Chemistry

# Class-XI

# CHEMICAL BONDING AND MOLECULAR STRUCTURE HYDROGEN BONDING

# HYDROGEN BOND

- (a) An atom of hydrogen linked covalently to a strongly electronegative atom can establish an extra weak attachment to another electronegative atom in the same or different molecules. This attachment is called a hydrogen bond.
- (b) To distinguish from a normal covalent bond, a hydrogen bond is represented by a broken line,
- **Ex.** X H ... Y where X and Y are two electronegative atoms. The strength of hydrogen bond is quite low about 2-10 kcalmol<sup>-1</sup> or 8.4-42 kJmol<sup>-1</sup>.
- (c) Conditions of hydrogen bonding:
  - (i) The molecule must contain a highly electronegative atom linked to H-atom.
    (If E.N. ↑ polarity of bond ↑)
  - (ii) The size of the electronegative atom should be small.





Ex.

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(d) Strength of H-bond:

H F	bond dissociation energy = $41.8 \text{ kJ mol}^{-1}$
Н О	bond dissociation energy = 29.3 kJ mol $^{-1}$
H N	bond dissociation energy = $12.6 \text{ kJ mol}^{-1}$

- (e) Effect of H-bond
  - (i) It causes the association of many molecules.
  - (ii) Due to hydrogen bond molecules are associated and show high molecular weight.
  - (iii) M.P. & B.P. of the molecules increases
  - (iv) Viscosity & surface tension of the molecules increases.
  - (v) The compounds which can form H-bond with the covalent molecules are soluble in such solvents.
  - **Ex.** : Alcohol & Ammonia are water soluble.

# **TYPE OF H-BONDING**

- (a) Intermolecular
- (b) Intramolecular
- (a) Intermolecular H-bond:
  - (i) This type of H-bonding takes place between two molecules.

**Ex.** ROH, H<sub>2</sub>O, R - OH & H<sub>2</sub>O

- (ii) In such compounds molecular wt., M.P, & B.P. are high.
- (iii) Extent of H-bonding  $\uparrow$  viscosity & density  $\uparrow$ .

# (b) Intramolecular Bond

- (i) It is the H-bonding in the same molecule of a compound. The bonding also known as chelation.
- (ii) Solubility in water, M.P. & B.P. of these compounds decreases.

(iii) The value of acid strength of acid depends on the relative stability of the acid and its conjugated base if the intramolecular H-bonding stablises the conjugate base then, the acid strength increases and if the conjugate acid is stabilised in this way, then the acid strength decreased.

# H-bond has serious consequences on the physical properties. These are -

- (i) H<sub>2</sub>O is liquid at room temperature whereas H<sub>2</sub>S is gas at room temperature although
  H<sub>2</sub>S has greater molecular weight.
- (ii) Ice is lighter than water, although it solid because in ice H<sub>2</sub>O molecules are extending their H-bonds to full length and six water molecules produce a cage like structure which is porous in nature leading to smaller mass and larger volume, thus lowering the density.
- (iii) Alcohols have higher boiling points than corresponding alkanes and there of the same molecular mass. This can be explained by the intermolecular H-bonds existing among the R-OH molecules whereas ethers and hydrocarbon are not capable to have such strong intermolecular forces. thus, they have lower Boling points.

 $H_2O > R-OH > R-OH \rightarrow Exceptional$ 

 $H_2S < R-SH < R-S-R \rightarrow Normal$ 

H-bond increases

 $H_2O > R\text{-}O\text{-}R$ 

B.P. increases

R-O-R → no H-bond H<sub>2</sub>O → H-bonds R-OH → H-bond.

- (iv) Alcohol and water are miscible in any proportion due to formation of H-bonds.
- (v) Ammonia is excessively soluble in water whereas other gases are partially soluble.This is due to the tremendous capacity of NH<sub>3</sub> molecule to generate 4-H-bonds.

 $NH_3 > RNH_2 > R_2NH$ 

- (vi) Solubility order of different amines and ammonia in water follows the order  $NH_3 > RNH_2 > R_2NH$ . This can be explained by the capacity of these elements to form H-bonds.
- (vii) KHF<sub>2</sub> exists whereas KHCl<sub>2</sub>, KHBr<sub>2</sub>, KHI<sub>2</sub> do not because KHF<sub>2</sub> is constituted by 2

ions i.e.  $K^+ \& HF_2^-$ 

$$\begin{bmatrix} - & \delta^+ & \delta^- \\ F & \dots & H - F \end{bmatrix}$$
 [Cl<sup>-</sup> ... H - Cl]

exist does not exist

 ${\rm KHF}_2$  is a red orange coloured solid.

