

Law of Corresponding states :-

A reduced Van der Waal's equation in terms of reduced pressure (π), reduced temperature (θ) & reduced volume (ϕ) is known as law of corresponding state.

Van der Waal's eq^s for 1-mole of gas is written as -

$$\left(P + \frac{a}{V^2}\right) (V - b) = RT \quad \text{--- (1)}$$

We know that -

$$V_c = 3b \quad \Rightarrow \quad b = \frac{V_c}{3}$$

$$P_c = \frac{a}{27b^2} = \frac{a}{27\left(\frac{V_c}{3}\right)^2} = \frac{a}{3 \times 27 \frac{V_c^2}{9}} = \frac{a}{3V_c^2}$$

$$\Rightarrow a = 3P_c V_c^2$$

$$\& T_c = \frac{8a}{27bR} = \frac{8 \times 3P_c V_c^2}{27 \frac{V_c}{3} R} = \frac{8P_c V_c}{3R}$$

$$\therefore R = \frac{8P_c V_c}{3T_c}$$

Putting all these values in eq^s (1) we get.

$$\left(P + \frac{3P_c V_c^2}{V^2}\right) \left(V - \frac{V_c}{3}\right) = \frac{8P_c V_c}{3T_c} \cdot T$$

On dividing it by $P_c V_c$ throughout, we get

$$\frac{\left(P + \frac{3P_c V_c^2}{V^2}\right) \left(V - \frac{V_c}{3}\right)}{P_c V_c} = \frac{8}{3} \frac{P_c V_c / P_c V_c \times T}{T_c}$$

$$\Rightarrow \frac{P}{P_c} + \frac{3}{\cancel{P_c}} \left(\frac{V_c}{V}\right)^2 \left(\frac{V}{V_c} - \frac{1}{3}\right) = \frac{8}{3} \frac{T}{T_c} \quad \text{--- (2)}$$

Putting $\frac{P}{P_c} = \pi$, $\frac{V}{V_c} = \phi$ & $\frac{T}{T_c} = \theta$ in eq^s (2), we get.

$$\left(\pi + \frac{3}{\phi^2} \right) \left(\phi - \frac{1}{3} \right) = \frac{8}{3} \phi \quad \text{--- (3)}$$

$$\text{or } \left(\pi + \frac{3}{\phi^2} \right) (3\phi - 1) = 8\phi$$

This eqn (3) is independent of a, b & R and holds good for any mass of the substances. It has been assumed that molecular state remains the same throughout it gives value of pressure, volume & temperature. This is known as law of corresponding state.

* Test of law of corresponding state :-

from eqn (3)

$$\pi + \frac{3}{\phi^2} = \frac{8\phi}{3\phi - 1}$$

$$\pi = \frac{8\phi}{3\phi - 1} - \frac{3}{\phi^2}$$

if ϕ and number are constant. then,

$$\pi = \phi$$

This eqn suddenly state that there is a linear relationship between π and ϕ if ϕ is constant.

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$$\text{or } Z = \frac{PV}{nRT}$$

→ When $Z = 1$, $PV = nRT$ (Gases show ideal behaviour)

→ When $Z \neq 1$, $PV \neq nRT$ (Gases show Real behaviour)

Thus, Compressibility factor is a measure of deviation from ideality.

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* Cause of deviation from ideal behaviour :-

Deviations from the ideal gas behaviour are large at high pressure and low temperature. Under such conditions, the total volume of the gas is small. Thus, the two postulates of kinetic molecular theory of gases are faulty. These are -

- 1) There is no force of attraction or repulsion between the molecules of a gas.
- 2) Volume of the gas molecules is negligible in comparison to the total volume of the gas.

Thus, real gases show deviation from ideal behaviour. At high pressure, molecules of gases are very close to each other. Due to molecular attraction, the molecules do not strike the walls of the container with full impact because they are dragged back by other gas molecule due to molecular attractive force. Thus the pressure exerted by the real gas is lower in comparison with the ideal gas.

At high pressure, the molecules are almost in contact and repulsive force become significant. The volume occupied by the gas molecule become significant. Thus instead of moving in volume V , the gas molecules are restricted to move $(V - nb)$, where nb is the total volume occupied by the gas molecules themselves.

* Vander Waal's Equations (Reduced equation of state)
(Equation of state for Real gas) :-

Vander Waal's equation is the modified form of an ideal gas equation by applying the correction in pressure and volume.

