3. Surface Tension

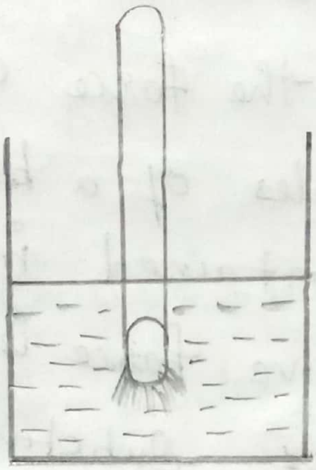
Introduction.

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.

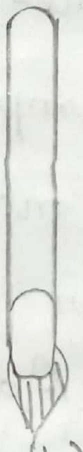
The following experiment illustrates the tendency of a liquid to decrease its surface area.

When a camel hair brush is dipped into water, the bristles spread out (Fig). When the brush is dipped into water, the bristles ~~spread~~ cling together on account of the films of water between them contractiong. This experiment clearly shows that the surface of 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.

" ~~It~~



(a)



(b)

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

Unite of surface tension : newton per metre (Nm^{-1})

Dimensions of Surface tension:

$MLT^{-2}/L = MT^{-2}$

Molecular forces:

There are two kinds of molecular forces.

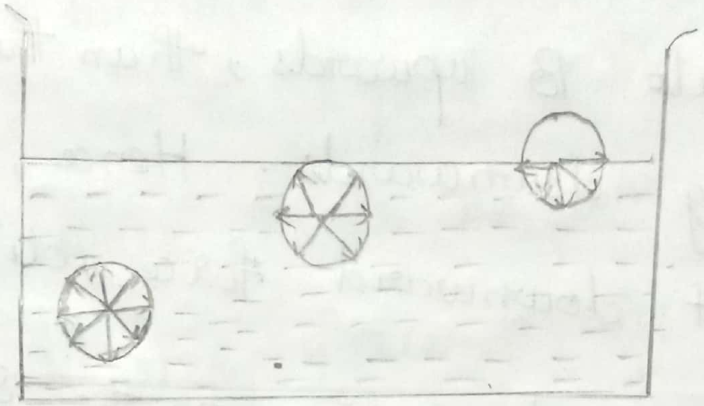
(i) adhesive forces and

(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.

Explanation of Surface tension on kinetic theory.



Consider three molecules A, B and C of a liquid. The Circles around them indicate their respective Spheres of influence.

(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)

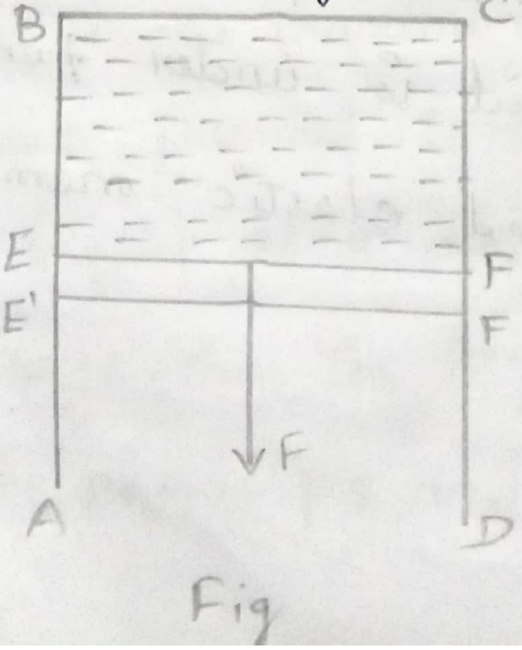
The sphere of influence of molecule B lies partly outside the liquid. The upper half of the sphere contains fewer molecules attracting the molecule B upwards, than the lower half attracting downwards. Hence, there is a resultant downward force acting on B.

(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 liquid is under tension and behaves like a strectched elastic membrane.

Work done in increasing the area of a surface.

