REAL GAS

1. Introduction :

An ideal gas is a hypothetical gas whose pressure, volume and temperature behaviour is completely described by the ideal gas equation. Actually no gas is ideal or perfect in nature. All gases are real gases.

Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure.

Real gases deviates from ideal behaviour because of mainly two assumptions of "Kinetic theory of gases".

(i) The volume of gas particle is negligible compared to volume of container (while the real gas particle may have some significant volume).

(ii) There is no interaction between gaseous particles (while attraction forces exist between real gas particles).
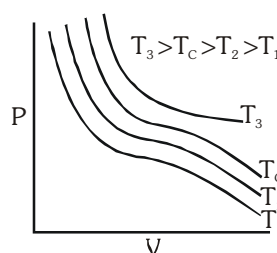
1.1 Comparision between Real and Ideal gas :
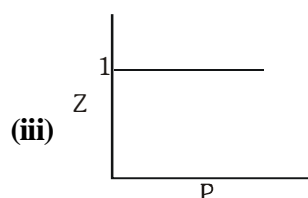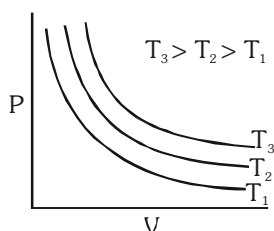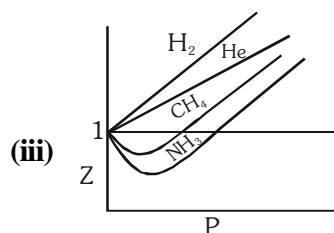
IDEAL GAS	REAL GAS
(i) $PV = nRT$	**(i)** $PV \neq nRT$
	$\Rightarrow$ If $PV > nRT$ (Gas is less compressible than ideal gas).
	If $PV < nRT$ (Gas is more compressible than ideal gas).
(ii) No liquifaction is possible.	**(ii)** Liquifaction is possible below a certain temperature.

$T_3 > T_2 > T_1$

$T_3 > T_C > T_2 > T_1$

$\Rightarrow$ Follow critical phenomena and can not liquefy above T_C.

(iii)

(iii)

(iv) No interaction force is present between gas particles.

(iv) Interaction force exist between gas particles which vary depending upon conditions.

(v) Volume of gas particles is negligible w.r.t. volume of container.

(v) Volume of gas particles has significant value and can not be neglected normally w.r.t. volume of container.

1.2 VANDER WAAL EQUATION OF REAL GASES

The ideal gas equation does not consider the effect of attractive forces and molecular volume.

Van der Waal corrected the ideal gas equation by taking the effect of

(a) Molecular volume

(b) Molecular attraction

(A) **Volume correction :**

In the ideal gas equation, $P_iV_i = nRT$, V_i represents the ideal volume where the molecules can move freely. In real gases, a part of the total volume is occupied by the gas molecules. Hence the free volume V_i is the total volume V minus the volume occupied by the gas molecules.

Real volume of gas = Actual volume of container – volume occupied by molecules in motion.

V_i = V – nb for n mole of gas

Where b is termed the 'excluded volume' or 'co-volume' per mole.

It is constant and characteristic for each gas.

$b = 4 \times$ volumes of one molecules $\times N_A$

Illustration of excluded volume

(B) **Pressure correction :**

In order to take account the effect of intermolecular forces of attraction, let us consider a molecule A in the midst of the vessel.

This molecule is surrounded by other molecules in a symmetrical manner and is being attracted uniformly on all sides by the neighbouring molecules with the result that this molecule on the whole experiences no net force of attraction.
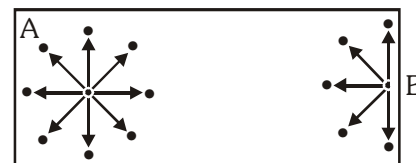

Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only in one side of the vessel, i.e. towards its centre, with the result of that, this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no force of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas.

Van der Waals noted that the total force of attraction on any molecule about to hit a wall is proportional to the concentration of neighbouring molecules, n/V. However, the number of molecules about to hit the wall per unit wall area is also proportional to the concentration n/V. Therefore, the force per unit wall area, or pressure, is reduced from that assumed in the ideal gas wall by a factor proportional to n^2/V^2. Letting a be the proportionality constant, we can write

$$P \text{ (actual)} = P(\text{ideal}) - \frac{an^2}{V^2} \quad \text{or} \quad P \text{ (ideal)} = P(\text{actual}) + \frac{an^2}{V^2}$$

'a' is a constant which depends upon the nature of the gas,

Combining the two corrections,

for 1 mole of gas

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

and for n mole of gas $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

The constants 'a' and 'b' :

Van der Waals constant for attraction 'a' and volume 'b' are characteristic constants for a given gas.

(i)   The 'a' values for a given gas are measure of intermolecular forces of attraction. More are the intermolecular forces of attraction, more will be the value of a.

(ii)   The gas having higher value of 'a' can be liquefied easily and therefore H_2 and He are not liquefied easily.

(iii)   Unit of 'a' is atm lit^2 $mole^{-2}$ or dyne cm^4 $mole^{-2}$ or Nm^4mol^{-2}

(iv)   Unit of 'b' is lit $mole^{-1}$ or cm^3 $mole^{-1}$ or m^3 mol^{-1}

❑   **The van der Walls constants for some common gases**

| Gas	a (atmL^{2}mol^{-2})	b (L mol^{-1})
Ammonia	4.17	0.0371
Argon	1.35	0.0322
Carbon dioxide	3.59	0.0427
Carbon monoxide	1.49	0.0399
Chlorine	6.49	0.0562
Ethane	5.49	0.0638
Ethanol	2.56	0.087
Ethylene	4.47	0.0571
Helium	0.034	0.0237
Hydrogen	0.024	0.0266
Hydrogen chloride	3.67	0.0408
Hydrogen bromide	4.45	0.0433
Methane	2.25	0.0428
Neon	0.21	0.0171
Nitric oxide	1.34	0.0279
Nitrogen	1.39	0.0319
Oxygen	1.36	0.0318
Sulphur dioxide	3.71	0.0564
Water	5.44	0.0305

1.3   COMPRESSIBILITY FACTOR (Z) :

The extent to which a real gas departs from the ideal behaviour may be expressed in terms of compressibility factor (Z),

$$Z = \frac{(PV)_{real}}{(PV)_{ideal}} = \frac{V_m}{V_{m(ideal)}} = \frac{PV_m}{RT} \quad [V_m = \text{molar volume}]$$

1.4   Plots of compressibility factor vs pressure :

(i)   For an ideal gas Z = 1 and is independent of temperature and pressure.

(ii)   Exceptional behaviour of H_2 and He :

For these gases Z > 1 at 0ºC.

(iii)   Effect of pressure :

At very low P, $PV_m \approx RT$ i.e. Z ≈ 1

At low P, $PV_m < RT$ i.e. Z < 1 $\Rightarrow$ attractive forces dominant

At high P, $PV_m > RT$ i.e. Z > 1 $\Rightarrow$ repulsive forces dominant

(iv)   For the gases which are easily liquefied (e.g. CO_2) Z dips sharply below the ideal line in the low pressure region.

(v)   Effect of temperature : An increase in temperature shows a decrease in deviation from ideal behaviours, Z approaches unity with increase in temperature.
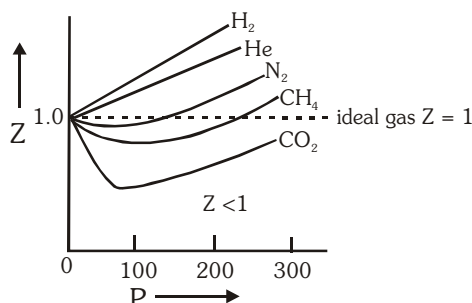
1.5   Verification of compressibility factor using Van Der Waal's equation :

Variation of Z with P for real gas at any temperature is given by following graph.
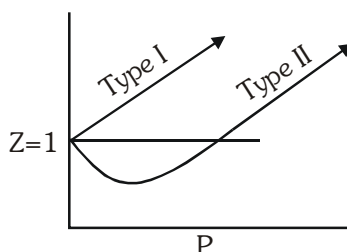
Van der waal equation :

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

(i)   **At low pressure and constant temperature**

At low pressure V_m will be high hence b can be neglected in comparision to V_m. But $\dfrac{a}{V_m^2}$ can't be neglected as pressure is low. Thus equation would be

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

$$PV_m + \frac{a}{V_m} = RT$$

$$\frac{PV_m}{RT} + \frac{a}{V_m RT} = 1$$

$$\mathbf{Z = 1 - \frac{a}{V_m RT}} \quad \Rightarrow \quad Z < 1$$

Substituting $V_m = \dfrac{RT}{P}$ in above equation ; $\quad \mathbf{Z = 1 - \dfrac{aP}{R^2 T^2}}$

At low pressure, real gas is easily compressible as compared to an ideal gas.

