# Derivation of Kinetic Gas Equation

The kinetic gas equation may be derived by the following steps :

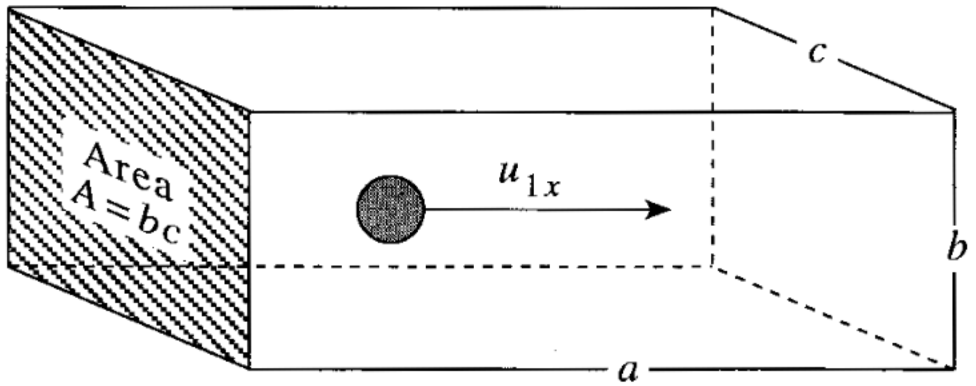


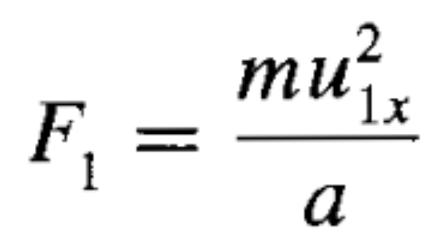
**FIGURE 25.1**
A molecule with its $x$-component of velocity equal to $u_{1x}$ moving perpendicular to one face of a rectangular parallelepiped of lengths $a$, $b$, and $c$.

The rate of change of momentum due to collisions with the right-hand wall is

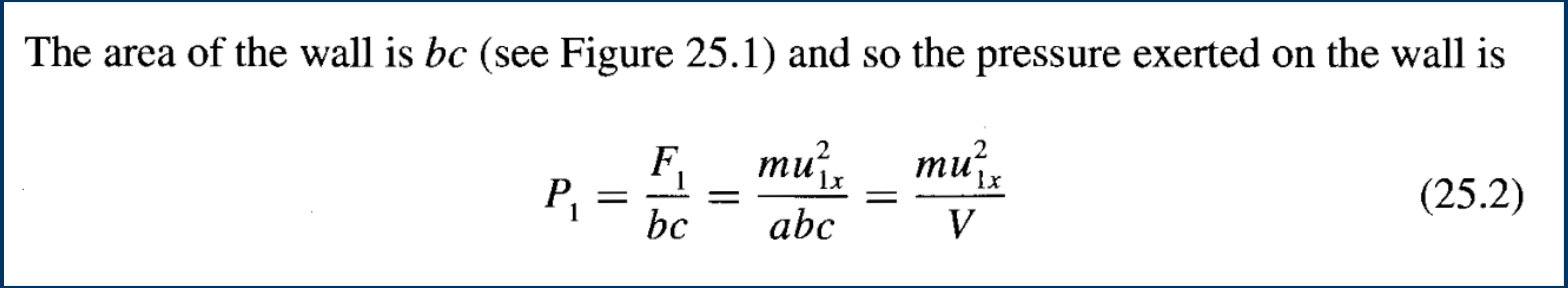
$$\frac{\Delta(mu_{1x})}{\Delta t} = \frac{2mu_{1x}}{2a/u_{1x}} = \frac{mu_{1x}^2}{a} \qquad (25.1)$$

# Derivation of Kinetic Gas Equation

The force that molecule-1 exerts on the right-hand wall is

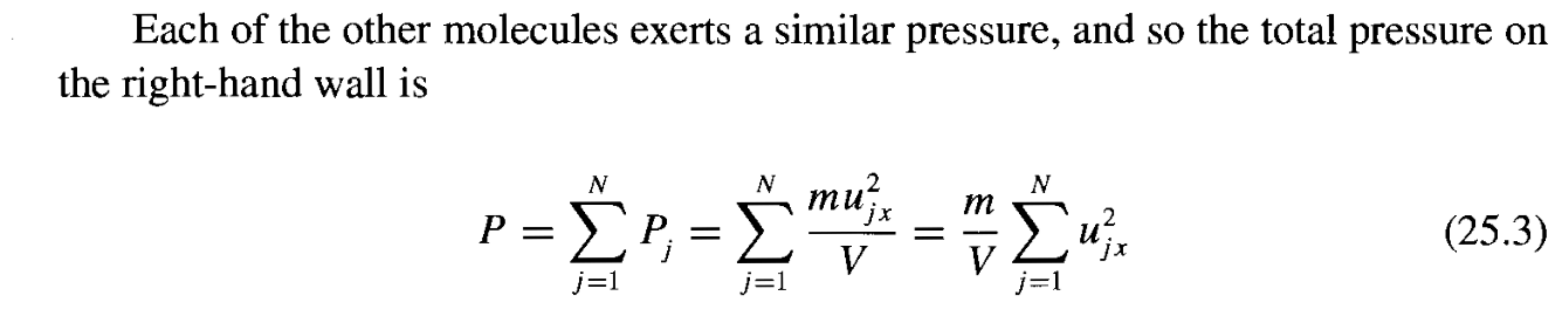


$$F_1 = \frac{mu_{1x}^2}{a}$$



The area of the wall is *bc* (see Figure 25.1) and so the pressure exerted on the wall is

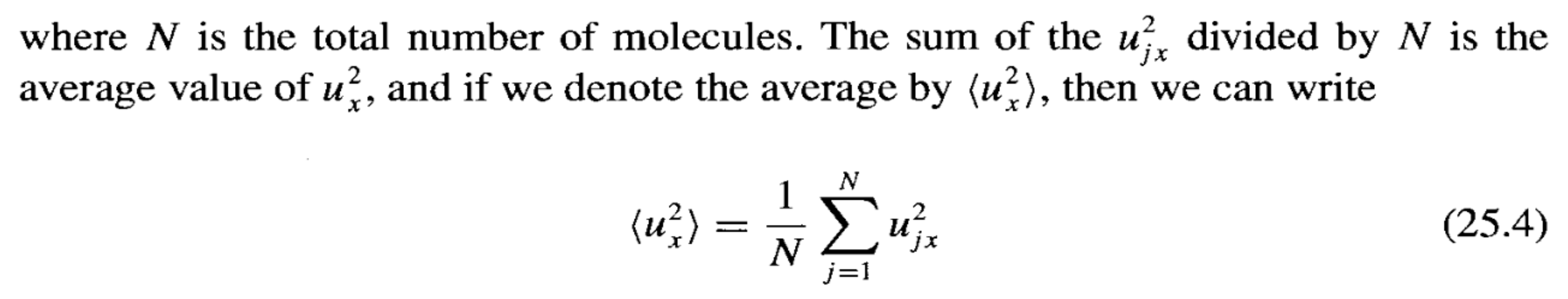
$$P_1 = \frac{F_1}{bc} = \frac{mu_{1x}^2}{abc} = \frac{mu_{1x}^2}{V} \tag{25.2}$$



Each of the other molecules exerts a similar pressure, and so the total pressure on the right-hand wall is

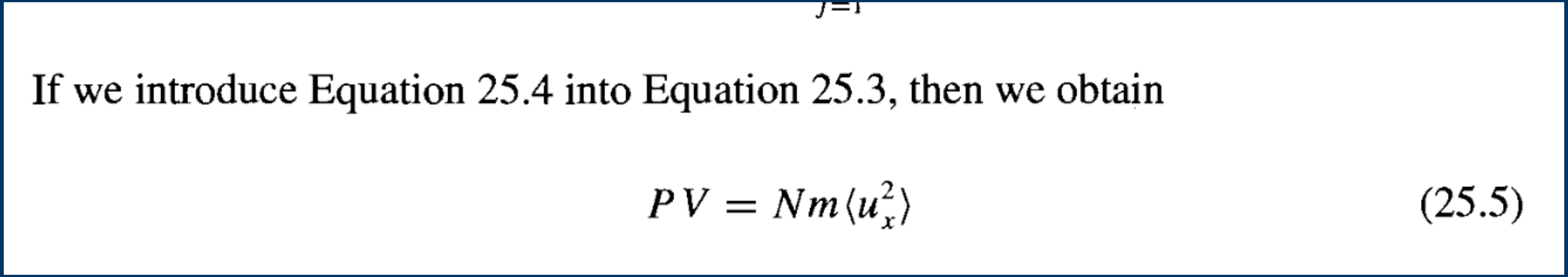
$$P = \sum_{j=1}^{N} P_j = \sum_{j=1}^{N} \frac{mu_{jx}^2}{V} = \frac{m}{V} \sum_{j=1}^{N} u_{jx}^2 \tag{25.3}$$

# Derivation of Kinetic Gas Equation



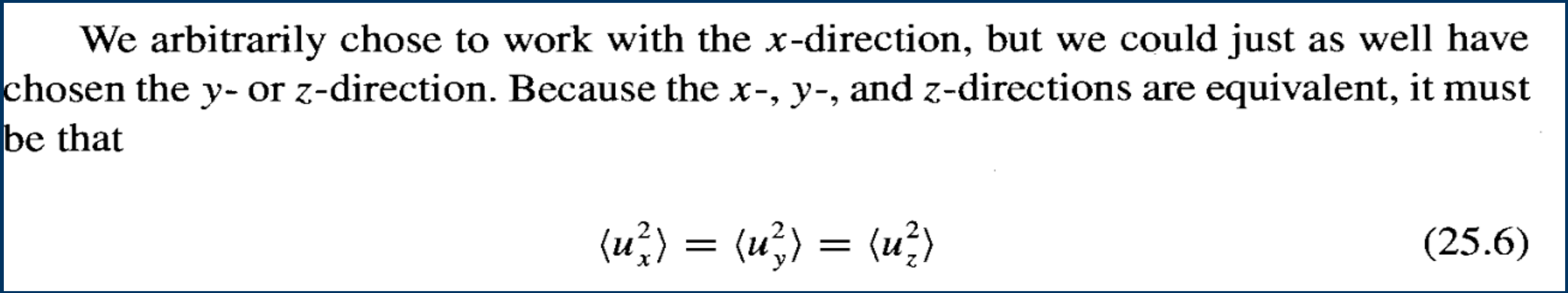
where $N$ is the total number of molecules. The sum of the $u_{jx}^2$ divided by $N$ is the average value of $u_x^2$, and if we denote the average by $\langle u_x^2 \rangle$, then we can write

$$\langle u_x^2 \rangle = \frac{1}{N} \sum_{j=1}^{N} u_{jx}^2 \qquad (25.4)$$



If we introduce Equation 25.4 into Equation 25.3, then we obtain

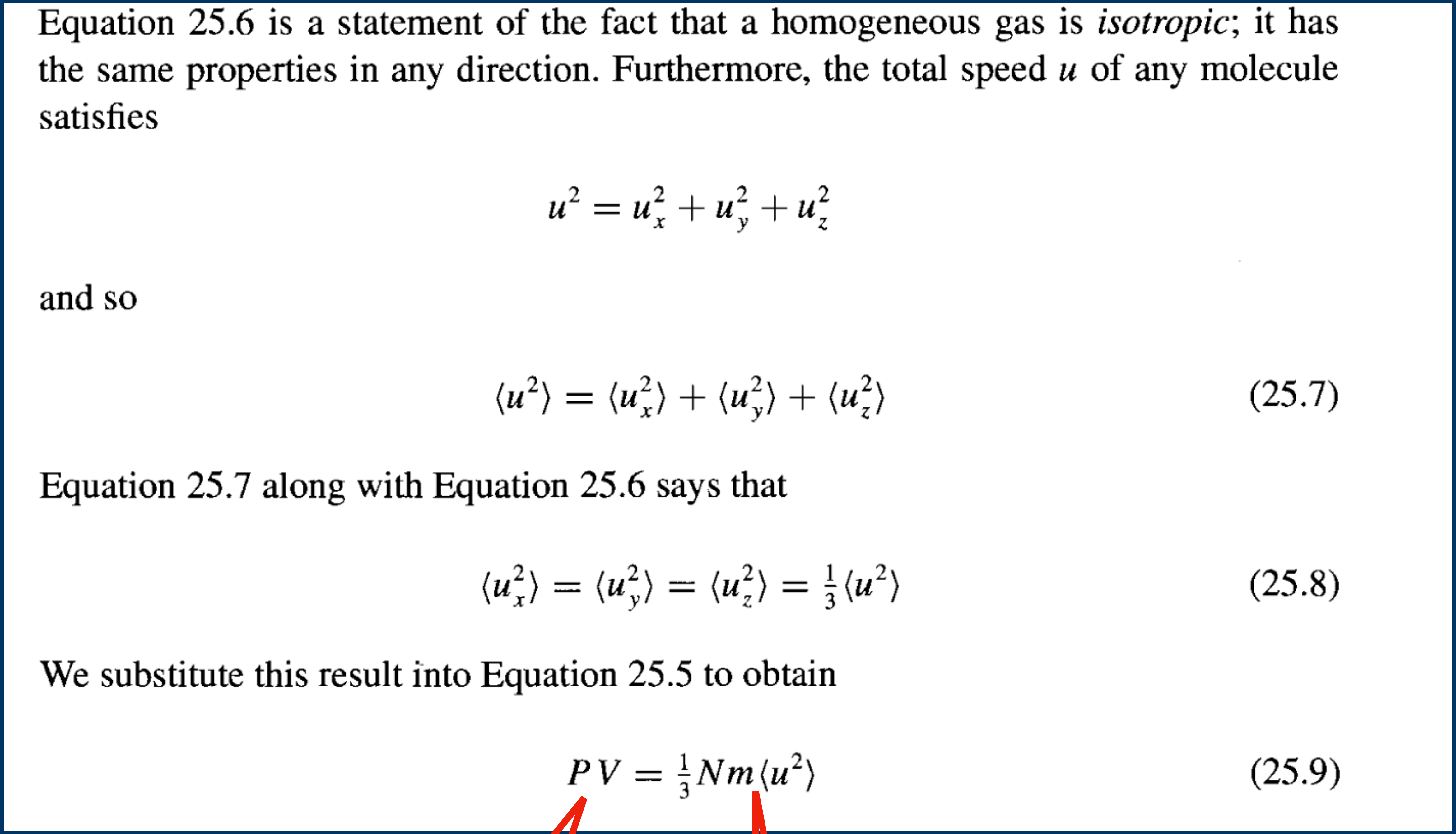
$$PV = Nm\langle u_x^2 \rangle \qquad (25.5)$$



We arbitrarily chose to work with the $x$-direction, but we could just as well have chosen the $y$- or $z$-direction. Because the $x$-, $y$-, and $z$-directions are equivalent, it must be that

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle \qquad (25.6)$$

# Derivation of Kinetic Gas Equation



Equation 25.6 is a statement of the fact that a homogeneous gas is *isotropic*; it has the same properties in any direction. Furthermore, the total speed $u$ of any molecule satisfies

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

and so

$$\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle \tag{25.7}$$

Equation 25.7 along with Equation 25.6 says that

$$\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle = \tfrac{1}{3}\langle u^2 \rangle \tag{25.8}$$

We substitute this result into Equation 25.5 to obtain

$$PV = \tfrac{1}{3} N m \langle u^2 \rangle \tag{25.9}$$

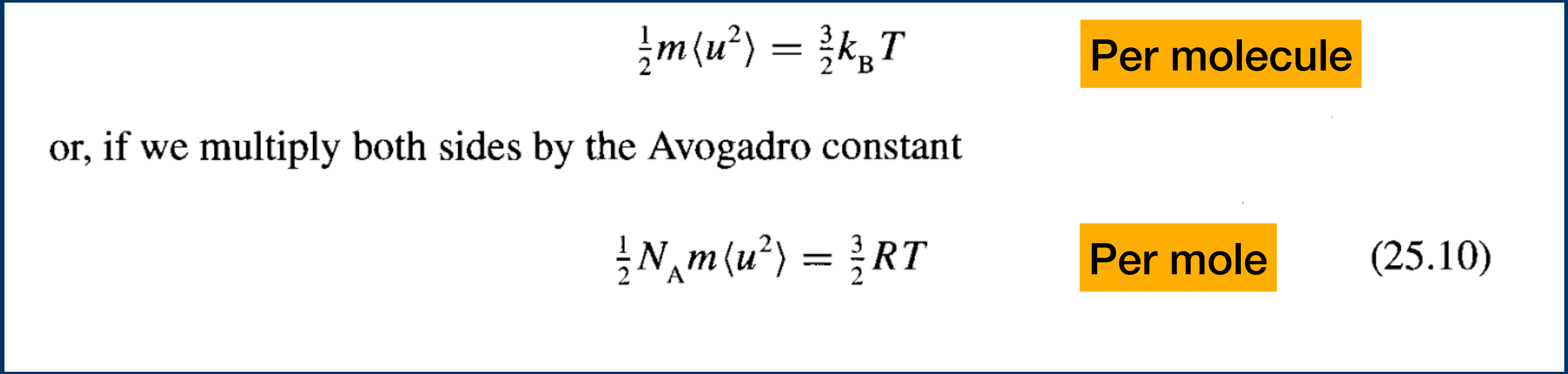
Macroscopic Property

Molecular Property (mu2)

This is the fundamental equation of the kinetic molecular theory of gases

# Derivation of Kinetic Gas Equation

The average translational (kinetic) energy of an ideal gas is



$$\tfrac{1}{2}m\langle u^2\rangle = \tfrac{3}{2}k_BT$$

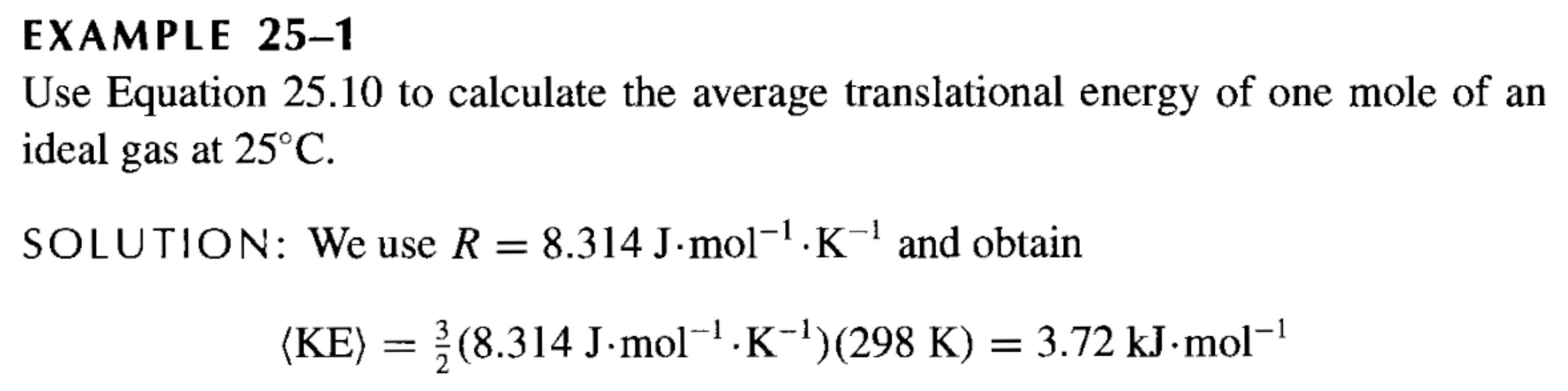
Per molecule

or, if we multiply both sides by the Avogadro constant

$$\tfrac{1}{2}N_Am\langle u^2\rangle = \tfrac{3}{2}RT \qquad (25.10)$$

Per mole

The Average Translational Kinetic Energy of the Molecules in a Gas Is Directly Proportional to the Kelvin Temperature



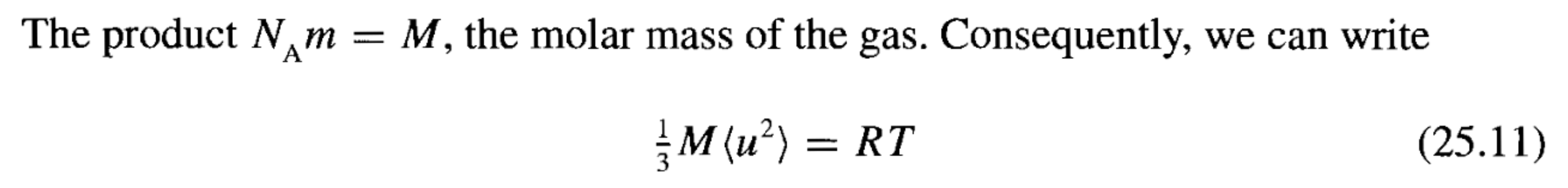
**EXAMPLE 25–1**

Use Equation 25.10 to calculate the average translational energy of one mole of an ideal gas at 25°C.