Take a rectangular frame work of wire ABCD, with a horizontal wire EF placed across it, free to move up and down (Fig a). From a soap flim across BCFE by dipping it in a soap solution. The wire EF will now be pulled upwards by the surface tension of the film acting in the plane of the film and perpendicular to EF. Therefore to keep the wire EF in equilibrium, a force F (including the weight of the wire EF) ~~Therefore, to keep the wire EF in equilibrium a force F (including the weight of the~~



Fig

has to be applied downwards. If σ = the force per unit length of the film (i.e; S.T) and l = the length of the wire EF, then the upward force due to S.T = $2l\sigma$ [$\because$ The film has two surface and each has a S.T. σ]

Hence $F = 2l.\sigma$

If the wire is pulled downwards through a small distance x to the position E'F'

the workdone = $Fx = 2l\sigma.x = \sigma 2l.x$

$= S.T \times$ Increase in surface area

$\therefore$ the work done in increasing the surface area of the liquid film by unity $\Bigg\} = \dfrac{\sigma 2l.x}{2l.x} = \sigma$.

$\therefore$ The surface tension of a liquid may be defined as the amount of work done in increasing the surface area of the liquid film by unity.

The work required to enlarge the surface of separation between two immiscible or partially miscible liquids is called the interfacial surface energy and is often expressed as the interfacial tension in newton per metre.

Work done in blowing a bubble.

Let the radius of the bubble blown be r. A bubble has two surfaces, an inner and an outer one, each of surface area $4\pi r^2$

∴ The surface area of the film forming the bubble $= 2 \times 4\pi r^2 = 8\pi r^2$

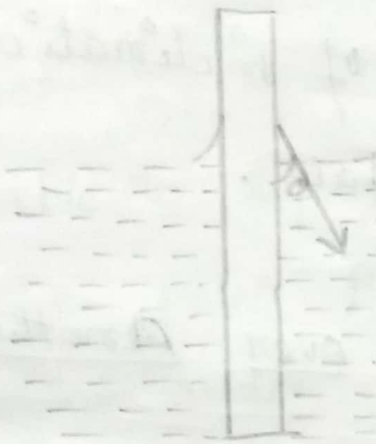
Workdone in blowing the bubble =

Surface tension × Surface area of the film formed

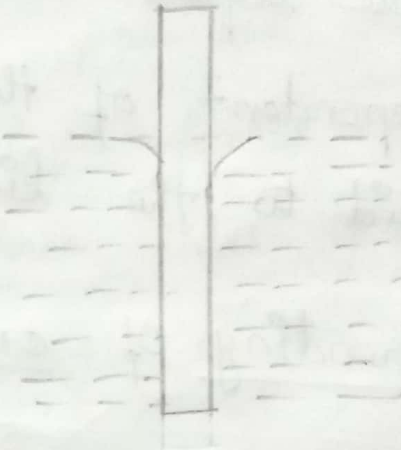
$$= \sigma \times 8\pi r^2 = 8\pi r^2 \sigma$$

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(1)



Water



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 (2)

"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".

The 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.

Spreading of one liquid over Another.

