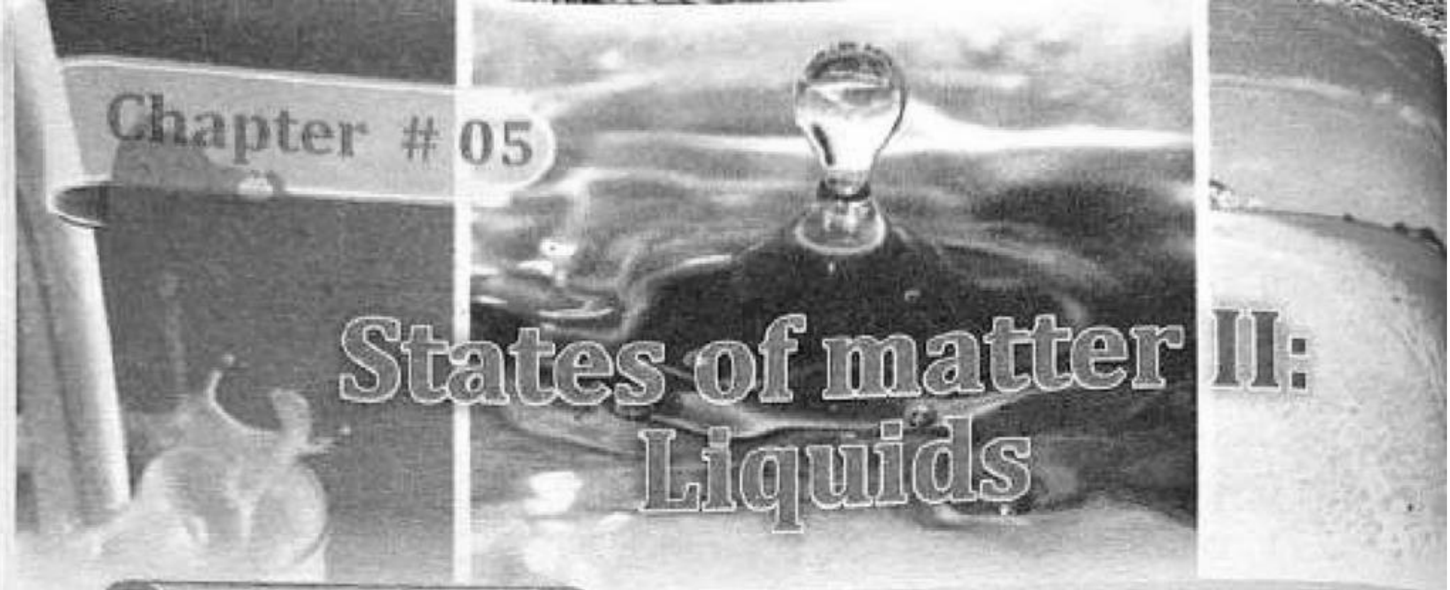


Chapter # 05

States of matter II: Liquids

Major Concepts

5.1 Kinetic Molecular interpretation of Liquids
5.2 Intermolecular forces (Van der Wall's forces)
5.3 Physical properties of Liquids
5.4 Energetics of Phase Changes
5.5 Liquid Crystals

Learning Outcomes

The student 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, vapor 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. And anomalous behavior of water when its density shows maximum at 4°C. (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)

Introduction

Do you know, what is liquid? The water you use for drinking, washing, swimming, and as a solvent, the blood running in the veins and arteries of your body, the milk you use for drinking and making tea, the mercury in thermometer which is used to measure the temperature, the petrol and diesel used as motor fuels, the oils used in engines, gear boxes, in the hydraulic brakes and other hydraulic systems and the vegetable oil used for cooking are all liquids. Out of 118 elements only two elements (bromine and mercury) are liquid at room temperature and normal pressure. There are four more elements which have melting points slightly above room temperature, these elements are, gallium, rubidium, cesium and francium. Liquids have definite volume but they do not have definite shape. In this chapter we focus on the properties of liquids and the forces of attractions that exist between them.

5.1 Kinetic Molecular Interpretation of Liquids

The key points of kinetic molecular theory are given below:

i) Liquids consist of atoms or molecules.

ii) The molecules of liquid are so close together that there is very little empty space. For that reason, liquids are much denser and are much more difficult to compress as compared to gases. The spaces between liquid molecules are greater than solids and smaller than gases.

iii) Liquids do not show an appreciable increase in volume, when they are heated.

iv) The intermolecular forces in liquids are stronger than gases but weaker than solids. Because of this, liquids have lower melting and boiling points than solids and higher melting and boiling points than gases.

v) The liquid molecules have high kinetic energy than solids and low kinetic energy than gases. Their kinetic energy decreases by decreasing temperature and increase by increasing temperature. They are converted into solids by decreasing kinetic energy (on cooling) and are converted into vapours by increasing kinetic energy (on heating).

vi) The liquid molecules are in state of constant motion that are why their molecules slip and slide over one another. That are, therefore, able to flow and are poured in the container. Hence, it has no definite shape and adopts the shape of container in which they are placed.

vii) Liquids diffuse into other liquids with which they are miscible. The diffusion is due to movement of liquid molecules. The diffusion in liquids occur slowly because the molecules of one liquid slowly past the molecules of other liquid.

5.2 Intermolecular Forces (Van der Waal's Forces)

To know the properties of liquid, we have to know the types of attractive forces present in them. There are two types of attractive forces which are associated with a liquid; that is, intramolecular forces and the Intermolecular forces. The forces of attraction exist between atoms within each molecule are called intramolecular forces whereas the forces of attractions exist between molecules of a substance are called intermolecular forces. Intramolecular forces are chemical bonds (discussed in 2[nd] chapter). Physical properties of a substance such as boiling point, vapour pressure, surface tension, viscosity, heat of vaporization, heat of fusion, heat of sublimation etc. depend upon intermolecular forces. The stronger the intermolecular forces in a substance, the more difficult it is to separate molecules. The chemical properties, shapes of molecules and bond energies depend upon intramolecular forces. Intramolecular forces are much stronger than intermolecular forces.

Consider the example of water; it exists in liquid state at room temperature and one atmospheric pressure. Water molecule has two hydrogen atoms and one oxygen atom which are linked through strong covalent bonds. It is important to note that the conversion of liquid into vapours to overcome intermolecular forces needs little energy as compared to decompose the molecules into their component atoms to overcome the covalent bonds. Consider the following conversions:

$$H_2O_{(l)} \xrightarrow{\text{Vaporization}} H_2O_{(g)} \qquad \Delta H = +40.67 kJmol^{-1}$$

$$H_2O_{(g)} \xrightarrow{\text{Decomposition}} 2H_{(g)} + O_{(g)} \qquad \Delta H = +934 kJmol^{-1}$$

From the above conversions, it is noted that 40.67kJ/mol energy is required to vaporize one mole of liquid water and 934kJ/mole energy is required for the dissociation of one mole of gaseous water molecules into hydrogen and oxygen atoms. Now it is clear that the intramolecular forces are stronger than intermolecular forces because the strong attractive forces need much energy to break.

Keep In Mind

The intermolecular forces are broken during the process of evaporation of water molecules whereas the intramolecular forces are broken during the decomposition of water molecules.

Types of Intermolecular Forces

Intermolecular forces as a whole are usually known as Van der Waals forces after the Dutch scientist Johannes Van der Waals (1837-1923) who suggest the importance intermolecular forces and studied the non-ideal behavior of real gases. There are three major types of intermolecular forces; that are,

Dipole-dipole interactions, hydrogen bonding and London forces

5.2.1 Dipole-dipole Interactions

The attractive forces between the positive ends of one molecule with the negative end of other molecule are called dipole-dipole interactions or dipole-dipole forces.

These forces are present in polar molecules of the same or a different type. A polar molecule is sometimes described as dipole. The diatomic molecules which have elements of different electronegativities like HCl, has an unequal distribution of electron density and therefore has partial positive charge at one end and partial negative charge at the other end. In HCl molecule, chlorine is more electronegative than hydrogen atom. Due to this chlorine gains partial negative charge whereas hydrogen gains partial positive charge. When the molecules come close to each other, the positive end of one HCl molecule attracts the negative end of other HCl molecule, called dipole-dipole interaction.

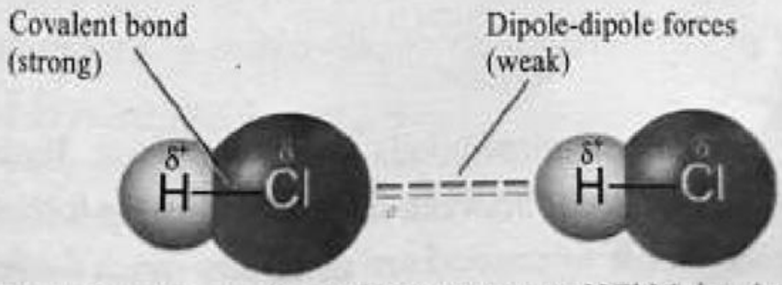


Figure 5.1: Dipole-dipole Forces between HCl Molecules

The repulsions can also occur when negative ends or positive ends of two molecules come close to each other. In liquids, the molecules which are attracting each other spend more time near each other than other molecules that are repelling each other. The overall effect is a net attraction strong enough to keep the molecules of liquid from moving apart to form a gas. Dipole-dipole forces are only about 1-4% percent as strong as a covalent or ionic bonds. These forces are very weak in gases & strong in liquids. The compounds having these forces generally have high melting points, boiling points, heat of vaporization (ΔH_{vap}) and heat of sublimation (ΔH_{sub}). The strength of dipole-dipole forces depends upon the distance between the molecules and electronegativity difference. Greater the electronegativity difference (ΔEN) of two bonded atoms in a molecule, greater will be its polarity. The greater the polarity of a substance, the greater will be the strength of dipole-dipole forces and higher will be the boiling point of the substance. For example, propane and acetaldehyde both have same molar masses ($44 gmol^{-1}$) but different strengths of dipole-dipole forces. The boiling point of polar acetaldehyde (20.85°C) is higher than that of non-polar propane (-42.15°C). This is because polar molecules have stronger intermolecular attractions than non-polar molecules. The electrons in polar molecules can form instantaneous dipoles, so all polar molecules also show London forces.

