

UNIT III:

Surface tension:

Definition of surface tension with unit and dimension – Surface energy – formation of drops – angle of contact – excess of pressure inside curved surface – Experimental determination of surface tension (Jaeger's method) – drop weight method of determining surface tension and interfacial surface tension – Quincke's method

Osmosis: Definition – experimental determination of osmotic pressure – Laws of osmosis – osmotic pressure and vapour pressure of a solution.

3

Surface Tension

CHAPTER

3.1 INTRODUCTION

Any liquid in small quantity, so that gravity influence is negligibly small, will always assume the form of a spherical drop e.g., rain drops, small quantities of mercury placed on a clean glass plate etc. So a liquid must experience some kind of force, so as to occupy a minimum surface area. This contracting tendency of a liquid surface is known as surface tension of liquid. This is a fundamental property of every liquid.

The following experiment illustrates the tendency of a liquid to decrease its surface area.

When a camel hair brush is dipped into water, the bristles spread out [Fig. 3.1 (a)]. When the brush is taken out, the bristles cling together on account of the films of water between them contracting [Fig. 3.1. (b)]. This experiment clearly shows that the surface of a liquid behaves like an elastic membrane under tension with a tendency to contract. This tension or pull in the surface of a liquid is called its *surface tension*.

Definition : It may be defined as the force per unit length of a line drawn in the liquid surface, acting perpendicular to it at every point and tending to pull the surface apart along the line.

Unit of surface tension. Surface tension being force per unit length, its SI unit is newton per metre (Nm^{-1}).

Dimensions of surface tension : Since it is the ratio of a force to a length, its dimensions are $MLT^{-2}/L = MT^{-2}$.

Molecular forces : There are two kinds of molecular forces :

(i) adhesive forces and (ii) cohesive forces.

(i) Forces of attraction between molecules of different substances are known as adhesive forces. For example, the force of attraction between the glass molecules of a beaker and molecules of water contained in it is an adhesive force. Adhesive force is different for different pairs of substances.

(ii) Force of attraction between molecules of the same substance is called cohesive force. This force varies inversely probably as the eighth power of the distance between two molecules. Hence, it is very appreciable when the distance between two molecules is small. It is the greatest in solids, less in liquids and the least in gases. Therefore, a solid has a definite shape, a liquid has a definite free surface and a gas has neither.

The maximum distance up to which a molecule exerts a force of attraction on another is called the range of *molecular attraction* and is generally of the order of 10^{-9} m. A sphere with the molecule as centre and the range of molecular attraction as radius is called the *sphere of influence* of the molecule. The molecule attracts and is, in turn, attracted by the molecules present inside this sphere.

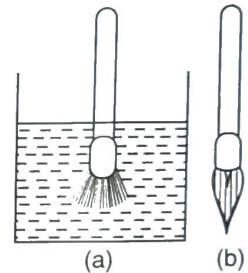


Fig. 3.1

3.2 EXPLANATION OF SURFACE TENSION ON KINETIC THEORY

Consider three molecules A , B and C of a liquid [Fig. 3.2]. The circles around them indicate their respective spheres of influence.

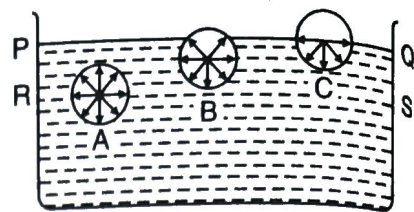


Fig. 3.2

- (i) The molecule A is well within the liquid and it is attracted equally in all directions by the other molecules lying within its sphere of influence. Therefore, it does not experience any resultant force in any direction. This happens only as long as the sphere of influence is well within the liquid.
- (ii) The sphere of influence of molecule B lies partly outside the liquid. The upper half of the sphere contains fewer molecules attracting the molecule B upwards, than the lower half attracting it downwards. Hence, there is a resultant downward force acting on B .
- (iii) The molecule C lies on the surface of the liquid. Half of its sphere of influence lies above the surface of the liquid and contains only a few vapour molecules, whereas there are many liquid molecules in its entire lower half. Thus the resultant downward force in this case is the maximum. If a plane RS is drawn parallel to the free surface PQ of the liquid at a distance equal to the molecular range, then the layer of the liquid between the planes PQ and RS is called the *surface film*. Hence all the molecules in the surface film are pulled downward due to the cohesive force between molecules.

If a molecule is to be brought from the interior of the liquid to the surface of the liquid, work has to be done against the downward cohesive force acting upon it. Hence molecules in the surface film have greater potential energy than the molecules inside the liquid. Since the potential energy of a system tends towards a minimum, the surface film tends to contract, so as to contain minimum number of molecules in it. Thus the surface of the liquid is under tension and behaves like a stretched elastic membrane.

Surface energy : The potential energy per unit area of the surface film is called its *surface energy*.

Example 1 : A glass plate of length 0.1 m, breadth 0.0154 m and thickness 0.002 m weighs 8.2×10^{-3} kg in air. It is held vertically with the long side horizontal and the lower half under water. Find the apparent weight of the plate. Surface tension of water $= 73 \times 10^{-3}$ N/m, $g = 9.8$ m/s².

Volume of the portion of the plate immersed in water is

$$\left(0.1 \times \frac{1}{2}\right)(0.0154)(0.002) = 1.54 \times 10^{-6} \text{ m}^3$$

$$\begin{aligned} \text{Upthrust} &= \text{Weight of water displaced} \\ &= (1.54 \times 10^{-6}) \times 1000 \times 9.8 \\ &= 1.509 \times 10^{-2} \text{ N} = 0.01509 \text{ N} \end{aligned}$$

Now, total length of the plate in contact with the water surface is $2(0.1 + 0.002) = 0.204$ m.

