IV.5. Surface Tension

Surface tension is the most significant of the characteristic properties of liquids. Consider a liquid in contact with its vapour. A molecule in the bulk of the liquid is subjected to forces of attraction from all directions by the surrounding molecules and is practically in a uniform field of force. But for a molecule at the surface, the net attraction towards the bulk of the liquid is much greater than that towards the vapour where the attracting molecules are more widely dispersed (Fig. IV.3). This means that the molecules at the surface are pulled inwards. The result is liquid surfaces in absence of other forces tend to contract to minimum areas. The surface layer seems to behave as a stretched membrane and this psuedomembrane tends to contract. It explains why a small amount of liquid, left freely, such as mercury, rain drop, etc. always takes spherical shape; because the sphere, for a given volume, has the least surface area.

That there is such a pull on the molecules of the surface layer can be easily demonstrated. If a circular copper-wire ring having a silk-thread tied loosely to the two opposite points be dipped into a soap solution so that on withdrawal a thin film stretches across the entire ring, the thread will freely swim in the film being attracted in all directions (Fig. IV.4*a*). But if the film is punctured in one part, say *A*, the thread will be pulled now in the direction of *B* only (Fig. IV.4*b*) where the film is intact. The thread will immediately assume the most-stretched position.

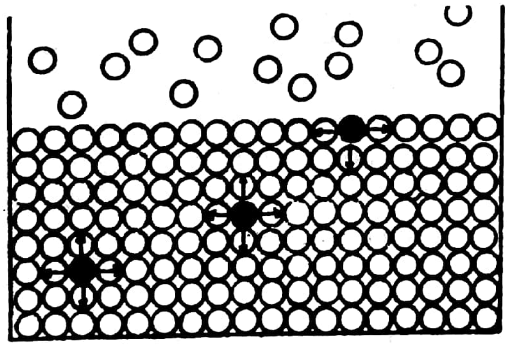
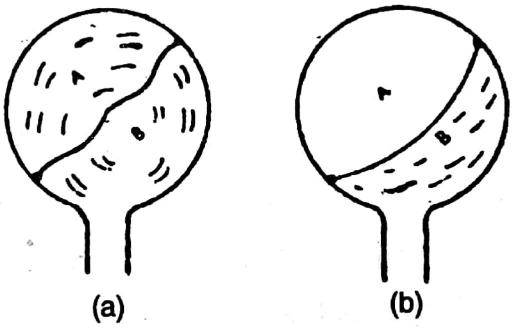


Fig. IV.3



(a) (b)

Fig. IV.4

The floating of metallic needles in water, the dancing of camphor on water, the rise of water-level in capillary tubes are all phenomena due to surface tension.

Now, since the surface is in a state of tension, an attempt to make a penetration along any line in the surface will require an application of force to hold the separate portions of the surface together. This force is called the *surface tension,* denoted usually by the symbol γ. It is expressed as the force in dynes per unit length acting at right angles to the line along the surface of the liquid.

Any increase in the area of the surface of a liquid against its natural tendency to contract will require performance of work. Consider a liquid film *PQRS* contained in a rectangular wire-frame, in which the side *PQ* is movable (Fig. IV.5). Suppose now the film is stretched by moving the boundary *PQ* by *x* cms to $P'Q'$. The length of *PQ* is *l* cms. If γ be the surface tension acting per cm, the force acting towards the film is $\gamma.2l$. It is to be remembered that there are two surfaces of the film.

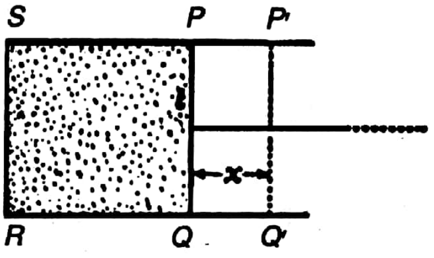


Fig. IV.5

The work done in stretching the film,

$$W = \gamma.2l \times x = \gamma.2xl = \gamma.\Delta A \qquad \text{... (IV.6)}$$

