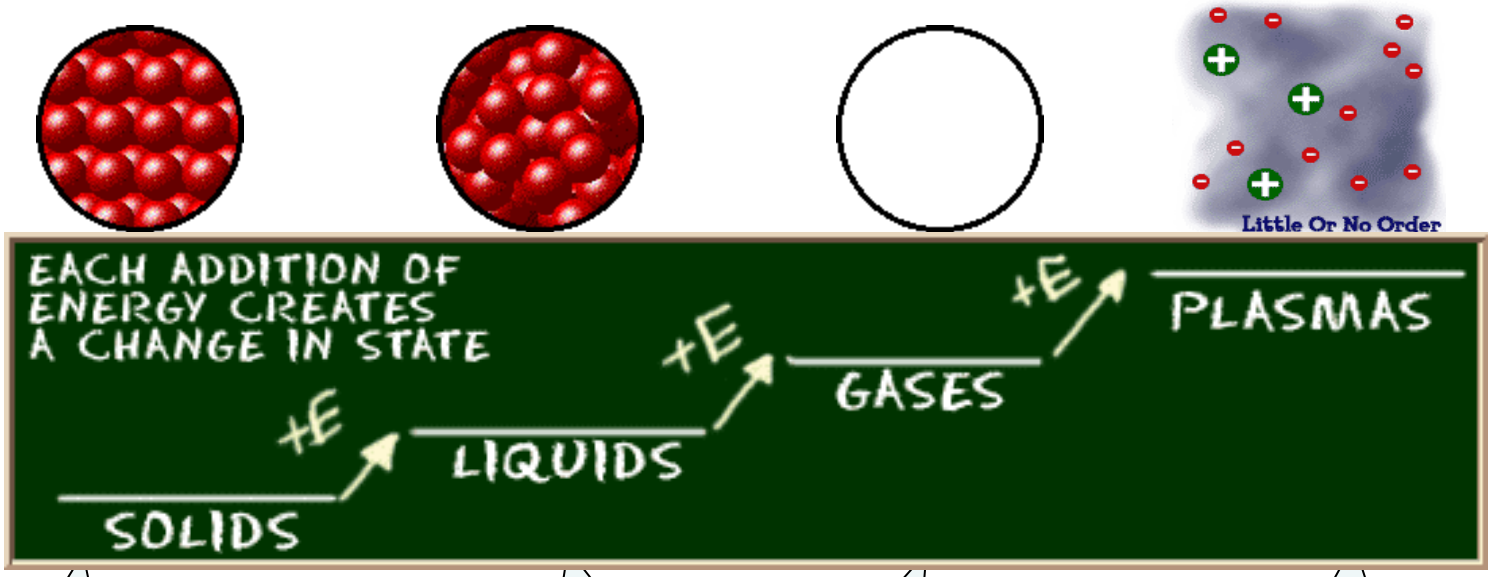
States of matter
Liquids

Md Khairul Islam (Ph.D)
Applied Chemistry & Chemical Engineering
University of Rajshahi

States of matter



SOLID

Tightly packed, in a regular pattern Vibrate, but do not move from place to place

LIQUID

Close together with no regular arrangement. Vibrate, move about, and slide past each other

GAS

Well separated with no regular arrangement. Vibrate and move freely at high speeds

PLASMA

Has no definite volume or shape and is composed of electrical charged particles

Phase changes

Description of Phase Change	Term for Phase Change	Heat Movement During Phase Change
Solid to liquid	Melting	Heat goes into the solid as it melts.
Liquid to solid	Freezing	Heat leaves the liquid as it freezes.
Liquid to gas	Vaporization, includes boiling & evaporation	Heat goes into the liquid as it vaporizes.
Gas to liquid	Condensation	Heat leaves the gas as it condenses.
Solid to gas	Sublimation	Heat goes into the solid as it sublimates.

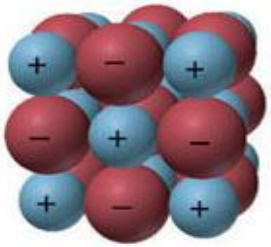
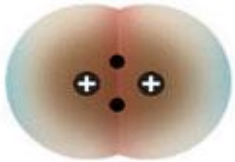
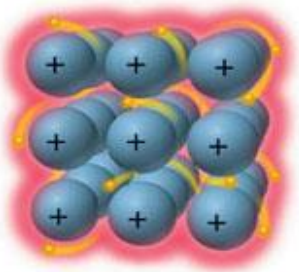
Intermolecular Forces

Intermolecular forces: attractions and repulsions between molecules that hold them together. Intermolecular forces (van der Waals forces) hold molecules together in liquid and solid phases.