Pressure Correction :-

At high pressure, molecules of gases are very close together. Due to molecular attraction, the molecule do not strike the walls of the container with full impact. Thus, the pressure exerted by the real gas is lower in comparison to an ideal gas.

Thus,

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2} \quad (\text{for } n \text{ mole}) \quad \text{--- (1)}$$

Volume Correction :-

At high pressure, the molecules are almost in contact and repulsive force becomes significant. The volume occupied by the gas molecule become significant. Thus instead of moving in volume V , the gas molecules are restricted to move $(V - nb)$, where 'nb' is the total volume occupied by the gas molecules.

Thus,

$$V_{\text{ideal}} = V_{\text{real}} - nb \quad (\text{for } n\text{-mole}) \quad \text{--- (2)}$$

from an ideal gas equation -

$$PV = nRT \quad \text{--- (3)}$$

Putting the value of P and V from eqs (1) & (2) in eqs --- (3) we get -

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad \text{--- (4)} \\ (\text{for } n\text{-mole})$$

for 1-mole, $n = 1$

$$\therefore \left(P + \frac{a}{v^2} \right) (v - b) = RT \quad \text{--- (5)}$$

Where, 'a' & 'b' are called Vander waal's constant.

* Unit of a & b :-

Unit of 'a' -

$$P = \frac{an^2}{v^2}$$

$$\begin{aligned} \text{or } a &= \frac{Pv^2}{n^2} = \frac{\text{atm L}^2}{\text{mol}^2} \\ &= \text{atm L}^2 \text{mol}^{-2} \\ &\equiv (\text{bar dm}^6 \text{mol}^{-2}) \end{aligned}$$

Unit of 'b' -

$$V = nb$$

$$\begin{aligned} \text{or } b &= \frac{V}{n} = \frac{\text{L}}{\text{mol}} = \text{L mol}^{-1} \\ &\equiv (\text{dm}^3 \text{mol}^{-1}) \end{aligned}$$

$$(1 \text{ L} = \text{dm}^3)$$

* Significance of Vanderwaal's Constant 'a' & 'b'.

The Vander waal's constant 'a' is the measure of strength of the Vander waal's force between the molecules of the gas. Greater is the magnitude of 'a' stronger are the Vander waal's forces, and thus greater is the case with which gas can be liquefied.

The Vander waal's constant 'b' represents effective volume of gas molecules. It has been observed that its value remains constant over a wide range of temperature & pressure for a gas. This show that gas molecules are incompressible.

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Assignment :-

- ① Derive an Equation of state for real gas. At what conditions gases deviates from ideal behaviour.
- ② Using Vanderwaal's equation, calculate the pressure exerted by 1-mole of CO₂. when it occupies a volume of 0.05 litre at 100°C. Given that $a = 3.592 \text{ atm L}^2 \text{ mol}^{-2}$,
 $b = 0.0426 \text{ L mol}^{-1}$,
 $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$.
- ③ Compare the above result with the pressure calculated using an ideal gas equation.
- ④ Two moles of ammonia are enclosed in a five litre flask at 27°C. calculate the pressure exerted by the gas assuming that :
 - (a) the gas behaves like an ideal gas -
 - (b) the gas behaves like a real gas -

Given, $a = 4.17 \text{ atm L}^2 \text{ mol}^{-2}$,
 $b = 0.037 \text{ L mol}^{-1}$,
 $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$.

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Solution (Answer) of Test Exam. -

(1) a (2) c (3) b (4) c

(5) d (6) d (7) b (8) b.

* Relationship between Vanderwaal's constants and critical constants :-

From Vanderwaal's eqⁿ -

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

$$\Rightarrow pv + \frac{a}{v} - pb - \frac{ab}{v^2} = RT$$

Multiply throughout by v^2 , we get.

$$pv^3 + av - pbv^2 - ab = RTv^2$$

$$\Rightarrow pv^3 + av - pbv^2 - ab - RTv^2 = 0$$

$$\Rightarrow pv^3 - pbv^2 - RTv^2 + av - ab = 0$$

on dividing by p , we get -

$$\frac{pv^3}{p} - \frac{pbv^2}{p} - \frac{RTv^2}{p} + \frac{av}{p} - \frac{ab}{p} = 0$$

$$\Rightarrow v^3 - bv^2 - \frac{RTv^2}{p} + \frac{av}{p} - \frac{ab}{p} = 0$$

$$\Rightarrow v^3 - bv^2 - \left(b + \frac{RT}{p}\right)v^2 + \frac{av}{p} - \frac{ab}{p} = 0. \quad \text{--- (1)}$$

This is a third-degree equation in terms of v (cubic equation in v) and below a certain value of temperature T , the equation can have three real roots. with rise in temperature, these roots approach one another and become identical ultimately.

