

REAL GASES

- Ideal gases obey the gas laws and the ideal gas equation ($PV=nRT$) at all temperatures and pressures.
- When gases do not obey gas laws and the ideal gas equation ($PV=nRT$), then they are called **real gases**.
- But real gases obey the ideal conditions at very high temperatures and very low pressures.
- At all other intermediate conditions, real gases deviate from ideal behavior.

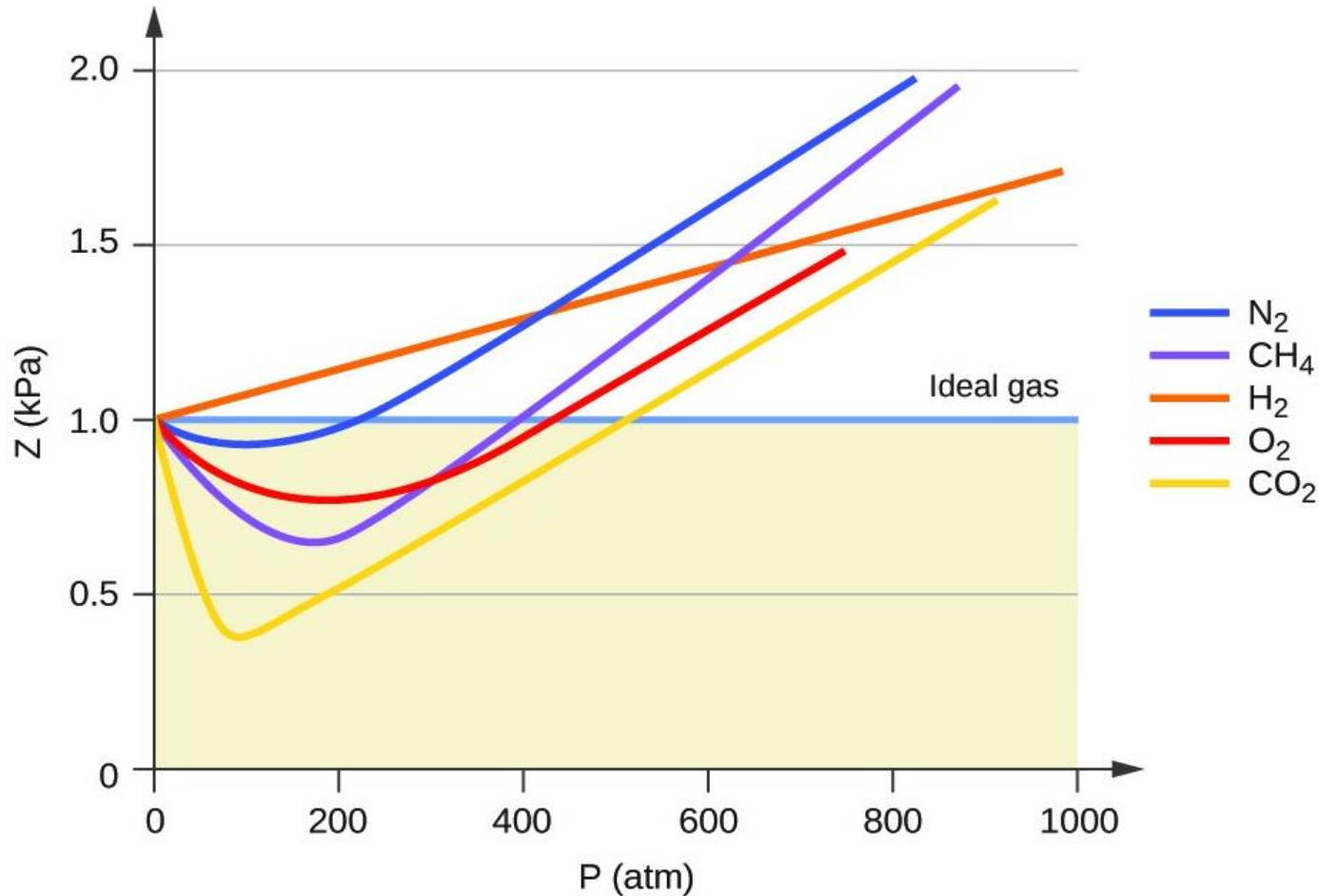
Compressibility Factor:

The extent of deviation from ideal behavior is represented by the function compressibility factor, Z. It is given be:

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

For ideal gases, Z=1 at all conditions. The deviation of value from unity is a measure of its deviation from ideal behavior.