- **Ion-dipole force:** interaction between an ion and partial charges in a polar molecule.
- **Hydrogen bond:** attraction between two atoms that already participate in other chemical bonds . One of the atoms is H, while the other may be any electronegative atom, i.e., O, N, or F.
- **Dipole-dipole force:** attractive force between polar molecules with positive end of one molecule is aligned with negative side of other.
- **London dispersion forces:** interactions bet$^{n.}$ instantaneously formed electric dipoles on neighboring polar or nonpolar molecules.

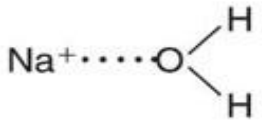
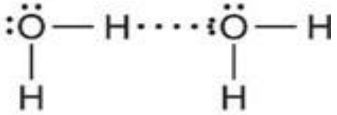
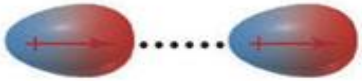
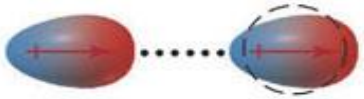
Intermolecular Forces

Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe

Intermolecular Forces

Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces

Nonbonding (Intermolecular)				
Ion-dipole		Ion charge–dipole charge	40–600	
H bond		Polar bond to H–dipole charge (high EN of N, O, F)	10–40	
Dipole-dipole		Dipole charges	5–25	
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	
Dispersion (London)		Polarizable e^- clouds	0.05–40	

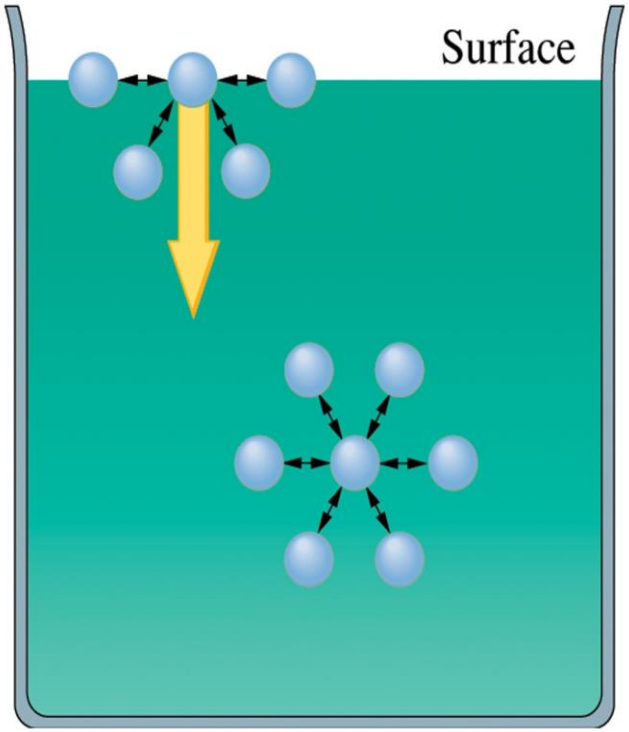
Importance of polarizability!

Properties of Liquids

Vapor pressure: Equilibrium pressure, exerted by a vapour with its condensed phases in a closed system at a given temperature.

Surface tension: The energy required to increase the surface area of a liquid by a unit amount. The net pull toward the interior of the liquid makes the surface tend to as small a surface area as possible and a substance does not penetrate it easily.

