States of Matter:

General Behaviour of Gases:

The Gas Laws The volume of a given mass of a gas depends upon the temperature and pressure under which the gas exists. It is, therefore, possible to describe the behaviour of gases in terms of the four variables: temperature,T ; pressure p; volume Vand amount (number of moles, n). For a given amount of gas the volume of gas changes with change in variables such as temperture and pressure. The relationship between any two of the variables is studied under Gas Laws.

INTERMOLECULAR FORCES:

An intermolecular force (IMF) (or secondary force) is the force that mediates interaction between molecules, including the electromagnetic forces of attraction or repulsion which act between atoms and other types of neighbouring particles, e.g. atoms or ions. Intermolecular forces are weak relative to intramolecular forces – the forces which hold a molecule together. For example, the covalent bond, involving sharing electron pairs between atoms, is much stronger than the forces present between neighboring molecules. Both sets of forces are essential parts of force fields frequently used in molecular mechanics.

Attractive intermolecular forces are categorized into the following types:

- Hydrogen bonding
- Ion–dipole forces and ion–induced dipole forces
- Van der Waals forces – Keesom force, Debye force, and London dispersion force
Information on intermolecular forces is obtained by macroscopic measurements of properties like viscosity, pressure, volume, temperature (PVT) data. The link to microscopic aspects is given by virial coefficients and Lennard-Jones potentials.

Hydrogen Bonding:

A hydrogen bond is an extreme form of dipole-dipole bonding, referring to the attraction between a hydrogen atom that is bonded to an element with high electronegativity, usually nitrogen, oxygen, or fluorine.[2] The hydrogen bond is often described as a strong electrostatic dipole–dipole interaction. However, it also has some features of covalent bonding: it is directional, stronger than a van der Waals force interaction, produces interatomic distances shorter than the sum of their van der Waals radii, and usually involves a limited number of interaction partners, which can be interpreted as a kind of valence. The number of Hydrogen bonds formed between molecules is equal to the number of active pairs. The molecule which donates its hydrogen is termed the donor molecule, while the molecule containing lone pair participating in H bonding is termed the acceptor molecule. The number of active pairs is equal to the common number between number of hydrogens the donor has and the number of lone pairs the acceptor has.

Beta Bonding (Ionic Bonding):

The attraction between cationic and anionic sites is a noncovalent, or intermolecular interaction which is usually referred to as ion pairing or salt bridge.[4] It is essentially due to electrostatic forces, although in aqueous medium the association is driven by entropy and often even endothermic. Most salts form crystals with characteristic distances between the ions; in contrast to many other noncovalent interactions, salt bridges are not directional and

show in the solid state usually contact determined only by the van der Waals radii of the ions. Inorganic as well as organic ions display in water at moderate ionic strength I similar salt bridge as association ΔG values around 5 to 6 kJ/mol for a 1:1 combination of anion and cation, almost independent of the nature (size, polarizability, etc.) of the ions.[5] The ΔG values are additive and approximately a linear function of the charges, the interaction of e.g. a doubly charged phosphate anion with a single charged ammonium cation accounts for about 2x5 = 10 kJ/mol. The ΔG values depend on the ionic strength I of the solution, as described by the Debye-Hückel equation, at zero ionic strength one observes ΔG = 8 kJ/mol.

Van der Waals Forces:
The van der Waals forces arise from interaction between uncharged atoms or molecules, leading not only to such phenomena as the cohesion of condensed phases and physical absorption of gases, but also to a universal force of attraction between macroscopic bodies.

Keesom force (permanent dipole – permanent dipole interaction):

The first contribution to van der Waals forces is due to electrostatic interactions between rotating permanent dipoles, quadrupoles (all molecules with symmetry lower than cubic), and multipoles. It is termed the Keesom interaction, named after Willem Hendrik Keesom. These forces originate from the attraction between permanent dipoles (dipolar molecules) and are temperature dependent

They consist of attractive interactions between dipoles that are ensemble averaged over different rotational orientations of the dipoles. It is assumed that the molecules are constantly rotating and never get locked into place. This is a good assumption, but at some point molecules do get locked into place. The energy of a Keesom interaction depends on the inverse sixth power of the distance, unlike the interaction energy of two spatially fixed dipoles, which depends on the inverse third power of the distance. The Keesom interaction can only occur among molecules that possess permanent dipole moments, i.e., two polar molecules. Also Keesom interactions are very weak van der Waals interactions and do not occur in aqueous solutions that contain electrolytes.