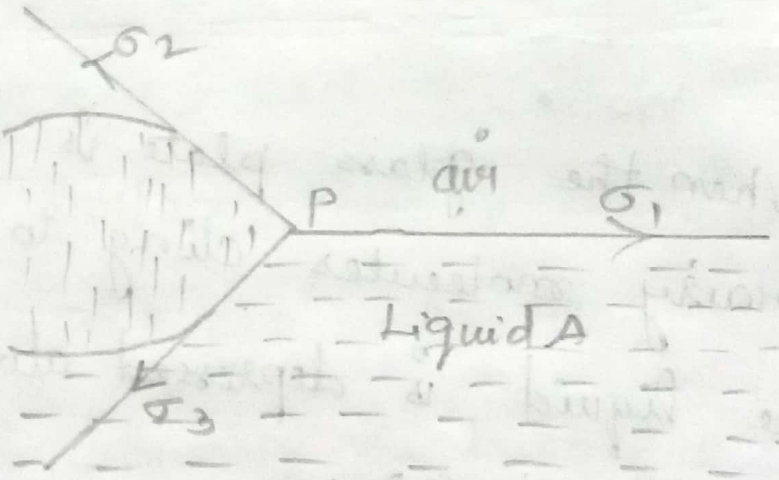


Fig 1

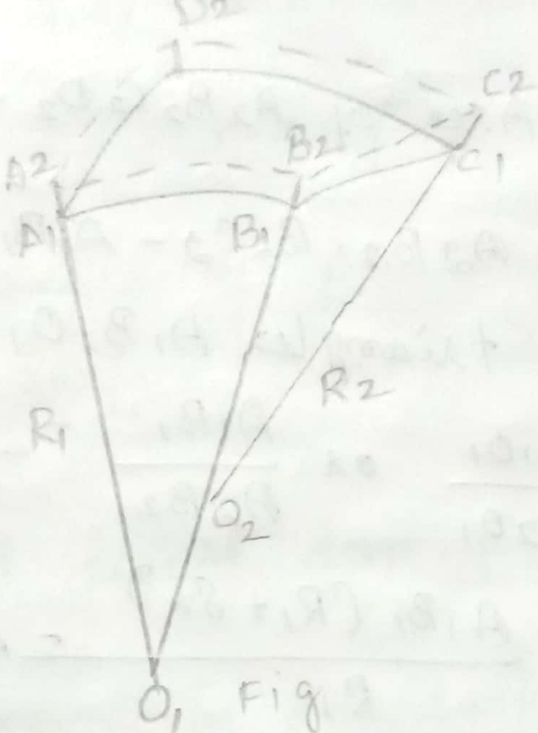
Let a liquid (liquid A) be in contact with another liquid (liquid B) as shown in Fig. The free surfaces of both liquids are in contact with air. Three forces are acting at the point of contact P of the three substances. (1). S.T σ_1 between liquid A and air (2) S.T σ_2 between liquid B and air and (3) S.T σ_3 between liquids A and B. The directions of these tensions are along the tangent at the lines of common contact. If equilibrium is possible, we should be able to represent the three forces acting at the 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 that 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 surface of liquids, the construction of Neumann's triangle can be possible.

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 $A_1B_1C_1D_1$ of a liquid surface Fig (1)



Fig

A_1B_1 has a radius of Curvature R_1 with Centre at O_1. B_1C_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 $A_1B_1C_1D_1$ = p × Area of the element

$A_1B_1C_1D_1 = p \times A_1B_1 \times B_1C_1$

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

Let the new position of the Surface be $A_2B_2C_2D_2$.

Work done in the displacement $= P \cdot A_1B_1 \cdot B_1C_1 \delta x$ .... (1)

Now increase in surface area $\Big\}$ = Area of $A_2B_2C_2D_2$ − Area of $A_1B_1C_1D_1$

$$= A_2B_2 \cdot B_2C_2 - A_1B_1 \cdot B_1C_1$$

From similar triangles $A_1B_1O_1$ and $A_2B_2O_1$.

$$\frac{A_1B_1}{A_2B_2} = \frac{A_1O_1}{A_2O_1} \quad \text{or} \quad \frac{A_1B_1}{A_2B_2} = \frac{R_1}{R_1+\delta x}$$

$$A_2B_2 = \frac{A_1B_1(R_1+\delta x)}{R_1} = A_1B_1\left[1+\frac{\delta x}{R_1}\right]$$

Similarly

$$B_2C_2 = B_1C_1\left(1+\frac{\delta x}{R_2}\right)$$

Hence
$$A_2B_2 \cdot B_2C_2 = A_1B_1\left(1+\frac{\delta x}{R_1}\right)B_1C_1\left(1+\frac{\delta x}{R_2}\right)$$

$$= A_1B_1 \cdot B_1C_1\left(1+\frac{\delta x}{R_1}+\frac{\delta x}{R_2}\right)$$

