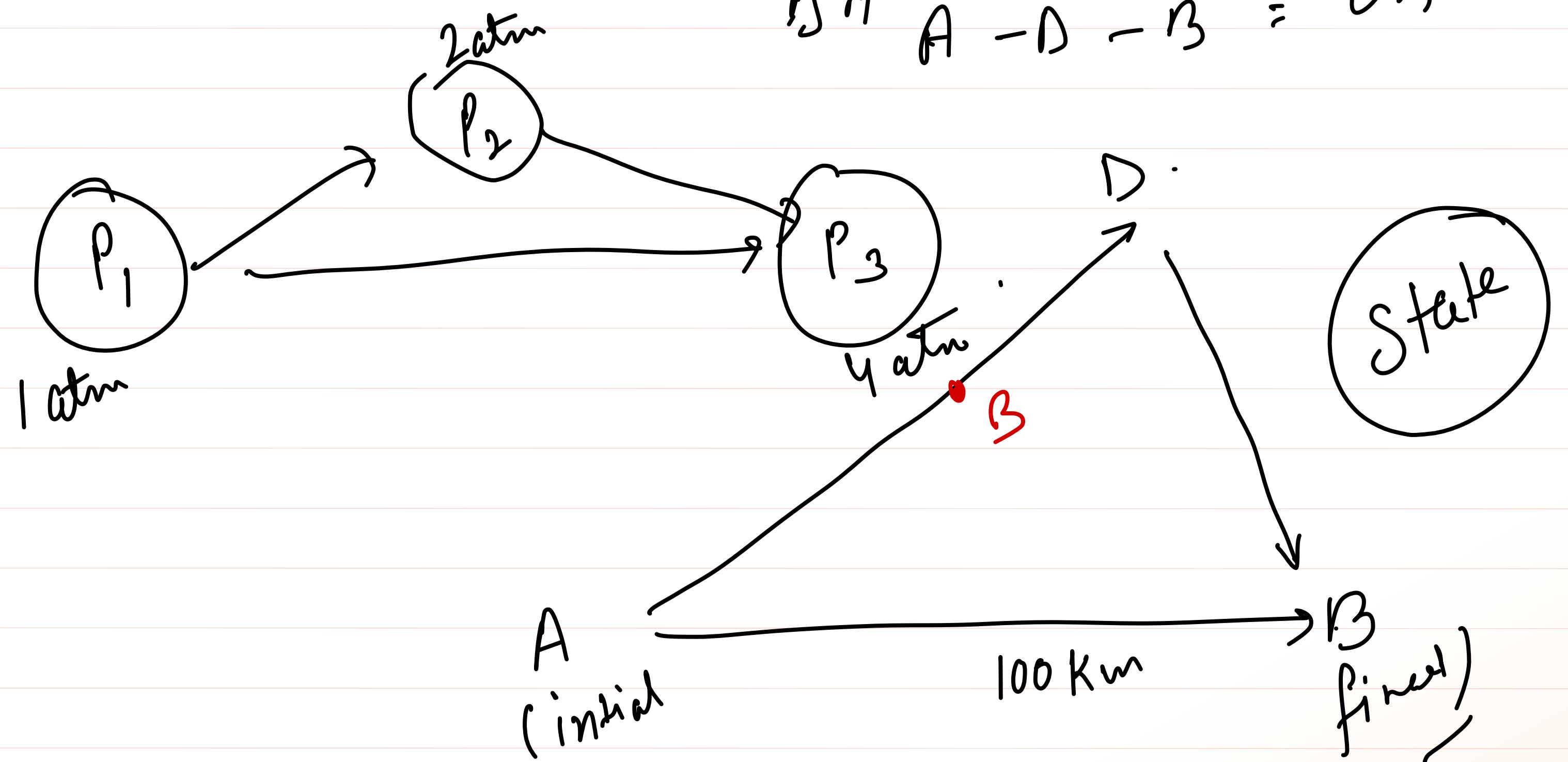
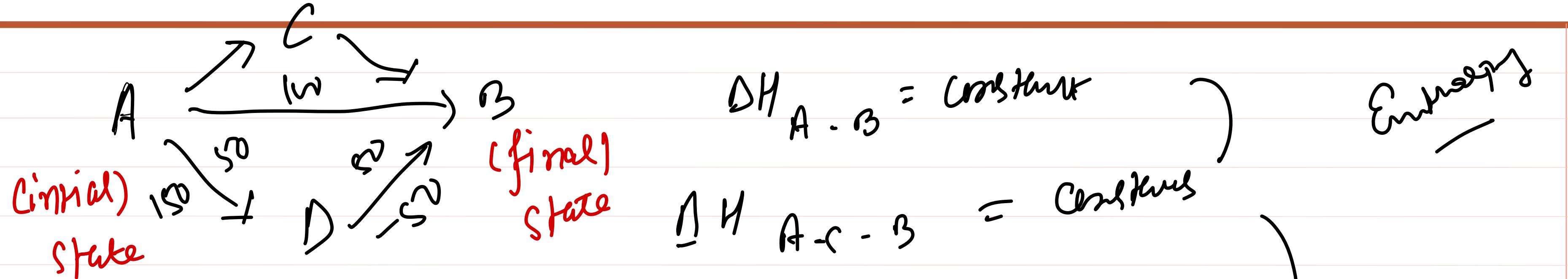
Hess's law:

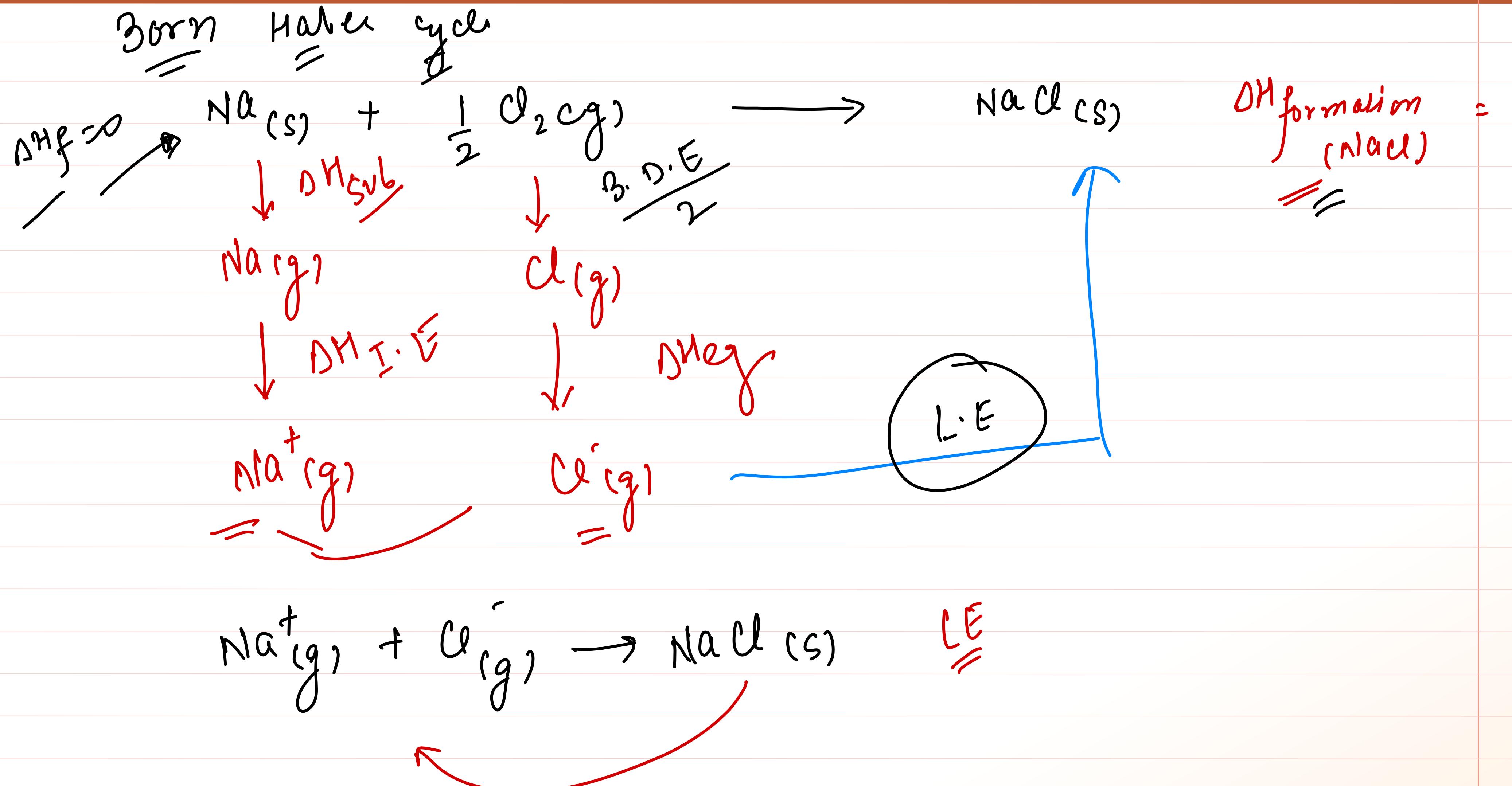
* Hess's law is the net enthalpy change of a chemical reaction or of any process always remains same whether the reaction takes place in one step or many steps.



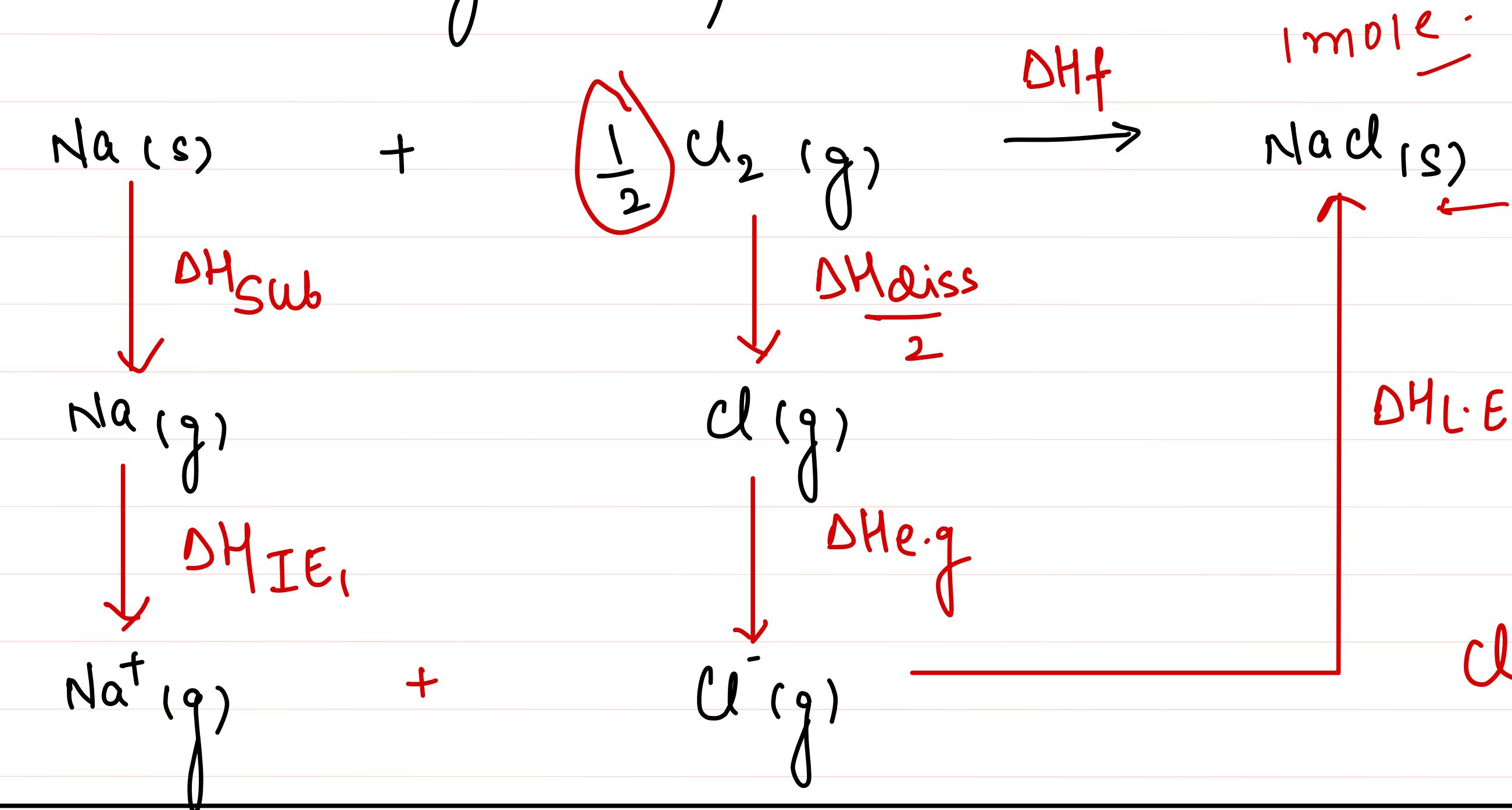
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$







Born Haber cycle (for NaCl)



(ΔH_f = Enthalpy of formation 1mole)

(always ΔH_f is for 1 mole of ionic compound)

ΔH_f = Enthalpy of formation-
1mole of Compound from its Standard State.

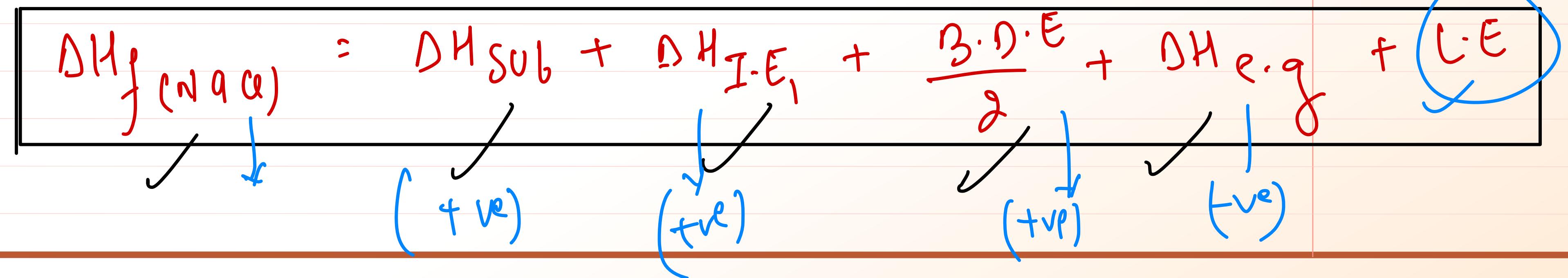
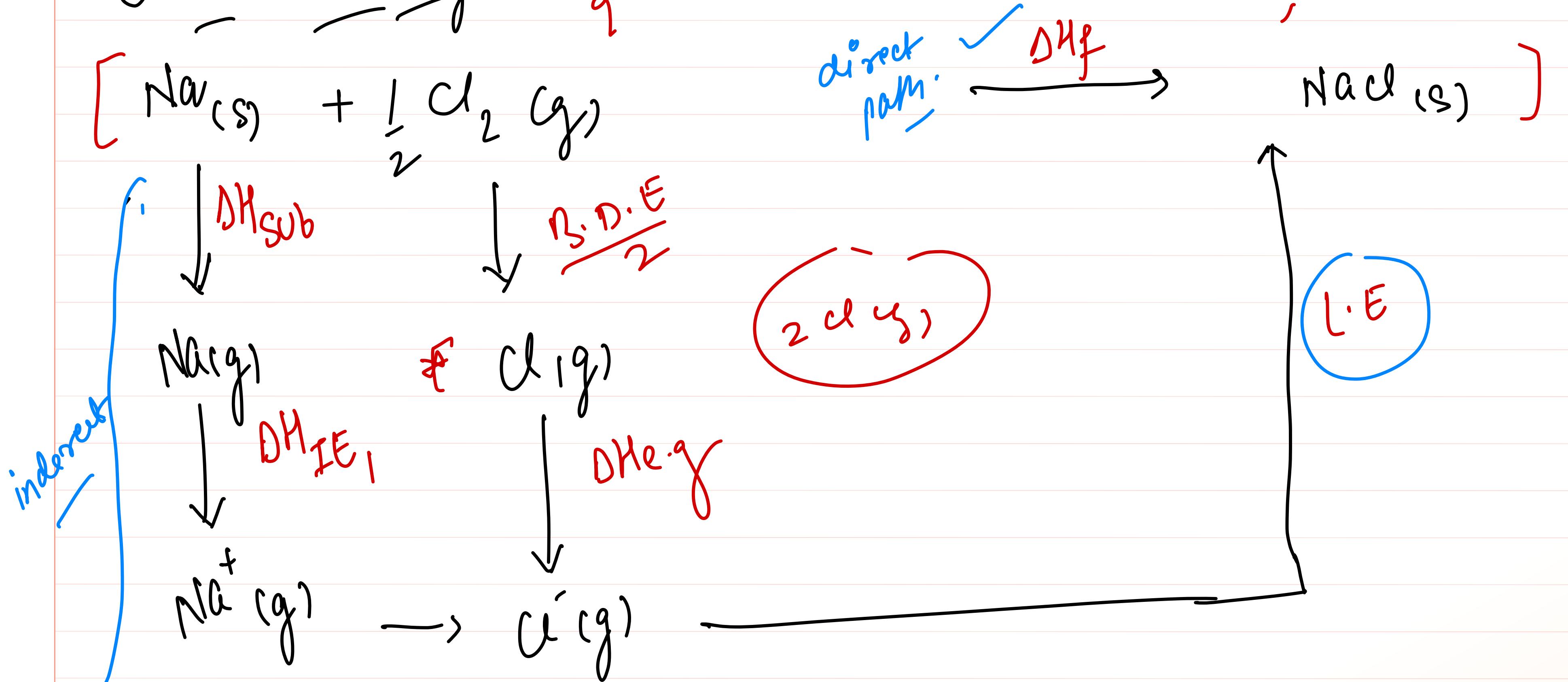
$$\Delta H_f = \Delta H_{\text{Sub}} + \Delta H_{\text{IE},1} + \frac{\Delta H_{\text{diss}}}{2} + \Delta H_{\text{e.g}} + \Delta H_{\text{L.E}}$$

ΔH_f = 1mole ionic compound.
Standard element Na(s) Cl₂(g)

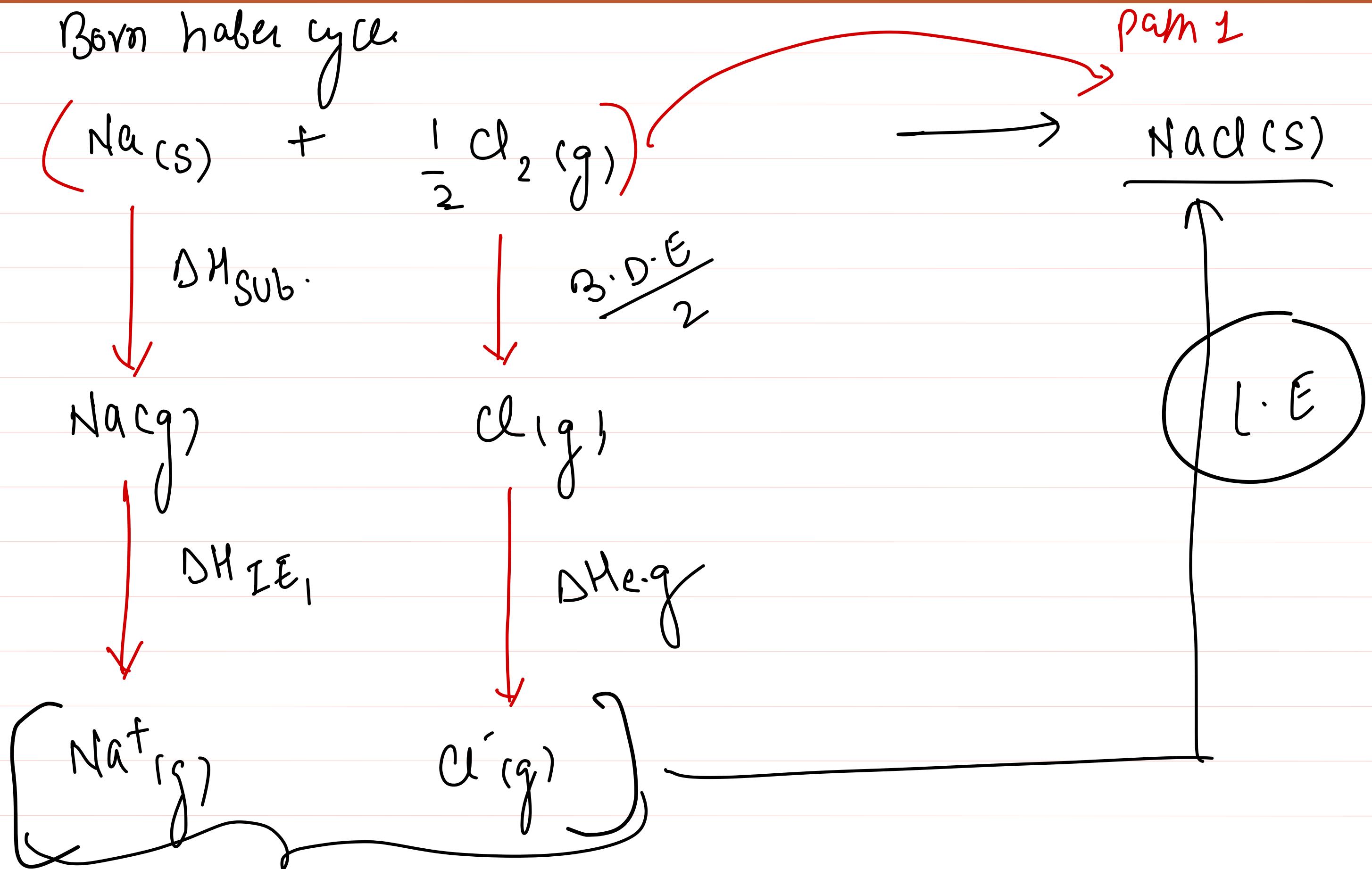
using Hess's Law of Constant Heat Summation

$$= \Delta H_{\text{diss}}$$

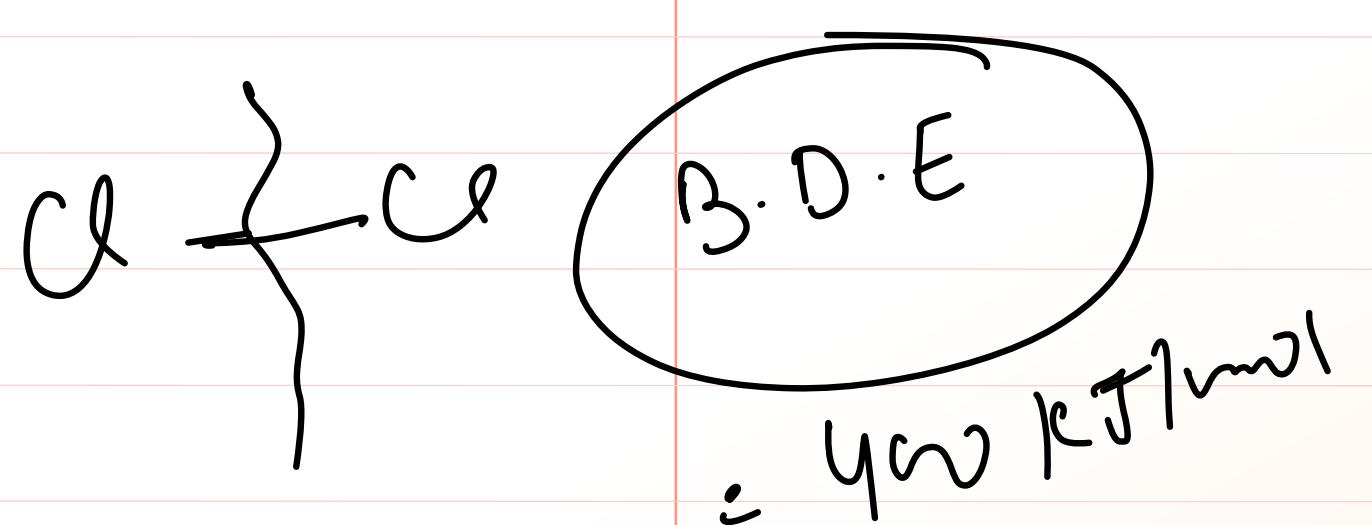
Born - haber cycle: { to calculate lattice energy? } all



Born haber cycle



ΔH_f : Enthalpy of formation
constituent element standard form.



$$\Delta H_f = \Delta H_{\text{Sub.}} + \Delta H_{\text{I.E.}} + \frac{3 \cdot \text{D.E.}}{2} + \Delta H_{\text{E.g.}} + \text{L.E.}$$

(Q) Use Born - Haber cycle to calculate the lattice energy of NaCl

Given data :

$$I^{\text{st}} \text{ I.E of Na} = 460 \text{ kJ/mol} \checkmark$$

~~$$2^{\text{nd}} \text{ I.E of Na} = 4560 \text{ kJ/mol}$$~~

$$\Delta H_{\text{diss}} \text{ Na} = -50 \text{ kJ/mol}$$

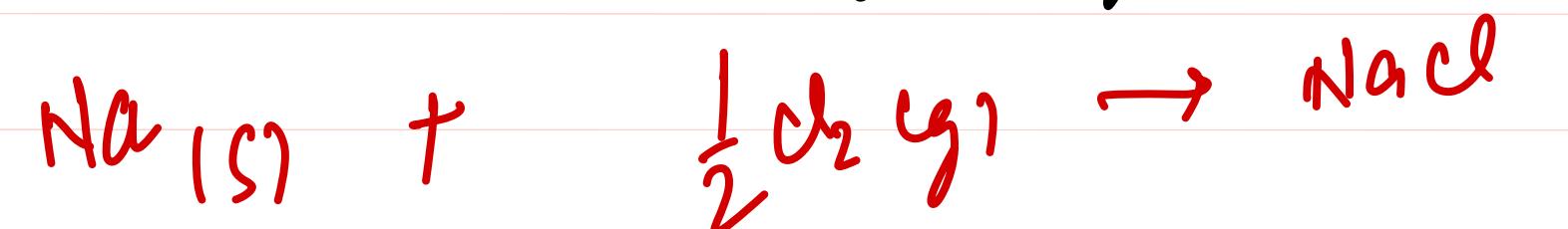
$$\Delta H_f \text{ (Cl)} = 350 \text{ kJ/mol}$$

$$\Delta H_{\text{diss}} \text{ Cl}_2 = -350 \text{ kJ/mol}$$

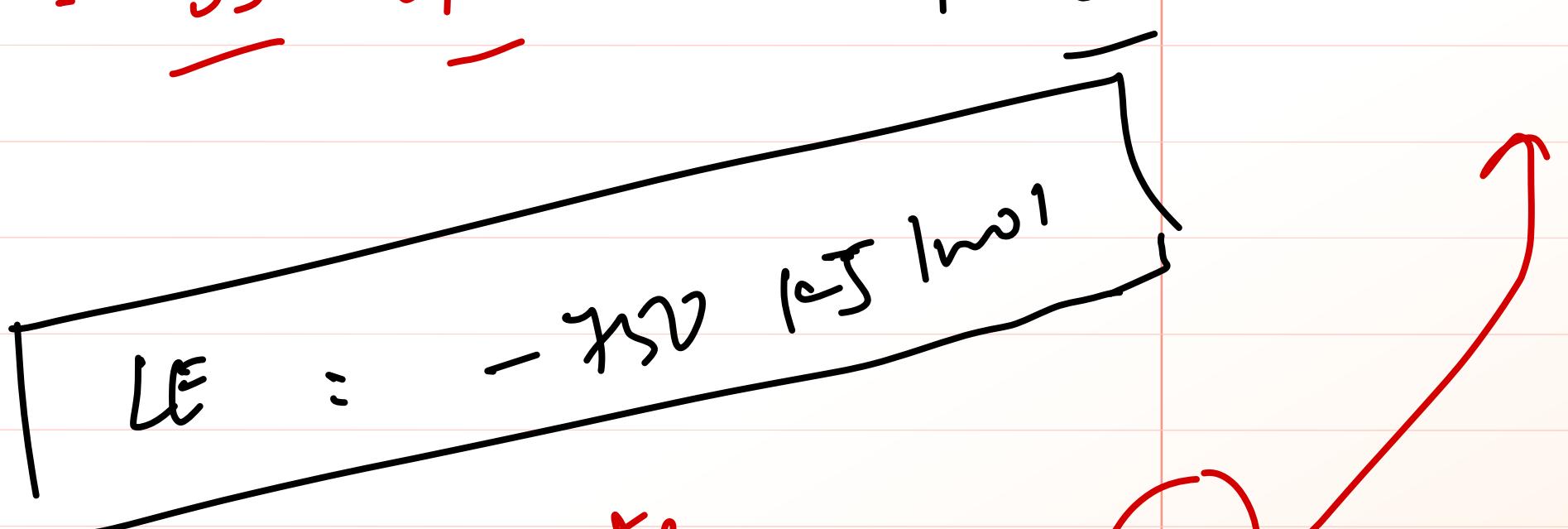
$$(\Delta H)_{\text{B.D.E}} \text{ Cl}_2 = 240 \text{ kJ/mol}$$

$$\Delta H_{\text{sub}} \text{ (Na)} = 110 \text{ kJ/mol} \checkmark$$

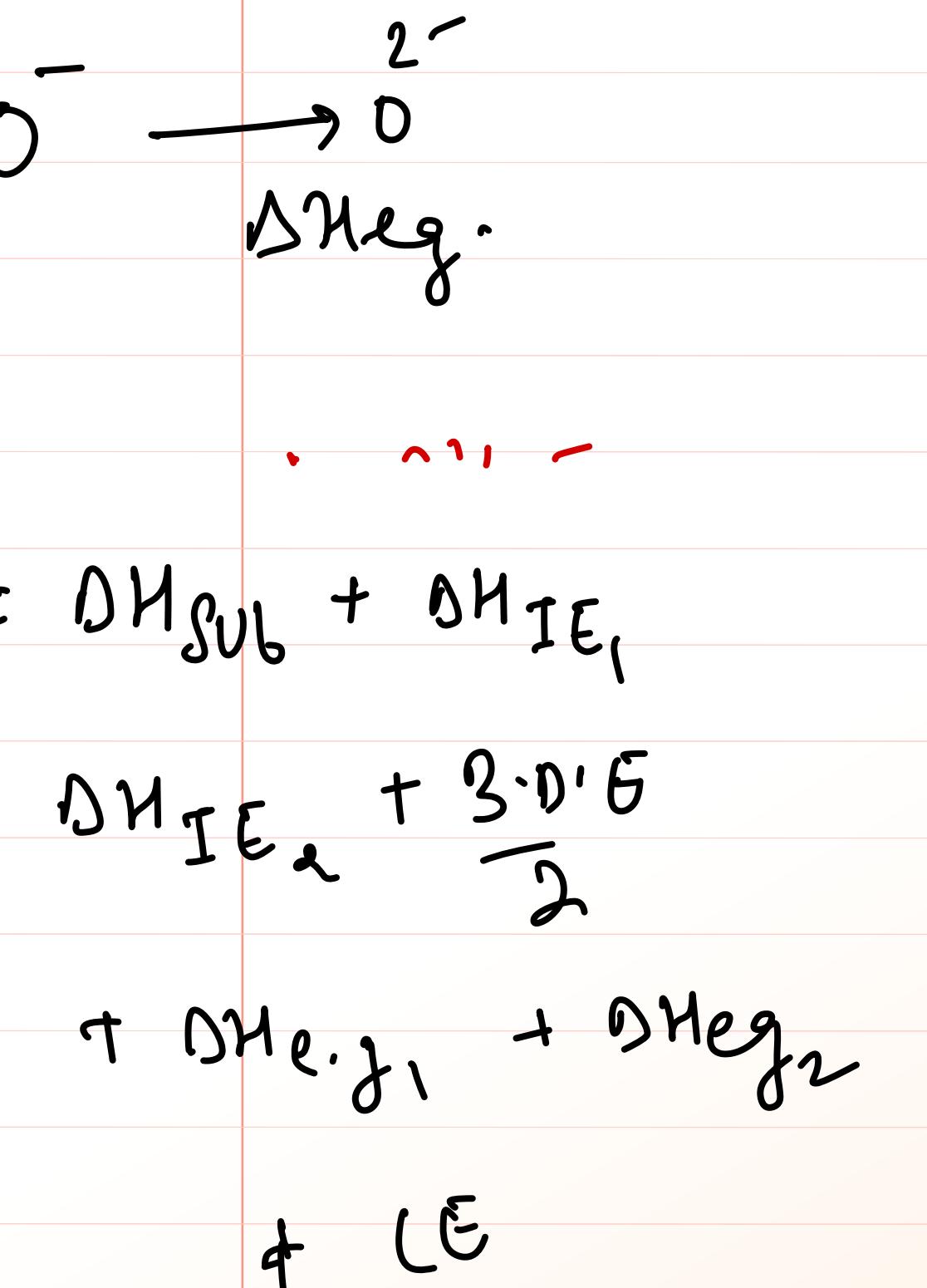
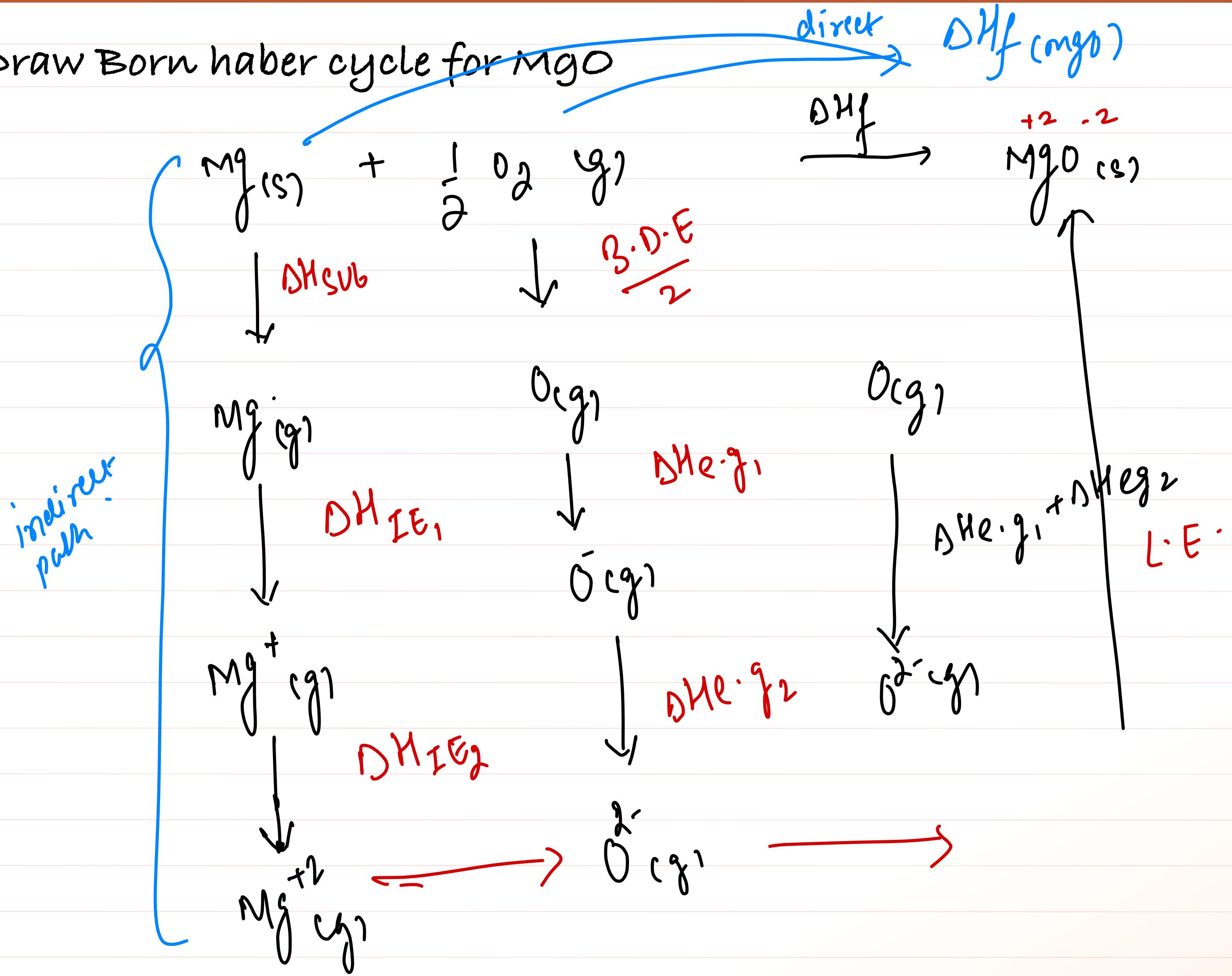
$$\Delta H_f^\circ \text{ (NaCl)} = -410 \text{ kJ/mol}$$



