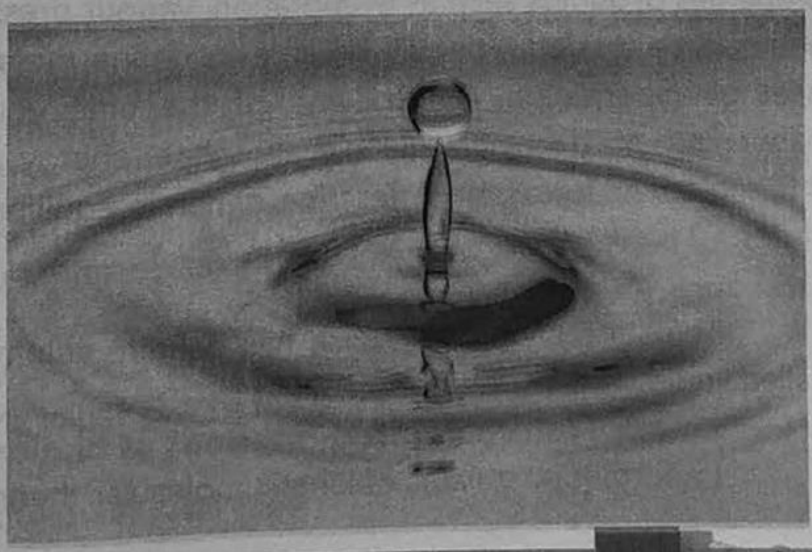
Unit - 05

States of Matter II: Liquids

After studying this unit, the students will be able to:

- 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. (Understanding)
- Explain applications of dipole – dipole forces, hydrogen bonding and London forces. (Applying)
- Explain physical properties of liquids such as evaporation, vapour pressure, boiling point, viscosity and surface tension. (Understanding)
- 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. Anomalous behaviour of water when its density shows maximum at 4 degree centigrade. (Applying)
- Define molar heat of fusion and molar heat of vaporization. (Remembering)
- Describe how heat of fusion and heat of vaporization affect the particles that make up matter. (Understanding)
- Relate energy changes with changes in intermolecular forces. (Applying)
- Define dynamic equilibrium between two physical states. (Remembering)
- Describe liquid crystals and give their uses in daily life. (Applying)
- Differentiate liquid crystals from pure liquids and crystalline solids. (Applying)

Teaching	09
Assessment	01
Weightage %	11



Introduction

It is well known that there is a complete absence of order in gases, a complete regularity in the structure of perfectly crystalline solids, while some of the properties of the liquids resemble those of the gases at one extreme and solids at the other.

Both gases and liquids are fluids and offer no resistance to deformation. They adopt the shape of the container. The similarities in density and compressibility of the liquids and solids suggest some sort of resemblance in arrangement of the molecules in the liquid and the solid states of the matter near the melting point.

The cohesion in a liquid may be due to ionic forces in molten electrolytes, metallic forces in molten metal's, hydrogen bonding in water or Van der Waal's forces in organic liquids and in some cases more than one of these forces may operate.

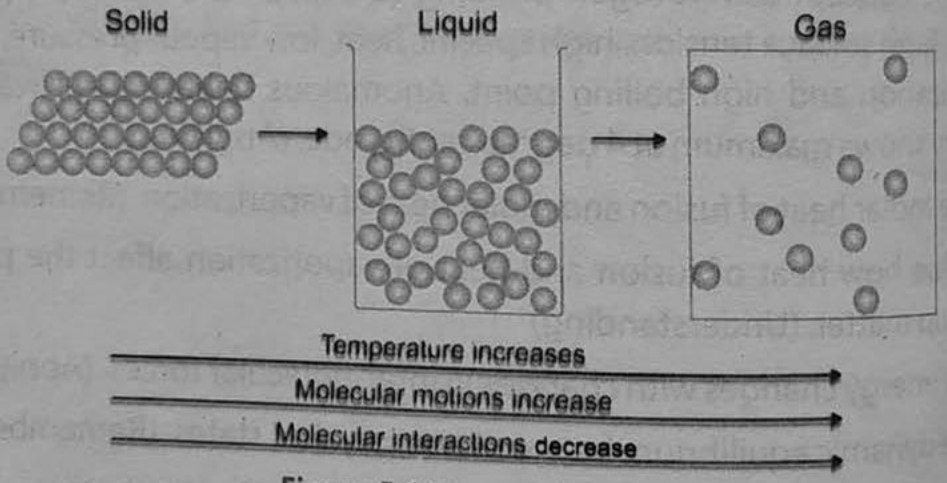


Figure 5.1 States of Matter

In this unit, you will study the intermolecular forces, the physical properties of liquids such as evaporation, vapour pressure, boiling point, viscosity and surface tension. You will be able to define molar heat of fusion and molar heat of vaporization. By the end of the unit, you will understand what is happening at the molecular level; relate energy changes with changes in intermolecular forces, and describe dynamic equilibrium between two physical states.

Liquid

The state of matter, which has definite volume but no definite shape is called liquid.

5.1 Kinetic molecular interpretations of liquids

Important postulates of kinetic molecular theory are,

1. The liquid molecules have kinetic energy greater than solids and lesser than gas molecules at a given temperature.
2. The intermolecular forces of liquids are stronger than in gases and weaker than in solids.
3. The molecules are close to each other. Empty spaces are negligible. Thus, liquids have definite volume and are very difficult to compress.
4. The molecules are in constant motion by sliding over each other. Thus,liquids have no definite shape and so a liquid can flow, can be poured and assume the shape of the container.

5.1.1 Simple properties of liquids

Some simple properties of liquids can be explained on the basis of kinetic molecular theory.

i. Diffusion

According to kinetic molecular theory, the molecules of liquid are in constant random motion. So, they move from one place to another due to kinetic energy that is why the liquid molecules diffuse and form a homogenous mixture. However, this diffusion takes place very slowly, due to intermolecular attractive forces among liquid molecules and small empty space among the molecules.

ii. Compression (Effect of Pressure on Liquids)

As in Liquids, there is very little empty space among their molecules, so they cannot be compressed significantly by increasing pressure.

iii. Expansion (Effect of Temperature)

Liquids do not have a definite shape. They take the shape of the container. Thus, a liquid can be specified by its volume. Hence, we can speak of volume expansion for liquids, as expansion of liquids is greater than that of solids. Liquids have ability to expand at all temperatures.

When a liquid is heated in a container, heat flows through the container to the liquid, which means that the container expands first, due to which the level of the liquid falls. When the liquid gets heated, it expands more and beyond its original level. We cannot observe the intermediate state. We can only observe the initial and the final levels. This observed expansion of the liquid is known as the apparent expansion of the liquid. If we consider the expansion of the container also and measure the total expansion in volume of the liquid, then the expansion is termed as the absolute expansion of the liquid.

iv. Motion of molecules

The molecules of liquids have intermolecular attractive force. Because of

these intermolecular attractive forces, they have less kinetic energy. However, th kinetic energy of these liquid molecules increases with increase in temperature.

v. Kinetic Energy Based on Kinetic Molecular Theory

According to kinetic molecular theory, the molecules of the liquids are in constant random motion. However, they have less free movement as compared to gas molecules, due to strong intermolecular forces. This less movement of molecules results minimum collisions.

Liquids have definite volume but no definite shape because intermolecular forces are not so strong to stop the molecules from sliding over each other. Thus it takes the shape of its container. A liquid has the ability to flow also that is why it can be poured from one container to another.

Molecular forces

There are two types of molecular forces.

a. Intra-molecular and
b. Intermolecular

a. Intra-molecular Forces

The attractive forces within a molecule of a liquid are called intra-molecular forces. The example of intra-molecular forces are (1). Covalent bond (2). Co-ordinate covalent bond etc.

b. Intermolecular Forces

The attractive forces among the molecules of a substance are called intermolecular forces. The examples of intermolecular forces are hydrogen bonding, dipole – dipole interactions and London dispersion forces. Collectively these three weak forces are named as Van der Waals forces.

Generally, intermolecular forces are much weaker than intra-molecular forces. Very small amount of energy is required to evaporate a liquid than to break the bonds in the molecules of the liquid. For example in equation (5.1), it require 40.7kJ of energy to break the hydrogen bonding and to vaporize 1 mole of water at its boiling point; but in equation (5.2), about 930kJ of energy is required to break the two O – H covalent bonds in 1 mole of water molecules. The intra-molecular forces hold the atoms in H_2O molecules together are 23 times stronger than intermolecular forces between water molecules.

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta H = 40.7kJ/mol \qquad (5.1)$$

$$H_2O_{(g)} \longrightarrow 2H_{(g)} + O_{(g)} \qquad \Delta H = 930kJ/mol \qquad (5.2)$$

5.2 Intermolecular Forces (Van der Waals Forces)

Water (H_2O) and hydrogen sulphide (H_2S) have the same bent molecular shape. Both are polar molecules. However, water (H_2O), with a molar mass of 18g/mol, is a liquid at room temperature, while hydrogen sulphide (H_2S), with a molar mass of 34g/mol is a gas. Water's boiling point is 100°C, while hydrogen sulphide's (H_2S) boiling point is −61°C.