SOLUTION: We use $R = 8.314\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ and obtain

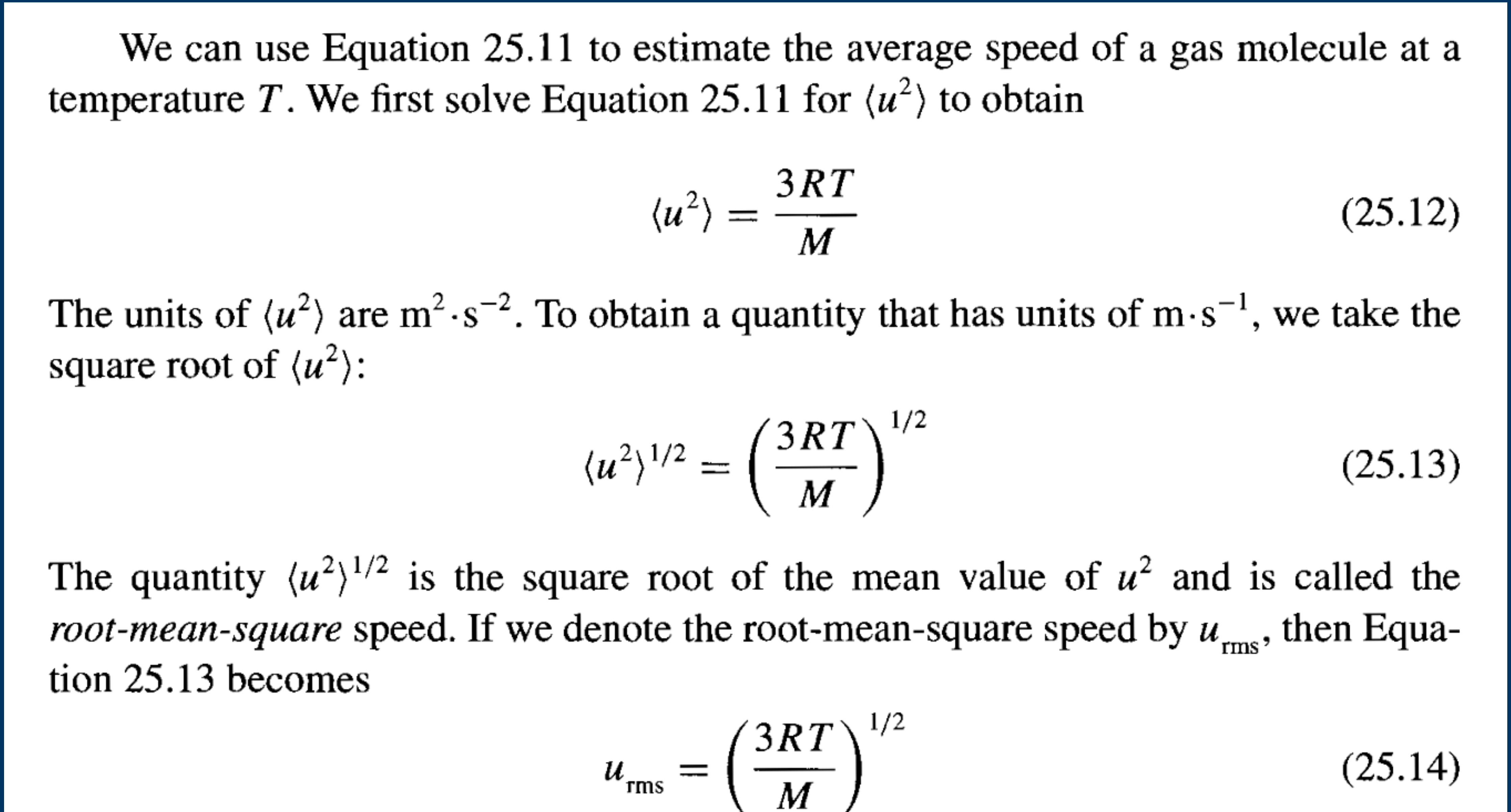
$$\langle \mathrm{KE}\rangle = \tfrac{3}{2}(8.314\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}})(298\ \mathrm{K}) = 3.72\ \mathrm{kJ\cdot mol^{-1}}$$

# Derivation of Kinetic Gas Equation



The product $N_A m = M$, the molar mass of the gas. Consequently, we can write

$$\tfrac{1}{3} M \langle u^2 \rangle = RT \tag{25.11}$$



We can use Equation 25.11 to estimate the average speed of a gas molecule at a temperature $T$. We first solve Equation 25.11 for $\langle u^2 \rangle$ to obtain

$$\langle u^2 \rangle = \frac{3RT}{M} \tag{25.12}$$

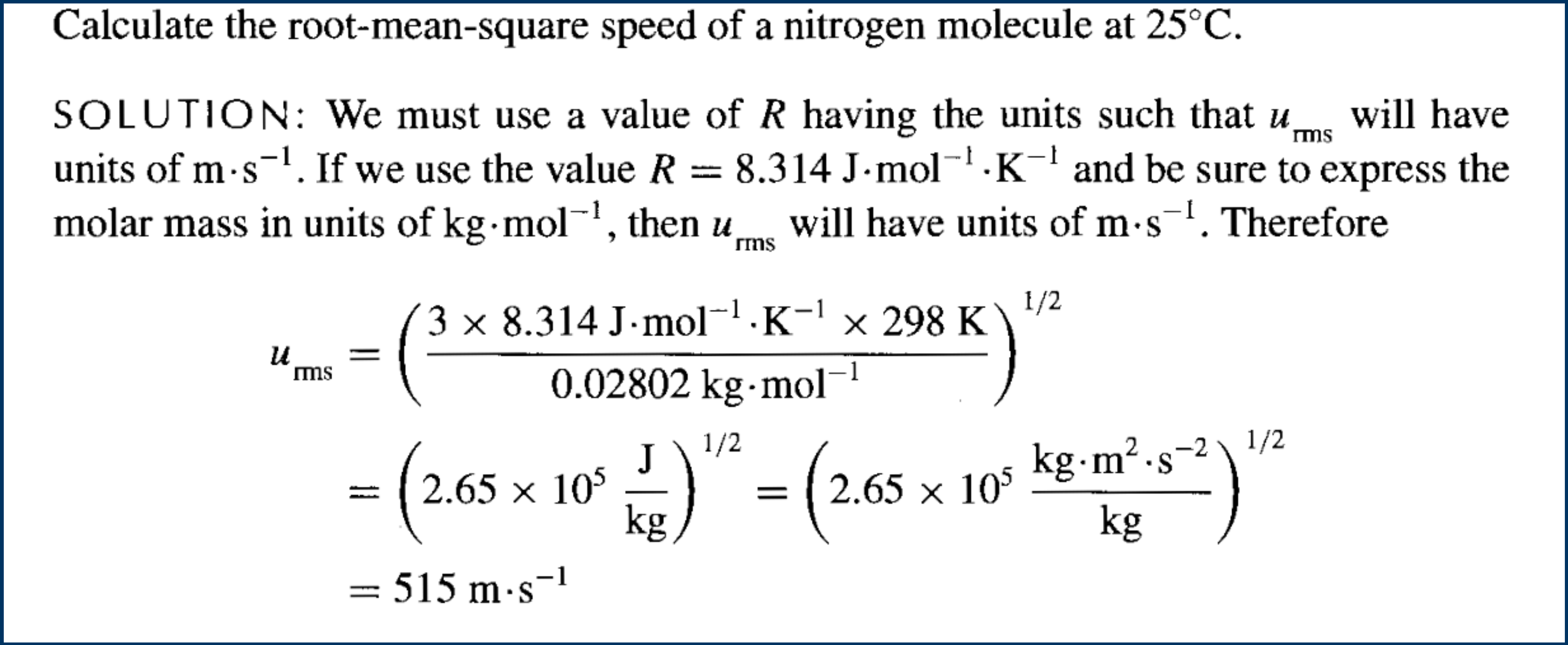
The units of $\langle u^2 \rangle$ are $\mathrm{m^2 \cdot s^{-2}}$. To obtain a quantity that has units of $\mathrm{m \cdot s^{-1}}$, we take the square root of $\langle u^2 \rangle$:

$$\langle u^2 \rangle^{1/2} = \left( \frac{3RT}{M} \right)^{1/2} \tag{25.13}$$

The quantity $\langle u^2 \rangle^{1/2}$ is the square root of the mean value of $u^2$ and is called the *root-mean-square* speed. If we denote the root-mean-square speed by $u_{\mathrm{rms}}$, then Equation 25.13 becomes

$$u_{\mathrm{rms}} = \left( \frac{3RT}{M} \right)^{1/2} \tag{25.14}$$

# Derivation of Kinetic Gas Equation

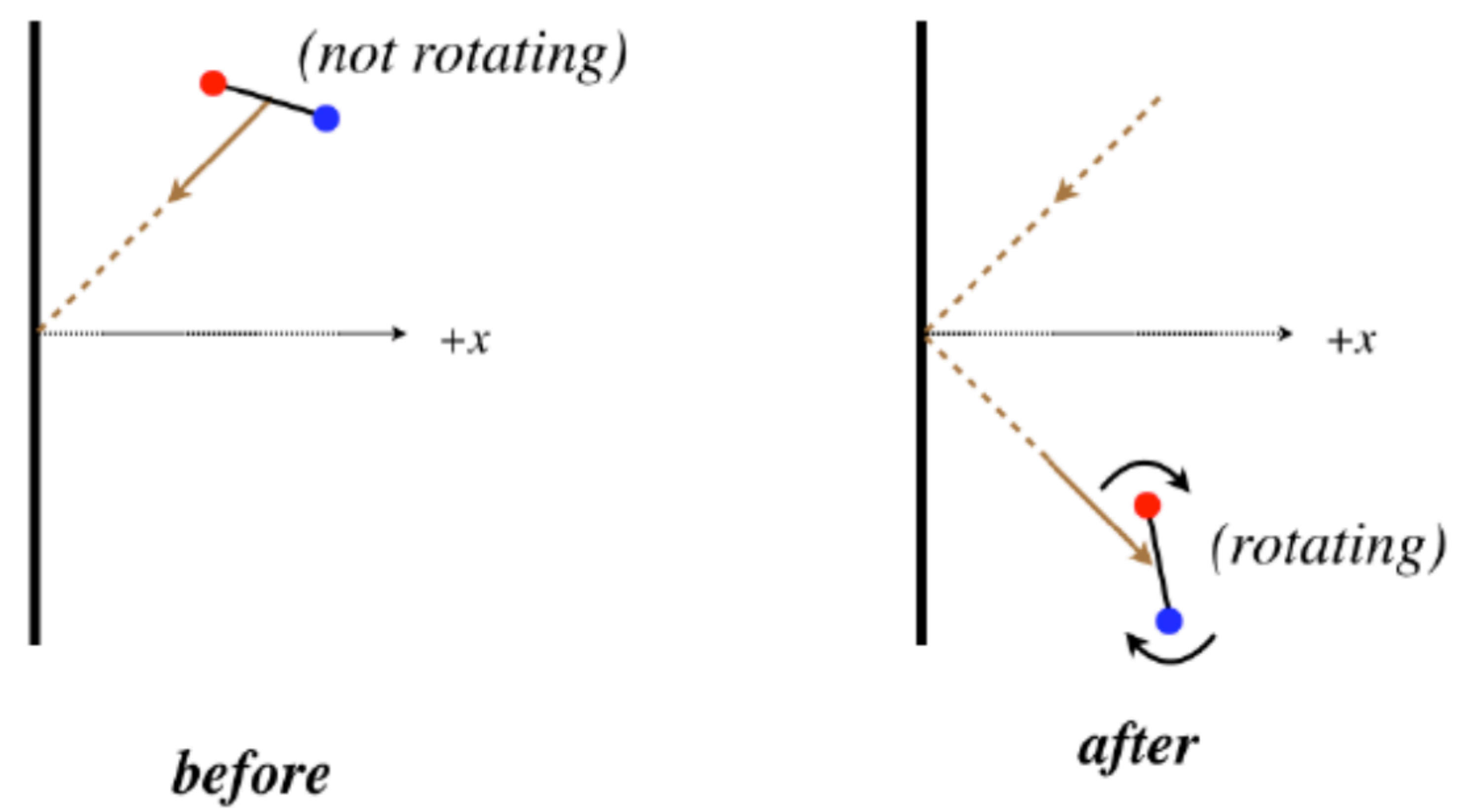


Calculate the root-mean-square speed of a nitrogen molecule at 25°C.

SOLUTION: We must use a value of $R$ having the units such that $u_{\mathrm{rms}}$ will have units of $\mathrm{m \cdot s^{-1}}$. If we use the value $R = 8.314\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ and be sure to express the molar mass in units of $\mathrm{kg \cdot mol^{-1}}$, then $u_{\mathrm{rms}}$ will have units of $\mathrm{m \cdot s^{-1}}$. Therefore

$$\begin{aligned} u_{\mathrm{rms}} &= \left( \frac{3 \times 8.314\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}} \times 298\ \mathrm{K}}{0.02802\ \mathrm{kg \cdot mol^{-1}}} \right)^{1/2} \\ &= \left( 2.65 \times 10^5\ \frac{\mathrm{J}}{\mathrm{kg}} \right)^{1/2} = \left( 2.65 \times 10^5\ \frac{\mathrm{kg \cdot m^2 \cdot s^{-2}}}{\mathrm{kg}} \right)^{1/2} \\ &= 515\ \mathrm{m \cdot s^{-1}} \end{aligned}$$

# Diatomic Molecule Bouncing Off a Container Wall



By assumption, the molecule cannot gain or lose energy when it strikes the wall, and we used that fact to show that the speed of the molecule stays constant, but if the molecule can now gain rotational kinetic energy upon striking the wall, then energy conservation requires that the kinetic energy that comes from its linear motion be reduced.

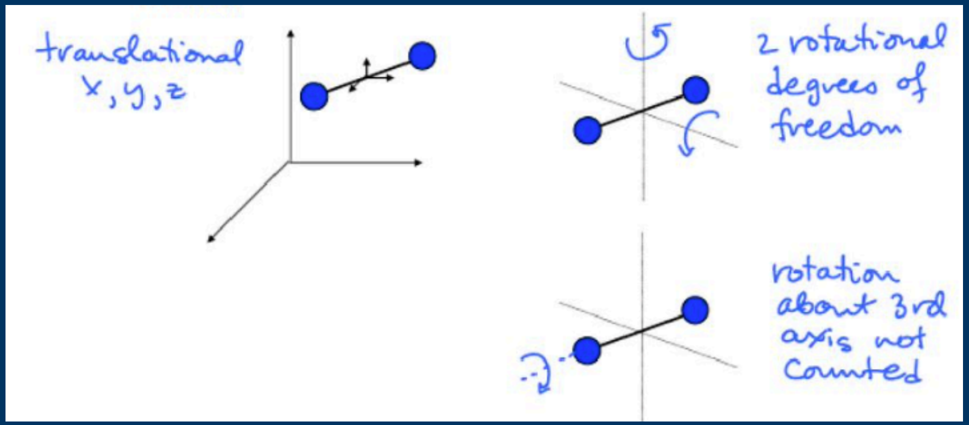
# Degrees of freedom (DF)

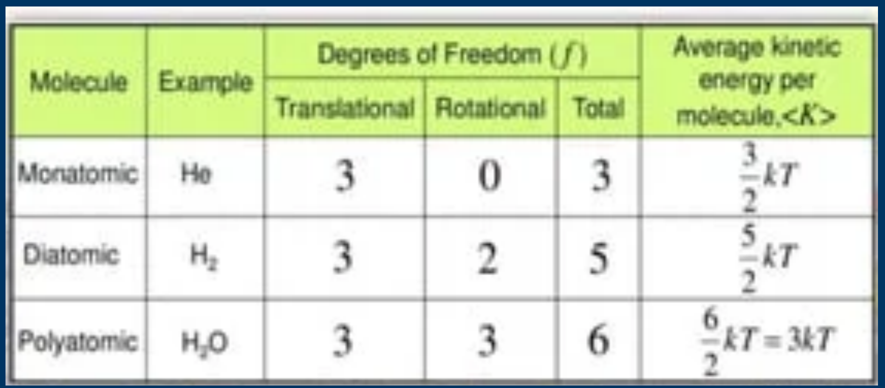
**The minimum number of independent coordinates, which can specify the configuration of the system completely.**

**For a single particle in plane two coordinates define its location, so it has two degrees of freedom.**

**Two particle in space have a combined 6 DF**

**If two particles in space are constrained to maintain a constant distance from each other, such as in the case of diatomic molecule, then the six coordinate must satisfy a single constraint equation defined by the distance formula. This reduce s the degree of Freedom of the system to five, because the distance formula can be used to solve for the remaining coordinate once the other five are specified.**



