... an interface with no molecules.

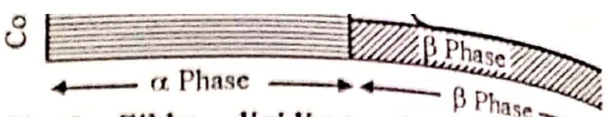

Fig. 2. Gibbs dividing plane between two surfaces.

CURVED SURFACES

The minimisation of the surface area of a liquid may result in the formation of a curved surface as in a bubble (A bubble is a region in which vapour and possibly air too is trapped by a thin film). We shall now see that there are two consequences of curvature, and hence of the surface tension that are relevant to the properties of liquids. One is that the vapour pressure of a liquid depends on the curvature of its surface. The other is the capillary rise or fall of liquid in narrow tubes.

[I] The Laplace-Young Equation

This equation relates pressure across a surface to the curvature of the surface. First we will derive it and then examine some of its applications.

For the system in figure (1), the energy of the α phase is given by

$$dE_\alpha = T\,dS_\alpha = P_\alpha dV_\alpha + \mu_\alpha dn_\alpha \quad \ldots (1)$$

and the energy of the β phase by

$$dE_\beta = T\,dS_\beta - P_\beta\,dV_\beta + \mu_\beta\,dn_\beta \quad \ldots (2)$$

If we place the Gibbs dividing plane such that the number of molecules in that plane disappear as shown in figure (2), the energy of the interface is given by

$$dE_\sigma = T\,dS_\sigma + \gamma d\sigma \quad \ldots (3)$$

To simplify the derivation of Laplace-Young equation, we have assumed that $T_\alpha = T_\beta = T_\sigma = T$. It is not necessary to do so. At equilibrium,

$$dE = dE_\alpha + dE_\beta + dE_\sigma = 0 \quad \ldots (4)$$

and

$$dS = dS_\alpha + dS_\beta + dS_\sigma = 0 \quad \ldots (5)$$

From these equations, we get

$$-P_\alpha dV_\alpha - P_\beta dV_\beta + \mu_\alpha dn_\alpha + \mu_\beta dn + \gamma d\sigma = 0 \quad \ldots (6)$$

Since there are no molecules in the interface, $dn_\alpha = -\,dn_\beta$, so

$$\mu_\alpha = \mu_\beta \quad \ldots (7)$$

for a material equilibrium between the two phases. The condition for equilibrium between two phases is not altered by the presence of an interface between them.

Since the interfacial region has zero volume, we have

$$dV_\alpha = -\,dV_\beta \quad \ldots (8)$$

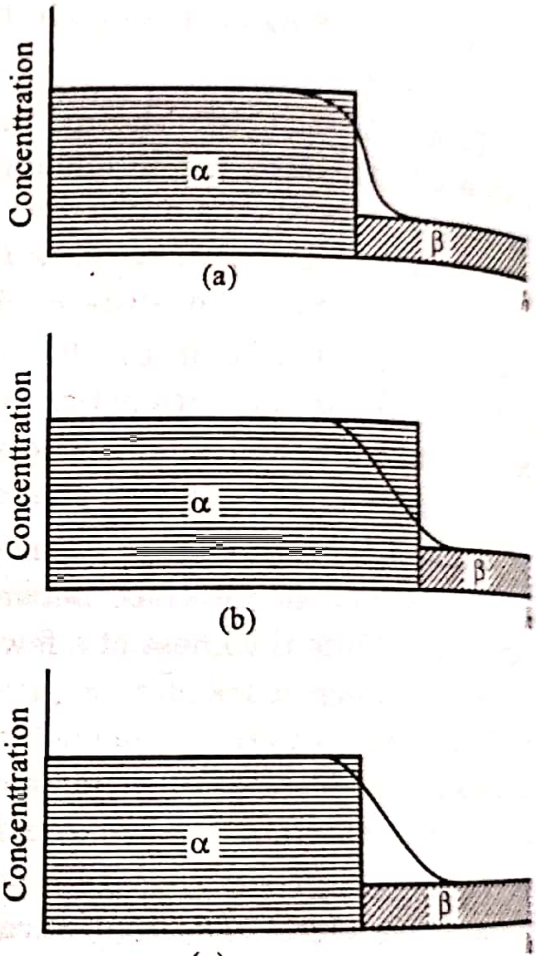

Fig. 3. Surface excess concentration. (a) The amount added to the α phase equals the amount subtracted from the β phase; hence $n_\sigma = 0$ (b) The amount added to the α phase is greater than the amount subtracted from the β phase; hence $n_\sigma > 0$. (c) The amount added to the α phase is smaller than the amount subtracted from the β phase; hence $n_\sigma < 0$.