Effect of Pressure on Deviations from Ideal Behaviour:



There are three types of curves in the Z vs P diagram.

For ideal gases, $Z = 1$

Horizontal Line

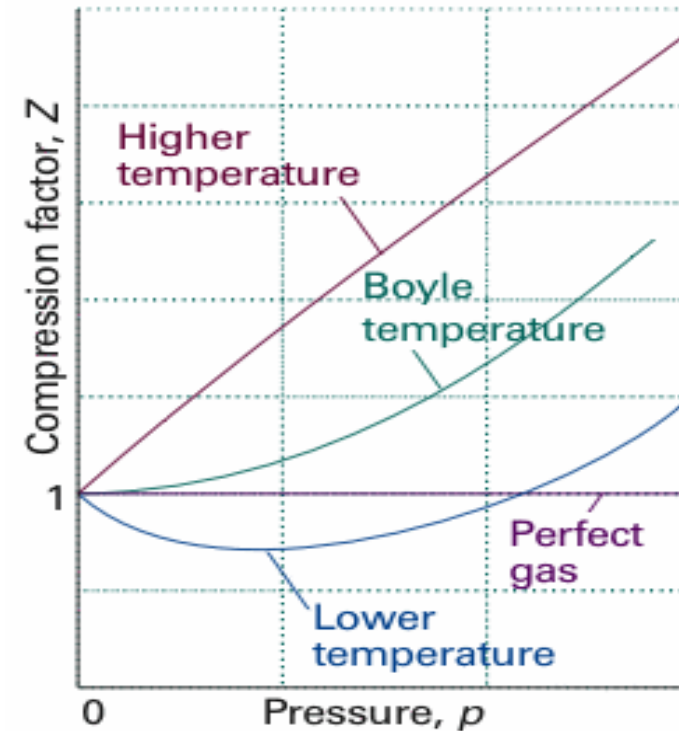
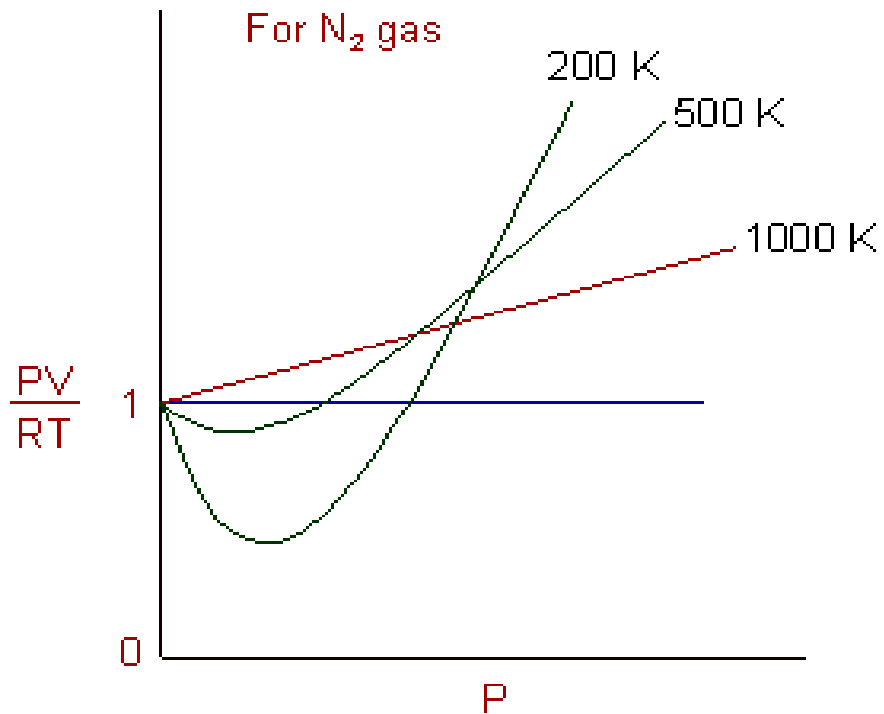
Gases like N_2 , O_2 , CO_2 , CH_4 :