Intermolecular forces also have an effect on solubility. As you know, like dissolves like, the polar molecules dissolve (mix) in polar solvents and non-polar molecules dissolve in non-polar solvents. The polar molecules are not dissolving in non-polar solvents. Water, for instance, is a polar liquid and can mix with other polar liquids such as ethanol, acetic acid etc. and can't mix with non-polar liquids like gasoline, oil etc. therefore the oily stains on cloth cannot be washed away with water and it can be washed away with gasoline a non-polar solvent.

5.2.2 Hydrogen Bonding

The force of attraction between partial positive hydrogen atom of one molecule and lone pair of highly electronegative atom of another molecule is called hydrogen bonding.

These are not real chemical bonds in formal sense. Hydrogen bonds are intermolecular forces that occur between molecules. These forces are special type of very strong dipole-dipole forces and are generally much weaker than chemical bonds. Hydrogen bond is about five to ten times stronger than other dipole-dipole forces. Hydrogen bond is formed between those two same or different molecules which have the following characteristics:

i) One molecule has a hydrogen atom covalently bonded to a small, highly electronegative atom such as fluorine, oxygen, nitrogen and rarely chlorine.

ii) The other molecule has a small, highly electronegative atom such as fluorine, oxygen, nitrogen and rarely chlorine

For example, the molecules like HF, NH_3 and H_2O, experience hydrogen bonding. In a molecule such as HF, the fluorine atom pulls the electrons away from the hydrogen atom which has no inner electrons, and as a result of this the hydrogen atom acquires a significant positive charge and the nucleus of hydrogen atom is unshielded. This unshielded positive hydrogen is strongly attracted to the lone pair of highly electronegative fluorine atom of a nearby HF molecule. The hydrogen atom is small in size and can approach a highly electronegative atom very closely and thus results in an extra strong dipole-dipole attraction. This unusual strong attraction between polar molecules is called hydrogen bonding. The strength of hydrogen bonds depends upon the polarity of the bond and the distance between the molecules.

The amount of energy needed to break hydrogen bond is 15–40kJmol^{-1} whereas the amount of energy needed to break covalent bonds between hydrogen and oxygen atoms is 150 –1100kJmol^{-1}. Hydrogen bonds are shown by dotted lines (…) and covalent bonds are shown by solid lines (—). Some examples of hydrogen bonds are given in figure 5.2.

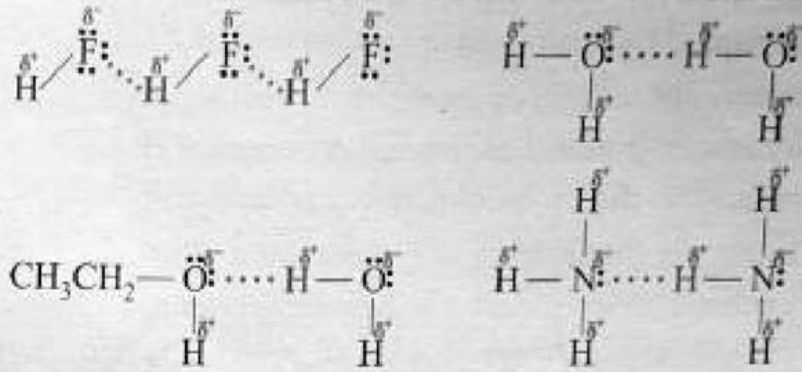


Figure 5.2: Hydrogen Bonding

Hydrogen bonding acts as a bridge between two electronegative atoms. Ience, it is also called bridge bonding. Due to Hydrogen bonding, molecules are oined with each other in a zigzag manner.

pplications of Hydrogen Bonding

Iydrogen bonds play an important role in our life. It helps in explaining the roperties of some substances.

Physical Properties

Iydrogen bonding affects thermodynamic properties like melting point, boiling oint and heat of vaporization of compounds. The molecules that form hydrogen onds have much higher heat of vaporization, melting and boiling points. For xample, the hydrides of group IVA(14) have low boiling points than group VA(15), IA(16) and VIIA(17) hydrides. This is due to lack of hydrogen bonds among drides of less electronegative elements of group IVA.

Table 5.1: The Boiling Points of Group IVA, VA, VIA, and VIIA Hydrides

ydrides Group IVA	Boiling Points (°C)	Hydrides of Group VA	Boiling Points (°C)	Hydrides of Group VIA	Boiling Points (°C)	Hydrides of Group VIIA	Boiling Points (°C)
CH_4	-164	NH_3	-33.3	H_2O	100	HF	19.9
SiH_4	-112	PH_3	-88	H_2S	-60.3	HCl	-85
GeH_4	-88	AsH_3	-55	H_2Se	-41.2	HBr	-67
SnH_4	-52	SbH_3	-17	H_2Te	-2	HI	-36

ii) Hydrogen Bonding and Structure of Ice

Water molecules have tetrahedral structures. Two lone pairs of electrons on oxygen atom occupy two corners of the tetrahedron and other two corners are occupied by hydrogen atoms. In the liquid state, the water molecules experience hydrogen bonds that continually break and reform as the molecules move around and thus, the molecules are associated with each other irregularly. When temperature is decreased, the molecules of water arrange themselves in a regular hexagonal pattern in such a way that empty spaces are created in the structure of ice and expands. Hence, ice occupies 10% more space and its density decreases. The result is that, the ice cubes and icebergs float on water. Hence, ice is an insulator of heat and it prevents the underneath water from freezing.

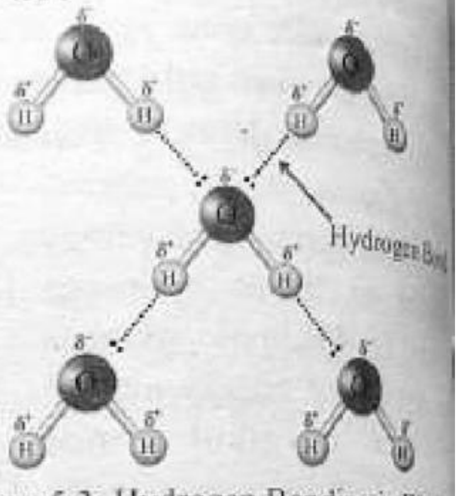


Figure 5.3: Hydrogen Bonding in Water

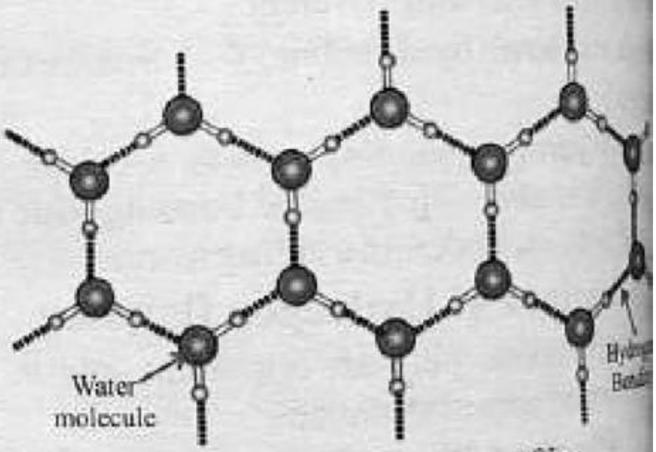


Figure 5.4: Structure of Ice

Therefore, fish and other aquatic life (animals and plants) can survive without being frozen under this layer of ice in the winter season. If ice were a typical solid, it would have high density than liquid water. Then the lakes and oceans would freeze from bottom to top. This would have harmful effects for aquatic life.

The expansion of water upon freezing shows adverse effects too. In cold winter nights, it causes water pipes to burst and cracks the radiators of car. To prevent this we use antifreeze in the radiators of car. In cold weather cities, it breaks up streets and produces potholes in it. The ice formation is also responsible for splitting of rocks where water leaks through cracks of rocks.

iii) Biological Significance

Biological molecules such as proteins and Deoxyribonucleic acid (DNA) play roles in biochemistry. The typical structures of proteins and DNA which required for their functions are due to hydrogen bonding. Proteins are made up of long chain of amino acids. The long chains of amino acids are coiled around each other into a spiral, called helix. Helix may either be right handed or left handed the right handed helix the –NH– groups of one spiral form hydrogen bonds with C=O of other spiral. On the other hand DNA has two spiral chains. These two long molecular chains (strands) of DNA coiled around each other are also held together by hydrogen bonds. Life would be impossible without hydrogen bond.

Interesting information:

Proteins are the major components of skin, hair, and muscle and are essential for the contraction of muscles, digestion of food, and clotting of blood. DNA, present in the cells of organisms, carries genetic information from one generation to other.

(v) Extraordinary High Specific Heat Capacity of Water

The strong hydrogen bonding is responsible for the extraordinary high specific heat of water. Specific heat is the amount of energy required to raise the temperature of one gram of a substance by one degree Celsius. Due to high values of specific heat, the water in swimming pools, lakes and oceans takes time in gaining the energy from the sun in the daytime to become warm. Once it has warmed up, it does not cool down rapidly. Because of this property, water has an enormous effect on weather and moderates the temperature at the surface of earth. If there were no water on the surface of earth, the temperature would shoot up in the daytime and would fall steeply at night because the rocks have much lower specific heat and has the capacity to gain energy in the daytime from the sun and release that energy at night. It is water that absorbs much heat from the sun during the daytime and released this stored heat at night and helps to keep up the temperature of the air of coastal cities such as Karachi and Gwadar.