or

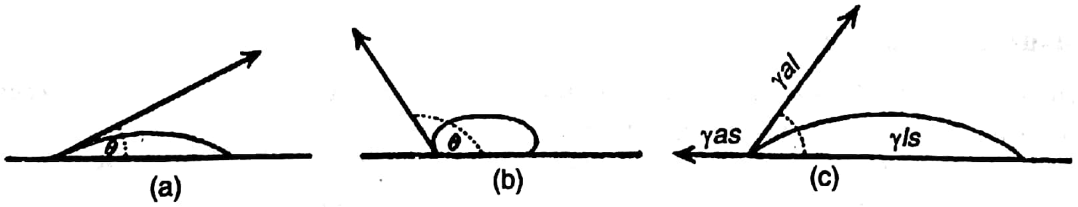
$$\gamma = \frac{W}{\Delta A}$$

ΔA is the total area of the new surfaces created on the two sides of the film.

The work (in ergs) necessary to create or extend one sq. cm. of surface area is called the surface *energy of* the liquid per sq. cm. In other words, the surface tension is numerically the same as the surface energy per unit area of the liquid. The total surface energy is obtained by multiplying the surface tension of the liquid by its area.

IV.6. Angle of Contact and Wetting of Surface

The surface of contact near its point of contact with a solid is generally a curved one. The angle between the tangent to the liquid surface at the point of contact and the solid surface, inside the liquid, is called the *angle of conctact* for that pair of liquid and solid.' The angle *of contact,* which depends upon the nature of the liquid and the solid, may obviously have values between 0^0 and 180^0 (Fig. IV.6). For water and glass it is approximately 18^0, whereas for mercury and glass it is nearly 140^0.



(a) (b) (c)

Fig. IV.6

It is also common experience that some liquids spontaneously wet the surface of some solids and spread over them while other liquids do not wet and spread on certain surfaces. Thus water on glass, alcohol on glass or cement, oil on cloth will easily wet the surface and spread over them but mercury on glass, water on solid paraffin, etc. will not wet or spread. This can be understood from the following consideration. In Fig. IV.6(*c*), let $\gamma_{ls}, \gamma_{as}, \gamma_{al}$ denote the surface tensions for liquid-solid, air-solid and air-liquid respectively. The liquid on solidification does not lose its surface-tension, though the outward manifestations are not seen on account of the rigidity of the solid. When there is equilibrium,

$$\gamma_{as} = \gamma_{ls} + \gamma_{al}\cos\theta \qquad \text{... (IV.7)}$$

where θ is the angler of contact of the liquid with the solid.

If $\gamma_{as} > \gamma_{ls} + \gamma_{al}\cos\theta$ then there cannot be any equilibrium and the, liquid will spread over the solid. From above, we have,

$$\cos\theta = \frac{\gamma_{as} - \gamma_{ls}}{\gamma_{al}}$$

if $\gamma_{as} > \gamma_{ls}$, then $\cos\theta$ is positive, *i.e.*, θ is less than 90^0. If $\gamma_{ls} > \gamma_{as}$, $\cos\theta$ is negative and θ is more than 90^0. The first is the case with water on glass and the second with mercury on glass.

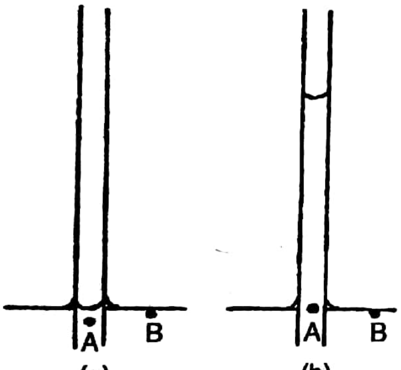
IV.7. Rise of a liquid in a capillary tube

As already mentioned, very often the free surface of a liquid is curved. There exists the inward pressure due to surface tension (γ). Evidently, the pressure on the concave side is higher than that on the convex side. It can be easily shown that the resultant pressure (ΔP) on the curved surface of a liquid is given by

$$\Delta P = 2\gamma / r \quad \text{(see appendix)} \qquad \text{... (IV.8)}$$

where r is the radius of curvature.