However, the variations in volume and area are not independent of each other. Hence grouping the remaining terms in equation (6), we get

$$P_\alpha \, dV_\alpha + P_\beta \, dV_\beta - \gamma d\sigma = 0 \quad ...(9)$$

On rearrangement, we get

$$P_\alpha - P_\beta = \gamma\left(\frac{\partial \sigma}{\partial V_\alpha}\right)_T \quad ...(10)$$

This equation was independently derived by Marquis de Laplace and Thomas Young (1805) in a different way from the one followed above.

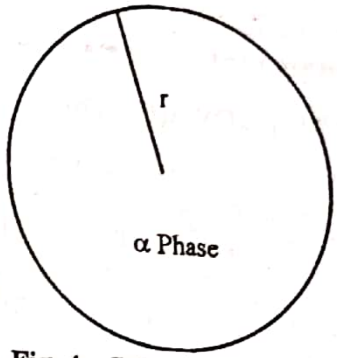

Fig. 4. Spherical drop. The pressure inside is greater than the pressure outside.

[II] Pressure Across a Spherical Surface

Let us consider application of the Laplace-Young equation to a spherical drop [Fig. (4)] For a sphere.

$$\left(\frac{\partial \sigma}{\partial V_\alpha}\right)_T = \frac{2}{r} \quad ...(11)$$

where α refers to the phase of the drop. Therefore,

$$P_\alpha - P_\beta = \frac{2\gamma}{r} \quad ...(12)$$

We see from this that the pressure inside a spherical drop is greater than the pressure outside. As an example, consider a spherical water drop of 5-μm radius. For this,

$$P_\alpha - P_\beta = \frac{2(7 \times 10^{-2} \text{Nm}^{-1})}{5 \times 10^{-6} \text{m}}$$

$$= 0.3 \times 10^5 \text{Pa} \simeq 0.3 \text{ bar}$$

where pressure is quite significant. However, when the radius is 1 mm, the pressure difference falls to 1.4×10^{-3} bar. For a planar surface $r \equiv \infty$ and the pressure difference across the surface disappears.

Equation (12) has to be modified for bubbles. A bubble has two surfaces (double the surface area of a drop), therefore Laplace-Young equation becomes

$$P_\alpha - P_\beta = \frac{4\gamma}{r} \quad ...(13)$$

The utility of the Laplace-Young equation is not confined to spherically symmetric systems. The curvature at a given point is related to two radii for any surface, and for a minimum energy surface it may be shown that

$$\left(\frac{\partial \sigma}{\partial V_\alpha}\right)_+ = \frac{1}{r_a} + \frac{1}{r_{b\alpha}} \quad ...(14)$$

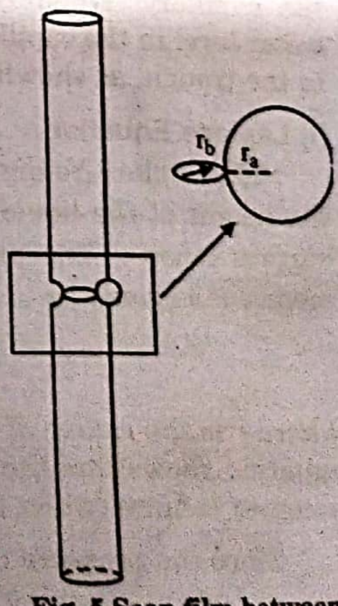

Fig. 5 Soap film between two tubes.

For a sphere $r_a = r_b$ and equation (14) becomes identical to equation (11). So, the general form of the Laplace-Young equation is

$$P_\alpha = P_\beta + \left(\frac{1}{r_{a\alpha}} + \frac{1}{r_{b\alpha}}\right) \quad ...(15)$$

Let us consider an illustration of equation (15). Figure (5) shows a soap film between two glass tubes. At certain distance between the glass tubes, the film appears curved as shown in the figure.

Since the system is open to the surroundings, the pressure in the region enclosed by the soap film must be equal to the external pressure. Therefore, in this special case, there is no pressure difference across a curved surface. This result does not violate the Laplace-Young equation. The soap film in fig. (5) has two radii of curvature. Let r_a be the radius in the plane of the paper, and r_b the radius at the minimum in the horizontal plane perpendicular to the paper. If we place the origin at the centre of the apparatus, we will see that r_b is positive and r_a is negative. The shape of the soap film is such that these two radii have the same magnitude. So, the term in parentheses in equation (15) disappears, leading to $\Delta P = 0$.