\therefore Downward pull upon the plate due to surface tension is

$$0.204 \times (73 \times 10^{-3}) = 0.0149 \text{ N}$$

\therefore Resultant upthrust $= 0.01509 - 0.0149 = 0.00019 \text{ N}$

\therefore Apparent weight of the plate in water $= \text{Weight of the plate in air} - \text{resultant upthrust}$

$$= 8.2 \times 10^{-3} - 1.939 \times 10^{-5} = 8.18 \times 10^{-3} \text{ kg}$$

3.5. FORMS OF LIQUID DROPS

When a quantity of liquid rests upon a horizontal solid plate, which it does not wet, the shape of the drop is determined by surface tension and gravity. For extremely small drops, the S.T. effects are great and the gravitational effects small. So S.T. determines the shape of the drop. It is therefore spherical. Rain drops, a small quantity of mercury on a glass plate, water drops on leaves, all assume spherical shapes on account of this.

On increasing the size of the drop, the effect of gravitation becomes greater and that of S.T. less. Now, the effect of gravitation alone would be to make the drop spread out, so that its centre of gravity may be the lowest. Hence, a large drop of a heavy liquid spreads out when placed on a glass plate. Therefore, a large drop of mercury is always flat.

3.6. ANGLE OF CONTACT

When a glass plate is dipped in water, the water molecules cling to the surface of glass and the water molecules rise along the plate. The shape of water is as shown in Fig. 3.4 (i). When the glass plate is dipped in mercury, the mercury molecules cling to the surface and the liquid is depressed along the plate as shown in Fig. 3.4 (ii).

The angle of contact θ is defined as the angle made by the tangent at the point of contact of the liquid surface with the glass surface inside the liquid.

This angle may have any value between 0° and 180° . For most liquids and glass, it is less than 90° ; for mercury and glass, it is about 140° . It really depends upon the nature of the liquid and the solid. It is quite independent of the angle of inclination of the solid to the liquid surface.

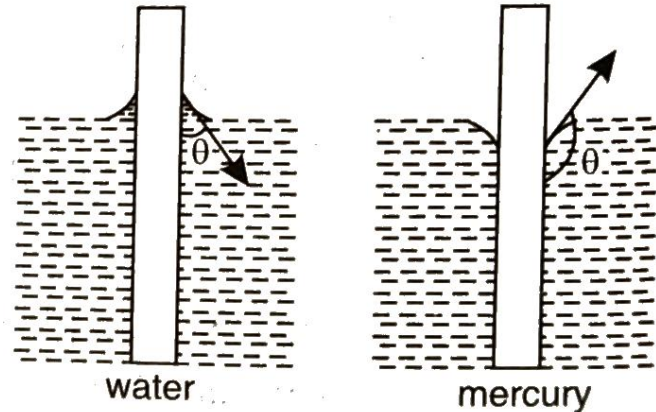


Fig. 3.4

point P by the three sides of a triangle, taken in order. Such a triangle is known as the *Neumann's triangle*. The sum of any two sides of a triangle is always greater than the third side. Therefore, the sum of any two of the three surface tensions σ_1 , σ_2 and σ_3 should be greater than the third. No two pure liquids satisfy this condition. Thus it is not possible to have a drop of one liquid remaining in equilibrium over another liquid. The liquid B , if it is lighter than the liquid A , will spread over the surface of A . Quincke showed that pure water spreads over pure mercury. But, if the mercury surface is contaminated with grease, the water will form a drop on the mercury surface. For contaminated surfaces of liquids, the construction of *Neumann's triangle* can be possible.

3.8. PRESSURE DIFFERENCE ACROSS A LIQUID SURFACE

- (a) If the free surface of the liquid is plane, as in Fig. 3.6 (a), the resultant force due to S.T. on a molecule on the surface is zero.
- (b) If the free surface of the liquid is concave, as in Fig. 3.6 (b), the resultant force due to S.T. on a molecule on the surface acts vertically upwards.
- (c) If the free surface of the liquid is convex, as in Fig. 3.6 (c), the resultant force due to S.T. on a molecule on the surface acts vertically downwards (into the liquid).

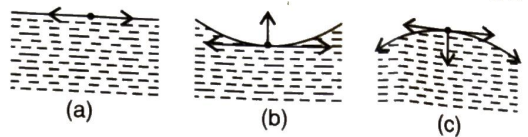


Fig. 3.6

Excess pressure inside a liquid drop : A spherical liquid drop has a convex surface, as in Fig. 3.7 (i). The molecules near the surface of the drop experience a resultant force, acting inwards due to surface tension. Therefore, the pressure inside the drop must be greater than the pressure outside it. Let this excess pressure inside the liquid drop over the pressure outside it be p .

Imagine the drop to be divided into two exactly equal halves. Consider the equilibrium of the upper-half (or the upper hemisphere) of the drop as shown in Fig. 3.7 (ii). If r is the radius of the drop, and σ its S.T.

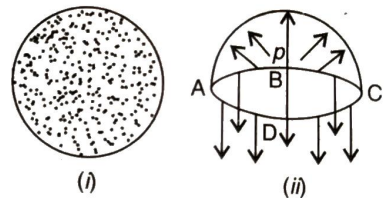


Fig. 3.7

$$\left. \begin{array}{l} \text{the upward force on the plane face} \\ ABCD \text{ due to the excess pressure } p \end{array} \right\} = p \pi r^2$$

$$\left. \begin{array}{l} \text{the downward force due to surface tension acting} \\ \text{along the circumference of the circle } ABCD \end{array} \right\} = \sigma 2\pi r$$

Since the hemisphere is in equilibrium, the two forces are equal.

$$\therefore p \pi r^2 = \sigma 2\pi r \quad \text{or} \quad p = 2\sigma/r$$

Excess pressure inside a soap bubble : A soap bubble has two liquid surfaces in contact with air, one inside the bubble and the other outside the bubble.

$$\text{The force due to S.T. in this case} = 2 \times \sigma 2\pi r = 4\pi r \sigma$$

Therefore, for equilibrium of the hemisphere,

$$p \pi r^2 = 4\pi r \sigma \quad \text{or} \quad p = 4\sigma/r$$

Thus the excess pressure inside a drop or a bubble is inversely proportional to its radius (i.e., $p \propto 1/r$). Since $p \propto 1/r$, the pressure needed to form a very small bubble is high. This explains why one needs to blow hard to start a balloon growing. Once the balloon has grown, less air pressure is needed to make it expand more.

