

REAL GAS

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JEE (Advanced) Syllabus

Gaseous and liquid states : Absolute scale of temperature, ideal gas equation; Deviation from ideality, van der Waals equation; Kinetic theory of gases, average, root mean square and most probable velocities and their relation with temperature; Law of partial pressures; Vapour pressure; Diffusion of gases, Graham's Law.

Board Syllabus

Three states of matter, intermolecular interactions, types of bonding, Boyle's law, Charles's law, Gay Lussac's law, Avogadro's law, ideal gas equation. Kinetic energy and molecular speeds (elementary idea), deviation from ideal behaviour, liquefaction of gases, critical temperature.

Liquid State – Vapour pressure.

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).

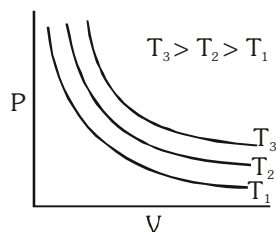
1.1 Comparison between Real and Ideal gas :

IDEAL GAS

(i) $PV = nRT$

⇒

(ii) No liquifaction is possible.



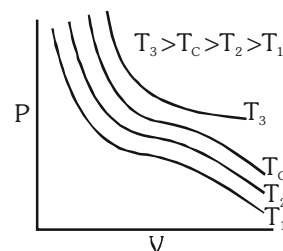
REAL GAS

(i) $PV \neq nRT$

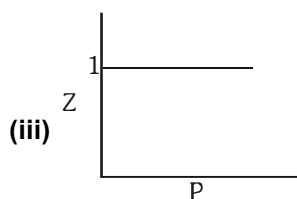
If $PV > nRT$ (Gas is less compressible than ideal gas).

If $PV < nRT$ (Gas is more compressible than ideal gas).

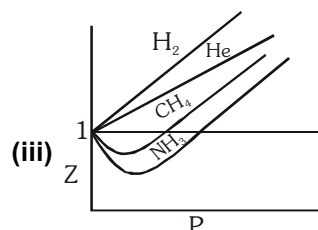
(ii) Liquifaction is possible below a certain temperature.



⇒ Follow critical phenomena and can not liquefy above T_c .



(iii)



(iii)

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

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

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

(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 :

Ideal gas equation :

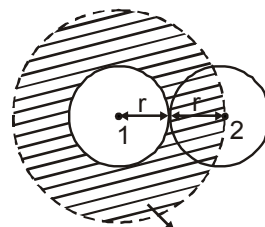
$P_i V_i = nRT$; In the equation ' V_i ' stands for the volume which is available for free movement of the molecules.

V_{ideal} = volume available for free movement of gaseous molecule

hence, $V_i = V - \{\text{volume not available for free movement}\}$ For an ideal gas $V_i = V$ { V = volume of container} but for a real gas $V_i \neq V$, as all the volume is not available for free movement

Molecules have finite volume :

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



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

let us see, how this excluded volume is calculated.

Excluded volume
(not available for free movement)

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.

$$\text{Hence for this pair of real gas molecules, excluded volume per molecule} = \frac{1}{2} \left\{ \frac{4}{3} \pi (2r)^3 \right\} = 4 \left\{ \frac{4}{3} \pi r^3 \right\}$$

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

for n moles, excluded volume = nb

$$V_i = V - nb \quad \text{volume correction}$$

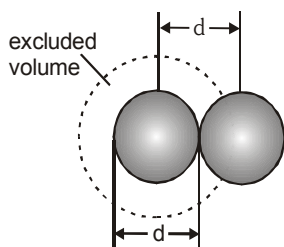
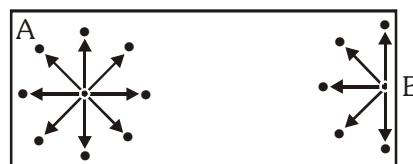


Illustration of excluded volume

(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

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

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

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 $\text{atm lit}^2 \text{mole}^{-2}$ or $\text{dyne cm}^4 \text{mole}^{-2}$ or $\text{Nm}^4 \text{mol}^{-2}$

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



The van der Waals constants for some common gases

Gas	a ($\text{atmL}^2\text{mol}^{-2}$)	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

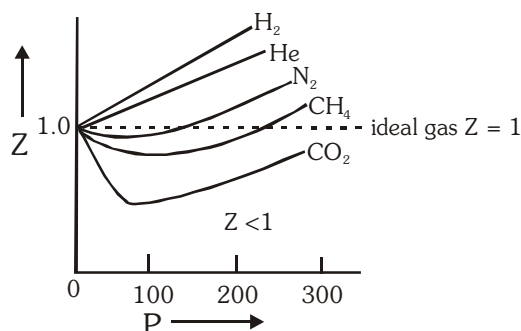
1.3 COMPRESSIBILITY FACTOR (Z) :

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

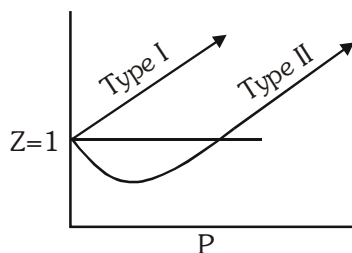
$$Z = \frac{(PV)_{\text{real}}}{(PV)_{\text{ideal}}} = \frac{V_m}{V_{m(\text{ideal})}} = \frac{PV_m}{RT} \quad [V_m = \text{molar volume}]$$

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 0°C .
- (iii) Effect of pressure :
At very low P, $PV_m \approx RT$ i.e. $Z \approx 1$
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 comparison to V_m . But $\frac{a}{V_m^2}$ can't be neglected as pressure is low. Thus equation would be

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

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

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

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

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

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

Then van der Waals' equation will be

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

$$PV_m - Pb = RT$$

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

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

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 $\frac{a}{V_m^2}$ can also be neglected as V_m is very large.

$$PV_m = RT \text{ (ideal gas condition)}$$

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

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

$$\text{So } Z = 1 + \frac{Pb}{RT}$$

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 $a = 3.592 \text{ atm L}^2 \text{ mol}^{-2}$, $b = 0.0427 \text{ L/mol}$. 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

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

$$n_{\text{CO}_2} = 5, V = 1 \text{ litre}, T = 320 \text{ K}, a = 3.592, b = 0.0427$$

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

$$\therefore P = 77.218 \text{ atm}$$

For ideal behaviour of gas, $PV = nRT$

$$\therefore P \times 1 = 5 \times 0.0821 \times 320$$

$$\therefore P = 131.36 \text{ atm}$$

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

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

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

$$\therefore P = 0.9922 \text{ atm}$$

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

- Ex.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 $0.05 \text{ litre mol}^{-1}$.