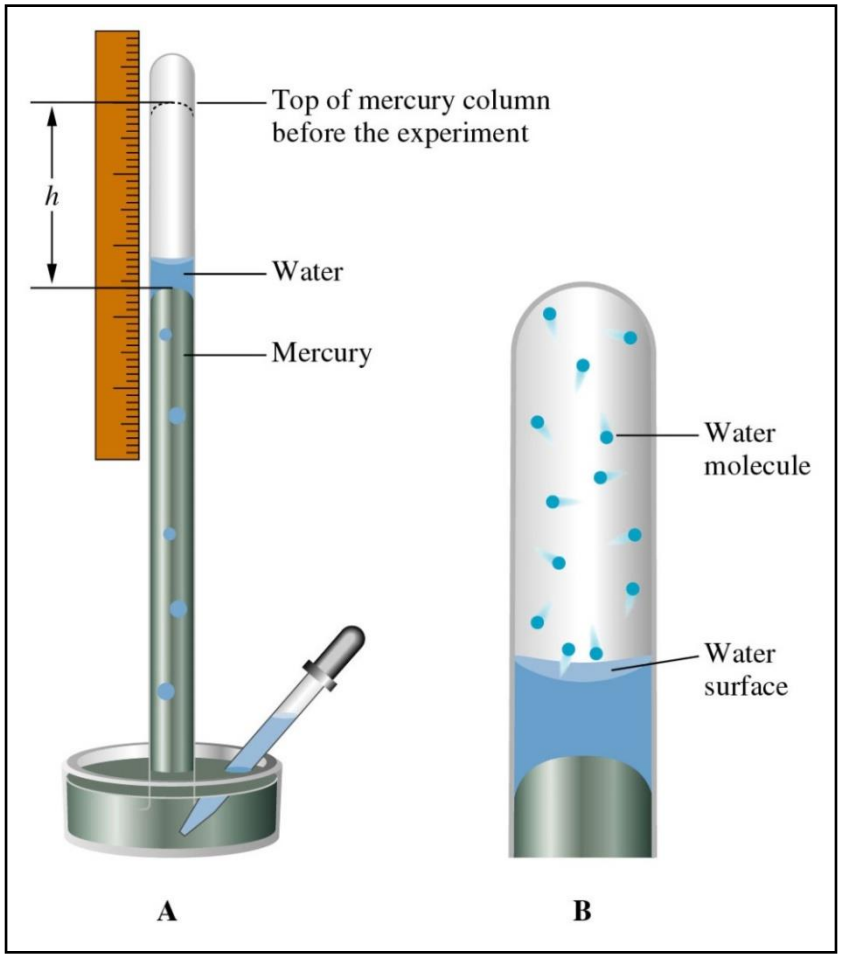
Viscosity: A measure of a liquid's resistance to flow. Related to mobility of a molecule (proportional to the size and types of interactions in the liquid).



Viscosity decreases as the temperature increases since increased temperatures tend to cause increased mobility of the molecule.

Vapor Pressure

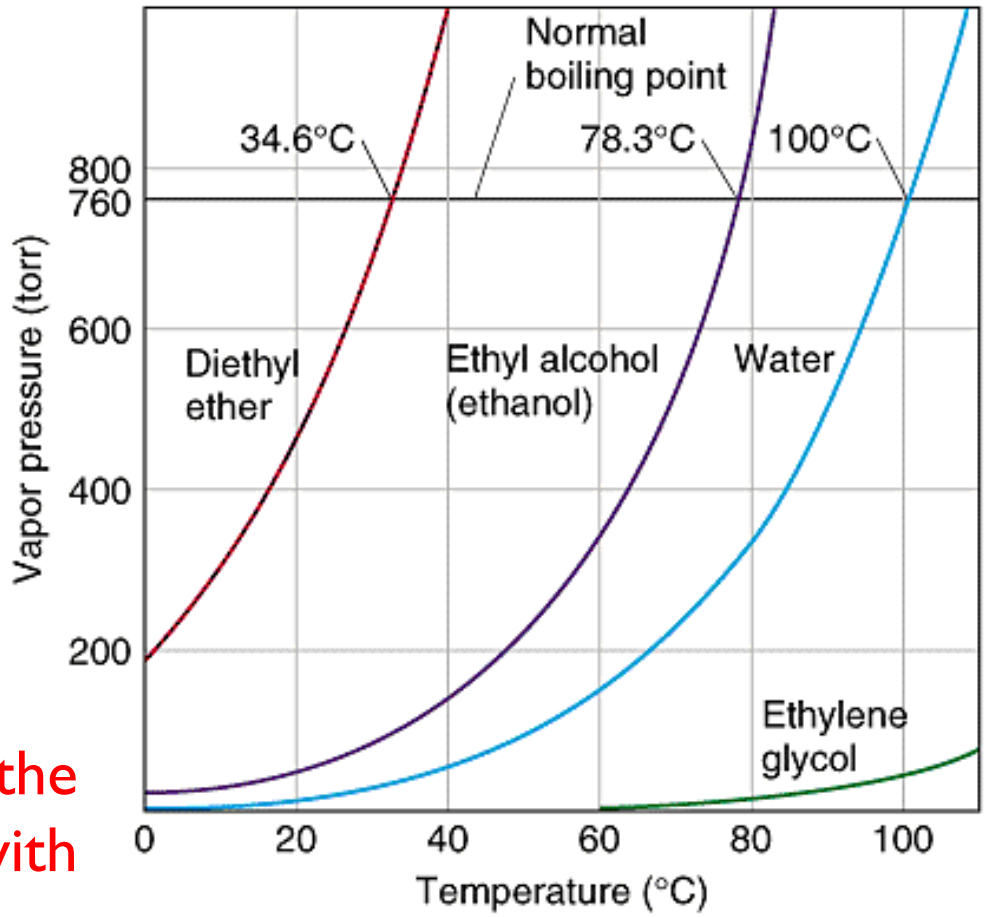
- In a sealed container, some of a liquid evaporates to establish a pressure in the vapor phase.
- Vapor pressure: partial pressure of the vapor over the liquid measured at equilibrium and at some temperature.
- Dynamic equilibrium



