Chapter 12
Kinetic Theory

Introduction

Kinetic theory explains the behaviour of gases based on the idea that the gas consists of rapidly moving atoms or molecules. The kinetic theory was developed in the nineteenth century by Maxwell, Boltzmann and others.

Behaviour of Gases

Ideal gas equation

Gases at low pressures and high temperatures much above that at which they liquefy (or solidify) approximately satisfy a simple relation

$$\mathbf{PV = \mu RT} \text{------------}(1)$$

where μ is the number of moles
R is universal gas constant.
$R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$
T is absolute temperature.

A gas that satisfies this eqn exactly at all pressures and temperatures is defined to be an ideal gas.

But $\mathbf{R = N_A k_B}$
N_A is Avogadro number
k_B is Boltzmann constant
$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$

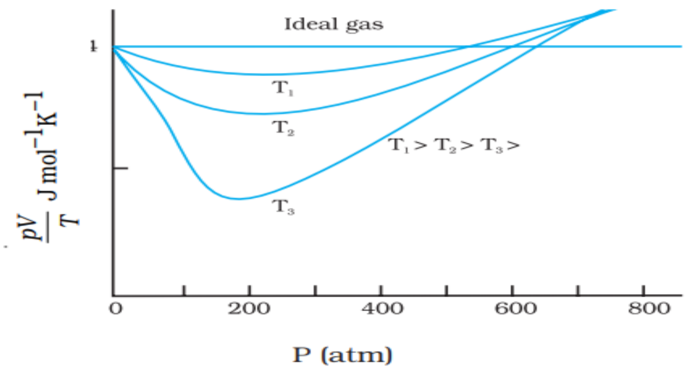
$$\mathbf{PV = \mu N_A k_B T}$$

$\mu N_A = N$
N is the number of molecules of gas

The perfect gas equation canalso be written as

$$\mathbf{PV = N k_B T} \text{ -------------}(2)$$

From above eq , $\frac{PV}{T} = \text{constant}$



From graph it is clear that **real gases approach ideal gas behaviour at low pressures and high temperatures.**
At low pressures or high temperatures the molecules are far apart and molecular interactions are negligible. Without interactions the gas behaves like an ideal one.

Boyle's Law

$$PV = \mu RT$$

If we fix μ and T,

$$\mathbf{PV = Constant}$$

$$P \propto \frac{1}{V}$$

i.e., **for a fixed temperature , pressure of a given mass of gas varies inversely with volume. This is the famous Boyle's law.**

Charles'Law

$$PV = \mu RT$$

If we fix P

$$\frac{V}{T} = \text{constant}$$

$$V \propto T$$

i.e., for a fixed pressure, the volume of a gas is proportional to its absolute temperature T (Charles' law).

Dalton's law of partial pressures.

Consider a mixture of non-interacting ideal gases μ_1 moles of gas 1, μ_2 moles of gas 2, etc

$$PV = (\mu_1 + \mu_2 + \ldots)\, RT$$

$$P = \mu_1 \frac{RT}{V} + \mu_2 \frac{RT}{V} + \ldots\ldots\ldots\ldots\ldots$$

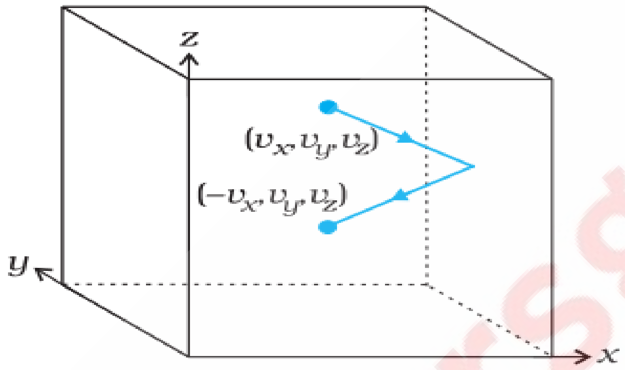
$$P = P_1 + P_2 + \ldots\ldots\ldots\ldots\ldots\ldots$$

Thus, the total pressure of a mixture of ideal gases is the sum of partial pressures. This is Dalton's law of partial pressures.

