

SURFACE TENSION – RISE IN CAPILLARY TUBE

OBJECT: To determine the value of the surface tension of a liquid from the height of rise in a capillary tube.

METHOD: A capillary tube is held vertically with the lower end immersed in the liquid whose surface tension is to be measured. A comparator (measuring microscope) is used to determine the height of rise of the liquid in the tube and the inside diameter (bore) of the tube. The surface tension of the liquid is computed from the height of rise, the bore of the tube, and the density of the liquid.

THEORY: The fact that molecules cling together to form a liquid indicates that between the molecules there must be attractive forces. When two molecules are close together the attractive force is considerable, but when separated by a distance equal to a very few times the diameter of a molecule the force becomes negligible. For many types of phenomena in physics the force between two particles varies inversely as the square of the distance. There is plenty of evidence, however, that the inverse square law does not apply to these intermolecular forces but that the force decreases as some higher power of distance. The nature and causes of these forces are not completely known but it is probable that they are the same kind of forces as those involved in chemical bonds.

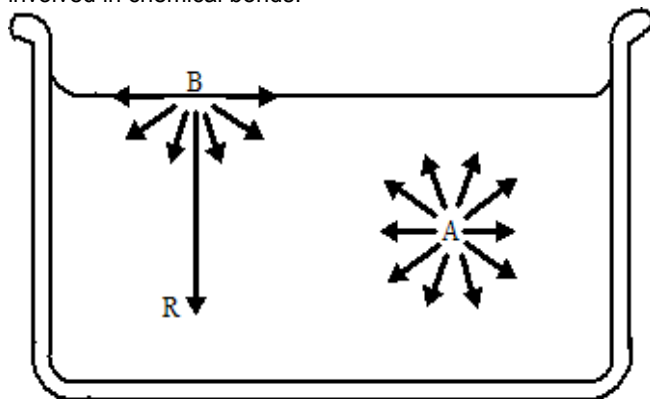


Fig. 1. A molecule on a surface is acted upon by an inward force R perpendicular to the surface.

A molecule in the interior of a liquid, A in Fig. 1, is attracted equally in all directions by the neighboring molecules and the vector sum of all these forces is zero. For a molecule at B on the surface, however, this is not true. Since there are relatively few molecules in the vapor above the surface the resultant is an inward force R perpendicular to the surface. Each molecule transferred from the interior to the surface

must be moved against this force. Since this requires that work be done on it, a molecule in the surface layer has more energy than a molecule in the interior. The excess free surface energy per unit area of surface is called the surface tension T of the liquid and may be expressed in ergs per square centimeter. This surface layer is only a few molecules thick.

The shaded portion of Fig. 2 represents a liquid surface between the U-shaped frame, width l , and the movable rod. If the rod is moved to the right a distance d , the area of the liquid surface is increased by an amount ld and, since T ergs of energy reside in each square centimeter of surface, the increase in free surface energy is Tld . The source of this energy is the work Fd done by the force F in moving the rod

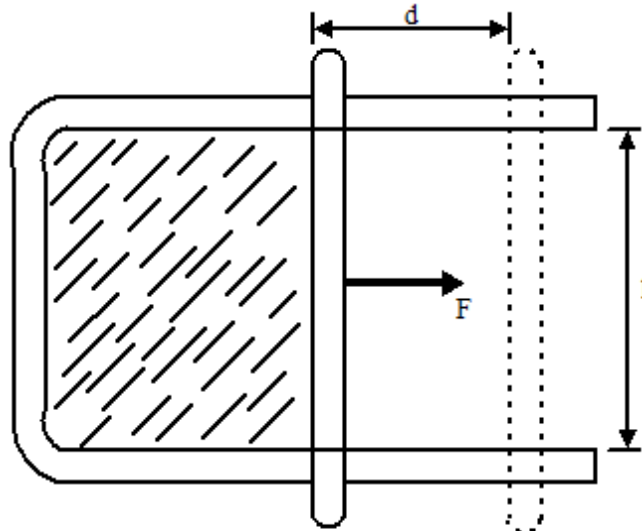


Fig. 2. Work is required to expand the surface of a liquid.

a distance d . Equating the work done by the force F and the increase in free surface energy gives

$$Fd = Tld \quad (1)$$

from which it follows that

$$T = F/l \quad (2)$$

This indicates that surface tension which has been expressed in ergs per square centimeter may be, and usually is, expressed in dynes per centimeter. Not only are these two methods of expressing surface tension

numerically the same but they have the same physical dimensions. From the above discussion it is evident that the result is the same as if the surface of the liquid were covered with an elastic membrane under a tension of T dynes per centimeter. For this reason some authors define surface tension as the force with which molecules on one side of a one-centimeter line on the surface attract the molecules on the other side of the line. This definition is unsatisfactory since it gives a false picture of the cause of surface tension. It is true that the molecules on one side of a line attract the molecules on the other side but this is not strictly a surface phenomenon for it would also be true for the interior of the liquid.