3.9. EXCESS PRESSURE INSIDE A CURVED LIQUID SURFACE

When the pressure on both sides of a liquid surface is same, then the surface is flat, without any curvature. But when it is curved convex upwards, then the pressure inside must be greater than the pressure outside and the excess pressure inside is balanced by the force of S.T.

To find the excess pressure, consider a small curvilinear rectangular element $A_1 B_1 C_1 D_1$ of a liquid surface [Fig. 3.8]. $A_1 B_1$ has a radius of curvature R_1 with centre at O_1 . $B_1 C_1$ has a radius of curvature R_2 with centre at O_2 . Let p be the excess of pressure inside the surface over that outside. Then the outward thrust on the surface $A_1 B_1 C_1 D_1 = p \times \text{Area of the element } A_1 B_1 C_1 D_1 = p \times A_1 B_1 \times B_1 C_1$.

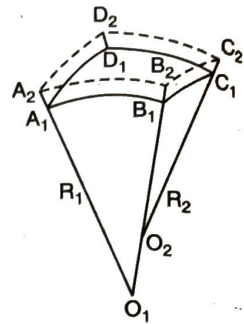


Fig. 3.8

Now, let the surface be moved outward through a very small distance δx .

Let the new position of the surface be $A_2 B_2 C_2 D_2$.

Work done in the displacement $= p \cdot A_1 B_1 \cdot B_1 C_1 \cdot \delta x \dots(1)$

Now, increase in surface area $\left. \begin{aligned} &= \text{Area of } A_2 B_2 C_2 D_2 - \text{Area of } A_1 B_1 C_1 D_1 \\ &= A_2 B_2 \cdot B_2 C_2 - A_1 B_1 \cdot B_1 C_1 \end{aligned} \right\}$

From similar triangles, $A_1 B_1 O_1$ and $A_2 B_2 O_1$,

$$\frac{A_1 B_1}{A_2 B_2} = \frac{A_1 O_1}{A_2 O_1} \quad \text{or} \quad \frac{A_1 B_1}{A_2 B_2} = \frac{R_1}{(R_1 + \delta x)}$$

$$\therefore A_2 B_2 = \frac{A_1 B_1 (R_1 + \delta x)}{R_1} = A_1 B_1 \left[1 + \frac{\delta x}{R_1} \right]$$

Similarly, $B_2 C_2 = B_1 C_1 \left(1 + \frac{\delta x}{R_2} \right)$

Hence $A_2 B_2 \cdot B_2 C_2 = A_1 B_1 \left(1 + \frac{\delta x}{R_1} \right) B_1 C_1 \left(1 + \frac{\delta x}{R_2} \right)$

$$= A_1 B_1 \cdot B_1 C_1 \left(1 + \frac{\delta x}{R_1} + \frac{\delta x}{R_2} \right)$$

Increase in surface area $\left. \begin{aligned} &= A_1 B_1 \cdot B_1 C_1 \left(1 + \frac{\delta x}{R_1} + \frac{\delta x}{R_2} \right) - A_1 B_1 \cdot B_1 C_1 \\ &= A_1 B_1 \cdot B_1 C_1 \cdot \delta x \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \end{aligned} \right\}$

Work done in increasing the area of a surface $\left. \begin{aligned} &= \{ \text{Surface tension} \times \text{increase in surface area} \} \\ &= \sigma \cdot A_1 B_1 \cdot B_1 C_1 \cdot \delta x \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \end{aligned} \right\}$

Equating (1) and (2) we have,

$$p \cdot A_1 B_1 \cdot B_1 C_1 \cdot \delta x = \sigma \cdot A_1 B_1 \cdot B_1 C_1 \cdot \delta x \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

or $p = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$

The excess of pressure inside any particular surface can be deduced from the above expression.

1. Spherical liquid drop (an air bubble in a liquid).

It has only one surface and the radius of curvature is the same everywhere, i.e., $R_1 = R_2 = r$.

$\therefore p = 2\sigma/r$

Handwritten notes:
 $A_1 B_1 B_1 C_1 \left[1 + \dots \right]$
 $(A_1 B_1 + A_1 B_1 \frac{\delta x}{R_1}) (B_1 C_1 + B_1 C_1 \frac{\delta x}{R_2})$
 $A_1 B_1 B_1 C_1 + A_1 B_1 \frac{\delta x}{R_1} B_1 C_1 + B_1 C_1 \frac{\delta x}{R_2} A_1 B_1 + \dots$
 $A_1 B_1 B_1 C_1 \frac{\delta x}{R_1} + \dots$
 $A_1 B_1 B_1 C_1 \frac{\delta x}{R_1} + \dots$
 $\left[\frac{\delta x}{R_1} + \frac{\delta x}{R_2} \right]$
 $\sigma [A_1 B_1 B_1 C_1 \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \delta x]$

2. **Spherical soap bubble.** Here there are two surfaces having the same radius of curvature.

$$\therefore p = 4\sigma/r$$

3. **Cylindrical drop.** $R_1 = r =$ Radius of the cylinder and $R_2 = \infty$.

$$\therefore p = \sigma/r$$

4. **Cylindrical bubble.** $p = 2\sigma/r$ since it has two surfaces.