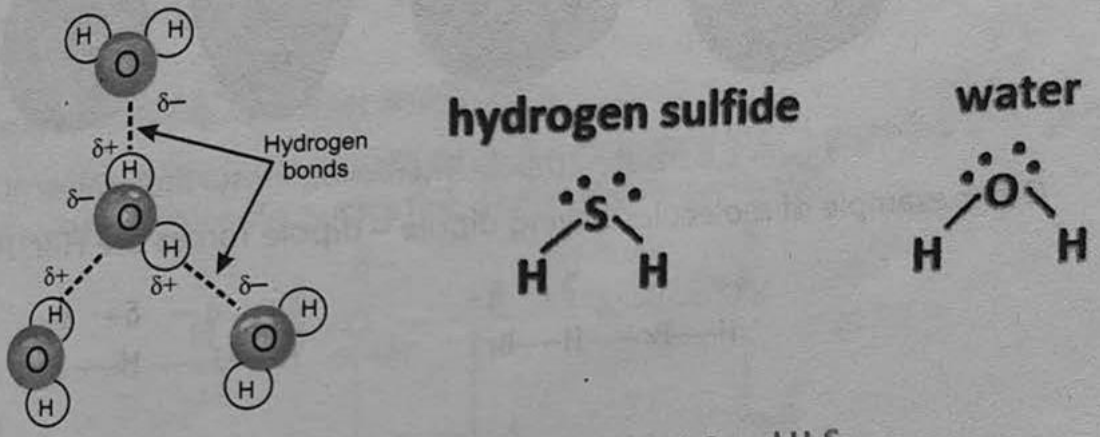


Figure 5.2 Intermolecular forces in H_2O and H_2S

The difference in such properties can be explained on the basis of intermolecular forces.

The intermolecular forces are (1) dipole – dipole interaction, (2) hydrogen bonding and (3) London dispersion forces. These intermolecular forces are called *Van der Waals forces,* after the Dutch physicist Johannes Van der Waals. These three forces follow the following order in strength.

Hydrogen Bonding > Dipole – Dipole Forces > London Dispersion Forces

5.2.1 Dipole – Dipole Interaction

Dipole-dipole forces are attractive forces between polar molecules, that is, between molecules that possess dipole moments.

The attractive forces between the positive pole of one polar molecule and negative pole of other polar molecule are called dipole – dipole forces.

Polar molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule and a separation of charge causes a *dipole.* Therefore, they are also called dipole molecules.

Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom has the partial negative charge, whereas the less electronegative H atom has the partial positive charge. An attractive force between HCl molecules results from the attraction between the

positive end of one HCl molecule and the negative end of another. This attracti force is called a dipole-dipole attraction – the electrostatic force between t partially positive end of one polar molecule and the partially negative end o another, as shown in figure 5.4.

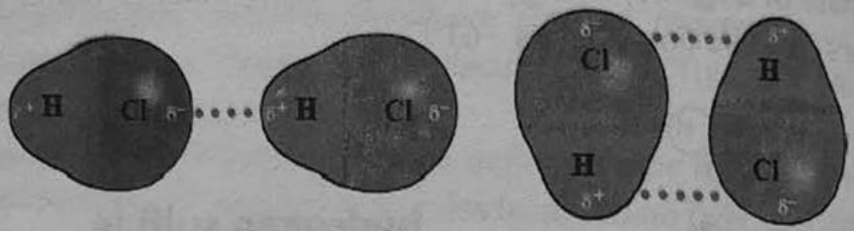


Figure 5.3 Dipole – Dipole Interaction in HCl Molecules

Other example of molecules having dipole – dipole forces are HBr, HI, etc

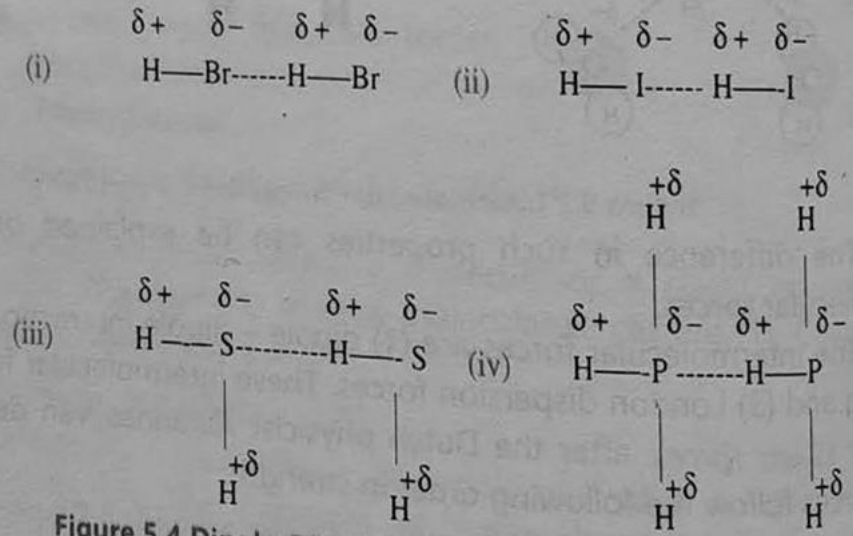


Figure 5.4 Dipole-Dipole Forces in HBr, HI, H_2S and PH_3

As a result of dipole-dipole forces of attraction, polar molecules will attra one another more at room temperature than similar sized non-polar molecule The energy required to separate polar molecules from one another is greater tha non-polar molecules of similar molar mass. Generally, stronger the dipole – dipo forces , greater the values of thermodynamic properties like melting point, boi points, heat of vaporization and heat of sublimation etc.

5.2.2 Hydrogen Bonding

Hydrogen bonding is the strongest type of intermolecular force. It is particularly strong form of dipole-dipole attraction that exists in molecules which hydrogen is bonded to a highly electronegative atom, such as fluorin oxygen or nitrogen. The strong force of attraction by these electronegative ato draws the electron from the hydrogen atom, leaving the hydrogen atom with a

partial positive charge. This dipole is easily attracted to the partially negative and lone pair of electron on a nearby electronegative atom (such as, F, O or N). The intermolecular force acting between these polar molecules is called a *hydrogen bond*, which acts like a very weak bond between polar molecules.

Thus, *the force of attraction between partially positive charged hydrogen atom which is covalently bonded to a small size, high electronegative (F, O, N) and active lone pair of another electronegative atom (F, O, N) is called hydrogen bonding.*

Hydrogen bonding in water molecules

In water, a link is developed between hydrogen of one molecule with oxygen atom of another molecule. Such a link is called hydrogen bond.

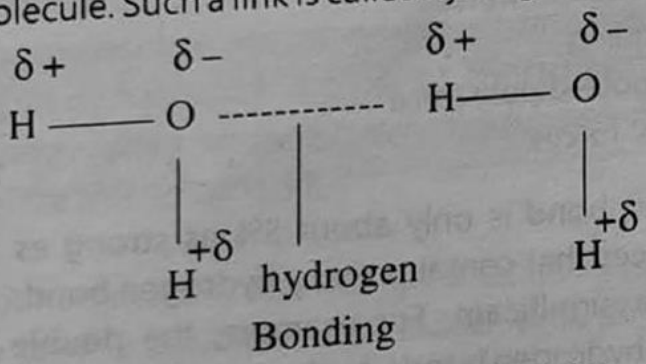


Figure 5.5 Hydrogen Bonding in water

Hydrogen bonding in HF molecules

In HF molecule, there is a hydrogen bond between the hydrogen atom of one molecule and the fluorine atom of another molecule. The hydrogen bond acts as a bridge between two F atoms.

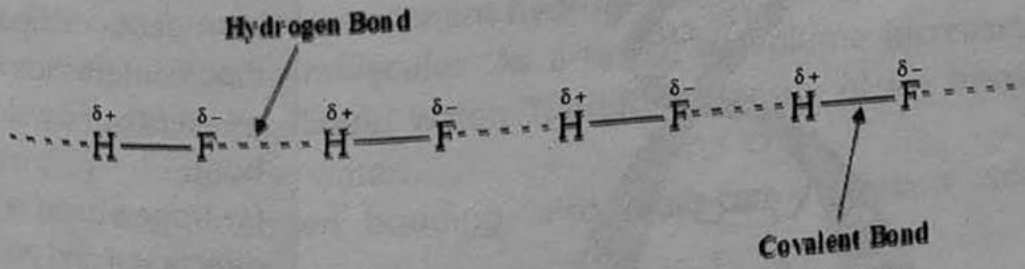


Figure 5.6 Hydrogen Bonding in HF

In the structure above, the dotted line (– – –) shows the hydrogen bond and the solid line shows the covalent bond.