A very interesting effect of surface tension is the rise of liquid in a capillary tube. If a capillary tube is partly immersed vertically in a liquid, which wets the surface, the meniscus of liquid within the tube will be concave upwards, as in Fig. (IV.7*a*). The result is that at the point A just below the surface in the tube, pressure will be less than that on the vapour side above by an amount $\frac{2\gamma}{a}$ where a is the radius of curvature of the meniscus. On the other hand, the pressure at the point B where the surface is flat, there is scarcely any difference of pressure on the two sides of the surface. But the pressure on the vapour side both in the tube and outside are the same. Hence inside the liquid the pressure at the point B will be higher than the pressure at the point A. The liquid therefore is pushed up the capillary tube until the level reaches the point C. The pressures at A and B are now equal because of the excess hydrostatic pressure over A. The equilibrium is thus attained, (Fig. IV.7*b*). It can be easily understood that if the liquid does not wet the tubesurface, the meniscus would be convex upwards, and the liquid-level inside will be depressed.



(a) (b)

Fig. IV.7

IV.8. Measurement of Surface Tension

A variety of methods are employed for measuring surface tension. Only a few of these will be mentioned here.

(*a*) ***Capillary Rise Method*** : *A* thoroughly cleaned capillary glass tube of uniform bore is kept partly immersed in the experimental liquid in a vertical position. The liquid rises in the tube and attains a particular height. The height h of the liquid from the surface of the bulk outside to the bottom of the meniscus (Fig. IV.8) is carefully measured with a travelling microscope. The radius r of the capillary tube is predetermined by the usual method of inserting a pellet of mercury and measuring its length and weight.

The upper meniscus is concave and if θ be the angle of contact then. the vertical component of the surface tension (γ) will he $\gamma\cos\theta$. The contact line of the meniscus with the wall of the tube is $2\pi r$. Hence the net upward pull is $2\pi r\gamma\cos\theta$. This is balanced by the weight of the liquid which has been drawn up. The weight of the liquid column is $(\pi r^2 h + v)\rho.g$, where v is the volume of the liquid in the curved meniscus

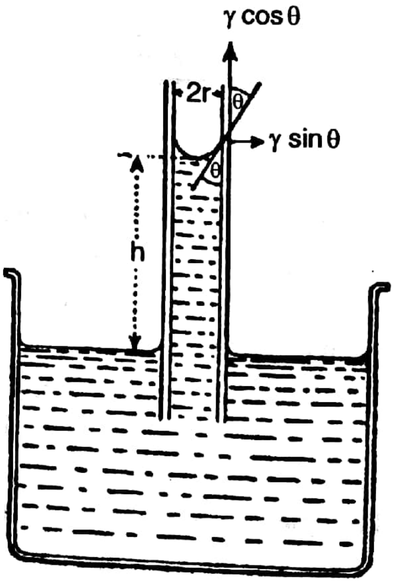


Fig. IV.8 Capillary rise

itself, and ρ is the density of the liquid. Then,

$$2\pi r\gamma\cos\theta = (\pi r^2 h + v)\rho g$$

The radius of curvature of the concave meniscus may be taken. to be the same as the radius of the capillary tube.

So, $$v = \pi r^3 - \frac{2}{3}\pi r^3 = \frac{1}{3}\pi r^3$$

Substituting, $$2\pi r\gamma\cos\theta = \left(\pi r^2 h + \frac{1}{3}\pi r^3\right)\rho g$$

or $$\gamma = \frac{r\rho g\left(h + \frac{1}{3}r\right)}{2\cos\theta} \qquad \text{... (IV.9)}$$

often θ is found to be nearly zero, so that cos $\theta \approx 1$, hence

$$\gamma = \frac{r\rho g\left(h + \frac{1}{3}r\right)}{2} \text{ dynes/cm} \qquad \text{. . . (IV.10)}$$

Thus, the measurement of h and r with a knowledge of the density ρ will enable us to determine the surface tension. Various precautions are of course taken in making the measurements. An alternative method is to make use of (IV.8) directly to arrive at the expression for γ from the capillary rise of liquid.