The forces responsible for surface tension are normal to the surface, but these forces manifest themselves as tangential forces. Fig. 3 may help in the understanding of the nature of these forces and the way in which the normal force R , Fig. 1, manifests itself as a tangential force in Fig. 2. A paper strip

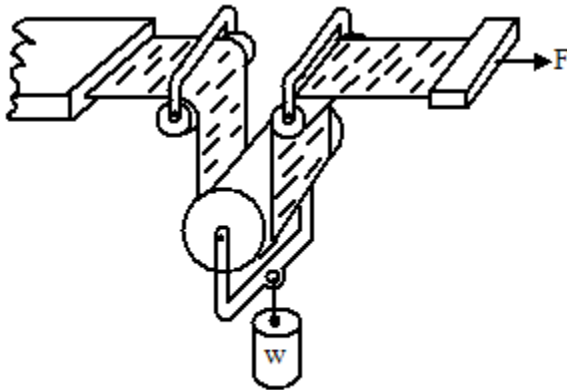


Fig. 3. The forces responsible for surface tension are normal to the surface but the measured forces are tangent to the surface.

passes over two fixed pulleys and supports a weight W attached to a movable pulley. Obviously, if the strip is sufficiently strong, the force F required to extend the strip to the right depends upon the magnitude of the weight W and not upon the tensile strength of the strip. This analogy is helpful but should not be pushed too far.

Although there is no elastic skin on the surface of a liquid, the results are exactly the same and in many cases the computations are more simple if surface problems are treated from the standpoint of the tension in this equivalent elastic skin rather than in terms of surface energy. This is done in the discussion that follows. The student should remember, however, that the forces responsible for surface tension are normal to the surface and that the tension in an elastic skin, while mathematically equivalent, is a convenient fiction.

In the discussion above, Fig. 2 was treated as if there were only one surface. In the case of a thin film (for example, a soap film) there are two surfaces (front and back) but an analysis of this case leads to the same conclusions as those given above.

In the development of the theory above, the work done was set equal to the change in free surface energy. Free surface energy will now be defined. When a surface contracts, the

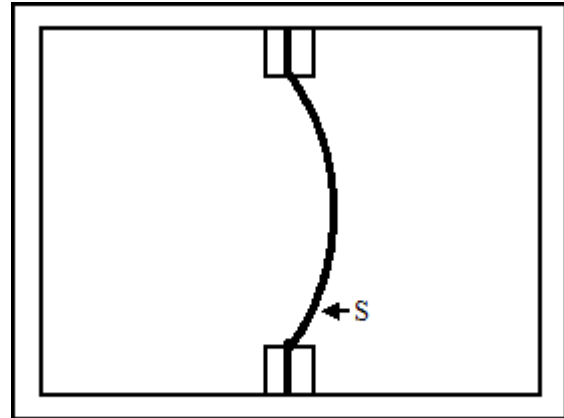


Fig. 4. The pressure is greater on the concave side of a surface.

surface layer is heated slightly and this heat flows to the interior of the liquid. Therefore part of the potential energy of the surface molecules is converted into heat and the rest is available for doing work on the movable rod, Fig. 2. That part of the potential energy of the surface layer that is available for doing work is called the free surface energy.

