Vapour Pressure

Molecules in a liquid possess varying amounts of kinetic and potential energy due to differences in their speeds and interactions with neighboring molecules. Some molecules near the surface have enough energy to break free from the liquid and enter the gas (or vapour) phase. This process is called evaporation.

When a liquid evaporates, its temperature drops because the molecules that escape take energy with them. The rate of evaporation depends on:

1. Temperature – Higher temperature means faster evaporation.
2. Attractive forces – Stronger forces in the liquid slow down evaporation.
3. Surface area – A larger surface speeds up evaporation.
4. Pressure above the liquid – Higher pressure slows evaporation.

If the liquid is in a closed container, the molecules that escape into the vapour phase cannot leave the container. These vapour molecules move around and collide with each other and the container walls. Some lose energy during collisions and return to the liquid. This is called condensation. At first, evaporation is faster than condensation. But after some time, the rate of evaporation and condensation becomes equal. This balance is called dynamic equilibrium.

For example:

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

At equilibrium, the number of molecules in the liquid and vapour remains constant. The vapour molecules exert pressure on the container walls. This pressure at equilibrium is called vapour pressure.

Definition

The vapour pressure of a liquid is the pressure exerted by its vapour when the liquid and vapour are in equilibrium at a given temperature.

Factors Affecting Vapour Pressure

The vapour pressure of a liquid is influenced by the following factors:

1. Nature of the Liquid

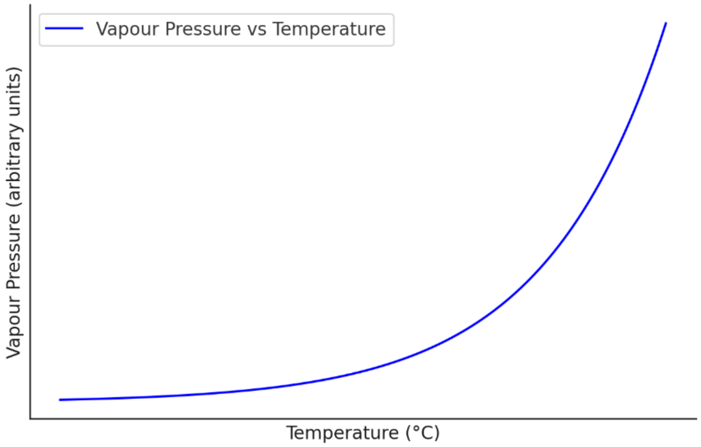
   The strength of intermolecular forces in a liquid determines how easily molecules can escape into the vapour phase.

   Strong intermolecular forces: Molecules have a low tendency to escape, so the liquid has low vapour pressure.

Weak intermolecular forces: Molecules escape easily, resulting in high vapour pressure.

2. Effect of Temperature

   As the temperature increases, the average kinetic energy of the molecules also increases. Higher kinetic energy helps molecules overcome the attractive forces in the liquid, making it easier for them to escape. This increases the vapour pressure of the liquid. The relationship between vapour pressure and temperature is exponential. A graph of vapour pressure vs. temperature shows a steep upward curve. Above the critical temperature the escaping tendency of the molecules is so high that only the vapours exist.



Boiling Point

The boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the external pressure. At this temperature, the liquid starts to boil, and bubbles of vapour form within the liquid.

1. Normal Boiling Point: When the external pressure is 1 atm (760 mmHg), the boiling point of a liquid is called the normal boiling point. For example, the normal boiling point of water is 100°C.
2. Effect of External Pressure: If the external pressure is higher, the boiling point increases because more heat is needed to make the vapour pressure equal to the higher external pressure. If the external pressure is lower, the boiling point decreases. This is why water boils at a lower temperature at a place of high altitude (low pressure) than at sea level (high pressure).

Enthalpy of Vaporization ($\Delta_{vap}H$)

When a liquid boils, it requires extra heat to overcome the attractive forces between its molecules. This heat is used to change the liquid into vapour, without raising the temperature of the liquid. During boiling, the temperature remains constant until the entire liquid becomes vapour.