Ans. $6.52 \text{ atm L}^2 \text{ mol}^{-2}$

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

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

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

- Ex.3.** 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'.

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

Sol. $Z = 1 - \frac{a}{V_m RT}$

$$Z = \frac{PV_m}{RT} \Rightarrow V_m = \frac{RTZ}{P} \quad ; \quad Z = 1 - \frac{a}{(RT)^2} \times \frac{P}{Z}$$

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

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

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 $\left(\frac{1}{V_m}\right)$

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

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 negative 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 :

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

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

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

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

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

comparing vander waals equation with virial equation

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

at low pressure : V_m will be larger

hence $\frac{1}{V_m^2}, \frac{1}{V_m^3}, \dots$ can be neglected

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

$$\text{If } \left(b - \frac{a}{RT}\right) = 0 \Rightarrow \quad \text{at } T = \frac{a}{Rb}; \quad Z = 1$$

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

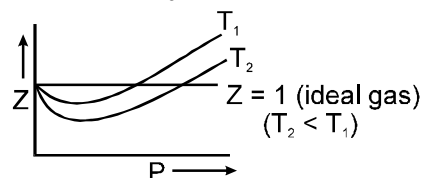
But at constant temperature, ideal gas equation is obeying Boyles law as $T = \frac{a}{Rb}$, so the temperature is called Boyles' temperature.

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

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

For a single gas, if we have two graphs as above, we must conclude $T_2 < T_1$.

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



2. BOYLE TEMPERATURE :

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

(ii) (a) Temperature < Boyle temperature

$Z < 1$, low pressure range

$Z > 1$, high pressure range

(b) Temperature = Boyle temperature

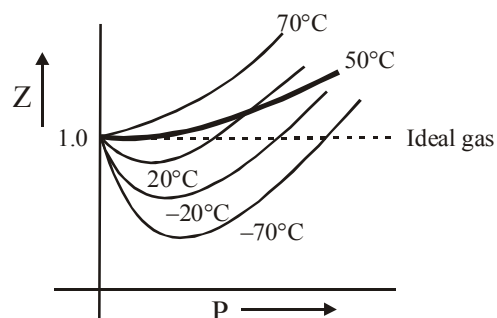
$Z = 1$, low pressure range

$Z > 1$, high pressure range

(c) At temperature > Boyle temperature

$Z > 1$, at all pressure

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



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 than 1.

Ex.4 Calculate the volume occupied by 2 moles of a vanderwall gas at 5 atm 800 K.

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

Sol. $T_B = \frac{a}{Rb} = 800\text{K}$

Gas behave ideally at given condition.

$$PV = nRT$$

$$5 \times V = 2 \times 0.08 \times 800 \quad ; \quad V = 25.6 \text{ litre}$$

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 liquefied.

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.

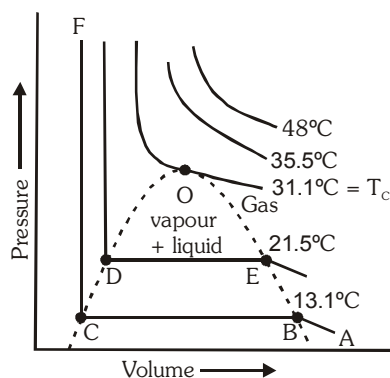


Fig : Isotherms for carbon dioxide

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, $\frac{dP}{dV} = 0$.

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 exist 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 .

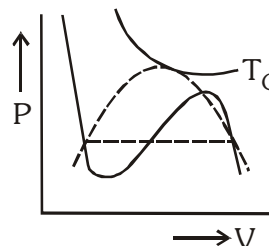
Critical volume (V_c) : The volume occupied by one mole of the system at critical temperature, T_c and critical pressure, P_c is called the critical volume (V_c) of the gas.

3.3 Determination of value of P_c , V_c and T_c :

The Vander waal's equation is

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

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



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 $V' = V'' = V''' = V_c$

\therefore the equation becomes,

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

$$\text{or } V_m^3 - V_c^3 - 3V_c V_m^2 + 3V_c^2 V_m = 0 \quad \dots (2)$$

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.

Ex.5 The critical temperature and pressure of CO₂ gas are 304.2 K and 72.9 atm respectively. What is the radius of CO₂ molecule assuming it to behave as vander Waal's gas ?

Sol. $T_c = 304.2 \text{ K}$ $P_c = 72.9 \text{ atm}$

$$T_c = \frac{8a}{27Rb} \quad P_c = \frac{a}{27b^2}$$

$$\therefore \frac{T_c}{P_c} = \frac{\frac{8a}{27Rb}}{\frac{a}{27b^2}} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R}$$

$$\text{or } b = \frac{RT_c}{8P_c} = \frac{1}{8} \times \frac{0.082 \times 304.2}{72.9} = 0.04277 \text{ lit mol}^{-1}$$

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

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

$$\therefore \text{radius of CO}_2 \text{ molecule} = 1.62 \text{ \AA}$$

Ex.6. Calculate vander waal's constant a and b if critical temperature and critical pressure are 30°C and 72 atm respectively.

