UNIT 3: GASEOUS STATE:

A. Kinetic molecular model of a gas:

Gases were among the first substances studied using the modern scientific method, which was developed in the 1600s. It did not take long to recognize that gases all shared certain physical behaviours, suggesting that gases could be described by one all-encompassing theory. The kinetic molecular theory of gases is a model that helps us understand the physical properties of gases at the molecular level.

- Kinetic molecular theory states that gas particles are in constant motion and exhibit perfectly elastic collisions.
- Kinetic molecular theory can be used to explain both Charles's and Boyle's laws.
- The average kinetic energy of a collection of gas particles is directly proportional to absolute temperature only.

Key Terms

- **ideal gas**: A hypothetical gas whose molecules exhibit no interaction and undergo elastic collision with each other and the walls of the container.
- **macroscopic properties**: Properties that can be visualized or measured by the naked eye; examples include pressure, temperature, and volume.

B. Postulates of molecular model of a gas:

The following are the basic assumptions of the kinetic molecular theory:

- A gas consists of a large number of very small spherical tiny particles, which may be identified with the molecules. The molecules of a given gas are completely identical in size, shape and mass.
- The volume occupied by the molecules is negligible in comparison to the total volume of the gas.
- The molecules are in rapid motion which is completely random. During their motion, they collide with one another and with the sides of the vessel. The pressure of the gas is due to the collisions of molecules with the sides of the vessel.
- The molecules are perfectly elastic, i.e. there occurs no loss of energy when they collide with one another and with the sides of the vessel.
- The laws of classical mechanics, in particular Newton's second law of motion, are applicable to the molecules in motion.
- There is no force of attraction or repulsion amongst the molecules, i.e. they are moving independent of one another.
- At any instant, a given molecule can have energy ranging from a small value to a very large value, but the average kinetic energy remains constant for a given temperature, i.e. the average kinetic energy is proportional to the absolute temperature of the gas.

C. Derivation of the Kinetic Gas Equation:

Derivation of the Kinetic Gas Equation

Imagine a cube of edge-length l, containing N molecules, each having a mass of m. Molecules are moving at random in all directions, with speed covering a considerable range of values.

The velocity u_1 of any molecule may be resolved into three-component velocities designated as u_x, u_y and u_z. These are in the three directions at right angles to each other and parallel to the sides of the cube as shown in Fig. 1.6.1. The component velocities are related by the expression

$$u_1^2 = u_x^2 + u_y^2 + u_z^2 \tag{1.6.1}$$

Considering the x-component motion of a molecule, we will have

Momentum of the molecule before collision with the side ABCD = mu_x

Momentum of the molecule after collision with the side ABCD = $-mu_x$

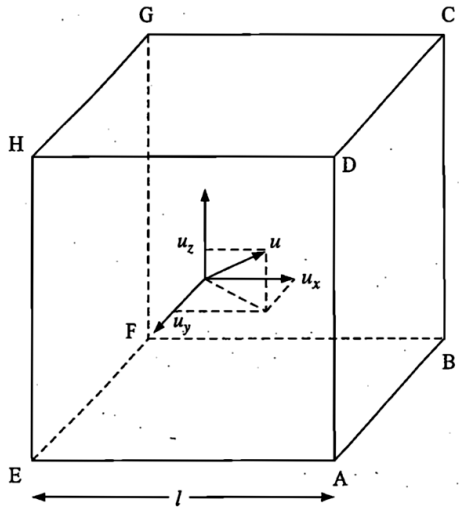


Fig. 1.6.1 Molecular velocity and its components

Change of momentum of the molecule in a single collision with the side ABCD $= |2mu_x|$.

Since l is the edge length of the cube, the molecule has to travel a distance $2l$ to arrive back at the wall ABCD. The number of collisions per unit time with the wall ABCD will be equal to $u_x/2l$.

The total change of momentum per unit time due to such impacts is

$$2mu_x\left(\frac{u_x}{2l}\right) = \frac{mu_x^2}{l}$$

According to Newton's second law of motion

$$\text{Force} = \text{mass} \times \text{acceleration}$$

$$= \text{mass} \times \frac{\text{d(velocity)}}{\text{d}t} = \frac{\text{d}}{\text{d}t}(\text{mass} \times \text{velocity})$$

$$= \frac{\text{d}}{\text{d}t}(\text{momentum}) = \text{rate of change of momentum}$$

Hence, total force due to impacts of a single molecule with the wall ABCD of the vessel is mu_x^2/l.

The area of the wall is l^2. Hence, the pressure exerted due to the collision of x-component velocity of a single molecule with the side ABCD is

$$p_x = \frac{mu_x^2/l}{l^2} = \frac{mu_x^2}{V} \tag{1.6.2}$$

where V is the volume of the vessel.

Since each molecule will exert similar pressure, the total pressure exerted on the wall ABCD will be

$$p = \sum_{i=1}^{N} p_{ix} = \frac{m}{V}\sum_{i=1}^{N} u_{ix}^2 \tag{1.6.3}$$

Defining the mean square speed as

$$\overline{u_x^2} = \frac{1}{N}\sum_{i=1}^{N} u_{ix}^2 \tag{1.6.4}$$

we can write

$$p = \frac{mN}{V}\overline{u_x^2} \tag{1.6.5}$$

Since the directions x, y and z are equivalent, we will also have

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} \tag{1.6.6}$$

But from Eq. (1.6.1), we will have

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2} \tag{1.6.7}$$

From Eqs (1.6.6) and (1.6.7), we can write

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{u^2} \tag{1.6.8}$$

Substituting this in Eq. (1.6.5), we get

$$p = \frac{mN}{V}\left(\frac{1}{3}\overline{u^2}\right) \quad \text{or} \quad pV = \frac{1}{3}mN\overline{u^2} \tag{1.6.9}$$

Root Mean Square Speed

Root mean square (rms) speed is defined as the square root of the average of the squares of speeds, i.e.

$$\sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots + u_N^2}{N}}$$

According to Eq. (1.7.2), this is given as

$$\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}} \tag{1.7.3}$$

or $$\sqrt{\overline{u^2}} = \sqrt{\frac{3pV}{M}} \tag{1.7.4}$$

Thus, rms speed is directly proportional to the square root of temperature and inversely proportional to the square root of molar mass. Hence, at a given temperature lighter molecules (say H_2, He) move faster than the heavier molecules (say O_2, N_2). There is no effect of change of pressure or volume on the rms speed since, at a given temperature, pV = constant.

D. Collision Diameter: ***The distance between the centres of the two molecules at the point of their closest approach is known as the collision diameter.***

While considering collisions of the molecules among themselves we assume the molecules to be rigid, non-interacting, and spherical with diameter σ. It is also assumed that all the molecules move with the same average speed $\bar{u}$.

Collision Cross-Section of Molecules

Two identical molecules of diameter σ will just touch each other when the distance separating their centres is σ. Thus, a moving molecule will collide with other molecules whose centres come within a distance of σ from its centre. The quantity $(\pi\sigma^2)$ is called the *collision cross-section* for the rigid spherical molecule. From Fig. 1.19.1 it is obvious that this collision cross-section is an area of an imaginary sphere of radius σ around the molecule within which the centre of another molecule cannot penetrate.

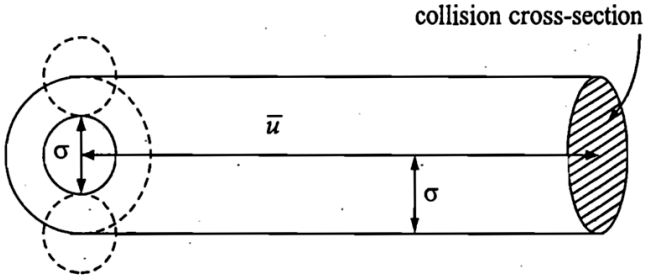


Fig. 1.19.1 Collision cross-section of a molecule

Collision Frequency: Collisional Frequency is the average rate in which two reactants collide for a given system and is used to express the average number of collisions per unit of time in a defined system.

Expression of Number of Collisions

The volume swept by a single molecule in unit time is

$$V = (\pi\sigma^2)\bar{u}$$

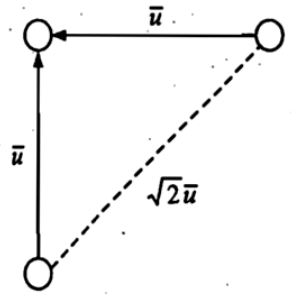
If N^* is the number of molecules per unit volume, then the number of molecules within the volume V is

$$N = VN^* = (\pi\sigma^2\bar{u})N^*$$

Hence, the number of collisions made by a single molecule in unit time will be

$$Z_1 = N = (\pi\sigma^2\bar{u})N^*$$

So far, it is assumed that only one molecule is moving and all the others are stationary. In practice, however, this is not true. In order to account for the movements of all molecules, one must consider the average velocity along the line of centres of two colliding molecules instead of the average velocity of a single molecule. If it is assumed that, on an average, molecules collide while approaching each other perpendicularly, then the average velocity along their centres is $\sqrt{2}\bar{u}$ as shown below.



Number of collisions made by a single molecule with other molecules per unit time is given by

$$Z_1 = \pi\sigma^2(\bar{u}_{rel})N^* = \sqrt{2}\pi\sigma^2\bar{u}\,N^* \tag{1.19.1}$$

The total number of bimolecular collisions Z_{11} per unit volume per unit time is given by

$$Z_{11} = \frac{1}{2}(Z_1\,N^*)$$

or
$$Z_{11} = \frac{1}{2}(\sqrt{2}\pi\sigma^2\bar{u}\,N^*)N^* = \frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}\,N^{*2} \tag{1.19.2}$$

(Note that the division by two is essential since the simple multiplication of Z_1 by N^* would count every collision twice.)

