Illustration - 21 *A gaseous mixture of helium and oxygen is found to have a density of 0.518 g dm^{-3} at 25°C and 720 torr. What is the per cent by mass of helium in this mixture ?*

SOLUTION :

We know, $PM_o = dRT$

$$\Rightarrow \frac{720}{760} \times M_o = 0.518 \times 0.0821 \times 298$$

$$\Rightarrow M_o = 13.37 \text{ g/mol}$$

Let mole fraction of He in mixture be α.

$$\Rightarrow \chi_{He} = \alpha, \quad \chi_{O_2} = (1-\alpha)$$

Average molecular mass $= \alpha \times M_{He} + (1-\alpha) M_{O_2}$

$$\Rightarrow 13.37 = \alpha \times 4 + (1-\alpha)\,32$$

$$\Rightarrow \alpha = 0.666$$

$$\% \text{ by mass of He} = \frac{0.666 \times 4}{0.666 \times 4 + 0.334 \times 32} \times 100 = 19.95\%$$

THE LIQUID STATE Section - 5

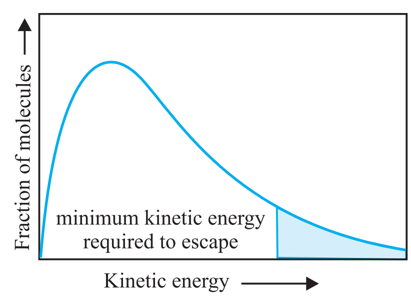
The liquid state is intermediate between gaseous and solid states. In the gaseous state the molecular interactions are very weak practically negligible and molecules are in random motion. Molecules continue to move unless they are reflected back by the walls of the vessel. Otherwise molecules would continue to move and the gas would expand to any volume. This is why gases do not have a definite volume.

In case of liquid, the molecular interactions are quite strong and a given quantity of liquid occupies a definite volume. Molecules of the liquid have so much freedom that they can flow readily and take up the shape of the container due to continuous breaking and making of weak van der Waal's bonds between the neighbouring molecules.

Molecules in solids completely lack in translation motion. The thermal motion of the molecules is so greatly reduced that they can only oscillate with respect to their fixed positions in the crystals. Each molecule in a solid has generally 6 to 12 nearest neighbours called coordination number. In the liquid state the coordination number of a molecule is not fixed but is only slightly less than in solid. The distance between the nearest neighbours in liquid is only slightly higher than that in solids. This is why there is very little expansion of solids on melting.

Vapour Pressure

The kinetic theory is the idea that there is distribution of kinetic energies and hence the molecular speeds, depending on the absolute temperature. Therefore, in any gas, liquid or solid at room temperature, a small fraction of molecules have relatively high kinetic energy. Some of these high energy molecules at the liquid surface become free resulting into its evaporation. With the departure of high energy molecules the average kinetic energy decreases leading to a fall in temperature of the liquid. This explains why evaporation causes cooling.



In a closed vessel, some free space above the liquid, the evaporated molecules cannot escape to the atmosphere. Initially the vapour pressure increases and then comes to a constant value. The volume of the liquid decreases initially and then becomes constant over a period of time. Increase in pressure means more number of collisions with the walls of the container.

Inside a closed vessel, the liquid and its vapours are in *dynamic equilibrium.* The pressure exerted by the vapours is then known as *equilibrium vapour pressure*. Since the vapour pressure is a kinetic phenomena, it is independent of the amount of a liquid .It only depends on the temperature. The temperature must, therefore, be specified with the vapour pressure of a liquid.

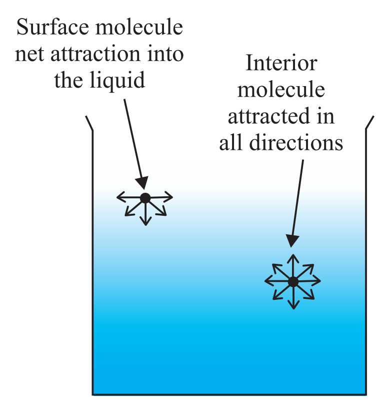
A liquid is said to be at its boiling temperature if its vapour pressure is equal to external pressure. Therefore, the boiling point of water in particular and of liquids in general decreases as altitude of a place increases where the external pressure is less than one atmospheric pressure.