Note: We have, $p = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$. This expression holds good for surfaces such as spherical or ellipsoidal, for which the principal radii of curvature are on the same side. Such surfaces are called synclastic surfaces [Fig. 3.9 (a)]. But in cases where the two radii are in opposite directions, the surface is called anticlastic [Fig. 3.9 (b)]. The expression for such surfaces is

$$p = \sigma \left(\frac{1}{R_1} - \frac{1}{R_2} \right)$$

Combining the two cases, the general relation is

$$p = \sigma \left(\frac{1}{R_1} \pm \frac{1}{R_2} \right)$$

Example 5 : There is a minute circular hole at the bottom of a small hollow vessel. The vessel has to be immersed in water to a depth of 0.4 m, before any water penetrates inside. Find the radius of the hole, if the surface tension and density of water be $73 \times 10^{-3} \text{ Nm}^{-1}$ and 1000 kg m^{-3} respectively.

Water cannot penetrate till the hydrostatic pressure is greater than the excess of pressure that comes into play due to surface tension. At the limiting condition, when water just penetrates, the two pressures should be equal; i.e., $h \rho g = 2\sigma/r$ where r is the radius of the hole.

$$\therefore r = 2\sigma/(h \rho g)$$

Here, $\sigma = 73 \times 10^{-3} \text{ Nm}^{-1}$; $h = 0.4 \text{ m}$; $\rho = 1000 \text{ kg m}^{-3}$; $r = ?$

$$r = \frac{2 \times (73 \times 10^{-3})}{0.4 \times 1000 \times 9.8} = 3.724 \times 10^{-5} \text{ m}$$

Example 6 : What would be the pressure inside a small air bubble of 10^{-4} m radius, situated just below the surface of water? S.T. of water may be taken to be $70 \times 10^{-3} \text{ Nm}^{-1}$ and the atmospheric pressure to be $1.012 \times 10^5 \text{ Nm}^{-2}$.

$$\left. \begin{array}{l} \text{Excess of pressure inside the spherical} \\ \text{air bubble over that of the atmosphere} \end{array} \right\} = p = \frac{2\sigma}{r}$$

Here, $\sigma = 70 \times 10^{-3} \text{ Nm}^{-1}$; $r = 10^{-4} \text{ m}$

$$\left. \begin{array}{l} \text{Excess} \\ \text{pressure} \end{array} \right\} = p = \frac{2\sigma}{r} = \frac{2 \times (70 \times 10^{-3})}{10^{-4}} = 1400 \text{ Nm}^{-2}$$

$$\therefore \left. \begin{array}{l} \text{Total pressure inside} \\ \text{the air bubble} \end{array} \right\} = \left\{ \begin{array}{l} \text{Atmospheric pressure} \\ + \text{Excess pressure} \end{array} \right\}$$

$$= 1.012 \times 10^5 + 1400 = 1.026 \times 10^5 \text{ Nm}^{-2}$$

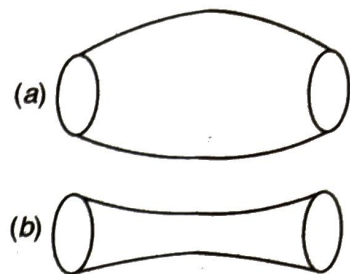


Fig. 3.9

EXPERIMENTAL DETERMINATION OF SURFACE TENSION

3.11. JAEGER'S METHOD

Principle : The experiment is based on the principle that the pressure inside an air bubble in a liquid is greater than the pressure outside it by $2\sigma/r$. Here σ is the S.T. of the liquid and r the radius of the air bubble. This excess pressure can be directly found and hence σ can be calculated.

Apparatus : An aspirator A is closed with a two-holed rubber stopper through which pass two glass tubes [Fig. 3.11]. One of these is connected to a water reservoir through a stopcock B and the other is joined through a tap C to a manometer M and a vertical tube DE . The tube DE ends in a narrow orifice at E and dips into the experimental liquid contained in a beaker.

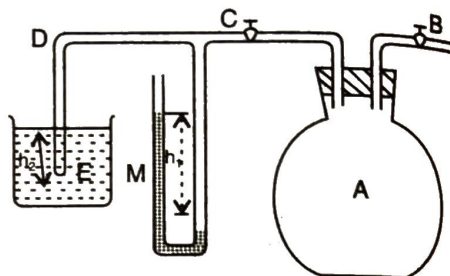


Fig. 3.11

Experimental details : If the stopcock B is opened, water flows into the aspirator and the air in the aspirator is displaced. The displaced air forces its way through the tube DE and forms air bubbles at E . The size of each air bubble gradually grows. When its radius becomes equal to the radius of the tube at E , it becomes unstable and breaks away. During the growth of the bubble, the pressure inside increases and reaches a maximum value at the instant of detachment. The difference in manometer levels h_1 is noted just when the bubble detaches itself. At the moment of detachment,

the pressure inside the bubble $= p_1 = H + h_1 \rho_1 g$, where

H = atmospheric pressure,

h_1 = the difference in manometer levels

and

ρ_1 = density of the manometric liquid

The pressure outside the bubble }
at the same time } $= p_2 = H + h_2 \rho_2 g$

where h_2 = Length of the tube dipping in the experimental liquid and ρ_2 = Density of the experimental liquid.

$$\therefore \left. \begin{array}{l} \text{Excess pressure} \\ \text{inside the bubble} \end{array} \right\} = p = (H + h_1 \rho_1 g) - (H + h_2 \rho_2 g) \\ = (h_1 \rho_1 - h_2 \rho_2) g$$

But the excess pressure inside the bubble $= 2\sigma/r$

$$\text{Hence} \quad 2\sigma/r = (h_1 \rho_1 - h_2 \rho_2)g \quad \text{or} \quad \sigma = \frac{1}{2} r g (h_1 \rho_1 - h_2 \rho_2)$$

Advantages of the method : (1) The angle of contact need not be known.