Temperature vs. Vapor pressures

The Clausius-Clapeyron equation shows how the vapor pressure and temperature are related. It can be written as:

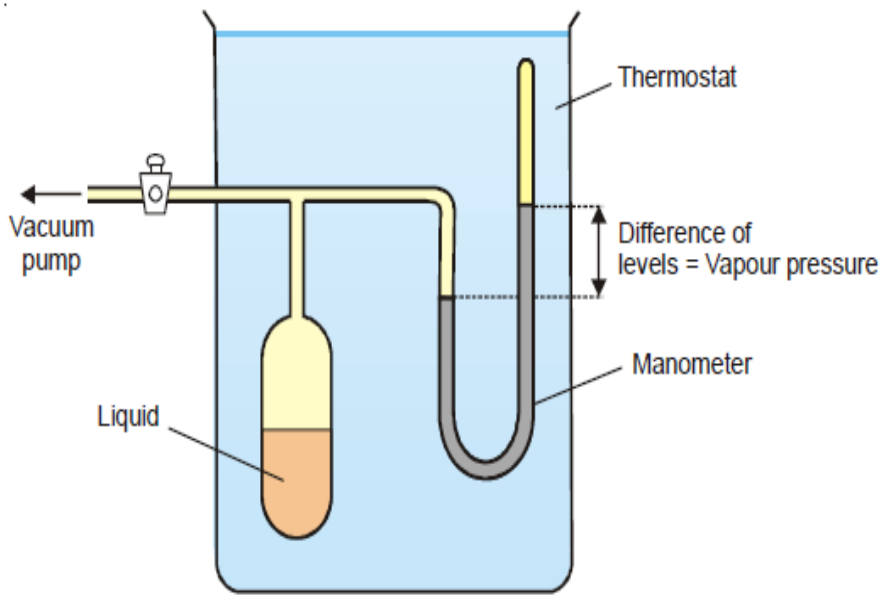
$$\ln P = -\frac{\Delta H_{vap}}{RT} \times \frac{1}{T} + C$$



The vapor pressure above the liquid varies exponentially with changes in the temperature.

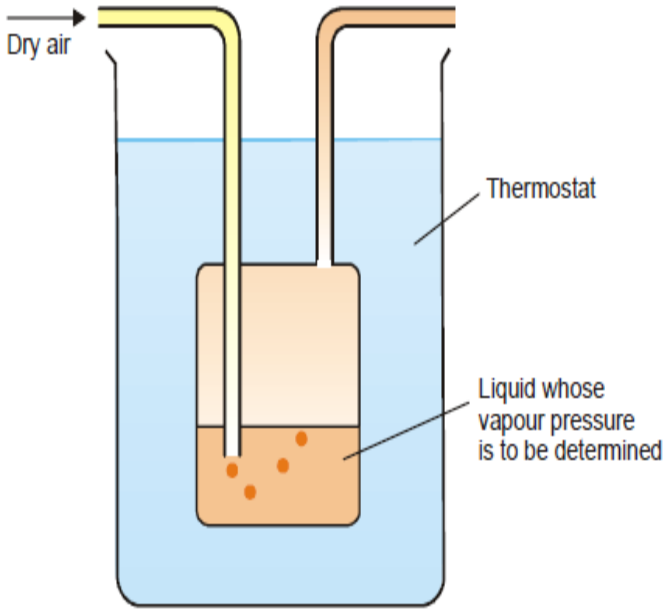
Determination of vapor pressure

Static method



Determination of vapour pressure by Static method.

Dynamic method



Determination of vapour pressure by Dynamic method.

Vapor Pressure & Boiling Point

- Liquids boil when the external pressure equals the vapor pressure.
- The vapor pressure of a liquid increases with temperature
- The temperature of boiling increases as pressure increases.
- There are two ways to get a liquid to boil: increase temperature or decrease pressure.
  - Pressure cookers operate at high pressure. At high pressure the boiling point of water is higher than at 1 atm. Therefore, there is a higher temperature at which the food is cooked, reducing the cooking time required.
- Normal boiling point is the boiling point at 760 torr (1 atm).

