Unit - 5

STATES OF MATTER

Atoms and molecules constitute most of the matter that is around us. Every molecule or an atom exerts a force of attraction or repulsion on the other constituent. This force is known as the Intermolecular Force.

- These forces are responsible for holding together a substance.
- Intermolecular forces are of two types:
  1) Attractive forces
  2) Repulsive forces

- The attractive intermolecular forces are also called van der waals force which in honour of a Dutch scientist Johannes van der waals. Using these forces van der waals describs the deviation of a real gas fron the ideal gas law. The attraction is mainly a result of the electrostatic forces.

- We have many types of Intermolecular forces :

1) <u>London forces or Dispersion forces</u>.

first demonstrated by Fritz London, these forces are the weakest amongst the other van der waals forces.

The following example will clearly describe the dispersion forces:

Atom A

Atom B

Atom A with instaneous dipole, more electron density on the right hand side.

Atom B with induced dipole

Atom 'A' more electron density on the left hand side

Atom 'B' with induced dipole

- The above figure illustrates the london forces between two atoms close to each other. When moving randomly in an atom, the electrons may get collected at a point hence making that part electrically denser than the other. This unsymmetric placement of electrons leads to the development of an instantaneous dipole for a very short interval in atom A.

- Now, this temporary dipole disturbs the electron density of the closeby atom B, hence resulting in an induction of dipole in atom B as well.

- This temporarily formed dipole between the two atoms is gradually induced in other molecules as well. A force of attraction is thus present that binds the atoms A and B for a small time.

- The London forces are always attractive in nature and the interaction energy of the atoms here is inversely proportional to the 6^{th} power of the distance between two atoms.

2) Dipole - Dipole Forces

- The molecules possessing permanent dipole show the dipole- dipole type of force. The end of the dipoles in an atom generally possess a small 'partial charge'.

- In the dipole-dipole forces, the interaction takes place between two neighbouring atoms or molecules that have a permanent dipole moment.

- since the dipole attraction is between two atoms in close vicinity to each other the force of attraction decreases with the increasing distance.

- The dipole - dipole forces varies with movement. For the stationary molecules, the dipole- dipole interaction energy is inversely proportional to the third power of r ($1/r^3$) while for molecules showing movement in the form of rotation the interaction energy is $1/r^6$.

Where r is the distance between polar molecule.

3) Dipole - Induced Dipole Forces

- These forces come into being between the molecules having a permanent dipole moment and the neutral molecules. In other words, a molecule with permanent dipole polarizes the other molecule which has less or no dipole at all. The polar molecule with a permanent dipole instigates dipole in an electrically neutral molecule by deforming the electronic cloud of that atom. This results in induction of dipole in the other molecule.

- Like london forces, the interaction energy is proportional to $1/r^6$; where r is the distance between two molecules.

- Induced dipole moment depends on the dipole moment present in a permanent dipole particle and the polarizability of the other electrically neutral molecule.