Table 5.2: Specific Heats of Some Substances

Substance	Specific Heat (J/g°C)	Substance	Specific Heat (J/g°C)
Iron (Fe)	0.45	Wood	1.76
Glass	0.84	Ethanol ($CH_3CH_2OH_{(l)}$)	2.46
Cement (concrete)	0.88	Water ($H_2O_{(l)}$)	4.18

Interesting information:

The air temperatures near large mass of water such as in Karachi are usually lower in the summer and higher in the winter than those areas which are far away from large bodies of water (sea) such as Sibi.

v) Solubility of Hydrogen Bonded Molecules

Compounds which contain hydrogen bonds are soluble in each other. For example ethanol and acetic acid are soluble in water due to presence of hydrogen bonds whereas methane and benzene are insoluble in water due to absence of hydrogen bonding.

vi) Cleaning Action

Cleaning action of detergents and soaps is because of hydrogen bonding. We use soaps and detergents for washing our bodies, clothes, dishes and so on. The one end of soaps and detergents is polar and the other is non-polar. The polar ends form hydrogen bonds with water and are soluble in water. The non-polar end attracts oil and grease that are present at the surface of dishes and cloths.

vii) Hydrogen Bonding in Food Materials

The food materials (carbohydrates) also form hydrogen bond due to presence of OH groups in their structures.

viii) Hydrogen Bonding in Paints and Dyes

The adhesive properties of paints and dyes are because of hydrogen bonding. The stickiness of honey and glycerin is also due to hydrogen bonding.

ix) Surface Tension and Viscosity

Water has high surface tension and viscosity as compared to many other liquids due to presence of hydrogen bonding. This is because the presence of hydrogen bonds make it more difficult for molecules to escape from the liquid state; additional energy is required to overcome the hydrogen bonds.

Conceptual Check Point:

- Which has the higher boiling point, H_2O or H_2S? Why?
- What bonds are broken when water boils?
- Why the boiling point of water is higher than that of hydrogen fluoride and ammonia?

5.2.3 London Forces

The weakest types of intermolecular forces which occur between all atoms and molecules (polar or non-polar) and produced due to temporary dipoles are called London forces. These forces of attraction are also known as London dispersion forces or instantaneous dipole-induced dipole forces.

In 1930, Fritz London a German physicist, recognized these weak forces of attraction between non-polar molecules and for this reason these forces of attraction are known as London forces. He found that the non-polar gases can be liq under the right conditions of pressure and temperature, therefore the non-polar molecules must show intermolecular forces that are different from other intermolecular forces because they originate from motion of electrons in an atom or molecule and produce an instantaneous dipole. These forces are present in halogens, noble gases, and non-polar molecules such as H_2, N_2, CH_4, CO_2, SO_3, SiH_4 and CCl_4 and so on. In the absence of London forces, such substances could not condense to form liquids or solidify to form solids. Condensation of some substances occurs only at very low temperatures and/or high pressures.

Fritz London
(1900-1954)

Let us consider the example of neon to understand how non-polar atoms and molecules attract each other. The distribution of electron density in a non-polar atoms and molecules like neon atom is uniform and symmetrical. When atoms of neon come close to each other, then the electrons of one atom repel the electrons of other atom. In this way, symmetry or equality of electronic cloud is disturbed. Therefore, electronic cloud bends towards one side and nucleus (positive portion) towards other side. This is called instantaneous dipole. This instantaneous dipole disturbs the electronic cloud of the other nearby atom. So a dipole is induced (produced) in second atom. This is called induced dipole. As a result of this, weak attractive forces are generated, called London forces or London dispersion forces. This process occurs with other nearby atoms and, thus, throughout the sample. These forces disappear when the electrons again become symmetrical around nucleus.

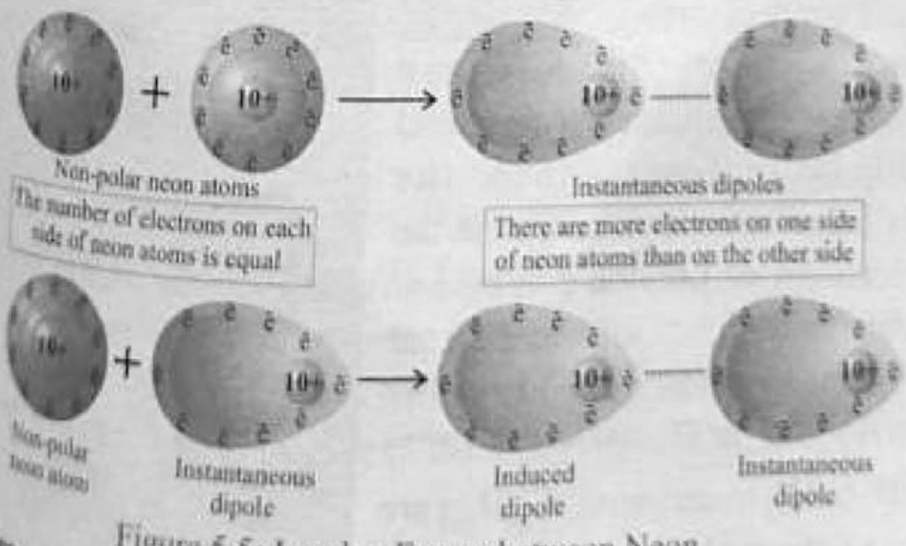


Figure 5.5: London Forces between Neon

…Affecting London Forces

These forces depend upon the following factors:

Atomic or molecular sizes

Shape of molecules

i) Atomic or Molecular Sizes

The strength of London forces depend upon the size of atoms and molecules. The larger atoms and molecules, with greater number of electrons and heavy mass, polarize more easily as compared to small atoms and molecules. We may say that the strength of London forces is directly proportional to the polarizability of the atom or molecule. For example, in VIIA group (Halogens), the fluorine and chlorine are gases, bromine is liquid, and iodine is solid at room temperature and one atmosphere pressure. The big difference in the physical states of halogens indicates that the polarizability of the halogens increases down the group because of which the strength of attractive forces (London forces) increases down the group. The boiling points of both polar and non-polar molecules increase when the sizes and molar masses of molecules increase. For example, the boiling points of halogens and noble gases increase from top to bottom in a group of periodic table due to increase in atomic size and molar masses.

When the molar masses and molecular sizes of alkanes (saturated hydrocarbons) increase, then the polarizability increases which results in the increase of strength of London forces. For example, the first four alkanes (from methane to butane) are gases due to smaller molecular size, the next sixteen alkanes (from pentane, C_5H_{12} to eicosane, $C_{20}H_{42}$) are liquids due to relatively higher molar masses and molecular sizes and the higher alkanes (from heneicosane, $C_{21}H_{44}$ on ward) are solids because of greater molar masses and molecular sizes.

Keep In mind

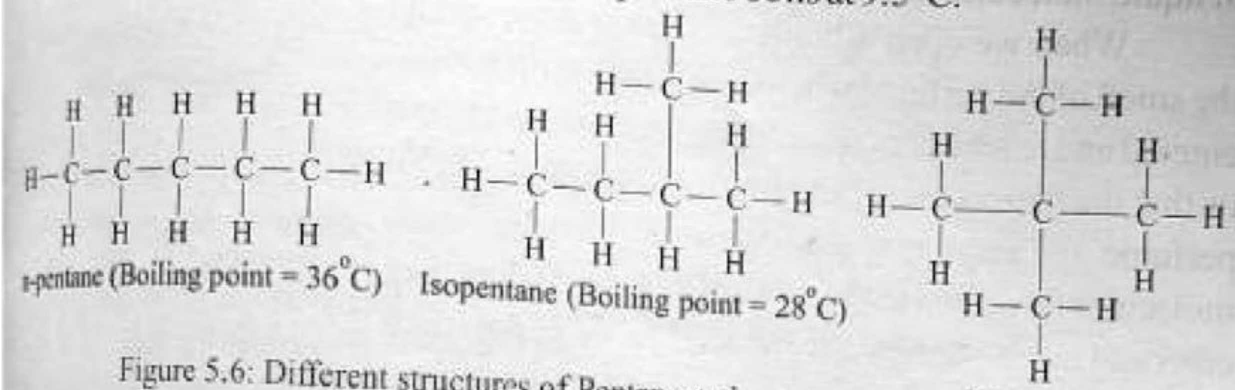
Polarizability is the extent to wh[...] the electronic cloud of a substance [...] distorted or polarized.
The polarizability increases as the number of electrons in an atom or molecule increases. The greater the polarizability, the more easily the electron cloud can be distorted (polarized). Hence, more polarizable atoms and molecules have strong[er] London forces.

Table 5.3: The Boiling Points of Halog[ens] and Noble Gases

Halogen	Molar Mass(g/mol)	Boiling Point(°C)
Fluorine (F_2)	38.0	-188.0
Chlorine (Cl_2)	70.9	-34.6
Bromine (Br_2)	159.8	58.9
Iodine (I_2)	253.8	184.5
Noble Gases	**Molar Mass(g/mol)**	**Boiling Point(°C)**
Helium (He)	4.0	-268
Neon (Ne)	20.2	-245
Argon (Ar)	39.9	-185
Krypton (Kr)	83.8	-152
Xenon (Xe)	131.3	-107
Radon (Rn)	222.0	[illegible]

Shape of Molecules

Greater the polarizability of a molecule, stronger would be the London forces. Hence molecules have strong forces of attractions. For example, three compounds with same molecular formula, C_5H_{12}, boil at different temperatures, n-pentane boils at 36°C, iso-pentane boils at 28°C and neo-pentane boils at 9.5°C.



n-pentane (Boiling point = 36°C) Isopentane (Boiling point = 28°C) Neopentane (Boiling point = 9.5°C)

Figure 5.6: Different structures of Pentane and their Boiling Points

All have the same molecular formula, C_5H_{12} and thus the same molar mass, but they differ in the arrangement of the atoms. Boiling points increase as the forces of attraction between molecules increase.

The valence electrons in the carbon-carbon bonds of n-pentane and iso-pentane are closer to the surface of the molecules while in neo-pentane the valence electrons in the carbon-carbon bonds are well inside the molecule. Hence London forces in n-pentane and iso-pentane are stronger than those in neo-pentane.

Keep In Mind

London forces are present among both the polar and non-polar molecules because electrons are in constant motion in all molecules whereas dipole-dipole forces are present only among polar molecules.

5.3 Physical Properties of Liquids

The properties of liquids depend on the nature and strength of intermolecular forces. In this section we consider five such properties which are associated with liquids in general: evaporation, vapour pressure, boiling point, viscosity and surface tension.

