

Topic 3D - Molecular Motion

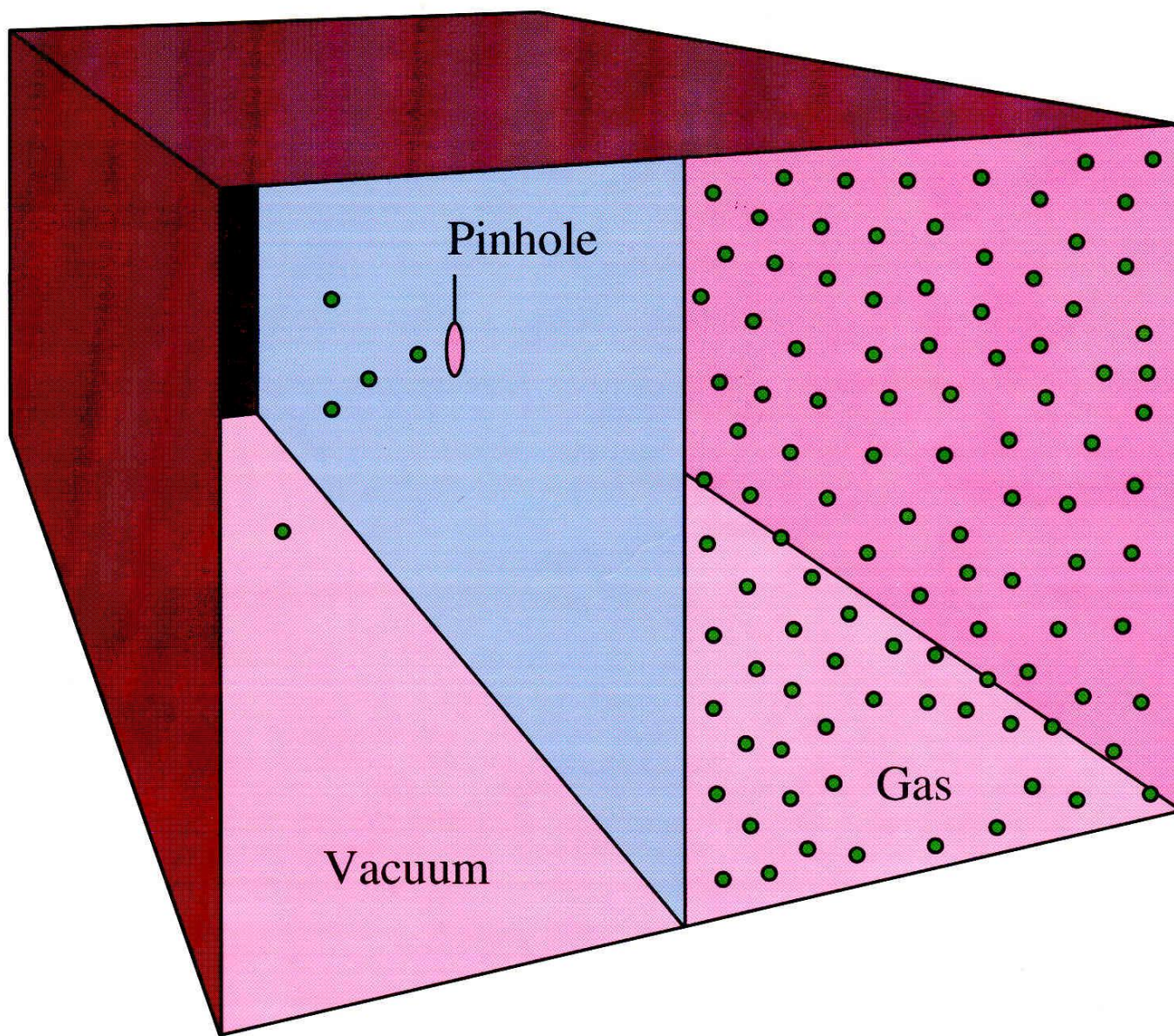


Figure 5.17
Effusion of a gas

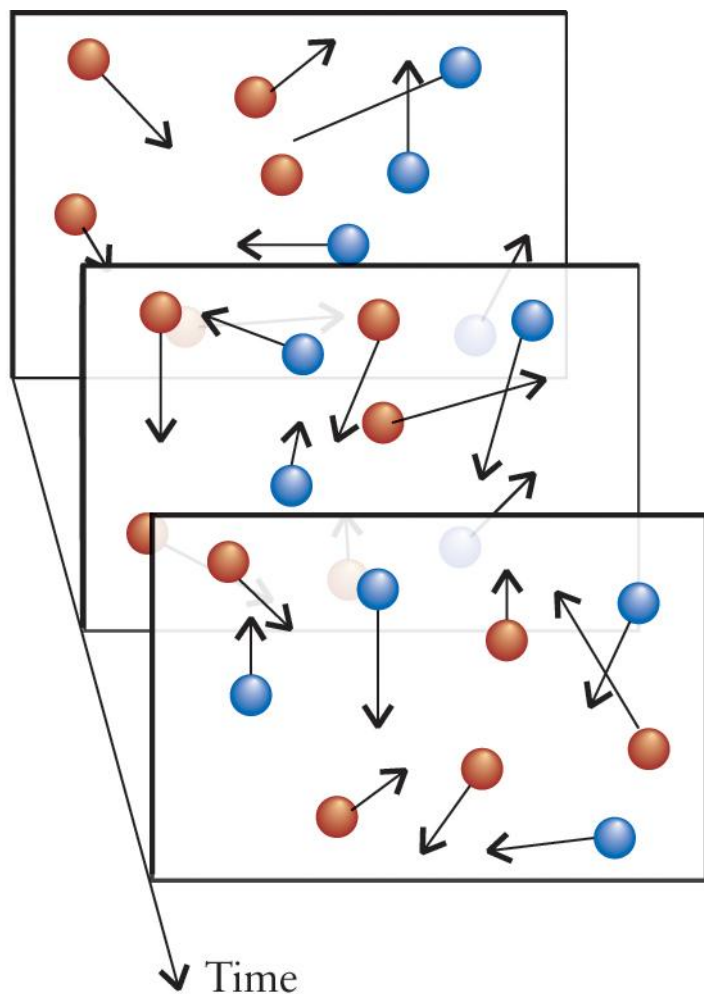


FIGURE 5.21 In diffusion, the molecules of one substance spread into the region occupied by molecules of another in a series of random steps, undergoing collisions as they move.