Definition:

The enthalpy of vaporization ($\Delta_{vap}H$) is the amount of heat required to convert one mole of a liquid into its vapour at the boiling point and at constant pressure.

Example:

The enthalpy of vaporization of water at 100°C is 40.67 kJ/mol. This means that 40.67 kJ of heat is needed to convert one mole of water into steam at 100°C. The same amount of heat is released when one mole of steam condenses into water at 100°C.

Relation to Intermolecular Forces:

- Liquids with strong intermolecular forces require more heat to overcome these forces, so they have a higher enthalpy of vaporization.
- For example, water has a much higher enthalpy of vaporization than liquids like ether or benzene because the hydrogen bonds in water are stronger than the forces in these other liquids.

Determination of Vapour Pressure

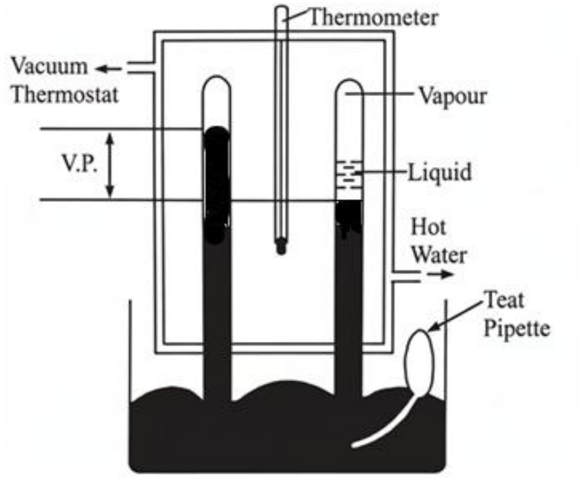
Static Methods

1. **Barometric Method**

   The Barometric Method is a classic static method used to determine the vapour pressure of a liquid. The setup involves two barometric tubes filled with mercury, which are placed inverted in a trough of mercury. Here's how the method works:

   The two barometric tubes are filled with mercury. One of these tubes is used as a control and remains empty, while the other contains a small amount of the liquid whose vapour pressure is to be determined. The space above the mercury in the second tube is filled with the vapour of the liquid. The liquid should be free from dissolved air to ensure accurate results. A thermometer is used to monitor the temperature of the system. The experiment is carried out at a constant temperature. To achieve this, the tubes and the liquid are placed in a vacuum thermostat, which ensures a stable temperature throughout the experiment.

The liquid in the second tube starts evaporating, and its vapour builds up in the empty space above the mercury. This creates an equilibrium between the liquid and its vapour. The difference in the height of the mercury in the two tubes is measured. This difference is directly related to the vapour pressure of the liquid at the given temperature. The difference in mercury levels (V.P.) between the two barometric tubes gives the vapour pressure of the liquid at the measured temperature.



2. The Isoteniscopic Method

This is a reliable static method used for measuring the vapour pressure of a liquid. This method, developed by A. Smith and A.W.C. Menzies, works by allowing the liquid and its vapour to reach equilibrium in a closed system without disturbance. The vapour pressure is measured by balancing the liquid levels in the apparatus and using a manometer to determine pressure differences.

Apparatus Setup:

The setup consists of the following key components:

- Isoteniscope: The central apparatus for this method. It includes:
- A bulb (A): Half-filled with the liquid whose vapour pressure is to be measured.
- A U-shaped tube (B): Partially filled (about 2–3 cm below the level of bulb A) with the same liquid, forming two limbs: L1 and L2.
- Manometer (C): Measures the pressure difference in the system.

- Bottle (D): Acts as a buffer to smooth out pressure fluctuations. It can be connected to either a vacuum pump or to air.
- Water Bath with Thermometer: Maintains the isoteniscope at a constant temperature, as temperature strongly influences vapour pressure.

Procedure:

The bottle (D) is connected to a vacuum pump, and the entire apparatus is evacuated. This causes the liquid in bulb A to boil vigorously, expelling all the dissolved and trapped air from the isoteniscope (AB).

