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SURFACE TENSION – BUBBLE PRESSURE METHOD

OBJECT: To determine, from the pressure inside a bubble of air under the surface of a liquid, the surface tension of the liquid.

METHOD: The lower end of a vertical capillary tube is immersed in a liquid and the liquid rises in the tube. The air pressure inside the tube is increased, forcing the liquid out of the tube and forming a bubble of air on the end of the tube. A manometer is used to measure the pressure inside the tube and bubble. The surface tension of the liquid is computed from the pressure and the inside diameter (bore) of the tube.

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.

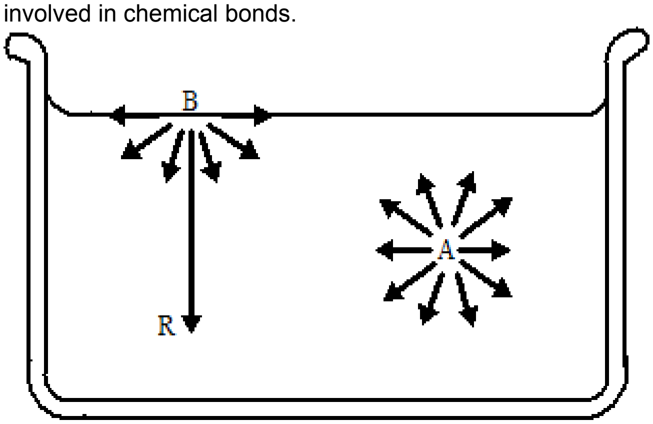

Fig. 1. A molecule on a surface is acted upon by an inward force R perpendicular to the surface.

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

$$Fd = Tld \tag{1}$$

from which it follows that

$$T = F/l \tag{2}$$

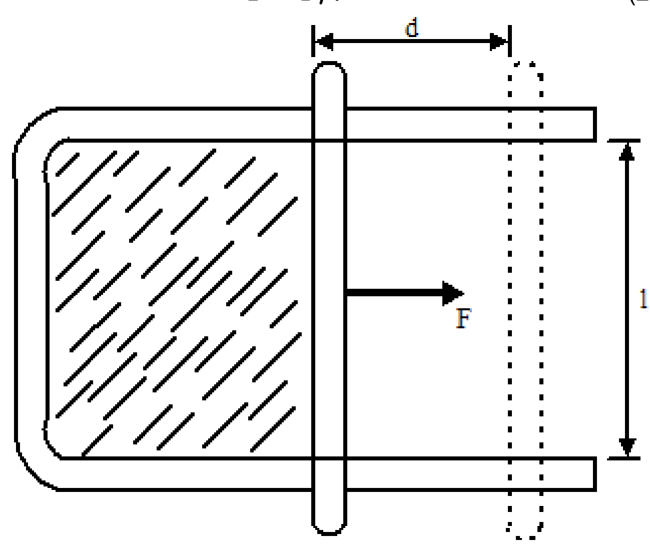

Fig. 2. Work is required to expand the surface of a liquid.

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.

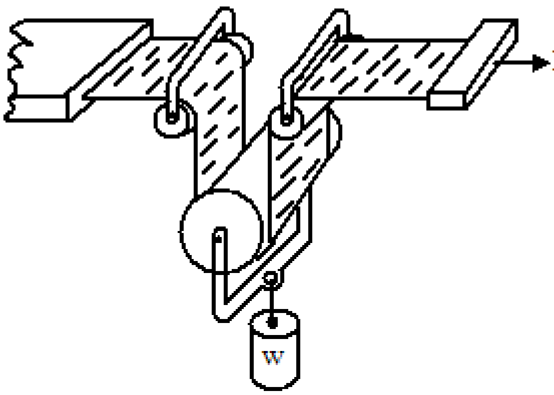

Fig. 3. The forces responsible for surface tension are normal to the surface but the measured forces are tangent to the surface.

