

Diffusion is a transport phenomenon. You will learn about it in this unit.

MEAN FREE PATH AND TRANSPORT PHENOMENA

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STUDY GUIDE

In the previous unit, you have learnt about Maxwell distribution function for molecular speeds and used it to obtain expressions for average speed, most probable speed and root mean square speed. In this unit, you will learn about mean free path and transport phenomena. The study of free paths involves simple concepts of probability, which you have learnt in your school mathematics classes. You are, therefore, advised to refresh your earlier knowledge of probability. Also, you are familiar with the concept of viscosity, diffusion and thermal conductivity. It will be a good idea to revise your school physics about these concepts. This unit is slightly longer but the concepts are simple. Yet we advise you to master sub-topics one at a time. Moreover, if you solve numerical problems given here as also in other texts, you should get extra rewards.

“Atoms and molecules from their very nature can never be made the objects of sensuous contemplations.”

Ernst Mach

3.1 INTRODUCTION

In the previous units you have learnt that molecules of an ideal gas can be considered as point masses, which move randomly with varying speeds. We have seen that even at room temperature, the molecules of a gas, say oxygen, move with very large speeds: $v_{rms} = 480 \text{ ms}^{-1}$. It means that a small amount of scent released in a large room from a vessel should spread throughout the room in no time. But this is not supported by our observation; when we open the lid of a perfume bottle in one corner of the room, the perfume is smelt at the other corner after a considerable time. This apparent paradox led to a serious objection in the early stages of development of kinetic theory of gases. However, this paradox was resolved by Clausius when he argued that **gas molecules have finite size and as they move, they collide with one another leading to increase in diffusion time**. This amounts to modifying the basic assumption about the size of gas molecules.

You may now like to know: What is the average distance travelled by a molecule between successive collisions? What is the mechanism of these collisions? To answer these and such other questions, we use the concept of **mean free path**. We have derived an expression for mean free path in Sec. 3.2 under simplified assumptions. These help us to get a feel of the basic physics. The distribution of free paths is also discussed in this section.

Suppose that a gas moves with a flow velocity towards the right. If its molecules experience velocity gradient in a direction normal to the direction of flow, the gas experiences net transport of momentum across an imaginary plane in the gas along the direction of flow. This is characterised by the **coefficient of viscosity**. You will note that in gases, unlike the case of liquids, random thermal motion associated with gas molecules rather than frictional force between successive layers, gives rise to the phenomenon of viscosity. We will just quote the expression for the coefficient of viscosity in terms of mean free path and discuss its temperature as well as pressure dependence.

When a temperature gradient exists in the body of such a gas in a direction perpendicular to the direction of flow, random motion of gas molecules leads to net transport of thermal energy in the direction of flow. This gives rise to the phenomenon of thermal conduction. This is characterised by **thermal conductivity**. You will learn how to correlate it with the coefficient of viscosity in Sec 3.3.2.

When concentration gradient exists inside a gas normal to the direction of flow, there is net transport of mass in the direction of preferential motion. This is characterised by the **coefficient of diffusion**. You will learn how to express the coefficient of diffusion in terms of mean free path, discuss its temperature dependence and correlate it with coefficient of viscosity in Sec. 3.3.3. These processes (viscosity, thermal conduction and diffusion) are collectively referred to as **transport phenomena**, since we observe net transfer of momentum, energy or matter.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define mean free path and obtain its expressions using elementary derivation;
- ❖ describe the law of free paths;
- ❖ explain the term transport phenomena;
- ❖ discuss physical implications of viscosity of a gas;
- ❖ discuss how thermal conductivity is related to the coefficient of viscosity; and
- ❖ establish the relation between mean free path and coefficient of self-diffusion.

3.2 MEAN FREE PATH

You may recall that in elementary kinetic theory, gas molecules are considered point masses (Assumption 2, Sec. 1.2) and intermolecular collisions are ignored. But as mentioned earlier, to explain the finite time taken by a gaseous mass in an open container to disperse, Clausius assigned a *finite size to gas molecules*. He argued that when a molecule moves within the gas under equilibrium conditions, it necessarily collides with other molecules it encounters in its path and undergoes frequent changes in its direction of motion. This results in a series of zig-zag paths. These are called **free paths**.

The trajectory of a molecule moving with average speed \bar{v} is shown in Fig. 3.1. The concept of mean free path may be visualised if you consider a person shooting aimlessly in a thick forest. The bullets fired by him may eventually hit trees but some will travel farther than others.

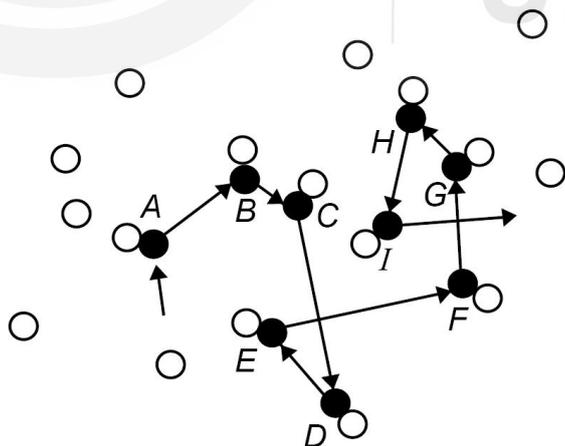


Fig. 3.1: The trajectory of a molecule moving in a gas.

Now carefully examine Fig. 3.1. You will note that free paths are of unequal length; some are short while others are long. The *average length of the free paths is referred to as mean free path*. Thus, **mean free path is the average distance travelled by a molecule between two successive collisions**. We denote it by the symbol λ (pronounce as lambda).

If $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_N$ are the successive free paths traversed by a molecule in time t and N denotes the total number of collisions suffered in this period, we can write

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_N}{N}$$

$$= \frac{\text{total distance travelled}}{\text{total number of collisions}}$$

If \bar{v} is the average speed with which a molecule moves in the body of the gas, then you can write

$$\lambda = \frac{\bar{v} t}{N} \quad (3.1)$$

Under normal conditions, the mean free path of oxygen molecules is about 2×10^{-7} m. This is smaller than the wavelength of visible light, which is in the range 4×10^{-7} m – 6×10^{-7} m. However, mean free path is greater than the average intermolecular separation (3×10^{-9} m).

If $\tau = t/N$ denotes the mean time between two successive collisions, then you can also write

$$\lambda = \bar{v} \tau = \frac{\bar{v}}{P_c} \quad (3.2)$$

Here $P_c = (\tau^{-1})$ denotes the collision frequency, which is a measure of the average number of collisions per second. You may now ask: How can we relate λ to the microscopic properties of a gas? To answer this question, we first make an elementary calculation.

3.2.1 Elementary Derivations

Suppose that a gas consisting of a large number of molecules, each of mass m and diameter d , is in thermal equilibrium. We assume that gas molecules undergo random collisions. Mathematically speaking, we can say that the probability of a molecule suffering a collision in a small interval of time dt is independent of the history of past collisions made by it. As a simple analogy, you can consider that if you throw a dice, the probability of getting a six does not depend on the preceding throw, where a six may or may not have appeared. Similarly, winning or losing toss before a match is independent of earlier results.