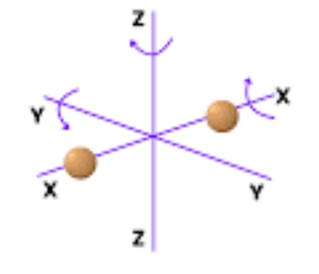


| Molecule | Example | Degrees of Freedom ($f$) | | | Average kinetic energy per molecule, $\langle K \rangle$ |
|---|---|---|---|---|---|
| | | Translational | Rotational | Total | |
| Monatomic | He | 3 | 0 | 3 | $\frac{3}{2}kT$ |
| Diatomic | $H_2$ | 3 | 2 | 5 | $\frac{5}{2}kT$ |
| Polyatomic | $H_2O$ | 3 | 3 | 6 | $\frac{6}{2}kT = 3kT$ |

# Law of equipartition of energy

The equipartition (or equal division) of energy theorem involves the concept that, **in thermal equilibrium, energy is shared equally among all of its various possible forms (or degree of freedom).**

$$\frac{1}{2}mv_{rms}^{2}=\frac{3}{2}K_bT$$



$$\frac{1}{2}mv_x^{2}$$

$$\frac{1}{2}mv_y^{2}$$

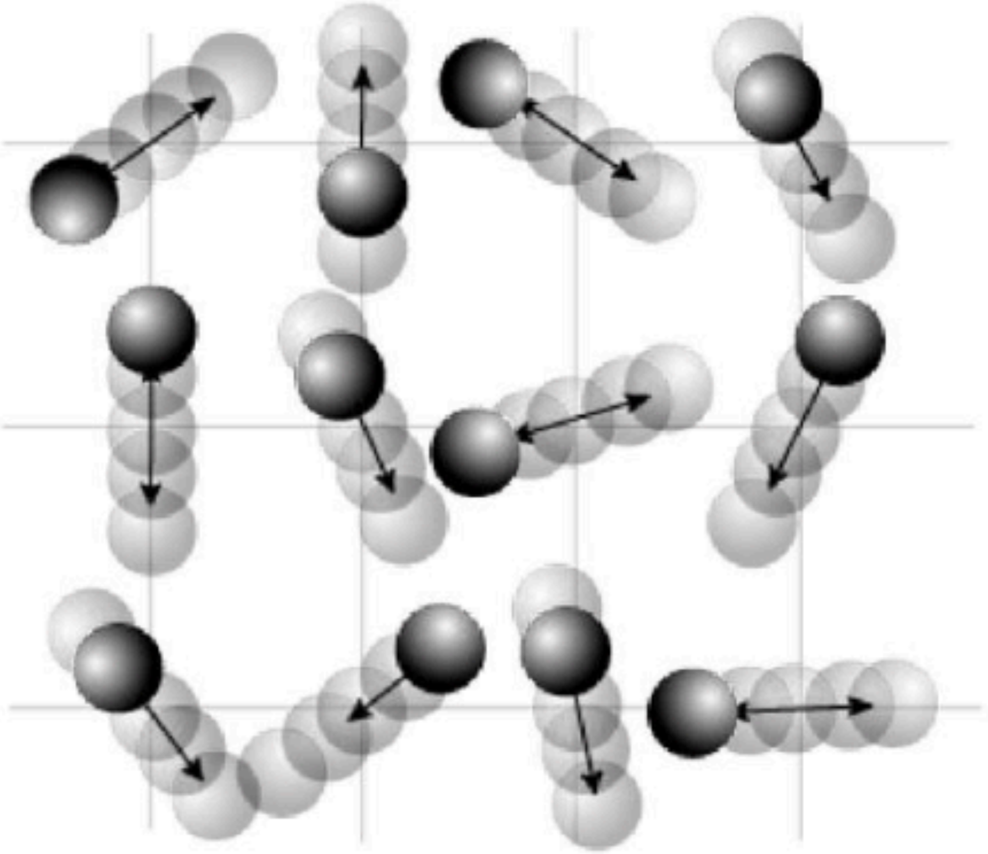
$$\frac{1}{2}mv_z^{2}$$

where Vrms is the root-mean-square velocity of the molecules,

*K*b is the Boltzmann constant

and T is the temperature of the gas.

# Application of equipartition of energy

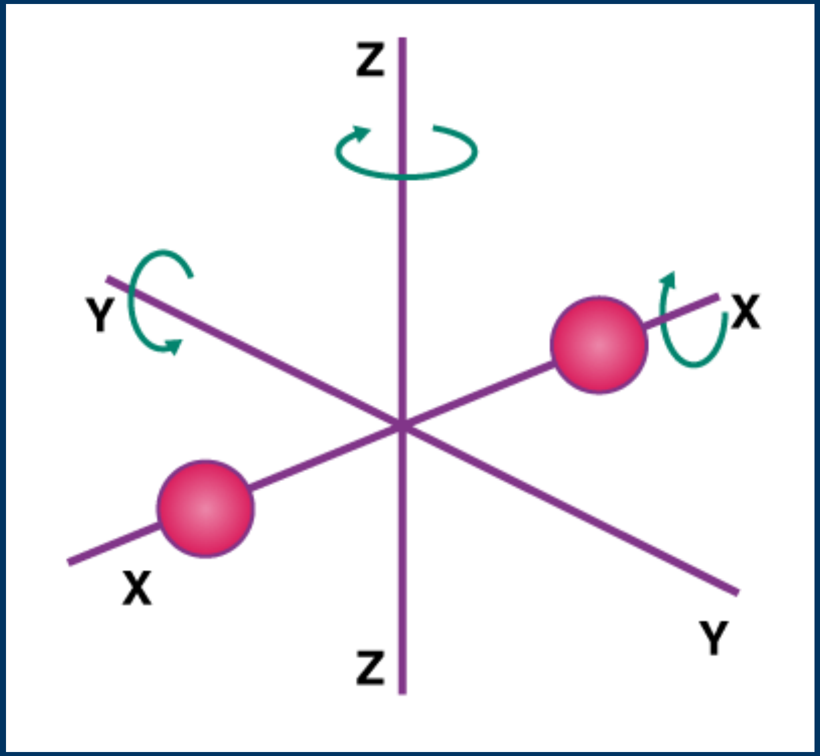


An important application of the equipartition theorem is to the specific heat capacity of a crystalline solid. Each atom in such a solid can oscillate in three independent directions, so the solid can be viewed as a system of $3N$ independent simple harmonic oscillators, where N denotes the number of atoms in the lattice. Since each harmonic oscillator has average energy $kT$, the average total energy of the solid is $3NkT$, and its heat capacity is $3Nk$.

# Law of equipartition of energy

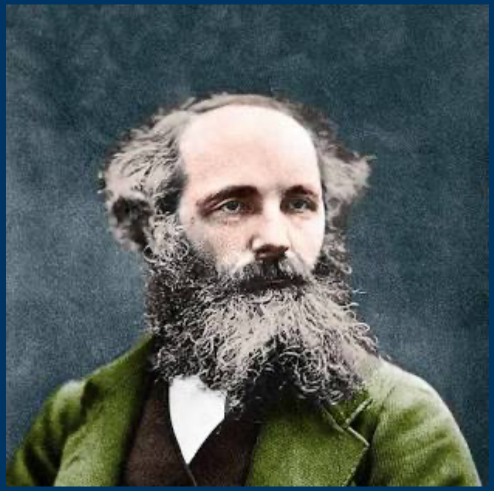
If a molecule is free to move in space, it needs three coordinates to specify its location, thus, it possesses **three translational degrees of freedom.** Similarly, if it is constrained to move in a plane, it **possesses two translational degrees of freedom** and if it is a straight line, it possesses **one translational degree of freedom**. In the case of a triatomic molecule, **the degree of freedom is 6 [ 3 rotational, 3 translational and ~~3 vibrational~~)**. And the kinetic energy of the per molecule of the gas is given as,

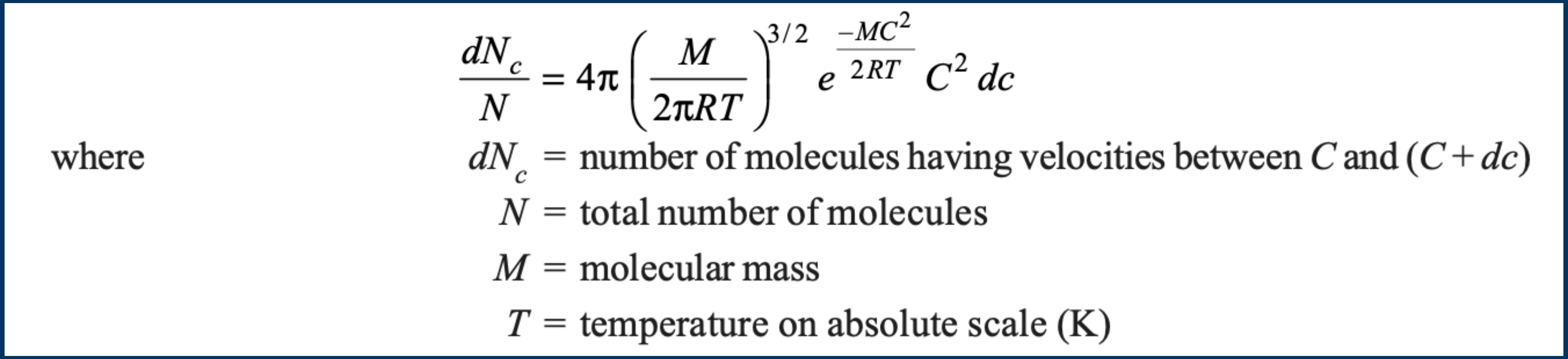
$$6\times N \times \frac{1}{2}K_bT = 3\times \frac{R}{N}NK_bT = 3\text{RT}$$



# Maxwell’s Law

While deriving Kinetic Gas Equation, it was assumed that all molecules in a gas have the same velocity. But it is not so. When any two molecules collide, one molecule transfers kinetic energy $(\frac{1}{2}mv^2)$to the other molecule





$$\frac{dN_c}{N} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} e^{\frac{-MC^2}{2RT}} C^2\,dc$$

where $dN_c$ = number of molecules having velocities between $C$ and $(C + dc)$

$N$ = total number of molecules

$M$ = molecular mass

$T$ = temperature on absolute scale (K)

# How the molecular velocity depends on Temperature

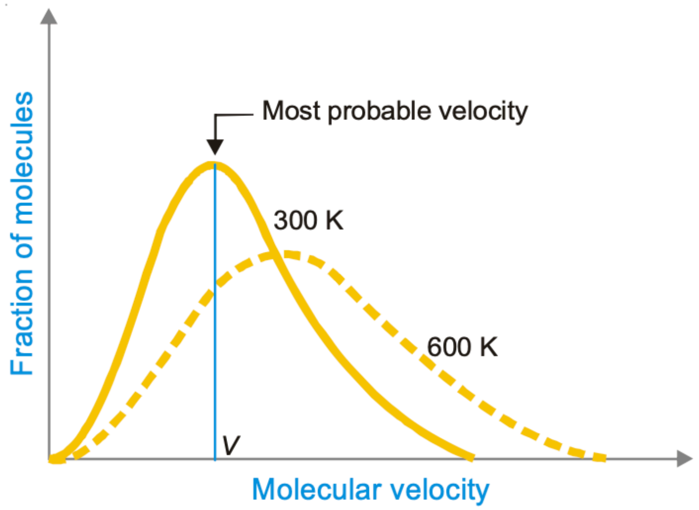
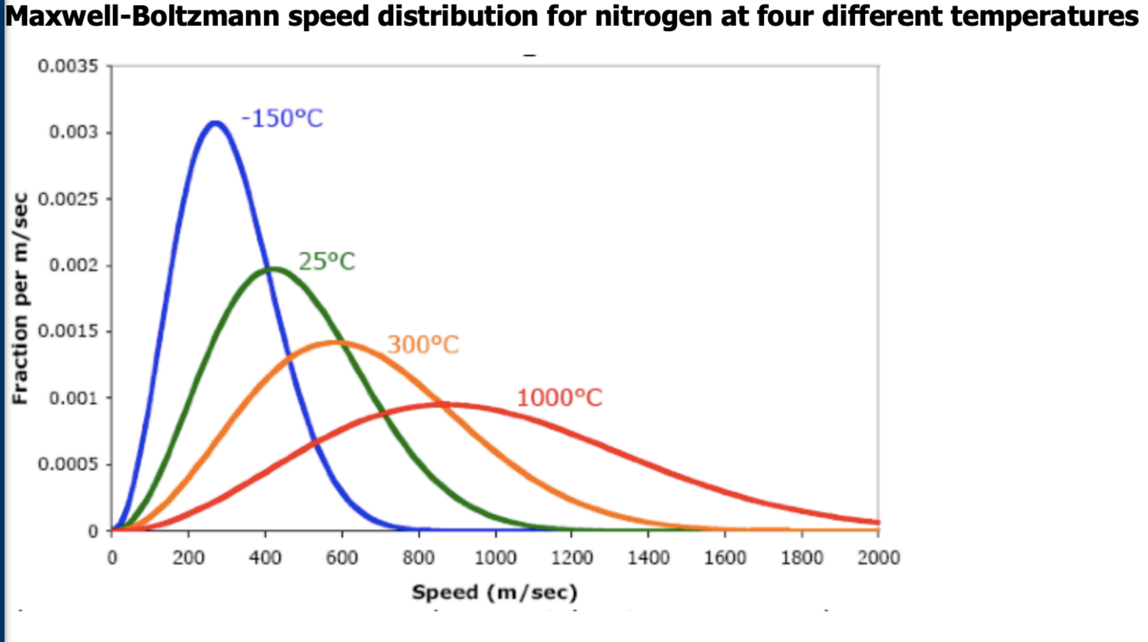
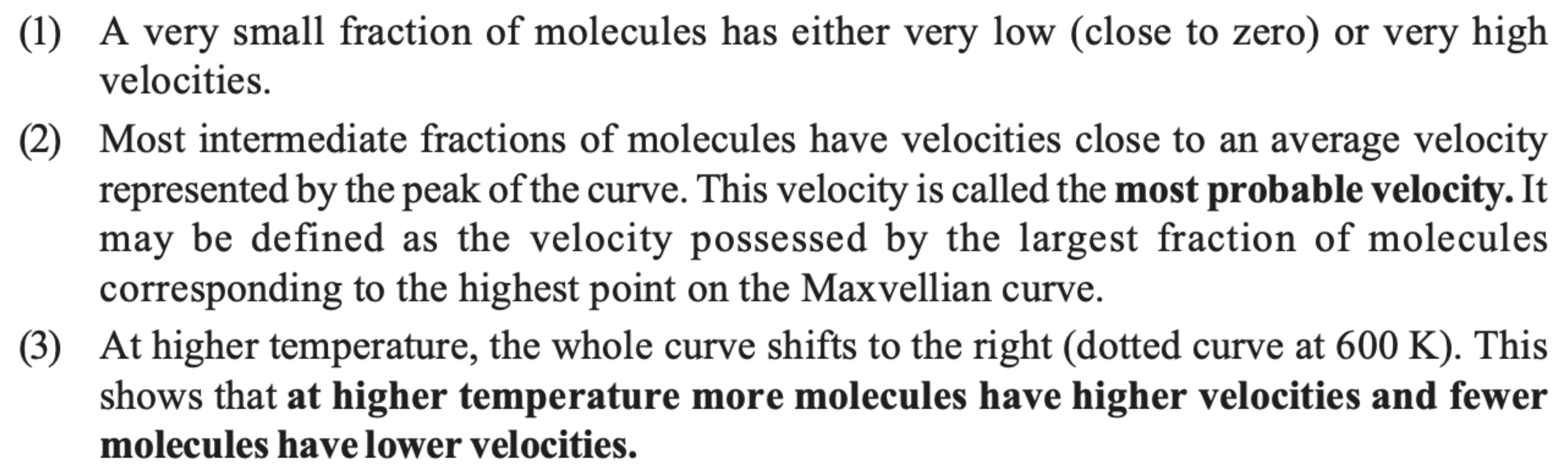


**Figure 10.20**

**Distribution of molecular velocities in nitrogen gas, $N_2$, at 300 K and 600 K.**


**Maxwell-Boltzmann speed distribution for nitrogen at four different temperatures**

# The characteristics of the Maxwell's plot:



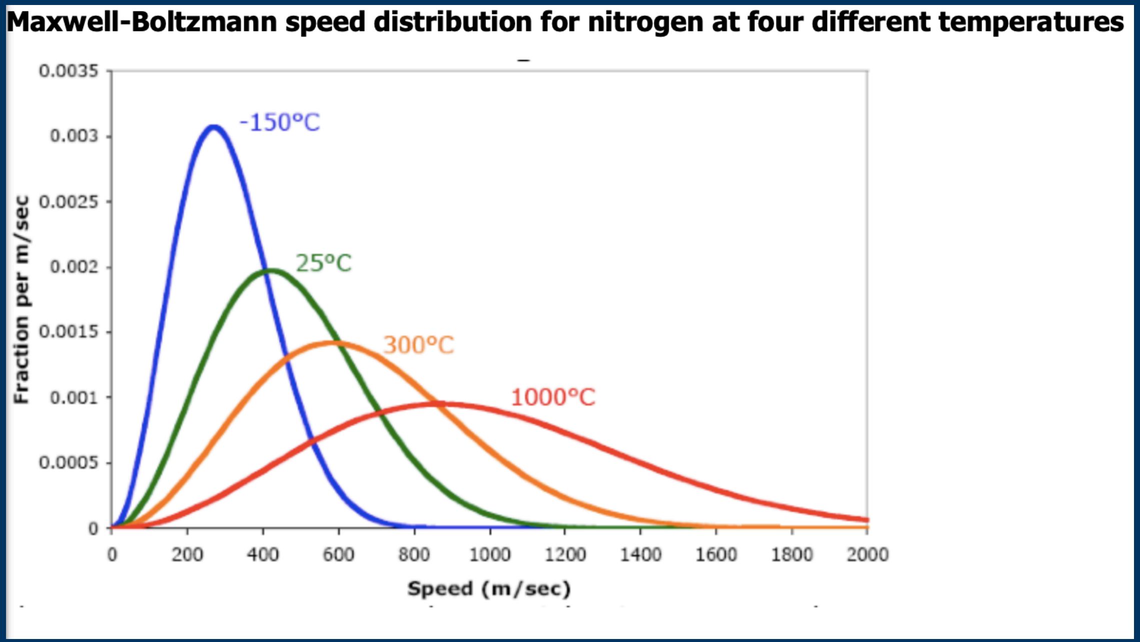
(1) A very small fraction of molecules has either very low (close to zero) or very high velocities.