5.3.1 Evaporation

The spontaneous conversion of liquid molecules into vapours in an open container at a given temperature is called evaporation. In this process, molecules escape from the liquid surface and change into vapours spontaneously.

Consider the example of a liquid which is present in the beaker. At a given temperature, all the liquid molecules do not have same kinetic energies in the beaker. Molecules having low kinetic energy move slowly while the molecules having high kinetic energy move faster. If one of the higher speed molecules approaches the surface, then it may escape and overcome the attractions of its neighboring molecules and leaves the bulk of the liquid. This spontaneous change of liquid molecules into vapours is called evaporation.

When we open a bottle of perfume, we detect the smell of the perfume when their gaseous molecules entered and reached our nose. Here our experience tells us that the molecules escape from the liquid surface of perfume and enter into gaseous state. These gaseous molecules travelling in the upward direction when they enter and reach our nose, we become aware of the smell of the perfume.

Evaporation is an endothermic process because energy is required to overcome the intermolecular forces of attraction holding the molecules together.

Keep in mind

Vaporization is the process by which liquid or solid changes to a gas while evaporation is the process by which molecules escape from the surface of a non-boiling liquid and enter the gas phase. Evaporation is a type of vaporization.

Interesting Information:

It is interesting to know that your body regulates its temperature through evaporation in the warm weather or when you exercise. During hot summer days your body passes water to the surface of your skin by means of sweat glands. As the water on the surface of your body evaporates, it removes high energy molecules from your body and low energy molecules are left behind. In this way the temperature of your body falls and your body becomes cool down.

Factors Affecting Evaporation

Temperature

Evaporation occurs at all temperatures. Rate of evaporation increases with the increase in temperature and decreases with the decrease in temperature. By increasing temperature, the kinetic energy of molecules increases which results in the rise of rate of evaporation. If you warm the glass of water, it evaporates quickly because the greater the temperature, the greater is the kinetic energy and the greater is the evaporation.

Conceptual Check Point:

Why wet laundry hung on a clothes-line dries faster in the hot days of summer than in cold days of winter?

Surface Area

Evaporation is the surface phenomenon. It occurs on the surface of the liquid. Greater the surface area, greater will be the evaporation and vice versa. The greater surface area provides a greater chance for molecules to come to the surface of the liquid and changes into the gas phase.

Conceptual Check Point:

Which water dries faster, the water present in the bottle or the water sprinkled on the ground? The water in both the cases has the same volume.

Intermolecular Forces

Different liquids have different rates of evaporation at the same temperature. This is due to the different nature and strength of intermolecular forces. Stronger the intermolecular forces, lower will be the rate of evaporation and vice versa. For example, Gasoline evaporates more quickly than water. Because the intermolecular forces between the gasoline molecules are weaker than the intermolecular forces between water molecules.

Conceptual Check Point:

- Which liquid evaporates more quickly: gasoline or gas oil?

5.3.2 Vapour Pressure

The pressure exerted by liquid vapours in equilibrium with its pure liquid at a given temperature is called vapour pressure.

Consider we have a liquid in an evacuated closed container. Its vapours are formed because of evaporation which begins together above the surface of liquid. These molecules move freely colliding with each other, with the walls of container and also with the surface of liquid. Condensation (the conversion of vapours into liquid) occurs because a molecule striking the liquid surface becomes captured by intermolecular forces in the liquid. In the beginning, the traffic is only one way: Molecules are moving from the liquid to the empty space and rate of evaporation is greater than rate of condensation. By the passage of time, the pressure of vapours above the liquid increases as the number of vapours molecule increases. But after some times, the rate of evaporation and condensation becomes equal, as shown in figure 5.7(c). At this stage, number of molecules leaving liquid

Keep in mind

- The term vapour is usually used for the gas phase of a substance that is found as liquid or solid at normal temperature and pressure.
- The processes of vaporization and condensation are examples of *phase changes*.

surface is equal to number of molecules going back to liquid. This state is called equilibrium state. Thus, at this stage, there is no net change in the masses of the two phases.

$$\text{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \text{Vapours}$$

The pressure of the vapours of a substance in equilibrium with its pure liquid is called its equilibrium vapour pressure (or just the *vapour pressure*). It is important to note that the value of the vapour pressure of liquid is maximum at equilibrium state at a given temperature and that it is constant at constant temperature. At equilibrium the volume of the liquid does not change.

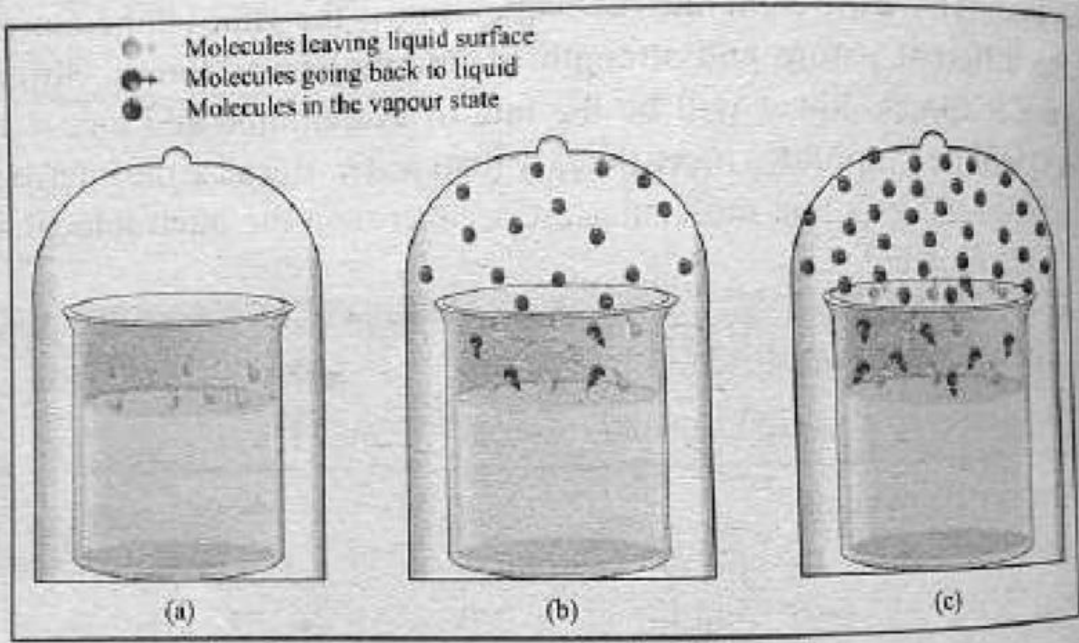


Figure: 5.7: A liquid is allowed to evaporate in a closed vessel.
(a) initially only evaporation occurs,
(b) condensation begins but the rate of evaporation is greater than rate of condensation
(c) dynamic equilibrium is established, now the rate of evaporation is equal to the rate of condensation

Equilibrium in which evaporation and condensation are going on is called dynamic equilibrium.

Factors Affecting Vapour Pressure

The vapour pressure of a liquid depends on the magnitude of the intermolecular forces present in them and on the temperature. Vapour pressure does not depend upon amount of liquid. It also does not depend on the surface area of liquid because an increase in surface area at equilibrium equally affects the rate of evaporation and the rate of condensation.

Intermolecular Forces

Vapour pressure is inversely related to intermolecular attractions. Weaker the intermolecular forces, greater will be the vapour pressure. For example the vapour pressure of water (18 mmHg) is lower than chloroform (170mmHg). The lower vapour pressure of water is due to the presence of strong hydrogen bonds which are absent in chloroform. Chloroform has weak London forces. In general, the liquids with large molecular sizes or greater molar masses have relatively low vapour pressure due to strong dispersion forces. For example, the vapour pressures of liquid alkanes (saturated hydrocarbons) decrease with increase in the molecular size. The larger the molecular size of a liquid is, the more polarizable it is, and the greater the dispersion forces are.

Keep In Mind

The liquids which evaporate easily and have high vapour pressures are said to be volatile, while those that do not vaporize easily and have low vapour pressures are said to be nonvolatile. Volatile liquids such as nail polish remover evaporate readily while non-volatile liquids such as motor oil evaporate slowly if not heated.

Temperature

Vapour pressure increases with increase in temperature. For example, the vapour pressure of water at 25°C is 24 mmHg and at 100°C its value is 760 mmHg. This is because with the rise in temperature the average kinetic energy of the liquid molecules increases which is high enough for molecule to escape from the liquid surface. It results in the increase of the number of vapours, thus the vapour pressure of the liquid increases.

Measurement of Vapour Pressure

A simple mercury barometer can be used to measure the vapour pressure of a liquid. A drop of liquid whose vapour pressure is to be determined is place under the barometer tube filled with Hg, with the help of a bent tube or dropper. The liquid drop will rise above mercury column, because most of the liquids are less dense than mercury and on reaching above the surface of mercury, a part of liquid will evaporates. The vapours will now push the Hg column downwards. As a result of this, the length of Hg column decreases. This change in length of mercury level from its initial position to its final position is equal to the vapour pressure of liquid.