From Eq. (3.2), we note that to derive an expression for λ , we must first know the expression for P_c . We shall make this calculation by assuming that only one molecule is in motion. We refer to it as Zeroth order approximation. You will realise that essential physics involved in this phenomenon can be understood well through simple arguments.

Case 1: Zeroth order approximation: Only one molecule in motion

We assume that only one molecule, labelled as A , criss-crosses a sea of other molecules that are at rest. (As such, this is an over-simplification of the actual situation.) You can easily visualise that for a collision to take place, the

centre-to-centre distance between the moving and a stationary molecule should be equal to $2r(=d)$, as shown in Fig. 3.2a.

Note that the centre-to-centre distance at the time of collision between the moving and a stationary molecule will also be equal to the diameter d of a gas molecule, if the stationary molecules were shrunk to geometrical points and the moving molecule is taken to be of radius d (Fig.3.2b). You can visualise this as if the moving molecule carries with it a circular disc of radius d . Therefore, the moving molecule can be thought of as sweeping out a cylinder of cross-sectional area πd^2 and length $\bar{v}t$ in time t . This is illustrated in Fig. 3.2c. During this time, it will collide with all other molecules whose centres lie within a cylinder of volume $\bar{v}t\pi d^2$. You must convince yourself about this before proceeding further.

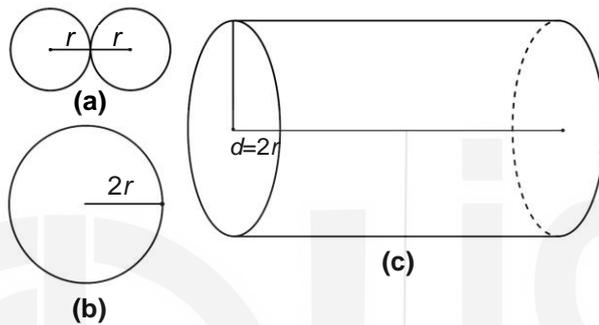


Fig. 3.2: a) Collision of two molecules of radii r : Instantaneous representation; b) equivalent representation of collision in (a) where radius of the moving molecule is increased to $2r$ and the stationary molecule is shrunk to a geometrical point; c) cylindrical volume mapped by the moving molecule of radius $2r$.

If the number of molecules per unit volume is n , the number of molecules contained in the cylinder of volume $\bar{v}t\pi d^2$ will be equal to $\bar{v}t\pi d^2n$. You will agree that this number also equals the number of collisions suffered by the moving molecule in time t .

The collision frequency, which defines the number of collisions per second, is given by

$$P_c = \bar{v} \pi d^2 n = n\sigma \bar{v} \quad (3.3)$$

where $\sigma = \pi d^2$ is known as *microscopic collision cross-section*. It is expressed in m^2 .

Substituting this result in Eq. (3.2), we get

$$\lambda = \frac{\bar{v}}{P_c} = \frac{1}{\pi d^2 n} = \frac{1}{\sigma n} \quad (3.4)$$

The quantity $n\sigma$ is called *macroscopic collision cross-section* and its unit is m^{-1} . Note here that the unit of macroscopic collision cross-section is *reciprocal length*, not an area.

Let us pause for a moment and ask: What is good about the relation contained in Eq. (3.4)? What are its implications? To seek answers to these questions, we note that Eq. (3.4) predicts that mean free path is inversely proportional to the macroscopic collision cross-section or number density and second power of diameter of the molecule. It means that mean free path will

be less for a denser and/or a heavier gas. This is in perfect agreement with common observation and lends support to the basic tenets of kinetic theory. The aesthetic beauty of kinetic theory is in its ability to relate experimentally measurable macroscopic quantity such as mean free path to a microscopic quantity – size of a molecule.

You may now logically ask: What is the typical magnitude of mean free path in a gas at STP? The answer to this question is contained in the following example. You should go through it carefully.

EXAMPLE 3.1: COLLISION CROSS-SECTION

The average speed of hydrogen molecules is 1840 ms^{-1} . The radius of a hydrogen molecule is $1.37 \times 10^{-10} \text{ m}$. Calculate (i) collision cross section, (ii) collision frequency and (iii) mean free path. Take $n = 3 \times 10^{25} \text{ m}^{-3}$.

SOLUTION ■ Since the radius of a hydrogen molecule is $1.37 \times 10^{-10} \text{ m}$ and number density n is $3 \times 10^{25} \text{ m}^{-3}$, we can easily calculate the collision cross-section, collision frequency and mean free path using Eqs. (3.3) and (3.4):

$$(i) \quad \sigma = \pi d^2 = 4\pi (1.37)^2 \times 10^{-20} \text{ m}^2 = 23.6 \times 10^{-20} \text{ m}^2$$

$$(ii) \quad P_c = \pi d^2 n \bar{v} = n \bar{v} \sigma \\ = (3 \times 10^{25} \text{ m}^{-3}) \times (1.84 \times 10^3 \text{ ms}^{-1}) \times (23.6 \times 10^{-20} \text{ m}^2) \\ = 1.3 \times 10^{10} \text{ s}^{-1}$$

$$(iii) \quad \lambda = \frac{1}{n\pi d^2} = \frac{1}{(3 \times 10^{25} \text{ m}^{-3}) \times (23.6 \times 10^{-20} \text{ m}^2)} \\ = 141 \times 10^{-9} \text{ m} = 141 \text{ nm}$$

Note that the number of collisions per second is of the order of 10^{10} , which is a very large number. For this reason, the path of a molecule is made up of so many kinks and zigzags that it is almost impossible to follow its trajectory.

Also note that λ is large compared to intermolecular distance, which is only a few nanometer ($\approx 3 \text{ nm}$).

To ensure that you have grasped the ideas and your progress is satisfactory, we would like you to solve an SAQ before proceeding further.

SAQ 1 – Mean free path

The mean speed of oxygen molecules at room temperature is 450 ms^{-1} . If the radius of an oxygen molecule is 1.8 \AA , calculate σ , P_c , λ , and τ . Take $n = 3 \times 10^{25} \text{ m}^{-3}$.

From ideal gas equation, we know that the pressure exerted by a gas can be expressed in terms of its temperature as

$$p = nk_B T$$

On using this result to substitute for n in Eq. (3.4), the expression for mean free path takes the form

$$\lambda = k_B T / \sigma p \quad (3.5)$$

This result is very interesting; it suggests that mean free path is directly proportional to absolute temperature of a gas and inversely proportional to the pressure exerted by it on the walls of the container. It means that the value of λ will increase as pressure decreases and/or temperature increases. Now suppose we reduce pressure to a very small value using a vacuum pump. According to Eq. (3.5), the mean free path can approach infinity. But in actual practice, this is forbidden by physical considerations. At the most, the value of λ can equal the dimensions of the container.

