5 STATES AND PHASES OF MATTER

Student Learning Outcomes [C-11-A-79 to C-11-A-92]

After studying this chapter, students will be able to:

- Describe the physical properties of gases (including compressibility, expandability, and pressure exerted by gases). (Understanding)
- Describe origin of pressure in terms of collisions between molecules and the walls of container, Understand that ideal gas have zero partial volume.
- State and use the ideal gas equation PV=nRT in Calculations including determination of M_r. (Understanding)
- 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)
- Describe types of intermolecular forces. (Understanding)
- Explain the strength and applications of dipole-dipole forces, hydrogen bonding and London forces. (Understanding)
- Describe physical properties of liquids such as evaporation, vapor pressure, boiling point, viscosity and surface tension. (Understanding)
- Apply the concept of hydrogen bonding to explain the properties of water (specifically high surface tension, high specific heat, low vapor pressure, high heat of vaporization, and high boiling point). (Application)
- Define molar heat of fusion and molar heat of vaporization. (Knowledge)
- Describe how heat of fusion and heat of vaporization affect the particles that make up matter. (Understanding)
- Outline the importance of heat of fusion in the study of glaciers and ice sheets (particularly while studying polar ice caps). (Understanding)
- Describe liquid crystals and give their uses in daily life. (Understanding)
- Differentiate liquid crystals from pure liquids and crystalline solids. (Understanding)
- Describe simple properties of solids e.g., compression, expansion, motion of molecules inter-particle space, intermolecular forces and kinetic energy based on kinetic molecular theory. (Understanding)
- Differentiate between amorphous and crystalline solids. (Knowledge)
- Describe properties of crystalline solids like geometrical shape, melting point, habit of a crystal, cleavage, and crystal growth. (Understanding)

Web version of PCTMA textbook Not for sale

Matter exists in four states i.e., solid, liquid, gas and plasma. The simplest form of matter is the gaseous state and most of matter around us is in the solid state. Liquids are less common than solids, gases and plasmas. The reason is that the liquid state of any substance can exist only within a relatively narrow range of temperature and pressure.

Let us look at the general properties of gases, liquids, and solids. Kinetic molecular theory of gases can help us to understand their properties.

5.1 PROPERTIES OF GASES

i. Gases do not have a definite shape and volume. The volume of a gas is the volume of the container.

ii. Ideal gases have zero particle volume.

iii. The molecules of gases are widely separated from one another and most of the volume of the gas is empty space (nearly 99.9%). That is why gases can be compressed easily. When sudden expansion of gases occurs cooling takes place. It is called Joule-Thomson effect.

iv. Pressure of a gas is due to the collisions of gas molecules with the walls of the container.

v. There are negligible intermolecular forces in ideal gases.

5.2 IDEAL GAS EQUATION

It is a matter of common observation that when external conditions of temperature and pressure are changed, the volume of a given quantity of a gas is affected. The gas laws describe the relationships between volume of a given amount of gas and the prevailing conditions of temperature and pressure.

While describing Boyle's and Charles' laws, some of the variables are held constant during the changes produced in the gases. According to Boyle's law.

$$V \propto \frac{1}{P} \quad \text{(when 'n' and 'T' are held constant) ..... (1)}$$

According to Charles' law

$$V \propto T \quad \text{(when 'n' and 'P' are held constant)..... (2)}$$

According to Avogadro's law volume of the given gas at constant temperature and pressure is directly proportional to the number of moles.

$$V \propto n \quad \text{(when P and T are held constant) ..... (3)}$$

If we think for a moment that none of the variables are to be kept constant, then all the above three relationships can be joined together as:

$$V \propto \frac{nT}{P}$$

$$V = \text{constant } \frac{nT}{P}$$

Web version of PLCTAA textbook
Not for sale

The constant suggested here is 'R' which is called **Ideal gas constant**. Its value is 0.0821 atm dm^3 K^{-1} mol^{-1}.

$$\text{Hence } V = R\ \frac{nT}{P}$$

$$PV = nRT \quad \ldots\ldots\ldots (4)$$

Equation (4) is called the **ideal gas equation**.

Calculation of Relative Molecular Mass (M_r) of a Gas

Equation (4) can be employed to calculate the relative molecular mass of a gas whose P, T, V and mass in grams are known. This is achieved by rearranging equation (4)

Putting $n = \frac{m}{M}$ in equation (4)

Where m= mass in g and M = molar mass of the gas

$$PV = \frac{mRT}{M} \quad \ldots\ldots\ldots (5)$$

Now rearranging equation (5)

$$M = \frac{mRT}{PV} \quad \ldots\ldots (6)$$

At molecular level, the molar mass becomes relative molecular mass of a compound, therefore, we can write

$$M_r = \frac{mRT}{PV} \quad \ldots\ldots\ldots (7)$$

Web version of PCTB A textbook
Not for sale

Sample Problem 5.1

The volume of 134 g of a gas at -73 °C under 10 atm pressure is 5 dm^3. Determine the relative molecular mass of the gas.

Solution: The molecular mass of the gas can be calculated by using the formula:

$$M = \frac{mRT}{PV}$$

$$M = \frac{(134\ g)(0.0821\ atm\ dm^3\ mol^{-1}\ K^{-1})(200\ K)}{(10\ atm)(5\ dm^3)}$$

$$M = 44\ g\ mol^{-1}$$

Therefore, the relative molecular mass of the gas is 44 amu.

Quick Check 5.1

a) Explain why gases can be compressed easily?

b) What is Joule-Thomson effect?

c) The volume of 84g of a gas is 8 dm^3 at -90 °C under 7 atm pressure. Calculate the relative molecular mass of the gas.

5.3 PROPERTIES OF LIQUIDS

i. Liquids also diffuse like gases, however the rate of diffusion in liquids is much lower than that in gases.