Suppose that a rubber membrane S separates the two parts of a box and that the membrane is curved as indicated in Fig. 4. It is evident that the pressure on the concave side of the membrane is greater than the pressure on the convex side. In fact, the difference in pressure may be expressed in terms of the tension in the membrane and its radius of curvature. In a similar manner the difference in pressure between the two sides of a liquid surface may be expressed in terms of surface tension and the radius of curvature of the surface. This relation is easily derived in the case of a spherical surface. Suppose the spherical drop of liquid in Fig. 5 has a radius ρ and is divided into two parts by passing an imaginary plane through the center. The upper hemisphere is in equilibrium under two sets of forces. The pull down due to surface tension acting along the circumference of a great circle is $2\pi\rho T$. The upward thrust due to the hydrostatic pressure p inside the drop is $\pi\rho^2 p$. Equating these two forces gives

$$\pi\rho^2 p = 2\pi\rho T \quad (3)$$

from which it follows that

$$p = 2T/\rho \quad (4)$$

This difference in pressure between the two sides of a curved surface may be used to explain the rise of liquids in capillary tubes. When the tube U , Fig. 6, is dipped into a liquid, the glass wall attracts the molecules of the liquid and the liquid surface inside the tube becomes concave. Since the pressure just above the surface at d is atmospheric pressure B , the pressure just under the surface at d is less than B . At the point of c , however, where the surface is plane, the pressure in the liquid is B . It is this difference in pressure between points at the same level in a liquid that causes the liquid to rise in the tube. The liquid will rise until

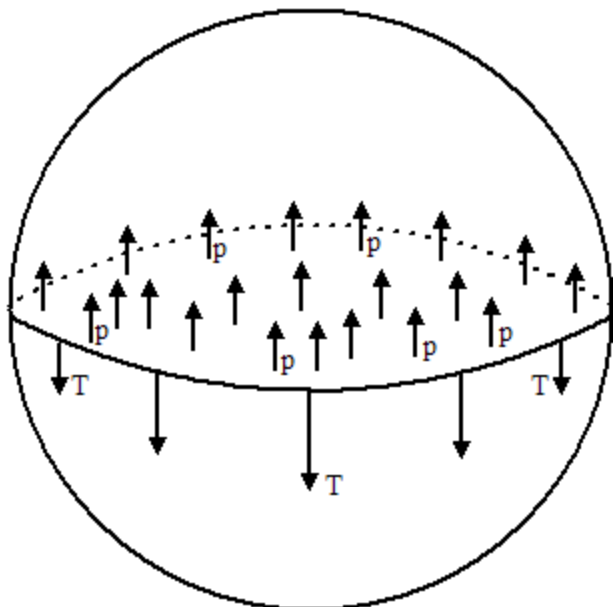


Fig. 5. As a result of surface tension the pressure inside a drop of liquid is greater than the pressure outside.

all points at the same level in the liquid are at the same pressure.

Eq. (4) may be used to determine the value of the surface tension T of a liquid from the height of rise in a capillary tube. Suppose that the liquid in the capillary tube V comes to equilibrium after rising a vertical height h , where h is measured from the flat surface of the liquid in the vessel to the bottom of the meniscus of the liquid surface in the tube. If the angle that the meniscus makes with the wall of the tube (contact angle) is a , it follows that $\rho = r/\cos a$, where ρ is the radius of curvature of the surface and r is the

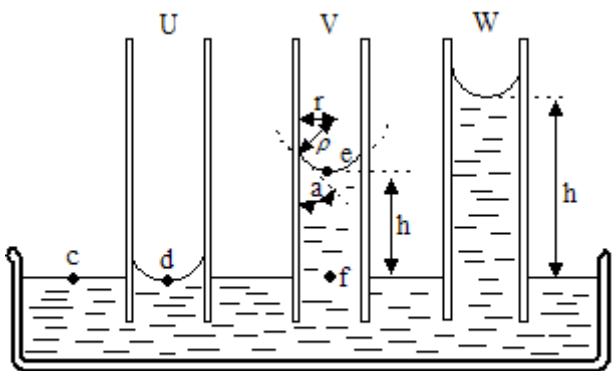


Fig. 6. The decreased pressure under a concave surface causes the liquid to rise in the tube.

radius of the tube. From the preceding paragraph it should be evident that the pressure at f is B , that the pressure in the liquid at e is $B - hdg$, and that the difference in pressure ρ between the two sides of the surface at e is hdg . Substituting for p and ρ in Eq. (4) gives

$$hdg = \frac{2T \cos a}{r} \quad (5)$$

which yields the equation

$$T = \frac{rhdg}{2 \cos a} \quad (6)$$

from which T may be computed. Since it is extremely difficult to measure a , the use of the capillary tube method is usually limited to those liquids for which the contact angle is zero. In this case (tube W , Fig. 6), the radius of curvature of the surface is equal to the radius of the tube and Eq. (6) becomes

$$T = \frac{1}{2}rhdg \quad (7)$$

In the discussion above, the meniscus was treated as if it were spherical. Since the pressure under the meniscus varies with height, the pressure difference on the two sides of the meniscus is not constant. This indicates that the curvature is not constant and that the surface is, therefore, not quite spherical. It can be shown that when this fact is taken into account, a more exact relation is given by

$$T = \frac{1}{2}rhdg \left(1 + \frac{1}{3} \frac{r}{h}\right) \quad (8)$$

which may be written

$$T = \frac{1}{2}rdg \left(h + \frac{1}{3}r\right) \quad (9)$$

This is the equation that will be used in this experiment to determine T .