(ii)   **At high pressure and constant temperature**

At high pressure the V_m will be low. So b can't be neglected in comparision to V_m but $\dfrac{a}{V_m^2}$ can be neglected as compared to much higher values of P.

Then van der Waals' equation will be

$$P(V_m - b) = RT$$
$$PV_m - Pb = RT$$

$$\frac{PV_m}{RT} = \frac{Pb}{RT} + 1$$

$$\mathbf{Z = \frac{Pb}{RT} + 1} \Rightarrow \quad (Z > 1)$$

At high pressure, gas is more difficult to compress as compared to an ideal gas.

(iii)   **At low pressure and very high temperature.**

V_m will be very large, hence 'b' can be neglected and $\dfrac{a}{V_m^2}$ can also be neglected as V_m is very large.

$PV_m = RT$ (ideal gas condition)

(iv)   For H_2 or He $a \simeq 0$ because molecules are smaller in size or vander Waal's forces will be very weak.

$$P(V_m - b) = RT$$

So $\mathbf{Z = 1 + \dfrac{Pb}{RT}}$

This explains type I plot.

Ex.1. Calculate the pressure exerted by 5 mole of CO_2 in one litre vessel at 47°C using van der waal's equation. Also report the pressure of gas if it behaves ideal in nature.

Given that a = 3.592 atm lt^2 mol^{-2}, b = 0.0427 L/mol. Also, if the volume occupied by CO_2 molecules is negligible, then calculate the pressure exerted by one mole of CO_2 gas at 273 K.

Sol. Vander waal's equation

$$\left[p + \frac{n^2 a}{V^2}\right][V - nb] = nRT$$

n_{CO_2} = 5, V = 1 litre, T = 320 K, a = 3.592, b = 0.0427

∴　$\left[P + 25 \times \dfrac{3.592}{1}\right][1 - 5 \times 0.0427] = 5 \times 0.0821 \times 320$

∴　P = 77.218 atm

For ideal behaviour of gas, PV = nRT

∴　P × 1 = 5 × 0.0821 × 320

∴　P = 131.36 atm

For one mole $\left[P + \dfrac{a}{V^2}\right][V - b] = RT$

∴　$P = \dfrac{RT}{V} - \dfrac{a}{V^2}$

∴　$P = \dfrac{0.0821 \times 273}{22.4} - \dfrac{3.592}{(22.4)^2}$

∴　P = 0.9922 atm

The volume occupied by 1 mole at 273 K is 22.4 litre if b is negligible.

Ex.2 One mole of CCl_4 vapours at 77°C occupies a volume of 35.0 L. If vander waal's constants are a = 20.39 L^2 atm mol^{-2} and b = 0.1383 L mol^{-1}, calculate compressibility factor Z under,

(a) low pressure region.　　　　　　　　　(b) high pressure region.

Sol. (a)　Under low pressure region, V is high

∴　$(V - b) \approx V$

$$\left(P + \frac{a}{V^2}\right)V = RT$$

$$PV + \frac{a}{V} = RT$$

$$\frac{PV}{RT} + \frac{a}{RTV} = 1$$

$$Z = \frac{PV}{RT} = \left(1 - \frac{a}{RTV}\right) = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

(b)　Under high pressure region, P is high,

$$\left(P + \frac{a}{V^2}\right) \approx P$$

∴　P (V − b) = RT

PV − Pb = RT

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$\therefore \quad Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT} \qquad\qquad \left(\because \frac{PV}{RT} = 1, \text{ or } \frac{P}{RT} = \frac{1}{V} \right)$$

$$Z = 1 + \frac{b}{V} = 1 + \frac{0.1383}{35} = 1 + 0.004 = 1.004$$

Ex.3 One way of writing the equation of state for real gases is $PV = RT \left[1 + \frac{B}{V} + ... \right]$ where B is a constant. Derive an approximate expression for B in terms of van der Waal's constants a and b.

Sol. According to van der Waal's equation

$$\left[P + \frac{a}{V^2} \right] [V - b] = RT \text{ or } \quad P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

Multiply by V, then

$$PV = \frac{RTV}{(V-b)} - \frac{a}{V} \qquad \text{or} \qquad PV = RT \left[\frac{V}{V-b} - \frac{a}{VRT} \right]$$

$$\text{or} \quad PV = RT \left[\left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{VRT} \right]$$

$$\because \quad \left[1 - \frac{b}{V} \right]^{-1} = 1 + \frac{b}{V} + \left(\frac{b}{V} \right)^2 + ...$$

$$\therefore \quad PV = RT \left[1 + \frac{b}{V} + ... - \frac{a}{VRT} \right]$$

$$PV = RT \left[1 + \left(b - \frac{a}{RT} \right) . \frac{1}{V} + ... \right]$$

$$\therefore \quad B = b - \frac{a}{RT}$$

2. BOYLE TEMPERATURE :

(i)   It is temperature at which a real gas behave ideally in a wide range of pressure.

(ii)   (a)   Tamperature < Boyle temperature

Z < 1, low pressure range

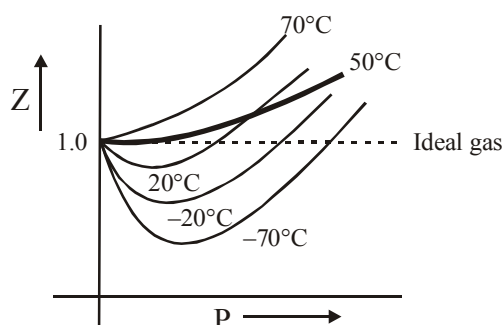Z > 1, high pressure range

(b)   Temperature = Boyle temperature

Z = 1, low pressure range

Z > 1, high pressure range

(c)   At temperature > Boyle temperature

Z > 1, at all pressure

(d) $T \to \infty, Z \to 1$

On increasing the temperature, the thermal energy increases and simultaneously the attractive forces decreases. Hence a temperature comes at which the thermal energy become too high that it balances the effect of attraction and gas molecules becomes independent.

If at Boyle temperature, pressure is increased, molecules come more closer. Due to repulsive force, Z becomes greater that 1.

2.1 CALCULATION OF T_B :

(i) $PV_m = RT = \left(1 + \dfrac{B}{V_m} + \underbrace{\dfrac{C}{V_m^2}}_{\text{negligible}} + ... \right)$ at low pressure.

At $T = T_B$, the second initial coefficient should be 0

   $B = 0$

   or $b - \dfrac{a}{RT_B} = 0$

   $\therefore$ $\boxed{T_B = \dfrac{a}{Rb}}$

(ii)   Calculus method :

At Boyle temperature, $\left(\dfrac{\partial Z}{\partial P} \right)_T = 0$ at low pressure.

Ex.4 Derive the expresion for compresibility factor of a vanderwaal gas at Boyle temperature.

Solution : $Z = \dfrac{V_m}{V_m - b} - \dfrac{a}{V_m - RT}$

At Boyle temperature,

$Z = \dfrac{V_m}{V_m - b} - \dfrac{a}{V_m R \times \dfrac{a}{Rb}}$

$Z = \dfrac{V_m}{V_m - b} - \dfrac{b}{V_m}$

$Z = \dfrac{V_m^2 - V_m b + b^2}{V_m (V_m - b)}$

$Z = 1 + \dfrac{b^2}{V_m (V_m - b)}$

Ex.5 Calculate the volume occupied by 2 moles of a vanderwall gas at 5 atm 800 K.

Given : a = 4.0 atm $\ell^2\,mol^{-2}$, b = 0.0625 $\ell\,mol^{-1}$, R = 0.08 ℓ-atm/K-mol

Solution : $T_B = \dfrac{a}{Rb} = 800K$

Gas behave ideally at given condition.

PV = nRT

$5 \times V = 2 \times 0.08 \times 800$

V = 25.6 litre

3. LIQUEFACTION OF GASES AND CRITICAL POINTS

The phenomenon of converting a gas into liquid is known as liquefaction. The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that they exist in liquid state. A gas can be liquefied by :

(a) **Increasing pressure :** An increase in pressure results decrease in intermolecular distance.

(b) **Decreasing temperature :** A decrease in temperature results decrease in kinetic energy of molecules.

Note : Due to absence of intermolecular forces, ideal gases can never be liquified.

