

Liquid State (2nd Sem CBCS H62)

Introduction:

Any substance which can melt at a temperature lower than room temperature i.e. 25°C is said to be liquid. While those substances which can boil at a temperature lower than room temperature are called gas.

The distinction between solids and liquids arises from different configuration at absolute zero. At absolute zero, atoms, molecules or ions are in a perfect crystal and in a regular space lattice. As the temperature is raised the vibrational motion achieve high amplitudes so that the ordered lattice structure breaks down abruptly. This phenomenon is called melting. At any temperature there is a competition between the intermolecular attraction which tends to produce orderly motion and the kinetic energy which tends to destroy the arrangement and produce the liquid.

If we consider a particular molecule in a liquid, its immediate neighbour will not be grouped around it in a completely random process, but will be arranged that shows some resemblance to the structure in the solid. The next nearest neighbours show a much smaller degree of order. Liquids, therefore exhibit short range order. The fluidity of liquid arises as a result of absence of long range order.

Physical properties of liquids:

The most important physical properties of liquids are —

- ① Vapour pressure
- ② Surface tension

- ③ Viscosity
- ④ Refraction.

Surface Tension:

The force that tends to contract the surface of a liquid is known as surface tension.

Let us consider a liquid in equilibrium with its vapour. Molecules at the surface of the liquid experience fewer attractions from other liquid phase molecules compared with the molecules in the bulk liquid phase and would have higher potential energy of the molecules in the bulk.

In order to increase the area of the liquid-vapour interface, work must be done. Since, such an increase means fewer molecules in the bulk and more in the surface layer, the systems tend to assume a configuration of minimum surface area. Thus an isolated drop of liquid is spherical. Since, the sphere is the shape with minimum ratio of surface area to volume.

Let, σ be the area of interphase between two faces α and β . The no. of molecules in the interface region is proportional to σ . If we want to increase the area by $d\sigma$, then dW amount of work is needed.

$$\therefore dW \propto d\sigma$$

$$\Rightarrow dW = \gamma \cdot d\sigma$$

The quantity γ is called interfacial tension or surface tension.

Effects of surface tension:

Tendency of a liquid to rise up of capillary tube is consequence of surface tension.

Let a glass capillary is emerged in a liquid which

has a tendency to stick to the wall. The energy is lowest when a thin film covers as much as possible. As this film creeps up inside the wall it has the effect of curving the surface of the liquid inside the tube. As a result of this, the pressure just beneath the curving meniscus is less than the atmospheric pressure by $\frac{2\gamma}{r}$ where r is the radius of the tube. The excess external pressure forces the liquid to climb up the tube until hydrostatic equilibrium is reached. The equilibrium is established when a column of liquid of density ρ has reached at a height h such that,

$$\frac{\rho \pi r^2 h g}{\pi r^2} = \frac{2\gamma}{r}$$

$$\Rightarrow \boxed{h = \frac{2\gamma}{r \rho g}}$$

Effect of Temperature on Surface Tension:

According to the kinetic theory, molecular kinetic energy is proportional to absolute temperature. Therefore, increase in molecular energy increases the temperature of a liquid. Since, intermolecular forces decrease with increase in the energy of molecules, the intermolecular forces of attraction decrease with rise in temperature. Hence, surface tension of a liquid decreases with rise in temperature.

Eotvos suggested the following expression for the variation of surface tension with temperature:

$$\gamma (M/\rho)^{\frac{2}{3}} = a - kt. \quad \longrightarrow \text{①}$$

where M is molar mass, ρ is density and γ is surface tension

of the liquid at temperature t , 'a' and 'k' are constants.

When $t = t_c$, $\gamma = 0$.

$$\therefore \text{Eqn (1)} \Rightarrow 0 = a - kt_c$$

$$\Rightarrow a = kt_c \quad \text{--- (2)}$$

\therefore Eqn (1) can be written as,

$$\gamma (M/\rho)^{\frac{2}{3}} = k(t_c - t)$$

\therefore Surface tension varies roughly \propto above the critical temp rather than at the critical temperature, Ramsay and Shields proposed the following equation for the temperature dependence of surface tension:

$$\gamma (M/\rho)^{\frac{2}{3}} = k(t_c - t - b)$$

Determination of Surface Tension by Stalagmometer method
or Drop number method:

A stalagmometer consists of a pipette like tube having a smooth capillary end. It is filled with the liquid up to the mark M by sucking the upper end of the tube. The liquid is then allowed to come down in the form of drops. The size of the drops depends on the radius of the capillary tube and on the surface tension of the liquid. The drop is supported



Fig: Stalagmometer

by the force of surface tension = $2\pi r\gamma$ where r is the radius of the drop. The drop falls when the weight of the drop mg just exceeds the force of surface tension.

At equilibrium,

$$2\pi r\gamma = mg$$

For drops of two liquids having weights w_1 and w_2 and masses m_1 and m_2 and surface tensions γ_1 and γ_2 ,

$$m_1 g = 2\pi r \gamma_1 \longrightarrow \textcircled{i}$$

$$m_2 g = 2\pi r \gamma_2 \longrightarrow \textcircled{ii}$$

$$\textcircled{i} \div \textcircled{ii} \Rightarrow \frac{m_1 g}{m_2 g} = \frac{2\pi r \gamma_1}{2\pi r \gamma_2}$$

$$\Rightarrow \frac{m_1}{m_2} = \frac{\gamma_1}{\gamma_2} \longrightarrow \textcircled{iii}$$

Let, n_1 and n_2 be the number of drops formed from the same volume V of the two liquids.