Proof of Hydrogen bonding

The evidence for existence of hydrogen bonding has been derived from the study of boiling points of hydrides. When the molecular mass of hydrides of group IV

elements increases, their boiling points also increase. This is due to increas London dispersion forces (absence of polarity). The boiling point of V, VI and groups elements shows exactly the same trends as VI group elements except hydride of first elements of each group which are abnormally high. This shows th there must be some additional intermolecular forces of attraction, which responsible for high boiling point. This additional intermolecular force is hydrogen bonding.

Table 5.1 Comparison of the relative strength of intermolecular forces and other bon

Type of bond	Bond strength / kJ mol^{-1}
Ionic bonding in sodium chloride	760
OH^- covalent bond in water	464
Hydrogen bonding	20 – 50
Permanent dipole–dipole force	5 – 20
Van der Waals' forces	1 – 20

A hydrogen bond is only about 5% as strong as a single covalent bon However, substances that contains many hydrogen bonds, the impact of hydrog bonding becomes significant. For example, the double-helix structure of DN occurs because of hydrogen bonds, as shown in Figure 5.8.

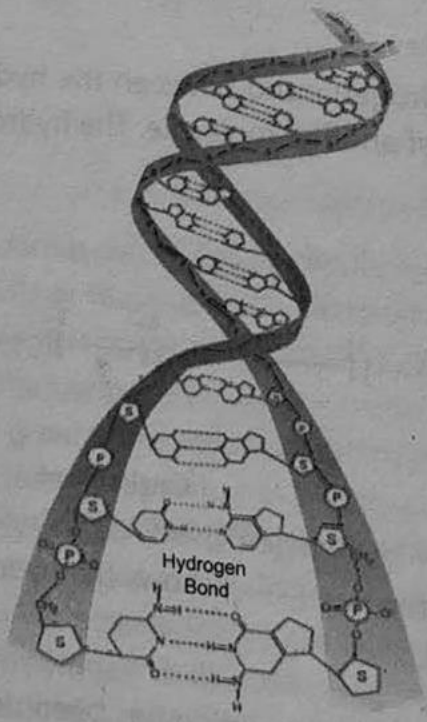


Figure 5.7 Hydrogen Bonding in DNA (deoxyribonucleic acid) molecule

Tidbit

Properties of hydrogen bond

Hydrogen bond is stronger than dipole-dipole interaction but weaker than covalent bond.

Hydrogen bond is directional and results in the formation of long chains and networks of molecules.

Application of Hydrogen Bonding

i. Strength of Acids

H – F is weaker acid than H–Cl, H–Br and H–I because hydrogen atom is entrapped between two highly electronegative atoms in H – F due to hydrogen bonding.

ii. Solubility

Organic substances which can form hydrogen bonds with water molecules, are soluble in water, for example, ethyl alcohol (C_2H_5OH) is miscible with water in all proportions because its molecules can form hydrogen bonds with molecules of water.

iii. In Biological Compounds

Large protein molecules in living organisms are stabilized due to hydrogen bondings. Fibers, hair, muscle proteins consist of long chains of amino acids. These chains are coiled around each other and form a spiral helix. Hydrogen bonds stabilize this spiral helix.

iv. DNA in Cells

DNA (Deoxyribonucleic acid) has two spiral strands which are coiled about a common axis. They form a double – helix ladder type structure. The steps of these ladders are formed by hydrogen bonds.

v. Structure of Ice

In liquid water, molecules form hydrogen bonding with each other. However, due to movement of molecules, bonds are broken and reformed. Hence, there is less regularity and less free space among them. However, when temperature of water is lowered below 4°C, its molecules start to become regularly arranged and form permanent hydrogen bonds. Thus, empty spaces are developed in between the molecules. As a result, its volume increases and ice occupies more space than liquid water. Therefore, density of ice becomes less than water and it floats over water.

Besides this, hydrogen bonding also plays an important role in the following:

- Cleaning action of soaps and detergents.
- Adhesive action of paints and dyes.
- Sticking action of glue and honey.
- Stabilization of large food material such as carbohydrates etc.

5.2.3 London Forces

In noble gases, like helium, neon, argon, etc atoms and molecules are

non-polar and experience a weak intermolecular attraction. In any atom molecule, polar or non-polar, the electrons are in constant motion but motion of electrons of one atom affects the motion of electrons of the ot atom. As a result, at any instant the electron distribution may be slightly uneve The momentary uneven distribution of charge creates a positive pole in one p of the atom or molecule and a negative pole in another. In other words, a no polar molecule becomes slightly polar for an instant. This is called instantaneo dipole.

The formation of this temporary dipole affects the electron distribution a neighbouring molecule. An *instantaneous dipole* that occurs in a molecule ca then *induce* a similar dipole in a neighbouring molecule. This is called induc dipole.

This phenomenon leads to an inter molecule-attraction that is relative weak and short-lived but that can be very significant especially for lar molecules, as shown in figure 5.8. The momentary force of attraction creat between instantaneous dipole and the induced dipole is called dipole - induc dipole interaction or London force.

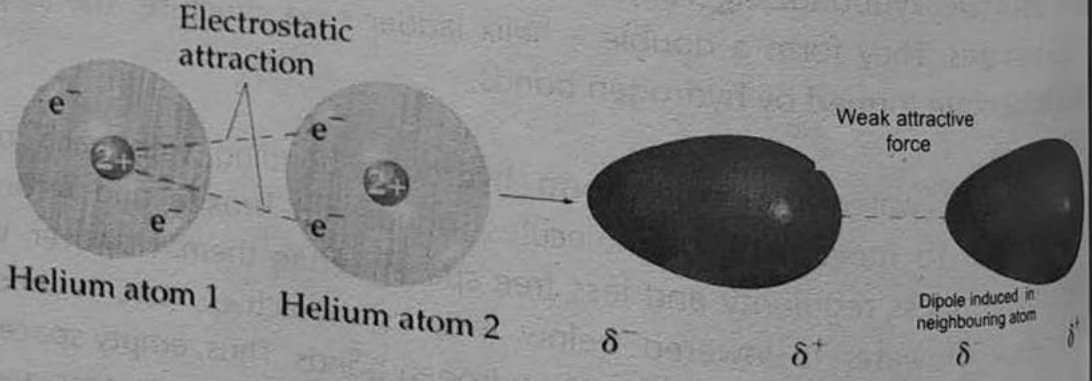


Figure 5.8 London Forces in Helium Atom

The weak intermolecular attractive forces resulting from the const motion of electrons and the creation of instantaneous dipoles are called Lond dispersion forces.

London forces are also known as Dispersion forces. These forces named after German physicist, Fritz London, who studied this force in 19 London forces act between all atoms and molecules. However, they are the o intermolecular forces acting among noble-gas atoms and non-polar molecu like H_2, Cl_2 etc.

London force is weaker than dipole – dipole interactions. The strength London forces are dependent on the,

- The number of electrons, and
- The shape of the molecule

(i) Effect of the number of electrons (size of molecules) on the strength of London dispersion forces

The sizes of atoms increase down a group in the periodic table due to increase in the electrons of valence shells. These create stronger temporary dipoles increasing the strength of London dispersion forces e.g. in group VIIIA, Neon has smaller size than xenon. Thus, neon molecules have weaker London dispersion forces than xenon molecules.

London forces usually increase with molar mass because molecules with larger molar mass tend to have more electrons and dispersion forces increase in strength with the number of electrons. As larger molecular mass often means larger atoms, which are more polarisable (more easily distorted to give instantaneous dipoles because the electrons are farther from the nuclei). The relationship of London forces to molecular mass is only approximate

(ii) Effect of shape of molecules on the strength of London dispersion forces

A molecule with a spherical shape has a smaller surface area than a straight chain molecule with the same number of electrons. The smaller surface area has less opportunity for the molecule to induce a charge on a nearby molecule. Therefore, for two substances that have a similar number of electrons, the substance with molecules that have a more spherical shape will have weaker dispersion forces and has a lower boiling point.

Shape of a molecule may be straight and long chain or branched and short chain. The straight – long chain molecules have greater London dispersion forces than the branched – short chain molecules, even if they have the same number of electrons.

Reading Check

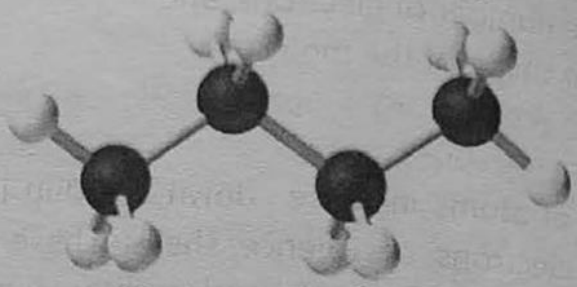
1. Define liquid and kinetically interpret the liquids.
2. What are the different properties of liquids?
3. What is dipole – dipole forces?
4. Explain the application of hydrogen bonding.