If the collisions involve two unlike molecules, then the number of collisions Z_{12} per unit volume per unit time is given as

$$Z_{12} = \pi\sigma_{12}^2\left(\sqrt{\frac{8kT}{\pi\mu}}\right)N_1N_2 \tag{1.19.3}$$

where N_1 and N_2 are the number of molecules per unit volume of the two types

of molecules, σ_{12} is the average diameter of the two molecules (i.e. $\sigma_{12} = (\sigma_1 + \sigma_2)/2$) and μ is the reduced mass such that

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

The Mean Free Path The mean free path is *the average distance travelled by a molecule between two successive collisions*. We can express it as follows:

$$\lambda = \frac{\text{Average distance travelled per unit time}}{\text{No. of collisions made by a single molecule per unit time}}$$

$$= \frac{\bar{u}}{Z_1}$$

Substituting Z_1 from Eq. (1.19.1), we get

$$\lambda = \frac{\bar{u}}{\sqrt{2}\pi\sigma^2\bar{u}N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 N^*} \qquad (1.19.4)$$

Effect of Temperature and Pressure on Mean Free Path and Molecular Collisions

In order to discuss the effect of temperature and pressure on λ, Z_1 and Z_{11}, first we express the pressure and temperature dependence of N^* and $\bar{u}$. This can be done as follows.

Dependence of N^* on p and T

According to the ideal gas equation, we have

$$pV = nRT = \frac{N'}{N_A}RT \quad \text{or} \quad p = \left(\frac{N'}{V}\right)\left(\frac{R}{N_A}\right)T = \left(\frac{N'}{V}\right)kT$$

Thus, the number of molecules per unit volume is given by

$$N^* = \frac{N'}{V} = \frac{p}{kT} \tag{1.19.5}$$

Thus, $$N^* \propto \frac{p}{T} \tag{1.19.6}$$

Dependence of $\bar{u}$ on T

The average speed $\bar{u}$ is given as

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}$$

Thus, $$\bar{u} \propto \sqrt{T} \tag{1.19.7}$$

Effects on Mean Free Path

Now from Eq. (1.19.4), we get

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

Thus, $$\lambda \propto \frac{1}{N^*}$$

Employing Eq. (1.19.6), we get

$$\lambda \propto \frac{T}{p} \tag{1.19.8}$$

Thus; $\lambda \propto T$ provided p is held constant

and $\lambda \propto \frac{1}{p}$ provided T is held constant.

Since, according to Gay Lussac's law, $p \propto T$ at constant volume, therefore, Eq. (1.19.8) under these conditions modifies to

$$\lambda \propto \text{(constant)}$$

that is, there will be no effect of changing T or p on λ if the volume of the gas is kept constant.

Effects of p and T on Molecular Collisions

From Eq. (1.19.1), we have

$$Z_1 = \sqrt{2}\pi\sigma^2 \bar{u} N^*$$

or $$Z_1 \propto \bar{u} N^*$$

Employing Eq. (1.19.6) and Eq. (1.19.7), this modifies to

$$Z_1 \propto (\sqrt{T})\left(\frac{p}{T}\right) \quad \text{or} \quad Z_1 \propto \frac{p}{\sqrt{T}} \tag{1.19.9}$$

Thus, $Z_1 \propto p$ when temperature is held constant and $Z_1 \propto 1/\sqrt{T}$ when pressure is held constant.

The effect of changing p or T at constant volume can be described by making use of Gay-Lussac's law in Eq. (1.19.9). Thus, we have

$$Z_1 \propto \frac{T}{\sqrt{T}} \propto \sqrt{T} \qquad \text{(volume constant)}$$

and $$Z_1 \propto \frac{p}{\sqrt{p}} \propto \sqrt{p} \qquad \text{(volume constant)}$$

From Eq. (1.19.2), we have

$$Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2 \bar{u} N^{*2} \quad \text{or} \quad Z_{11} \propto \bar{u} N^{*2}$$

Employing Eq. (1.19.6) and Eq. (1.19.7), this modifies to

$$Z_{11} \propto (\sqrt{T})\left(\frac{p}{T}\right)^2 \quad \text{or} \quad Z_{11} \propto \frac{p^2}{T^{3/2}}$$

Thus, $Z_{11} \propto p^2$ provided temperature is held constant and $Z_{11} \propto T^{-3/2}$ provided pressure is held constant.

The effect of changing p or T at constant volume can again be described by making use of Gay-Lussac's law. Thus

$$Z_{11} \propto \frac{p^2}{T^{3/2}} \propto \frac{T^2}{T^{3/2}} \propto T^{1/2} \qquad \text{(volume constant)}$$

and $$Z_{11} \propto \frac{p^2}{T^{3/2}} \propto \frac{p^2}{p^{3/2}} \propto p^{1/2} \qquad \text{(volume constant)}$$

1.20 VISCOSITY

Introduction

The internal friction which opposes the relative motion of adjacent layers of a fluid is known as viscosity.

Viscosity of Gases

In a laminar flow of a fluid in a cylindrical tube, layers just touching the sides of the tube are stationary, and velocities of the adjacent layers increase towards the centre of the tube, the layer in the centre of the tube has a maximum velocity. There thus exists a velocity gradient amongst different layers of a liquid.

In case of gases, because of their continuous movement, there occurs an interchange of molecules between two layers, with the result that a fraction of momentum of one layer is passed over to the other layer. The net effect is to decrease the relative rate of movement of one layer with respect to the other. In order to maintain a uniform velocity gradient, one has to apply a force along the direction of movement of the layers. This applied force is a measure of internal friction or viscosity of the fluid.

Definition of Coefficient of Viscosity

The tangential force F required to maintain uniform velocity of layers will depend upon two factors, viz.,

(i) Area A of contact between the two adjacent layers
(ii) Velocity gradient du/dz

Thus, $$F \propto A\frac{du}{dz} \quad \text{that is} \quad F = \eta A\frac{du}{dz} \tag{1.20.1}$$

where η is known as the *coefficient of viscosity* (or simply viscosity). It is the tangential force that must be applied in order to maintain a velocity difference of unity between two parallel layers unit distance apart and having unit area of contact. SI unit of the coefficient of viscosity is N m^{-2} s. In CGS units, it has the unit of dyn cm^{-2} s and is known as the poise unit.

Expression of Viscosity of Gases

Viscosity in case of a gas arises because of transfer of momentum across the layers of the gas. Consider a layer P–P′ at a height z, (Fig. 1.20.1), moving with a velocity u_z. Let the velocity gradient be du/dz. Let us consider the molecules entering and leaving this layer. We assume:

(i) That the flow velocity u_z is very small as compared with the mean gas velocity $\bar{u}$.

(ii) That the only molecules reaching P–P′ are those which, on an average, have just made their last collision at a distance λ from the height z.

(iii) The number of molecules passing downwards or upwards through a unit area per unit time = $N^* \bar{u}/4$, where N^* is the number of molecules per unit volume and $\bar{u}$ is the average speed of gaseous molecules.[†]

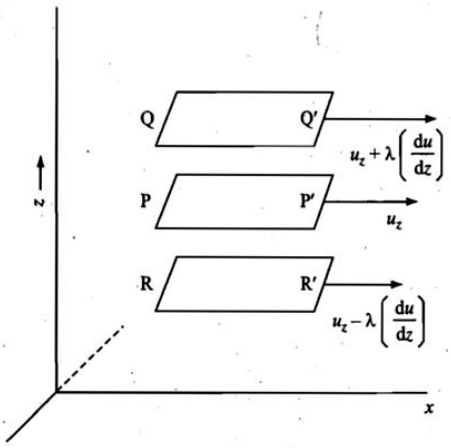


Fig. 1.20.1 Display of velocity gradient with the height of layer

In the plane P–P′, the amount of horizontal momentum coming up through a unit area per unit time is

$$(mu)\uparrow = m\left(\frac{1}{4}N^*\bar{u}\right)\left(u_z - \lambda\frac{du}{dz}\right)$$

and the amount of horizontal momentum coming down

$$(mu)\downarrow = m\left(\frac{1}{4}N^*\bar{u}\right)\left(u_z + \lambda\frac{du}{dz}\right)$$

The net downward flow of x momentum in unit time

$$(mu)\downarrow - (mu)\uparrow = \frac{1}{2}N^*\bar{u}\, m\lambda\frac{du}{dz}$$

Since momentum transfer in unit time is numerically equal to the force, therefore, the force acting in the x-direction on a unit area of the layer is

$$F = \frac{1}{2}mN^*\bar{u}\lambda\frac{du}{dz}$$

Comparing this with Eq. (1.20.1) with A = unit area, we get

$$\eta = \frac{1}{2}mN^*\bar{u}\lambda = \frac{1}{2}\rho\bar{u}\lambda \qquad (1.20.2)^\dagger$$

where ρ is the density of the medium.

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† The more rigorous calculations based on the hard sphere model gives the expression of viscosity as $\eta = (5\pi/32)\, mN^*\bar{u}\lambda$.

Calculation of σ from η and variation of viscosity with temperature and pressure

Effect of *p* and *T* on Viscosity of Gases

We have $\bar{u} = \sqrt{\frac{8kT}{\pi m}}$ and $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$

Substituting these in Eq. (1.20.2), we have

$$\eta = \frac{1}{2} m N^* \left(\sqrt{\frac{8kT}{\pi m}} \right) \left(\frac{1}{\sqrt{2}\pi\sigma^2 N^*} \right)$$

or $$\eta = \frac{(mkT)^{1/2}}{\pi^{3/2}\sigma^2} \qquad (1.20.3)$$

According to this equation, η is independent of pressure. Experimentally this is found to be true. When the pressure is so low that the mean free path becomes comparable with the dimensions of the apparatus, the collisions of molecules are primarily with the walls, and under such circumstances, Eq. (1.20.2) is not applicable.

Equation (1.20.3) shows that η should also be independent of density of gas and this is in agreement with the experimental observations. This equation also suggests that $\eta \propto T^{1/2}$, but a somewhat larger exponent more like $T^{0.7}$ is observed for real gases, partly due to the fact that the cross-sectional diameter becomes smaller at higher temperatures due to increased penetration of the potential energy barrier by gas molecules of higher velocities. In contrast with the viscosity of ideal gases, the viscosity of liquids decreases with the rise in temperature.

