

## 5. STATES OF MATTER

Matter is anything that occupies space and has a definite mass. Matter mainly exists in three different states – solid, liquid and gaseous state.

Solids have a definite shape and definite volume. This is because in solids the particles are closely packed and so the intermolecular force of attraction is greater.

Liquids have no definite shape but have definite volume. In liquids, the intermolecular force of attraction is smaller than that in solids. So the particles do not have a fixed position.

Gases have no definite shape and volume. Here the particles are far apart and hence they have no force of attraction.

### Comparison between the three states of matter

Properties	Solid state	Liquid state	Gaseous state
Shape and volume	Have definite shape and volume	No definite shape but have definite volume	Have no definite shape and volume
Inter molecular force of attraction	Strong	In between solids and gases	Very small
Arrangement of particles	Closely packed	Loosely packed	Far apart
K.E of particles	Very low	In between solids and gases	Very high
Diffusability	Very low	In between solids and gases	Very high
Compressibility	Very low	In between solids and gases	Very high

### INTERMOLECULAR FORCES

Intermolecular forces are the forces of attraction and repulsion between interacting particles (atoms and molecules). Attractive intermolecular forces are known as **van der Waals forces**. These forces include *dispersion forces or London forces, dipole-dipole forces, and dipole-induced dipole forces*. A particularly strong type of dipole-dipole interaction is *hydrogen bonding*.

#### 1) Dispersion Forces or London Forces

Atoms and non-polar molecules are electrically symmetrical and have no dipole moment. But in an atom, at a particular moment, the nucleus is shifted towards one side and the electrons, to the other side. So a temporary dipole (momentarily dipole) is created. This results in the development of instantaneous dipole on the adjacent atom for a very short time. These temporary dipoles of atoms attract each other. This force of attraction between temporary dipoles is termed as London forces or dispersion forces. These forces are important only at short distances.

#### 2) Dipole - Dipole Forces

Dipole-dipole forces act between the molecules possessing permanent dipole (polar molecules). These molecules interact with the neighbouring molecules. This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved. The attractive force decreases with the increase of distance between the dipoles. E.g.: HCl

#### 3) Dipole–Induced Dipole Forces

This type of attractive forces operates between the polar molecules and the non-polar molecules. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud. Thus an induced dipole is developed in the other molecule. The attraction between these molecules is termed as dipole – induced dipole force.

## Gas Laws

These are some relationships connecting the measurable properties of gases like pressure (P), temperature (T), volume (V) and number of moles (n). These are:

### **1) Boyle's Law (Pressure – Volume Relationship)**

It states that at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure. Mathematically,

$$P \propto 1/V$$

$$P = k \times 1/V, \text{ where } k \text{ is the proportionality constant.}$$

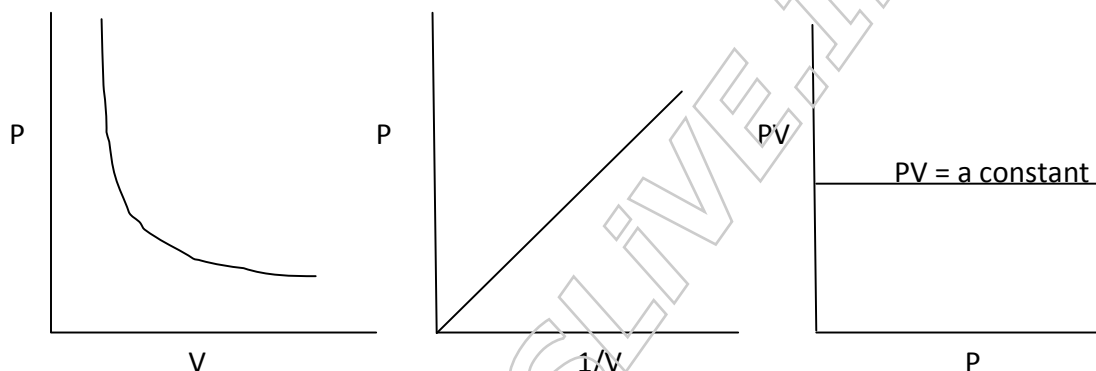
Or,  $PV = k$ , a constant

Consider a fixed amount of gas at constant temperature T. Let  $V_1$  &  $P_1$  are its initial volume and pressure respectively. Let the gas undergoes expansion, so that its final volume and pressure becomes  $V_2$  and  $P_2$ .