For those students who are interested in a more complete treatment of surface tension the following treatises, the first two of which contain extensive bibliographies, are recommended:

N. K. Adam, *The Physics and Chemistry of Surfaces*, Oxford University Press, 1938;

N. E. Dorsey, *The Investigation of Surface Tension and Associated Phenomenon*, Bulletin of the National Research Council, No.69, 1929;

F. C. Champion and N. Davy, *Properties of Matter*, Prentice-Hall, 1938.

APPARATUS: Comparator, thermometer, capillary tube, glass rod, two glass vessels, holder for tube and rod, and cleaning solution are required.

A comparator is shown in Fig. 7. It consists of a low power microscope M , mounted on a micrometer slide L , which is in turn mounted on a heavy rigid support B . The object under observation may be placed on the horizontal surface of B and the microscope adjusted so that its image is in the plane of cross hairs inside the tube of the microscope. This image and the cross hairs are viewed together through the ocular (eyepiece) of the microscope. The crank K is attached to an accurately cut screw thread and by turning K the microscope may be made to slide smoothly along the bed plate on which is mounted a scale S .

In a common form of this instrument the pitch of the screw is one millimeter. Therefore, turning the screw one complete turn advances the microscope one-millimeter.

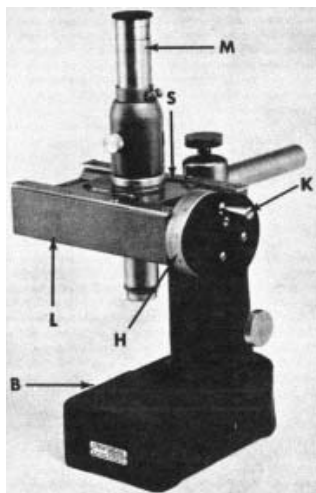


Fig. 7. The Comparator

Since the circular head H is divided into 100 divisions, each one of these divisions represents one hundredth of a turn and indicates that the microscope has advanced 0.01mm. By estimating tenths of a division on H, distances may be measured to thousandths of a millimeter. It is customary to mark the scale S directly in millimeters. If, therefore, the index on the movable slide is between 23 and 24 on scale S and the circular scale on the head H reads 16.3, the complete reading is 23.163mm. Precautions must be taken to avoid error due to "lost motion." To prevent injury to the screw it is made to fit loosely in the nut. It will be observed that K may be rotated back and forth a considerable distance without moving the microscope. It is obvious, therefore, that when a set of readings is taken all observations must be made with the microscope advancing in the same direction. If the screw has been turned too far, turn it back about a half turn and again approach the setting from the proper direction.

In using a comparator, first adjust the microscope so that the cross hairs are in sharp focus without eyestrain. This is accomplished by sliding the ocular in the tube. Next, the image is made to coincide with the cross hairs by adjusting the distance between the objective (front) lens and the object being viewed. This may be done either by moving the object or by sliding the microscope tube in its holder. Some instruments are provided with a rack and pinion to facilitate this adjustment. When the image and the cross hairs coincide there should be no parallax. That is, when the eye is moved slightly back and forth, perpendicular to the axis of the microscope, there is no relative motion between the image and the cross hairs.

PROCEDURE: Clean all glassware, including the inside of the capillary tube, with chromic acid and rinse thoroughly in tap water. Partially fill the glass vessel with water and mount the capillary tube C and the glass rod R in the holder P as indicated in Fig. 8. The glass rod R is drawn down to a fairly sharp point and serves as an index. It should be mounted about 5mm above the surface of the water.

Set the comparator with the scale S vertical and focus it on the lowest point of the rod R. Read both scales of the micrometer. Carefully add water to the vessel until the

surface just touches the rod. The reading taken above indicates, therefore, the position of the flat surface of the liquid. Use the crank K to elevate the microscope somewhat above the level of the water in the vessel. Being careful not to disturb the vessel or the comparator, shift the holder P bringing the tube C into focus in the microscope. Again using K, adjust the comparator so that the horizontal cross hair is tangent to the meniscus and read the instrument. The difference between the two readings is the vertical height h that the water rises in the tube. Record the temperature of the water.