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 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 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

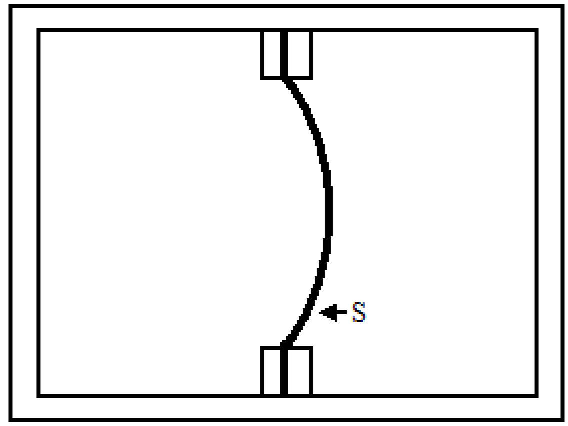

Fig. 4. The pressure is greater on the concave side of a surface.

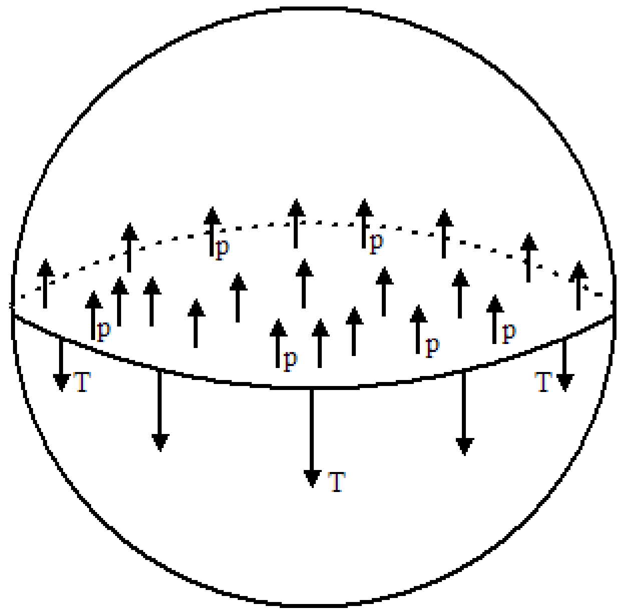

Fig. 5. As a result of surface tension the pressure inside a drop of liquid is greater than the pressure outside.

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 p 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

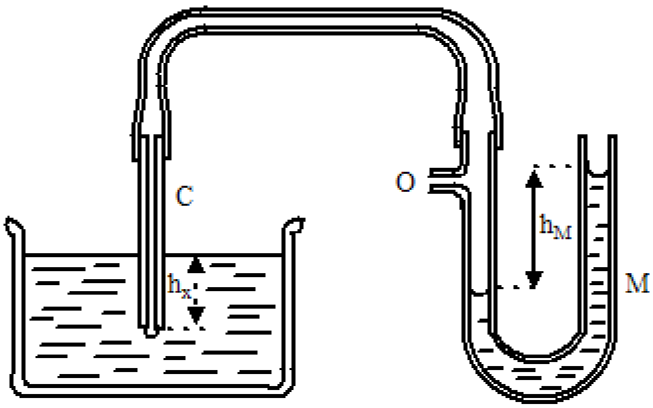

Fig. 6. The pressure inside the bubble is measured with a manometer.