Since the value of the three roots of the Vander Waal's equation at critical point,

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

$$\approx V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \quad \text{--- (2)}$$

Under critical conditions, $T = T_c$ & $P = P_c$

On substituting these values in eqn- (1) we get -

$$V^3 - V^2 \left(b + \frac{RT_c}{P_c} \right) + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \quad \text{--- (3)}$$

Both eqn- (2) & (3) are identical. Hence,

$$3V_c = b + \frac{RT_c}{P_c} \quad \text{--- (4)}$$

$$3V_c^2 = \frac{a}{P_c} \quad \text{--- (5)}$$

$$V_c^3 = \frac{ab}{P_c} \quad \text{--- (6)}$$

On dividing eqn- (6) by (5) we get.

$$\frac{V_c^3}{3V_c^2} = \frac{ab}{P_c} \times \frac{P_c}{a}$$

$$\approx \frac{V_c}{3} = b \quad \approx \boxed{V_c = 3b}$$

Substituting the value of V_c in eqn- (5) we get -

$$3(3b)^2 = \frac{a}{P_c}$$

$$\approx 27b^2 = \frac{a}{P_c} \quad \approx \boxed{P_c = \frac{a}{27b^2}}$$

On substituting the value of V_c & P_c in eqn- (4) we get -

$$3 \times 3b = b + \frac{RT_c}{\frac{a}{27b^2}}$$

$$\approx 3 \times 3b = b + RT_c \times \frac{27b^2}{a}$$

$$\Rightarrow 9b = b + RT_c \times \frac{27b^2}{a}$$

$$\Rightarrow 8b = RT_c \times \frac{27b^2}{a}$$

$$\Rightarrow T_c = 8b \times \frac{a}{27b^2} \times \frac{1}{R}$$

$$\Rightarrow T_c = \frac{8a}{27bR}$$

Where, V_c , T_c & P_c are critical Volume, Critical Temperature & Critical Pressure respectively.

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Problems:-

1) Use the equation of state of Vander Waals to calculate the pressure of 8g of gaseous CO_2 occupying a volume of 3 L at 27°C (Gives, $a = 3.6 \text{ L}^2 \text{ atm mol}^{-2}$, $b = 0.043 \text{ L mol}^{-1}$, $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$). Compare the above result with the pressure calculated using ideal gas equation.

2) 2 mole of NH_3 at 300K occupy a volume of $5 \times 10^{-3} \text{ m}^3$. Calculate the pressure using Vander Waals equation.
 $a = 0.417 \text{ Nm}^4 \text{ mol}^{-2}$ and $b = 0.037 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$.
 $R = 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1}$.
 Compare the above result with the pressure calculated using ideal gas equation.

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Problem (1). (Page no-25)

Using Vanderwaal's gas eqⁿ for n mole-

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad \text{--- (1)}$$

$$\approx P + \frac{an^2}{V^2} = \frac{nRT}{V - nb}$$

$$\therefore P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad \text{--- (2)}$$

Given,

$$n = \frac{8}{44} = 0.181 \quad (\text{for } CO_2)$$

$$a = 3.6 \text{ L}^2 \text{ atm mol}^{-2}$$

$$b = 0.043 \text{ L mol}^{-1}$$

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

$$V = 8 \text{ L}$$

$$T = 27 + 273 = 300 \text{ K}$$

$$P = ?$$

Putting all these values in eqⁿ (2) we get.

$$P = \frac{0.181 \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{8 \text{ L} - 0.181 \times 0.043 \text{ L mol}^{-1}} - \frac{3.6 \text{ L}^2 \text{ atm mol}^{-2} \times (0.181)^2}{(8 \text{ L})^2}$$

on solving this -

$$P \approx 5.56 \times 10^1 \text{ atm.}$$

Again, from an ideal gas eqⁿ -

$$PV = nRT \quad \therefore P = \frac{nRT}{V} \quad \text{--- (3)}$$

Putting all these value in eqⁿ (3) we get -

$$P \approx 5.58 \times 10^1 \text{ atm.}$$