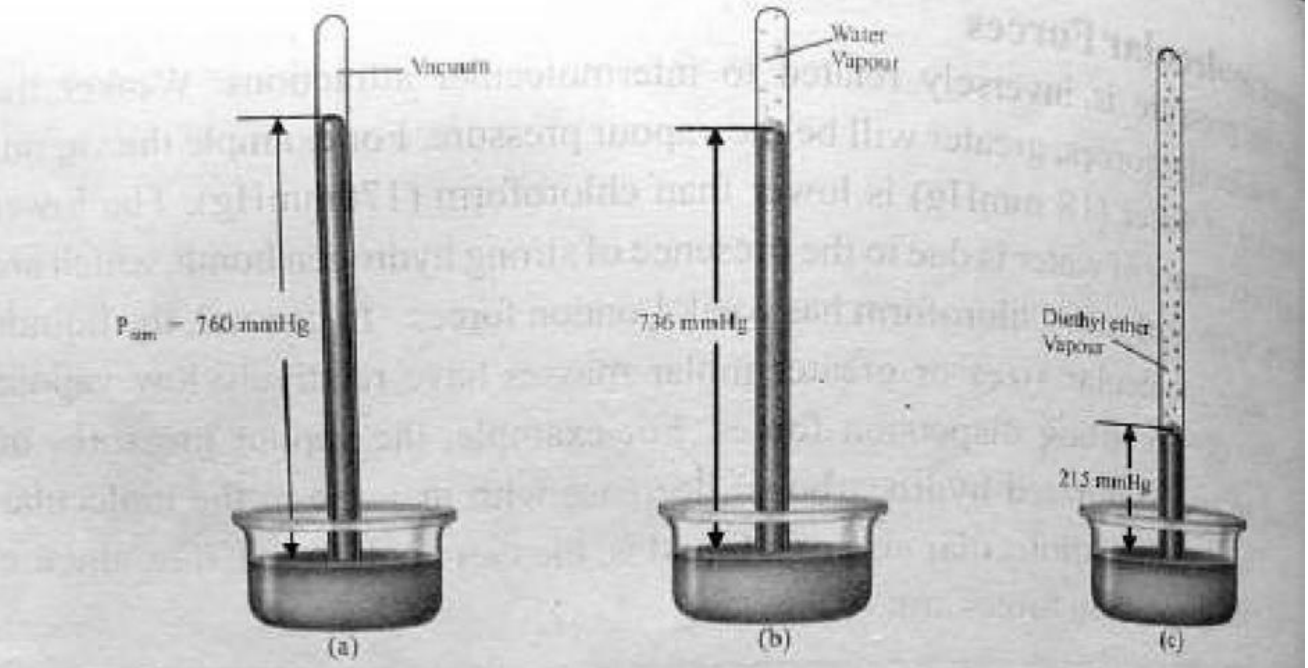


Figure 5.8: Measurement of Vapour Pressures of Water and Diethyl Ether

The vapour pressure of water and diethyl ether at 25°C and 760 mm Hg is 24 mm Hg and 545 mm Hg respectively.

Vapour pressure of liquids can be measured at various temperatures.

Table 5.4: Vapour Pressure of Water at Various Temperatures

Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)
0.0	4.6	50.0	92.5	90.0	525.8
10.0	9.2	60.0	149.4	100.0	760.0
20.0	17.5	70.0	233.7	110.0	1074.6
30.0	31.8	80.0	355.1	120.0	1489.1
40.0	55.3				

5.3.3 Boiling Point

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

When liquid is heated, its average kinetic energy is increased. As a result of this, more molecules escape from liquid surface, hence vapour pressure increases. It goes on increasing till it becomes equal to atmospheric pressure or external pressure. Then the liquid starts boiling. Small bubbles of vapours produced spontaneously below the surface of liquid and they start rising. The bubbles formed consist of vapourized molecules of the liquid, not of air. Temperature at this point is called boiling point.

Table 5.5: Boiling Points of Some Common Liquids at One Atmosphere Pressure

Liquid	Boiling Point (°C)	Liquid	Boiling Point (°C)
Acetic acid	118.5	Carbon tetrachloride	76.5
Acetone	56.0	Ethyl alcohol	78.3
Ammonia	-33.3	Ethylene glycol	197
Benzene	80.5	Mercury	356.6
n-Butyl alcohol	117	Phenol	181.8
Carbon disulphide	46.3	Water	100.0

Temperature of a liquid remains constant during boiling, why? When a liquid is heated, the average kinetic energy of its molecules increased, so the temperature of the liquid also increased. At boiling, the kinetic energy of molecules is the maximum. Now the heat supplied is only used to break the intermolecular forces and convert the liquid into vapours. Any more heat supplied will not increase the temperature of liquid. In this way, the temperature of the liquid molecules remains constant.

Factors Affecting the Boiling Point

The boiling points of the liquid are affected by the factors given below:

Intermolecular Forces

The boiling point of a pure liquid is directly related to the strength of intermolecular forces. The stronger the intermolecular forces, the higher are the boiling points of the liquids and vice versa. For example, the boiling point of water (100°C) is higher than ethyl alcohol (78.26°C). This is due to stronger intermolecular forces among water molecules as compared to ethyl alcohol.

Keep in mind

Each liquid has its own particular boiling point. The boiling points of liquids do not depend upon amount of liquid.

External (Atmospheric) Pressure

Boiling points depend upon external pressure. It increases with increase in external pressure and decreases with decrease in external pressure. For example, the boiling point of water at one atmosphere (760mmHg) is 100°C. At high altitude, atmospheric pressure is less than 760mmHg; hence water boils at temperature lower than 100°C. So the boiling point of water at Murree hills where atmospheric pressure is 0.921atm (700mmHg) is about 98°C and at the top of Mount Everest where atmospheric pressure is 0.316atm (240mmHg) is about 71°C. On the other hand the boiling point increases when the external pressure increases. For example, the boiling point of water at 1.414atm (1074.6mmHg) is 110°C.

Keep In Mind

The boiling point depends on the pressure of the atmosphere because the bubbles of vapour cannot even form until the temperature of the liquid raises to a point at which the vapour pressure of the liquid becomes equal the atmospheric pressure.

Applications

The change of boiling point of a liquid with external pressure has very important applications in chemistry as well as in our daily life.

Boiling Point and External Pressure (Pressure Cooker)

Boiling point of a liquid increases with increase in external pressure. This property is used in pressure cooker e.g. When a liquid is heated in a closed vessel i.e. pressure cooker, more and more vapours are gathered over the liquid surface. These vapours cannot go out from cooker, hence pressure is developed. It increases with increase in temperature. Due to high external pressure, boiling point of a liquid i.e. water is increased. A commercial pressure cooker reaches an internal temperature of 140°C.An increase in temperature of only 10°C will cause food to cook in approximately half the normal time. Therefore food cooks more quickly in cooker. It saves time and greater energy costs. In the hospitals, the same principle is used for the sterilization of instruments and laundries in autoclaves where temperature is high enough to destroy bacteria. Autoclave produces steam at 2atm because of high pressure, temperature of steam is increased and it destroys bacteria at such a high temperature and pressure efficiently.

Conceptual Check Point:

How does the pressure cooker balance the effects of the lower atmospheric pressure on the boiling of liquid at higher altitude?

Vacuum Distillation (Reduced Pressure Distillation)

Distillation at low pressure is called vacuum distillation. Boiling point of a liquid decreases with decrease in external pressure. This process is used to purify those liquids which decompose at their boiling points. In order to boil (distil) them at lower temperature, distillation is carried out under reduced pressure e.g. Glycerol boils and decomposes at 290°C at 760torr (1atm) but on lowering pressure to 90 it can be boiled at 120°C without decomposition.

Conceptual Check Point:

Is it possible to condense steam and recover the water as a liquid? If yes, then how?

5.3.4 Viscosity

Some liquids such as honey and glycerin flow very slowly while others such as gasoline and water flow speedily. The internal resistance to flow of a liquid is called viscosity. It is denoted by eta (η). The greater the viscosity of the liquid, the more slowly it flows. Consider the example of oil which is flowing through a pipeline in the form of layers. Each layer experiences resistance to the flow of other layer due to internal friction. The internal friction is produced because of cohesive force (forces of attraction among liquid molecule) that reduces the rate of flow of oil.

Keep in mind

The liquids which flow slowly are called viscous liquids. They show greater internal resistance to flow because of strong cohesive forces.

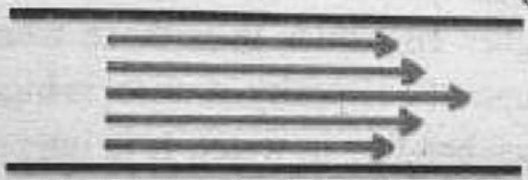


Figure shows the internal resistance to flow of a liquid. The velocity of flow of a liquid nearer to the sides of tube is less than the velocity of flow in the center of tube

The rate of flow of the oil close to the margins of pipeline is not as much as the rate of flow in the middle of the pipeline.

Table 5.6: Viscosity of Some Common Liquids at 20°C

Liquid	Formula	Viscosity ($Kgm^{-1}s^{-1}$)
Acetone	C_3H_6O	3.16×10^{-4}
Benzene	C_6H_6	6.25×10^{-4}
Blood	-----	4.00×10^{-3}
Carbon tetrachloride	CCl_4	9.69×10^{-4}
Diethyl ether	$CH_3CH_2O\ CH_2CH_3$	2.33×10^{-4}
Ethyl alcohol	CH_3CH_2OH	1.20×10^{-3}
Ethylene glycol	$HOCH_2CH_2OH$	26×10^{-3}
Glycerine	$C_3H_8O_3$	1.49
Mercury	Hg	1.55×10^{-3}
Water	H_2O	1.01×10^{-3}

Conceptual Check Point:

Which liquid takes much time, the olive oil or water, when they are pouring in the cups?

Factors Affecting Viscosity

The viscosity of a liquid is related to its intermolecular forces, temperature, molecular size and molecular shape.

Intermolecular Forces

The stronger the intermolecular forces, the greater the viscosity of liquids because liquid molecules cannot move around each other freely so the resistance to flow increases. In general, the liquids with small non-polar molecules such as benzene have relatively low viscosities due to weak intermolecular forces and the liquids with polar molecules such as ethyl alcohol have higher viscosities due to stronger intermolecular forces. On the other hand, the liquids which have ability to form hydrogen bonds have higher viscosities than those which are unable to form hydrogen bonds. For example, the viscosity of water is higher than methyl alcohol because of strong hydrogen bonding in water. It is interesting to know that, the glycerine has higher viscosity than that of all other liquids. It is more viscous than water because its molecule has more sites for making hydrogen bonds as compared to water. Each water molecule has only one –OH group and glycerine has three –OH groups for making hydrogen bonds.

Conceptual Check Point:

Why water, H_2O is more viscous than hydrogen fluoride, HF?