Debye force (permanent dipoles–induced dipoles interaction):

The second contribution is the induction (also termed polarization) or Debye force, arising from interactions between rotating permanent dipoles and from the polarizability of atoms and molecules (induced dipoles). These induced dipoles occur when one molecule with a permanent dipole repels another molecule's electrons. A molecule with permanent dipole can induce a dipole in a similar neighboring molecule and cause mutual attraction. Debye forces cannot occur between atoms. The forces between induced and permanent dipoles are not as temperature dependent as Keesom interactions because the induced dipole is free to shift and rotate around the polar molecule. The Debye induction effects and Keesom orientation effects are termed polar interactions. The energy of a Debye interaction depends on the inverse sixth power of the distance.

One example of an induction interaction between permanent dipole and induced dipole is the interaction between HCl and Ar. In this system, Ar experiences a dipole as its electrons are attracted (to the H side of HCl) or repelled (from the Cl side) by HCl.

This kind of interaction can be expected between any polar molecule and non-polar/symmetrical molecule. The induction-interaction force is far weaker than dipole–dipole interaction, but stronger than the London dispersion force.

London dispersion force (fluctuating dipole–induced dipole interaction):

The third and dominant contribution is the dispersion or London force (fluctuating dipole–induced dipole), which arises due to the non-zero instantaneous dipole moments of all atoms and molecules. Such polarization can be induced either by a polar molecule or by the repulsion of negatively charged electron clouds in non-polar molecules. Thus, London interactions are caused by random fluctuations of electron density in an electron cloud. These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles. An atom with a large number of electrons will have a greater associated London force than an atom with fewer electrons. The dispersion (London) force is the most important component because all materials are polarizable, whereas Keesom and Debye forces require permanent dipoles. The London interaction is universal and is present in atom-atom interactions as well. For various reasons, London interactions (dispersion) have been considered relevant for interactions between macroscopic bodies in condensed systems.

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 particles is called thermal motion.

Intermolecular forces vs. Thermal interactions:

We have already learnt that intermolecular forces tend to keep the molecules 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.

When molecular interactions are very weak, molecules do not cling together to make liquid or solid unless thermal energy is reduced by lowering the temperature. Gases do not liquify on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum. However, when thermal energy of molecules is reduced by lowering the temperature; the gases can be very easily liquefied and finally can also be solidified.

Characteristics of Gaseous State:

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much 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

The Gas Laws:

The gas laws were developed at the end of the 18th century, when scientists began to realize that relationships between pressure, volume and temperature of a sample of gas could be obtained which would hold to approximation for all gases.

Boyle's Law:

In 1662 Robert Boyle studied the relationship between volume and pressure of a gas of fixed amount at constant temperature. He observed that volume of a given mass of a gas is inversely proportional to its pressure at a constant temperature. Alternatively we can say that at constant temperature, the product of the pressure and volume of a given mass of an ideal gas in a closed system is always constant.

It can be verified experimentally using a pressure gauge and a variable volume container. It can also be derived from the kinetic theory of gases: if a container, with a fixed number of molecules inside, is reduced in volume, more molecules will strike a given area of the sides of the container per unit time, causing a greater pressure.

Mathematically, it can be written as

$p \propto \dfrac{1}{V}$

$\Rightarrow p = k . \dfrac{1}{V}$ [At constant T and n]

Where k is the proportionality constant. The value of constant k depends upon the amount of the gas, temperature of the gas and the units in which p and V are expressed.
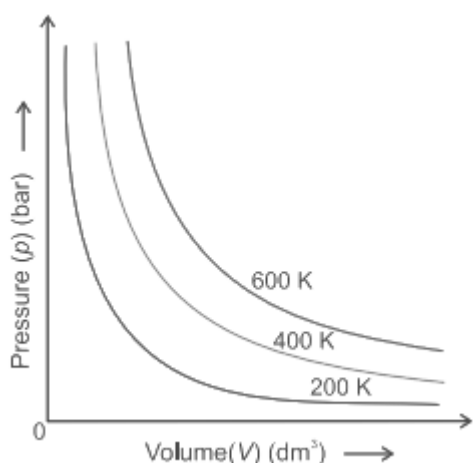
On rearranging equation we obtain