Sol. $T_c = \frac{8a}{27Rb}$ and $P_c = \frac{a}{27b^2}$

$$\therefore \frac{T_c}{P_c} = \frac{8b}{R} \text{ or } b = \frac{RT_c}{8P_c}$$

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

$$a = 27P_c \times b^2 = 27 \times 72 \times (0.043)^2 \\ = 3.59 \text{ litre}^2 \text{ atm mol}^{-2}$$

Reduced Equation of state :

Reduced Temp : Temperature in any state of gas with respect to critical temp of the gas

$$T_r = \frac{T}{T_c}$$

Reduced pressure : $P_r = \frac{P}{P_c}$

Reduced volume : $V_r = \frac{V_m}{V_c}$

Vander waals' equation, $\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$

Substitute values : $\left(P_r P_c + \frac{a}{V_r^2 V_c^2}\right)(V_r V_c - b) = R T_r T_c$

Substitute the value of P_c , T_c and V_c

$$\left(P_r \frac{a}{27b^2} + \frac{a}{V_r^2 (3b)^2}\right)(3b V_r - b) = R T_r \frac{8a}{27Rb}$$

$$\left(\frac{P_r}{3} + \frac{1}{V_r}\right)(3V_r - 1) = \frac{8RT_r}{3}$$

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8 T_r \quad (\text{Reduced equation of state})$$

Above equation is independent from a, b and R, so will be followed by each and every gas, independent of its nature.

Example-7 The vander waals constant 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

- Highest critical temperature
- The largest molecular volume
- Most ideal behaviour around STP ?

Solution : $T_c = \frac{8a}{27Rb}$ 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/dm ⁶ KPa mol ⁻²	b/dm ³ mol ⁻¹	T_c	V_c	a/b
A	405.3	0.027	534.97 K	0.081	1.501×10^4
B	1215.9	0.030	1444.42 K	0.09	4.053×10^4
C	607.95	0.032	677.07 K	0.096	1.89×10^4

- B gas has the largest critical temperature.
- C gas has the largest molecular volume.
- A gas has the most ideal behaviour around STP

Example-8 Under critical states of a gas for one mole of a gas, compressibility factor is :
 (A) 3/8 (B) 8/3 (C) 1 (D) 1/4

Solution : For 1 mole of gas $Z = \frac{P_C V_C}{RT_C}$ (Under critical condition)

$$\text{But, } P_C = \frac{a}{27b^2}, V_C = 3b, T_C = \frac{8a}{27Rb}$$

$$\therefore Z = \left(\frac{a}{27b^2} \right) \times \frac{3b}{R} \times \frac{27Rb}{8a} = \frac{3}{8}$$

Hence, Ans. (A)

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 $a = 5.46 \text{ atm litre}^{-2}$ and $b = 0.031 \text{ litre mol}^{-1}$.

Sol. Given, $P = 50 \text{ atm}$, $V = 25 \text{ litre}$, $n = 10$
 $a = 5.46 \text{ atm litre}^2 \text{mol}^{-2}$, $b = 0.031 \text{ litre mol}^{-1}$
 Now vander waal's equation for n mole of gas.

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

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

$$\therefore T = 1529.93 \text{ K} = 1256.93^\circ\text{C}$$

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

$$P[V - b] = RT \text{ (neglecting } a)$$

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

$$\text{or } 100 [V_1 - b] = 0.0821 \times 273 = 22.41 \quad \dots(1)$$

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

$$\text{or } [V_2 - b] = 22.41 \quad \dots(2)$$

$$\text{by eq. (1)} \quad V_1 - b = 0.2241 + b \quad \dots(3)$$

$$\text{by eq. (2)} \quad V_2 - b = 22.41 + b \quad \dots(4)$$

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

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

$$(V_1 = 0.011075 V_2 \text{ is given})$$

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

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

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

$$\therefore r = 1.33 \times 10^{-8} \text{ cm}$$

3. 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

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

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

b = 0.05 litre mol⁻¹ ; n = 2

$$\text{Thus, } \left[11 + \frac{2^2 a}{4^2} \right] [4 - 2 \times 0.05] = 2 \times 0.082 \times 300.$$

$$\therefore a = 6.46 \text{ atm litre}^2 \text{ mol}^2$$

4. Positive deviation from ideal behaviour takes place because of

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

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

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

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

Ans. (C)

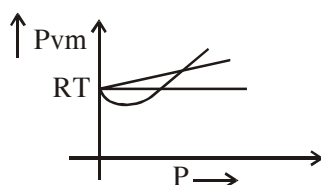
Sol. Positive deviation from ideal behavior takes place because of finite size of atoms & compressibility factor Z > 1.

5. 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.

Ans. RT

Sol. $\lim_{P \rightarrow 0} PV_m = RT$

Since, at very low P, all gases behave ideally.

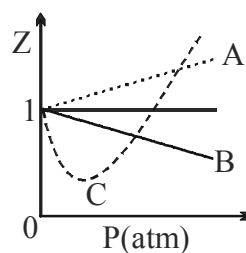


6. The given graph represents the variation of Z

(compressibility factor = $\frac{PV}{nRT}$) 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.



Ans. (D)

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

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

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

$$\text{So, } z = 1 - \frac{a}{V_m RT} \Rightarrow b = 0$$

(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) in terms 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.

Exercise-1

Marked Questions may have for Revision Questions.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Vander waal equation and compresibility factor (Z)

Commit to memory :

Vander waal's equation is $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

$Z = 1$ for ideal gas ; at all pressures for He/H₂ ($Z = \frac{Pb}{RT} + 1$); $Z < 1$ at low pressure (for all other gases)

($Z = 1 - \frac{a}{V_m RT}$) ; $Z > 1$ at high pressure (for all other gases) ($Z = \frac{Pb}{RT} + 1$)

A-1. Using the van der Waals equation, calculate the pressure of 10.0 mol NH₃ gas in a 10.0 L vessel at 27°C.

$$\left(P + n^2 \frac{a}{V^2}\right)(V - nb) = nRT \quad a = 4.2 \text{ L}^2 \cdot \text{atm/mol}^2 \quad b = 0.037 \text{ L/mol}, R = 0.08 \text{ atm L/mol} \times K$$

A-2. Calculate the pressure exerted by 22 g of carbon dioxide in 0.5 dm³ at 300 K using:

(a) the ideal gas law and

(b) Van der Waal's equation respectively.

Given : [a = 3.6 atm litre²mol⁻², b = 0.04 litre mol⁻¹, R = 0.08 L-atm/K-mol]

A-3. The density of mercury is 13.6 g/cm³. Estimate the value of 'b' (in cm³/ mole).

Atomic mass of Hg = 200

A-4. The molarity of O₂ gas at 72 atm and 300K is 6M. Calculate the value of Z for O₂.

