

the slower one and so there is more of the lighter molecule (enrichment) outside the porous cylinder (Fig. 13.5). The method is not very efficient and has to be repeated several times for sufficient enrichment.]

When gases diffuse, their rate of diffusion is inversely proportional to square root of the masses (see Exercise 13.12). Can you guess the explanation from the above answer?

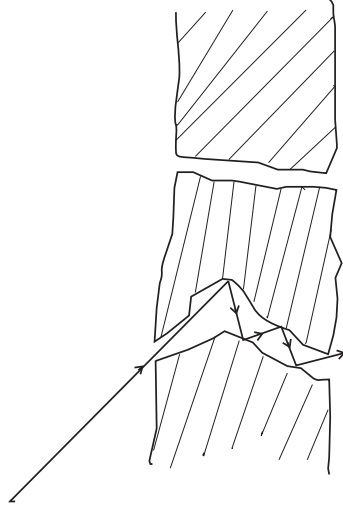


Fig. 13.5 Molecules going through a porous wall.

Example 13.7 (a) When a molecule (or an elastic ball) hits a (massive) wall, it rebounds with the same speed. When a ball hits a massive bat held firmly, the same thing happens. However, when the bat is moving towards the ball, the ball rebounds with a different speed. Does the ball move faster or slower? (Ch.6 will refresh your memory on elastic collisions.)

(b) When gas in a cylinder is compressed by pushing in a piston, its temperature rises. Guess at an explanation of this in terms of kinetic theory using (a) above.

(c) What happens when a compressed gas pushes a piston out and expands. What would you observe?

(d) Sachin Tendulkar used a heavy cricket bat while playing. Did it help him in anyway?

Answer (a) Let the speed of the ball be u relative to the wicket behind the bat. If the bat is moving towards the ball with a speed V relative to the wicket, then the relative speed of the ball to bat

is $V + u$ towards the bat. When the ball rebounds (after hitting the massive bat) its speed, relative to bat, is $V + u$ moving away from the bat. So relative to the wicket the speed of the rebounding ball is $V + (V + u) = 2V + u$, moving away from the wicket. So the ball speeds up after the collision with the bat. The rebound speed will be less than u if the bat is not massive. For a molecule this would imply an increase in temperature.

You should be able to answer (b) (c) and (d) based on the answer to (a).

(Hint: Note the correspondence, piston \rightarrow bat, cylinder \rightarrow wicket, molecule \rightarrow ball.)

13.5 LAW OF EQUIPARTITION OF ENERGY

The kinetic energy of a single molecule is

$$\epsilon_i = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \quad (13.22)$$

For a gas in thermal equilibrium at temperature T the average value of energy denoted by $\langle \epsilon_i \rangle$ is

$$\langle \epsilon_i \rangle = \left\langle \frac{1}{2}mv_x^2 \right\rangle + \left\langle \frac{1}{2}mv_y^2 \right\rangle + \left\langle \frac{1}{2}mv_z^2 \right\rangle = \frac{3}{2}k_B T \quad (13.23)$$

Since there is no preferred direction, Eq. (13.23) implies

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle = \frac{1}{2}k_B T, \quad \left\langle \frac{1}{2}mv_y^2 \right\rangle = \frac{1}{2}k_B T, \\ \left\langle \frac{1}{2}mv_z^2 \right\rangle = \frac{1}{2}k_B T \quad (13.24)$$

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. Motion of a body as a whole from one point to another is called translation. Thus, a molecule free to move in space has three translational degrees of freedom. Each translational degree of freedom contributes a term that contains square of some variable of motion, e.g., $\frac{1}{2}mv_x^2$ and similar terms in v_y and v_z . In, Eq. (13.24) we see that in thermal equilibrium, the average of each such term is $\frac{1}{2}k_B T$.

