

GASEOUS STATE

PART- III

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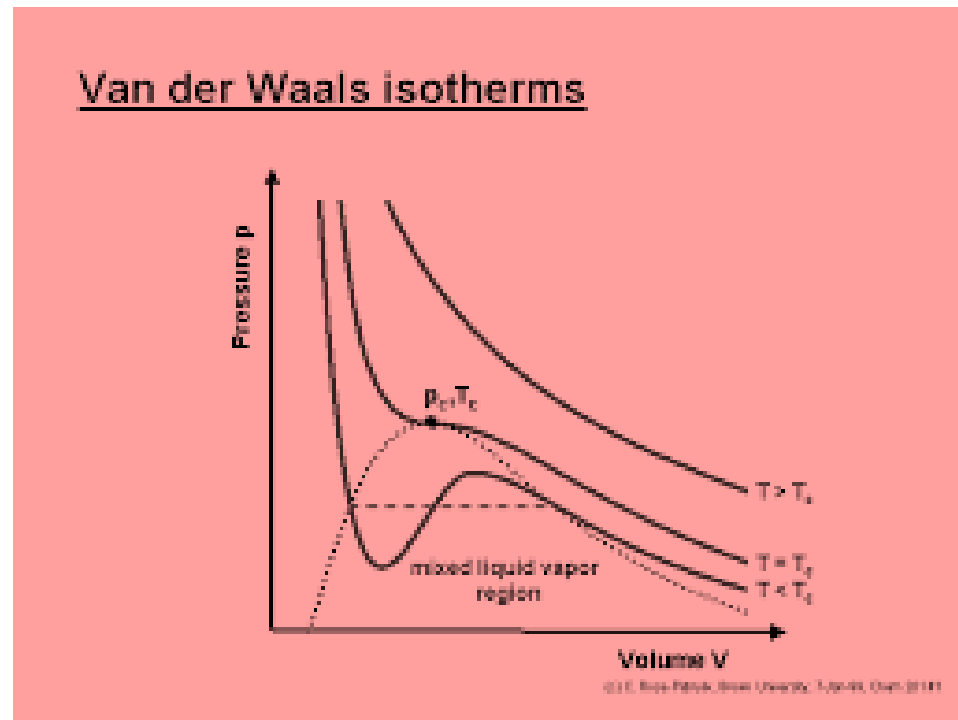
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Sem I Honours (CC – 2)

van der Waals equation

- Accounts for:
 - Non-zero volumes of gas particles
 - Attractive forces between gas particles (*attractive effect*)



- Correction for volume

$$V_i = V - nb$$

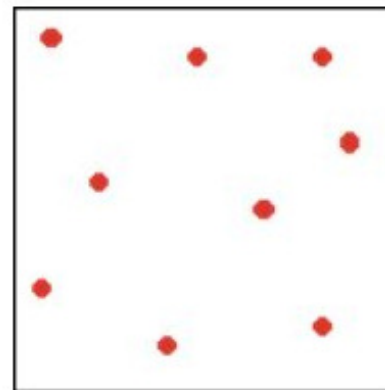
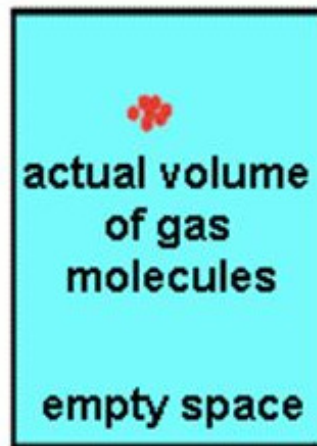
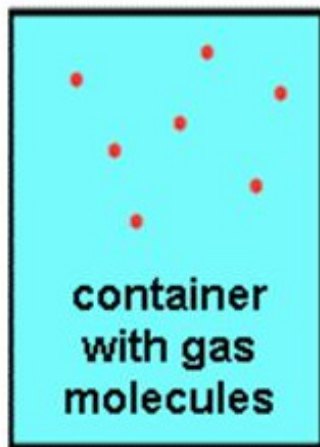
n = no. of moles

b = effective volume occupied by molecules in 1 mole of a gas (excluded volume/ co-volume)

