

XI

Chemistry

States of Matter

- Matter can exist (mainly) in three states- solid, liquid and gas.
- State of matter is determined by the nature of intermolecular forces, molecular interactions and thermal energy of particles.
- Change in the physical state does not change the chemical properties of a substance.
- Rates of Chemical reactions depend upon the physical state.
- Physical laws govern the behavior of matter in different states.

1. Intermolecular Forces

- Forces of attraction and repulsion between interacting particles (atoms and molecules).
- Covalent bonding is not intermolecular force.

2. Van der Waals Forces

- Attractive intermolecular forces.
- These forces include dispersion forces or London forces, dipole-dipole forces and dipole-induced dipole forces.
- Ion-dipole forces are not van der Waals forces.

a) Dispersion forces or London Forces

- Force of attraction between two temporary instantaneous dipoles.
- These forces are always attractive.
- Interaction energy $\propto 1/r^6$, where r is the distance between the two particles.

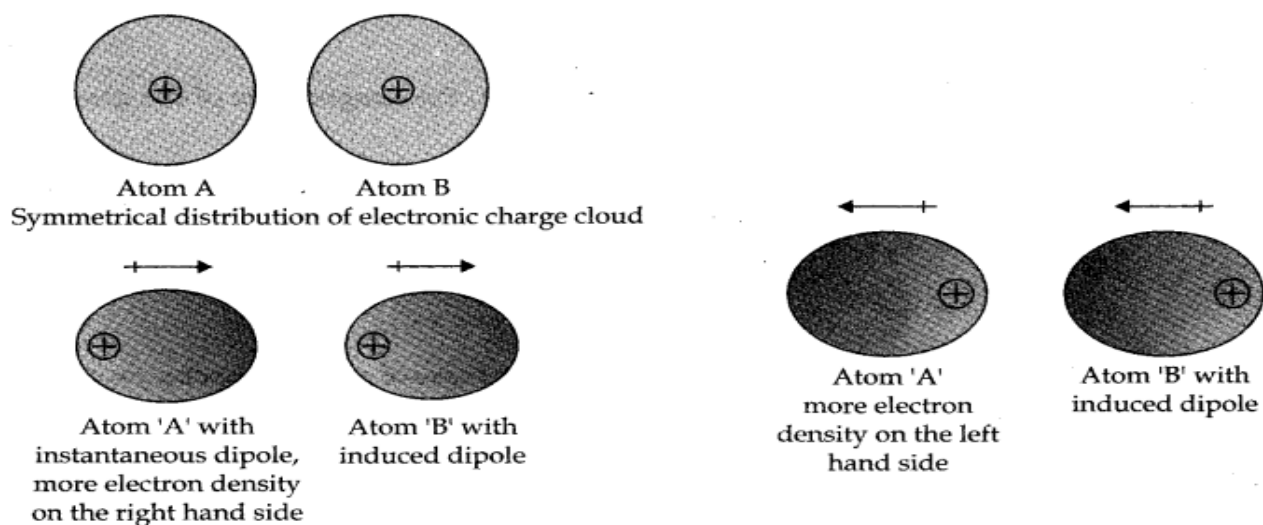
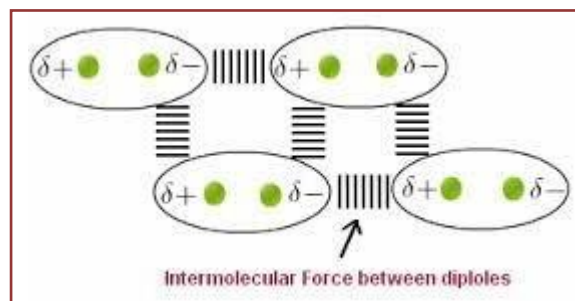


Fig. 5.2 Dispersion forces or London forces between atoms.