(*b*) ***Drop-Weight Method*** : When a drop of liquid is at the point of being detatched from the circular end of a vertical capillary tube, the upward and downward forces must balance one another. The upward force is $2\pi r\gamma$. The downward force consists of the weight of the liquid drop and the excess pressure inside the drop, which has a curved surface. The drop at the moment of detatchment is considered cylindrical at the mouth. So, the excess pressure inside the drop is $\frac{\gamma}{r}$. Hence, the total downward force $= mg + \pi r^2.\frac{\gamma}{r}$. At equilibrium, $2\pi r\gamma = mg + \pi r^2.\frac{\gamma}{r}$

or $$\gamma = \frac{mg}{\pi r}$$

The determination of the weight of a liquid drop and the radius of the capillary mouth would give the desired surface tension. In fact the relation is not so simple. The quantity of the liquid released in a drop depends on various factors. From a careful study of it with liquids of known surface tensions Harkins and Brown have established an empirical relation,

$$\gamma = \frac{mg}{r}\phi$$

where ϕ is a factor depending upon $\frac{v}{r^3}$ v being the volume of the liquid drop. The values of ϕ for tubes of different dimensions have also been tabulated by them.

If ρ denotes the density of the liquid, we may write

$$\gamma = \frac{vp}{r}\phi$$

This relation is often used to compare the relative surface tensions of two or more liquids. A pipette-like tube (Fig. IV.9), called *Stalagmometer,* having a very smooth capillary end is used for the purpose. The tube is thoroughly cleaned and the experimental liquid is sucked in. The apparatus is kept in a vertical position in an enclosure free from disturbances or air currents. The liquid is allowed to drop very slowly, ensuring that every drop is fully formed. A definite volume of the liquid (say v. c.c.) determined by marks in the stalagmometer is allowed to come out and the number of drops (n) counted. The density of the liquid is separately determined Then,

$$\gamma = \frac{(v/n)}{r}\rho\phi$$

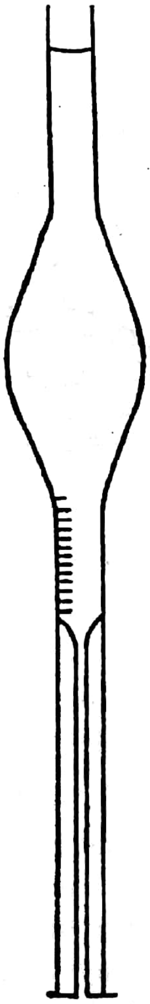


Fig. IV.9
Stalagmometer

The experiment is repeated with a second liquid of known surface tension γ'

That is, $$\gamma' = \frac{(v/n')\rho'}{r}\phi$$

Since, the same stalagmometer is used and the external factors are unaltered, v and r are the same and ϕ is assumed to be the same, *i.e.,*

$$\frac{\gamma}{\gamma'} = \frac{n'\rho}{n\rho'} \qquad \text{... (IV. 11)}$$

γ is easily calculated from a knowledge of surface of a given liquid

(c) The Ring Detachment Method (du Nouy) : *This* is now a commonly used method for quick determination of surface tension with appreciable accuracy. It is based on measurement of the force P, required to detatch a horizontal platinum ring (radius R) from the surfaces of the experimental liquid. The force will be required to overcome the pull due to surface tension. So,

$$P = 4\pi R\gamma, \ \ i.e., \ \ \gamma = \frac{P}{4\pi R} \qquad \text{. . . (IV.12)}$$

To be precise, the relation is to be expressed as $\gamma = \frac{P}{4\pi R}\phi$, where ϕ is Harkins and Jordan correction factor,* which depends on the size of the ring, the thickness of the wire, density of the liquid, etc. The apparatus used is the du Nouy's torsion balance (Fig. 10). The Pt-ring is thoroughly cleaned and suspended from the hook of the beam balanced at the other end by the torsionwire. One end of the torsion wire carries a pointer on a circular scale and is previously calibrated with known-weights taken by the beam. In a flat dish, the liquid is taken and placed in such a way that the Pt-ring just touches the surface. The knob of the torsion wire is then slowly turned until the ring is just detatched from the surface, keeping the beam always in horizontal position. The reading of the pointer gives the force P just at the moment of detatchment of the ring from the liquid surface. The magnitude of γ is then evaluated from equation (IV. 12)

