Chapter- 13

KINETIC THEORY

Equation of state of a perfect gas

Gases at low pressures and high temperatures much above that at which they liquefy (or solidify) approximately satisfy a simple relation between their pressure, absolute temperature and volume given by

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

where μ is the number of moles and $R = N_A k_B = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is a universal constant, T is absolute temperature, N_A is Avogadro's number, $k_B = 1.38 \times 10^{-23} JK^{-1}$ is Boltzmann constant.

A gas that satisfies Eq. (1) exactly at all pressures and temperatures is defined to be an ideal gas or perfect gas.

If we fix μ and T in Eq. (1), we get

$$PV = \text{constant} \text{ ---eq.(2)}$$

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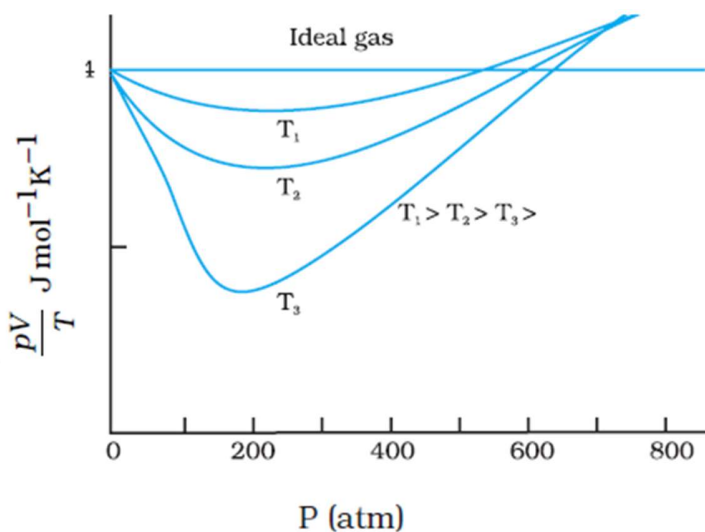
This is Charles' law.

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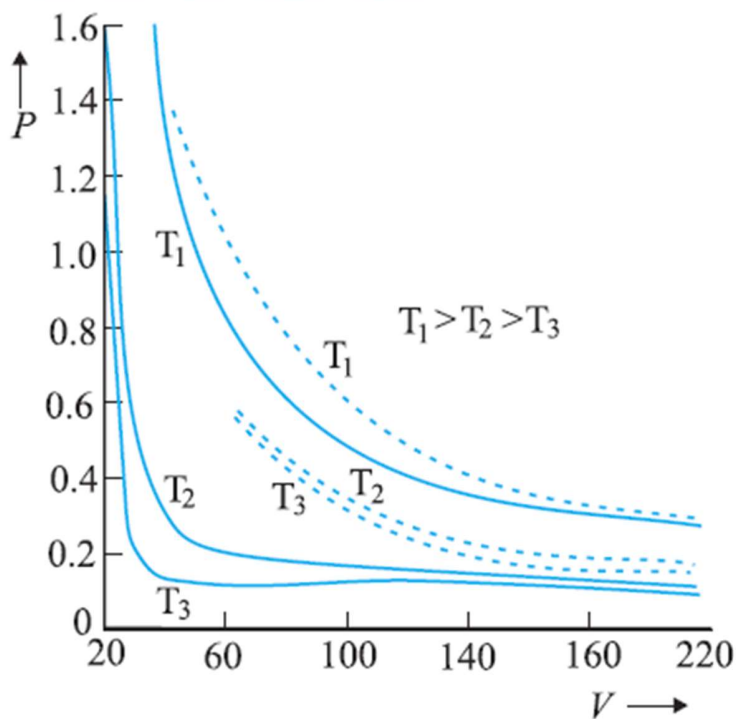