Trouton's rule

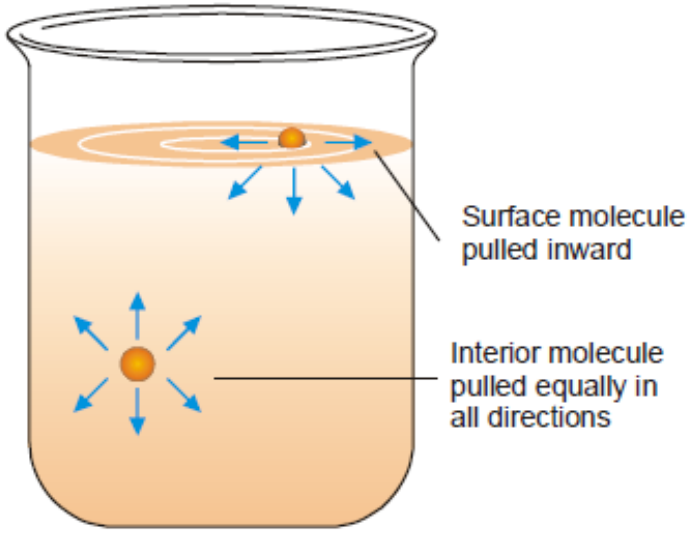
The entropy of vaporization is almost the same value, about 85–88 J K−1 mol−1, for various kinds of liquids. The entropy of vaporization is defined as the ratio between the enthalpy of vaporization and the boiling temperature. It is named after Frederick Thomas Trouton.

Mathematically, it can be expressed as: $\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$

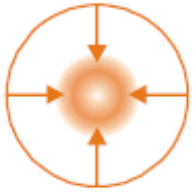
where R is the gas constant. Trouton's rule is valid for many liquids; for instance, the entropy of vaporization of toluene is 87.30 J K−1 mol−1, that of benzene is 89.45 J K−1 mol−1, and that of chloroform is 87.92 J K−1 mol−1. Because of its convenience, the rule is used to estimate the enthalpy of vaporization of liquids whose boiling points are known.

Surface Tension

The force in dynes acting along the surface of a liquid at right angle to any line 1 cm in length. Units; 1 dyne cm^{-1} (CGS) = 1 m Nm^{-1} (SI)



Surface tension is caused by the net inward pull on the surface molecules.



The inward forces on the surface molecules minimize the surface area and form a drop.

Effect of Temperature on Surface Tension

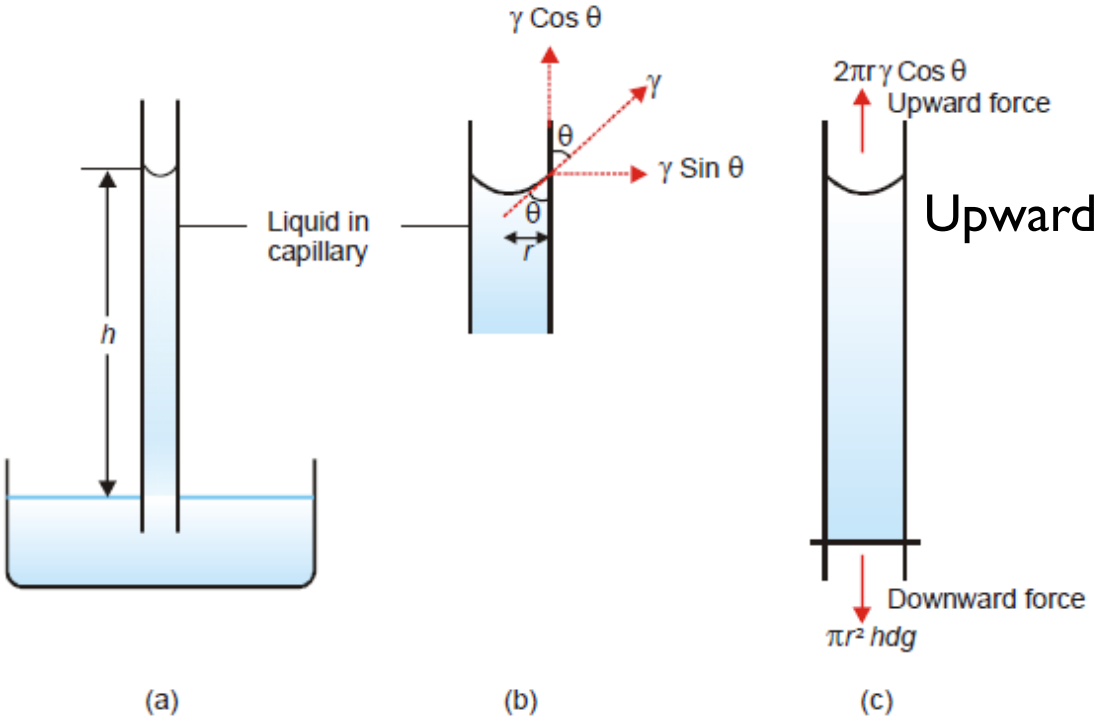
TABLE 11.2. SURFACE TENSION OF SOME LIQUIDS AT VARIOUS TEMPERATURES (dynes cm^{-1})