$pV = k$

$\Rightarrow p_1 V_1 = p_2 V_2 = \text{constant}$

Graphical representation of Boyle's Law:
1. p vs. V graph (Rectangular hyperboplic):

The value of k for each curve is different because for a given mass of gas, it varies only with temperature. Each curve corresponds to a different constant temperature and is known as an isotherm (constant temperature plot). Higher curves correspond to higher temperatures

2. p vs. 1/V graph(straight line):
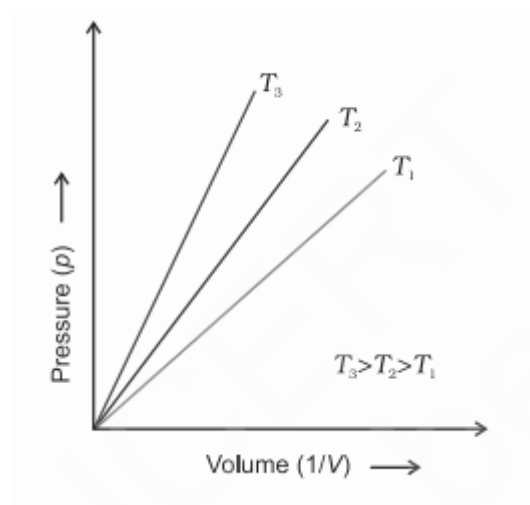
It is a straight line passing through origin. However at high pressures, gases deviate from Boyle's law and under such conditions a straight line is not obtained in the graph

Relation between density and pressure at constant temperature for a given mass of gas:

By definition, density 'd' is related to the mass 'm' and the volume 'V' by the relation

$$d = \frac{m}{V}$$

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

$$d = \frac{m}{k} P$$

$$= k_1 p$$

This shows that at a constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

Charle's Law:

Charles' law (also known as the law of volumes) is an experimental gas law that describes how gases tend to expand when heated. A modern statement of Charles' law is:

When the pressure on a sample of a dry gas is held constant, the kelvin temperature and the volume will be in direct proportion.

This relationship of direct proportion can be written as:

$V \propto T$

$\Rightarrow V = kT,$

or, $\dfrac{V}{T} = k$

where:

- V is the volume of the gas,
- T is the temperature of the gas (measured in kelvins), and
- k is a non-zero constant.

This law describes how a gas expands as the temperature increases; conversely, a decrease in temperature will lead to a decrease in volume. For comparing the same substance under two different sets of conditions, the law can be written as:

$$\frac{V1}{T1} = \frac{V2}{T2}$$

Charles also stated:

The volume of a fixed mass of dry gas increases or decreases by $\frac{1}{273}$ times the volume at 0 °C for every 1 °C rise or fall in temperature. Thus:

$$V_T = V_0 + \left(\frac{1}{273} \times V_0\right) \times T$$

$$V_T = V_0\left(1 + \frac{T}{273}\right)$$

where V_T is the volume of gas at temperature T, V_0 is the volume at 0 °C.

Relation to Absolute Zero of Temperature:

Charles's law appears to imply that the volume of a gas will descend to zero at a certain temperature (−266.66 °C according to Gay-Lussac's figures) or −273.15 °C. At absolute zero temperature, the gas possesses zero energy and hence the molecules restrict motion.

However, the "absolute zero" on the Kelvin temperature scale was originally defined in terms of the second law of thermodynamics, which Thomson himself described in 1852.[8] Thomson did not assume that this was equal to the "zero-volume point" of Charles's law, merely that Charles's law provided the minimum temperature which could be attained.

