

5

LIQUIDS



After completing this lesson, you will be able to:

This is 9 days lesson
(period including homework)

- Define molar heat of fusion and molar heat of vaporization.
- Define dynamic equilibrium between two physical states
- Describe simple properties of liquids e.g., diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces and kinetic energy based on Kinetic Molecular Theory.
- Explain physical properties of liquids such as evaporation, vapour pressure, boiling point, viscosity and surface tension.
- Describe how heat of fusion and heat of vaporization affect the particles that make up matter.
- Explain applications of dipole-dipole forces, hydrogen bonding and London forces
- Use the concept of Hydrogen bonding to explain the following properties of water: high surface tension, high specific heat, low vapour pressure, high heat of vaporization, and high boiling point. And anomalous behaviour of water when its density shows maximum at 4 degree centigrade.
- Relate energy changes with changes in intermolecular forces.
- Describe liquid crystals and give their uses in daily life.
- Differentiate liquid crystals from pure liquids and crystalline solids.

INTRODUCTION

A simple definition of a liquid is that "it is a material that assumes the shape of a container without filling it completely". A gas on the other hand takes the shape of the vessel and has the characteristics to fill it completely. A solid neither takes the shape of the vessel nor fills the container completely. The definition of a liquid is satisfactory on the whole with the exception of glasses, polymers (e.g. PVC etc); they appear in the solid but at higher temperatures they behave like liquid even before they melt. The cohesive force i.e. force of attraction between molecules of substance in a liquid are stronger than those in a gas even at high pressure.

5.1 KINETIC MOLECULAR INTERPRETATION OF LIQUIDS

The kinetic molecular theory also applies to liquids. Postulates of kinetic molecular theory of liquids are given below:

- (a) A liquid is made up of molecules which touch one another.



- (b) The molecules within the liquid are in constant motion but the movement of molecules is restricted due to their close packing together.
- (c) Attractive forces among liquid molecules are greater than those among gas molecules. However these attractive forces are not sufficient to hold molecules in fixed position. The liquid molecules can slide each other.
- (d) The average Kinetic Energy of liquid molecules is directly proportional to the Absolute Temperature.
- (e) At constant temperature, the average K.E of the molecules is equal to the K.E of the vapours of liquids.

a. Properties of Liquids

There are some simple properties of liquid e.g. diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces, and Kinetic Energy based on Kinetic Molecular Theory. We can use the Kinetic Molecular Theory to account for the simple properties of liquids.

i. Diffusion

The diffusion in liquids takes place because the molecules move from one place to another due to K.E. The restricted movement of the molecule reduces the rate of diffusion e.g. a drop of ink when added to water diffuses slowly due to relatively small empty spaces between the molecules. The diffusion between closely packed molecules of liquids is slow due to less collision between them.

ii. Compression (effect of pressure)

A liquid cannot be compressed significantly by increasing the pressure because the molecules are already in close contact with one another e.g. an increase of pressure from one to two atmospheres reduces the volume of water to 0.0045 percent which is negligible. However the same pressure reduces the volume of a gas up to 50 percent.

iii. Expansion (effect of temperature)

The liquids expand on heating because the intermolecular forces between them decrease. Moreover the increase of temperature increases the effective collisions between the molecules. If the temperature is decreased, contraction of volume takes place. This property is useful for making thermometers, e.g. mercury thermometer. In it, if the temperature rises, the mercury expands in the capillary tube. As the volume of capillary is much less than the volume of the bulb containing mercury, a small expansion gives a large movement of mercury thread.

iv. Motion of molecules

The molecules move with lesser speed due to larger forces of attraction among them, As a result they have lesser kinetic energy. However the kinetic energy increases with the increase of temperature.

v. Spaces between them

The molecules forming the liquid states are fairly close to each other. There is very little



space between them. As a result the numbers of collisions among the molecules are moderate. Therefore, the average kinetic energy is also moderate.

vi. Intermolecular forces

The attractive forces existing between the individual particles of a substance are called intermolecular forces. The physical properties of liquids such as boiling point, vapour pressure, surface tension, viscosity and heat of vaporization depend upon the strength of intermolecular attractive forces.

vii. Kinetic Energy based on Kinetic Molecular Theory

According to the kinetic molecular theory, the molecules due to strong inter-molecular attractions have minimum movements and minimum collisions. Let us consider the example of water, as the molecules are closer to each other and have strong forces of attractions due to hydrogen bonding so have low kinetic energy.

5.2 INTERMOLECULAR FORCES

The forces of attractions among the molecules of a liquid are called inter-molecular forces. For example, water exists as a liquid due to inter-molecular attractions called hydrogen bonds. The forces of attraction existing

between the molecules of a substance are also known as Vander Waal's forces. The physical properties of liquids can be explained in terms of their intermolecular forces.

