REAL GAS

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 particles have some significant volume).

(ii)   There is no interaction between gaseous particles (while attraction forces exist between real gas particles).
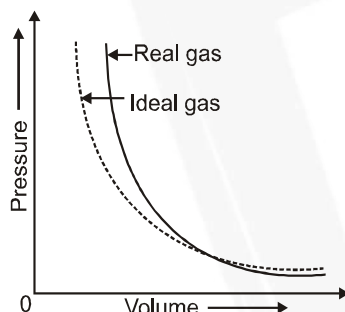
1.   **Deviation from Ideal behaviours :**

1.1   **Compressibility factor :**

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

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

When $Z > 1$, $V_m > 22.7$ L at STP ;

When $Z < 1$, $V_m < 22.7$ L at STP

1.2   **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 $Z > 1$. For such gases repulsive forces predominants.

(iii)   Effect of pressure :

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

At low P, $PV < RT$ i.e. $Z < 1$

At moderate P, $PV \approx RT$ i.e. $Z \approx 1$

At high P, $PV > RT$ i.e. $Z > 1$

(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 i.e. PV approaches unity or Z approaches unity with increase in temperature.
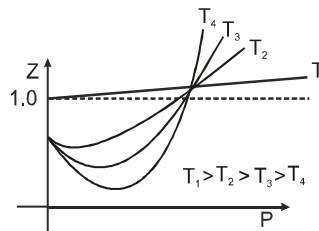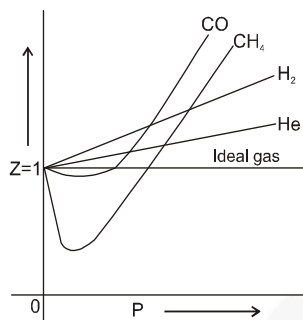
Conclusions :

$Z = 1$ for ideal gas ; $Z > 1$ at all pressures for He/H_2

$Z < 1$ at low pressure (for all other gases) ; $Z > 1$ at high pressure (for all other gases)

2.   **Vander Waal Equation of real gases :**

The ideal gas equation does not consider the effect of attractive forces and molecular volume. Vander Waal's corrected the ideal gas equation by taking the effect of

(a) Molecular volume   **(b)** Molecular attraction

2.1   **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 will be less than volume of container.

Excluded volume per molecule $= \dfrac{1}{2}\left\{\dfrac{4}{3}\pi(2r)^3\right\}$ = Co-volume per molecule.

The volume that is not available for free movement is called excluded volume.

let us see, how this excluded volume is calculated.

For above example, the entire shaded region is excluded, as its centre of mass cannot enter this region.

If both molecules were ideal, then they would not have experienced any excluded volume but not in the case, of real gas as the centre of mass of '2' cannot go further.
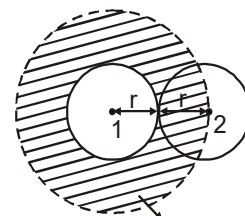
Hence for this pair of real gas molecules, excluded volume per

Excluded volume
(not available for free momement)

molecule $= 4\left\{\dfrac{4}{3}\pi r^3\right\}$

Excluded volume per mole of gas (b) $= N_A \times 4 \times \left\{\dfrac{4}{3}\pi r^3\right\}$ = 4 x N_A x Volume of individual molecule.

For n moles, excluded volume = nb

$V_i = V - nb$ volume correction

2.2   Pressure correction :

Due to these attraction, speed during collisions will be reduced

Momentum will be less

Force applied will be less

Pressure will be less.

$P_{ideal} = P + \{\text{correction term}\}$

Correction term $\propto$ a no. of molecules attracting the colliding molecule $\propto (n/v)$.

Correction term $\propto$ density of molecules $\propto \left(\dfrac{n}{v}\right)$

no. of collision $\propto$ a density of molecules $\propto \left(\dfrac{n}{v}\right)$

So net correction term $\propto \left(\dfrac{n}{v}\right)\left(\dfrac{n}{v}\right)$

So net correction term $= \dfrac{an^2}{V^2}$

'a' is constant of proportionality and this is dependent on force of attraction

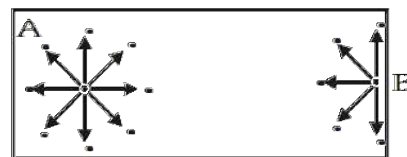Stronger the force of attraction greater will be 'a' (Constant)

$$P_i = P + \dfrac{an^2}{v^2}$$

'a' is a constant which depends upon the nature of the gas, V is the volume of 1 mole of gas.

Combining the two corrections, for 1 mole of gas

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

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

2.3   Significance of '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)   For a given gas van der Waals constant of attraction 'a' is always greater than van der Waals constant of volume 'b'.

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

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

(v)   Unit of 'b' is lit $mole^{-1}$ or cm^3 $mole^{-1}$.

REAL GAS

Gas	a $(\text{dm}^6 \text{ atm mol}^{-2})$	b $(\text{dm}^3 \text{ mol}^{-1})$
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

Ex.1 Arrange following in decreasing 'a' factor (H_2O, CO_2, Ar)

Sol. H_2O > CO_2 > Ar
polar

Ex.2 Arrange following gases according to 'a' (He , Ar, Ne, Kr).

Sol. $aKr_{Kr} > a_{Ar} > a_{Ne} > a_{He}$

Ex.3 Arrange the following according to liquification pressure (n-pentane ; iso-pentane , neo pentane).

Sol. $a_{n\text{-pentene}} > a_{\text{iso-pentane}} > a_{\text{neo-pentane}}$

Ex.4 Two Vander Waals gases have same value of b but different a values. Which of these would occupy greater volume under identical conditions ?

Sol. If two gases have same value of 'b' but different values of 'a', then the gas having a larger value of 'a' will occupy lesser volume. This is because the gas with a larger value of 'a' will have larger force of attraction and hence lesser distance between its molecules.

2.4 VERIFICATION OF VANDER WAAL'S EQUATIONS :

Variation of Z with P for vander waals' equation at any temperature.

Vander waal equation for 1 mole

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

V_m = volume of 1 mole of gas

2.4.1 AT LOW PRESSURE :

At low pressure V_m will be high.

Hence b can be neglected in comparision to V_m. but $\frac{a}{V_m^2}$ can't be neglected as pressure is low
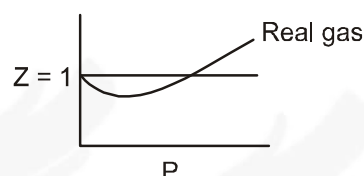
Thus equation would be

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

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

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

$$Z = 1 - \frac{a}{V_m RT} \qquad Z < 1$$

Real gas is easily compressible as compared to an ideal gas.

2.4.2 At high pressure (moderate temp.)

V_m will be low

so b can't be neglected in comparison to V_m

but $\frac{a}{V_m^2}$ can be neglected as compared to much higher values of P.

