Chemical Bonding

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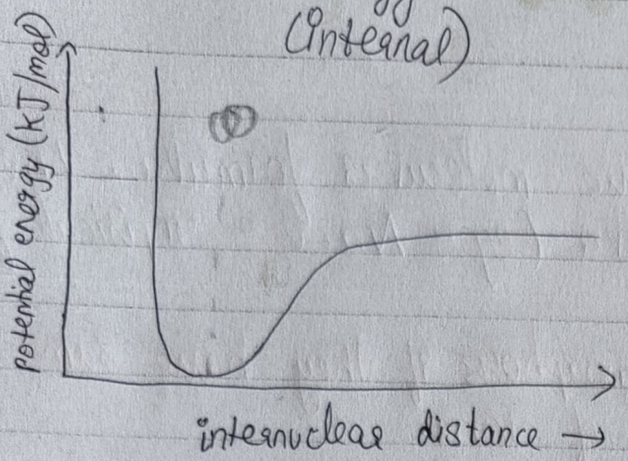
1. Attraction $\propto \frac{1}{\text{energy (internal)}} \propto$ stability $\propto$ strength of bond.



- Bond formation is an exothermic process ($\Delta H = -ve$)
∴ internal energy ↓es.

2. Valency = combining capacity of the element.
For group IA to IVA ⇒ Valency = no. of valence e^-s
group VA to O ⇒ Valency = |8 − (no. of valence e^-s)|.
All the elements of a group have same valencies.

3. The tendency of atoms to achieve 8 e^-s in their outer most shell is called Lewis octet rule.
→ Incomplete octet = electron deficient = hypovalent
→ expansion of octet = e^- rich/efficient = hypervalent
→ pseudo inert gas config. = presence of 18 e^- in the outer most orbit of cations.
Eg- Ga^{+3}, Zn^{+2}, Ag^+, etc.
→ odd e^- species = NO, NO_2, ClO_2, etc.

4. Ionic/Electrovalent Bond
→ Electronegativity difference $\propto$ nature of ionic bond
→ total no. of e^-s lost or gained = electrovalency.

→ Conditions for Ionic Bond - ↓IE (Ionisation energy)
↑EA (electron affinity) ↑LE (lattice energy).

$$\Delta H_f = \underbrace{SE + IE + BDE}_{\Delta H = +ve} + \underbrace{EA + LE}_{\Delta H = -ve} \quad \text{(for AB)}$$

SE = sublimation energy ($A_{(s)} \rightarrow A_{(g)}$)
BDE for ($B_2 \rightarrow 2B$).

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5. Factors Affecting LE

$LE \propto z^+ z^-$ (ionic charge)

$LE \propto \frac{1}{r^+ + r^-}$ (ionic radius)

6. Ionic bond - non-directional
   - Crystal lattice is formed
   - Ionic compounds do not have molecular formula. They have only empirical formula (eg - NaCl = empirical formula)
   - hard, crystalline, brittle
   - Compounds are said to be isomorphous if they have same no. of e^-s and same no. of ions.
   - high MP, High BP
   - Conductivity ⇒ solid state < fused state < aqueous soln.
   - Ionic reactions are faster than molecular reactions.

7. Solubility -

→ Extent of hydration $\propto (z^+ + z^-) \propto \frac{1}{\text{size of ion}}$

→ radii in aqueous medium $\propto$ extent of hydration

→ Conductivity in aqueous medium $\propto \frac{1}{\text{hydration}}$

→ solubility $\propto \frac{1}{\text{lattice energy}} \propto$ hydration energy.

An ionic compound gets dissolved in water when the hydration energy exceeds the lattice energy.

→ solubility $\propto$ dielectric constant of medium. (ability of medium to break down into opposite poles).

→ if common ion is small ⇒ LE dominates.
(Na^+, Li^+, O^{-2}, F^-, OH^-, IIA)

→ if common is large or polyatomic anion ⇒ hydration energy dominates.
(Cs^+, Rb^+, Br^-, I^-) (SO_4^{2-}, CO_3^{2-})

↳ Explains covalent character in ionic compounds.

8. **Polarization** - C^+ A^- → C^+ A^-.

Fajan's Rule

→ polarization power / ionic potential / charge density = ϕ = $\frac{\text{charge on cation}}{\text{size of cation}}$.

∴ Polarization $\propto$ $\frac{\text{charge on cation}}{\text{size of cation}}$ $\propto$ charge of anion $\propto$ size of anion.

→ Polarization $\propto$ $\frac{\text{covalent character}}{\text{ionic character}}$

→ order of polarization power : $8e^- < (18+2)e^- < 18e^-$ (for cation).

9. MP, BP $\propto \frac{1}{\text{Polarization}}$ → Solubility $\propto \frac{1}{\text{Polarization}}$

→ **For fluoride, hydride, normal oxide**
Thermal stability $\propto$ LE

For polyatomic anions
Thermal stability $\propto \frac{1}{\text{Polarization}}$.

10. $LiHCO_3$, IIA bicarbonates do not exist in solid state.