(2) The continual renewal of the liquid air interface helps in avoiding contamination.

(3) The experiment does not require a large quantity of liquid.

(4) The liquid in the beaker may be heated to various temperatures. Hence the S.T. of a liquid can be determined at various temperatures.

Drawbacks: (1) The exact value of the radius of the bubble when it breaks away cannot be ascertained.

(2) The drop may not be hemispherical and of quite the same radius as the aperture at E .

(3) The calculations are based on the assumption of static conditions but the phenomenon is not entirely statical.

For these reasons, this method does not give very accurate results for the surface tension.

3.17. DROP-WEIGHT METHOD OF DETERMINING THE SURFACE TENSION OF A LIQUID

Experiment : A short glass tube is connected to the lower end of a burette (or funnel) clamped vertically, by means of a rubber tube [Fig. 3.17]. The funnel is filled with the liquid whose S.T. is to be determined. A beaker is arranged under the glass tube to collect the liquid dropping from the funnel. The stopcock is adjusted so that the liquid drops are formed slowly. In a previously weighed beaker a known number of drops (say, 50) are collected.

The beaker is again weighed. The difference between this weight and the weight of the empty beaker gives the weight of 50 drops of the liquid. From this the mass m of each drop is calculated. The inner radius r of the tube is determined using a vernier calipers. The S.T. of the liquid at the room temperature is calculated using the formula,

$$\sigma = \frac{m \cdot g}{3.8 r}$$

Theory : Here, we consider the vertical forces that keep a small drop of liquid in equilibrium, just before it gets detached from the end of a vertical glass tube of circular aperture. At the instant the drop gets detached, it assumes a cylindrical shape at the orifice of the tube [Fig. 3.17(ii)]. Let σ = S.T. of the liquid and r = radius of the orifice.

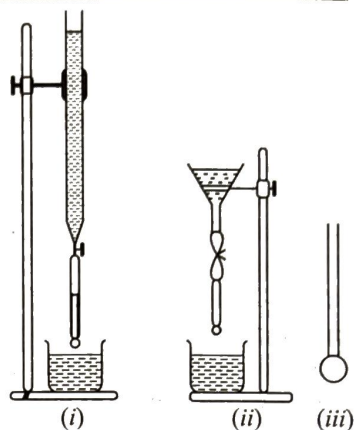


Fig. 3.17

Excess pressure (p) inside the drop over the outside atmospheric pressure } = $\frac{\sigma}{r}$

The area of the section is πr^2 . Therefore, downward force on the drop due to this excess of pressure } = $\pi r^2 \frac{\sigma}{r}$

The weight mg of the drop also acts vertically downwards.

\therefore Total downward force on the drop = $(\pi r^2 \sigma / r) + mg$

This downward force is balanced by the upward pull due to surface tension $2\pi r \sigma$ acting along a circle of radius r . Therefore

$$2\pi r \sigma = \frac{\pi r^2 \sigma}{r} + mg \quad \text{or} \quad 2\pi r \sigma = \pi r \sigma + mg$$

$$\therefore \sigma = \frac{m \cdot g}{\pi \cdot r}$$

But the equilibrium of the drop at the instant of its detachment is dynamic and not static. Lord Rayleigh, taking dynamical aspect into account, showed that

$$\sigma = \frac{m \cdot g}{3.8 r}$$

Example 14 : In a drop weight method for the determination of S.T. between water and air, a glass tube of external diameter 2 mm is used, and 100 drops of water are collected. The mass of these drops is 2.8 gms. Find the S.T. of water in air.

Here, $r = 10^{-3}$ m. $m = 2.8 \times 10^{-3} / 100 = 2.8 \times 10^{-5}$ kg

$$\therefore \sigma = \frac{m \cdot g}{3.8 r} = \frac{(2.8 \times 10^{-5}) \times 9.8}{3.8 \times 10^{-3}} = 0.07221 \text{ Nm}^{-1}$$

Interfacial Tension: At the surface of separation between two immiscible liquids there is a tension similar to surface tension. It is called the interfacial tension.

Definition: *When one liquid rests on another without mixing with it, the interface between the two liquids possesses energy just like the surface of a liquid. The interfacial tension is the value of the force acting per metre normal to a line drawn on the interface.*

Example 12. In a Jaeger type of experiment to measure the S.T. of a liquid, the vertical capillary tube of radius 0.0005 m was dipped inside a liquid of density 1100 kg/m³ to a depth 0.04 m below its surface. When an air bubble was formed at the end of the capillary tube dipping inside the liquid, it was observed from manometric reading that the pressure inside the bubble exceeded the atmospheric pressure by 0.00547 m of mercury. Calculate the S.T. of the liquid.

$$\sigma = \frac{rg}{2} (h_1\rho_1 - h_2\rho_2)$$

Here, $r = 0.0005$ m, $g = 9.8$ m/s², $h_1 = 0.00547$ m, $\rho_1 = 13600$ kg/m³, $h_2 = 0.04$ m and $\rho_2 = 1100$ kg/m³, $\sigma = ?$

$$\begin{aligned}\sigma &= \frac{0.0005 \times 9.8}{2} (0.00547 \times 13600 - 0.04 \times 1100) \\ &= 0.07446 \text{ Nm}^{-1}\end{aligned}$$

3.12. VARIATION OF SURFACE TENSION WITH TEMPERATURE

Liquids are of two types, viz., (i) unassociated liquid and (ii) associated liquid. An unassociated liquid contains the individual molecules of that liquid. **Example:** Benzene and carbon tetrachloride. An associated liquid contains groups of molecules of quite another type. These groups, however, tend to break up into single molecules with a rise in temperature. At the ordinary temperatures, water is known to consist of groups, consisting of two H₂O molecules, in addition to ordinary single H₂O molecules. Thus water is an associated liquid at these temperatures.

