

Chapter 13 Kinetic Theory

Kinetic Theory

- Atomic Hypothesis: All things are made of atoms
- Kanada in India and Democritus in Greece had suggested that matter may consist of indivisible constituents.
- The scientific 'Atomic Theory' is proposed by John Dalton.
- The size of an atom is about an angstrom.
- From many observations, in recent times we now know that molecules (made up of one or more atoms) constitute matter.
- Electron microscopes and scanning tunnelling microscopes enable us to see the molecules.
- In solids, which are tightly packed, atoms are spaced about a few angstroms (2 \AA) apart.
- In liquids the separation between atoms is also about the same.
- In liquids the atoms are not as rigidly fixed as in solids, and can move around. This enables a liquid to flow.
- In gases the interatomic distances are in tens of angstroms.
- The atoms attract when they are at a few angstroms but repel when they come closer.

Behaviour Of Gases

- Gases at low pressures and high temperatures shows ideal gas behaviour.
- The ideal gas equation can be written as

$$PV = \mu RT$$

- where μ is the number of moles and R is universal gas constant.

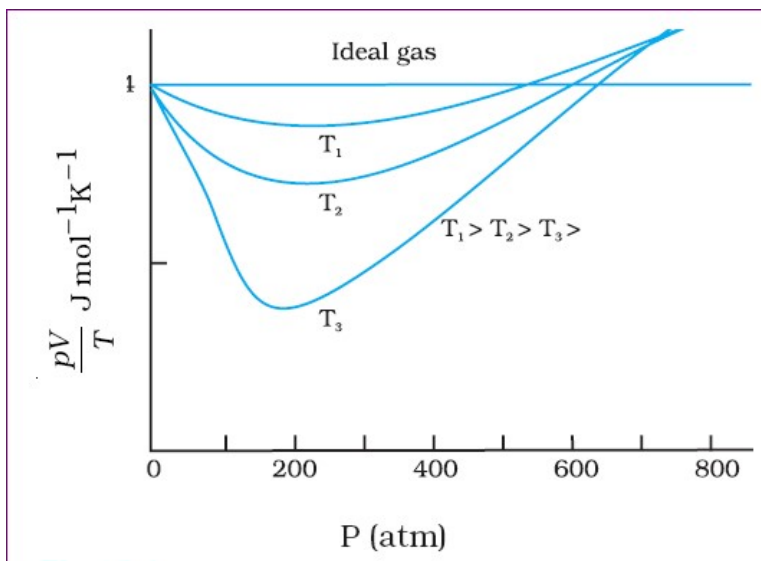
$$R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$$

- Also in terms of Boltzmann's constant ideal gas equation can be written as

$$PV = k_B NT \quad \text{or} \quad P = k_B nT$$

- Where $n = N/V$
- The value of Boltzmann constant in SI units is

$$1.38 \times 10^{-23} \text{ J K}^{-1}$$



Kinetic Theory Of An Ideal Gas

- Kinetic theory of gases is a theory, which is based on the concept of molecular motion as is able to explain the behaviour of gases.

Postulates of Kinetic Theory :

- The molecules of a gas are supposed to be point masses, the size of a molecule being negligible compared to the distance between them.
- There is no force of attraction or repulsion between molecules.
- The molecules are in a state of random motion, moving with all possible velocities in all possible directions.
- During their motion, they collide with one another and also with the walls of the container. These collisions are elastic.
- Between successive collisions, the molecules move in straight lines with uniform velocity. The distance travelled between two successive collisions is called free path. Average distance between the successive collisions is called mean free path
- Time for a collision is negligibly small compared to the time taken to traverse mean free path.
- The mean KE of the molecule is a constant at a given temperature and is proportional to absolute temperature.

Concept of Pressure.