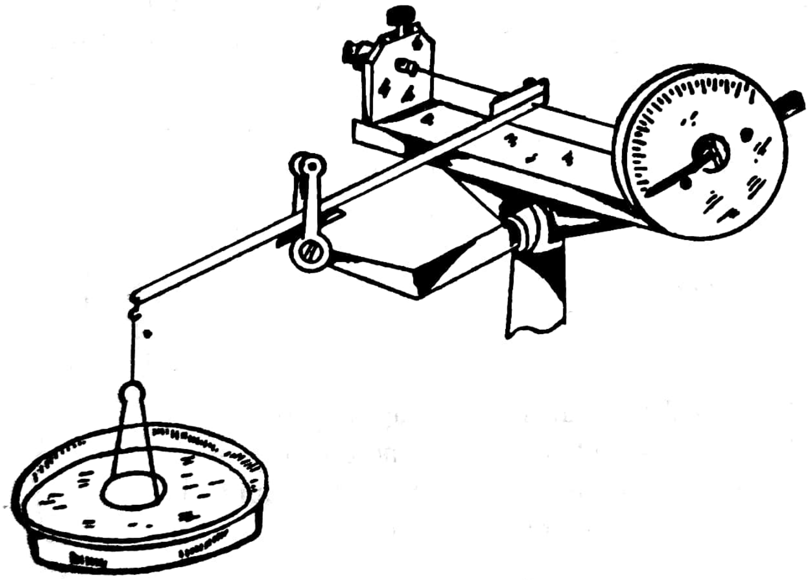


Fig. IV.10. –du Nouy torsion balance

IV.9. Surface Tension and Vapour Pressure

Surface tension is connected with the attraction between the molecules. The process of evaporation *in* which the molecules escape from the surface also depends upon the intermolecular attraction. A relation therefore must exist between the vapour pressure and the surface tension. We may proceed to find out the relation in the following way.

A capillary tube is dipped into a liquid and the capillary rise AB is h, when $\gamma = \frac{1}{2}h\rho gr$,where r is the radius of the tube and ρ is the density of the *liquid.* Further imagine the system is enclosed in a chamber and is in equilibrium (Fig. IV. 11). There is a vapour pressure difference at A and B. If p be the vapour pressure at B, then the vapour pressure at A *is* $p - hdg$, where d is the density of the vapour. This must be the maximum vapour pressure in contact with the curved surface at A. If it were not so, then there would have been condensation or evaporation at A, and a circulation would

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* J. Am. Chem. Soc. 1930, 52, 1756

set up without any supply of energy. This is contrary to our experience. The difference of vapour pressure,

$$dp = hdg$$

But we know, $$h = \frac{2\gamma}{\rho g r}$$

$$\therefore \qquad dp = \frac{2\gamma dg}{\rho g r} = \frac{2\gamma d}{\rho r}$$

Assuming ideal gas laws for the vapour, $d = \frac{Mp}{RT}$

we have,

$$dp = \frac{2\gamma p M}{\rho RTr}, \quad i.e. \quad \frac{dp}{p} = \frac{2\gamma M}{\rho RTr} \qquad \text{... (IV.13)}$$

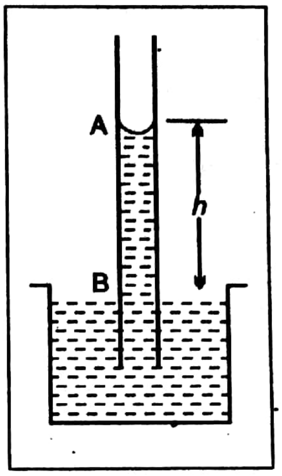

Fig. IV.11

This is the relation between the surface tension and the vapour pressure.

A more precise thermodynamically derived relation is given by

$$ln\frac{p}{p_0} = \frac{2\gamma . M}{\rho RT} . \frac{1}{r}$$

where p_0 and p are the vapour pressures over the liquid in bulk and over a curved surface, having a radius of curvature, r.

Since r occurs in the denominator, the smaller the droplet of a liquid higher will be its vapour-pressure. This is indeed so, as given in the table below, for water droplets of different sizes.

