CHAPTER 5
LIQUIDS

INTRAMOLECULAR FORCES

The attractive forces within a molecule of a liquid are called intramolecular forces. e.g

1. Covalent Bond
2. Ionic Bond
3. Co-ordinate covalent bond etc

These forces are stronger as compared to intermolecular forces.

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INTERMOLECULAR FORCES

The attractive forces among the molecules of a substance are called intermolecular forces. e.g

1. Dipole - Dipole Forces
2. Hydrogen Bonding
3. London Dispersion Forces

Collectively these three weak forces are named as Van der Waal's forces.

→ All the intermolecular forces are electrical in origin and are resulted from the mutual attraction of unlike charges or the mutual repulsion of like charges.

→ Many of the physical properties of liquids can be explained on basis of intermolecular forces.

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DIPOLE - DIPOLE FORCES

"The electrostatic force of attraction produced when the positive end of one molecule attracts the negative end of neighbouring molecule are called dipole - dipole forces"

The more electronegative atom develops a partially negative charge on itself and a partially positive charge on less electronegative atom.

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$$H^{+\delta} - Cl^{-\delta}$$

→ Dipole - Dipole Forces are stronger than London Dispersion forces.

→ Stronger the dipole - dipole forces, greater the values of thermodynamic properties like melting point, boiling point, heat of vaporization and heat of sublimation etc.

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HYDROGEN BONDING

"The electrostatic force of attraction between the positive hydrogen ion of one molecule and a more electronegative element of another molecule is called hydrogen bonding"

→ NH_3 and HF can form only one hydrogen bond due to presence of only one utilizable lone pair ~~and~~ of electrons and one utilizable H-atom respectively

→ Water can form two hydrogen bonds as it has two utilizable hydrogen atoms and two utilizable lone pairs on oxygen atom.

→ As Fluorine is more electronegative than oxygen. One should expect hydrogen bonding to be stronger in HF than H_2O. But boiling point of H_2O is higher than that of HF. The reason is that fluorine can make only one hydrogen bond with hydrogen of neighbouring molecule. On the other hand oxygen atom can form two hydrogen bonds with neighbouring molecule. NH_3 can also form one hydrogen bond per molecule as it has only one lone pair

→ Exceptionally low acidic strength of HF molecule as compared to HCl, HBr and HI is due to strong hydrogen bonding.

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→ Greater the E.N difference, stronger will be hydrogen bond.

* ORDER OF STRENGTH OF HYDROGEN BONDING

$HF > H_2O > NH_3$

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* ORDER OF BOILING POINTS:

$H_2O > HF > NH_3$

→ Hydrogen bond is approximately twenty times weaker than covalent bond.

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LONDON DISPERSION FORCES

"The forces of attraction between non-polar molecules which become polar for an instant are called London Dispersion forces."

OR

"The short range forces of attraction created between one end of instantaneous dipole and the opposite end of the induced dipole are called dipole induced dipole interaction or London dispersion forces"

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* FACTORS AFFECTING LONDON DISPERSION FORCES:
  1. Atomic or Molecular size
  2. Polarizibility
  3. Number of atoms in a molecule

1. ATOMIC OR MOLECULAR SIZE

Greater the size of atom, greater the strength of London Dispersion forces

2. POLARIZIBILITY

Greater the polarizibility, greater the strength of LDF.

The polarizibility of an atom or molecule is a measure of the ease with which electron charge density is distorted. In large atoms, the outer electrons are more loosely bound, they can shift towards another

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atom more readily than the more tightly bound electrons in small atoms. This means polarizibility increases with increased atomic and molecular size.

3. No. Of Atoms In A Molecule

Elongated molecules make contact with neighbouring molecules over a greater surface than do small molecules. Greater the number of atoms, greater is the polarizibility and hence greater strength of LDF.

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4. Shape Of Molecules

The straight-long chain molecules have greater LDF than the branched short chain molecules, even if they have same number of electrons.

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PHYSICAL PROPERTIES OF LIQUIDS

1. ADDITIVE PROPERTIES

Such properties depend upon the number and kind of atoms present in the molecule e.g molecular weight.

2. CONSTITUTIVE PROPERTIES

Such properties depend upon the arrangement of atoms in the molecules and not their number e.g Optical Activity

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3. COLLIGATIVE PROPERTIES

Such properties depend on the number of ions and molecules present but donot depend upon the structure of molecules e.g Osmotic Pressure, Molar Volume etc.