Then vander Waals' equation will be

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

$$PV_m - Pb = RT$$

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

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

If Z > 1, then gas is more difficult to compress as compared to an ideal gas.

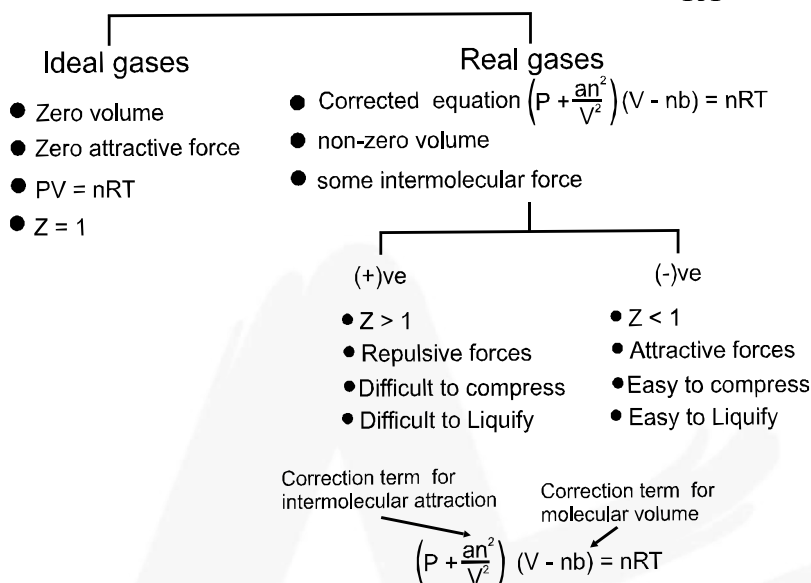### 2.4.3 At low pressure and very high temperature.

V_m will be very large

hence 'b' can't be neglected and $\frac{a}{V_m^2}$ can also be neglected as V_m is very large

2.4.3 For H_2 or He $a \simeq 0$ because molecules are smaller in size or vander Wall's forces will be very weak, these are non polar so no dipole-dipole interactions are present in the actions.

$$P(V_m - b) = RT \qquad \text{so} \qquad Z = 1 + \frac{Pb}{RT}$$

Ideal gases
- Zero volume
- Zero attractive force
- PV = nRT
- Z = 1

Real gases
- Corrected equation $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$
- non-zero volume
- some intermolecular force

(+)ve
- Z > 1
- Repulsive forces
- Difficult to compress
- Difficult to Liquify

(-)ve
- Z < 1
- Attractive forces
- Easy to compress
- Easy to Liquify

Correction term for intermolecular attraction

Correction term for molecular volume

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

Ex.5 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 L^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.

Ans. P = 77.218 atm, P_{Ideal} = 131.36 atm, P = 0.9922 atm

Sol. Vander waal's equation

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

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

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

$\therefore$ P = 77.218 atm

For ideal behaviour of gas, PV = nRT

$\therefore$ P × 1 = 5 × 0.0821 × 320

$\therefore$ P = 131.36 atm

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

$$\therefore \qquad P = \frac{RT}{V} - \frac{a}{V^2}$$

$$\therefore \qquad P = \frac{0.0821 \times 273}{22.4} - \frac{3.592}{(22.4)^2}$$

Ex.6 Two moles of ammonia gas are enclosed in a vessel of 5 litre capacity at 27°C. Calculate the pressure exerted by the gas, assuming that

      (i)   the gas behaves like an ideal gas (using ideal gas equation).

      (ii)   the gas behaves like a real gas (using van der Waal's equation)

      Given that for ammonia, a = 4.17 atm litre^2 mol^{-2} and b = 0.037 litre mol^{-1}.

Ans. 9.85 atm, 9.33 atm

Sol. Given,

$$n = 2 \text{ moles}$$
$$V = 5 \text{ litres}$$
$$T = 27°C = (27 + 273) \text{ K} = 300 \text{ K}$$
$$a = 4.17 \text{ atm litre}^2 \text{ mol}^{-2}$$
$$b = 0.037 \text{ litre mol}^{-1}$$

Also, we know that

$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

      (i)   If the gas behaves like an ideal gas, we have

$$PV = nRT$$

$$\therefore \quad P = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 300}{5} = 9.85 \text{ atm}$$

      (ii)   If the gas behaves like a real gas, we apply van der Waal's equation i.e.

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

or
$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} = \frac{2 \times 0.0821 \times 300}{5 - 2 \times 0.037} - \frac{4.17 \times (2)^2}{(5)^2} = 9.33 \text{ atm}$$

Ex.7 1 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.

Ans. (a) 0.98   (b) 1.004

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

$$\therefore \quad (V - b) \approx V$$

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

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

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

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

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

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

$\therefore$ $P(V-b)=RT$ $\Rightarrow$ $PV-Pb=RT$

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

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

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

2.   VIRIAL EQUATION OF STATE :

It is a generalised equation of gaseous state. All other equations can be written in the form of virial equation of state.

Z is expressed in power series expansion of P or $\left(\dfrac{1}{V_m}\right)$

$$Z=1+\frac{B}{V_m}+\frac{C}{V_m^2}+\frac{D}{V_m^3}+ ....$$

B – second virial coefficient, C – third virial coefficient, D – fourth virial coefficient.

The coefficients B, C...depend on the temperature but not the density and are known as virial coefficients. Both B and C are negatige at low temperature and positive at high temperature.

The virial coefficients are determined by the intermolecular potential.

B represents the effects of interactions between pairs of molecules, C interactions among triplets of molecules, and so forth.

Vander waals' equation in virial form :

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

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

$$Z=\frac{PV_m}{RT}=\frac{V_m}{(V_m-b)}-\frac{a}{V_m RT}=\frac{1}{(1-b/V_m)}-\frac{a}{V_m RT}$$

$$\frac{1}{1-x}=1+x+x^2+x^3+..........$$

$$Z=\left(1+\frac{b}{V_m}+\frac{b^2}{V_m^2}+\frac{b^3}{V_m^3}+.........\right)-\frac{a}{V_m RT}=1+\frac{1}{V_m}\left(b-\frac{a}{RT}\right)+\frac{b^2}{V_m^2}+\frac{b^3}{V_m^3}+................$$

comparing vander waals equation with virial equation

$$B=b-\frac{a}{RT}\ , C=b^2, D=b^3$$

So, $Z=1+\dfrac{B}{V_m}+\dfrac{C}{V_m^2}+\dfrac{D}{V_m^3}+ ....$

Nishant Jindal

2.1   BOYLE'S TEMPERATURE :

The temperature at which a real gas behaves like an ideal gas over an appreciable range of pressure is known as Boyle's temperature (T_B). It means that at this temperature, the value of PV remains constant for an appreciable range of pressure, i.e. Boyle's Law is obeyed. Mathematically we may express the Boyle temperature or Boyle point as the temperature where $\dfrac{\partial (PV)}{\partial P} = 0$ when $P \to 0$.