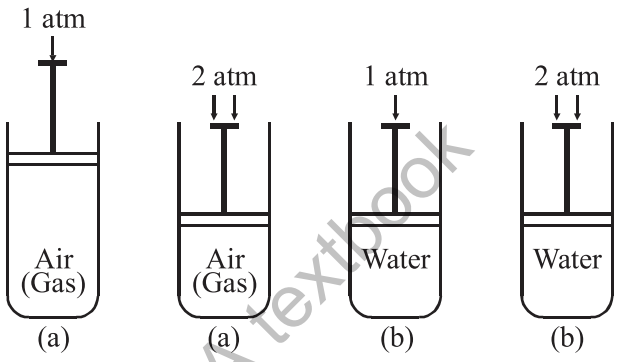
ii. There are little spaces among liquid molecules because of relatively stronger intermolecular forces.

iii. Liquids are 10^5 times less compressible than gases, but about 10 times more compressible than solids.

iv. The molecules of a liquid are in constant random motion, but their speed of movement is lower than gases. Diffusion among the miscible liquids is an evidence for the free motion of liquid molecules. Similarly, liquids can flow because of the free movement of their molecules.

v. Liquids expand when their temperature is increased. However, this expansion is negligible compared to that in gases .

vi. According to kinetic molecular theory, molecules of a liquid are in constant motion, therefore, they possess a certain amount of kinetic energy at any temperature. The K.E of the molecules may increase or decrease by the rise or fall in temperature respectively. For example, a liquid is converted into a solid by decreasing its kinetic energy (on cooling) and converted into vapour by increasing kinetic energy (on heating)



(a) Volume of gas is reduced to half when pressure is doubled

(b) Volume of a liquid changes by about 0.0045% when pressure is doubled.

Figure 5.1 Effect of pressure on the volumes of gases and liquids.

Web version of PECTA textbook Not for sale

5.4 INTERMOLECULAR FORCES

The intermolecular forces among the molecules of a liquid are reasonably stronger. Three types of such forces are mentioned here.

i. Instantaneous dipole-induced dipole forces (id-id)
ii. Permanent dipole-permanent dipole forces (pd-pd)
iii. Hydrogen bonding

5.4.1 Instantaneous dipole-induced dipole forces (id-id)

The creation of these forces is explained below:

Bromine is a liquid under ordinary conditions, but very volatile and gives dense fumes even at room temperature. It shows that its molecules are attracted by weak forces that can be easily broken. This force is actually **London Dispersion Force**. When two molecules of bromine come close, the electron cloud of one molecule influences the moving electrons

of the other as in **Figure 5.2**. In this way, the electrons of one molecule are pushed away while its nucleus is attracted by the electrons of the nearby molecule. As a result, this molecule becomes a dipole at any instant, which is called an **instantaneous dipole**. This molecule then disturbs the electron density of the molecule next to it and induces a polarity in it. A temporary dipole created due to the instantaneous dipole is called the **induced dipole**. A force of attraction develops between these two dipoles that holds them together temporarily. The momentary force of attraction between an instantaneous dipole and an induced dipole is called **instantaneous dipole-induced dipole force**.

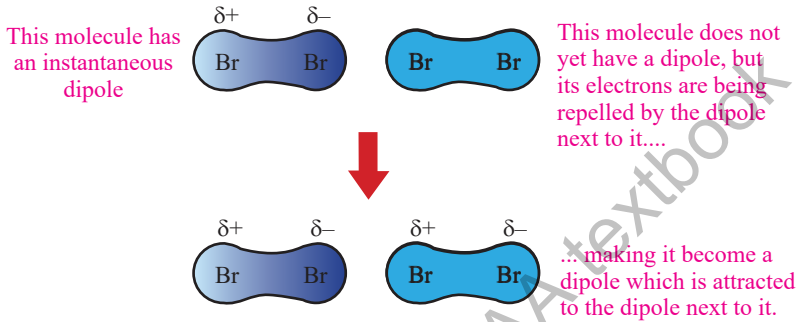


Figure 5.2 Creation of instantaneous dipole-induced dipole force

These are only forces that exist among the molecules of non-polar compounds. The strength of these forces depend upon the following factors

i. Molecular mass and size:

When the molecular mass (M_r) of a compound is greater, the id-id forces are stronger and vice versa. This is because in a larger atom or molecule the dispersion of electronic cloud and polarisation is relatively easier. This factor operates in the halogen and noble gas families. The physical state changes in the halogen family from top to bottom due to the increase in size and polarizability. The first two members in the halogen family (F_2 and Cl_2) are gases, but bromine is a liquid and iodine a solid (b.p. = 458 K). The boiling points of noble gases in group 18 also increase from helium (He) to xenon (Xe) as in **Table 5.1**.

Table 5.1 Molar masses and boiling points of group 17 and 18 of periodic table.

17 (VII-A)	Molecular Mass	Boiling points (K)	18 VIII	Molecular mass	Boiling points (K)
F_2	38	85	He	4.003	4.22
Cl_2	71	239	Ne	20.18	27.1
Br_2	159	333	Ar	39.95	87.3
I_2	253.8	458	Kr	83.8	120
			Xe	131.3	165

ii. Surface Area (shape of molecule)

A molecule with larger surface area has higher number of contacts for a nearby molecule. Thus the forces among the molecules of a compound having larger surface area are stronger.

Web version of PCTAA textbook
Not for sale

Consider saturated hydrocarbons. These have chains of carbon atoms linked with hydrogen atoms. Compare the length of the chains in C_2H_6 and C_6H_{14}. They have the boiling points –88.6°C and 68.7°C, respectively. It is evident that the molecules with larger chain length experiences stronger attractive forces. The reason is that longer molecules have more places along the length where they can be attracted to other molecules.

Three isomers of pentane have the same relative molecular mass (M_r), however, they differ in their surface areas. Straight chain pentane has largest surface area and so is its boiling point is the highest among the three isomers of pentane. 2-Methylbutane (Isopentane) has smaller surface area than n-pentane but larger than 2,2-Dimethylpropane (Neopentane). Therefore, the forces among 2-Methylbutane molecules are intermediate and the least strong forces occur in 2,2-Dimethylpropane. The isomers of pentane along with their boiling points are given in **Figure 5.3**.

