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11

Liquid State

CHAPTER

CONTENTS

We have seen that the molecules in a gas are in constant random motion. The spaces between them are large and the intermolecular attractions negligible. However, in a liquid the molecules are in contact with each other. The forces of attraction between the molecules are strong enough to hold them together. All the same, the molecules are able to move past one another through available intermolecular spaces. The molecules in a liquid move in a random fashion. At any instant the molecules may form clusters, leaving vacant space or 'hole' here and there. A molecule may be defined as : **a collection of molecules held close to each other and executing random motion through intervening spaces.**

Most of the physical properties of liquids are actually controlled by the strengths of intermolecular attractive forces. Therefore, before discussing the properties of liquids, we must have a look at the nature of intermolecular forces.

INTERMOLECULAR FORCES IN LIQUIDS

Intermolecular forces in liquids are collectively called **van der Waals forces**. These forces are essentially electrical in nature and result from the attraction of charges of opposite sign.

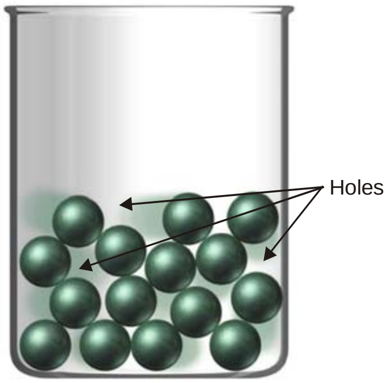


Figure 11.1
Molecular model of a liquid with holes indicated.

The principal kinds of intermolecular attractions are :

(1) Dipole-dipole attractions
(2) London forces
(3) Hydrogen bonding.

The relative size of these interactions is important so the relative effects are understood.

TABLE 11.1 : RELATIVE STRENGTHS FOR THE DIFFERENT INTERACTIONS

Covalent Bonds	Hydrogen Bonding	Dipole-Dipole Attractions	London Forces
400 kcal	12-16 kcal	2-0.5 kcal	Less than 1 kcal

Clearly normal covalent bonds are almost 40 times the strength of hydrogen bonds. Covalent bonds are almost 200 times the strength of dipole-dipole forces, and more than 400 times the size of London dispersion forces.

DIPOLE–DIPOLE ATTRACTIONS

Dipole-dipole attractions exist between molecules that are polar. This requires the presence of polar bonds and an unsymmetrical molecule. These molecules have a permanent separation of positive and negative charge. In the illustration the H and of HCl is permanently slightly positive charge. The Cl end of HCl has a permanent slight negative charge. The H atom in one molecule is attracted to the Cl in a neighbour. The intermolecular force is weak compared to a covalent bond, but this dipole-dipole interaction is one of the stronger intermolecular attractions.

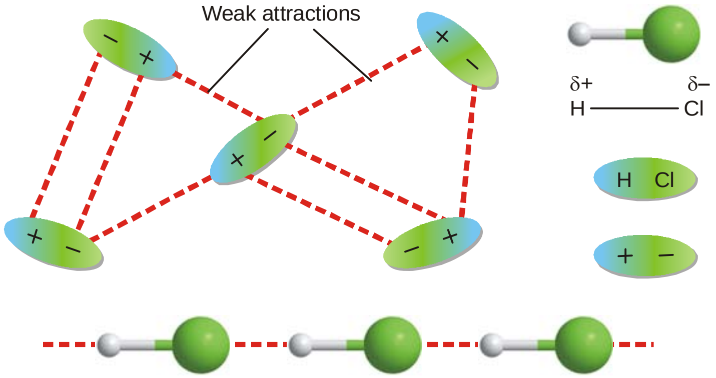


Figure 11.2
Weak attractions between polar HCl molecules.

LONDON DISPERSION FORCES

London dispersion forces exist in nonpolar molecules. These forces result from temporary charge imbalances. The temporary charges exist because the electrons in a molecule or ion move randomly in the structure. The nucleus of one atom attracts electrons form the neighbouring atom. At the same time, the electrons in one particle repel the electrons in the neighbour and create a short lived charge imbalance.

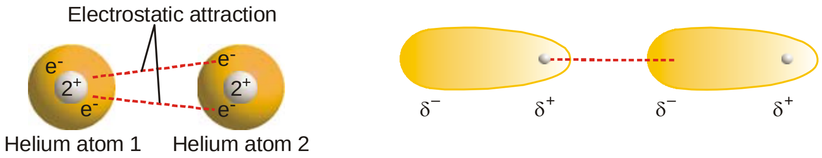


Figure 11.3
Explanation of London Forces.

These temporary charges in one molecule or atom attract opposite charges in nearby molecules or atoms. A local slight positive charge δ^+ in one molecule will be attracted to a temporary slight negative charge δ^- in a neighbouring molecule.

LONDON FORCES IN HYDROCARBONS AND ORGANIC MOLECULES

The temporary separations of charge that lead to the London force attractions are what attract one nonpolar organic molecule to its neighbours. The possibilities for these interactions go up with increasing molecular size and surface. The larger surface increases the chances for the "induced" charge separation. If the molecules are linear they have more surface area than if they are folded into a sphere. The linear molecules have higher melting and boiling points because of the increased attractions.

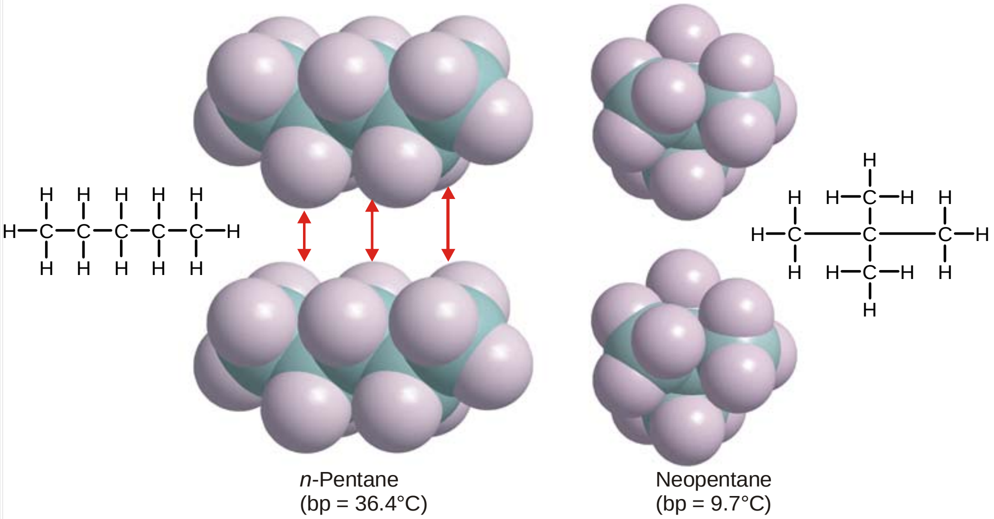


Figure 11.4
London Forces in hydrocarbons.

HYDROGEN BONDING

Hydrogen bonding is a unique type of intermolecular attraction. There are two requirements:

(1) Covalent bond between an H atom and either F, O, or N. These are the three most electronegative elements.

(2) Interaction of the H atom in this kind of polar bond with a lone pair of electrons on a nearby atom like F, O, or N.

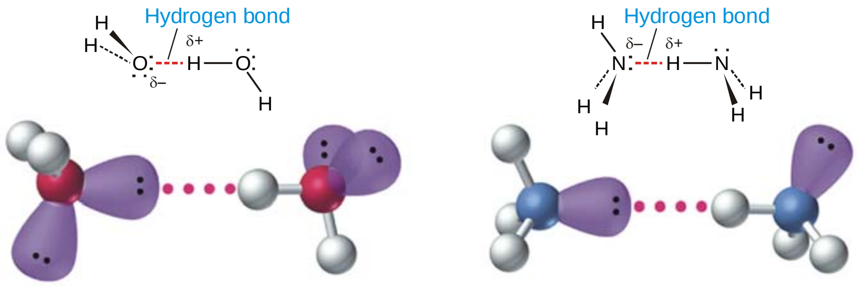


Figure 11.5
Hydrogen bonding in water and ammonia.

The normal boiling point for water is 100ºC. The observed boiling point is high compared to the expected value. The predicted boiling point from the trend of boiling points for H_2Te, H_2Se, H_2S and H_2O is very low. If the trend continued the predicted boiling point would be below –62ºC. The "anomalous" boiling point for water is the result of hydrogen bonding between water molecules.

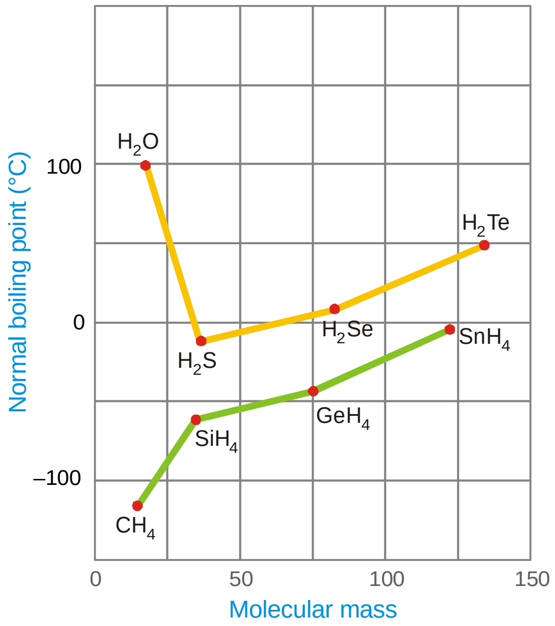


Figure 11.6
Effect of hydrogen bonding on boiling points.

Hydrogen bonding is responsible for the expansion of water when it freezes. The water molecules in the solid state have tetrahedral arrangement for the two lone pairs and two single bonds radiating out from the oxygen. The lone pairs on the "O" atom can be attracted to nearby water molecules through hydrogen bonds. A cage like structure results.