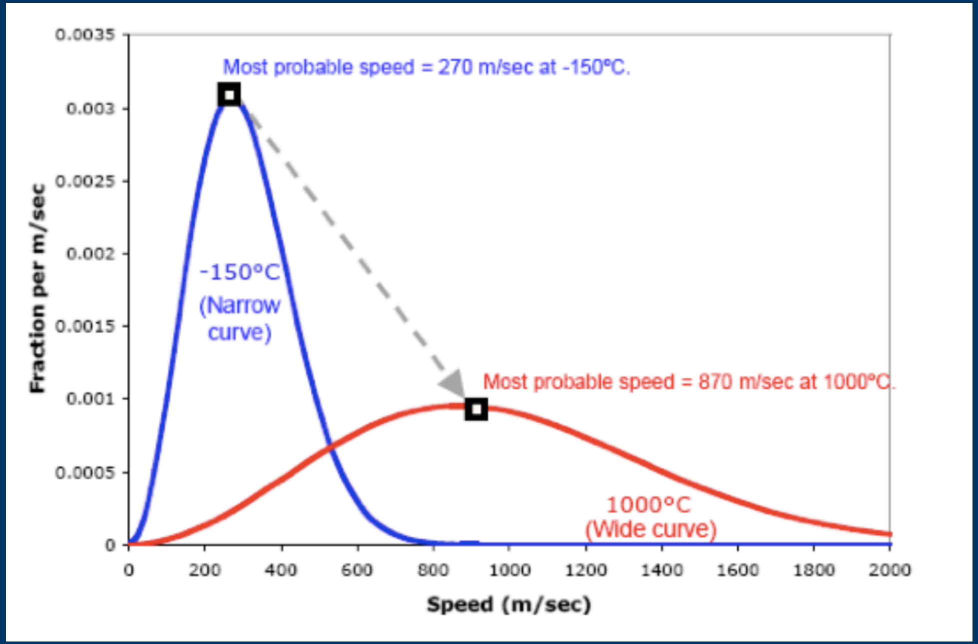
(2) Most intermediate fractions of molecules have velocities close to an average velocity represented by the peak of the curve. This velocity is called the **most probable velocity.** It may be defined as the velocity possessed by the largest fraction of molecules corresponding to the highest point on the Maxvellian curve.

(3) At higher temperature, the whole curve shifts to the right (dotted curve at 600 K). This shows that **at higher temperature more molecules have higher velocities and fewer molecules have lower velocities.**

# When we consider a gas at increasing temperature:

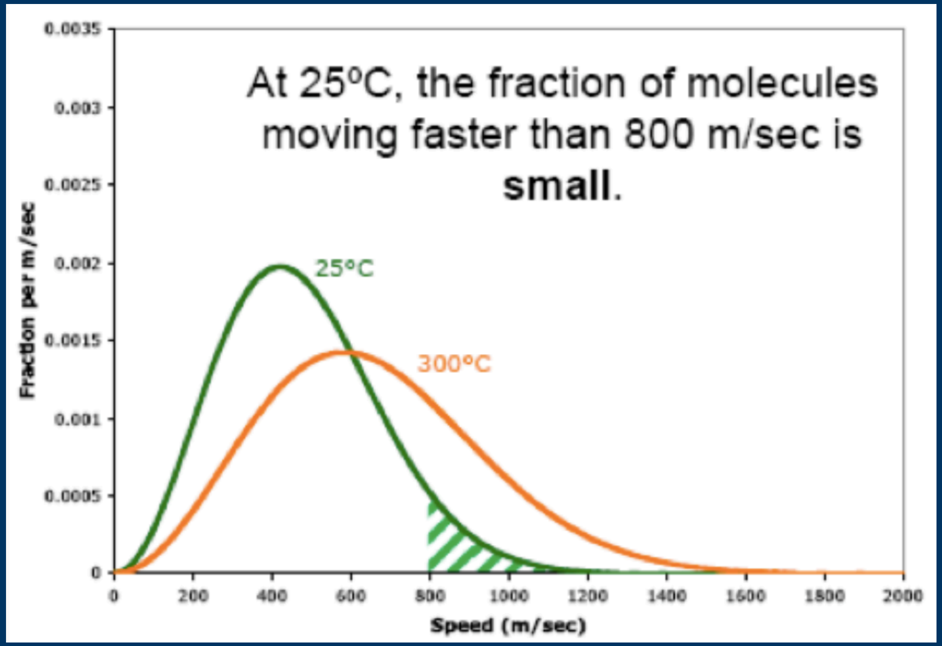
- The Maxwell-Boltzmann curve spreads and flattens out.
- The most probable speed increases (the peak shifts to the right).
- The fraction of fast-moving molecules increases.
- The fraction of slow-moving molecules decreases.

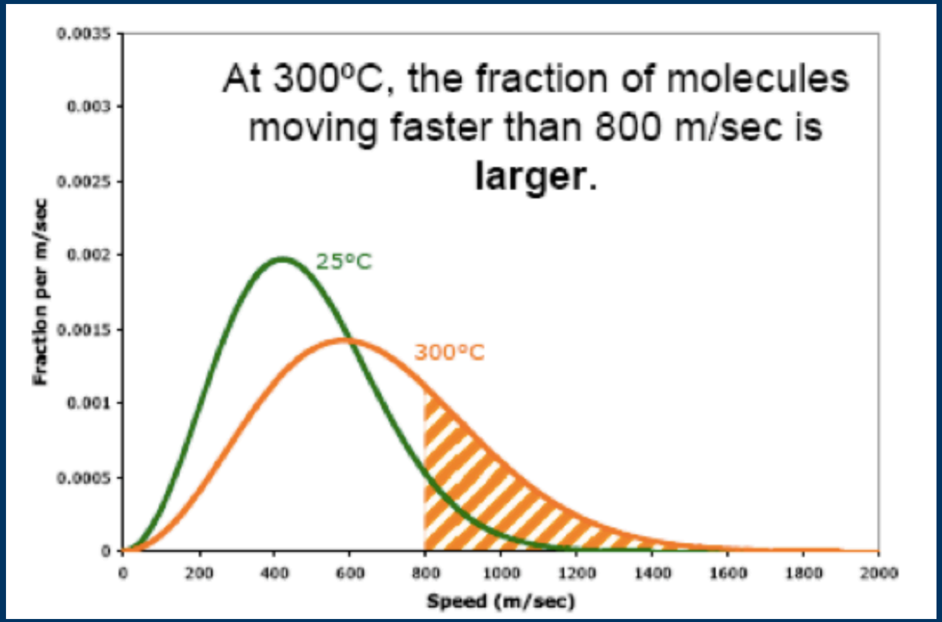

**Maxwell-Boltzmann speed distribution for nitrogen at four different temperatures**

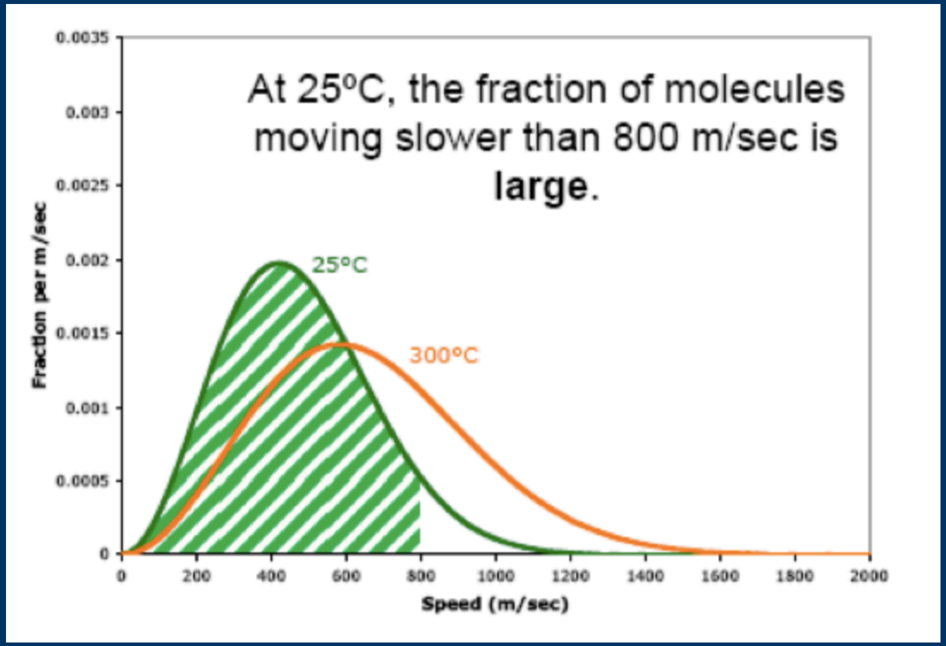


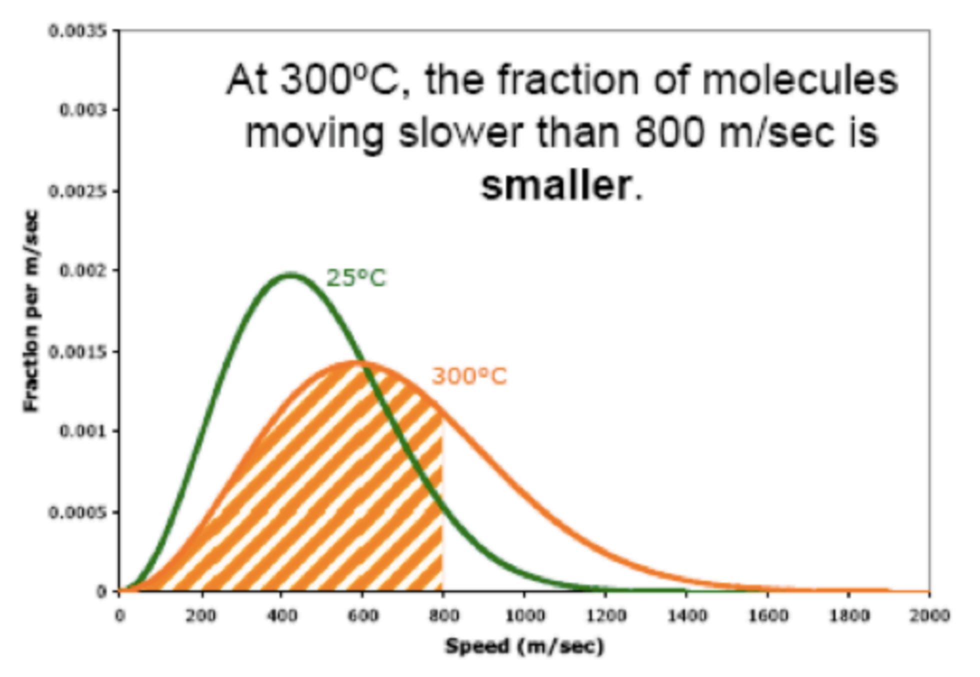
Observe that when the temperature goes up, the particles in a gas tend to move **faster**. As a result, the entire distribution shifts to the right, toward higher speeds. When we raise the temperature, the most probable speed increases (the highest point on the curve shifts to the right). In addition, the entire curve gets wider and lower: we have a wider range of speeds, but we have fewer molecules at the most probable speed

Also, when we raise the temperature, the fraction of molecules moving at **high** speeds **increases**. For example, when we raise the temperature from 25ºC to 300ºC, the fraction of molecules moving faster than 800 m/sec becomes larger.


At 25°C, the fraction of molecules moving faster than 800 m/sec is **small**.

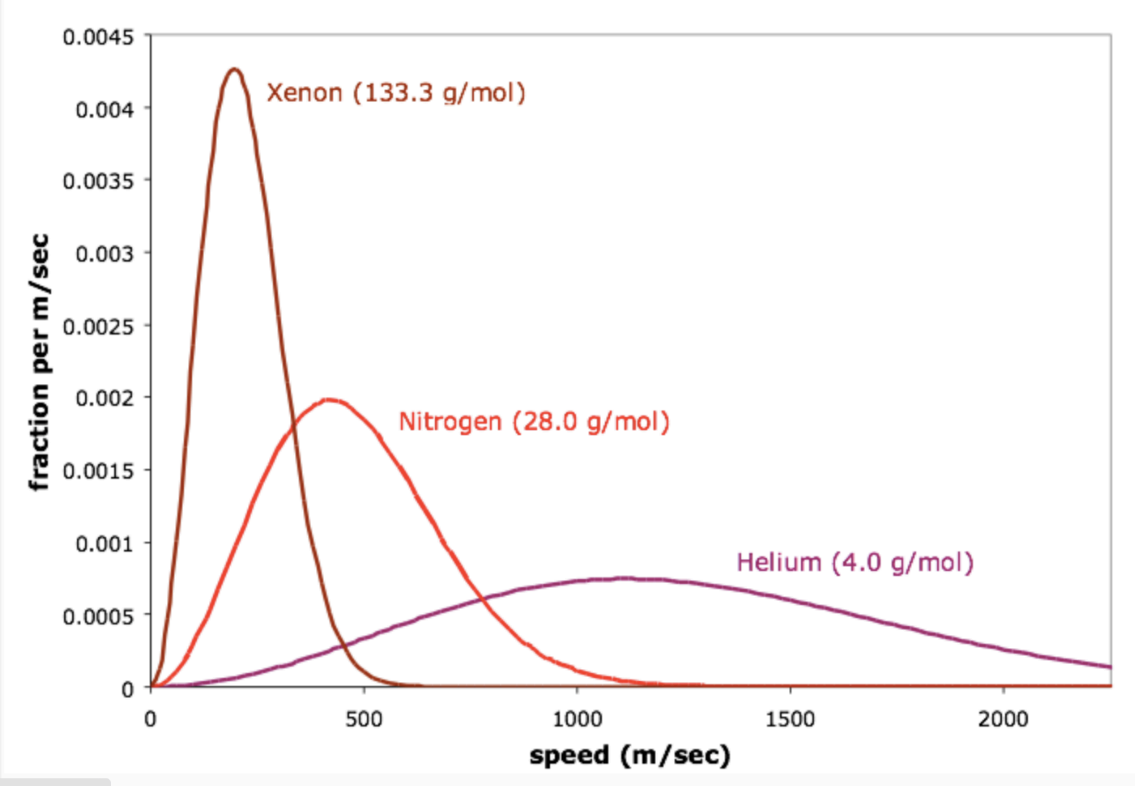

At 300°C, the fraction of molecules moving faster than 800 m/sec is **larger**.

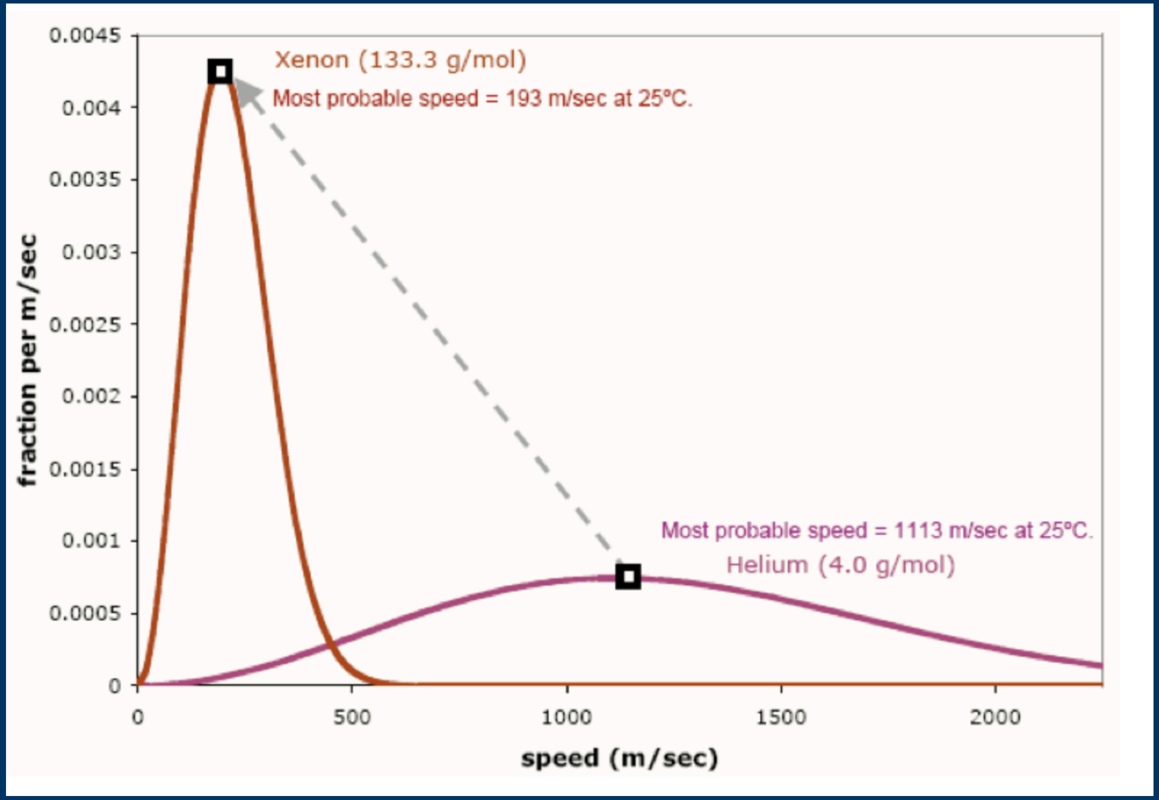

At 25°C, the fraction of molecules moving slower than 800 m/sec is **large**.


At 300°C, the fraction of molecules moving slower than 800 m/sec is **smaller**.

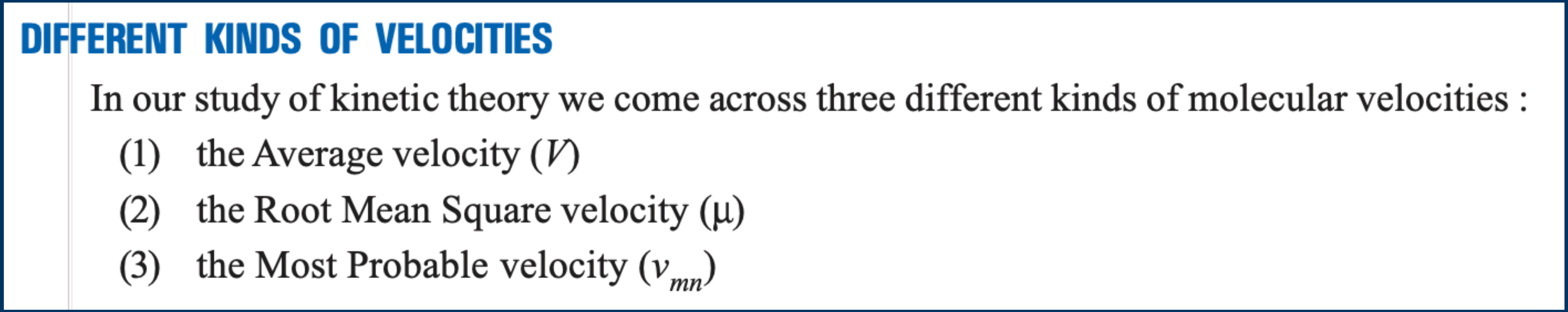
Likewise, when we raise the temperature, the fraction of molecules moving at **low** speeds **decreases**. For example, when we raise the temperature from 25ºC to 300ºC, the fraction of molecules moving slower than 800 m/sec becomes smaller.