due to the hydrostatic pressure p inside the drop is $\pi\rho^2 p$. Equating these two forces gives

$$\pi\rho^2 p = 2\pi\rho T \tag{3}$$

from which it follows that

$$p = 2T/\rho \tag{4}$$

One method in which the difference in pressure on the two sides of a curved surface is used to measure surface tension is illustrated in Fig. 6. When the lower end of the capillary tube C is immersed in a liquid, the liquid rises in the tube. If, however, the pressure above the liquid in C is increased by forcing air into the system through the opening O, the liquid is forced out of the tube and a bubble of air is formed on the end of C. Four stages in the development of the bubble are shown in Fig. 7. In the case illustrated the contact angle *a* (the angle the liquid surface makes with the wall of the tube) is not zero. An inspection of Fig. 7 shows that the minimum radius of curvature and hence the maximum pressure in the bubble will be realized when the bubble is hemispherical, stage c. For a hemispherical bubble the radius of curvature P is equal to the inside radius *r* of the tube. As the pressure in C is increased the surface falls from a to b. Further increase in pressure changes the shape of the surface to that indicated at c. Since stage *c* represents the maximum pressure, an attempt to increase the pressure beyond this point causes the air to rush in, expanding the bubble. The bubble then detaches itself from the tube and rises to the surface.

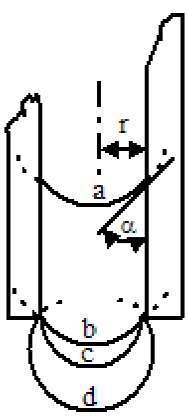

Fig. 7. Four stages in the formation of a bubble.

Assume in Fig. 6 that the bubble on C is hemispherical and that the pressure in the bubble as measured by the manometer M is, therefore, a maximum. The pressure p_o on the convex side of the surface is given by the equation

$$p_o = B + h_x d_x g \tag{5}$$

where B is atmospheric pressure, h x the depth of the bubble below the surface, d_x the density of the liquid, and g the acceleration due to gravity. The pressure p_I on the concave side of the surface is given by

$$p_I = B + h_M d_M g \tag{6}$$

where h_M is the manometer reading and d_M the density of the manometer liquid.
Substituting the pressures given by Eqs. (5) and (6) in Eq. (4), remembering that $p = p_I - p_o$ and $p = r$, yields

$$T = \tfrac{1}{2} rg\left(h_M d_M - h_x d_x\right) \tag{7}$$

By adjusting the position of the capillary tube, h_x may be made zero and Eq. (7) becomes

$$T = \tfrac{1}{2} rg h_M d_M \tag{8}$$

This method of measuring surface tension has two advantages over most other methods: (a) the contact angle need not be known; (b) since the surface is freshly formed, error due to contamination is minimized.

For those students who are interested in a more complete treatment of surface tension the following treatises, each of which contains an extensive bibliography, 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.

APPARATUS: Surface tension manometer, pinchcock, rubber tubing, capillary tube, thermometer, glass vessel, comparator and cleaning solution are required.
The surface tension manometer is illustrated in Fig. 8. The glass vessel containing the liquid under investigation is placed on the platform as shown. The support for the manometer and capillary tube is attached to the vertical rod by means of a friction clamp, thus providing a convenient method of regulating the vertical position of the capillary tube. Apiece of thin-wall rubber tubing is connected to the side tube in the left arm of the manometer. If the other end of this tube is closed with a pinchcock, the pressure inside the system may be raised by turning the pinchcock slowly. The pinchcock thus serves as a reel and the tubing is wound upon it. If the manometer is not equipped with aside tube, a T-tube should be inserted between the manometer and the capillary tube.
In using the comparator (Fig. 9), 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.

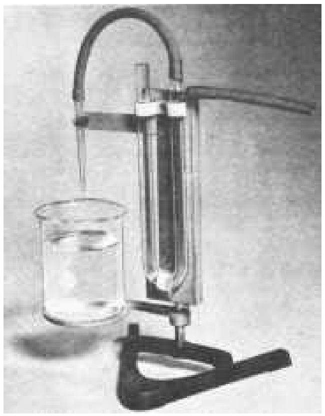

Fig. 8. The Surface Tension Manometer

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 with tap water. Instead of a capillary tube, a larger tube drawn down to a capillary point may be used. To prepare such a tube heat apiece of soft glass tubing in a Bunsen burner, turning it about its axis so that it is evenly heated, and draw it down until the inside diameter is not more than 0.03cm. Make a fine scratch on the tube with a glass knife (or file) and break the tube, making sure that the break is square across the tube. Heating the glass removes all traces of grease and, if care is taken to prevent contamination thereafter, it is not necessary to treat it with cleaning solution.

