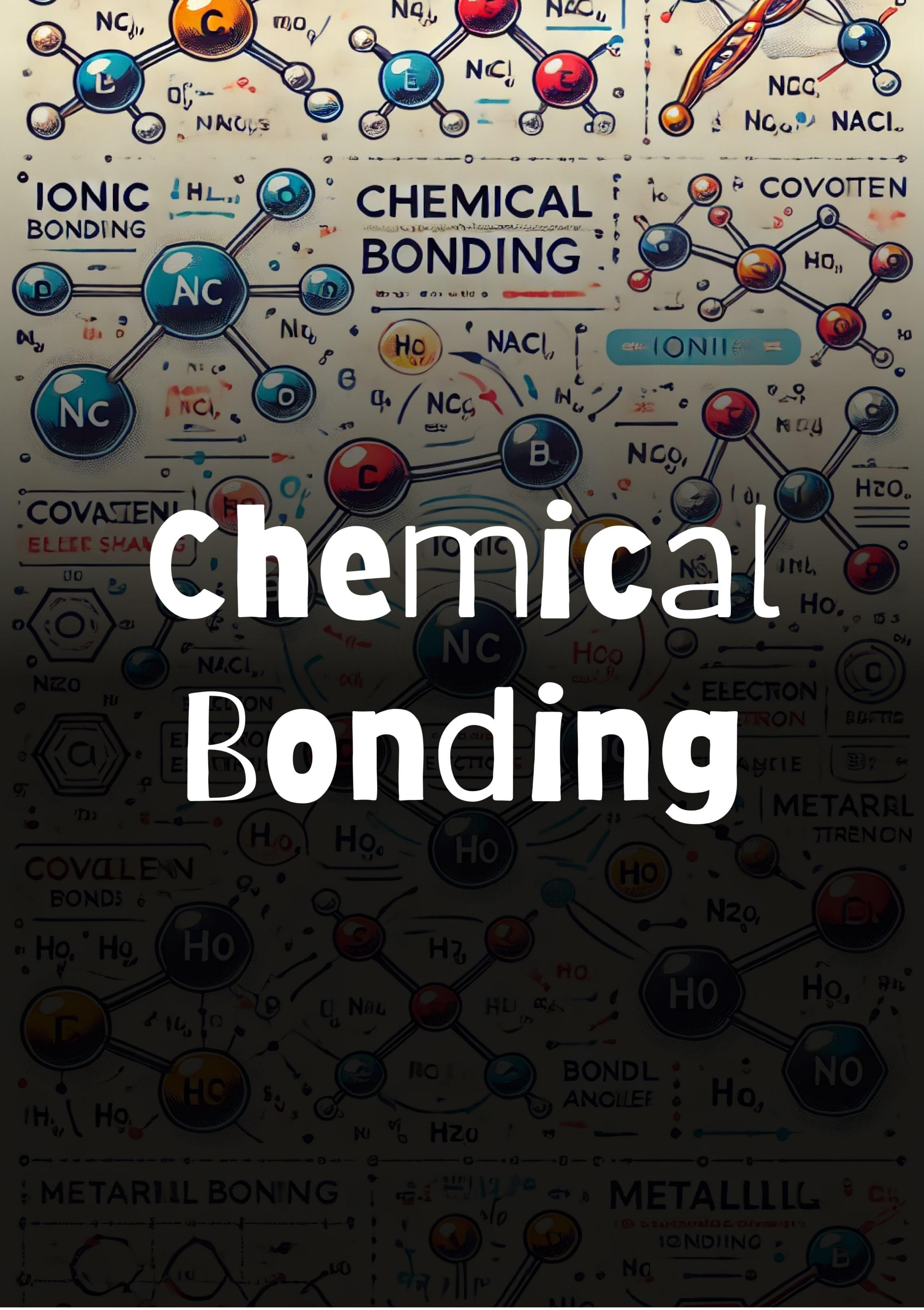

Chemical Bonding

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Chemical Bonding

Chemical Bond

Strong Bonds (≃ 200 KJ)

Weak Bonds (2 to 40 KJ)