→ carbonate, sulphate and hydroxide of Na, k, Rb, Cs do not decompose at high temp. They only melt.

→ $BeCO_3$ is kept in CO_2 atmosphere due to less thermal stability.

$BeCO_3 \rightleftharpoons BeO + CO_2$.

11. **Heating Effect**

(a) **Metal Carbonate**

$M_xCO_{3y} \longrightarrow M_xO_y + CO_2$. - For IA, only Li_2CO_3 decomposes - For IIA, all decompose.

(b) **Metal Nitrate**

metal nitrate → metal oxide + NO_2 + O_2.

Exception

→ $Na, K, Rb, Cs \xrightarrow{\text{low temp.}} MNO_2 + \frac{1}{2}O_2$

↓ high temp (> 800°C)

$M_2O + N_2 + O_2$.

→ $LiNO_3 \xrightarrow{\Delta} Li_2O + NO_2 + O_2$

→ all IIA nitrates decompose like Li.

(c) Metal hydroxide (metal hydroxide $\xrightarrow{\Delta}$ metal oxide + H_2O)

→ In IA, only LiOH decomposes, rest don't.

→ In IIA, all hydroxides decompose.

(d) Metal bicarbonate (metal bicarbonate $\rightleftharpoons$ metal carbonate + CO_2 + H_2O)

→ In IA and IIA, all bicarbonate decompose.

12. Covalent Bond

- Tendency to complete orbital or to pair the e^- is an essential condition of covalent bond.
- Completion of octet is not the essential condition.

→ Covalency = no. of covalent bonds an atom makes in a molecule.

→ Excitation ⇒ The energy required for excitation of e's is called promotion energy.

Promotion rule - excitation must take place in the same orbit.

13. VBT - Presented by Heitler & London - extended by Pauling & Slater.

→ directional bond (covalent bond)

→ strength of covalent bond ∝ extent of overlapping of orbitals.

→ bond strength ∝ $\frac{1}{n \text{ value}}$

→ p, d, f → directional orbitals ⇒ more overlapping
s → non-directional orbitals ⇒ less overlapping.

For same n value ⇒ p-p > p-s > s-s.

14. σ - bond = end to end overlapping (only one σ bond is possible between 2 atoms).
= directional = stronger
π - bond = sidewise (lateral) overlapping
= weaker. = non-directional.

15. Hybridisation - introduced by Pauling.

sp	Linear	BA = 180°	
sp^2	Trigonal Planar	BA = 120°	
sp^3	Tetrahedral	109° 28'	
sp^3d	Trigonal bipyramidal	3 = 120° 6 = 90°	dz^2
sp^3d^2	octahedral/square bipyramidal.	all angles = 90°	dx^2-y^2, dz^2
sp^3d^3	pentagonal bipyramidal	5 = 72° 10 = 90°	dx^2-y^2, dz^2, dxy.

16. VSEPRT
→ order of repulsion of e^- - lp - lp > lp - bp > bp - bp
→ by increasing one lp of e^-, BA is decreased by 2.5°.
→ position of lp and multiple bond -
- sp, sp^2, sp^3 = anywhere
- sp^3d = equatorial
- sp^3d^2 = anywhere (all positions are same)
- sp^3d^3 = 1 then equatorial
= 2 then axial.

→ See-saw = irregular tetrahedron (eg - SF_4)
angular = V-shaped = bent (eg - H_2O).
T-shape (eg - ClF_3)
Linear (eg XeF_2)
XeF_6 → 1 lp = equatorial = distorted octahedral/ capped octahedral.

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17. Bond Parameters

① **Bond Angle** α % s character (hybridisation)
$\alpha \frac{1}{\text{no. of lp}}$ (same hybridisation, diff. lp)
α EN of central atom (for same side atoms)
$\alpha \frac{1}{\text{EN of side atom}}$ α size of side atom (same central atom).

② **Bond Length**
→ If $\Delta EN = 0$ $\quad d_{AB} = r_A + r_B$
If $\Delta EN \neq 0$ $\quad$ Bond Length $= r_A + r_B - 0.09(\chi_A - \chi_B)$
Schomaker and Stevenson formula

→ BL $\alpha \frac{1}{\Delta EN} \alpha \frac{1}{\text{No. of bonds or bond order}} \alpha \frac{1}{\text{\% s character.}}$

③ **Bond Energy (BE)**
→ BE α ΔEN α Bond order $\alpha \frac{1}{\text{Atomic size}}$
→ BE α Bond polarity α resonance α % s character
→ BE $\alpha \frac{1}{\text{lp of } e^-s.}$

18. Co-ordinate Bond / Dative Bond
→ atom which donates e^- = Lewis base
atom which accepts e^- = Lewis acid

19. Dipole Moment (Ionic character in covalent compound).
$\mu = q \times d$. $\quad$ unit = Debye = 10^{-18} esu cm.
→ A non-polar molecule may have polar or non-polar bonds.
→ dipole moment = 1.85 D for H_2O $\quad H_2O > H_2S$ ($\because$ EN of O > S)
→ $CCl_4 < CHCl_3 < CH_2Cl_2 < CH_3Cl$.