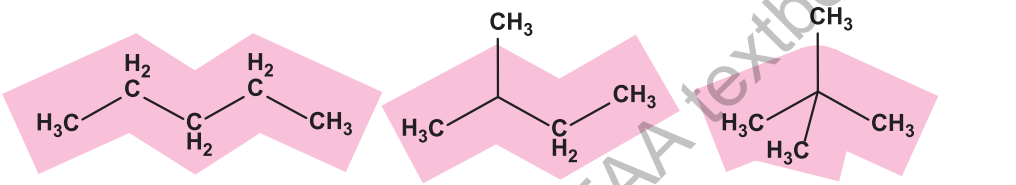


Figure 5.3 The three isomers of pentane have different structures, surface areas and intermolecular forces

Web version of PCTAA textbook
Not for sale

5.4.2 Permanent dipole-permanent dipole forces (pd-pd)

The force of attraction between the positive end of a polar molecule and the negative end of a nearby polar molecule is called **permanent dipole-permanent dipole force**. Whenever the HCl molecules are close to each other (as in liquid state), they tend to line up as in **Figure 5.4**. Similar type of forces is present among the molecules of chloroform ($CHCl_3$).

The molecule of chloroform has a positive center at the H atom and the negative center on the end with Cl atoms.

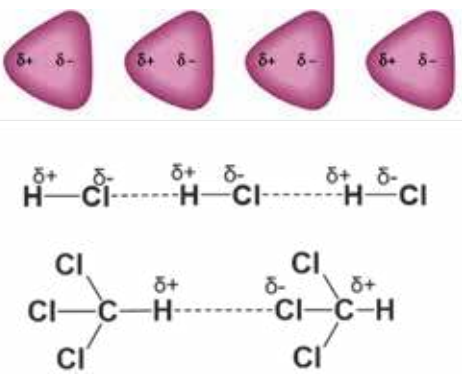


Figure 5.4 Permanent dipole-permanent dipole forces in HCl and chloroform

Quick Check 5.2

a) To improve the quality of gasoline(petrol), straight chain hydrocarbons in the gasoline fraction of petroleum are converted to branched chain ones. What could be the possible reason?

b) Which forces are present among the molecules of the following substances? CCl_4, SiF_4

c) Differentiate id-id and pd-pd forces with examples.

5.4.3 Hydrogen Bonding

Hydrogen bond is a special type of dipole-dipole force. It is the strongest force among intermolecular forces, but is weaker than all the major types of bond, i.e. ionic, metallic, and covalent bonds. A hydrogen bond is formed when the following conditions are fulfilled:

i. The hydrogen atom is connected to a highly electronegative atom, such as F, O, or N

ii. The electronegative atom must have a lone pair of electrons on it.

The covalent bond between a highly electronegative atom and hydrogen is highly polarized. It means the hydrogen atom carries a sufficient δ+ charge and the electronegative atom δ- charge. The presence of lone pair on the electronegative atoms allows the partial positively charged hydrogen atom to make a bond with F, O, or N called a hydrogen bond. This bond is represented by a dotted line (…) and its strength is one tenth of an ordinary covalent bond. The number of hydrogen bonds a molecule can form on average depends on:

- The number of hydrogen atoms bonded to the electronegative atom
- The number of lone pairs present on F, O, or N

A water molecule contains two hydrogen atoms and two lone pairs on oxygen. Therefore, it can form two bonds on average. This is why water molecules are extensively hydrogen bonded with one another. This unique feature is responsible for its characteristic properties, e.g. high boiling point of water (100 °C). The water molecules in liquid form are arranged three dimensionally as shown in **Figure 5.5**. This bonding acts as a bridge between two electronegative oxygen atoms.

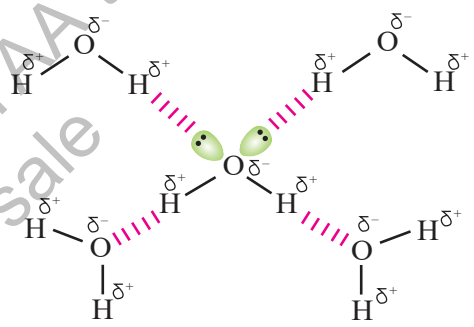


Figure 5.5 Hydrogen bonding in water

On the other hand, ammonia can form only one hydrogen bond per molecule despite having three hydrogen atoms. This is due to the availability of only one lone pair on the N atom as shown in **Figure 5.6.** The hydrogen bonding in liquid ammonia is much weaker than water. This is why its boiling point is much lower (-33°C). HF is even more distinct than water and ammonia. It has three lone pairs on the F atom which allows it to form three H-bonds. However, it has only one H atom and due to this reason, it is restricted to form only one bond again. Nevertheless, its hydrogen bond is strong enough compared to NH_3, which owes to its high electronegativity. Thus, its b.p (19.9°C) is much higher than ammonia (–33.5°C).

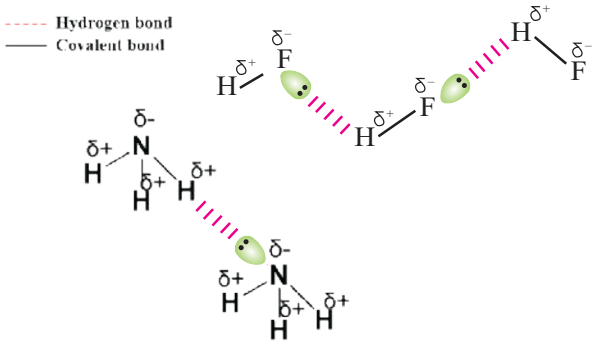


Figure 5.6 Hydrogen bonding in NH_3 and HF

Web version of PCTAA textbook
Not for sale

5.4.4 Influence of Hydrogen Bonding on the Properties of Water

i. Structure and low density of ice

The molecules of water have tetrahedral structure. Two lone pairs of electrons on oxygen atom occupy two corners of the tetrahedron. When the temperature of water is decreased and ice is formed, the molecules become more regular and this regularity extends throughout the whole structure. Empty spaces are created in the extensively hydrogen-bonded structure as shown in the following diagram **Figure 5.7**. This is why, when water freezes, it occupies 9% more space and its density decreases. For this reason, ice floats on water. Due to this so called anomalous behavior of ice, the fish and other living creatures survive under the frozen lakes and oceans. The ice blanket covers the water surface due to its low density and the water beneath is insulated from the environment.