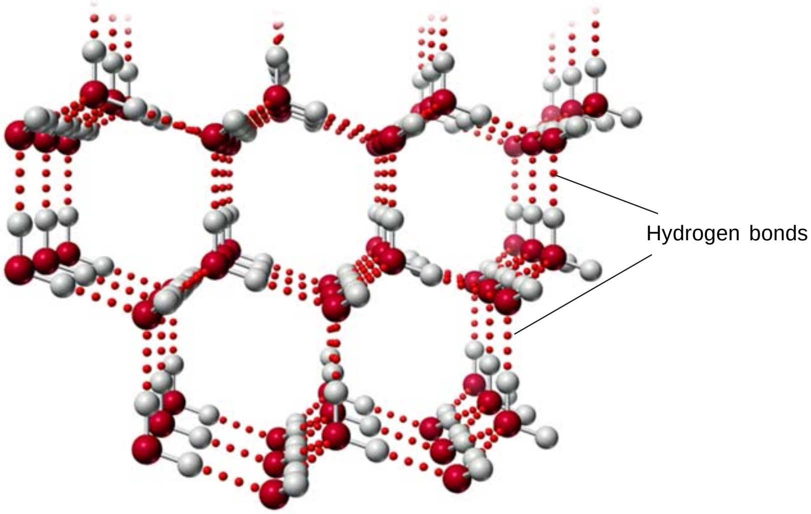
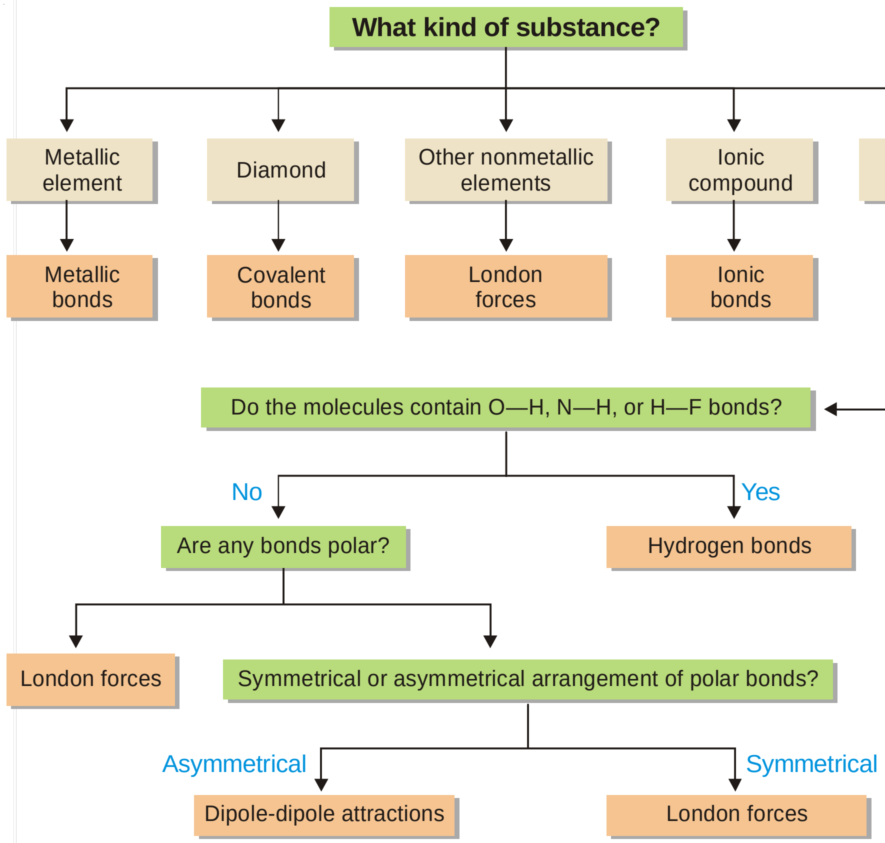
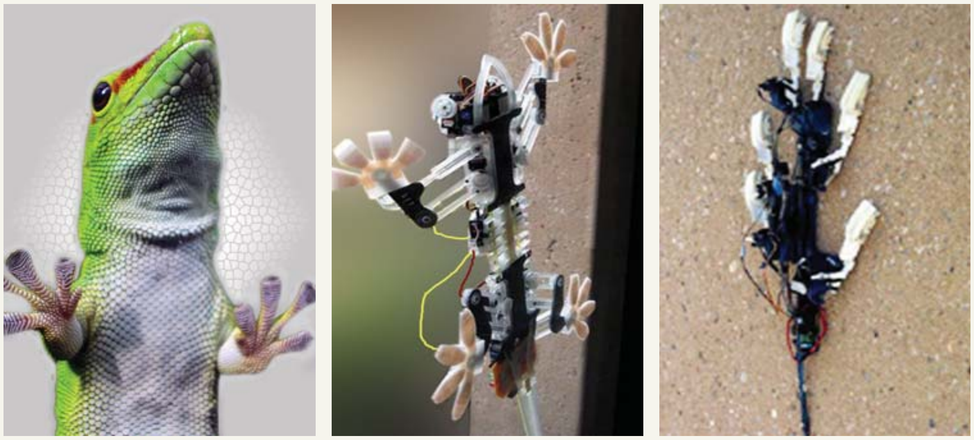


Figure 11.7
Hydrogen bonding in ice.

SUMMARY OF TYPES OF INTERMOLECULAR FORCES



GECKO-LIKE ROBOT WALKS–UP THE WALLS



Gecko-like robot developed in May, 2006 by Mark Cutkosky, Stanford University, USA

A Gecko-like robot with sticky feet could soon be scampering up a wall near you.

Geckos can climb up walls and across ceilings thanks to the millions of tiny hairs, or setae, on the surface of their feet. Each of these hairs is attracted to the wall by an intermolecular force called the van der Waals force, and this allows the gecko's feet to adhere.

Stickybot, developed in May, 2006, by Mark Cutkosky at Stanford University in California, has feet with synthetic setae made of an elastomer. These tiny polymer pads ensure a large area of contact between the feet and the wall, maximising the van der Waals forces. He is also developing gecko inspired climbing *gloves* and *shoes*. Gutkosky says a Stickybot-type robot would also make an adept planetary rover or rescue bot.

VAPOUR PRESSURE

When a liquid is placed in an open vessel, it evaporates. The molecules in the liquid are moving with different kinetic energies. The molecules that possess above-average kinetic energies can overcome the intermolecular forces that hold them in the liquid. These energetic molecules escape from the liquid surface as vapour. The process by which molecules of a liquid go into the gaseous state (vapours) is called **Vaporisation** or **Evaporation.** The reverse process whereby gas molecules become liquid molecules is called **Condensation.**

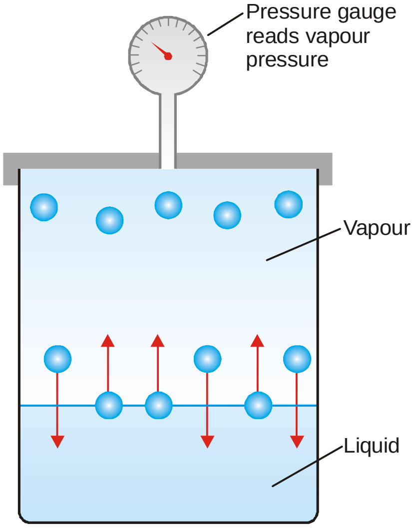


Figure 11.8
Illustration of vapour pressure.

If the liquid is placed in a closed vessel (Fig. 11.8.), the molecules with high kinetic energies escape into space above the liquid. As the number of molecules in the gas phase increases, some of them strike the liquid surface and are recaptured (condensation). A stage comes when the number of molecules escaping from the liquid is equal to the number of molecules returning to the liquid. In other words, the rate of evaporation exactly equals the rate of condensation. Thus a dynamic equilibrium is established between the liquid and the vapour at the given temperature.

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

Now the concentration of the vapour in the space above the liquid will remain unchanged with lapse of time. Hence the vapour will exert a definite pressure at the equilibrium. The vapour pressure of a liquid is defined as : **the pressure exerted by the vapour in equilibrium with the liquid at a fixed temperature.**

The vapour pressures of various liquids differ considerably, depending upon the identity of the liquid with its particular intermolecular forces. Thus ethanol having weaker hydrogen bonding than water, evaporates faster than water. Hence we expect that ethanol will have higher vapour pressure than water at a given temperature. As shown by the actual plot vapour pressure versus temperature, the vapour pressures of ethanol and water at 60ºC are about 350 torr and 150 torr respectively.

Effect of Temperature on Vapour Pressure

If the temperature of the liquid is increased, the vapour pressure will increase. This is so because at higher temperature more molecules in the liquid will have larger kinetic energy and will break away from the liquid surface. Therefore the concentration of vapour molecules will increase before the equilibrium is re-established. Also, at higher temperature, the average kinetic energy of the vapour molecules will increase. Both vapour concentration and kinetic energy are proportional to temperature. Therefore, any increase of temperature will result in the increase of vapour pressure. From the experimental curves shown in Fig. 11.9, it is clear that for both ethyl alcohol and water, the vapour pressure rises with increase of temperature.

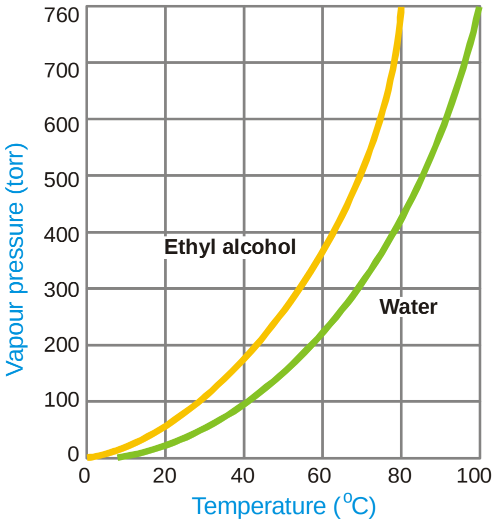


Figure 11.9
Vapour pressure increases with temperature for ethanol and water.

Determination of Vapour Pressure

The vapour pressure of a given liquid can be measured by *Static method* or *Dynamic method*.

(1) The Static Method

A simplified apparatus used for the static method is shown in Fig. 11.10. A sufficient amount of the liquid whose vapour pressure is to be determined is placed in the bulb connected to a mercury manometer and a vacuum pump. All the air from the bulb is removed by working the vacuum pump and the stopcock closed. A part of the liquid evaporates. The system is then maintained at a fixed temperature for enough time so that the equilibrium is established. **The difference in the levels of mercury in the manometer is equal to the vapour pressure of the liquid.** By adjusting the thermostat at a different temperature, the vapour pressure of the liquid at another temperature can be determined. This method is used for liquids having vapour pressures up to one atmosphere.

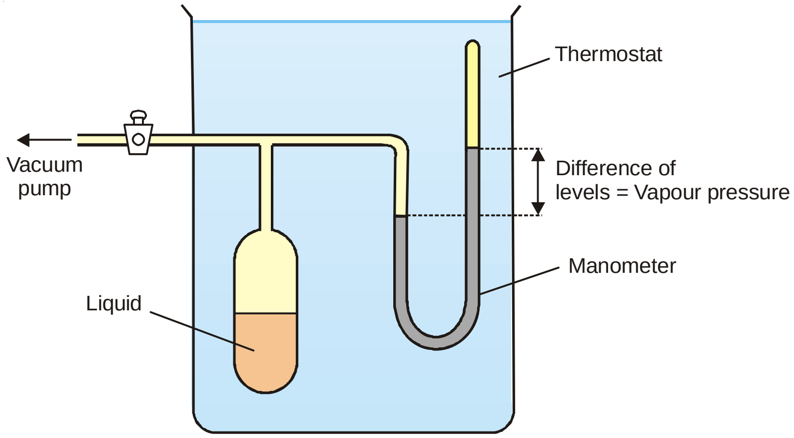


Figure 11.10
Determination of vapour pressure by Static method.

(2) The Dynamic Method

The apparatus used for the dynamic method is illustrated in Fig. 11.11. An inert gas is passed through the given liquid at a constant temperature (*T*). The gas saturated with the vapour of the liquid leaves the flask at the exit tube.

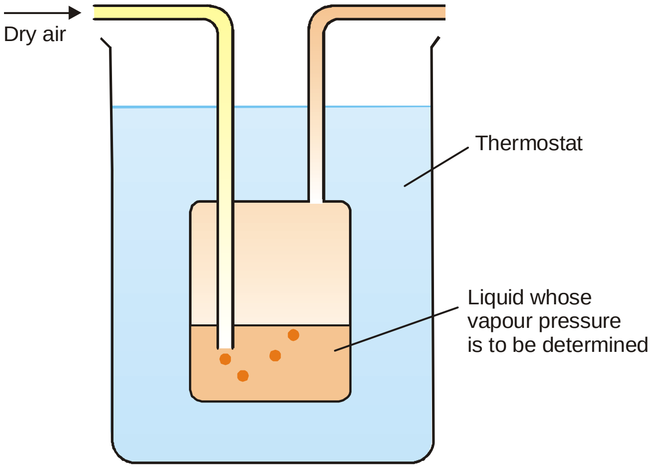


Figure 11.11
Determination of vapour pressure by Dynamic method.