After evacuation, the level of liquid in the limb L2 is higher than in L1, due to the vacuum. The isoteniscope is immersed in a water bath to maintain a constant temperature. The thermostat in the bath is adjusted to achieve the desired experimental temperature, as vapour pressure varies with temperature.Air is gradually introduced into the system by connecting the bottle D to the atmosphere. This is done until the liquid levels in both limbs (L1 and L2) of the U-tube are exactly equal.

At this point, the pressure in limb **L1** is the vapour pressure of the liquid in equilibrium with its vapour which is equal to the pressure in limb L2. And the pressure in the limb L2 is the atmospheric pressure minus the height of the mercury column in the manometer (C).

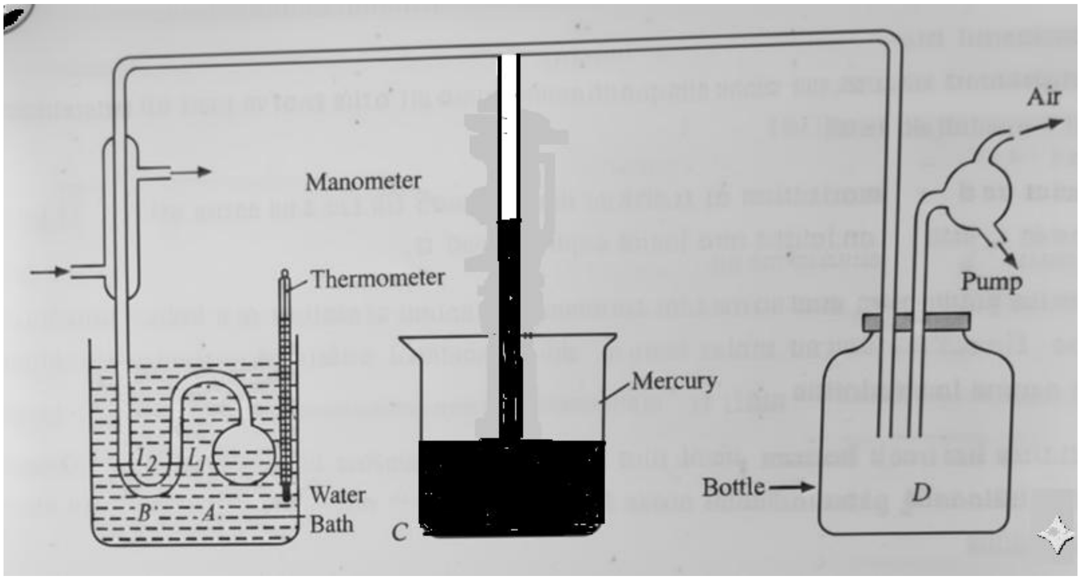


Figure: Apparatus Setup for Isoteniscopic Method

Surface Tension

Surface tension is a unique property of liquids arising from intermolecular forces, and it plays a vital role in determining the behavior of liquids at their surfaces.

Origin of Surface Tension (molecular interpretation)

In the bulk of a liquid, a molecule is surrounded by other molecules, experiencing equal and balanced attractive forces in all directions. At the surface, however, the molecule is only partially surrounded by other liquid molecules. It experiences an unbalanced force because there are no liquid molecules above it, only air. This downward force of attraction pulls the surface molecules inward, causing the surface of the liquid to contract to the smallest possible area. Because of this tendency to contract, the liquid surface behaves like a stretched elastic sheet. This phenomenon is termed surface tension.

Definition

Surface tension (γ) is defined as the force per unit length (acting perpendicular to the liquid surface) along the surface of a liquid.

In different systems, surface tension is measured as:

- CGS system: Dynes per centimeter (dynes cm^{-1}).
- SI system: Newton per meter (N m^{-1}).