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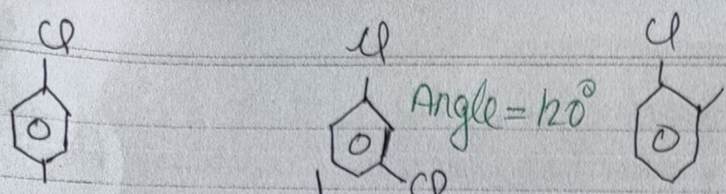
→ 

$\mu = 0$ $\mu \neq 0$

$\mu \propto \frac{1}{\text{angle}}$

→ % Ionic character = $\frac{\text{Experimental value of } \mu}{\text{Theoretical value of } \mu} \times 100$.

20. MOT - Put forward by Hund and Mulliken.

→ Bonding orbitals (BMO)	Antibonding Molecular Orbitals (ABMO)
(1) constructive interference, wave functions are added.	(1) destructive interference, wave functions are subtracted.
(2) generally it does not have a nodal plane.	(2) It always has a nodal plane between two nuclei of bonded atoms.
(3) energy of BMO is less	(3) energy of ABMO is high.
(4) e^- placed in BMO stabilizes the molecule. (σ, π)	(4) e^- placed in ABMO destabilizes the molecule. (σ^*, π^*)
$\psi_b = \psi_A + \psi_B$	$\psi_a = \psi_A - \psi_B$.

→ Order of filling

For total e^- (less than =) 14 (Atomic No. ≤ 7)

$\sigma 1s$ $\sigma^* 1s$ $\sigma 2s$ $\sigma^* 2s$

$[\pi_{2px} = \pi_{2py}]$ σ_{2pz} $[\pi^*_{2px} = \pi^*_{2py}]$ σ^*_{2pz}.

→ For total e^- > 14 (Atomic No. > 7)

$\sigma 1s$ $\sigma^* 1s$ $\sigma 2s$ $\sigma^* 2s$

σ_{2pz} $[\pi_{2px} = \pi_{2py}]$ $[\pi^*_{2px} = \pi^*_{2py}]$ σ^*_{2pz}

→ Bonder order = $\frac{1}{2}[N_b - N_a]$

→ stability $\propto$ BO.

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→ if unpaired e⁻s are present in MO → paramagnetic
if paired e⁻s only are present in MO → diamagnetic
fractional BO ⇒ paramagnetic
BO = 0 ⇒ molecule does not exist.

21. Resonance

→ Bonder order = Total no. of bonds / Resonating structures OR Total No. of bonds / total no. of side/surrounding atoms.

→ Formal charge = Total charge on surrounding atoms / No. of surrounding atoms.

22. Hydrogen Bonding (also known as dipole-dipole attraction)

→ stronger than vander Waal's forces
→ weak bond.
→ conditions for H-bonding - (H should be covalently bonded with highly EN element like FON.
→ strength of H-bond ∝ EN of element ∝ 1 / atomic size of element.
→ Intermolecular H-bonding has more association than intramolecular H-bonding ∴ it is having more strength
• homo intermolecular - H_2O, HF
One H_2O attaches with other H_2O molecules.
• hetero intermolecular - between alcohol and water.
→ Intramolecular H-bond - formed mostly in organic compounds
- results in ring formation (chelation)
Eg ⇒ o-nitrophenol, salicaldehyde, chloral hydrate.

① Solubility - Intermolecular H-bond ↑es solubility
Intramolecular H-bond ↓es solubility
② Viscocity - Viscosity ∝ extent of H-bonding ∝ -OH groups.
③ Surface Tension - surface tension ∝ extent of H-bonding.
④ MP, BP - due to intermolecular H-bonding, MP and BP ↑es
due to intramolecular H-bonding, MP and BP are low. ↓es.

⑤ Volatility - volatility $\propto \frac{1}{\text{H-bonding strength}}$

↓

Intra > Inter.

⑥ Molecular Weight - CH_3COOH dimerizes due to H-bonding
∴ molecular wt. is double of its formula mass.

→ strength of H-bond $\propto$ EN of element ($HF > H_2O$)
extent of H-bond $\propto$ no. of H-bonds formed ($H_2O > HF$)
∴ BP → $H_2O > HF$.

→ $F \overset{a}{\cdots} H \overset{b}{-} F$ H-bond a is strong.
∴ bond length ⇒ $a \approx b$.

23. Vander Waal's Forces.
- weak - non-directional
vander waal's forces $\propto$ size of atom/molecule $\propto$ at. wt. or molecular wt.

① Ion - dipole $\propto \frac{1}{r^2}$

② dipole - dipole (Keesom force) $\propto 1/r^3$
③ Ion - induced dipole $\propto 1/r^4$.
④ dipole - induced dipole $\propto 1/r^6$
(Debye Force)
⑤ Instaneous dipole induce dipole (London dispersion force) $\propto \frac{1}{r^6}$

decreasing strength order ↓

(Exception
CO^+ bonder order = 3.5.)