DO YOU KNOW

Lizards can stick to walls and ceilings because of Vander Waal's forces.

The intermolecular forces are of five types:

- Dipole-Dipole forces
- Ion-Dipole forces
- Dipole-induced dipole forces
- London Dispersion forces
- Hydrogen bonding

5.2.1 Dipole-Dipole Forces

Polar molecules have charges at different parts of a molecule. Due to these charges they attract each other.

The attractive forces between the positive ends of one molecule with the negative end of other molecule are called dipole – dipole forces. This means dipole – dipole interactions are electrostatic interactions between permanent dipoles in molecules. Examples of polar molecules include hydrogen chloride (HCl) chloroform (CHCl_3) etc.

Stronger these dipole-dipole forces, greater would be the value of thermodynamic parameters like melting point, boiling point, heat of vaporization, heat of sublimation etc.

5.2.2 London Dispersion Forces

The forces of attractions between non-polar molecules which become polar for an instant are called London dispersion forces.

Substances like hydrogen, helium, neon, argon, chlorine, fluorine, methane etc are non-

polar in nature. These gases can be liquefied and solidified under appropriate conditions. Some forces must be holding these molecules in contact with one another in the liquid and solid states.

In He gas, on the average, the electron charge density is evenly distributed in a spherical region about the nucleus. However, at any given instant, the actual location of two electrons relative to the nucleus can produce an instantaneous dipole. This temporary dipole, in turn, can influence the distribution of electrons in neighbouring helium atoms, producing induced dipoles in those atoms (Fig. 5.1).



Fig. 5.1: London dispersion forces Instantaneous dipole

The forces of attraction between an instantaneous dipole and an induced dipole are known as a dispersion force. It is also called as London dispersion force, named for Fritz London who offered a theoretical explanation for these forces in 1928.

Factors Affecting London Dispersion Forces

Factors affecting the London dispersion force are:

- Atomic or molecular size
- Polarizability
- Number of atoms in a molecules

(i) Atomic or Molecular Size

The strength of these forces depends upon the size of the electronic cloud of the atom or molecule. With the increase in size of atom or molecule, the dispersion becomes easy and these forces become prominent. Inert gases are all monoatomic gases. They do not make covalent bonds with other atoms because their valence shells are complete. Their boiling point increase down the group from He to Rn (Table 5.1). This is because of increase in molecular size.

Table 5.1: Boiling points of noble gasses

Noble Gas	He	Ne	Ar	Kr	Xe	Rn
Boiling Points (°C)	-268.6	-245.9	-185.7	-152.3	-107.1	-61.8

(ii) Polarizability

The polarizability of an atom or molecule is a measure of the ease with which electron charge density is distorted. Large atoms have more electrons and larger electron cloud than small atoms. In large atoms, the outer electrons are more loosely bound, they can shift

towards another atom more easily than the more tightly bonded electrons in small atoms. This means polarizability increases with increased atomic and molecular size. For example among halogens, the first member, F_2 is a gas at room temperature, the second member, Cl_2 is also a gas but it is more easily liquefied than F_2 . Bromine is a liquid and Iodine is solid at room temperature. Because large molecules are easily polarizable, the intermolecular forces between them are strong enough to form liquids or solids.

(iii) Number 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 in a molecule, greater is the polarizability of the molecule. Table 5.2 shows boiling points and physical states of some hydrocarbons.

Table 5.2: Boiling points and physical states of some hydrocarbons.

Molecular formula	B.P ($^{\circ}C$ at 1 atm)	Physical State at STP
CH_4	-161.5	Gas
C_2H_6	-88.6	Gas
C_3H_8	-42.1	Gas
C_4H_{10}	-0.5	Gas
C_5H_{12}	36.1	Liquid
C_6H_{14}	68.7	Liquid
$C_{10}H_{22}$	174.1	Liquid

Note that C_2H_6 and C_6H_{14} have the boiling points as $-88.6^{\circ}C$ and $68.7^{\circ}C$ respectively. This shows that the molecule with a large chain length experiences stronger attractive forces.

Hydrogen Bonding

A hydrogen bond is the attraction between the lone pair of an electronegative atom and a hydrogen atom that is bonded to either N, O or F. This limits hydrogen bonding mainly to the participation of nitrogen, oxygen and fluorine atoms. Hydrogen bonds are weaker than covalent bonds but stronger than dipole-dipole interactions, which are stronger than London dispersion forces. The boiling point and heat of vaporization of water are higher than those of H_2S because H_2O molecules attract each other through H-bonding whereas H_2S molecules attract each other by dipole-dipole interactions.