Presence of dip

Gases like He and H_2 :

Less Compressibility

Effect of Temperature on Deviations from Ideal Behaviour:



The temperature at which a gas obeys Boyle's law over an appreciable range of pressure is called the Boyle temperature. It is represented by T_B

Boyle temperature of nitrogen is 50°C ,
Hydrogen - - 165°C , Helium - - 240°C

Deviations from Avogadro's Law:

The volume occupied by 1 mole of a gas at STP is 22.41 Litres. But actual measurement of molar volume shows deviation from ideal behavior.

Hydrogen - 22.427 L

Nitrogen – 22.405 L

Oxygen – 22.394 L

Ammonia – 22.084 L

Causes of Deviations from Ideal Behaviors:

i) Definite Volume for Gases:

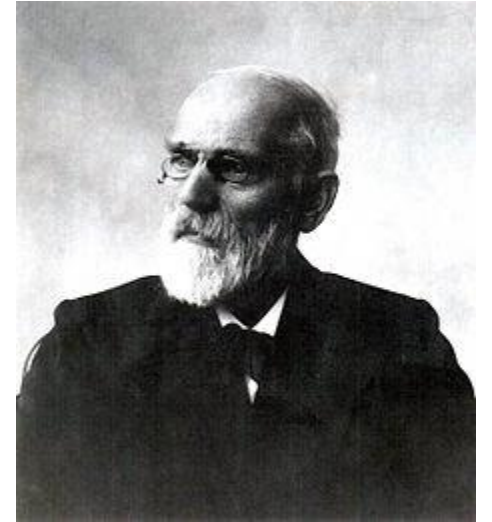
ii) Presence of intermolecular forces

Van der Waals equation of state

- Van der Waals equation was derived by *Johannes Diderik van der Waals* in the year 1873.
- The equation is basically a modified version of the Ideal Gas equation of state ($PV = nRT$).
- Kinetic theory fails to explain the behaviour of real gases.
- Van der Waals equation was devised and it helps us define the physical state of a real gas.
- The Van der Waals equation takes into consideration the **molecular size** and **molecular interaction forces** (attractive and repulsive forces).
- It is also referred to as Van der Waals equation of state.

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

‘a’ & ‘b’ are called van der Waal’s constants and are characteristic of each gas



Derivation of Van der Waals equation:

Van der Waals equation derivation is based on correcting the pressure and volume of the ideal gases given by [Kinetic Theory of Gases](#).

Kinetic theory of ideal gases assumes the gaseous particles as –

- Point masses without any volume,
- Independent having no interactions and
- Undergo perfectly elastic collisions.

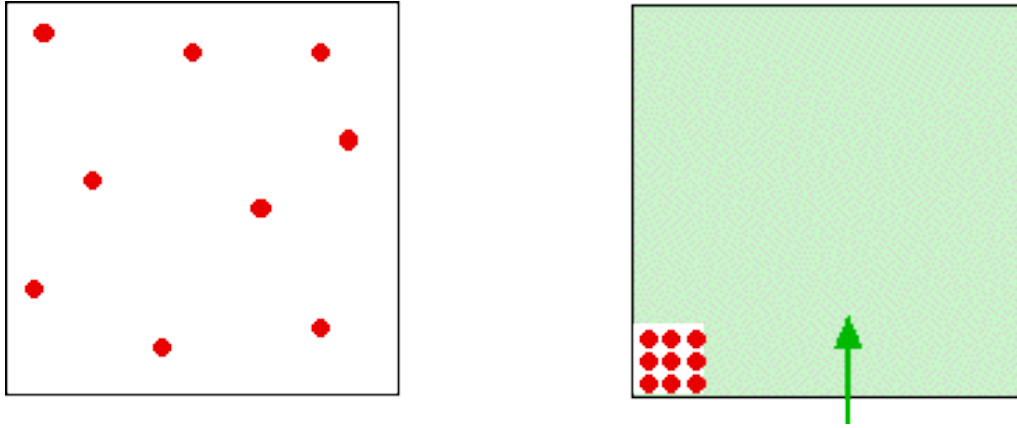
In practice, **Van der Waals** assumed that, gaseous particles –