Vapour pressure of solids

When a solid is directly converted to its vapour state, then the process is called *sublimation*. Substances like ammonium chloride, iodine, camphor, solid carbon dioxide sublime at ordinary temperature and pressure. The white cloud like trail that we see coming out of the high flying jet is water vapours issuing from the exhausts of high flying jets, getting converted directly into microcrystalline ice which is slowly reconverted into water vapour without passing through the liquid state. This property of sublimation is used in the process called **freeze drying.**

Surface Tension

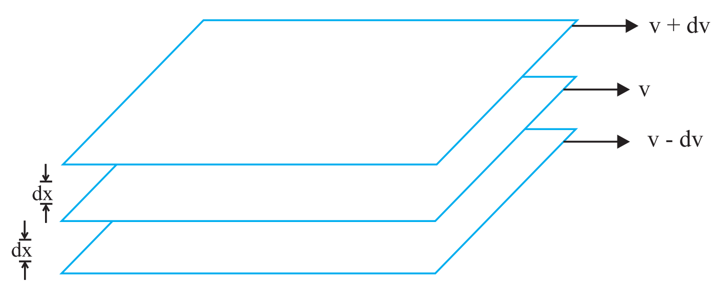
Surface tension is one of the characteristic properties of liquids. Each molecule in the liquid state is influenced by the nearest neighbour molecules. A molecule in the bulk of liquid experiences equal attractive forces from all sides. There is no resultant force on the molecule which tries to move it in any direction, whereas for a molecule at the surface of the liquid, the net attraction towards the liquid is greater than that towards the vapour state.



The energy required to increase the surface area of the liquid by one unit, is defined as its surface tension. It is represented by the *Greek letter* γ (gamma). The liquid surface, in the absence of any other force tends to attain a minimum area. Mathematically it can be shown that for a given volume, the sphere has a minimum area. Hence the water drop acquires a spherical shape. Liquid in a capillary tube rises due to its surface tension. Surface tension is also defined as the force acting per unit length perpendicular to the line drawn on the surface. The units of surface tension is Nm^{-1} .

Viscosity of liquids

The ease with which a fluid can flow is determined by its property called *viscosity*. Viscosity arises due to the internal friction between layers of fluids as they pass over each other. When a liquid is steadily flowing over a fixed horizontal surface the layer immediately in contact with the surface is stationary. The velocity of the layers increases with the distance from the fixed surface. if we select a layer, the layer immediately below tries to retard its flow(velocity),while the one above tries to accelerate the flow. Force required to maintain the flow in the three layers described above is directly proportional to the area of contact and velocity gradient.



Velocity gradient = dv/dx

Frictional force, $F \propto A\left(\frac{dv}{dx}\right)$

Force is proportional to area in contact and velocity gradient, i.e.,

$F \propto A$ (Area) ......(i)

and $F \propto \frac{dv}{dx}$ (velocity gradient) ......(ii)

On combining (i) & (ii) , we get : $F \propto \frac{dv}{dx}$

$\Rightarrow \quad F = \eta A \frac{dv}{dx}$

where η is a constant, called as the coefficient of viscosity and it has the unit of poise, g $cm^{-1}s^{-1}$.

THE SOLID STATE Section - 6

The substance is said to be in solid state if the molecular interaction energy predominates over the disruptive thermal energy.

Covalent Solids

A covalent solid is a giant molecule having a three dimensional network of covalent bonds. Examples are diamond, silicon carbide, silica. These are generally very hard.

Ionic Solids

Ionic solids are three dimensional arrangements of cations and anions bound by coulombic forces .The crystal on the whole are electrically neutral. Such solids are characterized by high melting and boiling points. The ionic solids do not conduct electricity as ions present therein are not free to move. Examples are sodium chloride, barium oxide and calcium fluoride.

Metallic Solids

Metals are orderly collection of positive ions surrounded by and held together by free electrons, each metal atom donating one or more electrons. The bonding is not directional. The metals are good conductors of heat and electricity. They are highly malleable and ductile. These sets of properties can be attributed to this structure of metals. Metals like sodium crystallize- in simple cubic lattice. The presence of a sea of mobile electrons in a metal accounts for its high electrical and thermal conductivity.

Molecular Solids

Many combinations of elements result into covalent molecules. These are discrete units capable of independent existence. Thus we have molecules like di-hydrogen, di-nitrogen, methane etc. which are called covalent compounds. They have weak molecular interaction. Even mono-atomic molecules like the noble gases, form molecular solids. These solids are characterized by low melting points.