Graphical representation of Charle's Law:

(i) Volume vs temperature (in celsius):
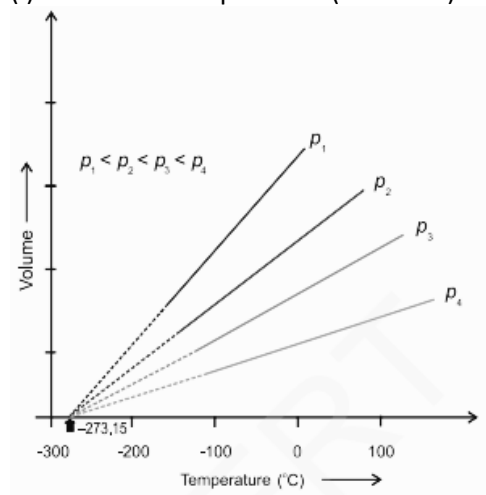
It is a straight line and on extending to zero volume, each line intercepts the temperature axis at − 273.15 ° C. Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at − 273.15 ° C.
Each line of the volume vs temperature graph is called **isobar**.

Gay-Lussac's law (PressureTemperature Relationship):

It states that **at constant volume, pressure of a fixed amount of a gas varies directly with the temperature**. Mathematically,

P$\propto T$

$$\Rightarrow \frac{p}{T} = k$$

Pressure vs temperature (Kelvin) graph at constant molar volume is shown below. Each line of this graph is called **isochore**.
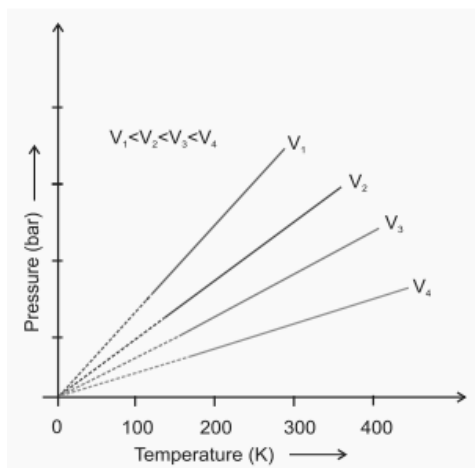
Avogadro Law (Volume - Amount Relationship):

It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. Mathematically we can write,

$$V \propto n$$

Ideal Gas Equation:

The three laws which we have learnt till now can be combined together in a single equation which is known as ideal gas equation.

At constant T and n; $V \propto \dfrac{1}{p}$ Boyle's Law

At constant p and n; $V \propto T$ Charles' Law

At constant p and T ; $V \propto n$ Avogadro Law

Thus,

$$V \propto \frac{nT}{p}$$

$\Rightarrow V = R\dfrac{nT}{p}$, where R is proportionality constant

On rearranging the equation we obtain

pV=nRT

R is same for all gases. Therefore it is also called **Universal Gas Constant.**

If temperature, volume and pressure of a fixed amount of gas vary from T1, V1 and p1 to T2, V2 and p2 then we can write

$$\frac{p_1 V_1}{T_1} = nR \quad \text{and} \quad \frac{p_2 V_2}{T_2} = nR$$

$$\Rightarrow \quad \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

This equation is also known as **Combined gas law**.

Density(d) and Molar Mass(M) of a Gaseous Substance:

The ideal gas equation:

pV=nRT

Replacing n by $\dfrac{m}{M}$ we get

$$\dfrac{m}{MV} = \dfrac{p}{RT}$$

$$\Rightarrow \dfrac{d}{M} = \dfrac{p}{RT}$$

On rearranging the equation we get the relationship for calculating molar mass of a gas as

$$M = \dfrac{dRT}{p}$$

Partial Pressure of Gas:

In a mixture of gases, each constituent gas has a partial pressure which is the notional pressure of that constituent gas as if it alone occupied the entire volume of the original mixture at the same temperature.

The partial pressure of a gas is a measure of thermodynamic activity of the gas's molecules. Gases dissolve, diffuse, and react according to their partial pressures but not according to their concentrations in gas mixtures or liquids. This general property of gases is also true in chemical reactions of gases in biology. For example, the necessary amount of oxygen for human respiration, and the amount that is toxic, is set by the partial pressure of oxygen alone.

Dalton's Law of Partial Pressures:

The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the individual gases in the mixture. This equality arises from the fact that in an ideal gas, the molecules are so far apart that they do not interact with each other.

Mathematically,

P_{total} = p_1+p_2+p_3+......(at constant T, V)

where p_{total} is the total pressure exerted by the mixture of gases and p1, p2 , p3 etc. are partial pressures of gases.

Gases are generally collected over water and therefore are moist. Pressure of dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas which contains water vapours also. Pressure exerted by saturated water vapour is called aqueous tension.