Practical Manifestations of Surface Tension

1. Spherical Shape of Drops or Bubbles:
   Due to surface tension, liquid drops and gas bubbles inside liquids adopt a spherical shape. This shape minimizes the surface area for a given volume, reducing the energy required to maintain the surface.
2. Rise or Fall in Capillary Tubes:
   The rise or fall of liquid levels in a container depends on the interaction between the liquid surface and the walls of the container (adhesive forces). If the intermolecular forces between liquid molecules (cohesive forces) are weaker than the forces between the liquid and the solid surface, the liquid will rise and wet the solid surface. If the solid-liquid interactions are weaker than the intermolecular forces in the liquid its level will fall and the liquid will not wet the solid surface. The angle between the tangent to the liquid surface at the point of contact and the solid surface inside the liquid is known as the contact angle (θ) for the pair of liquid and solid surface. The contact angle can have any value between

0 and 180°. For liquids which wet the solid surface, θ is less than 90° while those which do not wet the solid surface, is more than 90°.

  - Example: Water rises in a capillary tube due to adhesive forces (attraction to the walls of the tube) being stronger than cohesive forces (between water molecules).
  - Conversely, mercury falls because cohesive forces dominate.

3. **Formation of a Concave or Convex Meniscus:** The shape of the liquid's surface (concave or convex) in pipettes or burettes is caused by surface tension.
   Example: Water forms a concave meniscus because it adheres to the container walls. Mercury forms a convex meniscus because it does not adhere to the walls.

Surface Energy: As a result of the inward pull, surface of the liquid always tends to contract to the smallest possible surface area. In order to increase the surface area it is necessary to do work to bring molecules from the bulk of the liquid on to the surface against the inward attractive forces. The work required to increase the surface area by unity is called the surface energy.

Let us consider a liquid film in a rectangular wire frame ABCD (see diagram). The side CD=*l* is movable and fitted with a piston. When CD is pulled outward by a small distance *dl*, the liquid's surface area increases, and the work done against surface tension increases the surface energy. It is observed that the force acts on the movable side CD in a direction opposite to the movement of the side. The force per unit length acting on CD is the surface tension γ. So, the force acting on CD is given by

$$F = \gamma 2l$$

The work done to extend the side CD by distance dl is given by

$$W = F \times dl = \gamma 2l dl$$

The increase in area is given by $dA = 2ldl$

Therefore, $W = \gamma dA$

or $\gamma = \frac{W}{dA}$

Thus, it is evident that surface tension is defined as the work required to enlarge the surface area by unity and is, therefore, frequently referred to as the surface energy of a liquid per unit area. The surface tension (Nm^{-1}) is numerically and dimensionally equal to the rate of increase of surface energy with area.

Determination of surface tension

(a) The capillary rise method

If a capillary tube is placed in a liquid, it is found that the liquid usually rises in the tube (except for mercury in which it falls). Let us Consider a capillary tube of radius r immersed in a vessel containing a liquid that wets the glass. Let the liquid rise to a height $'h'$ above the level of the liquid and $'d'$ be the density of the liquid. The force due to surface tension acting upwards on the inner side of the capillary raising the liquid column upward is equal to $\gamma cos\theta\ \times$ inner circumference of the capillary, i.e.,

$$\text{Force} = \gamma cos\theta\ \times 2\pi r$$

where γ is the surface tension of the liquid and θ is the contact angle.

Force of gravity pulling the liquid downward = weight of the liquid column = Vdg

where V is the volume of the liquid in the tube.

But $V=\pi\, r^2 h$

Hence the weight of the liquid column = $\pi\, r^2hdg$

At equilibrium

$$\gamma cos\theta\ \times 2\pi r\ =\ \pi\, r^2hdg$$

$$\gamma = \frac{rhdg}{2\cos\theta}$$

If the angle of contact between the glass and liquid is zero then cos is unity and the expression reduces to

$$\gamma = \frac{rhdg}{2}$$

For the determination of surface tension of a liquid, it is required to measure the height (h) up to which the liquid rises and the radius (r) of the capillary tube. The height $'h'$ is measured by cathetometer and the radius of the capillary tube by a travelling microscope.