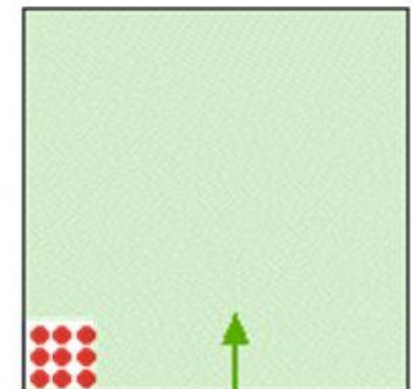
V_i = free volume

V = total volume

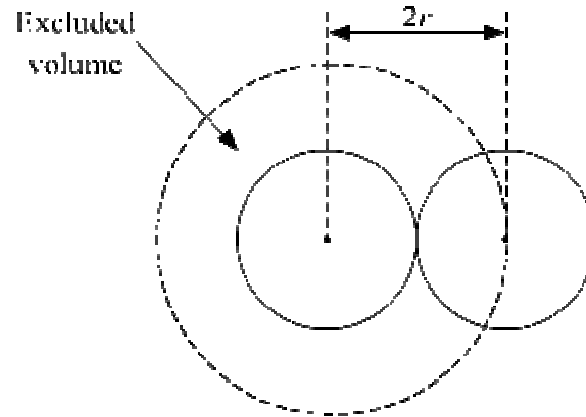
*Numerical value of 'b' is **four** times the actual volume occupied by the gas molecules.*



Kinetic Theory assumes that all of this space is available for the molecules to move around in . . .



. . . but, in fact, only this amount is available, because the rest is taken up by the molecules themselves.



- If we consider only bimolecular collisions, then the volume occupied by the sphere of radius $2r$ represents the excluded volume per pair of molecules which is given by, $\frac{4}{3}\pi(2r)^3 = 8\left(\frac{4}{3}\pi r^3\right)$
- Excluded volume per molecules = $4\left(\frac{4}{3}\pi r^3\right)$
- 'b' represent excluded volume per mole of the gas, $\therefore b = N_A \cdot 4\left(\frac{4}{3}\pi r^3\right)$

- Correction for pressure**

Consider a molecule in the bulk of the vessel, which is surrounded by other molecules symmetrically. As a result, it experiences no net force of attraction.

A molecule which is about to strike a side of the vessel is considered. There are molecules only on one side of the vessel. Hence, this molecule experiences a net force of attraction towards the centre of the vessel. Thus, there is a decrease in its velocity and hence in its momentum which results in decrease in pressure of the gas compared to ideal gas.

$$P_i = P + \text{correction term}$$

Correction term depends upon:

[1] No. of molecules per unit volume of the vessel

$$\text{Correction term} \propto \frac{n}{V}$$

[2] No. of molecules striking the side of the vessel in unit time (1 sec)

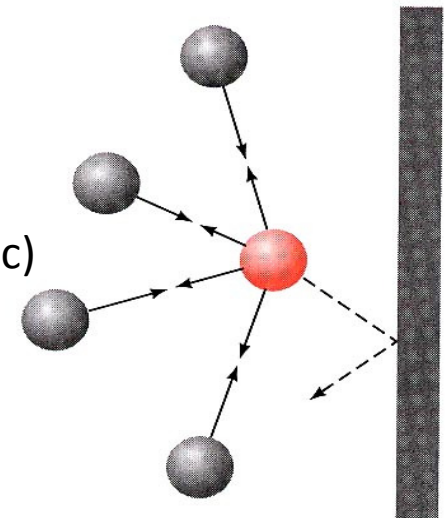
$$\text{Correction term} \propto \frac{n}{V}$$

$$\text{Thus, correction term} = a \cdot \frac{n^2}{V^2}$$

Thus,

$$P_i V_i = nRT$$

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



van der Waals equation

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

'a' and 'b' are called van der Waal's constants.