3.1 Andrews Isotherms :

The essential conditions for liquefaction of gases were discovered by Andrews (1869) as a result of his study of P–V–T relationship for CO_2. The types of isotherms are shown in figure.
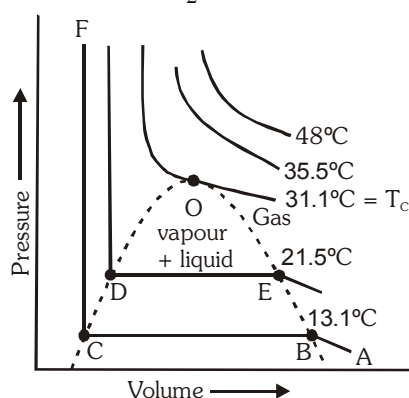

Fig : Isotherms for carbon dioxide

Observations from figure :

(a) **At low temperatures :** For the curve ABCF, as the pressure increases, volume of the curve decreases (curve A to B). At point B, at constant pressure, liquefaction commences and the volume decreases rapidly (because gas is converted to liquid with higher density). At point C, liquefaction is complete. The line CF represents the variation of V with P of the liquid state. The steepness of the line CF indicates that the liquid cannot be easily compressed. Thus AB, represent gaseous state, BC represent liquid and vapour in equilibrium and CF represent liquid state.

The pressure corresponding to the line BC is vapour pressure of the liquid at that temperature.

(b)   **At lower temperatures** : Similar type of curve as in case (A) is obtained but the width of the horizontal portion is reduced. The pressure corresponding to this portion is higher than at lower temperatures.

(c)   **At high temperatures** : (say 48°C), the isotherms are like those of ideal gas. Gas does not liquify, even at very high pressure.

(d)   **At temperature (31.1°C)** : The horizontal portion is reduced to a point.

The isotherm at T_C is called **critical isotherm**.

At point O, $\dfrac{dP}{dV} = 0$.

The point O is called the **point of inflection**.

3.2   Critical parameters or critical constants :

Critical temperature (T_C) : The temperature above which a system can never be liquefied by the application of pressure alone i.e. the temperature above which a liquid cannot exit is called the critical temperature T_C.

Critical pressure (P_C) :The minimum pressure required to liquefy the system at the temperature T_C is called the critical pressure P_C.

Critical volume (V_C) :The volume occupied by one mole of the system at critical temperature, T_C and critical pressure, P_C is called the critical volume (V_C) of the gas.

3.3   Determination of value of P_C, V_C and T_C :

The Vander waal's equation is

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

or $V_m^3 - \left(b + \dfrac{RT}{P}\right)V_m^2 + \dfrac{a}{P}V_m - \dfrac{ab}{P} = 0$ .... (1)

This equation has three roots in V_m for given values of a, b, P and T. It is found that either all the three roots are real or one is real and the other two are imaginary.

At temperature lower than T_C , the isotherm exhibits a maximum and a minimum for certain values of pressures, the equation gives three roots of volume e.g., V_1, V_2 and V_3 at pressure P_1. On increasing the temperature, the three roots become closer to each other and ultimately at critical temperature, they become identical. Thus, the cubic equation V_m can be written as
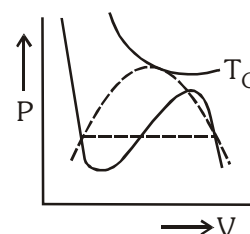
$(V_m - V')(V_m - V'')(V_m - V''') = 0$

At the critical point $V' = V'' = V''' = V_C$

∴   the equation becomes,

$(V_m - V_C)^3 = 0$

or $V_m^3 - V_C^3 - 3V_C V_m^2 + 3 V_C^2 V_m = 0$ .....(2)

By comparing the coefficients in eq.(1) and eq(2)

$$3V_C = b + \frac{RT_C}{P_C}, \quad 3V_C^2 = \frac{a}{P_C}, \quad V_C^3 = \frac{ab}{P_C}$$

By solving, $V_C = 3b$, $P_C = \frac{a}{27b^2}$ and $T_C = \frac{8a}{27Rb}$

- The value of critical compressibility factor in terms of vander wall's constants is given by

$$Z = \frac{P_C V_C}{RT_C} = \frac{\frac{a}{27b^2} \times 3b}{R \times \frac{8b}{27Rb}} = \frac{3}{8} = 0.375$$

If we compare the value of $\frac{P_C V_C}{RT_C} = 0.375$, with the experimental values, it has been found that the agreement is very poor.

Critical constants of gases

Gas	P_C (atm)	$V_{m,c}$ (cm^{3}mol^{-1})	T_C (K)
He	2.26	57.9	5.2
Ne	26.9	41.7	44.4
Ar	48.1	75.2	150.7
Xe	58.0	119.0	289.7
H_2	12.8	65.5	33.3
O_2	50.1	78.2	154.8
N_2	33.5	90.1	126.2
CO_2	72.8	94.0	304.2
H_2O	218.0	55.6	647.3
NH_3	111.5	72.5	405.0
CH_4	45.6	98.7	190.6
C_2H_6	48.2	148.0	305.4

Ex.6 The critical temperature and pressure of CO_2 gas are 304.2 K and 72.9 atm respectively. What is the radius of CO_2 molecule assuming it to behave as vander Waal's gas ?

Sol. $T_C = 304.2$ K $P_C = 72.9$ atm

$$T_C = \frac{8a}{27Rb} \qquad P_C = \frac{a}{27b^2}$$

$$\therefore \quad \frac{T_C}{P_C} = \frac{\frac{8a}{27Rb}}{\frac{a}{27b^2}} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R} \quad \text{or} \quad b = \frac{RT_C}{8P_C} = \frac{1}{8} \times \frac{0.082 \times 304.2}{72.9} = 0.04277 \text{ lit mol}^{-1}$$

$$b = 4 N_A \times \frac{4}{3}\pi r^3 = 42.77 \text{ cm}^3$$

or $r = (4.24)^{1/3} \times 10^{-8}$ cm $= 1.62 \times 10^{-8}$ cm

$\therefore$ radius of CO_2 molecule $= 1.62$ Å

4.   THE LIQUID STATE

Liquid state is intermediate between gaseous and solid states. The liquids posses fluidity like gases but incompressibility like solids.

The behaviour of liquids explained above gives some characteristic properties to the liquids such as definite shape, incompressibilty, diffusion, fluidity (or viscosity), evaporation (or vapour pressure), surface tension, etc.

The following general characteristics are exhibited by liquids :

(i)   Shape :

Liquids have no shape of their own but assume the shape of the container in which they are kept. No doubt, liquids are mobile but they do not expand like gases as to fill up all the space offered to them but remain confined to the lower part of the container.

(ii)   Volume :

Liquids have definite volume as the molecules of a liquid are closely packed and the cohesive forces are strong.

(iii)   Density :

As the molecules in liquids are closely packed, the densities of liquids are much higher than in gaseous state. For example, density of water at 100° C and 1 atmospheric pressure is 0.958 g mL^{-1} while that of water vapour under similar conditions as calculated from ideal gas law $\left(d = \dfrac{MP}{RT} \right)$ is 0.000588 g mL^{-1}.

(iv)   Compressibility :

The molecules in a liquid are held in such close contact by their mutual attractive forces (cohesive forces) that the volume of any liquid decreases very little on increasing pressure. Thus, liquids are relatively incompressible compared to gases.
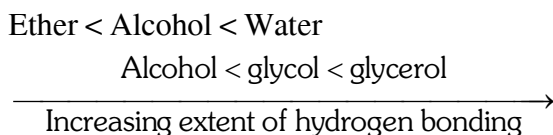
(v)   Diffusion :

When two miscible liquids are put together, there is slow mixing as the molecules of one liquid move into the other liquid. As the space available for movement of molecules in liquids is much less and their velocities are small. Liquids diffuse slowly in comparison to gases.

(vi)   Evaporation :

The process of changes of liquid into vapour state on standing is termed **evaporation**. Evaporation may be explained in terms of motion of molecules. At any given temperature all the motion of molecules do not possess the same kinetic energy (average kinetic energy is, however same). Some molecules move slowly, some at intermediate rates and some move very fast. A rapidly moving molecule near the surface of the liquid may possess sufficient kinetic energy to overcome the attraction of its neighbours and escape. Evaporation depends on the following factor.