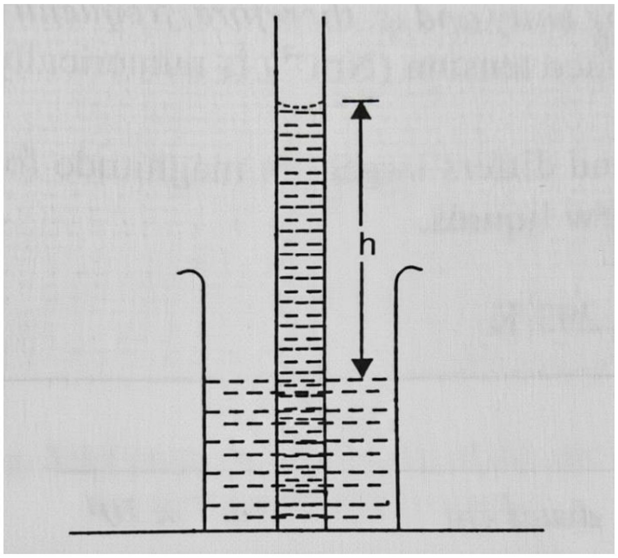


Figure: Surface Tension measurement by Capillary rise method

Problem: The surface tension of toluene at 293 K is 0.0284 Nm and its density at this temperature is 0.866 g cm^{-3}. What is the largest radius of the capillary that will permit the liquid to rise 2×10^{-2} m?

Problem: At 303 K, the surface tension of ethanol in contact with its vapour is 2.189 x 102 Nm^{-1}, and its density is 0.780 g cm^{-3}.

(a) How far up a tube of internal radius 0.2 mm will it rise?

(b) What pressure is needed to push the meniscus level back with the surrounding liquid?

(b) Drop Number Method: This method is generally used for the comparison of surface tension of a liquid with another liquid of which the absolute value of surface tension is already known. The instrument used is called a stalagmometer and consists of a bulbed capillary tube as shown in **Fig.** The tube is first cleaned thoroughly with chromic acid, and then with distilled water and dried. It is filled up to the mark A with the liquid whose surface tension is to be measured by sucking in the liquid. The liquid is allowed to flow completely through the stalagmometer to determine the number of drops. The number of drops is counted carefully. The purpose graduated portion of the tube is to enable fractions of a drop to be judged. The same procedure is repeated with the other liquid (water).

Let

n_1 = number of drops of the first liquid in a certain volume V

n_2 = number of drops of the second liquid (say water) in the same volume

d_1= density of first liquid

d_2= density of water

m_1 = mass of the first liquid in a certain volume V

m_2 = mass of the second liquid (say water) in the same volume

Then the average weight of liquid drops for the first liquid is given by

$$w_1 = \frac{m_1 g}{n_1} = \frac{V d_1 g}{n_1}$$

For the second liquid,

$$w_2 = \frac{m_2 g}{n_2} = \frac{V d_2 g}{n_2}$$

Hence,

$$\frac{\gamma_1}{\gamma_2} = \frac{w_1}{w_2} = \frac{\frac{V d_1 g}{n_1}}{\frac{V d_2 g}{n_2}}$$

Or, $$\frac{\gamma_1}{\gamma_2} = \frac{n_2 d_1}{n_1 d_2}$$

If the surface tension of water (γ_2) is known, that of the first liquid (γ_1) can be easily calculated.

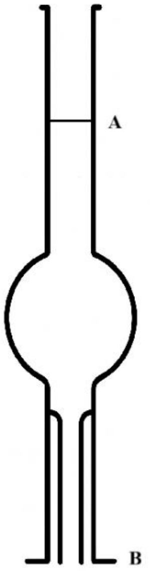


Fig. Stalagmometer

Problem: Equal volumes of an organic liquid and water gave 55 drops and 35 drops respectively. The densities of water and the organic liquid are 0.996 and 0.80 g cm^{-3} and the surface tension of water is 7.2×10^{-2} Nm^{-1}. Calculate the surface tension of the organic liquid. How many times a water drop is heavier than a drop of the organic liquid?