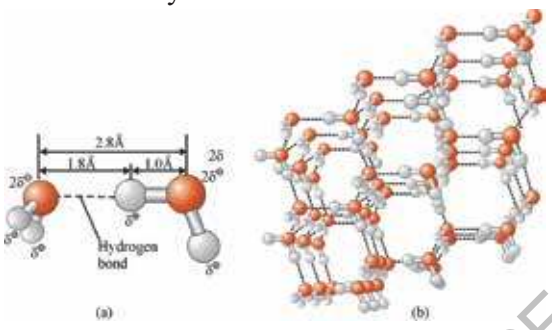


Figure 5.7 Extensive hydrogen bonding in ice and spaces among molecules

This part of a glacier is floating on the surface due to low density of ice

ii. High Heat Capacity

Water has a high specific heat capacity (4.18 J/g°C). This is due to its unique molecular structure which allows strong hydrogen bonds. Due to the high heat capacity of water, it can absorb and release a large amount of heat with small temperature changes.

iii. Anomalous heat of vaporization and boiling point

The general trend of enthalpy change of vaporization of group 16 hydrides is a regular increase from H_2S to H_2Po **Figure 5.8**. This is because the molecules of these compounds are bonded by weak London dispersion forces.

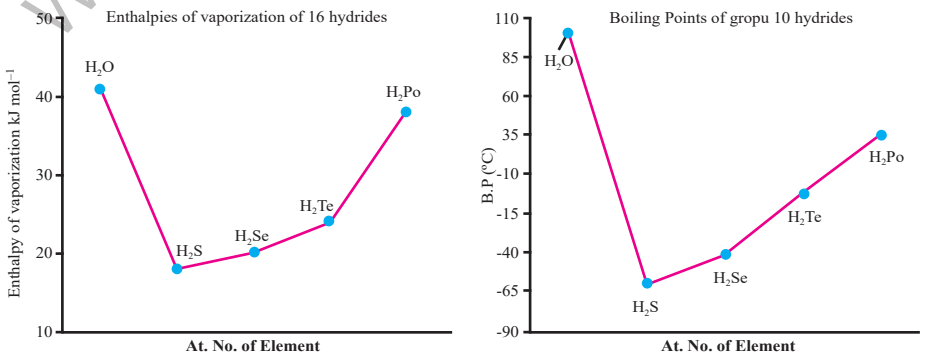


Figure 5.8 A graphical expression of variation in enthalpy of vaporization and B.Ps of group 16 hydrides

Web version of PECTAA textbook Not for sale

With the increasing atomic size down the group, from S to Po, the van der Waals forces also become stronger. If water had followed this trend, the heat of vaporization of water would be the lowest among the group members. However, water has the highest enthalpy change of vaporization (41 kJ mol^{-}) in the group. This is because water is exceptionally hydrogen bonded, which makes it difficult to break forces among water molecules and vaporize it. The boiling point of water is also remarkably higher than the rest of group 16 hydrides. Simply, the energy required to break the water molecules apart is very high due to the extensive hydrogen bonding in it. It needs high temperatures to provide so much energy as to boil water into its vapour.

iv. Surface tension and viscosity

The surface tension and viscosity of water are also very high. Surface tension is a downward pull of water molecules at the surface, making the water surface stretched and strained. This downward pull is due to the attraction of inner molecules through hydrogen bonds.

Viscosity is the resistance by a liquid to its flow. Water has higher viscosity than many of liquids including lower hydrocarbons and alcohols (e.g. hexane and ethanol). The high viscosity of water is also due to strong hydrogen bonds among the molecules. Alcohols can make hydrogen bonds, but the strength and extent of hydrogen bonding is far less than that in water. Hydrocarbons lack the ability to make the hydrogen bond.

Quick Check 5.3

a) Can the CHF_3 molecule make a hydrogen bond? Explain why or why not?

b) Show a hydrogen bond between two molecules of ethanol (CH_3CH_2OH).

c) Describe which forces are present in the following and arrange them in increasing order of boiling point.

i. $CH_3CH_2CH_3$ ii. CH_3CH_2OH iii. CH_3CH_2Cl

d) The boiling point difference in each of the following pairs is given

i. CH_3CH_3 (-89 °C) and CH_3OH (65 °C), difference = 154 °C

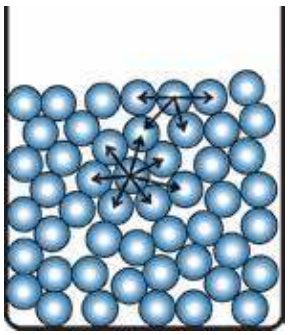
ii. $CH_3CH_2CH_2CH_3$ (0 °C) and $CH_3CH_2CH_2OH$ (97 °C), difference = 97 °C

Explain why the difference decreases as the size of the molecules increases.

e) Molecules of ethanoic acid (acetic acid) exist in the form of dimers in pure form but not in aqueous solution. How hydrogen bond can explain this?

Web version of PCTMA textbook Not for sale

5.5 SURFACE TENSION OF LIQUIDS



Surface tension is a property of liquids which depends upon the strength of intermolecular forces. The molecules located at the free surface of the liquid are pulled inward by the molecules below the surface of the liquid. This downward pull tends to contract the surface of the liquid.

Molecules at the surface experience a net force inward due to intermolecular forces, leading to a "skin" on the surface. Liquids tend to minimize their surface area due to surface tension, which

explains why droplets form spheres. Surface tension influences various phenomena, such as, capillary action, wetting of surfaces and formation of droplets and bubbles.

Factors Affecting Surface Tension

i) Temperature: Surface tension typically decreases with increasing temperature.

ii) Intermolecular forces: Stronger intermolecular forces lead to higher surface tension.