TABLE : T = 25°C, P_0 = 23.76 mm (Hg)

Radius of curvature, $r \rightarrow$	10^{-5}	10^{-6}	10^{-7} (cm)
Vapour pressure, $p \rightarrow$	24.02	26.40	68.43 (mm)

IV.10. Surface Tension and Temperature : Eötvös Ramsay-Shields Relation

It has generally been observed that the surface tension of a liquid decreases with rise in temperature. A quantitative relation, though empirical, between surface tension and temperature was given by Eötvös. If M be the molecular weight and v be the specific volume of a liquid, then molar surface of a liquid, assuming it to be a spherical mass, is proportional to $(Mv)^{2/3}$. The molar surface energy is then $k_1(Mv)^{2/3}\gamma$, where γ is the surface tension of the liquid and k_1 is an appropriate constant. Eötvös suggested that the molar surface energy bears a linear relationship to temperature (t), *i.e.*,

$$k_1(Mv)^{2/3}\gamma = -k_2 t + c_1 \text{ (constant)}$$

or $$(Mv)^{2/3}\gamma = -kt + c \text{ (constant)}$$

Remembering that at the critical temperature t_c the surface tension (γ) is zero, we have, the constant $c = kt_c$

Hence, $$(Mv)^{2/3}\gamma = k(t_c - t)$$

It follows that if we plot $(Mv)^{2/3}\gamma$ against temperature, the line will meet the temperature-axis at the critical temperature. Ramsay and Shields, however, showed from experimental results with many liquids that the lines actually cut the temperature-axis approximately six degrees below the critical temperature. Eötvös equation was therefore modified in order to conform to experimental results, as,

$$(Mv)^{2/3}\gamma = k(t_c - t - 6) \qquad \text{... (IV. 14)}$$

For many liquids, the constant k, often called Eötvös-Ramsay-Shields coefficient, has the same magnitude, 2.1. The constant is evaluated by measuring surface tension and specific volume (from density) at two temperatures for,

$$k = -\frac{\gamma_1(Mv_1)^{2/3} - \gamma_2(Mv_2)^{2/3}}{t_1 - t_2} \qquad \text{... (IV.15)}$$

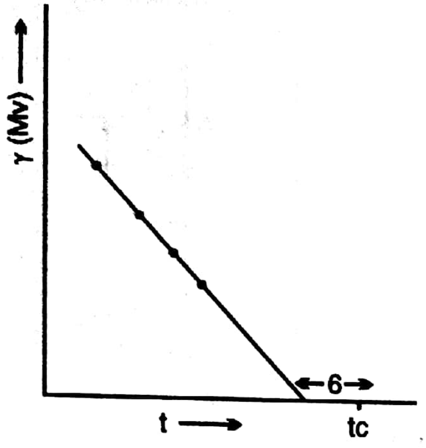

Fig. IV.12

In the case of water, alcohol, carboxylic acids, etc., the value of k was found to be less than 2.1 and the value also rises with temperature. This abnormality has been attributed to the associated state of the molecules in these liquids. That is, the value of k is 2.1 for normal liquids, but for the associated liquids the magnitude is less. Ramsay and Shields further suggested that if x molecules be associated to form each unit in the liquid state, *i.e.*, if x be the degree of association, then

$$-\frac{\gamma_1(xMv_1)^{2/3} - \gamma_2(xMv_2)^{2/3}}{t_1 - t_2} = k = 2.1, \qquad \text{... (IV.16)}$$

from which x the degree of association can be obtained. This relation is only a qualitative one. There are quite a number of non-associated liquids for which the k- value is less than 2.1. On the other hand, many liquids are known having k-values much above 2.1.

The surface tension values of some common liquids are given in the Table below.

SURFACE TENSIONS OF SOME LIQUIDS IN DYNES/CM

Liquids	*Temperature* (0^0C)			
	0^0	20^0	40^0	60^0
Benzene	31.6	28.9	26.3	23.7
Toluene	30.7	28.4	26.1	23.8
Carbon Tetrachloride	–	26.8	24.3	21.9
Acetone	26.2	23.7	21.2	18.6
Methanol	24.5	22.6	20.9	–
Ethanol	24.05	22.27	20.6	19.01
Water	75.64	72.75	69.56	66.18

Problem : A capillary tube of internal diameter 0.2 mm is dipped into water when water rises 15 cms. Calculate surface tension of water.