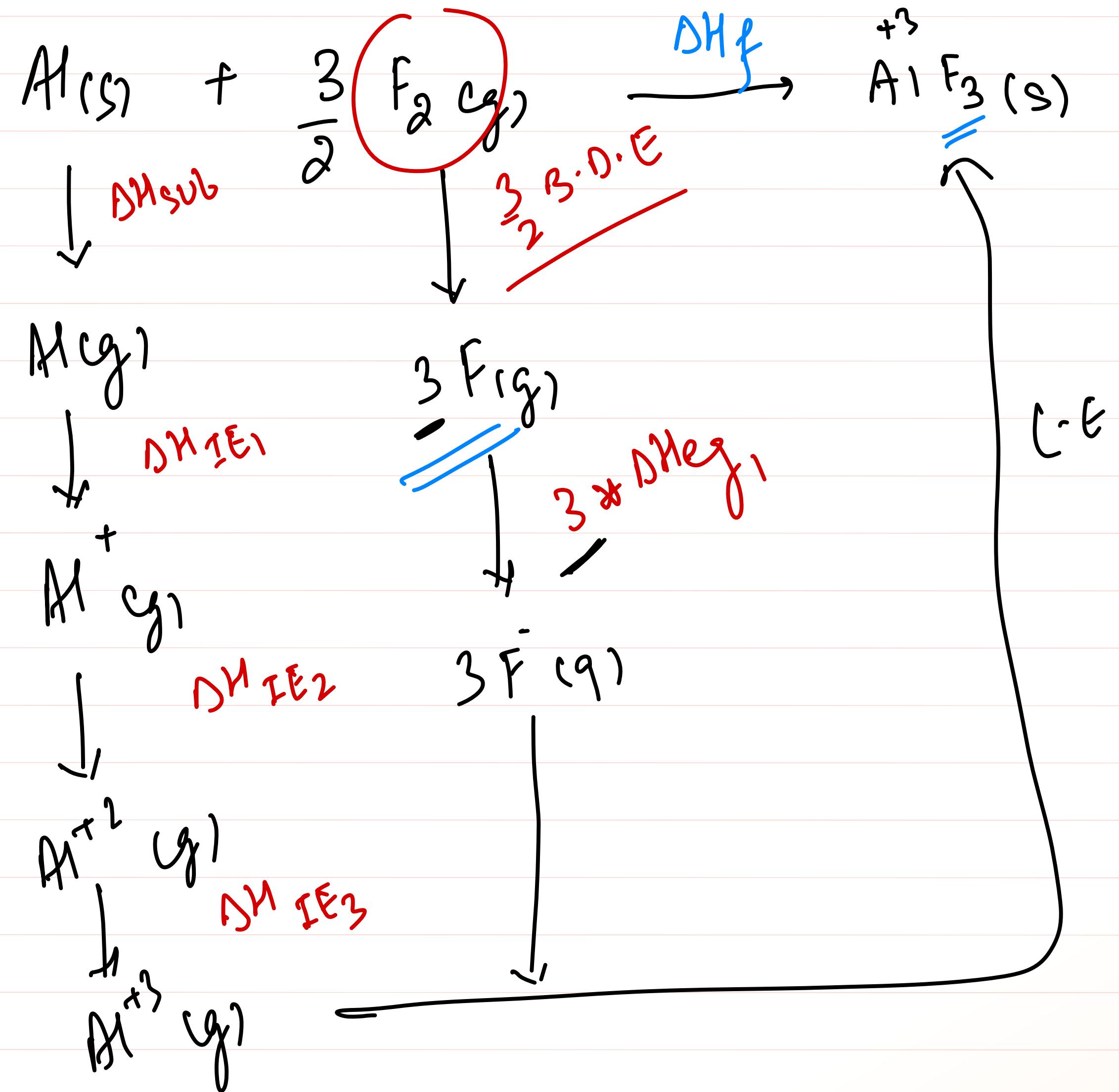
$$\Delta H_f^\circ \text{ (NaCl)} = 110 + 460 \\ + 2 \times 110 + (-350)$$



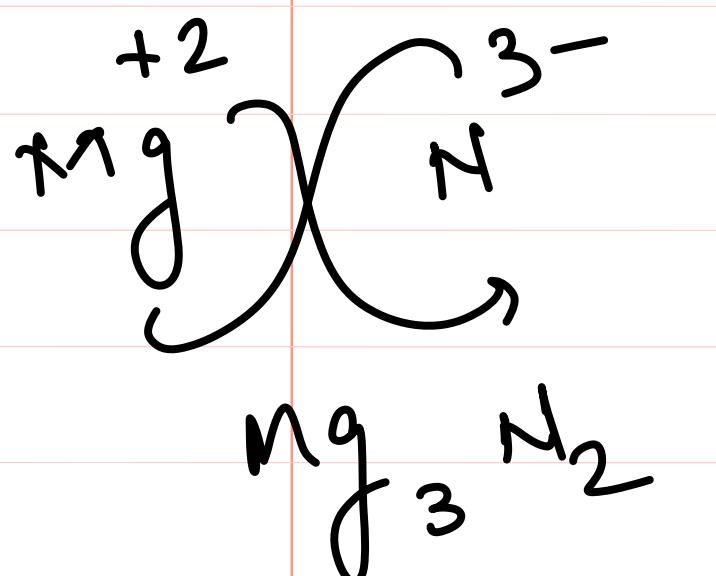
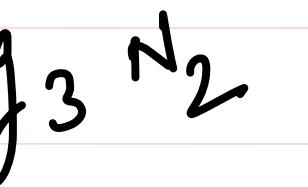
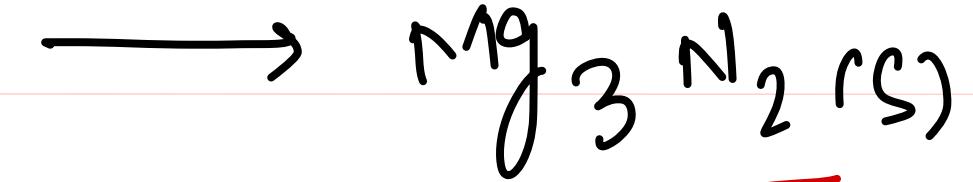
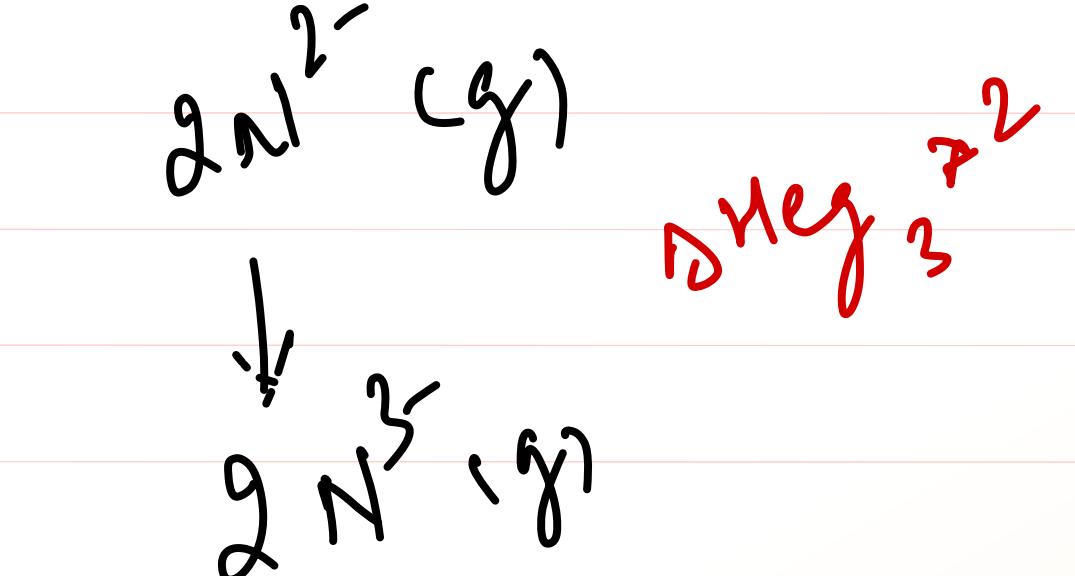
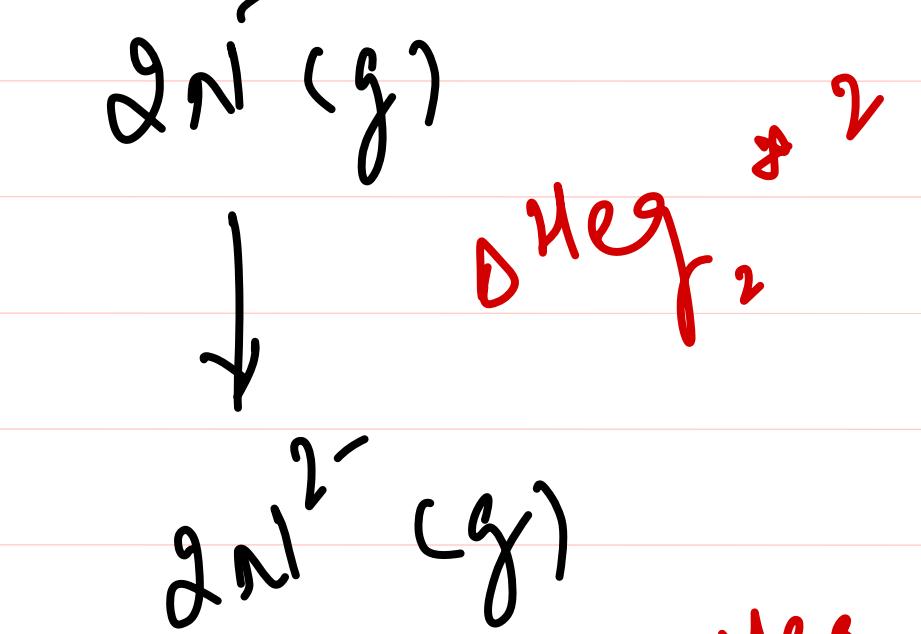
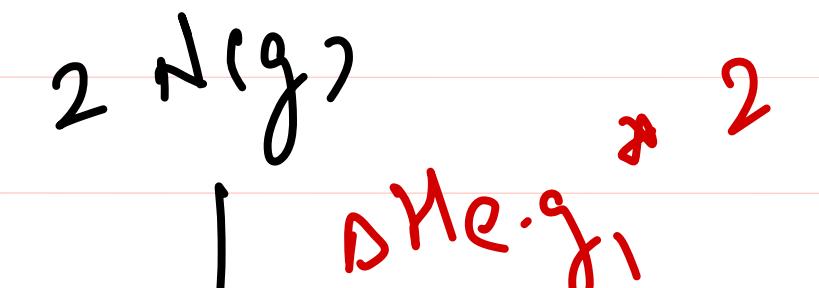
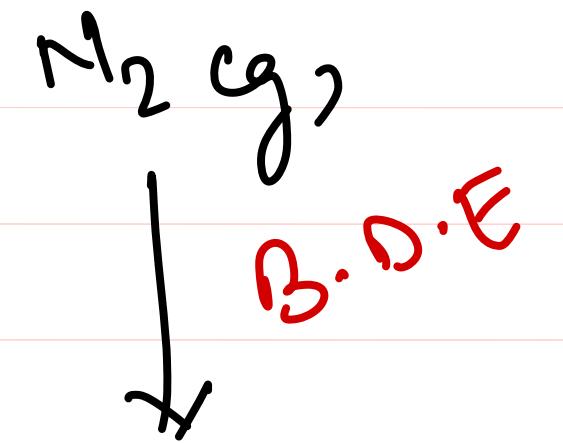
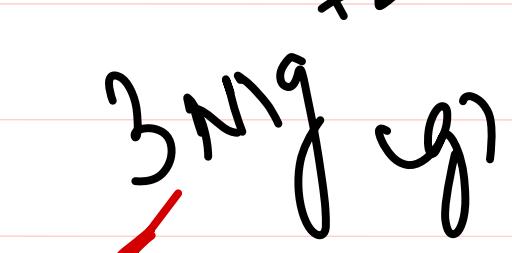
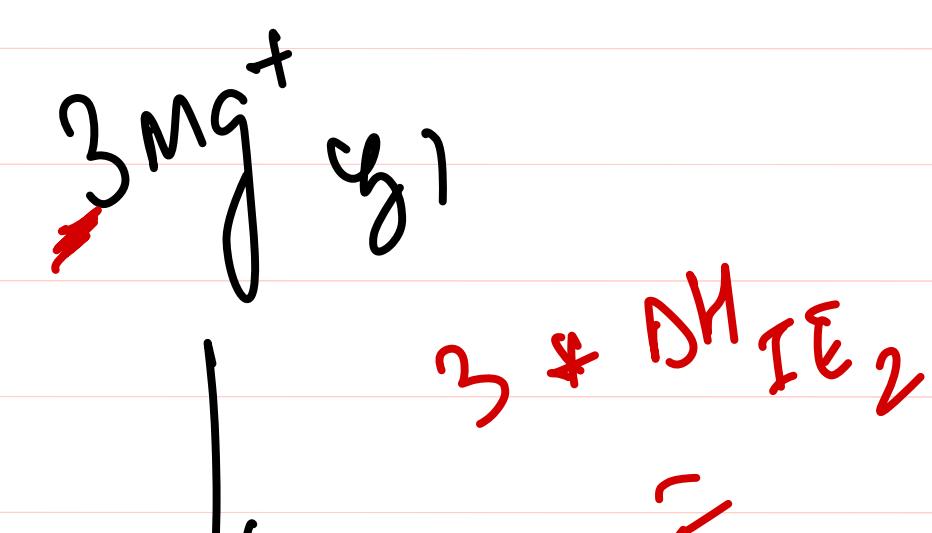
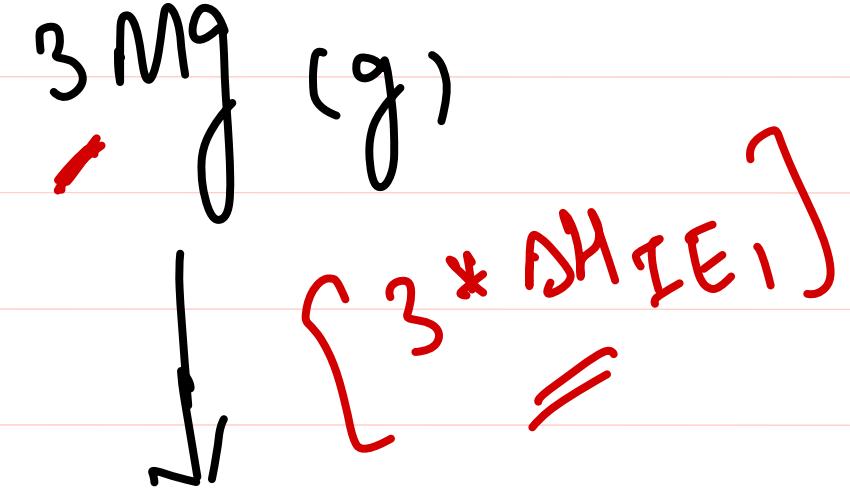
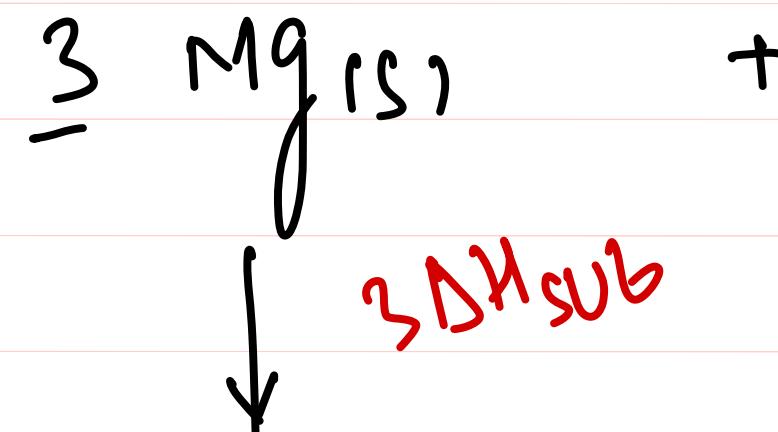
Draw Born haber cycle for MgO



Draw Born Haber cycle for AlF_3

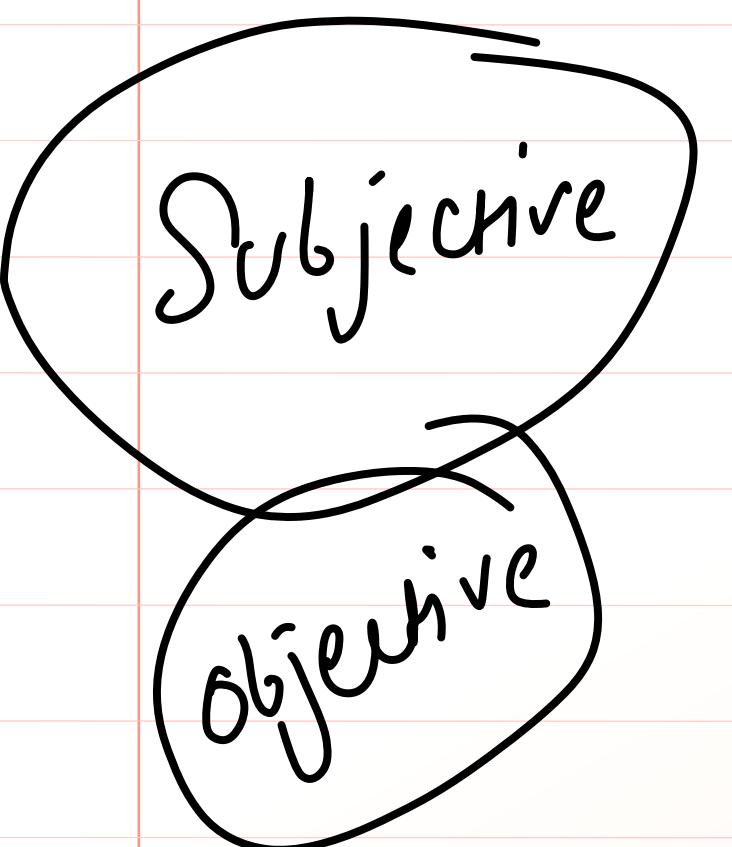
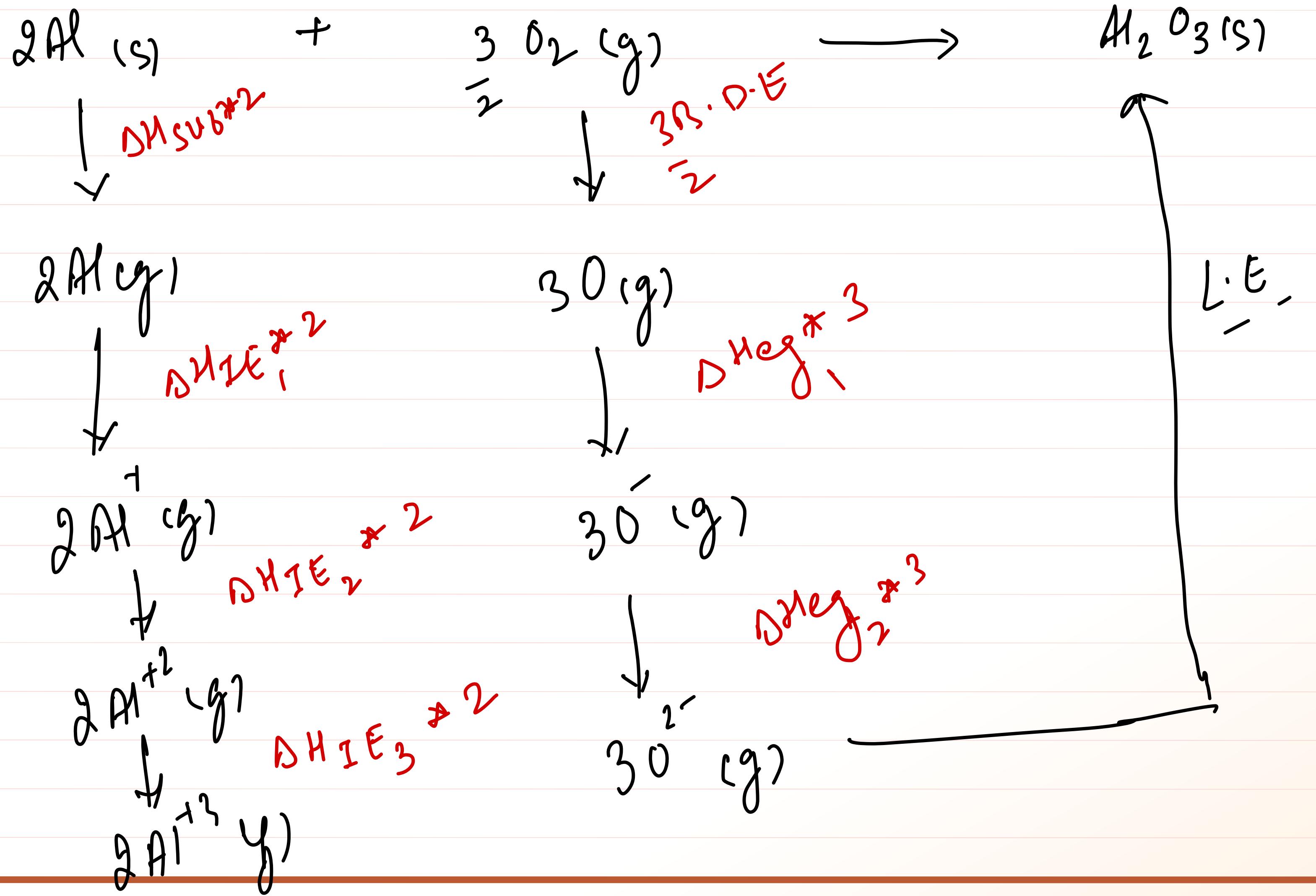


Draw Born haber cycle of Magnesium Nitride.



L.E

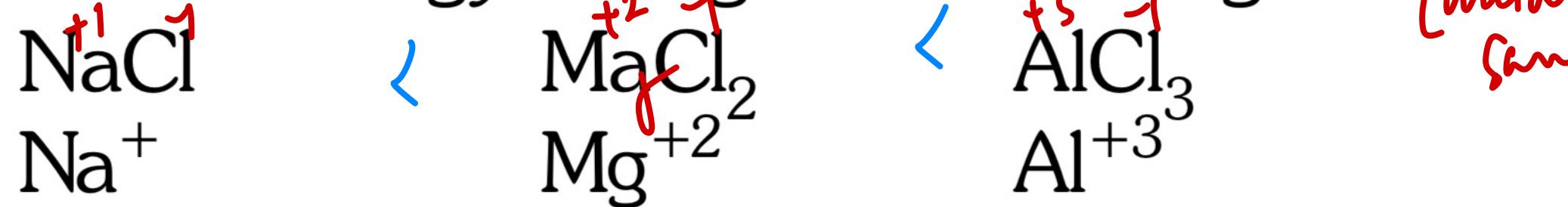
① Draw Born Haber cycle for $\text{Al}_2\text{O}_3(s)$



Factors affecting lattice energy

(i) Magnitude of charge $\rightarrow U \propto z^+ z^-$ (Ionic charge)

Lattice energy \propto Magnitude of charge



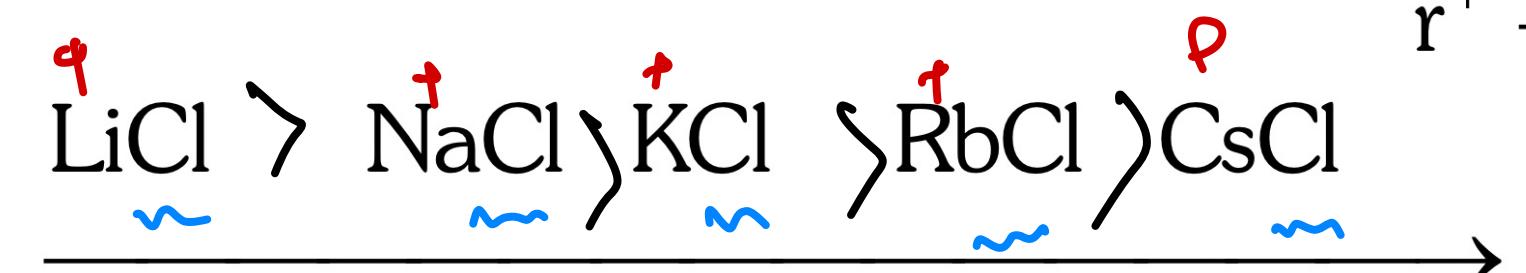
\longrightarrow

- Charge on cation increases.

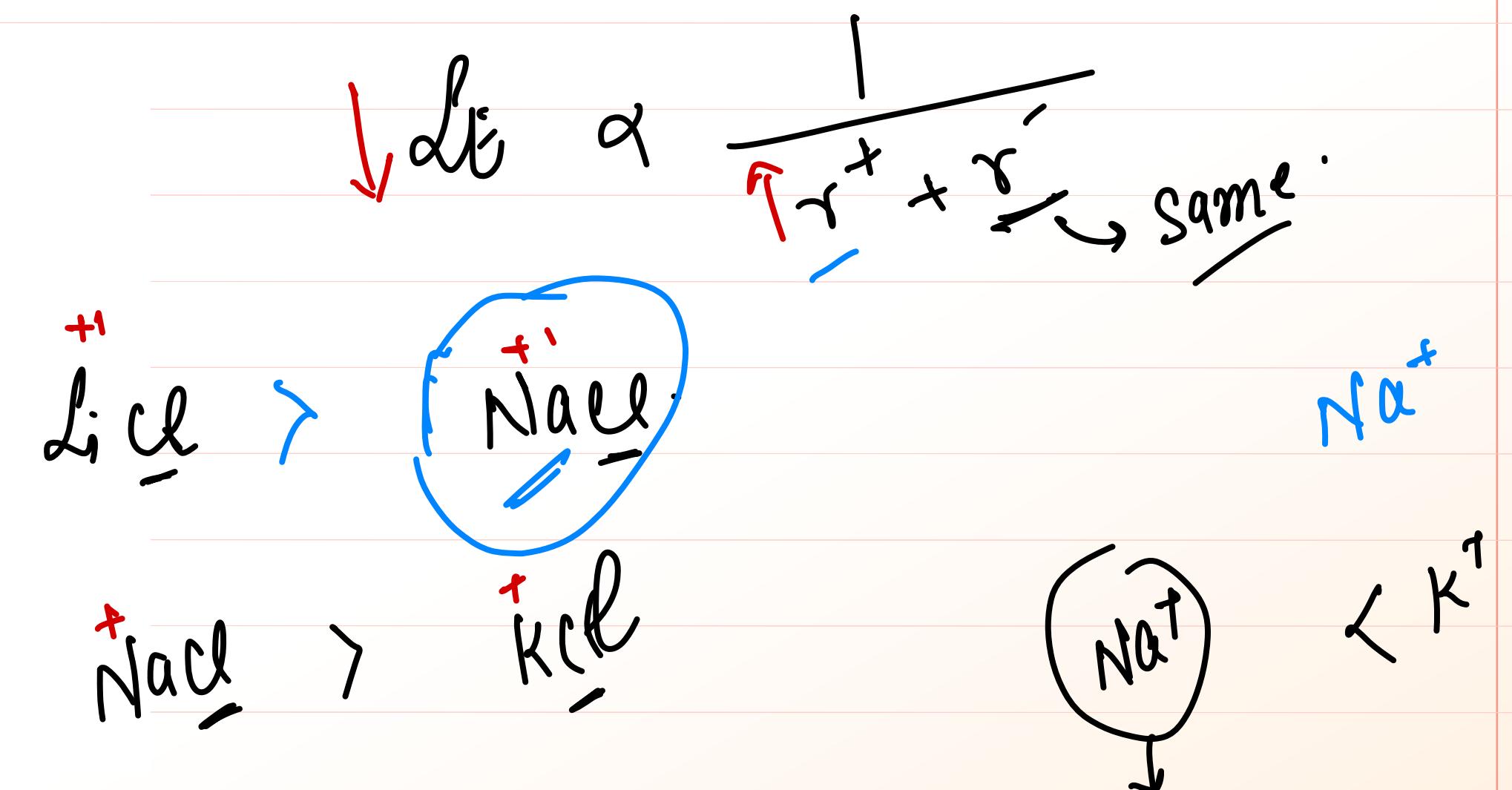
- Size of cation decreases.

- Lattice energy increases

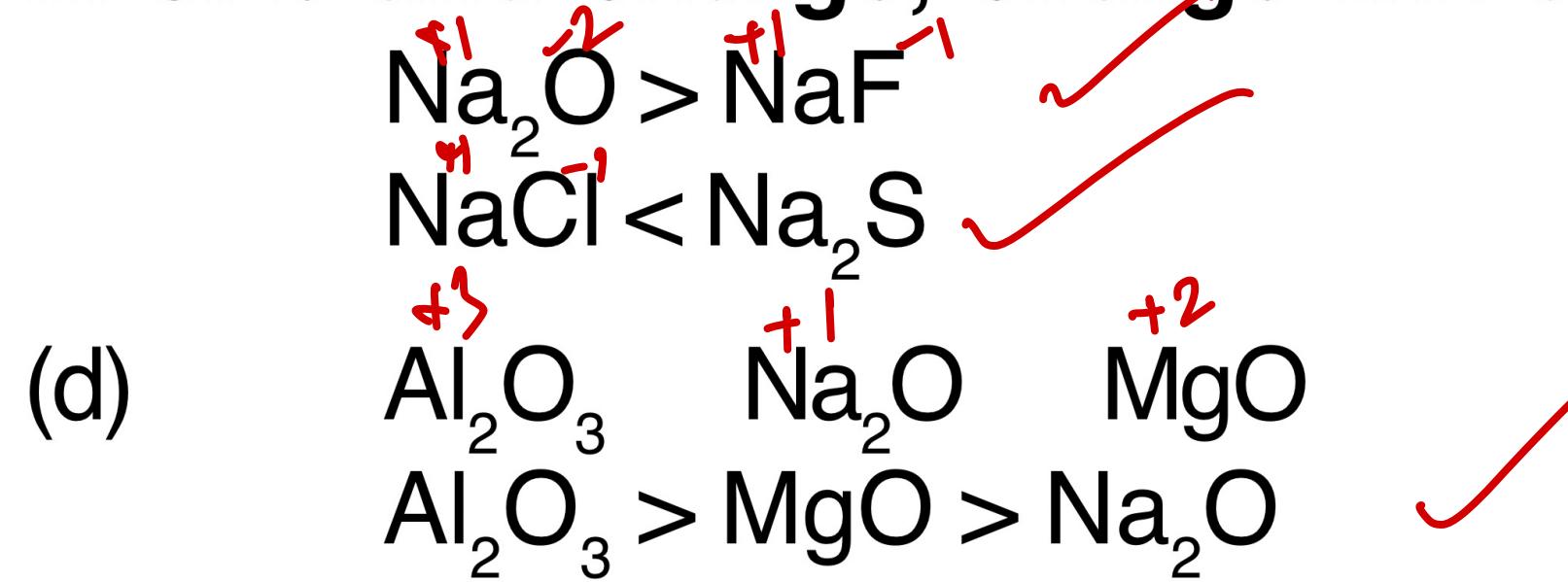
(ii) Size of Cation :- Lattice energy $\propto \frac{1}{r^+ + r^-}$



- Size of cation increasing
- Size of anion is constant
- Lattice energy decreases.