Now, density = $\frac{\text{mass}}{\text{volume}}$

$$\therefore \rho_1 = \frac{m_1 n_1}{V}$$

$$\text{and } \rho_2 = \frac{m_2 n_2}{V}$$

$$\Rightarrow m_1 = \frac{\rho_1 V}{n_1} \longrightarrow \textcircled{iv}$$

$$\Rightarrow m_2 = \frac{\rho_2 V}{n_2} \longrightarrow \textcircled{v}$$

Substituting the values of m_1 and m_2 in eqn \textcircled{iii} , we get,

$$\frac{\frac{\rho_1 V}{n_1}}{\frac{\rho_2 V}{n_2}} = \frac{\gamma_1}{\gamma_2}$$

$$\Rightarrow \boxed{\frac{\rho_1 n_2}{\rho_2 n_1} = \frac{\gamma_1}{\gamma_2}}$$

Note: S.I. unit of surface tension is $N m^{-1}$.

Viscosity:

Viscosity is defined as the resistance of a liquid to flow. Viscosity of the fluid is the measure of the frictional resistance it offers to an applied force.

If a fluid is flowing, the layer adjacent to the surface hardly moves. According to Newton's law of viscous flow, the frictional force resisting the relative motion of two adjacent layers in the liquid is proportional to the area 'A' and velocity gradient $\frac{dv}{dx}$.

$$\text{re. } F \propto A$$

$$F \propto \frac{dv}{dx}$$

$$\therefore F \propto A \left(\frac{dv}{dx} \right)$$

$$\Rightarrow \boxed{F = -\eta A \left(\frac{dv}{dx} \right)} \quad \text{--- } \textcircled{1}$$

Here, η is a proportionality constant known as coefficient of viscosity. The reciprocal of viscosity is fluidity, re. Fluidity, $\phi = \frac{1}{\eta}$. The negative sign in eqn $\textcircled{1}$ shows that viscous force on the faster layer is in the opposite direction to its motion.

Units of Viscosity:

S.I. unit is $\text{Nm}^{-2}\cdot\text{s}$ or Pa.s.

C.G.S unit is $\text{dyne cm}^{-2}\cdot\text{s}$ or Poise.

Effect of Temperature on Viscosity: The "Hole Theory":

The viscosity of a liquid generally decreases with rise in temp which is explained with the help of "Hole Theory" of liquids. According to this theory, there are vacancies

or 'holes' in a liquid. The liquid molecules keep on moving continuously into these vacancies. As a consequence, the vacancies also keep on moving around as otherwise the liquid will not be able to flow. For this process to occur, liquid molecules need some activation energy. As activation energy becomes increasingly available at increasing temperatures, a liquid can flow more easily at higher temperatures. Thus, coefficient of viscosity falls appreciably with rise in temperature.

The relationship between coefficient of viscosity of a liquid and temperature is expressed mathematically as:

$$\eta = Ae^{E_a/RT}$$

where A and E_a are constants for a given liquid.

Determination of viscosity by Ostwald's viscometer method.

This method is based on

Poiseuille's eqⁿ,

$$\eta = \frac{\pi r^4 P}{8Vt}$$

where, P is the pressure, r is the radius of the capillary tube, t is the time of flow of liquid from C to D , l is the length of the capillary tube, V is the volume of the liquid. By this method, the viscosity of an unknown liquid

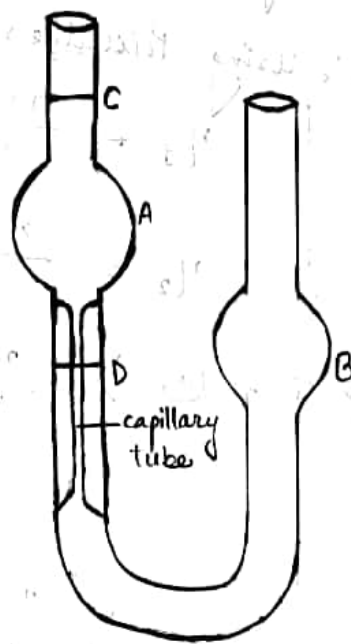


Fig: Ostwald's viscometer

can be calculated if the viscosity of one liquid is known.

Ostwald viscometer consists of a 'U-tube' having two bulbs A and B and also a capillary tube inside it. Before use, the viscometer is thoroughly cleaned by chromic acid and washed with water and then dried. A known volume of the liquid is put in the bulb B and then sucked into the bulb A, upto the mark C and then allowed to flow through the capillary tube upto the mark D. The time taken by the liquid to fall from C to D is noted. The experiment is repeated 3 times and the mean of the repeated time is taken. Let it be t_1 .

The viscometer is again cleaned, washed and dried. Now the same volume of another liquid (unknown) is taken to the bulb B and similar experiments are performed 3 times. In this stage let the time be t_2 .

∴ Using Poiseuille's eqⁿ,

$$\eta_1 = \frac{\pi r^4 t_1 \rho_1}{8Vr} \longrightarrow \textcircled{I}$$

$$\eta_2 = \frac{\pi r^4 t_2 \rho_2}{8Vr} \longrightarrow \textcircled{II}$$

$$\text{eqⁿ } \textcircled{I} \div \textcircled{II} \Rightarrow \frac{\eta_1}{\eta_2} = \frac{\frac{\pi r^4 t_1 \rho_1}{8Vr}}{\frac{\pi r^4 t_2 \rho_2}{8Vr}}$$

$$\Rightarrow \boxed{\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2}} \longrightarrow \textcircled{III}$$

∴ Hydrostatic pressure (P) is directly proportional to density (ρ),

$$\therefore \boxed{\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2}}$$