① Covalent Bond
② Ionic Bond
③ Co-ordinate Bond
④ Metallic bond

Vanderwaals Force (2 to 10 KJ)

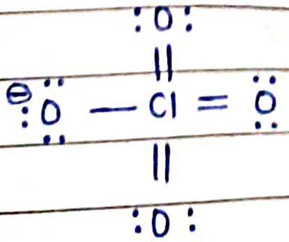
Hydrogen Bond (10 to 40 KJ)

① Covalent Bond – mutual sharing of e⊖
② Ionic Bond – complete transfer of e⊖
③ Co-ordinate Bond – shared e⊖ pair is contributed by only one atom.
④ Metallic Bond – Force between kernel and free e⊖.

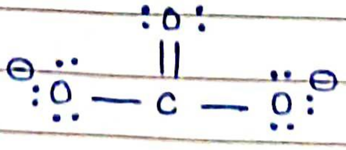
- Lewis Dot structure :

① Identify the central atom and surrounding atom.
② Assign -ve charge to more electronegative atom and +ve charge.
③ O atom form two bonds
but O⊖ form one bond.
④ Try to complete octet and duplet of all atoms.
⑤ But if central atom contains vacant d-orbital such as P, S, Cl etc then octet can expand.

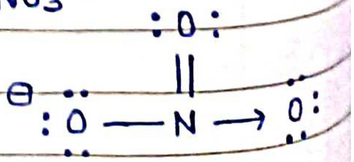
① ClO_4^-



② CO_3^{2-}



③ $NO_3^{\ominus}$



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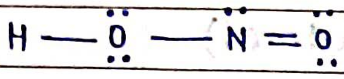
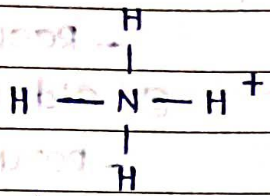
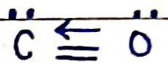
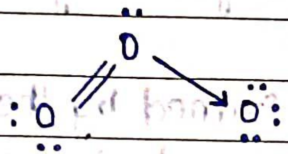
④ HNO_2 ⑤ NH_4^+ ⑥ CO

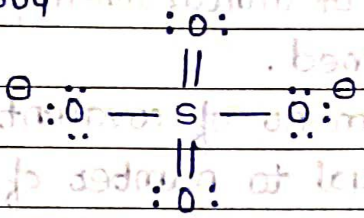


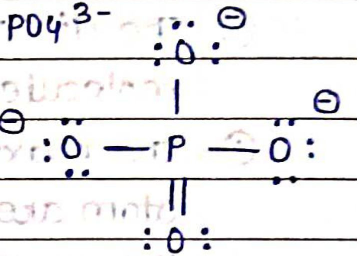




⑦ O_3 ⑧ SO_4^{2-} ⑨ PO_4^{3-}







- Formal charge :

Formal charge = Valence $e^{\ominus}$ − lone pair $e^{\ominus}$ − no. of surrounding Bonds.

- Bond order From Resonance :

$$B.O = \frac{\text{Total no. of Bonds}}{\text{Total no. of positions}}$$

- Average Formal charge on surrounding atom :

$$= \frac{\text{Net charge on species}}{\text{no. of surr. atoms}}$$

- Valence Bond Theory (VBT) :

① A covalent Bond is a result of overlap of atomic orbitals of two atoms.

② The atomic orbitals which overlap must contain unpaired electron with opposite spins. Also they must possess either same or nearly same energies.

③ Strength of covalent bond ∝ extent of overlap.

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④ Two types of overlap — ① Head to Head (axial)
— Result in σ bond.
② sidewise (lateral)
— Results in π bond.

⑤ The direction of orbital overlap decides geometry of molecule formed.

⑥ The maximum no. of covalent bonds formed by the particular atom are equal to number of the unpaired electron in its ground state.

ex: C in G.S — $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$
— carbon can form max. 2 bonds.