If *V* be the volume of the gas passed and *m* the loss in weight of the liquid, the vapour pressure is given by the expression

$$\text{Vapour pressure} = \frac{m}{MV} \times RT$$

where M = molecular weight of the liquid and R = gas constant. This method is particularly suited for liquids of very low vapour pressure.

Effect of Vapour Pressure on Boiling Points

When a liquid is heated, tiny bubbles are formed in it. These rise to the liquid surface and burst. The temperature at which it happens is the boiling point of the liquid. Let us consider an individual bubble. The liquid vaporises into it and the vapour pressure in the bubble keeps it in form. However, the pressure of the atmosphere exerted on the liquid top tends to collapse the bubble. As the bubble goes to the surface, the vapour pressure in the bubble equals the atmospheric pressure. Thus the bubble collapses. The **boiling point** of the liquid may, therefore, be defined as **the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure.**

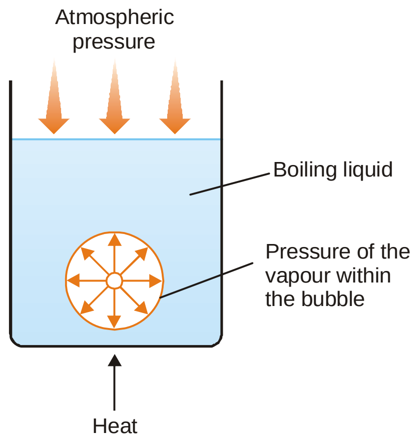


Figure 11.12
A liquid boils when the pressure of the vapour within the bubble equals the atmospheric pressure exerted on the bubble at the liquid surface.

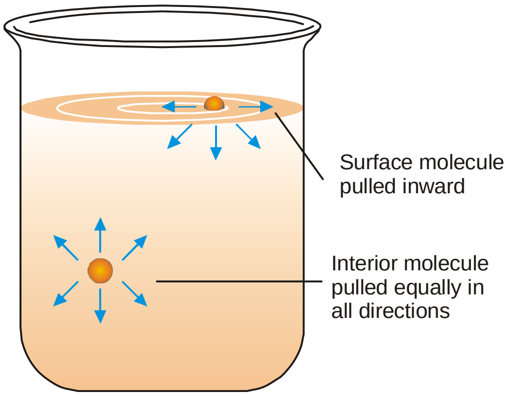
Because the atmospheric pressure varies with altitude and other conditions, the boiling points are reported at 760 torr (1 atm). Therefore the **normal boiling point** of a liquid is the temperature at which the vapour pressure of the liquid is 760 torr or 1 atm. As evident from Fig. 11.9, the boiling point of ethanol is 78ºC and of water, 100ºC.

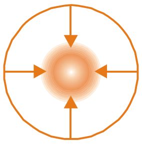
The boiling point of a liquid can be lowered by reducing the external pressure by vacuum pump. Then the vapour pressure of the liquid is equal to the external pressure at a lower temperature. The boiling point of a liquid can be increased by raising the external pressure. Thus the vapour pressure of the liquid is equal to the external pressure at a higher temperature. A domestic pressure cooker works on this principle. The pressure inside the cooker is maintained above one atmosphere and the liquid contained in it would boil at a higher temperature than 100ºC. Thus the food is cooked in a shorter time.

SURFACE TENSION

This property of liquids arises from the intermolecular forces of attraction. A molecule in the interior of a liquid is attracted equally in all directions by the molecules around it. A molecule in the surface of a liquid is attracted only sideways and toward the interior. The forces on the sides being counterbalanced the surface molecule is pulled only inward the liquid. Thus there is a tendency on the part of the surface molecules to go into the bulk of the liquid. The liquid surface is, therefore, under tension and tends to contract to the smallest possible area in order to have the minimum number of molecules at the surface. It is for this reason that in air, drops of a liquid assume spherical shapes because for a given volume a sphere has the minimum surface area.

The surface tension (γ) is defined as : **the force in dynes acting along the surface of a liquid at right angle to any line 1 cm in length.**





■ **Figure 11.13**
Surface tension is caused by the net inward pull on the surface molecules.

■ **Figure 11.14**
The inward forces on the surface molecules minimize the surface area and form a drop.

Units of Surface Tension

As included in the above definition the unit of surface tension in CGS system is dynes per centimetre (dyne cm^{-1}). In SI system, the unit is Newton per metre (Nm^{-1}). Both these units are related as : 1 dyne cm^{-1} = 1 m Nm^{-1}

Effect of Temperature on Surface Tension

A change in temperature causes a change in surface tension of a liquid. When temperature increases, there is an increase in kinetic energy of liquid molecules (KE ∝ T), thereby decreasing intermolecular forces. It results in decrease in the inward pull functioning on the surface of the liquid. In other words, **surface tension decreases with increase in temperature.** W. Ramsay and J. Shields gave the following relationship between surface tension of a liquid and its temperature

$$\gamma\,(\mathrm{M}/\rho)^{2/3} = k\,(t_c - t - 6) \qquad \text{....}(i)$$

where k is a constant (temperature coefficient), t_c is critical temperature and t any other temperature, $(\mathrm{M}/\rho)^{2/3}$ represents molar surface energy of the liquid.

TABLE 11.2. SURFACE TENSION OF SOME LIQUIDS AT VARIOUS TEMPERATURES (dynes cm^{-1})

Liquid	20°C	40°C	60°C	80°C
Water	72.75	69.56	66.18	62.61
Ethyl alcohol	22.27	20.60	19.01	–
Methyl alcohol	22.6	20.9	–	–
Acetone	23.7	21.2	18.6	16.2
Toluene	28.43	26.13	23.81	21.53
Benzene	28.9	26.3	23.7	21.3

SURFACE TENSION


Surface tension helps dew drops stick to the grass and prevents them from spreading.


Surface tension prevents this flower from sinking.


Surface tension prevents a paper clip from sinking.


Surface tension helps insects to walk on water.

Surface tension is an effect within the surface layer of a liquid that causes the layer to behave as an elastic sheet. It is the effect that allows insects (such as the water strider) to walk on water, and causes capillary action.

Surface tension is caused by the attraction between the molecules of the liquid, due to various intermolecular forces. In the bulk of the liquid each molecule is pulled equally in all directions by neighbouring liquid molecules, resulting in a net force of zero. At the surface of the liquid, the molecules are pulled inwards by other molecules deeper inside the liquid, but there are no liquid molecules on the outside to balance these forces.

All of the molecules at the surface are therefore subject to an inward force of molecular attraction which can be balanced only by the resistance of the liquid to compression. Thus the liquid squeezes itself together until it has the lowest surface area possible.

Determination of Surface Tension

The methods commonly employed for the determination of surface tension are :

(1) Capillary-rise Method

A capillary tube of radius r is vertically inserted into a liquid. The liquid rises to a height h and forms a concave meniscus. The surface tension (γ) acting along the inner circumference of the tube exactly supports the weight of the liquid column.

By definition, surface tension is force per 1 cm acting at a tangent to the meniscus surface. If the angle between the tangent and the tube wall is θ, the vertical component of surface tension is γ cos

θ. The total surface tension along the circular contact line of meniscus is $2\pi r$ times. Therefore,

$$\text{Upward force} = 2\pi r\gamma \cos\theta$$

where r is the radius of the capillary. For most liquids, θ is essentially zero, and $\cos\theta = 1$. Then the upward force reduces to $2\pi r\gamma$.

The downward force on the liquid column is due to its weight which is *mass* × *gravity*. Thus,

$$\text{Downward force} = h\pi r^2\, dg$$

where d is the density of the liquid.

But

$$\text{Upward force} = \text{Downward force}$$

or

$$2\pi r\gamma = h\pi r^2\, dg$$

$$\gamma = \frac{hr\ dg}{2}\ \text{dynes/cm} \qquad \text{...(1)}$$

In order to know the value of γ, the value of h is found with the help of a travelling microscope and density (d) with a pyknometer.

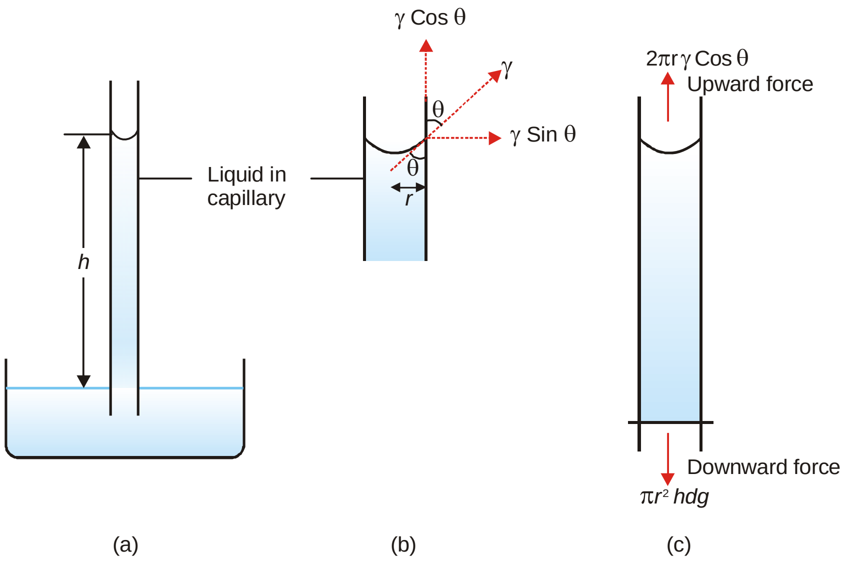


Figure 11.15
(*a*) Rise of liquid in a capillary tube; (*b*) Surface tension (γ) acts along tangent to meniscus and its vertical component is γ Cos θ; (*c*) Upward force 2πrγ Cos θ counterbalances the downward force due to weight of liquid column, πr^2 hgd.