☐ CAPILLARY ACTION

The tendency of liquids to rise up the capillary tube (tube of narrow bore) which is called the ***capillary action,*** is a consequence of surface tension. Consider what happens when a glass capillary tube is first immersed in water or any liquid that has a tendency to adhere to the walls. The energy is lowest when a thin film covers as much of the glass as possible. As this film creeps up the inside wall it has the effect of curving the surface of the liquid inside the tube. Suppose the water level in the tube is shown in fig. (6-a) when it is just immersed in water.

Let us examine the pressure at various points in the system. The pressure difference across a flat surface is zero, and pressure does not change appreciably with height in the gas phase. So, the pressure at all points marked 1 in Fig. (6-a) must be the same. Let this pressure be P_1.

Since water wets the glass to some extent; the angle between the liquid surface and the capillary wall will be less than 90°. So, in accordance with the Laplace-Young equation, $P_2 < P_1$ and $P_3 < P_1$. (The radius of curvature outside the capillary is large, and we may ignore the pressure difference there). However, the capillary radius is small, and P_2 will be appreciably lower than P_1. So, the liquid from the bulk migrates into the capillary. When equilibrium is attained the water level in the capillary will be higher than that in the trough, as shown in Fig. (6-b).

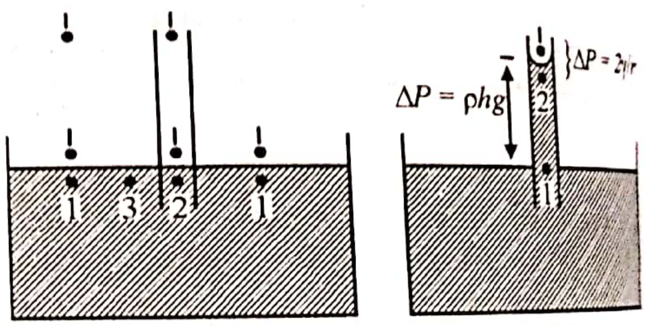

Fig.6. Capillary rise phenomenon.

[I] Laplace Equation

The Laplace-Young equation allows us to relate the height of the liquid column in the capillary to surface tension. The pressure difference across the meniscus is given by

$$\Delta P = P_1 - P_2 = \frac{2\gamma}{r} \quad \text{...(1)}$$

where r is the radius of the meniscus. Equation (1) is known as *Laplace equation*. This equation shows that the difference in pressure decreases to zero as the radius of curvature becomes infinite (when the surface is flat).

Since the pressure difference across a planar surface must vanish, we see from fig. (6-b) that

$$\Delta P = P_1 - P_2 = \rho g h \quad \text{...(2)}$$

where ρ is the density, g is the acceleration due to gravity, and h is the height of the liquid column as shown in Fig. (6-b). From equations (1) and (2), we get

$$\gamma = \rho \frac{ghr}{2} \quad \text{...(3)}$$

Since the radius of the capillary is easily measured, it is more convenient to relate surface tension to it than to the radius of curvature. Hence, equation (3) can be expressed as,

$$\gamma = \frac{\rho g h R}{2 \cos \theta} \quad \text{... (4)}$$

where R is the radius of the capillary tube and θ is the angle of contact.

Problem 1 : ***To what height does water rise at 25°C in a capillary tube of 1.00 mm diameter? The density of water is 997 kg m^{-3}. Assume that the contact angle is zero.***

Solution : Since $\cos \theta = 1$, we have, from equation (3),

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

$$\therefore \quad h = \frac{2(7.28 \times 10^{-2}\ \text{Jm}^{-2})}{(997\ \text{kg m}^{-3})\,(9.8\ \text{ms}^{-2})\,(5 \times 10^{-4}\text{m})}$$

$$= \mathbf{2.98\ cm}$$

Problem 2 : ***What is the size of a water drop falling from a tube 1.00 mm in diameter?***

Solution : Just before the drop falls, the surface tension holding it up equals the force of gravity pulling it down. (Fig. 7). So,

$$2\pi R\gamma = \frac{4}{3}\pi r_d^3 \rho g \quad \text{... (1)}$$

where r_d is the radius of the drop. Rearranging this equation, we have

$$r_d = \left(\frac{3R\gamma}{2\rho g}\right)^{1/3} \quad \text{... (2)}$$

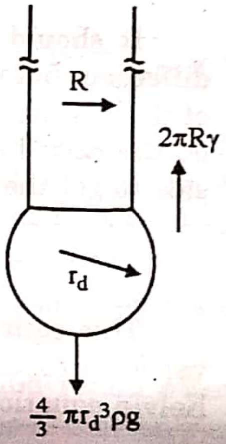

Fig. 7. Relation between the size of a drop and the surface tension.

On substituting the appropriate values for the quantities in the above equation and on solving, we get,

$$r_d = \mathbf{1.79\ mm}$$