Temperature

Viscosity generally decreases with increasing temperature and increases with decreasing temperature. Because at high temperature molecules have high kinetic energy and can overcome some of the intermolecular attractive forces to slip past one another between the layers. For example, the viscosity of honey and cooking oil decreases as their temperature rises.

Molecular size

The viscosity of a liquid increases by increasing molecular sizes or molar masses and decreases by decreasing molecular sizes or molar masses. For example, diesel is more viscous than petrol, because the larger size molecules (diesel molecules) with higher molar masses are difficult to slip past one another.

Conceptual Check Point:

Give reason which substance is more viscous, gasoline or kerosene oil?

Molecular Shape

Viscosity also depends on the shape of molecules. The viscosity of irregular shaped molecules such as glycerine is greater than regular shaped molecules such as ether. The molecules of viscous liquid become entangled rather than to slip past one another as the molecules of less viscous liquids do.

Measurement of Viscosity

It is difficult to measure the absolute value of viscosity; therefore relative viscosity of liquids is measured. The relative viscosity is the ratio of viscosity of a liquid to the viscosity of water taken as standard. The Ostwald viscometer is used to measure the viscosity of liquid. It has two bulbs, one at each limb. Definite amount of liquid is taken in bulb B and is sucked from bulb B to mark X. The liquid is, then, allowed to flow from mark X to Y. The time of flow of liquid is noted. The viscometer is now cleaned and the same process is repeated with the same amount of water at same temperature. The densities of both the water and given liquid are measured by specific gravity bottle at the same temperature. Relative viscosity of the liquid is calculated from the equation given below:

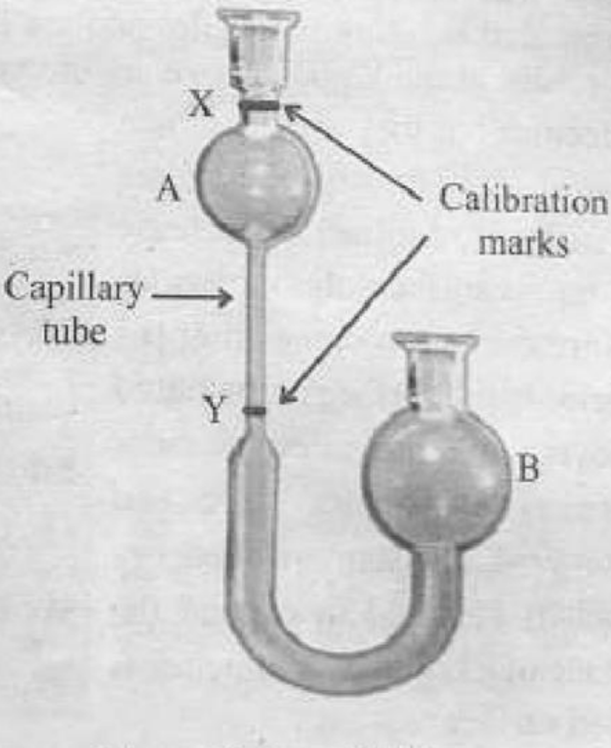


Figure 5.9: Ostwald's Viscometer

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

or

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

Where, η_l is the viscosity of liquid, η_w is the viscosity of water, d_l is the density of liquid, d_w is the density of water, t_l is the time of flow of liquid and t_w is the time of flow of water.

The unit of viscosity is poise (1 poise = 100 centipoise). The SI unit of viscosity is Newton-second per meter square, Nsm^{-2} (one Nsm^{-2} is equal to one kilogram per meter per second, $Kgm^{-1}s^{-1}$).

1 poise = $10^{-1}Kgm^{-1}s^{-1}$.

5.3.5 Surface Tension

A property common to all liquid is surface tension; it is defined as the amount of energy required to increase the surface of a liquid by a unit area. It is denoted by Greek letter γ (gamma). The unit of surface tension is erg per centimeter square (erg/cm^2) or dynes per centimeter (dynes/cm). Its SI unit is Newton per meter square (N/m^2) or joule per meter square (J/m^2).

The surface tension is due to variation of attractive forces at the surface of the liquid. The molecules present inside the body of the liquid are completely surrounded by other molecules and are drawn equally in all directions while the molecules at the liquid surface are drawn downward and from the sides by other molecules but they are not drawn upward. This inward pull causes the surface to contract. To increase the liquid surface, the molecules require energy to come from the interior to the surface of the liquid to overcome the intermolecular attractive forces directed downward. This amount of energy which is required to expand the surface of a liquid by a unit area is called surface tension.

Table 5.7: Surface Tension of Some Common Substances at 20°C

Substance	Formula	Surface Tension (J/m^2)
Ethyl alcohol	CH_3CH_2OH	2.23×10[illegible]
Benzene	C_6H_6	2.89×10[illegible]
Ethylene glycol	$HOCH_2CH_2OH$	4.8×10[illegible]
Glycerine	$C_3H_8O_3$	6.34×10[illegible]
Water	H_2O	7.29×10[illegible]
Mercury	Hg	4.60×10[illegible]

Due to surface tension the water surface behave like a stretched piece of rubber. A razor blade if kept carefully on the surface of the water can be made to float although it is made of steel.

Factors Affecting the Surface Tension

The magnitude of the surface tension of the liquid depends upon the following factors:

Intermolecular Forces

The liquids with strong intermolecular forces have higher surface tension than liquids with weak intermolecular forces. Water, for instance, has higher surface tension than many other liquids such as ethyl alcohol, benzene, and ether. This is due to the presence of strong hydrogen bonds in water molecules. Rain drops or the drops on the waxy surface of an apple or leaves are nearly spherical in shape. In a spherical drop, nearly all the attraction at the surface is inward, thus the sphere has the less surface area per unit volume than any other hape. Substances such as soaps and detergents which are used for washing are nown as surfactants. They can be added to water to reduce the surface tension of ater by the breakage of hydrogen bonds. This increases the interaction of water ith grease and dirt and it becomes easier to remove grease and dust particles from e fabrics.

> **Interesting information:**
>
> Because of high surface tension, some animals such as spider can stand, walk or run on water without breaking the surface.

emperature

e surface tension of the liquid decreases as the temperature is raised. By raising e temperature the kinetic energy of liquid molecules increases and hence, the rength of intermolecular forces decreases which results in the decrease of surface nsion.

easurement of Surface Tension

rface tension of liquid can be measured by agmometer method. It is also called drop thod. Stalagmometer consists of glass bulb etween tubes A and C as shown in the re 5.9.

Water is filled in the dry clean agmometer up to mark X and then it is wed to flow down slowly from mark X to the form of drops. The number of drops med with water is counted. The agmometer is now cleaned and the same ess is repeated with the same volume of the given liquid at same temperature. ensities of both the water and given liquid are measured by specific gravity e at the same temperature. Surface tension of the liquid is calculated by the tion given below:

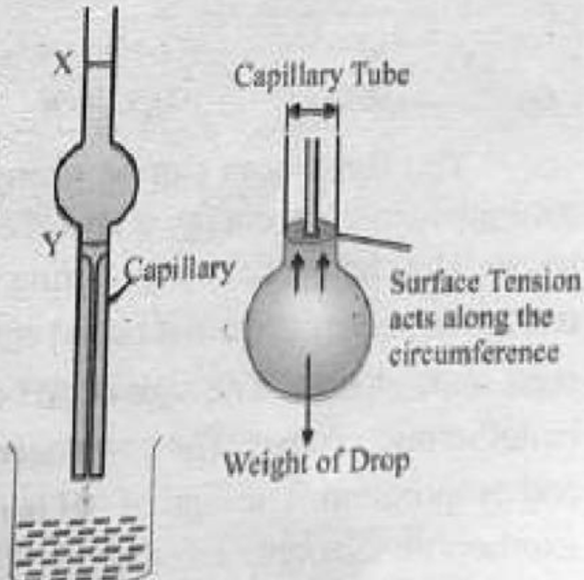


Figure 5.10: Stalagmometer

$$\frac{\gamma_l}{\gamma_w} = \frac{n_w d_l}{n_l d_w} \quad \text{or}$$

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

Where, γ_l is the surface tension of the liquid, γ_w is the surface tension of water, n_l is the number of drops formed with liquid, n_w is the number of drops formed with water, d_l is the density of liquid, and d_w is the density of water.

5.4 Energetics of Phase Changes

The process in which a substance is transformed from one physical state to another physical state is called phase change (state change). Phase change is an example of physical change. Six possible phase changes takes place among the states of matter.

Table 5.8:Possible Changes of States

Change of State	Process	Example
Solid → Liquid	Melting or fusion	Ice → Water
Solid → Gas	Sublimation	Iodine → Iodine vapours
Liquid → Solid	Freezing	Water → Ice
Liquid → Gas	Vaporization	Water → Steam
Gas → Liquid	Condensation	Steam → Water
Gas → Solid	Deposition	Iodine vapours → Iodine

The substances can be changed from one state to another by heating or cooling them. Heat energy is absorbed or evolved, when a phase changes to another phase. The change in energy during physical or chemical change of a substance at one atmosphere pressure is called enthalpy change. It is denoted by ΔH. The symbol Δ represents change. The sign of ΔH is positive, if energy is absorbed and is an endothermic change. The endothermic changes of state are melting, sublimation and evaporation. The sign of ΔH is negative, if heat energy is evolved and is an exothermic change. Exothermic changes are the reverse of the endothermic changes and they are freezing, condensation, and deposition.

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

The majority of substances experience two types of changes of state on heating. A solid changes to a liquid at its melting point, and a liquid changes at its boiling point. But we also experience, the change of solid into gas directly such as conversion of ice into vapours below 0°C. Therefore, we are going to discuss the enthalpy change of fusion, vaporization and sublimation.