SOLVED PROBLEM 1. A capillary tube of internal diameter 0.21 mm is dipped into a liquid whose density is 0.79 g cm^{-3}. The liquid rises in this capillary to a height of 6.30 cm. Calculate the surface tension of the liquid. (g = 980 cm sec^{-2})

SOLUTION

We know :

$$\gamma = \frac{hrdg}{2}\ \text{dynes/cm} \qquad \text{...(1)}$$

where h = height of liquid in capillary in centimetres
r = radius of capillary in centimetres

d = density of liquid in g cm^{-1}
g = acceleration due to gravity in cm sec^{-2}

Substituting the values from the above example,

$$h = 6.30 \text{ cm}$$

$$r = \frac{0.21}{2} \times \frac{1}{10} = 0.0105 \text{ cm}$$

$$d = 0.79 \, g \text{ cm}^{-3}$$

$$g = 980 \text{ cm sec}^{-2}$$

In relation (1), we have

$$\gamma = \frac{6.30 \times 0.0105 \times 0.79 \times 980}{2}$$

$$= \mathbf{25.6 \text{ dynes cm}^{-1}}$$

Thus the surface tension of the given liquid is **25.6 dynes cm^{-1}.**

SOLVED PROBLEM 2. How high will sap rise in a plant if the capillaries are 0.01 mm diameter, the density of the fluid is 1.3 g cm^{-1} and its surface tension 0.065 Nm^{-1}. (g = 981 cm s^{-2})

SOLUTION

We know that

$$h = \frac{2\gamma}{rdg} \text{ metres} \qquad ...(1)$$

where in SI units :

h = height of liquid in metres
γ = surface tension in Nm^{-1}
r = radius of capillary in metres
d = density in Kg m^{-3}
g = acceleration due to gravity in ms^{-2}

In this example,

$$\gamma = 0.065 \text{ Nm}^{-1}$$

$$r = \frac{1}{2}(0.00001) = \frac{10^{-5}}{2} \text{ metres}$$

$$d = 1.3 \times 10^{3} \text{ kg m}^{-3}$$

$$g = 9.81 \text{ ms}^{-2}$$

Substituting these values in equation (1)

$$h = \frac{2 \times 2 \times 0.065}{10^{-5} \times 1.3 \times 10^{3} \times 9.81} = \mathbf{2.04 \text{ m}}$$

Therefore in a plant with capillaries of 0.01 mm diameter, the sap will rise to a height of **2.04 metres.**

(2) Drop Formation Method

A drop of liquid is allowed to form at the lower end of a capillary tube (Fig. 11.17). The drop is supported by the upward force of surface tension acting at the outer circumference of the tube. The weight of the drop (mg) pulls it downward. When the two forces are balanced, the drop breaks. Thus at the point of breaking,

$$m g = 2 \pi r \gamma \qquad ...(1)$$

where m = mass of the drop
g = acceleration due to gravity
r = outer radius of the tube

The apparatus employed is a glass pipette with a capillary at the lower part. This is called a **Stalagmometer** or **Drop pipette (Fig. 11.16).** It is cleaned, dried and filled with the experimental liquid, say upto mark A. Then the surface tension is determined by one of the two methods given below.

(*a*) **Drop-weight Method.** About 20 drops of the given liquid are received from the drop-pipette in a weighing bottle and weighed. Thus weight of one drop is found. The drop-pipette is again cleaned and dried. It is filled with a second reference liquid (say water) and weight of one drop determined as before.

Then from equation (1)

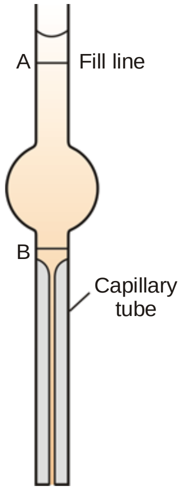
$$m_1 g = 2 \pi r \gamma_1 \qquad \text{...(2)}$$

$$m_2 g = 2 \pi r \gamma_2 \qquad \text{...(3)}$$

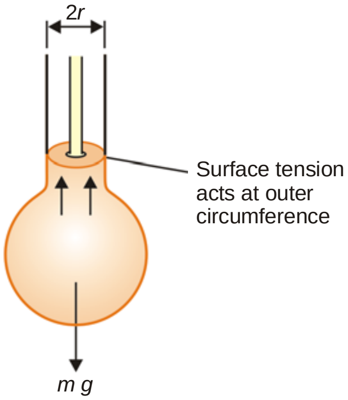
Dividing (2) by (3)

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} \qquad \text{...(4)}$$

Knowing the surface tension of reference liquid from Tables, that of the liquid under study can be found.



■ **Figure 11.16**
A stalagmometer.



■ **Figure 11.17**
A drop forming from a tube of radius *r*.

(*b*) **Drop-number Method.** The drop-pipette is filled upto the mark A with the experimental liquid (No. 1). The number of drops is counted as the meniscus travels from A to B. Similarly, the pipette is filled with the reference liquid (No. 2) as the meniscus passes from A to B. Let n_1 and n_2 be the number of drops produced by the same volume *V* of the two liquids. Thus,

$$\text{The volume of one drop of liquid 1} = V/n_1$$

$$\text{The mass of one drop of liquid 1} = (V/n_1)d_1$$

where d_1 is the density of liquid 1.

Similarly,

$$\text{The mass of one drop of liquid 2} = (V/n_2)d_2$$

Then from equation (4)

$$\frac{\gamma_1}{\gamma_2} = \frac{(V/n_1)\,d_1}{(V/n_2)\,d_2} = \frac{n_2 d_1}{n_1 d_2}$$

The value of d_1 is determined with a pyknometer. Knowing d_2 and γ_2 from reference tables, γ_1 can be calculated.

SOLVED PROBLEM. In the determination of surface tension of a liquid by the drop-number method, it gives 55 drops while water gave 25 drops for the same volume. The densities of the liquid and water are 0.996 and 0.800 g/cm^3 respectively. Find the surface tension of the liquid if that of water is 72.0 dynes/cm.

SOLUTION

We know that
$$\frac{\gamma_1}{\gamma_2} = \frac{n_2 d_1}{n_1 d_2} \qquad ...(1)$$
where γ_1 = surface tension of liquid; γ_2 = surface tension of water; n_1 = number of drops of liquid; n_2 = number of drops of water.

In the present case we have :

$$\gamma_2 = 72.0 \text{ dynes cm}^{-1}$$
$$n_1 = 55 \qquad n_2 = 25$$
$$d_1 = 0.996 \text{ g cm}^{-3} \qquad d_2 = 0.800 \text{ g cm}$$

From equation (1) we have
$$\gamma_1 = \gamma_2 \times \frac{n_2 d_1}{n_1 d_2} \qquad ...(2)$$

Substituting values in (2)
$$\gamma_1 = 72 \times \frac{0.996 \times 25}{0.800 \times 55} = 40.7 \text{ dynes cm}^{-1}$$

Therefore, the surface tension of the given liquid is **40.7 dynes cm^{-1}**.

(3) Ring-detachment Method

In this method the force required to detach a platinum ring (du Nouy ring) from the liquid surface is measured. **This force (*F*) is exactly equal to the downward pull due to surface tension γ acting along the circumference of the ring.** Twice the length of the circumference (2 × 2π*r*) is taken since the liquid is in contact with both the inside and the outside of ring. Thus,

$$F = 4\pi r \gamma$$

or
$$\gamma = \frac{F}{4\pi r} \qquad ...(1)$$

where *r* is the radius of the ring.

The apparatus employed is called the **du Nouy Tensiometer.** Its essential parts are shown in Fig. 11.19. One end of the torsion wire is fixed while the other is attached to a knob carrying a pointer. The pointer moves on a fixed scale. The scale is previously calibrated by taking different weights on the beam and noting the scale reading when it is lifted from the horizontal position. The liquid whose surface tension is to be determined is placed in a watch glass so that the Pt-ring just touches its surface. The knob of the torsion wire is then slowly turned till the ring is just detached from the surface. The reading shown by the pointer on the scale gives the force *F*. The surface tension is then calculated from equation (1).

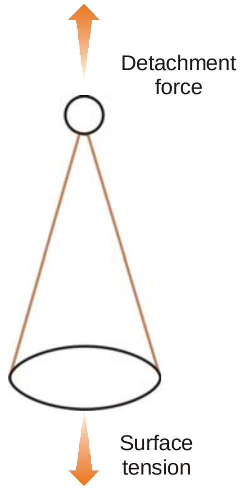


Figure 11.18
du Nouy ring with a suspending hook.

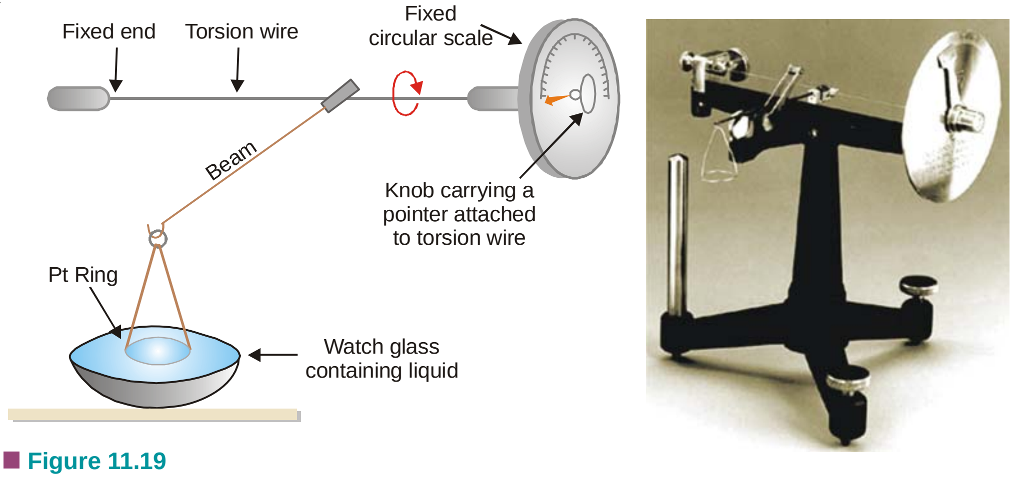


Figure 11.19
du Nouy Tensiometer.

(4) Maximum Bubble Pressure Method

In this method air-pressure is applied slowly through a capillary tube dipping in the experimental liquid (See Fig. 11.20).

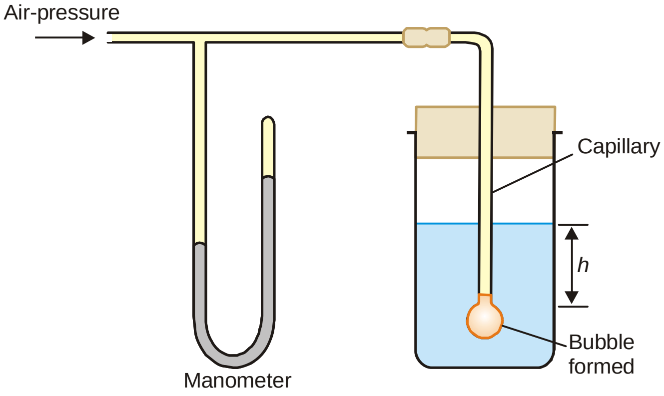


Figure 11.20
A simple apparatus for maximum bubble pressure method.

A bubble is formed at the end of the capillary. Slowly the bubble grows and becomes hemispherical. Then it breaks away when the pressure recorded by the manometer is noted. This is the maximum pressure required to make a bubble at the end of the capillary. At the moment of breaking, the forces due to maximum pressure P equals that of the opposing hydrostatic pressure P_h and the surface tension γ at the circumference of the capillary. Thus,

$$P \pi r^2 = P_h \pi r^2 + 2 \pi r \gamma$$

$$P = P_h + \frac{2\gamma}{r}$$

or
$$P = h d g + \frac{2\gamma}{r}$$

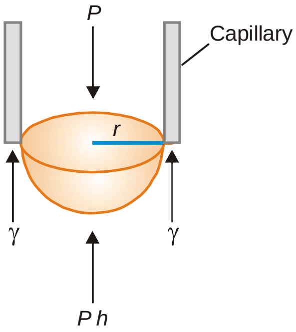


Figure 11.21
Applied pressure on bubble is opposed by hydrostatic pressure and surface tension.

where r = radius of capillary; d = density of the liquid; h = depth of liquid.

Knowing the value of P, h, d and r, γ can be found.

VISCOSITY

A liquid may be considered to be consisting of molecular layers arranged one over the other. When a shearing force is applied to a liquid, it flows. However, the forces of friction between the layers offer resistance to this flow. **Viscosity of a liquid is a measure of its frictional resistance.**

Let us examine a liquid flowing on a glass surface (Fig. 11.22). The molecular layer in contact with the stationary surface has zero velocity. The successive layers above it move with increasingly higher velocities in the direction of the flow.