Mosquitos can float on surface on water due to high surface tension

Table 5.2 Surface tension of some liquids at 20 °C in Nm^{-1}

Sr. No.	Liquid	Surface tension (10^{-3} Nm^{-1})	Sr. No.	Liquid	Surface tension (10^{-3} Nm^{-1})
1	Water H_2O	72.75	4	Acetone $(CH_3)_2CO$	23.70
2	Ethyl alcohol CH_3CH_2OH	22.75	5	Benzene C_6H_6	28.85
3	Methyl alcohol CH_3OH	22.61	6	Carbon tetrachloride CCl_4	26.95

Web version of PECTAA textbook
Not for sale

5.6 VISCOSITY OF LIQUIDS

Viscosity is a measure of a liquid's resistance to flow. It is a property that describes the thickness or stickiness of a liquid. Liquids with higher viscosity are thicker and offer more resistance to flow. While those with lower viscosity are thinner and are less resistant to flow. For example, honey is more viscous than water. Stronger intermolecular forces result in higher viscosity. Viscosity decreases with rise in temperature.

5.6.1 Factors affecting viscosity:

The factors affecting viscosity are as follows:

i. An increase of temperature increases the average kinetic energy of molecules. This allows the molecules to overcome the attractive forces. This lowers the viscosity.

ii. 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.

Quick Check 5.4

a) Arrange the following liquids in increasing order of surface tension, give reason:
Acetone (CH_3COCH_3), ethanol (C_2H_5OH), methoxy methane (dimethyl ether, CH_3OCH_3)

b) Why do you think tetracholro methane (carbon tetrachloride, CCl_4) has higher viscosity than chlroform ($CHCl_3$) but less than ethanol (C_2H_5OH)?

c) The viscosity of honey is higher than water, explain why.

d) Which of the following is more viscous: glycerine ($CH_2OHCHOHCH_2OH$) or hexane (C_6H_6)? Why?

5.7 EVAPORATION

Evaporation is the spontaneous conversion of a liquid into vapour at any temperature.

When high energy molecules leave the liquid and low energy molecules are left behind, the temperature of the liquid falls. The heat moves from the surrounding to the liquid and then the temperature of the surrounding also falls. This phenomenon helps to understand that evaporation causes cooling.

A person after bath feels a sense of cooling due to evaporation of water from his body when exposed to air. The molecules of H_2O take away the energy of body. Earthenware vessels keep water cooler under the same phenomenon. Earthenware vessels are porous.

The water molecules having sufficient K.E to overcome inter molecular forces come out of these pores and evaporate. This process of evaporation keeps on taking place and energy required for this process comes from the liquid. Thus, the average K.E of remaining water molecules decreases which results in decrease in temperature of the liquid. Hence, earthenware vessels keep water cool.

Web version of PECTAA textbook
Not for sale

5.8 VAPOUR PRESSURE

The molecules of a liquid which leave the open surface are mixed up with air above the liquid. If the vessel is open these molecules go on leaving the surface of liquid. But if we close the system the molecules of liquid start gathering above the surface. These molecules collide with the walls of the container, and also with the surface of the liquid as well. There are chances that these molecules are recaptured by the surface of liquid. This process is called **condensation**. The two processes, i.e., evaporation and condensation continue till a stage reaches when the rate of evaporation becomes equal to the rate of condensation **Figure 5.9**.

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

$$\text{Liquid} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \text{Vapour}$$

The magnitude of vapour pressure does not depend upon the amount of liquid in the container or the volume of container. It does not depend on surface area of a liquid. The larger surface area presents a larger target for returning the molecules, so the rate of condensation also increases.

The vapour pressure of liquids having stronger intermolecular forces are lower and vice versa. with increase in temperature, the vapour pressure of a liquid also increases.

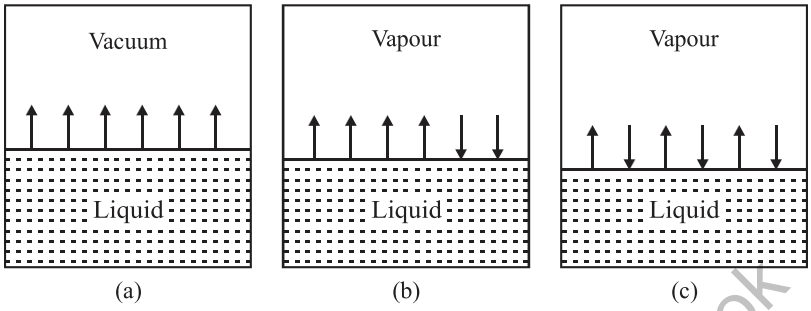


Figure. 5.9 Attainment of equilibrium when the evaporation of liquid is carried out in an evacuated closed vessel. (a) Initial state, with evacuated space above the liquid, (b) intermediate state, and (c) equilibrium state, when the rate of evaporation is equal to the rate of condensation.

Web version of PECTAA textbook
Not for sale

Quick Check 5.5

a) Which of the liquids in each of the following pairs has a higher vapour pressure?

i) Alcohol, glycerine ii) Petrol, kerosene, iii) Mercury, water

b) Which one in each of the following pairs is more viscous: Glycerine or kerosene?

c) Separate portions of acetone and water at the same temperature are poured on your hands. Acetone feels colder. Account for this in terms of attractive forces.

d) Why evaporation gets faster at higher temperatures?

e) Why do we feel cool near the bank of a river?

5.9 BOILING POINT

When a liquid is heated, its vapour pressure goes on increasing. A stage reaches when the vapour pressure of the liquid becomes equal to the atmospheric or external pressure. At this temperature the liquid starts boiling. The reason for this is that the bubbles of vapour which are formed in the interior of the liquid have greater internal pressure than atmospheric pressure on the surface of liquid. This makes the bubbles to come out of the liquid and burst at the surface. A constant stream of bubbles comes out at the boiling point of the liquid.

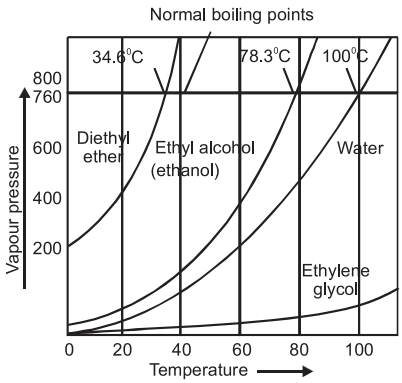


Figure 5.10 Vapour pressures (torr) of four common liquids shown as a function of temperature.

