

where η° is the standard unit viscosity. Thus, $\ln(\eta/\eta^\circ)$ varies linearly with $(1/T)$ as shown in Fig. 2.3.4. From the slope, the activation energy for viscous flow can be calculated.

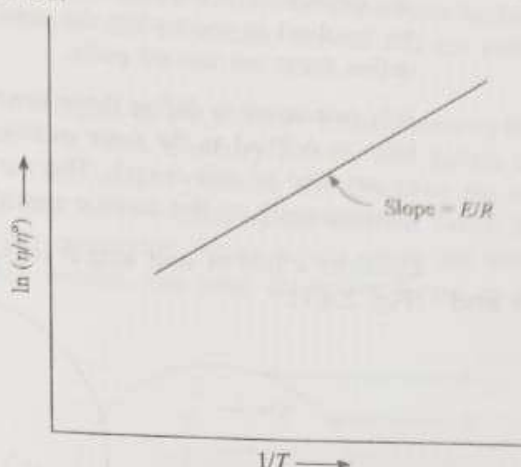


Fig. 2.3.4 Plot of $\ln(\eta/\eta^\circ)$ versus $1/T$

Viscosities of Mixtures

The fluidity of an ideal mixture which involves similar types of liquids, such as a mixture of benzene and toluene, is best represented by the following equations:

$$\phi = x_A \phi_A + x_B \phi_B \quad (\text{Bingham's equation})$$

$$\log(\phi/\phi^\circ) = x_A \log(\phi_A/\phi^\circ) + x_B \log(\phi_B/\phi^\circ) \quad (\text{Kendall's equation})$$

where ϕ° is the standard unit fluidity. These equations are not applicable to non-ideal solutions which involve dissimilar type of liquids. If the constituents of a solution strongly interact with each other then the observed fluidity is less than the calculated value, i.e., a considerable increase in viscosity occurs in such a case. One of the examples is the water and ethanol mixture. In this mixture, a strong interaction between the molecules of water and ethanol takes place due to the hydrogen bondings. If the mixture involves a polar and a nonpolar liquid such as alcohol and benzene then the observed fluidities are higher than the predicted fluidities as obtained by the use of either Bingham or Kendall equation.

2.4 SURFACE TENSION

Introduction

It was seen during the study of vapour pressure that the molecules at the surface of a liquid experience a net inward pull because of the larger number of molecules towards the liquid side than towards the vapour side. There is a tendency on the part of surface molecules to go in the bulk of the liquid. The surface of liquid is therefore in some sort of tension and it tends to contract to the smallest possible area in order to have the minimum number of molecules at the surface. It is for this reason that the surface of a liquid is spherically curved, since the surface area is minimum for a given volume in the case of a sphere.

Surface Energy

If the area of the surface is to be extended then one has to bring more molecules from the bulk of a liquid to its surface. This will require expenditure of some energy because work has to be done in bringing molecules from the bulk against

the inward attractive forces. The amount of work done in increasing the area by unity is known as the *surface energy*. Larger the forces of attraction amongst the molecules of a liquid, larger the net inward pull, and thus, larger work will be involved in increasing the area. Hence, the surface energy can be used to define these net inward pulls.

Surface Tension

It is customary to define these inward pulls in terms of the surface tension. The latter is defined as *the force acting along the surface of a liquid at right angle to any line of unit length*. The surface tension is equal, both numerically and dimensionally, to the surface energy. This can be proved as follows:

Equivalency of Surface Tension and Surface Energy

Consider a line of unit length (say, 1 cm) anywhere on the surface of a liquid (Fig. 2.4.1).