You will agree that in deriving Eq. (3.4), we made a rather unrealistic assumption that only one molecule moved while other molecules were at rest. But in Unit 2 you have learnt that molecules in a gas move about randomly. Therefore, a better way to represent the actual situation will be to assume that all molecules move with the same speed. When we consider this, Eq. (3.5) modifies to

$$\lambda_C = \frac{3}{4n\sigma} = \frac{0.75}{n\sigma} = 0.75 \frac{k_B T}{p\sigma} \quad (3.6)$$

It may be mentioned here that this result was obtained by Clausius. That is why we have put the subscript C with λ . It shows that mean free path of the molecules in a gas decreases when all molecules are moving.

You will recall that in actual practice, we should have considered Maxwellian distribution of velocities. However, the mathematical calculations are quite involved and it will be sufficient to quote the result. (Those of you who are interested in these details may refer to references given in the Further Readings):

$$\begin{aligned} \lambda_M &= \frac{1}{\sqrt{2} n\sigma} = (0.707) \frac{1}{n\sigma} \\ &= (0.707) \frac{k_B T}{p\sigma} \end{aligned} \quad (3.7)$$

Note that $\frac{\lambda_M}{\lambda_C} = 0.94$.

This result shows that there is a correction of only 6 per cent in the value of mean free path when we go from uniform speed model to Maxwell distribution. You will also note that for point molecules ($d \rightarrow 0$), collision cross-section $\sigma \rightarrow 0$ and mean free path $\lambda \rightarrow \infty$.

Before proceeding further, we would like you to revise what you have learnt so far in this unit.

Recap

MEAN FREE PATH

- The average distance covered by a gas molecule between two successive collisions defines the mean free path.
- The mean free path of a gas molecule when only one molecule moves with speed \bar{v} is given by

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

Now go through the following example carefully to get a feel of the values involved in real situations.

EXAMPLE 3.2: MOLECULAR DIAMETER

A gas is assumed to obey Maxwell's law of distribution of speeds. Calculate the (i) molecular diameter of a gas and (ii) the number of collisions per unit distance if mean free path at STP is 2.85×10^{-7} m. Take $n = 3 \times 10^{25} \text{ m}^{-3}$.

SOLUTION ■ From Eq. (3.7), we can write $\lambda = \frac{1}{\sqrt{2}} \frac{1}{\pi d^2 n}$

(a) To determine d , we rewrite the expression for mean free path as

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

On substituting the given values in this expression, we get

$$\begin{aligned} d^2 &= \frac{1}{\sqrt{2}} \cdot \frac{1}{3.14} \times \frac{1}{2.85 \times 10^{-7} \text{ m}} \times \frac{1}{3 \times 10^{25} \text{ m}^{-3}} \\ &= \frac{1}{37.96 \times 10^{18}} \text{ m}^2 = 2.63 \times 10^{-20} \text{ m}^2 \end{aligned}$$

so that

$$d = 1.62 \times 10^{-10} \text{ m}$$

Note that the order of magnitude of mean free path is 10^3 times that of molecular diameter.

(b) By definition, the number of collisions per unit distance is reciprocal of the mean free path. Therefore, we can write

$$\begin{aligned} N_c &= \frac{1}{\lambda} = \frac{1}{2.85 \times 10^{-7} \text{ m}} \\ &= 3.51 \times 10^6 \text{ m}^{-1} \end{aligned}$$

To test your understanding, you may like to answer the following SAQ.

SAQ 2 – Pressure and mean free path

The mean free path of the molecules of an ideal gas at 15°C is 6.28×10^{-8} m. If the radius of a gas molecule is 1.88 Å, calculate the pressure exerted by the gas. Also calculate the number of collisions suffered by a molecule in travelling a distance of one metre. Take $k_B = 1.38 \times 10^{-23}$ JK⁻¹.

You now know that molecules undergo collisions very frequently. It means that the distribution of free paths will be spread over a wide range. It is, therefore, interesting to know their distribution. This forms the subject of discussion of the following sub-section.

3.2.2 Distribution of Free Paths

Imagine a person shooting aimlessly in a thick forest. Every bullet eventually hits a tree, but some travel farther than others. This situation is analogous to the flights of gas molecules. We now wish to know the distribution of free paths. To do so, let us consider a molecule at the start of its journey (point O).

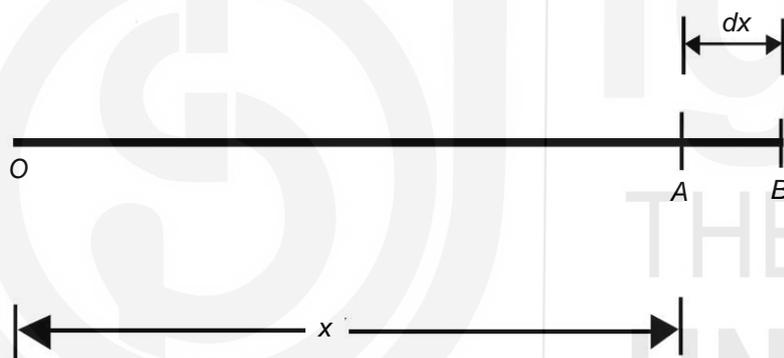


Fig. 3.3: A molecule travels from O to A without colliding with another molecule. It traverses a further distance AB in time dt .

We assume that past history of a molecule does not influence its subsequent motion in any way. Suppose that a molecule moving with average speed \bar{v} , travels a distance $OA = x$ without suffering any collision. The probability of this event will be a function of x . Let us denote it by $f(x)$. The probability that this molecule makes a collision in moving from A to B will be determined by the product of collision frequency and time interval in which it covers the given distance. So, we can take it to be equal to $P_c dt$, where P_c is the collision frequency. Since $dx = \bar{v} dt$, we can write

$$P_c dt = P_c \frac{dx}{\bar{v}} = \frac{dx}{\lambda}$$

where λ is the mean free path defined by Eq.(3.2). Hence, the probability that a molecule traverses a distance dx without making a collision is $\left(1 - \frac{dx}{\lambda}\right)$.

1. If the probability of occurrence of a collision is $p(x)$, the probability of its non-occurrence will be $1 - p(x)$.
2. The probability of occurrence of two mutually exclusive events is multiplicative.

Since motion from O to A and from A to B can be considered as two independent events, we can say that the probability $f(x + dx)$ of this molecule completing its journey from O to B without making any collision is equal to the product of probabilities for individual events. Mathematically, we express it as $f(x)\left(1 - \frac{dx}{\lambda}\right)$. Hence, we can write

$$f(x + dx) = f(x)\left(1 - \frac{dx}{\lambda}\right) \quad (3.8)$$

To simplify this expression, we use Taylor series expansion of $f(x + dx)$ and ignore second and higher order terms in dx . Then we can write

$$f(x + dx) = f(x) + \frac{df(x)}{dx} dx$$

On using this result in Eq. (3.8), we get

$$\frac{df(x)}{dx} = -\frac{f(x)}{\lambda}$$

You can easily integrate it to obtain

$$f(x) = A \exp(-x/\lambda). \quad (3.9)$$

The constant of integration A can be easily evaluated using the fact that $f(0) = 1$. (Physically it means that the particle is yet to move or collide.) This gives $A = 1$. Hence, Eq. (3.9) takes a compact form:

$$f(x) = \exp(-x/\lambda) \quad (3.10)$$

This is the law of *distribution of free paths*. It suggests that the probability of a molecule travelling very large distance without making a collision will be vanishingly small.