Liquid	20°C	40°C	60°C	80°C
Water	72.75	69.56	66.18	62.61
Ethyl alcohol	22.27	20.60	19.01	–
Methyl alcohol	22.6	20.9	–	–
Acetone	23.7	21.2	18.6	16.2
Toluene	28.43	26.13	23.81	21.53
Benzene	28.9	26.3	23.7	21.3

Surface tension decreases with increase in temperature

Determination of Surface Tension

1. Capillary rise method



Upward force = Downward force

$2\pi r\gamma = h\pi r^2 dg$

$\gamma = hrdg/2$ dynes/cm

Figure 11.15

(*a*) Rise of liquid in a capillary tube; (*b*) Surface tension (γ) acts along tangent to meniscus and its vertical component is γ Cos θ; (*c*) Upward force $2\pi r\gamma$ Cos θ counterbalances the downward force due to weight of liquid column, πr^2 hgd.

Determination of surface tension

Problem-I: A capillary tube of internal diameter 0.21 mm is dipped into a liquid whose density is 0.79 g cm–3. The liquid rises in this capillary to a height of 6.30 cm. Calculate the surface tension of the liquid. (g = 980 cm sec–2) [solution: 25.6 dynes cm–1]

Problem-II: How high will sap rise in a plant if the capillaries are 0.01 mm diameter, the density of the fluid is 1.3 g cm^{-1} and its surface tension 0.065 Nm^{-1}. (g = 981 cm s^{-2}) [solution: 2.04 meters]

Determination of surface tension

2. Drop Formation Method

(a) Drop-weight Method

(b) Drop-number Method

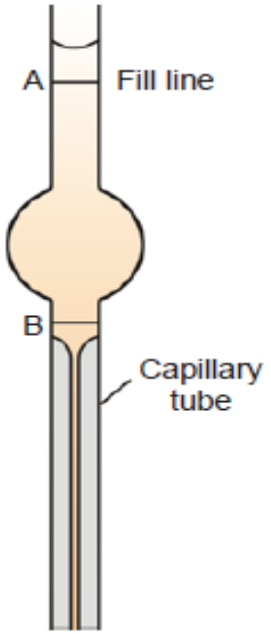


Figure 11.16
A stalagmometer.

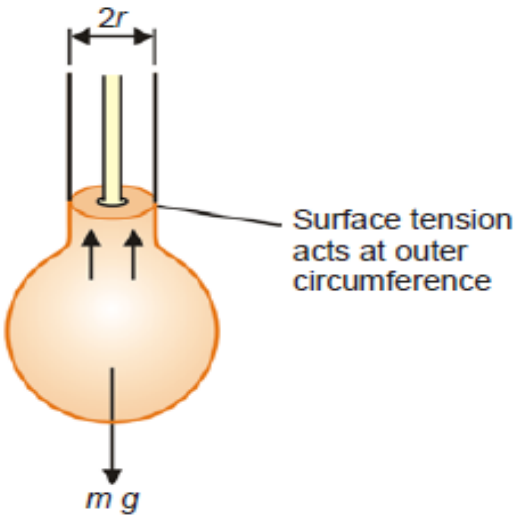


Figure 11.17
A drop forming from a tube of radius *r*.

Determination of surface tension

3. Ring-detachment method

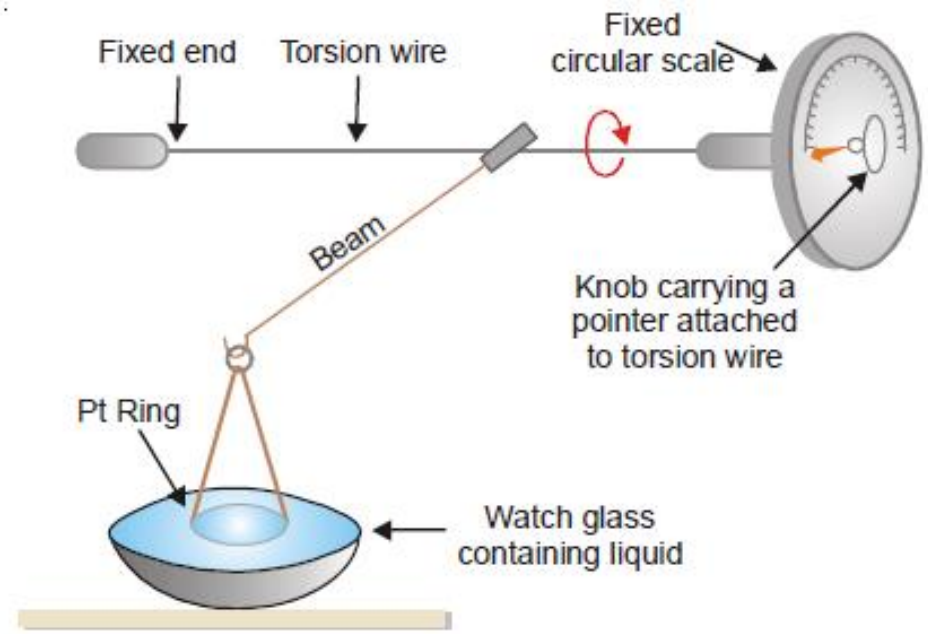


Figure 11.19
du Nouy Tensiometer.