Then according to Boyle's law,

$$P_1V_1 = P_2V_2$$

If we plot graphs between pressure against volume, pressure against 1/volume and PV against P at constant temperature, the graphs obtained are as follows:



These graphs are obtained at constant temperature and are called **isotherms**.

We know that density = mass/volume

$$\text{i.e., } d = m/V$$

If we put value of V in this equation from Boyle's law equation, we get the relationship,

$$d = (m/k) \times p$$

i.e. At constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

### **2) Charles' Law (Temperature – Volume Relationship)**

It states that at constant pressure, volume of a fixed mass of gas is directly proportional to its temperature.

$$\text{Mathematically, } V \propto T$$

Or,  $V = k \times T$

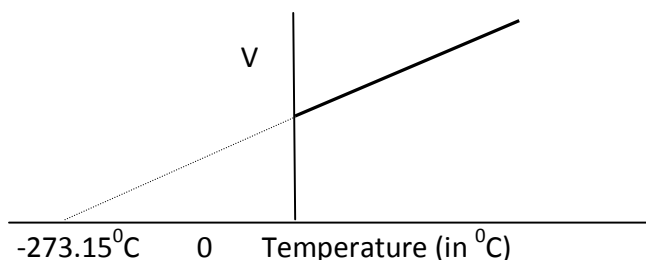
Or,  $V/T = k$ , a constant

Consider a fixed amount of gas at constant pressure P. Let  $V_1$  be its volume at a temperature  $T_1$  and  $V_2$  be its volume at a temperature  $T_2$ .

Then according to Charles' law:

$$V_1/T_1 = V_2/T_2$$

If volume is plotted against temperature at constant pressure, the graph obtained is as follows.



Since the graph is obtained at constant pressure, it is called **isobar**.

If we extend the graph to temperature axis (X-axis), the graph will meet at  $-273.15^{\circ}\text{C}$ . At this temperature, the volume of the gas becomes zero. This lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called **Absolute zero of temperature** and the scale of temperature based on absolute zero is called **Absolute scale of temperature**. All gases become solid or liquid before reaching this temperature.

### 3) Gay Lussac's Law (Pressure - Temperature Relationship)

It states that at constant volume, pressure of a fixed amount of a gas is directly proportional to the temperature.

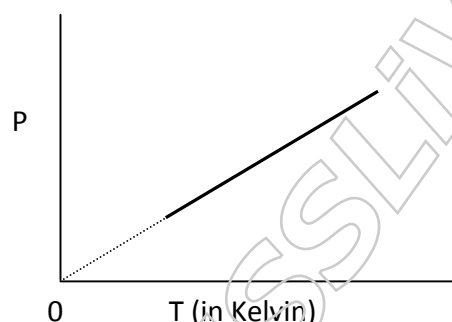
Mathematically,

$$P \propto T$$

$$\text{Or, } P = \text{a constant} \times T$$

$$\text{Or, } P/T = \text{a constant}$$

If we plot a graph between pressure and temperature of a fixed mass of gas at constant volume, the graph obtained is as follows:



The above is obtained at constant volume and is termed as an **isochore**

### 4) Avogadro Law (Volume – no. of moles or Amount Relationship)

It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of moles or molecules. This means that at constant temperature and pressure, the volume of a gas is directly proportional to its number of moles (n) or molecules (N).

$$\text{i.e., } V \propto n, \text{ the number of moles}$$

$$\text{or, } V = k \times n, \text{ where } k \text{ is a constant}$$

We know that number of moles (n) = mass in gram (w)/molar mass (M)

$$\text{i.e., } n = w/M$$

So the above equation becomes:

$$V = k \times w/M$$

$$\text{Or, } M = k \times w/V$$

$$\text{Or, } M = k \times d$$

$$\text{Or, } M \propto d$$

i.e., the density of a gas is directly proportional to its molar mass.

## Standard Temperature and Pressure (STP)

Standard temperature and pressure (also called NTP, the normal temperature and pressure) means 273.15 K (0°C) temperature and 1 bar pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level. At STP molar volume of an ideal gas or a combination of ideal gases is 22.71 L mol<sup>-1</sup>.

