

CHAPTER – 13

Kinetic Theory of Gases

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 by **Maxwell and Boltzmann** and others in the nineteenth century.

Molecular theory of matter

Dalton suggested that the smallest constituent of an element are atoms. Atoms of one element are identical but differ from those of other elements. A small number of atoms of each element combine to form a molecule of the compound.

Behaviour of gases

Gases at low pressures and high temperatures satisfy a simple relation between their pressure, temperature and volume by

$$PV = Nk_B T$$

Here k_B is the Boltzmann constant

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

'N' is the total no. of molecules.

$$\text{But the no. of moles } n = \frac{N}{N_A},$$

where N_A is the Avogadro number.

$$N_A = 6.023 \times 10^{23}$$

$$\therefore N = nN_A$$

$$\text{Hence } PV = nN_A k_B T$$

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

$$\therefore \boxed{PV = nRT} \text{ ----- (1)}$$

The above equation is called **Ideal gas equation**.

A gas that satisfies the equation $PV=nRT$ at all temperatures and pressures is defined to be an ideal gas.

An ideal gas is a simple theoretical model of a gas. No real gas is truly ideal.

The figure below shows deviation from ideal gas behaviour for a real gas at three different temperatures.

The figure shows that the real gases approach ideal gas behaviour at low pressures and high temperatures.

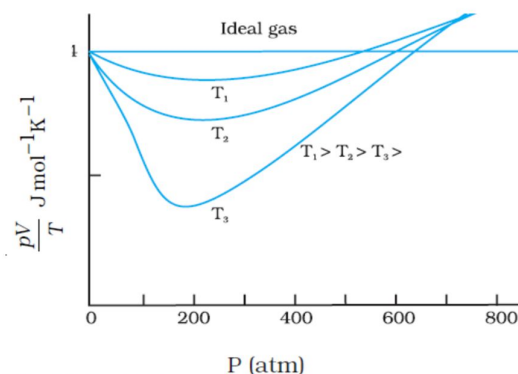


Fig.13.1 Real gases approach ideal gas behaviour at low pressures and high temperatures.

If we fix **n** and **T** in eqn (1), we get

$$PV = \text{Constant}$$

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

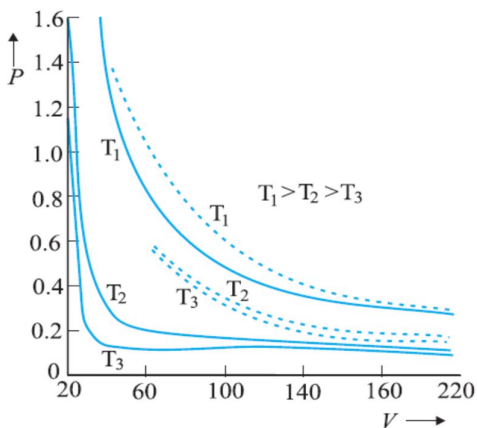


Fig.13.2 Experimental P-V curves (solid lines) for steam at three temperatures compared with Boyle's law (dotted lines). P is in units of 22 atm and V in units of 0.09 litres.

If we fix P, eq (1) shows that $V \propto T$ i.e., for a fixed pressure, the volume of a gas is proportional to its absolute temperature T (**Charles' law**).

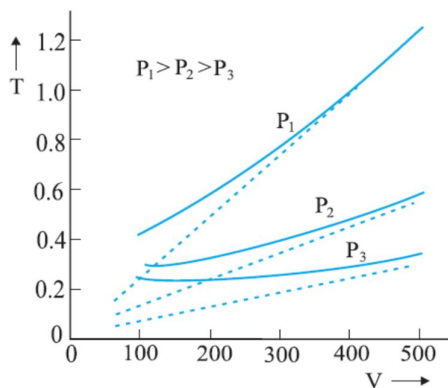


Fig. 13.3 Experimental T-V curves (solid lines) for CO_2 at three pressures compared with Charles' law (dotted lines). T is in units of 300 K and V in units of 0.13 litres.

Kinetic theory of an ideal gas

Kinetic theory of gases is based on molecular picture of matter. The main postulates of kinetic theory are:

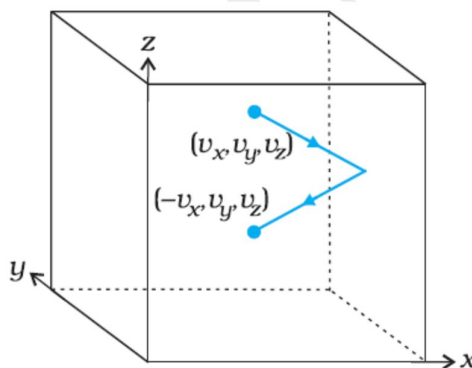
(i) A given amount of gas is a collection of large number of molecules that are in constant random motion. During their motion, they collide with each other and also collide with the walls of the container. These collisions are elastic. So the kinetic energy and linear momentum are conserved.

(ii) The actual volume of gas molecules can be neglected as compared to the volume of the container.