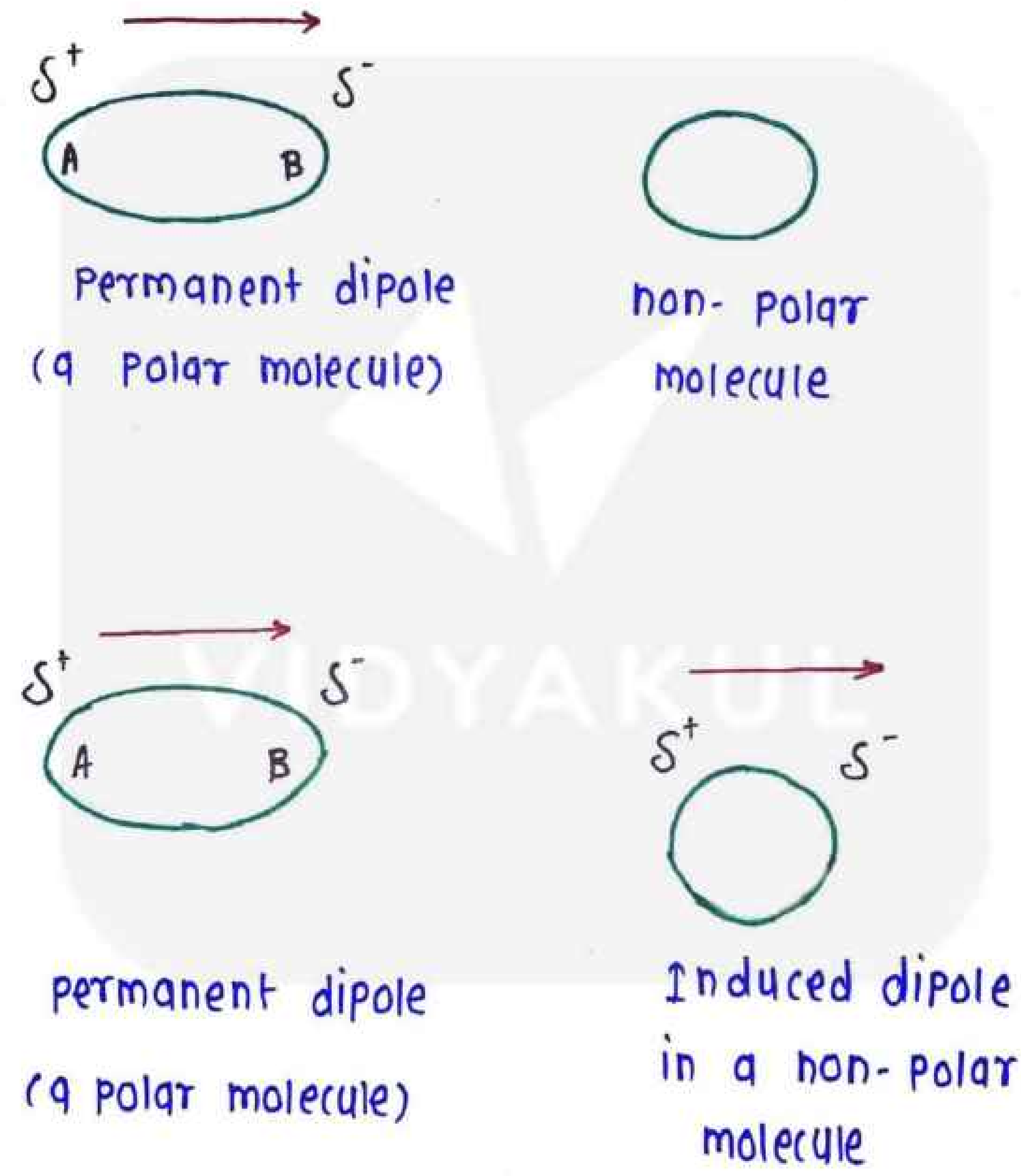


Fig: Dipole - induced dipole interaction between permanend and induced dipole.

4) Hydrogen bond

- Hydrogen bonds are the bonds associated with Hydrogen and a more electronegative aton like oxygen. This bond signifies special case of any dipole-dipole interaction and is found in molecules where N-H, O-H or H-F bonds are found.

- When hydrogen is bonded to a more electronegative atom, a positive charge is set up on it. As a result, the other atom gets a negative charge.

- When the Hydrogen of one atom comes closer to the oxygen of another atom, they strongly attract each other. Therefore a kind of 'bond' is formed which we call the Hydrogen bond.

- Generally, Hydrogen forms a bond with N (Nitrogen), O (oxygen), and F (Fluorine). It also bonds with Cl (chlorine) to form a Hydrogen bond.

- Hydrogen bonds have an extremely high energy, making these bonds a powerful force, approximately 10 to 100 kJ mol^{-1}. This bond plays an eminent role in many compounds, proteins and nucleic acid, because of their force.

- The Intermolecular Forces discussed above are forces of attraction. Molecules also experience a force of repulsion between them. These are the repulsive forces and come into play when two mole-cules come close to each other.