Applications of Hydrogen Bonding

(i) Thermodynamic properties

The boiling points of hydrides of group IVA, VA, VIA and VIIA plotted against period number of the periodic table is shown in figure 5.2.

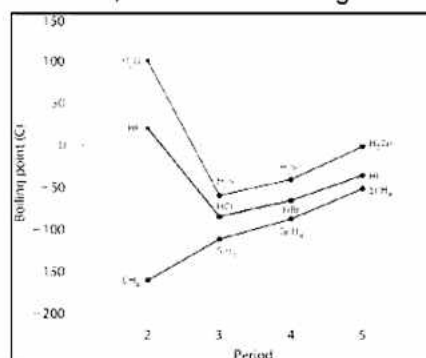


Fig. 5.2: A graph between period number and the boiling points of hydrides

**The boiling point of hydrides**

Note that hydrides of group IVA have lower boiling points. The reason is that these hydrides are non-polar and have only London dispersion forces among their molecules. Hydrides of group VA, VIA and VII-A have polar molecules. NH_3 , H_2O and HF show maximum boiling points in their respective series. This is due to hydrogen bonding in their molecules. The boiling point of H_2O seems to be more affected than that of HF . As F is more electronegative than O. One should expect H-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 the neighbouring molecule. On the other hand oxygen atom can form two hydrogen bonds with the neighbouring molecules. NH_3 can also form only one hydrogen bond per molecule as it has only one lone pair.

(iii) Solubility of Hydrogen Bonded Molecules

The compounds that have hydrogen bonds are soluble in each other. Ethyl alcohol can dissolve in water because both can form hydrogen bonds with each other. Similarly carboxylic acids are also soluble in water, if their molecular sizes are small.

(iii) Cleansing Action

Soaps and detergents perform the cleaning action. Their molecules contain both polar and non-polar ends. Their polar parts are water soluble due to hydrogen bonding and non-polar part dissolve oil or grease. Attraction between water and polar end of soap molecule carries the oil or grease droplet into the water.

(iv) Hydrogen Bonding in Paints and Dyes

Paints and dyes have adhesive action due to hydrogen bonding. Similarly hydrogen bonding also makes glue and honey sticky substances.

(v) Clothing

We use cotton, silk or synthetic fibres for clothing. Hydrogen bonding is of great importance in thread making materials. This hydrogen bonding is responsible in their rigidity and tensile strength.

(vi) Food Materials

Food materials like carbohydrates consist of glucose, fructose, sucrose, each of them contains $-\text{OH}$ groups which is responsible for H-bonding in them.

(vii) Hydrogen Bonding in Biological Molecules

The structure of proteins, substances essential to life, is determined partly by hydrogen bonding. The action of enzymes, the protein molecules that catalyze the reactions that sustain life, depends in part on the forming and breaking of hydrogen bonds. The hereditary information passed from one generation to the next is carried in nucleic acid molecules joined by hydrogen bonds into an elegant structure.

5.3 PHYSICAL PROPERTIES OF LIQUIDS

In a liquid the molecules are very close to each other due to the presence of intermolecular forces. As a result their independent motion is greatly hindered and the flow of liquid and the rate of diffusion are much less than in the case of gases. The existence of



powerful forces of cohesion (forces between similar types of molecules e.g. H_2O) is responsible for the main properties of liquids.

The properties of liquid molecules are as under:

i. Additive properties:

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

ii. Constitutive properties:

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

iii. Colligative properties:

Such properties depend on the number of ions and molecules present but do not depend upon the structure of molecules. e.g. Osmotic pressure etc.

Boiling Point of a Liquid

When a liquid is heated, its V.P. increases due to the decrease of intermolecular forces with rise in temperature. As a result more and more vapours escape in the air. A stage reaches at which the liquid begins to boil. So the **temperature at which the vapour pressure of the liquid equals to atmospheric pressure or some external pressure is called boiling point of that liquid.**

e.g. Boiling Point of water at 760mmHg = 100 °C

Boiling Point of water at 23.7mmHg = 25 °C

Effect of Pressure on boiling point of a Liquid:

There are two practical applications regarding the effect of pressure.

i. Effect of increase of Pressure:

Food can be cooked easily in pressure cookers, which is a closed container. The vapours are not allowed to escape out and, therefore, develop more pressure. This increases the B.P of water. Pressure cookers help us in cooking the food quickly even at high altitude e.g. B.P of water at 2026mm Hg is 130°C

ii. Effect of decrease of pressure:

The liquids which decompose at their B.P can be obtained in the pure form under reduced pressure by vacuum distillation e.g. Glycerine has a B.P of 290°C at 760mmHg but it decomposes at its B.P. Now in order to get it in the pure form, the V.P is decreased to 50mmHg by vacuum pump. The B.P decreases to 210°C at 50 mmHg, so it boils without decomposition. In this way the liquids can be purified.