When a liquid is heated, the kinetic energy of its molecules increases. This causes the increase of the temperature. At the boiling point, the kinetic energy of the molecules becomes maximum. Any further heating at this stage will not increase the temperature.

This further heating is utilized to break the intermolecular forces and convert the liquid into its vapour. The boiling points of some commonly available liquids at one atmospheric pressure are shown in the **Table 5.3**.

The **Figure 5.10** shows the variation of vapour pressure of water, ethyl alcohol, ethylene glycol and diethyl ether with temperature. The graphs show that the liquids reach upto their boiling points when their vapour pressures are equal to 760 torr at sea level.

5.9.1 Factors affecting boiling points of liquids

The boiling point of a liquid is affected by the factors given below.

1) Strength of intermolecular forces

Stronger the intermolecular forces, lower will be the vapour pressure and higher will be the boiling point. Higher boiling point of H_2O indicates stronger intermolecular forces than that of ethanol and methanol, **Table 5.3**.

Table 5.3 Boiling points of some common liquids at 760 torr (1 atm.)

Liquids	Formula	B.P (°C)	Liquids	Formula	B.P (°C)
Acetic acid	CH_3COOH	118.50	Carbon tetrachloride	CCl_4	76.50
Acetone	CH_3COCH_3	56.00	Ethanol	C_2H_5OH	78.30
Benzene	C_6H_6	80.15	Naphthalene	$C_{10}H_8$	218.00
Carbon disulphide	CS_2	46.30	Water	H_2O	100.00

2) External pressure

As already explained that when vapour pressure of a liquid becomes equal to the external pressure then the liquid boils. It means that when external pressure is changed, its boiling point will also change. When the external pressure is high the liquid requires greater amount of heat to equalize its vapour pressure to external pressure. In this way boiling point is raised. Similarly, at a lower external pressure a liquid absorbs less amount of heat and it boils at a lower temperature.

For example, water shows B.P of 120°C at 1489 torr pressure and boils at 25°C at 23.7 torr. Water boils at 98°C at Murree hills due to external pressure of 700 torr while at the top of Mount Everest water boils at only 69ºC at 323 torr.

We can increase the external pressure artificially on the surface of boiling water by using a pressure cooker. Pressure cooker is a closed container. The vapour of water formed is not allowed to escape. In this way, it exerts more pressure on the water surface in the cooker and the boiling temperature increases. As more heat is absorbed in water, so food is cooked quickly under increased pressure.

Web version of PCTAA textbook
Not for sale

Quick Check 5.6

a) Why food cooking is difficult in the areas with high altitudes?

b) The food cooks faster in the pressure cooker, explain.

c) Why the boiling point of water (100 °C) is higher than that of ethanol (78 °C), although both have hydrogen bonds?

5.10 ENERGETICS OF PHASE CHANGES

Whenever, matter undergoes a physical change, it is always accompanied by an energy change. This change in energy is the quantitative measurement of the difference in the strength of intermolecular forces.

Molar heat of fusion (ΔH_f)

The amount of heat absorbed by one mole of a solid to melt it into the liquid at its melting point at 1 atmospheric pressure is called molar heat of fusion.

$$H_2O_{(s)} \longrightarrow H_2O_{(l)} \quad \Delta H_f = 4.6 \text{ kJ mol}^{-1}$$

Heat of fusion plays a significant role in the study of glaciers and ice sheets. Heat of fusion determines the energy required for ice to melt. As water has high heat of fusion, ice requires a lot of energy to melt. Due to the low melting, glaciers gather mass which limits their flow. Also, it causes accumulation of ice on the earth poles, known as polar ice caps. Polar ice caps are important in regulating the earth's temperature by reflecting the sunlight. These ice caps also help regulate sea levels by storing fresh water ice. Both the ice caps and icebergs are stable due to the high heat of fusion of water. If the heat of fusion of water were low, melting of glaciers and ice caps would result in drastic changes in the sea and earth's ecosystems.

Molar heat of vaporization (ΔH_v)

The amount of heat absorbed by one mole of a liquid to convert it into one mole of vapour at its boiling point at 1 atmospheric pressure is called molar heat of vapourization.

The molar heats of vaporization depends upon the strength of intermolecular forces. When one mole H_2O is converted to vapour at 100ºC, then heat absorbed is **40.6 kJ mol^{-1}**.

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \quad \Delta H_v = 40.6 \text{ kJ mol}^{-1}$$

NH_3 and HCl only need 21.7 and 15.6 kJ mol^{-1} respectively to become vapours at their boiling points. This difference is due to the stronger intermolecular forces in water.

Effect of Molar heat of vaporization and fusion on matter particles

The molar heat of fusion and vaporization affect the particles that make up matter by providing them with enough energy. Due to this, the particle move away from one another and change the state of the substances from solids to liquids and liquids to gases respectively. Particles gain more freedom to move and rotate in the liquid and gas phases.

Web version of PCTAA textbook
Not for sale

5.11 SOLIDS

Solids are those substances which are rigid, hard, have definite shape and definite volume. The atoms, ions and molecules that make up a solid are closely packed. They are held together by strong cohesive forces. The constituent atoms, ions or molecules of solids cannot move at random.

5.11.1 General Properties of Solids

i) Compression of solids

The atoms, molecules or ions of a solid substance are closely packed. The particles of solids cannot move closer to each other unlike gases. It is true for metallic solids that their atoms are spherically symmetrical. So, when such particles are arranged, they can give birth to hexagonal and cubic close-packed structures. Here outer boundaries of constituent particles touch each other but due to their spherical shapes, they cannot occupy more than 74% space. It means the compression of solids is not possible.

ii) Expansion of solids

The expansion is the property in which spaces between constituent particles are increased. In case of solids the forces of attractions are so strong that increase of temperature hardly affects their relative positions. The particles in a solid have vibrational motions about their mean positions. Increase in temperature of solids hardly increases their volume. No doubt, there are parameters like **coefficient of linear** and **cubic expansions** of various solids, but these are negligible as compared to liquids and gases.

iii) Motion of particles in solids

The constituent particles of a solid do not undergo translatory motion and rotational motion. They only vibrate about their mean positions. These vibrations become more intense at higher temperature.

iv) Inter-particle space in solids

The interparticle spaces in solids are far less than liquids. This is due to the stronger forces among their particles. Due to closely packed atoms, molecules, and ions, solids are mostly hard, have high melting points and high stability.

v) Inter-particle forces in solids

In solids, the particles (atoms, ions, molecules) are held together by ionic, covalent, metallic or van der Waals forces. These forces are strong enough to fix the particles at their places thus allowing these particles to just vibrate about their mean positions.

vi) Kinetic energy based on KMT

Kinetic energy is due to the motion of constituent particles of a solid. Solid particles have only vibratory motion and they do not have translational or rotational motion. Therefore, the only kinetic energy that solids possess is vibrational kinetic energy.