Example:

C_4H_{10} is the molecular formula for two compounds with same number of electrons.

(i) **n – Butane**

It is straight and long chain compound and having boiling point of 272.5 K.

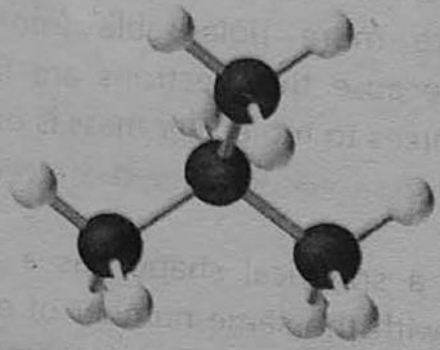


n-Butane, C_4H_{10}

Figure 5.9

ii) 2-Methylpropane

It is branched and short chain compound and having boiling point of 261 which is lower than the straight chain n-butane.



Isobutane (2-methylpropane), C_4H_{10}

Figure 5.10

5.3 Physical Properties of Liquids

Intermolecular forces give rise to a number of physical properties liquids.

1. Evaporation

The spontaneous change of a liquid into its vapours at any temperatu called evaporation.

According to kinetic molecular theory, the molecules of a liquid are alw in motion. The energy is not equally distributed among the molecules. It chang after each collision of a molecule. The molecules with greater kinetic ener move faster and reach to the surface. From the surface of liquid, these molec escape into vapours.

In an open container, at constant temperature evaporation continues the same rate until all the liquid is converted into vapours.

The process of evaporation rate depends on the surface area, temperature strength of intermolecular forces.

2. Vapours pressure

The pressure exerted by the vapours of the liquid when the rate of evaporation becomes equal to rate of condensation.

Consider a liquid in a closed container. The kinetic energy of all the molecules is not the same. The molecules of the liquid whose kinetic energy is greater than the average come to surface of the liquid and convert into the vapours. The vapours gather in the space above the surface of the liquid. Some vapours molecules strike back at the surface of the liquid and becomes liquid again by condensation. As the process of evaporation continues, the rate of condensation also increases. In the beginning, rate of evaporation is greater than rate of condensation, but after sometime both the rates become equal and a dynamic equilibrium is established as shown in the figure 5.11.

Therefore, the vapour pressure can be defined as *the pressure exerted by the vapours in state of equilibrium, at a given temperature.*

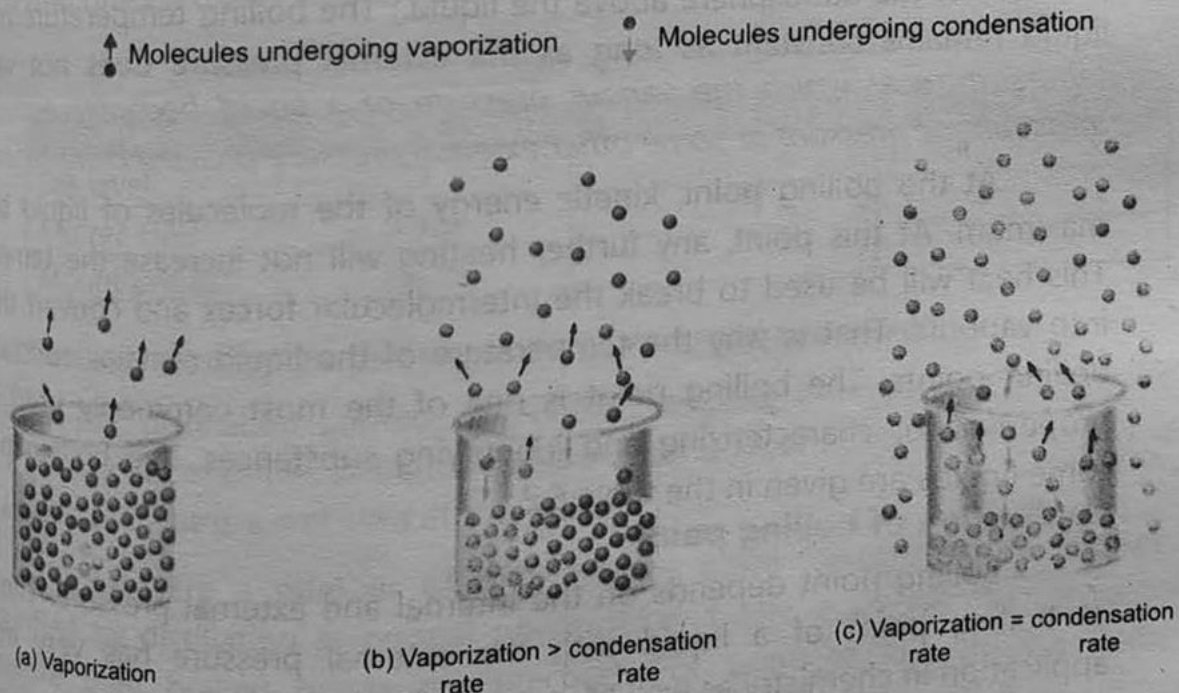


Figure 5.11 Vapour pressure

Tidbit

Barometer is used to measure vapour pressure. Barometer consists of long glass tube. One end of the glass tube is closed, while the other is open. Hold a finger over the open end and invert the tube into a dish of mercury. When the finger is removed, the mercury level falls up to certain height "h". The force of gravity and the atmospheric pressure exerts pressure on the mercury in the

container, air pressure pushing up. Therefore, it does not allow the mercury level fall down and keep it on certain height.

When these two forces balance each other, the mercury in the tube stops falling. The greater the air pressure, the higher the mercury stands in the tube above the level of mercury in the dish.

At sea level at 273.15 K temperature, the atmosphere can hold the mercury at a height of 760 mm Hg or 76cm Hg. It is considered as *one atmospheric pressure.*

3. Boiling point

When the internal or vapour pressure of a liquid becomes equal to external pressure, the liquid boils. (By external pressure, we usually mean pressure of the atmosphere above the liquid.) The boiling temperature of a liquid remains constant as long as the external pressure does not vary. *temperature at which the vapour pressure of a liquid becomes equal to atmospheric pressure or some other external pressure is called boiling point.*

At the boiling point, kinetic energy of the molecules of liquid becomes maximum. At this point, any further heating will not increase the temperature. This heat will be used to break the intermolecular forces and convert the liquid into vapours. That is why the temperature of the liquid remains constant at boiling points. The boiling point is one of the most commonly used physical properties for characterizing and identifying substances. The boiling points of some liquids are given in the table 5.2.

Application of boiling point

Boiling point depends on the internal and external pressure. The change of boiling point of a liquid with the external pressure has very important application in chemistry as well as in our daily life.

Table 5.2 Boiling Points of Some compounds

S. No	Compound	Boiling point (°C)at 760mm Hg
1.	CS_2	46.30
2.	CCl_4	76.50
3.	C_2H_5OH	78.26
4.	C_6H_6	80.15
5.	H_2O	100
6.	CH_3COOH	118.50

a. Pressure Cooker (An Example of Increased Pressure)

Cooking in pressure cooker is based on the fact that increase in external pressure increases the boiling point of a liquid. At higher altitudes, atmospheric pressure is lower than normal (1atm) pressure. Thus, water boils at lower temperature at high altitudes where external pressure is lower. At these places, cooking takes more time. The boiling point of water can be raised in a pressure cooker.

Tidbit

Boling point of a liquid with stronger intermolecular forces will be higher than a liquid with weaker intermolecular forces at the same atmospheric pressure.

Pressure cooker is a closed container, during heating the vapours formed are not allowed to escape from it. Therefore, they develop more pressure in the cooker and boiling point of water increases. As more heat is absorbed in water, therefore, food is cooked quickly under increased pressure.

Table 5.3 Boiling of Point of Water at Different Places

Place	Pressure (atm)	Boiling point on Celsius Scale (°C)
Sea level	1	100
Murree Hills	0.921	98
Mount Everest	0.425	72

b. Vacuum distillation (an example of reduced pressure)

The distillation carried out under reduced pressure is called vacuum distillation. For example, at 1 atm Pressure,water boils at 100°C but if the pressure is reduced to 0.5 atm, water boils at only 82°C.

There are a number of high boiling point liquids, which cannot be purified by distillation at normal pressure i.e. 1 atm, because they decompose before their boiling points are reached. For example, the boiling point of glycerine is 290°C under normal atmospheric pressure. However, it decomposes at this temperature. Hence, glycerine cannot be distilled at 290°C. In order to get pure glycerine, the pressure is reduced; the boiling point of glycerine is reduced to 210°C at 50mm Hg. At reduced pressure, the glycerine is easily purified without breaking.