Thoroughly dry the tube and vessels and repeat the experiment with some other liquid. It is advisable to have the meniscus at the same position in the tube as in the previous case. This may be done by adjusting the position of the tube in its holder.

Using a file or glass-knife, make a fine scratch at the point previously occupied by the meniscus and break the tube at this point. Mount the tube vertically and use the comparator to make at least five determinations of the inside diameter of the tube. Since the tube may not be round, all these observations should not be taken along the same diameter but should be distributed around the tube. It is very important in this part of the experiment that the microscope be adjusted for no parallax. If in doubt consult an instructor.

Use Eq. (9) to compute the values of the surface tension of the two liquids.

Optional: Partially fill the capillary tube with mercury and measure the length and mass of this thread of mercury. Use these observations and the density of the mercury to determine r . Compare this value of r with the one previously obtained.

QUESTIONS: 1. Show that the two members of Eq. (9) have the same dimensions.

2. What was the pressure just under the surface of the water in the capillary tube?

3. Assuming that the surface tension of a soap solution is 25 dynes/cm, compare the pressure inside a small soap bubble with the pressure inside a drop of water having the same radius.

4. Derive Eq. (9) by setting the total pull upward due to surface tension around the inside circumference of the tube equal to the weight of liquid lifted.

5. If the length of capillary tube projecting above the liquid in the vessel is less than h , will the liquid overflow from the top of the tube? Explain.

Optional: 6. Soap bubbles of different sizes are blown on two clay pipes and the stems of these pipes are connected by a short section of rubber tube. Explain the change in the sizes of these bubbles.

7. If the air is removed from the region above a liquid surface there is a slight increase in surface tension. Explain why.

8. The addition of a small amount of salt changes the surface tension of water only slightly but a small amount of oil will make a large change. Explain.

9. In deriving Eq. (9) it was stated that d is the density of the liquid. Actually a is the density of the liquid minus the density of the air. Why?

10. Derive Eq. (4) from the change in free surface energy of a drop of liquid which is caused to expand slightly.
11. A more accurate form of Eq. (8) is

$$T = \frac{1}{2}rhdg \left(1 + \frac{1}{3}\frac{r}{h} - 0.1288\frac{r^2}{h^2} + 0.1312\frac{r^3}{h^3} \right)$$

What percentage error was introduced into this experiment by neglecting the last two terms?

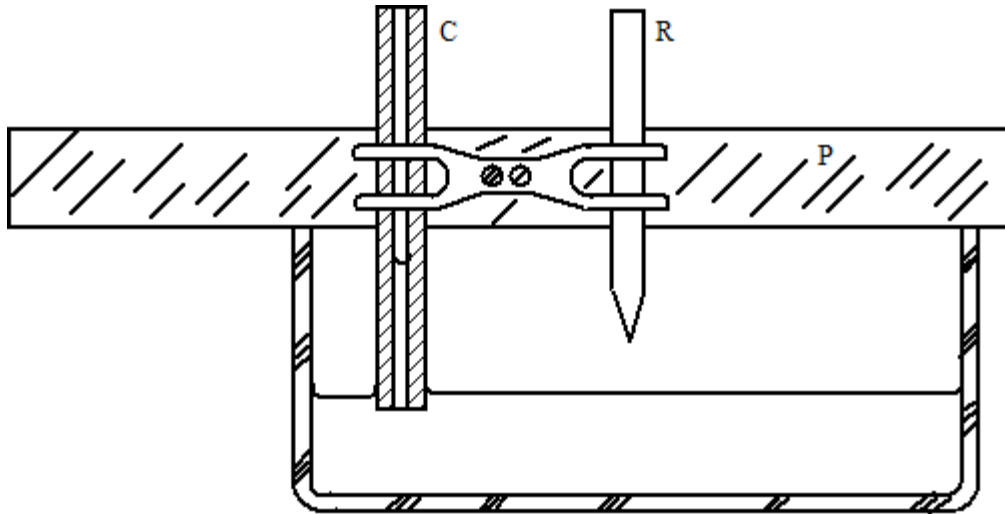


Fig. 8. Method of supporting capillary tube and rod.