Evaporation of a Liquid

Evaporation is the process in which liquid molecules escape from the surface and enter the gas phase. It can be explained in terms of the energy possessed by the molecules on the liquid's surface. Surface molecules whose kinetic energies are higher than

SCIENCE TITBITS

Sweat evaporation is a natural cooling system for the human body



average kinetic energies, overcome the intermolecular forces that bind them to the liquid and enter the gas phase. After their escape, the average kinetic energy of the remaining molecules decreases. Therefore temperature of the liquid decreases, thus evaporation is a cooling process.

The factors which can affect the rate of evaporation are as follow:

i. Surface Area

The rate of evaporation increases with increasing surface area. This is because large surface area allows more molecules to evaporate.

ii. Intermolecular Forces:

The escaping tendency of molecules depends upon attractive forces between the molecules. the liquids with strong intermolecular forces have less evaporation. Thus water has less evaporation rate than petrol. This is because water has stronger intermolecular forces (H-bonding) than petrol which has weak dispersion forces between the molecules. A liquid which can rapidly change into vapours is called **volatile** e.g. petrol is more volatile than water.

iii. Temperature

Evaporation takes place at all temperature. Rate of evaporation however is affected by the change in temperature. Increase in temperature increases the number of molecules having kinetic energy sufficient to overcome intermolecular forces and escape more readily from the surface of the liquid. Thus the rate of evaporation increases with increasing temperature. This is why clothes dry more readily in summer.

Evaporation and Condensation

In open containers, evaporation continues until all of the liquid disappear. But when a liquid is placed into a closed container, amount of liquid decreases for a period of time and then does not change. In closed containers, the vapours cannot escape. Therefore, as the vapour concentration increases, some of the vapour molecules lose energy and return to the liquid state. This process is called condensation.

Evaporation involves molecules leaving the liquid and condensation occurs when a vapour changes back to a liquid. When the liquid is placed in a closed container, it begins to evaporate at a constant rate, very little condensation takes place. But as the concentration of the vapour increases above the liquid, the rate of condensation increases. After some time the rate of condensation equals the rate of evaporation. At this stage, the number of molecules entering the gas phase equals the number returning to the liquid phase, the system is said to be in a dynamic equilibrium. **"The pressure exerted by vapours in equilibrium with its liquid state is called the liquid's vapour pressure at the given temperature".**

Factors affecting Vapour Pressure

Vapour pressure is measured in the same units used for gas pressure. Vapour pressure is independent of the amount of liquid, so this is called an **intensive property** of the liquid. Two factors affect liquid's vapour pressure:

- Intermolecular forces
- Temperature

i. Intermolecular forces

The vapour pressure of a liquid depends upon the strength of intermolecular forces. Liquids having stronger intermolecular forces possess low vapour pressure and vice versa.

For example, water having hydrogen bonding possesses low vapour pressure. On the other hand ether, petrol etc have high vapour pressure due to weak dispersion forces.

ii. Temperature

As the temperature increases, the vapour pressure increases. This is because increase in temperature increases the average kinetic energies of the molecules which in turn decreases the intermolecular forces. For example, vapour pressure of water at 0 °C is 4.6 mm of Hg but at 100°C it is 760mm of Hg. The relationship of vapour pressure and temperature is shown by the graph (see Fig 5.3).

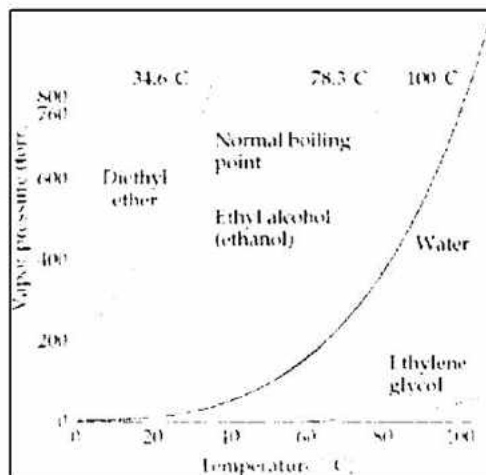


Fig 5.3: Effect of Temp on vapour pressure

Notice that the vapour pressure of diethyl ether (185mm Hg) at 0° C is much greater than that of ethanol (12mm Hg) or water (4.6mm Hg). Ether is non-polar in nature. Therefore, its high vapour pressure is due to its weak intermolecular forces (dispersion forces). Thus at the surface ether molecules require less energy to break free and change into vapour. Similarly, in ethanol intermolecular forces (H-bonding) are not as strong as those of water. Consequently vapour pressure of ethanol is greater than that of water at all temperatures.