Increase in Surface area $\Big\}$
$$= A_1B_1 \cdot B_1C_1\left(1+\frac{\delta x}{R_1}+\frac{\delta x}{R_2}\right) - A_1B_1 \cdot B_1C_1$$

$$= A_1B_1 \cdot B_1C_1\, \delta x\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$$

Workdone in increasing the area of a surface $\Big\}$ = {Surface tension × increase in Surface area}

$$= \sigma \cdot A_1B_1 \cdot B_1C_1 \cdot \delta x \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \cdots (2)$$

Equating (1) and (2) we have

$$P \cdot A_1B_1 \cdot B_1C_1 \cdot \delta x = \sigma \cdot A_1B_1 \cdot B_1C_1 \cdot \delta x \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

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 $R_1 = R_2 = r$,

$\therefore P = 2\sigma/r$

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

$P = 4\sigma/r$

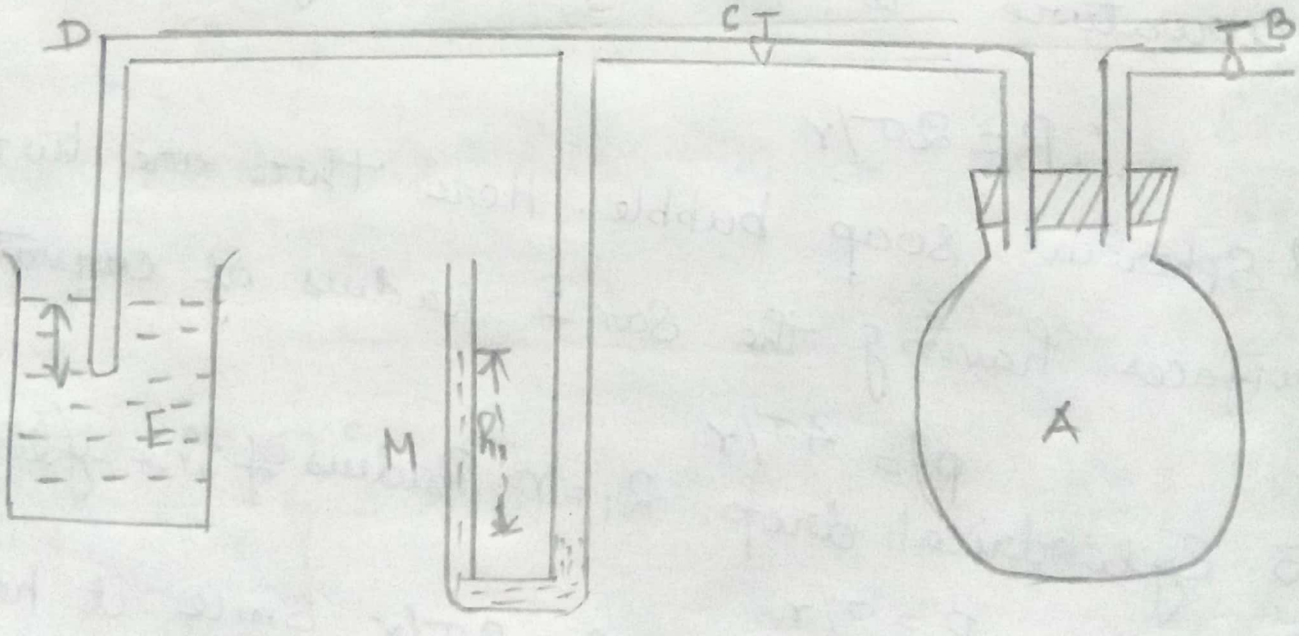
3. Cylindrical drop. $R_1 = r$ = Radius of the cylinder and $R_2 = \infty$ $P = \sigma/r$

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

Experimental determination of surface tension.

*JAEGAR'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 Surface Tension 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 ~~called~~ closed with a two holeded rubber stopper through which pass two glass tubes (Fig1). one of these is Connected to a water reservior through a stopcock B and the other is joined through a top 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.