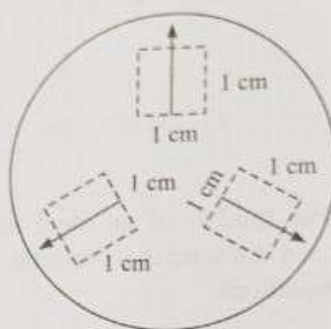


Fig. 2.4.1 Representation of surface tension

The surface area of the liquid can be increased by pulling this line perpendicularly by a force acting along the surface of the liquid. Let this line be extended by unity so as to enclose a unit area of the surface. Then

$$\text{Surface energy} = \frac{\text{amount of work done}}{\text{amount of area extended}} = \frac{\text{force} \times \text{distance}}{\text{area}}$$

Hence in CGS units, we have

$$\text{Surface energy} = \frac{\text{dyn} \times \text{cm}}{\text{cm}^2} = \frac{\text{dyn}}{\text{cm}} = \text{surface tension}$$

and in SI units, we have

$$\text{Surface energy} = \frac{\text{N} \times \text{m}}{\text{m}^2} = \text{N m}^{-1}$$

Obviously, $1 \text{ dyn cm}^{-1} = (10^{-5} \text{ N}) (10^{-2} \text{ m})^{-1} = 10^{-3} \text{ N m}^{-1}$

The surface tension is represented by the symbol γ .

Dimension of surface tension This can be determined as follows.

$$\gamma = \frac{\text{force}}{\text{distance}} = \frac{\text{mass} \times \text{acceleration}}{\text{distance}} = \frac{m l t^{-2}}{l} = m t^{-2}$$

Formation of Bubbles

The formation of a bubble is basically due to surface tension. It is obvious that the total pressure acting on a concave side must be larger than the pressure on the convex side. Therefore, the pressure inside a bubble must be larger

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Expression of Excessive Pressure

the external pressure. If this excess of pressure is not balanced by any other force, then the bubble will not be stable and will collapse immediately. Since stable bubbles are formed, this excessive pressure must be balanced by certain forces. These forces are due to surface tension and are called the *cementing forces*.

Let a gas bubble in a liquid be cut into two hemispheres by an imaginary plane (Fig. 2.4.2). There will be a tendency for the two halves to be driven apart by a force equal to the inward pressure multiplied by the surface area of the hemispheres. This will be prevented by the external forces due to atmospheric pressure and by the cementing forces acting along the circumference of the circle. For a stable bubble, the total disruptive forces must be equal to the binding forces.

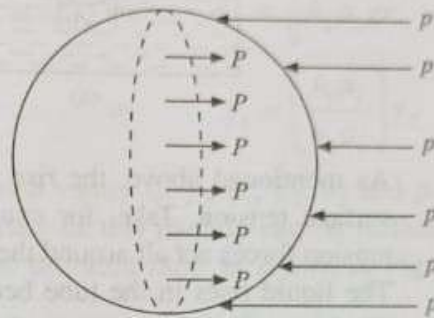


Fig. 2.4.2 Formation of a bubble

We have

$$\text{Disruptive forces} = P(\pi r^2)$$

$$\text{Binding forces} = p(\pi r^2) + \gamma(2\pi r)$$

Thus, for a stable bubble,

$$P(\pi r^2) = p(\pi r^2) + \gamma(2\pi r) \quad \text{i.e.} \quad \gamma(2\pi r) = (P - p)\pi r^2$$

$$\text{or} \quad (P - p) = \frac{2\gamma}{r}$$

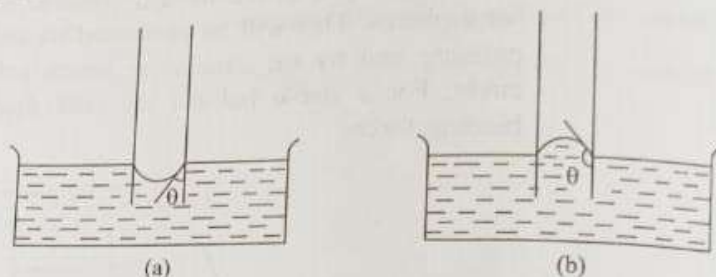
The excessive pressure inside the spherical bubble is thus inversely related to its radius. From this, it follows that the formation and maintenance of smaller bubbles will need greater values of excess pressure than the larger ones. This is, in fact, in agreement with the daily experience of blowing a balloon. It is difficult to blow a balloon initially but becomes easier later on as the excess pressure to be generated inside the balloon is inversely related to its radius.