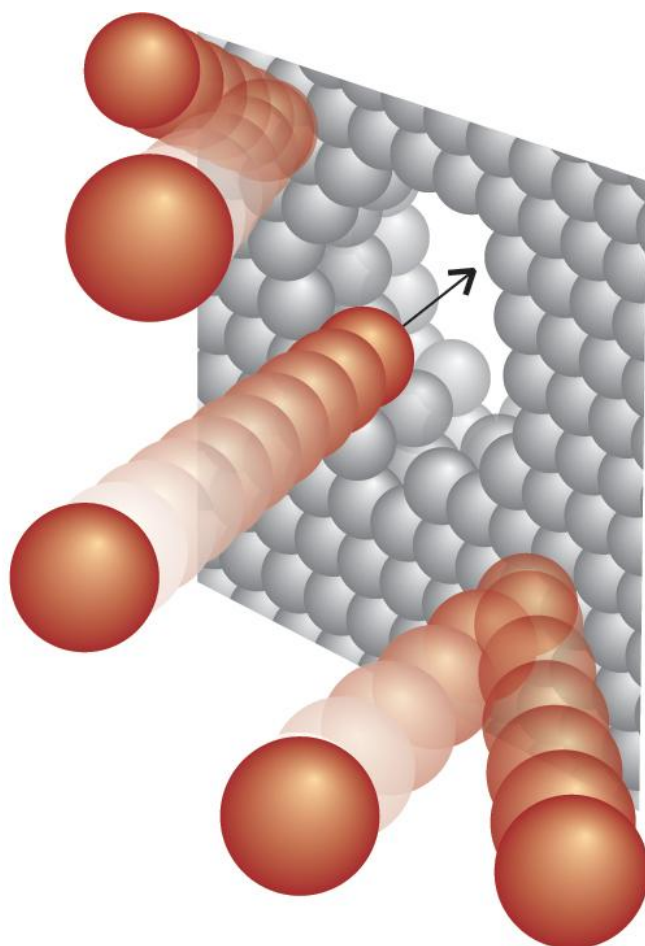


FIGURE 5.22 In effusion, the molecules of one substance escape through a small hole in a barrier into a vacuum or a region of low pressure.

Graham's Law: At constant temperature, the rate of effusion of a gas is inversely proportional to the square root of its molecular mass:

$$\frac{\text{Rate of Effusion of Gas A}}{\text{Rate of Effusion of Gas B}} = \sqrt{\frac{\text{M.W. of B}}{\text{M.W. of A}}}$$



$$\frac{\text{Ave. Speed of A "Particles"}}{\text{Ave. Speed of B "Particles"}} = \sqrt{\frac{\text{M.W. of B}}{\text{M.W. of A}}}$$

Effect of Temperature:

$$\frac{\text{Rate of Effusion at } T_2}{\text{Rate of Effusion at } T_1} = \sqrt{\frac{T_2}{T_1}}$$

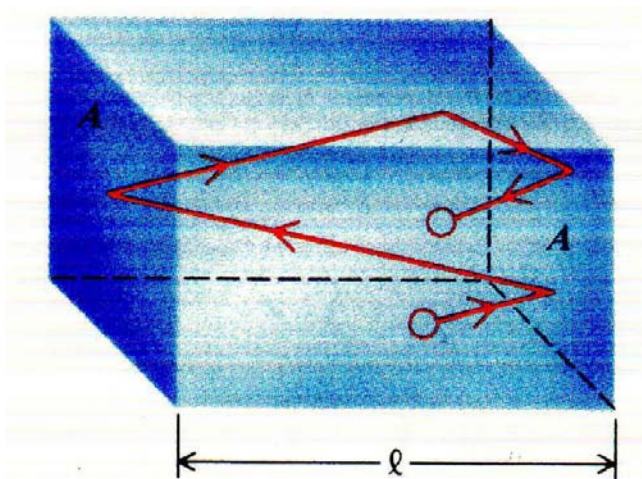
Thus, combining the effects of M.W. and Temp. on the rate of effusion:

$$\text{Ave. Speed of Gas "Particles"} \propto \sqrt{\frac{T}{\text{M.W.}}}$$

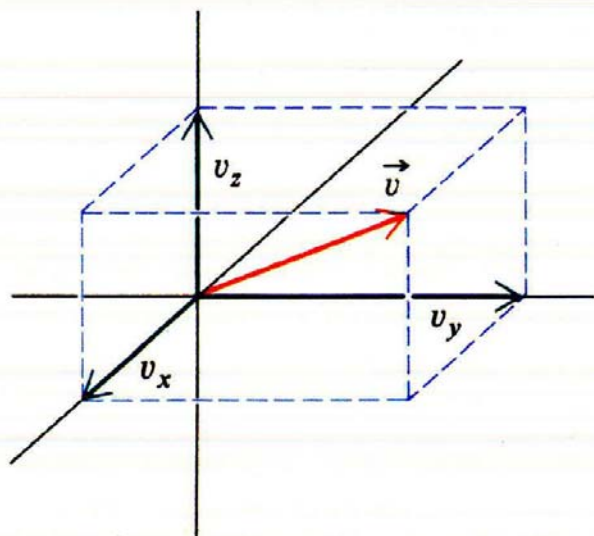
Kinetic Molecular Theory of Gases

Assumptions:

- 1.) Gases consist of a statistically large number of atoms or molecules that are separated by distances that are large compared to their size.
- 2.) The molecules are in constant random motion, with a distribution of speeds.
- 3.) Gas molecules exert no sustained forces on each other, so that between collisions individual molecules move in straight lines with constant velocities.
- 4.) Collisions of gas molecules with the walls of the container are perfectly elastic, *i.e.*, no energy is lost during a collision.
- 5.) The molecules are so small in comparison to the distances between them that the volume of the individual atoms or molecules can be assumed to be negligibly small (*i.e.*, zero).

**Figure 3-10**

The path of a molecule in a box.

**Figure 3-11**

The velocity is shown by an arrow of length v . It can be separated into three components, v_x , v_y , and v_z , along the three Cartesian coordinate axes.

Kinetic Molecular Theory of Gases

Goal is to derive an expression for pressure that agrees with the empirical ideal gas law.

Assume n moles of gas in a cubical container, with side length L , in meters. Each gas “particle” has a mass m and makes only elastic collisions (*i.e.*, momentum is conserved) with the container walls.

Thus, we want to compute the net force per unit area on the container walls, *i.e.*, the pressure ($P = F/A$).

The velocity (v) of each gas particle has x , y , and z components:

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

The collision frequency (# of collisions of gas particles with the container walls per unit time) is given by:

$$(\text{Collision Frequency})_{x,y,z} = \frac{v_{x,y,z}}{L}$$

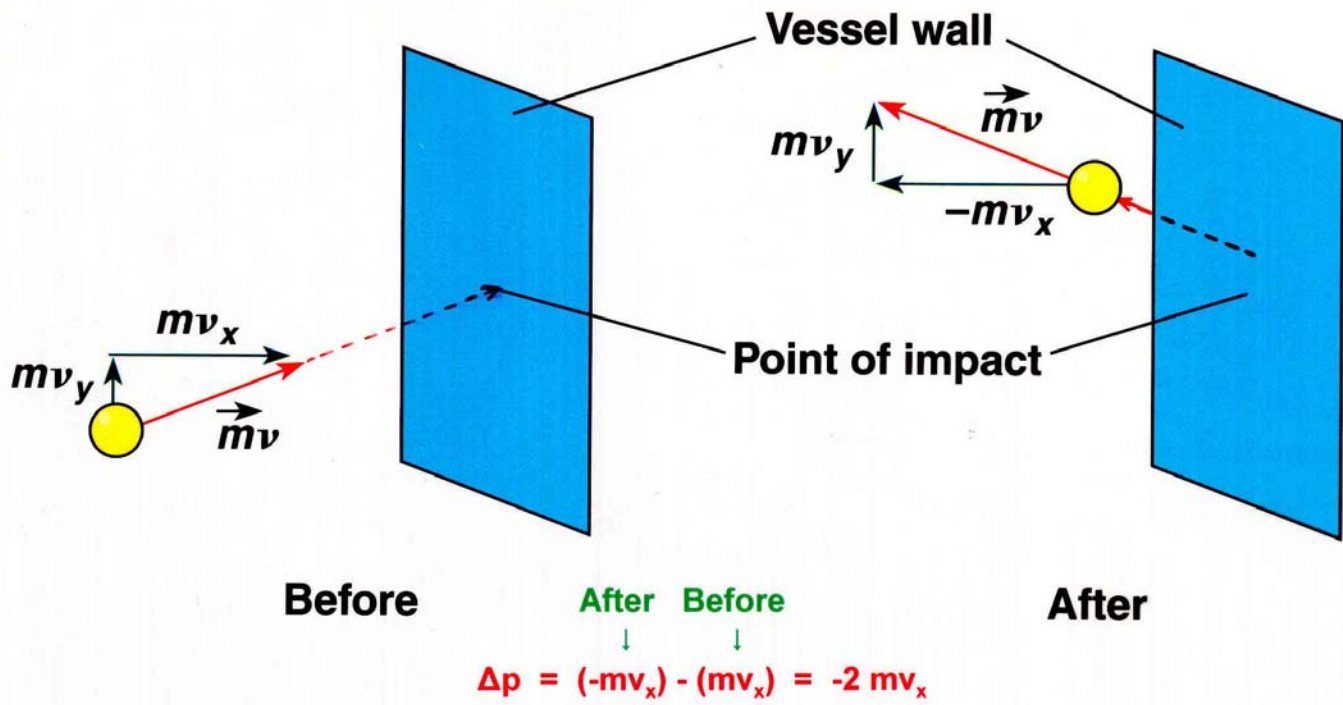
where L is the distance between walls.