Thus, vacuum distillation has the following advantages. (a) It decreases the time for distillation, (b) It also avoids the thermal decomposition of many compounds.

4. Surface Tension

Molecules within a liquid are attracted in all directions by intermolecular forces. However, molecules at the surface are attracted downward and sideways by other molecules, but not from above, as shown in the figure 5.12.

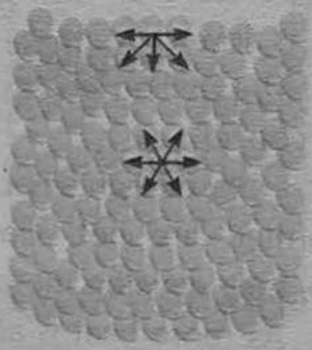
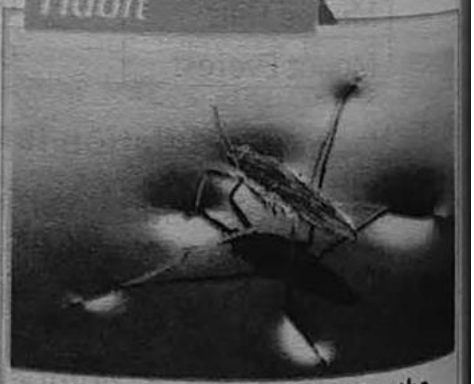


Figure5.12 Intermolecular forces acting on a molecule in the surface layer of a liquid and in the interior region of the liquid.

These intermolecular attractions, thus, tend to attract the molecules towards interior of liquid and cause the surface tightened like an elastic membrane due to net attraction inward, which creates surface tension.

The *surface tension* is *the amount of energy required to stretch or increase the surface of a liquid by a unit area.* It is measured in units of Nm^{-1} or Jm^{-2}. For a molecule to come to the surface, it must overcome the attractions directed towards interior of the liquid, it requires an input of energy and this energy is called liquid surface tension.

Tidbit



Surface tension enables the water strider to "walk" on water.

Surface tension of liquid depends on the intermolecular forces and temperature. Liquids that have strong intermolecular forces have high surface tension. Thus, because of hydrogen bonding, water has greater surface tension than most of other liquids. The surface tension of a liquid decreases with the increase in temperature. Because increase in kinetic energy of the molecules, decreases the effect of intermolecular forces of attraction.

Rain (water) drops have spherical shape due to surface tension. As the sphere has the least surface to volume ratio, which it acquires due to surface

tension, other liquids also show the same tendency.

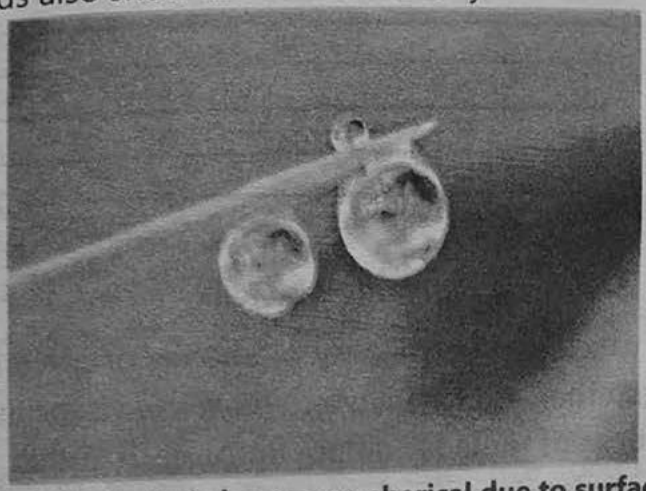


Figure 5.13 Rain (water) drops are spherical due to surface tension

Reduction in surface tension

When detergent is added into water (liquid), it reduces the surface tension of water by breaking up the hydrogen bonding. Detergents are the substances that reduce the intermolecular attractive forces between water molecules. These reductions of intermolecular forces increase the ability of water to wet a solid surface easily, thus, its cleaning action is increased. That is why detergents are used in laundry to wet fabrics easily and remove dirt particles.

5. Viscosity

Liquids have the ability to flow because molecules of the liquids can slide over each other. *The resistance of liquids to its flow is called viscosity.* In other words, viscosity of a liquid is a measure of its internal resistance to flow. Greater the viscosity, the more slowly the liquid will flow and vice versa. The viscosity of a liquid usually decreases as temperature increases; thus, hot honey flows much faster than cold honey.

Liquids that have strong intermolecular forces have higher viscosities than those that have weak intermolecular forces. The viscosity of water is higher than many other liquids because of hydrogen bonding in water molecules.

Consider the flow of the liquid in a tube as series of layers of liquid. The flow of liquid layers nearer to the sides of tube is less than the layers of liquid at the center of tube. The resistance to flow of a liquid is due to internal friction among the layers of molecules. Liquid layer, which flow near the walls of the tube, flow slowly or remains stationary. In the center of tube, the drag force decreases and flow increases as shown in the figure 5.14.

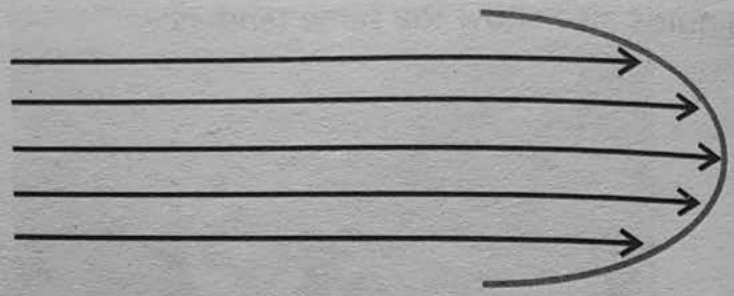


Figure 5.14 Viscosity of a Liquid

Liquids, which flow very slowly like honey or glycerine, have high viscosities as compared to ether and water, which have low viscosities.

Viscosities of liquids differ from each other mainly due to molecular size, shape and intermolecular attractions. Furthermore, shapes of the molecules also contribute to the viscosity of the liquids, regular shape and small molecules flow easily and irregular, large molecules offer more resistance and contribute to its high viscosity.

Reading Check

Define and explain surface tension.

Concept of Hydrogen Bonding to Explain Properties of Water

Many of the physical properties of water can be explained in terms of hydrogen bonding, e.g.

i. High Surface Tension

Surface tension of liquid depends on the intermolecular forces and temperature. In water, there occurs strong hydrogen bonding, so it has greater surface tension than most of other liquids. That is why surface of water acts like stretched membrane. As a result of high surface tension, there is a tendency for the surface area of water to be reduced as much as possible. This explains why falling raindrops (water) are nearly spherical. (The sphere has the smallest surface area for a given volume of any geometrical shape.)

ii. High Specific Heat

The amount of heat required to raise the temperature of one gram of substance by 1°C (or 1 K) is the heat capacity of the substance. Specific heat capacity is usually expressed in units of $J.g^{-1}\,°C^{-1}$.

Water has a relatively high specific heat (about 4.2 $J.g^{-1}\,°C^{-1}$) due to strong hydrogen bonding. It is much higher than metals, as most metals have much lower specific heats (usually less than 1 $J.g^{-1}\,°C^{-1}$). It takes almost ten times as much heat to raise the temperature of 1g of iron by 1°C. On the other hand, large amount of heat is given off by water even a small drop in temperature occurs

The water on the surface of earth acts like giant heat reservoir to moderate daily temperature variations.

iii. Low Vapour Pressure

The hydrogen bonding in water makes it difficult for the water molecules to escape into vapours. Therefore, the rate of conversion of water molecules into vapours is very low, so the vapour pressure of water is low.

iv. High Heat of Vaporization

Heat of vaporization is the heat required to change one gram of liquid to vapour at its boiling point.

High Heat of vaporization is the direct indication of the strong attraction between molecules in water. The strong attractive forces between the liquid molecules are due to hydrogen bonding. The hydrogen bonding in water molecules effectively gives the high heat of vaporization. As water is heated and energy is absorbed, hydrogen bonds are continually being broken until at 100°C, with the absorption of an additional 2.26 kJ/g, water separates into individual molecules, going into the gaseous state.

v. High Boiling Point

In water, there occurs stronger hydrogen bonding, so the vapour pressure of water is low. Water has high boiling point due to hydrogen bonding. Thus, the boiling point of water is 100°C at 1atm (760mm Hg).

It is clear from table 5.4, that boiling point is determined by the strength of hydrogen bonding. For example, methane (CH_4) and diethyl ether ($C_2H_5OC_2H_5$), has low boiling points due to weak intermolecular forces.

Both ethanol (C_2H_5OH) and water have strong hydrogen bonding, which accounts for their high boiling points.