Variation of Surface Tension with Temperature

Surface tension decreases with increase of temperature and vanishes at the critical temperature. Increase in temperature of the liquid is accompanied by an increase in the energy of the molecules; the intermolecular forces decrease with rise of temperature. The environment of the molecules in the bulk tend to become similar to that on the surface at higher temperatures. Consequently, less work would be required to bring molecules from the bulk of the liquid on to the surface. In other words, surface tension decreases with increase in temperature.

Eotvos found that surface tension varies linearly with temperature. He suggested the following expression for the variation of surface tension with temperature:

$$\gamma\left(\frac{M}{\rho}\right)^{2/3} = a - kt$$

Here, M is the molar mass of the liquid, ρ the density of the liquid, γ surface tension of the liquid at temperature t and a and k are constants

At the critical temperature (i.e. when $t = t_c$), the surface tension is zero. So, we may write

$$0 = a - kt_C$$

$$\text{or } a = kt_C$$

So, the Eotvos equation modifies to

$$\gamma\left(\frac{M}{\rho}\right)^{2/3} = k(t_C - t)$$

This equation has been found to be satisfactory in giving variation of surface tension with temperature in the case of a number of liquids over a wide range of temperature.

Since surface tension vanishes roughly 6° below the critical temperature rather than at the critical temperature, i.e., when $t = t_C - 6$. Ramsay and Shield proposed the following equation for the temperature dependence of surface tension:

$$\gamma\left(\frac{M}{\rho}\right)^{2/3} = k(t_C - t - 6)$$

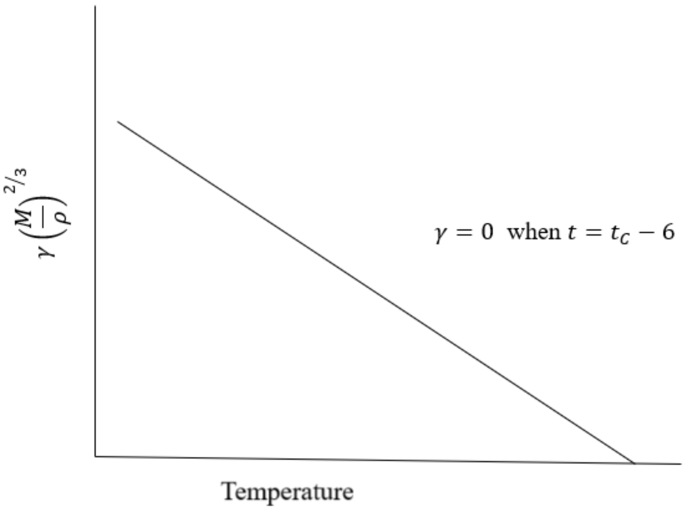


Figure: Variation of surface tension with temperature

Viscosity

The resistance to flow exhibited by liquid is known as viscosity. Because of this property some liquids flow slowly than others. For example, glycerine, castor oil, honey etc., which flow slowly are said to have high viscosity while water, alcohol and ether which flow rapidly are said to have low viscosity.

The phenomenon of viscosity may be elucidated by considering the flow of a liquid through a narrow pipe. When a liquid flows through a pipe, all parts of the liquid do not move with the same velocity. A thin layer immediately in contact with the wall of the pipe is almost stationary. The velocity of flow of each successive layer of the liquid gradually increases as we move towards the centre of the pipe. Each layer of the liquid moving with higher velocity over the other layer with low velocity will experience a retarding effect due to the friction between two layers. The resistance that one part of a liquid offers to a liquid flowing with one velocity offers to another part of a liquid flowing with different velocity is known as the viscosity. As with gases, the coefficient of viscosity η may be defined as the force per unit area required to maintain unit difference of velocity between two layers in the liquid unit distance apart.