THERMAL ENERGY

Thermal energy is the energy of a body arising from motion of its atoms or molecules. It is directly proportional to the temperature of the substance.

- It is the measure of average kinetic energy of the particles of the matter and is thus responsible for movement of particles.

- This movement of particle is called Thermal motion.

Intermolecular Forces vs Thermal Interactions.

Intermolecular forces tends to keep the

molecule together but thermal energy of the molecules tends to keep them apart

- Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.

Gas ⟶ Liquid ⟶ solid

predominance of intermolecular interactions.

Gas ⟵ Liquid ⟵ solid

predominance of thermal energy

The Gaseous State

Out of all states of matter, the gaseous state is considered one of the simplest. A slight increase in the physical condition of temperature or pressure can be easily observed.

- In the periodic table there are only eleven elements exists as gases under normal conditions.

Group No.	1	15	16	17	18
	H				He
		N	O	F	Ne
				Cl	Ar
					Kr
					Xe
					Rn

The gaseous state is characterized by the following physical properties.

- Gases are highly compressible
- Gases exert pressure equally in all directions
- Gases have lower density than the solids and liquids
- The volume and the shape of gases are not fixed. These assume volume and shape of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.

simplicity of gases is due to the fact that the forces of interaction between their molecules are neglibible.

The Gas Laws

All gases generally shows similar behaviour when the conditions are normal. But with a slight change in a physical conditions like pressure, temperature or volume, these show a deviation. Hence gas laws are relation between these variables.

Boyle's Law

Boyle's law states the relation between volume and pressure at constant tempe-rature and mass.

- Robert Boyle conducted an experiment on gases to study the deviation of its behaviour in changed Physical conditions.

- It states that under a constant temp-erature when the pressure on a gas increases, its volume decreases.

- According to Boyle's Law, volume is inversely proportional to pressure when the temperature and the number of molecules are constant.

$$P \propto \frac{1}{V}$$

$$P = k_1 \frac{1}{V}$$

K_1 here is a proportionality constant, V is the volume and P is the pressure.

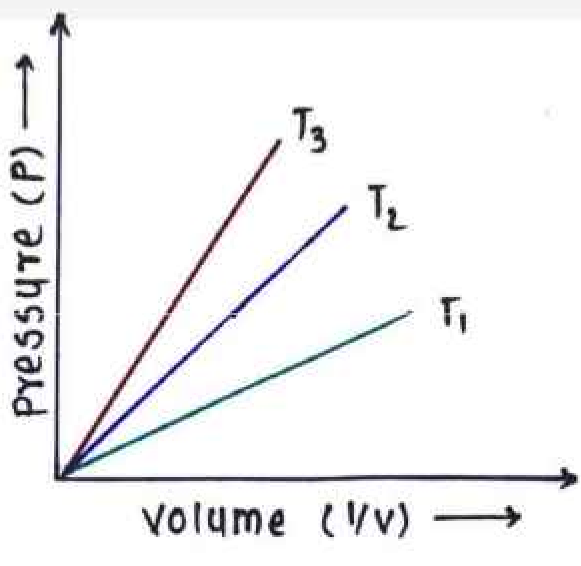
- Now, if a fixed mass of gas undergoes an expansion at constant temperature then the final volume and pressure shall be P_2 and V_2. The initial volume and initial pressure here is P_1 and V_1, then according to Boyle's law

$$P_1 V_1 = P_2 V_2 = \text{constant } (K_1)$$

$$\frac{P_1}{P_2} = \frac{V_2}{V_1}$$

- So, according to Boyle's law, if the pressure is doubled then at constant temperature the volume of that gas is reduced to half. The reason being the intermolecular force between the molecules of the gaseous substance.

- In a free state, a gaseous substance occupies a larger volume of the container due to the scattered molecules. When a pressure is applied to the gaseous substance, these molecules come closer and occupy a lesser volume.



$\therefore T_3 > T_2 > T_1$

Charle's law

- Jacques Charles in 1787 analyzed the effect of temperature on the volume of a gaseous substance at a constant pressure. He did this analysis to understand the technology behind the hot air balloon flight.

