

WANDER WAAL EQUATION OF STATE:

→ The molecules of ideal gas are point particles & their diameters are negligible according to the kinetic theory of gases.

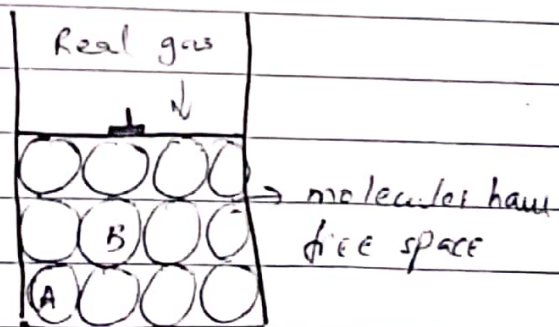
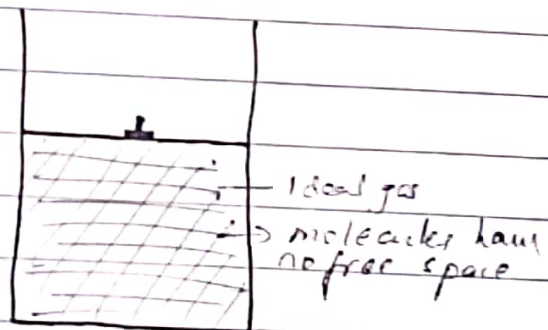
These molecules do not exert forces upon each other so have no intermolecular forces

The equation of ideal gas is written as

$$PV = nRT$$

$$P = \frac{nRT}{V} \quad \text{--- (1)}$$

Wander waal pointed out that these assumptions are not valid because molecules of real gases are ^{not} point particles. They have definite diameter.



The molecules of real gases exert intermolecular forces

∴

Under these conditions the ideal gas eq

Important:

$PV = nRT$ must be modified for

real gases

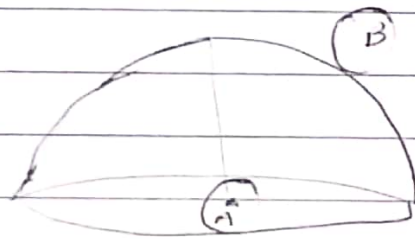
Van der Waal equation is derived taking into account following two facts

- 1- Definite diameter of molecules of real gases
- 2- Intermolecular forces among molecules of real gases.

1- Contribution of definite diameter of molecules

The molecules of real gas has definite diameter. Assume that each molecule of real gas is hard sphere having diameter 'd'

Now consider two molecules A & B of real gas having diameter 'd'



Draw a hemisphere whose center is at the center of molecule A & whose radius is equal to the diameter of molecule

The center of molecule B is not permitted to move within this hemisphere as shown in the figure.

It means free volume is available b/w two

Important: molecules

Therefore volume occupied by molecules of ideal gas reduces in real gas by amount of volume of such hemisphere

Now new volume of real gas can be calculated as

1 molecule gives free volume = volume of hemisphere = $\frac{1}{2} \left(\frac{4}{3} \pi d^3 \right)$

N molecules " " = $\frac{1}{2} \left(\frac{4}{3} \pi d^3 \right) N_n$
1 molecule = $\frac{1}{2} \left(\frac{4}{3} \pi d^3 \right)$

Putting $\frac{1}{2} \left(\frac{4}{3} \pi d^3 \right) \times N_n = b$

1 mole of real gas gives free volume = b
n " " " " " " = nb

⇒ The ideal gas has volume V. The same volume for real gas becomes V - nb

The ideal gas eq is $PV = nRT$

The eq of state for real gas under these conditions is

$P(V - nb) = nRT$

important

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

It shows pressure of real gas which is increased as compared to the pressure of ideal gas as in eq. (1) because $(V-nb)$ (is smaller than V) ~~&~~ V be under same conditions.

This increase in pressure is due to the fact the molecules make more collisions with the walls when the volume is reduced for the real gas.

2- Contribution of intermolecular forces:

The molecules of ideal gas ^{has} no intermolecular forces. The molecules of real gas has intermolecular forces.

The molecules of real gas in interior of container is attracted by other molecules surrounding it so attraction forces are cancelled out.

On the other hand the molecules experience force of attraction by other molecules when it collides with the walls of container because there is no molecule on the side when it collides w/ of wall

→ This attractive force decrease the force of impact on the wall. This molecule of real gas is unable to exert as much pressure on the wall as exerted by the molecules of ideal gas. Therefore pressure exerted by all molecules of real gas on the wall is reduced.

→ The total decrease in pressure resulting from intermolecular forces is proportional to $(\frac{n}{V})^2$

$$\text{decrease in pressure} \propto (\frac{n}{V})^2$$

$$\text{decrease in pressure} = a (\frac{n}{V})^2$$

where a is the constant of proportionality is called coefficient of attraction per molecule.