It is observed that each of the three vapour pressure curves cross the line corresponding to one atmosphere at different temperatures. Therefore they boil at different temperatures. Ether boils at 35 °C, ethanol at 78 °C and water at 100 °C.

5.2.2 Viscosity

It is common observation that water can be poured very quickly from one container to another as compared to honey and glycerine. **The resistance of a liquid's to flow is called its viscosity.** The larger the viscosity, the more slowly the liquid flows. Viscosity measures, how easily molecules slide by one another. To understand viscosity, consider a liquid flowing in a tube is made up of a series of concentric circular layers. The resistance to flow is due to the internal friction between the layers of the molecules. The layers adjacent to the walls have the lowest velocity. Each layer exerts a drag on one another and thus causes resistance to flow.

Units:

SI units of viscosity is Pascal Second (Pa.s). Non-SI unit of viscosity is poise.

1 poise = $0.1 \text{ kg m}^{-1} \text{ s}^{-1}$ or $\text{g cm}^{-1} \text{ s}^{-1}$

1 Pa.s = $1 \text{ kgm}^{-1} \text{ s}^{-1} = 10 \text{ poise}$

**Factors Affecting Viscosity:**

Viscosity depends on the following factors:

- Molecular shape and size
- Intermolecular forces
- Temperature

i. Molecular shape and size

Molecular size and shape strongly influence viscosity. Liquids such as water, acetone, benzene and methanol, whose molecules are small and compact have low viscosity. Whereas liquids having large and irregular shaped molecules like honey, glycerine tends to get tangled up with each other. This inhibits the flow of molecules and leads to high viscosity.

DO YOU KNOW

In winter the viscosity of blood increases due to cold. The arteries and veins of human body contract and become hard and their diameter decrease. As a result the flow of blood and blood pressure is affected. On sitting before fire, the viscosity of blood decreases and its circulation increases. So the man becomes normal.

ii. Intermolecular forces

Stronger the intermolecular force among the molecules higher is the viscosity. Liquids whose molecules form hydrogen bonds are more viscous than other without hydrogen bonding. For example water is more viscous than methanol mainly due to extensive hydrogen bonding.

iii. Temperature

Molecules move faster as temperature increases. This is because; an increase in temperature decreases the intermolecular forces. This dependence is quite noticeable for highly viscous liquids such as honey and syrup. It is easier to pour these liquids when hot than when cold.

3.12.2. Surface tension

Have you ever seen insects such as the water strider to walk on water? What allows it? Surface tension is the property of the surface of the liquids to act as if there is a membrane stretched across it. We can understand that the level of liquids exhibit surface tensions. All molecules below the surface of the liquid are surrounded in all directions by other molecules. Thus the force exhibited by such molecules is balanced in all directions whereas a molecule at a liquid surface has molecules beside it and beneath it but no one above it. This results in an unbalanced force pulling the surface molecules inward.

The molecules at the surface therefore, feel a net attraction inwards, which creates surface tension. **“The force in dynes acting at right angle on a unit length of surface of a liquid is called surface tension”**. For a molecule to come to the surface, it must overcome the attraction directed downward. This means work has to be done to pull it to surface. Therefore, increase in surface areas of a liquid requires an input energy. **Surface tension can also be defined as the amount of energy required to expand the surface of a liquid by a unit area**. Molecules at the surface of a liquid are less stable than those inside it, so a liquid is stable when the fewest molecules are at its surface. This occurs when the liquid has minimum

surface area. Spheres have less area per unit volume than any other. Therefore small drops of a liquid tend to be spherical.

Factors Affecting Surface Tension

Surface tension of a liquid depends upon the following factors.

i. Intermolecular forces

Surface tension of a liquid depends directly on the strength of intermolecular forces. Stronger the intermolecular forces among the molecules of liquid, greater is the surface tension and vice versa. For example the surface tension of water is higher than many liquids such as alcohols, ethers benzene etc. this is due to strong hydrogen bonding between water molecules.

ii. Temperature

Surface tension of a liquid decreases with the increase of temperature. This is because increased kinetic energy of the molecules decreases strength of intermolecular forces.

iii. Nature of Liquids

It is different for different liquids due to the presence of different types of intermolecular forces.

Units

SI unit of surface tension is joule per square meter, Jm^{-2} or Newton per meter, Nm^{-1} .