Table 5.4 Boling Points of Some Compounds

Compounds	Boling point (°C) at 1 atm
Diethyl ether ($C_2H_5OC_2H_5$)	34.6
Ethyl Alcohol (C_2H_5OH)	78.3
Methane (CH_4)	-164
Water(H_2O)	100

vi. Anomalous Behaviour of Water

The maximum density of water is 1.000 g/cm^3 at 4°C. Water has the unusual property of contracting in volume as it is cooled to 4°C and then expanding when cooled from 4°C to 0°C. Therefore, 1 g of water occupies a volume greater than 1 cm^3 at all temperatures except 4°C. Although, most liquids

contract in volume when temperature is decreased. However, a large increase (about 9%) in volume occurs when water changes from a liquid at 4°C to a solid (ice) at 0°C. The density of ice at 0°C is 0.917 g/ cm^3, which means that ice, being less dense than water, will float on the surface of water.

Self-Assessment

1. What are the different properties of liquids?
2. Explain the application of hydrogen bonding.
3. Use the concept of hydrogen bonding to explain the high surface tension,
4. high specific heat.
5. What is anomalous behaviour of water?

5.3 Energetics of Phase Changes

During physical and chemical changes, energy is evolved or absorbed; the change in energy at constant pressure, in a physical or chemical process is called enthalpy change. It is denoted as ΔH. It is expressed in kJ mol^{-1}. Three types of enthalpy changes are associated with physical changes at one atmospheric pressure.

The state of matter is often referred to as a *phase*. An ice cube floating in water makes up two phases of water, the solid phase (ice) and the liquid phase (water).

Any process of changing state (or phase) for a sample of matter is called a phase change. Phase changes, transformations from one phase to another, occur when energy (usually in the form of heat) is added or removed. When a solid changes to a liquid as a result of heating, the process is called melting or fusion. The process of changing a liquid to a gas is called evaporation or vaporization. A gas in contact with its liquid is often called a vapour state. Changing a solid directly into a gas is called sublimation. Changing a liquid to a solid is called freezing and changing a gas to a liquid is called condensation and to solid state directly is called deposition. These states and changes are summarized in figure 5.15.

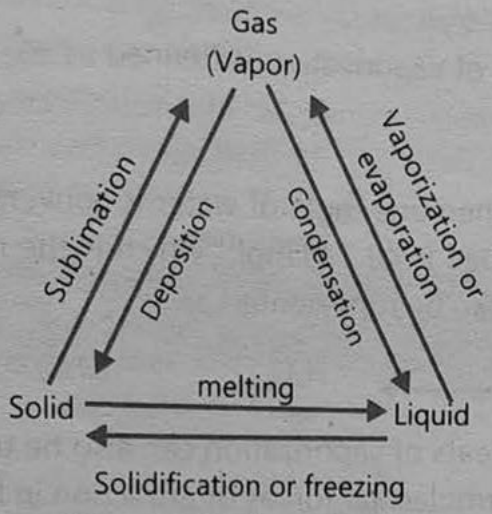


Figure 5.15 Phase Changes

As the temperature of the liquid increases, the particles move about more vigorously. The increased motion allows some particles to escape into the gas phase. As a result, the amount of vapours above the liquid surface increases with temperature. These gas-phase particles exert a pressure called vapour pressure. The vapour pressure increases with increasing temperature until it equals the external pressure or atmospheric pressure. At this point the liquid starts boiling and bubbles are formed within the liquid. The energy required to make the change of a given quantity of the liquid to the vapour state is called the heat of vaporization, ΔH_{vap}. For water, the heat of vaporization is 40.7 $kJ.mol^{-1}$.

$$H_2O_{(\ell)} \longrightarrow H_2O_{(g)} \qquad \Delta H_{vap} = 40.7 kJ.mol^{-1}$$

5.3.1 Molar Heat of Fusion, Molar Heat of Vaporization, Molar Heat of Sublimation

i. Molar Heat of Fusion (ΔH_{fus})

It is defined as *the amount of heat absorbed when one mole of a solid substance is converted into the liquid state at its melting point.*

As an example, we can take the melting of 1 mole of ice at its melting point, 0°C or 273 K. The process can be represented as,

$$\underset{\text{Ice}}{H_2O_{(s)}} \longrightarrow \underset{\text{Water}}{H_2O_{(\ell)}} \qquad \Delta H_{fus} = +\ 6.02 kJ.mol^{-1}$$

It is accompanied by the absorption of 6.02 $kJ.mol^{-1}$ of heat. From the values of heat of fusion of various substances, we can compare their magnitudes of intermolecular forces. Greater the heat of fusion of a substance, higher will be the magnitude of intermolecular forces.

ii. Molar Heat of Vaporization (ΔH_{vap})

The molar heat of vaporization is defined as *the amount of heat absorbed when one mole of a liquid is converted into vapour or gaseous state at its boiling point* (ΔH_{vap}).

For example, when one mole of water is converted into steam at 100°C or 373 K, the heat absorbed is 40.7 $kJ.mol^{-1}$, which is the molar heat of vaporization of water. The change can be represented as,

$$\underset{\text{water}}{H_2O_{(\ell)}} \longrightarrow \underset{\text{vapor}}{H_2O_{(g)}} \qquad \Delta H_{vap} = +\ 40.7\ kJ.mol^{-1}$$

The values of heats of vaporization can also be used for the comparison of the magnitude of intermolecular forces of attraction in liquids.

iii. Molar Heat of Sublimation (ΔH_{sub})

Heat of sublimation is defined as *the amount of heat absorbed when one mole of a solid is directly converted into the vapours or gaseous state at a constant value of pressure.*

For example, the heat of sublimation of iodine is 60.2 $kJ.mol^{-1}$. It can be represented as,

$$I_{2(s)} \longrightarrow I_{2(g)} \qquad \Delta H_{sub} = +\ 60.2\ kJ.mol^{-1}$$

The value of molar heats of sublimation can also be used for the comparison of magnitude of intermolecular forces.

5.3.2 Energy Changes and Intermolecular Attractions

When a liquid is heated, its temperature goes on increasing until its boiling point is reached. At boiling point, the temperature becomes constant. Now the heat supplied is used to convert the liquid into vapours by breaking intermolecular forces.

When a solid melts, small change occurs such as intermolecular distance changes and changes in potential energy of atoms, ions or molecules take place. However, when the liquid is converted into vapours (gaseous state), atoms, ions or molecules undergo large changes in their intermolecular distance and potential energy. Therefore, the heat of vaporization is much greater than heat of fusion.

It also depends on the nature of substance. Such as polar molecules have stronger intermolecular forces, thus large energy is required to change their physical state from solid to liquid or liquid to vapours or solid to vapours directly.

Hence, polar substances have higher values of ΔH_{vap}, ΔH_{sub} *e.g.* H_2O, and NH_3 etc, are polar substances and have considerably higher values of ΔH_{vap}. Thus, ΔH_{vap} is actually a measure of the strength of intermolecular forces.

Molar heat of fusion and molar heat of vaporization of some compounds are given below in the table 5.5.

Table 5.5 Molar Heat of Fusion and Molar Heat of Vaporization of Some Compounds

S. No	Substance	Molar heat of fusion $kJ.mol^{-1}$	molar heat of vaporization $kJ.mol^{-1}$
1.	H_2O	6.02	40.7
2.	NH_3	5.65	23.35

It clearly indicates that the values of molar heat of vaporization are higher than the molar heat of fusion. Beside this, the values of molar heat of vaporization of halogens are given below in the table 5.6.

Table 5.6 Molar Heat of Vaporization of Halogens

S. No	Compound	Molar heat of vaporization $kJ.mol^{-1}$
1.	I_2	20.27
2.	Br_2	15.43
3.	Cl_2	10.21
4.	F_2	3.26

It is evident from ΔH_{vap} of iodine, which is highest due to strong intermolecular forces, than the other halogens.

Non-polar molecules have weaker intermolecular forces, thus, their physical state can easily be changed. Hence, non polar substances have lower values of ΔH_{fus}, ΔH_{vap}, ΔH_{sub}.

5.3.3 Change of State and Dynamic Equilibrium

The physical or chemical processes in which both forward and reverse processes can occur are called reversible processes. The state of reversible process at which rate of forward change becomes equal to the rate of backward change is called equilibrium state. Since both changes are occurring simultaneously at equal rate, therefore, this equilibrium is called dynamic equilibrium.

When rates of two opposite changes are equal such as solid to liquid or liquid to solid, we say the system has reached a dynamic equilibrium. For example, at 0°C solid ice exists in dynamic equilibrium with liquid water.

$$\underset{\text{ice}}{H_2O_{(s)}} \overset{0^\circ C}{\rightleftharpoons} \underset{\text{water}}{H_2O_{(l)}}$$

5.4 Liquid Crystals

W. Heintz reported in 1850 that stearin melted from true solid to turbid liquid at 52°C. It changed to an opaque liquid at 58°C and became a clear and true liquid at 62.5°C. It means that stearin from 52.1°C to 62.6°C behaves like a liquid crystal. In 1888, an Austrian botanist Friedrich Reinitzer also reported an organic compound 'Cholesteryl Benzoate' as a liquid crystal substance. He observed that when cholesteryl benzoate was melted, it first became a cloudy liquid at 145°C and then cleared up as its temperature rose to 179 °C. Upon cooling, the liquid turned blue before finally crystallizing. This experiment showed the intermediate properties between those of liquid and solid that liquid crystal possessed.