Partially fill the glass vessel with water and place it on the platform. *Carefully* lower the support until the lower end of the capillary tube just touches the surface of the water and clamp it in this position. Very slowly reeling the free end of the rubber tubing on the pinchcock, as indicated above, determine the maximum manometer reading. The manometer reading is the difference between the levels of the liquid in the two arms of the manometer. A small piece of cardboard behind each arm of the manometer may help in this reading. Record the temperature of the water.

Repeat the experiment with other liquids designated by the instructor. Thoroughly dry the tube and vessel before starting with a new liquid.

Mount the capillary 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 uniformly distributed around the tube. Be sure to measure the proper end of the tube. It is very important that the microscope be adjusted for no parallax. If in doubt consult an instructor.

Use Eq. (8) to compute the value of the surface tension of the various liquids. In the case of water determine the value at 20˚C. The temperature coefficient for water is -0.154 dyne per centimeter per degree centigrade; the surface tension decreases 0.154 dyne per centimeter for each degree rise in temperature.

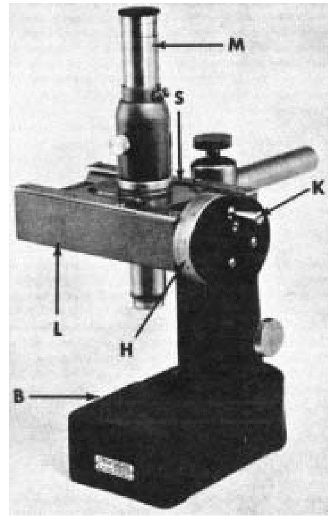

Fig. 9. The Comparator. This consists of a low power microscope M, mounted on a micrometer slide L, which is in turn mounted on a heavy rigid support B. The object under observation may be placed on the horizontal surface of B and the microscope adjusted so that its image is in the plane of the cross hairs inside the tube of the microscope. This image and the cross hairs are viewed together through the ocular (eye-piece) of the microscope. The crank K is attached to an accurately cut screw thread ad 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 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.

Precaution 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 form the proper direction.

Optional: In the theory above the bubble was considered to be spherical. Since, in descending from the top to the bottom of the bubble, the pressure outside increases while the pressure inside remains constant, the pressure difference across the surface is not constant. This indicates that the radius of curvature is not constant and the bubble is, therefore, not quite spherical. The error introduced by assuming that it is spherical is negligible for small bore tubes. If this factor is taken into account, however, the surface tension is given by the equation

$$T = \frac{pr}{2}\left(1 - \frac{2}{3}\frac{r}{h} - \frac{1}{6}\frac{r^2}{h^2}\right) \qquad (9)$$

where p is the difference in pressure across the surface at the end of the tube and $h = p/d_x g$. Show that, if the second and third terms in parenthesis are negligible, Eq. (9)

reduces to Eq. (7). Using Eq. (9) in place of Eq. (7), redetermine the surface tension of water. What percentage error was caused in the previous determination by neglecting the last two terms in Eq. (9)?

QUESTIONS: 1. Describe the nature and cause of the error that would be introduced into this experiment by forcing air into the system too rapidly.

2. Fig. 7 illustrates the formation of a bubble for the case where the contact angle is not zero. How would this be modified for zero contact angle?

3. Use Eq. (4) to derive the height of rise of a liquid in a capillary tube. Assume that the surface inside the tube is spherical and that the contact angle is zero.

4. Show that the two members of Eq. (8) have the same dimensions.

5. 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.

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 tubing. 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. Derive Eq. (4) from the change in free surface energy of a drop of liquid which is caused to expand slightly.