Molecules of a monatomic gas like argon have only translational degrees of freedom. But what about a diatomic gas such as O_2 or N_2 ? A molecule of O_2 has three translational degrees of freedom. But in addition it can also rotate about its centre of mass. Figure 13.6 shows the two independent axes of rotation 1 and 2, normal to the axis joining the two oxygen atoms about which the molecule can rotate*. The molecule thus has two rotational degrees of freedom, each of which contributes a term to the total energy consisting of translational energy ϵ_t and rotational energy ϵ_r .

$$\epsilon_t + \epsilon_r = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 \quad (13.25)$$

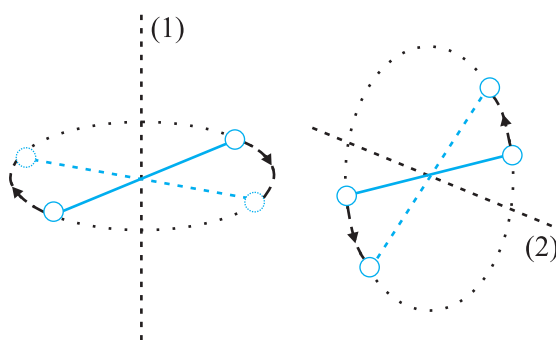


Fig. 13.6 The two independent axes of rotation of a diatomic molecule

where ω_1 and ω_2 are the angular speeds about the axes 1 and 2 and I_1, I_2 are the corresponding moments of inertia. Note that each rotational degree of freedom contributes a term to the energy that contains square of a rotational variable of motion.

We have assumed above that the O_2 molecule is a 'rigid rotator', i.e., the molecule does not vibrate. This assumption, though found to be true (at moderate temperatures) for O_2 , is not always valid. Molecules, like CO, even at moderate temperatures have a mode of vibration, i.e., its atoms oscillate along the interatomic axis like a one-dimensional oscillator, and contribute a vibrational energy term ϵ_v to the total energy:

$$\epsilon_v = \frac{1}{2}m\left(\frac{dy}{dt}\right)^2 + \frac{1}{2}ky^2$$

* Rotation along the line joining the atoms has very small moment of inertia and does not come into play for quantum mechanical reasons. See end of section 13.6.

$$\epsilon = \epsilon_t + \epsilon_r + \epsilon_v \quad (13.26)$$

where k is the force constant of the oscillator and y the vibrational co-ordinate.

Once again the vibrational energy terms in Eq. (13.26) contain squared terms of vibrational variables of motion y and dy/dt .

At this point, notice an important feature in Eq.(13.26). While each translational and rotational degree of freedom has contributed only one 'squared term' in Eq.(13.26), one vibrational mode contributes two 'squared terms': kinetic and potential energies.

Each quadratic term occurring in the expression for energy is a mode of absorption of energy by the molecule. We have seen that in thermal equilibrium at absolute temperature T , for each translational mode of motion, the average energy is $\frac{1}{2}k_B T$. The most elegant principle of classical statistical mechanics (first proved by Maxwell) states that this is so for each mode of energy: translational, rotational and vibrational. That is, in equilibrium, the total energy is equally distributed in all possible energy modes, with each mode having an 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.

The proof of the law of equipartition of energy is beyond the scope of this book. Here, we shall apply the law to predict the specific heats of gases theoretically. Later, we shall also discuss briefly, the application to specific heat of solids.

13.6 SPECIFIC HEAT CAPACITY

13.6.1 Monatomic Gases

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

$$U = \frac{3}{2} k_B T \times N_A = \frac{3}{2} RT \quad (13.27)$$

The molar specific heat at constant volume, C_v , is

$$C_v \text{ (monatomic gas)} = \frac{dU}{dT} = \frac{3}{2} RT \quad (13.28)$$

For an ideal gas,

$$C_p - C_v = R \quad (13.29)$$

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

$$C_p = \frac{5}{2} R \quad (13.30)$$

$$\text{The ratio of specific heats } \gamma = \frac{C_p}{C_v} = \frac{5}{3} \quad (13.31)$$