- According to his findings, at constant pressure and for constant mass, the volume of a gas is directly proportional to the temperature.

- This means that with the increase in temperature the volume shall increase while with decreasing temperature the volume decreases.

- In his experiment, he calculated that the increase in volume with every degree equals 1/273.15 times of the original volume. Therefore the volume is V_0 at $0°C$ and V_t is the volume at $t°C$ then,

$$V_t = V_0 + \frac{t}{273.15} V_0$$

$$V_t = V_0 \left(1 + \frac{t}{273.15}\right)$$

$$V_t = V_0 \left(\frac{273.15 + t}{273.15}\right)$$

For the purpose of measuring the observations of gaseous substance at temperature 273.15 K, we use a special scale called the kelvin Temperature scale. The observation of temperature (T) on this scale is 273.15 greater than the temperature (t) of the normal scale.

$$T = 273.15 + t$$

While, when $T = 0°c$ then the reading on the celsius scale is 273.15. The kelvin scale is called Absolute Temperature scale or Thermodynamic scale. In the equation $[V_t = V_0 (273.15 + t/273.15)]$ if we take the values $T_t = 273.15 + t$ and $T_0 = 273.15$ then:

$$V_t = V_0 (V_t / T_0)$$

which implies $V_t / V_0 = (T_t / T_0)$, which can also be written as :

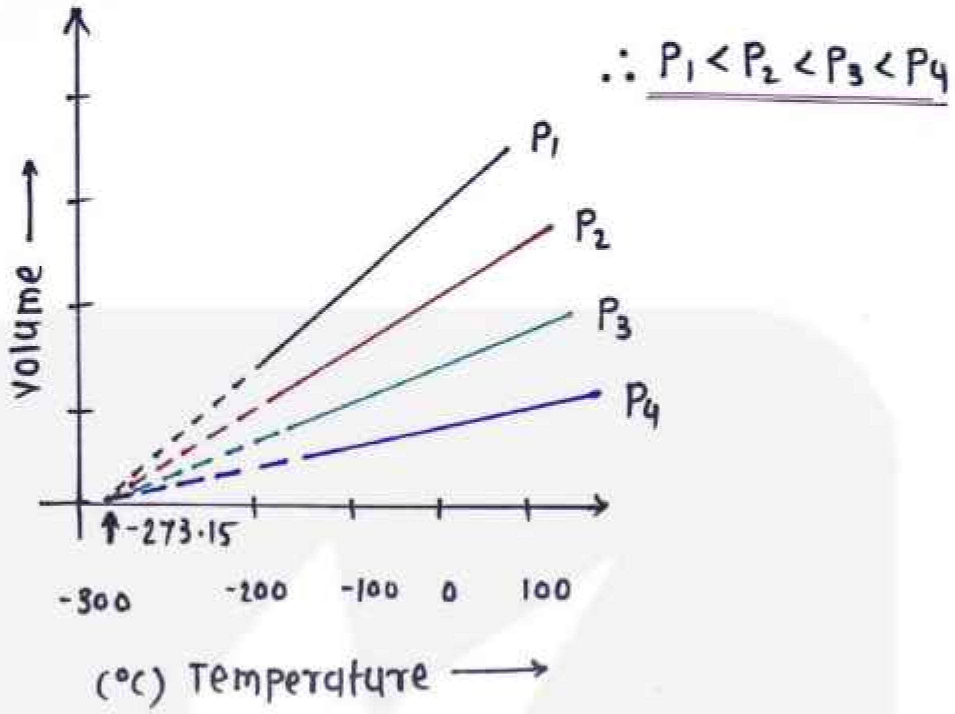
$$V_2 / V_1 = T_2 / T_1$$

$$\text{or} \quad V_1 / T_1 = V_2 / T_2$$

$$\frac{V}{T} = \text{constant} = k_2$$

$$\text{Thus} \quad V = k_2 T$$

- The graphical represantation of charles law is shown in Figure. Its an isobar graph as the pressure is constant with volume and the temperature changes under observa -tion.