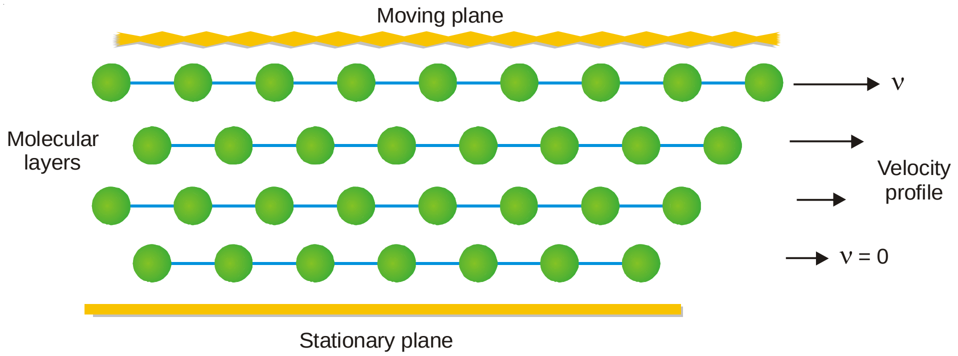


Figure 11.22
Flow of a liquid on a glass surface.

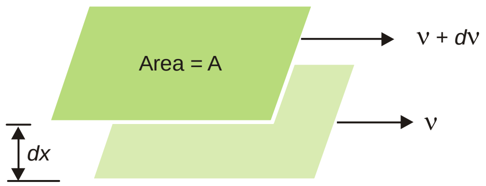


Figure 11.23
Two parallel layers moving in a liquid.

Now consider two adjacent moving layers of a liquid (Fig. 11.23). Let these be separated by a distance dx and have a velocity difference dv. The force of friction (F) resisting the relative motion of the two layers is directly proportional to the area A and the velocity difference dv, while it is inversely proportional to the distance between the layers.

That is,

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

or $$F = \eta A\frac{dv}{dx} \qquad \text{...(1)}$$

or $$\eta = \frac{F}{A} \times \frac{dx}{dv} \qquad \text{...(2)}$$

where η (Greek letter *eta*) is the proportionality constant. It is known as the **Coefficient of Viscosity** or simply viscosity of a liquid. η has a specific value for a given liquid at the same temperature. It may be defined from equation (2) as : **the force of resistance per unit area which will maintain unit velocity difference between two layers of a liquid at a unit distance from each other.**

The reciprocal of viscosity is called Fluidity and is denoted by ϕ.

$$\phi = \frac{1}{\eta}$$

Units of Viscosity

The dimensions of the coefficient of viscosity (η) may be derived from equation (2).

$$\eta = \frac{F}{A} \times \frac{dx}{dv} = \frac{\text{force}}{\text{area}} \times \frac{\text{distance}}{\text{velocity}}$$

or
$$\eta = \frac{\text{mass} \times \text{length} \times \text{time}^{-2}}{(\text{length})^2} \times \frac{\text{length}}{\text{length/time}}$$

$$= \text{mass} \times \text{length}^{-1} \times \text{time}^{-1}$$

Thus in CGS system the unit of η is expressed as g cm^{-1} s^{-1}. It is called poise (P). In practice smaller units **centipoise** (10^{-2} poise) and **millipoise** (10^{-3} poise) are used.

The SI unit is kg m^{-1} s^{-1}. One poise is equal to one-tenth of the SI unit *i.e.*

$$1 \text{ poise } = 1 \text{ g cm}^{-1} \text{ s}^{-1} = 0.1 \text{ kg m}^{-1} \text{ s}^{-1}$$

TABLE 11.3. COEFFICIENTS OF VISCOSITY OF SOME LIQUIDS AT 20ºC (293 K)

Liquid	Viscosity (P) CGS units	Viscosity SI units
Benzene	0.00652	0.000652
Carbon tetrachloride	0.0969	0.000969
Ethanol	0.01200	0.001200
Ether	0.00233	0.000233
Glycerine	14.9	1.49
Water	0.0101	0.00104

Measurement of Viscosity - The Ostwald Method

Viscosity of a liquid can be determined with the help of **Pioseulle's equation.** This expression which governs the flow of a liquid through a capillary may be written as :

$$\eta = \frac{\pi P r^4 t}{8 l V} \qquad \text{...(1)}$$

where V is the volume of the liquid flowing through capillary in time t, P the pressure-head, r the radius of the tube and l its length. The experimental measurement of P, r, l and V offers considerable difficulty. Therefore, it is not possible to find the absolute coefficient of viscosity (η) straight away from Poiseulle's equation.

Ordinarily, the viscosity of a liquid is determined with respect to that of water. This is called **Relative Viscosity.** Let t_1 and t_2 be the times of flow of a fixed volume (V) of the two liquids through the same capillary. The expression for relative viscosity (η_1/η_2) can be derived from equation (1).

$$\frac{\eta_1}{\eta_2} = \frac{\pi P_1 r^4 t_1}{8 l V} \cdot \frac{8 l V}{\pi P_2 r^4 t_2} = \frac{P_1 t_1}{P_2 t_2} \qquad \text{...(2)}$$

Since the pressure-head is proportional to density (d) of the liquid, from (2) we have :

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \qquad \text{...(3)}$$

Substituting the value of the viscosity coefficient of water (η_2) in (3), we can find the **absolute viscosity** of the given liquid (η_1).

Ostwald Viscometer

The apparatus commonly used for the determination of relative viscosity of a liquid is known as **Ostwald viscosimeter** *or* **viscometer.** A simple form of it is shown in Fig 11.24. The left-hand limb is essentially a pipette with two calibration marks *A* and *B*. A length of capillary tube joins the pipette to a bulb *C* in the right-hand limb.

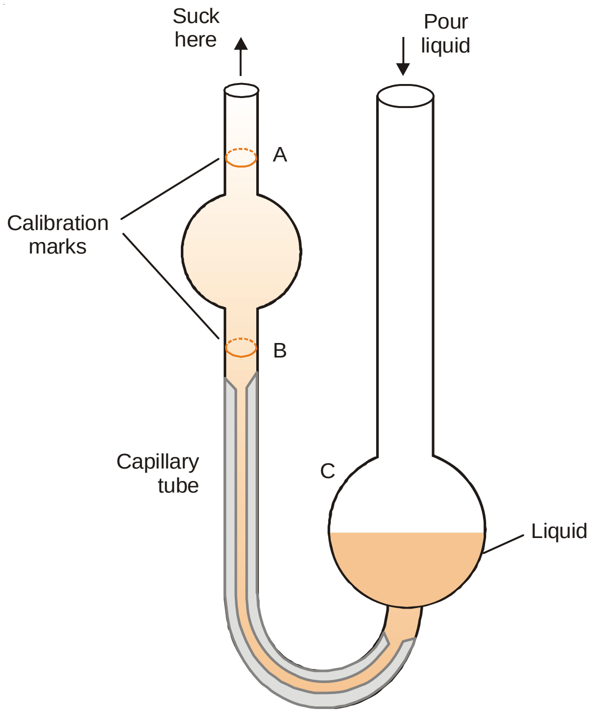


Figure 11.24
Ostwald Viscometer.

A definite volume of liquid (say 25 ml) is poured into the bulb *C* with a pipette. The liquid is sucked up near to the top of the left-limb with the help of a rubber tubing attached to it. The liquid is then released to flow back into the bulb *C*. The time (t_1) from *A* to *B* is noted with a stopwatch. Then the apparatus is cleaned and the experiment repeated with water, taking about the same volume. The time of flow of water (t_2) from *A* to *B* is recorded. The density of the liquid (d) and water (d_w) are determined with the help of a *pyknometer*. The relative viscosity coefficient is calculated from the expression

$$\frac{\eta}{\eta_w} = \frac{d\ t_1}{d_w\ t_2}$$

Knowing the value of the viscosity coefficient of water (η_w) at the temperature of the experiment, the absolute viscosity coefficient (η) of the given liquid can be found.

SOLVED PROBLEM 1. In an experiment with Ostwald viscometer, the times of flow of water and ethanol are 80 sec and 175 sec at 20ºC. The density of water = 0.998 g/cm^3 and that of ethanol = 0.790 g/cm^3. The viscosity of water at 20ºC is 0.01008 poise. Calculate the viscosity of ethanol.

SOLUTION

Substituting values in the expression

$$\eta = \eta_w \frac{d\ t_1}{d_w\ t_2}$$

or

$$\eta = 0.01008 \times \frac{0.790 \times 175}{0.998 \times 80}$$

$$= 0.01747 \text{ poise}$$

SOLVED PROBLEM 2. In an experiment with Ostwald viscometer, pure water took 1.52 minutes to flow through the capillary at 20ºC. For the same volume of another liquid of density 0.80 g cm^{-3} the flow time was 2.25 minutes. Find the relative viscosity of the liquid and its absolute viscosity in centipoise. Density of water at 20ºC is 0.9982 and absolute viscosity of water is 1.005 centipoise.

SOLUTION

Substituting values in the expression

$$\frac{\eta}{\eta_w} = \frac{d\,t_1}{d_w\,t_2}$$

we have

$$\frac{\eta}{\eta_w} = \frac{0.80 \times 2.25}{0.9982 \times 1.52} = 1.184$$

$$\therefore \quad \eta = 1.184 \times 1.005$$

$$= \mathbf{1.19 \text{ centipoise}}$$

Thus the relative viscosity of the liquid is **1.184** and its absolute viscosity is **1.19 centipoise.**

EFFECT OF TEMPERATURE ON VISCOSITY OF A LIQUID

In general, the viscosity decreases with increase in temperature. The variation of viscosity (η) with temperature can be expressed by the following relationship

$$\eta = Ae^{-E/RT} \qquad ....(i)$$

where A and E are constants.

Taking logarithms on both sides, we get

$$\text{In}\,\eta = A + E/RT$$

or

$$\text{In}\,\eta = \frac{E}{R} \times \frac{1}{T} + A \qquad ...(ii)$$

comparing equation (*ii*) with

$$y = mx + c \qquad \text{(equation of straight line)}$$

A plot of log η versus 1/T should be a straight line (Fig. 11.25). It has been verified for a variety of liquids.

It has also been found that there is 2% decrease in viscosity for every increase in one degree of temperature of the liquid.

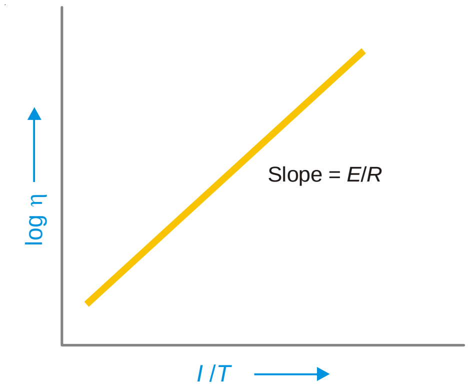


Figure 11.25
Plot of log η versus I/T

REFRACTIVE INDEX

The refractive index (*n*) of a substance is defined as the ratio of the velocity of light in vacuum or air, to that in the substance :

$$n = \frac{\text{Velocity of light in substance}}{\text{Velocity of light in air}}$$

When a ray of light passes from air into a liquid, its direction is changed. This change of direction is called *refraction*. The refractive index of the liquid with respect to air is given by **Snelle's Law.** According to it,

$$n = \frac{\text{Sin } i}{\text{Sin } r}$$

where i is the angle of incidence and r the angle of refraction.