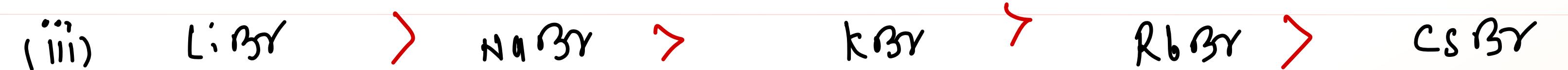
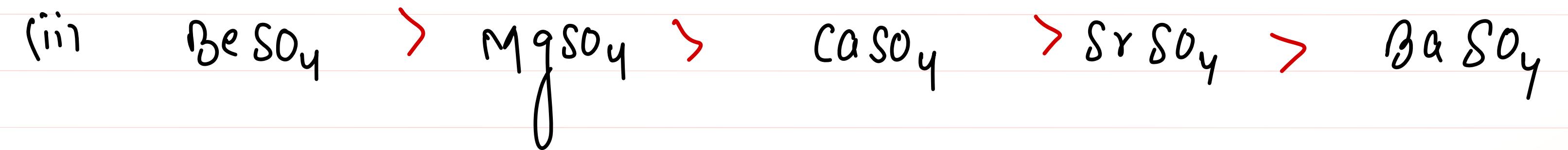


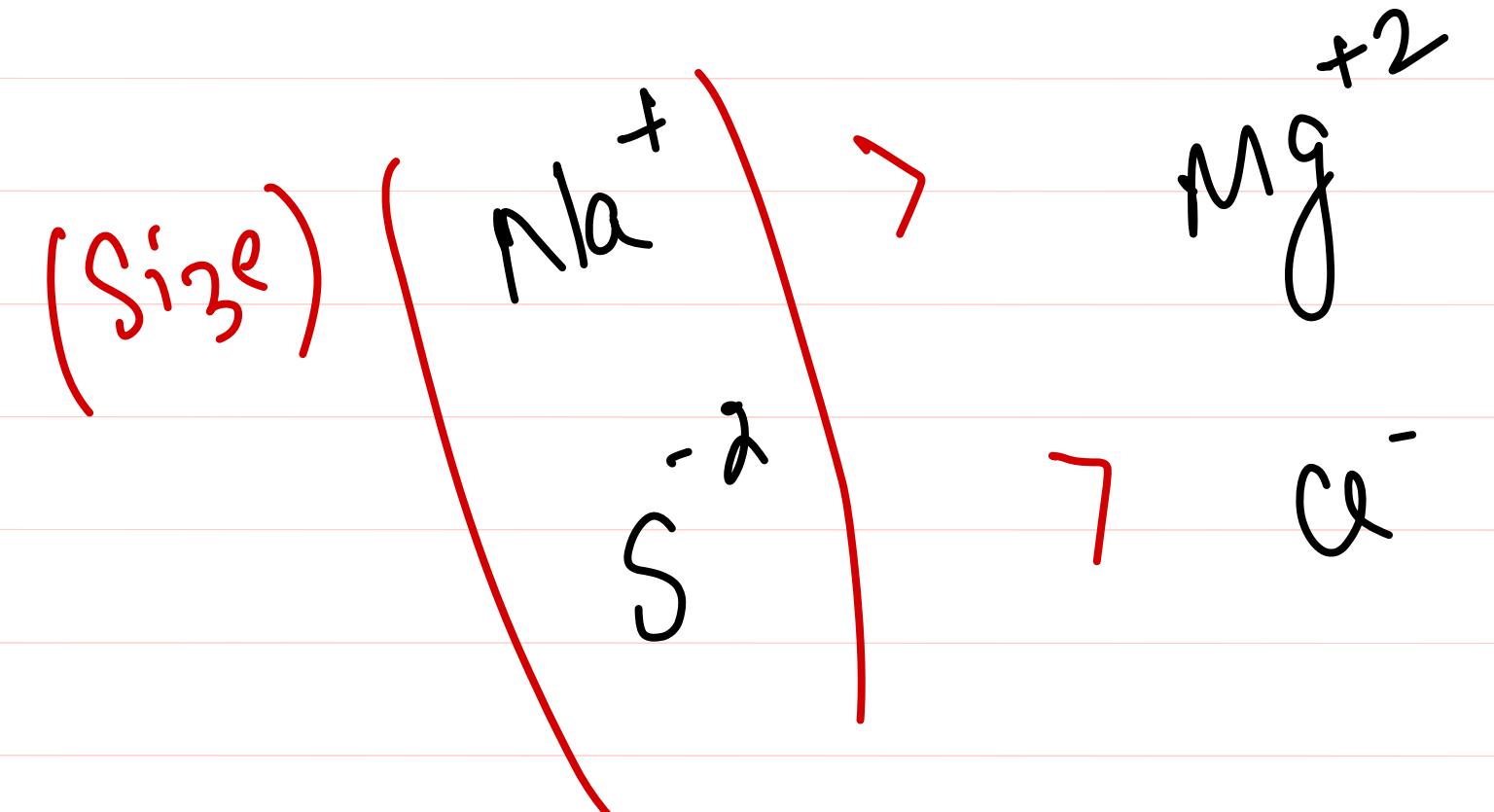
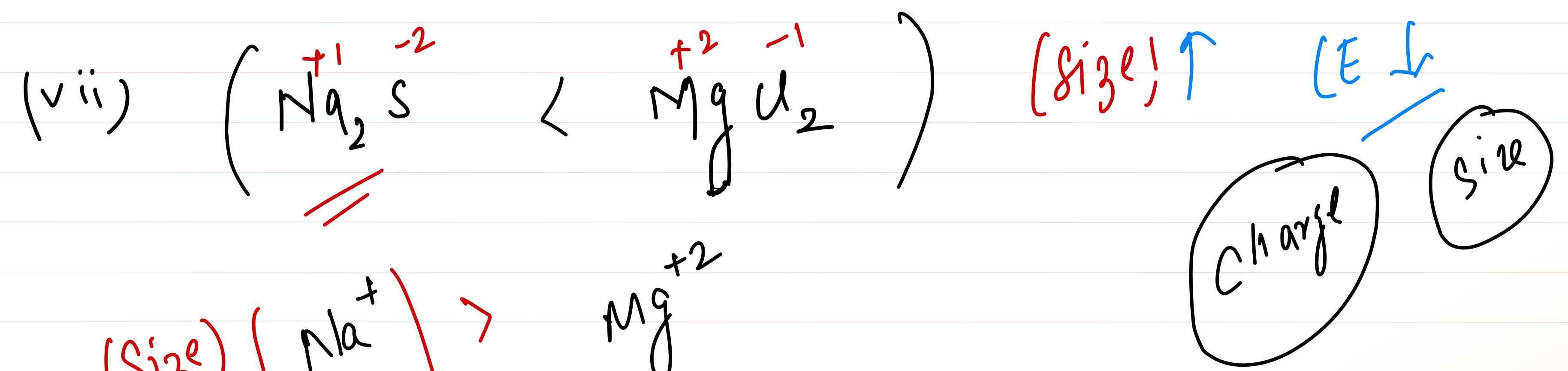
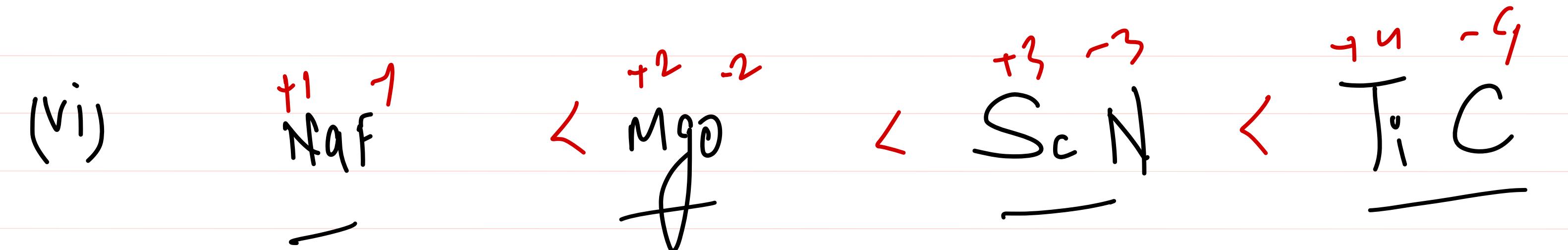
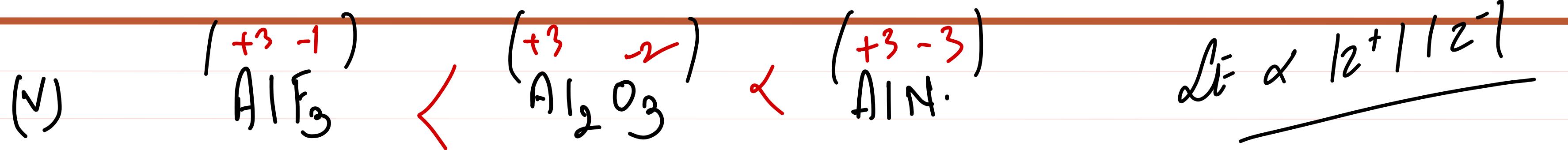
In size and charge, charge will dominate



charge

(d)





The correct expected order of decreasing lattice energy is

- (A) $\text{CaO} > \text{MgBr}_2 > \text{CsI}$
- (B) $\text{MgBr}_2 > \text{CaO} > \text{CsI}$
- (C) $\text{CsI} > \text{MgBr}_2 > \text{CaO}$
- (D) $\text{CsI} > \text{CaO} > \text{MgBr}_2$

Application of lattice Enthalpy

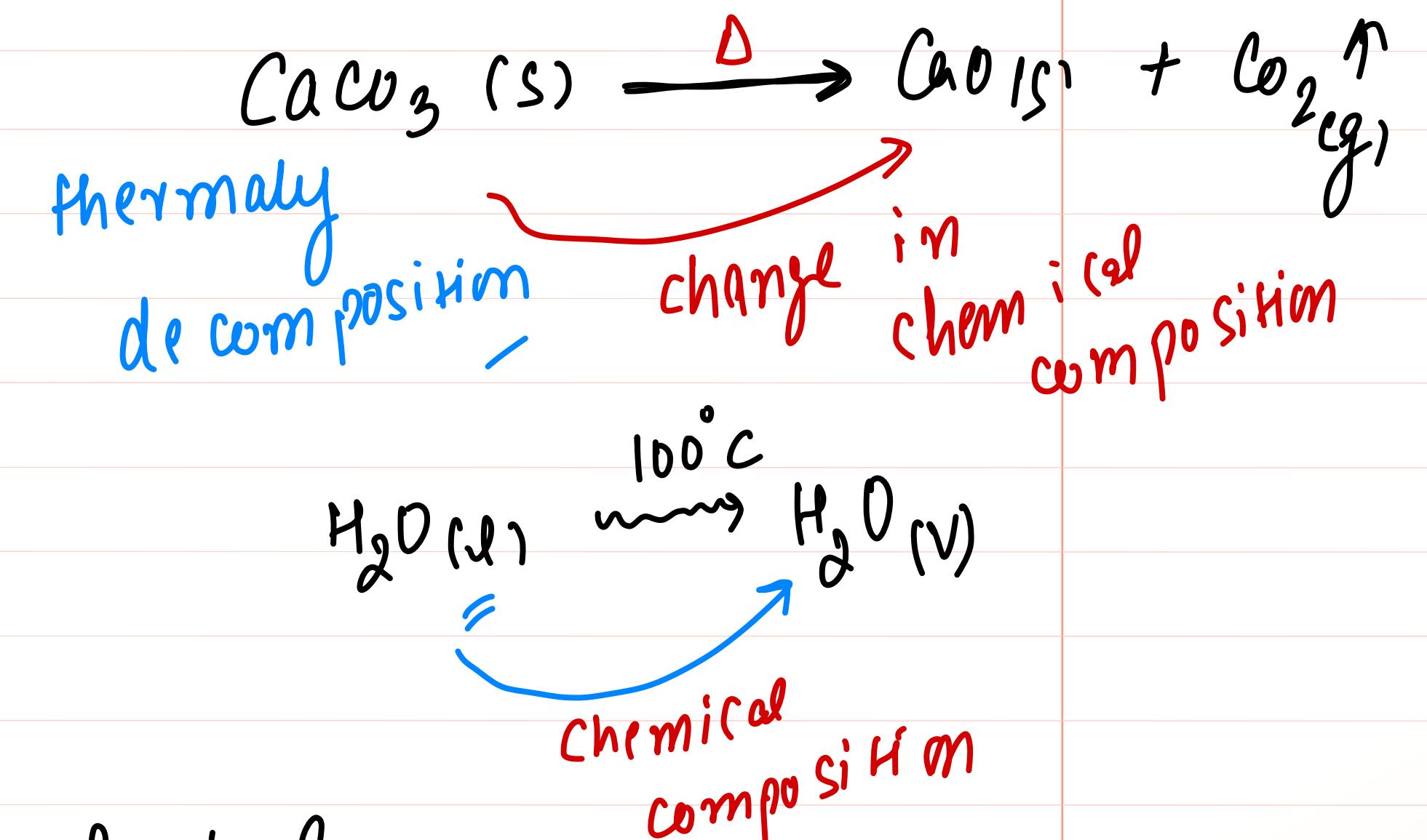
Order of thermal stability

1. $\text{Li}_3\text{N} > \text{Na}_3\text{N} > \text{K}_3\text{N}$
2. $\text{Li}_2\text{O} > \text{Na}_2\text{O} > \text{K}_2\text{O} > \text{Rb}_2\text{O} > \text{Cs}_2\text{O}$
3. ~~$\text{LiX} > \text{NaX} > \text{KX} > \text{RbX} > \text{CsX}$~~
 (where X = F, Cl, Br, I)
4. $\text{BeX}_2 > \text{MgX}_2 > \text{CaX}_2 > \text{SrX}_2 > \text{BaX}_2$
 (where X = F, Cl, Br, I)
5. $\text{Be}_3\text{N}_2 > \text{Mg}_3\text{N}_2 > \text{Ca}_3\text{N}_2 > \text{Sr}_3\text{N}_2 > \text{Ba}_3\text{N}_2$
6. $\text{BeO} > \text{MgO} > \text{CaO} > \text{SrO} > \text{BaO}$

Note : S-block halide, oxide and Nitride thermal stability is directly proportional to lattice energy

Halide (F^- , Cl^- , Br^- , I^-)

Oxides (O^{2-}), Nitrides (N^{3-})

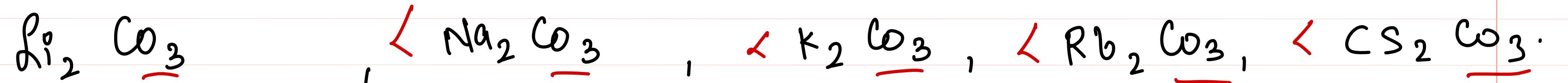


Lattice Energy

$\text{LiF} \approx \text{NaF} \approx \text{KF} \approx \text{RbF} \approx \text{CsF}$

Thermal Stability $\text{LiF} > \text{NaF} > \text{KF} > \text{RbF} > \text{CsF}$

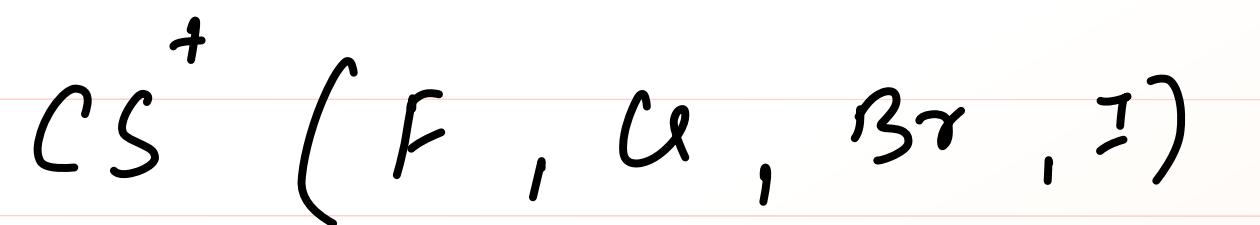
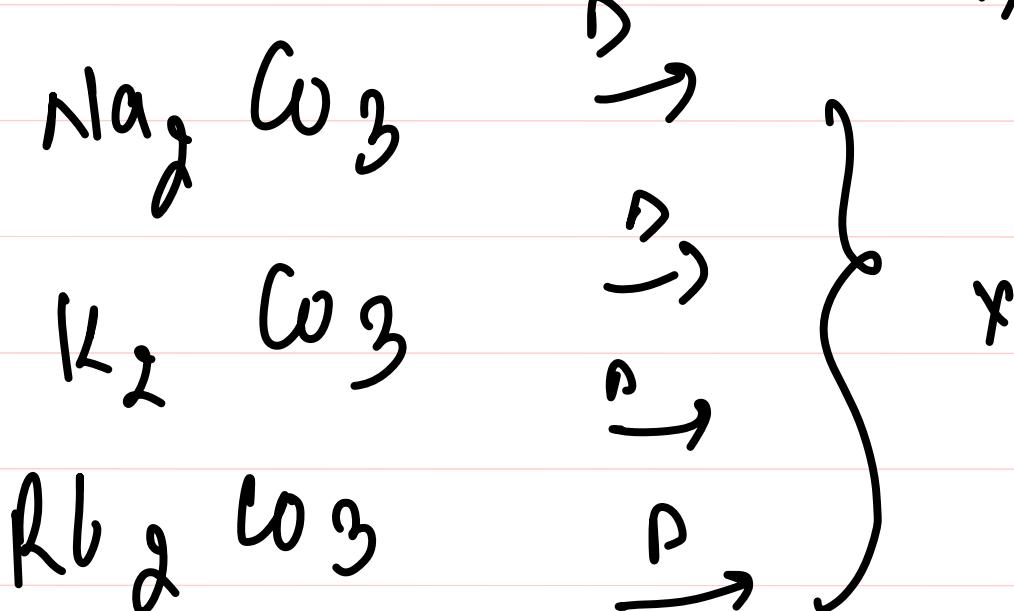
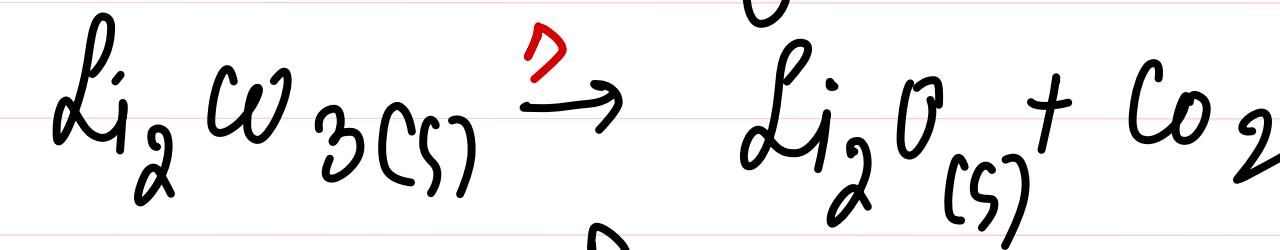
Stability of carbonates (S Block)



S Block harder, oxides, nitriles

Thermal stability & ionic character

* The thermal stability of S Block carbonates **increases** down the group

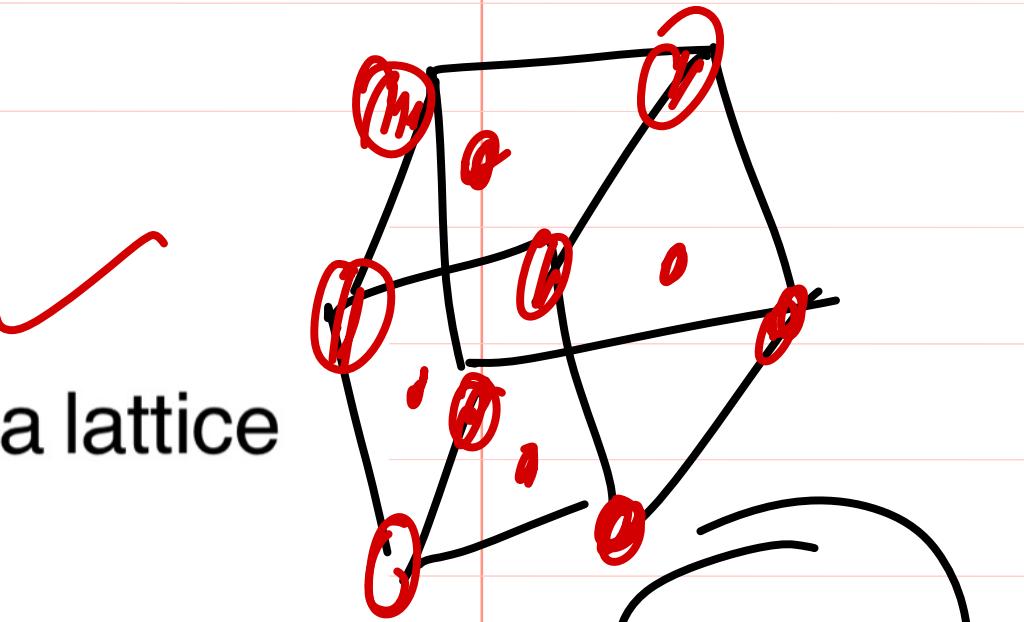


Characteristics (Properties) of Ionic Compound.

Physical state

(a) Electrovalent compounds are generally crystalline, hard & brittle in nature.

(b) These compounds are generally made from ions which are arranged in a regular way as a lattice structure.



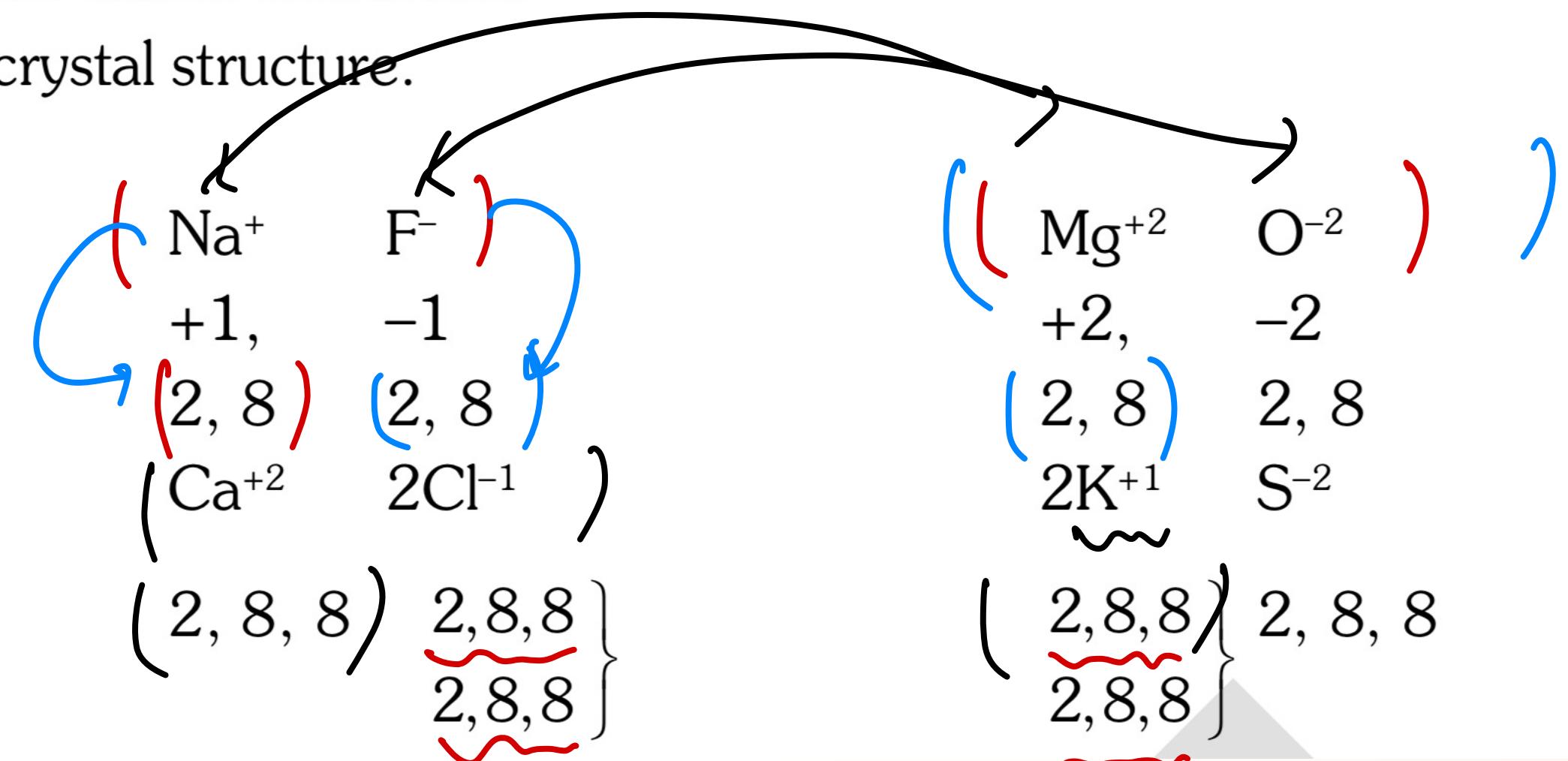
Isomorphism – Different ionic compounds, having same configuration/geometry of ions are isomorphs of each other and phenomenon is known as isomorphism

Ex. NaF, MgO, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. All alums $\text{M}_2'\text{SO}_4 \cdot \text{M}_2''(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.

- (1) Two compounds are said to be isomorphous if they have similar no. of electrons i.e. similar configuration of their cation and anion.
- (2) They have similar crystal structure.

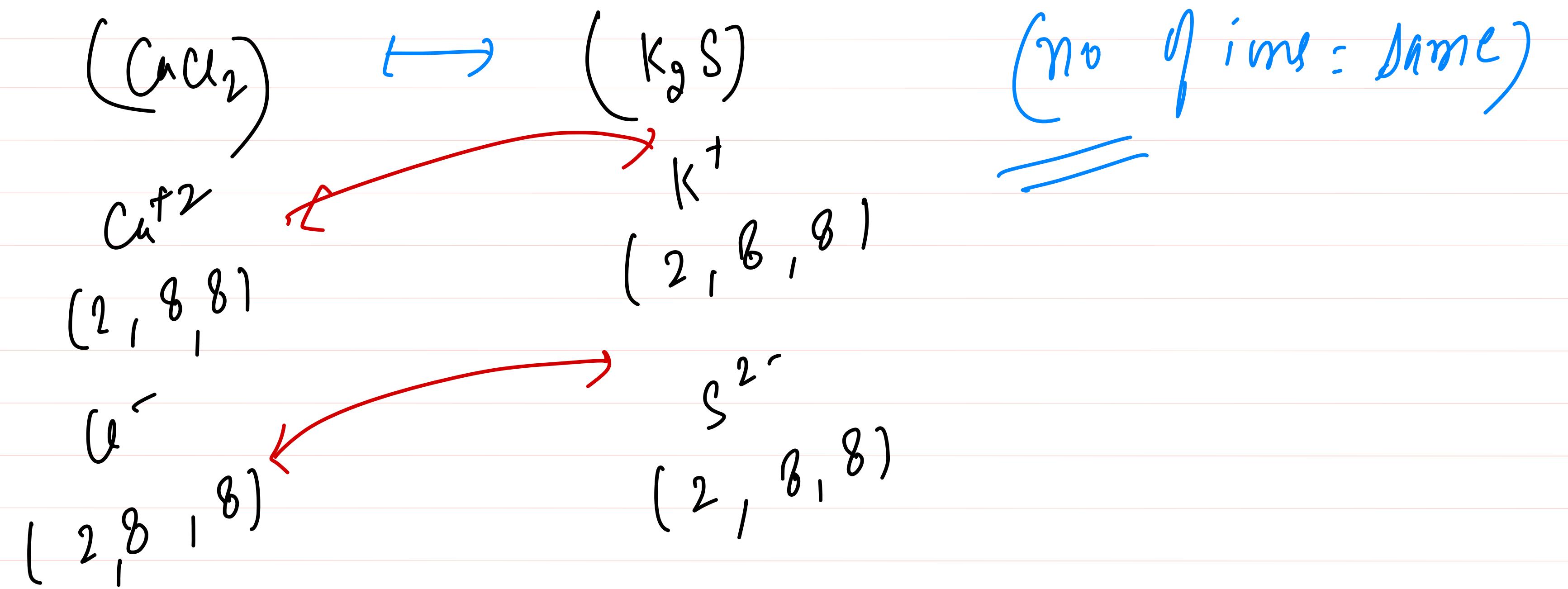
Example –

Valency
electronic configuration
similarly



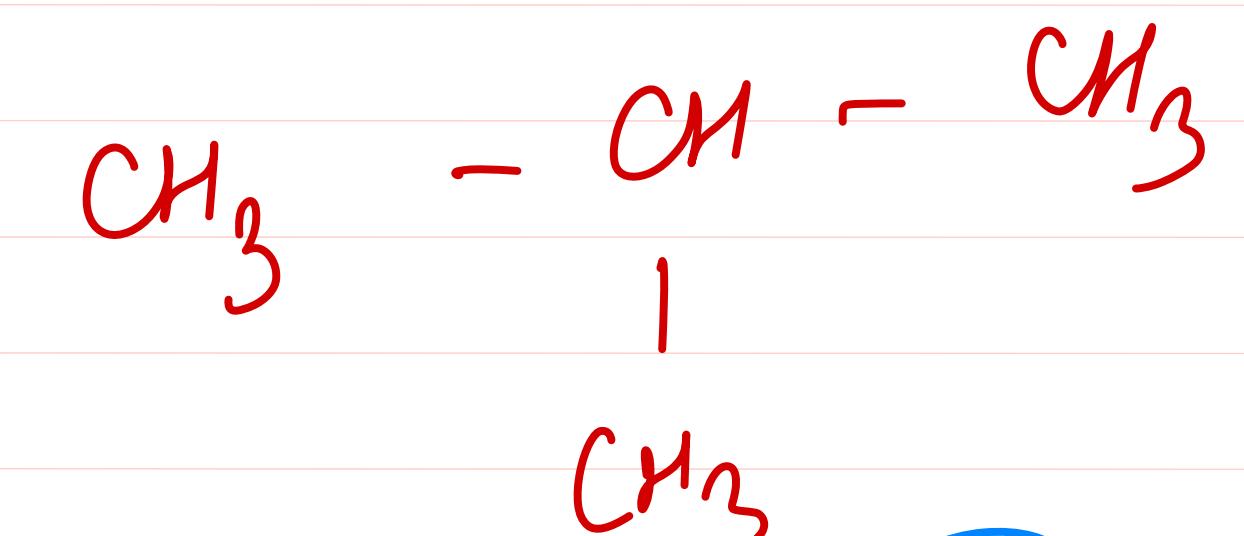
Same
Molecular
formula
but
different
physical
properties

isomer





Mf: C_4H_{10} ,



Mf: C_4H_{10}

Unsaturated
chemical
proposition
isomer

covalent

isomerism

(ii) Boiling point and melting point :

High boiling point and melting points are due to strong electrostatic force of attraction.

(iii) Electrical conductivity :

✓ It depends on ionic mobility. In solid state there are no free ions so they are bad conductors of electricity

In fused state or aqueous solution free ions are present so they are good conductors of electricity

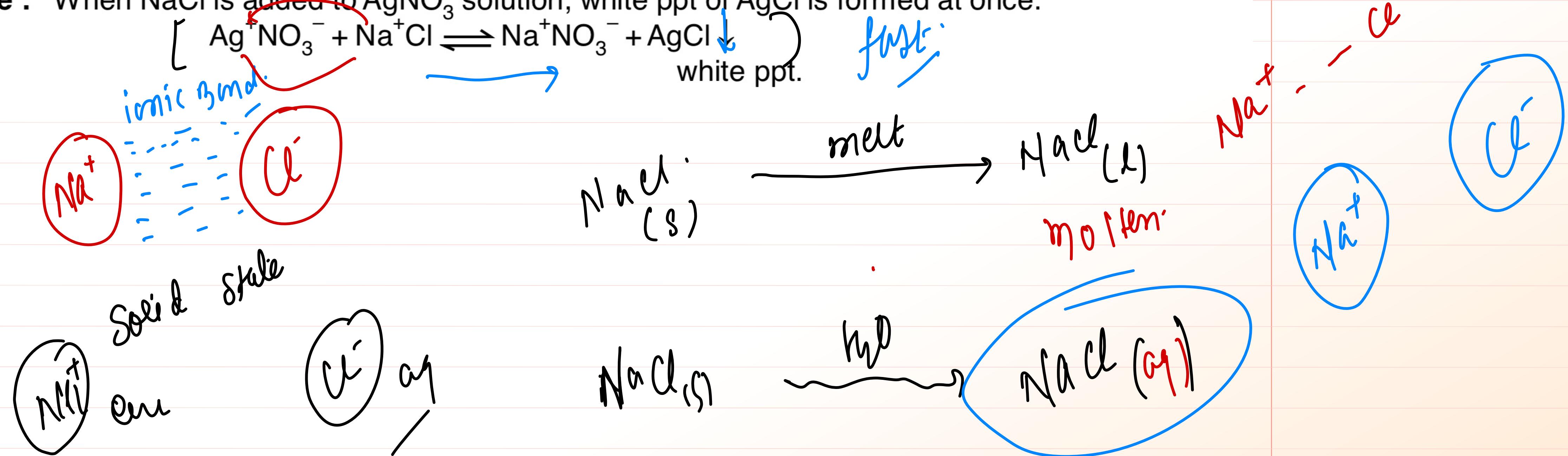
✓ (Conductivity order) Solid state < Fused state < Aqueous solution

(*from IITJEE*)

(iv) Ionic reactions :

* Ionic compounds show ionic reactions & covalent compounds show molecular reactions.
Ionic reactions are fast reactions.

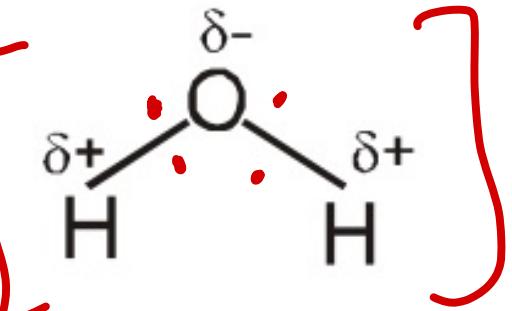
Example : When NaCl is added to AgNO₃ solution, white ppt of AgCl is formed at once.



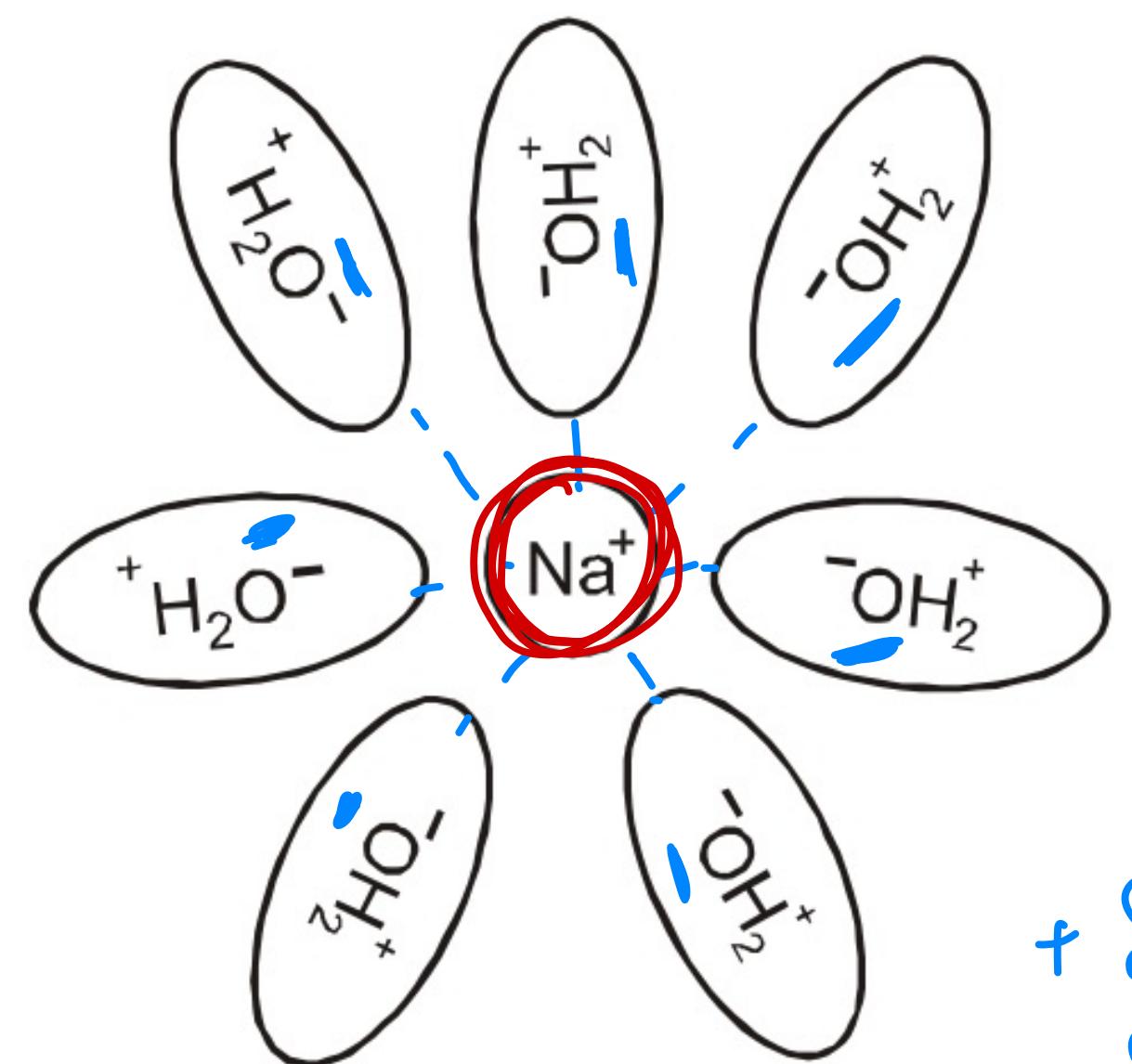
(v) **Solubility** – Ionic compounds are soluble in polar solvent like H_2O , HF etc.