Kinetic Theory of an Ideal Gas

- A given amount of gas is a collection of a large number of molecules that are in random motion.
- At ordinary pressure and temperature, the average distance between molecules is very large compared to the size of a molecule (2 Å).
- The interaction between the molecules is negligible.
- The molecules make elastic collisions with each other and also with the walls of the container .
- As the collisions are elastic , total kinetic energy and total momentum are conserved .

Pressure of an Ideal Gas



A gas is enclosed in a cube of side l

Consider a molecule moving in positive x direction makes an elastic collision with the wall of thecontainer.

$$\text{Momentum before collision} = mv_x$$

$$\text{Momentum after collision} = -mv_x$$

$$\text{The change in momentum of the molecule} = -mv_x - mv_x$$

$$= -2\,mv_x$$

By the principle of conservation of momentum

$$\text{Momentum imparted to wall in the collision} = 2mv_x$$

$$\text{Distnace travelled by the molecule in time } \Delta t = v_x\,\Delta t$$

$$\text{Volume covered by the molecule} = Av_x\,\Delta t$$

$$\text{No of molecules in this volume} = n\,Av_x\,\Delta t$$

(n is number density of molecules)

Only half of these molecules move in +x direction

$$\text{No of molecules} = \frac{1}{2}nA\,v_x\,\Delta t$$

The number of molecules with velocity v_x hitting the wall in time Δt

$$= \frac{1}{2}nA\,v_x\,\Delta t$$

The total momentum transferred to the wall

$$Q = (2mv_x)\left(\frac{1}{2} nA\, v_x\, \Delta t\right)$$

$$Q = nmAv_x{}^2\, \Delta t$$

The force on the wall, $F = \frac{Q}{\Delta t}$

$$F = nmAv_x{}^2$$

Pressure, $P = \frac{F}{A}$

$$P = nmv_x{}^2$$

All molecules in a gas do not have the same velocity; so average velocity is to be taken

$$P = nm\overline{v_x^2}$$

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

$$\overline{v^2} = 3\,\overline{v_x^2}$$

$$\overline{v_x^2} = \frac{1}{3}\overline{v^2}$$

but $\overline{v_x^2} = \frac{1}{3}\overline{v^2}$

$$\mathbf{P = \frac{1}{3} nm\overline{v^2}}$$

Kinetic Interpretation of Temperature

$$P = \frac{1}{3} nm\overline{v^2}$$

$$PV = \frac{1}{3} nVm\overline{v^2}$$

$$n = \frac{N}{V}, \quad N = nV$$

$$PV = \frac{1}{3} Nm\overline{v^2}$$

where N is the number of molecules in the sample.

$$PV = \frac{2}{3}\left(N\, \frac{1}{2} m\overline{v^2}\right)$$

The quantity in bracket is the average translational kinetic energy of the molecules in the gas.

$$N\, \frac{1}{2} m\overline{v^2} = E$$

$$PV = \frac{2}{3} E \text{---------------------}(1)$$

Ideal gas equation, $PV = Nk_BT$ -------------------(2)

From eq(1)and (2) $\frac{2}{3} E = Nk_BT$

$$E = \frac{3}{2} Nk_BT$$

$$\mathbf{E/N = \frac{3}{2} k_BT}$$

The average kinetic energy of a molecule is proportional to the absolute temperature of the gas; it is independent of pressure, volume or the nature of the ideal gas.

Note:

This is a fundamental result relating temperature(a macroscopic measurable parameter) to the average kinetic energy(microscopic quantity) of a gas molecule. The two domains are connected by the Boltzmann constant.

Root Mean Square (rms) Speed

$$E/N = \frac{3}{2}k_B T$$

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$$

$$\overline{v^2} = \frac{3k_B T}{m}$$

The square root of $\overline{v^2}$ is known as root mean square (rms) speed and is denoted by v_{rms}

$$\mathbf{v_{rms} = \sqrt{\frac{3k_B T}{m}}}$$

Degrees f Freedom

The total number of independent ways in which a system can possess energy is called degree of freedom.