When a capillary tube is dipped in a liquid, there occurs either a rise or a fall of liquid in the tube. This phenomenon is known as *capillary action* and is basically due to surface tension of the liquid. If the forces of attraction between the molecules of a liquid and those of the solid surface of the tube are greater than those existing amongst the molecules of the liquid, then the liquid has a tendency to spread on the solid surface and its meniscus in the tube is concave upwards. Such types of liquids are known as *wetting liquids* and they rise in the

Phenomenon of Capillary Action

capillary tube. The angle of contact, which is measured within the liquid from the side of the tube to the tangent drawn at the meniscus touching the surface of the tube, in this case, is less than 90° . This is shown in Fig. 2.4.3a. If the cohesive forces in the liquid are greater than the solid-liquid attraction forces, or if there occurs repulsion between the molecules of the liquid and those of the solid surface, the liquid detaches from the surface of the solid. The meniscus of such a liquid in the tube is convex upwards and its level falls within the tube. The angle of contact, in this case, is greater than 90° as shown in Fig. 2.4.3b.

Fig. 2.4.3 The angle of contact of the meniscus (a) wetting liquid, $< 90^\circ$ and (b) non-wetting liquid, $> 90^\circ$



Expression of Surface Tension

As mentioned above, the rise and fall of a liquid in a capillary tube is due to surface tension. Take, for example, the case of a wetting liquid. The surface tension forces act all around the capillary tube in the direction shown in Fig. 2.4.4. The liquid rises in the tube because of these upward forces. It continues to rise till the vertical component of the lifting force becomes equal to the weight of the liquid in the capillary tube. Thus,

$$\text{Lifting force} = (\gamma \cos \theta) (2\pi r_c)$$

$$\text{Weight of the liquid in the capillary tube} = \{(\pi r_c^2)h\}\rho g$$

At equilibrium, lifting force is equal to the downward force due to weight of the liquid in the capillary tube. Therefore,

$$(\gamma \cos \theta) (2\pi r_c) = \pi r_c^2 h \rho g$$

$$\text{or } \gamma = \frac{1}{2} h \rho g \frac{r_c}{\cos \theta} \quad (2.4.1)$$

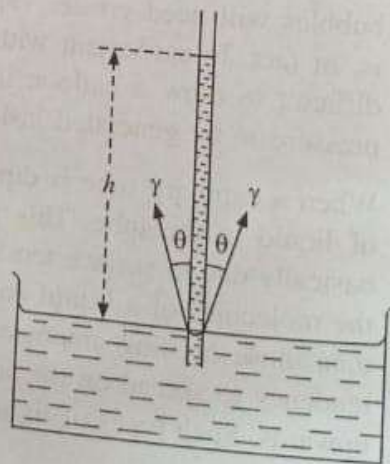


Fig. 2.4.4 Rise of a liquid in a capillary tube

For most of the wetting liquids, θ is very very small and thus $\cos \theta = 1$. Therefore, the value of γ for such liquids is

$$\gamma = \frac{1}{2} h \rho g r_c \quad (2.4.2)$$

For non-wetting liquids, Eq. (2.4.1) is still applicable. Here h denotes depression of the liquid level.