Maxwell distribution and its use in evaluating molecular velocities (average, root mean square and most probable) and average kinetic energy

Distribution of Molecular Speeds

The speed of a molecule of a gas changes continuously as a result of collisions with other molecules and with the walls of the container. Thus, the net result is that one cannot speak of the speed of an individual molecule; rather, one must consider the statistical average of the speeds of the whole collection of gas molecules. Since the observed properties such as pressure, volume and temperature of an isolated gaseous sample do not change with time, it is expected that the same is also true in the case of distribution of molecular speeds. That is, the fraction of total number of molecules having speeds between any definite range must be constant, even though the speeds of individual molecules may be changing as a result of molecular collisions.

Law of Distribution of Molecular Speeds

The manner in which the molecules of a gas are distributed over the possible speed ranges, from zero to very high values, was first investigated by J.C. Maxwell using the theory of probability. His results are expressed as the law of distribution of molecular speeds, one form of which is

$$dN_u = 4\pi N\left(\frac{M}{2\pi RT}\right)^{3/2} \exp(-Mu^2/2RT)\, u^2 du$$

$$= 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} \exp(-mu^2/2kT)\, u^2 du \qquad (1.16.1)$$

This expression gives the number of molecules dN_u having speeds between u and $u + du$ in terms of the total number N of molecules present, molar mass M (or mass of a single molecule m) of gas and the temperature. According to this expression the fraction dN_u/N of molecules having speeds between u and $u + du$ for a gas of molar mass M depends only on temperature. Thus, for a given temperature, this fraction has a constant value.

Consequence of Distribution of Speeds

A direct consequence of the distribution of speeds is that *the average kinetic energy of a gas is also constant for a given temperature.* Qualitatively, this may be verified as follows:

The average kinetic energy is defined as

$$\overline{\text{KE}} = \frac{1}{N}\left(\frac{1}{2}mu_1^2 + \frac{1}{2}mu_2^2 + \cdots + \frac{1}{2}mu_N^2\right)$$

$$= \frac{1}{2N}m(u_1^2 + u_2^2 + \cdots + u_N^2) = \frac{1}{2}m\overline{u^2}$$

Alternatively, it may be defined as

$$\overline{\text{KE}} = \frac{1}{N}\left(\frac{1}{2}m\sum_i dN_i\, u_i^2\right) = \frac{1}{2}m\left(\sum_i \frac{dN_i}{N}u_i^2\right) \qquad (1.16.2)$$

where dN_i is the number of molecules having speed equal to u_i. Since the fraction dN_i/N having speed u_i (or more precisely between speed range u_i and $u_i + du$) is constant at a given temperature, the right side of Eq. (1.16.2) has a constant value. Thus, the average kinetic energy has a constant value at a given temperature. This is, in fact, one of the assumptions of the kinetic theory of gases.

Plots of Maxwell Distribution of Speeds

The Maxwell distribution of speeds is customarily plotted with the fraction $(1/N)\,(dN_u/du)$ as the ordinate and u as the abscissa. The term $(1/N) \times (dN_u/du) = (1/du)\,(dN_u/N)$ gives the fraction of molecules in the speed range of u to $u + du$ per unit interval of speed. Roughly speaking, this gives the probability of finding a molecule with a speed between u and $(u + 1$ m/s). The distribution at two temperatures is shown in Fig. 1.16.1.

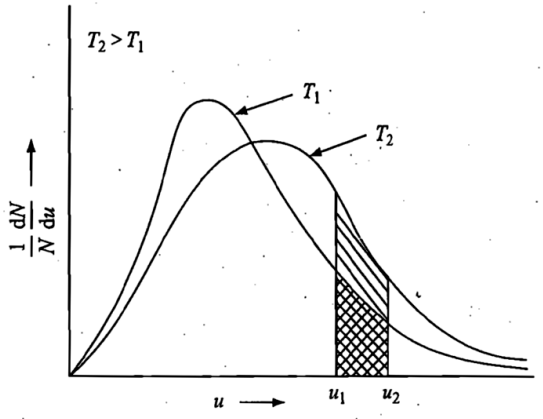

Fig. 1.16.1 Plots of $(1/N)\,(dN_u/du)$ versus u

The curve at any temperature is parabolic near the origin, since the factor u^2 is dominant in this region, the exponential function being approximately equal to unity. At high values of u, however, the exponential factor dominates the behaviour of the function, causing it to decrease rapidly in value.

Most Probable Speed

As a consequence of the contrasting behaviour of the two factors, the product function passes through a maximum at a speed known as the *most probable speed*, u_{mp}. Thus, the most probable speed is the speed possessed by the maximum fraction of the molecules. The expression of u_{mp} can be derived mathematically using the condition of maxima by setting the first derivative of $(1/N)\,(dN_u/du)$ with respect to speed equal to zero. Thus

$$\frac{d\left(\frac{1}{N}\frac{dN_u}{du}\right)}{du} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\left[2u\exp(-Mu^2/2RT) + u^2\left(-\frac{2Mu}{2RT}\right)\exp(-Mu^2/2RT)\right]$$

Hence at u_{mp}, we have

$$4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} u_{mp}\exp(-Mu_{mp}^2/2RT)\left[2-\frac{Mu_{mp}^2}{RT}\right] = 0 \qquad (1.16.3)$$

In fact, any of the terms u_{mp}, $\exp(-Mu_{mp}^2/2RT)$ and $(2 - Mu_{mp}^2/RT)$ being equal to zero will make the whole Eq. (1.16.3) equal to zero. The first two correspond to the minimum fraction of molecules having speeds zero and infinity, respectively. The third term gives

$$2-\frac{Mu_{mp}^2}{RT} = 0 \quad \text{or} \quad u_{mp}^2 = \frac{2RT}{M}$$

or
$$u_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2kT}{m}} \qquad (1.16.4)$$

Maxwell distribution expression (Eq. 1.16.1) can be used to derive expressions for average speed, root mean square speed, average kinetic energy and the fraction of molecules possessing kinetic energies greater than some specified energy.

Average Speed

The average value of speeds is given by the relation

$$\bar{u} = \frac{u_1 + u_2 + \cdots + u_N}{N} = \frac{1}{N}\sum_i u_i \qquad (1.17.1)$$

Equation (1.17.1) can be written in the form

$$\bar{u} = \frac{1}{N}\int_0^\infty u\,dN_u = \int_0^\infty u\frac{dN_u}{N} \tag{1.17.2}$$

where dN_u is the number of molecules having speed u. The summation of different speeds is replaced by integration since all types of speed ranging from zero to infinity are involved.

Substituting dN_u/N from Eq. (1.16.1) in Eq. (1.17.2), we get

$$\bar{u} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty u^3 \exp(-Mu^2/2RT)\,du$$

which on integration yields

$$\bar{u} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\left\{2\left(\frac{RT}{M}\right)^2\right\} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}} \tag{1.17.3}$$

Root Mean Square Speed

The mean square speed is given by

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \cdots + u_N^2}{N} = \frac{1}{N}\sum_i u_i^2 = \frac{1}{N}\int_0^\infty u^2\,dN_u \tag{1.17.4}$$

Using Eq. (1.16.1), we get

$$\overline{u^2} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty u^4 \exp(-Mu^2/2RT)\,du$$

which on integration yields

$$\overline{u^2} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\left\{\left(\frac{RT}{M}\right)^{5/2}\frac{3}{\sqrt{2}}\sqrt{\pi}\right\} = 3\frac{RT}{M}$$

Thus, $$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}} \tag{1.17.5}$$

Average Kinetic Energy

The average kinetic energy is given by

$$\bar{\varepsilon} = \frac{1}{N}\left(\frac{1}{2}m\,u_1^2 + \frac{1}{2}m\,u_2^2 + \cdots + \frac{1}{2}m\,u_N^2\right)$$

$$= \frac{1}{N}\frac{m}{2}\sum_i u_i^2 = \frac{1}{N}\frac{m}{2}\int_0^\infty u^2\,dN_u$$

Substituting dN_u/N from Eq. (1.16.1) and intergrating the resultant expression, we have

$$\bar{\varepsilon} = \frac{1}{2}m\left(\frac{3kT}{m}\right) = \frac{3}{2}kT \tag{1.17.6}$$

Expression of Energy Distribution

The Maxwell distribution of speeds (Eq. 1.16.1) can be converted into energy distribution by substituting

$$\varepsilon = \frac{1}{2}mu^2$$

which gives

$$u = \left(\frac{2}{m}\right)^{1/2} \varepsilon^{1/2}$$

Differentiating, we have

$$du = \left(\frac{1}{2m}\right)^{1/2} \varepsilon^{-1/2}\, d\varepsilon$$

The energy range $d\varepsilon$ corresponds to the speed range du, and so the number of particles dN_u having speeds between u and $u + du$ corresponds to the number of particles dN_ε having energies between ε and $\varepsilon + d\varepsilon$. Replacing u and du in Eq. (1.16.1) in terms of ε and $d\varepsilon$, we have

$$dN_\varepsilon = 2\pi N\left(\frac{1}{\pi kT}\right)^{3/2} \varepsilon^{1/2} \exp(-\varepsilon/kT)\, d\varepsilon \qquad (1.17.7)$$

Figure 1.17.1 shows the plot of $(1/N)\,(dN_\varepsilon/d\varepsilon)$ versus ε. Shape of this curve is different from that of the speed distribution curve. The energy distribution has a vertical tangent at the origin and thus it rises much more rapidly than the speed distribution curve which starts with a horizontal tangent. After passing the maximum, the energy distribution falls off more gently than does the speed distribution. As usual, the distribution is broadened at higher temperatures. Thus, a greater proportion of the molecules possess higher energies.