1. Are hard spheres.
2. Have definite volume and hence cannot be compressed beyond a limit.
3. Two particles at close range interact and have an exclusive spherical volume around them.

Volume Correction in Van der Waals Equation

As the particles have a definite volume, the volume available for their movement is not the entire container volume but less.

Volume in the ideal gas is hence an over-estimation and has to be reduced for real gases.

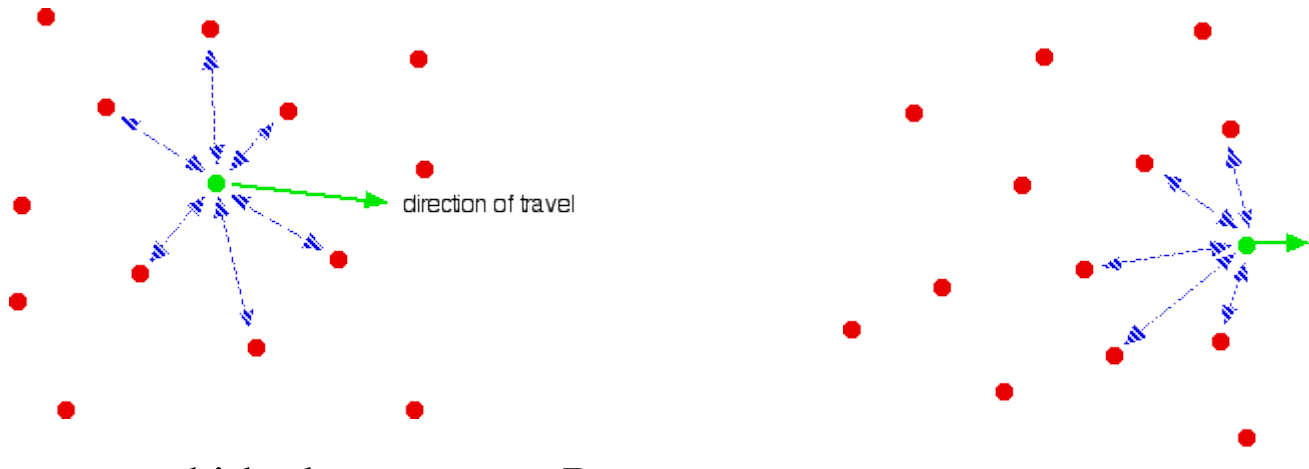


The corrected ideal volume = $V - b$

Where, 'b' is called the **co-volume or effective volume** or **excluded volume** and characteristic of each gas. **The co-volume 'b' is four times the actual volume of all the molecules in 1 mole of the gas.**

Pressure Correction:

- Intermolecular attractions are present in gases.
- Due to the resultant inward pull felt by the gas molecules near the walls of the container, it will strike the wall of the container with lower velocity.



The corrected ideal pressure = $P + p$

Where, ' p ' is known as the internal pressure of the gas.

The internal pressure depends on two factors:

- i) The attractive force exerted on a single molecule and
- ii) The number of molecules pulling the molecules inward.

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Both the above factors depends on the number density of gas molecules (ρ)

Hence, $p \propto \rho^2$

or, $p \propto \left(\frac{1}{V}\right)^2$ or, $p = \frac{a}{V^2}$ where 'a' is a constant.