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

A-5. 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 dm³ mol⁻¹ ; R = 0.08 atm lit mol⁻¹ K⁻¹.

A-6. Calculate from the Van der Waals equation, the temperature at which 192 g of SO₂ would occupy a volume of 6 dm³ at 15 atm pressure. [a = 5.68 atm L² mol⁻², b = 0.06 L mol⁻¹]

R = 0.08 atm L/mol × K

A-7. 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.

A-8. Certain mass of a gas occupy 500 ml at 2 atm and 27°C. Calculate the volume occupied by same mass of the gas at 0.3 atm and 227°C. The compressibility factors of gas at the given condition are 0.8 and 0.9, respectively.

A-9. 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)

Section (B) : Virial equation of state, Boyle's temperature, Critical constant, reduced equation of state

Commit to memory :

Critical point : At this point, all the physical properties of liquid phase will be equal to physical properties in vapour such that density of liquid = density of vapour.

T_c or critical temp : Temperature above which a gas can not be liquified.

P_c or critical pressure : Minimum pressure which must be applied at critical temperature to convert the gas into liquid.

V_c or critical volume : Volume occupied by one mole of gas at T_c & P_c .

$$P_c = \frac{a}{27b^2} \quad V_c = 3b \quad T_c = \frac{8a}{27Rb}$$

$$\text{Boyles' temperature } T_B = \frac{a}{Rb}$$

B-1. The Van der Waals constants for gases A, B and C are as follows

Gas	$a/[\text{atm L}^2 \text{mol}^{-2}]$	$b/[\text{L mol}^{-1}]$
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?

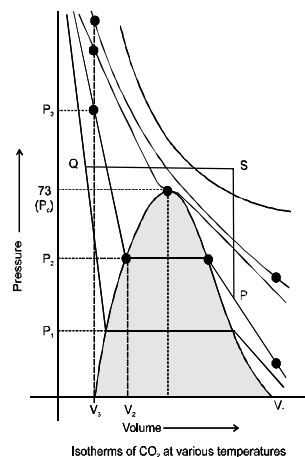
B-2. The critical temperature and critical pressure of a gas are 31°C and 728 atmospheres respectively. Calculate the constants 'a' and 'b'.

B-3. The vander waal's constant for a gas are $a = 1.92 \text{ atm L}^2 \text{mol}^{-2}$, $b = 0.06 \text{ L mol}^{-1}$. If $R = 0.08 \text{ L atm K}^{-1} \text{mol}^{-1}$, what is the Boyle's temperature of this gas.

B-4. Identify true and false statements for fixed amount of gas in following isotherm of real gas.

(i) From point P to point S volume is constant and temperature is increasing.

(ii) From point S to point Q pressure is constant and temperature is decreasing.



B-5. Calculate the volume occupied by 2.0 mole of N_2 at 200 K and 8.21 atm pressure, if $\frac{P_c V_c}{RT_c} = \frac{3}{8}$ and

$$\frac{P_r V_r}{T_r} = 2.4.$$

B-6. For a real gas (mol. mass = 30) if density at critical point is 0.40 g/cm^3 and its $T_c = \frac{2 \times 10^5}{821} \text{ K}$, then calculate Van der Waals constant a (in $\text{atm L}^2 \text{mol}^{-2}$).

B-7. Reduced temperature for benzene is 0.7277 and its reduced volume is 0.40. Calculate the reduced pressure of benzene.

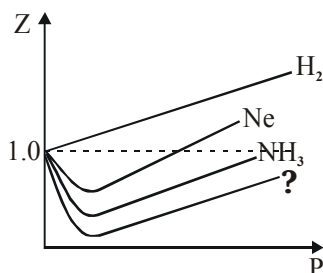
PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Vander waal equation and compresibility factor (Z)

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

- (A) $\left(P + \frac{a}{n^2 V^2}\right)(V - nb) = nRT$ (B) $\left(P + \frac{an^2}{V^2}\right)(V - nb) = \Delta nRT$
 (C) $\left(P + \frac{an^2}{V^2}\right)(V - b) = nRT$ (D) $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

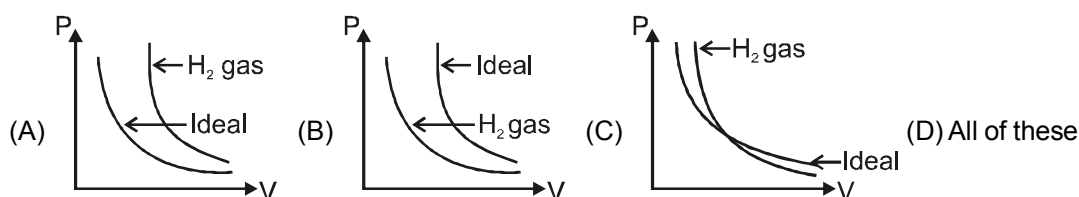
A-2. Observe the following Z vs P graph.



The missing gas in the above graph can be :

- (A) He (B) Ar (C) C_5H_{12} (D) All are correct
- A-3.** Consider the equation $Z = \frac{PV}{RT}$, 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
- A-4.** The density of a gaseous substance at 1 atm pressure and 750 K is 0.30 g/lit. 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
- A-5.** 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
- A-6.** The pressure of real gases is less than the pressure of an ideal gas because of :
 (A) Increase in number of collisions (B) Finite size of molecule
 (C) Increases in KE of molecules (D) Intermolecular forces of attraction
- A-7.** A real gas obeying Vander Waal's equation will resemble ideal gas, if the :
 (A) constants a & b are small (B) a is large & b is small
 (C) a is small & b is large (D) constant a & b are large

A-8. The correct graph to H_2 gas is : (at room temperature)



A-9. If temperature and volume are same, the pressure of a gas obeying Vander Waals equation is :

- (A) Smaller than that of an ideal gas (B) Larger than that of an ideal gas
(C) same as that of an ideal gas (D) none of these

A-10. For the non-zero values of force of attraction between gas molecules, gas equation will be :

- (A) $PV = nRT - \frac{n^2a}{V}$ (B) $PV = nRT + nbP$ (C) $PV = nRT$ (D) $P = \frac{nRT}{V-b}$

A-11. Compressibility factor for H_2 behaving as real gas is under normal condition :

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

A-12. At low pressures (For 1 mole), the Vander Waal's equation is written as

$$\left[p + \frac{a}{V^2}\right] V = RT$$

The compressibility factor is then equal to :

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

A-13. Calculate the radius of He atoms if its Vander Waal's constant 'b' is $\frac{\pi}{20} \text{ ml mol}^{-1}$.