Neglecting curvature and assuming that angle of contact is zero,

$$\gamma = \frac{rh\rho g}{2} = \frac{1}{2}(0.01 \times 15 \times 1 \times 981) = 73.6 \text{ dynes/cm}$$

Problem : What will be the pressure inside an air bubble of 0.1 mm radius situated just below the surface of water. [γ_{water} 72 dynes/cm, atm. $p = 1.013\times10^6$ dynes/cm^2]

The atm. pressure on the surface = 1.013×10^6

The excess pressure inside the bubble $= \frac{2\gamma}{r} = \frac{2\times72}{0.01} = 0.0144\times10^6$

Hence net pressure inside the bubble $= (1.013 + 0.0144)\times10^6 \ \frac{\text{dynes}}{\text{cm}^2}$

Problem **: A** drop of water, 0.4 cm in radius, is split up into 125 tiny drops. Find the increase in surface energy. [$\gamma_{\text{water}} = 72$ dynes/cm]

If r be the radius of the tiny drops, then

$4/3\pi(0.4)^3 = 4/3\pi(r)^3 n = 4/3\pi(r)^3 \times 125$ whence $r = 0.08$ cm.

The increase in surface area is

$$\begin{aligned} &4\pi(0.08)^2\times125 - 4\pi(0.4)^2 \\ &= 4\pi(0.64) \text{ sq.cm} \end{aligned}$$

The increase in surface energy = area × surface tension

$$= 4\pi\times0.64\times72 = 578.6 \text{ ergs}$$

Problem : The limbs of a vertical U-tube have internal diameters of 1 mm and 2 mm respectively. It is partially, filled with a liquid of density 0.82 gm/c.c. and surface tension 50 dynes/cm. What is the difference in level of the liquid in the two limbs?

Difference of Pressure in the two limbs is

$$\frac{2\gamma}{r_1} - \frac{2\gamma}{r} = 2\times50\left[\frac{1}{0.05} - \frac{1}{0.1}\right] = 1000 \text{ dynes / cm}^2$$

$$\therefore \quad hdg = 1000$$

$$\text{or} \quad h = \frac{1000}{dg} = \frac{1000}{0.82\times981} = 1.24 \text{ cm}$$

Interfacial tension : If a liquid x be separated to produce 1 sq. cm of new surface, the work w_a required for the same, called work of *adhesion.* is equal to $2\gamma_x$.

$$w_a = 2\gamma_x$$

When two immiscible liquids x and y are in contact (Fig. IV.13), the molecules of x attract those of y across the boundary of contact; similarly the molecules of y attract those of x. Thus at the boundary there is an interfacial tension, γ_{xy}, which acts in opposition to both γ_x and γ_y.

If the two liquids be pulled apart at the boundary by one sq. cm, the new surfaces will have surface energies $(\gamma_x + \gamma_y)$. The work of adhe- will he given by,

$$wa = \gamma_x + \gamma_y - \gamma_{xy}$$

Condition for spreading : If a small quantity of an immiscible liquid y be placed on the surface of another liquid x, then the former will spread over the latter, if the work of adhesion exceeds the work of its cohesion W_{cy}, which is called its spreading coefficient, ϕ.

$$\begin{aligned} \phi = w_a - w_{cy} &= \gamma_x + \gamma_y - \gamma_{xy} - 2\gamma_y \\ &= \gamma_x - \gamma_y - \gamma_{xy} \end{aligned}$$

Physically speaking, if $\gamma_x > \gamma_y + \gamma_{xy}$, then y will spread over x, such as oil over water. But if ϕ is negative, then, the added liquid y will not spread and will form a globule.

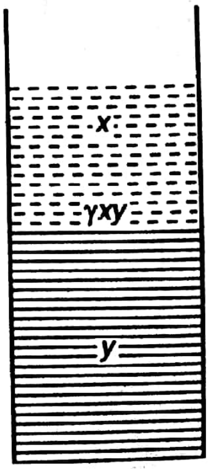

Fig. IV.13