If we have a sample of N_0 molecules to start with, only $N_0 \exp(-x/\lambda)$ of these will survive a collision in traversing a distance x . Let this number be denoted by $N(x)$. Then we can write

$$N(x) = N_0 \exp\left(-\frac{x}{\lambda}\right) \quad (3.11)$$

This equation is known as *survival equation*. You will come across similar equations in other areas of physics. For example, radioactive decay obeys the equation $N(x) = N_0 \exp(-\Lambda t)$, where $N(x)$ is the number of atoms which survive disintegration for time t and Λ is disintegration constant.

Now refer to Fig. 3.4. It shows the plot of distribution of free paths as a function of x/λ . Note that the fraction of molecules with free paths larger than λ is only $e^{-1} \approx 0.37$.

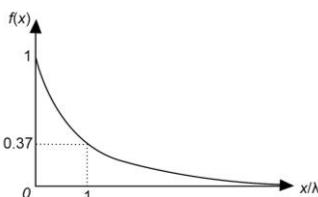


Fig. 3.4: The plot of the survival equation.

We now give a solved example to reinforce our discussion of this section.

EXAMPLE 3.3: SURVIVAL EQUATION

In a sample of 10^4 gas molecules, each molecule is moving with the same speed. Calculate the number of molecules that will continue to travel undeflected after traversing distances of 0.4λ , 0.5λ , λ , 2λ , and 10λ .

SOLUTION ■ The values of $N(x)$ are tabulated below for different distances traversed by the gas molecules and you can readily verify these using Eq. (3.11). To illustrate, for $x = 0.4\lambda$, we can write

$$N(x) = 10^4 e^{-0.4} = 6703$$

$\frac{x}{\lambda}$	0.4	0.5	1	2	10
N	6703	6065	3679	1353	0.4540

You will note that after traversing a distance of λ , 2λ and 10λ , nearly 37%, 13.5% and 0.5% molecule, respectively, will survive a collision.

You may now like to solve an SAQ to assess your understanding.

SAQ 3 – Law of free paths

The mean free path of the molecules of a gas at pressure p and temperature T is 5.2×10^{-8} m. Calculate the probabilities that a molecule will travel 10.4×10^{-8} m without making a collision, if (i) temperature is doubled, (ii) both temperature and pressure are doubled, and (iii) pressure is tripled.

Before proceeding further, let us revise what you have learnt in this section.

LAW OF FREE PATHS

Recap

- The law of distribution of free paths gives the probability that a gas molecule covers a distance x without making a collision:

$$f(x) = \exp(-x/\lambda)$$

- The law of distribution of free paths is supported by experimental results.

So far we confined ourselves to a gaseous system at uniform temperature and pressure in equilibrium so that there is no preferential motion of any kind. This is because the rate of migration of molecules across a given plane in the gas is exactly balanced by an equal number moving in the opposite direction. However, when the entire gas or a part of it moves as a whole in a particular direction, the preferential motion and random molecular motion combine to give rise to a new behaviour. Let us learn about it now.

3.3 TRANSPORT PHENOMENA

We know that each gas molecule has a finite mass and is characterised by random molecular motion. Therefore, it possesses momentum as well as energy. So, while moving from one part of the container to another, it is a potential carrier of these physical quantities under certain peculiar conditions. When a gas is in equilibrium, there is no *net* transport of matter, energy, or momentum. However, when a gas is endowed with macroscopic motion, i.e., the entire gas or a part of it moves as a whole in a particular direction, the following three cases may occur singly or jointly:

- *The different parts of the gas move with different velocities.* This will give rise to relative motion between different layers of the gas. As a result, the faster moving layers in the body of the gas will lose momentum to the slower moving layers. Therefore, *across an imaginary plane, there will be net transport of momentum in the preferential direction.* This results in a frictional force, which is characterised by the *coefficient of viscosity*.

Note that viscosity in gases arises due to the random thermal motion of molecules when it is endowed with macroscopic motion rather than a frictional force between any two adjacent layers, as in the case of liquids.

- *Different parts of a gas are at different temperatures.* In this case, the molecules of the gas will carry *thermal energy* from regions of higher temperature to regions of lower temperature and tend to attain thermal equilibrium. This gives rise to the phenomenon of *thermal conduction*.
- *Different parts of a gas have different concentrations.* The molecules from regions of higher concentration will migrate to the regions of lower concentration resulting in the transport of *mass (matter)*. This leads to the phenomenon of *diffusion*.

We thus find that viscosity, conduction and diffusion are bulk properties of gases signifying transport of momentum, energy and mass, respectively. These are collectively categorised under the title of *transport phenomena*. These processes are of vital importance in physical sciences and find several important applications. We will now discuss these in some detail on the basis of the simple molecular model discussed in the preceding chapters.

3.3.1 Viscosity: Transport of Momentum

In your school physics classes, you have learnt that the property by virtue of which a liquid opposes the motion between adjacent layers is referred to as viscosity. It is quantitatively expressed in terms of the coefficient of viscosity, η . Can you recall its definition? The *coefficient of viscosity is defined as the tangential force per unit area when a unit velocity gradient exists in a direction perpendicular to the direction of motion*. Mathematically, for small velocity gradient we write

$$F = -\eta A \frac{du}{dy} \quad (3.12)$$

Here F denotes the viscous force acting on an area A and du/dy is velocity gradient along the +ve y -direction. The negative sign signifies that the viscous force is directed against the velocity gradient. Note that η has dimensions

$\text{ML}^{-1}\text{T}^{-1}$. Its SI units are $\text{kgm}^{-1}\text{s}^{-1}$. It is also denoted as pascal-second. The CGS unit of η is poise ($= 10^{-1}\text{kgm}^{-1}\text{s}^{-1}$).

Let us consider a gas enclosed between two planes depicted as aa' and bb' in Fig. 3.5 and separated through a distance h . Suppose that the gas is endowed with mass motion from left to right and a positive velocity gradient exists along the y -axis, which is normal to the direction of flow.