- The pressure exerted by a gas may be defined as the total momentum imparted to unit area of the walls of the container per second due to molecular impacts (collisions). Root mean square (rms) velocity of gas molecules.
- rms velocity of gas molecules is the square root of the mean of the squares of individual velocities of the molecules.
- If c_1, c_2, \dots, c_n are the velocities of a gas molecules, then mean

square velocity,

$$\overline{c^2} = \frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}$$

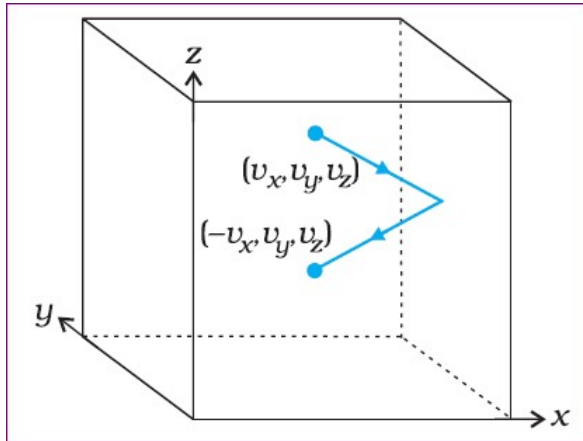
- Hence root mean square velocity

$$c_{\text{rms}} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}}$$

At a temperature $T = 300 \text{ K}$, the root mean square speed of a molecule in nitrogen gas is :

$$v_{\text{rms}} = 516 \text{ m s}^{-1}$$

Pressure of an Ideal Gas



- Consider a gas enclosed in a cube of side l .
- A molecule with velocity (v_x, v_y, v_z) hits the planar wall parallel to yz plane of area $A (= l^2)$.
- The velocity after collision is $(-v_x, v_y, v_z)$.
- The change in momentum of the molecule is : $-mv_x - (mv_x) = -2mv_x$.
- By the principle of conservation of momentum, the momentum imparted to the wall in the collision $= 2mv_x$.
- In a small time interval Δt , a molecule with x -component of velocity v_x will hit the wall if it is within the distance $v_x \Delta t$ from the wall.
- That is, all molecules within the volume $Av_x \Delta t$ only can hit the wall in time Δt .
- But, on the average, half of these are moving towards the wall and the other half away from the wall.
- Thus, the number of molecules with velocity (v_x, v_y, v_z) hitting the wall in time Δt is $\frac{1}{2}A v_x \Delta t n$, where n is the number of molecules per unit volume.
- The total momentum transferred to the wall by these molecules in time Δt is :

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

- The force on the wall is the rate of momentum transfer $Q/\Delta t$ and pressure is force per unit area :

$$P = Q / (A \Delta t) = n m v_x^2$$

- The above equation therefore, stands for pressure due to the group of molecules with speed v_x in the x-direction and n stands for the number density of that group of molecules.
- The total pressure is obtained by summing over the contribution due to all groups:

$$P = n m \overline{v_x^2}$$

- Now the gas is isotropic, i.e. there is no preferred direction of velocity of the molecules in the vessel.
- Therefore, by symmetry,

$$\begin{aligned} \overline{v_x^2} &= \overline{v_y^2} = \overline{v_z^2} \\ &= (1/3) [\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}] = (1/3) \overline{v^2} \end{aligned}$$

- Thus

$$P = (1/3) n m \overline{v^2}$$

Kinetic Interpretation of Temperature

- We have

$$P = (1/3) n m \overline{v^2}$$

- We may write

$$PV = (1/3) nV m \overline{v^2}$$

$$PV = (2/3) N \times \frac{1}{2} m \overline{v^2}$$

- where $N (= nV)$ is the number of molecules in the sample.
- The quantity in the bracket is the average translational kinetic energy of the molecules in the gas.
- Since the internal energy E of an ideal gas is purely kinetic,

$$E = N \times (1/2) m \overline{v^2}$$

- Thus

$$PV = (2/3) E$$

- But we have

$$PV = k_B NT \quad \text{or} \quad P = k_B nT$$

- Thus

$$E = (3/2) k_B NT$$

$$E/N = \frac{1}{2} m \overline{v^2} = (3/2) k_B T$$

- Thus, 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.

Pressure of a Mixture Of Non- reactive Gases

- For a mixture of non-reactive ideal gases, the total pressure gets contribution from each gas in the mixture.
- Thus

$$P = (1/3) [n_1 m_1 \overline{v_1^2} + n_2 m_2 \overline{v_2^2} + \dots]$$

- In equilibrium, the average kinetic energy of the molecules of different gases will be equal.