Virial equation of state ; $Z = 1 + \dfrac{B}{V_m} + \dfrac{C}{V_m^2} + \dfrac{D}{V_m^3} + \ldots\ldots\ldots$

At low pressure : V_m will be larger

hence   , $\dfrac{1}{V_m^2}, \dfrac{1}{V_m^3}$ .... can be neglected

$$Z = 1 + \dfrac{1}{V_m}\left(b - \dfrac{a}{RT}\right)$$

If $\left(b - \dfrac{a}{RT}\right) = 0$;   at $T_B = \dfrac{a}{Rb}$; $Z = 1$

so at $T_B = \dfrac{a}{Rb}$, gas will behave as an ideal gas (or follows Boyles law)

But at constant temperature, ideal gas equation is obeying Boyles law as $T_B = \dfrac{a}{Rb}$, so the temperature is called Boyles' temperature.

At Boyles' temperature 'a / RT' factor is compensated by 'b' factor, so Z = 1.

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 exist in the liquid. A gas can be liquefied by :

(a)   **Increasing pressure :** An increase in pressure results in an increase in attraction among molecules.

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

(Physical Chemistry)   **REAL GAS**

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.
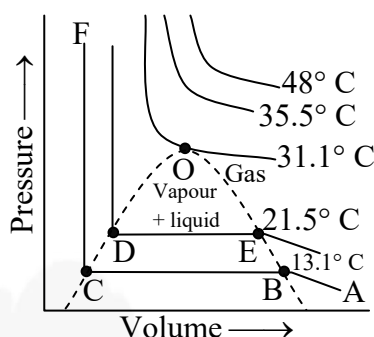
(fig. Isotherms for each carbon dioxide showing critical region)

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.

CF represent liquid state.

The pressure corresponding to the line BC is there vapour pressure of the liquid.

(b)   **At higher 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 :** (like 48ºC), the isotherms are like those of ideal gas.

(d)   **At temperature (31.1ºC) :** 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.

Critical temperature (T_C) : The maximum temperature at which gas can 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 gas at the temperature T_C is called the critical pressure P_C.

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

3.2　**Determination of value of P_C, V_C and T_C :**
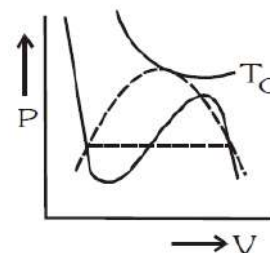
(a)　The vander waal's equation is

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

or　$$PV_m+\frac{a}{V_m}-Pb-\frac{ab}{V_m^2}=RT$$

or　$$V_m+\frac{a}{P}\ \frac{1}{Vm}-b-\left(\frac{ab}{P}\right)\frac{1}{V_m^2}=\frac{RT}{P}$$

or　$$V_m^3+\frac{a}{P}\ V_m-bV_m^2-\frac{ab}{P}=\frac{RTV_m^2}{P}$$

or　$$V_m^3-\left(b+\frac{RT}{P}\right)V_m^2+\frac{a}{p}V_m-\frac{ab}{P}=0 \qquad \ldots\ldots (1)$$

(b)　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.

(c)　The main characteristics of the figure are as follow :

(i)　At higher temperature 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.

(ii)　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 $V'=V''=V'''=V_C$

$\therefore$　the equation becomes,

$$(V_m-V_C)^3=0$$

or　$$V_m^3-V_C^3-3V_C\ V_m^2+3\ V_C^2\ V_m=0$$

from eq. (1)

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

(d)　By comparing the coefficients

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

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

Nishant Jindal

(e) At critical point, the slope of PV curve (slope of isotherm) will be zero

$$\left(\frac{\partial P}{\partial V_m}\right)_{T_C} = 0 \qquad ...(i)$$

at all other point slope will be negative 0 (zero) is the maximum value of slope.

$$\frac{\partial}{\partial V_m}\left(\frac{\partial P}{\partial V_m}\right)_{T_C} = 0 \qquad ....(ii)$$

{Mathematically such points are known as point of inflection (where first two differentiation becomes zero)}

(f) Therefore the value of critical compressibility factor in terms of vander wall's constants is given by

$$Z = \frac{P_C V_C}{RT_C} = \frac{\dfrac{a}{24b^2} \times 3b}{R \times \dfrac{8b}{27Rb}} = \frac{\dfrac{a}{9b}}{\dfrac{8a}{27b}}$$

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

(g) If we compart 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.

(iv) Boyle temperatures in terms of van der Waals constant :

$$T_B = \frac{a}{Rb}$$

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.	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

Ex.8 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 ?

Ans. T_C = 304.2 K P_C = 72.9 atm

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

$\therefore$ $\dfrac{T_C}{P_C} = \dfrac{\dfrac{8a}{27Rb}}{\dfrac{a}{27b^2}} = \dfrac{8a}{27Rb} \times \dfrac{27b^2}{a} = \dfrac{8b}{R}$

or $b = \dfrac{RT_C}{8P_C} = \dfrac{1}{8} \times \dfrac{0.082 \times 304.2}{72.9} = 0.04277$ lit mol^{-1}.

$b = 4\,N_A \times \dfrac{4}{3}\pi r^3 = 42.77$ cm3

$\therefore$ $4 \times N_A \times \dfrac{4}{3}\pi r^3 = 42.77$

or $r^3 = \dfrac{3 \times 42.77 \times 10^{-23}}{16 \times 6.023 \times 3.14}$

or $r^3 = 0.424 \times 10^{-23} = 4.24 \times 10^{-24}$

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

Ex.9 The vander waals constant for gases A, B and C are as follows :

Gas	a/dm⁶ KPa mol⁻²	b/dm³ mol⁻¹
A	405.3	0.027
B	1215.9	0.030
C	607.95	0.032

Which gas has
(i) Highest critical temperature
(ii) The largest molecular volume

Ans.   (i) B gas has the largest critical temperature.   (ii) C gas has the largest molecular volume.

Sol. $T_C = \dfrac{8a}{27Rb}$ Since, R is constant, higher the value of a/b, higher will be critical temperature.

$V_C = 3b$ and $V_C \propto V_m$ (for a particular gas) therefore higher the value of V_C, higher will be molar volume of the gas.

If the critical temperature is close to 273 K, gas will behave ideally around the STP. Let us illustrate the result in a tabular form.

Gas	a/dm⁶ KPa mol⁻²	b/dm³ mol⁻¹	T_C	V_C	a/b
A	405.3	0.027	534.97 K	0.081	1.501 x 10⁴
B	1215.9	0.030	1444.42 K	0.09	4.053 x 10⁴
C	607.95	0.032	677.07 K	0.096	1.89 x 10⁴

Nishant Jindal

(Physical Chemistry) REAL GAS

EXERCISE # (O-I)

PART - I ONLY ONE OPTION CORRECT TYPE

VANDER WAALS' EQUATION OF STATE

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

2. Consider a real gas placed in a container. If the intermolecular attractions are supposed to disappear suddenly which of the following would happen ?