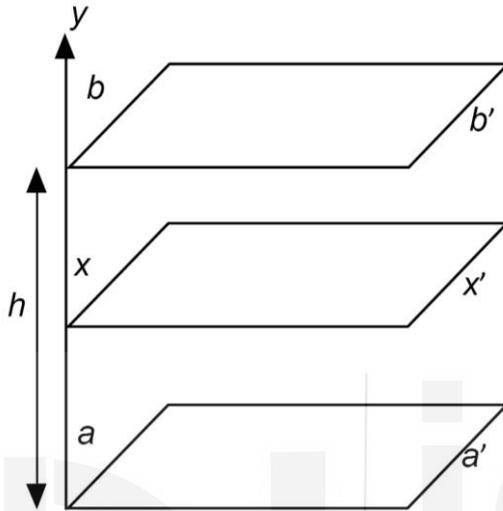


Fig. 3.5: Momentum transport across a plane in a gas having velocity gradient.

Mathematically, the coefficient of viscosity of a gas is given by

$$\eta = \frac{1}{3} mn\bar{v}\lambda = \frac{1}{3} \rho\bar{v}\lambda \quad (3.13)$$

On substituting the expression for λ corresponding to Maxwellian distribution of speeds in Eq. (3.13) from Eq. (3.7), we can express η in terms of σ :

$$\eta_M = \frac{1}{3\sqrt{2}} \frac{m\bar{v}}{\sigma} \quad (3.14)$$

This result provides us a useful way to estimate a microscopic property such as molecular diameter in terms of a macroscopic property such as viscosity η , which is directly measurable. This finding provided remarkable support to elementary kinetic theory.

To be able to discuss pressure and temperature dependence of η , we

substitute for $\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$ from Eq. (2.34) in Eq. (3.14). This gives

$$\eta_M = \frac{2}{3\sigma} \sqrt{\frac{mk_B T}{\pi}} = \frac{0.376}{\sigma} \sqrt{mk_B T} \quad (3.15)$$

Effect of Temperature and Pressure on Viscosity

- From Eq. (3.15) we note that the viscosity of a gas is directly proportional to the square root of absolute temperature. So, if we plot η versus $T^{1/2}$, we should obtain a straight line. However, experiments show that viscosity of a gas increases with temperature at a slightly faster rate than $T^{1/2}$.

The departure from the value 0.5 provides us an opportunity to review the assumptions of elementary kinetic theory.

- According to elementary kinetic theory, the viscosity of a gas is independent of pressure (or n). But in actual practice, pressure independence of η is observed only for a limited range – from a few mm of mercury to a few atmosphere. Experiments show that at very low pressures, viscosity decreases and at very high pressures, viscosity increases.

We can explain these observations as follows:

At very low pressures, intermolecular collisions become rare and as mentioned earlier, the mean free path becomes comparable to the dimensions of the apparatus. However, the number density decreases continuously with pressure. This makes the coefficient of viscosity to decrease as pressure decreases. On the other hand, at very high pressures, the mean free path is comparable to molecular size and the coefficient of viscosity increases with pressure (or n).

We now recapitulate important results of this sub-section.

Recap

COEFFICIENT OF VISCOSITY

- When different parts of a gas endowed with mass motion and its molecules move with different speeds, there is net transport of momentum in the direction of mass motion.
- The coefficient of viscosity of a gas is given by $\eta = \frac{1}{3} mn\bar{v}\lambda = \frac{1}{3} \rho\bar{v}\lambda$.
- Theory predicts that η is independent of pressure but varies as $T^{1/2}$.

EXAMPLE 3.4: COEFFICIENT OF VISCOSITY AND MEAN FREE PATH

The coefficients of viscosity of argon and helium are 22×10^{-6} Pa s and 19×10^{-6} Pa s, respectively. Calculate the mean free paths for these gases, if they are kept under identical conditions.

SOLUTION ■ Since the gases are under identical conditions, n is same for both gases. Then from Eq. (3.13) we can write

$$\frac{\eta_{\text{Ar}}}{\eta_{\text{He}}} = \frac{m_{\text{Ar}} \bar{v}_{\text{Ar}} \lambda_{\text{Ar}}}{m_{\text{He}} \bar{v}_{\text{He}} \lambda_{\text{He}}} \quad (\text{i})$$

Using the relation $\bar{v} = \sqrt{\frac{8k_{\text{B}}T}{\pi m}}$, we can rewrite (i) as

$$\frac{\eta_{\text{Ar}}}{\eta_{\text{He}}} = \sqrt{\frac{m_{\text{Ar}}}{m_{\text{He}}}} \frac{\lambda_{\text{Ar}}}{\lambda_{\text{He}}}$$

On re-arranging terms, we get

$$\frac{\lambda_{\text{Ar}}}{\lambda_{\text{He}}} = \sqrt{\frac{m_{\text{He}}}{m_{\text{Ar}}}} \frac{\eta_{\text{Ar}}}{\eta_{\text{He}}} = \left(\frac{4}{39.9}\right)^{1/2} \left(\frac{22 \times 10^{-6} \text{ Pa s}}{19 \times 10^{-6} \text{ Pa s}}\right) = 0.367$$

EXAMPLE 3.5: COEFFICIENT OF VISCOSITY AND MEAN FREE PATH

The molecules of helium gas move with an average speed of 1200 ms^{-1} . If $\eta = 19 \times 10^{-6} \text{ Pa s}$, calculate the mean free path for helium.

SOLUTION ■ We can rewrite Eq. (3.13) as

$$\lambda = \frac{3\eta}{\rho\bar{v}} = \frac{3\eta V}{M\bar{v}}$$

where M is molecular weight and V is volume occupied by one mole of the gas. On inserting the given numerical values, we get

$$\begin{aligned}\lambda &= \frac{3 \times (19 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}) \times (22.4 \times 10^{-3} \text{ m}^3)}{(4 \times 10^{-3} \text{ kg}) \times (1200 \text{ ms}^{-1})} \\ &= 2.66 \times 10^{-7} \text{ m}\end{aligned}$$

You may now like to solve an SAQ to assess your understanding.

SAQ 4 – Viscosity and molecular dimensions

Calculate the radius of an oxygen molecule, if coefficient of viscosity of oxygen is $19.6 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1}$ at 15°C and $\bar{v} = 436 \text{ ms}^{-1}$. Assume that it obeys Maxwellian law of distribution of speeds.

3.3.2 Thermal Conductivity: Transport of Energy

When a gas is endowed with mass motion and a temperature gradient exists between its different layers, a finite amount of energy is transported by gas molecules due to their random motion from regions of higher temperature to regions of lower temperature. As mentioned earlier, this gives rise to the phenomenon of thermal conduction. The rate at which thermal energy is transported across any surface per unit area is characterised in terms of thermal conductivity, K and we can write

$$Q = -K \frac{dT}{dy} \quad (3.16)$$

where (dT/dy) is temperature gradient and temperature of the gas at an imaginary surface xx' within the gas is T .

The expression for thermal conductivity is given by

$$K = \frac{f}{6} n \bar{v} \lambda k_B \quad (3.17)$$

From this equation, we note that thermal conductivity is directly proportional to average molecular speed. Therefore, theory predicts that thermal conductivity

You should not confuse the symbol K used for thermal conductivity with the symbol used for kelvin, the unit of temperature.

is directly proportional to square root of temperature. However, in actual practice, K increases somewhat more rapidly suggesting that when intermolecular forces come into play, they begin to influence energy transport.

