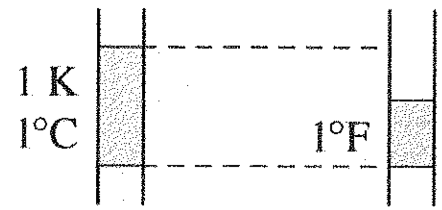
Lecture 42

(CH12:3-4)

Figure 12.2

Kelvins and Celsius degrees are larger than Fahrenheit degrees by 9/5:

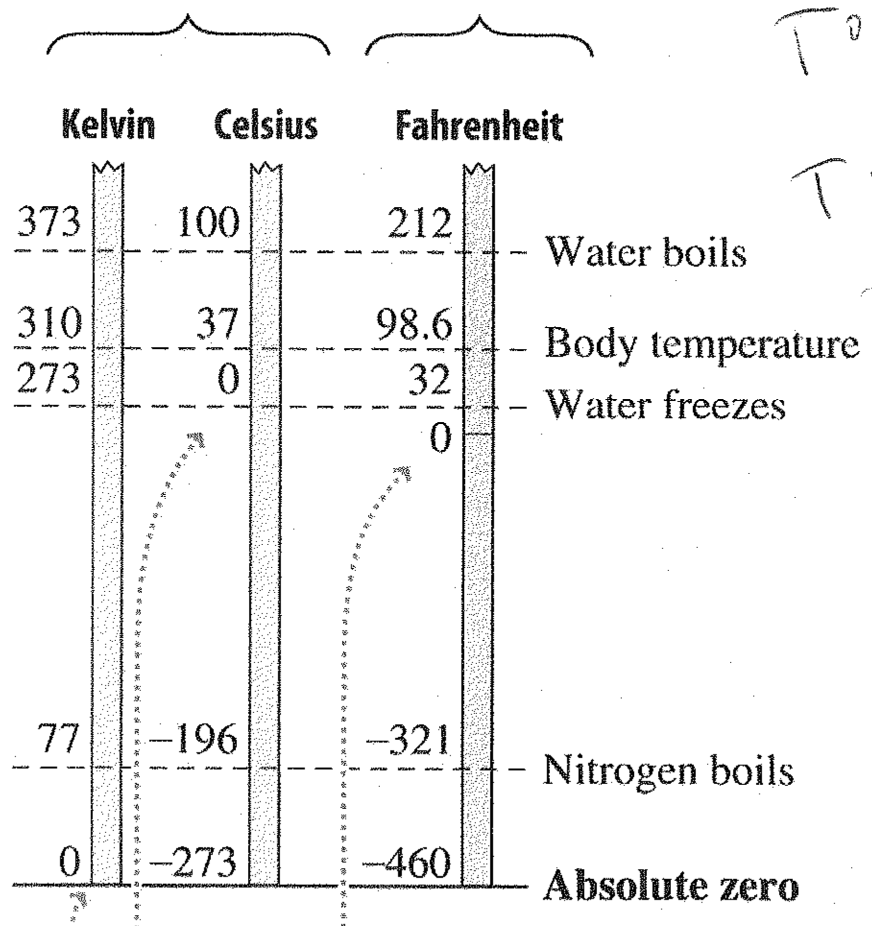


$$\frac{1\text{ K (or }1^\circ\text{C)}}{1^\circ\text{F}} = \frac{9}{5}$$

$T°C = \frac{5}{9}(T°F - 32°)$

$T\,K = T°C + 273.15$

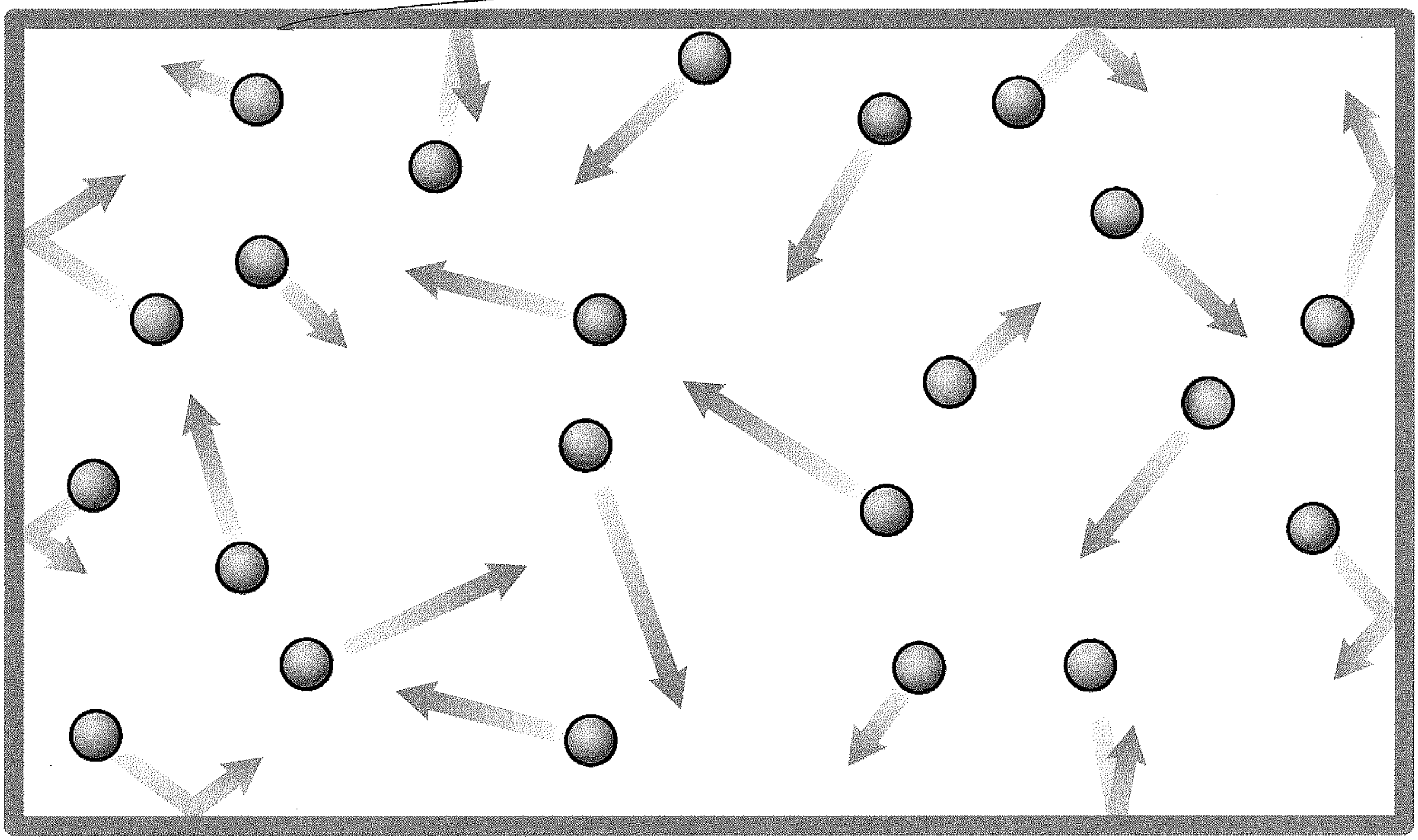
$T°F = \frac{9}{5}T°C + 32$



The three scales also have different zero points.

Figure 12.7

Ideal gases



The amount of gas:

1 mol $6.022 \times 10^{23} = N_A$

$N = N_A \cdot n$

2.85 mol $= (6.022 \times 10^{23})(2.85) = 1.72 \times 10^{24}$ molecules

$M_{molar}(O_2) = 32g = 16_{(O)} + 16_{(O)} = 32\ O_2$

EXAMPLE 12.5 Carbon Dioxide

How many molecules are in a 77.0-g sample of carbon dioxide (CO_2)?

ORGANIZE AND PLAN The molar mass comes from the periodic table and the formula CO_2: It's the sum of one mole of carbon atoms and two moles of oxygen atoms. Then the number of moles and number of molecules follow from the relations $m = nm_{molar}$ and $N = N_A n$.

Known: mass $m = 77.0$ g.

SOLVE From the periodic table (or Appendix D), the molar masses for carbon and oxygen are 12.0 g and 16.0 g, respectively. Therefore, CO_2's molar mass is

$$m_{molar} = 12.0\text{ g} + 2(16.0\text{ g}) = 44.0\text{ g}$$

With mass $m = 77.0$ g, our sample contains

$$n = \frac{m}{m_{molar}} = \frac{77.0\text{ g}}{44.0\text{ g/mol}} = 1.75\text{ mol}$$

Then the number of molecules is $N = N_A n = (6.022 \times 10^{23}\text{ molecules/mol})(1.75\text{ mol}) = 1.05 \times 10^{24}$ molecules.