Molar Heat of Fusion

The amount of heat required to convert one mole of solid into liquid state at its melting point is called molar heat of fusion (or molar enthalpy of fusion). It is denoted by ΔH_{fus}. The molar heat of fusion for ice is 6.02 KJ/mol.

$$\underset{Ice}{H_2O_{(s)}} \longrightarrow \underset{Water}{H_2O_{(l)}} \qquad \Delta H_{fus} = 6.02 kJ/mol$$

Table 5.9: Molar Heat of Fusion and Melting Point of Some Substances

Substance	Formula	Melting Point (°C)	ΔH_{fus} (kJ/mol)
Water	H_2O	0.0	6.02
Carbon tetrachloride	CCl_4	−23	2.51
Isopropyl alcohol (rubbing alcohol)	$(CH_3)_2CHOH$	−89.5	5.4
Dimethyl ketone (acetone)	CH_3COCH_3	−94.8	5.7
Diethyl ether	$CH_3CH_2OCH_2CH_3$	−116.3	7.3

Freezing is the reverse of fusion (melting). The amount of heat released in ezing a substance is equal to the amount of energy required to melt that substance lid), but the sign is negative.

$$\underset{Water}{H_2O_{(l)}} \longrightarrow \underset{Ice}{H_2O_{(s)}} \qquad \Delta H_{fus} = -6.02 kJ/mol$$

lar Heat of Vaporization

amount of heat required to convert one mole of a liquid into vapours at its ing point is called molar heat of vaporization (or molar enthalpy of orization). It is denoted by ΔH_{vap}. Molar heat of vaporization of water is 7kJ/mol.

$$\underset{Water}{H_2O_{(l)}} \longrightarrow \underset{Steam}{H_2O_{(g)}} \qquad \Delta H_{vap} = 40.67 kJ/mol$$

Table 5.10: Molar Heat of Vaporization and Boiling Point of Some Liquids

Substance	Formula	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
Water	H_2O	100.0	40.7
Benzene	C_6H_6	80.1	31.0
Ethyl alcohol	CH_3CH_2OH	78.3	39.3
Carbon tetrachloride	CCl_4	76.8	32.8
Diethyl ether	$CH_3CH_2OCH_2CH_3$	34.6	26.0

Condensation is the reverse of vaporization. The amount of heat releas[ed in] condensing a substance is equal to the amount of heat required to vaporize [the] substance (liquid), but the sign is negative.

$$\underset{\text{Steam}}{H_2O_{(g)}} \longrightarrow \underset{\text{Water}}{H_2O_{(l)}} \qquad \Delta H_{vap} = -40.67\text{kJ/mol}$$

Molar Heat of Sublimation

The amount of heat required to convert one mole of a solid into vapours direct[ly is] called molar heat of sublimation (or molar enthalpy of sublimation). It is deno[ted by] ΔH_{sub}. Molar heat of sublimation for iodine is 62.2 kJ/ mol.

$$\underset{\text{Solid Iodine}}{I_{2(s)}} \longrightarrow \underset{\text{Iodine vapours}}{I_{2(g)}} \qquad \Delta H_{sub} = 62.2\text{kJ/mol}$$

The reverse of sublimation is called deposition. The amount of heat rel[eased] in deposition of a substance is equal to the amount of heat required to subli[me the] substance (solid), but the sign is negative.

$$\underset{\text{Iodine vapours}}{I_{2(g)}} \longrightarrow \underset{\text{Solid Iodine}}{I_{2(s)}} \qquad \Delta H_{sub} = -62.2\text{kJ/mol}$$

The molar heat of sublimation is equal to the sum of the molar heats of [fusion] and vaporization:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

Dry ice (solid carbon dioxide) and iodine sublime at ordinary temp[erature]. The process of sublimation is used for the purification of iodine. This proce[ss is] used in frost-free refrigerators to remove frost from the inner cold su[rface by] increasing the temperature of freezer at regular intervals. The formation of [frost on] the cold surface is the example of deposition.

5.4.2 Energy Change and Intermolecular Forces

The substance that generally have stronger intermolecular attractive forces need greater amount of energy to change their physical states from solid to liquid or liquid to vapours. For example, the liquids having hydrogen bonds among their molecules such as water, ethylene glycol, and ethyl alcohol have high values of heats of vaporization. These liquids have stronger intermolecular attractive forces, hence need high amount of energy to separate their molecules from each other.

Heats of vaporization are generally much higher than heats of fusion. For fusion (to move around the particles freely) of a substance less amount of energy is provided because the small change occurs in the intermolecular distances during the melting process. On the other hand, large amount of heat is required for liquids to break the intermolecular attractive forces completely to separate their molecules from each other during vaporization.

5.4.3 Change of State and Dynamic Equilibrium

The process of conversion of liquid to vapours is called evaporation while the reverse process (conversion of vapours to liquid) is called condensation. The situation in which a forward process (evaporation) and a reverse process (condensation) are occurring simultaneously and at the same rate is called dynamic equilibrium. Dynamic equilibrium is established between liquid and vapours in a closed container. For a dynamic equilibrium to occur, the rates of two opposing change must be equal so that no net change occurs in the volume or amount of components (liquid or vapours) of the system because the two opposite processes counterbalance each other. The term dynamic equilibrium is not limited to evaporation and condensation processes. You will encounter it, in many of the systems, in chemistry. It indicates the equality in rate between two opposing process of any type (i.e. for all the reversible chemical reactions and all the physical changes). For example ice exists in dynamic equilibrium with water when the temperature is kept constant at 0°C.

$$\text{Ice} \xrightleftharpoons{0°C} \text{Water}$$

5.5 Liquid Crystals

5.5.1 Brief Description

The intermediate state between solids and liquids in which substances have arrangement of particles like solids but freedom of motion like liquids is called liquid crystals.

$$\text{Solid} \rightleftharpoons \text{Liquid Crystals} \rightleftharpoons \text{Liquid}$$

The crystalline solid have specific melting points. The temperature of solids remains constant at melting point until all the solid melts. However, there are some solids which change into turbid liquid before changing into clear liquid. These turbid liquids have the properties of solids such as optical activity and that of liquids such as fluidity, viscosity, and surface tension and are called liquid crystals. A crystalline solid may be isotropic or anisotropic while liquid crystals are always isotropic.

Liquid crystals were first discovered by an Austrian Botanist and chemist Frederick Reinitzer (1857 - 1927) in 1888. He was studying an organic compound cholesteryl benzoate. He found that this compound has an interesting and unusual property. This solid compound melts at 145.5°C and is transformed into viscous milky liquid and becomes a clear liquid at 178.5°C. By cooling, the reverse process occurs, the clear liquid first changes to viscous milky liquid at 178.5°C and then solidifies at 145.5°C. He concluded that he had discovered a new state of matter that has a place between the crystalline solid and liquid states: the liquid crystalline state.

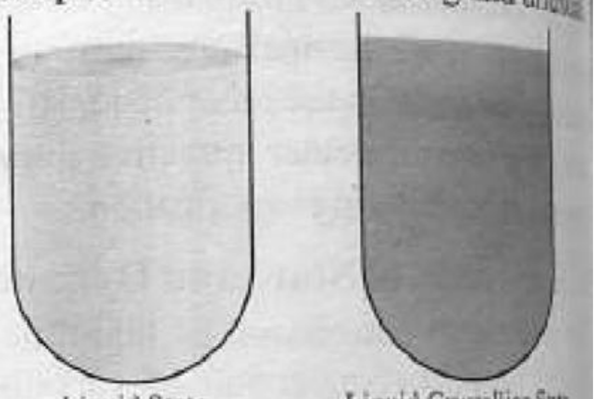


Figure 5.11: The liquid and liquid crystalline phases of cholesteryl benzoate

5.5.2 Applications (uses) of Liquid Crystals

This special kind of material has many applications in our daily life. Liquid crystals are not only used for your wrist watch and packet calculator, these materials are now used in the many fields of science and engineering and have been applied to many products in our society. Some uses of liquid crystals are:

i) They are used as temperature sensors to detect the faulty connections in microelectronic circuit boards.

ii) They are used in thermometers to measure the body temperature of infants.

iii) They are used to detect blockage of veins, arteries and infected areas by tumors. Special liquid crystal devices can be attached to the skin to show a "map" of temperatures. This is useful because of the physical problems, such as tumors, have a different temperature than the surrounding tissue.

iv) They are used as a solvent in chromatographic separations.

v) The most common application of liquid crystal technology is liquid crystal displays (LCDs.). They are used in display of electrical devices such as digital wristwatches, clocks, flat-panel televisions, computers, laptop screens, cell pH-meters and many other electronic devices. The devices, in which liquid crystals are used, are known as LCD devices.

vi) Some of the liquid crystals are used in hydraulic break due to their high viscosity values.

Summary of Facts and Concepts

- Liquid is the physical state of matter which has definite volume but no definite shape and adopts the shape of container in which they are poured. They are not easily compressed. They have high densities than gases.
- The forces of attractions among atoms present within a molecule are called intramolecular forces. These are true chemical bonds and large amount of energy is required to break these forces.
- The forces of attractions which act to hold molecules together in liquids and solids are called intermolecular forces. These are weak forces of attractions and a small amount of energy is required to break these forces. These forces are collectively known as van der Waal's forces. There are three principal types of intermolecular forces in liquids and they are dipole-dipole forces, hydrogen bonding, and London forces.
- Dipole-dipole forces are present in polar molecules. These forces of attraction are due to unequal sharing of electrons between two atoms in a molecule.
- Hydrogen bonding is the special type of dipole-dipole forces. These forces are present among those polar molecules which contain hydrogen bonded to a highly electronegative atom such as fluorine, oxygen, nitrogen, and rarely chlorine. Hydrogen bonds are generally stronger than dipole-dipole forces and London dispersion forces. The unusual high boiling points of some substance is due to hydrogen bonding. The extraordinary qualities of water are due to hydrogen bonding.
- London forces are short lived weak attractive forces and are produced by instantaneous dipoles in atoms or molecules. These forces increase in strength with molar masses. These forces are not only present in non-polar molecules but also present in polar molecules. These forces are more noteworthy in polar molecules.
- The change in which composition of a substance alters is called chemical change such as burning of wood and rusting of iron while the change in which

composition of a substance does not alter is called physical change such as melting and evaporation.