The force generated by each particle’s collision with a wall is given by Newton’s Second Law:

$$F = ma = m \frac{\Delta v}{\Delta t} = \frac{\Delta(mv)}{\Delta t}$$

where $\Delta(mv)$ is the change in momentum.

Only the x-component of a gas particle's velocity affects the frequency of its collisions with container walls that are perpendicular to the x-axis:



For each collision with a container wall, the change in a particle's momentum, $\Delta(mv_{x,y,z})$, is given by:

$$\begin{aligned}\Delta(mv_{x,y,z}) &= -\underset{\text{(final)}}{mv_{x,y,z}} - \underset{\text{(initial)}}{mv_{x,y,z}} \\ &= 2 |mv_{x,y,z}|\end{aligned}$$

Thus, the total force exerted by a gas particle in each direction may be determined by multiplying $\Delta(mv_{x,y,z})$ per impact by the total number of impacts per unit time (*i.e.*, the collision frequency):

$$F_{x,y,z} = (2mv_{x,y,z}) \left(\frac{v_{x,y,z}}{L} \right) = \frac{2m(v_{x,y,z})^2}{L}$$

Since $v^2 = v_x^2 + v_y^2 + v_z^2$, the total force exerted on the container walls by a gas particle is:

$$F_T = \frac{2m}{L} (v_x^2 + v_y^2 + v_z^2) = \frac{2mv^2}{L}$$

But since the particles have a range of energies, rather than a single energy, an average velocity is used:

$$\overline{F_T} = \frac{2m\overline{v^2}}{L}$$

The total area of the cubical container's walls is $6L^2$, and its volume (V) is L^3 . Thus, the total pressure (F/A) is given by:

$$P = \frac{\overline{F_T}}{A} = \frac{2m\overline{v^2} / L}{6L^2} = \frac{m\overline{v^2}}{3L^3} = \frac{m\overline{v^2}}{3V}$$

which is the pressure exerted by a single "average" gas particle.

In n moles of gas, the total number of gas particles is nN_A , where N_A is Avogadro's number. Thus, the total pressure exerted by n moles of gas is:

$$P = nN_A \frac{\overline{mv^2}}{3V}$$

or

$$\frac{PV}{n} = \frac{2}{3} (\overline{\text{K.E.}}) \propto T$$

$$\text{since } \overline{\text{K.E.}} = \frac{1}{2} \overline{mv^2}.$$

The above equation has the same form as the ideal gas law:

$$PV = nRT$$

Thus, the Kelvin temperature is a measure of the average kinetic energy of the gas particles:

$$\frac{PV}{n} = RT = \frac{2}{3} (\overline{\text{K.E.}})$$

$$\overline{\text{K.E.}} = \frac{3}{2} RT \quad (\text{per mole})$$

$$= \frac{3}{2} kT \quad (\text{per molecule})$$

where k = Boltzmann's constant.

The root-mean-square velocity of the gas particles is given by:

$$v_{\text{rms}} = \sqrt{v^2} = \sqrt{\frac{3RT}{N_A m}} = \sqrt{\frac{3RT}{M}}$$

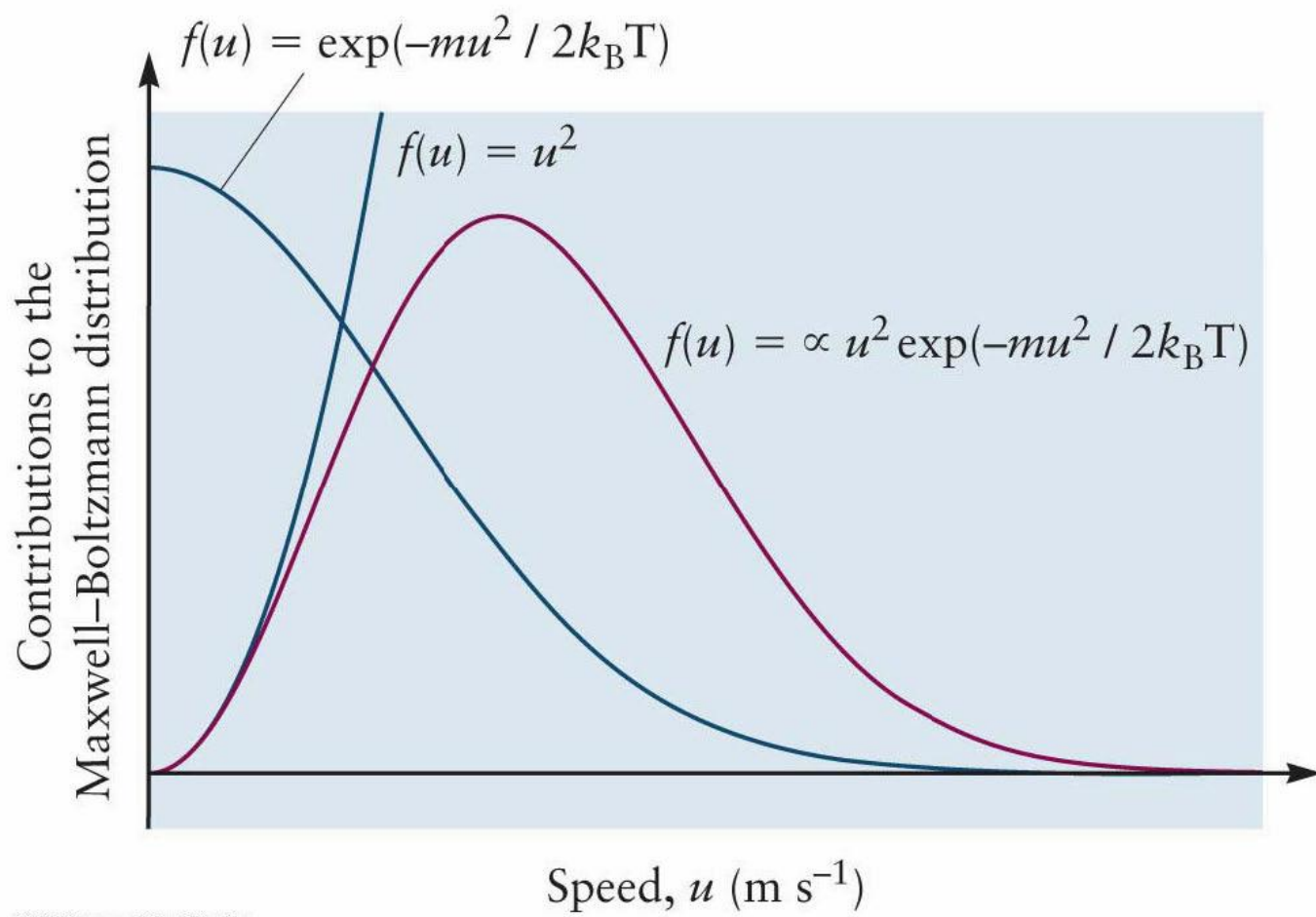
where $R = 0.08206 \text{ L-atm/mol-K} = 8.3145 \text{ J/mol-K}$.