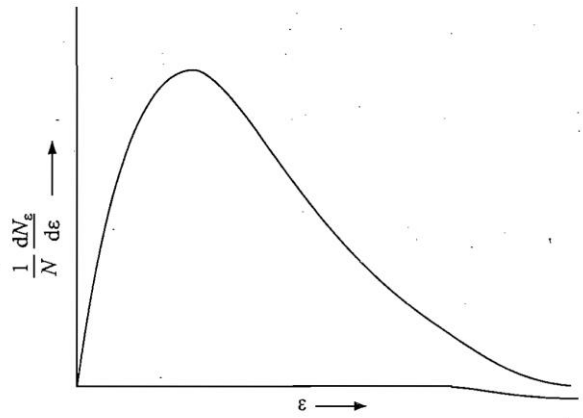

Fig. 1.17.1 Plot of $(1/N)$ $(dN_\varepsilon/d\varepsilon)$ versus ε

1.24 LAW OF EQUIPARTITION OF ENERGY

Classical Law of Equipartition of Energy

The average energy of a molecule can be calculated with the help of the classical law of equipartition of energy. The latter may be stated as follows:

If the energy of a molecule can be written in the form of a sum of terms, each of which is proportional to the square of a velocity component (or to the square of a position coordinate), then each of these square terms contributes (1/2)kT to the average energy.

The above law can be derived by evaluating the average value of the x-component of average kinetic energy with the help of Maxwell distribution law.† But here we follow a simple method based on the conceptual analysis of the average kinetic energy of molecules. According to Eq. (1.7.5), the latter is given as

$$\overline{\mathrm{KE}} = \bar{\varepsilon} = \frac{1}{2}m\overline{u^2} = \frac{3}{2}kT \tag{1.24.1}$$

Now the mean square velocity can be written in terms of its components as

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}$$

Since the designation of the components is arbitrary, it follows that

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2}$$

Thus, Eq. (1.25.1) can be written as

$$\bar{\varepsilon} = \frac{1}{2}m\overline{u^2} = \frac{1}{2}m(\overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}) = \frac{3}{2}m\overline{u_x^2} = \frac{3}{2}kT$$

which gives

$$\frac{1}{2}m\overline{u_x^2} = \frac{1}{2}kT \tag{1.24.2}$$

Similarly,

$$\frac{1}{2}m\overline{u_y^2} = \frac{1}{2}kT \tag{1.24.3}$$

$$\frac{1}{2}m\overline{u_z^2} = \frac{1}{2}kT \tag{1.24.4}$$

Thus, the average total kinetic energy can be divided into three components, each of which is proportional to the square of the velocity component and thus contributes $(1/2)kT$ to the average energy.

Average Energy of Different Modes of Motion

A polyatomic molecule, besides having translational motion, also has rotational and vibrational motions. The average energy stored in these motions can be calculated using the law of equipartition of energy as shown in the following.

Translational Motion

The translational energy of a gas molecule is

$$\bar{\varepsilon}_{\text{trans}} = \frac{1}{2}mu^2 = \frac{1}{2}mu_x^2 + \frac{1}{2}mu_y^2 + \frac{1}{2}mu_z^2$$

Since each term is proportional to the square of a velocity component, each contributes $(1/2)kT$ to the average energy. Thus, the translational contribution is

$$\bar{\varepsilon}_{\text{trans}} = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT \tag{1.24.5}$$

Rotational Motion

In order to describe the orientation of a linear molecule in space, we need to specify two angles about two axes while for a nonlinear molecule, three angles are required. Motion in these coordinates corresponds to rotation about two axes

† See Section 4.14 of Vol. 5 of this series of the book.

for a linear molecule and about three axes for a nonlinear molecule in space. The equation for the energy of rotation is given by

$$\varepsilon_{\text{rot}} = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 \qquad \text{(linear molecule)}$$

$$\varepsilon_{\text{rot}} = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2 \qquad \text{(nonlinear molecule)}$$

where ω_x, ω_y, ω_z are angular velocities and I_x, I_y, I_z are moments of inertia about the x-, y-, and z-axes, respectively. Since each term in the above expressions is proportional to the square of the velocity component, it contributes on an average $(1/2)kT$ towards the average rotational energy. Thus,

Average rotational energy of a linear molecule

$$= \frac{1}{2}kT + \frac{1}{2}kT = kT \tag{1.24.6}$$

Average rotational energy of a nonlinear molecule

$$= \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT \tag{1.24.7}$$

Vibrational Motion

If the vibrational motion is assumed to be harmonic, then the energy of each vibrational mode is given as

$$\varepsilon_{vib} = \text{kinetic energy} + \text{potential energy}$$

$$= \frac{1}{2}\mu\left(\frac{dr}{dr}\right)^2 + \frac{1}{2}k_f(r - r_0)^2$$

where μ is the reduced mass, k_f is the force constant, r_0 is the equilibrium value of the coordinate r, and dr/dt is the change of internuclear distance with time. Since both the terms in the above expression contain square of either the velocity or the coordinate, it follows that each will contribute $(1/2)kT$ towards the total average vibrational energy. Thus, the average energy stored in a vibrational motion is

$$\bar{\varepsilon}_{vib} = \frac{1}{2}kT + \frac{1}{2}kT = kT \qquad (1.24.8)$$

DEGREES OF FREEDOM:

The number of independent ways in which a molecule of gas can move is called the degree of freedom.

Types of degree of freedom

A gaseous molecule has a certain number of degrees of freedom, such as the ability to translate (the motion of its centre of mass through space), rotate around its centre of mass, or vibrate (as its bond lengths and angles change). Many physical and chemical properties depend on the energy associated with each of these modes of motion.

If a molecule has N number of independent particles, then total degree of freedom in three dimensions of the molecule is determined by: **F= 3N**

Translational Motion

The translational motion of a molecule as a whole can be described by the motion of its centre of mass. Since three coordinates are required to describe the position of centre of mass, it follows that the energy (kinetic only) stored in the translational motion as described by Eq. (1.24.5) is

$$\bar{\varepsilon}_{trans} = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT \qquad (1.25.1)$$

Rotational Motion

Linear molecule Since a linear molecule can rotate around two axes, the energy stored in the rotational motion as described by Eq. (1.24.6) is

$$\bar{\varepsilon}_{\text{rot}} = \frac{1}{2}kT + \frac{1}{2}kT = kT \qquad (1.25.2)$$

Nonlinear molecule Since a nonlinear molecule can rotate around three axes, the energy stored in this motion as described by Eq. (1.24.7) is

$$\bar{\varepsilon}_{\text{rot}} = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT \qquad (1.25.3)$$

Thus a linear molecule contributes, on an average, kT and a nonlinear molecule $(3/2)kT$, towards the total average energy due to rotational motion.

Vibrational Motion

The remaining $(3N - 5)$ coordinates for a linear molecule and $(3N - 6)$ coordinates for a nonlinear molecule, describe the bond distances and bond angles within the molecule. Motion in these coordinates corresponds to the vibrations (stretching or bending) of the molecule. Thus, linear molecules have $(3N - 5)$ and nonlinear molecules have $(3N - 6)$ vibrational modes. Vibrational energy stored in each of the vibrational mode as given by Eq. (1.24.8) is

$$\bar{\varepsilon}_{\text{vib}} = \frac{1}{2}kT + \frac{1}{2}kT = kT \qquad (1.25.4)$$

Thus, each vibrational mode contributes on an average kT towards the total average energy. Thus, linear molecules contribute $(3N - 5)kT$ and nonlinear molecules contribute $(3N - 6)kT$ towards the total average energy due to their vibrational motions.

Degree of freedom	Monatomic	linear molecules	Non-linear molecules
Translational	3	3	3
Rotational	0	2	3
Vibrational	0	3N-5	3N-6
Total	3	3N	3N

Points to be noted:

Energy contribution for linear molecules:

Degree of freedom	Translational	Rotational	Vibrational
Linear molecule	3	2	3N-5
Energy contribution			
At room temperature	3 x ½ kT	2 x ½ kT	Inactive (no contribution)
Energy contribution			
At high temperature	3 x ½ kT	2 x ½ kT	(3N-5) x Kt

Energy contribution for non-linear molecules

Degree of freedom	Translational	Rotational	Vibrational
non-linear molecule	3	3	3N-6
Energy contribution At room temperature	3 x ½ kT	3 x ½ kT	Inactive (no contribution)
Energy contribution At high temperature	3 x ½ kT	3 x ½ kT	(3N-6) x kT

Degree of freedom of monoatomic gas

- Since a monatomic molecule consists of only a single atom of point mass it has three degrees of freedom of translatory motion along the three coordinate axes x, y and z.
- Examples: Molecules of Inert gases like helium(He), Neon(Ne), Argon(Ar), etc.

Degree of freedom of diatomic molecule

- The diatomic molecule can rotate about any axis at right angles to its own axis. Hence it has **two** rotational degrees of freedom, in addition, it has **three** translational degrees of freedom along the three axes. A diatomic molecule shows **one** vibrational degree of freedom. So, a diatomic molecule has a total of **six** degrees of freedom at high temperatures.
- At room temperature the total degree of freedom of a diatomic molecule is **five** because vibrational motion is not contributed. Examples: molecules of O_2, N_2, CO, Cl_2, etc.

Degree of freedom of triatomic molecule

- In the case of a triatomic molecule of linear type, the centre of mass lies at the central atom.
- It, therefore, behaves like a diatomic molecule with **three** degrees of freedom of translation and **two** degrees of freedom of rotation, it has **five** degrees of freedom as shown at room temperature.
- At high temperatures, It shows four vibrational degrees of freedom. Hence, it shows a total of **nine** degrees of freedom. Examples: molecules of CO_2, CS_2, etc.
- At room temperature a triatomic **nonlinear molecule** possesses **three** degrees of freedom of rotation in addition to **three** degrees of freedom of translation. Hence it has **six** degrees of freedom.
- At high temperatures, it shows a total of **nine** degrees of freedom. Examples : molecules of H_2O, SO_2, etc.

Total Energy of Molecules

The total average energy contribution due to all the three modes is:

For linear molecule

$$\bar{\varepsilon}_{\text{linear}} = \left(\frac{3}{2}kT\right)_{\text{trans}} + \left(\frac{2}{2}kT\right)_{\text{rot}} + \{(3N-5)kT)\}_{\text{vib}} \qquad (1.25.5)$$

For nonlinear molecule

$$\bar{\varepsilon}_{\text{nonlinear}} = \left(\frac{3}{2}kT\right)_{\text{trans}} + \left(\frac{3}{2}kT\right)_{\text{rot}} + \{(3N-6)kT)\}_{\text{vib}} \qquad (1.25.6)$$

The total average energy stored by the molecules in one mole of the gas is

$$\bar{E}_{\text{linear}} = N_A\,\bar{\varepsilon}_{\text{linear}} = \frac{3}{2}RT + RT + (3N-5)RT \qquad (1.25.7)$$

$$\bar{E}_{\text{nonlinear}} = N_A\,\bar{\varepsilon}_{\text{nonlinear}} = \frac{3}{2}RT + \frac{3}{2}RT + (3N-6)RT \qquad (1.25.8)$$

Table 1.26.1 describes the average energies of molecules of different gases.