Measurement of Surface Tension

Method Using Capillary Action

The phenomenon of capillary action can be used to determine surface tension of a liquid. However, to avoid the necessity of determining r , we use the relative method in which the value of h is also determined for a liquid whose surface tension is known. Thus

$$\gamma_1 = \frac{1}{2} h_1 \rho_1 g r, \quad \text{and} \quad \gamma_2 = \frac{1}{2} h_2 \rho_2 g r$$

$$\text{Hence,} \quad \frac{\gamma_1}{\gamma_2} = \frac{h_1 \rho_1}{h_2 \rho_2} \quad \text{or} \quad \gamma_1 = \left(\frac{h_1 \rho_1}{h_2 \rho_2} \right) \gamma_2 \quad (2.4.3)$$

Hence, for known values of γ_2 , h_1 , ρ_1 , h_2 and ρ_2 , the value of γ_1 can be calculated. The accuracy of this method can be further increased by the use of two capillary tubes of different radii as shown in Fig. 2.4.5. We have

$$\gamma = \frac{1}{2} h_1 \rho g r_1 \quad \text{or} \quad \frac{\gamma}{r_1} = \frac{1}{2} h_1 \rho g$$

$$\text{and} \quad \gamma = \frac{1}{2} h_2 \rho g r_2 \quad \text{or} \quad \frac{\gamma}{r_2} = \frac{1}{2} h_2 \rho g$$

Subtracting, we have

$$\gamma \left(\frac{1}{r_1} - \frac{1}{r_2} \right) = \frac{1}{2} \rho g (h_1 - h_2) = \frac{1}{2} \rho g \Delta h$$

$$\text{or} \quad \gamma = \frac{\rho g \Delta h}{2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right)}$$

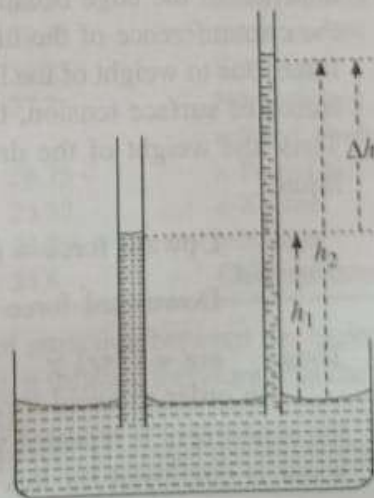


Fig. 2.4.5 Capillary rise method for measurement of surface tension

If the same pair of capillaries, after proper cleaning, are dipped in two different liquids one after the other, we will have

$$\gamma_A = \frac{\rho_A g \Delta h_A}{2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right)} \quad \text{and} \quad \gamma_B = \frac{\rho_B g \Delta h_B}{2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right)}$$

Dividing, we get

$$\gamma_A = \frac{\rho_A \Delta h_A}{\rho_B \Delta h_B} \gamma_B \quad (2.4.4)$$

Thus, knowing the values of various terms on the right side of Eq. (2.4.4), the value of surface tension of the liquid A can be determined.

The other method which is commonly employed in laboratories is to use a *stalagmometer* (Fig. 2.4.6).

A Laboratory Method



Fig. 2.4.6 The stalagmometer

A stalagmometer consists of a bulb attached to a fine capillary with a sharp edge. The liquid is allowed to fall drop by drop through the capillary tube. As the size of a liquid drop grows, its weight goes on increasing. It remains attached to the edge because of the forces of surface tension which act around the circumference of the tube and in the upward direction. When the downward force, due to weight of the liquid, becomes infinitesimally greater than the upward forces of surface tension, the drop detaches from the apparatus and falls down. Thus, the weight of the drop can be correlated with the surface tension of the liquid:

$$\text{Upward force} = (2\pi r) \gamma$$

$$\text{Downward force} = mg$$

$$\text{Thus, } mg = (2\pi r) \gamma$$

In order to avoid measurement of r , we use the relative method in which the experiment is repeated with a liquid whose surface tension is known. Usually water is employed for this purpose. Thus,

$$m_l g = 2\pi r \gamma_l \quad \text{and} \quad m_w g = 2\pi r \gamma_w$$

Dividing and rearranging, we get

$$\gamma_l = \left(\frac{m_l}{m_w} \right) \gamma_w \quad (2.4.5)$$

The values of m_l and m_w can be determined following either the drop weight method or the drop number method.

Drop Weight Method

In the drop weight method, the mass of about 20 to 30 drops of each liquid is found accurately, and then the mass of a single drop is calculated.