Web version of PECTAA textbook
Not for sale

5.12 TYPES OF SOLIDS

There are two types of solids on the basis of the way their particles are arranged;

i. Crystalline solids

ii. Amorphous solids.

5.12.1 Crystalline Solids

Crystal lattice

The regular arrangement of ions, atoms, or molecules in three dimensional space is called the crystall lattice.

The solids which have definite regular and three dimensional geometric shapes are called crystalline solids. For example, diamond, sodium chloride, ice, etc.

Properties of crystalline solids

i. Geometrical shape

All the crystalline solids have a definite, distinctive geometrical shape due to definite and orderly arrangement of atoms, ions or molecules in three-dimensional space. For a given crystal, the interfacial angles, at which the surfaces intersect, are always the same no matter in which shape they are grown. The faces and angles remain characteristic even when the material is ground to a fine powder.

ii. Melting points

Crystalline solids have sharp melting points. They can be identified from their definite melting points.

iii. Cleavage planes

Whenever the crystalline solids are broken they do so along definite planes. These planes are called the cleavage planes and they are inclined to one another at a particular angle for a given crystalline solid. The value of this angle varies from one solid to another solid.

iv. Growing of a crystal

When we have a saturated or super saturated solution of a crystalline material in a suitable solvent, it can give us same types of crystals by arranging atoms, ions or molecules. This happens through the process called **growth of crystals**. This can be done by slow evaporation of the solvent or by seeding process from saturated solution.

For example, the solubility of sodium thiosulphate ($Na_2S_2O_3$) in water at 100°C is 231g/100 cm^3. At room temperature, the solubility is 50 g / 100 cm^3. In case, we have saturated solution of $Na_2S_2O_3$ at 100°C, on cooling slowly no growth of crystal happens. It means that super saturated solution is not in equilibrium with solid substance. Now, if small crystal of $Na_2S_2O_3$ is added to super saturated solution, the crystallization happens rapidly.

Web version of PCTA textbook
Not for sale

v. Habit of a crystal

The shape of a crystal in which it usually grows is called habit of a crystal. If the conditions for growing a crystal are maintained, then the shape of the crystal always remains the same. If the conditions are changed the shape of the crystal may change. For example, a cubic crystal of NaCl becomes needle like when 10% urea is present in its solution as an impurity.

5.12.2 Amorphous solids

Amorphous solids, contrary to the crystalline solids, do not possess regular three dimensional geometrical shapes. The examples of amorphous solids are glass, wood, amorphous sulphur (plastic sulphur), charcoal, coal, coke, etc.

Properties of amorphous solids:

i. The amorphous solids can have small regions where orderly arrangement of particles is found, but they do not have long range of regularity. The regions where orderly arrangement of particles is present are known as crystallites.

ii. Amorphous solids like glass melts over a wide temperature range.

iii. They can be molded and blown to form different shapes.

iv. Amorphous solids do not have **definite value of heat of fusion**.

Table 5.4 Comparison of crystalline and amorphous solids.

Property	Crystalline solids	Amorphous solids
1. Geometry of solid	Crystalline solids show characteristic geometrical shapes.	Amorphous solids generally appear in lump or in a fine powder form.
2. Melting of solid	Crystalline solids melt sharply at their melting points.	Amorphous solids do not have sharp melting points and they melt over a range of temperature.
3. Directional character of the properties	Crystalline solids are anisotropic in nature. It means that their properties depend upon the direction along which the measurements are made.	Amorphous solids are isotropic. Their properties do not depend upon the direction of measurement.
4. Order of particles in solid	Crystalline solids have long-range order.	In amorphous solids, long-range order is absent.

Web version of PCTAA textbook
Not for sale

Quick Check 5.7

a) Why solids have very low compressibility and expansion?

b) What is meant by habit of a crystal?

c) Why solids do not undergo translatory motion?

5.13 LIQUID CRYSTALS

We know that the distinction between liquids and solids is clear-cut. Moreover, the phase transition between them is always sharply defined. However, at certain temperature, many substances exist in a phase that is neither fully liquid nor fully solid. The molecules in these substances can move around, as in viscous liquids, but have a restricted range of motion, as in solids. These substances are called **liquid crystals**.

Crystalline solid ⟶ Cloudy liquid (liquid crystal) ⟶ Clear liquid

In most liquid crystals, the molecules have a rigid, rod-like shape with a length four to eight times greater than their diameter. When packed together, the molecules tend to orient with their long axes roughly parallel, like logs in a stack of firewood. Individual molecules can migrate through the fluid. They can spin around their long axis, but they can't rotate end over end.

5.13.1 General properties of liquid crystals

The general properties of liquid crystals are as follows:

Liquid crystals:

i) have parallel ordered arrangement.
ii) are elongated, rod-like and linear
iii) flow like liquids
iv) show viscosity like liquids.
v) show optical properties like crystals.
vi) are somewhat rigid.
vii) are always anisotropic.

5.13.2 Uses of liquid crystals in daily life

The main application area of liquid crystals is in **electro-optic devices**. These are electrically controlled devices that **modulate light** in a desired way. Liquid crystals have many uses in daily life.

i) In diagnostics

Special liquid crystal devices can be used to diagnose the tumors and infections in the human body. This is because often physical problems, such as tumors, have a different temperature than the surrounding tissue. When cholesteric liquid crystals are applied to the breast, a tumor is located because of being warmer than the other parts. This technique is successfully applied to diagnose breast cancer in the early stage.

ii) Characteristic higher temperature determination

Liquid crystal temperature sensors can also be used to find faulty connections on a circuit board by detecting the characteristic higher temperature. As temperature sensors, they are used in thermometers.

iii) Liquid crystal displays (LCDs)

The most common application of liquid crystal technology is liquid crystal displays (LCDs). LCDs are used in the screens of T.Vs, computers, mobiles, etc.