Table 1.26.1 Average Energies of Gaseous Molecules

Gas	*N*	$\bar{\varepsilon}$	$\bar{E}$
Monatomic	1	(3/2) *kT*	(3/2) *RT*
Diatomic	2	(7/2) *kT*	(7/2) *RT*
Triatomic	3		
Linear		(13/2) *kT*	(13/2) *RT*
Nonlinear		6 *kT*	6 *RT*

1.26 HEAT CAPACITIES

Definition of Heat Capacities

The change in internal energy of a gaseous system is given by

$$\Delta U = q + w \tag{1.26.1}$$

where q is the heat absorbed (or released) by the system and w is the work of expansion (or compression) of the system.[†]

The work done due to expansion at constant pressure (Fig. 1.26.1) is given by

$$w = -F \times l = -p\,(A \times l)$$

or $$w = -p\,\Delta V$$

With this, Eq. (1.26.1) becomes

$$q = \Delta U + p\,\Delta V \tag{1.26.2}$$

If heat flows at constant volume condition, then $w = 0$ and the entire heat is utilized in increasing the internal energy of the gas, i.e.

$$q_V = \Delta U \quad \text{or} \quad dq_V = dU \tag{1.26.3}$$

and if the heat flows at constant pressure condition, then it is utilized both in increasing the internal energy and in doing the work of expansion, i.e.

$$q_p = \Delta U + p\,\Delta V \quad \text{or} \quad dq_p = dU + p\,dV \tag{1.26.4}$$

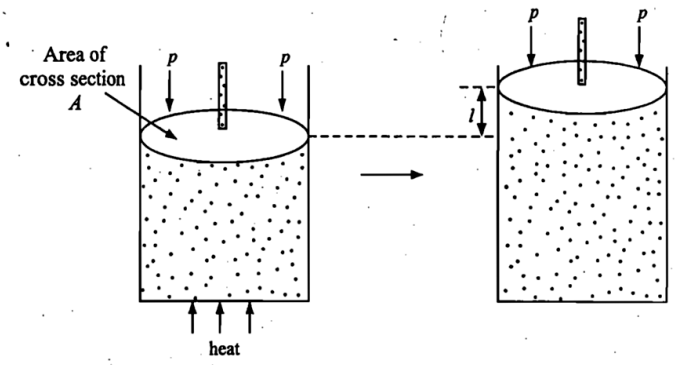

Fig. 1.26.1 Work done on account of expansion of a gas

Heat capacity of a system is defined as the amount of heat required to increase its temperature by 1 degree Celsius. Thus one can have two heat capacities, (i) heat capacity C_V at constant volume condition and (ii) heat capacity C_p at constant pressure condition. These are represented as:

$$C_V = \left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{1.26.5}$$

$$C_p = \left(\frac{\partial q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{1.26.6}$$

Difference in Heat Capacities of an Ideal Gas

If the gas is assumed to be ideal, then

$$pV = nRT, \quad p(\partial V/\partial T)_p = nR$$

Since for an ideal gas, the internal energy U depends only on T, we will have

$$(\partial U/\partial T)_V = (\partial U/\partial T)_p$$

Thus, for an ideal gas it follows that

$$C_p = C_V + nR \tag{1.26.7}$$

For one mole of the gas

$$C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + R \tag{1.26.8}$$

Molar Heat Capacities of Gases

Molar heat capacity at constant volume of a gas can be obtained by differentiating the molar energy with respect to temperature. Thus, from Eqs (1.25.7) and (1.25.8), and Table 1.26.1, we have

Monatomic gases

$$C_{V,\mathrm{m}} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R; \qquad C_{p,\mathrm{m}} = \frac{5}{2}R$$

$$\gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} = \frac{5}{3} \simeq 1.667$$

Polyatomic gases

$$\text{(Linear)}\quad C_{V,\mathrm{m}} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R + R + (3N-5)R \tag{1.26.9}$$

$$\text{(Nonlinear)}\quad C_{V,\mathrm{m}} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R + \frac{3}{2}R + (3N-6)R \tag{1.26.10}$$

The molar heat capacities for diatomic and triatomic molecules are as follows:

Diatomic molecule $N = 2$. Thus

$$C_{V,\mathrm{m}} = \frac{3}{2}R + R + R = \frac{7}{2}R; \qquad C_{p,\mathrm{m}} = \frac{9}{2}R$$

$$\gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} = \frac{9}{7} \simeq 1.286 \tag{1.26.11}$$

Triatomic molecule $N = 3$. Thus

$$\text{Linear}\quad C_{V,\mathrm{m}} = \frac{3}{2}R + R + 4R = \frac{13}{2}R; \qquad C_{p,\mathrm{m}} = \frac{15}{2}R \tag{1.26.12}$$

$$\gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} = \frac{15}{13} \simeq 1.154$$

$$\text{Nonlinear}\quad C_{V,\mathrm{m}} = \frac{3}{2}R + \frac{3}{2}R + 3R = 6R; \qquad C_{p,\mathrm{m}} = 7R \tag{1.26.13}$$

$$\gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} = \frac{7}{6} \simeq 1.167$$

BEHAVIOUR OF REAL GASES:

Deviations from ideal gas behaviour:

Deviation from Ideal Behaviour

Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure. Experiments show that at low pressure and moderately high temperatures, gases obey the laws of Boyle, Charles and Avogadro approximately, but as the pressure is increased or the temperature is decreased, a marked departure from ideal behaviour is observed. Figure 1.8.1 shows, for example, the type of deviation that occurs in Boyle's law for H_2 at room temperature.

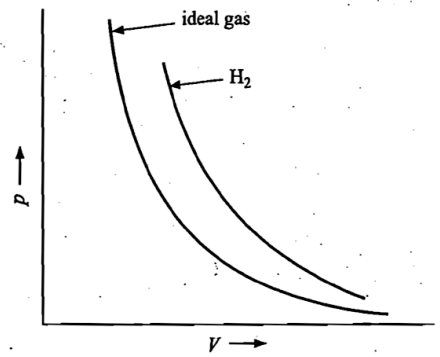

Fig. 1.8.1 Plot of p versus V of hydrogen, as compared to that of an ideal gas

The curve for the real gas has a tendency to coincide with that of an ideal gas at low pressures when the volume is large. At higher pressures, however, deviations are observed.

Compression Factor

The deviations can be displayed more clearly, by plotting the ratio of the observed molar volume V_m to the ideal molar volume $V_{m,ideal}$ (= RT/p) as a function of pressure at constant temperature. This ratio is called the compression factor Z and can be expressed as

$$Z = \frac{V_m}{V_{m,ideal}} = \frac{p}{RT}V_m \qquad (1.8.1)$$

Plots of Compression Factor versus Pressure

For an ideal gas, $Z = 1$ and is independent of pressure and temperature. For a real gas, $Z = f(T, p)$, a function of both temperature and pressure. Figure 1.8.2 shows a graph between Z and p for some gases at 273.15 K, the pressure range in this graph is very large. It can be noted that:

(1) Z is always greater than 1 for H_2.

(2) For N_2, $Z < 1$ in the lower pressure range and is greater than 1 at higher pressures. It decreases with increase of pressure in the lower pressure region, passes through a minimum at some pressure and then increases continuously with pressure in the higher pressure region.

(3) For CO_2, there is a large dip in the beginning. In fact, for gases which are easily liquefied, Z dips sharply below the ideal line in the low pressure region.

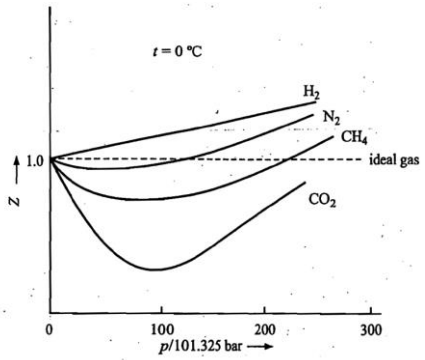

Fig. 1.8.2 Plots of Z versus p of a few gases

Figure 1.8.2 gives an impression that the nature of deviations depend upon the nature of the gas. In fact, it is not so. The determining factor is the temperature relative to the critical temperature (*see* p. 36) of the particular gas; near the critical temperature, the pV curves are like those for CO_2, but when far away, the curves are like those for H_2 (Fig. 1.8.3).

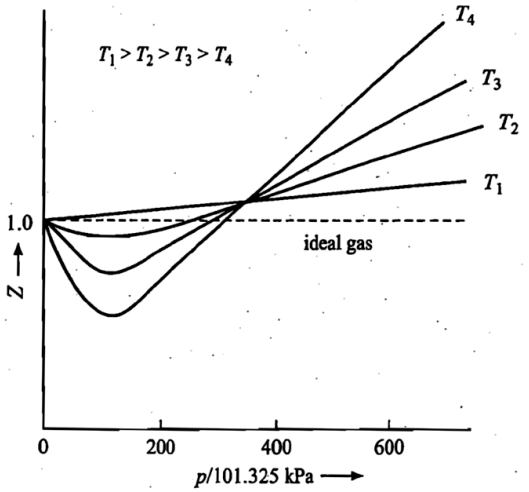

Fig. 1.8.3 Plots of Z versus p of a single gas at various temperatures

Provided the pressure is of the order of 1 bar or less, and the temperature is not too near the point of liquefaction, the observed deviations from the ideal gas laws are not more than a few per cent. Under these conditions, therefore, the equation $pV = nRT$ and related expressions may be used.