# How molecular velocity depends on molar mass





Observe that the gas with the lowest molar mass (helium) has the highest molecular speeds, while the gas with the highest molar mass (xenon) has the lowest molecular speeds. When we increase the molar mass, the most probable speed decreases (the highest point on the curve shifts to the left). In addition, the entire curve gets narrower and taller: we have a smaller range of speeds, but we have more molecules at the most probable speed.

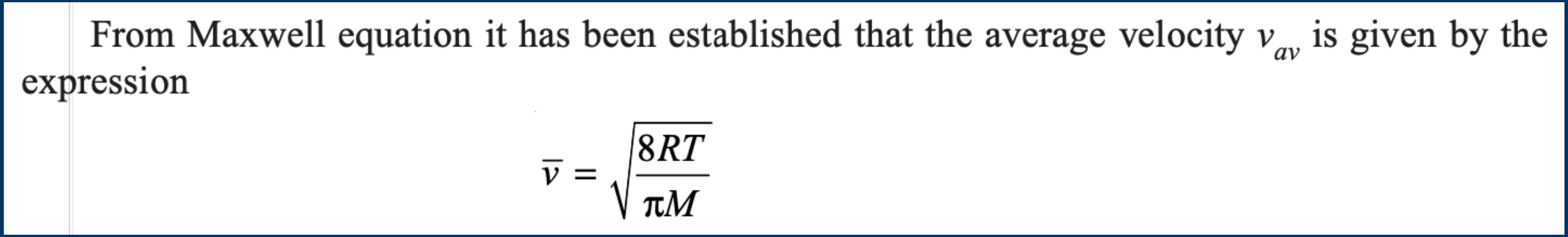


## DIFFERENT KINDS OF VELOCITIES

In our study of kinetic theory we come across three different kinds of molecular velocities :

(1) the Average velocity ($V$)
(2) the Root Mean Square velocity (μ)
(3) the Most Probable velocity ($v_{mn}$)

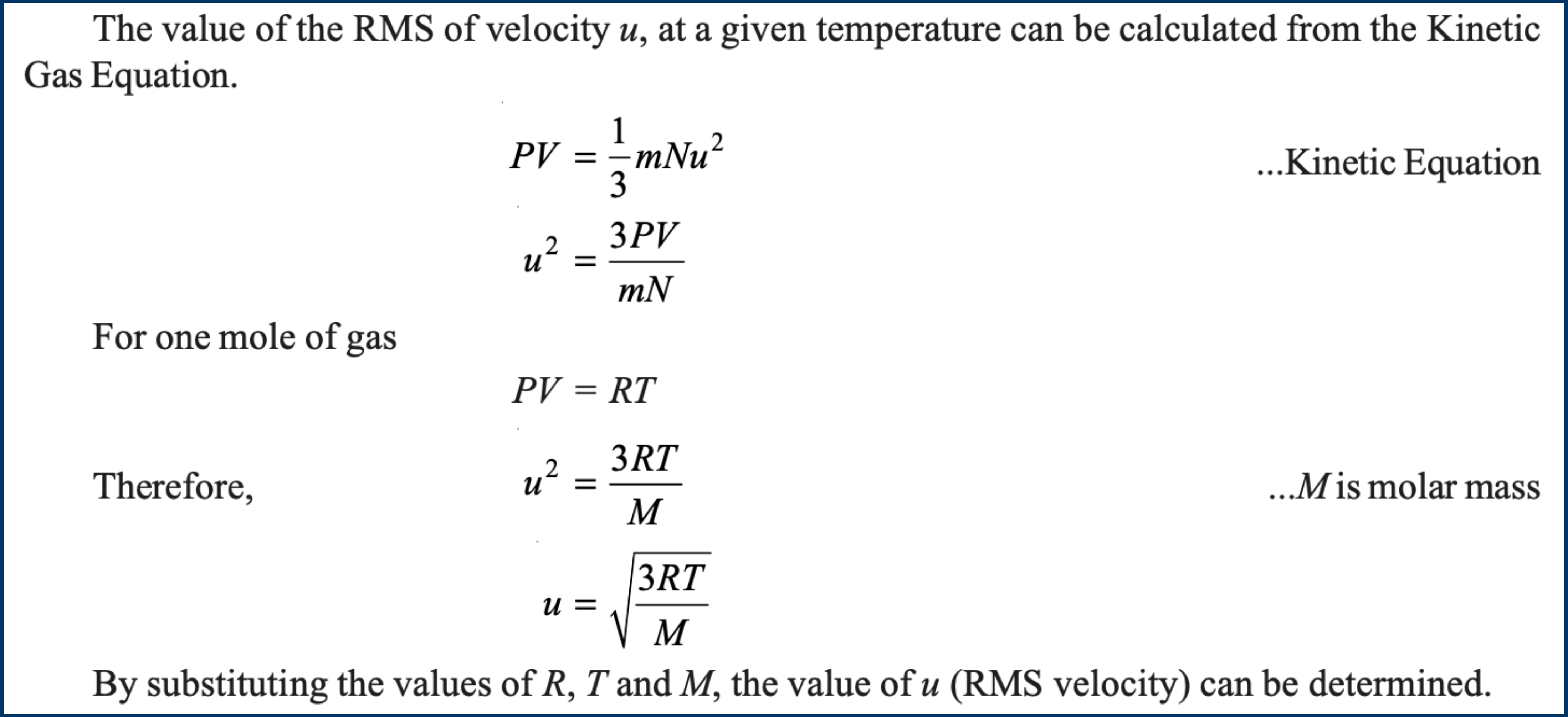
# Average velocity



From Maxwell equation it has been established that the average velocity $v_{av}$ is given by the expression

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

# RMS (Root mean Square Velocity)



The value of the RMS of velocity *u*, at a given temperature can be calculated from the Kinetic Gas Equation.

$$PV = \frac{1}{3} mNu^2 \qquad \text{...Kinetic Equation}$$

$$u^2 = \frac{3PV}{mN}$$

For one mole of gas

$$PV = RT$$

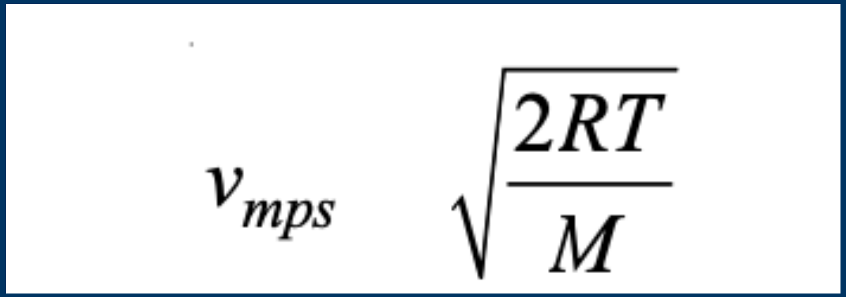
Therefore,

$$u^2 = \frac{3RT}{M} \qquad \text{...}M \text{ is molar mass}$$

$$u = \sqrt{\frac{3RT}{M}}$$

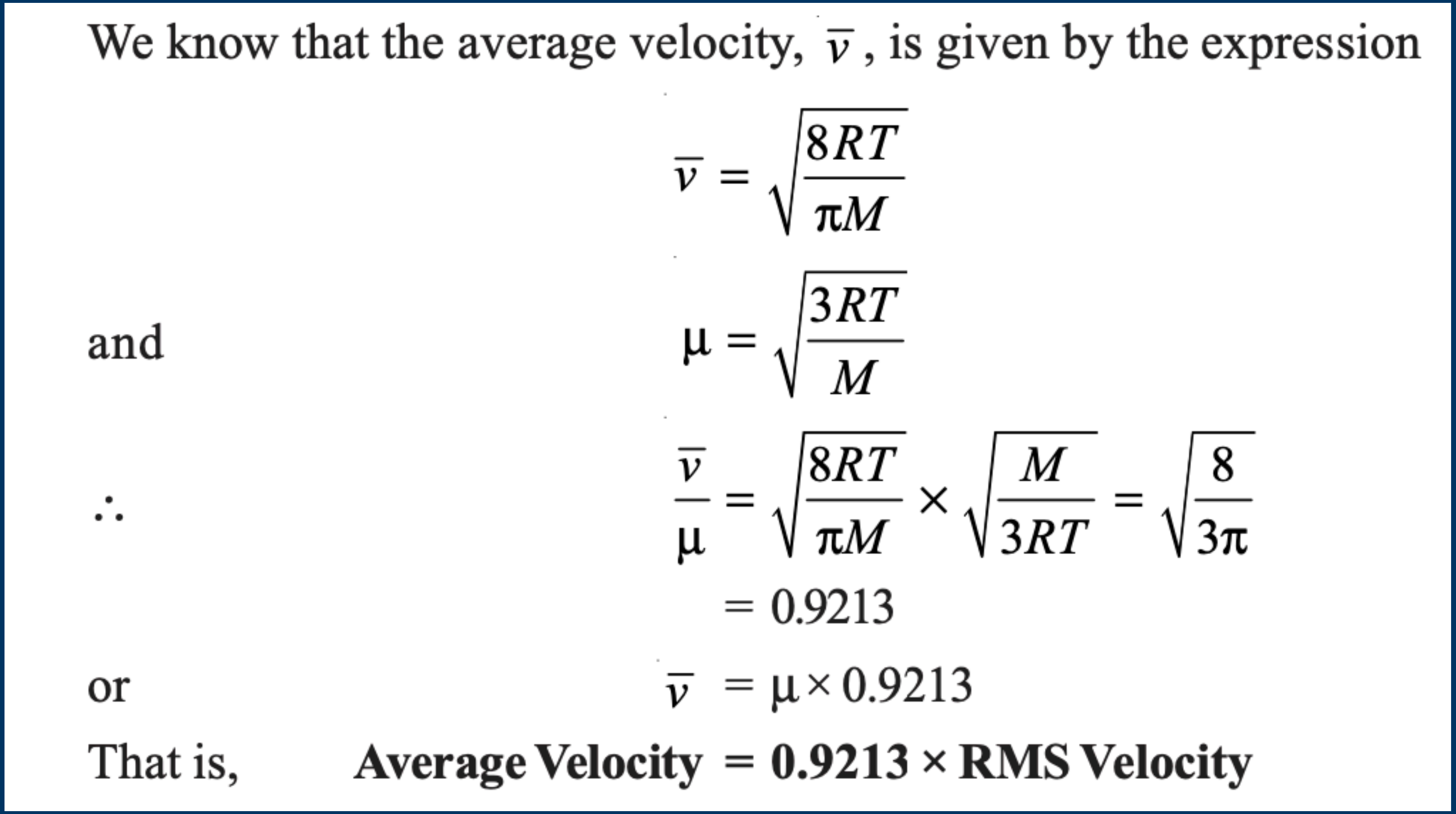
By substituting the values of *R*, *T* and *M*, the value of *u* (RMS velocity) can be determined.

## Most Probable Velocity



$$v_{mps} \qquad \sqrt{\frac{2RT}{M}}$$

## Relation between average velocity and RMS velocity



We know that the average velocity, $\overline{v}$, is given by the expression

$$\overline{v} = \sqrt{\frac{8RT}{\pi M}}$$

and

$$\mu = \sqrt{\frac{3RT}{M}}$$

∴

$$\frac{\overline{v}}{\mu} = \sqrt{\frac{8RT}{\pi M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{8}{3\pi}}$$

$$= 0.9213$$

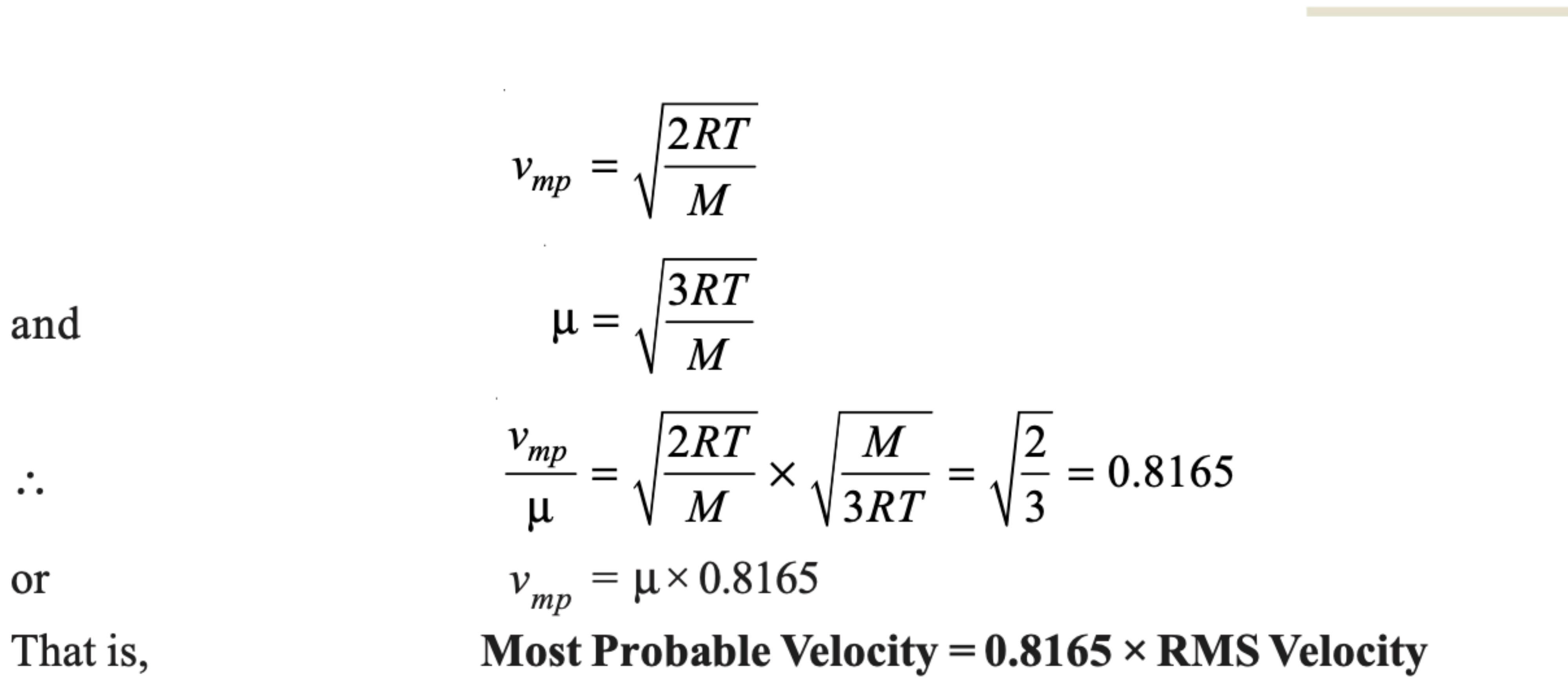
or

$$\overline{v} = \mu \times 0.9213$$

That is, **Average Velocity = 0.9213 × RMS Velocity**

# Relation between most probable velocity and RMS velocity

The expression for the most probably velocity, $v_{mp}$, is



$$v_{mp} = \sqrt{\frac{2RT}{M}}$$

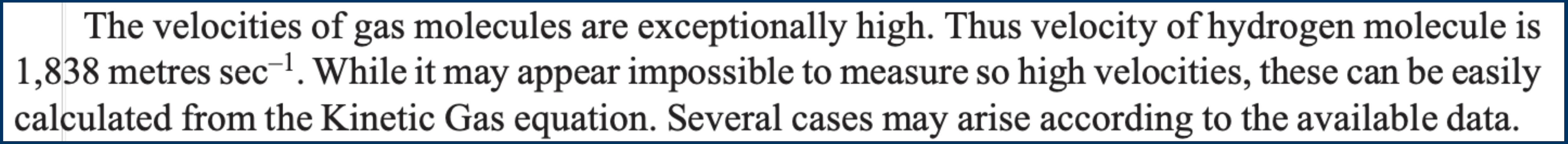
and $$\mu = \sqrt{\frac{3RT}{M}}$$

$\therefore$ $$\frac{v_{mp}}{\mu} = \sqrt{\frac{2RT}{M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{2}{3}} = 0.8165$$