- Evaporation is the process of conversion of liquid in vapours while condensation is the reverse of vaporization (the conversion of vapours into liquid). The direct evaporation of solid is known as sublimation. Evaporation is an endothermic process while condensation is an exothermic process. The evaporation and condensation both play key roles in moderating the temperature of climates. Evaporation is a cooling process and occurs at a great rate in the hot summer days to absorb heat and prevent the temperature increase while condensation is the reverse process and it occurs at night to prevent further temperature drop.
- The pressure exerted by vapours in dynamic equilibrium with its pure liquid at a given temperature in a closed system is called vapour pressure. It shows the evaporating tendency of the liquid.
- The temperature at which vapour pressure of the liquid becomes equal to external pressure or atmospheric pressure is called boiling point of the liquid. The temperature at which the vapour pressure of a liquid becomes equal to one atmosphere pressure is called normal boiling point.
- Liquids show properties such as viscosity (the resistance to flow of a liquid) and surface tension (a measure of how difficult it is to stretch or break the surface of liquid) that depend on the attractive forces among the particles of liquid. The viscosity and surface tension of a liquid increase as the strength of intermolecular forces increase and they decrease as temperature increase.
- The transformation of a substance from one physical state to another physical state is called phase change. The changes of states are the physical changes. They are not chemical changes. The matter can be changed from one physical state to another physical state by cooling, heating and changing pressure.
- The amount of energy required to vaporize one mole of the liquid at its boiling point is called molar heat of vaporization whereas the energy required to melt one mole of the solid at its melting point is called molar heat of fusion.
- The intermediate state of substance that displays properties of both of a liquid and a solid is called liquid crystal. Liquid crystals flow like a viscous liquid and it particles exist in highly ordered patterns as in a crystalline solid.

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) Greater the strength of intermolecular forces, greater will be:
(a) Heat of fusion (b) boiling point
(c) viscosity (d) all of these

ii) Which hydride of group VIIA has higher boiling point:
(a) HF (b) HCl
(c) HBr (d) HI

iii) Which liquid has weak intermolecular forces:
(a) Gas oil (b) water
(c) ethyl alcohol (d) gasoline

iv) The conversion of vapours into liquid is called:
(a) Condensation (b) fusion
(c) evaporation (d) sublimation

v) The vapour pressure of water at 100°C is:
(a) 260 mmHg (b) 760 mmHg
(c) 1074 mmHg (d) 1489 mmHg

vi) The boiling point of glycerine at 50 mmHg is:
(a) 100°C (b) 120°C
(c) 240°C (d) 360°C

vii) Food cooks more rapidly at:
(a) Karachi (b) Quetta
(c) Murree (d) Mt. Everest

viii) Surface tension is measured by:
(a) Stalagmometer (b) thermometer
(c) viscometer (d) manometer

ix) Viscosity of liquid increases with decrease in:
(a) molecular mass (b) intermolecular forces
(c) temperature (d) atmospheric presure

x) Which one of the following is more volatile?
(a) Water (b) methyl alcohol
(c) gasoline (d) diethyl ether

2. Fill in the blanks with suitable words given in the brackets:

i) The intramolecular attractive forces are __________ stronger than intermolecular attractive forces. (less/more)

ii) Hydrocarbons are insoluble in water due to absence of

__________.(ionic bond/ hydrogen bond)

iii) Internal resistance to flow of liquid is called ________ of liquid (fluidity / viscosity).

iv) Vapour pressure increases with increase in ________ of liquid. (surface area / temperature)

v) Substances which have both the properties of ________ are called liquid crystals. (solids and liquids/liquids and gases)

vi) Molar heat of vaporization is ________ than molar heat of fusion. (lesser/greater)

vii) Water is liquid while H_2S is gas at room temperature because of the presence of ________ in water molecules. (covalent bonds / hydrogen bonds)

viii) Ice occupies 10% ________ space than water. (more/less)

ix) The element ________ is found in the liquid state while the element ________ is found in the gaseous state. (chlorine / bromine)

x) The surface tension is denoted by Greek letter ________ (gamma, γ / eta, η)

Q.3. Label the following statements as True or False.

i) Liquids and gases both have definite volume.

ii) The thermal expansion for a liquid is generally less than that of its corresponding gas.

iii) The density of a liquid is nearly the same as that of its corresponding gas.

iv) The intermolecular forces between particles of a liquid are called cohesive forces (or cohesion) while the forces of attraction between particles of liquid and another surface are called adhesive forces (or adhesion).

v) The intermolecular forces and temperature are the two factors which affect the vapour pressure of a substance.

vi) London dispersion forces are the weak intermolecular forces that are absent in all of the molecules of liquids and solids.

vii) Viscosity is the inverse of the fluidity of liquid.

viii) Surface tension, viscosity, and vapour pressure are all temperature independent.

ix) Liquid crystal is a turbid liquid that displays some degree of order below the melting point of solid.

x) Specific heat is the amount of heat required to raise the temperature of 1g of a substance by 1°C.

Q4. Describe the properties of liquids on the basis of kinetic molecular theory of gases.

Q5. What are intramolecular and intermolecular attractive forces? Why intramolecular attractive forces are stronger than intermolecular attractive forces? Name the various types of intermolecular forces.

Q6. Why are the intermolecular forces stronger in liquids as compared to gases?

Q7. What are dipole-dipole forces? Explain dipole-dipole force with the help of an example. What factors determine the strength of dipole-dipole forces between molecules?

Q8. What is hydrogen bonding? What conditions are necessary for the formation of hydrogen bonding?

Q9. What are London dispersion forces? How are they affected by?

(a) The sizes of atoms or molecules;

(b) The shapes of molecules; and

(c) The polarizability of atoms or molecules.

Q10. Which one of the following molecules displays strong hydrogen bonding?

(a) HF (b) HCl (c) H_2O (d) NH_3 (e) CH_3CH_2OH

Q11. What type of intermolecular forces must be overcome when each of the following liquids are converted to vapours?

(a) CH_3OH (b) petrol (c) $CHCl_3$ (d) CCl_4 (e) bromine

Q12. Which substance in each of the following pair has the stronger London forces?

(a) H_2O or H_2S (b) F_2 or Cl_2 (c) CO_2 or CO

(d) argon or krypton (e) CH_4 or C_2H_6

Q13. Why does ice float on the surface of water and all other solids sink in their liquid phase? Give reason.

Q14. Explain why the water pipes are drained or insulated and the antifreeze is added to the radiators of cars in the cold climate areas such as Quetta, Ziarat and Murree in winter?

Q15. Explain why London forces are weaker than other intermolecular attractive forces?

Q16. What is the difference between dipole-dipole forces and London forces?

Q17. Why the boiling point and heat of vaporization of H_2O is higher than HF although their molar masses are nearly the same and hydrogen bonding between HF molecules is stronger than H_2O molecules?

Q.18. Define and explain evaporation. Explain the factors that affect evaporation.

Q.19. Why the rate of evaporation of liquid increase by increasing temperature?

Q.20. The evaporation is the cooling process and occurs at all temperature, how?

Q.21. Why the wet clothes hanged outdoors dry rapidly on a hot summer day than a cold winter day? Explain.

Q.22. How does perspiration cool the skin of your body in hot weather?

Q.23. Earthen ware such as pitcher keep water cool while those made of metal plastic or glass such as jerrycan and glass bottle are unable to keep water cool, why?

Q.24. What is the equilibrium vapour pressure of the liquid? Discuss the factors that affect vapour pressure. How is it measured?

Q.25. What is meant by dynamic equilibrium? Explain it between two physical states.

Q.26. The change in the surface area of a liquid does not cause the change in the equilibrium vapour pressure of liquid, how?

Q.27. Explain why we feel sense of cooling on the bank of lake after bath?

Q.28. Why autoclaves are considered as the efficient sterilization instrument?

Q.29. How would you change a substance from liquid state to gaseous state without increasing the temperature of the liquid?

Q.30. Define and explain the boiling point of liquid. What are the factors affecting boiling point of liquid? How does the boiling point of a liquid depend on external pressure?

Q.31. The bubbles are formed when water starts boiling. What is present inside the bubbles that form?

Q.32. Why does the boiling point of water is much higher than that of H_2S?

Q.33. Why the boiling point of water in pressure cooker is higher than an ordinary saucepan?

Q.34. Explain why the egg takes a longer time to cook it in boiling water at high altitude than does at lower altitude?

Q.35. Explain why each liquid has its own boiling point?

Q.36. Why the temperature of boiling liquid remains constant even though heat is being added continuously?

Q.37. Explain why the steam at 100°C burns your skin much more severely than liquid water at 100°C?

Q.38. Why the sprinkling of the boiling diethyl ether does not burn as severely as the sprinkling of boiling water on your skin? Explain.

Q.39. What is a phase change? Name all possible changes that can occur among the vapour, liquid, and solid phases of a substance.

Q.40. Define the terms molar heat of vaporization and molar heat of fusion. Give their units. Why the molar heat of vaporization is greater than that of molar heat of fusion?

Q.41. Which process is exothermic, the fusion or condensation?

Q.42. Why do the droplets appear on the outside of the glass full of ice cold water in the summer time?

Q.43. What is the viscosity of a liquid? How does viscosity change with increasing temperature? What is the effect of intermolecular forces on the viscosity of liquid? How is it measured experimentally?

Q.44. Why does gas oil flow at a higher speed through a pipe when the temperature of oil increases?

Q.45. The drivers are suggested to use the lower viscosity motor oils in the winter and higher viscosity motor oils in the summer, why?

Q.46. What is the surface tension of the liquid? Why are the molecules at the surface of the liquid act differently from those situated inside? What factors affects the surface tension of a liquid? How can it measured experimentally?

Q.47. A razor blade if kept carefully on the surface of water can be made to float although it is made of steel and is much denser than water, how?

Q.48. Explain why a small drop of water assumes nearly a spherical shape on the surface of waxy bonnet of car?

Q.49. What are surfactants? What is the role of surfactants?

Q.50. How does viscosity and surface tension change with temperature? Discuss the relation of intermolecular forces with these properties.

Q.51. What are liquid crystals? Give their applications in daily life.

Q.52. What is the difference between a liquid crystal and a typical solid crystal like that of NH_4Cl?