Gay - Lussac's Law

Also referred to as pressure - Temperature law, Gay Lussac's law was discovered in 1802 by a French scientist Joseph Louis Gay Lussac.

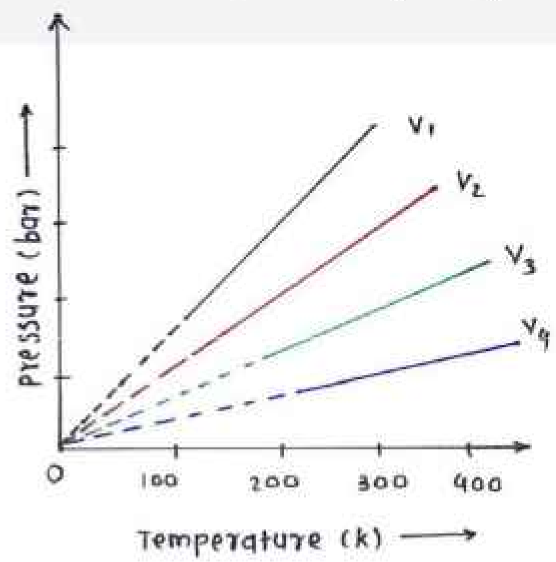
- While building an air thermometer, Gay Lussac accidentally discovered that at fixed volume, and mass of a gas, the pressure of that gas is directly proportional to the temperature. This mathematically can be written as :

$$P \propto T$$

$$\frac{P}{T} = \text{constant} = k_3$$

- The temperature here is measured on the kelvin scale. The graph for the Gay - Lussac's law is called as an Isochore because the volume here is constant.

$V_1 < V_2 < V_3 < V_4$



Avogadro's law

Amedeo Avogadro in 1811 combined the conclusions of Dalton's Atomic theory and Gay Lussac's law to give another important gas law called Avogadro's law.

- According to Avogadro's law, at constant temperature and pressure, the volume of all gases constitutes an equal number of molecules.

- This means that as long as the tempe-rature and pressure remain constant, the volume depends upon number number of molecules of the gas or in other words, amount of the gas

Mathematically we can write

$V \propto n$ ∴ Where n is the number of moles of the gas.

$V = k_4 n$

- The number of molecules in one mole of a gas has been determined to be 6.022×10^{23} and known as Avogadro constant.

- The values for temperature and pressure here are the standard values. For temperature, we take it to be 273.15 K while for the pressure it equals 1 bar or 10^5 Pascals.

At these standard Temperature pressure (STP) values, one mole of a gas is supposed to have the same volume.

Now,

$$n = \frac{m}{N}$$

According to Avogadro

equation, $V = K_4 \left(\frac{m}{M}\right)$

$$M = K_4 \left(\frac{m}{V}\right)$$

$\frac{m}{V} = d$ (density); Therefore

$$\therefore M = K_4 d$$

- This means that at an unchanged temperature and pressure conditions, the molar mass of every gas is directly proportional to its density

Ideal Gas Equation

- The ideal gas equation is a combination of all the individual gas laws.

  i) Boyle's law ii) Charle's law

  iii) Gay-Lussac's law iv) Avogadro's laws

  are the basis of the ideal gas equation.

- After the analysis of the experiments in various gas laws, we can understand the idea behind the ideal behaviour of gases.

- The law of Ideal gases states that the volume of a specified amount of gas is inversely proportional to pressure and directly proportional to volume and Temperature.

The Equation -

Now putting all the three laws together, we find that at standard conditions, volume of a gas can be represented as follows :

$\therefore$ At constant T and n ; $V \propto \frac{1}{P}$

— (Boyle's law)

$\therefore$ At constant P and n ; $V \propto T$

— (Charle's law)

$\therefore$ At constant P and T ; $V \propto n$

— (Avogadro law)

Thus,

$$= V \propto \frac{nT}{P}$$

$$= V = R\frac{nT}{P}$$

- Where R is proportionality constant. on rearranging the equation we obtain

$$= pV = nRT$$

$$\therefore \quad R = \frac{PV}{nT}$$

- R is called gas constant. It is same for all gases, therefore it is called universal Gas constant. The Equation we obtained above is called ideal gas equation.