Its value is constant for particular gas

→ The ^{net} corrected pressure of real gas when contribution of diameter of intermolecular forces is taken into account is given as

$$\text{Net corrected pressure} = \text{Increase pressure due to diameter of molecules} - \text{decrease in pressure due to intermolecular forces}$$

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

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

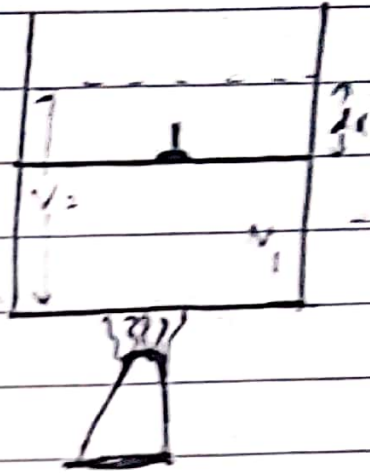
$$\left[P + a\left(\frac{n}{V}\right)^2 \right] (V-nb) = nRT$$

It is called Vander Waal equation of state of real gases

WORK DONE ON AN IDEAL GAS:

If we raise the Temperature of gas in a cylinder, the gas expands and raises the load

The upward force exerted by the gas due to pressure of gas is PA ($P = \frac{F}{A}$
 $\Rightarrow F = PA$) where A is the area of the piston



According to Newton's laws ~~the~~ force exerted by piston on the gas is $-PA$. ^{reverse} Work done on the gas

$$W = \int F dx$$

$$W = \int (-PA) dx \quad \text{--- (3)}$$

where dx represents displacement of piston & $-ve$ sign shows that force exerted by the piston on the gas is in the direction opposite to the displacement of the piston.

If we reduce the temperature of gas, it contracts and work done on the gas is

Important: this case is $+ve$, as both force

exerted on piston and displacement of the piston is place in same direction.

We assume that process is ~~carrying~~ carried slowly so that gas remains in equilibrium at all intermediate stages

→ If the piston moves through a distance dx then the volume of gas changes by an amount $dV = A dx$ and eq (1) assumes the form

$$W = - \int P dV \quad \text{--- (2)}$$

The integral is evaluated b/w the limits $V = V_1$ to $V = V_2$. Thus eq (2) becomes

$$\begin{aligned} W &= - \int_{V_1}^{V_2} P dV = - P \int_{V_1}^{V_2} dV \\ &= - P |V|_{V_1}^{V_2} \\ &= - P (V_2 - V_1) \quad \text{--- (3)} \end{aligned}$$

(where $V_2 > V_1$)

where $V_2 > V_1$

that is work done ~~on~~ by the gas during expansion is -ve. On the other hand if the gas contracts during a process

Important:

dV is -ve and work is +ve.

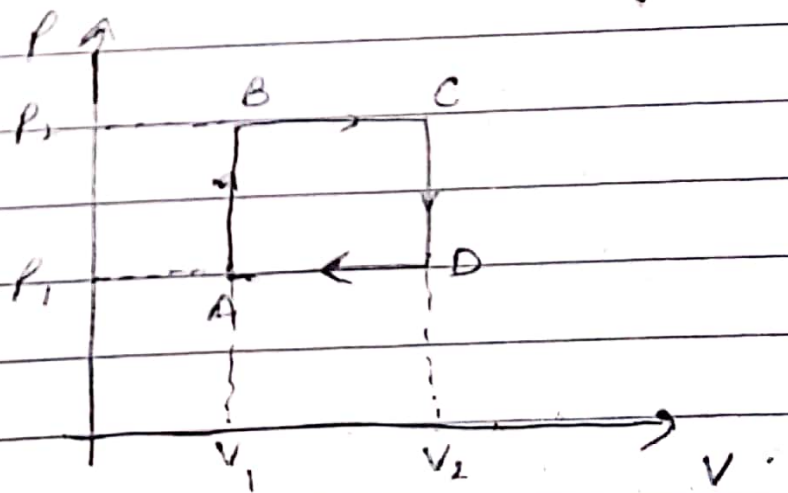
from eq (3) $W = P(V_1 - V_2) \quad (V_2 < V_1) \quad \text{--- (4)}$

That is work done on gas during compression is +ve.

NOTE:

Work done ^{by} on gas is -ve if ^{Process} pressure increases its volume and +ve if the process decrease its volume.

Magnitude of work done on the gas is represented by the area under the pressure - volume curve on the P-V diagram.



Work done on the gas is -ve on the path ABC and +ve along the path CDA.

Pressure force is nonconservative in behaviour.