Determination of surface tension

4. Maximum Bubble Pressure method

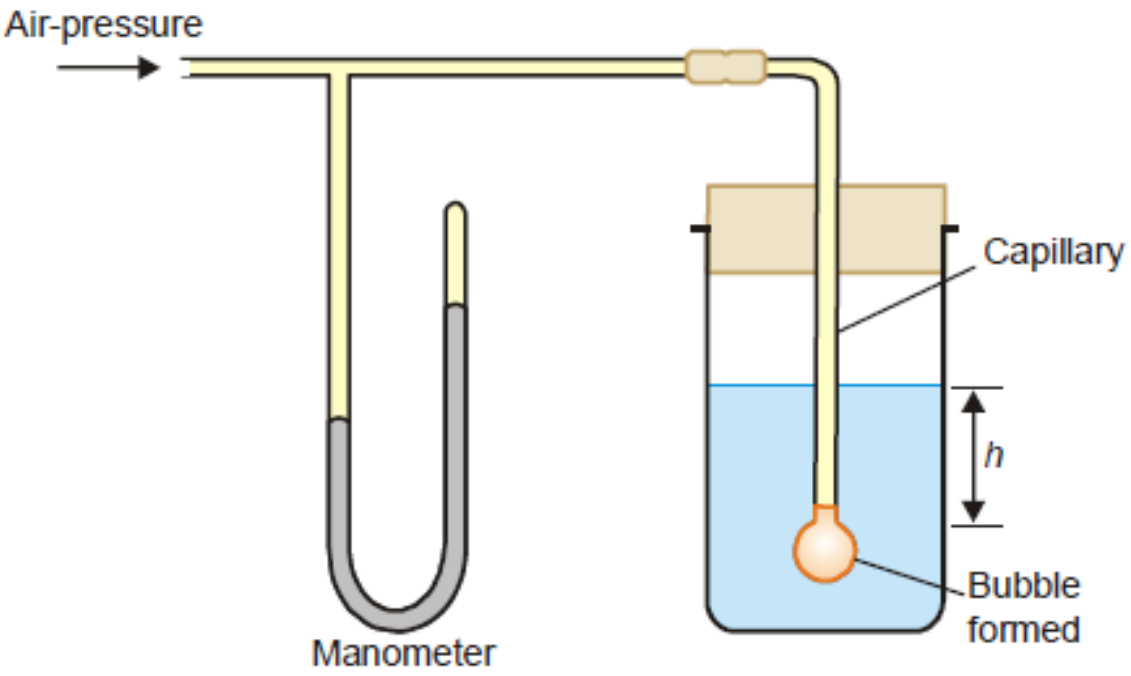
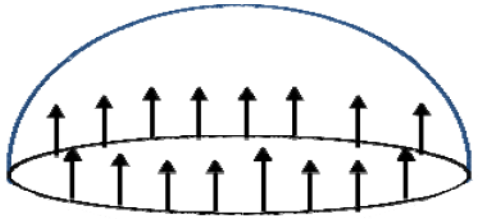


Figure 11.20
A simple apparatus for maximum bubble pressure method.

Excess pressure inside a soap bubble



Given:

r = radius of the bubble

S = surface tension of soap bubble

P = excess pressure inside the bubble

= Pressure on the concave side – Pressure on convex side

Let us imagine a section of bubble by a horizontal plane.

The length of the boundary of the circular section = $2\pi r$

Hence the total force acting on the section due to surface tension = $(S \times 2\pi r) \times 2$

(This factor 2 arises because there are two free surfaces)

The area of the circular section = πr^2

Force acting on the surface due to excess pressure = $P \times \pi r^2$

Since the surface is in equilibrium force due to surface tension must be balanced by the force due to excess pressure.

$$P \times \pi r^2 = 2 S \times 2 \pi r$$

$$P = \frac{4S}{r}$$

Equation gives the relation between excess pressure and surface tension.

Viscosity

Viscosity of a liquid is a measure of its frictional resistance.