Density and Molar Mass of a Gaseous Substance

Ideal gas equation can be rearranged as follows :

$$\frac{n}{V} = \frac{P}{RT}$$

Replacing n by $\frac{m}{M}$, we get

$$\frac{m}{MV} = \frac{P}{RT}$$

$$\frac{d}{M} = \frac{P}{RT} \quad \therefore (d = \text{density})$$

on rearranging equation we get the relationship for calculating molar mass of a gas.

$$\therefore \quad M = \frac{dRT}{P}$$

- This concludes that the under unchanged conditions of temperature and pressure the density of a gas is directly proportional to molar mass of the gas.

Dalton's Law of partial pressure

The law was formulated by John Dalton in 1801. It states that, The total pressure exerted by the mixture of the partial pressure of individual gases.

mathematically

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

where, P_{Total} is the total pressure exerted by the mixture of gases and P_1, P_2, P_3 etc. are partial pressure of gases.

Kinetic Molecular Theory of Gases.

- The kinetic molecular theory provides the microscopic model of gases. and gives us a picture of the behavious of gases. We have already had a look at the gas laws which depict the changing behaviour of gases with the changing physical conditions.

- Kinetic Molecular theory intensely outlines the molecular behavior of a gas. The theory is based on the following postulates.

1) Negligible molecules to space-volume Ratio

Gases consist of a large number of atoms or molecules that are generally identical in shape and size and are spaced very far apart. Due to the large space between these molecules, the volume of molecules is negligible as compared to the space that gas occupies.

2) No Force of Attraction

At normal temperatures and pressure, gaseous molecules generally lack attraction forces.

3) Always in motion

A large amount of space between the molecules gives them the room to be always in motion. Gases do not have a fixed shape, this shows that the gaseous molecules are always in random motion.

4) Elastic Collision

The collision between the molecules in a gas is perfectly elastic. collisions are of two types: Elastic and Inelastic.

- In an elastic collision, the energy stored in the molecules by virtue of their movement is same before and after the collision.

- In inelastic collision, after some time duration, the molecules would come to a rest.

5) constantly changing kinetic Energy.

The kinetic energy stored in the various molecules is never static or constant. The kinetic energy of an object is by virtue of its motion.

6) Average kinetic Energy.

The never ending, movement of molecules and particles results in a changed Kinetic Energy. since for calculating the kinetic energy, we use

$$K.E. = \frac{1}{2} mv^2$$

7) Effects of Physical conditions.

- According to the kinetic theory of gases, the kinetic energy of molecules is directly proportional to temperature.

- The increased kinetic energy of the molecules makes them strike with the walls of the container more often, hence leading to an increased pressure on the walls of the container.

Behaviour of Real Gases: Deviation From Ideal Gas Behaviour.

- We know the Ideal Gas Equation, $pV = nRT$. It defines the relationship between Temperature, pressure and volume of gasses.

- For checking the reliability of this relationship we first plot a graph between pV and p.

- Now we know that at a constant temperature, as the Boyle's law states, pV shall be a constant.

- Therefore the graphs between the two shall be straight line. But the case is not so. AT temperature 273 k the data for several gases is shown below:

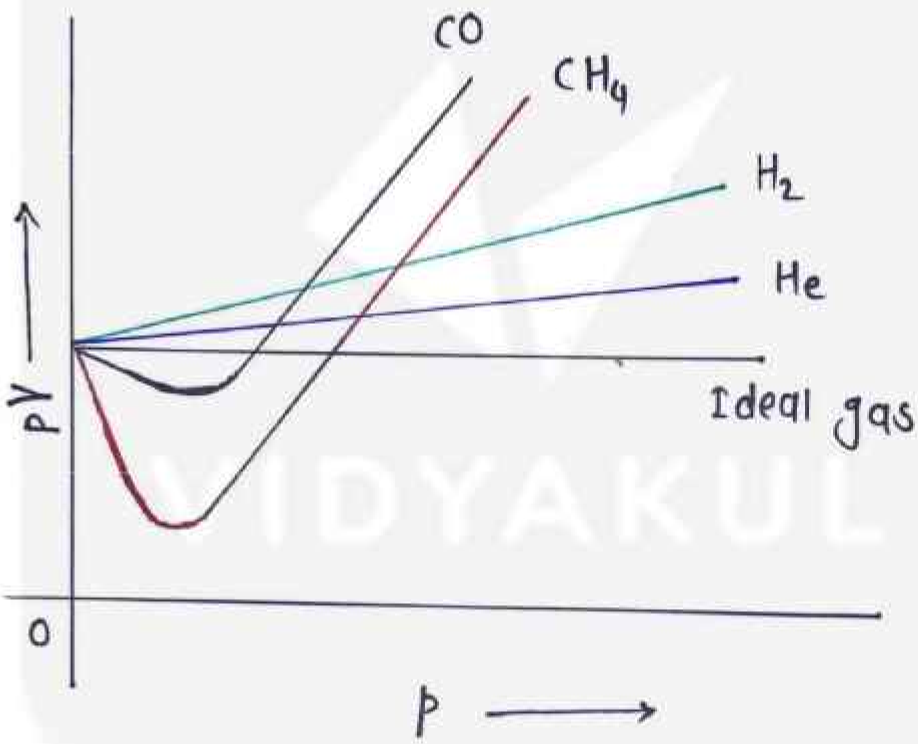


fig: Plot of pV vs P for real gas and Ideal gas.

- From the graph plotted in the figure we can easily conclude that despite the constant temperature, the real gases do not show behaviour as predicted by the Boyle's law. These gases show a significant deviation from the predicted ideal behaviour as per the Boyle's law.

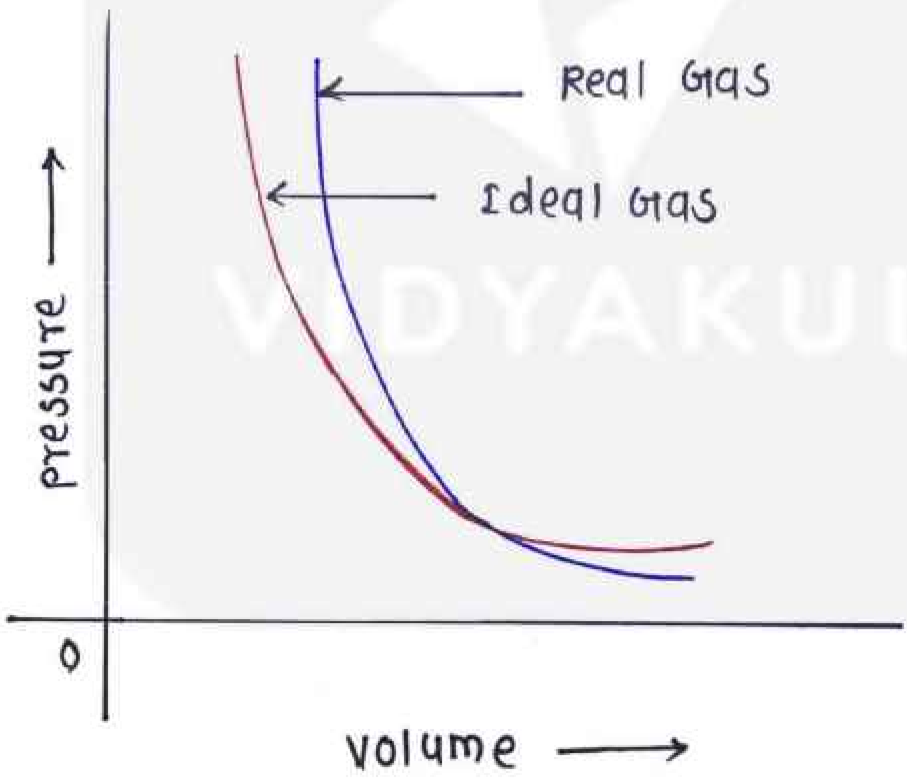


Fig : Plot of pressure vs volume for real gas and ideal gas.