Units of 'a' and 'b'

$$P + \frac{an^2}{V^2} \Rightarrow \text{pressure}$$

$$V - nb \Rightarrow \text{unit of volume}$$

$$\frac{an^2}{V^2} \Rightarrow Pa$$

$$b \Rightarrow dm^3 mol^{-1}$$

$$a \Rightarrow Pa dm^6 mol^{-2}$$

- "a" and "b" are **determined by experiment**
- "a" and "b" are **different for each gas**
- **bigger molecules** have **larger "b"**
- "a" depends on both **size** and **polarity**

Applicability of van der Waals equation

- At low pressure and high temperature

When pressure is low, volume is considerably high and 'b' can thus be ignored. Thus, for 1 mole of a gas,

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

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

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

Thus, in low pressure region, Z is less than 1. As $V \propto \frac{1}{P}$, thus on increasing P , Z will further decrease with increase in P .

- At high pressure

When P is high, V_m is low and value of ' b ' cannot be ignored. However, $\frac{a}{V_m^2}$ can be ignored.

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

$$\Rightarrow PV_m - Pb = RT$$

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

Thus, Z is greater than 1 and it increases linearly with pressure.

- At high temperature and low pressure

At high temperature, the value of V_m will be considerably high. The value of $\frac{a}{V_m^2}$ will be very small. The value of ' b ' may also be neglected in comparison to V_m .

$$PV_m = RT$$

Thus, van der Waal's gas equation reduces to ideal gas equation.

- Hydrogen and helium

For hydrogen and helium, the value of ' a ' is extremely low as these gases are difficult to liquify.

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

So, Z is greater than 1 and it increases linearly with pressure.

- Drawback of van der Waals equation

Generality of van der Waals equation is lost as it contains two constants whose values depend upon the nature of gas.

Determination of critical constants for van der Waals gas

- For 1 mole of van der Waal gas,
$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

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

- At critical point, the maxima and the minima coalesce, and it is thus, a point of inflexion.

- At critical point,
$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4}$$

- At critical point,
$$-\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

$$\Rightarrow \frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3} \dots\dots\dots(1)$$