(a) Nature of the liquid : The evaporation depends on the strength of intermolecular forces (cohesive forces). The liquids having low intermolecular forces evaporate faster in comparison to the liquids having high intermolecular forces. For example, ether evaporates more quickly than alcohol, and alcohol evaporates more quickly than water, as the intermolecular forces in these liquids are in the order :

Ether < Alcohol < Water

Alcohol < glycol < glycerol

$\xrightarrow{\hspace{4cm}}$
Increasing extent of hydrogen bonding

(b) Surface area : Evaporation is a surface phenomenon. Larger the surface area, greater is the oportunity of the molecules to escape. Thus, rate of evaporation increases with increase of surface area.

(c) Temperature : Rate of evaporation increases with the increase of temperature as the kinetic energy of the molecules increases with the rise of temperature.

(d) Flow of air current over the surface : Flow of air helps the molecules to go away from the surface of liquid and, therefore, increases the evaporation of liquid in open vessel.

(vii) Heat of vaporisation :

The quantity of heat required to evaporate a unit mass of a given liquid at constant temperature is known as heat of vaporisation. The heat of vaporisation depends on the strength of the intermolecular forces with in the liquid. The value of heat of vaporisation generally decreases with increase in temperature. It becomes zero at the critical temperature. When the vapour is condensed into a liquid, heat is evolved. This is called **heat of condensation**. It is numerically equal to the heat of vaporisation at the same temperature.

(viii) Vapour pressure :
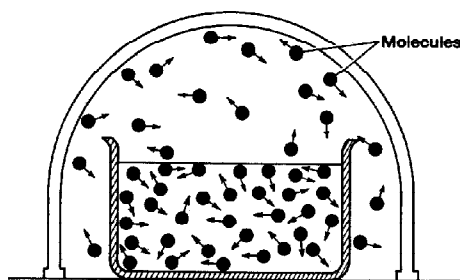
When the space above the liquids is closed, the molecules cannot escape into open but strike the walls of the container, rebound and may strike the surface of the liquid, where they may be trapped. The return of the molecules from the vapour state of the liquid state is known as **condensation**. As evaporation proceeds, the number of molecules in the vapour state increases and, in turn, the rate of condensation increases.

The rate of condensation soon becomes equal to the rate of the evaporation, i.e., the vapour in the closed container is in equilibrium with the liquid.
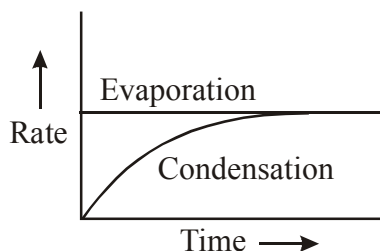
At equilibrium the concentration of molecules in the vapour phase remains unchanged. The pressure exerted by the vapour in equilibrium with liquid, at a given temperature, is called the **vapour pressure**. Mathematically, it may be given by ideal gas equation, assuming ideal behaviour.

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

where C is the concentration of vapour, in mol/litre.

Since the rate of evaporation increases and rate of condensation decreases with increasing temperature, vapour pressure of liquids always increases as temperature increases. At any given temperature, the vapour pressures of different liquids are different because their cohesive forces are different. Easily vaporisable liquids are called **volatile liquids** and they have relatively high vapour pressure. Vapour pressure values (in mm of Hg) for water, alcohol and ether at different temperatures are given in the following table :

| Substance	Temperatures				
	0° C	20° C	40° C	80° C	100° C
Water	4.6	17.5	55.0	355.5	760.3
Ethyl alcohol	12.2	43.9	812.6	1693.3	
Diethyl ether	185.3	442.2	921.1	2993.6	4859.4

The vapour pressure of a given liquid at two differnt temperatures can be compared with the help of **Clausius-Clapeyron equation.**

$$\log \times \frac{P_2}{P_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Where ΔH is the latent heat of vaporisation and R is the molar gas constant.

(ix)   Boiling point :

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the **boiling point** of the liquid. When a liquid is heated under a given applied pressure, bubbles of vapour begin to form below the surface of the liquid. They rise to the surface and burst releasing the vapour into the air. This process is called **boiling**. The normal boiling point is the temperature at which the vapour pressure of a liquid is equal to exactly one atmospheric pressure (760 mm of Hg). Figure shows that normal boiling points of di-ethyl ether, ethyl alcohol and water are 34.6° C, 78.5° C and 100° C respectively.
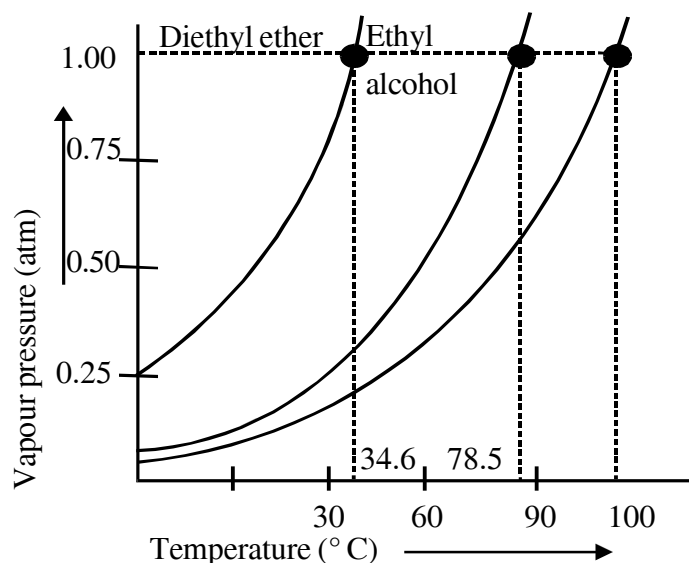
The temperature of the liquid remains constant until all the liquid has been vaporised. Heat must be added to the boiling liquid to maintian the temperature because in the boiling process, the high energy molecules are lost by the liquid.

The boiling point of a liquid changes with the change in external pressure. A liquid may boil at temperatures higher than normal under external pressures greater than one atmoshpere; conversely, the boiling point of a liquid may be lowered than normal below one atmosphere. Thus, at high altitudes where the atmospheric pressure is less than 760 mm, water boils at temperatures below its normal boiling water.

Boiling and evaporation are similar processes (conversion of liquid into vapour) but differ in following respects :

(a)   Evaporation takes place spontaneously at all temperatures but boiling occurs at a particular temperature at which the vapour prssure is equal to the atmospheric pressure.

(b)   Evaporation is surface phenomenon. It occurs only at the surface of the liquid whereas boiling involves formation of bubbles below the surface of the liquid.

Note. : Boiling does not occur when liquid is heated in a closed vessel.

(x)   Freezing point :

When a liquid is cooled, the kinetic energy of the molecules goes on decreasing. A stage comes when the intermolecular forces become stronger and the rotational motion is siezed. At this stage, the formation of solid begins and the liquid is seen to freeze out. The point (temperature) at which the vapour pressure of solid and liquid forms of a substance become equal is termed as **freezing point.**

Normal freezing point of a liquid is the temperature at which is liquid and solid forms are in equilibrium with each other under a pressure of one atmosphere. The freezing point of a liquid is the same as the melting point of its solid. The amount of heat that must be removed to freeze a unit mass of the liquid at the freezing point, which is called the **heat of fusion.**

The freezing point of a liquid is affected by the change of external pressure. With increased external pressure, the freezing point of some liquids rises while of others falls. But the effect of pressures is very small because solid as well as liquid are almost incompressible.

(xi)   Surface tension :

It is the property of liquids caused by the intermolecular attractive forces. A molecule within the bulk of the liquid is attracted equally in all the directions by the neighbouring molecules. The resultant force on any one molecule in the centre of the liquid is, therefore, zero. However, the molecules on the surface of the liquid are attracted only inward and sideways. This unbalanced molecular attraction pulls some of the molecules into the bulk of the liquid, i.e., are pulled inward and the surface area is minimized.
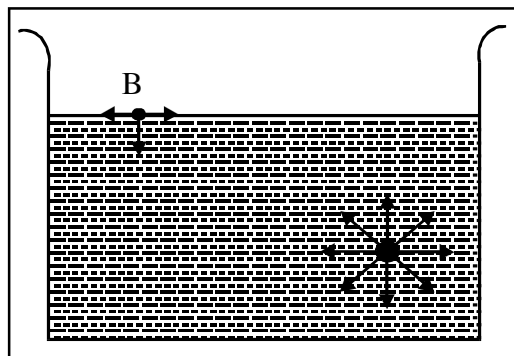
Surface tension is a measure of this inward force on the surface of the liquid. It acts downwards perpendicular to the plane of the surface. The unit of surface tension is dyne cm^{-1}. Surface tension is, thus, defined **as the force acting on the surface at right angles to any line of unit length.**

As the intermolecular forces of attraction decreases with the rise of temperature, the surface tension of a liquid, thus, decreases with increase in temperature. Similarly, addition of chemicals to a liquid may reduce its surface tension. For example, addition of chemicals like soaps, detergents, alcohol, camphor, etc., lowers the surface tension of water.