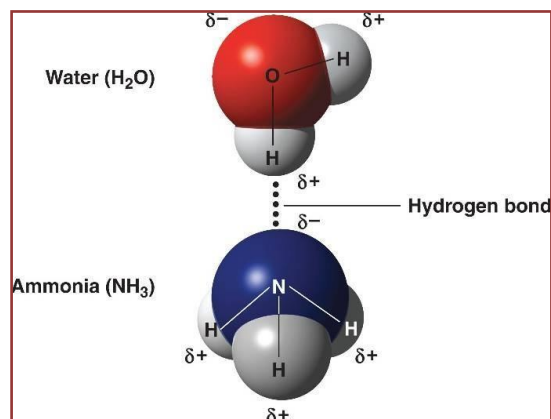
b) Dipole – Dipole Forces

- Present between the molecules possessing permanent dipoles.
- For stationary polar molecules : interaction energy $\propto 1/r^3$
- For rotating polar molecules : interaction energy $\propto 1/r^6$ where, r = distance between polar molecules.



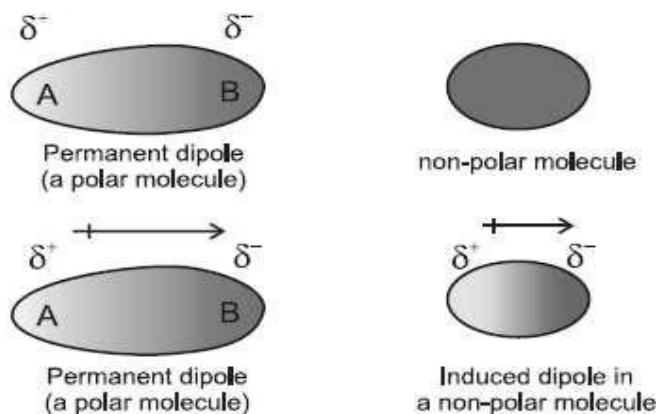
c) Hydrogen – bonding

- A special case of dipole-dipole interaction.
- Exists in the molecules which are highly polar containing N-H, O-H or H-F bonds.
- Energy of H-bond ≈ 10 to 100 kJ mol^{-1} .
- One of the important forces in proteins and nucleic acids.
- It determines the structure and properties of many compounds.
- INTERMOLECULAR HYDROGEN BOND



d) Dipole – Induced Dipole Forces

- Exists between polar molecules having permanent dipole and non-polar molecules.



- Existence of the three states of matter - It is due to the balance between intermolecular forces and the thermal energy of the molecules.
- Predominance of intermolecular interactions
Gas \rightarrow liquid \rightarrow solid
- Predominance of thermal energy
Gas \leftarrow liquid \leftarrow solid

Comparison between gaseous and liquid states

Gaseous State	Liquid State
• Highly compressible	• Not compressible
• Much lower density than solids and liquids	• Denser than gases
• Volume and shape are not fixed	• Volume is fixed but shape is not
• Interactive forces are negligible	• Interactive forces are stronger than those in gaseous state.
• Behaviour of gases is governed by general laws of gases	• No such general laws exist.

3.The Gas Laws

1. Boyle's Law ($p - V$ relationship)

At constant T & n (no. of moles)