The refractive index of a liquid can be easily determined to a high degree of accuracy. It is a characteristic property of a liquid. It varies with temperature and wavelength of light used.

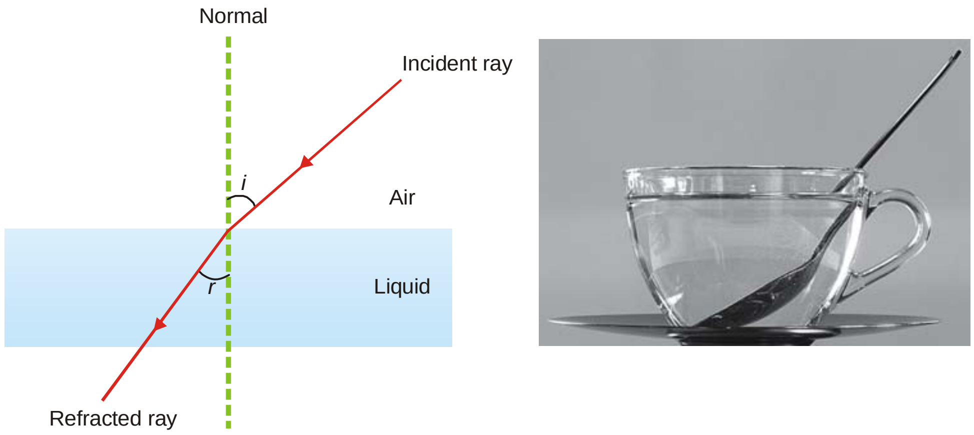
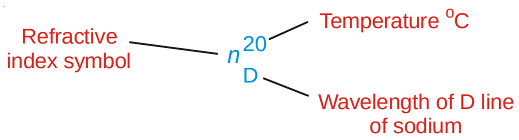


Figure 11.26
Refraction of light through a denser liquid medium.

The wavelength of D-line of the sodium spectrum is generally used for the purpose. If the refractive index of a liquid is measured at 20ºC and using D-line of sodium, it is represented by the following symbol.



Because refractive index is a ratio, it has no units.

SPECIFIC REFRACTION

Lorenz and Lorenz (1880) purely from theoretical considerations derived the following relation for the refractive power of substance.

$$R_s = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \qquad \text{....(1)}$$

where R_s is the **Specific Refraction,** d the density and n the refractive index. The value of R_s was constant at all temperatures.

MOLAR REFRACTION

It is defined as **the product of specific refraction and molecular mass.** Thus molar refraction of a liquid (R_M) is obtained by multiplying equation (1) by molecular mass (M).

$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \qquad \text{...(2)}$$

The value of molar refraction is characteristic of a substance and is temperature-independent. It can be determined by substituting the values of n, M and d in the equation (2). Since it depends on the wavelength of light, the values of molar refraction are generally reported for D-line of sodium. Since the value of refractive index (n) is dimensionless, from equation (2) it is evident that R_M has the units of the molar volume *i.e.*, $\text{cm}^3 \text{ mol}^{-1}$.

SOLVED PROBLEM. The refractive index of carbon tetrachloride for D-line of sodium has been found to be 1.4573. Calculate its molar refraction if the density is 1.595 g/cm^3.

SOLUTION

Substituting values in the expression

$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

Here

$$M = 12 + 35.5 \times 4 = 154$$

$$d = 1.595 \text{ g/cm}^3$$

$$n = 1.4573$$

$$\therefore \qquad R_M = \frac{(1.4573)^2 - 1}{(1.4573)^2 + 2} \times \frac{154}{1.595} = 26.31 \text{ cm}^3\text{mol}^{-1}$$

Determination of Refractive Index

The refractive index of a liquid can be determined with the help of an instrument called **Abbe Refractometer** (Fig. 11.27). A thin film of the liquid is placed between the two prisms. Light from a sodium lamp is made to fall on lower side of the lower prism with the help of a mirror. The hypotenuse surface of the lower prism is ground and, therefore, light enters the liquid at all angles of incidence. However, no ray can enter the upper prism with greater angle of refraction than the grazing incidence (*i.e.*, at an angle) slightly less than 90ºC. Thus the view in the telescope appears to be divided into two bands, one bright and one dark. The prism assembly is rotated with the help of a side knob till the cross wire of the telescope coincides with the edge of the bright band. A pointer attached to the prism assembly indicates the refractive index on the scale calibrated to read refractive indices directly.

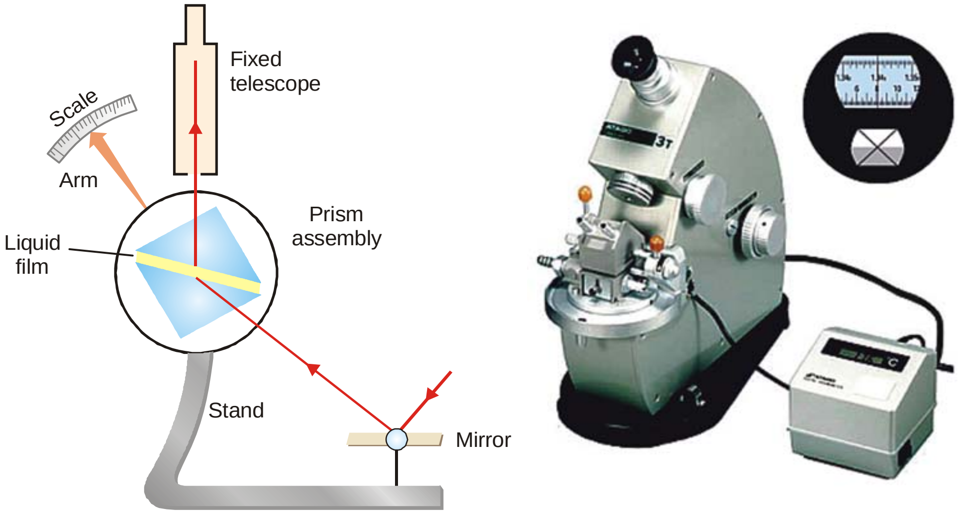


Figure 11.27
The Abbe refractometer.

Molar Refraction and Chemical Constitution

The molar refraction (R_M) is an additive property *i.e.* molar refraction of a molecule is the sum of the molar refraction of its constituent atoms. It is helpful in determining the constitution of a compound. The molar refraction values are calculated for various possible structures and the formula which is in accordance with the calculated molar refraction is the correct formula (or structure) of that compound. The molar refraction values for some atoms and bonds are given in Table 11.4.

TABLE 11.4. MOLAR REFRACTIONS ($cm^3\ mol^{-1}$)

Carbon C	2.418	3-membered ring	0.710
Hydrogen H	1.100	4-membered ring	0.480
Chlorine Cl	5.967	6-membered ring	0–0.15
Bromine Br	8.861	O in OH group	1.525
Iodine I	13.900	O is C = O group	2.211
Double bond	1.733	O in ethers	1.64
Triple bond	2.398		

Let us take the example of ethyl alcohol (CH_3CH_2OH). Its refractive index at 295.9 K for D-line is 1.3611 and its density is 0.7885 g cm^{-3}. The molar mass of ethyl alcohol is 46 ($2 \times 12 + 1 \times 6 + 1 \times 16$). The molar refraction can be calculated using the relation

$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

$$= \frac{(1.3611)^2 - 1}{(1.3611)^2 + 2} \times \frac{46}{0.7885}$$

$$= 12.9105\ \text{cm}^3\ \text{mol}^{-1}$$

Let us now compute the value of molar refraction using the values in Table 11.4.

$$
\begin{aligned}
\text{Contribution of 6 Hydrogens} &= 6 \times 1.100 = 6.600\\
\text{Contribution of 2 Carbons} &= 2 \times 2.418 = 4.836\\
\text{Contribution of O in OH group} &= 1.525\\
\text{Total contribution} &= 12.961\ \text{cm}^3\ \text{mol}^{-1}
\end{aligned}
$$

This value is in close agreement with the value calculated above. Therefore, the correct structure of ethyl alcohol is CH_3CH_2OH.

The molar refraction R_M of a solution is given by

$$R_M = \frac{n^2 - 1}{n^2 + 2}\left[\frac{x_1M_1 + x_2M_2}{d}\right]$$

where x_1 and x_2 are mole fractions of the solvent and solute with molecular masses M_1 and M_2 respectively, n is the refractive index of the solution and d is the density of the solution.

OPTICAL ACTIVITY

A beam of ordinary light consists of electromagnetic waves oscillating in many planes. When passed through a polarizer (*e.g.*, a Polaroid lens), only waves oscillating in a single plane pass through. **The emerging beam of light having oscillations in a single plane is said to be plane-polarized.**

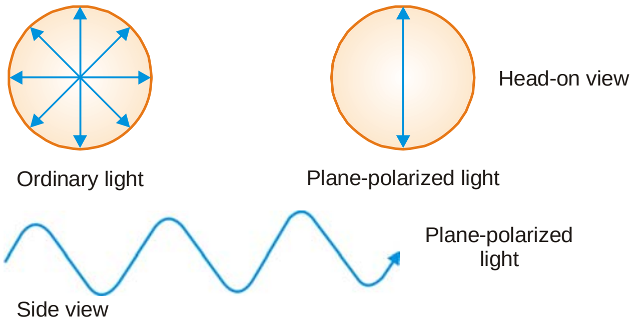


Figure 11.28
Plane-polarized light.

When plane-polarized light is passed through certain organic compounds, the plane of polarized light is rotated. **A compound that can rotate the plane of polarized light is called optically active.** This property of a compound is called **optical activity.**

A compound which rotates the plane-polarized light to the left (anticlockwise), is said to be **levorotatory.** A compound that rotates the plane-polarized light to the right (clockwise), is said to be **dextrorotatory**. By convention, rotation to the left is given a minus sign (–) and rotation to the right is given a plus sign (+). For example, (–)-lactic acid is levorotatory and (+)-lactic acid is dextrorotatory.

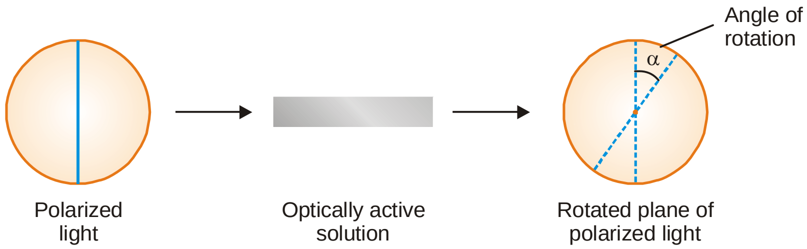
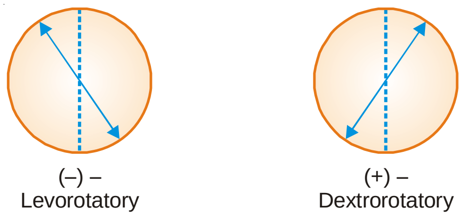


Figure 11.29
Optical Activity illustrated.



SPECIFIC ROTATION

The rotation of plane-polarized light is an intrinsic property of optically active molecules. When a polarized beam of light is passed through the solution of an optically active compound, its plane is rotated through an angle α (**angle of rotation**). This rotation depends on the number of optically active molecules encountered. Therefore, α is proportional to both the concentration and the length of the sample solution.