For 'n' molecules;

$$p \propto \left(\frac{n}{V}\right)^2 \quad \text{or,} \quad p = \frac{an^2}{V^2}$$

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

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

Applicability of van der Waal's Equation in Explaining Real Gas Behavior:

The van der Waal's equation is rearranged as:

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

$$PV - Pb + \left(\frac{a}{V}\right) - \left(\frac{ab}{V^2}\right) = RT$$

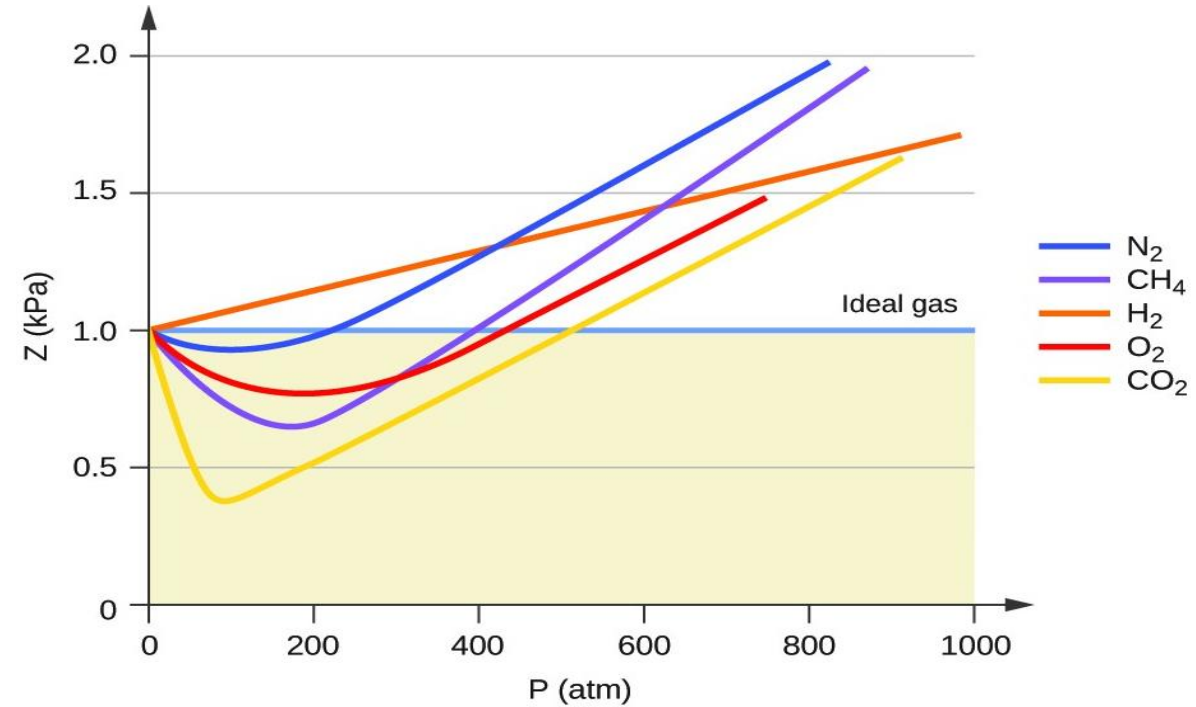
$$PV = RT + Pb - \left(\frac{a}{V}\right) + \left(\frac{ab}{V^2}\right)$$

(b) At low Pressure:

When P is low, V will be large. Hence Pb and (ab/V^2) becomes negligibly small. So the equation reduces to:

$$PV = RT - \left(\frac{a}{V}\right)$$

$$\frac{PV}{RT} = 1 - \left(\frac{a}{VRT}\right) \qquad Z = 1 - \left(\frac{a}{VRT}\right)$$