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EVAPORATION

* Evaporation is:
  - → spontaneous
  - → endothermic
  - → occurs at all temperature

* Rate of Evaporation Depends On:

1. Surface Area
   (Greater Surface Area, Greater rate of evaporation)

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2. Temperature
   (Greater temperature, greater rate of evaporation)

3. Inter molecular Forces
   (Greater strength of inter molecular forces, slower is the rate of evaporation)

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VAPOUR PRESSURE

"The pressure exerted by the vapours in equilibrium with the liquid at a given temperature is called vapour pressure of a liquid"

* Vapour Pressure is independant of :
  1. Surface Area
  2. Amount of Liquid

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* FACTORS AFFECTING VAPOUR PRESSURE

1. Intermolecular Forces (Nature of Liquid)

Liquids having strong intermolecular forces possess low vapour pressure and vice versa. e.g

V.P of water is 24 mmHg at 25°C
V.P of ether is 537 mm Hg at 25°C

2. Temperature

Vapour Pressure of Liquids increase with increase in temperature and vice versa e.g

V.P of water :
At 25°C = 24 mm Hg
At 50°C = 93 mm Hg
At 80°C = 355 mm Hg
At 100°C = 760 mm Hg

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MEASUREMENT OF VAPOUR PRESSURE

(1) BAROMETRIC METHOD

- 1m (1000mm) long glass tube is filled with mercury and inverted in a dish of mercury. The mercury level in the tube falls until it is stopped by atmospheric pressure.
- Small amount of liquid is placed at the lower end of mercury in the tube whose vapour pressure is to be measured.
- Liquid rises above the surface of mercury and evaporate.
- Liquid ~~pr~~ vapours exert pressure and push the mercury downwards.
- The vapour pressure of liquid is measured by fall of mercury level in the tube.

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(2) MANOMETRIC METHOD

- An accurate method
- The liquid in the flask is frozen and the space above the liquid is evacuated using vacuum pump.
- The vacuum pump end is closed and manometric end is opened.
- The liquid is evaporated and the vapours exert pressure on the left limb of manometer due to which mercury in the right limb will be pushed up against atmospheric pressure.
- After some time equilibrium is established.

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- The difference in mercury height gives the vapour pressure of liquid in the flask

$$V.P = P + \Delta h$$

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BOILING POINT

"The temperature at which the vapour pressure of a liquid becomes equal to atmospheric pressure or any other external pressure is called boiling point".

* Boiling Point of H_2O

At 1atm = 100°C

At 0.921 atm = 98°C

At 0.425 atm = 72°C

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FACTORS AFFECTING BOILING POINT

1. INTER MOLECULAR FORCES

Boiling point of a liquid with stronger inter-molecular forces will be higher than a liquid with weaker intermolecular forces at the same pressure.

2. EXTERNAL PRESSURE

Greater the external pressure, ~~strong~~ higher the boiling point e.g

Boiling Point of water:

At 1 atm = 100°C

At 0.921 atm = 98°C

At 0.425 atm = 72°C

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+ PRESSURE COOKING

It is an example of increased pressure.
Food is easily cooked at high pressure.

* VACCUM DISTILLATION

It is an example of reduced pressure.
The boiling point and decomposition point of glycerine is 290°C at. 760mm Hg.
Glycerine can be purified by vacuum distillation at 210°C and 50mm Hg.

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* Boiling Point of CCl_4 is greater than $CHCl_3$ although CCl_4 is non polar and $CHCl_3$ is polar bc2 size of CCl_4 is greater than $CHCl_3$.

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ENERGETICS OF PHASE CHANGE

The change in energy at constant pressure, in a physical or chemical process is called enthalpy change. It is denoted as ΔH. Expressed in $kJ\,mol^{-1}$.

Three types:-

1. MOLAR HEAT OF FUSION (ΔH_f)

"The amount of heat absorbed when one mole of a substance (solid) is converted into liquid form at its melting point"

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e.g

ΔH_f for ice (H_2O) is $6\,kJ\,mol^{-1}$

2. MOLAR HEAT OF VAPORIZATION (ΔH_{vap})

"The amount of heat absorbed when one mole of a liquid is converted into vapours at its boiling point"

e.g

ΔH_{vap} for water (H_2O) is 40.7 kJ/mol

3. MOLAR HEAT OF SUBLIMATION

"The amount of heat absorbed when one mole of a solid is converted directly into vapours at constant temp and one atm pressure"

e.g

ΔH_{sub} for one mol of Solid Iodine (I_2) to vapours is $62.3\,kJ\,mol^{-1}$

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ENERGY CHANGES AND INTERMOLECULAR ATTRACTIONS

Enthalpy change in a physical change e.g vaporization can determine the strength of intermolecular forces.