(Note 1 ml = 1 cubic centimeter)

$$(N_A = 6 \times 10^{23})$$

- (A) 0.25 Å (B) 1.25 Å (C) 0.5 Å (D) 1 Å

A-14. In vander Waal's equation of state for a non ideal gas the term that accounts for intermolecular forces is :

- (A) nb (B) nRT (C) n^2a/V^2 (D) $(nRT)^{-1}$

A-15. A gas obeys the equation of state $P(V-b) = RT$ (The parameter b is a constant). The slope for an isochore will be :

- (A) Negative (B) Zero (C) $R/(V-b)$ (D) R/P

A-16. If V is the volume of one molecule of a gas, then van der Waals constant 'b' is : (N_0 = Avogadro's number)

- (A) $\frac{4V}{N_0}$ (B) 4V (C) $\frac{N_0}{4V}$ (D) $4VN_0$

A-17. On heating vapours of $S_8(g)$ decomposes to $S_2(g)$. Due to this, the van-der Waal's constant 'b' for the resulting gas

- (A) increases (B) decreases (C) remains same (D) changes unpredictably

Section (B) : Virial equation of state, Boyle's temperature, Critical constant, reduced equation of state

- B-1.** 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 moment
- B-2.** Select incorrect statement :
 (A) we can condense vapour simply by applying pressure
 (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 applied, a gas cannot be liquified below its critical temp.
- B-3.** The values of Vander Waal's constant "a" for the gases O_2 , N_2 , NH_3 & CH_4 are 1.36, 1.39, 4.17, 2.253 $L^2 \text{ atm mole}^{-2}$ respectively. The gas which can most easily be liquified is:
 (A) O_2 (B) N_2 (C) NH_3 (D) CH_4
- B-4.** The correct order of normal boiling points of O_2 , N_2 , NH_3 and CH_4 , for whom the values of vander Waal's constant 'a' are 1.360, 1.390, 4.170 and 2.253 $L^2 \text{ atm. mol}^{-2}$ respectively, is :
 (A) $O_2 < N_2 < NH_3 < CH_4$ (B) $O_2 < N_2 < CH_4 < NH_3$
 (C) $NH_3 < CH_4 < N_2 < O_2$ (D) $NH_3 < CH_4 < O_2 < N_2$
- B-5.** The van der Waals parameters for gases W, X, Y and Z are
- | Gas | a(atm $L^2 \text{ mol}^{-2}$) | 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
- B-6.** One way of writing the equation of state for real gases is $PV = RT \left[1 + \frac{B}{V} + \dots \right]$
 where B is a constant. An approximate expression for B in terms of the van der Waals constant 'a' and 'b' is
 (A) $B = a - \frac{b}{RT}$ (B) $B = b - \frac{a}{RT}$ (C) $B = RT - \frac{a}{b}$ (D) $B = \frac{b}{a}$
- B-7.** The third virial coefficient of a He gas is $4 \times 10^{-2} (\text{lit/mol})^2$, 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) 45.2 lit
- B-8.** 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 |
- 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

PART - III : MATCH THE COLUMN

1. **Column – I**(A) H_2 gas at NTP(B) O_2 gas having density more than $\frac{10}{7}$ g/L at NTP(C) SO_2 gas at NTP having density more than $\frac{20}{7}$ g/L(D) He gas at NTP having density less than $\frac{1}{5.6}$ g/L**Column – II**

(p) Molar volume = 22.4 L

(q) Molar volume > 22.4 L

(r) More compressible with respect to ideal gas

(s) Less compressible with respect to ideal gas

2. Match the column :

Column-I

(A) Boyle's temperature(Consider low pressure region)

(B) Compressibility factor

(C) Real gas with very large molar volume

(At moderate temperature)

(D) Critical temperature

Column-II

(P) Depends on 'a' and 'b'

(Q) Depends on identity of real gas

(R) The temperature at which $\frac{dZ}{dP} = 0$ at low pressure region.(S) $PV = nRT$ (T) $\frac{8a}{27R.b}$

3.

Column – I

(A) At low pressure

(B) At higher pressure

(C) At low density of gas

(D) For H_2 and He at $0^\circ C$ **Column – II**(p) $Z = 1 + \frac{pb}{RT}$ (q) $Z = 1 - \frac{a}{V_m RT}$

(r) gas is more compressible

(s) gas is less compressible

Exercise-2

Marked Questions may have for Revision Questions.

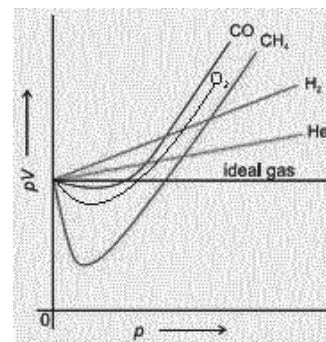
PART - I : ONLY ONE OPTION CORRECT TYPE

1. 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 incorrect (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.



2. At 273 K temp. and 9 atm pressure, the compressibility 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
3. 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
4. Calculate the compressibility factor for CO_2 , if one mole of it occupies 0.4 litre at 300 K and 40 atm. Comment on the result. ($R = 0.08 \text{ atm lit / mol} \times K$)
 (A) 0.40, CO_2 is more compressible than ideal gas
 (B) 0.67, CO_2 is more compressible than ideal gas
 (C) 0.55, CO_2 is more compressible than ideal gas
 (D) 0.62, CO_2 is more compressible than ideal gas

5. Consider the following statements:
 The coefficient B in the virial equation of state
 (i) is independent of temperature

(ii) is equal to zero at Boyle temperature

(iii) has the dimension of molar volume

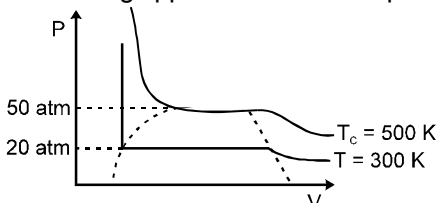
Which of the above statements are correct.