Relation Between η and K

When we closely examine the expressions for η and K , we expect some connection between them. It is instructive to ascertain it as both these quantities are physically measurable. Therefore, we divide Eq. (3.17) by Eq. (3.13) and obtain

$$\frac{K}{\eta} = \frac{f}{2} \frac{k_B}{m} = \frac{f}{2} \frac{k_B N_A}{M} = \frac{f}{2} \frac{R}{M} \quad (3.18)$$

where $m = \frac{M}{N_A}$ and M is molecular weight of the substance.

From Unit 2 you will recall that molar heat capacity at constant volume is given by

$$c_V = \frac{f}{2} R$$

Using this result, we can rewrite Eq. (3.18) as

$$\frac{K}{\eta} = \frac{c_V}{M}$$

or

$$\frac{KM}{\eta c_V} = 1 \quad (3.19)$$

Atomicity of a gas defines the number of atoms in its molecule.

From this result we note that the ratio $(KM/\eta c_V)$ is constant, same for all gases. But experiments show that this ratio is greater than one. A more rigorous calculation shows that this ratio varies between 1.5 and 2.5 and is different for different gases; decreasing with atomicity. There can be several reasons for this difference.

You should now go through the following example carefully.

EXAMPLE 3.6: THERMAL CONDUCTIVITY AND VISCOSITY

The coefficient of viscosity of helium is $18.6 \times 10^{-6} \text{ Nsm}^{-2}$, $M = 4 \text{ kg kmol}^{-1}$ and $c_V = 12.5 \times 10^3 \text{ Jkmol}^{-1} \text{ K}^{-1}$. Calculate the thermal conductivity of helium.

SOLUTION ■ From Eq. (3.19) we can write $K = \frac{\eta c_V}{M}$. On putting the given values, we get

$$\begin{aligned} K &= \frac{(18.6 \times 10^{-6} \text{ Nsm}^{-2}) \times (12.5 \times 10^3 \text{ Jkmol}^{-1} \text{ K}^{-1})}{4 \text{ kg kmol}^{-1}} \\ &= 5.8 \times 10^{-2} \text{ Jm}^{-1} \text{ s}^{-1} \text{ K}^{-1}. \end{aligned}$$

Before proceeding further, we recapitulate important result in this sub-section.

THERMAL CONDUCTIVITY

Recap

- When a temperature gradient exists between different layers of a gas endowed with mass motion, there is net transport of energy from regions of higher temperature to regions of lower temperature. This gives rise to phenomenon of thermal conduction.
- The thermal conductivity of a gas is given by

$$K = \frac{fn\bar{v}}{6} \lambda k_B$$

- In terms of the coefficient of viscosity, we can write $\frac{KM}{\eta c_V} = 1$.

3.3.3 Diffusion: Transport of Matter

Inter-mixing of gases is known as *diffusion*. This phenomenon is responsible for the smell of flowers/scent reaching us. This is also why while sitting in your study room, you can know what is being cooked in the kitchen. It is a direct consequence of random molecular motion when there are inequalities in concentration. Molecules diffuse from regions of higher concentration towards regions of lower concentration. Fig. 3.6a schematically depicts self-diffusion (diffusion of like molecules). Diffusion of unlike molecules is shown in Fig. 3.6b.

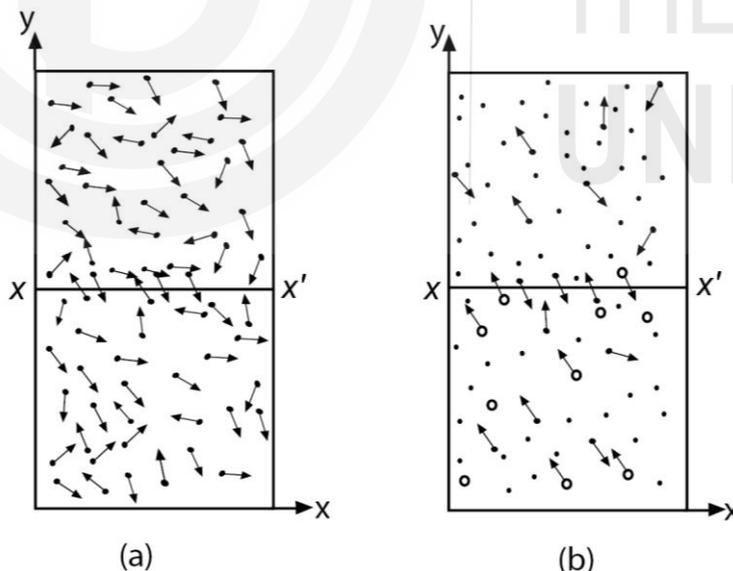


Fig. 3.6: a) Self-diffusion across a barrier; b) Diffusion of unlike molecules.

We describe intermixing of gases in terms of diffusion coefficient, D . If the molecular concentration along a horizontal plane xx' is n and there is positive concentration gradient dn/dy in the vertical plane, the number of particles crossing the given surface per unit area per unit time is given by

$$\Gamma = -D \frac{dn}{dy} \quad (3.20)$$

The concentration of ^{235}U isotope in natural uranium is 0.71%. For power generation in a nuclear power plant, it is desirable to increase its concentration to 2-3%, i.e., above its natural value. Then we say that uranium has been enriched.

The calculation of diffusion coefficient is complicated due to the fact that the rates of diffusion of two gases may not be the same. However, we can understand the essential ideas by considering the diffusion of like molecules, i.e., **self-diffusion**. The diffusion of the isotopes of the same element (say ^{235}U and ^{238}U) is an excellent example of self-diffusion. For self-diffusion, the expression for diffusion coefficients is

$$D = \frac{1}{3} \bar{v} \lambda \quad (3.21)$$

If we now substitute the values of \bar{v} and λ for a Maxwellian gas, we get

$$D = \frac{0.376 (k_B T)^{3/2}}{\sigma \rho \sqrt{m}} \quad (3.22)$$

For air at STP, $\lambda = 100 \text{ nm}$, and $\bar{v} = 450 \text{ m s}^{-1}$. It means that the diffusion coefficient for air is of the order of $10^{-5} \text{ m}^2 \text{ s}^{-1}$. Moreover, Eq. (3.22) implies that diffusion coefficient will vary inversely with pressure and directly with temperature as $T^{3/2}$. The predicted variation with pressure is in agreement with the observed results but the power of T lies between 1.75 and 2. The reason for the more rapid increase with temperature is attributed to the presence of intermolecular forces in real gases. To be precise, it is due to the attractive part of the intermolecular potential.

Relation between D and η

If we combine Eqs. (3.13) and (3.21), we can write

$$\frac{D\rho}{\eta} \equiv \xi = 1 \quad (3.23)$$

Though simple kinetic theory predicts that ξ is constant, equal to one for all gases, its observed value lies between 1.3 and 1.5. It means that simple calculations given here help us to know qualitative behaviour.