The semisolid substances, which have properties in between the true solids (crystalline solids) and true liquids (clear liquids), are called liquid crystals.

5.4.1 Brief Description

Liquid crystals are organic materials, which have an additional state of matter between the liquid state and the solid state. When a solid is melted, it is converted to liquid. However, many organic solids do not melt to give the liquid substance directly. They, instead, pass through an intermediate turbid liquid state called the liquid crystal state, before finally converting into clear liquid. Thus, the liquid crystal state is intermediate between the liquid state and the solid state.

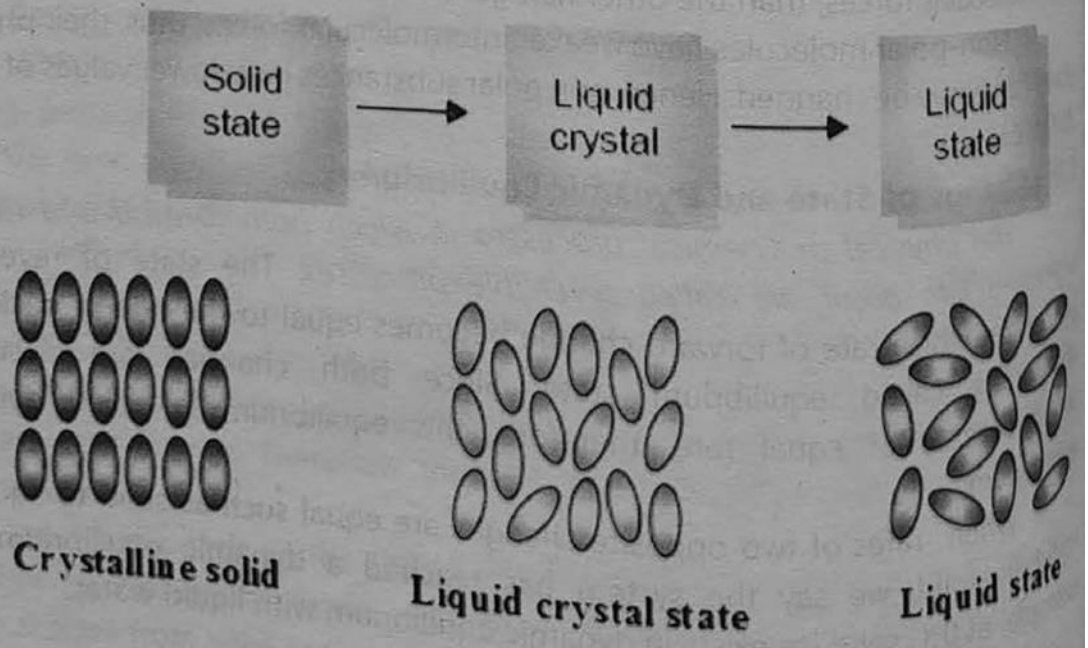


Figure 5.16 Liquid crystals

These are either semi-solids or turbid liquids. They show the optical properties like crystalline solids and surface tension or viscosity like liquids.

In a liquid, the molecules have a random arrangement and they are able to move. In a solid crystal, the molecules have an ordered arrangement and are in fixed positions. In liquid crystals, however, molecules are arranged parallel to each other and can flow like a liquid. Thus, the liquid crystals have the fluidity of liquid and optical properties of solid crystals.

Science, Technology and Society

Liquid crystals are used in a number of objects including liquid crystal display (LCD). A liquid crystal display is a flat panel display. Liquid crystal displays have replaced the old-fashioned heavy, bulky cathode ray tube (CRT) displays in nearly all appliances. Today LCD screens are available in a wider range of screen sizes than CRT. LCD screens are available in sizes ranging from small digital wrist watches to very large television displays.

Today liquid crystals objects are used in wide applications, including televisions, computer monitors, wrist watches, calculators, instrument panels, aircraft cockpit displays, thermometers. It is used in a number of medical instruments which are used for diagnoses of patients such as ultrasound, endoscopy etc. It is also used for indoor and outdoor signage.

Properties of Liquid Crystals

Some properties of liquid crystals are,

i. They have some degree of order like crystalline solids.
ii. They have fluidity like liquids.
iii. They have properties such as surface tension, viscosity etc like liquids.
iv. They have optical properties like crystalline solids.

5.4.2 Uses from Daily Life

Earlier the liquid crystals were limited to laboratories but in modern days liquid crystals have many useful practical applications in daily life. Liquid crystals are temperature sensors and have many other useful applications, so they are used:

1. In medical instruments such as clinical thermometers.
2. To find the point of potential failure in electrical circuits.

Figure 5.17Clinical Thermometer

3. To find the blockage in veins and arties by skin –thermography.
4. For display in calculators, digital watches, computers, cell phones, stop watches, room thermometers, etc.
5. For screen (LCD= liquid crystal display) in TV and Oscilloscope. (Oscilloscope: an instrument for indicating and recording time-varying electrical quantities, such as current and voltage).
6. As a solvent in liquid-solid chromatography.

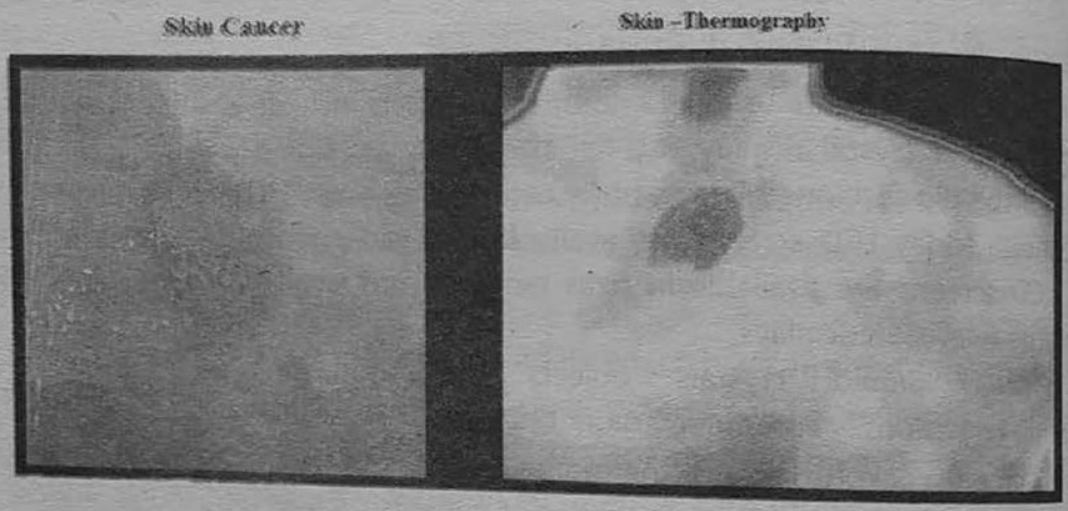
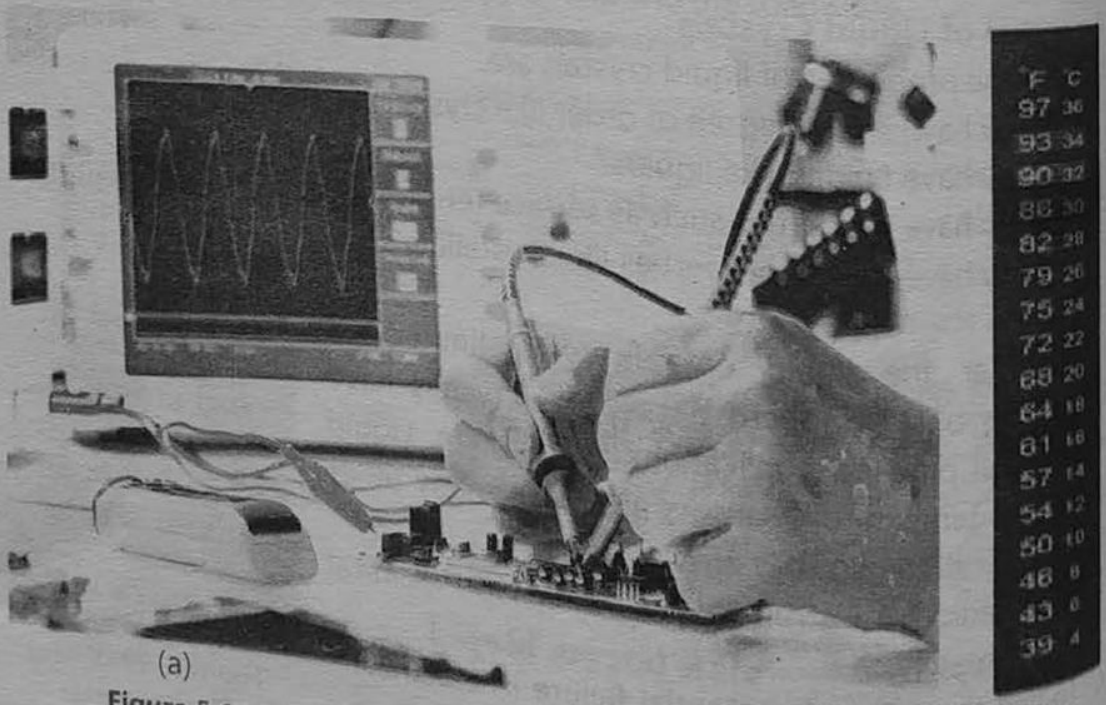