13.6.2 Diatomic Gases

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

$$U = \frac{5}{2} k_B T \times N_A = \frac{5}{2} RT \quad (13.32)$$

The molar specific heats are then given by

$$C_v \text{ (rigid diatomic)} = \frac{5}{2} R, C_p = \frac{7}{2} R \quad (13.33)$$

$$\gamma \text{ (rigid diatomic)} = \frac{7}{5} \quad (13.34)$$

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

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

$$C_v = \frac{7}{2} R, C_p = \frac{9}{2} R, \gamma = \frac{9}{7} R \quad (13.35)$$

13.6.3 Polyatomic Gases

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

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

$$\text{i.e., } C_v = (3 + f) R, C_p = (4 + f) R,$$

$$\gamma = \frac{(4 + f)}{(3 + f)} \quad (13.36)$$

Note that $C_p - C_v = R$ is true for any ideal gas, whether mono, di or polyatomic.

Table 13.1 summarises the theoretical predictions for specific heats of gases ignoring any vibrational modes of motion. The values are in good agreement with experimental values of specific heats of several gases given in Table 13.2. Of course, there are discrepancies between predicted and actual values of specific heats of several other gases (not shown in the table), such as Cl_2 , C_2H_6 and many other polyatomic gases. Usually, the experimental values for specific heats of these gases are greater than the predicted values as given in Table 13.1 suggesting that the agreement can be improved by including vibrational modes of motion in the calculation. The law of equipartition of energy is, thus, well

Table 13.1 Predicted values of specific heat capacities of gases (ignoring vibrational modes)

Nature of Gas	C_v (J mol ⁻¹ K ⁻¹)	C_p (J mol ⁻¹ K ⁻¹)	$C_p - C_v$ (J mol ⁻¹ K ⁻¹)	γ
Monatomic	12.5	20.8	8.31	1.67
Diatomic	20.8	29.1	8.31	1.40
Triatomic	24.93	33.24	8.31	1.33

Table 13.2 Measured values of specific heat capacities of some gases

Nature of gas	Gas	C_v (J mol ⁻¹ K ⁻¹)	C_p (J mol ⁻¹ K ⁻¹)	$C_p - C_v$ (J mol ⁻¹ K ⁻¹)	γ
Monatomic	He	12.5	20.8	8.30	1.66
Monatomic	Ne	12.7	20.8	8.12	1.64
Monatomic	Ar	12.5	20.8	8.30	1.67
Diatomic	H ₂	20.4	28.8	8.45	1.41
Diatomic	O ₂	21.0	29.3	8.32	1.40
Diatomic	N ₂	20.8	29.1	8.32	1.40
Triatomic	H ₂ O	27.0	35.4	8.35	1.31
Polyatomic	CH ₄	27.1	35.4	8.36	1.31

verified experimentally at ordinary temperatures.

► **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 ? ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$).

Answer Using the gas law $PV = \mu RT$, you can easily show that 1 mol of any (ideal) gas at standard temperature (273 K) and pressure (1 atm = 1.01×10^5 Pa) occupies a volume of 22.4 litres. This universal volume is called molar volume. Thus the cylinder in this example contains 2 mol of helium. Further, since helium is monatomic, its predicted (and observed) molar specific heat at constant volume, $C_v = (3/2) R$, and molar specific heat at constant pressure, $C_p = (3/2) R + R = (5/2) R$. Since the volume of the cylinder is fixed, the heat required is determined by C_v . Therefore,
Heat required = no. of moles \times molar specific heat \times rise in temperature
= $2 \times 1.5 R \times 15.0 = 45 R$
= $45 \times 8.31 = 374 \text{ J}$.