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 detechment. The difference in monometer 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 level

and ρ_1 = density of the monometric 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.

$\therefore$ Excess pressure inside the bubble } $p = (H + h_1\rho_1 g) - (H + h_2\rho_2 g)$

$= (h_1\rho_1 - h_2\rho_2)g$

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

Hence $2\sigma/r = (h_1\rho_1 - h_2\rho_2)g$ or

$$\sigma = \frac{1}{2} rg\,(h_1\rho_1 - h_2\rho_2)$$

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 temperature.

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 E.

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

Variation of surface tension with temperature

Liquids are of two types viz., (i) un-associated 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 breakup into single molecules with a rise in temperature. At the ordinary temperatures, water is known to consist of groups, consisting of two H_2O molecules, in addition to ordinary single H_2O 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 ST at tc, σ_0 at 0°c and α, the temperature coefficient of ST for liquid.

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Van der waals and Ferguson suggested other relations from which it could be easily deduced that the ST 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 presented by $\sigma (Mvx)^{3/2} = k.(\theta_c - \theta - d)$ where σ = surface tension at θ K, θ_c = critical temperature,

d = a constant, varying from 6 to 8 for most of the liquids,

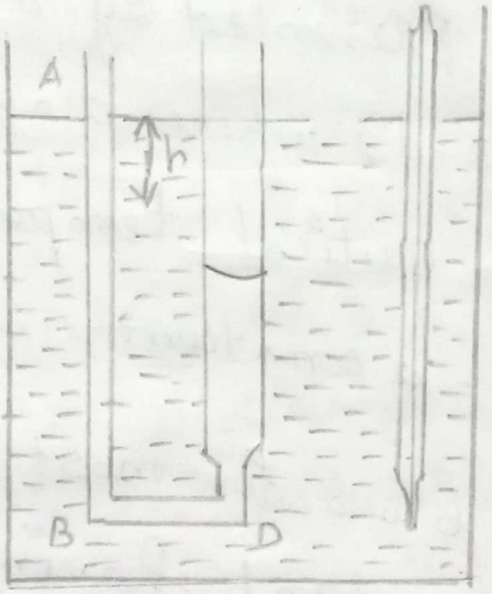
k = another constant having the value 2.12 for associated liquids and 2.22 for unassociated liquids.

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

M = molecular weight of the unassociated liqui
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.

Experimental Study of the variation of Surface Tension with Temperature.



A Capillary glass tube AB is Connected to another glass tube CD, of a Comparatively wider bore, So as to form a complete U tube. The experimental liquid is poured into the U tube. If the angle of contact (θ) for the liquid and glass is less than 90°, the liquid stands much higher in the narrower limb AB of the tube than in its wider limb CD. If $\theta > 90°$ (for example, in the case of mercury and glass), the liquid column in AB will be depressed into the tube to a position h below the liquid column in CD.

Let σ be the ST of the liquid θ, its angle of contact with glass. Let r_1 and r_2 be the radii of the bores of the two limbs respectively. Let P be the atmospheric pressure. Then

Pressure just below the liquid meniscus in AB $\Big\}$ $= P - \dfrac{2\sigma\cos\theta}{r_1}$

Pressure just below the liquid meniscus in CD $\Big\}$ $= P - \dfrac{2\sigma\cos\theta}{r_2}$

$\therefore$ Difference of Pressure in the two limbs $\Big\} = 2\sigma \cos\theta \left(\frac{1}{r_1} - \frac{1}{r_2}\right)$

This is balanced by the hydrostatic pressure $h\rho g$ due to the liquid column in the U-tube. Here, h is the difference of liquid levels in the two limbs. ρ is the density of the liquid

$$\therefore \ 2\sigma \cos\theta \left(\frac{1}{r_1} - \frac{1}{r_2}\right) = h\rho g$$

or

$$\sigma = \frac{h\rho g}{2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)\cos\theta}$$

The Experiment is repeated with the liquid maintainde at different temperature by means of suitable temperature baths.