Drop Number Method

In the drop number method, the number of drops obtained for the same volume, say V , of each liquid is counted. Then the mass of a single drop is determined as follows:

$$v_l = \frac{m_l}{\rho_l} \quad \text{and also} \quad v_l = \frac{V}{n_l}$$

$$\text{Therefore, } m_l = v_l \rho_l = \frac{V \rho_l}{n_l}$$

$$\text{Similarly, } m_2 = \frac{V \rho_2}{n_2}$$

$$\text{and thus, } \frac{\gamma_l}{\gamma_2} = \frac{m_l}{m_2} = \frac{\rho_l n_2}{\rho_2 n_l} \quad (2.4.6)$$

Values of Surface Tensions of a few Liquids

Table 2.4.1 records the surface tension values at 20 °C for some liquids.

Table 2.4.1 Surface Tensions of Some Common Liquids at 20 °C

Substance	Surface tension $\gamma/\text{dyn cm}^{-1}$ or $\gamma \times 10^3/\text{N m}^{-1}$	Substance	Surface tension $\gamma/\text{dyn cm}^{-1}$ or $\gamma \times 10^3/\text{N m}^{-1}$
Water	72.8	Acetic acid	27.42
Benzene	28.87	Methyl alcohol	22.55
Toluene	28.53	Ethyl alcohol	22.30
Carbon disulphide	32.25	Ethyl ether	17.05
Chloroform	27.2	Nitrobenzene	43.35
Carbon tetra- chloride	26.75	n-Butyl alcohol	24.52
Acetone	23.32	n-Propyl alcohol	23.75
Ethyl acetate	23.75	o-Xylene	30.03
Methyl acetate	24.8	p-Xylene	28.31
		Chlorobenzene	33.25

Effect of Temperature on Surface Tension

Since the effects of forces of attraction between the molecules of a liquid decrease with increase in temperature, it follows, therefore, that the surface tension decreases with increase in temperature.

Eötvös Equation R. von Eötvös proposed the following relation between surface tension and temperature.

$$\gamma(Mv)^{2/3} = a - kt \quad (2.4.7)$$

where a and k are constants and v is the specific volume of the liquid. The factor Mv represents the molar volume of the liquid. If the volume is considered to be spherical, the area of the sphere will be proportional to $(Mv)^{2/3}$. Since γ represents the surface energy per unit area, the factor $\gamma(Mv)^{2/3}$, therefore, represents some sort of surface energy which according to Eötvös, varies linearly with temperature. The value of surface energy will be zero at the critical temperature since at this temperature the surface of separation between a liquid and its vapour disappears. This fact can be utilized in deriving the value of a in terms of k . At critical temperature

$$\gamma(Mv)^{2/3} = 0 = a - kt_c$$

Therefore

$$a = kt_c$$

Ramsay and Shields Modification W. Ramsay and J. Shields made a study of Eötvös equation and found that the experimental results could be better expressed by the relationship:

$$\gamma(Mv)^{2/3} = k(t_c - t - 6) \quad (2.4.8)$$

According to this equation, the surface energy becomes zero when

$$t = t_c - 6$$

that is, it becomes zero at a temperature 6 °C below the critical temperature. This is also supported by experimental observations that for some liquids, the meniscus disappears at a temperature a few degrees before the critical temperature. For normal and non-associated liquids the constant k is found to have a value of 2.12. For associated liquids such as water and alcohol, k is found to have a value less than 2.12.