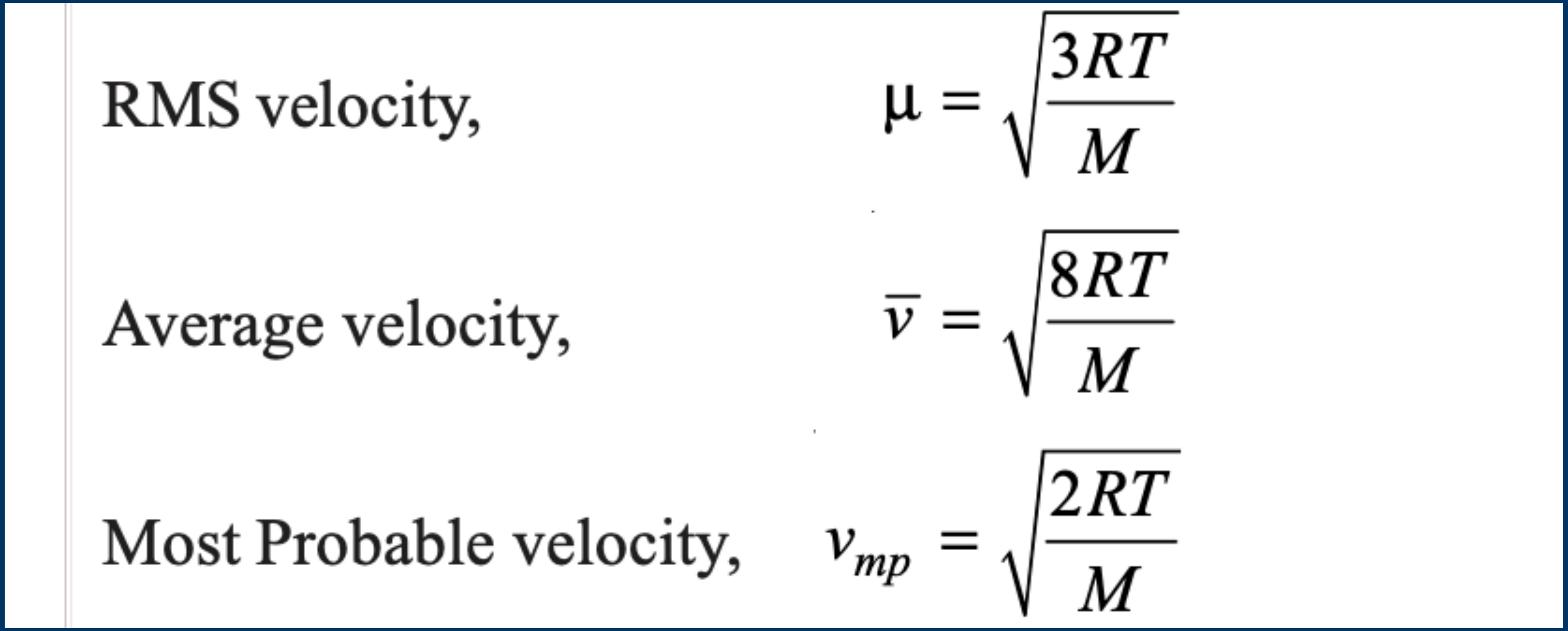
or $$v_{mp} = \mu \times 0.8165$$

That is, **Most Probable Velocity = 0.8165 × RMS Velocity**

# Calculation of Molecular Velocities



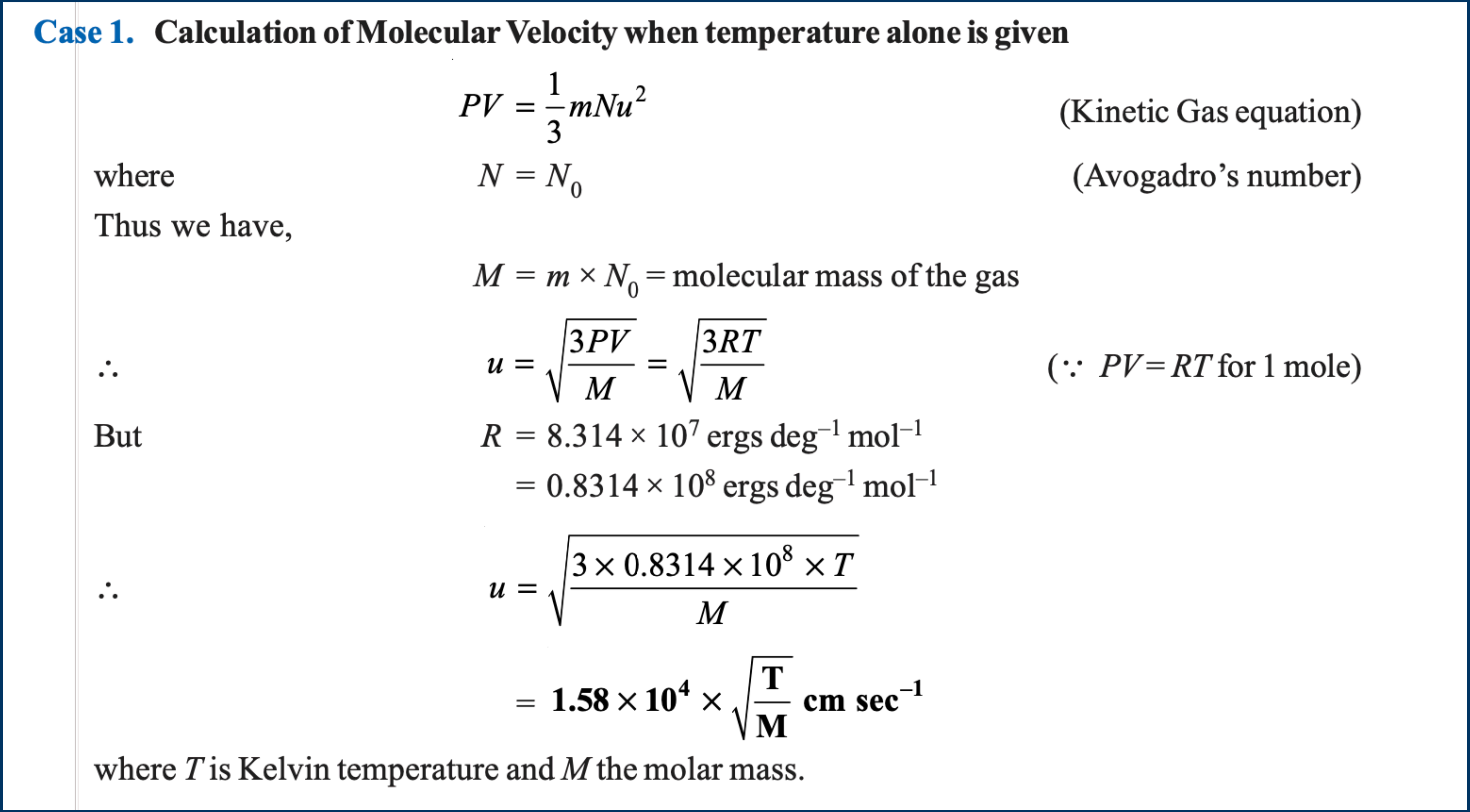
The velocities of gas molecules are exceptionally high. Thus velocity of hydrogen molecule is 1,838 metres sec$^{-1}$. While it may appear impossible to measure so high velocities, these can be easily calculated from the Kinetic Gas equation. Several cases may arise according to the available data.



RMS velocity, $\mu = \sqrt{\dfrac{3RT}{M}}$

Average velocity, $\bar{v} = \sqrt{\dfrac{8RT}{M}}$

Most Probable velocity, $v_{mp} = \sqrt{\dfrac{2RT}{M}}$



**Case 1.** **Calculation of Molecular Velocity when temperature alone is given**

$$PV = \frac{1}{3} mNu^2 \qquad \text{(Kinetic Gas equation)}$$

where $N = N_0$ (Avogadro's number)

Thus we have,

$$M = m \times N_0 = \text{molecular mass of the gas}$$

$$\therefore \quad u = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} \qquad (\because\ PV = RT \text{ for 1 mole})$$

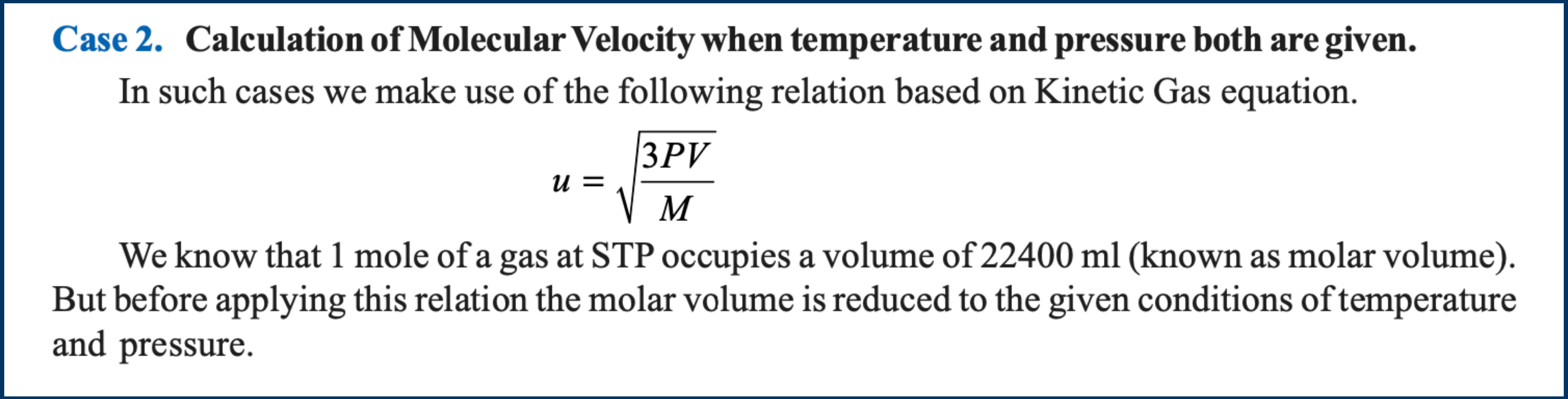
But

$$R = 8.314 \times 10^7 \text{ ergs deg}^{-1} \text{ mol}^{-1}$$
$$= 0.8314 \times 10^8 \text{ ergs deg}^{-1} \text{ mol}^{-1}$$

$$\therefore \quad u = \sqrt{\frac{3 \times 0.8314 \times 10^8 \times T}{M}}$$

$$= \mathbf{1.58 \times 10^4 \times \sqrt{\frac{T}{M}} \ cm\ sec^{-1}}$$

where $T$ is Kelvin temperature and $M$ the molar mass.

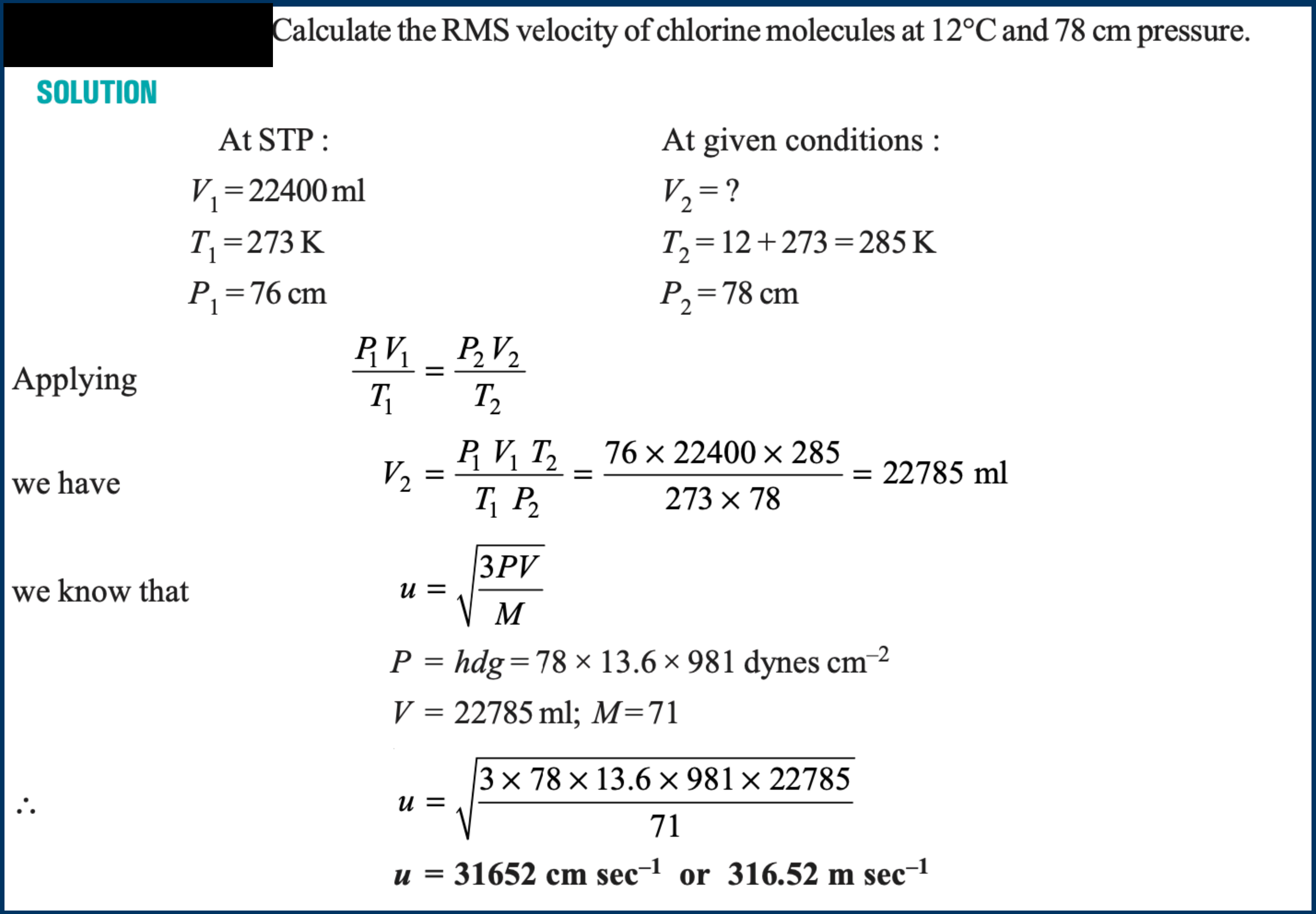


**Case 2.** **Calculation of Molecular Velocity when temperature and pressure both are given.**

In such cases we make use of the following relation based on Kinetic Gas equation.

$$u = \sqrt{\frac{3PV}{M}}$$

We know that 1 mole of a gas at STP occupies a volume of 22400 ml (known as molar volume). But before applying this relation the molar volume is reduced to the given conditions of temperature and pressure.



[redacted] Calculate the RMS velocity of chlorine molecules at 12°C and 78 cm pressure.

**SOLUTION**

| At STP : | At given conditions : |
|---|---|
| $V_1 = 22400$ ml | $V_2 = ?$ |
| $T_1 = 273$ K | $T_2 = 12 + 273 = 285$ K |
| $P_1 = 76$ cm | $P_2 = 78$ cm |

Applying
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

we have
$$V_2 = \frac{P_1\, V_1\, T_2}{T_1\, P_2} = \frac{76 \times 22400 \times 285}{273 \times 78} = 22785 \text{ ml}$$

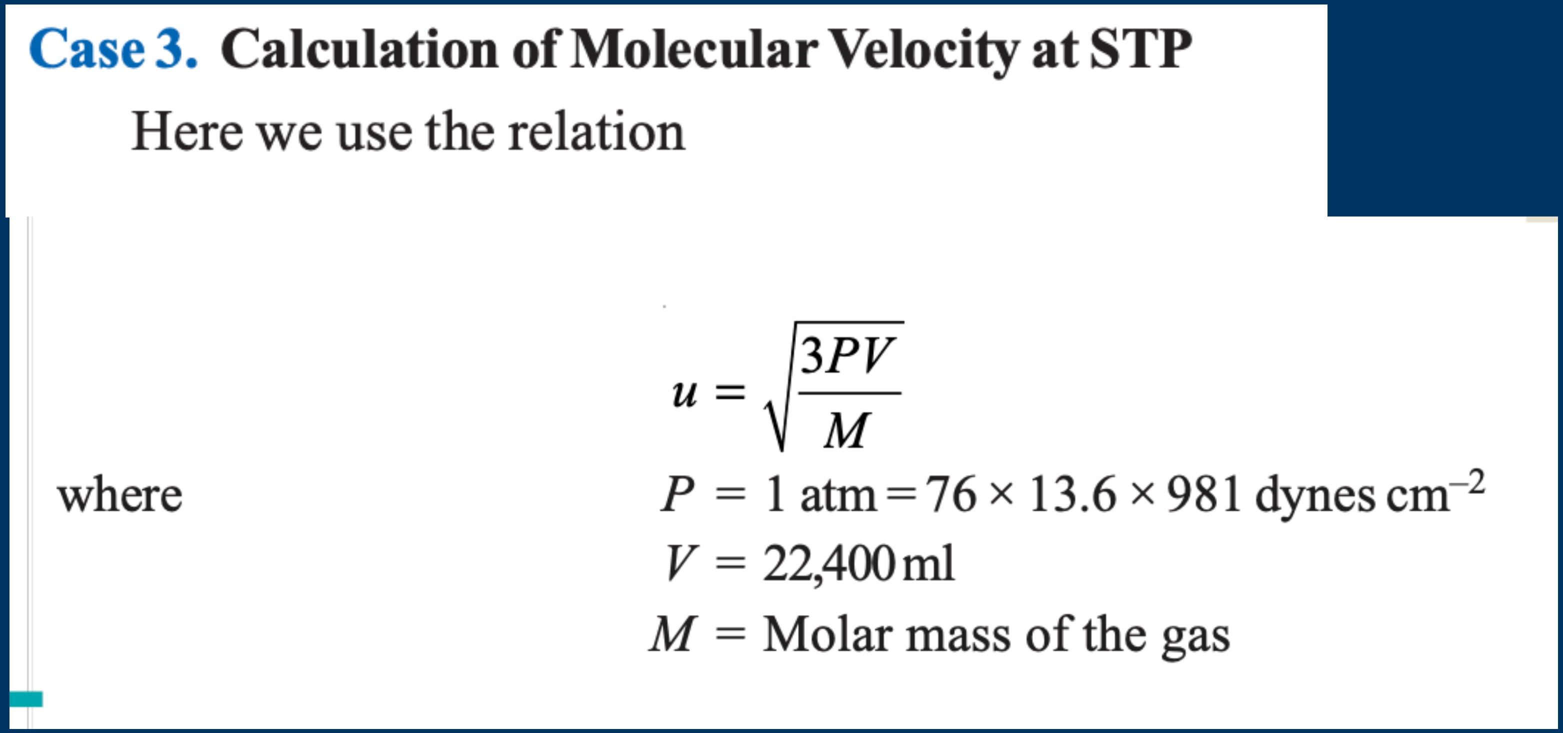
we know that
$$u = \sqrt{\frac{3PV}{M}}$$

$$P = hdg = 78 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$

$$V = 22785 \text{ ml};\ M = 71$$

$\therefore$
$$u = \sqrt{\frac{3 \times 78 \times 13.6 \times 981 \times 22785}{71}}$$

$$\mathbf{u = 31652 \text{ cm sec}^{-1} \text{ or } 316.52 \text{ m sec}^{-1}}$$



## Case 3. Calculation of Molecular Velocity at STP

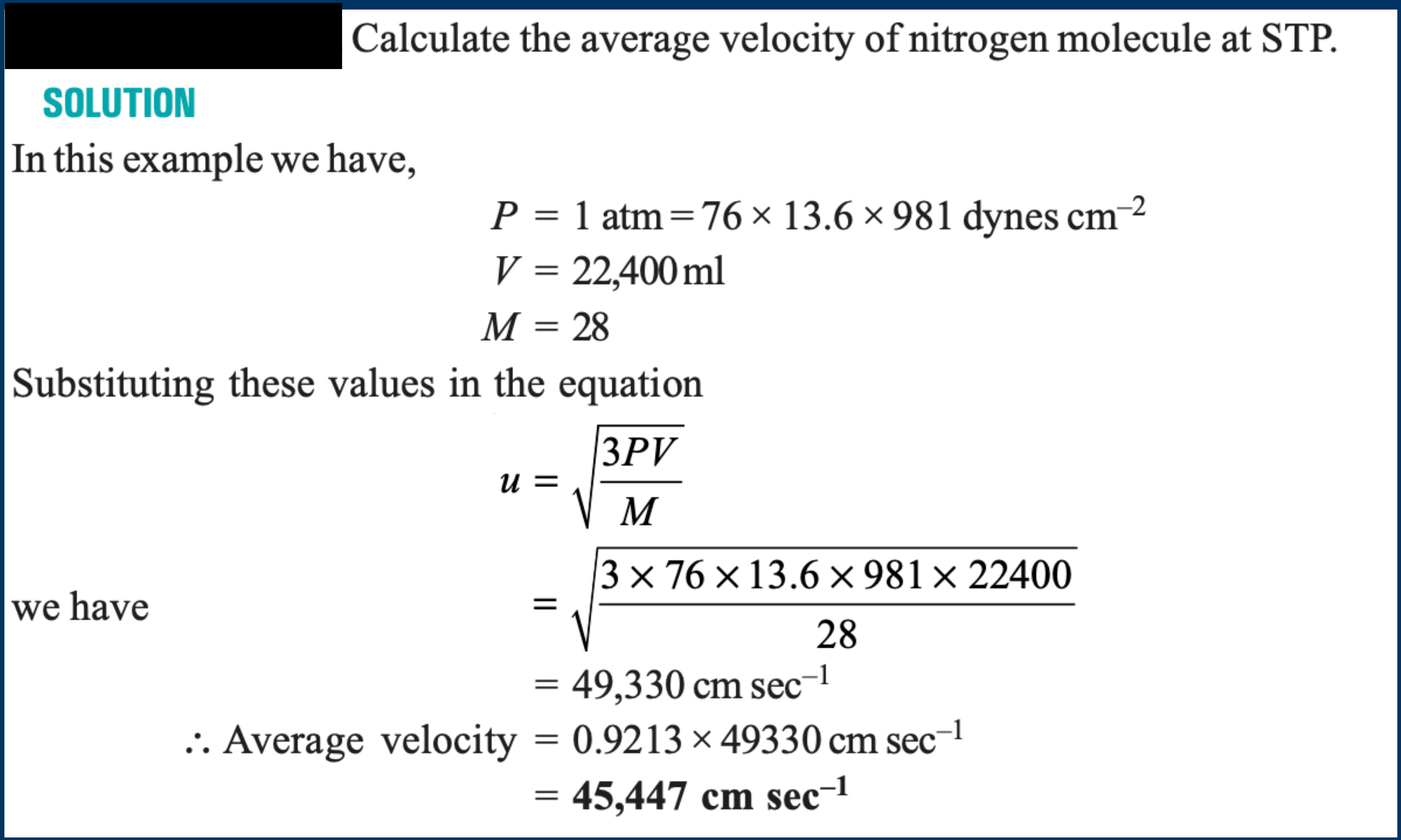
Here we use the relation

$$u = \sqrt{\frac{3PV}{M}}$$

where $P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$

$V = 22{,}400 \text{ ml}$

$M$ = Molar mass of the gas



[redacted] Calculate the average velocity of nitrogen molecule at STP.