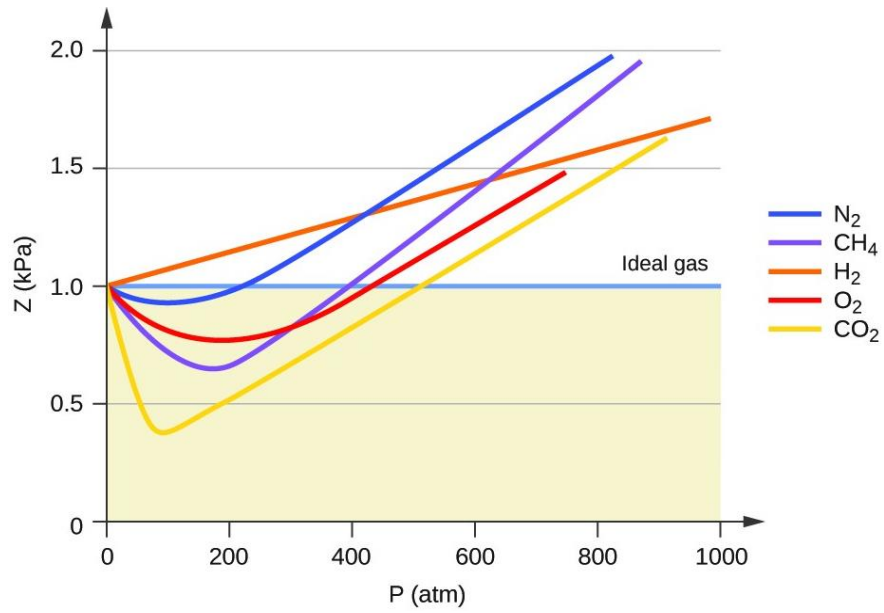
At high Pressure:

When P is very high, V will be small. The terms (a/V) and (ab/V²) becomes more or less equal in magnitude and cancel out each other.

$$PV = RT + Pb$$

$$\frac{PV}{RT} = 1 + \left(\frac{Pb}{RT}\right) \qquad Z = 1 + \left(\frac{Pb}{RT}\right)$$

Hence Z will be greater than unity. This explains the rising part of the Z vs P isotherms.



At very low Pressure:

When P is very low, V is very large. Then the terms having ‘a’ and ‘b’ becomes negligibly small.

So, $PV = RT$ or, $Z = 1$

i.e. Real gas approaches ideal behavior.

At very high temperature:

When T is very high, V is very large. Then the terms having 'a' and 'b' becomes negligibly small.

$$\text{So, } PV = RT \text{ or, } Z = 1$$

i.e. Real gas approaches ideal behavior.

Exceptional Behavior of Hydrogen and Helium:

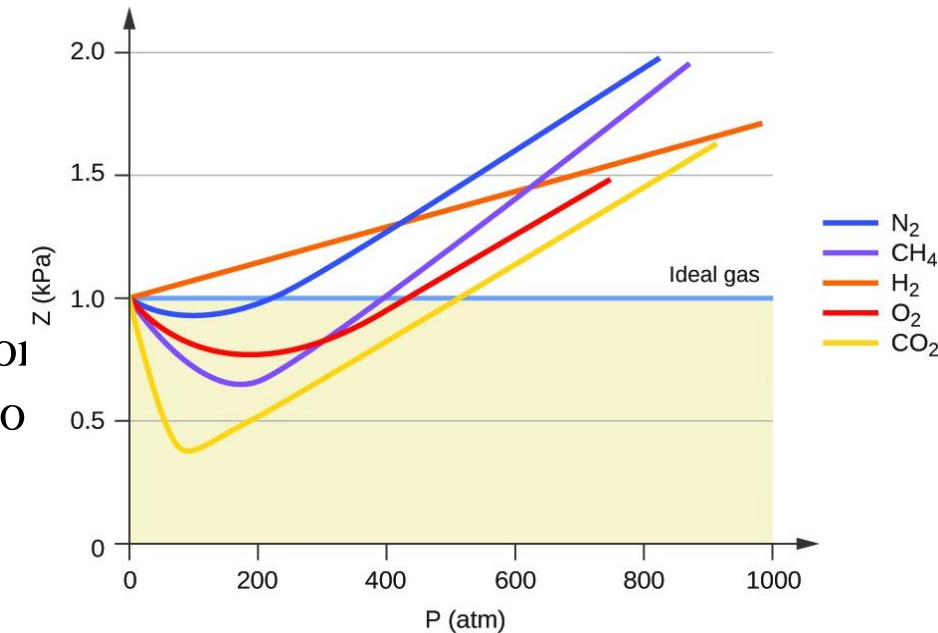
- The hydrogen and helium molecules have relatively smaller masses.
- Consequently these gases have smaller intermolecular forces of attraction.
- The pressure correction term due to the intermolecular forces of attraction becomes negligible at ordinary temperature.

$$PV = RT + Pb$$

$$\frac{PV}{RT} = 1 + \left(\frac{Pb}{RT} \right)$$

$$Z = 1 + \left(\frac{Pb}{RT} \right)$$

Thus Z is greater than unity even at low pressure. As P increases, the value of Z rises.