Interfacial Tension

Consider two immiscible liquids in contact with each other. The molecules at the surface of either of these liquids will experience an unbalanced force of attraction in the same way as the molecules at the surface of a liquid experience when they have the liquid on one side and the vapour on the other. These unbalanced forces at the surface of separation between the two immiscible liquids give rise to interfacial tension, which can be defined in the same way as surface tension. It is thus, the force acting along the surface of a liquid perpendicular to any line of unit length. According to Antonoff's rule, the interfacial tension γ_{AB} between two liquids A and B is equal to the difference of the respective surface tensions γ_A and γ_B , i.e.

$$\gamma_{AB} = |\gamma_A - \gamma_B| \quad (2.4.9)$$

Obviously, the interfacial tension will be smaller than the larger of the two surface tensions. This is because the attraction across the interface between the molecules of one liquid and those of the other, tends to reduce the inward pull of the molecules in the surface by those of the same kind. The numerical value of the interfacial tension can be determined experimentally by following either the

Surface
Mixtures

Surface A
Materials

Cleansing
Soap

Gibbs Ads
Isotherm

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Surface Tension of Mixtures

capillary rise method or the drop weight method. The interfacial tension plays a very important role in determining the properties of emulsions, detergents, etc.

When two liquids whose surface tensions do not differ very much are mixed in various proportions, the surface tension of the resultant mixture varies linearly with the mole fraction of either of the liquids. Ideal solutions follow this behaviour; an example of which is the benzene-toluene mixture. If the surface tension of liquids differ very much, the addition of even a small amount of the liquid of lower surface tension in the liquid of higher surface tension decreases the surface tension of the latter to a large extent. This is because such a liquid has a tendency to accumulate at the surface and thus the surface has a relatively richer constituent of the lower surface tension as compared to the bulk of the mixture. In such cases, the variation of surface tension is given by the following expression, provided the solution is not very dilute:

$$\frac{d\gamma}{d \ln c} = -X\gamma^* \quad (2.4.10)$$

In this expression, X is a constant and γ^* is the surface tension of the pure liquid. According to this, the surface tension of the mixture varies linearly with the logarithm of the concentration of the added liquid. A few examples are alcohol-water, acetone-water, and acetic acid-water mixtures.

Surface Active Materials

Certain substances like soap, salts of higher sulphonic acids and of higher amines, in water decrease the surface tension of the latter to a large extent and thus are called *surface active materials* (due to their tendency to accumulate at the surface.). These substances act as detergents and they have the characteristics of lowering the interfacial tension between water and grease and thus render wetting of the latter easier. This also explains why these substances are used to clean garments. We can now explain the cleansing action of soap as follows.

Cleansing Action of Soap

Most of the dirt or dust sticks on to grease or oily materials which gather on clothes. As grease is not readily wetted by water, it is difficult to clean the garment with water alone. If a soap solution is used, the interfacial tension between water and grease decreases and thus facilitating the mixing of the two. This decrease of interfacial tension is due to higher concentration of soap molecules at the surface. The orientations of these molecules at the surface is specific, $-\text{COO}$ groups pointing towards the surface of water and hydrocarbon chains pointing outwardly. These hydrocarbon chains act as a solvent for the grease and thus the latter is detached from the cloth along with the dust.

Gibbs Adsorption Isotherm

In general, the variation of surface tension of a solvent with the addition of solute is given by the Gibbs adsorption isotherm:

$$\Gamma_2 = -\frac{c}{RT} \frac{d\gamma}{dc} \quad (2.4.11)$$

where Γ_2 is the excessive concentration of the solute at the surface relative to that existing in the bulk of the solution. According to Eq. (2.4.11),

positive if Γ_2 is negative, and vice versa. For solutes like acetone, urea, and detergents, Γ_2 is positive and hence there occurs a decrease in surface tension of water with addition of such solutes. The solutes like NaCl, KCl, etc., (where Γ_2 is negative) and thus there occurs an increase in the surface tension of water when such electrolytes are added in this solvent.