To explain solubility of ionic compound consider an example of NaCl in water.

H_2O is polar solvent it can represent as

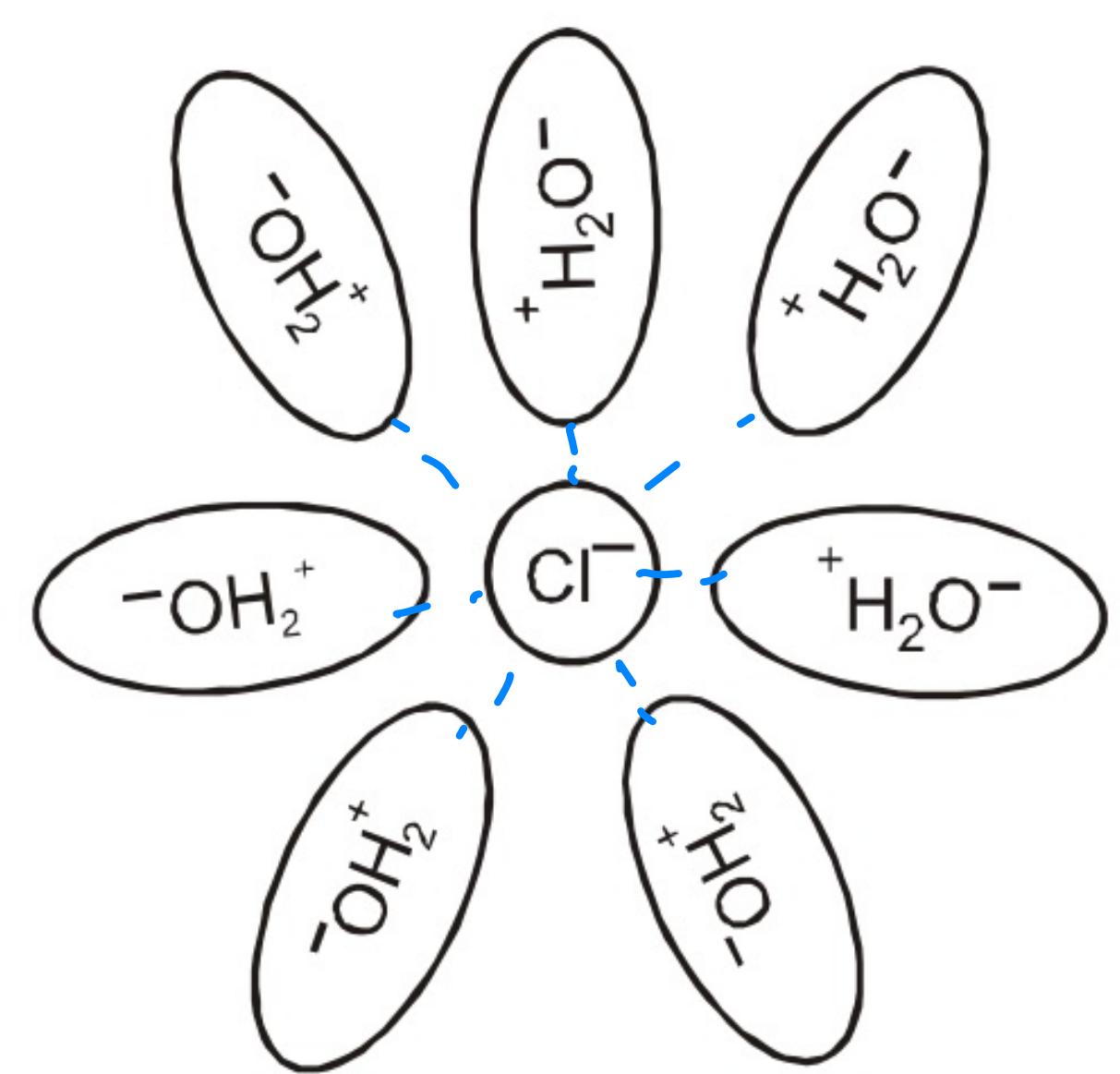


- * The Na^+ ions gets associated with partially negatively charged 'O' of water
- * And Cl^- ions gets associated with partially positively charged 'H' of water.



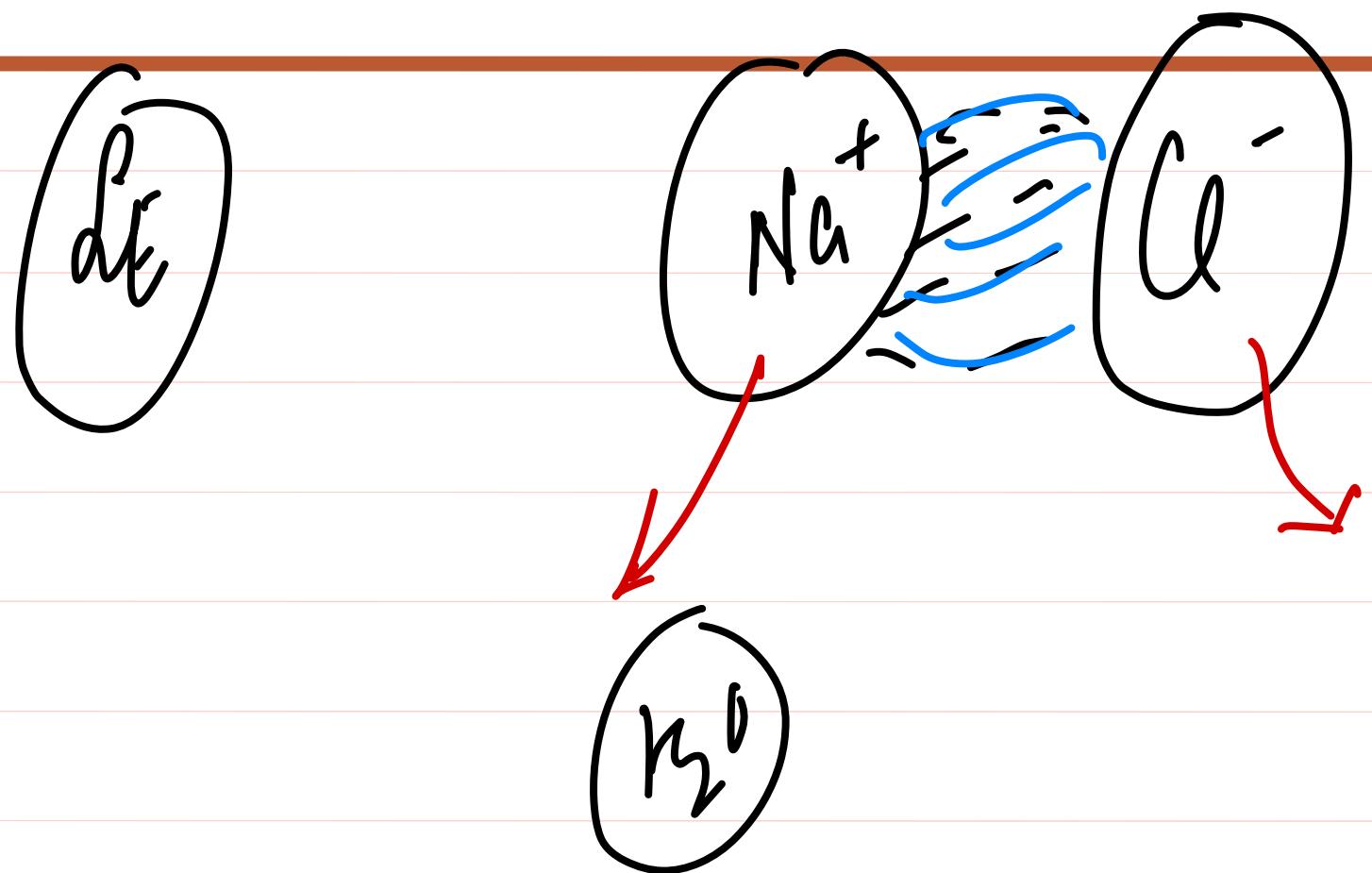
+ δ delta.
- δ delta.

Oxygen atom of H_2O gives its electron to Na^{+}

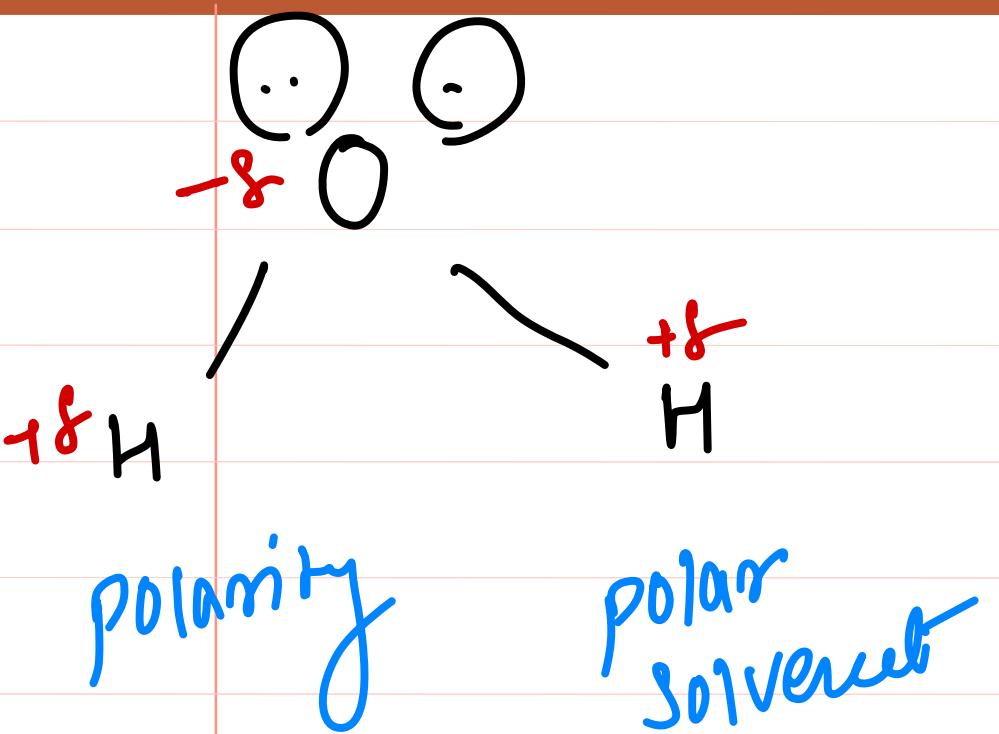
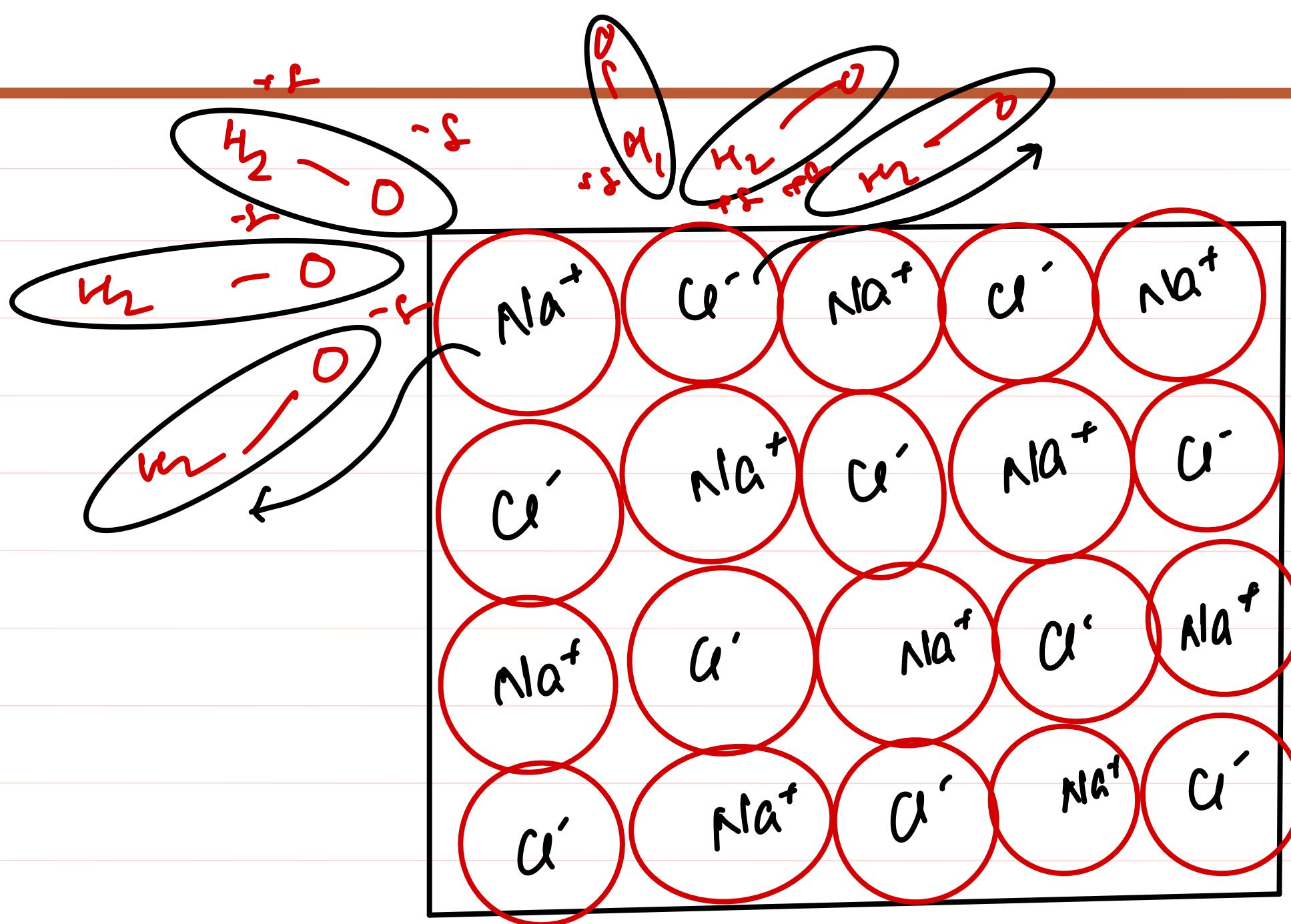


H atom of H_2O gain electron from Cl^{-}

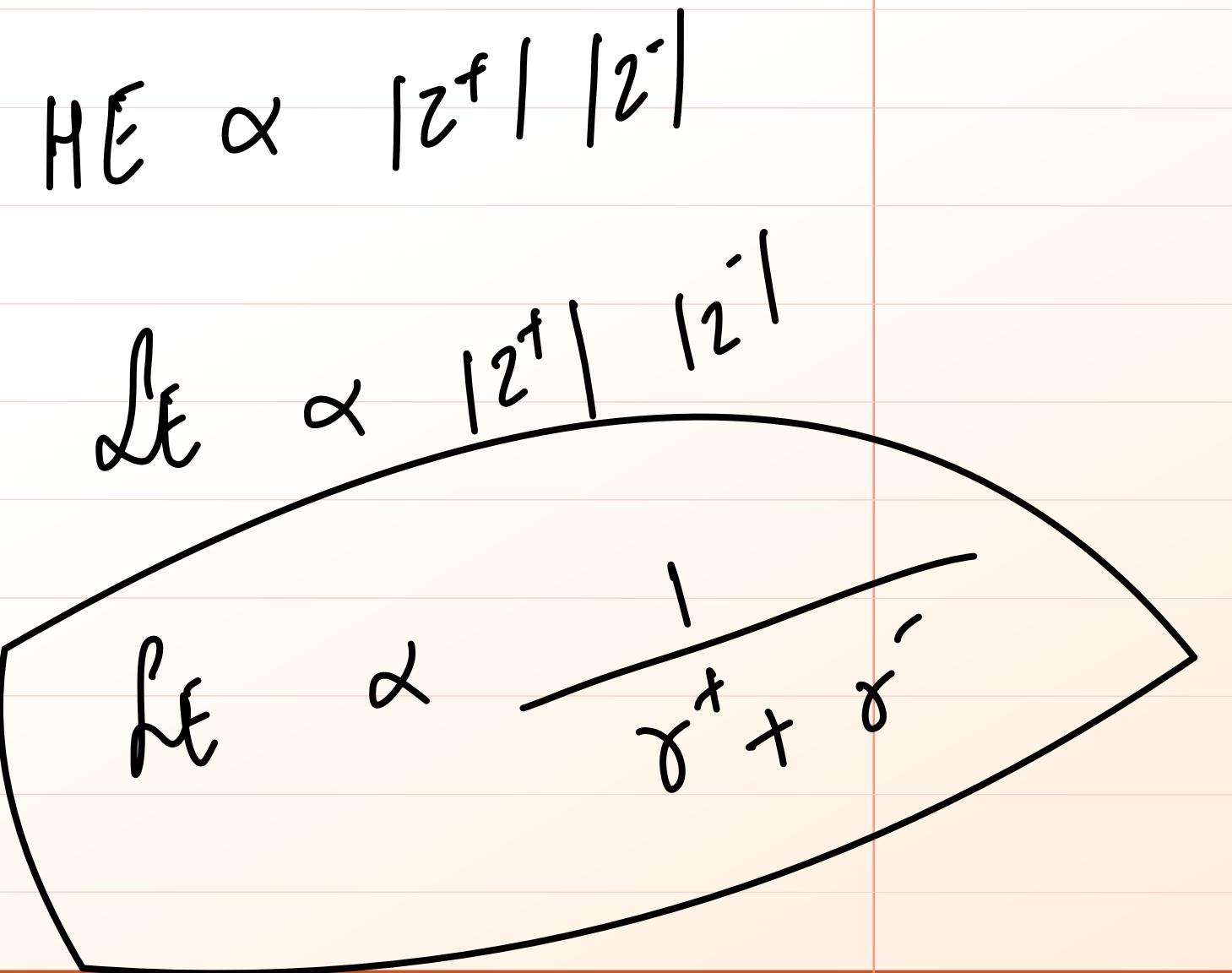
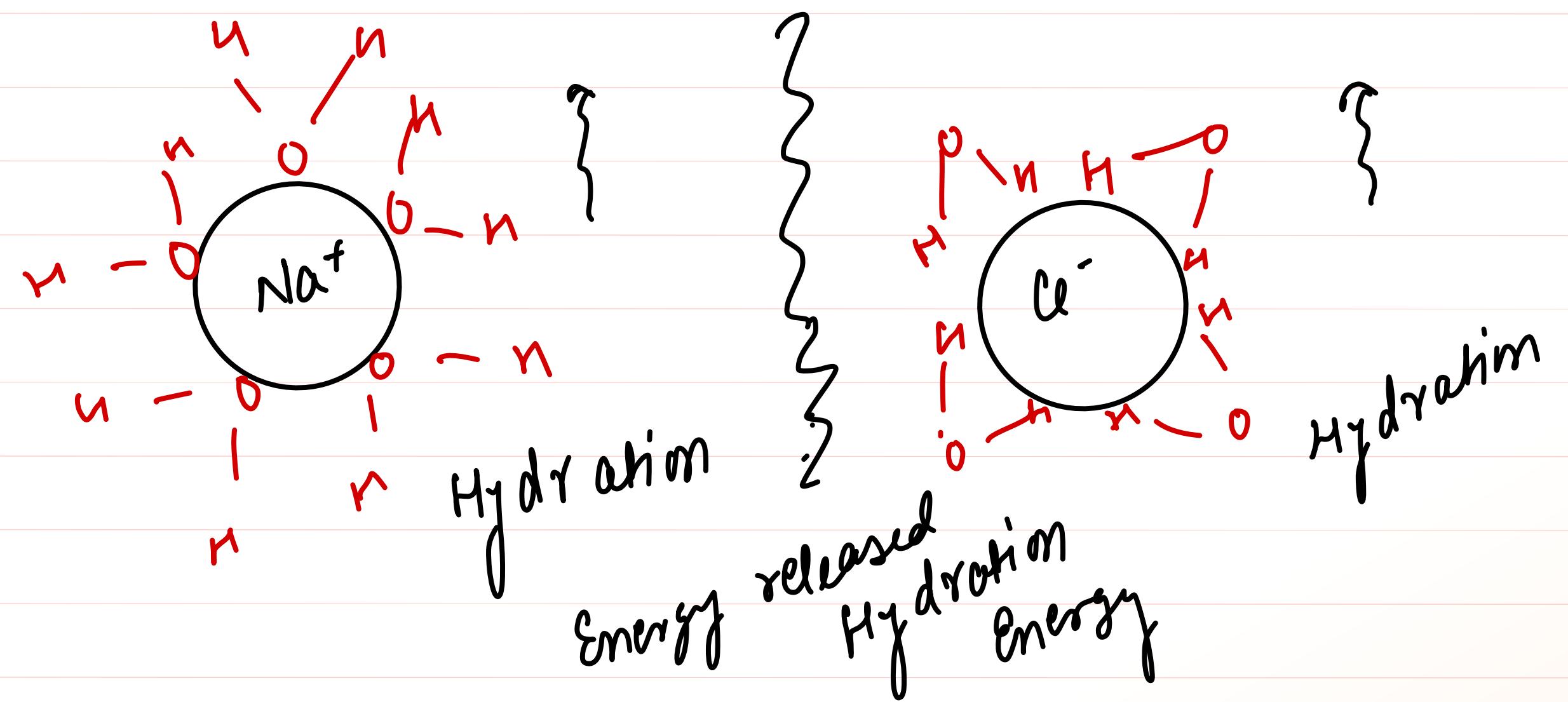
Solvent +
 'like' dissolve
 'like'
 [NOTE: Ionic Generally Compounds are more soluble than Covalent Compound in polar solvent (e.g. H_2O)
 Solvent



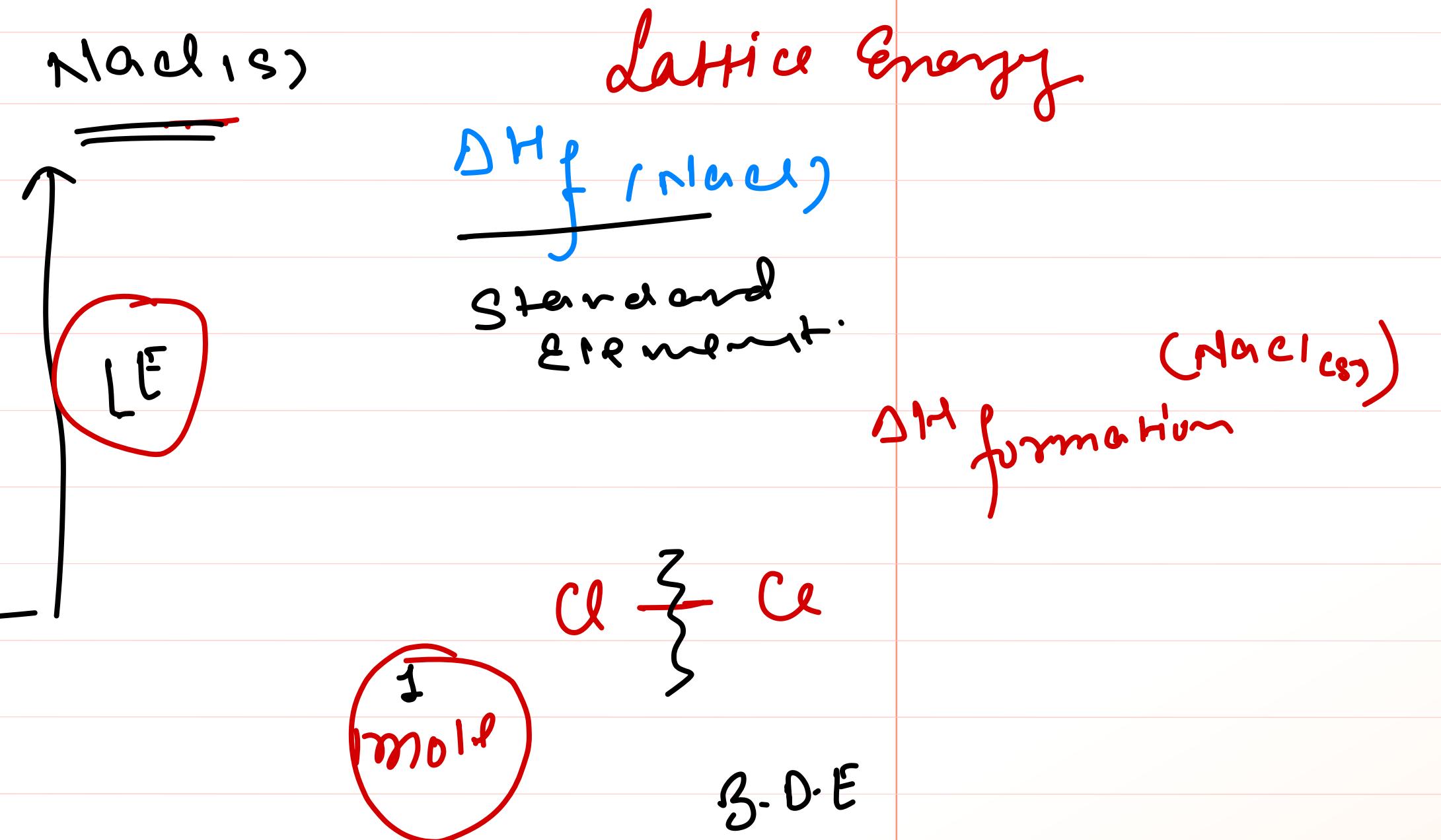
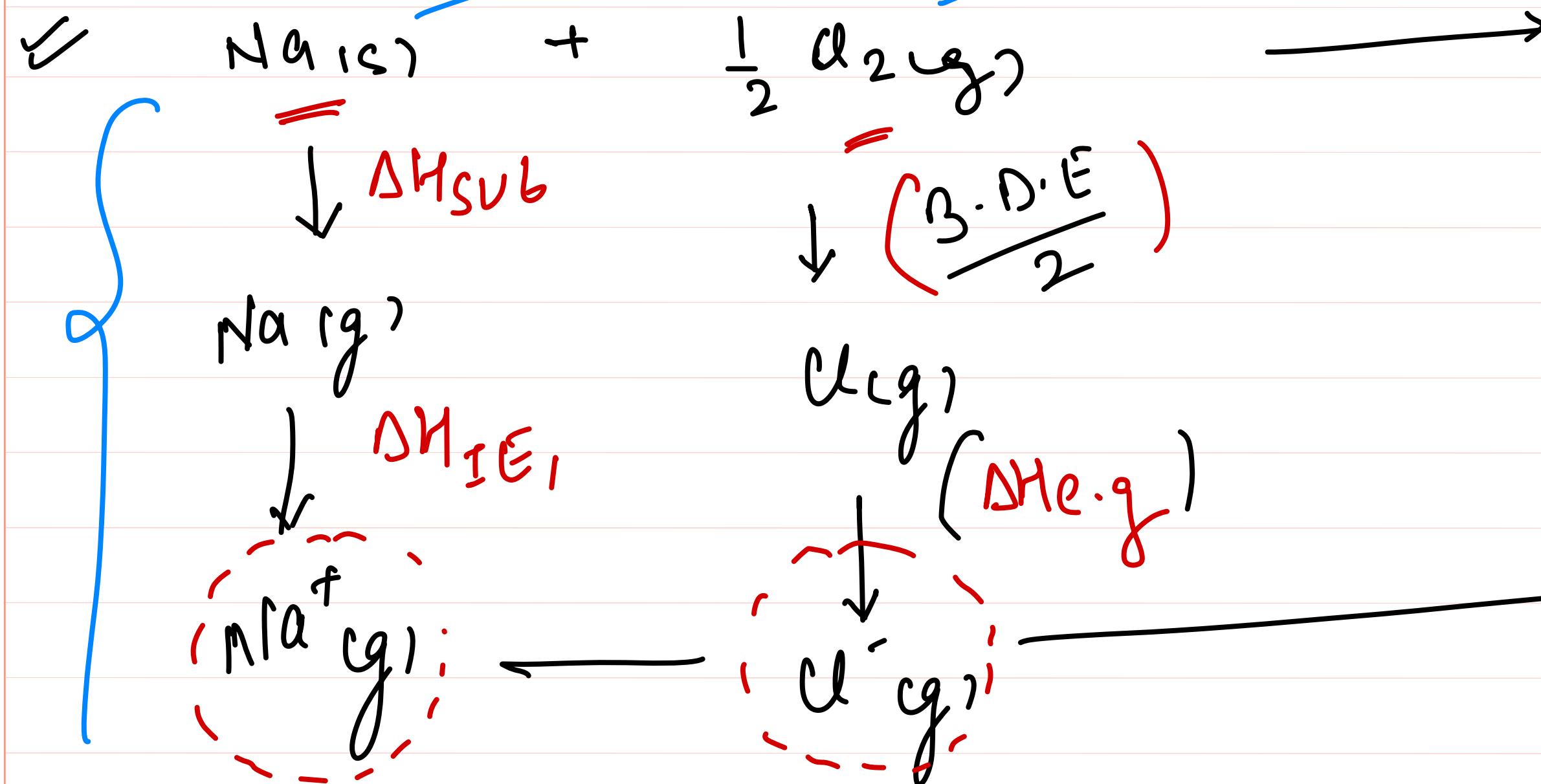
common im:-