(iii) The intermolecular force of attraction between gas molecules is very weak.

Pressure of an ideal gas:

Consider a large no. of molecules (N) of a gas enclosed in a cube of side L of volume V. Let the mass of a molecule be 'm'.



Suppose a molecule with velocity (v_x, v_y, v_z) hits the planar wall parallel to **yz- plane** of area $A (=L^2)$.

Since the collision is elastic, the molecule rebounds with same velocity; its y and z components of velocity do not change in the collision but the x-component reverses sign. That is, the velocity after collision is $(-v_x, v_y, v_z)$.

change in momentum of the molecule

$$= -mv_x - (mv_x) = -2mv_x$$

So by the principle of conservation of momentum, the momentum imparted to the wall in collision $= 2mv_x$

These collisions takes place after a time interval of $\Delta t = \frac{L}{v_x} + \frac{L}{v_x} = \frac{2L}{v_x}$

There fore change in momentum occurs during every $\frac{2L}{v_x}$ second.

The rate of change of momentum

$$= \frac{\Delta P}{\Delta t} = \frac{2mv_x}{\frac{(2L)}{v_x}} = \frac{mv_x^2}{L}$$

This rate of change in momentum is the force.

Since there are N molecules, the total force on the wall of area L^2 is

$$F = \frac{Nm v_x^2}{L}$$

Since gas molecules have different velocities, we take the root mean square velocity (rms velocity) $\bar{v}_x$ instead of v_x

$\therefore F = \frac{Nm \bar{v}_x^2}{L}$, $\bar{v}_x^2$ is the mean square velocity.

$$\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$$

The gas is isotropic, i.e., there is no preferred direction of velocity of the molecules in the vessel.

$\therefore$ By symmetry, $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2$

$$\therefore \bar{v}^2 = 3\bar{v}_x^2 \Rightarrow \bar{v}_x^2 = \frac{1}{3} \bar{v}^2$$

$$\therefore F = \frac{1}{3} \frac{Nm \bar{v}^2}{L}$$

The pressure acting on the wall,

$$P = \frac{F}{A} = \frac{\frac{1}{3} \frac{Nm \bar{v}^2}{L}}{L^2} = \frac{1}{3} \frac{Nm \bar{v}^2}{L^3}$$

$\therefore P = \frac{1}{3} \frac{Nm \bar{v}^2}{V}$, where V is the volume of the cubic vessel.

But $\frac{N}{V} = n$, the number density of molecules in the vessel.

$$P = \frac{1}{3} n m \bar{v}^2$$

Kinetic Interpretation of Temperature

We have $P = \frac{1}{3} \frac{Nm \bar{v}^2}{V}$

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

$$= \frac{2}{3} N \left(\frac{1}{2} m \bar{v}^2 \right) = \frac{2}{3} N(\text{KE})$$

Combinig these equation with the ideal gas equation $PV = NK_B T$

we get $\frac{2}{3} N(\text{KE}) = NK_B T$

$$\text{KE} = \frac{3}{2} K_B T$$

That is, **the average kinetic energy of a gas molecule is proportional to the absolute temperature.** But it is independent of pressure, volume or nature of the gas.

Problem1: At what temperature the rms speed of hydrogen is double its value at STP.

Ans:

Law of Equipartition of Energy:

The kinetic energy of a single molecule is,

$$KE = \frac{1}{2} m \overline{v_x^2} + \frac{1}{2} m \overline{v_y^2} + \frac{1}{2} m \overline{v_z^2}$$

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

$$\therefore \frac{1}{2} m \overline{v_x^2} = \frac{1}{2} m \overline{v_y^2} = \frac{1}{2} m \overline{v_z^2}$$

$$\begin{aligned} \therefore KE &= \frac{1}{2} m \overline{v_x^2} + \frac{1}{2} m \overline{v_y^2} + \frac{1}{2} m \overline{v_z^2} \\ &= \frac{3}{2} m \overline{v_x^2} \end{aligned}$$

For a gas at thermal equilibrium, the average kinetic energy

$$KE = \frac{3}{2} K_B T$$

$$\frac{3}{2} m \overline{v_x^2} = \frac{3}{2} K_B T$$

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} K_B T$$

$$\therefore \frac{1}{2} m \overline{v_x^2} = \frac{1}{2} m \overline{v_y^2} = \frac{1}{2} m \overline{v_z^2} = \frac{1}{2} K_B T$$

The law of equipartition of energy states that if a system is in equilibrium at absolute temperature T, the total energy is distributed equally in different degrees of freedom, the energy in each degree

of freedom being equal to $\frac{1}{2} K_B T$.

Problem2:

Two vessels of the same size are at the same temperature. One of them contains 1Kg of hydrogen

(Molecular weight=2) and the other contains 1 kg of nitrogen (molecular weight=28).

(a) Which of the vessels contains more molecules?

(b) In which vessel is the average molecular speed greater? How many times greater?

(c) Which of the vessels is at higher pressure? Why?