1.9 VAN DER WAALS EQUATION OF STATE FOR A REAL GAS

Causes of Deviations from Ideal Behaviour

The ideal gas laws can be derived from the kinetic theory of gases which is based on the following two important assumptions:

(i) The volume occupied by the molecules is negligible in comparison to the total volume of the gas.

(ii) The molecules exert no forces of attraction upon one another.

It is because neither of these assumptions can be regarded as applicable to real gases that the latter show departure from the ideal behaviour.

Derivation of Van Der Waals Equation

Van der Waals was the first to introduce systematically the correction terms due to the above two invalid assumptions in the ideal gas equation $p_i V_i = nRT$. His corrections are given below.

Correction for Volume

V_i in the ideal gas equation represents an ideal volume where the molecules can move freely. In real gases, a part of the total volume is, however, occupied by the molecules of the gas. Hence, the free volume V_i is the total volume V minus the volume occupied by the molecules. If b represents the *effective volume* occupied by the molecules of 1 mole of a gas, then for the amount n of the gas V_i is given by

$$V_i = V - nb \qquad (1.9.1)$$

where b is called the *excluded volume* or *co-volume*. The numerical value of b is four times the actual volume occupied by the gas molecules. This can be shown as follows.

Expression of Excluded Volume

If we consider only bimolecular collisions, then the volume occupied by the sphere of radius $2r$ represents the excluded volume per pair of molecules as shown in Fig. 1.9.1.

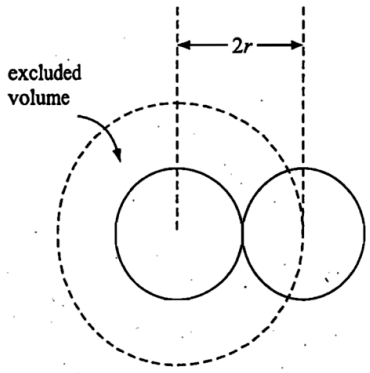

Fig. 1.9.1 Excluded volume per pair of molecules

Thus, excluded volume per pair of molecules

$$= \frac{4}{3}\pi(2r)^3 = 8\left(\frac{4}{3}\pi r^3\right)$$

Excluded volume per molecule

$$= \frac{1}{2}\left[8\left(\frac{4}{3}\pi r^3\right)\right] = 4\left(\frac{4}{3}\pi r^3\right) = 4\,(\text{volume occupied by a molecule})$$

Since b represents excluded volume per mole of the gas, it is obvious that

$$b = N_A\left[4\left(\frac{4}{3}\pi r^3\right)\right] \tag{1.9.2}$$

Correction for Forces of Attraction

Consider a molecule A in the bulk of a vessel as shown in Fig. 1.9.2. This molecule is surrounded by other molecules in a symmetrical manner, with the result that this molecule on the whole experiences no net force of attraction.

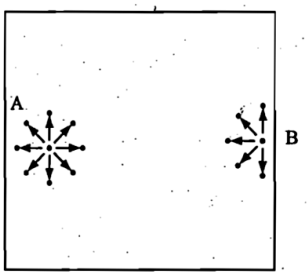

Fig. 1.9.2 Arrangement of molecules within and near the surface of a vessel

Now, consider a molecule B near the side of the vessel, which is about to strike one of its sides, thus contributing towards the total pressure of the gas. There are molecules only on one side of the vessel, i.e. towards its centre, with the result that this molecule experiences a net force of attraction towards the centre of the vessel. This results in decreasing the velocity of the molecule, and hence its momentum. Thus, the molecule does not contribute as much force as it would have, had there been no forces of attraction. Thus, the pressure of a real gas would be smaller than the corresponding pressure of an ideal gas, i.e.

$$p_i = p + \text{correction term} \tag{1.9.3}$$

This correction term depends upon two factors:

(i) *The number of molecules per unit volume of the vessel* Larger the number, larger the net force of attraction with which the molecule B is dragged behind. This results in a greater decrease in the velocity of the molecule B and hence a greater decrease in the rate of change of momentum. Consequently, the correction term also has a large value. If n is the amount of the gas present in the volume V of the container, the number of molecules per unit volume of the container is given as

$$N' = \frac{nN_A}{V} \quad \text{or} \quad N' \propto \frac{n}{V}$$

Thus, the correction term is given as:

$$\text{Correction term} \propto \frac{n}{V} \tag{1.9.4a}$$

(ii) *The number of molecules striking the side of the vessel per unit time* Larger this number, larger the decrease in the rate of change of momentum. Consequently, the correction term also has a larger value. Now, the number of molecules striking the side of vessel in a unit time also depends upon the number of molecules present in unit volume of the container, and hence in the present case:

$$\text{Correction term} \propto \frac{n}{V} \tag{1.9.4b}$$

Taking both these factors together, we have

$$\text{Correction term} \propto \left(\frac{n}{V}\right)\left(\frac{n}{V}\right)$$

or $$\text{Correction term} = a\frac{n^2}{V^2} \tag{1.9.5}$$

where a is the proportionality constant and is a measure of the forces of attraction between the molecules. Thus

$$p_i = p + a\frac{n^2}{V^2} \tag{1.9.6}$$

The unit of the term an^2/V^2 is the same as that of the pressure. Thus, the SI unit of a is Pa m^6 mol^{-2}. It may be conveniently expressed in kPa dm^6 mol^{-2}.

Expression of Van Der Waals Equation of State

When the expressions as given by Eqs (1.9.1) and (1.9.6) are substituted in the ideal gas equation $p_iV_i = nRT$, we get

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT \tag{1.9.7}$$

This equation is applicable to real gases and is known as the *van der Waals equation*.

Applicability of the Van Der Waals Equation

Since the van der Waals equation is applicable to real gases, it is worth considering how far this equation can explain the experimental behaviour of real gases, as represented by Fig. 1.8.2. The van der Waals equation for 1 mole of a gas is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT \tag{1.9.8}$$

At low pressure When pressure is low, the volume is sufficiently large and b can be ignored in comparison to V_m in Eq. (1.9.8). Thus, we have

$$\left(p + \frac{a}{V_m^2}\right)V_m = RT \quad \text{or} \quad pV_m + \frac{a}{V_m} = RT$$

or $$Z = 1 - \frac{a}{V_m RT} \tag{1.9.9}$$

From the above equation it is clear that in the low pressure region, Z is less than 1. On increasing the pressure in this region, the value of the term

$(a/V_m RT)$ increases as V is inversely proportional to p. Consequently, Z decreases with increase of p.

At high pressure When p is large, V_m will be small and one cannot ignore b in comparison to V_m. However, the term a/V_m^2 may be considered negligible in comparison to p in Eq. (1.9.8). Thus,

$$p(V_m - b) = RT$$

or
$$Z = 1 + \frac{pb}{RT} \tag{1.9.10}$$

Here Z is greater than 1 and it increases linearly with pressure. This explains the nature of the graph in the high pressure region.

At high temperature and low pressure If temperature is high, V_m will also be sufficiently large and thus the term a/V_m^2 will be negligibly small. At this stage, b may also be negligible in comparison to V_m. Under these conditions, Eq. (1.9.8) reduces to an ideal gas equation of state:

$$pV_m = RT$$

Hydrogen and helium The value of a is extremely small for these gases as they are difficult to liquefy. Thus, we have the equation of state as $p(V_m - b) = RT$, obtained from the van der Waals equation by ignoring the term a/V_m^2. Hence, Z is always greater than 1 and it increases with increase of p.

The van der Waals equation is a distinct improvement over the ideal gas law. It gives qualitative reasons for the deviations from ideal behaviour. However, the generality of the equation is lost as it contains two constants, the values of which depend upon the nature of the gas.

1.10 OTHER EQUATIONS OF STATE FOR REAL GASES

Berthelot's Equation The van der Waals equation is one of the many equations of state suggested in order to account for the behaviour of real gases. There are two other simple equations of state which involve just two arbitrary constants. The first of these, due to Berthelot, is

$$\left(p + \frac{n^2 a}{TV^2}\right)(V - nb) = nRT \tag{1.10.1}$$

where a and b are constants called the *Berthelot's constants* (different from van der Waals constants) and are characteristics of the gas.

Dieterici's Equation The second equation, due to Dieterici, is

$$\{p \exp(na/VRT)\}\ (V - nb) = nRT \tag{1.10.2}$$

Virial Equation All these three equations of state can be expressed approximately in one common form, called the *virial equation of state*, which has the following form for 1 mole of a gas

$$Z = \frac{pV_m}{RT} = 1 + B\frac{1}{V_m} + C\frac{1}{V_m^2} + D\frac{1}{V_m^3} + \cdots \tag{1.10.3}$$

where B, C, ... are temperature dependent constants known as second, third, etc., virial coefficients. These coefficients must be evaluated experimentally at each different temperature.

The second virial coefficient B may be obtained from the experimental data. Rearranging the virial equation, we get

$$V_m\left(\frac{pV_m}{RT} - 1\right) = B + \frac{C}{V_m} + \cdots$$

Thus, extrapolating the graph between $V_m\{(pV_m/RT) - 1\}$ versus $1/V_m$ to $1/V_m = 0$ gives the value of B, i.e.

$$B = \lim_{V_m \to \infty} V_m\left[\frac{pV_m}{RT} - 1\right] \tag{1.10.4}$$

The third virial coefficient C would be the slope of this plot if there were no higher terms in Eq. (1.10.3). These further terms cause the plot to be curved so that C must be evaluated from the initial slope.

1.11 REDUCTION OF VAN DER WAALS EQUATION TO VIRIAL EQUATION

Virial Equation in Volume The van der Waals equation of state for 1 mole of a gas is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad \text{or} \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Multiplying both sides by V_m/RT, we get

$$\frac{pV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{V_m RT} \quad \text{or} \quad Z = \left(1 - \frac{b}{V_m}\right)^{-1} - \frac{a}{V_m RT}$$

In the low pressure region, V_m is large and $b/V_m << 1$. Thus, the expression $(1 - b/V_m)^{-1}$ can be expanded into a power series in b/V_m:

$$\left(1 - \frac{b}{V_m}\right)^{-1} = 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \left(\frac{b}{V_m}\right)^3 + \cdots$$

Substituting this in the expression for Z, we get

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots \quad (1.11.1)$$

Thus for the second virial coefficient, we have

$$B = b - \frac{a}{RT}$$

Third virial coefficient $C = b^2$, and so on.