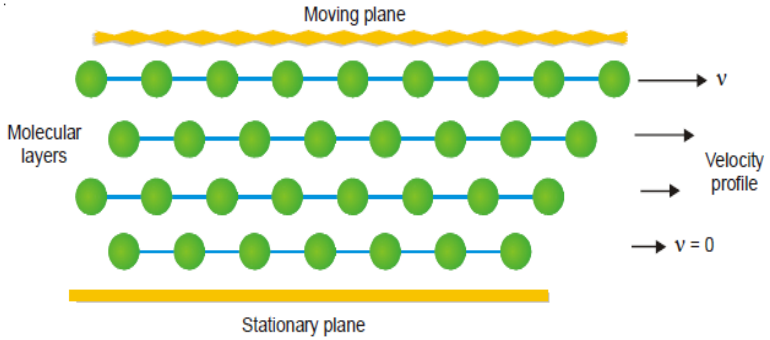


Figure 11.22
Flow of a liquid on a glass surface.

$$F \alpha A \frac{dv}{dx}$$

$$F = \eta A \frac{dv}{dx}$$

$$\eta = \frac{F}{A} \times \frac{dx}{dv}$$

η Coefficient of Viscosity
or simply viscosity of a liquid

The dimensions of the coefficient of viscosity (η) may be derived from equation

$$\eta = \frac{F}{A} \times \frac{dx}{dv} = \frac{\text{force}}{\text{area}} \times \frac{\text{distance}}{\text{velocity}}$$

or

$$\eta = \frac{\text{mass} \times \text{length} \times \text{time}^{-2}}{(\text{length})^2} \times \frac{\text{length}}{\text{length/time}}$$

$$= \text{mass} \times \text{length}^{-1} \times \text{time}^{-1}$$

1 poise (practice)= 1 g cm^{-1} s^{-1} (CGS)= 0.1 kg m^{-1} s^{-1}(SI)

Determination of Viscosity

Ostwald method: Viscosity of a liquid can be determined with the help of *Pioseulle's equation.*

$$\eta = \frac{\pi P r^4 t}{8 l V}$$

$$\frac{\eta_1}{\eta_2} = \frac{\pi P_1 r^4 t_1}{8 l V} \cdot \frac{8 l V}{\pi P_2 r^4 t_2} = \frac{P_1 t_1}{P_2 t_2}$$

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

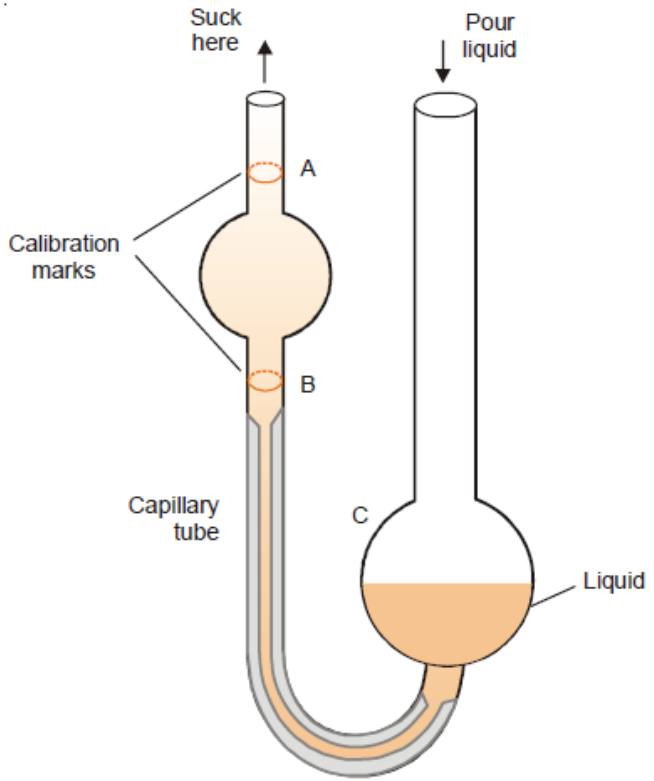


Figure 11.24
Ostwald Viscometer.

Determination of Viscosity

PROBLEM-111: In an experiment with Ostwald viscometer, the times of flow of water and ethanol are 80 sec and 175 sec at 20°C. The density of water = 0.998 g/cm3 and that of ethanol =0.790 g/cm3. The viscosity of water at 20°C is 0.01008 poise. Calculate the viscosity of ethanol. (0.01747 poise)

PROBLEM-1V: In an experiment with Ostwald viscometer, pure water took 1.52 minutes to flow through the capillary at 20°C. For the same volume of another liquid of density 0.80 g cm–3 the flow time was 2.25 minutes. Find the relative viscosity of the liquid and its absolute viscosity in centipoise. Density of water at 20°C is 0.9982 and absolute viscosity of water is 1.005 centipoise. (1.184 & 1.19)

Tutorial Marks