$$HE \propto \frac{1}{\gamma^+} + \frac{1}{\gamma^-}$$

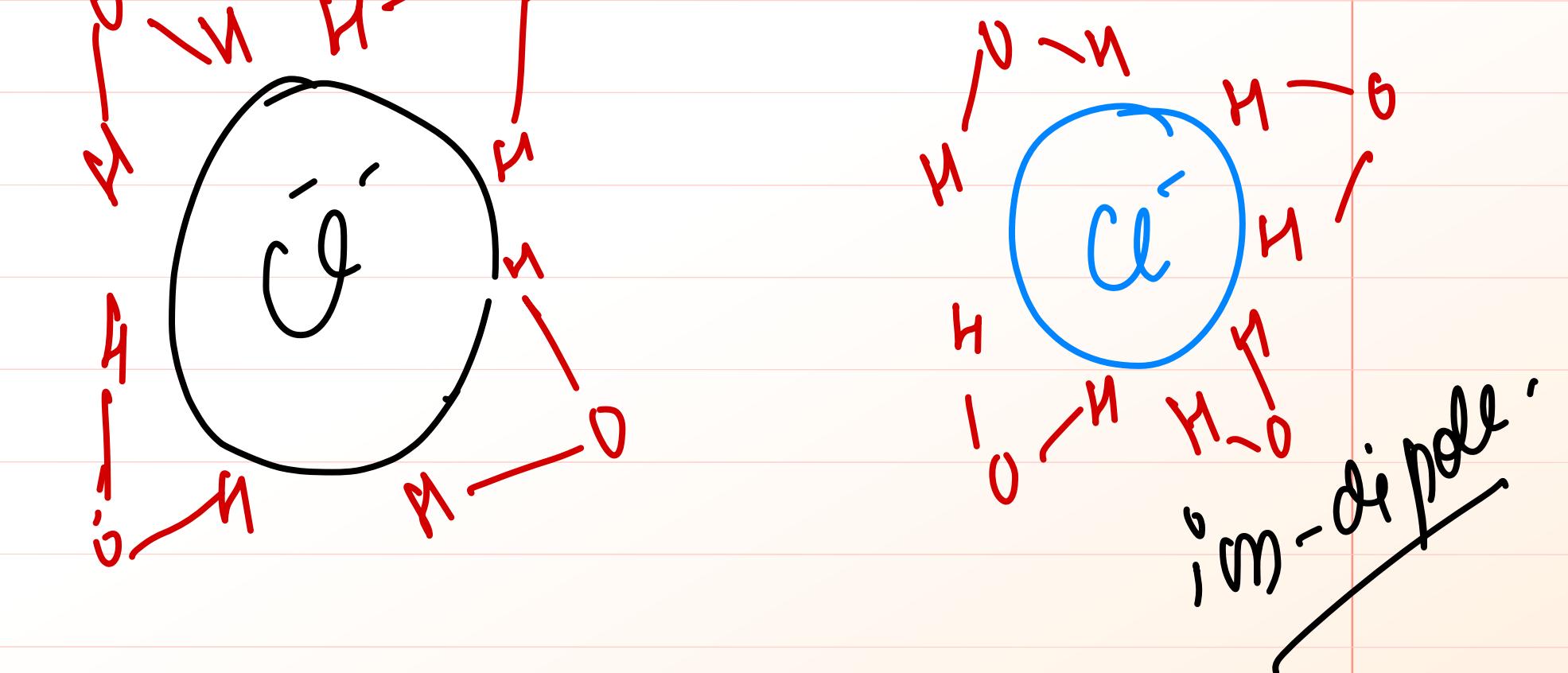
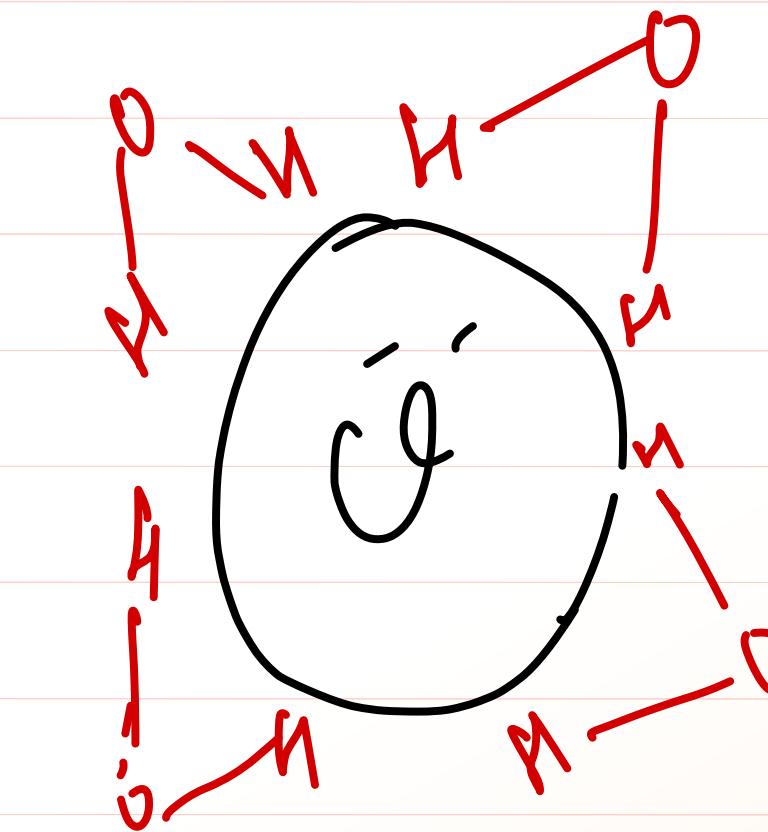
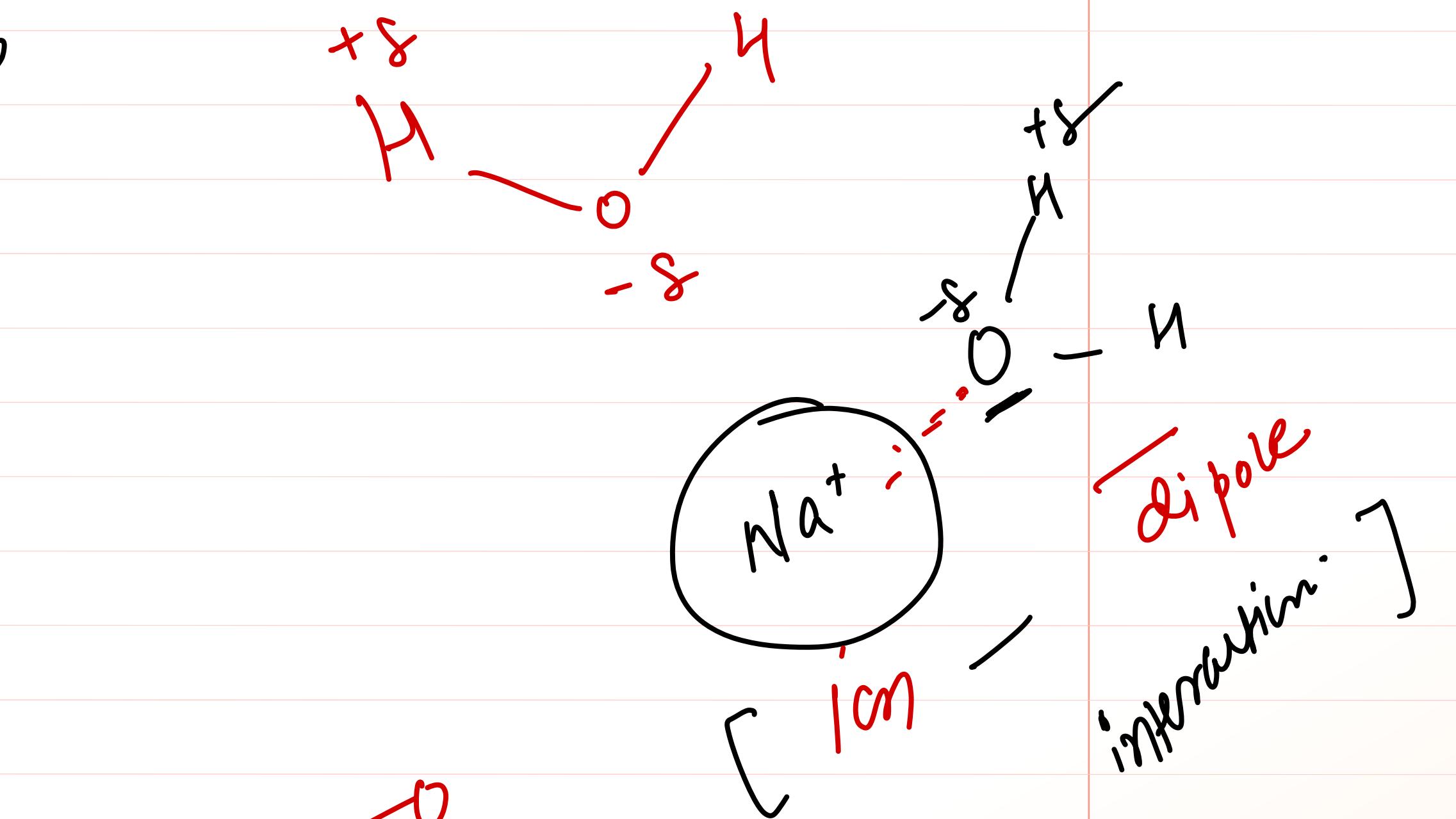
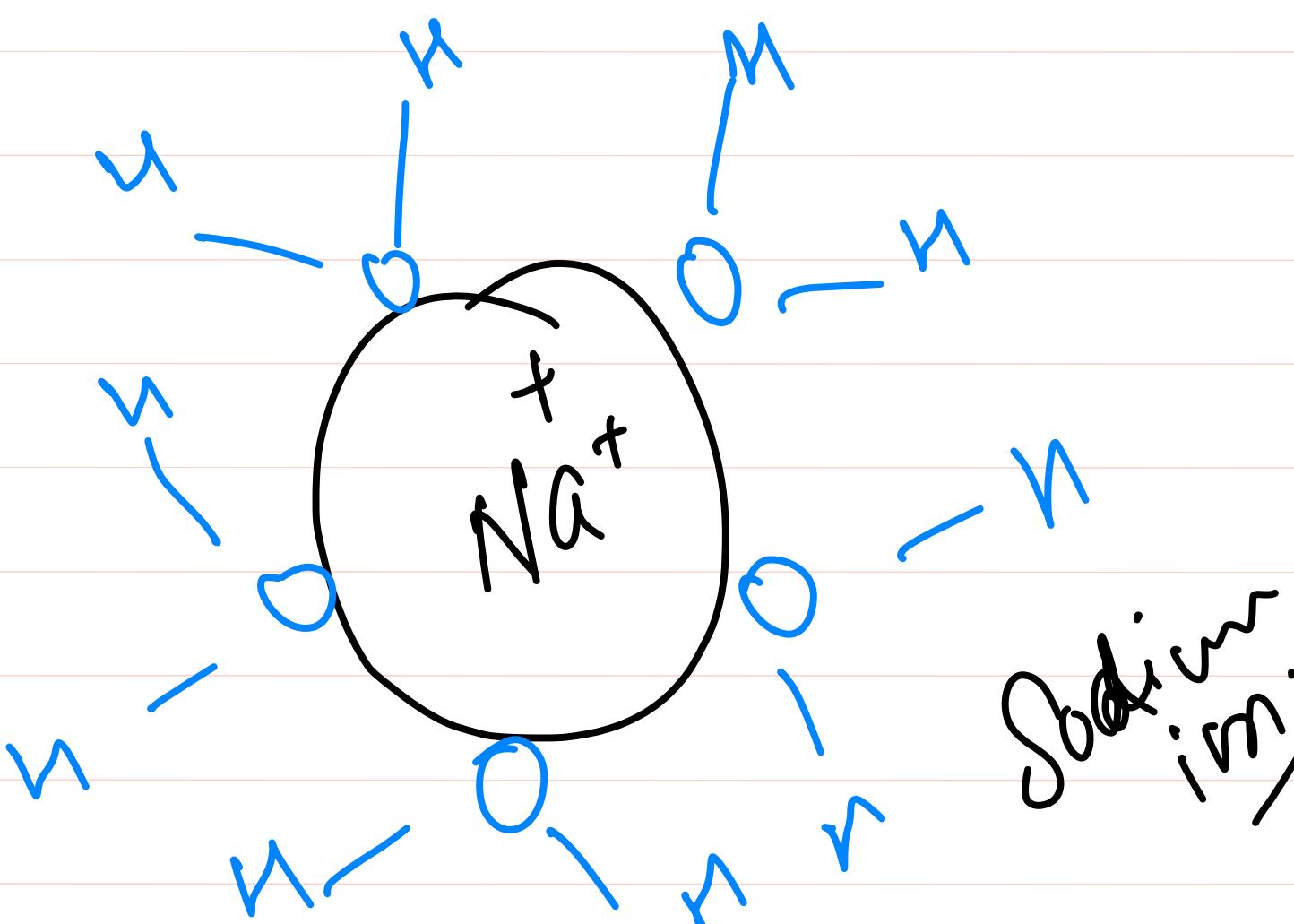
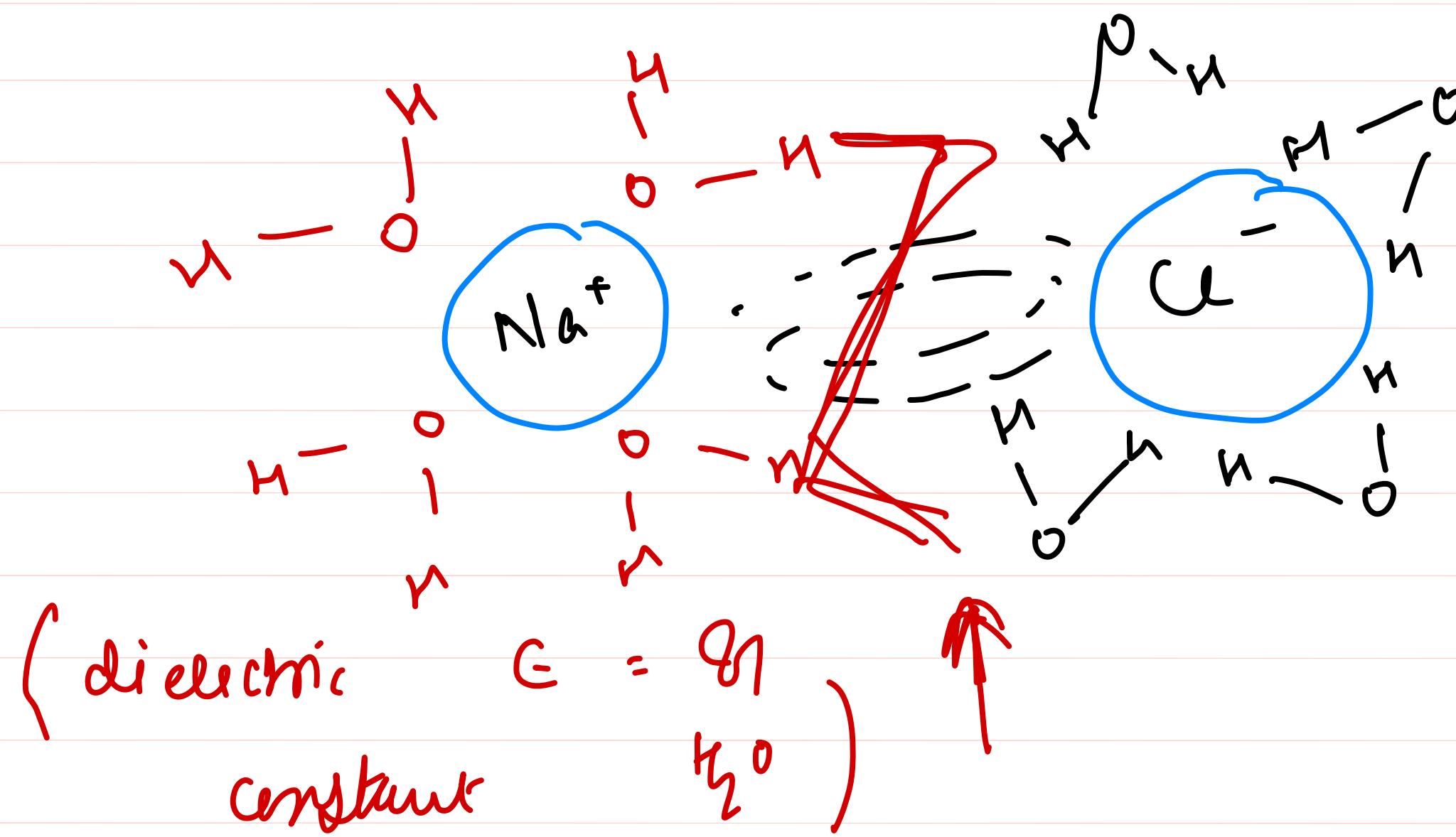


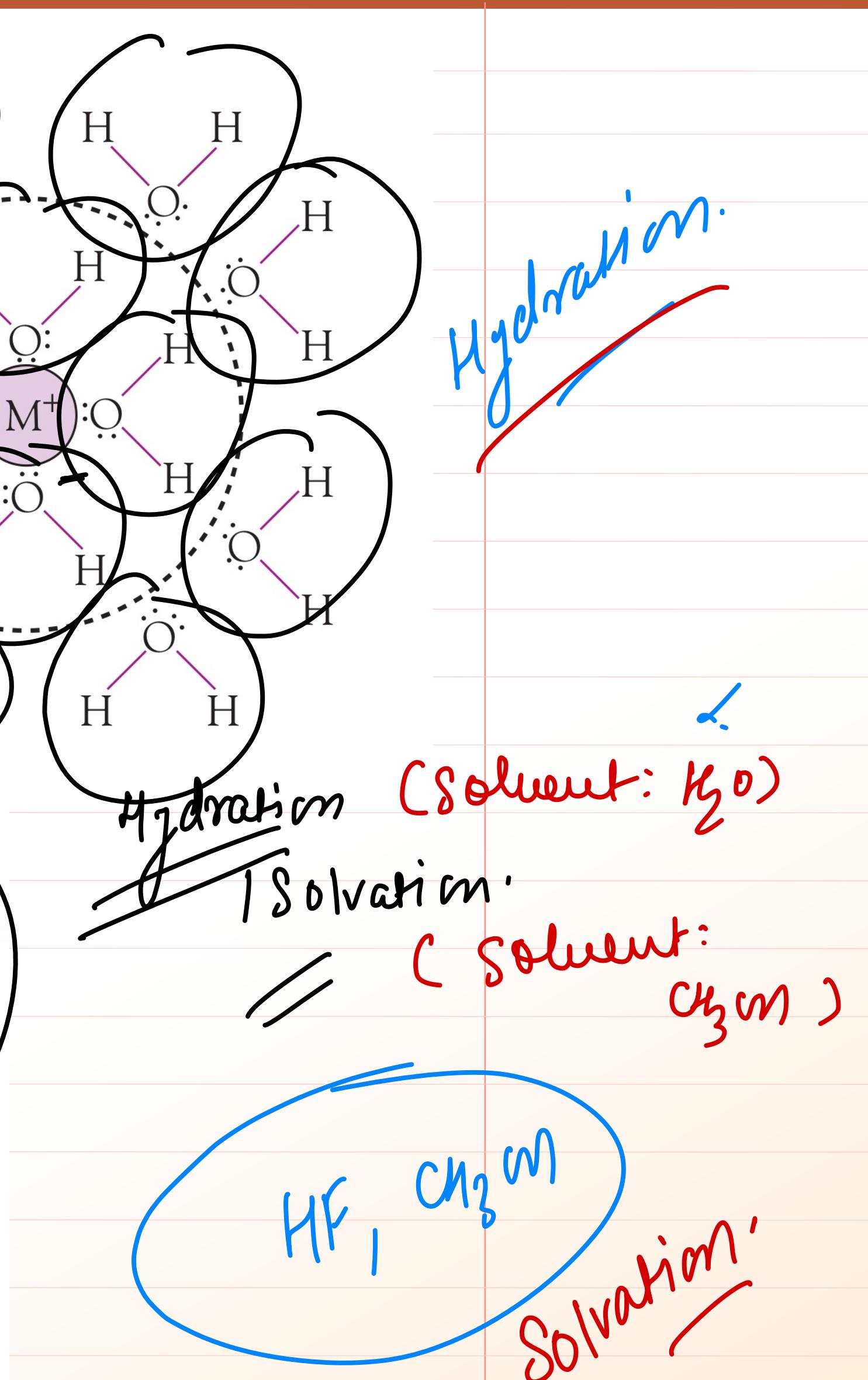
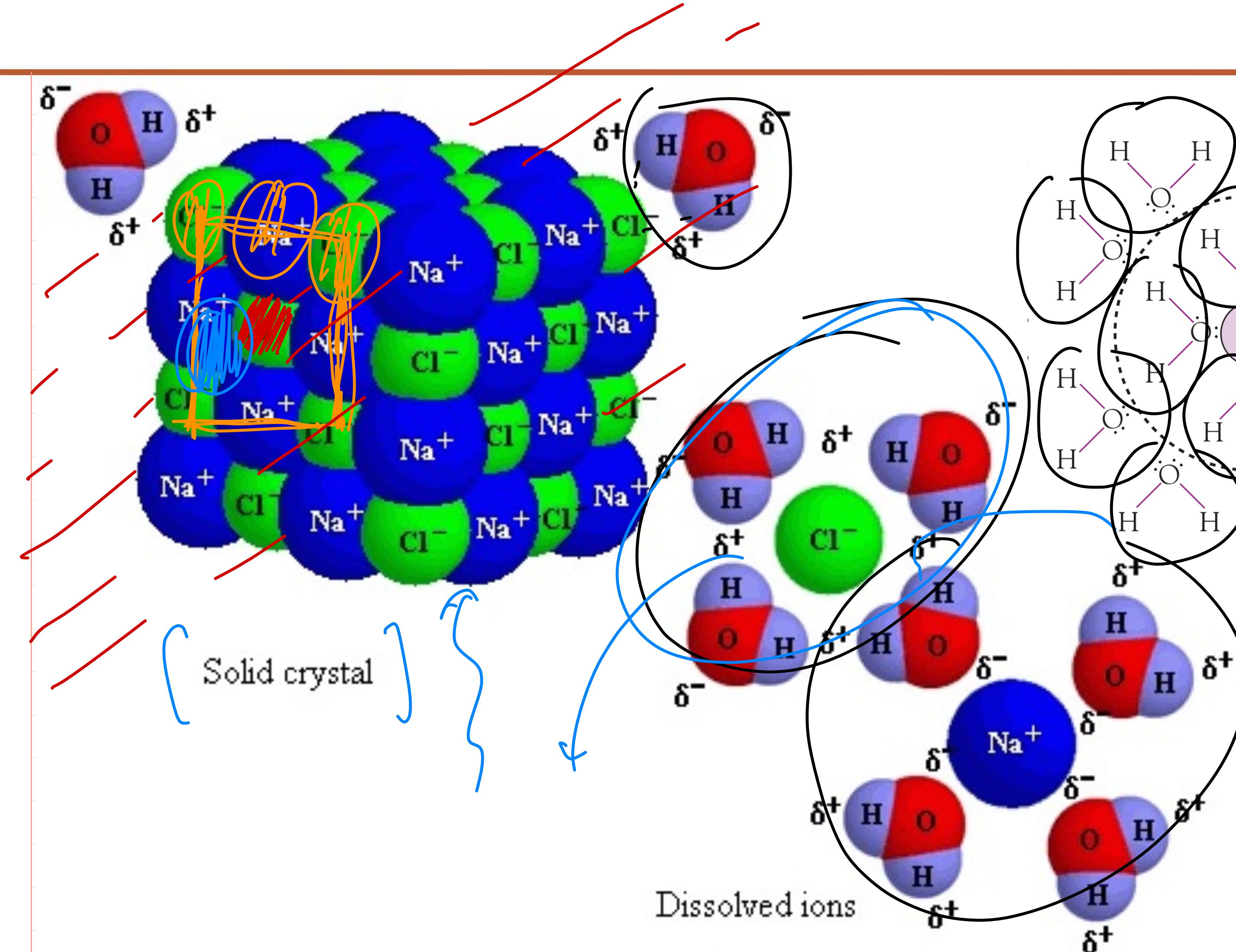
Born water cycle.



$$\Delta H_f(\text{NaCl}) = \Delta H_{\text{SUB}} + \Delta H_{\text{IE}} + \frac{1}{2} \Delta H_{\text{D.E.}} + \Delta H_{\text{E.g.}} + \text{LE}$$

direct/indirect lattice energy





Factor affecting solubility

AL

(a) **Dielectric constant of solvent** – The capacity of solvent to neutralise the charge of ionic compounds is called Dielectric constant. It is represented by ϵ .

(i) Water has maximum dielectric constant ($\epsilon = 80$)

$(CH_3OH \epsilon = 35)$, $(Acetone \epsilon = 21)$

$(C_2H_5OH \epsilon = 27)$, $(Ether \epsilon = 4.1)$

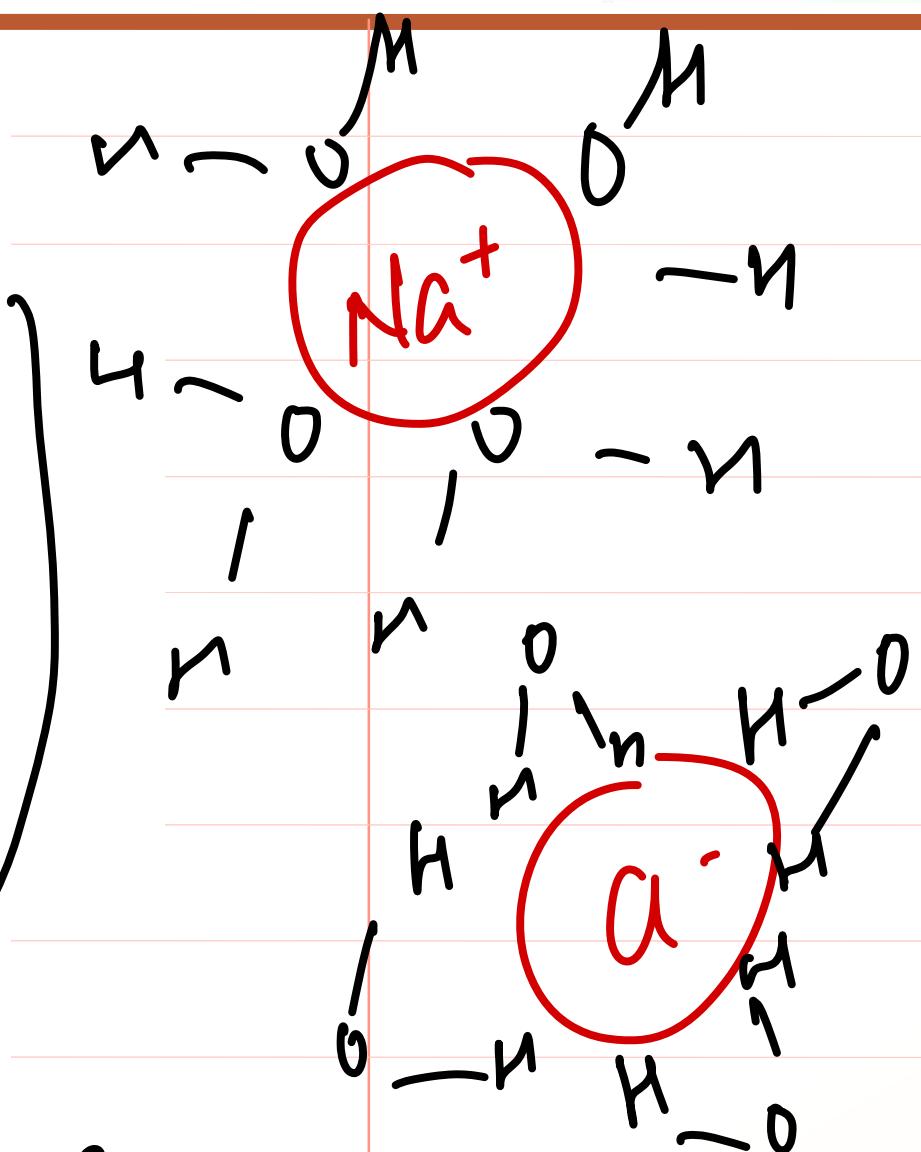
$(Benzene \epsilon = 2.3)$

$H_2O > CH_3OH > CH_3CH_2OH > CH_3COCH_3 > CH_3OCH_3 > C_6H_6$

(ii) Ionic compounds are more soluble in the solvents, having high dielectric constant.

HF	→	120
H_2SO_4	→	102
H_2O	→	81
D_2O	→	78

HF	→	120
H_2SO_4	→	102
H_2O	→	81
D_2O	→	78



(Q) Solubility of KI is maximum in which solvent?

(a) CH_3OH

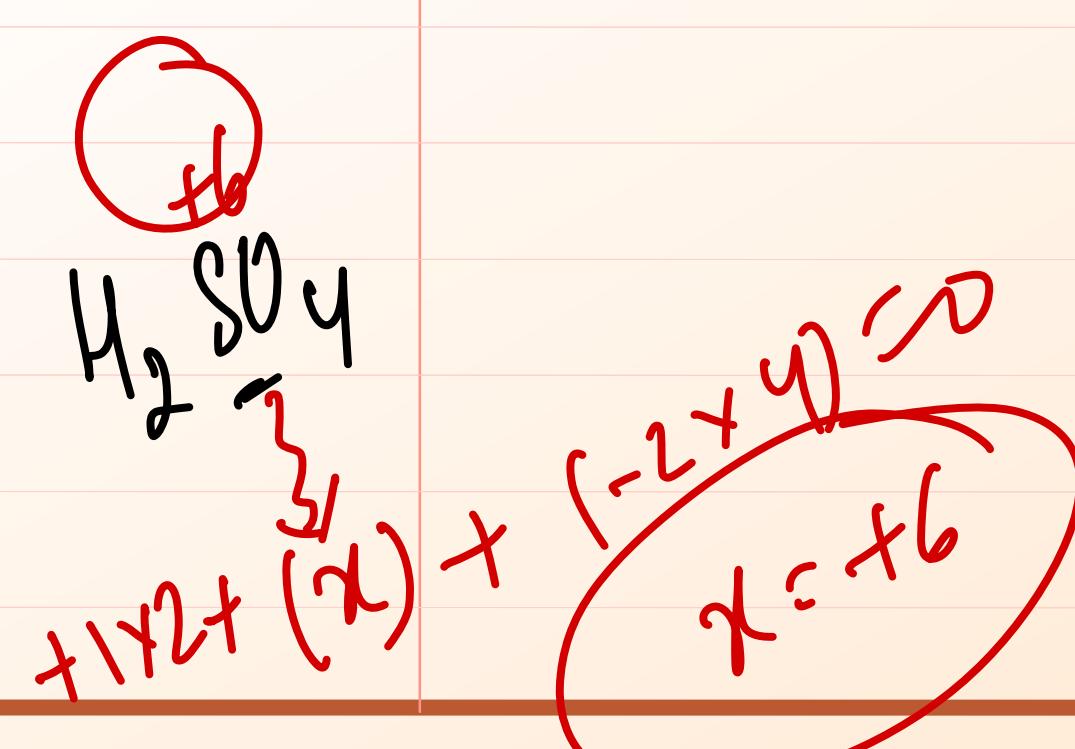
(b) C_2H_5OH

(c) CH_3OCH_3

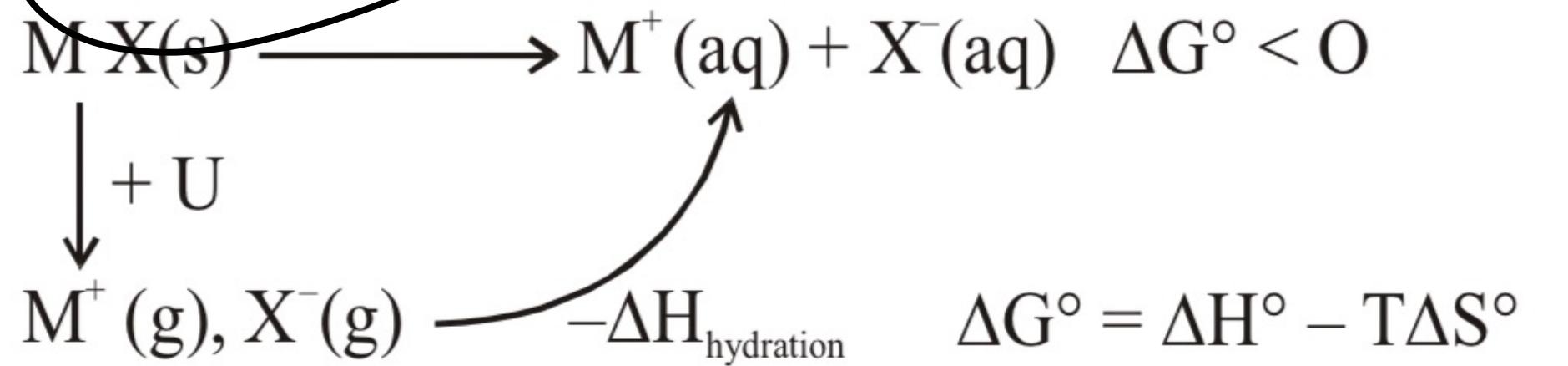
(d) C_6H_6 (non polar)

Note :

H_2SO_4 and H_2O_2 have high dielectric constant but these are not a good solvent due to oxidising nature.



(b) **Lattice energy and Hydration energy -**



For the solubility of ionic compounds in water, it is necessary that ΔG° must be negative.

Favourable conditions for solubility of ionic compound in water is

$$\Delta H_{\text{hydration}} > \Delta H_{\text{Lattice-energy}}$$

$$LE \propto \frac{1}{r^+ + r^-}, \quad HE \propto \frac{1}{r^+} + \frac{1}{r^-}$$

If lattice energy decreases, solubility increases

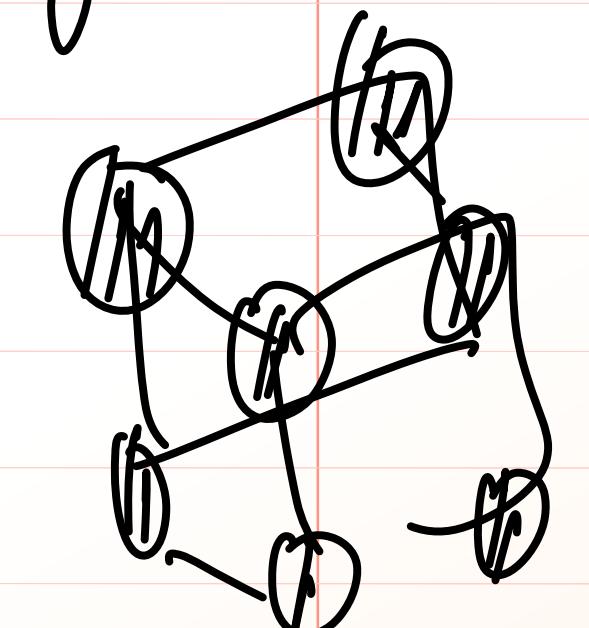
If hydration energy decreases, solubility decreases

In s-block moving down the group, solubility of most of the salts decreases because hydration energy decreases more rapidly as compared to lattice energy.

Solubility

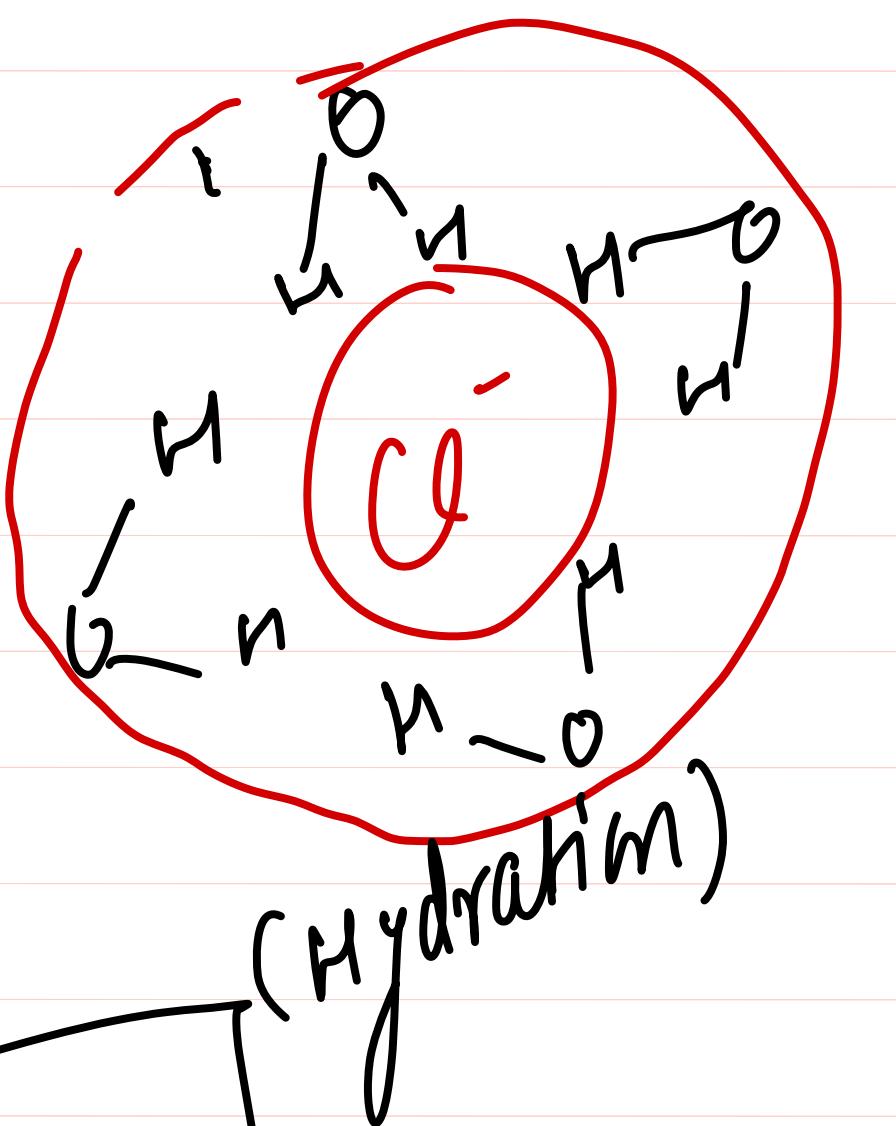
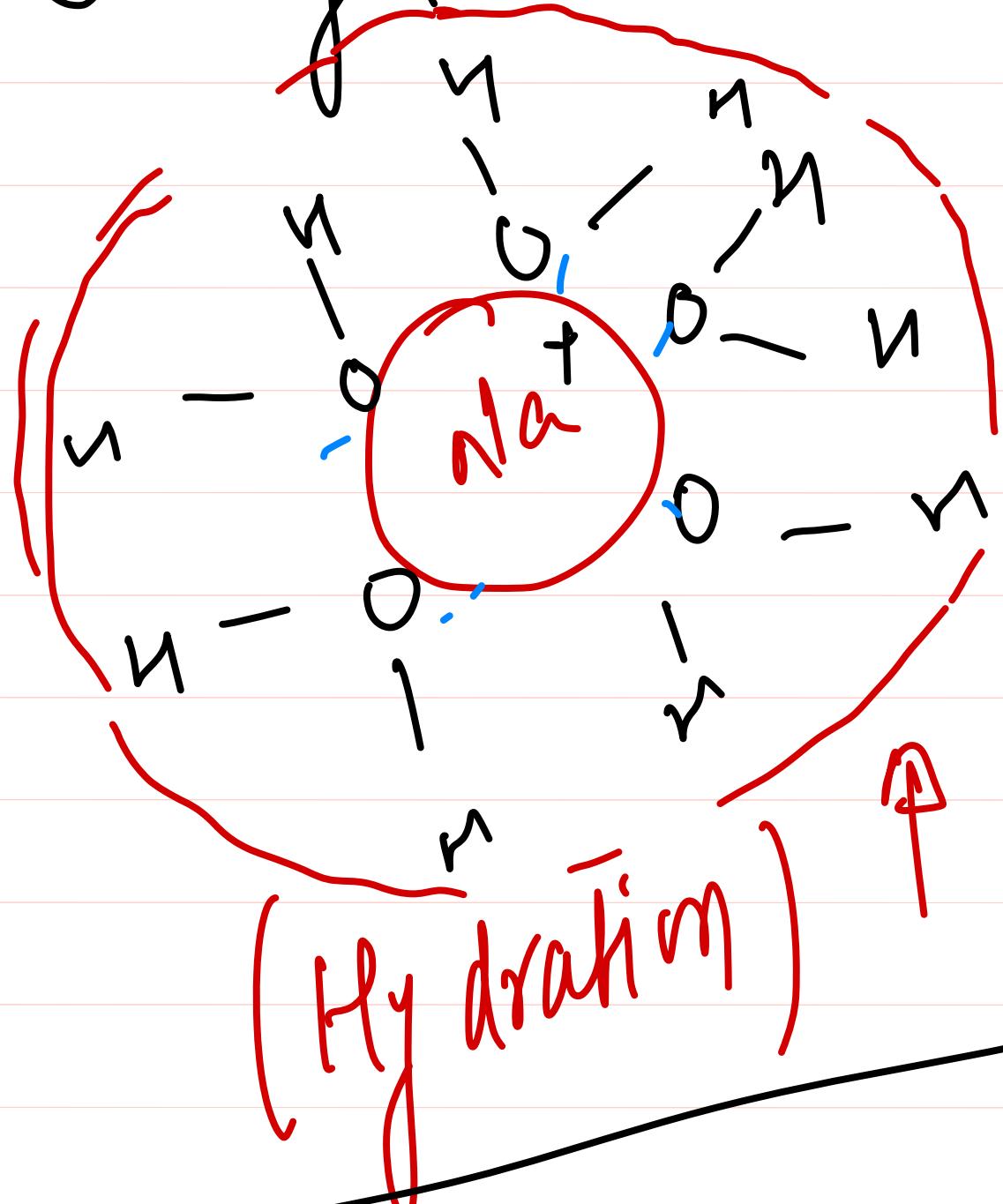
① dielectric Constant