- From the above graph that plots the volume to pressure data of gases, we find an apparent deviation from the theorètical prediction of gases in changed conditions.

- From the graph, we can figure out that at very high pressures the value of volume we calculated is less than the actual practical volume.

- Hence from the above two graphs, it is clear that generally real gases, under all conditions do not follow The Ideal Gas Behaviour or equation.

Vander walls Equation of State

- From the above difference, it is clear that in ideal gasses the pressure exerted by molecules on the container is greater than that exerted by real gases, so $P_{ideal} = P_{real} + \frac{an^2}{V^2}$

i.e $\therefore P_{real}$ is observed pressure

$$\therefore \frac{an^2}{V^2} = \text{correction term}$$

$$\therefore a = \text{constant.}$$

- Now, let's consider the repulsive forces. The forces which came into play when the molecules are in contact with each other are called repulsive forces.

- Being short range interactions, these forces make molecules behaviour like the impenetrable spheres. It is because of this force that the volumes of the molecules rise significantly and at high pressure volume V becomes $V - nb$. Here, nb is the volume occupied by the molecules.

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

- a and b are constants that depends on the nature of the gas. This equation is also known as the van der waals equation.

- n, here is number of moles.

Liquifaction of gases

Liquifaction is the transformation of a gaseous substance into its liquid state. This change is the outcome of change in physical conditions like temperature, pressure, and volume.

The liquid state

All the liquids show following characteristics

- Strong intermolecular forces:

The intermolecular forces in a liquid are stronger than a gas and weaker than a solid.

- Definite volume and density:

liquids have a definite volume. These unlike gases occupy a limited space, the reason being their low space between the molecules.

- Free flowing and shapeless:

liquids take the shape of the container in which they are stored. Due to free flowing molecules that move past each other liquids assume the flowing characteristics as well.

Vapour pressure

When a liquid is filled in a container, its walls are occupied by the vapours, from that liquid. Liquids show the unique property of turning into vapours, as soon as the temperature rises.

- Generally, vapours from the aqueous substance occupy the walls of the unfilled part of the container. and exert a pressure on the walls of that container, this pressure is called the vapour pressure.

Surface Tension

The molecules in a liquid experiences an equal intermolecular force from all the sides. The intermolecular force between the molecules on the surface is exerted perpendicularly downward.

This force is called the surface Tension of the liquid.

- The surface tension of a liquid depends upon the intermolecular forces directly, greater the force higher the surface tension.

- The unit of surface tension is Jm^{-2} and it is denoted by γ (gamma)

- The surface tension depends on the surface area. The lower the surface area the lower shall be the surface tension.

- surface tension is also inversely proportional to the temperature.

Viscosity

The viscosity of a liquid substance is a measure of resistance to flow. The molecular forces and internal friction between the moving molecules in the liquid makes them viscous to flow.

- When a liquid flows, the molecules in contact with the surface are stationary, while the upper layer tends to move, the velosity of this moving layer increases with the distance of layer from the stationary layer.

- This implies that the farther the moving layer, the faster it moves. This kind of increasing velocity is termed as laminar flow.

Coefficient of viscocity

If the velocity of the layer at a distance dx is changed by a value dy then velocity gradient is given by the amount dy/dx.

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.

$F \propto A$ (A is the area of contact)

$F \propto \frac{dy}{dx}$ (dy/dx is velocity gradient; the change in velocity distance)

$$F \propto A . \frac{dy}{dx}$$

$$\therefore \quad F = \eta A \frac{dy}{dx}$$

'η' is proportionality constant and is called coefficient of viscosity.

- 'η' is measure of viscosity. SI unit of viscosity is 1 Newton scond per square meter [$N s m^{-2}$]

- viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecu-lar forces to slip one another between the layers.