The S.T. of an unassociated liquid is found to decrease with rise of temperature, according to the simple formula $\sigma_t = \sigma_0 (1 - \alpha t)$ where σ_t is the S.T. at $t^\circ\text{C}$, σ_0 at 0°C and α , the temperature coefficient of S.T. for the liquid. Van der Waals and Ferguson suggested other relations from which it could be easily deduced that the S.T. is zero at the critical temperature. The best relation connecting S.T. and temperature, for both associated and unassociated liquids, is due to Eotvos. This formula was later modified by Ramsay and Shields.

This is represented by $\sigma (Mv^x)^{3/2} = k (\theta_c - \theta - d)$ where σ = Surface tension at θ K, θ_c = Critical temperature, d = a constant, varying from 6 to 8 for most of the liquids, k = another constant having the value 2.12 for associated liquids and 2.22 for unassociated liquids.

x = Coefficient of association

$$= \frac{\text{effective molecular weight of associated liquid}}{\text{mol wt of the unassociated liquid with the same molecules}}$$

M = molecular weight of the unassociated liquid and v its specific volume.

This shows that the S.T. is zero, when $\theta = (\theta_c - d)$ i.e., at a temperature a little below the critical temperature.

Note 1 : At higher temperature, the molecules themselves possess greater average kinetic energy and are moving about more rapidly. This reduces the effect of molecular attractions. So less work is needed to bring a molecule from the interior of the liquid to the surface. Hence the S.T. of all liquids decreases as the temperature rises.

Note 2 : Impurities, contaminations and dissolved substances all lower the S.T. of a liquid.

3.13. QUINCKE'S METHOD

The shape of a drop depends on the combined action of S.T. and gravity. When a large drop of mercury is placed on a clean horizontal glass plate, the drop flattens out until its top becomes perfectly horizontal as shown in Fig. 3.12 (a).



Fig. 3.12 (a)

Imagine that the drop is cut into two halves by a vertical plane $ABCD$ [Fig. 3.12 (b)]. Let the drop be further cut by two vertical planes BCG and ADH at a distance l from each other and perpendicular to $ABCD$. GH is the most protruding portion of the drop. Let h_1 be the height of the flat top AB above the horizontal plane $EFGH$ and h_2 the total height BC of the drop.

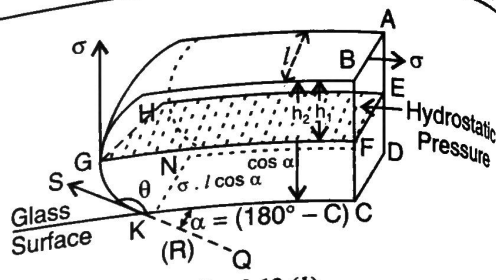


Fig. 3.12 (b)

The portion of the drop lying above the horizontal plane $EFGH$ is in equilibrium under the action of the following forces:

1. Force due to S.T. acting at right angles to AB from left to right horizontally $= \sigma \cdot l$.
2. Hydrostatic thrust acting horizontally from right to left on the plane $ABEF$ of the drop due to part of the liquid on the right. The hydrostatic pressure is zero at AB and increases to $h_1 \rho g$ at EF .

$$\therefore \text{Average pressure} = (0 + h_1 \rho g) / 2 = \frac{1}{2} h_1 \rho g$$

$$\therefore \text{Total hydrostatic thrust on the area } ABEF = \frac{1}{2} h_1 \rho g \times h_1 l$$

$$= \frac{1}{2} h_1^2 \rho g l$$

3. The S.T. at G , which acts vertically upwards, has no component along the horizontal.

Since the drop is in equilibrium, these horizontal forces must balance. Hence $\sigma \cdot l = \frac{1}{2} h_1^2 \rho g l$

$$\text{or } \sigma = \frac{1}{2} h_1^2 \rho g$$

Determination of the angle of contact : Consider the equilibrium of the whole drop. The forces acting on the face $ABCD$ are :

Pull due to S.T. acting horizontally from left to right and perpendicular to $AB = \sigma \cdot l$.

$$\left. \begin{array}{l} \text{Hydrostatic thrust acting horizontally} \\ \text{from right to left on the face } ABCD \end{array} \right\} = \frac{1}{2} h_2 \rho g \times h_2 l = \frac{1}{2} h_2^2 \rho g l$$

$$\left. \begin{array}{l} \text{The S.T. pull due to mercury on glass at } K \text{ acting} \\ \text{tangentially to the slice in the direction } KS \end{array} \right\} = \sigma \cdot l$$

The glass plate exerts an equal and opposite reaction along KQ .

$$\left. \begin{array}{l} \text{The horizontal component of this reactional force} \\ \text{due to glass along } KC, \text{ acting from left to right} \end{array} \right\} = \sigma \cdot l \cos \alpha$$

where $\alpha = (180 - \theta)$

In equilibrium, $\sigma \cdot l + \sigma \cdot l \cos \alpha = \frac{1}{2} h_2^2 \rho g \cdot l$

or $\sigma (1 + \cos \alpha) = \frac{1}{2} h_2^2 \rho \cdot g$

or $\frac{1}{2} h_1^2 \rho \cdot g (1 + \cos \alpha) = \frac{1}{2} h_2^2 \rho \cdot g$

$$\left[\therefore \sigma = \frac{1}{2} h_1^2 \rho g \right]$$

$$\text{or} \quad (1 + \cos \alpha) = \frac{h_2^2}{h_1^2} \text{ or } \cos \alpha = \frac{h_2^2}{h_1^2} - 1$$

$$\text{or} \quad \cos \alpha = (h_2^2 - h_1^2)/h_1^2$$

The value of α can be determined from this relation.