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

$PV = \text{Constant}$ OR

$$P_1 V_1 = P_2 V_2$$

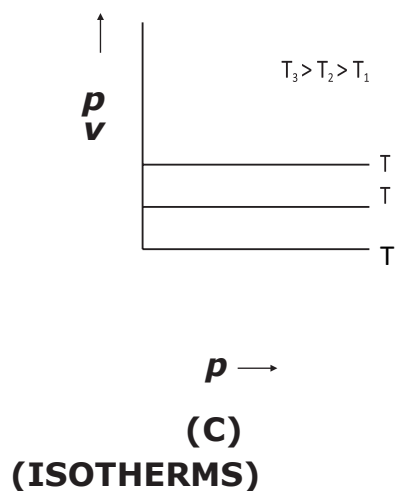
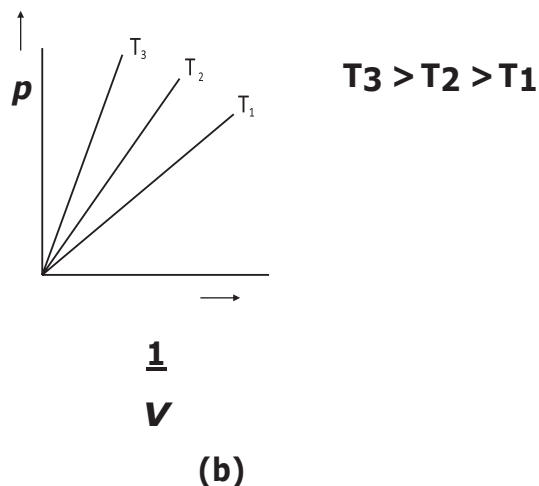
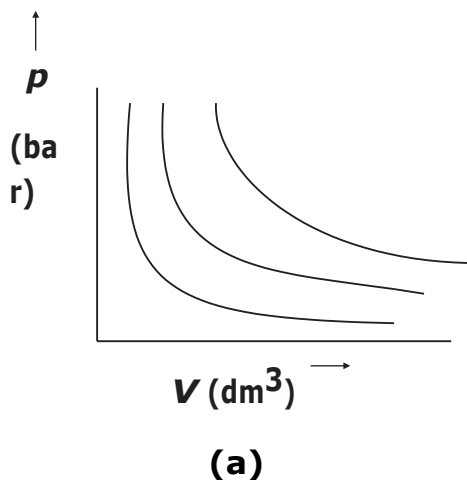
At a constant temperature, the pressure exerted by a fixed mass of a gas is inversely proportional to its volume.

Graphical Representation

Isotherm – line/plot between p & V at constant temperature for a given amount (n) of the gas.

Isobar – line/plot between V and I at constant pressure (p) and n .

Isochore – line/plot between p and I at constant volume (V) & n .



2. **Charles' Law (T-V relationship)**

At constant P and n

$$V \propto T$$

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

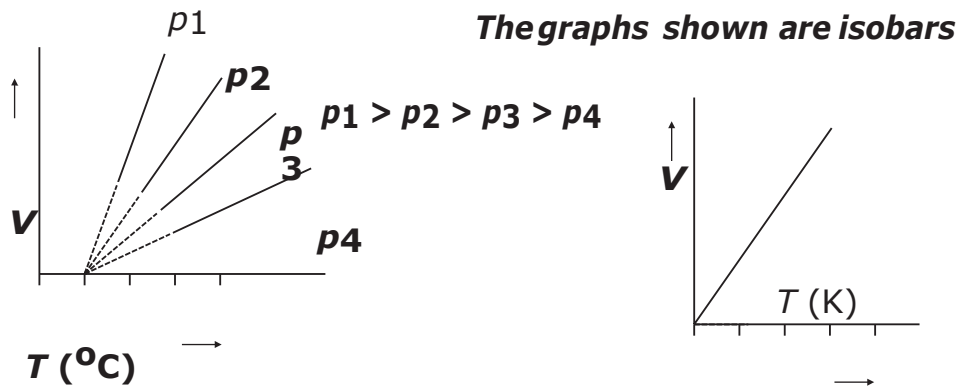
$$\text{i.e. } \boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}} \text{ or } \boxed{\frac{V_2}{V_1} = \frac{T_2}{T_1}}$$

For a fixed mass of a gas, at a constant pressure, the volume of a gas is directly proportional to its absolute temperature.

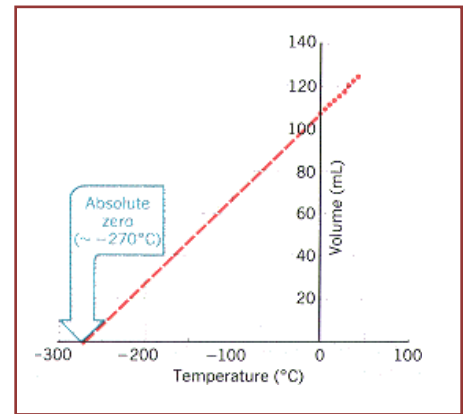
Kelvin Temperature Scale or Absolute Temperature Scale

$$T = (273.15 + t^{\circ}\text{C}) \text{ K}$$

Also, known as thermodynamic scale of temperature.