② Lattice energy & Hydration



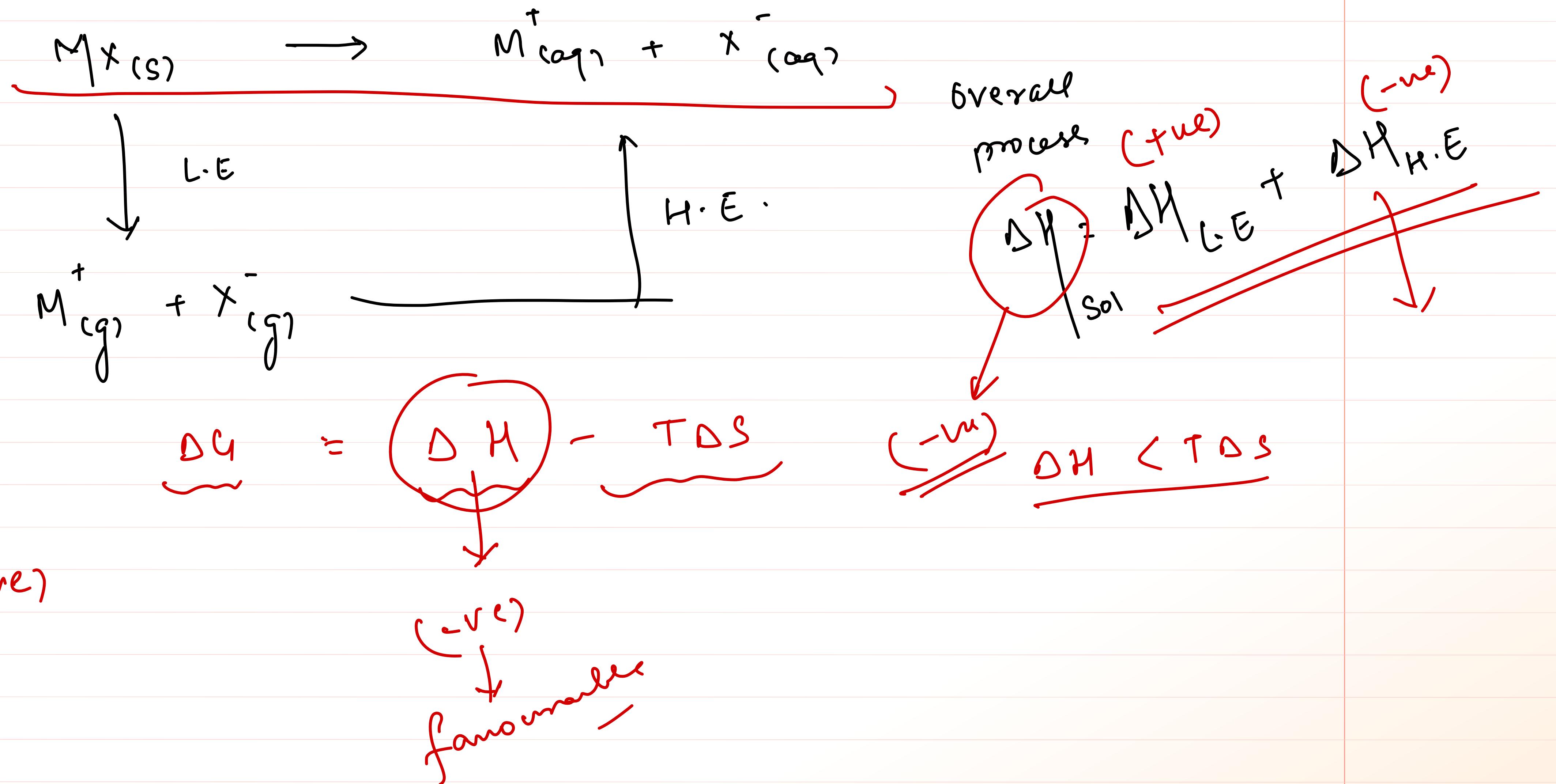
Lattice energy ↑ lattice strong Energy ↑
for solubility ↓ lattice energy ↓

① Hydration Energy ↑



Solubility P

\propto Hydration Energy
Lattice Energy

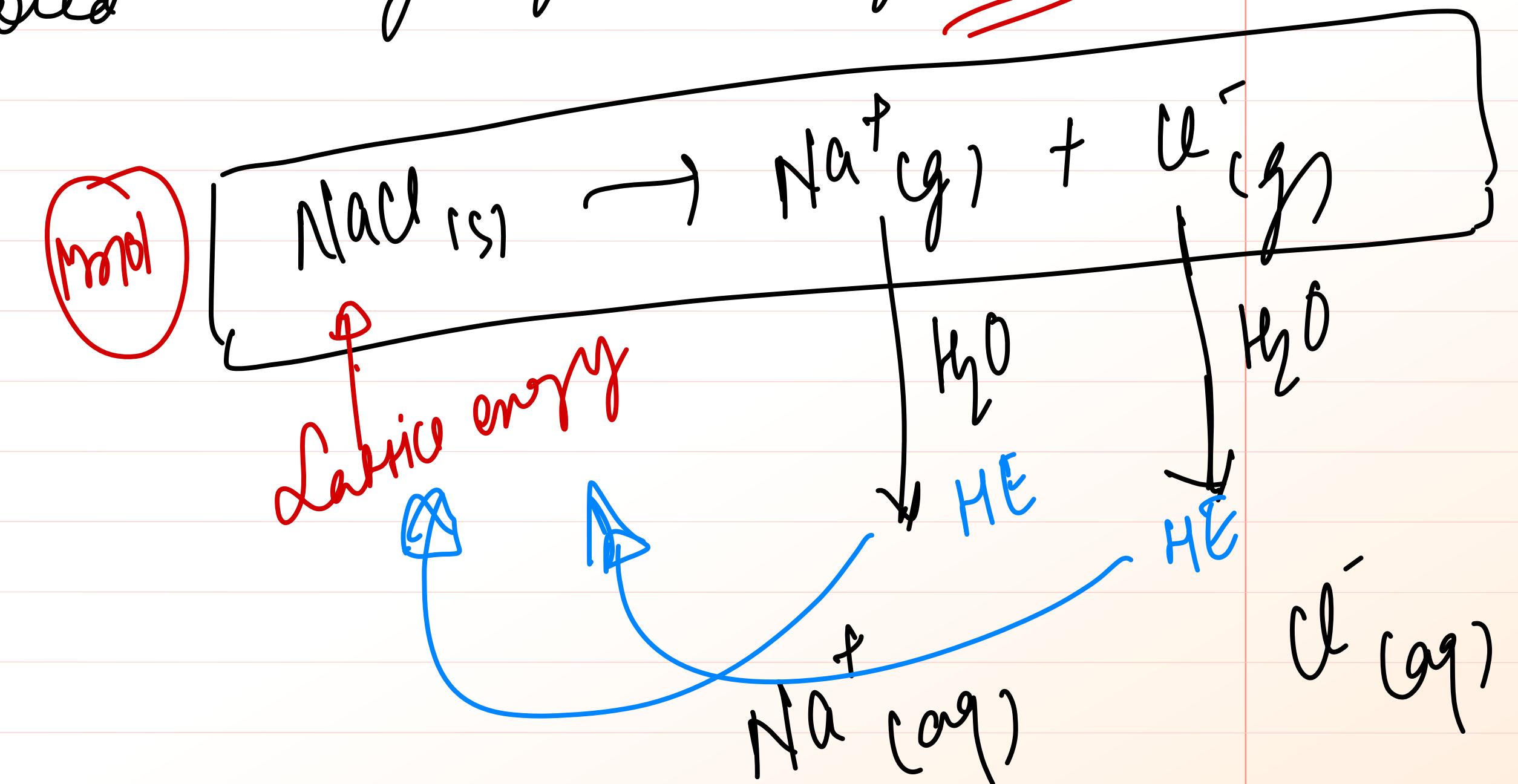
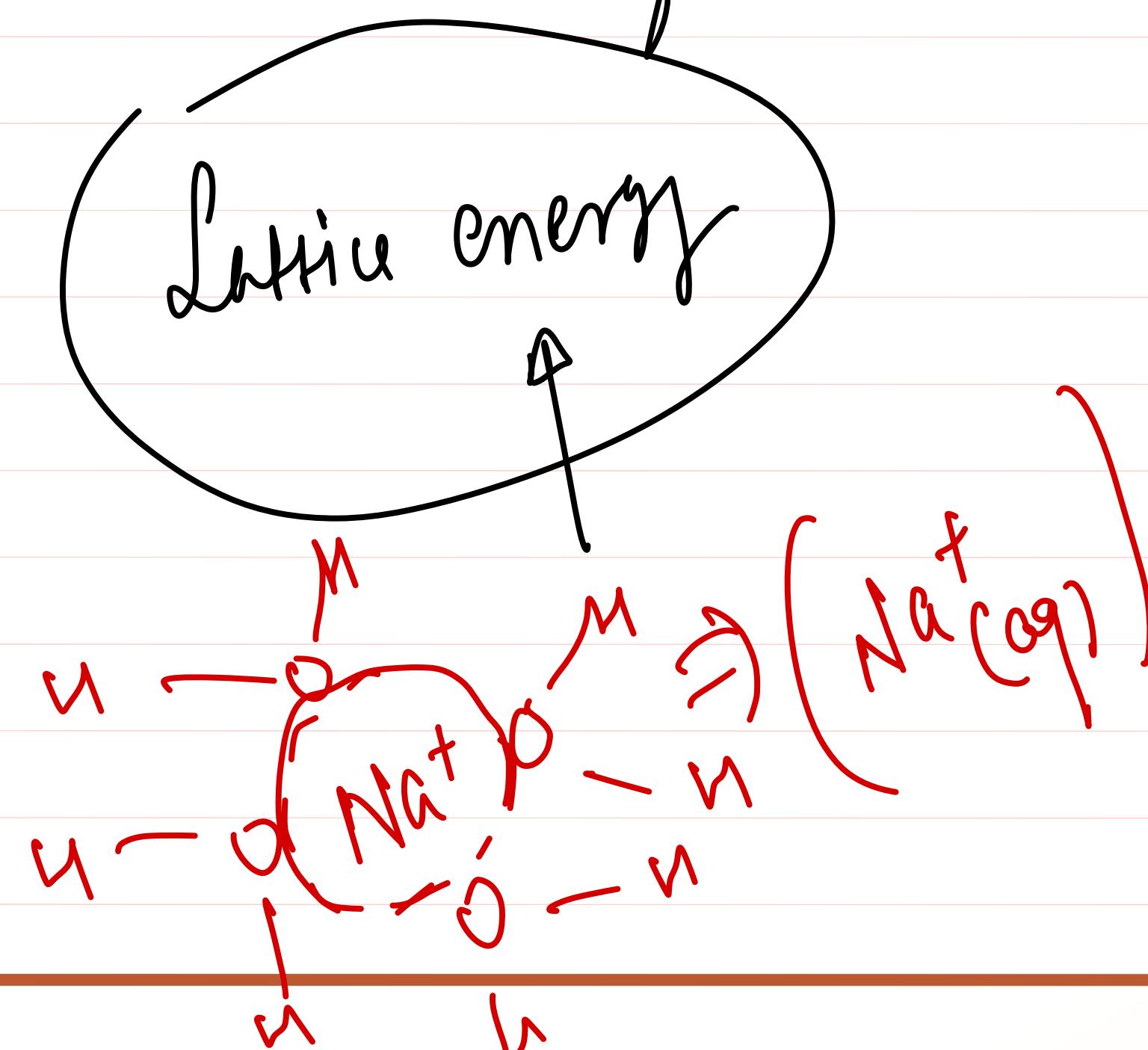


Thus charge on Na^+ and Cl^- decreases and electrostatic force also decreases which leads to free ion.

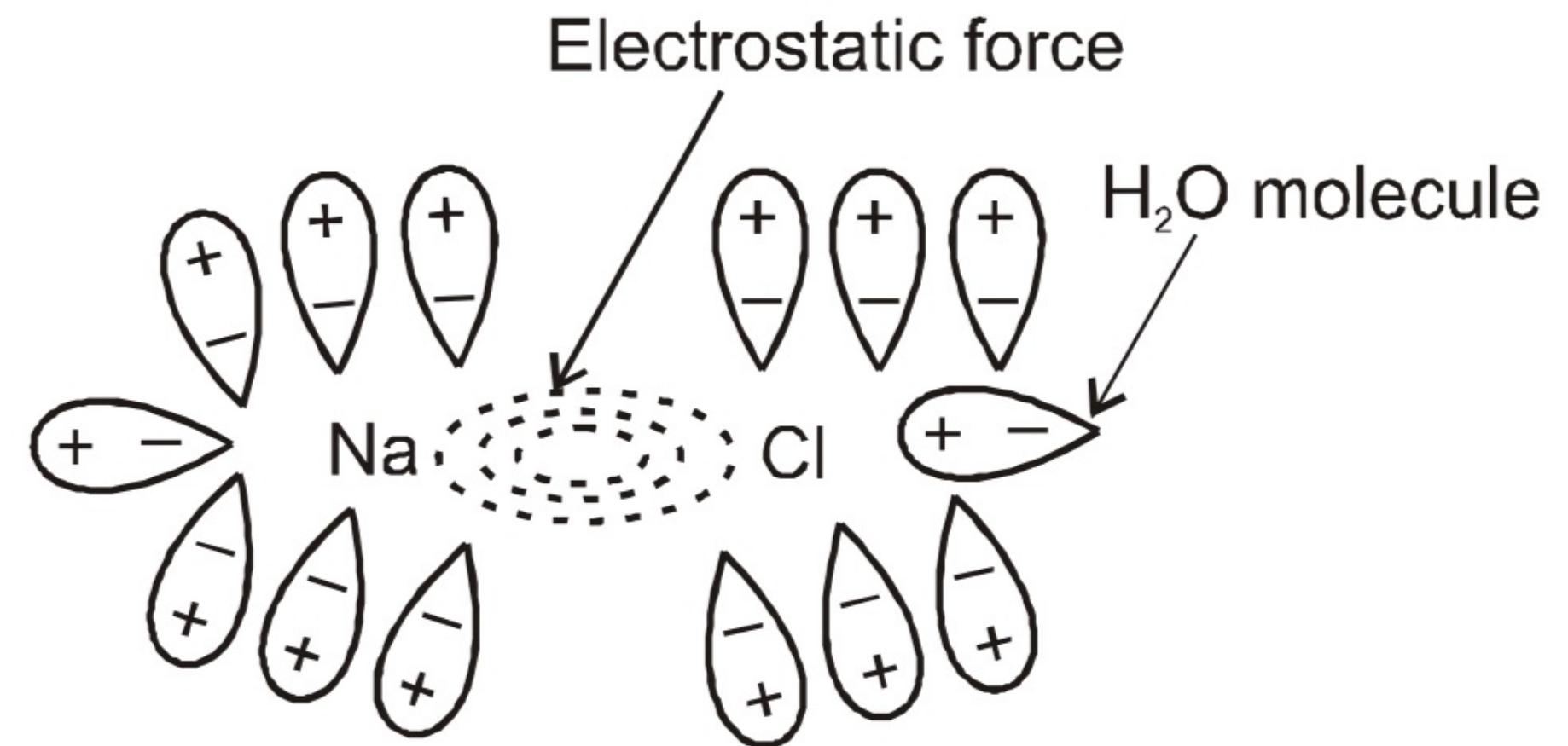
- * Here, attraction force between H_2O and Na^+ or Cl^- (Hydration energy) $>$ Electrostatic force between ions in lattice. (Lattice energy)
- * Energy released due to interaction between polar solvent molecule and ions of solute is called solvation energy. If water used as solvent it is called hydration energy.
- * Condition of the solubility of ionic compound in water is (Hydration energy > Lattice energy)

favourable condition

Hydration Energy: Energy released during hydration of 1 mol of ionic solid

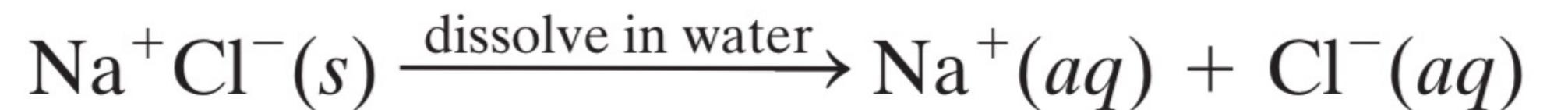


Solvation or Hydration :



Whenever any compound generally ionic or polar covalent is dissolved in an polar solvent or in water then., different ions of the compound will get separated and will get surrounded by polar solvent molecules. This process is known as solvation or hydration. Energy released in this process is known as solvation energy or hydration energy

Solubility of NaCl calculation at 298k



Breaking the process into steps, first, the lattice must be vaporized (dissociate into gaseous ions):



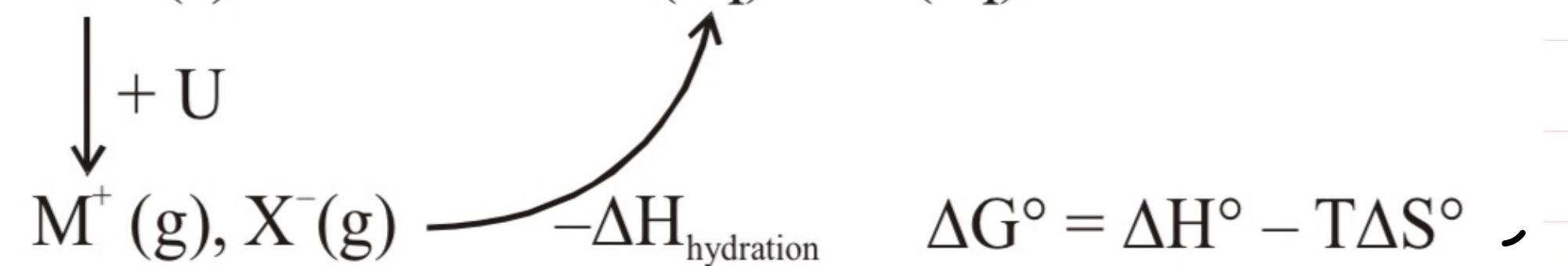
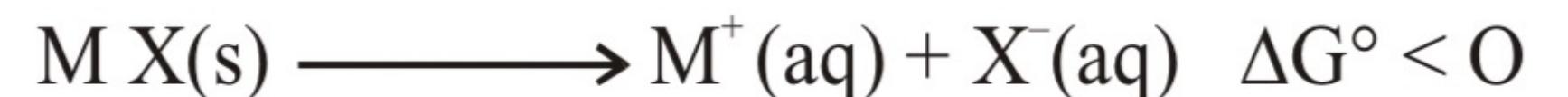
Then the ions are hydrated:



Thus, the enthalpy change ΔH^θ for the solution process is

$$[(+788 \text{ kJ}\cdot\text{mol}^{-1})] + [(-406 \text{ kJ}\cdot\text{mol}^{-1}) + (-378 \text{ kJ}\cdot\text{mol}^{-1})] \\ = +4 \text{ kJ}\cdot\text{mol}^{-1}$$

Lattice energy and Hydration energy –





Then the ions are hydrated:



Thus, the entropy change (as $T\Delta S^\Theta$) for the solution process is

$$[(+68 \text{ kJ}\cdot\text{mol}^{-1})] + [(-27 \text{ kJ}\cdot\text{mol}^{-1}) + (-28 \text{ kJ}\cdot\text{mol}^{-1})] \\ = +13 \text{ kJ}\cdot\text{mol}^{-1}$$

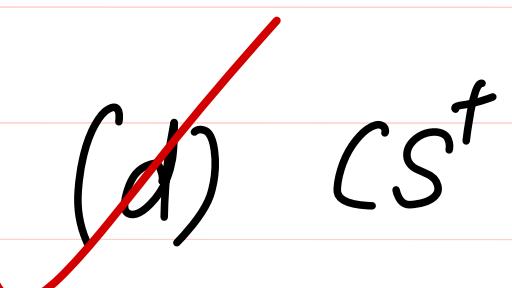
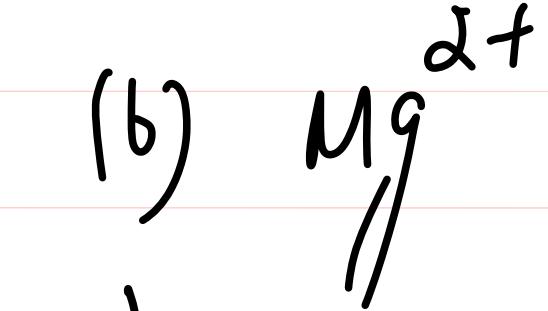
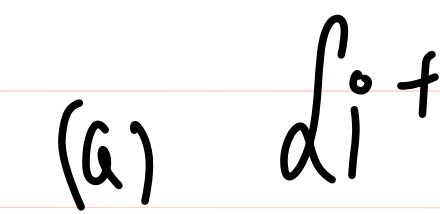
$$\begin{aligned} \Delta G^\Theta &= \Delta H^\Theta - T\Delta S^\Theta \\ &= (+4 \text{ kJ}\cdot\text{mol}^{-1}) - (+13 \text{ kJ}\cdot\text{mol}^{-1}) \\ &= -9 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

Applications of Hydration energy :

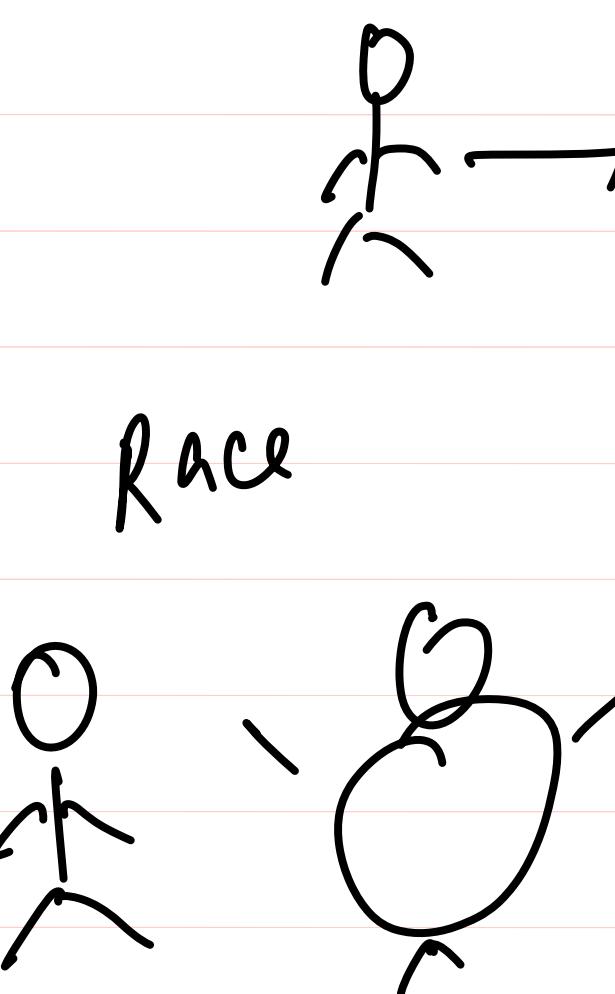
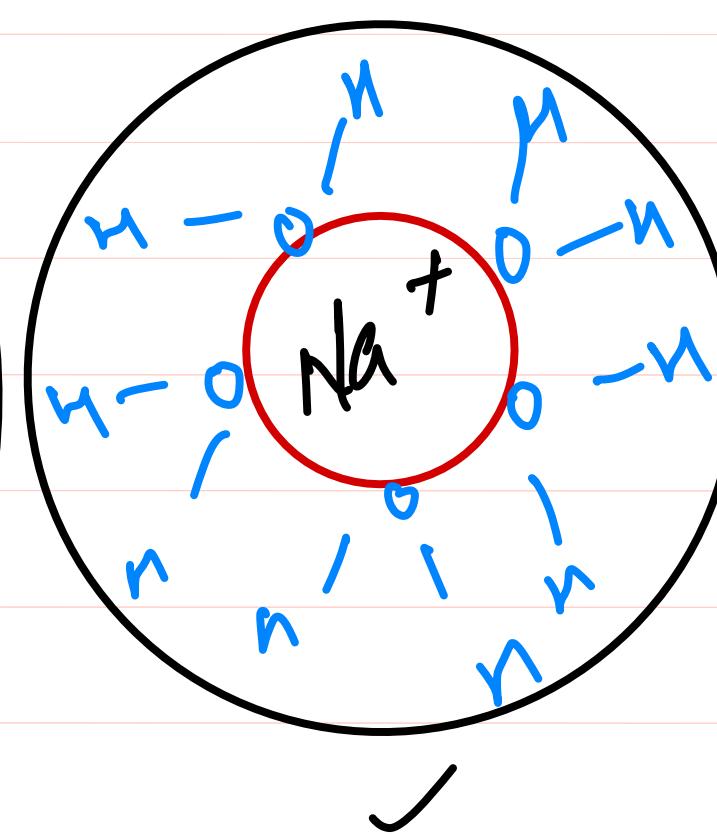
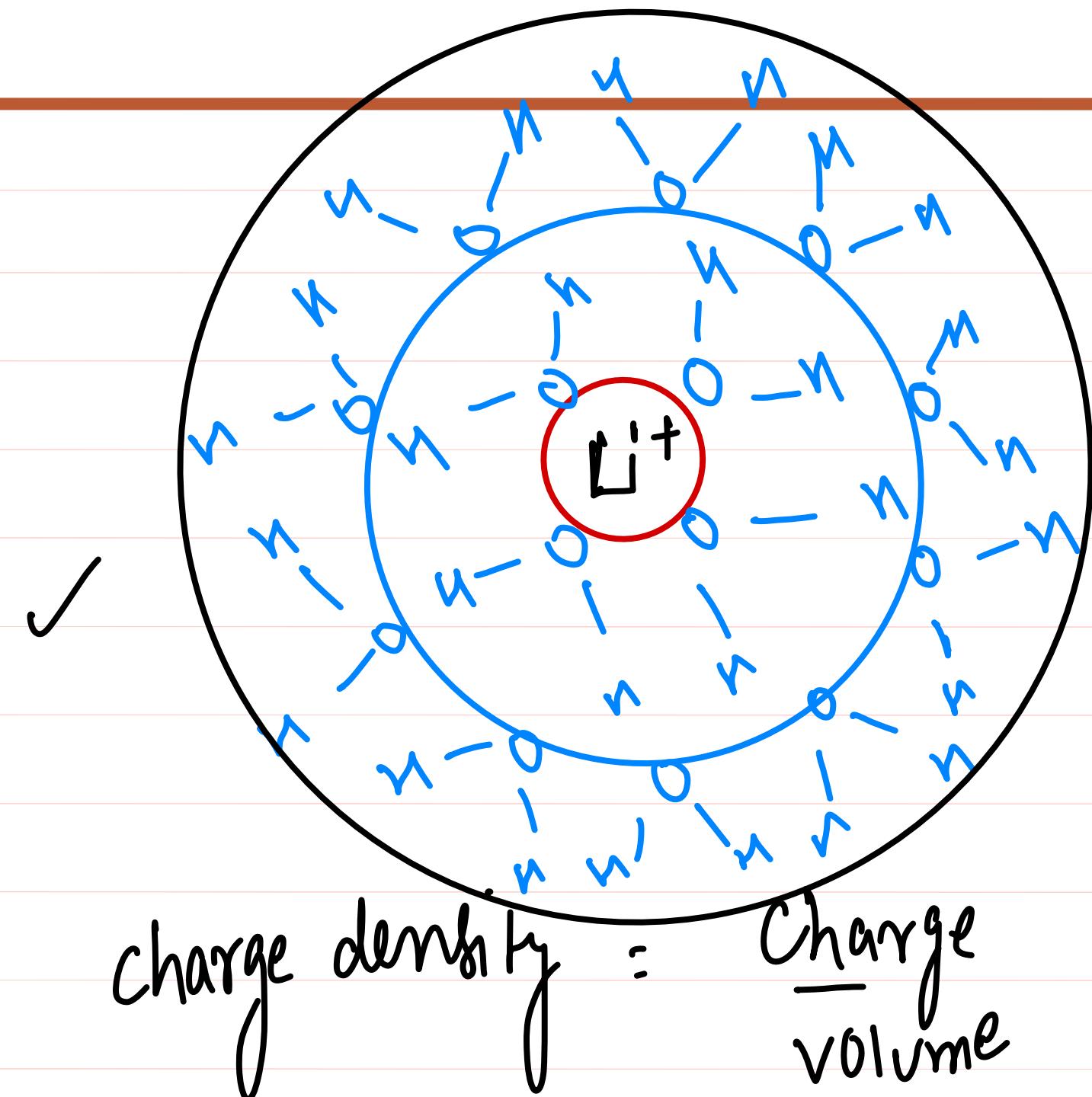
- (a) ✓ Size of the hydrated ions: Greater the hydration of the ion greater will be its hydrated radii
 $\text{Li}^+(\text{aq}) > \text{Na}^+(\text{aq})$
- (b) ✓ Mobility of the ion: more is the hydration smaller will be the mobility of the ions
 $\text{Li}^+(\text{aq}) < \text{Na}^+(\text{aq}) < \text{K}^+(\text{aq}) < \text{Rb}^+(\text{aq}) < \text{Cs}^+(\text{aq})$.
- (c) Electrical conductance : is related to mobility so follows the same order

+

(Q) which of the following has maximum mobility



Ans: He^+ $1s^1$ $2s^1$ $2p^1$
 He^+



$\text{Li}^+ >$
Charge density ↑
Hydration ↑



ionic mobility

ionic potential = $\frac{\text{charge}}{\text{radius}}$

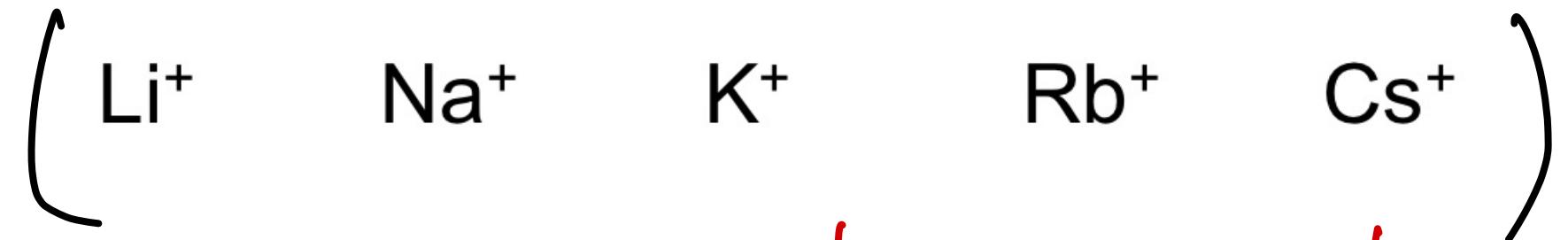
hydrated radius $\text{Li}^+ \text{(aq)} > \text{Li}^+ \text{(g)}$

ionic radius $\text{Li}^+ \text{(g)} < \text{Na}^+ \text{(g)} < \text{K}^+ \text{(g)} < \text{Rb}^+ \text{(g)} < \text{Cs}^+ \text{(g)}$

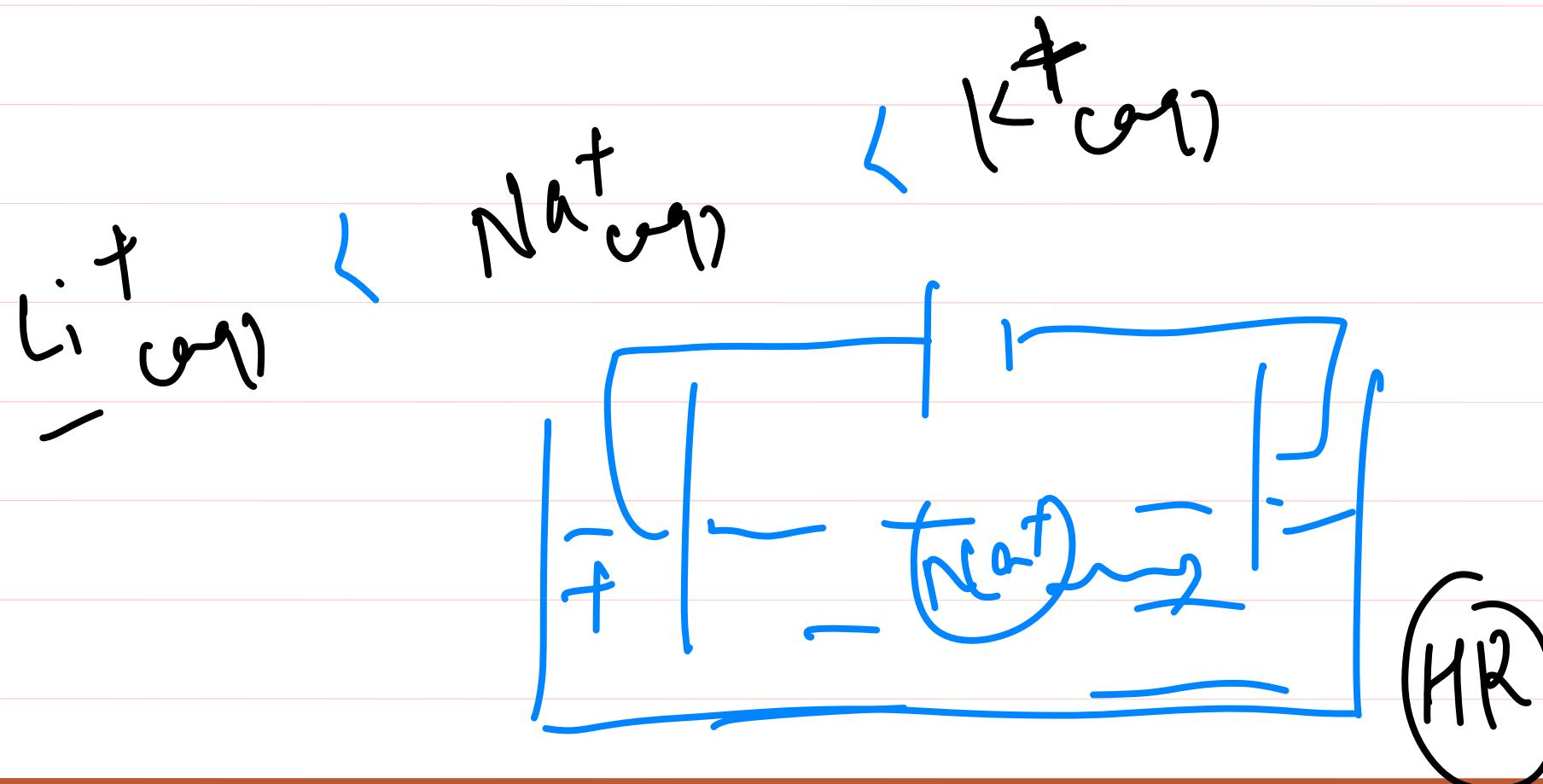
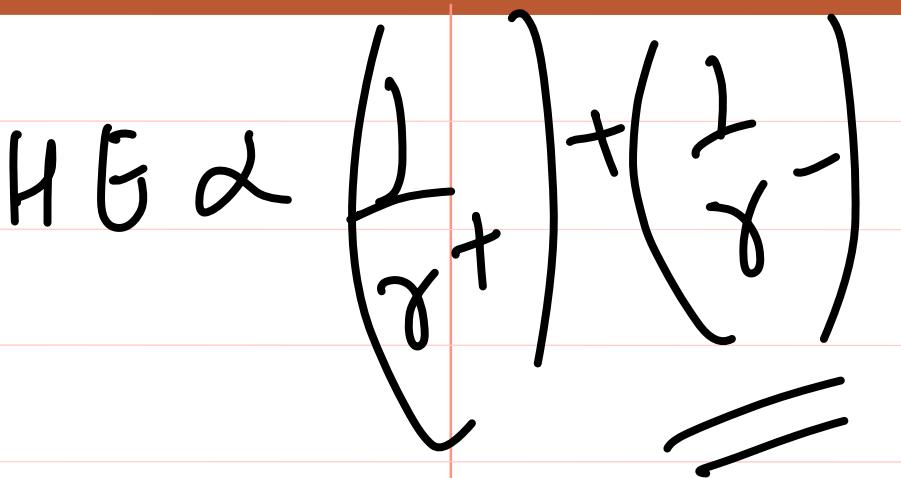
ionic mobility
hydration energy