Virial Equation in Pressure

An alternative form of the virial equation of state involves the expression of Z in terms of a power series in p, i.e.

$$Z = 1 + A_1 p + A_2 p^2 + \cdots \quad (1.11.2)$$

The expressions for A_1 and A_2 can be derived as follows:

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \left(\frac{b}{V_m}\right)^2 + \cdots$$

Since $Z = pV_m/RT$, therefore, $1/V_m = p/RTZ$. Hence

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + b^2\left(\frac{p}{RTZ}\right)^2 + \cdots \quad (1.11.3)$$

Comparing Eqs (1.11.2) and (1.11.3), we get

$$1 + A_1 p + A_2 p^2 + \cdots = 1 + \left(b - \frac{a}{RT}\right)\frac{p}{RTZ} + \left(\frac{b}{RTZ}\right)^2 p^2 + \cdots$$

or $$A_1 p + A_2 p^2 + \cdots = \frac{1}{RTZ}\left(b - \frac{a}{RT}\right)p + \left(\frac{b}{RT}\right)^2 \frac{p^2}{Z^2} + \cdots$$

Dividing by p, we get

$$A_1 + A_2 p + \cdots = \frac{1}{RTZ}\left(b - \frac{a}{RT}\right) + \left(\frac{b}{RT}\right)^2 \frac{p}{Z^2} + \cdots$$

In the limiting state of zero pressure, $Z = 1$ and this equation becomes

$$A_1 = \frac{1}{RT}\left(b - \frac{a}{RT}\right) \quad (1.11.4)$$

which is the required expression for A_1. Thus

$$A_1 + A_2 p + \cdots = A_1\left(\frac{1}{Z}\right) + \left(\frac{b}{RT}\right)^2 \frac{p}{Z^2} + \cdots$$

We repeat the procedure by subtracting A_1 from both sides of this equation, dividing by p and taking the limiting value at zero pressure. Note that $(Z - 1)/p = A_1$ at zero pressure. Then

$$A_2 = \left(\frac{b}{RT}\right)^2 - A_1^2 = \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right) \qquad (1.11.5)$$

Thus, the expression for Z correct up to the third coefficient is

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)p + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)p^2 + \cdots \qquad (1.11.6)$$

The correct coefficient for p could have been obtained by simply replacing $1/V_m$ in Eq. (1.11.1) by the ideal value; however, this would yield incorrect values of the coefficients of higher powers of pressures.

The slope of Z versus p curve is obtained by differentiating the above virial equation in Z with respect to pressure, keeping the temperature constant, i.e.

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right) + \frac{2a}{(RT)^3}\left(2b - \frac{a}{RT}\right)p + \cdots \qquad (1.11.7)$$

At $p = 0$, all higher terms drop out and this derivative simply reduces to

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right); \qquad (p = 0) \qquad (1.11.8)$$

Comment on the Plots of Compression Factor versus Pressure

The derivative in Eq. (1.11.8) is the initial slope of the plot of Z versus p (Fig. 1.8.2). Now if $b > a/RT$, the initial slope is positive and the size effect (i.e. b factor) will dominate the behaviour of the gas. However, if $b < a/RT$, the initial slope is negative and the effect of the attractive forces (i.e. a factor) will dominate. Thus, the van der Waals equation, which includes both the effects of size and of intermolecular forces, can interpret both the positive and negative slopes of the Z versus p plots. In interpreting Fig. 1.8.2, we can say that at 0 °C, the effect of attractive forces dominate the behaviour of methane and carbon dioxide, while the molecular size effect dominates the behaviour of hydrogen.

While interpreting Fig. 1.8.3 (graph of Z versus p of the same gas at different temperatures), we can say that if the temperature is low enough, the term a/RT will be larger than b and so the initial slope of Z versus p will be negative. As the temperature rises, a/RT becomes smaller. At a sufficiently high temperature it becomes less than b, and the initial slope of Z versus p curve turns positive.

Boyle Temperature

At some intermediate temperature T_B, called *Boyle temperature*, the initial slope is zero. This is obtained from Eq. (1.11.8) by putting $b - a/RT_B = 0$, which yields

$$T_B = \frac{a}{Rb} \tag{1.11.9}$$

At the Boyle temperature, the Z versus p line of an ideal gas is tangent to that of a real gas when p approaches zero. The latter rises above the ideal gas line only very slowly. In Eq. (1.11.6) the second term is zero at T_B and the remaining terms are small until the pressure becomes very high. Thus, at the Boyle temperature, the real gas behaves ideally over a wide range of pressure, because the effects of the size of molecules and intermolecular forces roughly compensate each other.

The Boyle temperature of some gases are given below:

$T_B(H_2) = -156$ °C $T_B(N_2) = 59$ °C

$T_B(He) = -249$ °C $T_B(CH_4) = 224$ °C

$T_B(NH_3) = 587$ °C

Thus we can see that for H_2 and He, the temperature of 0 °C is above their respective Boyle temperatures and so they have Z values greater than unity. The other gases at 0 °C are below their respective Boyle temperatures and so they have Z values less than unity in the low pressure range.

1.13. CONTINUITY OF STATE

In Fig. 1.12.1 end-points of the horizontal lines have been connected with a dotted line. This portion, known as the *surface of discontinuity*, separates the liquid state on one side and the gas on the other. Within this curve the liquid and the gas coexist. Because of this coexistence curve, it is possible to distinguish between the two states of matter, namely, gas and liquid. However, in practice, this is not always true because it is possible to convert matter from one state into another without any sharp discontinuity. This can be done as shown in Fig. 1.13.1.

(i) Increase the temperature of the gas keeping volume constant. The pressure rises along AL.

(ii) Having reached L, the pressure is kept constant and the gas is cooled; this decreases the volume along the line LD.

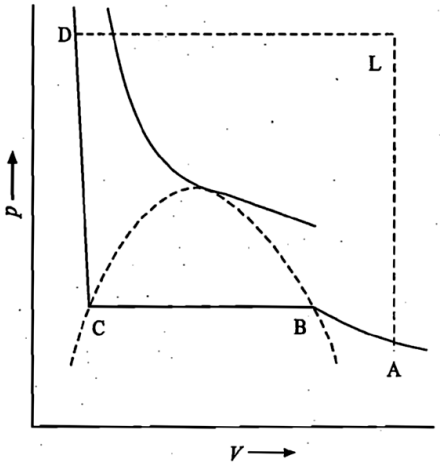

Fig. 1.13.1 Schematic representation of the continuity of state

Thus, we have passed from A to D without the gradual change as it occurs along the line BC, i.e. condensation in the usual sense of the term did not occur. Point D could be said to represent a highly compressed gaseous state of the substance. Whether we refer to the state in the region of point D as liquid state or as highly compressed gaseous state depends purely upon which of the two viewpoints happens to be convenient at the moment. Thus, in the absence of the surface of discontinuity, there is no way of distinguishing between liquid and gas.

1.14 ISOTHERMS OF VAN DER WAALS EQUATION

For one mole of a gas the van der Waals equation

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

can be written as

$$V_m^3 - \left(b + \frac{RT}{p}\right)V_m^2 + \frac{a}{p}V_m - \frac{ab}{p} = 0 \qquad (1.14.1)$$

This equation has three roots in V_m for given values of a, b, p and T. It is found that either all the three roots are real or one is real and the other two are imaginary (Fig. 1.14.1).

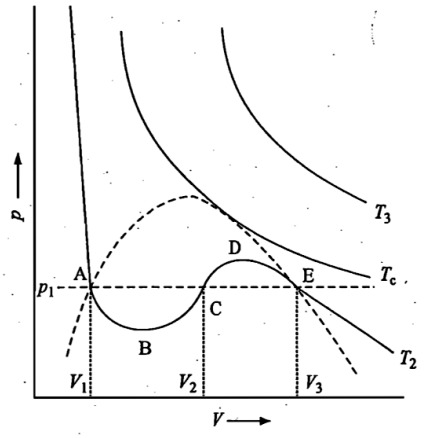

Fig. 1.14.1 Van der Waals isotherms

Main Characteristics of Van Der Waals Isotherms

The main characteristics of Fig. 1.14.1 are given in the following:

- At higher temperatures such as T_3 and in the higher volume region, the isotherms look much like the isotherms for a real gas.
- At a temperature lower than T_c the isotherm exhibits a maximum and a minimum. For certain values of pressure, the equation gives three roots of volume, e.g., V_1, V_2 and V_3 at pressure p_1. The sections AB and ED of the van der Waals curve at T_2 can be realized experimentally. ED represents supersaturated (or supercooled) vapour and AB represents superheated liquid. Both these states are metastable. These are realized only when the volume is changed very slowly. These states are unstable in the sense that slight disturbances are sufficient to cause the system to revert spontaneously into the stable state with the two phases present in equilibrium.
- The section BCD of the van der Waals isotherm cannot be realized experimentally. In this region the slope of the p–V curve is positive. Increasing (decreasing) the volume of such a system would increase (decrease) the pressure. The line BCD also represents the system in the metastable state.
- At the end points of the horizontal line AE, the conversion of gas into liquid or vice versa has just commenced, the system will have the same value of Gibbs function at the points A and E. Thus,

$$\Delta G_{A \to E} = 0$$

Since $dG = V\,dp$ at constant temperature, this leads to the fact that

$$\Delta G_{A \to E} = \int_A^E V\,dp = 0$$

Consequently, the line AE which divides the curly curve of van der Waals isotherm within the discontinuity region into two portions is so placed that the area ABCA and CDEC have the same value but of opposite sign so that their sum is equal to zero.