Web version of PECTAA textbook
Not for sale

Quick Check 5.8

a) Name the properties of liquid crystals in which they resemble solids.

b) Mention the properties of liquid crystals in which they resemble liquids.

c) Which property of liquid crystals make it possible to use them in temperature sensing devices?

EXERCISE

MULTIPLE CHOICE QUESTIONS

Q.1 Four choices are given for each question. Select the correct choice.

I. London dispersion forces are the only forces present among:

a) molecules of water in liquid state

b) atoms of helium in gaseous state at high temperature

c) molecules of solid iodine

d) molecules of hydrogen chloride gas

II. When the vapour pressure of a liquid equals the external pressure, what phenomenon occurs?

a) Sublimation b) Condensation

c) Boiling d) Freezing

III. When water freezes at 0 ^{o}C, its density decreases due to:

a) cubic structure of ice

b) empty spaces present in the structure of ice

c) decrease in volume

d) decrease in viscosity

IV. Which of following is the correct sequence of increasing ΔH_V values of substances mentioned?

a) $H_2O > NH_3 > F_2$ b) $F_2 > NH_3 > H_2O$

c) $NH_3 > H_2O > F_2$ d) $H_2O > F_2 > NH_3$

V. Surface tension of a liquid is due to:

a) inward pull of surface molecules b) upward pull from the surface

c) collision of molecules d) repulsive forces

VI. Which change of state involves overcoming only London dispersion forces?

a) Melting of ice ($H_2O_{(s)} \rightarrow H_2O_{(l)}$)

b) Boiling of ethanol ($CH_3CH_2OH_{(l)} \rightarrow CH_3CH_2OH_{(g)}$)

Web version of PECTAA textbook
Not for sale

c) Sublimation of iodine ($I_{2(s)} \rightarrow I_{2(g)}$)

d) Dissolving sodium chloride in water

VII. In which of the following substances are London dispersion forces the only significant intermolecular forces present?

a) Ammonia (NH_3)

b) Water (H_2O)

c) Methane (CH_4)

d) Hydrogen fluoride (HF)

VIII. Which of the following is a characteristic property of crystalline solids?

a) They have a range of melting points.

b) They are isotropic.

c) They have a definite and sharp melting point.

d) They lack a regular arrangement of particles.

IX. Which of the following liquids would you expect to have the highest viscosity at a given temperature?

a) Water (H_2O)

b) Ethanol (CH_3CH_2OH)

c) Diethyl ether ($CH_3CH_2OCH_2CH_3$)

d) Glycerol ($CH_2(OH)CH(OH)CH_2(OH)$)

X. Which type of intermolecular force is present in all types of molecule regardless of their polarity?

a) Dipole-dipole forces

b) Hydrogen bonds

c) London dispersion forces

d) Ion-dipole forces

XI. Liquid crystals exhibit properties:

a) Only like solids.

b) Only like liquids.

c) Between solids and liquids.

d) Unlike solids or liquids.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions

a. Explain, at the molecular level, why evaporation leads to a cooling effect.

b. Explain why liquids with stronger intermolecular forces tend to have lower rates of evaporation at a given temperature compared to liquids with weaker intermolecular forces.

c. One feels sense of cooling under the fan after bath. Explain.

d. How a dynamic equilibrium is established during evaporation of a liquid in a closed vessel at constant temperature?

e. The boiling point of water is different at Lahore and Murree hills.

f. Discuss two significant consequences of the lower density of ice compared to liquid water in natural environments.

g. Why B.P of a liquid increases when the external pressure rises?

h. Mention four items in which liquid crystals are used.

i. How do you differentiate between crystalline solids and amorphous solids?

Web version of PCTAA textbook
Not for sale

j. Propanone (CH_3COCH_3), propanol ($CH_3CH_2CH_2OH$) and butane ($CH_3CH_2CH_2CH_3$) have very similar relative molecular masses. List them in the expected order of increasing boiling points. Explain your answer.

k. Discuss how hydrogen bonding is responsible for the relatively high surface tension of water.

l. What type of intermolecular forces will dominate in the following liquids?

(i) NH_3 (ii) Ar (iii) CH_3COCH_3 (iv) CH_3OH

m. The boiling points and molar masses of hydrides of some first-row elements are tabulated below. Suggest reasons for the difference in their boiling points in terms of the type of molecules involved and the nature of the forces present between them.

Substance	Boiling Point (K)	Molar Mass (g mol^{-1})
CH_4	112	16
NH_3	240	17
H_2O	373	18

DESCRIPTIVE QUESTIONS

Q.3. What are London dispersion forces? Give examples, and discuss the factors affecting these forces.

Q.4 Hydrogen bonding is present in H_2O, NH_3, HF, $(CH_3)_2CO$ and $CHCl_3$ molecules. Sketch structures and discuss briefly.

Q.5 Discuss the structural changes when water turns into ice. Justify the empty spaces in its crystals as compared to H_2O at 4°C and lower density of ice.

Q.6 How liquid crystals resemble liquids and solids? Give their uses in daily life.

Q.7 Describe the following properties of crystalline solids.

i) Geometrical shape ii) Melting point

iii) Cleavage plan iv) Habit of a crystal

NUMERICAL PROBLEMS

Q8. A sample of an unknown gas has a mass of 0.560 g. It occupies a volume of 2.87×10^{-4} m^3 at a temperature of 300 K and a pressure of 1.01×10^5 Pa. Calculate the molar mass of the gas. (Gas constant, $R=8.31 JK^{-1}mol^{-1}$)

Q9. In a laboratory experiment, 150 cm^3 of a volatile liquid was completely vaporized at 98 °C and a pressure of 1.01×10^5 Pa. The mass of the vapor was found to be 0.495 g. Determine the molecular mass of the liquid ($R = 8.314$ J K^{-1} mol^{-1}).

Web version of PECTAA textbook
Not for sale