Many common phenomenon can be explained with the help of surface tension. Some are described here :

(a)   Small droplets are spherical in shape :

The surface tension acting on the surface of the liquid tries to minimise the surface area of a given mass of a liquid. It is known that for a given volume, a sphere has the minimum surface area. On account of this, drops of liquids acquire a spherical shape.

(b)   Insects can walk on the surface of water :

Many insects can walk on the surface of water without drowing. This is due to the existence of surface tension. The surface tension makes the water surface to behave like an elastic membrane and prevents the insects from drowning.

(c)   Cleaing action of soap and detergents :

Soap and detergent solutions due to their lower surface tensions penetrate into the fibre and surround the greasy substances and wash them away.

(d)   Capillary action :

The tendency of a liquid to rise into narrow pores and tiny openings is called capillary action. The liquids rise in the capillary tubes due to the surface tension.

(e)   Surface Energy :

The work required to be done to increase or extend surface area by unit area is called surface energy. The units of surface energy are, therfore, erg per sq. cm (or joule per sq. metre, i.e. J m^{-2} in S.I. system)

(xii)   Viscosity :

It 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. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.

When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increase as the distance of layers from the fixed layer increases. This 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 we choose any layer in the flowing liquid , the layer above it accelerates its flow and the layer below this retards its flow.

Gradation of velocity in the laminar flow
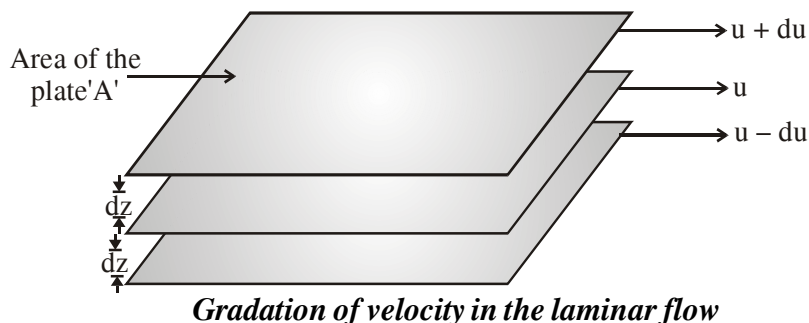
If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount $\dfrac{du}{dz}$. A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

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

$F \propto A \dfrac{du}{dz}$ (where, $\dfrac{du}{dz}$ is velocity gradient; the change in velocity with distance)

$F \propto A. \dfrac{du}{dz} \Rightarrow F = \eta A \dfrac{du}{dz}$

'η' is proportionality 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 'h' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre ($N\ s\ m^{-2}$) = pascal second ($Pa\ s = 1kg\ m^{-1}s^{-1}$). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

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

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. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top.

Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

SOME MISCELLANEOUS SOLVED EXAMPLES

1. Calculate the temperature of gas if it obeys vander waal's equation from the following data. A flask of 25 litre contains 10 moles of a gas under 50 atm. Given a = 5.46 atm litre^{-2} and b = 0.31 litre mol^{-1}.

Sol. Given , P = 50 atm, V = 25 litre, n = 10

a = 5.46 atm litre^{2}mol^{-2}, b = 0.031 litre mol^{-1}

Now vander waal's equation for n mole of gas.

$$\left[P + \frac{n^2a}{V^2}\right] [V - nb] = nRT$$

$$\left[50 + \frac{100 \times 5.46}{625}\right] [25 - 10 \times 0.031] = 10 \times 0.0821 \times T$$

$\therefore$ T = 1529.93 K = 1256.93ºC

2. The molar volume of He at 10.135 MPa and 273 K is 0.011075 of its molar volume of 101.325 kPa at 273K. Calculate the radius of helium atom. The gas is assumed to show real gas nature. Neglect the value of a for He.

Sol. For real gas : $\left[P + \dfrac{a}{V^2}\right] [V - b] = RT$

P [V - b] = RT (neglecting a)

$\therefore \dfrac{10.1325 \times 10^6}{101325} [V_1 - b] = 0.0821 \times 273$

or 100 [V$_1$ - b] = 0.0821 × 273 = 22.41 .....(1)

$\dfrac{101.325 \times 10^3}{101325} [V_2 - b] = 0.0821 \times 273$

or [V$_2$ - b] = 22.41 ....(2)

by eq. (1) V$_1$ - = 0.2241 + b ....(3)

by eq. (2) V$_2$ - = 22.41 + b ....(4)

By eqs. (3) and (4), $\dfrac{V_1}{V_2} = \dfrac{0.2241 + b}{22.41 + b}$

$\dfrac{0.011075V_2}{V_2} = \dfrac{0.2241 + b}{22.41 + b}$

(V$_1$ = 0.011075V$_2$ is given)

$\therefore$ b = 0.024 litre mol^{-1} = 24 cm^{3}mol^{-1}

$\therefore$ b = 4N × v = $4 \times 6.023 \times 10^{23} \times \dfrac{4}{3}\pi r^3$

or $24 = 4 \times 6.023 \times 10^{23} \times \dfrac{4}{3} \times \dfrac{22}{7} \times r^3$

$\therefore$ **r = 1.33 × 10^{-8} cm**

3. Calculate vander waal's constant a and b if critical temperature and critical pressure are 30ºC and 72 atm respectively.

Sol. $T_C = \dfrac{8a}{27Rb}$ and $P_C = \dfrac{a}{27b^2}$

$\therefore \dfrac{T_C}{P_C} = \dfrac{8b}{R}$ or $b = \dfrac{RT_C}{8P_C}$

$\therefore b = \dfrac{0.0821 \times 303}{8 \times 72} = 0.043$ litre mol^{-1}

$\alpha = 27P_C \times b^2 = 27 \times 72 \times (0.043)^2$
$= 3.59$ litre^{2}atm mol^{-2}

4. Using vander waal's equation, calculate the constant, 'a' when two mole of a gas confined in a four litre temperature of 300K. The value of 'b' is 0.05 litre mol^{-1}.

Sol. Vander waal's equation for n mole of gas is

$\left[P + \dfrac{n^2 a}{V^2} \right]$ [V−nb]=nRT

Given V = 4 litre ; P = 11.0 atm, T = 300 K

b = 0.05 litre mol^{-1} ; n =2

Thus, $\left[11 + \dfrac{2^2 a}{4^2} \right]$ [4 − 2 × 0.05] = 2 × 0.082 × 300.

$\therefore$ a = 6.46 atm litre^2 mol^2

5. One way of writing the equation for state for real gases is,   **[JEE 1997]**

$P\,\overline{V} = RT \left[1 + \dfrac{B}{\overline{V}} + \ldots \right]$ where B is a constant.

Derive an approximate expression for 'B' in terms of van der Waals' constants **'a'** & **'b'**.

Ans. $B = \left(b - \dfrac{a}{RT} \right)$

Sol. $\left[P + \dfrac{a}{Vm^2} \right]$ [Vm − b]

$P = \dfrac{RT}{Vm - b} - \dfrac{a}{Vm^2}$

$\dfrac{PVm}{RT} = \dfrac{Vm}{Vm - b} - \dfrac{a}{VmRT}$

$Z = \left(1 - \dfrac{b}{Vm} \right)^{-1} - \dfrac{a}{VmRT}$

$$= 1 + \frac{b}{Vm} + \frac{b^2}{Vm^2} + \ldots - \frac{a}{VmRT}$$

$$= 1 + \left[b - \frac{a}{RT} \right] \frac{1}{Vm} + \frac{b^2}{Vm^2} \ldots + \quad \ldots (1)$$

Also, $P\bar{V} = RT \left[1 + \frac{B}{V} + \ldots \right]$

$$\Rightarrow \frac{P\bar{V}}{RT} = \left[1 + \frac{B}{V} + \ldots \right] \qquad \ldots (2)$$

$\Rightarrow$ Comparing equation (1) & (2), we get

$$B = b - \frac{a}{RT}$$

6. Using Vander Waals equation, calculate the constant "a" when 2 moles of a gas confined in a 4 litre flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of "b" is 0.05 litre mol^{-1}.

[JEE 1998]

Ans. 6.52 atm L² mol⁻²

Sol. $\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$

$$\left[11 + \frac{2^2 \times a}{4 \times 4} \right] [4 - 2 \times 0.05] = 2 \times 0.0821 \times 300$$

$\Rightarrow a = 6.52$ atm L^2 mol^{-2}

7. A gas will approach ideal behaviour at :   **[JEE 1999]**

(A) low temperature and low pressure

(B) low temperature and high pressure

(C) low pressure and high temperature

(D) high temperature and high pressure .