A molecule has one degree of freedom for motion in a line.
Two degrees of freedom for motion in a plane.
Three degrees of freedom for motion in space.

Law of Equipartition of Energy

Law of Equipartition of Energy states that, in equilibrium, the total energy is equally distributed in all possible energy modes, with each mode having an average energy equal to $\mathbf{\frac{1}{2}k_B T}$

- Each translational degree of freedom contributes $\frac{1}{2}k_B T$
- Each rotational degree of freedom contributes $\frac{1}{2}k_B T$
- Each vibrational degree of freedom contributes , $2 \; x \; \frac{1}{2}k_B T = k_B T$ as a vibrational mode has both kinetic and potential energy modes.

Specific Heat capacity

Specific Heat capacities of Monoatomic Gases

The molecule of a monatomic gas has only 3 translational degrees of freedom.

$$\text{Average energy of a molecule} = 3 \; x \; \frac{1}{2} k_B T = \frac{3}{2} k_B \, T$$

The total internal energy of a mole of such a gas is,

$$U = \frac{3}{2} k_B \, T \text{ x } N_A$$

$$k_B N_A = R$$

$$U = \frac{3}{2} RT$$

Specific heat capacity at constant volume

$$C_V = \frac{dU}{dt}$$

$$= \frac{d}{dT} \left(\frac{3}{2} \, RT \right)$$

$$\mathbf{C_V = \frac{3}{2} R}$$

For an ideal gas, $C_P - C_V = R$ (Mayer's relation)

Specific heat capacity at constant pressure,

$$C_P = C_V + R$$

$$= \frac{3}{2} R + R$$

$$\mathbf{C_P = \frac{5}{2} R}$$

The ratio of specific heats

$$\frac{C_P}{C_P} = \gamma = \frac{\frac{5}{2} R}{\frac{3}{2} R}$$

Adiabatic constant , $\boldsymbol{\gamma = \frac{5}{3}}$

Specific heat capacities of Diatomic Gases

Rigid diatomic molecule

A diatomic rigid rotator has , 3 translational and 2 rotational degrees of freedom.i.e.,

$$\text{Average energy of a molecule} = 5 \ \text{x} \frac{1}{2} k_B T$$

$$= \frac{5}{2} k_B \ T$$

The total internal energy of a mole of such a gas is,

$$U = \frac{5}{2} k_B \ T \ \text{x} \ N_A$$

$$k_B N_A = R$$

$$U = \frac{5}{2} RT$$

Specific heat capacity at constant volume

$$C_V = \frac{dU}{dt}$$

$$= \frac{d}{dT} \left(\frac{5}{2} RT\right)$$

$$\mathbf{C_V = \frac{5}{2} R}$$

For an ideal gas, $C_P - C_V = R$ (Mayer's relation)

Specific heat capacity at constant pressure,

$$C_P = C_V + R$$

$$= \frac{5}{2} R + R$$

$$\mathbf{C_P = \frac{7}{2} R}$$

The ratio of specific heats

$$\frac{C_P}{C_P} = \gamma = \frac{\frac{7}{2} R}{\frac{5}{2} R}$$

Adiabatic constant , $\boldsymbol{\gamma = \frac{7}{5}}$

Non Rigid Diatomic Molecule

A non rigid diatomic molecule has , 3 translational , 2 rotational and 1 vibrational degrees of freedom.

(Each vibrational degree of freedom contributes ,2x $\frac{1}{2}k_BT = k_BT$)

$$\text{Average energy of a molecule} = \frac{5}{2}k_BT + k_B T$$

$$= \frac{7}{2}k_BT$$

The total internal energy of a mole of such a gas is,

$$U = \frac{7}{2}k_B T \text{ x } N_A$$

$$k_BN_A = R$$

$$\mathbf{U = \frac{7}{2}RT}$$

Specific heat capacity at constant volume

$$C_V = \frac{dU}{dt}$$

$$= \frac{d}{dT}\left(\frac{7}{2} RT\right)$$

$$\mathbf{C_V = \frac{7}{2}R}$$

For an ideal gas, $C_P - C_V = R$ (Mayer's relation)