## IDEAL GAS EQUATION

The combination of the three gas laws (Boyle's law, Charles' and Avogadro law) give a single equation which is known as **ideal gas equation**.

According to Boyle's law:  $V \propto 1/P$  (At constant T and n)

According to Charles' Law:  $V \propto T$  (At constant p and n)

According to Avogadro Law:  $V \propto n$  (At constant p and T)

On combining these three laws we get:

$$V \propto n \times T \times 1/P$$

Or,  $V = R \times n \times T \times 1/P$  (where R is a constant called **universal gas constant**)

Or,  **$PV = nRT$**  ..... (1)

This equation is known as **ideal gas equation**.

From equation (1),  $R = \frac{PV}{nT}$

The value of R depends upon units in which P, V and T are measured.

### Values of R in different units

1. L atm/K/mol	0.0821
2. L bar/K/mol	0.08314 (8.314x10 <sup>-2</sup> )
3. Pa m <sup>3</sup> /K/mol	8.314
4. J/K/mol	8.314

Ideal gas equation is a relation between four variables and it describes the state of any gas, therefore, it is also called **equation of state**.

## Combined Gas Law

From ideal gas equation  $PV = nRT$ ,  $\frac{PV}{T} = nR$

If temperature, volume and pressure of a fixed amount of gas vary from T<sub>1</sub>, V<sub>1</sub> and P<sub>1</sub> to T<sub>2</sub>, V<sub>2</sub> and P<sub>2</sub> then we can write,

$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
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This equation is known as **combined gas law**. By knowing the values of any 5 parameters, we can determine the sixth one.

## 5) Dalton's Law of Partial Pressures

*This law states that at constant temperature, the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of the component gases.* The partial pressure of a gas in a mixture of gases is the pressure that the gas would exert, when it alone occupies the whole volume.

Mathematically,

$$P_{\text{Total}} = P_1 + P_2 + P_3 + \dots \text{ (at constant T, V)}$$

where P<sub>Total</sub> is the total pressure exerted by the mixture of gases and P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub> etc. are partial pressures of gases.

**Application of Dalton's law:** Dalton's law can be used to calculate the pressure of a gas collected over water surface. Here the gas is always moist. Therefore, pressure of dry gas can be calculated by subtracting vapour

pressure of water from the total pressure of the moist gas. *Pressure exerted by saturated water vapour is called aqueous tension.*

$$P_{\text{Dry gas}} = P_{\text{Total}} - \text{Aqueous tension}$$

### **Partial pressure in terms of mole fraction**

Consider three gases at constant temperature T and constant volume V, exert partial pressures  $P_1$ ,  $P_2$  and  $P_3$ .

From ideal gas equation,  $P = nRT/V$

So,  $P_1 = n_1RT/V$ ,  $P_2 = n_2RT/V$  and  $P_3 = n_3RT/V$

$$\begin{aligned} \text{The total pressure exerted by the mixture, } P_{\text{Total}} &= P_1 + P_2 + P_3 \\ &= n_1RT/V + n_2RT/V + n_3RT/V = (n_1 + n_2 + n_3) \frac{RT}{V} \end{aligned}$$

On dividing  $P_1$  by  $P_{\text{Total}}$ , we get,  $P_1/P_{\text{Total}} = n_1/(n_1 + n_2 + n_3)$

$$\text{Or, } P_1/P_{\text{Total}} = x_1$$

$$\text{Or, } P_1 = x_1 \cdot P_{\text{Total}}$$

$$\text{Similarly, } P_2 = x_2 \cdot P_{\text{Total}} \quad \text{and} \quad P_3 = x_3 \cdot P_{\text{Total}}$$

$$\text{In general, } P_i = x_i \cdot P_{\text{Total}}$$

where  $P_i$  and  $x_i$  are partial pressure and mole fraction of  $i^{\text{th}}$  gas respectively.

### **KINETIC MOLECULAR THEORY OF GASES**

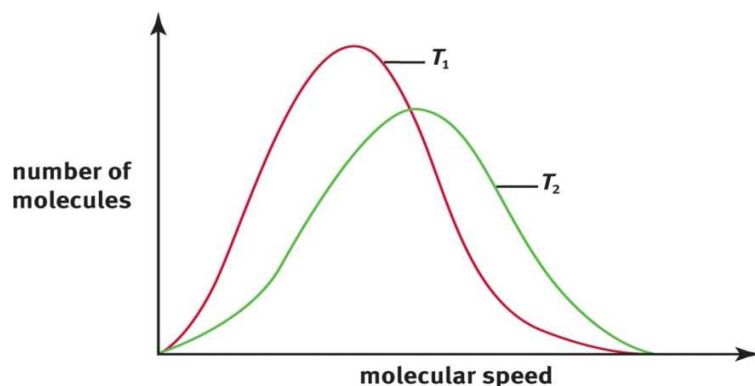
In order to explain the gas laws theoretically Maxwell, Boltzmann, Clausius etc. put forward a theory called *kinetic molecular theory of gases or microscopic model of gases*. The important postulates of this theory are:

1. Every gas contains a large number of minute and elastic particles (atoms or molecules). The actual volume of the molecules is negligible compared to the volume of the gas.
2. There is no force of attraction between the gas particles.
3. The particles of a gas are in constant and random motion in straight line. During this motion they collide with each other and also with the walls of the container.
4. The pressure of a gas is due to the wall collisions of the particles.
5. All collisions are perfectly elastic. i.e. the total energy of particles before and after collisions remains the same.
6. At any particular time, different particles of a gas have different speed and hence different kinetic energy.
7. The average kinetic energy of gas molecules is directly proportional to absolute temperature.

### **Maxwell-Boltzmann Distribution of molecular speeds**

According to Kinetic molecular theory of gases, the molecules of a gas are in continuous random motion and they collide with each other. So the speed and the kinetic energy of the molecules are different at any particular time. Thus we can obtain only an average value of speed of molecules.

The distribution of molecular speeds was first studied by Maxwell and Boltzmann by applying the theory of probability. This is known as *Maxwell-Boltzmann Distribution of molecular speeds*. They plotted a graph between number of molecules having different speeds against molecular speeds as follows:



The following conclusions are obtained from the graph:

1. The number of molecules having very low and very high speed is very small.
  2. Most of the molecules have a particular speed called most probable speed ( $u_{mp}$ ) which denotes the maximum in the curve.
  3. On increasing the temperature, the curve broadens and the  $u_{mp}$  increases.
- The speed distribution also depends on mass of molecules. At a constant temperature, heavier gas molecules have slower speed than lighter gas molecules.

#### Different types of molecular speeds

1. **Average speed ( $u_{av}$ ):** It is the arithmetic mean of the different speeds of molecules in a given sample of gas. If there are 'n' molecules in a sample and  $u_1, u_2, u_3, \dots, u_n$  are their individual speeds, then average speed is given by,

$$u_{av} = \frac{u_1 + u_2 + u_3 + \dots + u_n}{n}$$

2. **Root mean square (rms) speed:** It is the square root of the mean of the squares of the different speeds of the gas molecules. It is given by:

$$u_{rms} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2}{n}}$$

3. **Most probable speed ( $u_{mp}$ ):** It is the speed possessed by maximum number of gas molecules.

The three types of molecular speeds are related as:  $u_{rms} > u_{av} > u_{mp}$ .

The ratio between the three speeds is:

$$u_{mp} : u_{av} : u_{rms} = 1 : 1.128 : 1.224$$

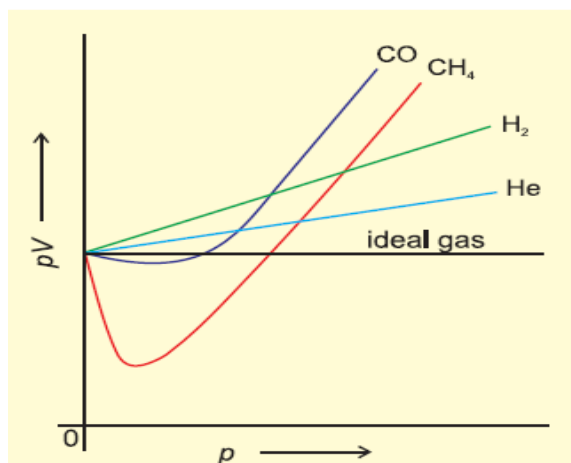
#### Behavior of real gases – Deviation of real gases from ideal behavior

Real gases do not obey ideal gas equation at all conditions of temperature and pressure. This can be understood from the PV against P graphs for different gases.