Ans. (C)

Sol. A gas approches ideal behavior at High T & low P

8. The compressibility of a gas is less than unity at STP. Therefore **,**   **[JEE 2000]**

(A) $V_m > 22.4$ L   (B) $V_m < 22.4$ L

(C) $V_m = 22.4$ L   (D) $V_m = 44.8$ L

Ans. (B)

Sol. $Z = \frac{(Vm)real}{(Vm)ideal} ; Z < 1$

$\Rightarrow (Vm)_{real} < (Vm)_{ideal}$

$\therefore (Vm)_{real} < 22.4$ L

9. The compression factor (compressibility factor) for one mole of a Van der Waals' gas at $0° C$ and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the Van der Waals' constant 'a'.   **[JEE 2001]**

Ans. $\mathbf{1.256\ atm\ L^2\ mol^{-2}}$

Sol. $Z = 1 - \dfrac{a}{VmRT}$

$Z = \dfrac{PVm}{RT} \Rightarrow Vm = \dfrac{RTZ}{P}$

$Z = 1 - \dfrac{a}{(RT)^2} \times \dfrac{P}{Z}$

$0.5 = 1 - \dfrac{a \times 100}{(273 \times 0.0821)^2 \times .5}$

$a = 1.256\ atm\ L^2\ mol^{-2}$

10. The density of the vapour of a substance at 1 atm pressure and 500 K is $0.36\ Kg\ m^{-3}$. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition. Determine   **[JEE 2002]**

(i) mol. wt.;   (ii) molar volume;   (iii) compression factor z of the vapour and

(iv) which forces among the gas molecules are dominating, the attractive or the repulsive

Ans. (i) 18 g/mol , (ii) 50 L mol⁻¹ , (iii) 1.218 , (iv) repulsive

Sol. (i) $\dfrac{r_{gas}}{r_{O_2}} = \sqrt{\dfrac{M_{O_2}}{M_{gas}}}$

$\Rightarrow \dfrac{4}{3} = \sqrt{\dfrac{32}{M_{gas}}}$

$\Rightarrow M_{gas} = 18$

(ii) $V_m = \dfrac{18}{0.36}\ 50\ L\ mol^{-1}$

(iii) $Z = \dfrac{PVm}{RT} = \dfrac{1 \times 50}{0.0821 \times 500} = 1.218$

(iv) since, $Z > 1$ = Repulsive forces are operative

11. Positive deviation from ideal behaviour takes place because of   **[JEE 2003]**

(A) molecular attractions between atoms and $\dfrac{PV}{nRT} > 1$

(B) molecular attractions between atoms and $\dfrac{PV}{nRT} < 1$

(C) finite size of atoms and $\dfrac{PV}{nRT} > 1$

(D) finite size of atoms and $\dfrac{PV}{nRT} < 1$

Ans. (C)

Sol. Positive deviation from ideal behavior takes place because of finite size of atoms & compressibility factor $Z > 1$.

12. For a real gas obeying van der Waals' equation a graph is plotted between PV_m (y-axis) and P(x-axis) where V_m is molar volume. Find y-intercept of the graph. **[JEE 2004]**
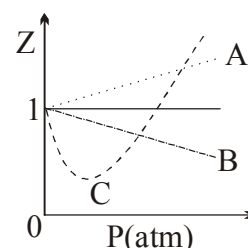
Ans. RT

Sol. $\text{Lim}_{P \to 0} PVm = RT$

Since, at very low P, all gases behave ideally.
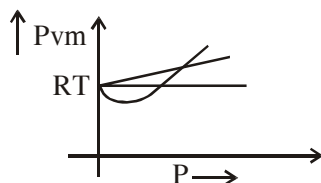
13. The given graph represents the variation of Z

(compressibility factor $= \dfrac{PV}{nRT}$) versus P, for three real

gases A, B and C. Identify the only **INCORRECT** statement.

(A) for the gas A, a = 0 and its dependence on P is linear at all pressure

(B) for the gas B, b = 0 and its dependence on P is linear at all pressure

(C) for the gas C, which is typical real gas for which neither a nor b = 0. By knowing the minima and the point of intersection, with Z = 1, a and b can be calculated.

(D) At high pressure, the slope is positive for all real gases A, B and C. **[JEE 2006]**

Ans. (D)

Sol. (A)   In case of A, repulsion dominate because Z > 1

               So, $Z = 1 + \dfrac{Pb}{RT} \Rightarrow a = 0$

    (B)   In case of B, attraction dominate because Z < 1

               So, $z = 1 - \dfrac{a}{VmRT} \Rightarrow b = 0$

    (C)   In case of C, a typical real gas :

               We can calculate the minima of curve to given equation (1) in terms of a & b.

               Similarly, at intersection point of the curve with Z = 1, we get another equation (2) interms of a & b. Solving the two equation we can calculate a & b.

    (D)   At high P, a Slope is negative for gas B.

               SO, (D) is incorrect.

14. Match gases under specific conditions listed in Column I with their properties / laws in Column II. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the ORS.

        Column I   **Column II**

(A) Hydrogen gas (P = 200 atm, T = 273 K)   (P) Compressibility factor $\neq 1$

(B) Hydrogen gas (P $\sim$ 0, T = 273 K)   (Q) Attractive forces are dominant

(C) CO_2 (P = 1 atm, T = 273 K)   (R) PV = nRT

(D) Real gas with very large molar volume   (S) P (V $-$ nb) = nRT   **[JEE 2007]**

Ans. (A) - P, S ; (B) - R ; (C) - P, Q ; (D) - R

Sol. (A) H_2 gas at high P,

                 Repulsions dominate

                 So, $Z \neq 1$

                 & P(V$-$nb) = nRT

       (B) H_2 gas at P $\to$ 0, will exhibit ideal behaviour PV = nRT

       (C) CO_2 at P = 1 atm, T = 273 K

                 CO_2 is easily liquefiable gas.

                 Z < 1, So attraction forces dominate.

       (D)   If volume is very large, no intermoleculer force exists. Moreover, moleculare volume can also be neglected.

                 SO, PV = nRT

**15.** A gas described by van der Waals' equation   **[JEE 2008]**

(A) behaves similar to an ideal gas in the limit of large molar volumes

(B) behaves similar to an ideal gas in the limit of large pressures

(C) is characterised by van der Waals' coefficients that are dependent on the identity of the gas but are independent of the temperature

(D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

Ans. (A,C,D)

Sol. (A) $PV_m \to RT$ as $V_m \to \infty$

       (B) $PV_m \to RT$ as P $\to$ O So (B) is incorrect

       (C) $\left(P + \dfrac{a}{V_m{}^2} \right) (V_m - b) = RT$

                 where, a & b are vander waals, coefficients independent of temperature

       (D) $P_{real} < P_{ideal}$
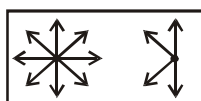
EXERCISE # S-I

1. Calculate the pressure exerted by 22 g of carbon dioxide in 0.5 dm^3 at 300 K using:

(a) the ideal gas law and

(b) Van der Waal's equation respectively.

Given : [a = 3.6 atm litre^{2}mol^{-2} , b = 0.04 litre mol^{-1}, R = 0.08 L-atm/K-mol]

RG0001

2. Calculate from the Van der Waals equation, the temperature at which 192 g of SO_2 would occupy a volume of 6 dm^3 at 15 atm pressure.[a = 5.68 atm L^2 mol^{-2}, b = 0.06 L mol^{-1}]

RG0002

3. The density of water vapour at 328.4 atm and 800 K is 135.0 g/dm^3. Determine the molar volume, V_m and the compression factor of water vapour .

RG0003

4. At 300 K and under a pressure of 10.1325 MPa, the compressibility factor of O_2 is 0.9. Calculate the mass of O_2 necessary to fill a gas cylinder of 45 dm^3 capacity under the given conditions.
[R = 0.08L-atm/K-mol]

RG0004

5. 1 mole of CCl_4 vapours at 27°C occupies a volume of 40 L. If Van der Waals constants are 24.6 L^2 atm mol^{-2} and 0.125 Lmol^{-1}, then, calculate compressibility factor in

(a) Low pressure region   (b) High Pressure region [R = 0.082 L -atm/K-mol]

RG0005

6. If at 200 K & 500 atm, density of CH_4 is 0.246 gm/ml then its compressibility factor (Z) is approx 2.0×10^x . 'x' is:

RG0006

7. Certain mass of a gas occupy 500 ml at 2 atm and 27ºC. Calculate the volume occupied by same mass of the gas at 0.3 atm and 227ºC. The compressibility factors of gas at the given condition are 0.8 and 0.9, respectively.