Charles saw a linear relationship between the volume and temperature of a gas. Extrapolating backwards, he found that the point where a gas would have no volume would be -273 degrees Celsius. Since that's as cold as he thought things could ever get, that originated the idea of **absolute zero**.



Absolute Zero (the lowest possible temperature) – The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume. Absolute Zero is equal to
 - 273.15 °C

$$-273.15^{\circ}\text{C} = 0\text{ K}$$

3. Gay Lussac's Law (p – T relationship)

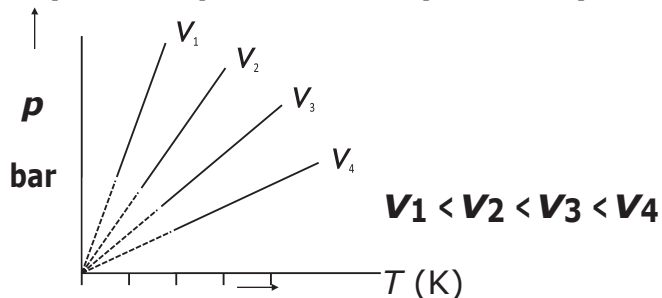
$$p \propto T \quad (V, n \text{ constant})$$

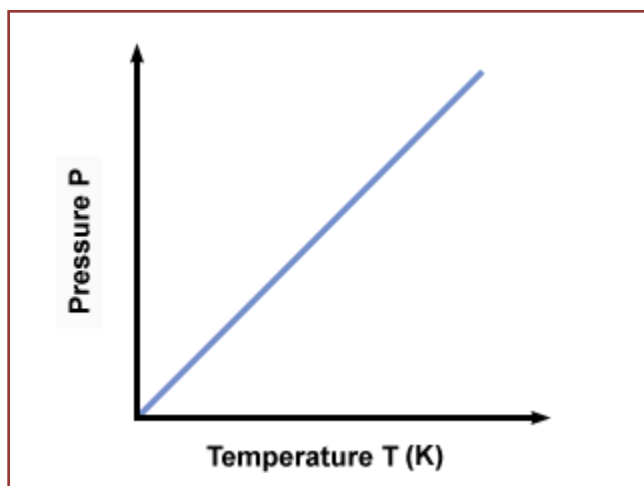
$$\frac{p}{T} = \text{constant}$$

$$T$$

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Graphical representation(isochore)





4. Avogadro's Law (V – n Relationship) : *At constant p and T*

$$V \propto n$$

$$V = kn$$

- This law states that equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules.
- No. of molecules in one mole of a gas = $6.022 \times 10^{23} = N_A$ (Avogadro constant).
- Molar Volume – Volume occupied by one mole of each substance.
- It contains the same number of molecules i.e. N_A .

Molar Volume at different T and P are as follows:

Conditions	Temperature	Pressure	Molar Volume
NTP (Earlier also called STP)	273.15 K	1 atm	22.4 L mol^{-1}
STP	273.15 K	1 bar	22.7 L mol^{-1}
SATP	298.15 K	1 bar	24.8 L mol^{-1}

- STP : Standard Temperature and Pressure
- NTP : Normal Temperature and Pressure
- SATP : Standard Ambient Temperature and Pressure

5. Density relationship

$$n = \frac{m}{M} \quad \begin{matrix} m = \text{mass of the gas} \\ (M = \text{molar mass}) \end{matrix}$$

$$V = k \frac{m}{M}$$

$$M = k \frac{m}{V}$$

$M = kd$

where, d = density of the gas

density of a gas \propto molar mass (M)

Ideal gas equation or Equation of State

Gases can be described in terms of four variables: pressure (P), volume (V), temperature (T), and the amount of gas (n). There are five relationships between pairs of these variables in which two of the variables were allowed to change while the other two were held constant.