Isotherm at Critical Temperature

On increasing the temperature, the three roots such as A, C and E, become closer to one another and ultimately at critical temperature, they become identical. Thus, the cubic equation in V_m can be written as

$$(V_m - V')(V_m - V'')(V_m - V''') = 0$$

which at the critical point (where $V' = V'' = V''' = V_c$) becomes

$$(V_m - V_c)^3 = 0$$

Expressions of Critical Constants in Terms of Van Der Waals Constants

Expanding the above expression, we obtain

$$V_m^3 - V_c^3 - 3V_cV_m^2 + 3V_c^2V_m = 0 \qquad (1.14.2)$$

Equation (1.14.1) with $p = p_c$ and $T = T_c$ and Eq. (1.14.2) must be completely identical and coefficients of the individual powers of V_m must be the same in both. Setting the corresponding coefficients equal, we obtain the following three equations:

$$3V_c = b + \frac{RT_c}{p_c}; \qquad 3V_c^2 = \frac{a}{p_c}; \qquad V_c^3 = \frac{ab}{p_c} \qquad (1.14.3)$$

Solving these equations for p_c, V_c and T_c in terms of a, b and R, we get

$$V_c = 3b; \qquad p_c = a/27b^2; \qquad T_c = 8a/27Rb \qquad (1.14.4)$$

Thus, if the values of p_c, V_c and T_c for a given gas are known, it is possible to calculate the values of a, b and R from the equations

$$b = \frac{V_c}{3}, \qquad a = 3p_cV_c^2, \qquad R = \frac{8p_cV_c}{3T_c} \qquad (1.14.5)$$

Since experimentally it is difficult to determine V_c accurately, it would be better if a and b could be obtained from p_c and T_c only. Thus

$$b = \frac{1}{3}\left(\frac{3RT_c}{8p_c}\right) = \frac{RT_c}{8p_c}; \qquad a = 3p_cV_c^2 = 3p_c\left(\frac{3RT_c}{8p_c}\right)^2 = \frac{27(RT_c)^2}{64p_c}$$

(Note that for an ideal gas $a = 0$ since there exists no forces of attraction between its molecules. Thus, for such a gas, $T_c = 0$ K. Since the essential condition for a gas to liquefy is to cool it up to or below its critical temperature, it is obvious that an ideal gas cannot be liquefied as it is not possible to attain 0 K.)

Comment on the Value of Gas Constant at the Critical State

The value of pV/RT at critical state is

$$\frac{p_cV_c}{RT_c} = \frac{3}{8} = 0.375 \qquad (1.14.6)$$

If we compare this value with the experimental values (Table 1.14.1), it is found that the agreement is very poor. The reason behind this poor agreement is that the van der Waals equation is not accurate enough to predict the behaviour of a gas near its critical state.

Table 1.14.1 Order of Observed Values of p_cV_c/RT_c for Some Gases

Type of molecules	*Examples*	*Value of* p_cV_c/RT_c
Molecules with small symmetrical nature (nonpolar and slightly polarizable)	He, Ne, Ar, O_2, CH_4	Very close to 0.29
Molecules having polarity or polarizability	Cl_2, CS_2, CCl_4, C_2H_4	About 0.26 or 0.27
Molecules having hydrogen bonding	NH_3, H_2O, CH_3OH	0.22 to 0.24

Alternative way of Expressing Critical Constants in Terms of Van Der Waals Constants

Another way of expressing critical constants in terms of a, b and R is to use the condition of maximum slope at the critical state. The slope of p–V curve is negative before and after the critical point and has a maximum value of zero at the critical point (the point of inflection). The condition of slope being equal to zero is given by

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \tag{1.14.7}$$

and the condition that this slope has a maximum value is

$$\frac{\partial}{\partial V}\left\{\left(\frac{\partial p}{\partial V}\right)_T\right\}_T = 0 \tag{1.14.8}$$

From the van der Waals equation

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

we get $\left(\frac{\partial p}{\partial V_m}\right)_T = \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3}$ and $\left(\frac{\partial^2 p}{\partial V_m^2}\right)_T = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4}$

Hence at the critical point,

$$-\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0 \tag{1.14.9}$$

and

$$\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0 \tag{1.14.10}$$

Solving Eqs (1.14.9) and (1.14.10) for V_c and T_c, we get

$$V_c = 3b \quad \text{and} \quad T_c = \frac{8a}{27Rb} \tag{1.14.11}$$

Substituting the values of V_c and T_c in the van der Waals equation, we have

$$p_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} = \frac{R(8a/27Rb)}{(3b - b)} - \frac{a}{(3b)^2}$$

$$= \frac{4a}{27b^2} - \frac{a}{9b^2} = \frac{a}{27b^2} \qquad (1.14.12)$$

1.15 THE LAW OF CORRESPONDING STATES

Reduced Equation of State

Van der Waals equation can be written in a form which does not contain any constant characteristics of individual gases. Such an equation will, therefore, be applicable to all gases. In order to obtain this equation, we define reduced pressure, reduced temperature and reduced volume as follows:

$$p_r = \frac{p}{p_c}, \qquad T_r = \frac{T}{T_c} \quad \text{and} \quad V_r = \frac{V_m}{V_c} \qquad (1.15.1)$$

Thus $p = p_r p_c$, $T = T_r T_c$ and $V_m = V_r V_c$

Substituting these expressions in the van der Waals equation

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

we obtain $\left(p_r p_c + \frac{a}{V_r^2 V_c^2}\right)(V_r V_c - b) = RT_r T_c$

Replacing p_c, V_c and T_c in terms of a, b and R, we get

$$\left\{p_r \frac{a}{27b^2} + \frac{a}{V_r^2(3b)^2}\right\}\{V_r(3b) - b\} = RT_r\left(\frac{8a}{27Rb}\right)$$

i.e. $$(p_r + 3/V_r^2)(3V_r - 1) = 8T_r \qquad (1.15.2)$$

Equation (1.15.2), known as the *reduced equation of state*, does not contain any constant which is characteristic of a gas and is thus applicable to all gases. According to it, *if two gases have the same values of reduced pressure and reduced temperature, they will have the same reduced volume.* Thus, they correspond to each other. This statement is known as the law of corresponding states.

In actual practice, the above reduced equation of state is not directly used. One makes use of the graphs between compression factor Z and the reduced pressure at different reduced temperatures. The same graphs are applicable to all gases. This can be seen from the following consideration.

Since $Z = pV_m/RT$, writing this in reduced terms gives

$$Z = \frac{pV_m}{RT} = \frac{(p_r p_c)(V_r V_c)}{R(T_r T_c)} = \frac{p_c V_c}{T_c}\left(\frac{p_r V_r}{T_r}\right) = \frac{3}{8}\frac{p_r V_r}{T_r} \qquad (1.15.3)$$

According to the law of corresponding states, if two gases have the same reduced temperature and reduced pressure they will have the same reduced volume. Thus, the right hand side of Eq. (1.15.3) is independent of the nature of gas and hence the value of Z is same for all gases.

Comment

Any equation of state which involves only two constants in addition to R can be written in terms of reduced variables only.

1.7 SOME DERIVATIONS FROM THE KINETIC GAS EQUATION

Kinetic Gas Equation Involving Kelvin Temperature

The kinetic gas equation (1.6.9) can be used to derive the various gaseous laws and to define expressions for some useful quantities such as the root mean square speed and the average kinetic energy. Before deriving these, it is helpful to write this equation in the following form:

One of the postulates of the kinetic theory of gases is

$$\text{Average kinetic energy} \propto T$$

i.e. $$\frac{1}{2}m\overline{u^2} \propto T \quad \text{or} \quad \frac{1}{2}m\overline{u^2} = KT$$

where K is the proportionality constant. Introducing this in Eq. (1.6.9) we have

$$pV = \frac{1}{3}mN\overline{u^2} = \frac{2}{3}N\left(\frac{1}{2}m\overline{u^2}\right) = \frac{2}{3}NKT \qquad (1.7.1)$$

Now, we proceed to derive the various gaseous laws from Eq. (1.7.1).

Boyle's Law

The essential conditions for Boyle's law to be applicable are:

(i) Temperature (T) should remain constant.
(ii) Mass of the gas should remain constant. In other words, the total number of molecules (N) remains unchanged.

Under these conditions, Eq. (1.7.1) yields

$$pV = \text{constant} \qquad \text{or} \qquad p \propto \frac{1}{V}$$

which is the expression for Boyle's law.

Charles Law

In this case:

(i) Pressure (p) remains fixed.
(ii) Mass of the gas remains unchanged, i.e. N is constant.

With these conditions, Eq. (1.7.1) yields

$$V = \left(\frac{2}{3}\frac{NK}{p}\right)T \qquad \text{i.e.} \qquad V = (\text{constant})\,T \qquad \text{or} \qquad V \propto T$$

as required by Charles law.

Avogadro's Law

It states that *under similar conditions of pressure and temperature, equal volume of all gases contain equal number of molecules.* Considering two gases, we have

$$p_1V_1 = \frac{2}{3}N_1KT_1 \quad \text{and} \quad p_2V_2 = \frac{2}{3}N_2KT_2$$

Since $p_1 = p_2$ and $T_1 = T_2$, therefore

$$\frac{p_1V_1}{p_2V_2} = \frac{(2/3)N_1KT_1}{(2/3)N_2KT_2} \quad \Rightarrow \quad \frac{V_1}{V_2} = \frac{N_1}{N_2}$$

If volumes are identical, obviously $N_1 = N_2$.

Graham's Law of Effusion

The rate of diffusion or effusion can be assumed to be directly proportional to the root mean square speed (or any other average speed). Thus

$$\frac{r_1}{r_2} = \sqrt{\frac{\overline{u_1^2}}{\overline{u_2^2}}}$$

From Eq. (1.6.9), we have

$$\overline{u^2} = \frac{3pV}{mN}$$

For 1 mol of an ideal gas

$$pV = RT$$

and $N = N_A$ (N_A is Avogadro constant)

With these, the above equation becomes

$$\overline{u^2} = \frac{3RT}{mN_A} = \frac{3RT}{M} \qquad (1.7.2)$$

where M is the molar mass of the gas.

Thus, $$\frac{r_1}{r_2} = \sqrt{\frac{\overline{u_1^2}}{\overline{u_2^2}}} = \sqrt{\frac{3RT/M_1}{3RT/M_2}} = \sqrt{\frac{M_2}{M_1}}$$

which is Graham's law of effusion.