$\text{Cs}^+ \text{ (aq)} > \text{Rb}^+ \text{ (aq)} > \text{K}^+ \text{ (aq)} > \text{Na}^+ \text{ (aq)} > \text{Li}^+ \text{ (aq)}$
 $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+ \text{ (aq)}$

E.g. :- (In Aqueous solution)



- ✓ Ionic radius (\uparrow) $\rightarrow \text{Cs}^+ (\text{aq}) > \text{Rb}^+ (\text{aq}) > \text{K}^+ (\text{aq}) > \text{Na}^+ (\text{aq}) > \text{Li}^+ (\text{aq})$
- ✓ Hydrated radii (\downarrow) $\rightarrow \text{Li}^+ (\text{aq}) > \text{Na}^+ (\text{aq}) > \text{K}^+ (\text{aq}) > \text{Rb}^+ (\text{aq}) > \text{Cs}^+ (\text{aq})$
- ✓ Movement of ions (\uparrow) $\rightarrow \text{Cs}^+ (\text{aq}) > \text{Rb}^+ (\text{aq}) > \text{K}^+ (\text{aq}) > \text{Na}^+ (\text{aq}) > \text{Li}^+ (\text{aq})$
- ✓ Ionic mobility (\uparrow) $\rightarrow \text{Cs}^+ (\text{aq}) > \text{Rb}^+ (\text{aq}) > \text{K}^- (\text{aq}) > \text{Na}^+ (\text{aq}) > \text{Li}^+ (\text{aq})$
- ✓ Ionic conductivity (\uparrow) $\rightarrow \text{Cs}^+ (\text{aq}) > \text{Rb}^+ (\text{aq}) > \text{K}^+ (\text{aq}) > \text{Na}^+ (\text{aq}) > \text{Li}^+ (\text{aq})$



radius $\text{Li}^+ (\text{aq}) > \text{Na}^+ (\text{aq}) > \text{K}^+ (\text{aq})$
ionic mobility $\text{Li}^+ (\text{aq}) < \text{Na}^+ (\text{aq}) < \text{K}^+ (\text{aq})$
 $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

TRANSITION FROM IONIC TO COVALENT BOND – FAJANS' RULE

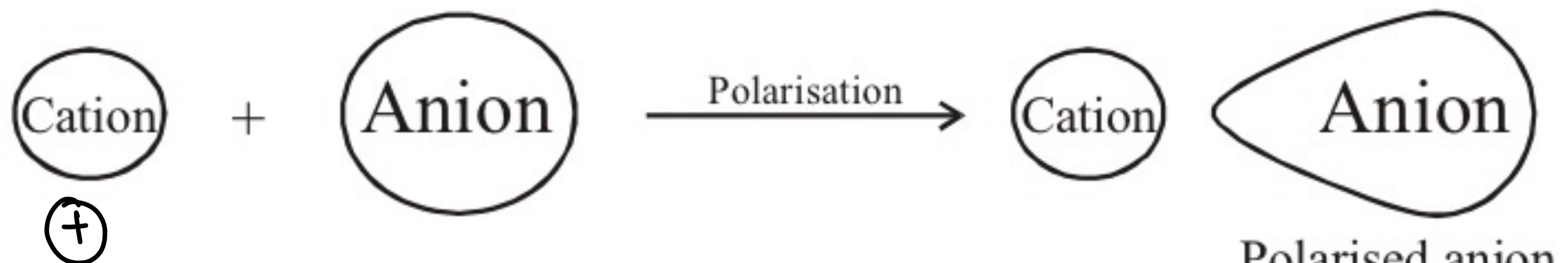
SL AL

Just as a covalent bond may have partial ionic character an ionic bond may also show a certain degree of covalent character. When two oppositely charged ions approach each other closely, the cation would attract the electrons in the outer shell of the anion and simultaneously repel its nucleus. This produces distortion or polarization of the anion, which is accompanied by some sharing of electrons between the ions, i.e., the bond acquires a certain covalent character.

Terms used in polarisation in ionic compounds.

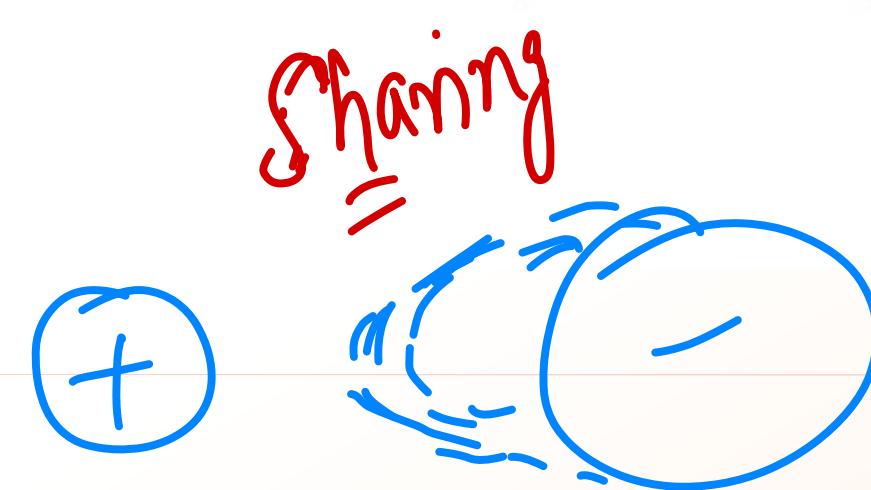
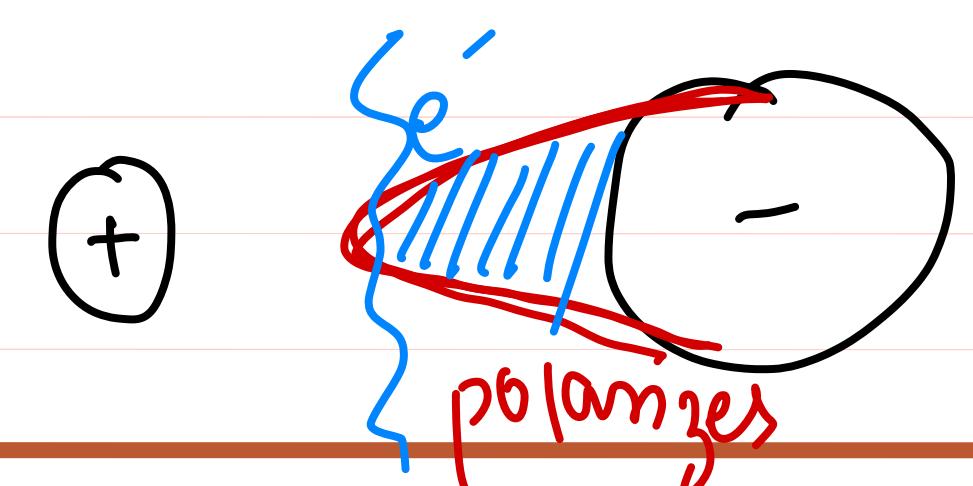
Polarisation Power :

The ability of cation to polarise a nearby anion is called Polarisation power of cation.



Polarisation power of a cation is usually called ionic potential or charge density.

$$\text{Ionic potential } \phi \text{ (phi)} = \frac{\text{Charge on cation}}{\text{Size of cation}}$$



$\text{Li}^+ > \text{Na}^+$
charge density

AgF AgCl AgBr AgI ?

SnCl_2

SnCl_4

ionic
character

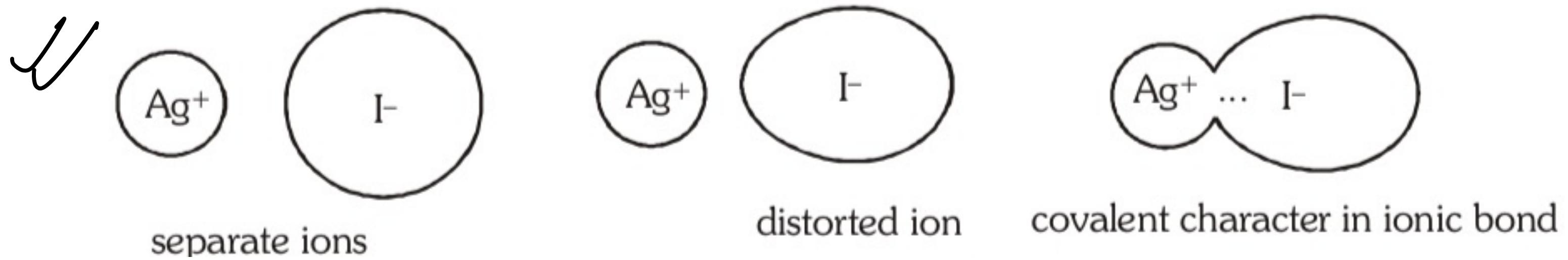
quality

qualitative
as per

Polarizability : (property of anion)

- (i) It is the ability of anion to get polarised by the cation.
- (ii) Polarisation of anion causes some sharing of electron between the ions so ionic bond acquires certain covalent character.
- (iii) Increase in polarisation increases covalent character.
- (iv) Magnitude of polarisation depends upon a number of factors, suggested by Fajan and are known as Fajan's rule.

The formation of a covalent bond between two ions may be illustrated with reference to formation of AgI.



p.p
 $\text{Fe}^{+2} < \text{Fe}^{+3}$

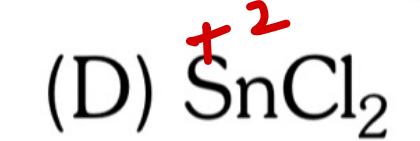
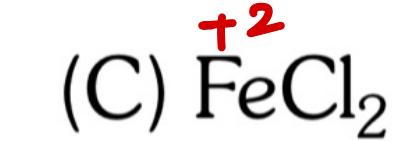
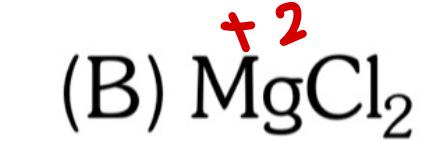
Factors influencing ion - Deformation or increasing covalent character

SL AL

(i)

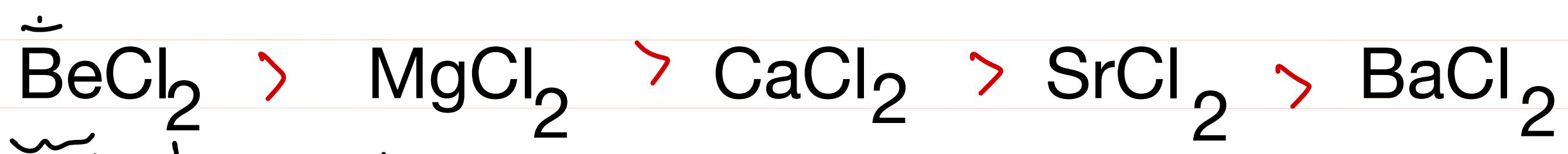
Large charge on the ions – The greater the charge on the cation, the more strongly will it attract the electrons of the anion. For example, Al^{3+} can distort Cl^- ion more than Na^+ ion. So aluminium chloride is a covalent compound whereas NaCl , AlF_3 , AgF are ionic.

(Q) Among the following the maximum covalent character is shown by the compound :-

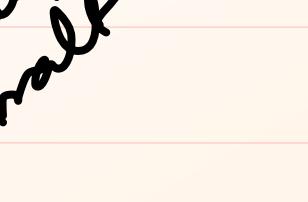
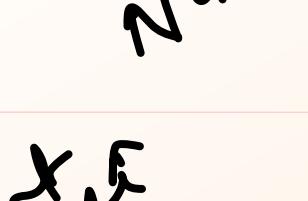
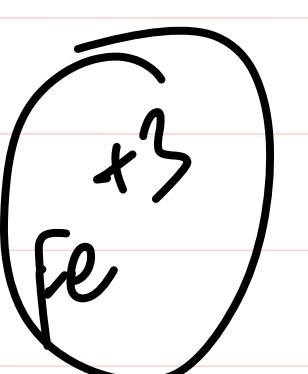
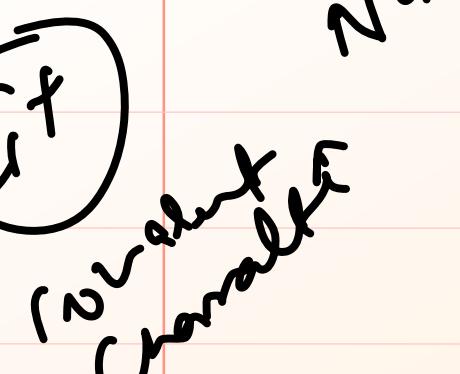
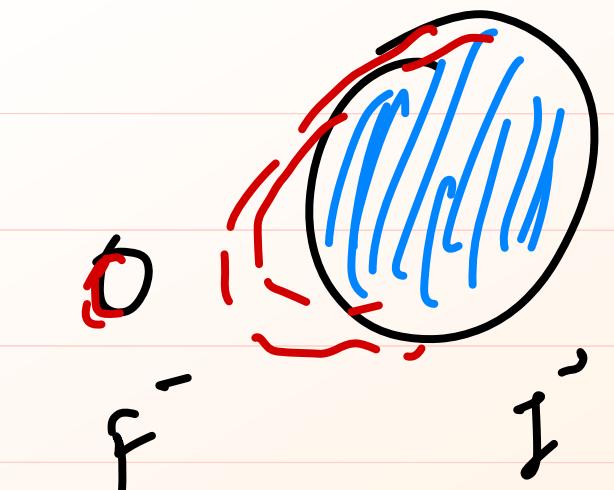
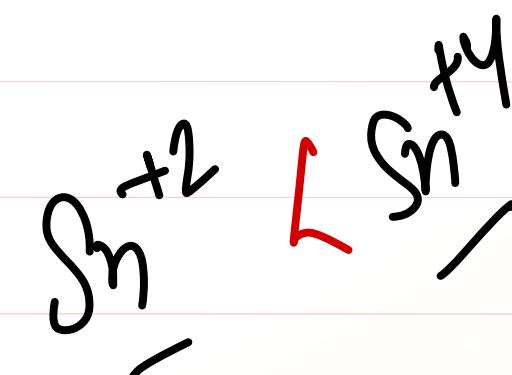
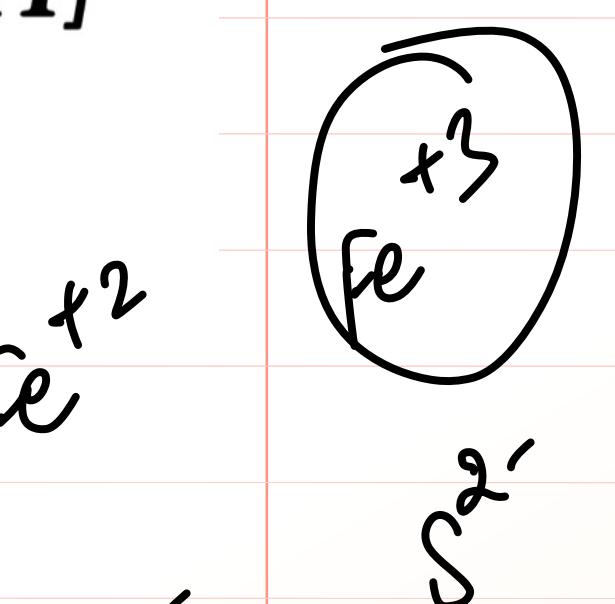
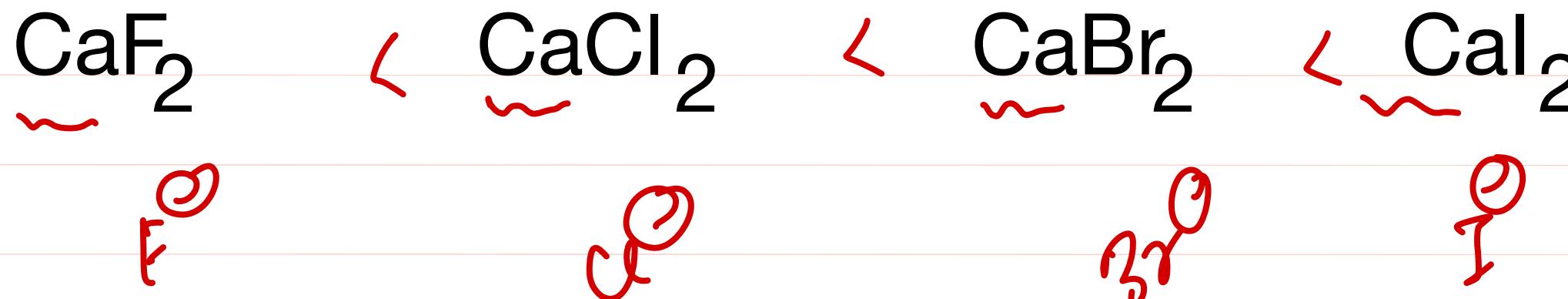


[AIEEE-2011]

Arrange in order of compound with more covalent character



\downarrow
cation
 \uparrow
p. r. \uparrow covalent



(ii) **Small cation and large anion** - For a small cation, the electrostatic force with which its nucleus will attract the anion will be more. Moreover a large anion cannot hold the electrons in its outermost shell, especially when they are attracted by a neighbouring cation. Hence there will be increased covalent character with a small cation and a large anion, as in AgI.

Maximum Covalent character is present in :

- ~~(a) LiCl. (b) NaCl. (c) KCl. (d) CsCl~~

$$\text{Lattice energy} \propto |z^+||z^-|$$

(Q) Which is more soluble in water?

~~(a) AgF~~

① AgF P

②

AgCl

③

AgBr

④

AgI

I

$$\alpha \frac{1}{r^+ + r^-}$$

anim

more

covalent

character

large

the

size

of anion

(AgI, AgBr, AgF)

(Q) MP of SnCl₂ > MP of SnCl₄.

(less covalent character more ionic character)

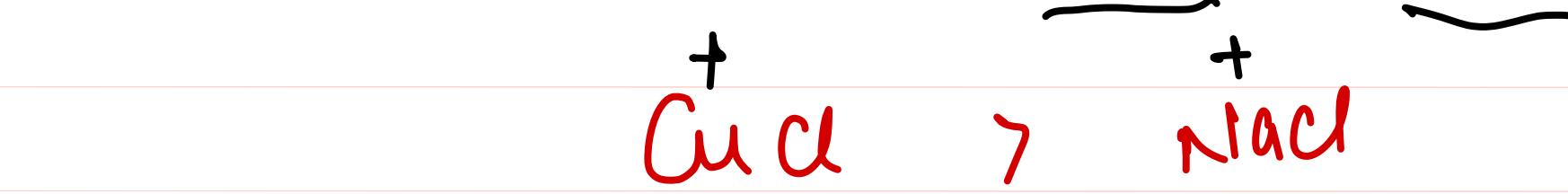
When ions are sticky

(iii) Cation with a pseudo-inert gas type of electronic configuration - A cation with a 18 electron in outermost shell such as Ag^+ ($[\text{Kr}] 4\text{d}^{10}$) polarizes anions more strongly than a cation with a 8 electron arrangement as in K^+ . The 'd' electrons in Ag^+ do not screen the nuclear charge as effectively as the 's' and 'p' electron shell in K^+ . Thus AgI is more covalent than KI , although Ag^+ and K^+ ions are nearly of the same size. Cuprous and mercurous salts are covalent.

A comparison of KI & AgI

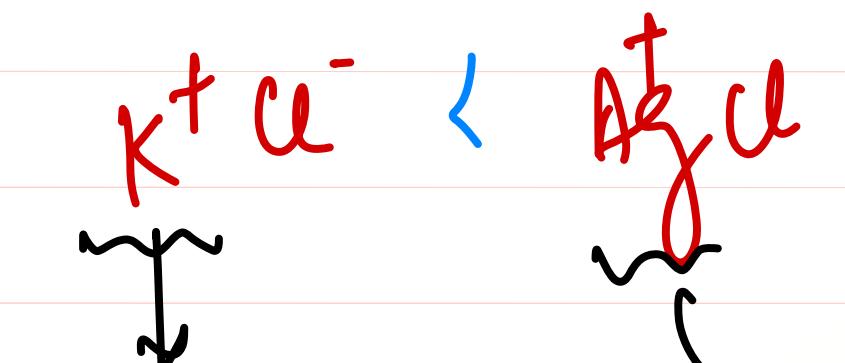
Compound	Melting point (°C)	Charge density (C·mm ⁻³)	Bonding classification
KCl	(770)	11	Ionic
AgCl	455	15	Partially covalent

Compare covalent character CuCl and NaCl .

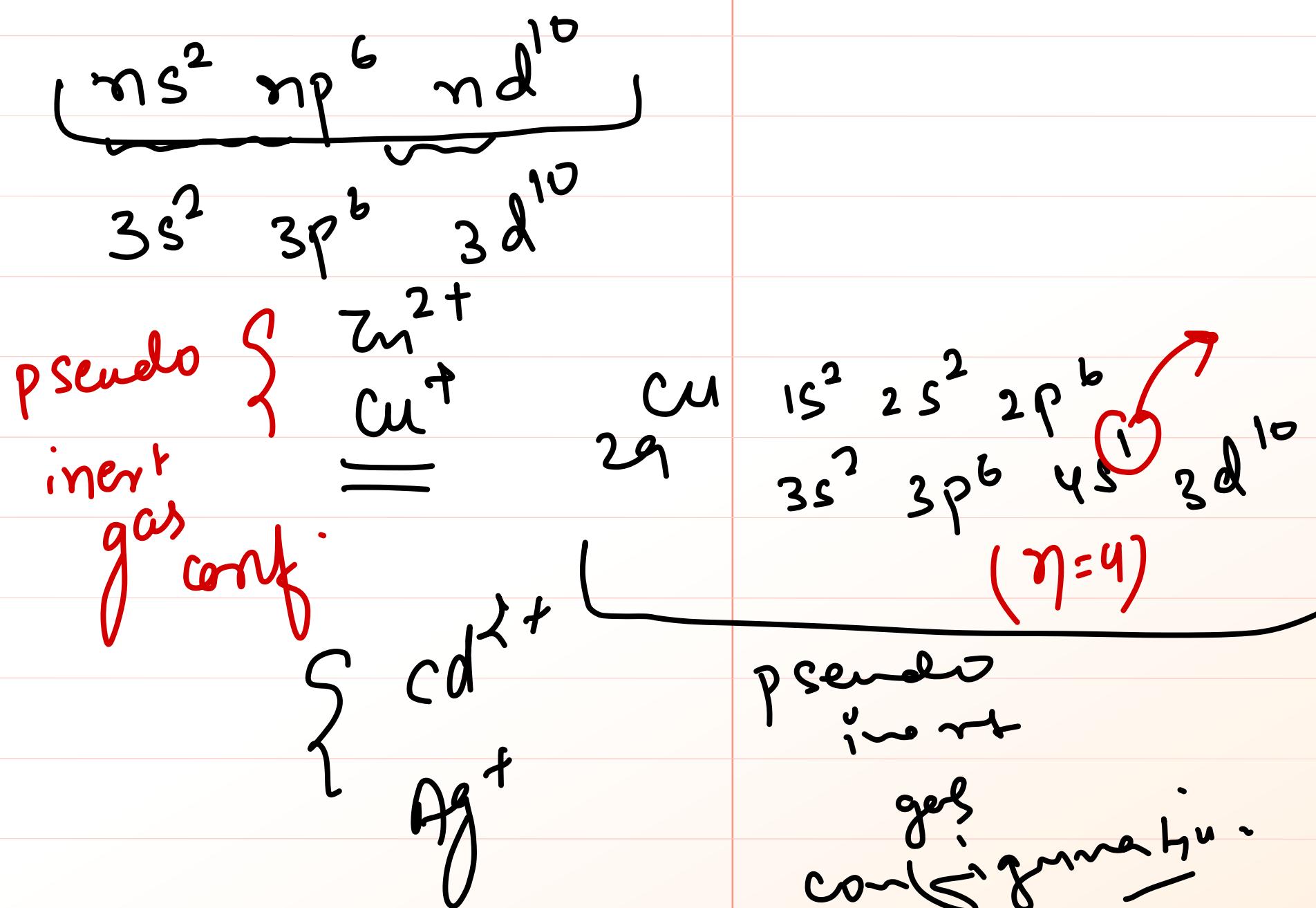


ψ = charge density
Covalent character

Covalent character



inert gas configuration



pseudo inert gas configuration =

Electronic configuration of cation :-

Order of Polarisation power : $8e^- < (18+2) e^- < 18e^-$

Spelling example:

$\text{Na}^+, \text{Sr}^{+2}$

Sn^{2+} Tl^+

Order of covalent character

- $\text{LiF} < \underline{\text{LiCl}} < \underline{\text{LiBr}} < \underline{\text{LiI}}$
 - $\text{CaCl}_2 < \overset{+2}{\text{FeCl}}_2 < \overset{+3}{\text{FeCl}}_3$
 - $\text{SrCl}_2 < \text{SnCl}_2 < \text{CdCl}_2$

inert gas / Same period. $(18+2)e$ Periodic table.

Note : order of covalent character $\text{ZnCl}_2^{+2} < \text{CdCl}_2^{+2} < \text{HgCl}_2^{+2}$



ϕ = charge density.

$18e^-$
 $ns^2 np^6$ nd¹⁰ (High z._{effective})

Example : Zn^{2+} Cd^{2+} Hg^{2+} Cu^+

The diagram illustrates four metal ions, each enclosed in a circle:

- Zn^{2+}
- Cd^{2+}
- Hg^{2+}
- Cu^+

1

O_2

6P

us² up⁶ ud¹

(18) +

2 5p⁶ 5d¹⁰
18 - 10

65.
re

* sch example

$$3\alpha < \beta \Rightarrow \text{True}$$

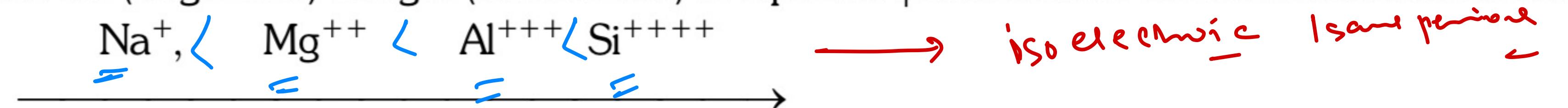
Application of the concept of polarisation

AL

(a) To determine covalent and ionic character of molecule

$$\phi \propto \frac{\text{Covalent character}}{\text{Ionic character}}$$

From left (larger size) to right (smaller size) in a period ϕ increases so covalent character increases.



- charge increases
- size decreases ϕ increases
- Covalent character increases with particular anion

From top to bottom in a group ϕ decreases so covalent character decreases.



Na^+ - Size increases (charge is fix)

K^+ - ϕ decreases

Rb^+ - Hence covalent character decreases with particular anion



(Q) compare the covalent character. NaCl \swarrow MgCl_2 \swarrow AlCl_3 \swarrow SiCl_4

(b) To determine the solubility of compound

In polar solvent: higher polarization will cause less solubility. For example,

- (i) $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$
- (ii) $\text{PbF}_2 > \text{PbCl}_2 > \text{PbBr}_2 > \text{PbI}_2$
- (iii) $\text{HgF}_2 > \text{HgCl}_2 > \text{HgBr}_2 > \text{HgI}_2$

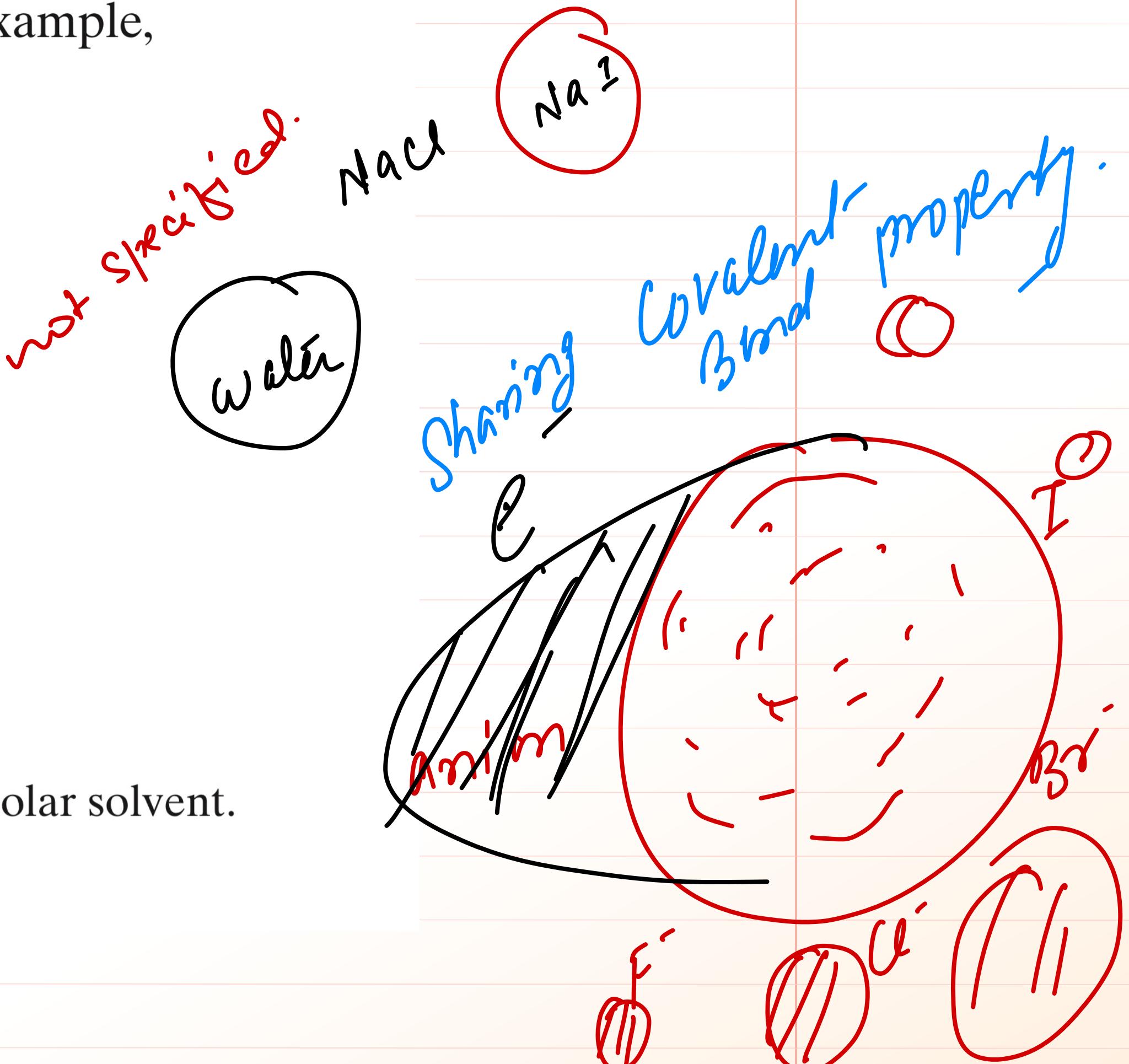
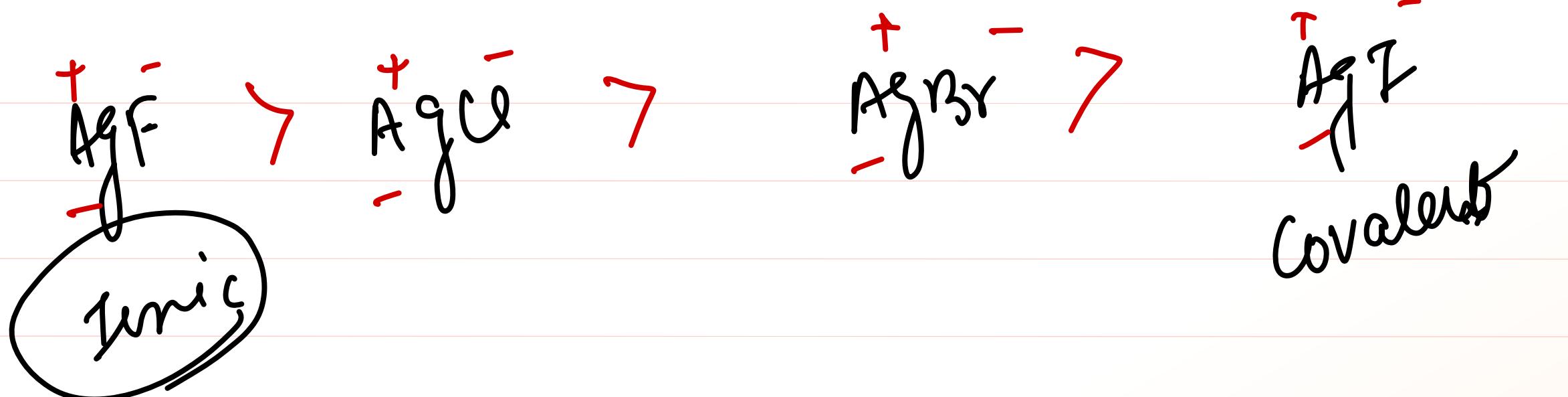
In relatively non-polar solvents, e.g. acetone, the solubility order is



Since the covalent character order is



more the covalent character, higher will be the solubility in relatively non-polar solvent.