$$P \propto n \quad (T \text{ and } V \text{ constant})$$

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

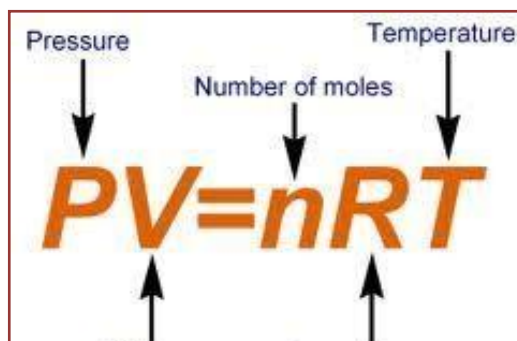
Gay Lussac's law: $P \propto T$ (V and n constant)

Charles' law: $V \propto T$ (P and n constant)

Avogadro's hypothesis: $V \propto n$ (P and T constant)

Each of these relationships is a special case of a more general relationship known as the ideal gas equation.

In this equation, R is a proportionality constant known as the ideal gas constant and T is the absolute temperature. The value of R depends on the units used'



Universal Gas Constant :R is called gas constant. It is same for all gases. $R = 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{-2} \text{ bar L K}^{-1} \text{ mol}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- Ideal gas equation in terms of density (Relationship between molar mass and density of a gas)

$$p = \frac{dRT}{M} \quad (M \text{ is the molar mass, } d \text{ is the density})$$

- Values of the gas constant :

$$0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$82.1 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

- In the C.G.S. units

$$8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}$$

- In S.I. units

$$8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad (10^7 \text{ erg} = 1 \text{ J})$$

- In terms of calories

$$1.987 \text{ calories K}^{-1} \text{ mol}^{-1} \quad (4.184 \text{ J} = 1 \text{ calorie})$$

Dalton's Law of Partial Pressures: Law is valid for non-reacting gases, at constant volume & constant Temperature.

$$P_1 = \frac{n_1 RT}{V}$$

$$P_2 = \frac{n_2 RT}{V}$$

$$P_3 = n_3 \frac{RT}{V}$$

$$\begin{aligned} P_{\text{total}} &= P_1 + P_2 + P_3 \\ &= (n_1 + n_2 + n_3) \frac{RT}{V} \end{aligned}$$

$$\begin{aligned} \frac{P_1}{P_{\text{total}}} &= \left(\frac{n_1}{n_1 + n_2 + n_3} \right) \frac{RTV}{RTV} \\ &= \frac{n_1}{n} = x_1 \end{aligned}$$

Where

$$(n = n_1 + n_2 + n_3)$$

∴

$$P_1 = n_1 P_{\text{total}}$$

- $p_{\text{Total}} = p_1 + p_2 + p_3 + \dots$ (at constant T, V)
where, p_{Total} = Total pressure exerted by the mixture of gases
 p_1, p_2, \dots = partial pressures of gases, 1, 2, ----- res.
- Gases are generally collected over water and therefore are moist.
 $p_{\text{dry gas}} = p_{\text{Total}} - \text{Aqueous Tension}$
- Aqueous Tension : Pressure exerted by saturated water vapour.
- p_{Total} : Total pressure of the moist gas.
- Partial Pressure in terms of mole fraction
 $p_i = x_i p_{\text{total}}$

where, p_i = Partial pressure of the i^{th} gas

x_i = mole fraction of the i^{th} gas.

Different Pressure units and their relation

$$1 \text{ Pa} = 1 \text{ Nm}^{-2} \text{ or}$$

$$1 \text{ kgm}^{-1} \text{ s}^{-2}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$1 \text{ atm} = 101.325 \text{ kPa}$$

$$1 \text{ Torr} = (101325 / 760) \text{ Pa} = 133.32 \text{ Pa}$$

$$1 \text{ mm Hg} = 1 \text{ Torr} = 133.322 \text{ Pa}$$

$$1 \text{ Psi} = 6.894 \text{ kPa}$$

* Psi = Pound per square inch Standard pressure = 1 bar Normal pressure = 1 atm

Kinetic Molecular Theory of Gases : This theory helps us to understand the behavior of gases. This theory provides a microscopic model of gases.