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

$$PV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$$

6. At Boyle's temperature, the value of compressibility factor $Z = (PV_m / RT = V_{\text{real}} / V_{\text{ideal}})$ has a value of 1, over a wide range of pressure. This is due to the fact that in the van der Waal's equation
 (A) the constant 'a' is negligible and not 'b'
 (B) the constant 'b' is negligible and not 'a'
 (C) both the constant 'a' and 'b' are negligible
 (D) the effect produced due to the molecular attraction compensates the effect produced due to the molecular volume
7. 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 : (N is Avogadro number)

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

8. Which of following statement (s) is true
 I – Slope of isotherm at critical point is maximum.
 II – Larger is the value of T_c easier is the liquification of gas.
 III – Vander waals equation of state is applicable below critical temperature at all pressure.
 (A) only I (B) I & II (C) II & III (D) only II
9. 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 options :
 (A) (i) alone (B) (i) and (ii) (C) (i), (ii) and (iii) (D) (ii) and (iii)
10. For a real gas the P-V curve was experimentally plotted and it had the following appearance. With respect to liquifaction. Choose the **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 - II : NUMERICAL TYPE QUESTIONS

1. Calculate the temperature ($^{\circ}\text{C}$) at which 0.2 mole of a Vander waal gas have 60 ltr. volume and 0.0821 atm pressure.
 $[a = 4.105 \text{ L}^2 \text{ atm mol}^{-2}, b = \frac{1}{6} \text{ Lmol}^{-1}]$
2. At what pressure and 127°C , the density of O_2 gas becomes 1.6 g/L ?
 $[a = 4.0 \text{ atm L}^2 \text{ mol}^{-2}, b = 0.4 \text{ Lmol}^{-1}, R = 0.08 \text{ L - atm/ K-mol}]$
3. The vander waals constant 'b' of a gas is $4\pi \times 10^{-4} \text{ L/mol}$. The radius of gas atom can be expressed in scientific notation as $z \times 10^{-9} \text{ cm}$. Calculate the value of z. (Given $N_A = 6 \times 10^{23}$)
4. 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.
5. 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.
 $[R = 0.08 \text{ L-atm/K-mol}]$
6. Calculate molecular diameter for a gas if its molar excluded volume is $3.2 \pi \text{ ml}$. (in nanometer).
7. 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 : $RT = 20 \text{ L atm mol}^{-1}$ and $a = 1000 \text{ atm L}^2 \text{ mol}^{-2}$
8. 1 mole of CCl_4 vapours at 127°C occupies a volume of 10 L. If van der Waal's constant are $a = 20 \text{ L}^2 \text{ atm mol}^{-2}$ and $b = 0.2 \text{ L mol}^{-1}$, calculate compressibility factor Z under,
 $R = 0.08 \text{ atm lit/ mol} \times \text{K}$
 (a) low pressure region (b) high pressure region
 Report your answer as nearest whole number of $(a + b) \times 10$.

9. 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 Van der waals equation of state. The van der waals constants for $\text{CO}_2(\text{g})$ are $a = 4 \frac{\text{L}^2 - \text{atm}}{\text{mol}^2}$, $b = 0.04 \frac{\text{L}}{\text{mol}}$. (Ca - 40, C - 12, O - 16).
($R = 0.08 \text{ atm lit/mol} \times \text{K}$)
10. If C & D are the third & fourth virial coefficients. If $\frac{D}{C} = \frac{V_C}{x}$ then find the value of x.
11. If the ratio of PV_m & RT for a real gas is $\frac{x}{24}$ at a temp where $\left(\frac{\partial P}{\partial V_m}\right) = 0$. The find value of x.

PART - III : 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) van der Waals constant 'b' is also called co-volume or excluded volume
(C) 'b' is expressed in L mol^{-1}
(D) 'a' is expressed in $\text{atm L}^2 \text{mol}^{-2}$
2. Which of the following statements are correct ?
(A) It is not possible to compress a gas at a temperature below T_c
(B) At a temperature below T_c , the molecules are close enough for the attractive forces to act and condensation occurs
(C) No condensation takes place above T_c
(D) Due to higher kinetic energy of gas molecules above T_c , it is considered as super critical fluid
3. Which of the following is correct for critical temperature ?
(A) It is the highest temperature at which liquid and vapour can coexist
(B) It is lesser than boyle's temprature
(C) At this temperature, the gas and the liquid phases have different critical densities
(D) All are correct
4. The vander waal gas constant 'a' is given by
(A) $\frac{1}{3} V_c$ (B) $3P_c V_c^2$ (C) $\frac{1}{8} \frac{RT_c}{P_c}$ (D) $\frac{27}{64} \frac{R^2 T_c^2}{P_c}$
5. Select the correct statement(s) :
(A) At Boyle's temperature a real gas behaves like an ideal gas at low pressure
(B) Above critical conditions, a real gas behave like an ideal gas
(C) For hydrogen gas 'b' dominates over 'a' at all temperature
(D) At high pressure van der Waals' constant 'b' dominates over 'a'
6. A 1 litre vessel contains 2 moles of a vanderwaal's gas.
Given data : $a = 2.5 \text{ atm-L}^2 \text{ mole}^{-2}$ $T = 240 \text{ K}$
 $b = 0.4 \text{ L-mole}^{-1}$ $RT = 20 \text{ L-atm mole}^{-1}$
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

7. 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 generally show negative deviation from ideal behaviour at low pressure condition.
8. 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) At Boyle's temperature a real gas behaves like an ideal gas in low pressure region
 (D) At high pressure Van der Waals constant 'b' dominates over 'a'.
9. Which is/are correct for real gases ?
 (A) $\lim_{P \rightarrow 0} (PV_m) = \text{constant}$ at constant high temperature
 (B) $\lim_{V_m \rightarrow 0} (PV_m) = \text{constant}$ at constant low temperature
 (C) $\lim_{P \rightarrow 0} \left(\frac{PV_m}{RT} \right) = 1$ at high temperature
 (D) $\lim_{V \rightarrow 0} \left(\frac{PV_m}{RT} \right) = R$
10. Which of the following statements are incorrect ?
 (A) Molar volume of every gas at STP is 22.4 L
 (B) Under critical state compressibility factor is 1
 (C) pressure of a real gas is always less than that of ideal gas (At same V,T,n)
 (D) At absolute zero, KE is $3/2 R$.