13.6.4 Specific Heat Capacity of Solids

We can use the law of equipartition of energy to determine specific heats of solids. Consider a solid of N atoms, each vibrating about its mean position. An oscillation in one dimension has average energy of $2 \times \frac{1}{2} k_B T = k_B T$. In three dimensions, the average energy is $3 k_B T$. For a mole of solid, $N = N_A$, and the total energy is

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

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

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 3R \quad (13.37)$$

Table 13.3 Specific Heat Capacity of some solids at room temperature and atmospheric pressure

Substance	Specific heat ($\text{J kg}^{-1} \text{K}^{-1}$)	Molar specific heat ($\text{J mol}^{-1} \text{K}^{-1}$)
Aluminium	900.0	24.4
Carbon	506.5	6.1
Copper	386.4	24.5
Lead	127.7	26.5
Silver	236.1	25.5
Tungsten	134.4	24.9

As Table 13.3 shows the prediction generally agrees with experimental values at ordinary temperature (Carbon is an exception).

13.6.5 Specific Heat Capacity of Water

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

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

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

This is the value observed and the agreement is very good. In the calorie, gram, degree units, water is defined to have unit specific heat. As 1 calorie = 4.179 joules and one mole of water is 18 grams, the heat capacity per mole is $\sim 75 \text{ J mol}^{-1} \text{ K}^{-1} \sim 9R$. However with more complex molecules like alcohol or acetone the arguments, based on degrees of freedom, become more complicated.

Lastly, we should note an important aspect of the predictions of specific heats, based on the classical law of equipartition of energy. The predicted specific heats are independent of temperature. As we go to low temperatures, however, there is a marked departure from this prediction. Specific heats of all substances approach zero as $T \rightarrow 0$. This is related to the fact that degrees of freedom get frozen and ineffective at low temperatures. According to classical physics, degrees of freedom must remain unchanged at all times. The behaviour of specific heats at low temperatures shows the inadequacy of classical physics and can be explained only by invoking quantum considerations, as was first shown by Einstein. Quantum mechanics requires a minimum, non-zero amount of energy before a degree of freedom comes into play. This is also the reason why vibrational degrees of freedom come into play only in some cases.

13.7 MEAN FREE PATH

Molecules in a gas have rather large speeds of the order of the speed of sound. Yet a gas leaking from a cylinder in a kitchen takes considerable time to diffuse to the other corners of the room. The top of a cloud of smoke holds together for hours. This happens because molecules in a gas have a finite though small size, so they are bound to undergo collisions. As a result, they cannot

Seeing is Believing

Can one see atoms rushing about. Almost but not quite. One can see pollen grains of a flower being pushed around by molecules of water. The size of the grain is $\sim 10^{-5}$ m. In 1827, a Scottish botanist Robert Brown, while examining, under a microscope, pollen grains of a flower suspended in water noticed that they continuously moved about in a zigzag, random fashion.

Kinetic theory provides a simple explanation of the phenomenon. Any object suspended in water is continuously bombarded from all sides by the water molecules. Since the motion of molecules is random, the number of molecules hitting the object in any direction is about the same as the number hitting in the opposite direction. The small difference between these molecular hits is negligible compared to the total number of hits for an object of ordinary size, and we do not notice any movement of the object.

When the object is sufficiently small but still visible under a microscope, the difference in molecular hits from different directions is not altogether negligible, i.e. the impulses and the torques given to the suspended object through continuous bombardment by the molecules of the medium (water or some other fluid) do not exactly sum to zero. There is a net impulse and torque in this or that direction. The suspended object thus, moves about in a zigzag manner and tumbles about randomly. This motion called now 'Brownian motion' is a visible proof of molecular activity. In the last 50 years or so molecules have been seen by scanning tunneling and other special microscopes.

In 1987 Ahmed Zewail, an Egyptian scientist working in USA was able to observe not only the molecules but also their detailed interactions. He did this by illuminating them with flashes of laser light for very short durations, of the order of tens of femtoseconds and photographing them. (1 femto-second = 10^{-15} s). One could study even the formation and breaking of chemical bonds. That is really seeing !

move straight unhindered; their paths keep getting incessantly deflected.