Ans:

Specific Heat Capacity

If we heat a sample of gas by keeping its volume constant, the heat supplied is used to increase its internal energy only.

Thus we have $\Delta U = nC_v \Delta T$. For one mole of a gas

$$\Delta U = C_v \Delta T \text{ (Since } n = 1\text{)}.$$

$$\boxed{\frac{dU}{dT} = C_v}$$

Degrees of Freedom

A molecule free to move in space needs three co-ordinates to specify its location.

If it is restricted to move in a plane it needs two; and if restricted to move along a line, it needs just one coordinate to locate it. Or, it has one degree of freedom for motion in a line, two for motion in a plane and three for motion in space.

Motion of a body as a whole from one point to another is called **translation**. Thus a molecule free to move in space has three translational degrees of freedom. In thermal equilibrium at absolute temperature T , for each translational mode of motion, the average energy is

$$\frac{1}{2} K_B T$$

But one vibration mode contributes two 'squared terms': Kinetic and potential energies.

Each **vibration** frequency has two modes of energy (kinetic and potential) with corresponding energy equal to

$$2 \times \frac{1}{2} K_B T = K_B T.$$

Monatomic Molecule

Molecules of a monatomic gas have *only translational degrees of freedom*.

The no. of degrees of freedom = 3

Internal Energy of a molecule,

$$u = 3 \times \frac{1}{2} K_B T = \frac{3}{2} K_B T$$

Internal Energy of one mole of monoatomic gas,

$$U = \frac{3}{2} K_B T \times N_A$$

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

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

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

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

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

Diatomic Molecule

(i) Diatomic Rigid Rotator

Rigid rotator means the molecule does not vibrate.

A molecule of a diatomic gas has three translational degrees of freedom. But in addition it can also rotate about its centre of mass. The molecule thus has two rotational degrees of freedom.

3 trans. degrees freedom

+ 2 rot. degrees freedom

The no. of degrees of freedom = 5

Internal Energy of a molecule,

$$u = 5 \times \frac{1}{2} K_B T = \frac{5}{2} K_B T$$

Internal Energy of one mole of monoatomic gas,

$$U = \frac{5}{2} K_B T \times N_A$$

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

$$C_V = \frac{dU}{dT} = \frac{5}{2} R$$

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

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

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

(ii) Diatomic Non-rigid Rotator

The molecules like **CO** even at moderate temperatures have a mode of **vibration**. I.e., its atoms oscillate along inter atomic axis like a one – dimensional oscillator, and contribute a vibration energy term to the total energy.

A non rigid rotator has 7 degrees of freedom.

3 trans. degrees freedom

+ 2 rot. degrees freedom

+ 1 vibra. degree of freedom

The no. of degrees of freedom = 7

Internal Energy of a molecule,

$$u = 7 \times \frac{1}{2} K_B T = \frac{7}{2} K_B T$$

Internal Energy of one mole of monoatomic gas,

$$U = \frac{7}{2} K_B T \times N_A$$

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

$$C_V = \frac{dU}{dT} = \frac{7}{2} R$$

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

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

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

Polyatomic Molecule

A polyatomic molecule has $6+2f$ degrees of freedom.

3 trans. degrees freedom

+ 3 rot. degrees freedom

+ f vibra. degree of freedom

The no. of degrees of freedom

$$= 6 + 2f$$

Internal Energy of a molecule,

$$u = (6 + 2f) \frac{1}{2} K_B T = \frac{6 + 2f}{2} K_B T \\ = (3 + f) K_B T$$

Internal Energy of one mole of monoatomic gas,

$$U = (3 + f) K_B T \times N_A \\ = (3 + f) R T \\ C_V = \frac{dU}{dT} = (3 + f) R \\ C_P = C_V + R = (3 + f) R + R \\ = (4 + f) R \\ \gamma = \frac{C_P}{C_V} = \frac{(4 + f) R}{(3 + f) R} \\ = \frac{(4 + f)}{(3 + f)}$$

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 $3K_B T$. For a mole of solid, $N = N_A$, and the total energy is $U = 3K_B T \times N_A = 3RT$

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

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

SPECIFIC HEAT CAPACITY OF WATER

Like solids here also for each atom the average energy is $3k_B T$. Water molecule has three atoms, two Hydrogen and one Oxygen. So it has $U = 3 \times 3K_B T \times N_A = 9RT$ and

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 9R.$$

The predicted specific heats are independent of temperature. As we go to low temperature, however, there is a marked departure from this prediction. Specific heats of all substances approach zero as T tends to 0. This is related to the fact that degrees of freedom get frozen and ineffective at low temperatures.

Problem3: For a gas $\gamma=3/2$ and R is the universal gas constant, find the values of C_P and C_V

Ans:

MEAN FREE PATH

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

It is given by the expression:

$$\ell = \frac{1}{\sqrt{2} \pi n d^2}, \text{ where 'n' is the}$$

number density of gas molecules & 'd' the diameter of the molecule.