D.B. Macleod observed that the surface tension of a liquid was related to the orthobaric densities ρ_l and ρ_v of liquid and saturated vapour, respectively, through the equation

$$\frac{\gamma^{1/4}}{\rho_l - \rho_v} = C$$

where C is a constant, whose value depends upon the nature of the liquid. If the above equation is multiplied by M , the molar mass of the liquid, then we have

$$\frac{M\gamma^{1/4}}{\rho_l - \rho_v} = MC = \text{constant} = [P]$$

If the liquid is not very near to its critical temperature, then ρ_l is much greater than ρ_v , and the approximate form of the above expression becomes

$$\left(\frac{M}{\rho_l}\right)\gamma^{1/4} = [P] \quad \text{or} \quad V_m\gamma^{1/4} = [P]$$

Thus, if the surface tension is unity, the value of the constant $[P]$ is equal to the molar volume of the liquid. The symbol $[P]$ is known as *parachor*, meaning *comparative volume*, since the comparison of the parachors of different liquids is equivalent to a comparison of molar volumes under the condition of equal (unit) surface tension.

Parachor has been found to be largely an *additive* property and particularly a *constitutive* property. It is possible to evaluate the parachor equivalents of various atoms and for various structural units (Table 2.4.2).

Table 2.4.2 Vogel's Values of Atomic and Structural Parachor

Unit	Parachor ([P]/[P ^o])	Unit	Parachor ([P]/[P ^o])
C	8.6	—OH	30.1
H	15.7	—COOH	75.7
O	19.8	—NO ₂	75.8
S	48.2	Single bond	
Cl	55.2	Double bond	
Br	68.8	Triple bond	
I	90.3	3-membered ring	
CO	44.4	4-membered ring	
		5-membered ring	
		6-membered ring	

$$[P^o] = 1 \text{ cm}^3 \text{ mol}^{-1} (\text{dyn cm}^{-1})^{1/4} \equiv 10^{-6} \text{ m}^3 \text{ mol}^{-1} (10^{-3} \text{ N m}^{-1})^{1/4}$$

With the help of these values, we can calculate the parachor values of different isomers of a given compound. The comparison of these values with the experimentally determined values can help in deciding the structure of the given compound.

REVISIONARY PROBLEMS

- 2.1 Discuss the general characteristics of liquids and compare them with those of gases and solids.
- 2.2 What is the vapour pressure of a liquid? How does it arise and what is the effect of temperature on it?
- 2.3 The variation of vapour pressure with temperature can quantitatively be expressed by Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}} H_m}{T(V_{m,v} - V_{m,l})}$$

Explain the various terms involved in this equation. Discuss the Clausius approximations and hence derive the Clausius-Clapeyron equation.

- 2.4 Draw a graph indicating:
 - (i) The variation of vapour pressure with temperature. What are the lower and the upper limits of this graph?
 - (ii) The variation of $\ln(p/p^\circ)$ versus $1/T$. What is its slope?
- 2.5 Discuss how vapour pressure and boiling point are intimately connected to each other. Explain how a plot of the variation of vapour pressure with temperature can be considered to represent a graph of the variation of boiling point of a liquid with the external pressure.
- 2.6 Describe the methods commonly employed for the measurement of vapour pressure of a liquid.
- 2.7 (a) Discuss the effects of nonvolatile impurities on vapour pressure and boiling point of a liquid. (b) What is Trouton's rule?
- 2.8 What do you understand by the term viscosity of a liquid? How does it arise and what are its units? What is the effect of temperature on the viscosity of a liquid?
- 2.9 Describe the methods commonly employed for the measurement of viscosity of a liquid.
- 2.10 Explain why the viscosity of ethyl alcohol is greater than that of ether.
- 2.11 According to the Arrhenius equation, the variation of viscosity with temperature is given by

$$\ln(\eta/\eta^\circ) = \ln(A/\eta^\circ) + \frac{E}{RT}$$

Explain the various terms involved in this. Give a schematic plot of $\ln(\eta/\eta^\circ)$ versus $1/T$. What is its slope?

- 2.12 Discuss the origin of surface tension of a liquid. Show that the surface tension and surface energy have the same dimensions.
- 2.13 Show that the excessive pressure inside a spherical bubble is given by

$$\Delta p = (P - p) = \frac{2\gamma}{r}$$

where P and p are the pressures inside and outside the bubble, respectively. With the help of this, justify the statement: