## STATE OF MATTER

## INTRODUCTION

Any substance that has mass and occupies space is called Matter. Matter is composed of atoms or molecules. The arrangement of these building blocks gives matter various states, physical and chemical properties. The force of interaction between these particles give matter its physical properties based on which matter can be classified into solid, liquid or gases. The force of interaction between atoms/ molecules is highest in solids and least in liquids.
In this unit, we will learn more about these three physical states of matter particularly liquid and gaseous states.

## 1. INTERMOLECULAR FORCES

The forces of attraction existing among the molecules of a substance (gaseous, liquid or solid) are called intermolecular forces.
Dipole-dipole, dipole-induced dipole and dispersion forces are collectively called as van der Waals forces. Ion-dipole and ion-induced dipole forces are not van der Waals forces. Further, hydrogen bonding is only a special type of dipoledipole attraction shown only by limited number of elements. The different types of intermolecular forces are :

### 1.1 Dipole-Dipole Interactions

These forces of attraction occur among the polar molecules. Polar molecules have parmanent dipoles. The positive ple of one molecule is thus attracted by the negative pole of the other molecule.
HCl in which chlorine being more electronegative acquires a slight negative charge whereas the hydrogen end becomes slightly positively charged. The dipole-dipole interactions then take place among the HCl molecules :

PERMANENT DIPOLES


### 1.2 Ion-Dipole Interactions

This is the attraction between an ion (cation or anion) and a polar molecule. For example, when NaCl is dissolved in water, the polar water molecules are attracted towards $\mathrm{Na}^{+}$ion as well as towards $\mathrm{Cl}^{-}$ion.



Ion-dipole attractions between $\mathrm{Na}^{+}$and $\mathrm{H}_{2} \mathrm{O}$ molecules and Cl - ion and $\mathrm{H}_{2} \mathrm{O}$ molecules

### 1.3 Ion-Induced dipole Interactions

A non-polar molecule may be polarized by the presence of an ion near it, i.e., it becomes an induced dipole. The interactions between them are called ion-induced dipole interactions.

$$
\begin{gathered}
\mathrm{NO}_{3}^{-} \frac{\delta+}{\mathrm{I}-\mathrm{I}} \\
\text { betweinduced dipole attractions } \mathrm{NO}_{3}^{-} \text {ion and } \mathrm{I}_{2} \text { molecule }
\end{gathered}
$$

For example, in the presence of nitrate ion $\left(\mathrm{NO}_{3}^{-}\right)$, iodine molecule $\left(I_{2}\right)$, which is non-polar, gets polarized as $\stackrel{\delta+}{(\mathrm{I}-\mathrm{I})}$ as shown in fig.

### 1.4 Dipole-Induced dipole Interactions

A non-polar molecule may be polarized by the presence of a polar molecule (dipole) near it, thereby making it an induced dipole. The interactions between them are then called dipoleinduced dipole interactions.


## Dipole-induced dipole attractions

For example, noble gases get polarized in the presence of polar molecules.

### 1.5 London forces or Dispersion forces

At any instant of time, the electron cloud of the molecule may be distorted so that an instantaneous dipole or momentary dipole (i.e., a dipole for a short while) is produced in which one part of the molecule is slightly more negative than the rest. The momentary dipoles induce dipoles in the

## STATE OF MATTER

neighbouring molecules. These are then attracted to each other. The forces of attraction between the induced momentary dipoles are called London dispersion forces.


Forces of attraction between momentary dipoles and induced dipoles (London forces) in helium atoms

## 2. INTERMOLECULAR FORCES VERSUS

## THERMAL ENERGY

Whether a substance will exist as a solid or a liquid or a gas is the result of competition between :
(i) intermolecular forces, i.e., the forces of interaction between the molecules of that substance which try to bring the molecules closer, and
(ii) thermal energy possessed by the molecules due to temperature which results into the movement of the molecules and hence tries to keep them apart.


## 3. IDEAL GAS

An ideal gas is a hypothetical concept of matter and is treated as a standard of comparison while studying the various states of matter. There are various assumptions associated with an ideal gas. The most notable of these assumptions are:

* Volume of the molecules are infinitely small and the force of interaction between the molecules is zero
* The molecules of the gas undergo random motion colliding with each other and the walls of the container
* Laws of classical mechanics are applicable on the molecules.


## 4. STATE OF A GAS AND STATE VARIABLES

"State" of a gas means the physical condition of the system. Certain variables are used to represent physical condition of the gas which are termed as state variables.

There are majorly three variables for a given sample of a gas, i.e. Pressure, Volume and Temperature ( $\mathbf{P}, \mathbf{V}$ and T). When the values of these three parameters are fixed for a gas, we say it to be in a fixed state.

### 4.1 Pressure

A force is exerted on the walls of the container due to the collisions of the atoms/molecules. This force averaged per unit area is called the pressure.

### 4.1.1 Measurement of pressure of a gas

The most common instrument used to measure the pressure of a gas is called a barometer. Another instrument used to measure pressure is manometer.

### 4.2 Volume

In case of rigid containers, the volume of the gas is same as the volume of the container it is kept in. However, for containers which can expand (e.g. balloon), the volume of the gas is determined by the other two state functions and moles of the gas taken.

### 4.3 Temperature

Temperature is a measure of the amount of heat contained in the gas. When the temperature of the gas equals the surrounding temperature, no heat flows in or out of the gas and the gas is said to be in a state of Thermal Equilibrium.

### 4.3.1 Measurement of Temperature

The instrument used to measure the temperature of a gas is called a thermometer. There are three units used in measuring temperature viz. ${ }^{\circ} \mathrm{C},{ }^{\circ} \mathrm{F}$ and K .

| Pressure relations | Temperature relations | Volume relations |
| :--- | :---: | :---: |
| $1 \mathrm{~atm}=1.0132 \times 10^{5} \mathrm{~Pa}$ | $1.8 \mathrm{~T}\left({ }^{\circ} \mathrm{C}\right)=\mathrm{T}\left({ }^{\circ} \mathrm{F}\right)-32$ | $1 \mathrm{~L}=1000 \mathrm{~mL}$ |
| $1 \mathrm{bar}=10^{5} \mathrm{~Pa}$ | $\mathrm{~T}(\mathrm{~K})=\mathrm{T}\left({ }^{\circ} \mathrm{C}\right)+273.15$ | $1 \mathrm{~m}^{3}=1000 \mathrm{~L}$ |
| $76 \mathrm{~cm} \mathrm{Hg}=1 \mathrm{~atm}=760 \mathrm{mmHg}$ |  | $1 \mathrm{~mL}=1 \mathrm{cc}$ |
| $1 \mathrm{torr}=1 \mathrm{~mm} \mathrm{Hg}$ |  | $1 \mathrm{dm}^{3}=1 \mathrm{~L}$ |
| $1 \mathrm{kPa}=1000 \mathrm{~Pa}$ |  |  |

## 5. IDEAL GAS LAW

There are four laws which relate the state variables of a gas in two states. These four laws are :

### 5.1 Boyle's Law (Pressure - Volume Relationship)

It states that at constant temperature, the pressure of a fixed amount (i.e. number of moles $n$ ) of gas varies inversely with its volume. This is known as Boyle's law Mathematically
$\mathrm{p} \propto \frac{1}{\mathrm{~V}}($ at constant T and n$)$
$\mathrm{PV}=$ constant
$\Rightarrow \mathrm{p}_{1} \mathrm{~V}_{1}=\mathrm{p}_{2} \mathrm{~V}_{2}$


Graph of pressure, p vs. Volume, $V$ of a gas at different temperature

Each curve corresponds to a different constant temperature and is known as an isotherm.

### 5.2 Charles's Law (Temperature - Volume Relationship)

It states the pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.


Each line of the volume vs temperature graph is called isobar.

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

It states that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature. Mathematically,
$p \propto T$
$\Rightarrow \frac{\mathrm{P}}{\mathrm{T}}=$ constant
Each line of pressure is temperature graph is called isochore.


### 5.4 Avogadro Law (Volume - Amount Relationship)

It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.
Mathematically
$\mathrm{V} \propto \mathrm{n}$ where n is the number of moles of the gas.

## 6. IDEAL GAS EQUATION

The above laws can be combined together in a single equation which is known as ideal gas equation.

At constant $T$ and $n ; V \propto \underset{\mathrm{p}}{ }$ Boyle's Law
At constant p and $\mathrm{n} ; \mathrm{V} \propto \mathrm{T}$ Charles's Law
At constant p and $\mathrm{T} ; \mathrm{V} \propto \mathrm{n}$ Avogadro Law
Thus,

$$
\begin{aligned}
& \mathrm{V} \propto \frac{\mathrm{nT}}{\mathrm{p}} \\
\Rightarrow \quad \mathrm{~V} & =\mathrm{R} \frac{\mathrm{nT}}{\mathrm{p}}
\end{aligned}
$$

where R is proportionality constant. On rearranging the equation we obtain
$\mathrm{pV}=\mathrm{n} \mathrm{RT}$
This equation is called ideal gas equation.

$$
\Rightarrow \mathrm{R}=\frac{\mathrm{pV}}{\mathrm{nT}}
$$

R is called gas constant. It is same for all gases. Therefore it is also called universal gas constant.
Values of R :
(i) $\mathrm{R}=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$, (ii) $\mathrm{R}=0.0821 \mathrm{~L} \mathrm{~atm} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$.
(iii) $\mathrm{R}=2 \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$.

If temperature, volume and pressure of a fixed amount of gas vary from $T_{1}, V_{1}$ and $p_{1}$ to $T_{2}, V_{2}$ and $p_{2}$ then we can write

$$
\begin{aligned}
& \frac{\mathrm{p}_{1} \mathrm{~V}_{1}}{\mathrm{~T}_{1}}=\mathrm{nR} \text { and } \frac{\mathrm{p}_{2} \mathrm{~V}_{2}}{\mathrm{~T}_{2}}=\mathrm{nR} \\
\Rightarrow & \frac{\mathrm{p}_{1} \mathrm{~V}_{1}}{\mathrm{~T}}=\frac{\mathrm{p}_{2} \mathrm{~V}_{2}}{\mathrm{~T}_{2}}
\end{aligned}
$$

This equation is alos known as combined gas law.

## 7. VARIATION OF THE IDEAL GAS EQUATION

Ideal gas equation can be rearranged as follows :
$\frac{\mathrm{n}}{\mathrm{V}}=\frac{\mathrm{p}}{\mathrm{RT}}$

Replacing n by $\frac{\mathrm{m}}{\mathrm{M}}$, we get
$\frac{m}{M V}=\frac{p}{R T}$
$\frac{\mathrm{d}}{\mathrm{M}}=\frac{\mathrm{p}}{\mathrm{RT}}$ (where d is the density)
$\Rightarrow \mathrm{pM}=\mathrm{dRT}$

## 8. DALTON'S LAW OF PARTIAL PRESSURES

It states that the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases i.e., the pressures which these gases would exert if they were enclosed separately in the same volume and under the same conditions of temperature. In a mixture of gases, the pressure exerted by the individual gas is called partial pressure. Mathematically,
$\mathrm{p}_{\text {Total }}=\mathrm{p}_{1}+\mathrm{p}_{2}+\mathrm{p}_{3}+\ldots . .($ at constant $\mathrm{T}, \mathrm{V})$
where $p_{\text {Total }}$ is the total pressure exerted by the mixture of gases and $p_{1}, p_{2}, p_{3}$ etc. are partial pressures of gases.

## Partial pressure in terms of mole fraction

Suppose at the temperature T, three gases, enclosed in the volume $V$, exert partial pressure $p_{1}, p_{2}$ and $p_{3}$ respectively. then,

$$
\begin{aligned}
& \mathrm{p}=\frac{\mathrm{n}_{1} \mathrm{RT}}{\mathrm{~V}} \\
& \mathrm{p}_{2}=\frac{\mathrm{n}_{2} \mathrm{RT}}{\mathrm{~V}} \\
& \mathrm{p}_{3}=\frac{\mathrm{n}_{3} \mathrm{RT}}{\mathrm{~V}}
\end{aligned}
$$

where $n_{1} n_{2}$ and $n_{3}$ are number of moles of these gases. Thus expression for total pressure will be
$\mathrm{p}_{\text {Total }}=\mathrm{p}_{1}+\mathrm{p}_{2}+\mathrm{p}_{3}$
$=\mathrm{n} \frac{\mathrm{RT}}{\mathrm{V}}+\mathrm{n}_{2} \frac{\mathrm{RT}}{\mathrm{V}}+\mathrm{n}_{3} \frac{\mathrm{RT}}{\mathrm{V}}$
$=\left(n_{1}+n_{2}+n_{3}\right) \frac{R T}{V}$
On dividing $\mathrm{p}_{1}$ by $\mathrm{p}_{\text {total }}$ we get
$\frac{\mathrm{p}_{1}}{\mathrm{p}_{\text {total }}}=\left(\frac{\mathrm{n}_{1}}{\mathrm{n}_{1}+\mathrm{n}_{2}+\mathrm{n}_{3}}\right) \frac{\text { RTV }}{\text { RTV }}$
$=\frac{\mathrm{n}_{1}}{\mathrm{n}_{1}+\mathrm{n}_{2}+\mathrm{n}_{3}}=\frac{\mathrm{n}_{1}}{\mathrm{n}}=\mathrm{x}_{1}$
where $\mathrm{n}^{=} \mathrm{n}_{1}+\mathrm{n}_{2}+\mathrm{n}_{3}$
$x_{1}$ is called mole fraction of first gas.
Thus, $\mathrm{p}_{1}=\mathrm{x}_{1} \mathrm{p}_{\text {total }}$
Similarly for other two gases we can write
$\mathrm{p}_{2}=\mathrm{x}_{2} \mathrm{p}_{\text {total }}$ and $\mathrm{p}_{3}=\mathrm{x}_{3} \mathrm{p}_{\text {total }}$
Thus a general equation can be written as
$\mathrm{p}_{\mathrm{i}}=\mathrm{x}_{\mathrm{i}} \mathrm{p}_{\text {total }}$

## 9. GRAHAM'S LAW OF DIFFUSION

Diffusion is a process of intermixing of gases. This is a natural tendency of any gas to occupy the whole volume available to it. So even without pressure difference gases mix with each other. If the pressure difference is increased the diffusion process becomes faster.
Effusion is flow of a gas through small openings due to pressure difference that is it is a case of fast diffusion.

(a) Diffusion is mixing of gas molecules by random motion under conditions where molecular collisions occur.
(b) Effusion is the escape of a gas through a pinhole without molecular collisions.
According to Graham's Law the rate of diffusion depends on pressure and molecular weight of a gas. Rate of Diffusion is directly proportional to Partial Pressure of the gas and inversely proportional to the square root of molar mass of the gas. That is, greater the pressure faster is the movement of molecules and heavier the molecules, slower are their movement.

## Rate of diffusion $\propto \mathbf{P}$ (partial pressure)

$$
\text { Also, } \propto 1 / \sqrt{M}
$$

Therefore we can write:

$$
\text { Rate, } \mathbf{r} \propto \mathbf{P} / \sqrt{\mathbf{M}}
$$

Rate of diffusion may be defined in various ways. It may be number of moles transferred per unit time, Volume transferred per unit time, distance travelled per unit time and even pressure drop per unit time. While comparing the rates of two gases, we should take similar definitions of rate, it may be $\mathrm{n} / \mathrm{t}$, $\mathrm{V} / \mathrm{t}$ or $\mathrm{d} / \mathrm{t}$.

$$
\frac{r_{2}}{r_{1}}=\frac{P_{2}}{P_{1}} \sqrt{\frac{M_{1}}{M_{2}}}
$$

Graham's Law can be applied to diffusion and effusion both.

## 10. KINETIC THEORY OF GASES

Assumptions or postulates of the kinetic-molecular theory of gases are given below. These postulates are related to atoms and molecules which cannot be seen, hence it is said to provide a microscopic model of gases.
(i) Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the actual volume of the molecules is negligible in comparison to the empty space between them.
(ii) There is no force of attraction between the particles of a gas at ordinary temperature and pressure.
(iii) Particles of a gas are always in constant and random motion.
(iv) Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.
(v) Collisons of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same.
(vi) At any particular time, different particles in the gas have different speeds and hence different kinetic energies.
It is possible to show that though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature.

If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances, we can talk only about average kinetic energy. In kinetic theory it is assumed that average kinetic energy of the gas molecules is directly proportional to the absolute temperature.
The important mathematical results from this Theory are ;
K.E. per mole $=3 / 2 \mathrm{nRT}$
K.E. per molecule $=3 / 2 \mathrm{kT}$
where $\mathrm{R}=8.314$ and $\mathrm{k}=\mathrm{R} / \mathrm{N}_{\mathrm{A}}=1.38 \times 10^{-23} \mathrm{~J} / \mathrm{K}$

## 11. Molecular Distribution of speeds

## (Max well Boltzmann Distribution)

The Maxwell Boltzmann Distribution is a plot of fraction of molecules in the gas sample vs. the speed of the gas molecules. The distribution is shown below followed by the salient features of the graph.


The graph shows that :

* The fraction of molecules having very low or very high speeds is very less.
* Most of the molecules have a speed somewhere in the middle, this is called the most probable speed. $\left(\mu_{\mathrm{MP}}\right)$
* The area covered between any two velocities is the number of molecules in that velocity range.
* The total area covered by the graph gives the total number of molecules in the sample and is constant.
* There are two more molecular speeds defined for a sample called average speed $\left(\mathrm{u}_{\mathrm{AVG}}\right)$ and root mean square speed ( $\mathrm{u}_{\mathrm{RMS}}$ )
$\mathrm{u}_{\mathrm{RMS}}=\sqrt{\frac{3 R T}{\mathrm{M}}} \quad \mathrm{u}_{\mathrm{MP}}=\sqrt{\frac{2 \mathrm{RT}}{\mathrm{M}}} \quad \mathrm{u}_{\mathrm{AVG}}=\sqrt{\frac{8 \mathrm{RT}}{\pi \mathrm{M}}}$
NB: Always remember to take molecular mass in kg in the above relations.

It's useful to remember the ratio of $u_{M P}: u_{A V G}: u_{\text {RMS }}$ 1:1.128:1.224 for a given gas at the same temperature.

## 12. REAL GASES

In case of real gases two of assumption taken for ideal gases become invalid or restricted only to some particular conditions.
(i) We assumed that there are no interactions between molecules of an ideal gas.
(ii) We assumed that volume of the molecules of a gas is negligible as compare to entire volume of gases.
In case of real gases, we cannot ignore the molecular interactions any more.

There are two types of forces of interaction :

## Long Ranged attractive forces. \&

## Short Ranged repulsive forces.

When the molecules of a real gas are far apart, the interactive forces are negligible. When the molecules are brought closer to each other attractive forces start to develop and when the molecules are too close they start repelling each other. The following curve represents the variation of potential energy of a system of two molecules of a real gas with distance between them.


## 13. COMPRESSIBILITY FACTOR

The deviation from ideal behaviour can be measured in terms of compressibility factor $(Z)$.
$\mathrm{Z}=\mathrm{V}_{\mathrm{m}}($ real $) / \mathrm{V}_{\mathrm{m}}$ (ideal)

* At very low pressures, there are no interactions between the molecules of the real gas and $\mathrm{Z}=1$.
* At low or moderate pressure, there are attractive forces dominant due to which a real gas is compressed to a greater volume than expected, therefore $\mathrm{Z}<1$.
* At high pressures, repulsions dominate and it is tough to compress the real gas so it is compressed to smaller volume
than expected thus $\mathrm{Z}>1$.
Z is always 1 for ideal gases.
For real gases $\mathrm{Z}=\mathrm{PV} / \mathrm{nRT}$.


### 13.1 Variation of $Z$ with $P$ and $T$

The graph of compressibility factor, Z, with pressure for an ideal gas is a straight line. However, for real gases the value of Z is $<1$ for low pressures and then Z becomes $>1$ as pressure increases and keeps on increasing. On increasing the temperature the graph tends more towards $\mathrm{Z}=1$ i.e. ideal gas.


It can be concluded from the above graphs that real gas follows ideal behavior at low pressure and high temperature. This does not mean that if you keep on increasing the temperature a real gas will convert to ideal gas. There is a characteristic temperature at which a gas follows ideal behavior most closely; this is called Boyle's temperature.

## 14. VANDERWALL'S EQUATION

This equation was formulated taking into account correction factors for pressure and volume into the ideal gas equation.

$$
\left(\mathrm{P}+\mathrm{an}^{2} / \mathrm{V}^{2}\right)(\mathrm{V}-\mathrm{nb})=\mathrm{nRT}
$$

Constants a and b are called vander waals constants and their value depends on the characteristic of a gas.

## Note:

(i) Unit of $a \equiv \frac{\mathrm{~L}^{2} \mathrm{~atm}}{\mathrm{~mol}^{2}} ; b \equiv \frac{\mathrm{~L}}{\mathrm{~mol}}$
(ii) $\mathrm{a} \equiv$ Relates to the forces interacting between the gas molecules and modifies the pressure term.
(' $a$ ' is high if the gas molecules have more attractive forces)
(iii) $\mathrm{b} \equiv$ Relates to the volume occupied by the gas molecules and takes into account the fact that the space actually occupied by the molecules themselves is unavailable for the molecules to move in and is given by :
$\mathrm{b}=4 \times$ volume of 1 mol of gas molecules.
(iv) For a given gas Van der Waal's constant ' $a$ ' is always greater than ' $b$ '.
(v) The gas having higher values of ' $a$ ' can be liquefied easily.

### 14.1 Applicability of Vanderwaal's Equation

Under the conditions of high temperature and low/moderate pressure and also under very low pressure $\mathrm{Z}=1$ and the above equation becomes $\mathrm{PV}_{\mathrm{m}}=\mathrm{RT}$.

### 14.2 At low/moderate Pressure

The volume correction factor can be ignored and $\mathrm{Z}<1$ where the attractive forces dominate. The equation becomes:
$\mathrm{Z}=\left(1-\frac{\mathrm{a}}{\mathrm{V}_{\mathrm{m}} \mathrm{RT}}\right)$

### 14.3 At high Pressure

The volume correction factor cannot be ignored but the pressure correction factor can be ignored. $\mathrm{Z}>1$ and the equation is:
$\mathrm{P}\left(\mathrm{V}_{\mathrm{m}}-\mathrm{b}\right)=\mathrm{RT}$
$\Rightarrow \mathrm{Z}=\left(1+\frac{\mathrm{Pb}}{\mathrm{RT}}\right)$

## 15. LIQUEFICATION OF GASES

When the molecules of a gas are brought closer to each other, due to increase in the attractive forces, a stage may be reached when the gas changes its phase to liquid. This phenomenon is called Liquefaction of gases.

### 15.1 Critical Temperature, $\mathrm{T}_{\mathrm{C}}$

The characteristic temperature of a real gas above which it cannot be liquefied.
$\mathrm{T}_{\mathrm{C}}=8 \mathrm{a} / 27 \mathrm{Rb}$

### 15.2 Critical Pressure, $P_{C}$

It is the minimum pressure required for liquefaction to take place at critical temperature
$\mathbf{P}_{\mathrm{C}}=\mathbf{a} / \mathbf{2 7} \mathbf{b}^{2}$

### 15.3 Critical Volume, $\mathrm{V}_{\mathrm{c}}$

It is the volume occupied by one mole of a gas under critical temperature and pressure.
$\mathbf{V}_{\mathrm{C}}=\mathbf{3 b}$
NB: The compressibility factor at critical point is constant for all gases and has a value of 0.375 .

For liquefication of real gases, we can do either of the following:
(1) Increase the pressure on the gas
(2) Decrease the temperature of gas but temperature is the dominant factor and pressure assumes a secondary role.

## 16. LIQUID STATE

Intermolecular forces are stronger in liquid state than in gaseous state.

1. Properties of liquids : Molecules in liquids are so close that there is very little empty space between them and under normal conditions liquids are denser than gases.
2. Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other.
3. Molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored.
4. Vapour pressure of a liquid at any temperature may be defined as the pressure exerted by the vapour present above the liquid in equilibrium with the liquid at that temperature.

## Factors affecting vapour pressure

Two important factors on which the vapour pressure of a liquids depends are :
(a) Nature of the liquid : If the intermolecular forces of attraction in the liquid are weak, the molecules can easily leave the liquid and come into the vapour phase and hence the vapour pressure is higher.
(b) Effect of temperature : As the temperature of a liquid is increased, the vapour pressure of the liquid increases.

Boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid becomes equal to the external pressure (i.e., the atmospheric pressure).
When the external pressure is normal atmospheric pressure (i.e., 760 mm ), the boiling point is called the normal boiling point.

When the external pressure is equal to 1 bar, the boiling point is called standard boiling point of the liquid.

## Some Applications of Effect of External Pressure on Boiling point.

(i) Obviously, if the external pressure is higher, more heat will be required to make the vapour pressure equal to the external pressure and hence higher will be the boiling point. That is why in hospitals, surgical instrumnts are sterilized in autoclaves in which boiling point of water is raised by using a weight to cover the vent.
(ii) Similarly, if the external pressure is decreased, the boiling point is lowered. This is the reason that a liquid boils at a lower temperature on the top of a mountain (where pressure is low) than on the sea shore. That is why at hills, use of pressure cooker is essential for cooking food.
5. Surface tension is a characteristic property of liquids which arises due to the fact that the molecules of the liquid at the surface are in different situation than those in the interior of the liquid.

Surface tension of a liquid is defined as the force acting at right angles to the surface along one centimetre length of the surface. Thus, the units of surface tension are dynes per cm (or Newtons per metre, i.e., $\mathrm{N} \mathrm{m}^{-1}$ in the S.I. system.

## Some important Results

(i) Spherical shape of drops the lowest energy state of a liquid will be when the surface area is minimum. Surface tension tries to decrease the surface area of the liquid to the minimum. The drops of a liquid (or the bubbles of a gas) are spherical because for a given volume, a sphere has minimum surface area.
(ii) Fire polishing of glass. Sharp glass edges are heated to make them smooth. This is because on heating, the glass melts and takes up rounded shape at the edges which has minimum surface area.
(iii) Rise of a liquid in a capillary tube. This rise is obviously due to the inward pull of surface tension acting on the surface which pushes the liquid into the capillary tube.
(iv) Effect of nature of the liquid on surface tension. Surface tension is a property that arises due to the intermolecular forces of attraction among the molecules of the liquid. Greater are the intermolecular forces of attraction, higher is the surface tension of that liquid.
(v) Effect of temperature on surface tension. The surface tension of liquids generally decreases with increase of temperature and becomes zero at the critical temperature (where the meniscus between the liquid and the vapour disappears). The decrease in surface tension with increase of temperature is obviously due to the fact that with increase of temperature, the kinetic energy of the molecules (and hence the speeds of molecules) increases and, therefore, the intermolecular attraction decreases.
6. Viscosity is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows.
The type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow.
If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount $\frac{\mathrm{du}}{\mathrm{dz}}$.
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.
$\mathrm{F} \propto \mathrm{A}(\mathrm{A}$ is the area of contact)
$\mathrm{F} \propto \frac{\mathrm{du}}{\mathrm{dz}}$ (where, $\frac{\mathrm{du}}{\mathrm{dz}}$ is velocity gradient; the change in velocity with distance)
$\mathrm{F} \propto \mathrm{A} . \frac{\mathrm{du}}{\mathrm{dz}}$
$\Rightarrow \mathrm{F} \propto \eta \mathrm{A} \frac{\mathrm{du}}{\mathrm{dz}}$
' $\eta$ ' is proportional constant and is called coefficient of viscosity. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus ' $\eta$ ' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre $\left(\mathrm{N} \mathrm{s} \mathrm{m}^{-2}\right)=$ pascal second ( $\mathrm{Pa} \mathrm{s}=1 \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$ ). In cgs system the unit of coefficient of viscosity is poise.
1 poise $=1 \mathrm{~g} \mathrm{~cm}^{-1} \mathrm{~s}^{-1}=10^{-1} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$

* Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid.
* Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

17. MEASUREMENT OF PRESSURE OF A GAS

The pressure of a gas can be measured by various methods. Mostly it is measured in terms of heights of liquid column. We know that a liquid exerts pressure on the bottom of a container or a tube due to gravity.
Suppose there is a liquid of density $\rho$ filled in a tube (cross sectional area A) up to a height h and there is vacuum above it.
Then :
Volume of the liquid $=\mathbf{A} \times \mathbf{h}$
Mass of the liquid $=\boldsymbol{\rho} \times \mathbf{A} \times \mathbf{h}$
Force applied at the bottom $=$ weight of the liquid
$=\boldsymbol{\rho} \times \mathbf{g} \times \mathbf{A} \times \mathbf{h}$
Pressure $=\mathbf{F} / \mathbf{A}=\boldsymbol{\rho g h}$
If a tube filled with a liquid is kept at an angle $\theta$ then only the vertical component of weight is taken.
Pressure $=\rho \mathrm{gh} \times \sin \theta$
A common arrangement to measure pressure of a gas is called "Barometer" as shown in the figure.
A mercury barometer is used to measure atmospheric pressure by determining the height of a mercurry column supported in a sealed glass tube.


## TABLE FOR FORMULAE USED IN THE CHAPTER

*. For a U tube manometer; $\Delta \mathrm{h}=\frac{\mathrm{P}_{1}-\mathrm{P}_{2}}{\rho \mathrm{~g}}$

* Boyle's Law : $\mathrm{PV}=$ constant $\Rightarrow \mathrm{P}_{1} \mathrm{~V}_{1}=\mathrm{P}_{2} \mathrm{~V}_{2}$
* $\quad$ Charles' Law : $V / T=$ constant $\Rightarrow V_{1} / T_{1}=V_{2} / T_{2}$
* Gay Lussac's Law : $\mathrm{P} / \mathrm{T}=$ constant $\Rightarrow \mathrm{P}_{1} / \mathrm{T}_{1}=\mathrm{P}_{2} / \mathrm{T}_{2}$
* Avogadro's Law : V $\propto \mathrm{n}$
* Ideal Gas Equation : $\mathrm{PV}=\mathrm{nRT}$
* Variation of ideal gas equation: $\mathrm{PM}=\rho \mathrm{RT}$
* Dalton's Law of Partial Pressure : Pressure due a gas in a gas mixture $\mathrm{P}_{\mathrm{A}}=\mathrm{X}_{\mathrm{A}} \mathrm{P}_{\text {Total }}$
* Graham's Law of diffusion :
rate of diffusion $\propto$ Pressure $/ \sqrt{ }$
* $\quad u_{R M S}=\sqrt{\frac{3 R T}{}} \quad u_{M P}=\sqrt{\frac{2 R T}{}}$
$\mathrm{u}_{\mathrm{AVG}}=\sqrt{\frac{8 \mathrm{RT}}{\pi \mathrm{M}}}$
\& $\quad u_{M P}: u_{A V G}: u_{R M S}=1: 1.128: 1.224$
- Compressibility Factor, $Z=V_{\text {real }} / V_{\text {ideal }}$
* Vander waal's Equation :
$\left(\mathbf{P}+\mathbf{a n}^{2} / \mathbf{V}^{2}\right)(V-n b)=n R T$
* Vanderwaal's constant or co-volume:
$\mathrm{b}=4 \times\left(4 / 3 \pi \mathrm{r}^{3}\right) \mathrm{N}_{\mathrm{A}}$
* At low/moderate pressure $\left(\mathrm{P}+\mathrm{an}^{2} / \mathrm{V}^{2}\right) \mathrm{V}=\mathrm{nRT}$
and $\mathbf{Z}=\mathbf{P V} / \mathbf{n R T}=\mathbf{1}-\frac{\text { an }}{\text { VRT }}$
* At high pressure: $\mathrm{P}(\mathrm{V}-\mathrm{nb})=\mathrm{nRT}$ and
$\mathbf{Z}=(\mathbf{1}+\mathbf{P b} / \mathbf{R T})$
* At very low pressure or at high temperature and moderate/low pressure: $\mathrm{Z}=1$ and $\mathrm{PV}=\mathrm{nRT}$
* Critical Temperature : $\mathrm{T}_{\mathrm{c}}=8 \mathrm{a} / 27 \mathrm{Rb}$

Critical Pressure: $\mathbf{P}_{\mathrm{C}}=\mathbf{a} / 2 \mathbf{7 b}^{\mathbf{2}}$

* Critical Volume: $\mathrm{V}_{\mathrm{C}}=3 \mathrm{~b}$