- Types of overlap :

① s-s overlap — H_2 formation — Always form σ bond.
② p-p overlap — Cl_2, F_2, O_2 — can form σ and π bond.
(σ) (σ) (σ and π)
③ s-p overlap — HCl Formation — always form σ bond.
HF Formation

- strength order :

1s-1s > 1s-2p > 2p-2p > 2s-2p > 2s-2s > 3p-3p > 3s-3p > 3s-3s

- concept of Hybridisation (modified VBT)

- The mixing and recasting of atomic orbitals of same atom to form new orbitals called hybrid orbitals which are identical in all respect.

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- Covalent Bond is a result of any of the Following overlap:

① Hybrid orbital of one atom and atomic orbital of another atom.
ex: CH_4 Formation.

② Hybrid orbital of one atom and hybrid orbital of another atom.
ex: Graphite.

- Types of hybridisation:

① sp – (2) – Linear
② sp^2 – (3) – Trigonal planar.
③ sp^3 – (4) – Tetrahedral.
④ sp^3d – (5) – Trigonal Bipyramidal.
⑤ sp^3d^2 – (6) – octahedral.
⑥ sp^3d^3 – (7) – Pentagonal Bipyramidal.
⑦ dsp^2 – (4) – square planar
⑧ d^3s – (4) – Tetrahedral.
⑨ dsp^3 – (5) – Trigonal Bipyramidal.
⑩ d^2sp^3 – (6) – octahedral.
⑪ d^3sp^3 – (7) – Pentagonal Bipyramidal.
⑫ sp^2d – (4) – square planar.

- Method of Finding hybridisation:

X ⟶ Indicate valence $e^{\ominus}$ of central atom.

- If surrounding atom is monovalent (H, F, Cl, Br, I, etc) then allot 1 'X' form 1 atom.
- If surrounding atom is divalent (O, S) then allot 2 'X' Form 1 atom.

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- $H = \sigma$ bond + no. of lone pair.

If $H = 2$ — sp　　$H = 5$ — sp^3d
　$H = 3$ — sp^2　　$H = 6$ — sp^3d^2
　$H = 4$ — sp^3　　$H = 7$ — sp^3d^3

- Valence shell electron pair repulsion (VSEPR Theory):

① If central atom is surrounded by only bond pairs and no lone pairs then geometry and shape both are same. ex. CH_4.

② If central atom is surrounded by both bond pairs and lone pairs then geometry and shape both are different.

③ The order of repulsion of various types of $e^{\ominus}$ pairs is
$lp-lp > lp-bp > bp-bp$.

④ Lone pair of central atom reduces bond angle from expected value.
Decrease in bond angle from expected value ∝ no. of lone pairs on central atom.

Code number	Hybridisation	Geometry	Shape
220	sp	Linear	Linear (CO_2, $BeCl_2$)
330	sp^2	Trigonal planar	Trigonal planar (BF_3)
321	sp^2	"	V-shape ($SnCl_3$)
440	sp^3	Tetrahedral	Tetrahedral (CH_4)
431	sp^3	"	Pyramidal (NH_3)
422	sp^3	"	V-shape (H_2O)
550	sp^3d	TBP	TBP (PCl_5)
541	sp^3d	"	See-saw (SF_4)
532	sp^3d	"	T-shape (ClF_3)
523	sp^3d	"	Linear (XeF_2)
660	sp^3d^2	Octahedral	Octahedral (SF_6)
651	sp^3d^2	"	Square pyramidal (BrF_5)

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642	sp^3d^2	"	square planar (XeF_4)
770	sp^3d^3	PBP	PBP (IF_7)
761	sp^3d^3	"	Distorted octahedral
752	sp^3d^3	"	Pentagonal planar.

- Bond parameters (measurable properties of covalent bond):

① Bond angle – angle between two adjacent covalent bonds.