REFLECT This large number is one reason scientists use moles to measure the amount of a substance; the smaller numbers of moles are much more manageable.

MAKING THE CONNECTION Air is 78% nitrogen (N_2), 21% oxygen (O_2), and 1% argon (Ar). What's the average molar mass of air?

ANSWER The three molar masses are, respectively, 28.0 g, 32.0 g, and 39.9 g. Taking their weighted average gives 29.0 g.

Ideal Gasses: no interaction between molecules

N_A

$1\ mol \rightarrow 6.022 \times 10^{23}$ molecules

$N = n \cdot N_A$

$g \cdot mol^{-1}$

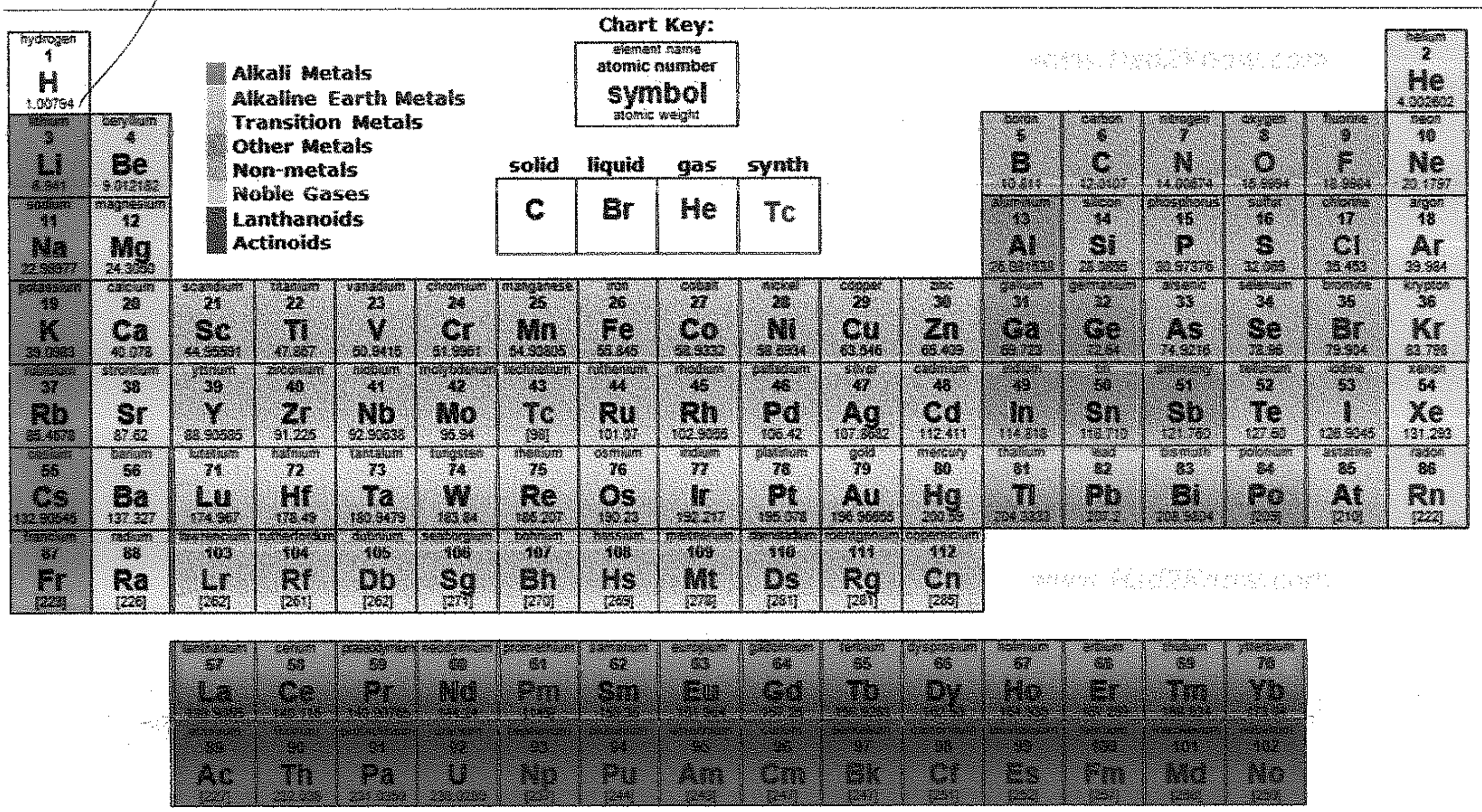


Figure 12.8

Ideal Gas Laws

State variables

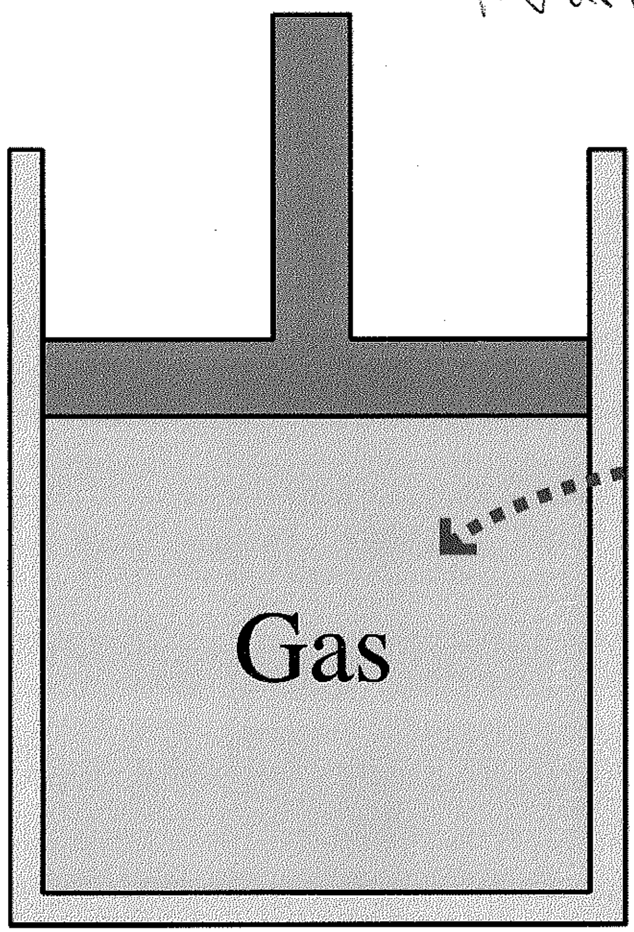
$p \cdot V = \text{const}$; $n, T = \text{const}$

$V \sim T$; $n, p = \text{const}$

$p \sim n$; $T, V = \text{const}$

$p \sim T$; $n, V = \text{const}$

$\boxed{p \cdot V = n \cdot R T}$ $R = 8.31 \left[mol^{-1} \cdot J \cdot K^{-1} \right]$ molar gas constant