RG0007

BOYLE TEMPERATURE

8. The vander waal's constant for a gas are a = 1.92 atm L^2 mol^{-2}, b = 0.06L mol^{-1}. If R = 0.08 L atm K^{-1}mol^{-1}, what is the Boyle's temperatrue of this gas.

RG0008

9. The Van der Waals constant for O_2 are a = 1.642 atm L^2 mol^{-2} and b = 0.04 L mol^{-1}. Calculate the temperature at which O_2 gas behaves ideally for longer range of pressure.

RG0009

LIQUIFICATION OF GASES, CRITICAL PHENOMENON

10. The Van der Waals constants for gases A, B and C are as follows

Gas	a[/atm L^2 mol^{-2}]	b[/L mol^{-1}]
A	8.21	0.050
B	4.105	0.030
C	1.682	0.040

Which gas has (i) the highest critical temperature, (ii) the largest molecular volume, and (iii) most ideal behaviour around 500 K?

RG0010

11. For a real gas, if at critical conditions molar volume of gas is 8.21 litre at 3 atm, then critical temperature (in K) will be :

RG0011

12. An unknown gas behaves ideally at 540K in low pressure region, then calculate the temperature
(in K) below which it can be liquified by applying pressure.

RG0012

EXERCISE # S-II

1. The density of mercury is 13.6 g/cm^3. Estimate the value of **'b'** (in cm^3/ mole).

RG0013

2. The molarity of O_2 gas at 72 atm and 300K is 6M. Calculate the value of Z for O_2.

(Use : R = 0.08 atm-litre/K-mole).

RG0014

3. Calculate the amount of He (in gm) present in the 10 litre container at 240 atm and 300K. Given value of "b" for He is 0.08 dm^3 mol^{-1} ; R = 0.08 atm lit mol^{-1} K^{-1}.

RG0015

4. For a real gas (mol. mass = 30) if density at critical point is 0.40 g/cm^3 and its $T_c = \dfrac{2 \times 10^5}{821}$ K, then calculate Van der Waals constant a (in atm L^{2}mol^{-2}).

RG0016

5. Calculate the volume occupied by 0.2 mole of a Vander waal gas at 27ºC and 0.0821 atm.

[a = 4.105 L^2 atm mol^{-2}, b = $\dfrac{1}{6}$Lmol^{-1}]

RG0017

6. At what pressure and 127ºC, the density of O_2 gas becomes 1.6 g/L ?

[a = 4.0 atm L^2 mol^{-2} , b = 0.4 Lmol^{-1}, R = 0.08 L - atm/ K-mol]

RG0018

EXERCISE # O-I

1. The correct expression for the Van der Waals equation of state is :

(A) $\left(P + \dfrac{a}{n^2V^2}\right)(V - nb) = nRT$

(B) $\left(P + \dfrac{an^2}{V^2}\right)(V - nb) = \Delta nRT$

(C) $\left(P + \dfrac{an^2}{V^2}\right)(V - b) = nRT$
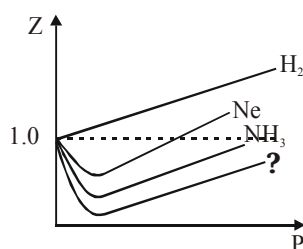
(D) $\left(P + \dfrac{an^2}{V^2}\right)(V - nb) = nRT$

RG0019

2. At relatively high pressure, Van der Waals equation reduces to :

(A) $PV_m = RT$
(B) $PV_m = RT + \dfrac{a}{V_m}$
(C) $PV_m = RT + Pb$
(D) $PV_m = RT - \dfrac{a}{V_m^2}$

RG0020

3. Observe the following Z vs P graph.

The missing gas in the above graph can be :

(A) He
(B) Ar
(C) C_5H_{12}
(D) All are correct

RG0021

4. Correct option regarding a container containing 1 mol of a gas in 22.4 litre container at 273 K is

(A) If compressibility factor (Z) > 1 then 'P' will be less than 1 atm.

(B) If compressibility factor (Z) > 1 then 'P' will be greater than 1 atm.

(C) If 'b' dominates, pressure will be less than 1 atm.

(D) If 'a' dominates, pressure will be greater than 1 atm.

RG0022

5. If 'V' is actual volume of 1 molecule of gas then, excluded volume (b) of 1 mole of gaseous molecule is -

(A) $4 N_A V$
(B) $N_A V$
(C) V/N_A
(D) V

RG0023

6. Consider the equation $Z = \dfrac{PV}{RT}$, Which of the following statements is correct :

(A) When Z > 1 real gases are easier to compress

(B) When Z = 1 real gases are easier to compress

(C) When Z > 1 real gases are difficult to compress

(D) When Z < 1 real gases are difficult to compress

RG0024

7. Compressibility factor of ideal gas is :-

(A) z > 1   (B) z > 1   (C) z = 1   (D) z = ∞

RG0025

8. The density of a gaseous substance at 1 atm pressure and 750 K is 0.30 g/lt. If the molecular weight of the substance is 27, the dominant forces existing among gas molecules is -

(A) Attractive   (B) Repulsive   (C) Both (A) and (B)   (D) None of these

RG0026

9. The third virial coefficient of a He gas is 4×10^{-2} $(\text{lit/mol})^2$, then what will be volume of 2 mole He gas at 1 atm 273K ($273K > T_B$)

(A) 22.0 lit   (B) 44.0 lit   (C) 44.8 lit   (D) 45.3 lit

RG0027

10. At low pressure the vander waals equation is reduced to -

(A) $Z = \dfrac{pV_m}{RT} = 1 - \dfrac{a}{RTV_m}$ (B) $Z = \dfrac{pV_m}{RT} = 1 + \dfrac{a}{RT}p$

(C) $pV_m = RT$ (D) $Z = \dfrac{pV_m}{RT} = 1 - \dfrac{a}{RT}$

RG0028

11. The values of Van der Waals constant 'a' for the gases O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 L atm mol^{-2} respectively. The gas which can most easily be liquefied is :

(A) O_2 (B) N_2 (C) NH_3 (D) CH_4

RG0029

12. The values of critical temperatures of few gases are given gases :

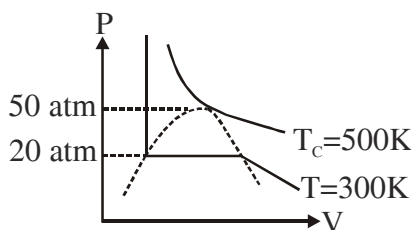| Gases :	H_2	He	O_2	N_2
T_C(K)	33.2	5.2	154.3	126

From the above data arrange the given gases in the increasing order of ease of their liquification.

(A) O_2, N_2, H_2, He   (B) He, N_2, O_2, H_2

(C) He, H_2, N_2, O_2 (D) H_2, N_2, O_2, He

RG0030

EXERCISE # O-II

1. For real gas the P–V curve was experimentally plotted and it had the following appearance. With respect to liquification, choose the incorrect statement :

(A) At T = 500 K, P = 40 atm, the state will be liquid

(B) At T = 300 K, P = 50 atm, the state will be gas

(C) At T < 300 K, P = 20 atm, the state will be gas

(D) At 300 K < T < 500 K, P > 50 atm, the state will be liquid

RG0031

2. Select the incorrect statement (s)

(A) The critical constant for a Vander Waal's gas is $V_C = 3b$, $P_C = \dfrac{a}{27b^2}$ and $T_C = \dfrac{a}{27Rb}$

(B) At 56 K a gas may be liquified if its critical temperature is –156°C.

(C) U_{avg} of gas in a rigid container can be doubled when the pressure is quadrupled by pumping in more gas at constant temperature

(D) At extremely low pressure, all real gases behave ideally.

RG0032

3. A 1 litre vessel contains 2 moles of a vanderwaal's gas.

Given data :   **a = 2.5 atm-L^2 mole^{-2}**   **T = 240 K**

                 b = 0.4 L-mole^{-1} RT = 20 L-atm mole^{-1}

Identify the correct options about the gas sample :

(A) Pressure of gas = 190 atm

(B) Compressibility factor = 4.75

(C) Attraction forces are dominant in the gaseous sample

(D) T_B (Boyle temperature) = 75 K

RG0033

4. Choose the correct statement(s) among the following -

(A) A gas having higher value T_C is easy to liquify

(B) The radius of molecules of gas having same value of T_C/P_C is same

(C) Hydrogen gas can be liquified at its boyle temperature by application of pressure.