Hyb^n	expected B·A
sp	180°
sp^2	120°
sp^3	109° 28'
sp^3d	90°, 120°
sp^3d^2	90°, 180°
sp^3d^3	90°, 72°
dsp^2	90°

① B·A ∝ s% character (H is diff)

sp	sp^2	sp^3
50% s	33·33% s	25% s

② No. of lone pairs

I. same – Hybridisation, surrounding atom
Different – central atom, no. of lone pairs then

$$B \cdot A \propto \frac{1}{\text{no. of lone pairs}}$$

ex: $CH_4 > NH_3 > H_2O$

II. Same – Hybridisation, surrounding atom, lone pair.
Different – central atom.

B·A ∝ EN of central atom

$NH_3 > PH_3 > AsH_3 > SbH_3$

$H_2O > H_2S > H_2Se > H_2Te$

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III. Same – Hybridisation, central atom, lone pair
Different :- Surrounding atom $F_2O < Cl_2O < Br_2O$

$B \cdot A \propto \dfrac{1}{\text{EN of surr. atom}}$

- Bond order : The number of bonds between two atoms. calculat by using any of the following :

① MOT — Total e⊖ ≤ 20, species is diatomic.
② Resonance — $B \cdot O$ = total no. of Bonds / total no. of positions.
③ Use structure.

- Bond energy : Energy required to break 1 mole of particular bonds.

① Bond energy ∝ Bond multiplicity
② Bond energy ∝ % s character.
③ Bond energy $\propto \dfrac{1}{\text{atomic size}}$
④ Bond energy ∝ Bond polarity
⑤ Bond energy $\propto \dfrac{1}{\text{no. of lone pairs}}$ (use this factor when there is single bond betn 2 identi. bon

- Big exception :
Bond energy in halogens

Expected order : F–F > Cl–Cl > Br–Br > I–I
Actual order : Cl–Cl > Br–Br > F–F > I–I

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- **Bond length:** The distance between the centres of nuclei of two closely bonded atoms.

① $B.L \propto \frac{1}{\text{Bond multiplicity}}$

② $B.L \propto$ Atomic size

③ $B.L \propto \frac{1}{\%\ s\text{-character}}$

④ $B.L \propto \frac{1}{\text{Bond order}}$

$\xleftarrow{\text{Bond order}}$

ex: ① O_2 O_3 H_2O_2

$\xleftarrow{B.O}$ $\xrightarrow{\text{Bond length}}$

② CO CO_2 CO_3^{2-}

$\xrightarrow{\text{Bond length}}$

- **Dipole moment:** Measure of polarity of bond.

$\mu = q \times r$ Units: esu · cm, C·m, Debye.

$1D = 10^{-18}$ esu·cm.

$1D = 3.33 \times 10^{-30}$ C.m.

$$\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

$$\%\ \text{ionic character} = \frac{\mu\ \text{observed}}{\mu\ \text{theory}} \times 100$$

Polar molecule = $\mu_R \neq 0$ (permanant dipole moment)

Non-polar molecule = $\mu_R = 0$

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- **Molecular orbital theory:**
(Applicable only for diatomic species having total $e^{\ominus} \leqslant 20$)

① During molecule or ion formation through covalent bonding, Atomic orbitals combine together to form new orbitals called molecular orbitals.

② The number of molecular orbitals formed are exactly equal to number of Atomic orbitals combined.

③ Two types of Molecular orbitals formed:

a) Bonding MO. (denoted by σ and π)
b) Anti-Bonding MO. (denoted by σ^* and π^*)

AO's combined	BMO's combined	ABMO's formed
$ns + ns$	σns	$\sigma^* ns$
$np_z + np_z$	σnp_z	$\sigma^* np_z$
$np_x + np_x$	πnp_x	$\pi^* np_x$
$np_y + np_y$	πnp_y	$\pi^* np_y$

- Filling of electrons in MO's:

① Configuration I: when total $e^{\ominus} \leqslant 14$.
ex: N_2, N_2^+, B_2, C_2 etc (2S-2P mixing occurs)

$\sigma 1S < \sigma^* 1S < \sigma 2S < \sigma^* 2S < \pi 2P_x = \pi 2P_y < \sigma 2P_z < \pi^* 2P_x = \pi^* 2P_y$
$< \sigma^* 2P_z$

BABA BBB AAA — Trick

② Configuration II: when total $e^{\ominus}$ = 15 to 20 ex:
ex: O_2, O_2^-, F_2, Ne_2 etc (2S-2P mixing do not occurs)

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$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y$
$< \sigma^* 2p_z$.