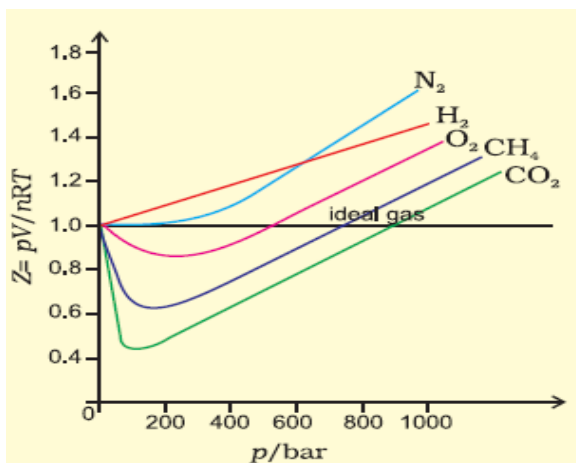
For ideal gases, PV is constant for any pressure. So the graph obtained is a straight line parallel to the pressure axis (X – axis). For  $H_2$  and He, PV increases with increase of pressure. But for CO and  $CH_4$ , the value of PV first decreases, reaches a minimum value and then increases.

The deviation from ideal behaviour can be measured in terms of compressibility factor Z, which is the ratio of product PV and nRT. Mathematically,  $Z = \frac{PV}{nRT}$

For ideal gas  $Z = 1$  at all temperature and pressures. So the graph of Z vs P will be a straight line parallel to pressure axis. For real gases value of Z deviates from unity.



PV vs P graph



Z vs P graph for real & ideal gases

From the graph it is clear that all gases behave ideally at low pressure. As the pressure increases the deviation from ideal behaviour also increases.

The deviation from real gases from ideal behaviour is due to two wrong assumptions of kinetic theory of gases. They are:

1. The actual volume of the molecules is negligible compared to the volume of the gas.
2. There is no force of attraction between the gas particles.

These two assumptions become wrong at *high pressure and low temperature*. When the pressure increases, the volume of the gas decreases. Then the volume of the gas molecule is also considered. At this condition, there arises inter molecular forces of attraction.

**Thus real gases obey ideal gas equation at low pressure and high temperature. Or, real gases deviate from ideal behaviour at high pressure and low temperature.**

By considering the above two assumptions, van der Waal proposed an equation, which is applicable to real gases. The equation is known as **van der Waal's equation** and is given as:

$$(P + n^2a/V^2)(V - nb) = nRT$$

Where P is the pressure of the gas, V is the volume, R is the universal gas constant, T is the absolute temperature, n is the no. of moles, 'a' and 'b' are called van der Waal's constants. 'a' is a measure of magnitude of inter molecular attractive forces within the gas and 'b' is related to the volume of the particles. The unit of 'a' is  $L^2\text{atm mol}^{-2}$  and that of 'b' is  $L\text{ mol}^{-1}$ . The term  $n^2a/V^2$  is related to pressure correction and term 'nb' is related to volume correction.

### Boyle Temperature or Boyle Point

The temperature at which real gases obey ideal gas equation over an appreciable range of pressure is called Boyle temperature or Boyle point. It depends on the nature of the gas.

### Liquification of gases

Gases can be liquefied by applying pressure at low temperature. The temperature below which a gas can be liquefied by the application of pressure is called **Critical Temperature** ( $T_c$ ). The pressure that must be applied at the critical temperature to liquefy a gas is called **Critical Pressure** ( $P_c$ ). The volume of 1 mole of a gas at its critical temperature and critical pressure is called **Critical Volume** ( $V_c$ ).  $T_c$ ,  $P_c$  and  $V_c$  are called **Critical constants**.

A gas below its critical temperature can be liquefied by applying pressure and is called the *vapour* of the gas.

### THE LIQUID STATE

In liquids the particles are loosely packed and so there is some inter molecular force of attraction. But this force is not strong enough to bind the molecules together. So liquids have a definite volume but no



definite shape. Due to the weak force of attraction, the molecules can move and so liquids can flow. Some of the important properties of liquids are:

### 1. Vapour pressure

In a liquid, all the molecules do not have the same energy. The molecules having higher energy are escaped to vapour phase. This process is called **evaporation**. As the density of the vapour increases the molecules collide with each other and so their energy decreases and returns to the liquid state. This process is called **condensation**. After some time, the rate of evaporation becomes equal to rate of condensation and the two processes attain equilibrium. At this condition, the pressure exerted by the vapour is called **vapour pressure**. It is defined as *the pressure exerted by the vapour in equilibrium with its own liquid*. It depends on the nature of the liquid and the temperature. As the temperature *increases*, the vapour pressure also *increases*.