(A) The pressure decreases   (B) The pressure increases

(C) The pressure remains unchanged   (D) The gas collapses

3. The pressure of real gases is less than the pressure of an ideal gas because of :

(A) higher number of collisions   (B) Finite size of molecule

(C) higher KE of molecules   (D) Intermolecular forces of attraction

4. Calculate the radius of He atoms if its Vander Waal's constant 'b' is 24 ml mol^{-1}.

(A) 1.355 Å   (B) 1.314 Å   (C) 1.255 Å   (D) 0.355 Å

COMPRESSIBILITY FACTOR

5. 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) $PV_m = RT - \dfrac{a}{V_m^a}$

6. Compressibility factor at room temperature for H_2 behaving as real gas is :

(A) 1   (B) $\left(1 - \dfrac{a}{RTV}\right)$ (C) $\left(1 + \dfrac{Pb}{RT}\right)$ (D) $\dfrac{RTV}{(1-a)}$

APNI KAKSHA 14

7. At low pressures (For 1 mole), the Vander Waal's equation is written as $\left[p + \dfrac{a}{V^2} \right] V = RT$

The compressibility factor is then equal to :

(A) $\left(1 - \dfrac{a}{RTV} \right)$ (B) $\left(1 - \dfrac{RTV}{a} \right)$ (C) $\left(1 + \dfrac{a}{RTV} \right)$ (D) $\left(1 + \dfrac{RTV}{a} \right)$

8. What is the compressibility factor (Z) for 0.02 mole of a van der Waals' gas at pressure of 0.1 atm. Assume the size of gas molecules is negligible.

Given : RT = 20 L atm mol^{-1} and a = 1000 atm L^2 mol^{-2}

(A) 2   (B) 1   (C) 0.02   (D) 0.5

9. At 273 K temp. and 9 atm pressure, the compressibility factor for a gas is 0.9. The volume of 1 milli-mole of gas at this temperature and pressure is :

(A) 2.24 litre   (B) 0.020 mL   (C) 2.24 mL   (D) 22.4 mL

10. 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.

11. Observe the following Z vs P graph.
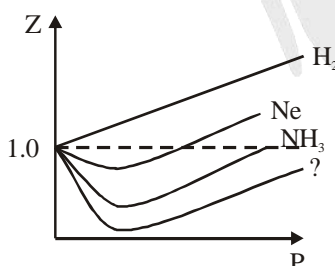
The missing gas in the above graph can be :

(A) He   (B) Ar   (C) H_2O (D) CH_4

12. A real gas most closely approaches the behaviour of an ideal gas at –

(A) 15 atm and 200 K   (B) 1 atm and 273 K

(C) 0.5 atm and 500 K   (D) 15 atm and 500 K

BOYLE'S TEMPERATURE

13. Consider the following statements:

The coefficient B as per Vander Waal's equation

(i) is independent of temperature

(ii) is equal to zero at Boyle temperature $PV_m = RT\left(1 + \dfrac{B}{V_m} + \dfrac{C}{V_m^2} + \ldots\ldots\right)$

(iii) has the dimension of molar volume

Which of the above statements are correct.

(A) i and ii   (B) i and iii   (C) ii and iii   (D) i, ii and iii

CRITICAL PHENOMENON

14. The critical temperature of water is higher than that of O_2 because the water molecule has

(A) Fewer electrons than O_2 (B) two covalent bonds

(C) V-shape   (D) dipole-dipole attraction

15. The van der Waals parameters for gases W, X, Y and Z are

Gas	a(atm L^2 mol^{-2})	b(L mol^{-1})
W	4.0	0.027
X	8.0	0.030
Y	6.0	0.032
Z	12.0	0.027

Which one of these gases has the highest critical temperature ?

(A) W   (B) X   (C) Y   (D) Z

16. Consider the following statements: If the van der Waal's parameters of two gases are given as

	a (atm lit^2 mol^{-2})	b (lit mol^{-1})
Gas X:	6.5	0.056
Gas Y:	8.0	0.011

then   (i) : V_C (X) < V_C (Y)   (ii) : P_C (X) < P_C (Y)   (iii) : T_C (X) < T_C(Y)

Select correct alternate:

(A) (i) alone   (B) (i) and (ii)   (C) (i), (ii) and (iii)   (D) (ii) and (iii)

17. The critical density of the gas CO_2 is 0.44 g cm^{-3} at a certain temperature. If r is the radius of the molecule, r^3 in cm^3 is approximately. (N is Avogadro number)

(A) $\dfrac{25}{\pi N}$ (B) $\dfrac{100}{\pi N}$ (C) $\dfrac{6}{\pi N}$ (D) $\dfrac{25}{4N\pi}$

18. 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

19. Which set of conditions represents easiest way to liquefy a gas :

(A) Decreasing temperature and Increasing pressure

(B) Increasing temperature and decreasing pressure

(C) Decreasing temperature and decreasing pressure

(D) Increasing temperature and Increasing pressure

20. 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, which of the following is true?
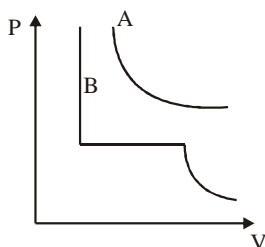
(A) $T_A < T < T_B$ (B) $T_A > T > T_B$ (C) $T_A > T_B > T$ (D) none of above

VAN DER WAALS' EQUATION OF STATE

1. Using the van der Waals equation, calculate the pressure of 10.0 mol NH_3 gas in a 10.0 L vessel at 27ºC.

Given :   a = 4.2 L^2. atm/mol^2 ; b = 0.037 L/mol

2. Calculate the pressure (in kPa) exerted by 22 g of carbon dioxide in 0.5 dm^3 at 298.15 K using:

(a)   Ideal gas equation

(b)   Vander Waals' equation respectively.

Given : [a = 363.76 kPa $dm6$ mol^{-2} and b = 42.67 cm^3 mol^{-1}]

3. Calculate from the van der Waals' equassssssssstion, the temperature at which 192 gm of SO_2 would occupy a volume of 10 dm^3 at 15 atm pressure.[a = 6.7 atm lit^2 mol^2, b = 0.0564 lit mol^{-1}]

4. The molar volume of He at 10.1325 MPa and 273 K is 0.011075 of its molar volume at 101.325 KPa at 273 K. Calculate the radius of helium atom. The gas is assumed to show real gas nature. Neglect the value of **'a'** for He.