(D) Real gas show negative deviation from ideal behaviour at low pressure condition.

RG0034

5.   Select the **INCORRECT** statement(s):

(A) At Boyle's temperature a real gas behaves like an ideal gas irrespective of pressure.

(B) At critical condition, a real gas behaves like an ideal gas.

(C) On increasing the temperature four times, collision frequency (Z_1) becomes double at constant volume.

(D) At high pressure Van der Waals constant 'b' dominates over 'a'.

RG0035

Question No. 6 & 7 (2 questions)

For two gases A and B, P v/s V isotherms are shown at same temperature, T K . T_A & T_B are critical temperatures of A & B respectively
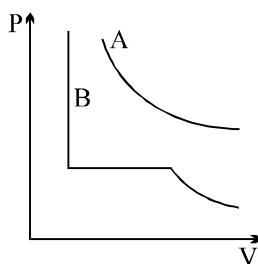
6.   Which of the following is true?

(A) $T_A < T < T_B$ (B) $T_A > T > T_B$

(C) $T_A > T_B > T$ (D) none of above

RG0036

7.   The correct statement(s) is/are

(I)   Pressure correction term will be more negligible for gas B at T K.

(II)   The curve for gas 'B' will be of same shape as for gas A if $T > T_B$

(III) Gas 'A' will show same P v/s V curve as of gas 'B' if $T > T_A$

(A) III only   (B) II and III   (C) II only   (D) All

RG0037

Match the column:

8.   Match the column :

Column-I	Column-II
(A) Boyle's temperature	(P) Depends on 'a' and 'b'
(B) Compressibility factor	(Q) Depends on identity of real gas
(C) Real gas with very large molar volume	(R) The temperature at which $\dfrac{dZ}{dP} = 0$ at low pressure region.
(D) Critical temperature	(S) $PV = nRT$
	(T) $\dfrac{8a}{27R.b.}$

RG0038

EXERCISE # JEE-MAINS

1. 'a' and 'b' are Van der Waals constants for gases. Chlorine is more easily liquefied than ethane because :-   **[AIEEE-2011]**

(1) a for Cl_2 < a for C_2H_6 but b for Cl_2 > b for C_2H_6

(2) a for Cl_2 > a for C_2H_6 but b for Cl_2 < b for C_2H_6

(3) a and b for Cl_2 > a and b for C_2H_6

(4) a and b for Cl_2 < a and b for C_2H_6

RG0039

2. When does a gas deviate the most from it's ideal behaviour ?   **[JEE-MAINS(ONLINE)-2015]**

(1) At high pressure and low temperature

(2) At high pressure and high temperature

(3) At low pressure and low temperature

(4) At low pressure and high temperature

RG0040

3. If Z is the compressibility factor, Van der Waals equation **at low** pressure can be written as :

[JEE-MAINS-2014]

(1) $Z = 1 - \dfrac{Pb}{RT}$ (2) $Z = 1 + \dfrac{Pb}{RT}$ (3) $Z = 1 + \dfrac{RT}{Pb}$ (4) $Z = 1 - \dfrac{a}{V_m RT}$

RG0041

4. Among the following, the incorrect statement is :   **[JEE-Mains-2017(ONLINE)]**

(1) At low pressure, real gases show ideal behaviour

(2) At very large volume, real gases show ideal behaviour

(3) At Boyle's temperature, real gases show ideal behaviour

(4) At very low temperature, real gases show ideal behaviour

RG0042

5. The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressures of the gases for equal number of moles are :

[JEE-MAINS-2019]

(1) $2P_A = 3P_B$ (2) $P_A = 3P_B$ (3) $P_A = 2P_B$ (4) $3P_A = 2P_B$

RG0043

6. At a given temperature T, gases Ne, Ar, Xe and Kr are found to deviate from ideal gas behaviour.

Their equation of state is given as $p = \dfrac{RT}{V - b}$ at T.   **[JEE-MAINS-2019]**

Here, b is the van der Waals constant. Which gas will exhibit steepest increase in the plot of Z (compression factor) vs p?

(1) Ne   (2) Ar   (3) Xe   (4) Kr

RG0044

7. Consider the van der Waals constants, a and b, for the following gases.

Gas   Ar   Ne   Kr   Xe   **[JEE-MAINS-2019]**

a/ (atm dm^6 mol^{-2})   1.3   0.2   5.1   4.1

b/ (10^{-2} dm^3 mol^{-1} 3.2   1.7   1.0   5.0

Which gas is expected to have the highest critical temperature?

(1) Kr   (2) Ne   (3) Ar   (4) Xe

RG0045

8. Consider the following table :   **[JEE-MAINS-2019**

Gas	a/(k Pa dm^6 mol^{-1})	b/(dm^3 mol^{-1})
A	642.32	0.05196
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

a and b are vander waals constant. The correct statement about the gases is :

(1) Gas C will occupy lesser volume than gas A; gas B will be lesser compressible than gas D

(2) Gas C will occupy more volume than gas A; gas B will be lesser compressible than gas D

(3) Gas C will occupy more volume than gas A; gas B will be more compressible than gas D

(4) Gas C will occupy lesser volume than gas A; gas B will be more compressible than gas D

RG0046

EXERCISE # JEE-ADVANCED

1. For one mole of a Van der Waals gas when b = 0 and T = 300 K, the PV vs. 1/V plot is shown below. The value of the Van der Waals constant a (atm. litre^2 mol^{-2}) is   **[JEE 2012]**
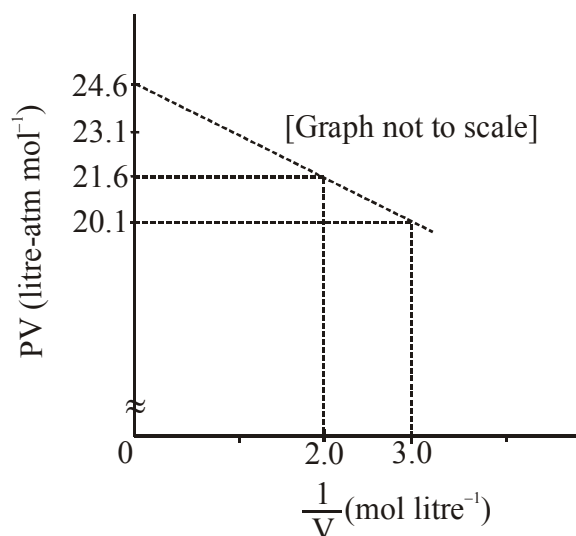
(A) 1.0   (B) 4.5   (C) 1.5   (D) 3.0

RG0047

E

ANSWER KEY

EXERCISE # S-I

1.	**(a) 24.0 atm, (b) 21.4 atm**	**2.**	**388 K**
3.	**Molar vol. = 0.1333 L/mol; Z = 0.667**	**4.**	**6.67 kg**
5.	**(a) 0.975 ; (b) 1.003**	**6.**	**Ans. 0**
7.	**6.25 L**	**8.**	**Ans. 400 K**
9.	**500 K**	**10.**	**(i) A, (ii) A, (iii) C**
11.	**Ans. 800**	**12.**	**Ans. 160 K**

EXERCISE # S-II

1.	**58.82**	**2.**	**0.5**
3.	**222.22**	**4.**	**1.6875**
5.	**60 L**	**6.**	**1.622 atm.**

EXERCISE # O-I

1.	**Ans.(D)**	**2.**	**Ans.(C)**	**3.**	**Ans.(C)**	**4.**	**Ans.(B)**
5.	**Ans.(A)**	**6.**	**Ans.(C)**	**7.**	**Ans.(C)**	**8.**	**Ans.(B)**
9.	**Ans.(D)**	**10.**	**Ans.(A)**	**11.**	**Ans.(C)**	**12.**	**Ans.(C)**

EXERCISE # O-II

1.	**Ans. (A,B,C)**	**2.**	**Ans. (A,C)**	**3.**	**Ans. (A,B,D)**	**4.**	**Ans. (A,B,D)**
5	**Ans.(A,B**	**6.**	**Ans.(A)**	**7.**	**Ans. (C)**		

8.   **(A) - P,Q,R,S ; (B) - P, Q ; (C) - S ; (D) - P, Q, T**

EXERCISE # JEE-MAINS

1	**Ans. (2)**	**2.**	**Ans. (1)**	**3.**	**Ans. (4)**	**4.**	**Ans. (4)**
5.	**Ans. (1)**	**6.**	**Ans.(3)**	**7.**	**Ans. (1)**	**8.**	**Ans.(3)**

EXERCISE # JEE-ADVANCED

1.	**Ans.(C)**