The amount of gas remains constant, but its volume, temperature, and pressure may change.

$\boxed{T \text{ in K!!}}$

$N = n \cdot N_A \rightarrow n = \frac{N}{N_A}$

$p \cdot V = N \frac{R}{N_A} \cdot T = N k_B T$, where

$k_B = 1.38 \times 10^{-23} \frac{J}{K}$ molecular gas constant

A 10 liter tank contains ideal gas at 30 °C and a pressure of 15 atm. How many moles of gas are in the tank ?

Equation of state for ideal gas: p.V = n.R.T so n = (P.V)/(R.T)

Where p – pressure in Pa, V – volume in m^3, n – number of moles, R – gas constant = 8.31 $J.mol^{-1}\,K^{-1}$ and T – temperature in "K". Note T [K] = T °C + 273 = 303 K. Also, note 1 atm = 1.013×10^5 Pa and 1 liter = $10^{-3}\,m^3$

Then $n = (15 \times 1.013 \times 10^5\ [Pa] \times 10\ [liters] \times 10^{-3}\ [m^3]) / (8.31\ [J.mol^{-1}\,K^{-1}] \times 303\ [K]) = 6$ moles

Ideal gas is in a closed metal cylinder. If its pressure is 1000 Pa initially, and its temperature is 293 K, what is its pressure after its temperature is raised to 333 K ?