The angle of contact $\theta = 180 - \alpha$.

Experiment : Place a clean glass plate on a small table provided with levelling screws. Arrange it horizontally with the help of a spirit level. Form a large drop of mercury on the glass plate so that its upper surface is perfectly plane.

Sprinkle a fine layer of lycopodium powder at the top of the drop. Adjust the microscope so that the horizontal cross-wire is in line with the lycopodium powder. Lower the microscope and focus it on the line of separation of mercury and glass. The difference between the two readings gives h_2 .

Move the microscope to one edge of the drop. Focus the microscope so that the horizontal cross-wire is in line with the most protruding part of the drop. To find this position very accurately, light from an incandescent lamp S is focussed by a lens L and the plane glass plate P , acting as a mirror, on to the edge of the drop (Fig.3.13). A bright, thin, horizontal line is seen at G , where the drop protrudes out most. The horizontal cross-wire is placed coinciding with this bright horizontal line and the reading is noted. The difference between the top surface reading and this reading gives h_1 . Using the relations given above, S.T. of mercury and angle of contact are determined.

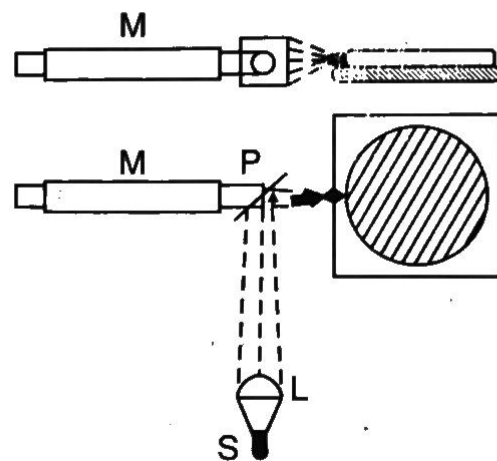


Fig. 3.13

5

Osmosis

CHAPTER

5.1. INTRODUCTION

When a semi-permeable membrane separates a solution from its pure solvent, both being at the same hydrostatic pressure, a diffusion of the solvent takes place into the solution, causing a dilution of the solution. This is known as osmosis.

Osmosis may be demonstrated using the following simple experimental arrangement. A semi-permeable membrane is stretched across the mouth of a thistle funnel and tied firmly. A concentrated solution of sugar in water is poured into the funnel through the stem, keeping the funnel inverted. The funnel is then supported vertically in water kept in a beaker (Fig. 5.1).

The funnel is raised or lowered until the level of the solution in the funnel is the same as the level of water in the beaker. Water is observed to pass from the beaker into the funnel through the semi-permeable membrane. The level of the solution in the tube gradually rises. Therefore, the pressure on the solution side of the membrane gradually increases. This process continues until the excess of pressure on the solution side over the solvent side of the membrane is just sufficient to prevent further diffusion of the solvent into the solution.

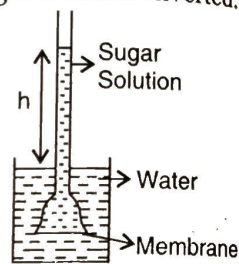


Fig. 5.1

The excess of pressure on the solution side over the solvent side of the membrane when there is no further diffusion of the solvent into the solution is called the osmotic pressure of the sugar solution.

5.2. EXPERIMENTAL DETERMINATION OF OSMOTIC PRESSURE [BERKELEY AND HARTLEY METHOD]

The semi-permeable membrane is in the form of a cylindrical porous pot AB with a deposit of copper ferro-cyanide in its pores (Fig. 5.2). The ends of AB are closed by air-tight one-holed rubber bungs. Through one of them a capillary tube C , closed at one end, is passed. Through the other end, a tube connected to a funnel F is passed. The pot is surrounded by a steel cylinder D containing the given solution. A side-tube in the cylinder is connected to a pump and a nitrogen manometer M .

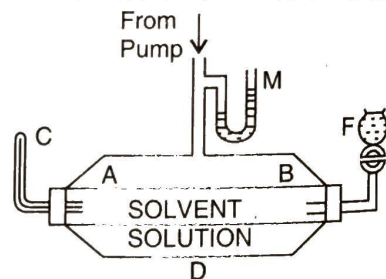


Fig. 5.2

The pure solvent is poured into the pot through the funnel F . Pressure is applied by means of the pump on the solution until the level of solvent in the capillary tube C remains steady. The solvent in the pot is then just prevented from entering the solution due to the pressure applied on the solution. This pressure is noted from the manometer M . It gives the osmotic pressure of the solution of the given concentration.

5.3. LAWS OF OSMOTIC PRESSURE

It is found that a dilute solution of a non-electrolyte behaves in the same way as a perfect gas. The following laws hold good for non-electrolytes.

1. At constant temperature, the osmotic pressure of a dilute solution is directly proportional to the concentration of the solution.
If m kg of a solute are dissolved in V m³ of a solvent, the concentration $C = m/V$.
 $\therefore P \propto m/V$ or PV is constant. This is similar to Boyle's law.
2. When the concentration of the solution is constant, its osmotic pressure is directly proportional to the absolute temperature, ($P \propto T$). This is similar to Charles' law for gases.
3. Solutions of non-electrolytes dissolved in the same solvent and having the same osmotic pressure at the same temperature, contain the same number of gram molecules of the solute in the same volume. This is similar to Avogadro's law.