BABA <u>BBB</u> <u>AAA</u>

- Applications of MOT :

① Bond order = $B.O = \frac{1}{2}(N_b - N_a)$ If B.O = 0 species do not exist
B.O ≠ 0 species exist.

Total e⊖	B.O
1	0.5
2	1.0
3	0.5
4	0
5	0.5
6	1.0
7	0.5
8	0

Total e⊖	B.O
9	0.5
10	1.0
11	1.5
12	2.0
13	2.5
14	3.0
15	2.5
16	2.0
17	1.5
18	1.0
19	0.5
20	0

exception :
$CO^+ = 3.5$

② Bond length $\propto \frac{1}{\text{Bond order}}$.

③ Bond energy
Bond strength $\propto$ Bond order.
Thermal stability

④ Prediction of magnetic nature :

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① Total $e^\ominus$ are odd or 10 or 16 → Paramagnetic

② Total $e^\ominus$ are even → Diamagnetic.

- **Ionic Bond :**

(The Bond which is formed by complete transfer of $e^\ominus$ from one atom to another atom).

① $\Delta EN \geq 1.6$.

② Low IE of element forming cation.

③ High electron gain enthalpy with −ve sign of element forming anion.

④ High lattice enthalpy.

⑤ Overall decrease in energy of system. ← IE (+ve)
$\Delta_{eg}H$ (−ve)
L.E (−ve)
(−ve)

- **Imp. note :**

① The Bond formed between metal and non metal is generally ionic.

② The Bond formed between two complex ions or in between simple ion and complex ion is also ionic.

③ There are some substance which contains ionic, covalent as well as co-ordinate bond.

ex: NH_4Cl

$[Ni(H_2O)_6]SO_4$

④ Electrovalency : no. of electron lost or gained by one atom.

- **Lattice energy or lattice enthalpy ($\Delta_L H$)**

Amount of energy released when 1 mole of ionic compound is formed from constituent gaseous cation and gaseous anion. $\Delta_L H = -ve$.

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or Amount of energy required to break 1 mole of ionic compound into its constituent gaseous cation and gaseous anion.

$\Delta_L H = +ve$.

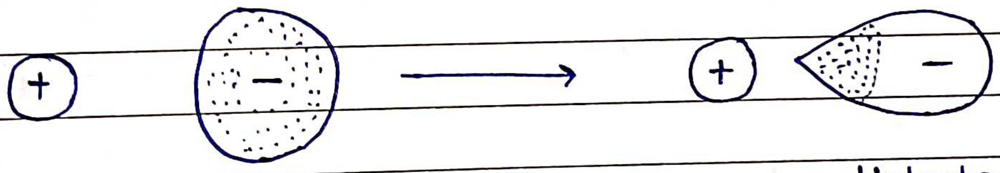
- V. Imp:

① stability of ionic compound $\propto \Delta_L H$.

② solubility of ionic compound in $H_2O \propto \frac{1}{\Delta_L H}$

③ $\Delta_L H \propto \frac{q_c \cdot q_a}{r_c + r_a}$

- covalent nature in ionic bond: (concept of polarisation)



symmetrical anion   distorted anion

For cation ⟶ polarising power.
For anion ⟶ polarisibility
covalent character in ionic substance ∝ extent of polarisation

- Fajan's rules:

① Polarisation $\propto \frac{\text{size of anion}}{\text{size of cation}}$

SHILA: small cation ↓ High charges ↳ large anion

② Polarisation $\propto q_c$ and q_a.

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⑧ Polarising power is exceptionally more if cation posess pseudo inert gas configuration ($ns^2np^6nd^{10}$)

ex : $\overset{+}{Na}X < \overset{+}{Cu}X$, $\overset{+}{K}X < \overset{+}{Ag}X$

- V.Imp :

Melting point, thermal stability, ionic nature, solubility in H_2O $\propto \frac{1}{\text{Polarisation}}$

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