The distribution of particle velocities in an ideal gas is given by the Maxwell-Boltzmann Law:

$$\begin{aligned} f(v) &= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \\ &= 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-mv^2/2kT} \end{aligned}$$

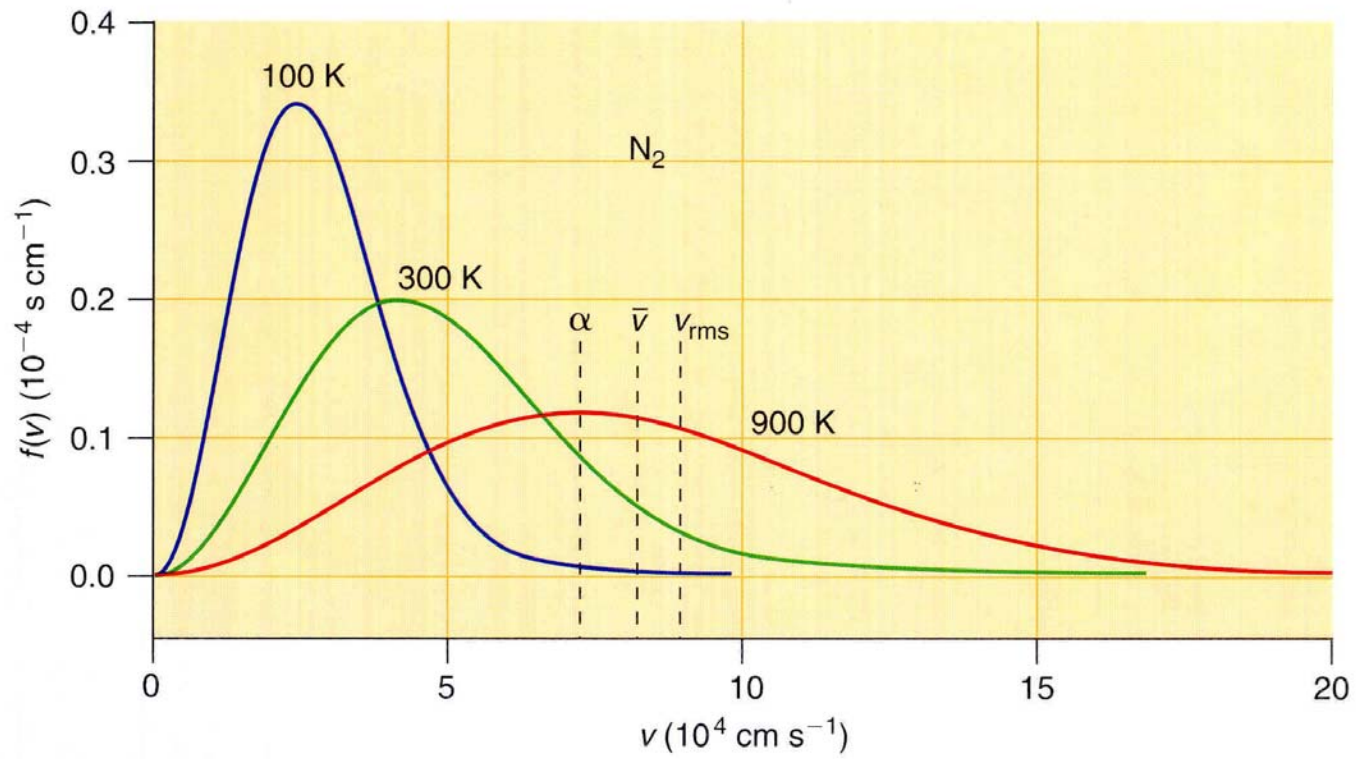
where $k = \text{Boltzmann's Constant} = 1.38 \times 10^{-27} \text{ J/K}$.

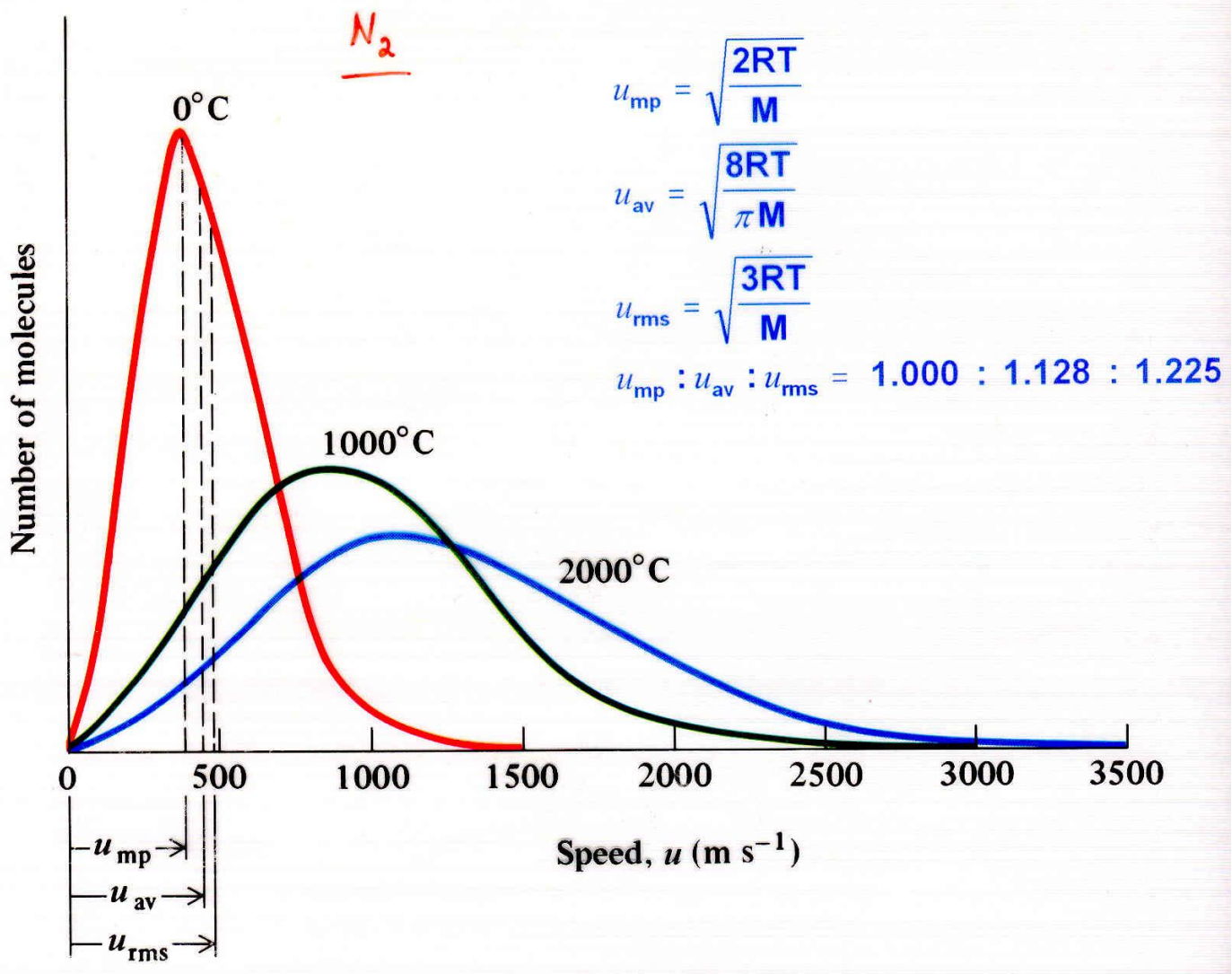
In the above expression, $f(v)$ is the fraction of gas particles having velocities between v and $v+dv$.