The first two laws can be combined and expressed as $PV = KT$ where K is a constant and V is the volume containing 1 gram molecule of the solute. $K = R$ for non-electrolytes.

The osmotic pressure of electrolytes is much higher than that of non-electrolytes, under the same temperature and concentration. This abnormal behaviour of electrolytes is attributed to the dissociation of the electrolyte in solution. In the case of electrolytes, the relation between P , V and T is $PV = iRT$ where i is a factor which depends on the degree of dissociation.

5.4. OSMOSIS AND VAPOUR PRESSURE OF A SOLUTION

The vapour pressure of a solution is always less than that of the pure solvent. A tube AB containing a solution is closed at B by a semi-permeable membrane. The tube AB dips vertically into the solvent contained in a beaker. The tube and the beaker are enclosed in an evacuated chamber (Fig. 5.3). The solution rises in the tube due to osmosis to the point M . Let the height of the solution in the tube above the level of the solvent be h . The vapour at M is in contact with the surface of the solution. The vapour at N is in contact with the solvent. Let p_1 and p_2 be the pressures of the vapour at M and N respectively. Let σ be the uniform density of the vapour in the enclosure. Then

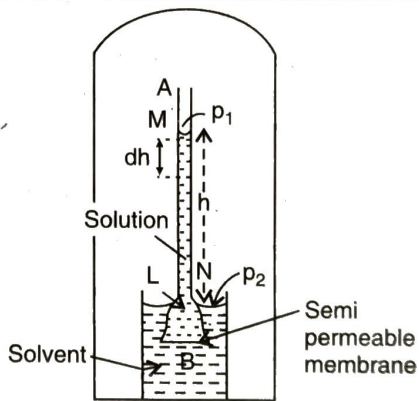


Fig. 5.3

$$p_2 - p_1 = h\sigma g \quad \dots(1)$$

Let ρ be the density of the solution. Let L be a point inside the tube at the same level as N outside. If P is the osmotic pressure, then

$$P = h g (\rho - \sigma) = h g \rho \quad (\because \sigma \ll \rho) \quad \dots(2)$$

Dividing (1) by (2),

$$\frac{p_2 - p_1}{P} = \frac{\sigma}{\rho} \quad \dots(3)$$

$$\therefore p_2 - p_1 = P \sigma / \rho$$

or

$$p_2 - p_1 \propto P$$

$p_2 - p_1$ represents the lowering of vapour pressure. The lowering of vapour pressure of the solvent is directly proportional to the osmotic pressure P .

Now, σ is the density of the vapour at the pressure p_2 . Let σ_0 be the density of the vapour at normal atmospheric pressure P_0 . Then,

$$\frac{p_2}{\sigma} = \frac{P_0}{\sigma_0} \quad \text{or} \quad \sigma = \frac{p_2}{P_0} \sigma_0$$

Substituting this value of σ in Eq. (3),

$$\frac{p_2 - p_1}{p_2} = \frac{P \sigma_0}{P_0 \rho}$$

$$p_2 - p_1 = \frac{P \cdot p_2 \sigma_0}{P_0 \rho}$$

It is not correct to assume the density of the vapour to be uniform, if the osmotic pressure is high.

Let p be the pressure of the vapour at a height h above the surface and σ the density of the vapour at that height.

For a small height dh , let the pressure difference be dp .

$$dp = -g\sigma dh$$

Let σ_0 be the density of the solvent vapour at the normal atmospheric pressure P_0 . Then, at constant temperature T ,

$$\frac{p}{\sigma} = \frac{P_0}{\sigma_0} \text{ or } \sigma = \frac{p\sigma_0}{P_0}$$

$$\therefore dp = -g \frac{p\sigma_0}{P_0} dh$$

$$\text{or } \frac{dp}{p} = -\frac{g\sigma_0}{P_0} dh$$

$$\text{Integrating, } \int_{p_2}^{p_1} \frac{dp}{p} = -\frac{g\sigma_0}{P_0} \int_0^h dh$$

$$\log_e \left(\frac{p_2}{p_1} \right) = -\frac{\sigma_0}{P_0} (hg)$$

But, the osmotic pressure $P = hg\rho$ or $hg = P/\rho$.

$$\therefore \log_e \left(\frac{p_2}{p_1} \right) = -\frac{\sigma_0 P}{P_0 \rho}$$

Example 1 : Calculate the lowering of vapour pressure of a molar solution of a non-electrolyte in water.

A molar solution is one which contains 1 mole of the solute in 1000 cm^3 . A dilute solution behaves as a gas. Therefore, the volume of the solution containing 1 mole of the dissolved substance exerting an osmotic pressure of 1 atmosphere at 0°C is 22400 cm^3 . Hence, the osmotic pressure exerted by 1000 cm^3 of the solution containing 1 mole of the dissolved substance is 22.4 atmospheres.

Thus $P = 22.4$ atmospheres. $P_0 = 1$ atmosphere.

Further, 1 mole of water vapour at N.T.P. occupies 22400 cm^3 .

\therefore density of water vapour at N.T.P.

$$= \sigma_0 = (18 \times 10^{-3}) / (22400 \times 10^{-6})$$

$$= 0.8036 \text{ kg m}^{-3}.$$

Density of water

$$= \rho = 1000 \text{ kg m}^{-3}.$$

We have the relation, $\frac{p_2 - p_1}{p_2} = \frac{P\sigma_0}{P_0\rho}$

$$\therefore \frac{p_2 - p_1}{p_2} = \frac{22.4 \times 0.8036}{1 \times 1000} = 0.018 = 1.8\%$$

The percentage decrease of 1 mole dissolved in 100 c.c. of the solution would be about 1.8%.