### 2. Boiling Point

The vapour pressure of a liquid increases with temperature. At a particular temperature, the vapour pressure becomes equal to atmospheric pressure. At this temperature, the liquid boils. This temperature is called **boiling point**. At 1 atm pressure the boiling point is called **normal boiling point**. If pressure is 1 bar then the boiling point is called **standard boiling point** of the liquid. The normal boiling point of water is 100 °C (373 K), its standard boiling point is 99.6 °C (372.6 K).

At high altitudes (heights) atmospheric pressure is low. Therefore liquids at high altitudes boil at lower temperatures than at sea level. Since water boils at low temperature on hills, the pressure cooker is used for cooking food.

As depth increases, the atmospheric pressure also increases. So water boils at a higher temperature in a mine than at sea level.

Boiling does not occur when liquid is heated in a closed vessel. On heating continuously vapour pressure increases. At first there is a clear boundary between liquid and vapour phase because liquid is denser than vapour. As the temperature increases more and more molecules go to vapour phase and density of vapours rises. At the same time liquid becomes less dense. When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called critical temperature. At critical temperature boiling does not occur.

### 3. Surface Tension

It is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is denoted by Greek letter  $\gamma$  (Gamma). Its SI unit is  $\text{N m}^{-1}$ .

The energy required to expand the surface of a liquid by unit area is called surface energy. Its SI unit is  $\text{Jm}^{-2}$ .

Every liquid tries to reduce their energy by decreasing the surface area. For a given volume sphere has the minimum surface area. So liquid drops assume spherical shape.

Sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface of the liquid tends to take the rounded shape at the edges, which makes the edges smooth. This is called fire polishing of glass.

The magnitude of surface tension of a liquid depends on the attractive forces between the molecules and the temperature. When the attractive forces are large, the surface tension is large. As temperature increases, surface tension decreases.

The phenomenon like rise (or fall) of a liquid in a capillary tube (Capillary rise/depression) is due to surface tension.

### 4. Viscosity

When a liquid flows over a fixed surface, we can assume that there are a large number of layers.



The layer of molecules which is in contact with the surface is stationary. The velocity of upper layers increases as the distance of layers from the fixed layer increases. *This type of flow in which there is a regular change of velocity in passing from one layer to the next is called **laminar flow**.*

**Viscosity is a measure of internal resistance offered by the different layers of a liquid.**

If the velocity of the layer at a distance  $dz$  is changed by a value  $du$ , then velocity gradient is given by the amount  $du/dz$ . A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient

i.e.  $f \propto A$  (Where  $A$  is the area of contact).

$f \propto \frac{du}{dz}$  (Where  $\frac{du}{dz}$  is the velocity gradient. i.e. the change in velocity with distance)

or,  $f \propto A \cdot \frac{du}{dz}$

or,  $f = \eta \cdot A \cdot \frac{du}{dz}$

The proportionality constant ' $\eta$ ' is called coefficient of viscosity. It is defined as the force when velocity gradient and the area of contact are unity. Thus ' $\eta$ ' is measure of viscosity.

SI unit of viscosity coefficient is newton second per square metre ( $\text{N s m}^{-2}$ ) or pascal second (Pa sec). In cgs system the unit of coefficient of viscosity is **poise**.

$1 \text{ poise} = 1 \text{ g cm}^{-1} \text{ s}^{-1} = 10^{-1} \text{ kg m}^{-1} \text{ s}^{-1}$ .

Greater the viscosity, the more slowly the liquid flows. i.e. viscosity is inversely proportional to fluidity. The presence of Hydrogen bonding and van der Waals forces, increases viscosity.

Glass is a very viscous liquid. So it has a tendency to flow though very slightly. Hence the windowpanes of old buildings are thicker at the bottom than at the top.

Viscosity of liquids decreases as the temperature rises because at high temperature, molecules have high kinetic energy and can overcome the intermolecular forces.

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