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Figure 9.12: Maxwell-Boltzmann Velocity Distributions



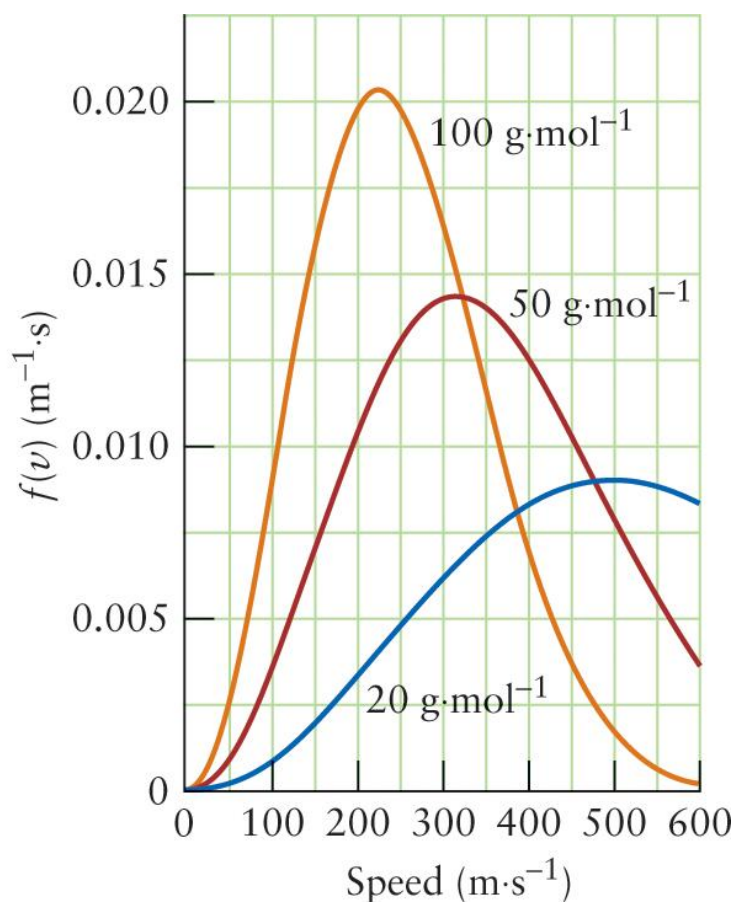


FIGURE 5.26 The range of molecular speeds for three gases, as given by the Maxwell distribution. All the curves correspond to the same temperature (300 K). The greater the molar mass, the lower is the average speed and the narrower the spread of speeds. To obtain the fraction of molecules with speeds in the range from v to $v + \Delta v$, multiply $f(v)$ by Δv .