Fig.13.2 Experimental P-V curves (solid lines) for steam at three temperatures compared with Boyle's law (dotted lines). P is in units of 22 atm and V in units of 0.09 litres.
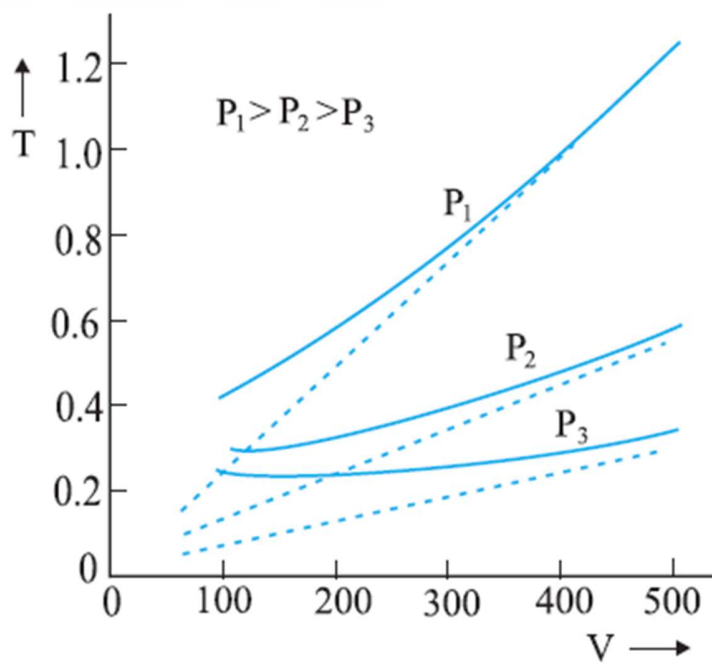
Fig. 13.3 *Experimental T-V curves (solid lines) for CO_2 at three pressures compared with Charles' law (dotted lines). T is in units of 300 K and V in units of 0.13 litres.*

Finally, consider a mixture of non-interacting ideal gases: μ_1 moles of gas 1, μ_2 moles of gas 2, etc. in a vessel of volume V at temperature T and pressure P. It is then found that the equation of state of the mixture is :

$$PV = \left(\mu_1 + \mu_2 + ... \right) RT$$

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

$$\Rightarrow P = P_1 + P_2 + ... \text{ ---eq.(3)}$$

Clearly, P is the pressure gas 1 would exert at the same conditions of volume and temperature if no other gases were present. This is called the partial pressure of the gas. Thus, the total pressure of a mixture of ideal gases is the sum of partial pressures. This is Dalton's law of partial pressures.

NCERT Example 13.1

The density of water is $1000 kg / m^3$. The density of water vapour at 100 °C and 1 atm pressure is $0.6 kg / m^3$. The volume of a molecule multiplied by the total number gives, what is called, molecular volume. Estimate the ratio (or fraction) of the molecular volume to the total volume occupied by the water vapour under the above conditions of temperature and pressure.

SOLUTION

The density of water is $1000 kg / m^3$. When water is converted to vapour its density becomes $0.6 kg / m^3$. So the mass of water and vapour are the same. So

$$\frac{1000kg/m^3}{0.6kg/m^3} = \frac{\text{volume of vapour}}{\text{volume of water}} = \frac{1}{6\times10^{-4}}$$

NCERT Example 13.2

The density of water is $1000kg/m^3$. Estimate the volume of a

water molecule.

Solution

1 mole of water has a mass approximately equal to 18 g. The mass of a molecule of water is

$\frac{18g}{6\times10^{23}}$. If V is the volume of a water molecule, then

$$1000kg/m^3 = \frac{\frac{18g}{6\times10^{23}}}{V} \Rightarrow V = \frac{18}{6\times10^{29}} m^3 = 3\times10^{-29} m^3$$

NCERT Example 13.4

Example 13.4 A vessel contains two nonreactive gases: neon (monatomic) and

oxygen (diatomic). The ratio of their partial pressures is 3:2. Estimate the ratio of (i)

the number of molecules and (ii) mass density of neon and oxygen in the vessel. The atomic

mass of Ne = 20.2 u, the molecular mass of O2 = 32.0 u.