**SOLUTION**

In this example we have,

$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$

$V = 22{,}400 \text{ ml}$

$M = 28$

Substituting these values in the equation

$$u = \sqrt{\frac{3PV}{M}}$$

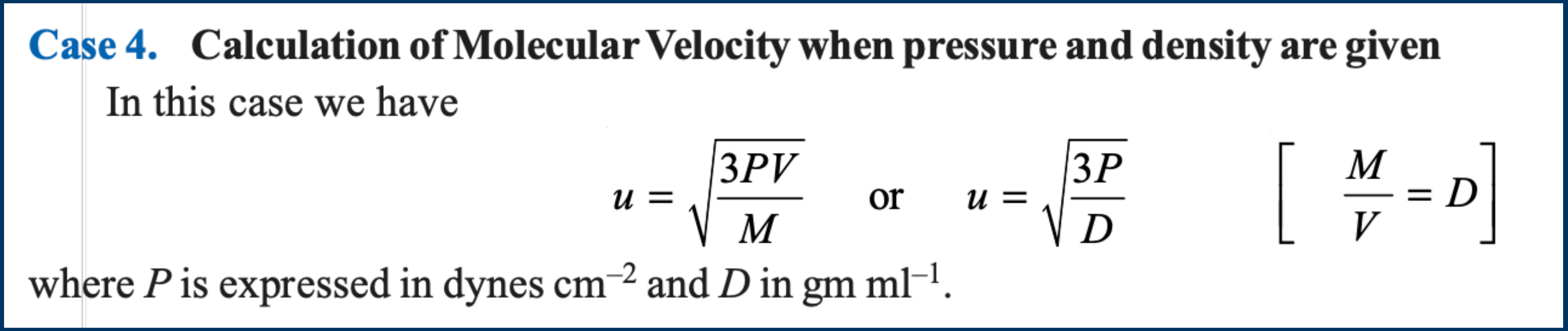
we have

$$= \sqrt{\frac{3 \times 76 \times 13.6 \times 981 \times 22400}{28}}$$

$$= 49{,}330 \text{ cm sec}^{-1}$$

$$\therefore \text{ Average velocity } = 0.9213 \times 49330 \text{ cm sec}^{-1}$$

$$= \mathbf{45{,}447 \text{ cm sec}^{-1}}$$

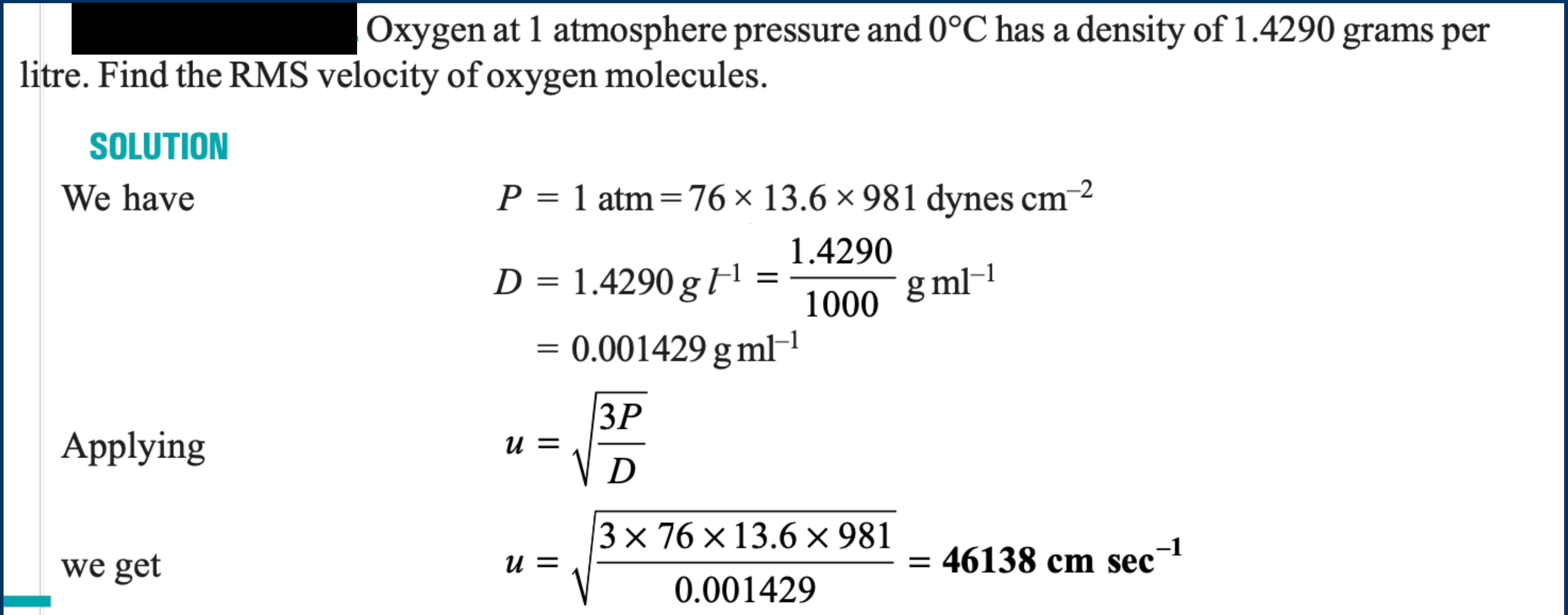


**Case 4. Calculation of Molecular Velocity when pressure and density are given**

In this case we have

$$u = \sqrt{\frac{3PV}{M}} \quad \text{or} \quad u = \sqrt{\frac{3P}{D}} \qquad \left[\frac{M}{V} = D\right]$$

where $P$ is expressed in dynes cm$^{-2}$ and $D$ in gm ml$^{-1}$.



[redacted] Oxygen at 1 atmosphere pressure and 0°C has a density of 1.4290 grams per litre. Find the RMS velocity of oxygen molecules.

**SOLUTION**

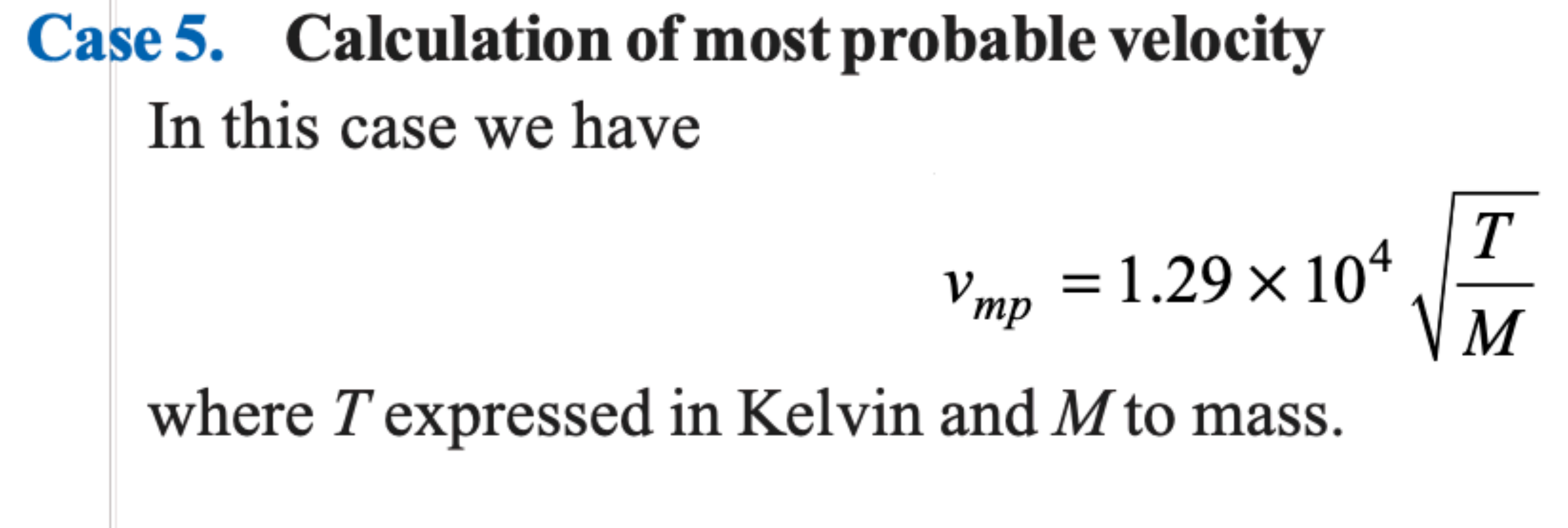
We have $$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$

$$D = 1.4290 \text{ g } l^{-1} = \frac{1.4290}{1000} \text{ g ml}^{-1}$$

$$= 0.001429 \text{ g ml}^{-1}$$

Applying $$u = \sqrt{\frac{3P}{D}}$$

we get $$u = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.001429}} = \mathbf{46138\ cm\ sec^{-1}}$$

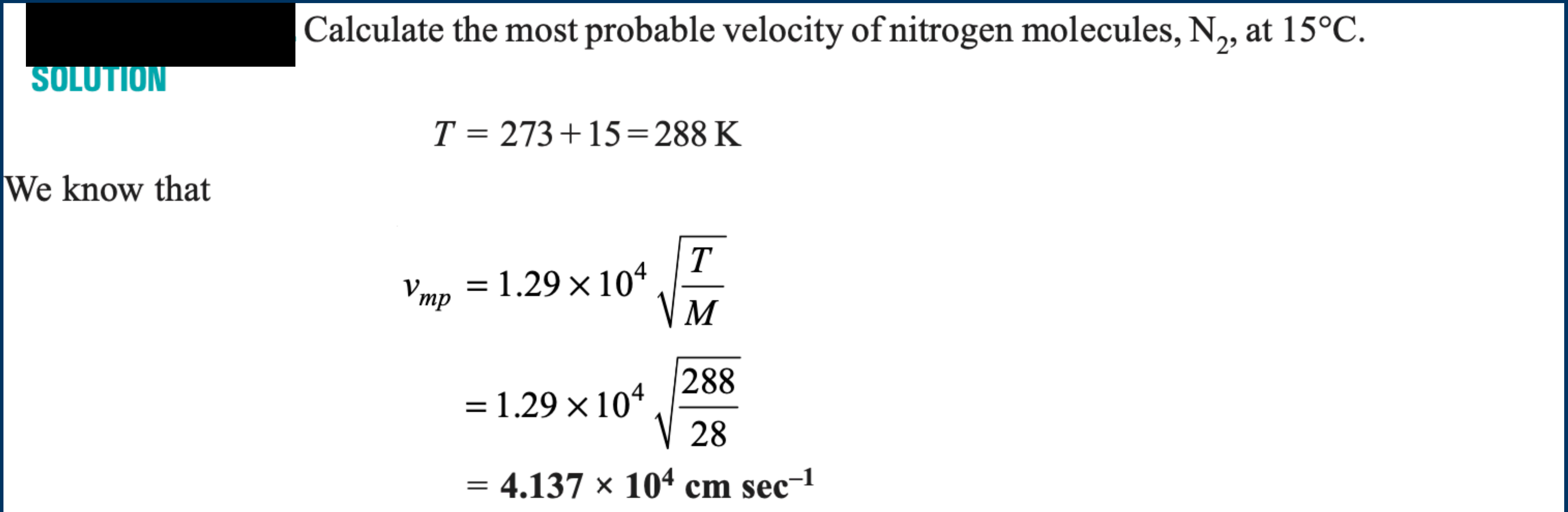


**Case 5.** **Calculation of most probable velocity**

In this case we have

$$v_{mp} = 1.29 \times 10^4 \sqrt{\frac{T}{M}}$$

where $T$ expressed in Kelvin and $M$ to mass.



[redacted] Calculate the most probable velocity of nitrogen molecules, $N_2$, at 15°C.

**SOLUTION**

$$T = 273 + 15 = 288\text{ K}$$

We know that

$$v_{mp} = 1.29 \times 10^4 \sqrt{\frac{T}{M}}$$

$$= 1.29 \times 10^4 \sqrt{\frac{288}{28}}$$

$$= \mathbf{4.137 \times 10^4\ cm\ sec^{-1}}$$

[redacted]. Calculate the root mean square velocity of $CO_2$ molecule at 1000°C.

**SOLUTION**

$$T = 273 + 1000 = 1273 \text{ K}; M = 44$$

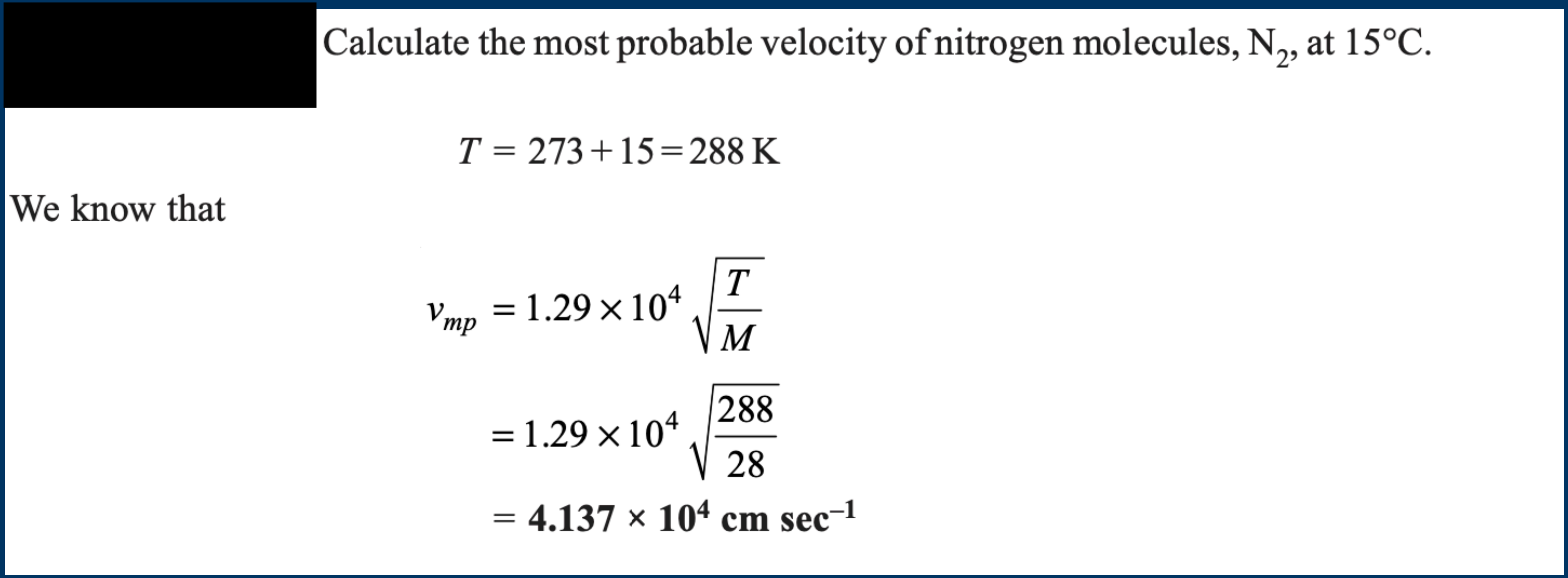
Applying the equation

$$u = 1.58 \times 10^4 \times \sqrt{\frac{T}{M}}$$

we have

$$u = 1.58 \times 10^4 \times \sqrt{\frac{1273}{44}}$$

$$u = \mathbf{84985\ cm\ sec^{-1}\ or\ 849.85\ m\ sec^{-1}}$$



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$$= 1.29 \times 10^4 \sqrt{\frac{288}{28}}$$