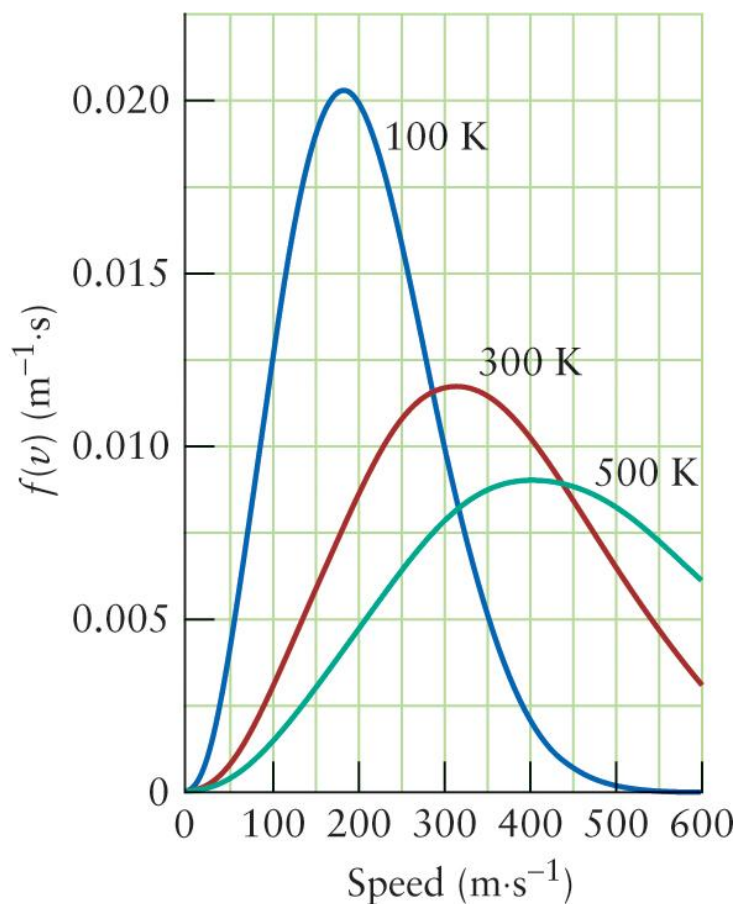
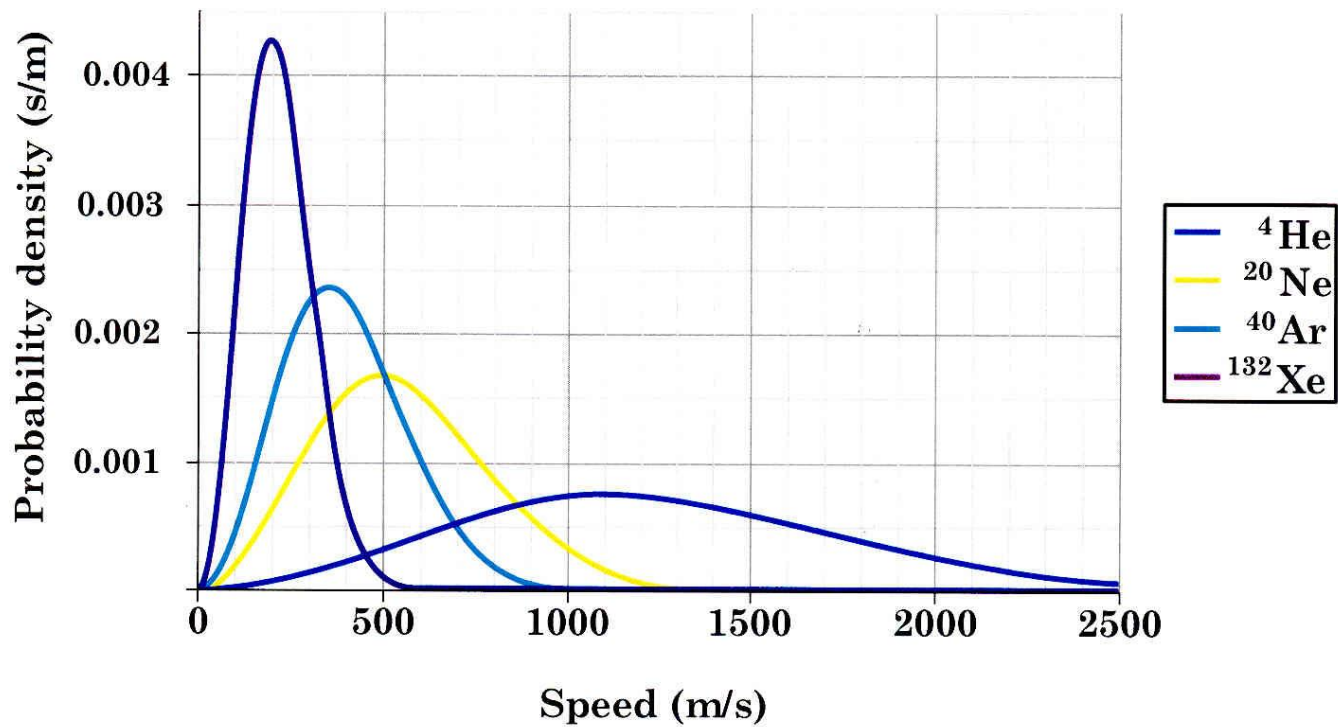
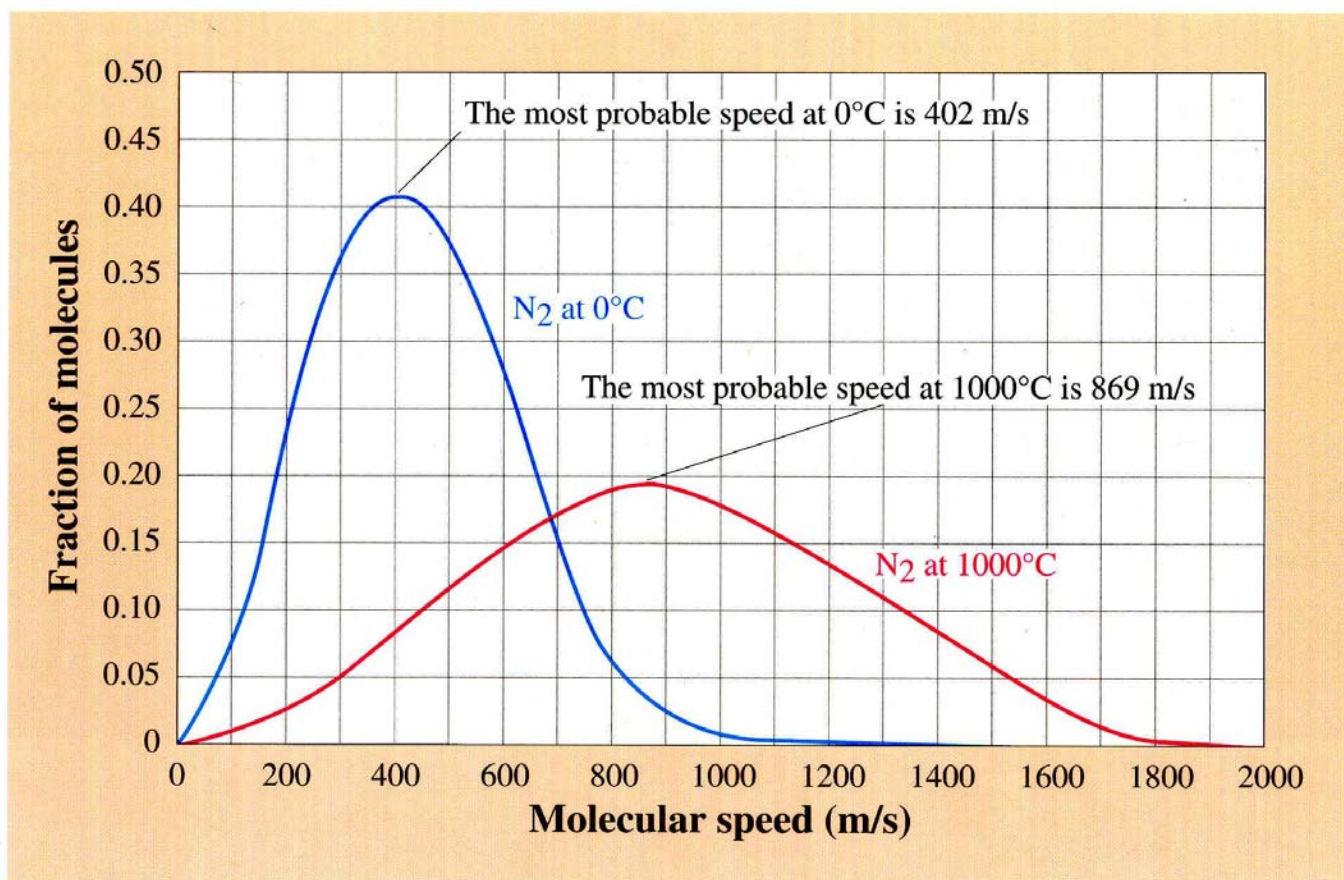


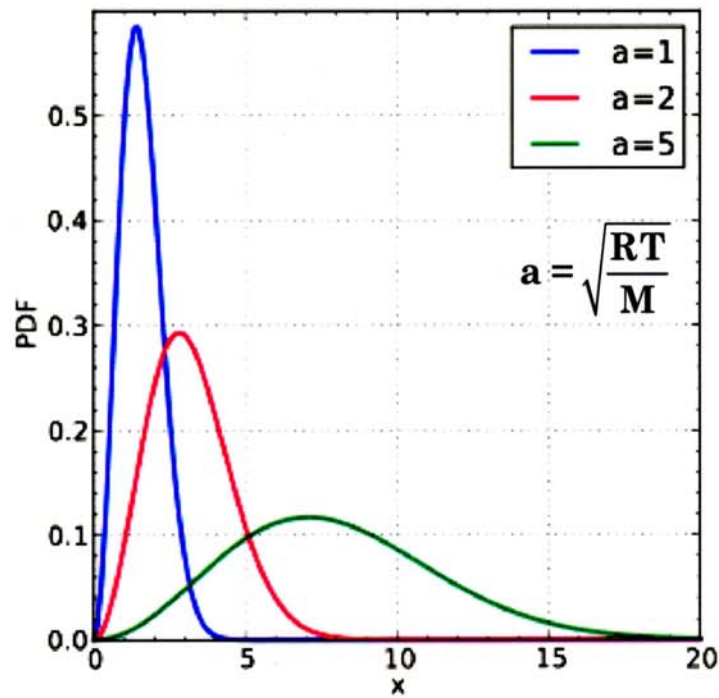
FIGURE 5.27 The Maxwell distribution again, but now the curves correspond to the speeds of a single substance (of molar mass 50 g·mol⁻¹) at different temperatures. The higher the temperature, the higher is the average speed and the broader the spread of speeds.

Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases

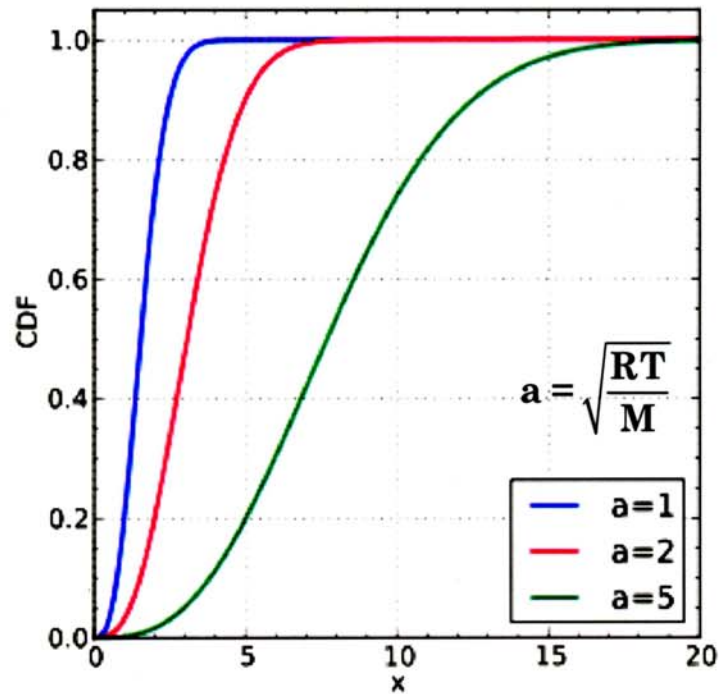


Maxwell-Boltzmann Distribution Curves for Molecular Speed

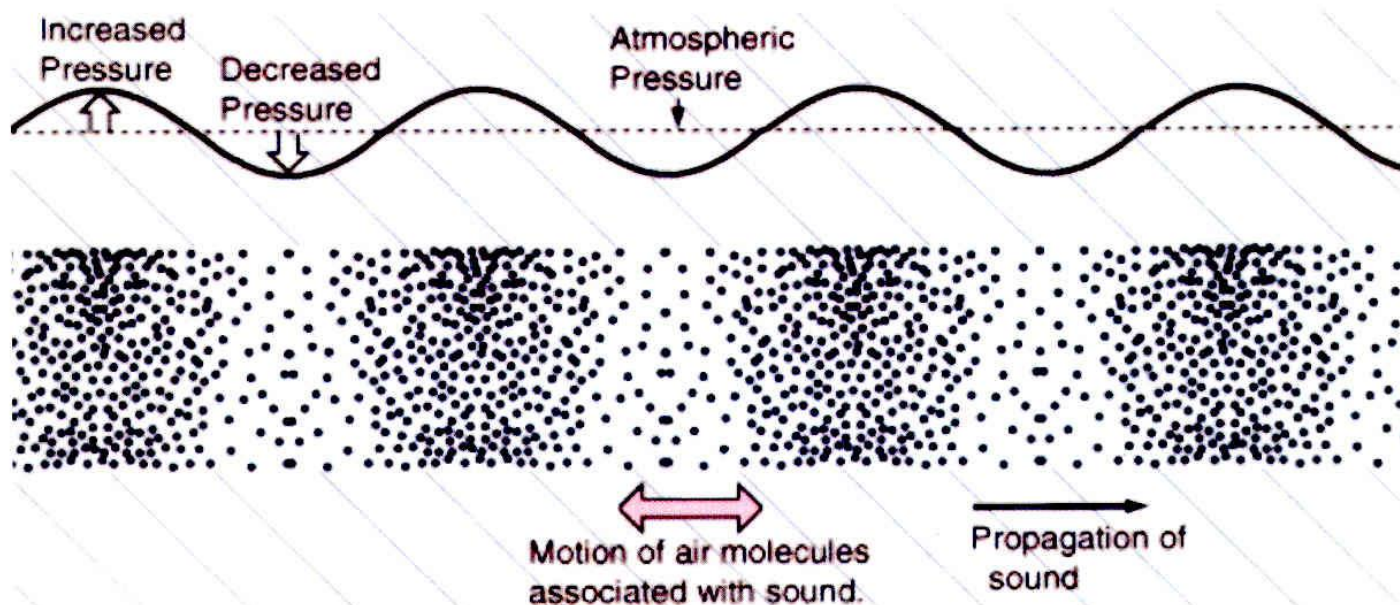
Maxwell-Boltzmann Probability Distribution Function (PDF):



Maxwell-Boltzmann Cumulative Distribution Function (CDF):



Propagation of Longitudinal Sound Waves in Air



VELOCITY OF SOUND IN DRY AIR

Data in this table apply only to dry air. These data have been calculated with air being treated as a perfect gas.