5. To an evacuated 504.2 mL steel container is added 25 g $CaCO_3$ and the temperature is raised to 1500 K causing a complete decomposition of the salt. If the density of CaO formed is 3.3 g/cc, find the accurate pressure developed in the container using the Vander Waals equation of state.

The Vander Waal's constants for CO_2(g) are a = 4 $\dfrac{L^2 - atm}{mol^2}$, b = 0.04 $\dfrac{L}{mol}$.

(Ca - 40, C - 12, O - 16). Report your answer as nearest whole number.

6. N_2 molecule is spherical of radius 100 pm.

(a)   What is the volume (in cm^3) of one mole of molecules of a gas?

(b)   What is the value of van der Waals' constant **b** (in cm^3/mole)

COMPRESSIBILITY FACTOR

7. If density of vapours of a substance of molar mass 18 gm at 1 atm pressure and 500 K is 0.36 kg m^{-3}, then calculate the value of Z for the vapours. (Take R = 0.082 L atm $mole^{-1}$ K^{-1})

8. 1 mole of CCl$_4$ vapours at 27°C occupies a volume of 40 lit. If van der Waals' constants are 24.6 L^2 atm mol^{-2} and 0.125 Lmol^{-1}, then, calculate compressibility factor in

    (a) Neglecting 'b' (b) Neglecting 'a'

9. One litre gas at 400 K and 300 atm pressure is compressed to a pressure of 600 atm and 200 K. The compressibility factor is changed from 1.2 to 1.6 respectively. Calculate the final volume of the gas.

10. At 273.15 K and under a pressure of 10.1325 MPa, the compressibility factor of O$_2$ is 0.927. Calculate the mass of O$_2$ necessary to fill a gas cylinder of 100 dm^3 capacity under the given conditions.

11. The density of water vapour at 327.6 atm and 776.4 K is 133.2 gm/dm^3.

    Determine the molar volume, V$_m$ and the compression factor of water vapour .

12. For a fixed amount of real gas when a graph of z v/s P was plotted then at very high pressure slope was observed to be 0.01 atm^{-1}. At the same temperature if a graph is plotted b/w pv v/s P then for 2 moles of the gas 'Y' intercept is found to be 40 atm-liter. Calculate excluded volume in litres for 20 moles of the real gas.

BOYLE'S TEMPERATURE

13. Sign of initial slope of compressibility factor (Z) versus P curve is _____ if a gas is below its Boyle's temperature and _____ if it is above its Boyle's temperature.

14. The van der Waals' constant for O$_2$ are a = 1.36 atm L^2 mol^{-2} and b = 0.0318 L mol^{-1}. Calculate the temperature at which O$_2$ gas behaves ideally for longer range of pressure.

CRITICAL PHENOMENON

15. The van der Waals' constants for gases A, B and C are as follows

Gas	a/dm^6 kPa mol^{-2}	b/dm^3 mol^{-1}
A	405.3	0.027
B	1215.9	0.030
C	607.95	0.032

   Which gas has (i) the highest critical temperature, (ii) the largest molecular volume ?

16. For a real gas (mol. mass = 30) if density at critical point is 0.40 g/cm^3 and its $T_c = \dfrac{2\times10^5}{821}$ K,

then calculate van der Waals' constant a (in atm L^{2}mol^{-2}).

EXERCISE # (O-II)

### ONE OR MORE THAN ONE OPTION CORRECT TYPE

1. Which of the following are correct statements ?

    (A) Vander Waals constant 'a' is a measure of attractive force

    (B) Vander Waals constant 'b' is also called co-volume or excluded volume

    (C) 'b' is expressed in L mol^{-1}

    (D) 'a' is expressed in atm L^2 mol^{-2}

2. The curve of pressure volume (PV) against pressure (P) of the gas at a particular temperature is as shown, according to the graph which of the following is correct (in the low pressure region):
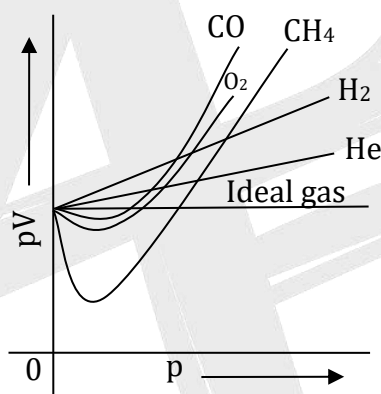

    (A) H$_2$ and He shows +ve deviation from ideal gas equation.

    (B) CO, CH$_4$ and O$_2$ show negative deviation from ideal gas equation.

    (C) H$_2$ and He show negative deviation while CO, CH$_4$ and O$_2$ show positive deviation.

    (D) H$_2$ and He are less compressible than that of an ideal gas while CO, CH$_4$ and O$_2$ more compressible than that of ideal gas.

3.   If critical temperature for the real gas is 500K then the value of-
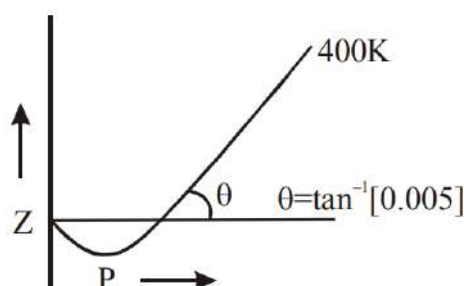
(A) Boyle's temperature is 1687.5 K

(B) Vander Waal's constant a for the gas is 21.6 atm-L^2/mol^2

(C) Gas will show ideal behaviour at high temperature & low pressure.

(D) At Boyle's temperature behaviour of gas is always ideal

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

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

(B) For hydrogen gas 'b' dominates over 'a' at all temperature.

(C) AT low pressure Vander Waals' constant 'b' dominates over 'a'.

(D) At very high pressure Vander Waals' constant 'b' dominates over 'a'.

5.   Select correct statement :

(A) we can condense vapour simply by applying pressure below critical temperature.

(B) to liquefy a gas one must lower the temperature below T_C and also apply pressure

(C) at T_C, there is no distinction between liquid and vapour state hence density of the liquid is nearly equal to density of the vapour

(D) However great the pressure is applied a gas cannot be liquified below it's critical temperature.

6.   Which of the following is correct for critical temperature ?

(A) It is the highest temperature at which liquid and vapour can coexist

(B) Below this temperature, the gas and the liquid phases have different density

(C) At this temperature and critical pressure, the gas and the liquid phases have different densities

(D) At this temperature real gas behaves like ideal gas.

7.   Which of following statement (s) is true

(A) Slope of isotherm at critical point is maximum.

(B) Larger is the value of T_C easier is the liquification of gas.

(C) Ideal gas equation is applicable above critical temperature

(D) Above critical condition, a real gas behaves like an ideal gas.