Specific heat capacity at constant pressure,

$$C_P = C_V + R$$

$$= \frac{7}{2}R + R$$

$$\mathbf{C_P = \frac{9}{2}R}$$

The ratio of specific heats

$$\frac{C_P}{C_P} = \gamma = \frac{\frac{9}{2}R}{\frac{7}{2}R}$$

$$\text{Adiabatic constant , } \boldsymbol{\gamma = \frac{9}{7}}$$

Polyatomic Gases

A polyatomic molecule has 3 translational, 3 rotational degrees of freedom and a certain number (f) of vibrational modes.

$$\text{Average energy of a molecule} = \frac{3}{2}k_BT + \frac{3}{2}k_BT + f\,k_BT$$

The total internal energy of a mole of such a gas is,

$$U=\left(\frac{3}{2}k_BT + \frac{3}{2}k_BT + f\,k_BT\right)N_A$$

$$U=(3 + f)k_BTN_A$$

$$k_BN_A = R$$

$$U=(3 + f)RT$$

Specific heat capacity at constant volume

$$C_v = \frac{dU}{dt}$$

$$\mathbf{C_V = (3 + f)R}$$

Specific heat capacity at constant pressure,

$$C_P = C_V + R$$

$$=(3 + f)R + R$$

$$\mathbf{C_P = (4 + f)R}$$

The ratio of specific heats

$$\gamma = \frac{C_P}{C_P} = \frac{(4+f)R}{(3+f)R}$$

Adiabatic constant , $\boldsymbol{\gamma = \frac{(4+f)}{(3+f)}}$

Specific Heat Capacity of Solids

Consider a solid of N atoms, each vibrating about its mean position.

A vibration in one dimension has average energy $= 2x\,\frac{1}{2}k_BT$

$$= k_BT$$

In three dimensions, the average energy $= 3k_BT$

The total internal energy of a mole of solid is,

$$U = 3k_BT \times N_A$$

$$k_BN_A = R$$

$$U = 3RT$$

Specific heat capacity $\quad C = \frac{dU}{dt}$

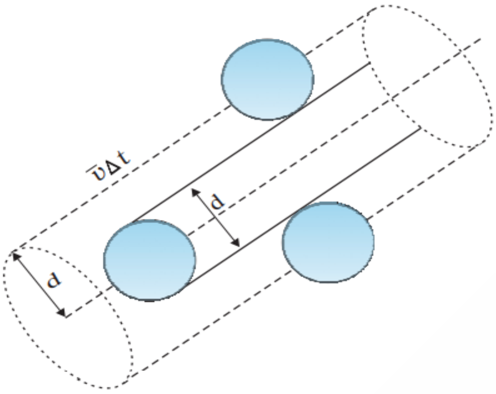
$$=\frac{d}{dT}(3\,RT)$$

$$\mathbf{C = 3R}$$

Mean Free Path

The mean free path l is the average distance covered by a molecule between two successive collisions.

$$\boldsymbol{l = \frac{1}{\sqrt{2}n\pi d^2}}$$



Consider the molecule of a gas as spheres of diameter d. Focus a single molecule.

The volume swept by a molecule in time Δt in which any molecule will collide with it $= \text{Area x distancd covered}$

$$= \pi d^2 \times \langle v \rangle \Delta t$$

The number of collisions suffered by the molecule in time Δt.

$$= n\pi \langle v \rangle d^2 \Delta t$$

where n is the number of molecules per unit volume,

$$\text{Rate of collision} = n\pi \langle v \rangle d^2$$

Time between two successive collisions is on the average,

$$\tau = \frac{1}{n\pi \langle v \rangle d^2}$$

The average distance between two successive collisions, called the mean free path l, is

$$l = \langle v \rangle \tau$$

$$l = \langle v \rangle \frac{1}{n\pi \langle v \rangle d^2}$$

$$l = \frac{1}{n\pi d^2}$$

As all molecules are moving , average relative velocity of the moleculesis to be considered. So the exact equation is

$$\boldsymbol{l = \frac{1}{\sqrt{2}n\pi d^2}}$$