$P_{dry\ gas}$ = p_{total} - aqueous tension

Partial pressure in terms of mole fraction: Suppose at the temperature T, three gases, enclosed in the volume V, exert partial pressure p1, p2 and p3 respectively. then,

$P_1 = \dfrac{n1RT}{V}$,

$P_2 = \dfrac{n2RT}{V}$,

$P_3 = \dfrac{n3RT}{V}$ etc.

where n1 n2 and n3 are number of moles of these gases. Thus, expression for total pressure will be

p_{total} = p1 + p2 + p3

$\quad = \dfrac{n1RT}{V} + \dfrac{n2RT}{V} + \dfrac{n3RT}{V}$

$\quad = (n_1+n_2+n_3)\dfrac{RT}{V}$

On dividing p_1 by p_{total} we get

$$\frac{p1}{p} = \frac{n1}{n}$$

$$= x_1$$

where n = n1+n2+n3 , and x1 is called mole fraction of first gas.

Thus,

$$P_1 = x_1 p_{total}$$

Similarly for other two gases we can write,

$$P_2 = x_2 p_{total}$$

$$P_3 = x_3 p_{total}$$

In general, we can write,

$$P_i = x_i p_{total}$$

Thus, partial pressure of a component is directly proportional to the mole fraction of that component.

Diffusion :

Diffusion is the net movement of anything (for example, atoms, ions, molecules, energy) generally from a region of higher concentration to a region of lower concentration. Diffusion is driven by a gradient in Gibbs free energy or chemical potential.

Graham's law of diffusion:

Graham found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the molar mass of its particles. This formula is stated as:

$$\frac{r1}{r1} = \frac{M1}{M2}$$

Graham's law is most accurate for molecular effusion which involves the movement of one gas at a time through a hole. It is only approximate for diffusion of one gas in another or in air, as these processes involve the movement of more than one gas.

In the same conditions of temperature and pressure, the molar mass is proportional to the mass density. Therefore, the rates of diffusion of different gases are inversely proportional to the square roots of their mass densities.

$$r \propto \frac{1}{\sqrt{d}}$$

KINETIC MOLECULAR THEORY OF GASES:

The assumptions of Kinetic theory of gas are:

- The gas consists of very small particles. This smallness of their size is such that the sum of the volume of the individual gas molecules is negligible compared to the volume of the container of the gas. This is equivalent to stating that the average distance separating the gas particles is large compared to their size, and that the elapsed time of a collision between particles and the container's wall is negligible when compared to the time between successive collisions.
- The number of particles is so large that a statistical treatment of the problem is well justified. This assumption is sometimes referred to as the thermodynamic limit.
- The rapidly moving particles constantly collide among themselves and with the walls of the container. All these collisions are perfectly elastic, which means the molecules are perfect hard spheres.
- Except during collisions, the interactions among molecules are negligible. They exert no other forces on one another.

BEHAVIOUR OF REAL GASES: DEVIATION FROM IDEAL GAS BEHAVIOUR:

An ideal gas obeys the ideal gas equation PV=nRT at all pressures and temperatures. No gas, on the other hand, is excellent. Almost all gases vary in some manner from the ideal behaviour. Non-ideal or actual gases, such as H_2, N_2, and CO_2, do not obey the ideal-gas equation.

The reason behind the deviation of gases from the ideal behavior is few assumptions of kinetic theory. The assumptions are as follows:

1. The first assumption is that the particles are point sized. This means that the particles have no volume as compared to the volume of the vessel.
2. The second assumption is that there is no force of attraction between the molecules of gas, hence the collisions of molecules are treated as perfectly elastic.

However, these two assumptions are applicable for real gases only under the conditions of high temperature and low pressure.

Due to these two assumptions we can see the deviations from the ideal behavior of gases.

Compressibility Factor:

A new function called the Compressibility factor, denoted by Z, can be used to quantify the degree to which real gas deviates from ideal behaviour. It's described as

$$Z = \frac{PV}{RT}$$

Plotting the compressibility factor, Z, vs. P (or PV vs. P, reveals the degree of departure from optimum behaviour. Temperature and pressure have no effect on an ideal gas, which has a Z value of 1. The value of Z is more or less than 1 determines the difference between ideal and real gas behaviour. The degree of gas nonideality is represented by the difference between unity and Z. Pressure and temperature cause deviations from optimal behaviour in a real gas. Using pressure and temperature to examine the compressibility curves of some of the gases discussed below.

