

## CHAPTER THIRTEEN

### 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 tunneling microscopes** enable us to see the molecules.
- In solids, which are tightly packed, atoms are spaced about a few angstroms ( $2 \text{ \AA}$ ) 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 behavior**.
- The ideal gas equation can be written as

$$PV = \mu RT$$

- where  $\mu$  is the number of moles and  $R$  is **universal gas constant**.

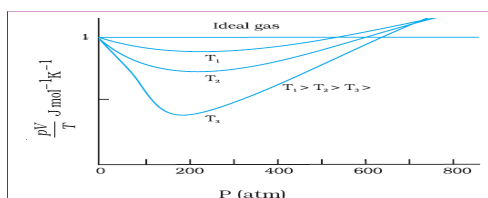
$$R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$$

- 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 behavior 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,

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

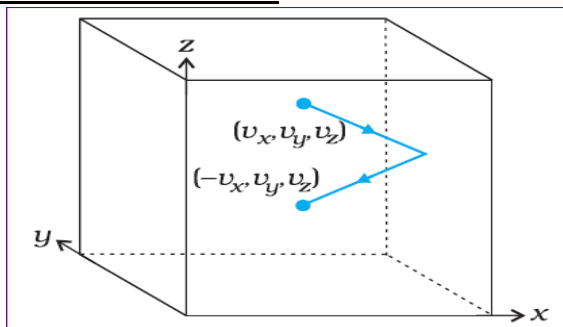
- Hence root mean square velocity

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

- 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  $\Delta t$ , 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  $\Delta t$ .
- 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  $\Delta t$  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  $\Delta t$  is :  

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

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

so that

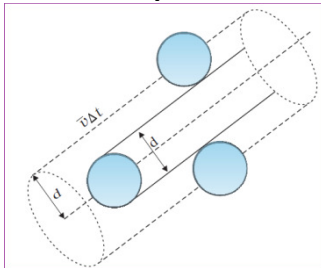
$$P = (n_1 + n_2 + \dots) k_B T$$

### 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 given 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  $\lambda = \text{distance travelled} / \text{number of collisions}$

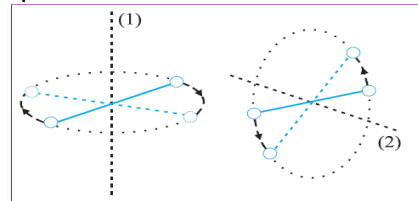
$$\lambda = \frac{\text{distance travelled}}{\text{no. of collisions}} = \frac{l}{n \pi d^2 l} = \frac{1}{n \pi d^2}$$

- 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  $\frac{1}{2} k_B T$ .
- The kinetic energy of a single molecule is

$$\mathcal{E}_t = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

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

$$\langle \mathcal{E}_t \rangle = \left\langle \frac{1}{2} m v_x^2 \right\rangle + \left\langle \frac{1}{2} m v_y^2 \right\rangle + \left\langle \frac{1}{2} m v_z^2 \right\rangle = \frac{3}{2} k_B T$$

- Since there is no preferred direction

$$\left\langle \frac{1}{2} m v_x^2 \right\rangle = \frac{1}{2} k_B T$$

$$\left\langle \frac{1}{2} m v_y^2 \right\rangle = \frac{1}{2} k_B T$$

$$\left\langle \frac{1}{2} m v_z^2 \right\rangle = \frac{1}{2} k_B T$$

- Thus the average energy for translational, rotational and vibrational mode of motion is  $\frac{1}{2} k_B T$
- Each translational and rotational degree of freedom of a molecule contributes  $\frac{1}{2} k_B T$  to the energy.

- Each vibrational frequency contributes  $2 \times \frac{1}{2} k_B T = k_B T$ , 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

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

- The molar specific heat at constant volume,  $C_v$  is  $C_v = \frac{dU}{dT} = \frac{3}{2} R$

- 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

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

- 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

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

$$C_v = \frac{7}{2} R, \quad C_p = \frac{9}{2} R, \quad \frac{C_p}{C_v} = \frac{9}{7}$$

#### 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  $\Delta V$  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

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

$$\text{and } C = \Delta Q / \Delta T = \Delta U / \Delta T = 9R$$

#### 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.

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