- That is,

$$\frac{1}{2} m_1 \overline{v_1^2} = \frac{1}{2} m_2 \overline{v_2^2} = \left(\frac{3}{2}\right) k_B T$$

so that

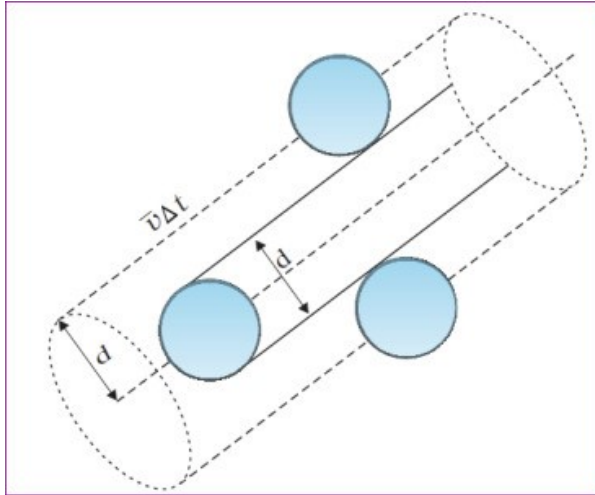
$$P = (n_1 + n_2 + \dots) k_B T$$

Mean free path

- Mean free path of a molecule in a gas is the average distance travelled by the molecule between two successive collisions.
- The mean free path, in gases, is of the order of thousands of angstroms.
- Let $\lambda_1, \lambda_2, \dots, \lambda_n$ are the free paths travelled by the molecules in n successive collisions, then mean free path is give by

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n}{n}$$

Equation for mean free path



- Assume that only one molecule is in motion and all other molecules are at rest.
- Let d be the diameter of each molecule.
- Suppose l is the distance travelled by the moving molecule.
- The moving molecule will make a collision with all those molecules whose centres lie inside a volume $\pi d^2 l$
- Thus the number of collisions = the number of molecules in the volume $\pi d^2 l = n \pi d^2 l$
- Where n is the number of molecules per unit volume.
- Now mean free path λ = distance travelled / number of collisions

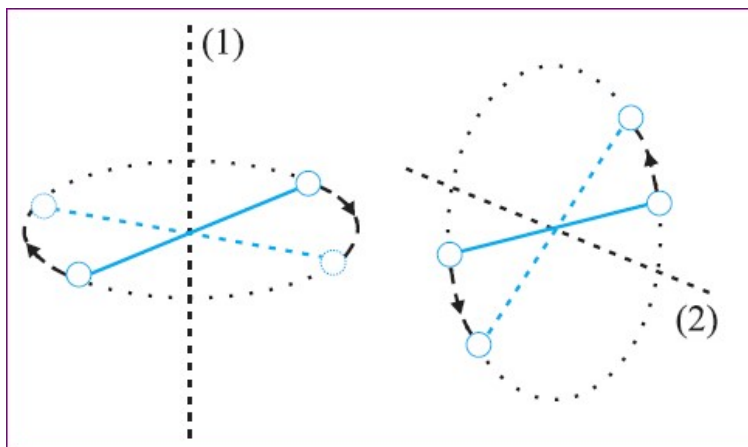
$$\lambda = \frac{\text{distance travelled}}{\text{no. of collisions}} = \frac{l}{n\pi d^2 l} = \frac{1}{n\pi d^2}$$

- A more exact treatment gives

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

Degrees Of Freedom

- The total number of co-ordinates or independent quantities required to completely specify the position and configuration of a system is called the degrees of freedom of that system.
- A molecule has only one degree of freedom for motion in a line, two for motion in a plane and three for motion in space.