The **specific rotation** which is characteristic of an optically active substance, is expressed as

$$[\alpha] = \frac{\alpha}{l \times c} \qquad \text{...(1)}$$

where $[\alpha]$ = specific rotation in degrees
α = observed angle of rotation in degrees
l = length of the sample solution in decimeters (dm; 10 cm)
c = concentration of the sample solution in g/ml

Thus from equation (1), the specific rotation can be defined as **the observed angle of rotation at a concentration of 1 g/ml and path length of 1 dm.** Conventionally, a specific rotation is reported as $[\alpha]_D^t$, where t stands for temperature and D for D-line of sodium used for determination.

Measurement of Optical Activity

Optical activity is measured with the help of an instrument known as **polarimeter** (Fig. 11.30). This is basically a system of *polarizers* with a sample tube placed in between. First, an optically inactive medium (air or solvent) fills the sample tubes and polarized sodium light emerging from the *polarizer* passes through it. The *analyzer* is then turned to establish a dark field. This gives a zero reading on the circular scale around the analyzer.

Then the solution of the given optically active compound is placed in the sample tube. The plane of polarized light passing through it is rotated. The analyzer is turned to re-establish the dark field. The angle of rotation (α) is then noted in degrees on the circular scale. The specific rotation is calculated using the expression (1) above.

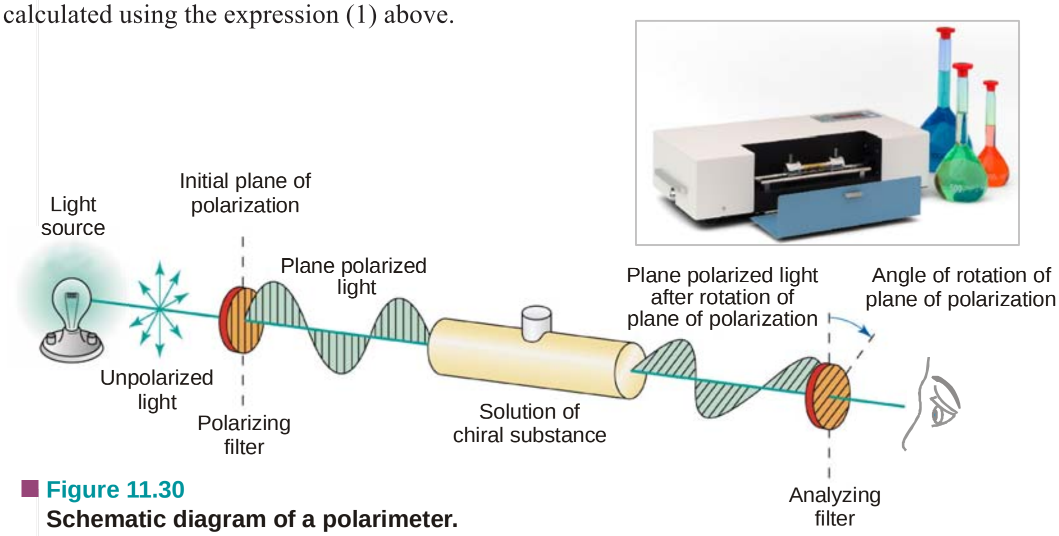


Figure 11.30
Schematic diagram of a polarimeter.

EXAMINATION QUESTIONS

1. Define or explain the following terms :

(*a*) van der Waal's forces
(*b*) Hydrogen bond
(*c*) Vapour pressure
(*d*) Boiling point
(*e*) Surface tension
(*f*) Viscosity
(*g*) Ostwald's method
(*h*) Refractive index
(*i*) Specific Refraction
(*j*) Molar Refraction
(*k*) Optical activity
(*l*) Specific rotation

2. (*a*) Define the term coefficient of viscosity. Describe Ostwald's viscometer method for determining it.

(*b*) In a measurement of viscosity by Ostwald's viscometer at 20.2°C, water takes 30 seconds to flow between the upper and lower marks while the flow of another liquid of density 1.500 gm cm^{-3}, takes 35 seconds. Taking density of water at 20.2°C to be 0.9982 gm cm^{-3}, calculate the viscosity of the other liquid if the viscosity of water at this temperature is 10 centipoise.

Answer. (*b*) 0.1735 poise

3. The density of a liquid at 25°C is 1.203 g ml^{-1}. Its refractive index n^{25}_D is 1.552. Calculate its molar refractivity. (Molecular weight of liquid = 123)

Answer. 32.66 cm mol^{-1}

4. In an Ostwald viscometer, the flow times for two liquids A and B are in the ratio 4:5. If the density of liquid B is twice as high as that of A, calculate the ratio of their viscosities.

Answer. 2:5

5. (*a*) Define : (*i*) Poise (*ii*) Surface Tension and (*iii*) Specific viscosity.

(*b*) Time taken for the same volume of water and benzene to flow in viscometer at 20°C have been found to be 120 seconds and 88 seconds respectively. The density of benzene at this temperature is 9.879 g cm^{-3}. If the absolute viscosity of water at 20°C is 10.05×10^{-3} poise, calculate the specific viscosity of benzene at this temperature.

Answer. (*b*) 6.478×10^{-4} poise

6. (*a*) Define viscosity and coefficient of viscosity. Describe one method of determining the viscosity of liquids.

(*b*) It takes 100 sec for water to flow through a capillary tube at fixed pressure. How long will it take toluene to do so under similar conditions. Given that : (*i*) density of water = 0.998 g cm^{-3}; absolute viscosity of water = 0.01 dyne sec cm^2; density of toluene = 0.866 g cm^{-3}; viscosity = 0.006 dyne sec cm^{-2}.

Answer. (*b*) 69.14 sec

7. (*a*) Define surface tension. What is the influence of temperature on surface tension?

(*b*) Describe drop number method of determining surface tension of a liquid.

8. At 20°C, pure water required 102.2 sec to flow the capillary of an Ostwald viscometer, while toluene at 20°C required 68.9 sec. Calculate the relative viscosity of toluene. Densities of water and toluene are 0.998 and 0.866 g cm^{-3}.

Answer. 0.5849 poise

9. Define coefficient of viscosity. How does it vary with temperature? (*Punjabi BSc, 2000*)

10. Explain the following terms :

(*a*) Fluidity
(*b*) Surface Tension (*Kurukshetra BSc, 2000*)

11. What is the effect of temperature on surface tension of a liquid? (*MD Rohtak BSc, 2000*)

12. Why do you use the same viscometer for the liquid and water during the experimental determination of viscosity by the Ostwald viscometer? Describe the experiment. (*Delhi BSc, 2000*)

13. (*a*) How is the surface tension of a liquid affected by temperature?

(*b*) Describe the relationship between the viscosity of a liquid and its chemical constitution.

(*Madurai BSc, 2000*)

14. What is meant by viscosity of a liquid? How it is experimentally determined? Discuss the effect of temperature on it. (*Lucknow BSc, 2000*)

15. Define viscosity of fluids. Explain determination of coefficient of viscosity for a liquid using Ostwald's viscometer. How does the change in temperature affect the viscosity of a liquid. (*Aligarh BSc, 2002*)

16. (*a*) Define the term viscosity, coefficient of viscosity and fluidity. What are the factors affecting the viscosity of liquid?

(*b*) Describe a method for measuring surface tension of a liquid.

(*Arunachal BSc, 2002*)

17. Describe the terms : Viscosity and coefficient of viscosity. Give their units.

(*Guru Nanak Dev BSc, 2002*)

18. What is the effect of temperature on viscosity of a liquid? (*Nagpur BSc, 2002*)

19. How is relative surface tension of a liquid with reference to that of water measured by drop weight method? Write the dimensions of surface tension.

(*Jammu BSc, 2002*)

20. Explain : Viscosity of liquids decreases with increase in temperature. (*Delhi BSc, 2002*)

21. Define surface tension. What are its units? Describe drop weight method for the determination of the surface tension. Why do liquids have surface tension? Show diagrammatically the direction in which surface tension acts. (*Guru Nanak Dev BSc, 2003*)

22. What do you mean by laminar flow of a liquid? Define coefficient of viscosity. Describe a method for its determination. (*Kalyani BSc, 2003*)

23. (*a*) When a liquid is warmed, initially many small bubbles begin to form. Why?

(*b*) Surface tension of a liquid vanishes at its critical temperature. Explain.

(*c*) What is coefficient of viscosity of a liquid? What are its units in CGS and SI systems? How do you determine it for a liquid by capillary method? How does it vary with temperature?

(*Guru Nanak Dev BSc, 2003*)

24. (*a*) What is surface tension? Why rain drops are spherical? Write SI units of surface tension.

(*b*) Write short note on parachor. (*Arunachal BSc, 2003*)

25. Water passes through a viscometer in 30 seconds. The same volume of oil required 2263.7 seconds. Calculate the viscosity of oil if its density is 1.1×10^3 kg m^{-3}. Density of water is 0.998×10^3 kg m^{-3}, viscosity of water is 0.00101 kg m^{-1} s^{-1}.

Answer. 0.8400 poise (*Nagpur BSc, 2003*)

26. Define the terms : relative viscosity, specific viscosity, reduced viscosity and intrinsic viscosity as applied to the solutions of high polymers. How is the intrinsic viscosity related to molecular mass of a polymer? (*Burdwan BSc, 2003*)

27. Describe stalagmometer and what for it is used? (*HS Gaur BSc, 2003*)

28. What are the factors on which surface tension of a liquid depends? What are its units? Describe drop number method to measure surface tension of liquid. (*Delhi BSc, 2004*)

29. (*a*) What is stalagmometer and how is it used in the determination of surface tension of a liquid?

(*b*) When 12.0 cc of water is allowed to flow through a stalagmometer, 50.0 drops of water were obtained and when the same volume of liquid is allowed to flow, the number of drops formed was 35. If the density of the liquid is 1.2 g per c.c. and the surface tension of water is 72 dynes cm^{-1}, calculate the surface tension of the liquid.

Answer. (*b*) 123.428 dynes cm^{-1} (*Jammu BSc, 2004*)

30. (*a*) Find the dimension of viscosity coefficient η and translate poise into SI units.

(*b*) At 20°C flow times of water and another liquid in a viscometer are 2 min. 24 sec. and 1 min. respectively. Take density of water = 1 g per cc, density of liquid = 0.8 g per cc, viscosity coefficient of water = 1 centipoise (all at 20°C). Calculate the coefficient of viscosity for the liquid at 20°C.

Answer. (*b*) 0.33 centipoise (*Sambalpur BSc, 2004*)

31. At 20°C, toluene rises 1.95 cm in a capillary tube of radius 0.3412 mm. Calculate the surface tension of toluene. The density of toluene at 20°C is 0.866 g per cc.

Answer. 28.42 dyne cm^{-1} (*Sri Venkateswara BSc, 2004*)

32. The refractive index of a liquid of molar mass 72 is 1.34 and its density is 0.98 g cm^{-3}. Find its molar refraction.

Answer. 15.40 cm^3 mol^{-1} (*Jiwaji BSc, 2005*)

33. The surface tension of a liquid at 300 K is 27.1 dyne cm^{-1} and its density at this temperature is 0.9880 g cm^{-3}. What is the radius of the largest capillary that will allow the liquid to rise 2.0 cm ? (Assume the angle of contact to be zero and $g = 981$ cm sec^{-2})

Answer. 0.028 cm (*Panjab BSc, 2005*)

34. The surface tension of water at 293 K is 72.73×10^{-3} Nm^{-2}. How high will water rise in a capillary of diameter 0.01 cm?

Answer. 29.7 cm (*Bundelkhand BSc, 2005*)

35. Calculate the optical rotation when sodium D light passes through a solution of a compound in chloroform, containing 25 g per 100 ml, placed in a cell of 20 cm. [α] for the compound in chloroform is 37.5º.