- (viii) o-nitro phenol is steam volatile and less H<sub>2</sub>O soluble than its corresponding para isomer because in o-nitro phenol, intra molecular H-bond exists which reduces the capacity of the molecule to produce intermolecular H-bonds with other molecules like water. This brings intermolecular forces among the o-nitrophenol molecules resulting into high volatility.
- (ix) Acetic acid has a molecular weight of 60 in benzene and it shows a very high boiling point. This is due to dimerization of molecule.



 (x) Salicylic acid has very high acidity due to chelation of salicylate ion through the Hbond



- (xi) Chelation means to grab atoms in vicinity as much as possible.
- (xii) Maleic acid has greater acidity than furmaric acid. This can also be explained by chelation of monooleate anion which has a H-bond between carboxylate anion and the unionized carboxylic acid.



(xiii) Normally when 2 hydroxyl groups are present on the same carbon atom i.e. gem diols are unstable, but "chloralhydrate" is a stable molecule due to formation of H-bond.



(xiv)  $CH_3 - C - CH_2 - C - CH_3$  In the above compound, (acetyl acetone) enol form is stable because of the intramolecular H-bond.

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 $C_2H_2$  is not soluble in  $H_2O$  but it is highly soluble in acetone.



Sol.

In hybridization as %S character increase, electronegativity increases hence  $C_2H_2$  forms H-bonds with O-atom of acetone and get dissolved. But  $H_2O$  molecules are so much associated that it is not possible for  $C_2H_2$  molecules to break that association, hence  $C_2H_2$  is not soluble in  $H_2O$ .

# **DIPOLE MOMENTS & MOLECULAR POLARITY**

- (a) The degree of polarity of covalent bond is given by the dipole moment ( $\mu$ ), which is the product of either charge (e) and the distance (d) between them.  $\mu = d \times e$ . 'e' is the order of magnitude of the electronic charge, i.e., about  $10^{-10}$  esu and d is the distance between the atomic centres, i.e., about  $10^{-8}$  cm.
- (b) Hence dipole moments may be expected to have value around  $10^{-10} \times 10^{-8} = 10^{-18}$  esu-cm. It is however, general particle to express dipole moments in **Debye units** (D),  $1 \text{ D} = 10^{-18} \text{ esu-cm}.$



Electronegativity of A < Electronegativity of B

If the charge is in SI units (Coulomb's) and d in meter,  $\mu$  will be coulomb-meter (cm) unit.

 $1D = 3.336 \times 10^{-30} \text{ cm}$ 

(c) Any covalent bond which has a certain degree of polarity will have a corresponding dipole moment, though it does not follow that compound containing such bonds will

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have dipole moment, for the polarity of the molecule as a hole is the vector sum of the individual bond moment.

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

 $\mu_{resultant} = \bullet$ 

- (i) For example, CO<sub>2</sub> is a linear molecule, O = C = O, so that the dipole moments of the two C = O bonds cancel out.
- (ii) The C → Cl bond has a definite polarity and a definite dipole moment but carbon tetrachloride has zero dipole moment because it is a tetrahedral molecule, and the resultant of the 4C Cl bond moments is zero.
- (iii) On the contrary CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> have definite dipole moments. (Order of dipole moment  $CH_3Cl > CHCl_3 > CH_2Cl_2 > CCl_4 = CH_4$ )

# ELECTROVALENT OR IONIC BOND

- (a) The chemical bond formed between two or more atoms as a result of the complete transfer of one or more electrons from one atom to another is called Ionic or electrovalent bond.
- (b) Electro positive atom loses electron (group IA to IIIA)
- (c) Electro negative atom gains electron (group VA to VIIA)
- (d) Electrostatic force of attraction between cation and anion is called ionic bond or electrovalent bond.
- (e) Total number of electrons lose or gained is called electro valency.

Ex.