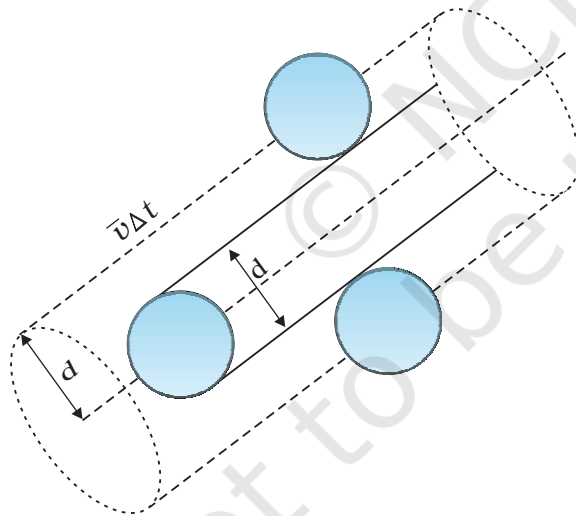


Fig. 13.7 The volume swept by a molecule in time Δt in which any molecule will collide with it.

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 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 (see Fig. 13.7). 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,

$$\tau = 1/(n\pi \langle v \rangle d^2) \quad (13.38)$$

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

$$l = \langle v \rangle \tau = 1/(n\pi d^2) \quad (13.39)$$

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. (13.38). A more exact treatment gives^r

$$l = 1/(\sqrt{2} n\pi d^2) \quad (13.40)$$

Let us estimate l and τ for air molecules with average speeds $\langle v \rangle = (485 \text{ m/s})$. At STP

$$n = \frac{(0.02 \times 10^{23})}{(22.4 \times 10^{-3})}$$

$$= 2.7 \times 10^{25} \text{ m}^{-3}$$

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

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

$$\text{and } l = 2.9 \times 10^{-7} \text{ m} \approx 1500d \quad (13.41)$$

As expected, the mean free path given by Eq. (13.40) depends inversely on the number density and the size of the molecules. In a highly evacuated tube n is rather small and the mean free path can be as large as the length of the tube.

Example 13.9 Estimate the mean free path for a water molecule in water vapour at 373 K. Use information from Exercises 13.1 and Eq. (13.41) above.

Answer The d for water vapour is same as that of air. The number density is inversely proportional to absolute temperature.

$$\text{So } n = 2.7 \times 10^{25} \times \frac{273}{373} = 2 \times 10^{25} \text{ m}^{-3}$$

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

Note that the mean free path is 100 times the interatomic distance $\sim 40 \text{ \AA} = 4 \times 10^{-9} \text{ m}$ calculated earlier. It is this large value of mean free path that leads to the typical gaseous behaviour. Gases can not be confined without a container.

Using, the kinetic theory of gases, the bulk measurable properties like viscosity, heat conductivity and diffusion can be related to the microscopic parameters like molecular size. It is through such relations that the molecular sizes were first estimated.

SUMMARY

- The ideal gas equation connecting pressure (P), volume (V) and absolute temperature (T) is

$$PV = \mu RT = k_B NT$$

where μ is the number of moles and N is the number of molecules. R and k_B are universal constants.

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \quad k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

Real gases satisfy the ideal gas equation only approximately, more so at low pressures and high temperatures.

- Kinetic theory of an ideal gas gives the relation

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

where n is number density of molecules, m the mass of the molecule and $\overline{v^2}$ is the mean of squared speed. Combined with the ideal gas equation it yields a kinetic interpretation of temperature.

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T, \quad v_{rms} = (\overline{v^2})^{1/2} = \sqrt{\frac{3k_B T}{m}}$$

This tells us that the temperature of a gas is a measure of the average kinetic energy of a molecule, *independent of the nature of the gas or molecule*. In a mixture of gases at a fixed temperature the heavier molecule has the lower average speed.

- The translational kinetic energy

$$E = \frac{3}{2} k_B NT.$$

This leads to a relation

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

- The law of equipartition of energy states that if a system is in equilibrium at absolute temperature T , the total energy is distributed equally in different energy modes of