Postulates:

- Gases consist of large number of very small identical particles (atoms or molecules) which are so far apart on the average that the actual volume of the molecules is negligible as compared to the empty space between them.
This explains the high compressibility of gases
- No force of attraction between the particles of a gas.
- Particles, within the container, are in ceaseless random motion during which they collide with each other and with the walls of the container.
- All the collisions are perfectly elastic i.e. total energy of molecules before and after the collision remains same. The energy may, however, be transferred from one molecule to the other on collision.
- Due to the bombardment of the molecules on the walls of the containing vessel, pressure is exerted by the gas on the walls of the containing vessel.
- Particles of the gas move in straight line (i.e. it obeys Newton's first law of motion).
- At any particular time, different particles in the gas have different speeds and hence different kinetic energies.
- Average K.E. of the gas molecules is directly proportional to the absolute temperature.

Ideal gas and real gas

A gas which obeys ideal gas equation, $pV = nRT$ under all conditions of temperature and pressure.

No gas obeys ideal gas equation under all conditions of temperature and pressure.

Real gas

A gas which obey gas laws at low pressure and high temperature. All gases are real gases.

Causes of Deviation from Ideal Behaviour

Assumptions of Kinetic theory of gases which do not hold good in all conditions :

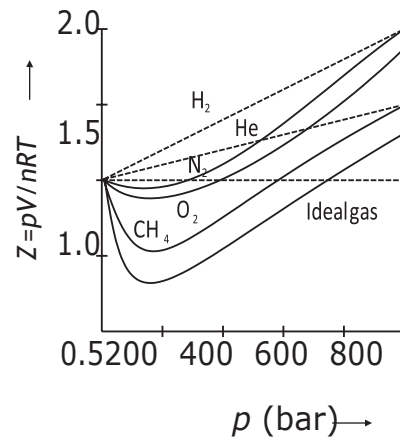
1. The intermolecular force of attraction between gaseous molecules is negligible.
2. The volume occupied by the gas molecules is negligible in comparison to the total volume of the gas.

Compressibility Factor (Z) - Gives the extent to which real gas deviates from ideal behaviour.

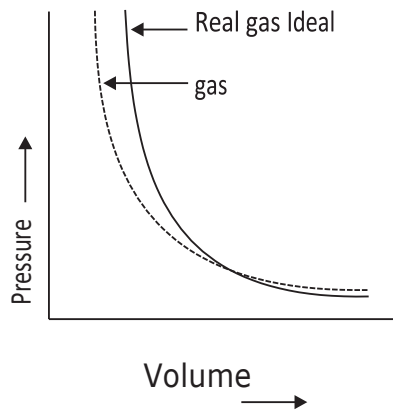
$$Z = \frac{pV}{nRT}$$

- For 1 mole of gas, $Z = \frac{PV}{RT}$
- $Z = 1$ A Gas is ideal ; $pV = nRT$
- $Z = 1$ A Gas is real ; $PV \neq nRT$
- $Z < 1$ A Gas shows -ve deviation and it is more compressible than ideal gas (usually at low pressure).
- $Z > 1$ A Gas shows +ve deviation and it is less compressible than ideal gas (usually at high pressure).
-

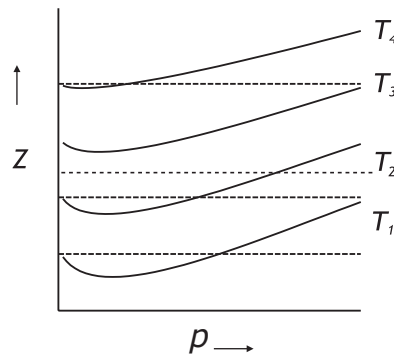
Plot : variation of Z with p for some gases



1. Plot of p vs V for ideal and real gases



The variation of Z with different temperatures $T_4 > T_3 > T_2 > T_1$



The deviation from ideal behavior becomes less and less with increase in temperature.