We now sum up what you have learnt in this unit.

3.4 SUMMARY

Concept	Description
Mean free path	<ul style="list-style-type: none"> The mean free path is the average distance travelled by a molecule between two successive collisions. If we assume that all but one molecule moves with average speed \bar{v}, the expressions for λ is given by $\lambda = \frac{1}{\pi n d^2} = \frac{1}{n \sigma}$ <p>where n is the molecular number density and σ is the collision cross-section. For a sphere of diameter d, $\sigma = \pi d^2$.</p>

$$dN_v = NA^3 e^{-Bv^2} d^3v$$

Survival equation

- For a sample of N_0 molecules, the number of molecules which travel a distance x without making any collision is given by **survival equation**:

$$N = N_0 \exp(-x/\lambda)$$

Transport phenomena

- When a gas is endowed with mass motion, random molecular motion can lead to **transport of energy, momentum and mass**, depending on the physical conditions, which lead to the phenomena of **thermal conduction, viscosity and diffusion**, respectively. These are collectively referred to as transport phenomena.

Coefficient of viscosity

- The **coefficient of viscosity** for a gas having velocity gradient is given by

$$\eta = \frac{1}{3} mn\bar{v}\lambda = \frac{1}{3}\rho\bar{v}\lambda$$

where m is molecular mass and \bar{v} is average speed of a molecule.

Thermal conductivity

- The thermal conductivity K is given by

$$K = \frac{f}{6} n\bar{v}\lambda k_B$$

where f denotes the number of degrees of freedom.

- K and η are connected by the relation

$$\frac{KM}{\eta c_V} = 1$$

Coefficient of diffusion

- The coefficient of diffusion D is given by

$$D = \frac{\bar{v}}{3}\lambda$$

3.5 TERMINAL QUESTIONS

1. Calculate the diffusion coefficient of hydrogen molecules at 27°C when pressure is 2 atm. Assume that it behaves as a Maxwellian gas. Take

$$r_{\text{H}_2} = 1.37 \times 10^{-10} \text{ m and } k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

2. Calculate the radius of the nitrogen molecule using the following data:

$$K = 23.7 \times 10^{-3} \text{ Js}^{-1} \text{ m}^{-1} \text{ K}^{-1}, c_V = 29.1 \times 10^3 \text{ Jkmol}^{-1} \text{ K}^{-1} \text{ at } 273 \text{ K}$$

$$M = 28.02 \text{ kg, } N_A = 6.023 \times 10^{26} \text{ and } k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

3. Calculate the mean free path for hydrogen molecules at STP. The diameter of a hydrogen molecule is 2.9 Å. Take $n = 3 \times 10^{25} \text{ molecules m}^{-3}$.

4. The coefficient of viscosity of a gas is $16.6 \times 10^{-6} \text{ N s m}^{-2}$. Calculate the diameter of the gas molecule at STP, when average molecular velocity $\bar{v} = 4.5 \times 10^2 \text{ m s}^{-1}$; number density $= 2.7 \times 10^{25} \text{ molecules m}^{-3}$, and molecular weight of nitrogen $= 28$. Take Avogadro's number $= 6.023 \times 10^{23} \text{ mol}^{-1}$.
5. Calculate the thermal conductivity of air using the following data:
 $\bar{v} = 470 \text{ m s}^{-1}$, $\rho = 1.29 \text{ kg m}^{-3}$, $\lambda = 5.6 \times 10^{-8} \text{ m}$, $M = 29$, $\gamma = 1.4$, and $R = 8.31 \text{ kJ mol}^{-1} \text{ K}^{-1}$.

3.6 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. We have

$$\sigma = 4\pi r^2 = 4\pi(1.8 \times 10^{-10} \text{ m})^2 = 40.7 \times 10^{-20} \text{ m}^2$$

$$P_c = n\sigma \bar{v} = (3 \times 10^{25} \text{ m}^{-3}) \times (40.7 \times 10^{-20} \text{ m}^2) \times (450 \text{ m s}^{-1}) \\ = 5.49 \times 10^9 \text{ s}^{-1}$$

$$\tau = P_c^{-1} = 1.8 \times 10^{-10} \text{ s}$$

and
$$\lambda = \frac{1}{(3 \times 10^{25} \text{ m}^{-3}) \times (40.7 \times 10^{-20} \text{ m}^2)} = 82 \text{ nm}$$

2. From Eq. (3.7), we recall that

$$\lambda = \frac{k_B T}{\rho \sigma}$$

Here $\sigma = 4\pi r^2 = 4 \times 3.14 \times (1.88 \times 10^{-10} \text{ m})^2 = 44.42 \times 10^{-20} \text{ m}^2$

On substituting the given values of Boltzmann constant and temperature (in kelvin), we get

$$\rho = \frac{k_B T}{\lambda_M \sigma} = \frac{(1.38 \times 10^{-23} \text{ JK}^{-1}) \times (288 \text{ K})}{(6.28 \times 10^{-8} \text{ m}) \times (44.4 \times 10^{-20} \text{ m}^2)} \\ = 1.43 \times 10^5 \text{ Nm}^{-2}$$

For a Maxwellian gas, the value for ρ will be lower by a factor of $\frac{1}{\sqrt{2}}$.

Hence, its magnitude will be

$$\rho = 1.01 \times 10^5 \text{ Nm}^{-2}.$$

The number of collisions suffered by a molecule per metre of the path

$$N_s = \frac{1}{6.28 \times 10^{-8} \text{ m}} = 16 \times 10^6 \text{ m}^{-1}.$$

3. From Eq. (3.10) we recall that the probability of a molecule travelling a distance x without making a collision is given by $f(x) = \exp\left(-\frac{x}{\lambda}\right)$, where λ is a function of p and T . Here $x = 10.4 \times 10^{-8} \text{ m}$ and

$$\lambda(p, T) = 5.2 \times 10^{-8} \text{ m}$$

i) Using Eq. (3.7) we can write $\lambda(p, 2T) = 2 \times \lambda(p, T) = 10.4 \times 10^{-8} \text{ m}$.

$$\therefore \text{Required probability} = e^{-1} = 0.37$$

ii) $\lambda(2p, 2T) = \lambda(p, T) = 5.2 \times 10^{-8} \text{ m}$

$$\therefore \text{Required probability } e^{-2} = 0.14$$

iii) $\lambda(3p, T) = \frac{1}{3} \lambda(p, T) = \frac{5.2}{3} \times 10^{-8} \text{ m} = 1.73 \times 10^{-8} \text{ m}$

$$\therefore \text{Required probability } e^{-6} = 2.48 \times 10^{-3}$$

$$4. \quad m = \frac{32}{6 \times 10^{26}} = 5.33 \times 10^{-26} \text{ kg}$$

From Eq. (3.13) we recall that

$$\eta = \frac{1}{3} \frac{m\bar{v}}{\pi d^2}$$

On re-arrangement, we can write

$$d^2 = \frac{m\bar{v}}{3\pi\eta}$$

On substituting the values of various physical quantities, we get

$$d^2 = \frac{(5.33 \times 10^{-26} \text{ kg}) \times (436 \text{ ms}^{-1})}{3\pi \times (19.6 \times 10^{-6} \text{ kg m}^{-1} \text{ s}^{-1})}$$