Law of Equipartition Of Energy

- The law of equipartition of energy states that, in equilibrium, the total energy of a molecule is equally distributed in all possible energy modes, with each mode having an average energy equal to $\frac{1}{2} kBT$.
- The kinetic energy of a single molecule is

$$\epsilon_t = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

- For a gas in thermal equilibrium at temperature T the average value of energy is

$$\langle \epsilon_t \rangle = \left\langle \frac{1}{2}mv_x^2 \right\rangle + \left\langle \frac{1}{2}mv_y^2 \right\rangle + \left\langle \frac{1}{2}mv_z^2 \right\rangle = \frac{3}{2}kT$$

- Since there is no preferred direction

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle = \frac{1}{2}kT_B$$

$$\left\langle \frac{1}{2}mv_y^2 \right\rangle = \frac{1}{2}kT_B$$

$$\left\langle \frac{1}{2}mv_z^2 \right\rangle = \frac{1}{2}kT_B$$

- Thus, the average energy for translational, rotational and vibrational mode of motion is $\frac{1}{2}kT$
- Each translational and rotational degree of freedom of a molecule contributes $\frac{1}{2}kT$ to the energy .Each vibrational frequency contributes $2 \times \frac{1}{2}kT = kT$, since a vibrational mode has both kinetic and potential energy modes.

Specific Heat Capacity

Monatomic Gases

- The molecule of a monatomic gas has only three translational degrees of freedom. Thus, the average energy of a molecule at temperature T is $(3/2)k_B T$.
- The total internal energy of a mole of such a gas is

$$U = \frac{3}{2} k_B T N_A = \frac{3}{2} RT$$

$$\frac{dU}{dT} = \frac{3}{2} R$$

- The molar specific heat at constant volume, C_v , is $C_v =$
- For an ideal gas $C_p - C_v = R$
- Thus

$$C_p = \frac{5}{2} R \quad \frac{C_p}{C_v} = \frac{5}{3}$$

Diatomic Gases

- A diatomic molecule treated as a rigid rotator like a dumbbell has 5 degrees of freedom : 3 translational and 2 rotational.
- Using the law of equipartition of energy, the total internal energy of a mole of such a gas is

$$U = \frac{3}{2} k_B T N_A = \frac{3}{2} RT$$

- The molar specific heats are then given by

$$C_v \text{ (rigid diatomic)} = \frac{5}{2} R, \quad C_p = \frac{7}{2} R$$

$$\gamma \text{ (rigid diatomic)} = \frac{7}{5}$$

- If the diatomic molecule is not rigid but has in addition a vibrational mode

$$U = \left(\frac{5}{2} k_B T + k_B T \right) N_A = \frac{7}{2} RT$$

Polyatomic Gases

- In general a polyatomic molecule has 3 translational, 3 rotational degrees of freedom and a certain number (f) of vibrational modes.
- According to the law of equipartition of energy, it is easily seen that one mole of such a gas has

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

- Thus

$$C_v = (3 + f) R, \quad C_p = (4 + f) R,$$

- And

$$\gamma = \frac{4 + f}{3 + f}$$

Specific Heat Capacity of Solids

- Consider a solid of N atoms, each vibrating about its mean position.
- An oscillation in one dimension has average energy of $2 \times \frac{1}{2} k_B T = k_B T$
- In three dimensions, the average energy is $3 k_B T$.
- For a mole of solid, $N = N_A$,
- The total energy is

$$U = 3 k_B T \times N_A = 3 RT$$

- Now at constant pressure $\Delta Q = \Delta U + P\Delta V = \Delta U$, since for a solid ΔV is negligible.
- Hence,

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 3R$$

Specific Heat Capacity of Water

- We treat water like a solid. For each atom average energy is $3k_B T$. Water molecule has three atoms, two hydrogen and one oxygen.
- So it has

$$U = 3 \times 3 k_B T \times N_A = 9 RT$$

and $C = \Delta Q / \Delta T = \Delta U / \Delta T = 9R$.

Inadequacy of classical physics

- The predicted specific heats are independent of temperature. As we go to low temperatures, however, there is a marked departure from this prediction.
- Specific heats of all substances approach zero as $T \rightarrow 0$. This is related to the fact that degrees of freedom get frozen and ineffective at low temperatures.
- According to classical physics degrees of freedom must remain unchanged at all times.
- The behaviour of specific heats at low temperatures shows the inadequacy of classical physics and can be explained only by invoking quantum considerations, as was first shown by Einstein.