If A is the area of the layer, *dz* the distance between them and dv_x the velocity difference of the layer, then the tangential force required to maintain a constant velocity difference dv_x is directly proportional to A and dv_x and inversely proportional to *dz*. Consequently,

$$F \propto A\left(\frac{dv_x}{dz}\right)$$

$$F = -\eta A\left(\frac{dv_x}{dz}\right) \dots\dots\dots\dots\dots\dots\dots.(1)$$

where η is the proportionality constant called the coefficient of viscosity of the liquid. The equation (1) is known as Newton's law of viscosity. This law is experimentally obeyed by several liquids under the condition that their rate of flow is not very high. This equation is applied for laminar flow, not for turbulent flow.

A liquid which does not obey Newton's law of viscosity is called a non-Newtonian liquid. The liquids which follow this equation are called Newtonian liquid. For Newtonian liquids, η is independent of $\frac{dv_x}{dz}$, whereas for non-Newtonian fluids, η changes as $\frac{dv_x}{dz}$ changes.

The reciprocal of the coefficient of viscosity is called the fluidity and is denoted by φ, that is,

$$\varphi = \frac{1}{\eta}$$

Units of viscosity:

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

In CGS system, $\eta = \frac{(dyne)(cm)}{(cm^2)(\frac{cm}{s})}$

$$= dyne\ cm^{-2}s$$

$$= gcms^{-2}cm^{-2}s\ \ (1dyne = 1\ gcm\ s^{-2})$$

$$= gcm^{-1}s^{-1}$$

The CGS unit of viscosity $dyne\ cm^{-2}s$ is known as *poise.*

In SI system, $\eta = \frac{Nm}{(m^2)(\frac{m}{s})}$

$$= N\ m^{-2}s$$

$$= kgms^{-2}m^{-2}s\ \ (1N = 1\ kgm\ s^{-2})$$

$$= kgm^{-1}s^{-1}$$

This is equal to pascal-second (Pa *s*).

Relation between poise and Pa s:

1 poise $= 1\ gcm^{-1}s^{-1}$

$$= 10^{-3}\ kg\ (10^{-2}m)^{-1}s^{-1}$$

$$= 10^{-1}\ kg\ m^{-1}s^{-1}$$

$$= 0.1\ kg\ m^{-1}s^{-1}$$

$$= 0.1\ Pa\ s$$

Measurement of Viscosity

The viscosity of a liquid is measured by observing the rate of laminar flow of the liquid through a capillary tube. The rate of laminar flow of a liquid through a capillary tube at a constant pressure is related to the viscosity of the liquid. This relationship was first derived by Poiseuille and is given by the equation

$$\eta = \frac{\pi r^4 Pt}{8Vl}$$

where *V* is the volume of the liquid of viscosity which flows in time *t* through a capillary of radius *r* and length *l* under a driving pressure *P*.

Driving pressure *P* is given by

$$P = hdg$$

where h is the height of the liquid column,
d the density of the liquid
and g the acceleration due to gravity.

Substituting P in Poiseuille equation, we get

$$\eta = \frac{\pi r^4 hdgt}{8Vl}$$

It is to determine the relative viscosity of a liquid (1) with respect to some reference liquid (2) whose viscosity is known (e.g. water). Commonly used method is Ostwald's viscometer method. Ostwald viscometer consists of a capillary tube BD through which a definite volume of liquid (between the marks A and B) is allowed to flow under the force of its own weight. To start with, a definite quantity of a liquid 1 is introduced into the viscometer and is then drawn up by suction into the bulb E until the liquid level is above the mark A. The liquid is then allowed to drain, and the time necessary for the liquid level to fall from A to B is measured with a stop Watch. Let this time be t_1. The viscometer is now washed, dried and the whole operation is repeated with the reference liquid 2(water). Let the time of flow for water be t_2.