8.   For a real gas the P-V curve was experimentally plotted and it had the following appearance. With respect to liquifaction. Choose the in**correct** statement.
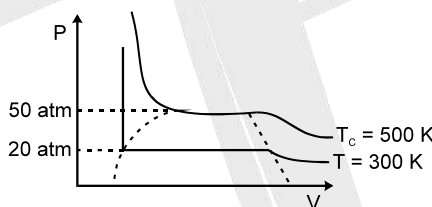
(A) at T = 500 K, P = 40 atm, the state will be liquid.

(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.

PART- III MATCH THE COLUMN

---

9.   **Column – I**   **Column – II**

(A)   At low pressure   (p) $Z = 1 + \dfrac{pb}{RT}$

(B)   At higher pressure   (q) $Z = 1 - \dfrac{a}{V_m RT}$

(C)   At low density of gas   (r)   gas is more compressible

(D)   For H_2 and He at 0°C   (s)   gas is less compressible

EXERCISE # (JEE-MAINS)

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

     (A) At high pressure and low temperature

     (B) At high pressure and high temperature

     (C) At low pressure and low temperature

     (D) At low pressure and high temperature

2   If Z is the compressibility factor, van der Waals' equation at low pressure can be written as :

                                                                            [JEE-MAINS-2014]

     (A) $Z = 1 - \dfrac{Pb}{RT}$ (B) $Z = 1 + \dfrac{Pb}{RT}$ (C) $Z = 1 + \dfrac{Pb}{RT}$ (D) $Z = 1 - \dfrac{a}{V_m RT}$

3.   The compressibility factor for a real gas at high pressure is :-   **[AIEEE-2012]**

     (A) $1 - \dfrac{Pb}{RT}$ (B) $1 + \dfrac{PT}{Pb}$ (C) 1   (D) $1 + \dfrac{Pb}{RT}$

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

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

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

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

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

5.   In van der Waals' equation of state of the gas law, the constant 'b' is a measure of : **[AIEEE-04]**

     (A) intermolecular repulsions

     (B) intermolecular attractions

     (C) volume occupied by the molecules

     (D) intermolecular collisions per unit volume

6. Consider the van der Waals constants, a and b, for the following gases.   **[JEE-MAINS-2019]**

Gas	At	Ne	Kr	Xe
a/(atm dm⁶ mol⁻²)	1.3	0.2	5.1	4.1
b/(10⁻² dm³ mol⁻¹)	3.2	1.7	1.0	5.0

    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 ?

    (A) Xe   (B) Kr   (C) Ne   (D) Ar

7. 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

    $$P = \frac{RT}{V-b} \text{ at T.}$$

    Here, b is the Vander Waals constant. Which gas will exhibit steepest increase in the plot of Z (compression factor) v_s p?   **[JEE-MAINS-2019]**

    (A) Kr   (B) Ar   (C) Xe   (D) Ne

8. Consider the following table :

Gas	a/(k Pa dm⁶ mol⁻¹)	b/(dm³ mol⁻¹)
A	642.32	0.05196
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

    [JEE-MAINS-2019]

    a and b are van der Waals constants. The correct statement about the gases is :

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

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

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

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

9. 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]

    (A) $P_A = 3P_B$ (B) $3P_A = 2P_B$ (C) $2P_A = 3P_B$ (D) $P_A = 2P_B$

10. The unit of the van der Waals gas equation parameter ' a' in $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ is :

    [JEE-Mains-2021]

    (A) $kgms^{-2}$ (B) $dm^3 \, mol^{-1}$
    (C) $kgmsm^{-1}$ (D) $atmdmdmol^{-2}$

11. for a real gas at 25°C temperature and high pressure (99 bar) the value of compressibility factor is 2, so the value of Vander Waal's constant ' b ' should be $\times 10^{-2} \, L \, mol^{-1}$ (Nearest integer) Given $R = 0.083 \, L \, bar^{-1} \, mol^{-1}$)   **[JEE-Mains-2022]**
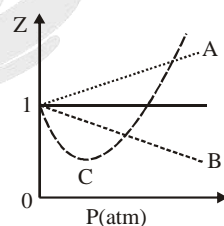
EXERCISE # (JEE-ADVANCE)

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

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

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

2. 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]**

3. 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 .

4. 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

5. 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]**

6. 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

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

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

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

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

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

8. 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]**

9. 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. 　　**[JEE 2006]**

(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.

10. 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. 　　**[JEE 2007]**

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

11. 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

12. The term that corrects for the attractive forces present in a real gas in the Vander Waals' equation is   **[JEE 2009]**

(A) nb   (B) $\frac{an^2}{V^2}$ (C) $-\frac{an^2}{V^2}$ (D) – nb

13. 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]**

$\frac{1}{V}$ (mol litre^{-1})
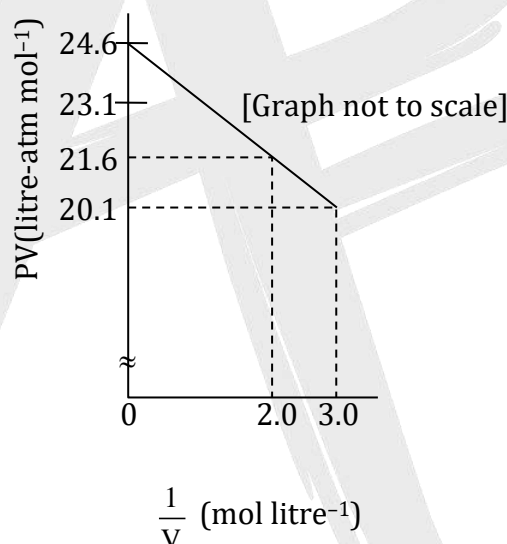
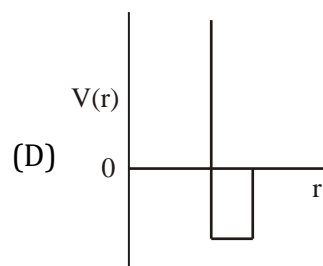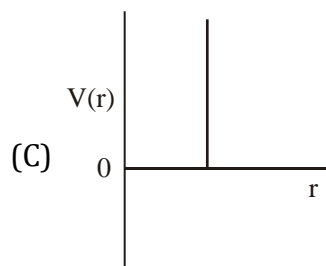(A) 1.0   (B) 4.5   (C) 1.5   (D) 3.0

14. One mole of a monoatomic real gas satisfies the equation P(V– b) = RT where b is a constant. The relationship of interatomic potential V(r) and interatomic distance r for the gas is given by-

[JEE 2015]

(C)