Boyle's temperature: Temperature at which a real gas obeys ideal gas equation over an appreciable range of pressure.

Compressibility Factor The most useful way of displaying this new law for real molecules is to plot the compressibility factor, Z :

For $n = 1$

$$Z = PV / RT$$

Ideal Gases have $Z=1$

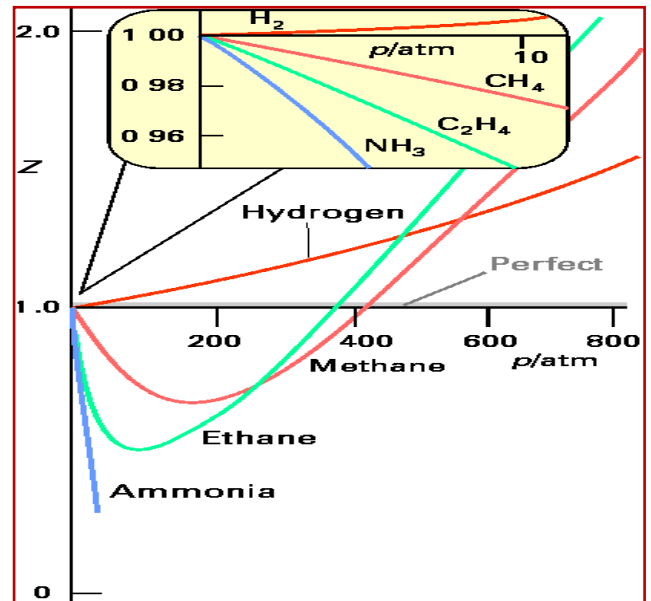
Significance of compressibility factor (Z)

$$Z = \frac{p V_{\text{real}}}{nRT}$$

$$\text{for the ideal gas, } V_{\text{ideal}} = \frac{nRT}{p}$$

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

Z is the ratio of actual volume of a gas to the calculated volume of an equal amount of an ideal gas.



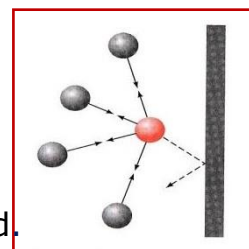
Van der Waal's equation

Volume Correction

- ❖ The actual volume free to move in is less because of particle size.
- ❖ More molecules will have more effect.
- ❖ Corrected volume $V' = V - nb$
- ❖ "b" is a constant that differs for each gas.

Pressure Correction

- ❖ Because the molecules are attracted to each other, the pressure on the container will be less than ideal.
- ❖ Pressure depends on the number of molecules per liter.
- ❖ Since two molecules interact, the effect must be squared.



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

Significance of van der Waals constants

- *a* : It is a measure of magnitude of intermolecular attractive forces within the gas.
 - Greater the value of 'a', stronger are the intermolecular forces of attraction and gas can be liquefied more easily.
- *b* : It is a measure of the effective size of the gas molecules. It is related to incompressible volume of the molecules

NOTE: "a" and "b" are determined by experiment.

"a" and "b" are different for each gas, bigger molecules have larger "b" "a" depends on both size and polarity.

Value of the Gas Constant

The value of the gas constant 'R' depends on the units used for pressure, volume and temperature.

- $R = 0.0821 \text{ liter}\cdot\text{atm/mol}\cdot\text{K}$
- $R = 8.3145 \text{ J/mol}\cdot\text{K}$
- $R = 8.2057 \text{ m}^3\cdot\text{atm/mol}\cdot\text{K}$
- $R = 62.3637 \text{ L}\cdot\text{Torr/mol}\cdot\text{K}$ or $\text{L}\cdot\text{mmHg/mol}\cdot\text{K}$

Also refer to the given video link:

https://youtu.be/Qw_Jy1Ydfrk