SOLUTION

(i) $\dfrac{P_n}{P_o} = \dfrac{\mu_n \dfrac{RT}{V}}{\mu_o \dfrac{RT}{V}} = \dfrac{\mu_n}{\mu_o} = \dfrac{N_n}{N_o} = \dfrac{3}{2}$

(ii) $\dfrac{\rho_n}{\rho_o} = \dfrac{m_n N_n}{m_o N_o} = \dfrac{20.2u}{32.0u} \times \dfrac{3}{2} = 0.947$

work done in compressing a gas

Suppose the volume an ideal gas changes from V_1 to V_2. At any intermediate stage with

pressure P and volume change from V to $V + \Delta V$ (ΔV small)

$\Delta W = P\Delta V$

Taking ($\Delta V \to 0$) and summing the quantity ΔW over the entire process,

$W = \int_{V_1}^{V_2} P dV$

Kinetic theory of gases - assumptions, the concept of pressure

Kinetic theory of gases is based on the molecular picture of the matter. A given amount of gas is

a collection of a large number of molecules (typically of the order of Avogadro's number) that

are in incessant random motion. At ordinary pressure and temperature, the average distance

between molecules is a factor of 10 or more than

the typical size of a molecule. Thus, the interaction between molecules is negligible and

we can assume that they move freely in straight lines according to Newton's first law.

Molecules of a gas are in incessant random motion, colliding against one another and with the walls of the container. All collisions between molecules among themselves or between molecules and the walls are elastic. This implies that the total kinetic energy is conserved. The total momentum is conserved as usual.

The pressure of an Ideal Gas

Consider a gas enclosed in a cube of side l. Take the axes to be parallel to the sides of the cube. A molecule with velocity $\left(v_x, v_y, v_z \right)$ hits the planar wall parallel to yz plane of area $A = l^2$. Since the collision is elastic, the molecule rebounds with the 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 the collision is $\left(-v_x, -v_y, -v_z \right)$. 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 $A v_x \Delta t$ only can hit the wall in time Δt. But, on average, half of these are moving towards the wall and the other half away from the wall. Thus, the number of molecules with velocity $\left(v_x, v_y, v_z \right)$ hitting the wall in time Δt is

$\dfrac{1}{2} A v_x n \Delta t$, where n is the number of molecules per unit volume. The total momentum

transferred to the wall by these molecules in time Δt is:

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

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

area :

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

The above equation 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

the contribution due to all groups:

$$P = Q / A \Delta t = n m \overline{\left(v_x\right)^2}$$

where $\overline{v_x^{\,2}}$ is the average of $v_x^{\,2}$.

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

the vessel.

Therefore, by symmetry,
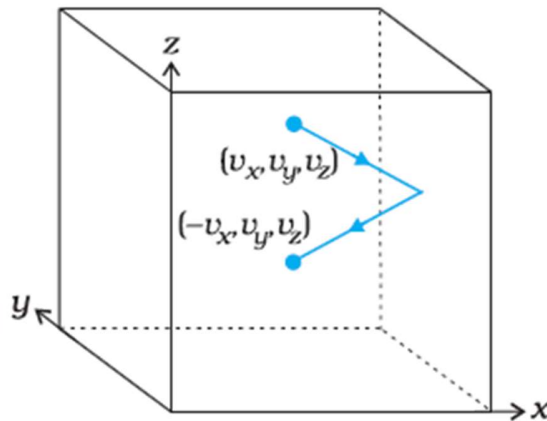
$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2}$$

where v is the speed and $\overline{v^2}$ denotes the mean of the squared speed. Thus

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

By Pascal's law, pressure in one portion of the gas in equilibrium is the same as anywhere else.