(D)
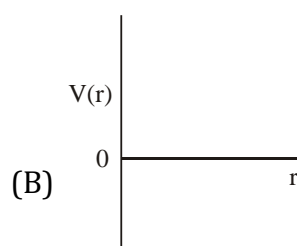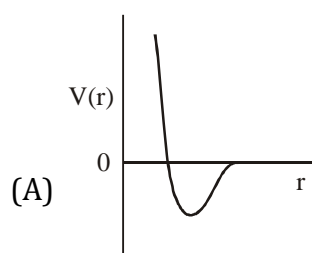
15. A gas has a compressibility factor of 0.5 and a molar volume of $0.4\,dm^3\,mol^{-1}$ at a temperature of 800 K and pressure **x**atm. If it shows ideal gas behaviour at the same temperature and pressure, the molar volume will be **y dm^3**mol^{-1}. The value of **x/y** is
[Use: Gas constant, $R = 8 \times 10^{-2}$ L atm K $^{-1}$ mol^{-1}]   **[JEE ADVANCE 2023]**

ANSWER KEY

EXERCISE O-I

1.	(C)	2.	(B)	3.	(D)	4.	(A)	5.	(C)	6.	(C)	7.	(A)
8.	(D)	9.	(C)	10.	(B)	11.	(C)	12.	(C)	13.	(C)	14.	(D)
15.	(D)	16.	(D)	17.	(D)	18.	(C)	19.	(A)	20.	(A)		

EXERCISE S-I

1. (21.37 atm.) 2. (2479 kPa, (b) 2225.55 kPa) 3. (622.78K)

4. (0.561Å) 5. (62 atm.) 6. ((a) 2.523 cm³, (b) 10.09 cm³mol⁻¹)

7. $(\frac{50}{41})$ 8. ((a) 0.975; (b) 1.003) 9. $(\frac{1}{3}$ litre)

10. (15.39 kg) 11. (Molar vol = 0.1351 L/mol; Z = 0.694)

12. (4) 13. (–ive, +ive) 14. (521 K)

15. ((i) B, (ii) C) 16. (1.6875)

EXERCISE O-II

1.	(ABCD)	2.	(ABD)	3.	(ABC)	4.	(ABC)	5.	(ABC)
6.	(AB)	7.	(AB)	8.	(ABC)				

9. ((A) - q,r (B) – p,s ; (C) – q,r ; (D) – p,s)

JEE MAIN

1.	(A)	2.	(D)	3.	(D)	4.	(B)	5.	(C)	6.	(B)	7.	(C)
8.	(B)	9.	(C)	10.	(D)	11.	(25)						

JEE ADVANCED

1. $(B = \left(b - \dfrac{a}{RT} \right))$ 2. (6.52 atm L2 mol⁻²) 3. (C) 4. (B)

5. (1.256 atm L² mol⁻²)

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

7. (C) 8. (RT) 9. (D)

10.   ((A)→P,S; (B)→R; (C)→P,Q; (D)→R)

11.   (ACD) 12.   (B)   13.   (C)   14.   (C)   15.   (100)

SOLUTION

EXERCISE O-I

VANDER WAALS' EQUATION OF STATE

4. $4 \times \dfrac{4}{3} \pi r^3 \times N_A = 24$

COMPRESSIBILITY FACTOR

6. $PV = Pb + RT$

$\dfrac{PV}{RT} = 1 + \dfrac{Pb}{RT}$

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

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

$\dfrac{PV}{RT} = 1 - \dfrac{a}{VRT}$

8. $\left(P + \dfrac{an^2}{V^2}\right)(V - nb) = n R T$

$PV + \dfrac{an^2}{V} = n R T$

$0.1 \times V + \dfrac{1000(0.02)^2}{V} = 0.02 \times 20$

$V = 2C$

$Z = \dfrac{PV}{nRT} = 0.5$

9. $Z = \dfrac{PV}{nRT}$; $V = \dfrac{0.9 \times 0.0821 \times 273}{9} = 2.24$ litre/mol

∴ Volume of 1 milli-mole of gas = 2.24 mL

12. High T, low P

CRITICAL PHENOMENON

16. $T_C \propto \dfrac{a}{b}$

17. $V_C = 3 \times N \times \dfrac{4}{3} \pi r^3 \times 0.44$

1. $\left(P + \dfrac{n^2 \times 4.2}{(10)^2}\right)(V - nb) = nRT$

$\left(P + \dfrac{(10)^2 \times 4.2}{(10)^2}\right)(10 - 10 \times 0.037) = 10 \times 0.082 \times 300$

2.   (a) 2479 kPa, (b) 2225.55 kPa

3.   622.78K

4.   0.561Å

5. $CaCO_3 \ (s) \xrightarrow{\Delta} CaO \ (s) + CO_2(g)$
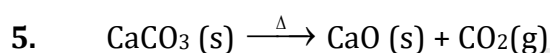
Moles of $CaCO_3$ used = $\dfrac{25}{100}$

Moles of CaO formed = $\dfrac{25}{100}$ = moles of CO_2 formed

Mass of CaO formed = $\dfrac{25}{100} \times 56$ g = 14 g

Volume occupied by CaO = $\dfrac{14}{3.3}$ cc $\simeq$ 4.2 mL

∴ Volume available for CO_2 (g) = 504.2 − 4.2 mL = 0.5 L

Now applying the van der waals equation of state

$\left(p + \dfrac{an^2}{v^2}\right)(v - nb) = nRT$

$\left[p + \dfrac{4 \times (0.25)^2}{(0.5)^2}\right][0.5 - 0.25 \times 0.04] = 0.25 \times 0.082 \times 1500$

$\Rightarrow \quad p = 62.83 - \dfrac{4 \times (0.25)^2}{(0.5)^2} = 61.83$ atm.

6.   (a) 2.523 cm³,   (b) 10.09 cm³ mol⁻¹

COMPRESSIBILITY FACTOR

7. Volume of one mole of given vapour = $\dfrac{18}{0.36}$ L = 50 L

volume of one mole of an ideal gas = $\dfrac{RT}{P}$ = $\dfrac{0.082 \times 500}{1}$ = 41 L

so value of. Z = $\dfrac{V_m, \text{real}}{V_m, \text{ideal}}$ = $\dfrac{50}{41}$

8. (a) 0.975;   (b) 1.003

9. $Z_1 = \dfrac{P_1 V_1}{RT_1}$ and $Z_2 = \dfrac{P_2 V_2}{RT_2}$

$\dfrac{Z_1}{Z_2}$ = $\dfrac{P_1}{P_2} \times \dfrac{T_2}{T_1} \times \dfrac{V_1}{V_2}$ $\Rightarrow V_2 = \dfrac{1}{3}$ litre

10. 15.39 kg

11. Molar vol = 0.1351 L/mol;   Z = 0.694

12. ∵ very high pressure ∴ neglect (a)

∴ Z = 1 + $\dfrac{Pb}{RT}$ Pb ...(1)

Comparing above equation with y = mx + c

∴ m = $\dfrac{b}{RT}$

$\Rightarrow \dfrac{b}{RT}$ = 0.01 (given m = 0.01)

b = 0.01 RT   .....(2)

Z = $\dfrac{(PV)_{\text{real}}}{(PV)_{\text{ideal}}}$

Z = $\dfrac{(PV)_{\text{real}}}{nRT}$ (given for n = 2, PV = 40)