(i) 
$$Mg + O \\ 2, 8, 2 & 2, 6 \\ 2e^{-} \qquad \longrightarrow Mg^{+2} + O^{-2} \\ electro valency of Mg = 2 \\ electro valency of 0 = 2$$

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- (f) The force of attraction is equal in all direction so ionic bond is non-directional.
- (g) A definite three-dimensional structure is formed called crystal lattice.
- (h) Ionic compound does not have molecular formula. It has only empirical formula.
- **Ex.** NaCl is empirical formula of sodium chloride

# FORMATION OF IONIC COMPOUND - BORN HABER CYCLE

- (a) When elements react to form compounds,  $\Delta G$  (the free energy of formation) is negative. For a reaction to proceed spontaneously, the free energy of the products must to lower than that of the reactants.
- (b) Usually, the energy changes are measured as enthalpy values  $\Delta H$ , and  $\Delta G$  is related to  $\Delta H$  by the equation

$$\Delta G = \Delta H - T \Delta S$$

In many cases enthalpy values are used instead of free energy values, and the two are almost the same if the term T S is small. At room temperature T is almost 300 K, so G and  $\Delta$ H are similar when the change in entropy  $\Delta$ S is very small. Entropy changes are

large when three is a change in physical state,

Ex. solid to liquid, or liquid to gas, but otherwise entropy changes are usually small.

(c) A whole series of energy changes is involved when one starts from the elements and finishes with an ionic crystal. These changes are shown in the Born-Haber cycle.
 Formation of NaCl (s) involves



thus  $S + I.P. + - EGE - U = \Delta H_f$ 

here S = heat of sublimation of Na(s)

I.P. = ionisation potential of Na(g)

 $D = bond dissociation energy of Cl_2$ 

EGE = electron gain enthalpy of Cl(g)

U = lattice energy

 $\Delta H_f$  = enthalpy heat of formation of NaCl(s)

If lattice is  $MgX_2(s)$  then

 $S + (IP_1 + IP_2) + D - 2EGE - U = \Delta H_f$ 

where  $(IP_1 + IP_2) = \text{total ionisation energy to form Mg}^{2+}(g)$  from Mg(g).

#### FACTORS FAVOURING IONIC BONDING

# (a) Ionisation Energy

Amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom to form the +ve ion or cation. (Energy absorbed)

Lesser Ionization energy  $\rightarrow$  Greater tendency to form cation.

**Ex.** 
$$Na^+ > Mg^{+2} > Al^{+3}$$

 $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$  Cation formation tendency

# (b) Electron Affinity

Amount of energy released when an electron is added to an isolated gaseous atom to form -ve ion (anion) energy released.

Higher electron affinity  $\rightarrow$  Greater tendency to form anion

**Ex.**  $Cl^- > F^- > Br^- > I^-$ 

 $F^- > 0^{-2} > N^{-3}$ 

(c) Lattice Energy - (Energy released)

The energy released in the formation of 1g mole electrovalent compound from isolated gaseous ions is called lattice energy (U) of that compound.

Higher lattice energy  $\rightarrow$  Greater will be the stability or strength of ionic compound.

# FACTOR AFFECTING SOLUBILITY

# (a) Dielectric Constant of Solvent

The capacity of solvent to neutralise the charge of ionic compounds is called Dielectric constant. It is represented by  $\epsilon$ .

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

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

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

(Benzene  $\varepsilon = 2.3$ )

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

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

 (iii) H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> have high dielectric constant but these are not a good solvent due to oxidising nature.

# (b) Size of Ion

(i) Keeping size of cation constant, the lattice energy decreases with the increase of anionic radius. Hence order of solubility of LiX in water is LiF < LiCl < LiBr < LiI</p>

As solubility  $\alpha$   $\frac{1}{1}$  lattice energy

- (ii) In LiI covalent nature is more according to Fajan's rule but HE > LE therefore LiI is more soluble in water.
- (iii) Keeping size of anion constant, the hydration energy decreases with the increase of cationic radius. Hence order of solubility of MSO<sub>4</sub> will be BeSO<sub>4</sub> > MgSO<sub>4</sub> > CaSO<sub>4</sub> > SrSO<sub>4</sub> > BaSO<sub>4</sub> (Exception of Fajan's rule)
- (iv) If size of cation and anion is very large, solubility decreases from top to bottom.
- (v) Solubility decreases in a period (as ionic nature decreases and covalent nature increases)

 $NaCl > MgCl_2 > AlCl_3$