Kinetic interpretation of temperature

$$P = \frac{1}{3}mn\overline{v^2} \text{ ---eq.(1)}$$

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

$$\Rightarrow PV = \frac{2}{3}nV\frac{1}{2}m\overline{v^2}$$

$$\Rightarrow PV = \frac{2}{3}N\frac{1}{2}m\overline{v^2} \text{ ---eq.(2)}$$

where $N = nV$ is the number of molecules in the sample, $\frac{1}{2}m\overline{v^2}$

is the average translational kinetic energy of the molecules in the gas. Since the internal energy

E of an ideal

gas is purely kinetic,

$$E = N\frac{1}{2}m\overline{v^2} \text{ ---eq.(3)}$$

Equation (1) then gives :

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

$$\Rightarrow \mu RT = \frac{2}{3}E$$

$$\Rightarrow E = \frac{3}{2}\mu RT = \frac{3}{2}\mu N_A k_B T = \frac{3}{2}N k_B T$$

$$\Rightarrow \frac{E}{N} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T \text{ ---eq.(4)}$$

i.e., 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. This is a fundamental

result relating to temperature, a macroscopic

measurable parameter of gas (a thermodynamic variable as it is called) to a

molecular quantity, namely the average kinetic energy of a molecule.

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

the mixture. Equation (1) becomes

$$P = \frac{1}{3}\left(m_1 n_1 \overline{v_1^2} + m_2 n_2 \overline{v_2^2} + m_3 n_3 \overline{v_3^2} + ... \right)$$

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

is,

$$\frac{1}{2}m_1 \overline{v_1^2} = \frac{1}{2}m_2 \overline{v_2^2} = \frac{1}{2}m_3 \overline{v_3^2} = \frac{3}{2}k_B T$$

So

$$P = \left(n_1 + n_2 + n_3 + ...\right)k_BT$$

which is Dalton's law of partial pressures.

PROBLEM

Calculate the mean square speed of a molecule in nitrogen gas at a temperature *T* = 300 K.

SOLUTION

Since

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

So

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

$$m = \frac{28g}{6.02\times10^{23}} = \frac{28}{6.02\times10^{26}}kg$$

So

$$\overline{v^2} = \frac{3}{m}k_BT = \frac{3\times6.02\times10^{26}}{28kg}\times1.38\times10^{-23}\frac{J}{K}\times300K = \left(516\right)^2 m^2/s^2$$

Root mean square (RMS) speed is $v_{rms} = 516 m/s$

NCERT Example 13.5

A flask contains argon and chlorine in the ratio of 2:1 by mass. The temperature of the mixture

is 27 °C. Obtain the ratio of (i) average kinetic energy per molecule, and (ii) root mean square

speed v_{rms} of the molecules of the two gases. Atomic mass of argon = 39.9 u; Molecular mass

of chlorine = 70.9 u.

SOLUTION

(i)The average kinetic energy (per molecule) of any (ideal) gas is always equal to $\dfrac{3}{2}k_BT$. Since

argon and chlorine both have the same temperature in the flask, the ratio of average kinetic

energy (per molecule) of the two gases is 1:1.

(ii) $v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\dfrac{3}{m}k_BT}$

$$\frac{\left(v_{\text{rms}}\right)_{\text{Ar}}}{\left(v_{\text{rms}}\right)_{\text{Cl}}} = \sqrt{\frac{m_{\text{Cl}}}{m_{\text{Ar}}}} = \sqrt{\frac{70.9}{39.9}} = \sqrt{1.77} = 1.33$$

Degrees of freedom

A molecule free to move in space needs three coordinates to specify its location. If it is

constrained to move in a plane it needs two; and if constrained to move along a line, it needs

just one coordinate to locate it. This can also be expressed in another way. We say that it has

one degree of freedom for motion in a line, two for motion in a plane and three for motion in

space. A molecule free to move in space has three translational degrees of freedom. Molecules

of a monatomic gas like argon have only translational degrees of freedom. A diatomic molecule

having a rigid bond has three translational degrees of freedom. But in addition, it has two

rotational degrees of freedom. Some diatomic molecules have a mode of vibration, i.e., its

atoms oscillate along the interatomic axis like a one-dimensional oscillator.