Answer. 18.75º (*Delhi BSc, 2006*)

36. A glass capillary of diameter 0.1 cm is dipped into water. Calculate the level of the water that rises in the capillary if surface tension of water = 72.75 dyne cm^{-1} density = 0.9984 g cm^{-3} and contact angle for water = 10º.

Answer. 2.93 cm (*Madurai BSc, 2006*)

37. The refractive index of a liquid at 25 ºC is 1.6 and its density is 0.87 g cm^{-3}. Find the molar refraction. (Molar mass of the liquid is 78)

Answer. 26.36 cm^3 mol^{-1} (*Kolkata BSc, 2006*)

38. The molar refraction of a liquid is 12.95 cm^3 mol^{-1} and its density is 1.046 g cm^3. Calculate the refractive index (molar mass of liquid is 60 g mol^{-1})

Answer. 1.369 (*Banaras BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. The molecules which have partial positive charge at one end and a partial negative charge at the other are called

(*a*) ion-pairs (*b*) charged molecules

(*c*) dipoles (*d*) electric molecules

Answer. (*c*)

2. The momentary attractions between the molecules of a liquid caused by instantaneous dipole and induced-dipole attractions are called

(*a*) van der Waals forces (*b*) polar forces

(*c*) French forces (*d*) London forces

Answer. (*d*)

3. The strength of H-bonding is about _______ as that of a covalent bond (*a*) 1/2 (*b*) 1/3

(*c*) 1/10 (*d*) 1/100

Answer. (*c*)

4. Which of the following statements is incorrect?

(*a*) the pressure exerted by the vapour in equilibrium with the liquid at a fixed temperature is called vapour pressure

(*b*) the vapour pressure increases with rise in temperature

(*c*) at equilibrium, liquid $\rightleftharpoons$ vapour

(*d*) at equilibrium, the rate of evaporation is not equal to the rate of condensation

Answer. (*d*)

5. The boiling point of a liquid is that temperature at which

(*a*) the vapour pressure of the liquid is equal to the atmospheric pressure

(*b*) the vapour pressure of the liquid is less than the atmospheric pressure

(*c*) the vapour pressure of the liquid is greater than the atmospheric pressure

(*d*) the vapour pressure of the liquid is equal to the square root of the atmospheric pressure

Answer. (*a*)

6. With rise in temperature, the surface tension of a liquid

(*a*) increases (*b*) decreases

(*c*) remains the same (*d*) none of the above

Answer. (*b*)

7. The unit in which surface tension is measured is

(*a*) dyne cm (*b*) dyne cm^{-1}

(*c*) dyne^{-1} cm (*d*) $\text{dyne}^{-1}\ \text{cm}^{-1}$

Answer. (*b*)

8. The formula used for the determination of surface tension by capillary rise method is

(*a*) $2\gamma = hrdg$ (*b*) $2\gamma = hr^2dg$

(*c*) $2\gamma = \pi\, r \cos\theta$ (*d*) $2\gamma = \pi\, hr^2dg$

Answer. (*a*)

9. In drop weight method for determination of surface tension of liquids, the formula used is

(*a*) $\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2}$ (*b*) $\frac{\gamma_1}{\gamma_2} = \frac{m_2}{m_1}$

(*c*) $\frac{\gamma_1}{\gamma_2} = \frac{m_2^2}{m_1^2}$ (*d*) $\frac{\gamma_1}{\gamma_2} = \frac{m_1^2}{m_2^2}$

Answer. (*a*)

10. The formula used in drop-number method for determination of surface tension of liquids is

(*a*) $\frac{\gamma_1}{\gamma_2} = \frac{n_2\, d_1}{n_1\, d_2}$ (*b*) $\frac{\gamma_1}{\gamma_2} = \frac{n_1\, d_1}{n_2\, d_2}$

(*c*) $\frac{\gamma_1}{\gamma_2} = \frac{n_1\, d_2}{n_2\, d_1}$ (*d*) $\frac{\gamma_1}{\gamma_2} = \frac{n_2\, d_2}{n_1\, d_1}$

Answer. (*a*)

11. Viscosity of a liquid is a measure of

(*a*) repulsive forces between the liquid molecules

(*b*) frictional resistance

(*c*) intermolecular forces between the molecules (*d*) none of the above

Answer. (*b*)

12. The reciprocal of viscosity is called

(*a*) surface tension

(*b*) frictional resistance

(*c*) fluidity

(*d*) none of these

Answer. (*c*)

13. The dimensions in which coefficient of viscosity is expressed are

(*a*) mass × length × time^{-1}

(*b*) mass × length^{-1} × time^{-1}

(*c*) mass × length^{-1} × time

(*c*) mass^{-1} × length^{-1} × time^{-1}

Answer. (*b*)

14. The SI unit of coefficient of viscosity is

(*a*) kg m^2 sec

(*b*) kg m sec^{-1}

(*c*) kg m^{-1} sec

(*d*) kg m^{-1} sec^{-1}

Answer. (*d*)

15. The formula used for the determination of relative viscosity by Ostwald's method is

(*a*) $\dfrac{\eta_1}{\eta_2} = \dfrac{d_1\, t_1}{d_2\, t_2}$

(*b*) $\dfrac{\eta_1}{\eta_2} = \dfrac{d_1\, t_2}{d_2\, t_1}$

(*c*) $\dfrac{\eta_1}{\eta_2} = \dfrac{d_2\, t_1}{d_1\, t_2}$

(*d*) $\dfrac{\eta_1}{\eta_2} = \dfrac{d_2\, t_2}{d_1\, t_1}$

Answer. (*a*)

16. In general, the viscosity ________ with temperature

(*a*) decreases

(*b*) increases

(*c*) remains the same

(*d*) none of these

Answer. (*a*)

17. The specific refraction is given by the formula

(*a*) $R_s = \dfrac{n^2 - 1}{n^2 + 2} \times \dfrac{1}{d}$

(*b*) $R_s = \dfrac{n^2 + 1}{n^2 - 2} \times \dfrac{1}{d}$

(*c*) $R_s = \dfrac{n^2 - 1}{n^2 - 2} \times \dfrac{1}{d}$

(*d*) $R_s = \dfrac{n^2 + 1}{n^2 + 2} \times \dfrac{1}{d}$

Answer. (*a*)

18. The molar refraction is given by the formula

(*a*) $R_M = \dfrac{n^2 + 1}{n^2 + 2} \cdot \dfrac{M}{d}$

(*b*) $R_M = \dfrac{n^2 - 1}{n^2 + 2} \cdot \dfrac{M}{d}$

(*c*) $R_M = \dfrac{n^2 + 1}{n^2 - 2} \cdot \dfrac{M}{d}$

(*d*) $R_M = \dfrac{n^2 - 1}{n^2 - 2} \cdot \dfrac{M}{d}$

Answer. (*b*)

19. The units in which molar refraction is expressed are

(*a*) cm^3 mol^1

(*b*) cm^{-3} mol

(*c*) cm^{-3} mol^{-1}

(*d*) cm^3 mol^{-1}

Answer. (*d*)

20. The specific rotation, a characteristic of an optically active substance, is expressed as

(*a*) $[\alpha] = \dfrac{\alpha}{\ell \times c}$

(*b*) $[\alpha] = \dfrac{\alpha}{\ell^2 \times c}$

(*c*) $[\alpha] = \frac{\alpha}{\ell \times c}$ (*d*) $[\alpha] = \frac{\alpha^2}{\ell \times c}$

Answer. (*c*)

21. Association of molecules in water is due to

(*a*) surface tension (*b*) viscosity

(*c*) hydrogen bonding (*d*) optical activity

Answer. (*c*)

22. With the increasing molecular mass of a liquid, the viscosity

(*a*) increases (*b*) decreases

(*c*) no effect (*d*) none of these

Answer. (*a*)

23. Which of the following liquids has the maximum viscosity

(*a*) water (*b*) acetone

(*c*) ethyl alcohol (*d*) glycerine

Answer. (*d*)

24. The fluidity of liquids _______ with increase in temperature

(*a*) decreases (*b*) remains the same

(*c*) increases (*d*) none of these

Answer. (*c*)

25. A liquid rises in a capillary tube. It is due to

(*a*) surface tension (*b*) viscosity

(*c*) osmosis (*d*) effusion

Answer. (*a*)

26. A liquid is in equilibrium with its vapours at its boiling point. On the average, the molecules in the two phases have equal

(*a*) potential energy (*b*) kinetic energy

(*c*) van der Waal's forces (*d*) total energy

Answer. (*b*)

27. The rate of evaporation of a liquid depends upon

(*a*) surface area (*b*) temperature

(*c*) nature of liquid (*d*) all of these

Answer. (*d*)

28. The highest temperature at which vapour pressure of a liquid can be measured is

(*a*) boiling point of the liquid (*b*) freezing point of the liquid

(*c*) inversion temperature (*d*) critical temperature

Answer. (*d*)

29. Small droplets are spherical in shape. It is due to

(*a*) high viscosity

(*b*) their tendency to acquire minimum surface area

(*c*) their tendency to acquire maximum surface area

(*d*) less viscosity

Answer. (*b*)

30. Insects can walk on the surface of water due to

(*a*) viscosity (*b*) surface tension

(*c*) refractivity (*d*) optical activity

Answer. (*b*)

31. The cleansing action of soaps and detergents is due to

(*a*) internal friction
(*b*) high hydrogen bonding
(*c*) surface tension
(*d*) viscosity

Answer. (*c*)

32. The work in ergs required to be done to increase the surface area by 1 sq. cm is called

(*a*) surface tension
(*b*) internal friction
(*c*) fluidity
(*d*) surface energy

Answer. (*d*)

33. While determining viscosity of a liquid with the help of a viscometer, the liquid was sucked with great difficulty. The liquid may be

(*a*) water
(*b*) acetone
(*c*) ether
(*d*) glycerine

Answer. (*d*)

34. The vapour pressure of a liquid at a given temperature is given by

(*a*) $\frac{n}{V}RT$
(*b*) $\frac{n}{V}RT^2$
(*c*) $\frac{n}{2V}RT$
(*d*) $\frac{n}{V}RT^3$

Answer. (*a*)

35. Which of the following is incorrect?

(*a*) the rate of condensation is equal to the rate of evaporation at equilibrium in a closed container
(*b*) the concentration of the molecules in vapour phase decreases continuously
(*c*) the concentration of the molecules in vapour phase remains unchanged at equilibrium
(*d*) none of the above

Answer. (*b*)

36. The vapour pressure of non-polar liquids is

(*a*) fairly high as compared to polar liquids
(*b*) fairly low as compared to polar liquids
(*c*) the same as that of polar liquids
(*d*) none of these

Answer. (*a*)

37. The boiling point of a liquid ________ with external pressure

(*a*) changes
(*b*) always increases
(*c*) always decreases
(*d*) remains the same

Answer. (*a*)

38. The units of coefficient of viscosity are

(*a*) dyne cm^{-2} sec
(*b*) poise
(*c*) centipoise
(*d*) all of these

Answer. (*d*)

39. Liquids with high molecular masses have ________ viscosity

(*a*) greater
(*b*) lesser
(*c*) zero
(*d*) none of these

Answer. (*a*)

40. The liquids with high intermolecular attractive forces have ________ viscosity

(*a*) low
(*b*) intermediate
(*c*) high
(*d*) none of these

Answer. (*c*)

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