$$= \mathbf{4.137 \times 10^4\ cm\ sec^{-1}}$$

# Men free path

**The mean distance travelled by a molecule between two successive collisions is called the Mean Free Path**

$$\lambda = \frac{l_1 + l_2 + l_3 + \ldots.. + l_n}{n}$$

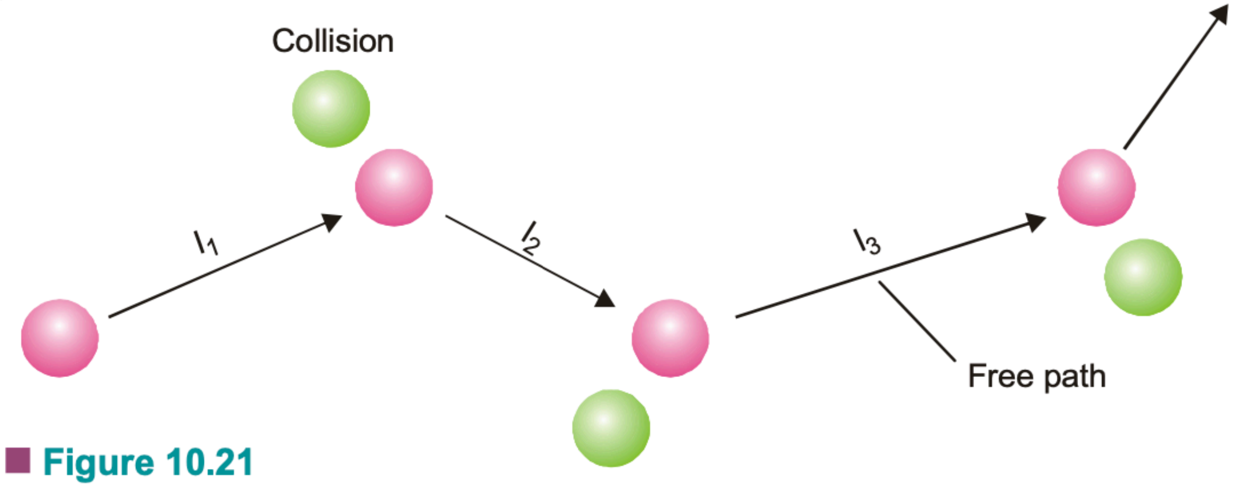


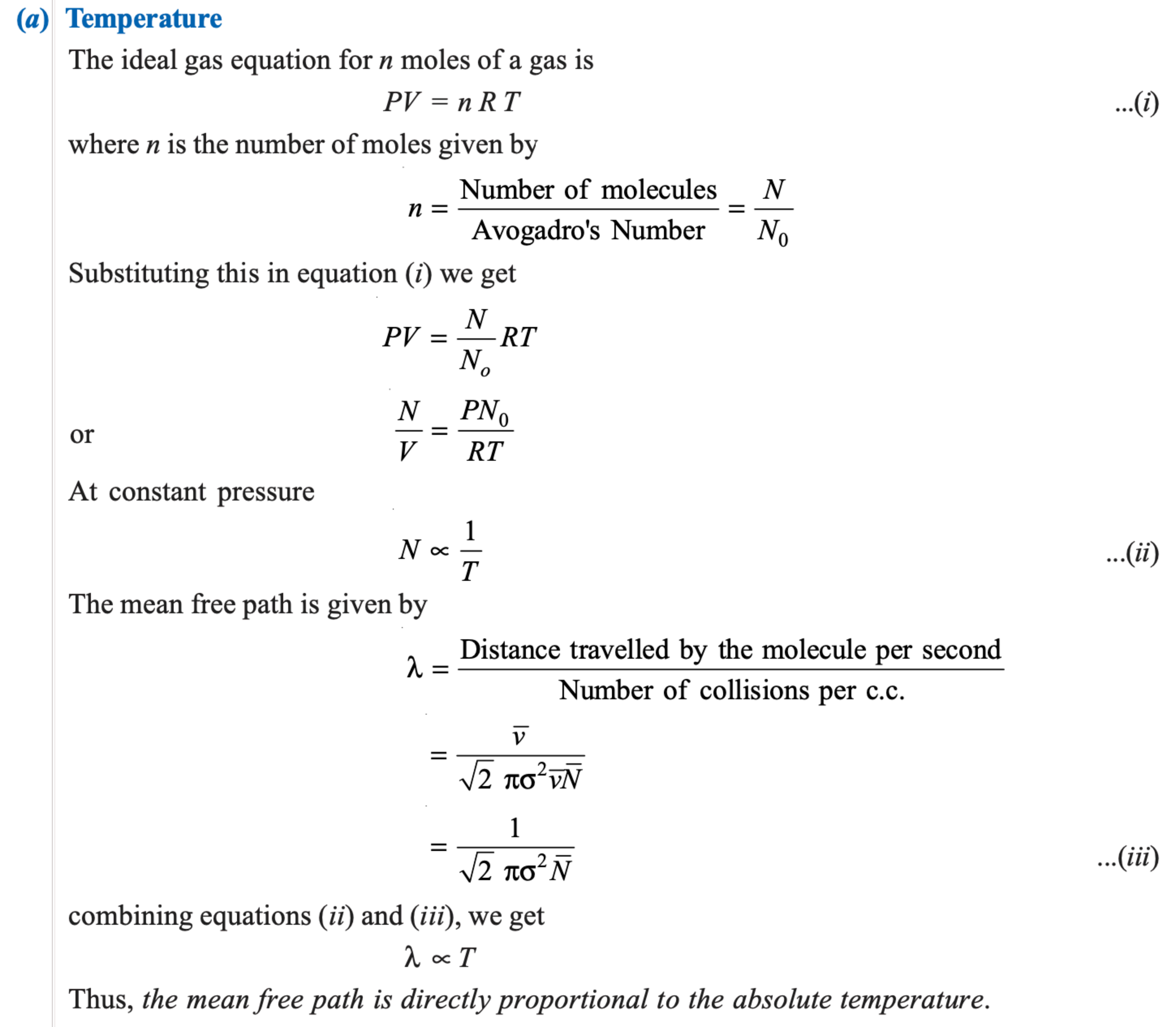
**Figure 10.21**
**The mean free path illustrated.**

The mean free path, $\lambda$, is given by the expression

$$\lambda = \eta\sqrt{\frac{3}{Pd}}$$

where
$P$ = pressure of the gas
$d$ = density of the gas
$\eta$ = coefficient of viscosity of the gas

# Effect of Temperature and Pressure on Mean Free Path



**(*a*) Temperature**

The ideal gas equation for $n$ moles of a gas is

$$PV = nRT \qquad \text{...}(i)$$

where $n$ is the number of moles given by

$$n = \frac{\text{Number of molecules}}{\text{Avogadro's Number}} = \frac{N}{N_0}$$

Substituting this in equation (*i*) we get

$$PV = \frac{N}{N_o} RT$$

or

$$\frac{N}{V} = \frac{PN_0}{RT}$$

At constant pressure

$$N \propto \frac{1}{T} \qquad \text{...}(ii)$$

The mean free path is given by

$$\lambda = \frac{\text{Distance travelled by the molecule per second}}{\text{Number of collisions per c.c.}}$$

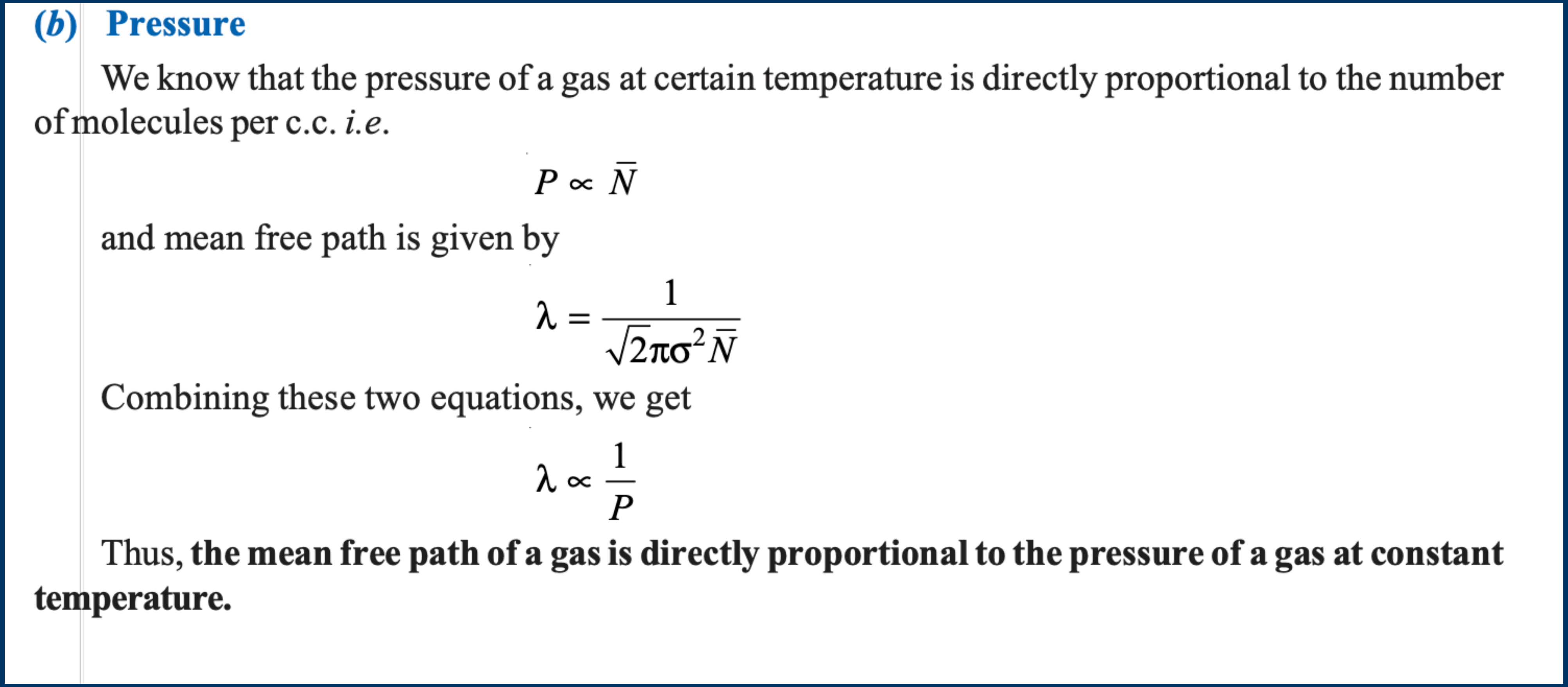
$$= \frac{\bar{v}}{\sqrt{2}\,\pi\sigma^2 \bar{v} \bar{N}}$$

$$= \frac{1}{\sqrt{2}\,\pi\sigma^2 \bar{N}} \qquad \text{...}(iii)$$

combining equations (*ii*) and (*iii*), we get

$$\lambda \propto T$$

Thus, *the mean free path is directly proportional to the absolute temperature.*



### (*b*) Pressure

We know that the pressure of a gas at certain temperature is directly proportional to the number of molecules per c.c. *i.e.*

$$P \propto \bar{N}$$

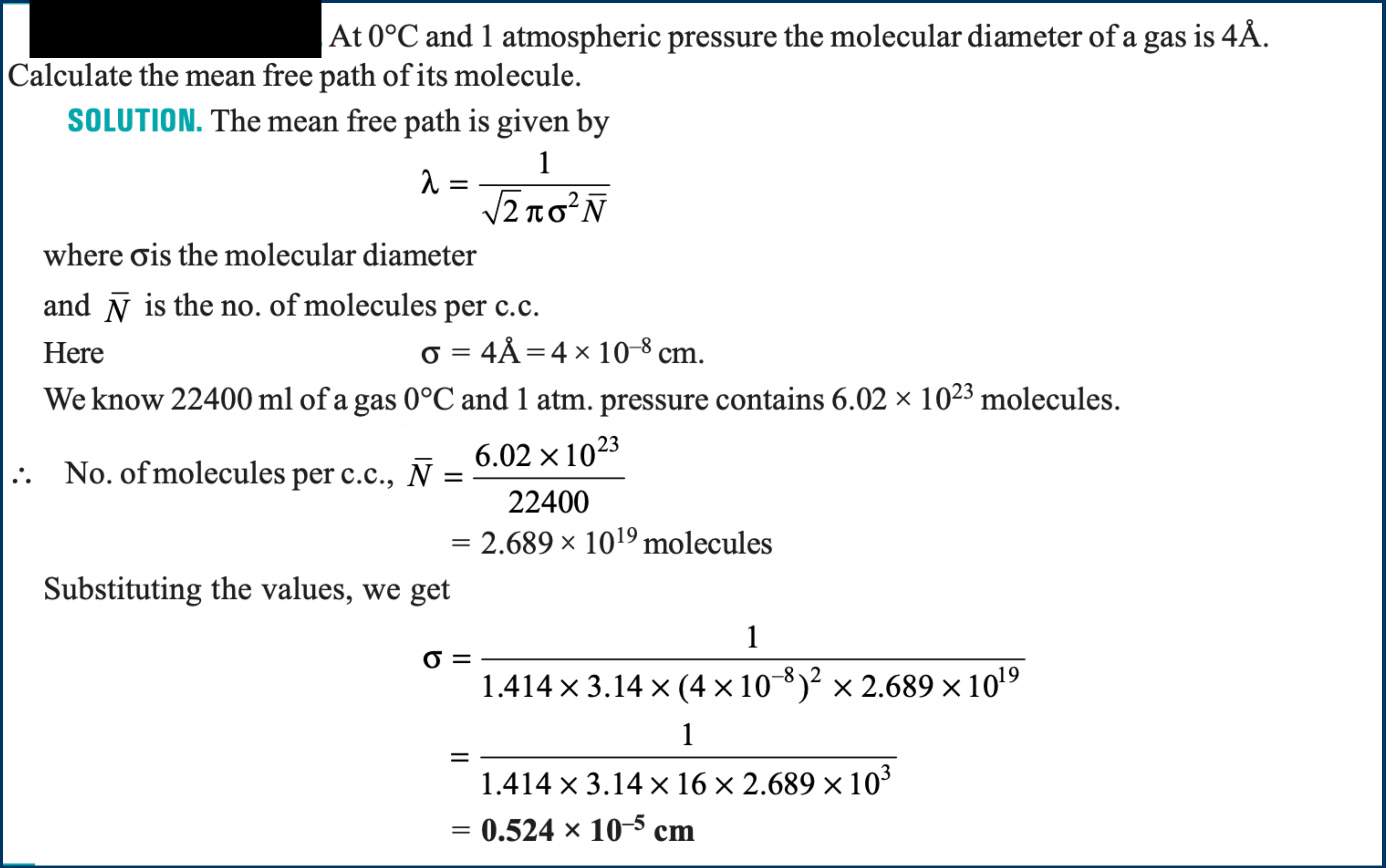
and mean free path is given by

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

Combining these two equations, we get

$$\lambda \propto \frac{1}{P}$$

Thus, **the mean free path of a gas is directly proportional to the pressure of a gas at constant temperature.**



[redacted] At 0°C and 1 atmospheric pressure the molecular diameter of a gas is 4Å. Calculate the mean free path of its molecule.

**SOLUTION.** The mean free path is given by

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

where σ is the molecular diameter

and $\bar{N}$ is the no. of molecules per c.c.

Here $\sigma = 4\text{Å} = 4 \times 10^{-8}$ cm.

We know 22400 ml of a gas 0°C and 1 atm. pressure contains $6.02 \times 10^{23}$ molecules.

$$\therefore \quad \text{No. of molecules per c.c., } \bar{N} = \frac{6.02 \times 10^{23}}{22400}$$

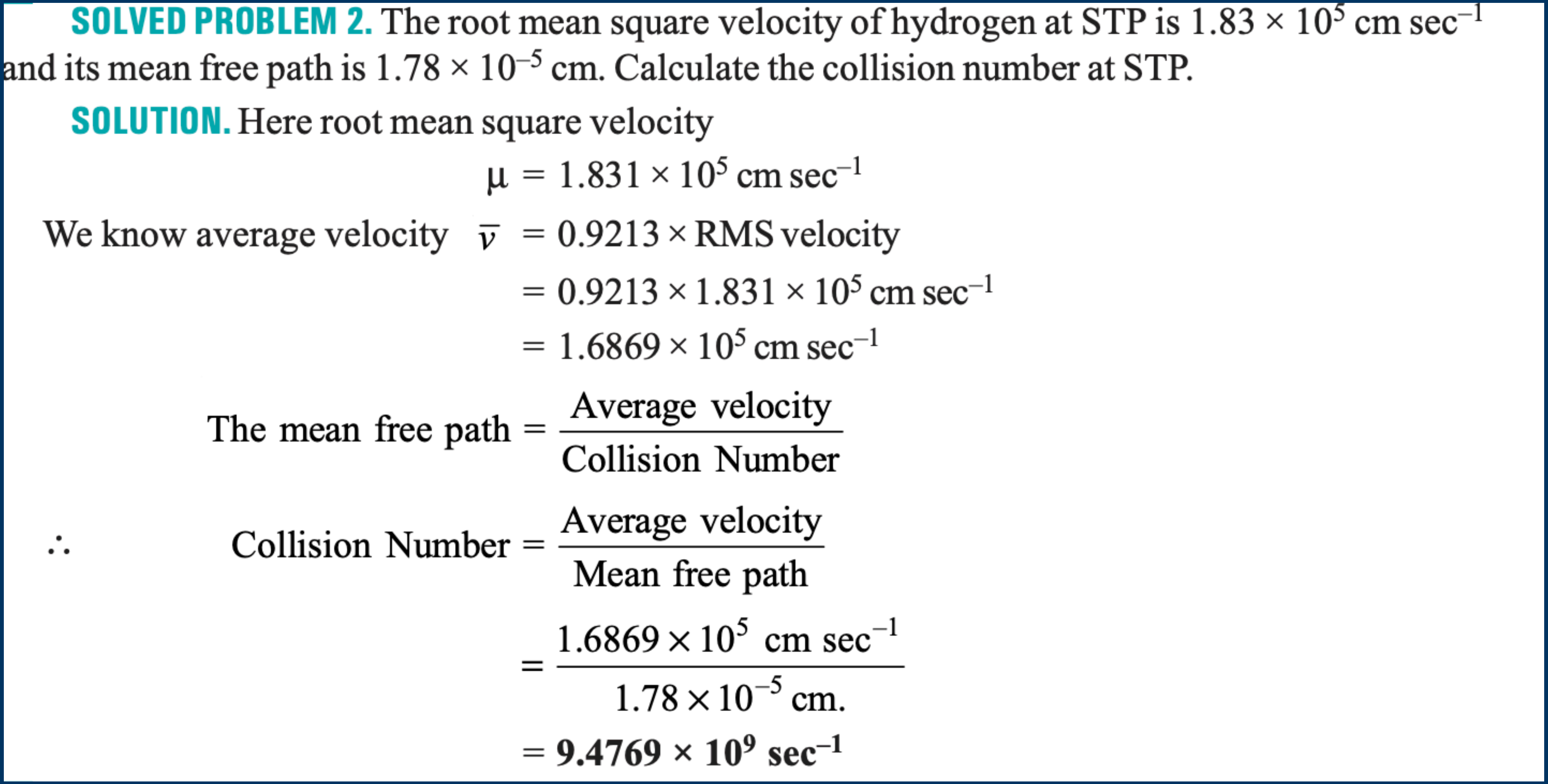
$$= 2.689 \times 10^{19} \text{ molecules}$$

Substituting the values, we get

$$\sigma = \frac{1}{1.414 \times 3.14 \times (4 \times 10^{-8})^2 \times 2.689 \times 10^{19}}$$

$$= \frac{1}{1.414 \times 3.14 \times 16 \times 2.689 \times 10^{3}}$$

$$= \mathbf{0.524 \times 10^{-5}\ cm}$$



**SOLVED PROBLEM 2.** The root mean square velocity of hydrogen at STP is 1.83 × $10^5$ cm $\text{sec}^{-1}$ and its mean free path is 1.78 × $10^{-5}$ cm. Calculate the collision number at STP.

**SOLUTION.** Here root mean square velocity

$$\mu = 1.831 \times 10^5 \text{ cm sec}^{-1}$$

We know average velocity $\bar{v}$

$$\begin{aligned} \bar{v} &= 0.9213 \times \text{RMS velocity} \\ &= 0.9213 \times 1.831 \times 10^5 \text{ cm sec}^{-1} \\ &= 1.6869 \times 10^5 \text{ cm sec}^{-1} \end{aligned}$$

$$\text{The mean free path} = \frac{\text{Average velocity}}{\text{Collision Number}}$$

$$\therefore \quad \text{Collision Number} = \frac{\text{Average velocity}}{\text{Mean free path}}$$

$$= \frac{1.6869 \times 10^5 \text{ cm sec}^{-1}}{1.78 \times 10^{-5} \text{ cm.}}$$

$$= \mathbf{9.4769 \times 10^9\ sec^{-1}}$$