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

One of the important approach to the study of real gases involves the analysis of a parameter Z called the compressibility factor $Z = \frac{PV_m}{RT}$ where P is pressure, V_m is molar volume, T is absolute temperature and R is

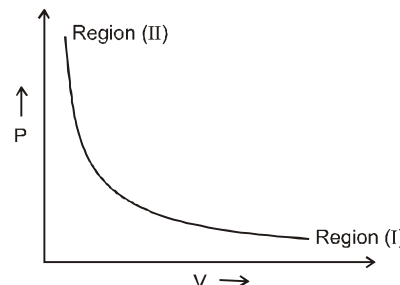
the universal gas constant. Such a relation can also be expressed as $Z = \left(\frac{V_{m \text{ real}}}{V_{m \text{ ideal}}} \right)$ (where $V_{m \text{ ideal}}$ and $V_{m \text{ real}}$ are

the molar volume for ideal and real gas respectively). Gas corresponding $Z > 1$ have repulsive tendencies among constituent particles due to their size factor, whereas those corresponding to $Z < 1$ have attractive forces among constituent particles. As the pressure is lowered or temperature is increased the value of Z approaches 1. (reaching the ideal behaviour)

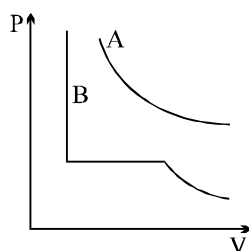
1. Choose the conclusions which are appropriate for the observation stated.

Observation	Conclusion
I. $Z = 1$	I. The gas need not be showing the ideal behaviour
II. $Z > 1$	II. On applying pressure the gas will respond by increasing its volume
III. $Z < 1$	III. The gas may be liquefied.
IV. $Z \rightarrow 1$ for low P	IV. The gas is approaching the ideal behaviour.
(A) All conclusions are true	(B) Conclusions I, II & IV are true
(C) Conclusions I, III & IV are true	(D) Conclusions III & IV are true

2. For a real gas 'G' $Z > 1$ at STP Then for 'G' :
Which of the following is true :
(A) 1 mole of the gas occupies 22.4 L at NTP
(B) 1 mole of the gas occupies 22.4 L at pressure higher than that at STP (keeping temperature constant)
(C) 1 mole of the gas occupies 22.4 L at pressure lower than that at STP (keeping temperature constant)
(D) None of the above
3. Following graph represents a pressure (P) volume (V) relationship at a fixed temperature (T) for n moles of a real gas. The graph has two regions marked (I) and (II). Which of the following options is true.
(A) $Z < 1$ in the region (II)
(B) $Z = 1$ in the region (II)
(C) $Z = 1$ for the curve
(D) Z approaches 1 as we move from region (II) to region (I)

**Comprehension # 1**

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



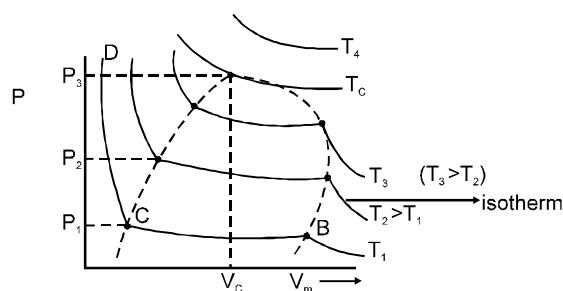
4. Which of the following is true?
(A) $T_A < T < T_B$
(B) $T_A > T > T_B$
(C) $T_A > T_B > T$
(D) none of above
5. The correct statement(s) is/are
(I) Pressure correction term will be more negligible for gas B at T K.
(II) The curve for gas 'B' will be of same shape as for gas A if $T > T_B$
(III) Gas '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

Comprehension # 2**Critical constant of A gas**

When pressure is increased at constant temp volume of gas decreases

AB → gases, BC → vapour + liquid, CD → liquid

critical point : At this point all the physical properties of liquid phase will be same as the physical properties in vapour such as, density of liquid = density of vapour



T_c or critical temp : Temperature above which a gas can not be liquified

P_c or critical pressure : minimum pressure which must be applied at critical temp to convert the gas into liquid.

V_c or critical volume : volume occupied by one mole of gas at T_c & P_c

CRITICAL CONSTANT USING VANDER WAAL EQUATIONS :

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

$$PV_m^3 + aV_m - PbV_m^2 - ab - RTV_m^2 = 0 \quad \Rightarrow \quad V_m^3 + V_m^2 \left(b + \frac{RT}{P}\right) + \frac{a}{P} V_m - \frac{ab}{P} = 0$$

since equation is cubic in V_m hence there will be three roots of equation at any temperature and pressure. At critical point all three roots will coincide and will give single value of $V_m = V_c$
at critical point, Vander Waal equation will be

$$V_m^3 - V_m^2 \left(b + \frac{RT_c}{P_c}\right) + \frac{a}{P_c} V_m - \frac{ab}{P_c} = 0 \quad \dots(1)$$

But at critical point all three roots of the equation should be equal, hence equation should be :

$$\begin{aligned} V_m &= V_c \\ (V_m - V_c)^3 &= 0 \\ V_m^3 - 3V_m^2 V_c + 3V_m V_c^2 - V_c^3 &= 0 \quad \dots(2) \end{aligned}$$

comparing with equation (1)

$$b + \frac{RT_c}{P_c} = 3V_c \quad \dots(i) \quad \frac{a}{P_c} = 3V_c^2 \quad \dots(ii) \quad \frac{ab}{P_c} = V_c^3 \quad \dots(iii)$$

From (ii) and (iii), $V_c = 3b$

$$\text{From (ii)} \quad P_c = \frac{a}{3V_c^2} \quad \text{substituting} \quad P_c = \frac{a}{3(3b)^2} = \frac{a}{27b^2}$$

$$\text{From (i)} \quad \frac{RT_c}{P_c} = 3V_c - b = 9b - b = 8b \quad \Rightarrow \quad T_c = \frac{8a}{27Rb}$$