Significance of van der Waal's Constants:

- The van der Waal's constant ' a ' account for the intermolecular attraction present in real gases.
 - It also indicates the relative ease of liquefaction of gases.
 - Greater the value of ' a ' of a gas, the stronger the intermolecular forces of attraction present in it and the greater is the ease of its liquefaction.
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- The van der Waal's constant ' b ' account for the actual volume of the molecules.
 - A larger value of ' b ' for a gas therefore indicates a larger volume of the gas molecule and thus a larger size for the molecule.

Units of van der Waal's Constants:

$$\frac{(\text{Unit of } a) \times (\text{mol}^2) n^2}{(\text{m}^3)^2} = \text{Nm}^{-2}$$

$$\text{Unit of } a = \text{Nm}^4 \text{mol}^{-2} \quad \text{or} \quad \text{Pa m}^6 \text{mol}^{-2}$$

$$\text{Unit of } a = \text{atmL}^2 \text{mol}^{-2} \quad \text{or} \quad \text{atm dm}^6 \text{mol}^{-2}$$

$$(\text{mol})(\text{Unit of } b) = \text{m}^3$$

$$\text{Unit of } b = \text{m}^3 \text{mol}^{-1}$$

$$\text{Unit of } b = \text{Lmol}^{-1} \quad \text{or} \quad \text{dm}^3 \text{mol}^{-1}$$

Limitation of van der Waal's equation:

- Real gases show deviations from the van der Waal's equations at low temperature and high pressure.
- This is because the van der Waal's constants 'a' and 'b' are not exact constants for a gas and they vary with temperature.

VIRIAL EQUATION OF STATE

$$PV = RT$$

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

Virial equation of state proposed by Kammerlingh Onnes is in the form of a power series of $(1/V)$. For 1 mole of a gas it is given by:

$$PV = RT \left[1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \right]$$

- Where, B, C, D are called second, third, fourth etc. virial co-efficients which are functions of temperature and are characteristic of each gas.
- The virial coefficients represent the contribution to deviation from ideal behavior by the interaction between specific number of molecules.
- For eg., second virial co-efficient B represents deviation due to interaction between two molecules.

Significance of Second Virial Co-efficient (B):

- The second virial coefficient B is negative at moderately low temperatures, becomes zero and then positive as the temperature is raised.
- The temperature at which the second virial coefficient B is zero for a gas is called its Boyle temperature.

Virial equation of state can also be expressed as a power series of pressure (P).

$$PV = RT(1 + B'P + C'P^2 + D'P^3 + \dots)$$

Where B', C', D' etc are temperature-dependent virial co-efficients.

Van der Waal's equation expressed in virial form:

Van der Waal's equation for 1 mole of a gas is given by:

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

Upon rearranging the above expression, we get

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

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

$$PV = RT \left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{V}$$

$$PV = RT \left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{V}$$

Since 'b' is smaller than 'V', Applying binomial theorem,

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

$$PV = RT \left(1 + \frac{b}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots \right) - \frac{aRT}{VRT}$$

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

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

The above equation is the van der Waal's equation in virial form for 1 mole of a gas.

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

$$PV = RT \left[1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \right]$$

Equation for Boyle temperature:

The second virial coefficient is given by:

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

Boyle temperature is the temperature at which $B=0$, so

$$b - \frac{a}{RT_B} = 0$$

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

The Redlich-Kwong equation

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m (V_m + b) T^{1/2}}$$

Berthelot equation

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

The Dieterici equation

$$Pe^{\frac{an}{RTV}} (V - nb) = nRT$$