Why water does not expand like many substance? In ice hydrogen bonds hold water molecules in a rigid but open hexagonal structure. As ice melts, some of the hydrogen bonds are overcome, and water molecules move into the holes that were present in ice structure. As a result, the H_2O molecules are closer together in liquid water than in ice. When ice melts, there is a about 9% decrease in volume and a corresponding increase in density. So, water is most unusual in this regard, because the liquid state is less dense than the solid for most substances. If we continue to heat water just above the melting point, more hydrogen bonds are overcome. The molecules become still more closely packed and the density of liquid increases to a maximum density at 3.98°C . Below 3.98°C the density of water decreases with temperature, as we expect for a liquid. These density phenomena explain why a freshwater lake freezes from the top down in winter. When temperature falls below 4°C , the more dense water sinks to the bottom of the lake. The colder surface water freezes first. Since ice is less dense than water, the water that freezes remain at the top to cover the lake with a layer of ice. This layer of ice insulates the water underneath. Thus under this thick blanket of ice, fish and plants survive for months.

Hydrogen bonding in water contributes to its unique properties, which are as follows.

i. High surface tension

A stretched membrane is formed on the surface of water. The force on the surface acting downwards is due to strong hydrogen bond in water. Therefore a high surface tension is



observed. This has been proved by the following data. Which liquid has lowest surface tension.

Solvent	Surface tension ($\gamma \times 10^{-2}$) (Nm ⁻¹)
Water	7.275
Methanol	2.26
Ethanol	2.28
Benzene	2.888
Hexane	1.84
CCl ₄	2.70

ii. High specific heat:

Specific heat is the quantity of heat required to raise the temperature of 1g of the substance by 1°C (or by 1K). For example specific heat of water is 4.180J/g°C. It is much higher than those of metals. It takes almost ten times as much heat to raise the temperature of 1g of water 1°C as to raise the temperature of 1g of iron by 1°C. Conversely, much heat is given off by water even a small drop in temperature. The vast amounts of water on the surface of Earth thus acts as a giant heat reservoir to moderate daily temperature variations. That is why the climate near large bodies of water such as lakes, ponds, oceans etc, is more moderate than interior of the land.

iii. High heat of Vaporization:

Water has a high heat of vaporization due to extensive hydrogen bonding. A large amount of heat is required to evaporate a small amount of water. This is of enormous importance to us because large amounts of body heat can be dissipated by the evaporation of small amounts of water (perspiration) from the skin. This effect also accounts for the climate-modifying property of lakes and oceans.

iv. High boiling points

Water has a high B.P. due to strong H-bonding. It is practically observed that the B.P. of water is 100°C at one atmospheric pressure (760mm) at sea level, however, the organic solvents like benzene (B.P80°C), ether (35°C) etc. have lower B.P. due to poor interactions between the molecules.

5.4 ENERGETIC OF PHASE CHANGES

Physical and chemical changes are accompanied by energy change in the form of heat. A physical change in energy is the quantitative measurement of the strength of intermolecular forces. Energy change at constant pressure is known as enthalpy change denoted by ΔH . It is expressed in kJ mole⁻¹. When a substance undergoes a phase change (change of state), its temperature remains constant, even though heat is being added.

5.4.1 Molar Heat of Fusion, Molar Heat of Vaporization and Molar Heat of Sublimation

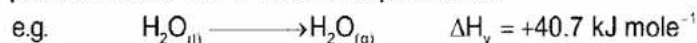
Molar heat of fusion (ΔH_f) is the amount of heat required to convert one mole of a solid into its liquid state at its melting point is called molar heat of fusion (ΔH_f)

e.g. Molar heat of fusion for ice is $+6.02 \text{ kJ mole}^{-1}$



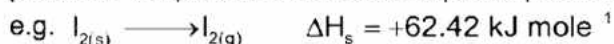
Molar heat of vaporization (ΔH_v)

The amount of heat required to convert one mole of a liquid into its vapours at its boiling point is called molar heat of vaporization.



Molar heat of Sublimation (ΔH_s)

The amount of heat absorbed when one mole of a solid sublimates to give vapour at a particular temperature at one atmospheric pressure is called molar heat of sublimation.



5.4.2 Energy Changes and Intermolecular Forces

As a result of melting of a solid, a small change in intermolecular distance and potential energy takes place in atoms, molecules or ions. On the other hand on evaporation of a liquid atoms, molecules or ions undergo large changes in their intermolecular distance and potential energy. Therefore, heat of vaporisation is much greater than that heat of fusion.