Effect of Pressure Variation on Deviations:

In the graph below, the compressibility factor, Z, for H_2, N_2, and CO_2 at constant temperature is plotted against pressure.
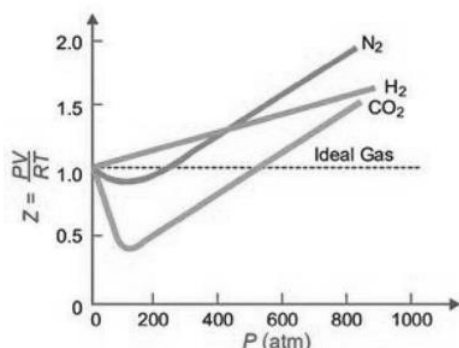
For all of these gases, Z is practically equal to one at very low pressure. Real gases behave almost perfectly at low pressures (up to 10 atm). As the pressure rises, H2 exhibits a steady increase in Z (from Z=1). As a result, the H_2 curve is higher than the ideal gas curve at all pressures. For N_2 and CO_2, Z decreases at first , then reaches a minimum, and finally increases with increasing pressure (Z>1). Because CO_2 is the most easily liquefied gas, it has the greatest drop in the curve.

Effect of Temperature on Deviations:

The graph below shows plots of Z or PV/RT against P for N2 at various temperatures.
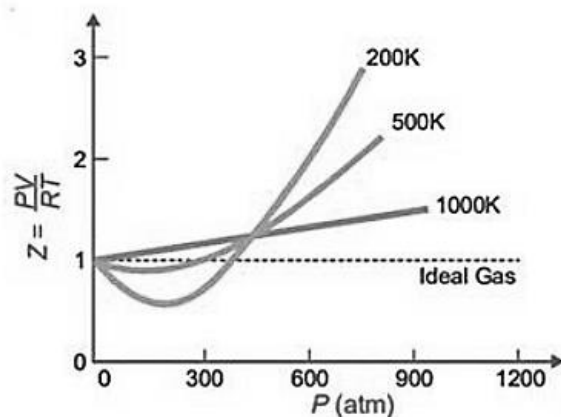
As the temperature rises, the deviations from ideal gas behaviour become smaller and smaller, as shown by the shape of the graphs. At lower temperatures, the curve dips significantly, and the slope of the curve is negative. In this situation, Z<1. As the temperature rises, the dip in the curve decreases. The curve's minimum vanishes at a certain temperature and remains horizontal for a wide range of pressures. At this temperature, PV/RT is nearly equal, thus Boyle's law is satisfied. As a result, Boyle's temperature refers to the temperature of the gas. Each gas has its own Boyle temperature, such as 332K for N_2.

Evidence for Molecular Attractions and Molecular Volume Gases can be liquefied by decreasing its temperature and applying high pressure. Since liquids have definite volume due to the close presence of molecules, it indicates that the molecules of a gas do occupy certain volume. This volume is negligible when the pressure of the gas is low. At high pressure, when the volume of the gas is small, the molecular volumes are not negligible. Liquefaction of the gas is possible because there exist molecular attractions among them. When the volume of the gas is small, these molecular attractions are not negligible.

Van Der Waals Equation of State for a Real Gas:

How can the ideal gas law be modified to yield an equation that will represent the experimental data more accurately? We begin by correcting an obvious defect in the ideal gas law, namely the prediction that under any finite pressure the volume of the gas is zero at the absolute zero of temperature: $\overline{V} = \dfrac{RT}{P}$. On cooling, real gases liquefy and ultimately solidify ; after liquefaction the volume does not change very much. We can arrange the new equation so that it predicts a finite, positive volume for the gas at 0 K by adding a positive constant **b** to the ideal volume:

$$\overline{V} = b + \dfrac{RT}{P} \ ----------(1)$$

Now it would be interesting to see how this equation predicts theZ vs P curves. Since by definition

$Z = \dfrac{PV}{RT}$, multiplication of Eq. (1) by p/RT yields

$$Z = 1 + \dfrac{bp}{RT} \quad \text{----------------(2)}$$

According to the equation the molar volume at 0 K is b, and we expect that **b** will be roughly comparable with the molar volume of the liquid or solid. It also predicts that as the pressure becomes infinite the molar volume approaches the limiting value b. This prediction is more in accord with experience than the prediction of the ideal gas law that the molar volume approaches zero at very high pressures.