and
$$\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0$$

$$\Rightarrow \frac{RT_c}{(V_c - b)^3} = \frac{3a}{V_c^4} \dots\dots\dots(2)$$

(1) *divided by* (2)
$$V_c - b = \frac{2}{3}V_c$$

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

$$\Rightarrow \boxed{V_c = 3b} \dots\dots\dots(3)$$

- Putting (3) in (1), $\frac{RT_c}{4b^2} = \frac{2a}{27b}$

$$\Rightarrow T_c = \frac{8a}{27Rb} \dots\dots\dots(4)$$

- Now,
$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2}$$

$$= \frac{8aR}{27Rb \cdot 2b} - \frac{a}{9b^2}$$

$$= \frac{4a}{27b^2} - \frac{a}{9b^2}$$

$$= \frac{4a - 3a}{27b^2}$$

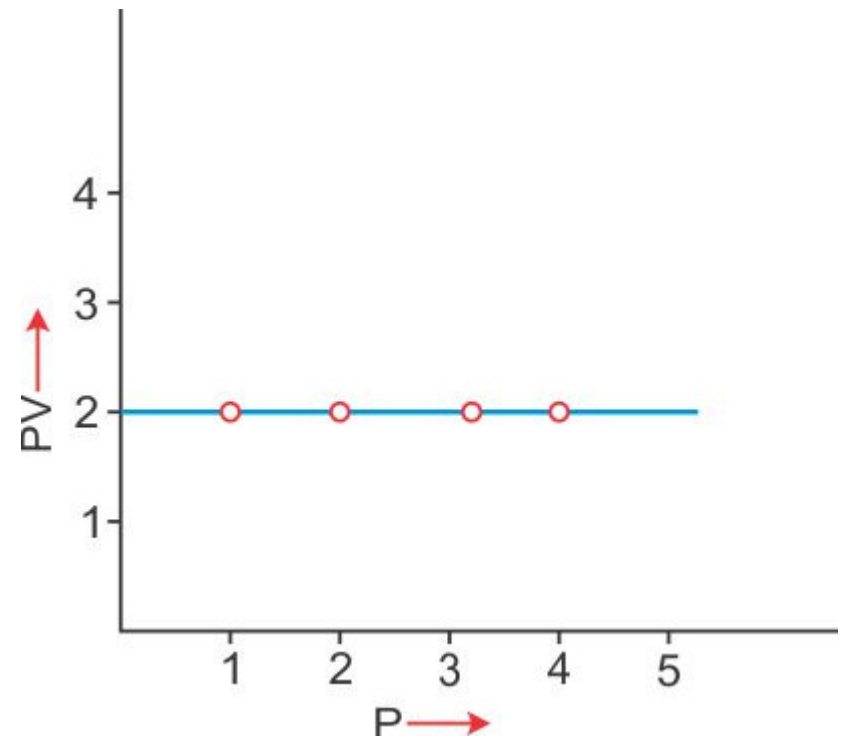
$$P_c = \frac{a}{27b^2} \dots\dots\dots(5)$$

- Critical co-efficient i.e. $\frac{RT_c}{P_c V_c} = R \cdot \frac{8a}{27Rb} \cdot \frac{27b^2}{a} \cdot \frac{1}{3b} = \frac{8}{3} = 2.66$

Boyle's temperature

- There exists for every gas a characteristic temperature where the curve (PV vs P) runs almost parallel to P axis from zero pressure to moderate values of pressure. It means at this temperature, the value of PV remains constant for an appreciable range of pressure, i.e. Boyle's law is obeyed. This temperature is known as Boyle temperature (T_B).
- Mathematically, at T_B ,

$$\frac{\partial(PV)}{\partial P} = 0, \quad P \rightarrow 0$$



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

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

$$\Rightarrow PV = \frac{RTV}{V - b} - \frac{a}{V}$$

$$\begin{aligned} \left[\frac{\partial(PV)}{\partial P}\right]_T &= \frac{RT}{V - b} - \frac{RTV}{(V - b)^2} + \frac{a}{V^2} \\ &= \frac{RTV - RTb - RTV}{(V - b)^2} + \frac{a}{V^2} \\ &= -\frac{RTb}{(V - b)^2} + \frac{a}{V^2} \end{aligned}$$

$$\text{At } T_B, \left[\frac{\partial(PV)}{\partial P}\right]_T = 0$$

$$\Rightarrow \frac{-RT_B b}{(V - b)^2} + \frac{a}{V^2} = 0$$

$$\Rightarrow T_B = \frac{a}{Rb} \left(\frac{V - b}{V}\right)^2$$

When $P \rightarrow 0$, V is infinitely large,
i.e. $V - b \approx V$

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

$$\text{Thus, } \frac{T_B}{T_c} = \frac{a}{Rb} \cdot \frac{27Rb}{8a} = \frac{27}{8}$$

Reduced equation of state

$$P = \pi P_c$$

reduced
pressure

$$V = \phi V_c$$

reduced
volume

$$T = \theta T_c$$

reduced
temperature

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

$$\left(\pi P_c + \frac{a}{(\phi V_c)^2} \right) (\phi V_c - b) = R \theta T_c$$

$$\left(\frac{a\pi}{27b^2} + \frac{a}{9b^2\phi^2} \right) (3b\phi - b) = \frac{8aR\theta}{27Rb}$$

$$\frac{ab}{27b^2} \left(\pi + \frac{3}{\phi^2} \right) (3\phi - 1) = \frac{8aR\theta}{27Rb}$$

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

This equation is independent of a , b and R and hence applicable to all gases.

Law of corresponding states

If two substances have same reduced pressure and are also at the same reduced temperature, then their reduced volumes should be the same. The substances under such conditions are said to be in the corresponding states and the principle stated above is called the **law of corresponding states**.