Particular examples:

- i. ΔH_v (heat of vapourization) for H_2O ($40.6 \text{ kJ mole}^{-1}$ at 373.15K , for NH_3 ($23.35 \text{ kJ mole}^{-1}$ at 239K) and CO_2 ($25.23 \text{ kJ mole}^{-1}$ at 194.5K) are high due to their polar nature and strong intermolecular forces ΔH_f (Heat of fusion) will be as under:

$$\text{H}_2\text{O} = 6.02 \text{ kJ mole}^{-1} \text{ at } 273.15\text{K}$$

$$\text{NH}_3 = 6.652 \text{ kJ mole}^{-1} \text{ at } 195.4\text{K}$$

$$\text{CO}_2 = 8.33 \text{ kJ mole}^{-1} \text{ at } 217.0\text{K}$$

- ii. I_2 , a volatile solid has the highest value of Heat of sublimation i.e $62.42 \text{ kJ mole}^{-1}$ at 458.4K . The values for other halogens are

$$\Delta H_v \text{ for } \text{Br}_2 = 29.4 \text{ kJ mole}^{-1} \text{ at } 332.4\text{K}$$

$$\text{for } \text{Cl}_2 = 20.21 \text{ kJ mole}^{-1} \text{ at } 239.1\text{K}$$

$$\text{for } \text{F}_2 = 3.16 \text{ kJ mole}^{-1} \text{ at } 85.0\text{K}$$

This shows that ΔH_v (heat of vapourization) of I_2 is the highest because of strong intermolecular forces than the other halogens.



5.4.2 Dynamic Equilibrium in Solids, Liquids and Gases

Dynamic equilibrium is a reversible process where the two opposite changes occurring simultaneously at equal rates. For example solid to liquid or liquid to gas and vice versa. The system moves towards the condition of dynamic equilibrium.

example At 0 °C, ice exists in dynamic equilibrium with liquid water.



5.4.3 Liquid Crystals and their Applications

In 1888 an Austrian Botanist, Frederick Reintizer discovered that when crystals of cholesteryl benzoate are heated, it forms a milky liquid at 145°C. On further heating, the milky liquid suddenly becomes clear. When the clear liquid is cooled, the reverse process occurs. The milky or turbid liquid is called liquid crystal. The liquid crystal state exists between two temperature i.e. melting temperature and clear temperature. It is a form of matter intermediate in characteristics between a liquid and solid crystal. They have properties of liquids and show viscosity, surface tension etc.

Definition

- (i) The substance which can flow like a liquid and also have some of the properties of liquids within a certain temperature range are called liquid crystals.
- (ii) The intermediate phase lying between the solid phase and the normal liquid phase is called liquid crystal.

Uses in daily life

- i. Liquid crystals are used as temperature sensors. This is because the liquid crystals change their colour with change in temperature.
- ii. They are used to monitor temperature changes where conventional methods are not feasible, e.g. they are used in thermometer for measuring skin temperature of infants.
- iii. Some of the modern room thermometers contain liquid crystals with a suitable temperature range. As temperature changes, the liquid crystal show up the figure in different colours.
- iv. They are used to find the point of potential failure in micro-electronic circuits.
- v. They are used to locate the veins, arteries and tumours, e.g. when a layer of liquid crystal is painted on the surface of the breast, a tumour shows up as a hot area which is coloured blue. Thus this technique helps in early diagnosis of breast tumours.
- vi. Liquid crystals are used in the display of numbers and letters of electrical devices such as digital watches, calculators and computers etc.
- vii. Liquid crystals are used in LCD screens of oscillographs and TV.



Science Titbits

The mucous secreted by slugs and snails behaves like liquid crystals. Its rod-shaped molecular arrangements align in varying degrees to control the viscosity of the mucous to adapt to different ground conditions.



1. A liquid crystal is a state of matter which is in between pure liquid (transparent) and crystalline solid.

- A liquid crystal is a state of matter which is in between pure liquid (transparent) and crystalline solid.
i.e. crystalline solid $\rightleftharpoons$ liquid crystals $\rightleftharpoons$ pure liquid
- A liquid crystal resembles the crystalline solid in certain respects, e.g. optical properties. However pure liquids remain as such.
- A crystalline solid may be isotropic (A substance showing same properties in all directions) and an anisotropic (A substance showing different properties in different direction) but liquid crystals are always isotropic. Pure liquids remain as such.
- Liquid crystal is intermediate in between pure liquid and crystalline phase.

References for additional information

- Holderness & Lambert, A New Certificate Chemistry.
- John Olmsted III and Gregory M. Williams, Chemistry, The Molecular Science.
- Osei Yaw Ababio, New School Chemistry.
- George M. Bodner and Harry L. Pardue, Chemistry, an experimental Science.