→ Higher the value of ΔH_v, stronger the intermolecular forces and vice versa

→ Polar molecules have stronger intermolecular forces. Hence, polar substances have higher values of ΔH_v, ΔH_s, ΔH_f

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SURFACE TENSION

" Tendency of liquids to minimize their surface area due to intermolecular forces".

The tension experienced by the molecule on the surface due to imbalanced attractive forces is called surface tension. Surface tension tends to minimize surface ~~air~~ area.

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" The amount of energy required to expand the surface of a liquid by a unit area"

Unit :- Nm^{-1} or Jm^{-2}

* FACTORS AFFECTING SURFACE TENSION

1. INTERMOLECULAR FORCES

Stronger the intermolecular forces, greater is the surface tension.

2. TEMPERATURE

Surface Tension decrease with increase in temperature.

* Surface Tension is due to cohesion.

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→ Water has high surface tension because of hydrogen bonding. Rain drops have spherical shape because a sphere has least surface to volume ratio which it acquires due to surface tension.

→ Detergents reduce the surface tension of water by breaking up the hydrogen bonding. The reduction of cohesive forces increases the ability of ~~wet~~ water to wet a solid surface by adhesion, thus its cleaning action is increased.

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MEASUREMENT OF SURFACE TENSION

1. The torsion method
2. The capillary method
3. The drop or stalagmometer method

DROP METHOD FORMULA:

$$\gamma_l = \frac{n_w d_l}{n_l d_w} \times \gamma_w$$

γ_l : Surface Tension of Liquid
d_l : Density of Liquid
n_l = No. of drops of Liquid
γ_w = Surface Tension of water
d_w = Density of water
n_w = No. of drops of water

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VISCOSITY

→ The resistance of a liquid to its flow is called viscosity.

→ The velocity of flow of liquid nearer to the sides of tube is less than the velocity of flow at the centre of the tube.

→ The layer of the liquid in contact with the walls of the tube remains stationary.

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FACTORS AFFECTING VISCOSITY

1. MOLECULAR SIZE

The viscosity of a liquid increases with increasing molecular size.

2. MOLECULAR SHAPE

Irregular molecules offer more resistance to their flow as compared to more regularly shaped molecules. Molten sulphur at 140°C with ring shaped S_8 molecules is less viscous than long chain entangled S_n molecules at 190°C.

3. INTERMOLECULAR FORCES

Stronger the intermolecular forces between molecules, higher will be viscosity of liquid.

Liquids with hydrogen bonding among their molecules

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are more viscous than others.

→ Sulphuric Acid and Glycerine are more viscous bcz of the extensive possibility of hydrogen bonding in their molecules.

→ The viscosity of water is more than methyl alcohol (CH_3OH) mainly due to hydrogen bonding in water.

4. TEMPERATURE

Viscosity of a liquid decrease with increase in temperature.

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MEASUREMENT OF VISCOSITY

The relative viscosity is defined as the ratio of viscosity of a liquid to the viscosity of water taken as a standard.

→ The viscosity of water is taken as 1 centipoise at 25°C.

→ To measure the relative viscosity of a liquid, Ostwald's viscometer is used.

$$\frac{\eta_l}{\eta_w} = \frac{d_l t_l}{d_w t_w}$$

η_l : Viscosity of liquid

η_w : Viscosity of water

d_l : density of liquid

d_w : density of water

t_l : time of flow of liquid

t_w : time of flow of water

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SI Unit of Viscosity:

$kg\,m^{-1}s^{-1}$

1 Poise = $10^{-1}\ kg\,m^{-1}s^{-1}$

or $0.1\ kg\,m^{-1}s^{-1}$

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POINTS TO REMEMBER

* Only two of the known elements in periodic table are liquids at room temperature - Bromine and Mercury.

* Helium at 21.8K becomes a super fluid liquid, its viscosity is zero.

* DNA when placed in solutions of salt and water form liquid crystal phases.

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The highest temperature at which vapour pressure of a liquid can be measured is:
Boiling Point of Liquid

Kerosine oil is liquid at room temperature due to molecular size.

Arsenic (As) and Antimony (Sb) are metalloids.

Dipole-Dipole Forces Require Four Poles
$H^+ - Cl^- \ldots . H^+ - Cl^-$
H^+, Cl^-, H^+, Cl^- are four poles.

Stronger intermolecular forces would make the substance less volatile.

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