At critical point, the slope of PV curve (slope of isotherm) will be zero at all other point slope will be negative zero is the maximum value of slope.

$$\left(\frac{\partial P}{\partial V_m}\right)_{T_c} = 0 \quad \dots(i) \quad \frac{\partial}{\partial V_m} \left(\frac{\partial P}{\partial V_m}\right)_{T_c} = 0 \quad \dots(ii)$$

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

using the two T_c , P_c and V_c can be calculated by

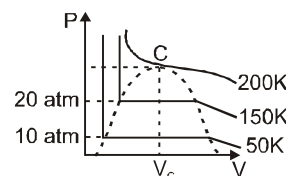
$$\begin{array}{c} \uparrow \\ V_c \quad T_c \quad \& \quad P_c \\ \downarrow \\ a \end{array}$$

6. A scientist proposed the following equation of state $P = \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3}$. If this equation leads to the critical behaviour then critical temperature is :

- (A) $\frac{8B}{27RC}$ (B) $\frac{B}{8RC}$ (C) $\frac{B^2}{3RC}$ (D) None of these

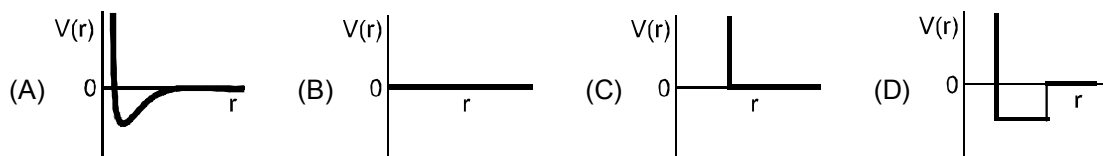
7. Identify the wrong statement related to the above graph :

- (A) between 50 K and 150 K temperature and pressure ranging from 10 atm to 20 atm matter may have only liquid state.
(B) zero is the maximum value of the slope of P-V Curve
(C) If Vander Waal equation of state is applicable above critical temperature then cubic equation of V_m will have one real and two imaginary roots.
(D) At 100 K and pressure below 20 atm it has liquid state only



6. 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(Advanced)-2015, 4/168]



PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. In vander Waal's equation of state of the gas law, the constant 'b' is a measure of :
[AIEEE-2004, 3/225]
(1) Intermolecular collisions per unit volume (2) Intermolecular attractions
(3) Volume occupied by the molecules (4) Intermolecular repulsions
2. 'a' and 'b' are van der Waals' constants for gases. Chlorine is more easily liquefied than ethane because :
[AIEEE-2011, 4/120]
(1) a and b for $\text{Cl}_2 > a$ and b for C_2H_6
(2) a and b for $\text{Cl}_2 < a$ and b for C_2H_6
(3) a and $\text{Cl}_2 < a$ for C_2H_6 but b for $\text{Cl}_2 > b$ for C_2H_6
(4) a for $\text{Cl}_2 > a$ for C_2H_6 but b for $\text{Cl}_2 < b$ for C_2H_6
3. The compressibility factor for a real gas at high pressure is :
[AIEEE-2012, 4/120]
(1) $1 + RT/pb$ (2) 1 (3) $1 + pb/RT$ (4) $1 - pb/RT$
4. If Z is a compressibility factor, vander Waals equation at low pressure can be written as :
[JEE(Main) 2014, 4/120]
(1) $Z = 1 + \frac{RT}{Pb}$ (2) $Z = 1 - \frac{a}{VRT}$ (3) $Z = 1 - \frac{Pb}{RT}$ (4) $Z = 1 + \frac{Pb}{RT}$
5. When does a gas deviate the most from its 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
6. 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
7. 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) $3P_A = 2P_B$

8. 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 $p = \frac{RT}{V-b}$ 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

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

Gas	Ar	Ne	Kr	Xe
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

[JEE-MAINS-2019]

Which gas is expected to have the highest critical temperature?

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

10. 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

ANSWER KEY

EXERCISE # 1

PART - I

A-1.	20.72 atm.	A-2.	(a) 24.0 atm, (b) 21.4 atm	A-3.	58.82
A-4.	0.5	A-5.	222.22	A-6.	398 K
A-7.	$\frac{1}{3}$ litre	A-8.	6.25 L	A-9.	$\frac{50}{41}$
B-1.	(i) A, (ii) A, (iii) C	B-2.	$a = 0.36 \text{ atm litre}^2 \text{ mole}^{-2}$, $b = 4.28 \times 10^{-3} \text{ litre/mole}$		
B-3.	400 K	B-4.	(i) T (ii) T	B-5.	3.6 L
B-6.	1.6875	B-7.	10.358 atm		

PART - II

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

PART - III

1.	(A) – q,s ; (B) – r ; (C) – r ; (D) – q,s	2.	(A) – P,Q,R,S ; (B) – P,Q ; (C) – S ; (D) – P,Q,T
3.	(A) – q,r (B) – p,s ; (C) – q,r ; (D) – p,s		

EXERCISE # 2

PART - I

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

PART - II

1.	27	2.	1.622 atm.	3.	5	4.	4	5.	6.67 kg	6.	0.2
7.	0.5	8.	20	9.	60.22 atm.	10.	3	11.	9		

PART - III

1.	(ABCD)	2.	(BCD)	3.	(AB)	4.	(BD)	5.	(AD)	6.	(ABD)
7.	(ABD)	8.	(AB)	9.	(AC)	10.	(ABCD)				

PART - IV

1.	(D)	2.	(B)	3.	(D)	4.	(A)	5.	(C)	6.	(C)	7.*	(AD)
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EXERCISE # 3

PART - I

1.*	(ABC)	2.	A – p, s ; B – r ; C – p, q ; D – r	3.	(ACD)	4.	(B)
5.	(C)	6.	(C)				

PART - II

1.	(3)	2.	(4)	3.	(3)	4.	(2)	5.	(1)	6.	(4)	7.	(1)
8.	(3)	9.	(1)	10.	(3)								