Z = $\dfrac{40}{2RT}$

$Z = \dfrac{20}{RT}$ .....(3)

as, $Z = 1 + \dfrac{Pb}{RT}$

from equation (3)

$\dfrac{20}{RT} = 1 + \dfrac{Pb}{RT}$ .....(4)

10 = RT + Pb

Pb = 20 – RT .....(5)

$(PV)_{real} = 40 = ZnRT = \left(1 + \dfrac{Pb}{2RT}\right)2RT$

$\Rightarrow 40 =$

40 = 2RT + 20 – RT

20 = RT .....(6)

From (2) & (4)

b = 0.01 × 20

b = 0.2

excluded volume for 20 moles

nb = 20 × 0.2

nb = 4

BOYLE'S TEMPERATURE

13. Negative, positive

14. $T_b = \dfrac{a}{Rb} = \dfrac{1.36}{0.0821 \times 0.0318}$

= 521 K

CRITICAL PHENOMENON

15.   (i) $T_C = \dfrac{8}{27}\dfrac{a}{Rb}$

For Gas B T_C is maximum

(ii)   For Gas C,   b is maximum

16. $V_C = \dfrac{\text{Molar mass}}{\text{Density}} = \dfrac{30}{0.4} = 75 \text{ cm}^3$

= 0.075 lit

$V_C = 3b$

b = 0.025

$T_C = \dfrac{8}{27}\dfrac{a}{Rb}$

$\dfrac{2\times10^5}{821} = \dfrac{8}{27}\times\dfrac{a}{0.0821}\times 0.025$

a = 1.6875 atm L^2 mol^{-2}

EXERCISE O-II

2.   If Z > 1 positive deviation

Z < 1 negative deviation

7.   (A)   Slope of isotherm below critical point < 0.

Slope of isotherm above critical point < 0.

Slope of isotherm at critical point = 0.

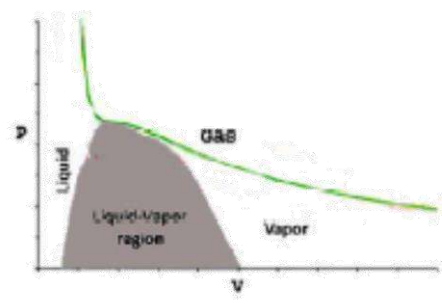So slope of isotherm at critical point is maximum.

(B) $T_C = \dfrac{8a}{27Rb}$

$T_C \propto a$

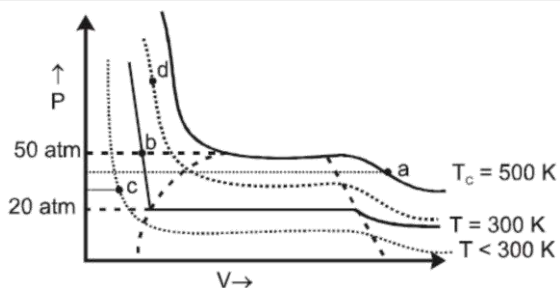Larger value of T_C It means less decreases in temperature is required to liquifly the gas.

Gas will liquify at higher temperature. So, easier'll be liquification.

(C) –   No

(D)   No

8.

(a) at T = 500 K, P = 40 atm corresponds to 'a' substance - gas

(b) at T = 300 K, P = 50 atm corresponds to 'b' substance - liquid

(c) at T < 300 K, P > 20 atm corresponds to 'c' substance - liquid

(d) at T < 500 K, P > 50 atm corresponds to 'd' substance - liquid

So, Answer **(D)**

JEE MAIN

4.   Ease of liquification $\propto \dfrac{a}{b}$

6. $T_C \propto \dfrac{a}{b}$

7. $P = \dfrac{RT}{V-b}$

   $PV - Pb = RT$

   $Z = \dfrac{Pb}{RT}$

   $Z = \left(\dfrac{b}{RT}\right) \cdot P$

   b is maximum for Xe

8. $\Rightarrow$ Gas A and C have same value of 'b' but different value of 'a' so gas having higher value of 'a' have more force of attraction so molecules will be more closer hence occupy less volume.

   $\Rightarrow$ Gas B and D have same value of 'a' but different value of 'b' so gas having lesser value of 'b' will be more compressible.

1. According to the van der Waals equation,

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

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

or $Pv = \dfrac{RTV}{V - b} - \dfrac{a}{V}$

or $Pv = RT\left(1 - \dfrac{b}{V}\right)^{-1} - \dfrac{a}{V} = RT\left(1 + \dfrac{b}{V}\right) - \dfrac{a}{V}$

Neglecting higher powers of b/V

or $PV = RT\left(1 + \dfrac{b}{V} - \dfrac{a}{VRT}\right) = RT\left[1 + \dfrac{1}{V}\left(b - \dfrac{a}{RT}\right)\right]$

Comparing with the given form of the equation. We get

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

2. Vander Waal's equation for n moles of gas is,

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

Given, $v = 4L$, $P = 11$ atm, $T = 300$ K, $b = 0.05$ litre/mol
$n = 2$

Thus, $\left[11 + a\dfrac{2^2}{4^2}\right][4 - 2(0.05)] = 2 \times 0.082 \times 300$

$a = 6.46$ atm litre^2 mol^{-2}

5. We know that, compressibility factor, $Z = PV/RT$

$0.5 = 100 * V/0.082 * 273$

$\therefore V = 0.1117$ L

Note :- Further when volume of a gas molecule is negligible, van der Waal's equation becomes

$(P + a/V^2)(V - 0) = RT$

Or $PV = RT - a/V$ or $a = RTV - PV^2$

Substituting the values

$A = (0.082 * 0.1119 * 173) - (100 * 0.1119 * 0.1119)$

$= 1.253$ atm L^2 mol^{-2}

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

$PV_m - Pb - \dfrac{a}{V_m} + \dfrac{ab}{V_m^2} = RT$

at y intercept, $x = 0$

i.e. $P = 0$

$\Rightarrow \quad V_m \longrightarrow \infty$

So the equation becomes

$PV_m - Pb = RT$

$PV_m = Pb + RT$

$y = m\,x + c$

c is the y intercept

$\therefore \quad c = RT$

14. Since $a = 0$

Hence, only repulsive forces are present which are contributive only at very close distance.

Thus, the potential energy will increase abruptly.

15. $Z = \dfrac{PVm}{RT}$

$0.5 = \dfrac{X0.4}{RT}$

$X \times 0.4 = 0.5RT$

$X \times 0.4 = 0.5R \times 800$

$X = R \times 1000$

$PVm = RT$

$R \times 1000 \times Y = R \times 800$

$Y = 0.8$

$\dfrac{X}{Y} = \dfrac{R \times 1000}{0.8} = \dfrac{0.08 \times 1000}{0.8}$

$\dfrac{X}{Y} = 100$