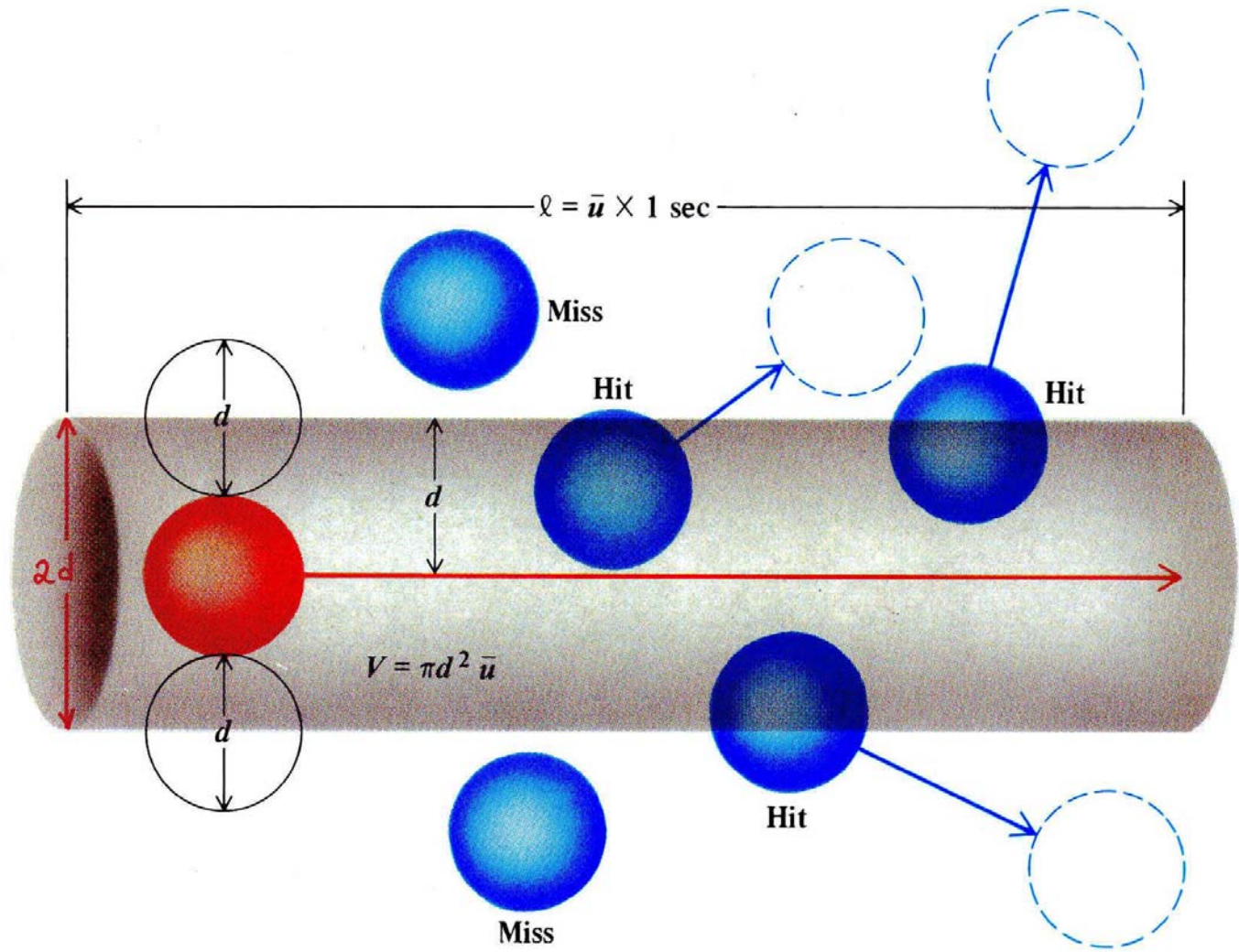
Temp °C	0 m/s	1 m/s	2 m/s	3 m/s	4 m/s	5 m/s	6 m/s	7 m/s	8 m/s	9 m/s
60	366.05	366.60	367.14	367.69	368.24	368.78	369.33	369.87	370.42	370.96
50	360.51	361.07	361.62	362.18	362.74	363.29	363.84	364.39	364.95	365.50
40	354.89	355.46	356.02	356.58	357.15	357.71	358.27	358.83	359.39	359.95
30	349.18	349.75	350.33	350.90	351.47	352.04	352.62	353.19	353.75	354.32
20	343.37	343.95	344.54	345.12	345.70	346.29	346.87	347.44	348.02	348.60
10	337.46	338.06	338.65	339.25	339.84	340.43	341.02	341.61	342.20	342.78
0	331.45	332.06	332.66	333.27	333.87	334.47	335.07	335.67	336.27	336.87
-10	325.33	324.71	324.09	323.47	322.84	322.22	321.60	320.97	320.34	319.72
-20	319.09	318.45	317.82	317.19	316.55	315.92	315.28	314.64	314.00	313.36
-30	312.72	312.08	311.43	310.78	310.14	309.49	308.84	308.19	307.53	306.88
-40	306.22	305.56	304.91	304.25	303.58	302.92	302.26	301.59	300.92	300.25
-50	299.58	298.91	298.24	297.56	296.89	296.21	295.53	294.85	294.16	293.48
-60	292.79	292.11	291.42	290.73	290.03	289.34	288.64	287.95	287.25	286.55
-70	285.84	285.14	284.43	283.73	283.02	282.30	281.59	280.88	280.16	279.44
-80	278.72	278.00	277.27	276.55	275.82	275.09	274.36	273.62	272.89	272.15
-90	271.41	270.67	269.92	269.18	268.43	267.68	266.93	266.17	265.42	264.66

VELOCITY OF SOUND IN

GASES AND VAPORS

Substance	Formula	Density g/l	Velocity m/s	$\delta v/\delta t$ m/sec °C	<u>M.W.</u>
Gases (0°C)					
Air, dry		1.293	331.45	0.59	~ 29
Ammonia	NH ₃	0.771	415		17
Argon	Ar	1.783	319*	0.56	
Carbon monoxide	CO	1.25	338	0.6	
Carbon dioxide	CO ₂	1.977	259	0.4	44
Chlorine	Cl ₂	3.214	206		71
Deuterium	D ₂		890	1.6	
Ethane (10°C)	C ₂ H ₆	1.356	308		30
Ethylene	C ₂ H ₄	1.260	317		28
Helium	He	0.178	965	0.8	4
Hydrogen	H ₂	0.0899	1284	2.2	2
Hydrogen bromide	HBr	3.50	200		
Hydrogen chloride	HCl	1.639	296		
Hydrogen iodide	HI	5.66	157		
Hydrogen sulfide	H ₂ S	1.539	289		
Illuminating (Coal gas)			453		
Methane	CH ₄	0.7168	430		16
Neon	Ne	0.900	435	0.8	
Nitric oxide (10°C)	NO	1.34	324		
Nitrogen	N ₂	1.251	334	0.6	
Nitrous oxide	N ₂ O	1.977	263	0.5	
Oxygen	O ₂	1.429	316	0.56	
Sulfur dioxide	SO ₂	2.927	213	0.47	64
Vapors (97.1°C)					
Acetone	C ₃ H ₆ O		239	0.32	
Benzene	C ₆ H ₆		202	0.3	
Carbon tetrachloride	CCl ₄		145		
Chloroform	CHCl ₃		171	0.24	
Ethanol	C ₂ H ₆ O		269	0.4	
Ethyl ether	C ₄ H ₁₀ O		206	0.3	
Methanol	CH ₄ O		335	0.46	
Water vapor (134°C)	H ₂ O		494		

* At 20°C.



For an individual molecule having a diameter of d and an average velocity of \bar{v} , the volume of a “collision cylinder” swept out by the molecule in 1 sec is:

$$V_{\text{cyl}} = \pi d^2 \bar{v}$$

If N/V is the number of molecules per unit volume in the gas (*i.e.*, the number density of the gas), then the number of collisions per second experienced by the moving molecule is:

$$\text{Collision Frequency} = Z = \sqrt{2} \frac{N}{V} V_{\text{cyl}} = \sqrt{2} \frac{N}{V} \pi d^2 \bar{v}$$

where the factor $\sqrt{2}$ accounts for the fact that the other molecules are also moving.

Inserting the value for \bar{v} ($= \sqrt{8RT / \pi M}$) gives the frequency at which gas particles collide with other particles:

$$Z = 4 \frac{N}{V} d^2 \sqrt{\frac{\pi RT}{M}} \text{ collisions / sec}$$

The average distance traveled by a gas particle between collisions with other particles is called the **Mean Free Path**, λ , and is inversely related to the collision frequency:

$$\text{Mean Free Path} = \frac{1}{Z} \times \bar{v} = \lambda = \frac{1}{\sqrt{2} \left(\frac{N}{V} \right) (\pi d^2)}$$

For N_2 , for example, at 25°C , $Z = 4.1 \times 10^9$ collisions/sec, and $\lambda = 2.3 \times 10^{-7} \text{ m} = 2,300 \text{ \AA}$. Thus, an “average” N_2 molecule at 25°C travels approximately 1,000 molecular diameters between collisions with other N_2 molecules.

Diffusion is the process by which initially separated gases gradually mix, or by which differing gases penetrate a porous barrier at different rates. Diffusion rates are proportional to $(\text{M.W.})^{-0.5}$, similar to effusion rates. The **diffusion constant** of a gas is a quantitative measure of its rate of diffusion. For a single-component gas, it is given by:

$$D = \frac{3}{8} \sqrt{\frac{RT}{\pi M}} \frac{1}{d^2 (N/V)} \text{ m}^2 / \text{ s}$$