Hence,

$$d = \left(\frac{5.33 \times 436}{3\pi \times 19.6} \right)^{1/2} \times 10^{-10} \text{ m}$$

$$= 3.55 \times 10^{-10} \text{ m}$$

$$\text{and } r = 1.77 \times 10^{-10} \text{ m}$$

Terminal Questions

1. From Eq. (3.22), we recall that

$$D = \frac{0.376}{\sigma} \frac{(k_B T)^{3/2}}{p\sqrt{m}}$$

On substituting the given values, we get

$$\begin{aligned}
 D &= \frac{0.376}{(3.1417 \times 4) (1.37 \times 10^{-10} \text{ m})^2} \frac{[(1.38 \times 10^{-23} \text{ JK}^{-1}) \times (300 \text{ K})]^{3/2}}{(2.026 \times 10^5 \text{ Nm}^{-2}) (3.3 \times 10^{-27} \text{ kg})^{1/2}} \\
 &= \frac{0.376}{(23.59 \times 10^{-20} \text{ m}^2)} \frac{266.4 \times 10^{-33} \text{ J}^{3/2}}{(2.026 \times 10^5 \text{ Nm}^{-2}) (5.74 \times 10^{-14} \text{ kg}^{1/2})} \\
 &= 3.56 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}
 \end{aligned}$$

2. We have from Eq. (3.19)

$$K = \frac{\eta c_V}{M} = 0.376 \frac{\sqrt{m}}{\sigma} (k_B T)^{1/2} \frac{c_V}{M} = \frac{0.376}{\sigma} (k_B T)^{1/2} \frac{c_V}{\sqrt{M N_A}}$$

where we have used Eq. (3.15) for η and $m = M/N_A$.

Hence,

$$\begin{aligned}
 \sigma &= 4\pi r^2 = \frac{(0.376)(k_B T)^{1/2} c_V}{K \sqrt{M}} \\
 \text{or } r^2 &= \frac{(0.376)(k_B T)^{1/2} c_V}{4\pi K \sqrt{M}}
 \end{aligned}$$

On substituting the given values, we get

$$\begin{aligned}
 r^2 &= \frac{(0.376)(1.38 \times 10^{-23} \text{ JK}^{-1})^{1/2} \times (273 \text{ K})^{1/2} \times (29.1 \times 10^3 \text{ Jk mol}^{-1} \text{ K}^{-1})}{4\pi \times (23.7 \times 10^{-3} \text{ Jm}^{-1} \text{ s}^{-1} \text{ K}^{-1}) \times [(6.02 \times 10^{26} \text{ kmol}^{-1}) \times (28.02 \text{ kg})]^{1/2}} \\
 &= \frac{671.5 \times 10^{-9}}{3869.0 \times 10^{10}} = 1.74 \times 10^{-20} \text{ m}^2
 \end{aligned}$$

Hence $r = 1.32 \times 10^{-10} \text{ m}$

3. From Eq. (3.7) we recall that $\lambda = \frac{1}{n\sigma}$

Here $\sigma = \pi d^2 = \pi (2.9 \times 10^{-10})^2 \text{ m}^2 = 26.42 \times 10^{-20} \text{ m}^2$

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

Hence,

$$\begin{aligned}
 \lambda &= \frac{1}{(3 \times 10^{25} \text{ m}^{-3}) \times (26.42 \times 10^{-20} \text{ m}^2)} \\
 &= 1.26 \times 10^{-7} \text{ m}
 \end{aligned}$$

4. $m = \frac{28 \text{ kg kmol}^{-1}}{6.023 \times 10^{26} \text{ kmol}^{-1}}$

$$= 4.649 \times 10^{-26} \text{ kg}$$

$$\eta = 16.6 \times 10^{-6} \text{ N s m}^{-2}$$

$$\bar{v} = 4.5 \times 10^2 \text{ m s}^{-1}$$

From Eq. (3.13), we can write

$$\lambda = \frac{3\eta}{m\bar{v}}$$

On inserting the values of various physical quantities, we get

$$\lambda = \frac{3 \times (16.6 \times 10^{-6} \text{ N s m}^{-2})}{(4.65 \times 10^{-26} \text{ kg}) \times (2.7 \times 10^{25} \text{ m}^{-3}) \times (4.5 \times 10^2 \text{ m s}^{-1})} = 8.85 \times 10^{-8} \text{ m}$$

Now, the diameter of a gas molecule can be determined by using the

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

and rewriting it as

$$d = \left[\frac{1}{\sqrt{2} \pi n \lambda} \right]^{1/2}$$

On substituting the values of n and λ , we get

$$d = \left(\frac{1}{1.414 \times 3.14 \times (2.7 \times 10^{25} \text{ m}^{-3}) \times (8.85 \times 10^{-8} \text{ m})} \right)^{1/2}$$

$$= 3.07 \times 10^{-10} \text{ m}$$

and $r = 1.53 \times 10^{-10} \text{ m}$

Note that the values of radius calculated in TQ 2 and TQ 4 are slightly different. These deviations point to limitations of theory, or values of physical quantities used in two calculations.

5. Using Eq. (3.17), we can write

$$K = \frac{f}{6} n \bar{v} \lambda k_B$$

But we know that $k_B = \frac{R}{N_A}$, therefore we can rewrite the above

expression as

$$K = \frac{f}{6} n \bar{v} \lambda \frac{R}{N_A} \quad (i)$$

You will recall that molar heat capacity

$$c_v = \frac{f}{2}R \quad (\text{ii})$$

Substituting the value of c_v in Eq. (i), we get

$$\begin{aligned} K &= \frac{c_v}{3} \left(\frac{n}{N_A} \right) \bar{v} \lambda \\ &= \frac{1}{3} \rho \frac{c_v}{M} \bar{v} \lambda \end{aligned} \quad (\text{iii})$$

Since air is primarily a mixture of two diatomic gases (N_2 and O_2),

$$\begin{aligned} c_v &= \frac{5}{2}R = \frac{5}{2} \times 8.31 \times 10^3 \text{ J kmol}^{-1} \text{ K}^{-1} \\ &= \frac{41.55}{2} = 20.78 \times 10^3 \text{ J kmol}^{-1} \text{ K}^{-1} \end{aligned}$$

Now substituting the values of various physical quantities in Eq. (iii), we get the required result:

$$\begin{aligned} K &= \frac{1}{3} \times \frac{(1.29 \text{ kg m}^{-3}) \times (20.78 \times 10^3 \text{ J kmol}^{-1} \text{ K}^{-1}) \times (470 \text{ ms}^{-1}) \times (5.6 \times 10^{-8} \text{ m})}{29 \text{ kg kmol}^{-1}} \\ &= 8.1 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1} \end{aligned}$$