

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?

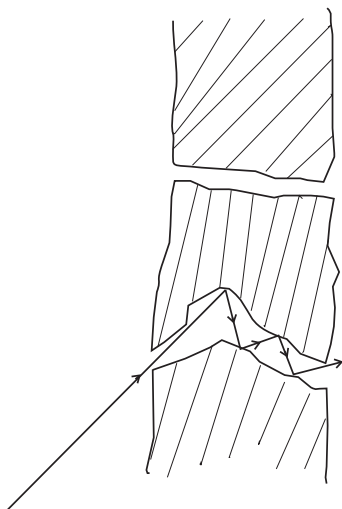


Fig. 13.5 Molecules going through a porous wall.

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 uses a heavy cricket bat while playing. Does 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

$$t \quad \frac{1}{2}mv_x^2 \quad \frac{1}{2}mv_y^2 \quad \frac{1}{2}mv_z^2 \quad (13.22)$$

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

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

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 .

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

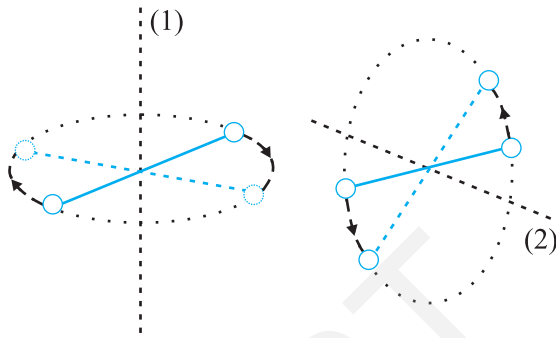


Fig. 13.6 The two independent axes of rotation of a diatomic molecule

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 $\frac{1}{2}k_B T$. A 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

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

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,

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

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

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

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

The molar specific heats are then given by

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

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

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

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

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

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

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

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

$$\frac{f}{f} \quad (13.36)$$

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 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 ($\text{J mol}^{-1} \text{K}^{-1}$)	C_p ($\text{J mol}^{-1} \text{K}^{-1}$)	$C_p - C_v$ ($\text{J mol}^{-1} \text{K}^{-1}$)	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 ($\text{J mol}^{-1} \text{K}^{-1}$)	C_p ($\text{J mol}^{-1} \text{K}^{-1}$)	$C_p - C_v$ ($\text{J mol}^{-1} \text{K}^{-1}$)	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_2O	27.0	35.4	8.35	1.31
Polyatomic	CH_4	27.1	35.4	8.36	1.31