Law of equipartition of energy

In equilibrium, the total energy is equally distributed in all possible energy modes, with each

mode having average energy equal to $\frac{1}{2} k_B T$. This is known as the law of equipartition of

energy. Accordingly, each

translational and rotational degree of freedom of a molecule contributes $\frac{1}{2} k_B T$ to the

energy, while 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 OF GASES

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 $\frac{3}{2} k_B T$. The total internal energy of a mole

of such a gas is

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

The molar specific heat at constant volume,

$$C_V = \frac{dU}{dT} = \frac{3}{2} RT \text{ is}$$

For an ideal gas,

$C_P - C_V = R$ (13.29)

where C_P is the molar specific heat at constant pressure. Thus,

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

The ratio of specific heats

$$\gamma = \frac{C_P}{C_V} = \frac{5}{3}$$

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 average energy of a molecule at temperature T is $\frac{5}{2}k_B T$. The total internal energy of a mole of such a gas is

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

The molar specific heat at constant volume,

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

For an ideal gas,

$C_P - C_V = R$ (13.29)

where C_P is the molar specific heat at constant pressure. Thus,

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

The ratio of specific heats

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

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

$$U = \frac{5}{2}N_A k_B T + k_B T = \frac{7}{2}RT$$

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

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

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

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 gas has

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

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

$$C_P = (4 + f)R$$

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

NCERT Example 13.8

A cylinder of fixed capacity 44.8 litres contains helium gas at standard temperature and pressure. What is the amount of heat needed to raise the temperature of the gas in the cylinder by 15.0 °C?

SOLUTION

In the given condition $\mu = 2$

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

$$\Delta Q = \mu C_V \Delta T = 2 \times 1.5 \times 8.314 \times 15 = 374J$$
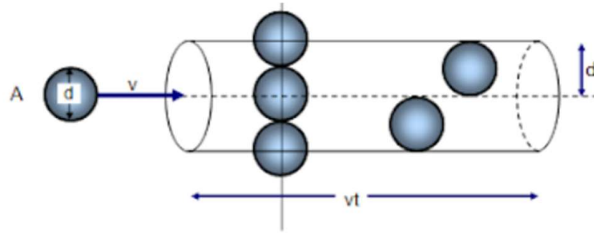
MEAN FREE PATH

Suppose the molecules of a gas are spheres of diameter *d*. Focus on a single molecule with the average speed $\langle v \rangle$. It will suffer a collision with any molecule that comes within a distance *d* between the centres. In time Δt, it sweeps a volume $\pi d^2 \langle v \rangle \Delta t$ wherein any other molecule will collide with it. If *n* is the

number of molecules per unit volume, the molecule suffers $n\pi d^2 \langle v \rangle \Delta t$ collisions in time Δt. Thus the rate of collisions is $n\pi d^2 \langle v \rangle$ or the time between two successive collisions is on the

average, $\tau = \dfrac{1}{n\pi d^2 \langle v \rangle}$

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

$$l = \langle v \rangle \tau = \langle v \rangle \dfrac{1}{n\pi d^2 \langle v \rangle} = \dfrac{1}{n\pi d^2} \text{---eq.(1)}$$

In this derivation, we imagined the other molecules to be at rest. But actually, all molecules are moving and the collision rate is determined by the average relative velocity of the molecules. Thus we need to replace $\langle v \rangle$ by $\langle v_r \rangle$ in Eq. (1). A more exact treatment gives

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

Let us estimate *l* and τ for air molecules with average speeds $\langle v \rangle = 485 m/s$

$$n = \frac{0.02 \times 10^{23}}{22.4 \times 10^{-3}} = 2.7 \times 10^{25} m^{-3}$$

Taking, $d = 2 \times 10^{-10} m$,

$$\tau = 6.1 \times 10^{-10} s$$

and $l = 2.9 \times 10^{-7} m$

NCERT Example 13.9

Estimate the mean free path for a water molecule in water vapour at 373 K.

SOLUTION

$$n = \frac{273}{373} \times 2.7 \times 10^{25} m^{-3}$$

Hence, the mean free path $l = 4 \times 10^{-7} m$

Note that the mean free path is 100 times the interatomic distance $4 \times 10^{-9} m$.