Since Eq. (2) requires Z to be a linear function of pressure with a positive slope b/RT, it cannot possibly fit the curve for nitrogen, which starts from the origin with a negative slope. However, it can represent the behavior of hydrogen in the low-pressure region.

We can conclude that the assumption that the molecules of a gas have finite size is sufficient to explain values of Z greater than unity. Apparently this size effect is the dominating one in producing deviations from ideality in hydrogen at 0^0c. It is also clear that some other effect must produce the deviations from ideality in gases such as nitrogen and methane, since the size effect cannot explain their behavior in the low pressure range. This other effect must now be sought.

We have already noted that the worst offenders in the matter of having values of Z less than unity are methane and carbon dioxide, which are easily liquefied. Thus we begin to suspect a connection between ease of liquefaction and the compressibility factor, and to ask why a gas liquefies. First of all, energy, the heat of vaporization, must be supplied to take a molecule out of the liquid and put it into the vapor. This energy is required because of the forces of attraction acting between the molecule and its neighbors in the liquid. The force of attraction is strong if the molecules are close together, as they are in a liquid, and very weak if the molecules are far apart, as they are in a gas. The problem is to find an appropriate way of modifying the gas equation to take account of the effect of these weak attractive forces.

The pressure exerted by a gas on the walls of a container acts in an outward direction. Attractive forces between the molecules tend to pull them together, thus diminishing the outward thrust against the wall and reducing the pressure below that exerted by the ideal gas. This reduction in pressure should be proportional to the force of attraction between the molecules of the gas.

Consider two small volume elements $v1$ and $v2$ in a container of gas. Suppose that each volume element contains one molecule and that the attractive force between the two volume elements is some small value f.
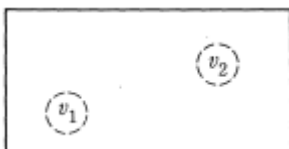
If another molecule is added to V_2, keeping one molecule in V_1 the force acting between the two elements should be $2f$; addition of a third molecule to V_2 should increase the force to $3f$, and so on. The force of attraction between the two volume elements is therefore proportional to $\bar{c}_2$, the concentration of molecules in V_2. If at any point in the argument, the number of molecules in V_2 is kept constant and molecules are added to V_1 then the force should double and triple, etc. The force is therefore proportional to $\bar{c}_1$, the concentration of molecules in V_1 Thus, the force acting between the two elements can be written as: $\text{force} \propto \bar{c}_1 \bar{c}_2$. Since the concentration in a gas is

everywhere the same, $\overline{c}_1 =; \overline{c}_2 = \overline{c}$, and so, force $\propto \overline{c}^2$. But $\overline{c} = n/V = 1/\overline{V}$; consequently, force $\propto 1/\overline{V}^2$.

We can rewrite the above equation in the form

$$p = \frac{RT}{\overline{V} - b}$$

Because of the attractive forces between the molecules, the pressure is less than that given by the above equation by an amount proportional to $1/\overline{V}^2$, so a term is subtracted from the right-hand side to yield

$$p = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

where a is a positive constant roughly proportional to the energy of vaporization of the liquid. Two things should be noted about the introduction of the $1/\overline{V}^2$ term.

This equation is known as **van der Waals equation**, proposed by van der Waals, who was the first to recognize the influence of molecular size and intermolecular forces on the pressure of a gas. These weak forces of attraction are called van der Waals forces. The van der Waals equation is frequently written in the equivalent but less instructive forms:

$$\left(p + \frac{a}{\overline{V}^2}\right)(\overline{V} - b) = RT \qquad \text{or} \qquad \left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT,$$

where $V = n\overline{V}$ has been used in the second writing.

Units of van der Waals Constants a and b   The unit of $n^2 a/V^2$ is that of pressure. Hence, the SI unit of a is Pa m^6 mol^{-2}. However, it is convenient to express it as kPa dm^6 mol^{-2}.