1. Choose the correct answer (MCQs).

1 Choose the correct answer (MCQs).

- Van Der Waal's forces are effective;
 - (a) At long distance
 - (b) Both at long as well as short distance
 - (c) Only at short distance
 - (d) Independent of distance
- Which one of the following forces are also called London forces?
 - (a) Ion-dipole forces
 - (b) Dipole-induced dipole forces
 - (c) Dipole-dipole forces
 - (d) Dispersion forces
- Which of the following two halogens are gases at room temperature?
 - (a) Fluorine and Iodine
 - (b) Chlorine and Bromine
 - (c) Fluorine and Chlorine
 - (d) Iodine and Bromine
- The intermolecular forces are of;
 - (a) Two types
 - (b) Three types
 - (c) Four types
 - (d) Five types
- Thermostat is an instrument which;
 - (a) Increases the temperature
 - (b) Decreases the temperature
 - (c) Maintains the temperature
 - (d) Fluctuate the temperature



- vi. The scientist who discussed the phenomenon of viscosity are;
(a) Poiseuille (b) Newton
(c) Fritz (d) Vander Wall
- vii. The distillation under reduced pressure is called;
(a) Fractional distillation (b) Vacuum distillation
(c) Steam distillation (d) Pressure distillation
- viii. The unit of surface tension is;
(a) Newton per metre (b) Newton per metre square
(c) 760mmHg (d) Newton square per metre
- ix. The intermediate phase lying between the solid phase and the normal liquid phase is called;
(a) Crystalline solid (b) liquid crystals
(c) Mesogens (d) Crystal lattice
- x. In which of the following are the particles the most disordered?
(a) Water at 100 °C (b) Steam at 100 °C
(c) Impure water at 102 °C (d) Water at 10 °C
- xi. Which of these statement best supports the idea that matter is made up of particles?
(a) Liquids always fill the space available to them
(b) Liquids are easily compressible
(c) 1 cm³ of water produces nearly 1700 cm³ of steam
(d) If a bottle of perfume is opened, the smell spread quickly
- xii. Which of these processes involve a weakening of the attraction between particles?
(a) Condensation (b) Freezing
(c) Crystallization (d) Evaporation
- xiii. A liquid is thought to be pure ethanoic acid (acetic acid), which of the following is the best way to test its purity?
(a) Measure its B.P
(b) React it with ethanol
(c) Burn it completely in oxygen
(d) Dehydrate it with concentrated H₂SO₄

2: Write brief answer to the following.

- i. Give the general properties of liquids as to
(a) Diffusion (b) Compression
- ii. What are the types of intermolecular forces, give examples?
- iii. What is hydrogen bonding, give particular examples?
- iv. What are the applications of H-bonding?
- v. What are the different types of physical properties of liquids?

- vi. Define vapour pressure. What are the factors affecting the V.P?
 - vii. What is
 - (a) Viscosity.
 - (b) Surface tension.
 - viii. Define molar heat of fusion and molar heat of vaporization.
 - ix. How will you differentiate liquid crystals from pure liquids?
 - x. Why distillation under reduced pressure is often used in the purification of chemicals?
- 3 (a) Give the simple properties of liquids with special reference to the following:
- Diffusion
 - Compression
 - Expansion
 - Inter molecular forces
 - Kinetic energy
- (b) Explain on the basis of kinetic molecular theory. Why the boiling point of a liquid remains constant although heat is continuously supplied to the liquid?
- 4 (a) Define and explain evaporation.
- (b) What are the factors affecting evaporation?
- (c) Different liquids have different rates of evaporation. Explain with reference to ether and alcohol?
- 5 (a) Define and explain vapour pressure. How equilibrium is established between evaporation and condensation?
- (b) What are the factors affecting vapour pressure of a liquid?
- (c) Kinetically how will you explain the effect of temperature on vapour pressure?
- 6 (a) Define and explain boiling point of a liquid?
- (b) How will you explain the effect of pressure on the boiling point of a liquid?
- (c) Practically how will you explain the
- (i) Effect of increase of pressure on boiling point.
 - (ii) Effect of decrease of pressure on boiling point.
- 7 (a) Define and explain the term viscosity of a liquid? How does the resistance to the layers causes viscosity?
- (b) What are the factors affecting the viscosity of a liquid?
- (c) Use the concept of hydrogen bonding to explain the following properties of water?
- (i) High surface tension
 - (ii) High heat of vaporization
 - (iii) High boiling point



- 8
 - (a) Define and explain the phenomenon of surface tension?
 - (b) What are the factors affecting surface tension?
 - (c) Define dynamic equilibrium between two physical states?
 - (d) Define?
 - (i) Molar heat of fusion
 - (ii) Molar heat of vapourization
- 9
 - (a) Define a liquid crystal?
 - (b) What are the uses of liquid crystals in daily life?
 - (c) How will you differentiate liquid crystals from pure liquids and crystalline solids?
- 10 What are the energetics of phase changes?
- 11
 - (a) Define and explain the boiling point of a liquid?
 - (b) How will you explain the two practical applications regarding the effect of pressure on the boiling point of a liquid?
- 12 How can you interpret the anomalous behaviour of water?