Correct order of covalent character of alkaline earth metal chloride in

- (A) $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{SrCl}_2$ (B) $\text{BeCl}_2 < \text{CaCl}_2 < \text{SrCl}_2 < \text{MgCl}_2$
~~(C) $\text{BeCl}_2 > \text{MgCl}_2 > \text{CaCl}_2 > \text{SrCl}_2$~~ (D) $\text{SrCl}_2 > \text{BeCl}_2 > \text{CaCl}_2 > \text{MgCl}_2$

Which of the compound is least soluble in water

- (A) AgF (B) AgCl (C) AgBr ~~(D) AgI~~

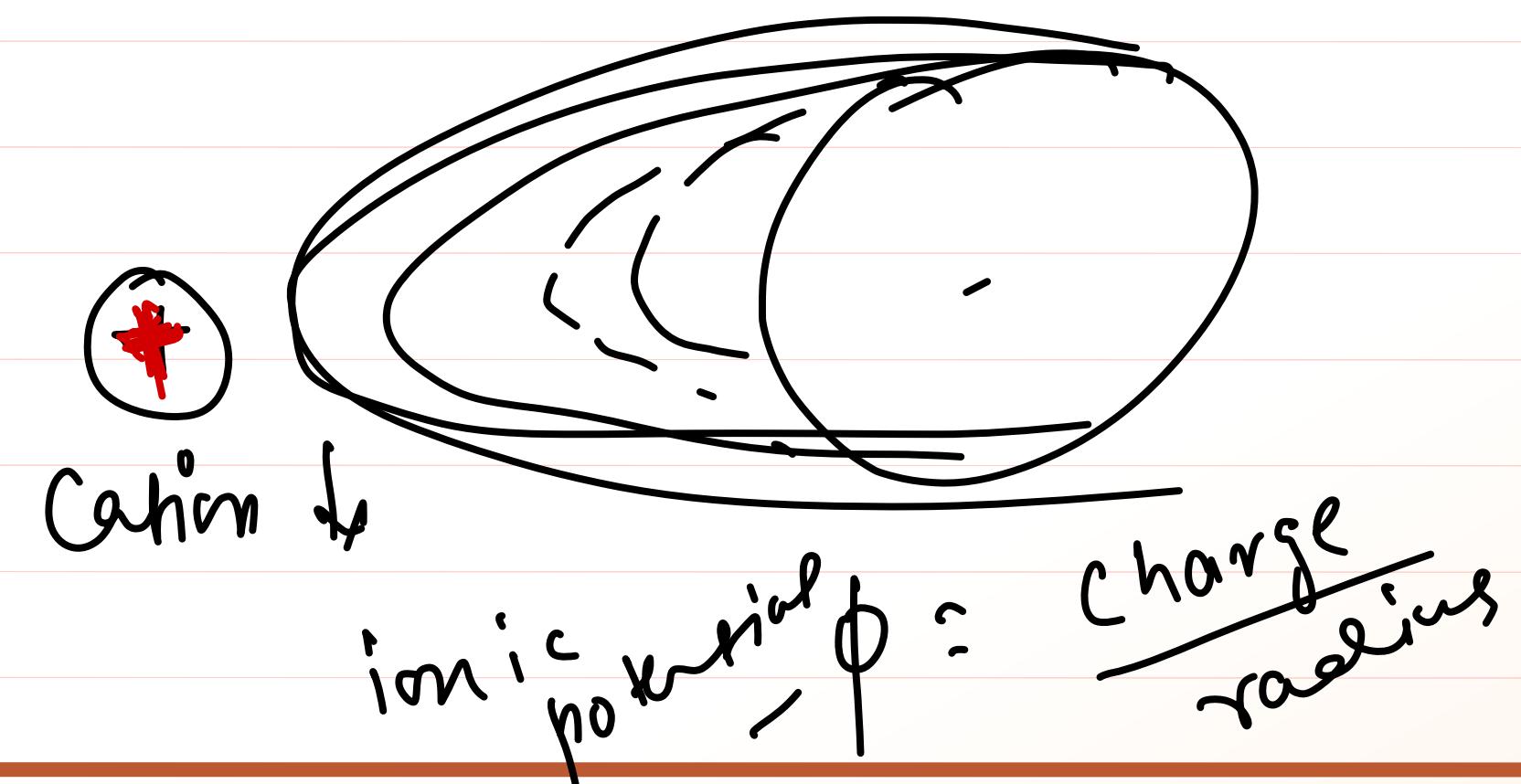
Which pair in the following has maximum and minimum ionic character respectively :

- (A) LiCl, RbCl (B) ~~RbCl, BeCl,~~ (C) BeCl₂, RbCl (D) AgCl, RbCl

The M.P. of SnCl_4 is less than that of SnCl_2 , the suitable reason for the observed fact is

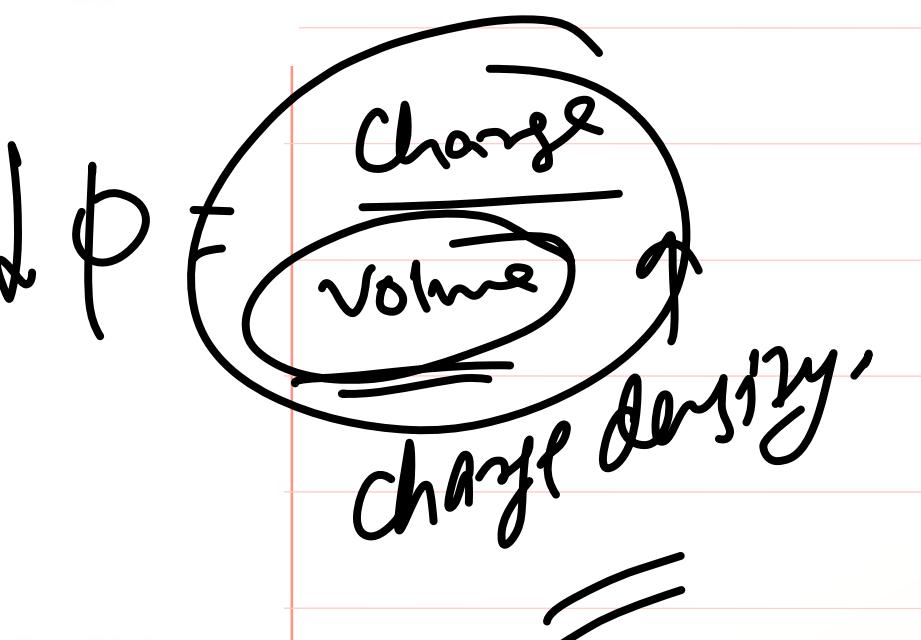
- (A) There is more charge on Sn^{+4}
(C) Ionic potential (ϕ) of Sn^{+4} is high

(B) The size of Sn^{+4} is small
(D) The shape of SnCl_4 is tetrahedral



favorable condition
correlation
chart area:

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



A graph illustrating two cost curves. The vertical axis represents cost, and the horizontal axis represents quantity. Two upward-sloping curves are shown: the Marginal Cost curve (MC^0) and the Average Cost curve (SC^0). The MC^0 curve is steeper than the SC^0 curve.

- ① cation: Small ✓
 - ② anion: Big ✓
 - ③ charge
 - ④ pseudo inert gas cert

Colour density $\propto \phi$ (Covalent character)

To explain colour of compounds

More the covalent character, more will be the colour intensity.

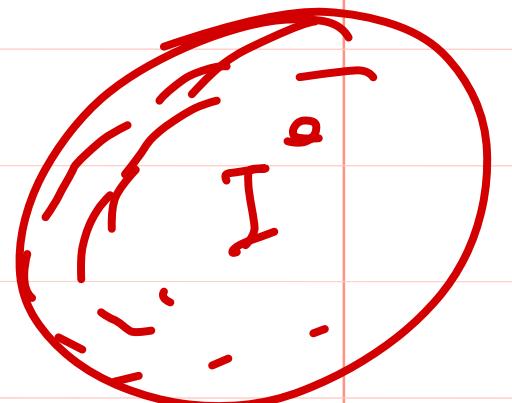
Ex.	AgCl	AgBr	AgI
	(White)	(Light yellow)	(Dark yellow)
	SnO ₂	SnS ₂	
	(White)	(Yellow)	

more covalent

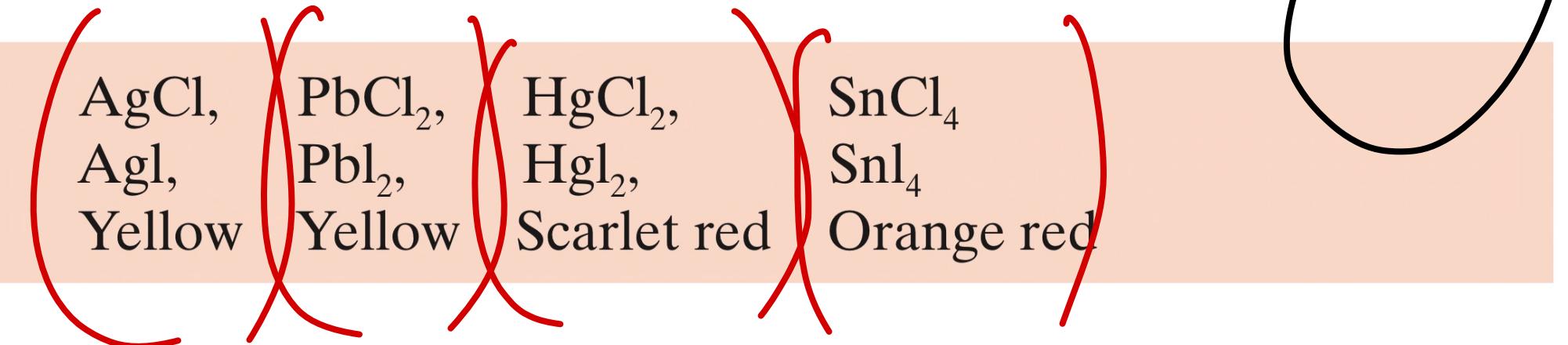
Polarization

(Q) Why Ag⁺ is yellow while

Ag⁺ is white?



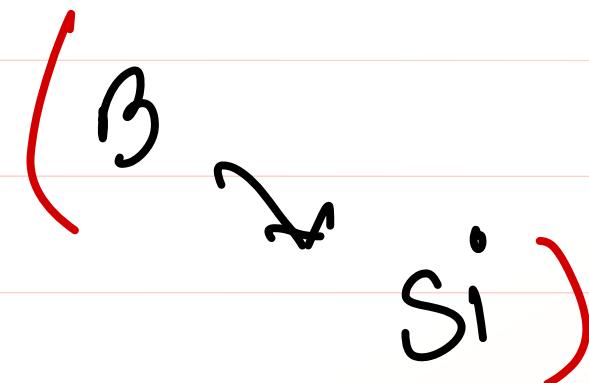
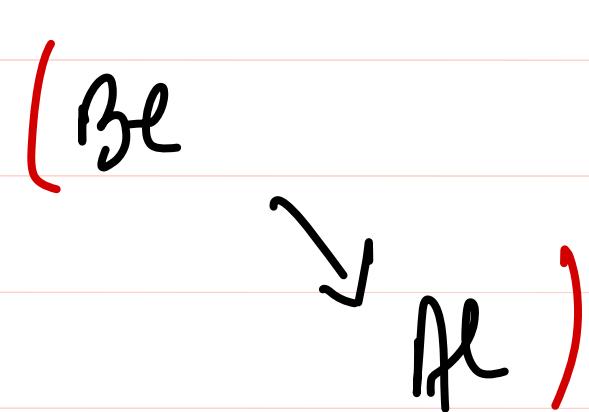
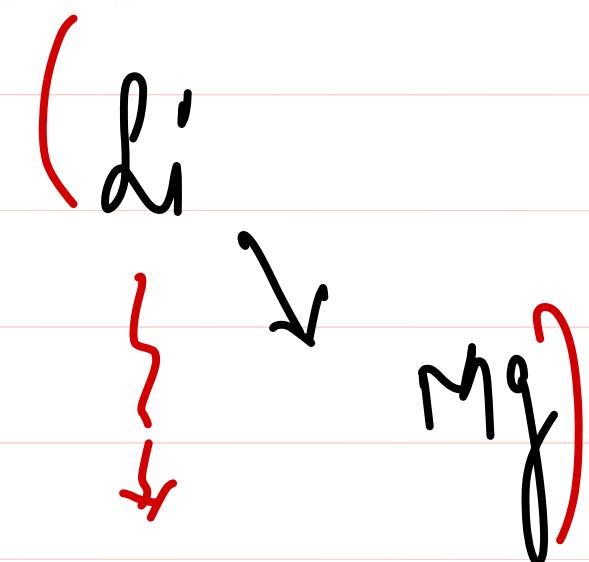
Colourless compounds:
Coloured compounds:



more polarizing union

To explain diagonal relationship :

Since the value of ϕ for Be²⁺ is almost of the same order as that of diagonally situated Al³⁺. Hence have many similar properties. Similarly value of ϕ for Li⁺ is equal to Mg²⁺, so have diagonal relationship.



ϕ ionic potential = Charge radius

To determine nature of oxide

$\sqrt{\phi} < 2.2$ (Basic oxides)

$\sqrt{\phi} = 2.2$ to 3.2 (Amphoteric oxides)

Neutral oxides doesn't react with acid & base eg. H_2O , CO etc.

Amphoteric oxides (Al_2O_3 etc.) reacts with acid & base

$\sqrt{\phi} > 3.2$ (Acidic oxide)

Ex. Li_2O , Na_2O , K_2O , Rb_2O , Cs_2O



- $\sqrt{\phi}$ decreases
- Basic character increases

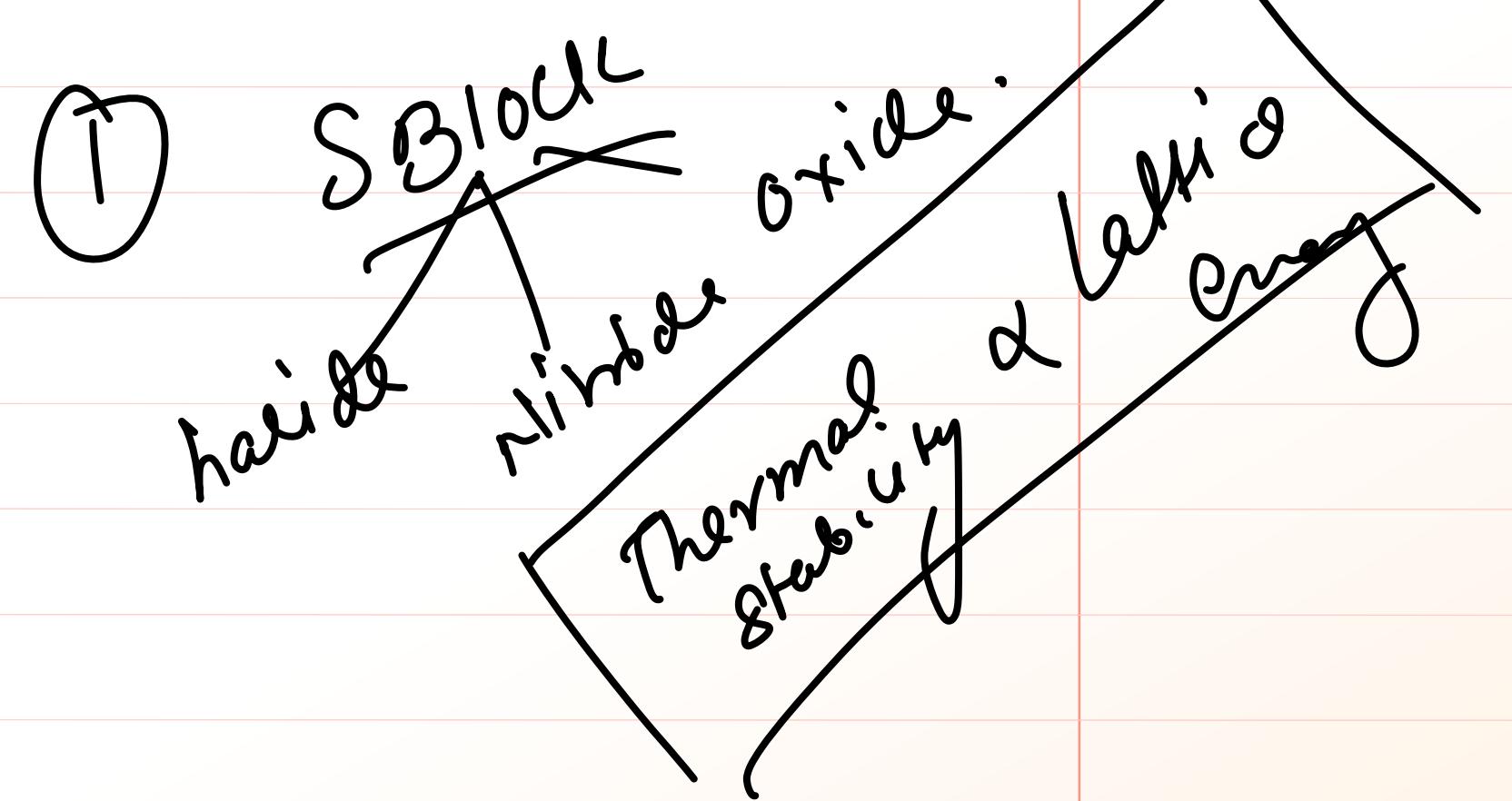
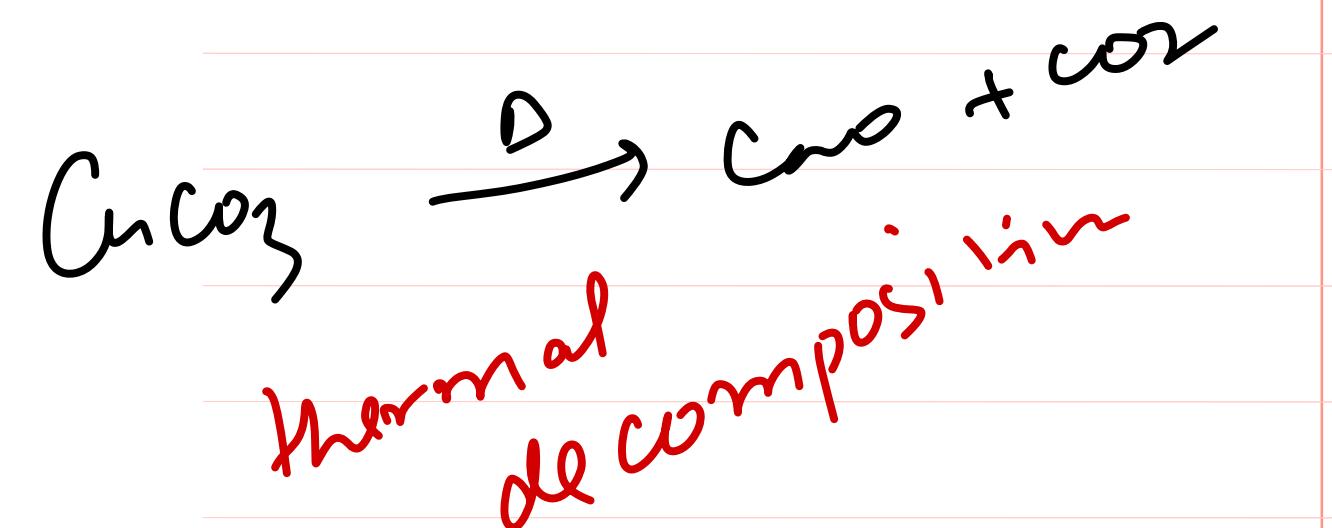
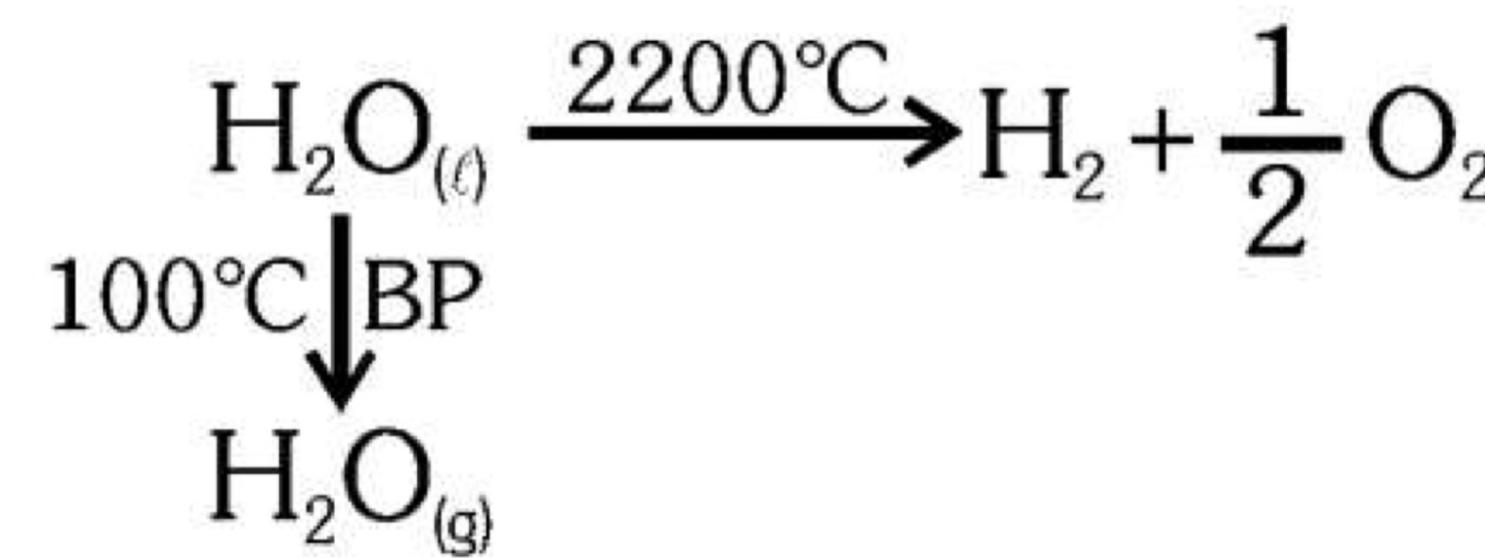
To determine conductivity of metal halides (MX)

If $\sqrt{\phi} < 2.2$ MX - ionic nature

If $\sqrt{\phi} > 2.2$ MX - covalent nature

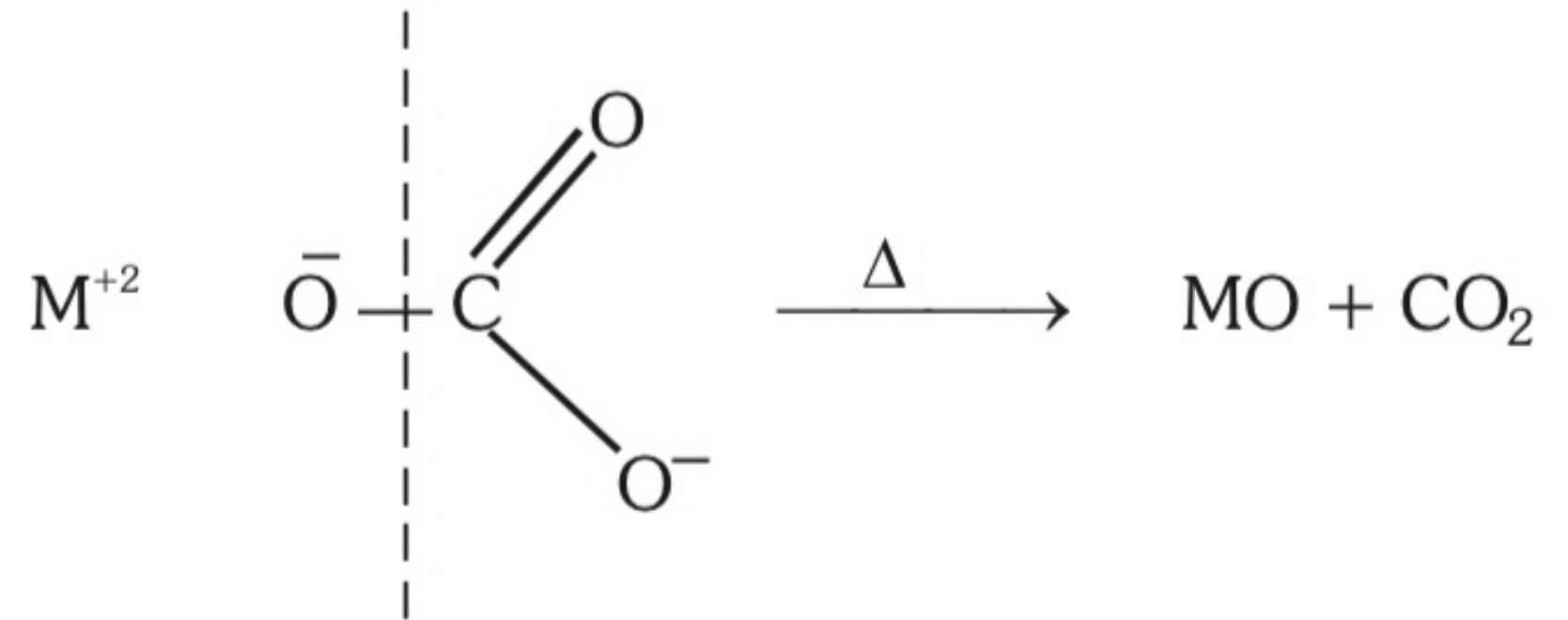
Thermal stability

Temperature up to which a substance can retain it's original composition.



To determine thermal stability of metal carbonates

Stability $\propto \frac{1}{\phi}$ (Covalent nature)



More smaller the size of metal cation, its polarisation capacity increases - strength of M—O bond increases and C—O bond decreases. So thermal stability of carbonates decreases.

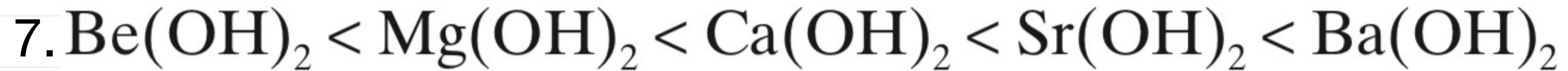
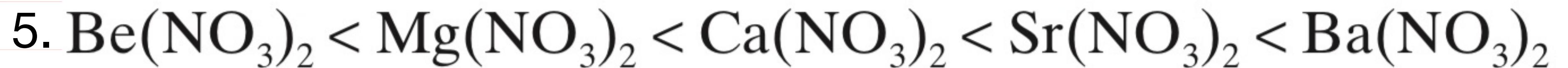


From top to bottom thermal stability of carbonates increases (as size of cation increases)
 (Ionic character increases or covalent character decreases)

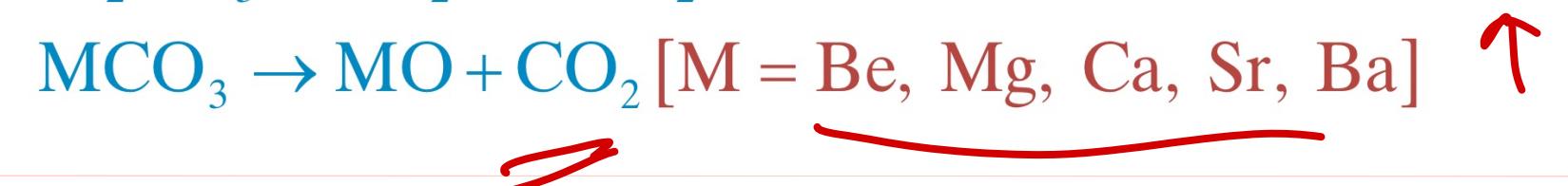
- (+) BeCO₃
 - (+) MgCO₃
 - (+) CaCO₃
 - (+) SrCO₃
 - (+) BaCO₃
- size of cation increases
 - ϕ decreases (covalent character decreases)
 - Thermal stability increases
- false note*

Carbomate Stability ↑

Order of thermal stability



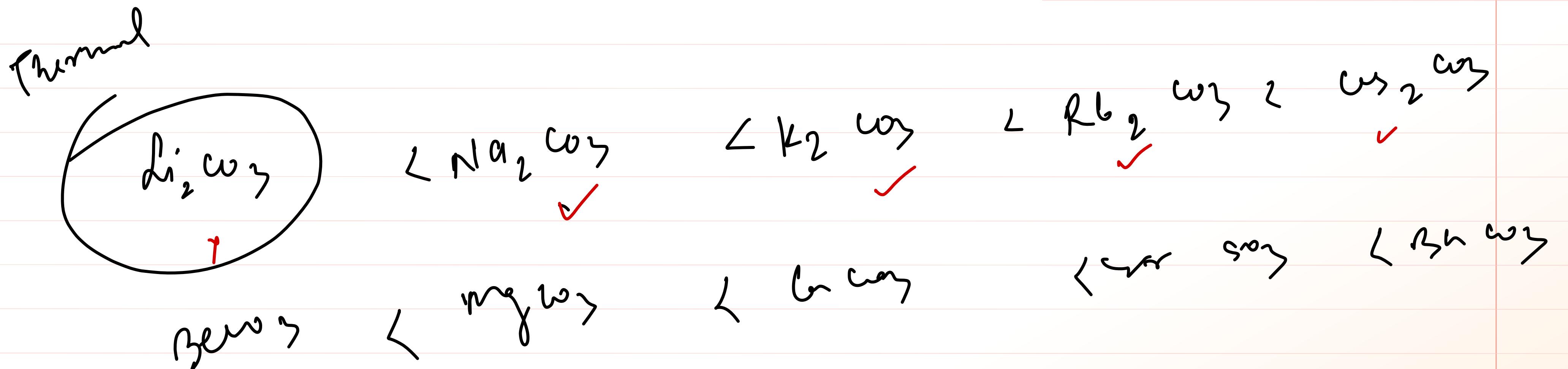
1. Heating effect on carbonate and bicarbonate salts: All carbonates except (Na, K, Rb, Cs) decompose on heating giving CO_2 . For example,



All bicarbonates decompose to give carbonates and CO_2 . For example,



General reaction: $2\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} + \text{CO}_2$

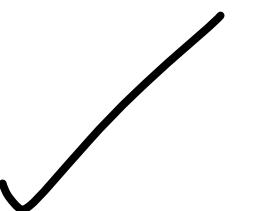


Solubility of ionic compound

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

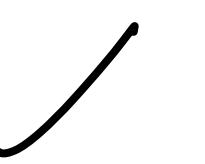
(i)

$$\text{Solubility} \propto \text{Hydration energy}$$



(ii)

$$\text{Solubility} \propto \frac{1}{\text{Lattice energy}}$$



- If common ion is smaller than apply L.E.

(F⁻, O⁻², OH⁻, Li⁺, Mg⁺², Be⁺² etc.)

Lattice energy

Solubility ↓

- If common ion is larger than apply H.E.

(CO₃⁻², SO₄⁻², NO₃⁻, ClO₄⁻, HCO₃⁻, Cs⁺ etc.)

Hydration energy

Solubility ↑

Q. Compare Solubility in following :-

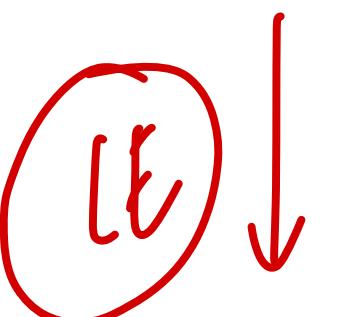


(Common ion O^{2-} , Apply L.E.)

Size(↑), L.E. (↓), Solubility (↑)

Common ion : O^{2-} (Smaller in Size)

Lattice energy
Solubility energy.



HE



(Common ion Cs^+ , Apply H.E.)

Common ion Cs^+ (charge in size)

Hydration
Energy.

Size(↑), H.E.(↓), Solubility (↓) chart

① Charge

② $\Delta E \propto [Z^+ | Z^-]$

$\{ E \propto \frac{1}{r^+ + r^-}$

③ $H.E \propto [Z^+ | Z^-]$

$H.E \propto \frac{1}{Z^+ + Z^-}$

Z^- S^{2-}
Size charge

(3)



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

OH^-
Lattice

Size(↑) , L.E. (↓) , Solubility (↑)

(4)



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

SO_4^{2-}
Lattice
H.E.

Size(↑) , H.E.(↓) , Solubility (↓)

Order of solubility in ionic compound

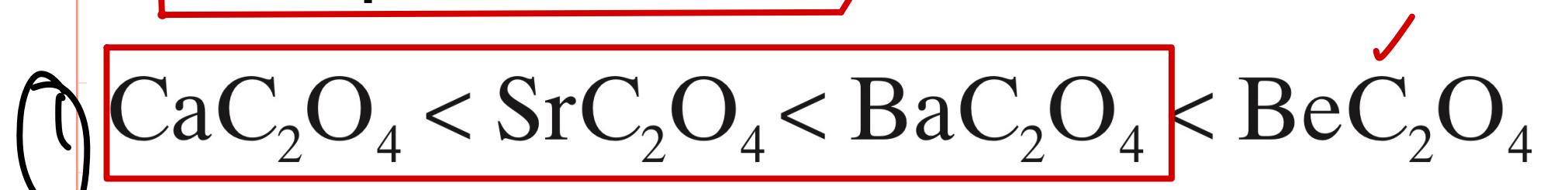
1. $\text{LiClO}_4 > \text{NaClO}_4 > \text{KClO}_4 > \text{RbClO}_4 > \text{CsClO}_4$
2. $\text{LiNO}_3 > \text{NaNO}_3 > \text{KNO}_3 > \text{RbNO}_3 > \text{CsNO}_3$
3. $\text{LiBr} > \text{NaBr} > \text{KBr} > \text{RbBr} > \text{CsBr}$
4. $\text{CaCrO}_4 > \text{SrCrO}_4 > \text{BaCrO}_4$
5. $\text{Be}(\text{NO}_3)_2 > \text{Mg}(\text{NO}_3)_2 > \text{Ca}(\text{NO}_3)_2 > \text{Sr}(\text{NO}_3)_2 > \text{Ba}(\text{NO}_3)_2$
6. $\text{BeCO}_3 > \text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$
7. $\text{BeSO}_4 > \text{MgSO}_4 > \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$
8. $\text{CaSO}_3 > \text{SrSO}_3 > \text{BaSO}_3$
9. $\text{CaS}_2\text{O}_3 > \text{Sr S}_2\text{O}_3 > \text{BaS}_2\text{O}_3$
10. $\text{BeX}_2 > \text{MgX}_2 > \text{CaX}_2 > \text{SrX}_2 > \text{BaX}_2$ (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$)

Order of solubility in ionic compound



~~Max~~ ~~Max~~

Exceptional order



BeC₂O₄ is the exception of this trend.



BeF₂ is the exception to the trend

Common: Hydratin.

Lattice energy

Learn
"it"

High Hydratin Enthalpy

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

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

E.g. :-	AgF	AgCl	AgBr	AgI
				↗
		Size of anion ↑		
			Covalent character ↑	
			Solubility ↑	

Q.

Compare solubility in following sequence.

(i)



~~Size of anion (↑)~~

Covalent character (↑)

Solubility (↓)

(ii)



~~Charge of cation (↑)~~

Covalent character (↑)

Solubility (↓)