The unit of nb is that of volume. Hence, the SI Unit of b is m^3 mol^{-1}. However, it is convenient to express it as dm^3 mol^{-1} or cm^3 mol^{-1}.

Comment on the values of a and b   Larger and bulkier molecules have larger value of van der waals constant b as compared to lighter gases. The gases which are easily liquefiable have larger values of van der Waals constant a.

Applicability of van der Waals Equation   For one mole of a real gas, the van der Waals equation of state is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

At low pressure   When pressure is low, the volume is sufficiently large and b can be ignored in comparison to V_m

$$\left(p + \frac{a}{V_m^2}\right)V_m = RT \quad \text{or} \quad pV_m + \frac{a}{V_m} = RT \qquad \text{or} \qquad Z = 1 - \frac{a}{V_m RT}$$

From the above equation it is clear that in the low pressure region, Z is less than 1. On increasing the pressure in this region, the value of the term $(a/V_m RT)$ increases as V is inversely proportional to p. Consequently, Z decreases with increase in p.

At high pressure   When p is large, V_m will be small and one cannot ignore b in comparison to V_m. However, the term a/V_m^2 may be considered negligible in comparison to p

Thus, $\qquad\qquad p(V_m - b) = RT \qquad\qquad \text{or} \qquad\qquad Z = 1 + \frac{pb}{RT}$

Here Z is greater than 1 and it increases linearly with pressure. This explains the nature of the graph in the high pressure region.

At high temperature and low pressure   If temperature is high, V_m will also be sufficiently large and thus the term a/V_m^2 will be negligibly small. At this stage, b may also be negligible in comparison to V_m.

Under these conditions the above equation reduces to the ideal gas equation.

Hydrogen and helium The value of *a* is extremely small for these gases as they are difficult to liquefy. Thus, we have the equation of state as $p(V_m - b) = RT$, obtained from the van der Waals equation by ignoring the term a/V_m^2. Hence, *Z* is always greater than 1 and it increases with increase in *p*.

Critical Constants of gas:

Critical temperature, T_c, is the maximum temperature which a gas can be liquefied, i.e. the temperature above which a liquid cannot exist.
Critical pressure, p_c, is the minimum pressure required to cause liquefaction at the temperature T_c.
Critical volume, V_c, is the volume occupied by one mole of a gas at critical temperature T_c and critical pressure p_c.

Critical Constants for van der Waals gases:

$$V_c = 3b; \qquad p_c = a/27b^2 \qquad \text{and} \qquad T_c = 8a/27Rb$$

The value of *pV/RT* at the critical state is

$$\frac{p_c V_c}{RT_c} = \frac{3}{8}$$

Inversion Temperature

If a gas at high pressure is passed through a porous plug or any other throttling device under adiabatic condition (i.e. no heat is absorbed from or released to the surroundings) to the low pressure region, cooling effects are produced provided the temperature of the gas is less than its characteristic temperature known as inversion temperature (T_i). Heating effect is produced if the temperature of the gas is larger than its inversion temperature. Under the condition of low pressure and high temperature, the inversion temperature is given by

$$T_i = \frac{2a}{Rb}$$

SURFACE TENSION : The surface tension is defined as the force per cm acting perpendicular to the tangential line on the surface of the liquid which tend to compress the surface area.
The units of surface tension are force per unit length i.e. dynes cm^{-1} or Nm^{-1} (in SI units)
Stronger the forces of intermolecular attraction (cohesive forces) greater is the surface tension.
The surface tension decreases with rise in temperature or surface tension in inversely proportional to temperature.
Surface tension μ 1/Temperature Measurement of surface tension of a liquid by the drop number method is the most convenient method.

VISCOSITY: Viscosity may be defined as the force of friction between two layers of a liquid moving past one another with different velocities.
The viscosities of liquids are compared in terms of coefficient of viscosity which is defined as the force per unit area needed to maintain a unit difference in velocities between two consecutive parallel layers which are one cm. apart.
The units of viscosity are **poise** (P) where $1P = g \, cm^{-1} \, sec^{-1}$. In SI units of viscosity $1P = 0.1 \, N \, sec \, m^{-2}$.
The liquid having stronger forces of attraction has a higher viscosity.
With the rise in temperature, viscosity of a liquid decreases because the intermolecular attractive force between consecutive layers decrease as temperature increases.