Applying Poiseuille equation for the two liquids η_1 and η_2 are given by:

$$\eta_1 = \frac{\pi r^4 hd_1gt_1}{8Vl}$$

$$\eta_2 = \frac{\pi r^4 hd_2gt_2}{8Vl}$$

where d_1 is the density of the liquid 1 and d_2 is the density of water.

$$\frac{\eta_1}{\eta_2} = \frac{\pi r^4 hd_1gt_1}{8Vl} \times \frac{8Vl}{\pi r^4 hd_2gt_2}$$

Or,

$$\frac{\eta_1}{\eta_2} = \frac{d_1t_1}{d_2t_2}$$

Or,

$$\eta_1 = \eta_2 \times \frac{d_1t_1}{d_2t_2}$$

Knowing the value of coefficient of viscosity of water(η_2) at the temperature of the experiment, the coefficient of viscosity of the liquid (η_1) can be determined.

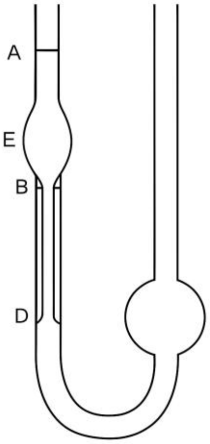


Figure: Ostwald Viscometer

Problem: Water requires 120.5 seconds to flow through a viscometer and the same volume of acetone requires 49.5 seconds. If the densities of water and acetone at 293 K are 9.982×10^2 kg m^{-3} and 7.92×10^2 kg m^{-3} respectively and the viscosity of water at 293 K is 10.05 pascal second, calculate the viscosity of acetone at 298 K.

Effect of temperature on viscosity:

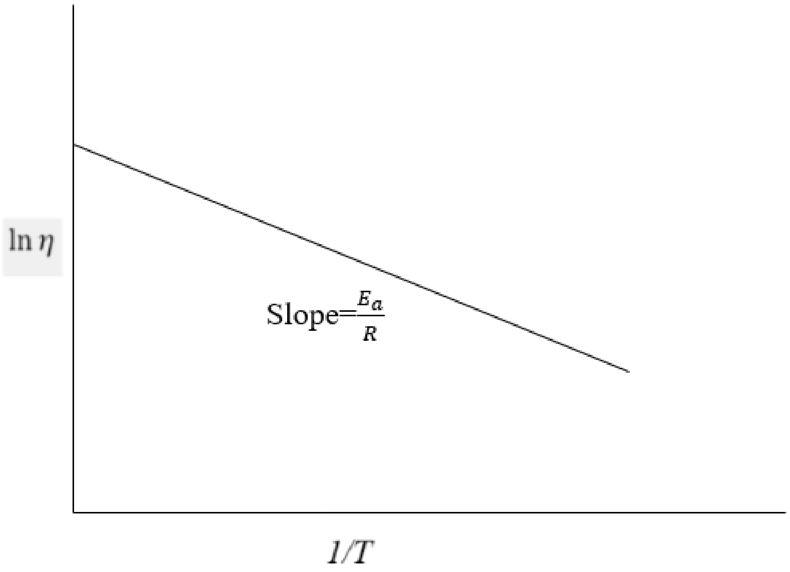
Viscosity of a liquid decreases with increase of temperature. In liquids, viscous forces are caused by molecules exerting attractive forces on each other across layers of flow. Increasing temperature results in a decrease in viscosity because a larger temperature means particles have greater thermal energy and are more easily able to overcome the attractive forces binding them together.

Various empirical equations relating viscosity with temperature have been proposed, but the expression given by Arrhenius and Guzman is the most satisfactory and is given by

$$\eta = Ae^{E_a/RT} \quad \text{……………………(1)}$$

$$ln\eta = lnA + \frac{E_a}{RT} \text{…………………..…(2)}$$

where A is a constant and E_a is the activation energy for the viscous flow and R is the gas constant and T the temperature in degree absolute. It follows from Eq. (2) that a plot of $ln\eta$ against $1/T$ will be straight line with slope $\frac{E_a}{R}$, from which E_a can be calculated.



The effect of temperature on the viscosity of a liquid is different from that of a gas. The coefficient of viscosity of a gas increases with increase in temperature.