Figure 5.18 Skin –Thermography



(a) (b)

Figure 5.19 (a) Oscilloscope (b) LCD Room thermometer without mercury

Self-Assessment

1. Define dynamic equilibrium between two physical states.
2. Define liquid crystals.
3. Differentiate liquid crystals from pure liquids and crystalline solids.
4. What is energetics of phase change?
5. Briefly explain the uses of liquid crystals in daily life.

KEY POINTS

- Liquid has definite volume but no definite shape.
- The attractive forces within a molecule are called intra-molecular forces. These are covalent bond, co-ordinate bond, etc.
- The attractive forces among the molecules are called intermolecular forces. These are hydrogen bond, dipole – dipole interactions and London dispersion forces. Collectively these three weak forces are named as Van der Waals forces.
- Dipole – dipole forces is the attractive forces between the positive pole of one polar molecule and negative pole of other polar molecule.
- Hydrogen bonding is a linkage formed between two molecules in such a way that partially positively charged hydrogen atom of one molecule is attracted to the lone pair of an electronegative atom of the other molecule.
- London forces (also called dispersion forces) are the weak attractive forces between molecules resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion about nuclei.
- Evaporation is the spontaneous change of a liquid into its vapours at any temperature.
- The pressure exerted by the vapours of the liquid when the rate of vaporization becomes equal to rate of condensation is vapour pressure.
- Barometer and manometer are used to measure vapour pressure of a liquid.
- Boiling point is the temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure or some other external pressure.
- Boiling point of a liquid is less at hilly areas like Murree.

- Cooking in pressure cooker is based on the fact that increase in external pressure increases the boiling point of a liquid.
- Vacuum distillation is the distillation that is carried out under reduced pressure.
- The surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area.
- Detergents reduce the surface tension of water by breaking the hydrogen bonding.
- Viscosity is the resistance of liquids to its flow. The S.I unit of viscosity is $kgm^{-1}s^{-1}$ (1poise = $10^{-1}kgm^{-1}s^{-1}$).
- The amount of energy required to raise the temperature of one gram of a substance by 1°C (or 1 K) is the specific heat capacity of the substance.
- Heat of vaporization is the heat required to change a liquid to vapour at its boiling point.
- The states of matter are often referred to as a phases.
- Phase change is any process of changing state (or phase) for a sample of matter.
- The amount of heat absorbed when one mole of a solid substance is converted into the liquid state at its melting point is molar heat of fusion.
- Sublimation is a process when a solid changes directly into gaseous state without changing into liquid state.
- Liquid crystals are the semisolid substances, which have properties in between the true solids (crystalline solids) and true liquids (clear liquids).

EXERCISE

Choose the Correct Option.

1. Forces of attraction which may be present between atoms of molecules are
   a. Intramolecular
   b. Intermolecular
   c. Van der Waal
   d. Dipole-induced dipole
2. When water freezes at 0°C its density decreases due to
   a. Change of bond angles
   b. Decrease in volume
   c. Empty space present in the structure of ice
   d. Change of bond length
3. London dispersion forces are only forces present among which of the following?
   a. Polar molecules of water at room temperature
   b. Molecules of HF at room temperature
   c. Molecules of solid iodine at room temperature
   d. Molecules of hydrogen chloride gas at room temperature
4. Molar heat of vaporization of water is
   a. 40.7 kJ/mole b. 40.7 J/mole c. 40.7 cal/mole d. 40.7 kcal/mole
5. The S. I unit of viscosity is
   a. $kgm^{-1}s$ b. $kgm.s^{-1}$ c. kgm.s d. $kg\,m^{-1}s^{-1}$
6. Liquid gets the shape of the container when it is poured into it. Which one of the following reasons justifies it?
   a. Liquid is incompressible
   b. Liquid does not has definite volume
   c. Liquid is highly compressible
   d. Liquid molecules can slide over each other
7. Hydrogen bonding is not involved in
   a. DNA structure
   b. The liquid properties of water
   c. Liquid HF
   d. Liquid CH_4
8. Which one is incorrect for evaporation
   a. Surface phenomenon
   b. Continuous process
   c. Exothermic process
   d. Causes cooling
9. Exceptionally low acidic strength of HF is due to
   a. strong polar bond
   b. small size of fluorine
   c. strong hydrogen bonding
   d. Van der Waals forces

10. Distillation under very reduced pressure is
    a. Vacuum distillation
    b. Steam distillation
    c. Destructive Distillation
    d. Fractional distillation
11. Which one of the following is more temperature sensitive
    a. Ionic crystals
    b. Solid crystals
    c. Liquid crystals
    d. Molecular crystals
12. Which of the following has weakest London dispersion forces
    a. F_2 b. Cl_2 c. Br_2 d. I_2
13. What is the boiling point of water at a mountain,
    a. It is 100°C
    b. It is < 100°C, since the atmospheric pressure is greater
    c. It is > 100°C, since the atmospheric pressure is greater
    d. It is < 100°C, since the atmospheric pressure is less.

Short Questions

Give at least two of the effects on our lives if water had weak hydro bonding among its molecules.

2. Give the reason that why HF is a liquid at ordinary temperature while HCl gas.
3. Why H_2O has high boiling point than HF, although fluorine is m electronegative than oxygen.
4. How would you justify that water and ethanol can mix easily in all proportio
5. How can you explain that neon and argon both are mono-atomic no gases of the same group, neon has boiling of -248°C, while argon has -189
6. How would you justify that different liquids have different rates evaporation even at the same temperature.
7. Justify the statement that earthenware vessels keep water cool even in summer days.
8. How vacuum distillation can be used to avoid decomposition of sensiti liquids?
9. Why evaporation of a liquid causes cooling?
10. Explain that why a liquid boils at different temperature at sea level and mountains.
11. Why water droplet is spherical?
12. Temperature of a liquid remains constant during boiling although heat being supplied continuously, why?

Descriptive Questions

1. (a) Briefly explain the properties of liquids (i) Diffusion, (ii) Compression, (iii) Expansion, (iv) Motion of Molecules, (v) Intermolecular Forces on the basis of Kinetic Molecular Theory.
   (b) What is anomalous behaviour of water when its density shows maximum at 4°C?
   (c) Wet clothes dry more quickly on a hot, dry day than on a hot, humid day. Explain.
2. (a) Define and explain these terms along with their units: (i) Molar Heat of Vaporization, (ii) Molar heat of Fusion, (iii) Molar Heat of Sublimation.
   (b) Explain the origin of the London Force that exists between molecules.
3. (a) Define boiling point and how does the boiling point of a liquid dependent on the external atmospheric pressure?
   (b) Briefly explain physical properties of water with special reference to (i) Evaporation (ii) Vapour Pressure (iii) Boiling Point (iv) Viscosity (v) Surface Tension
   (c) Why does the vapour pressure of a liquid depend on the intermolecular forces?
4. (a)What is the relationship between the intermolecular forces that exist in a liquid and its surface tension?
   (b) What do you know about dipole – dipole interactions?
5. (a) Differentiate liquid crystals from pure liquids and crystalline solids? Also give some uses of liquid crystals in daily life.
   (b) Define phase change. Name all possible changes that can occur among the vapour, liquid and solid states of a substance.

Project

- Develop a set of criteria that will allow you to classify the following substances on the basis of intermolecular force i.e. Dipole – dipole forces, Hydrogen bonding and London dispersion forces: Water, Milk, Honey, Methylated Sprit, Glycerine ($C_3H_8O_3$), Carbon Tetrachloride (CCl_4), Acetone (CH_3COCH_3), Chloroform ($CHCl_3$), Benzene (C_6H_6), Kerosene oil, Ammonia (NH_3), Hydrochloric Acid (HCl) and Methane (CH_4). Present it in the classroom and give reason of your criteria of classification based on their molecular structures.
- Classify the above given substances on the basis of more volatile, less volatile and non-volatile at the same temperature based upon intermolecular forces, with suitable reason.