Equation of state (atomic) for ideal gas: $p.V = n.R.T$

So for the initial state: $p_1 .V_1 = N.k_B .T_1$ Note: $V_1 = V_2$

And for the final state: $P_2 .V_2 = N.k_B .T_2$

Therefore, $(p_1)/(p_2) = T_1/T_2$

and isolating $p_2 = (p_1 \times T_2)/T_1$

$p_2 = (1000\,[Pa] \times 333\,[K]) / (293\,[K])$

$p_2 = 1137$ Pa

Kinetic theory of gas

Assumptions:

- **Dilute gas with negligible interactions.**
- **Elastic collisions between molecules and the container walls.** (Elastic collisions: gas doesn’t lose or gain energy.)
- **Pressure on the container walls results from collisions between gas molecules and the walls.**

Pressure

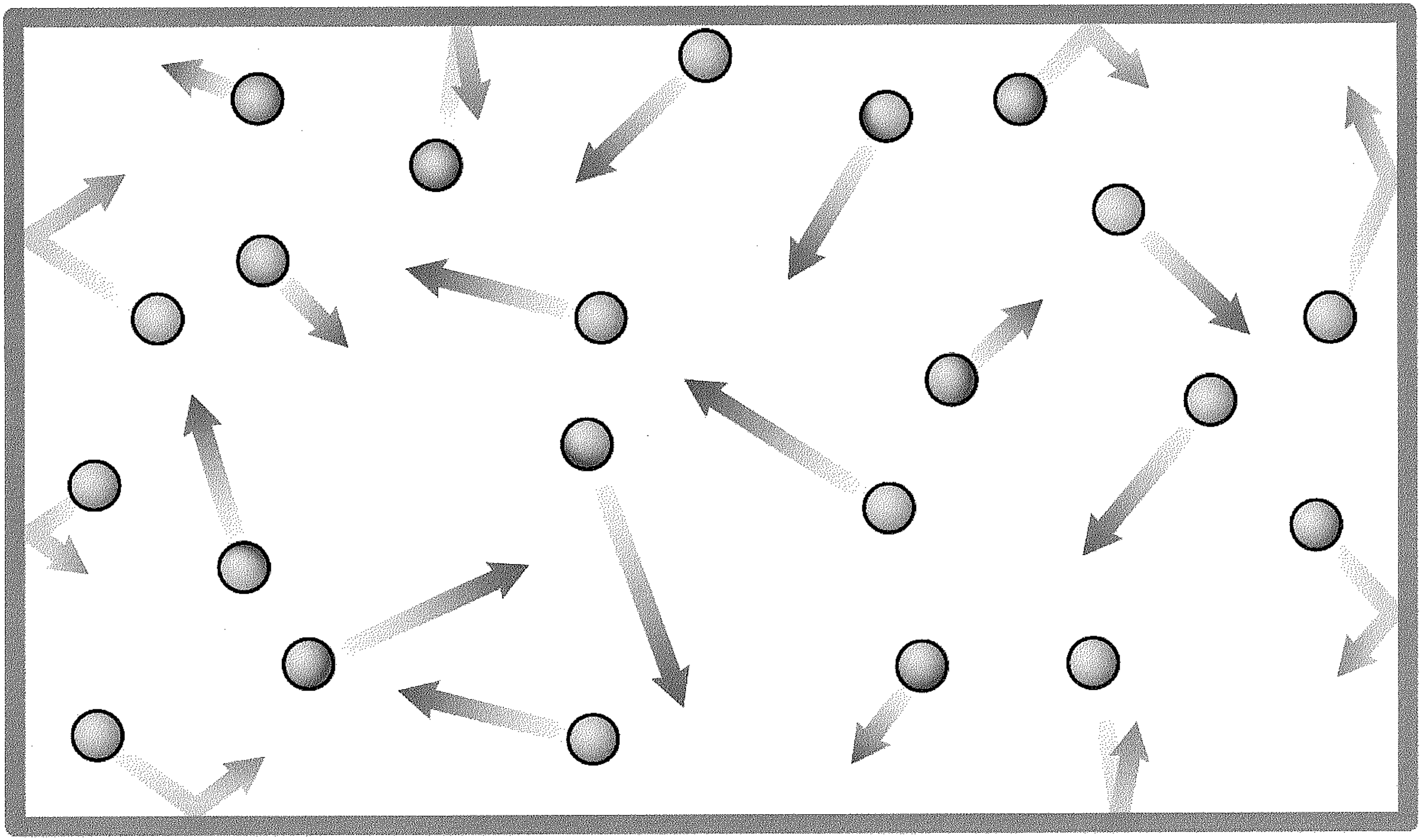
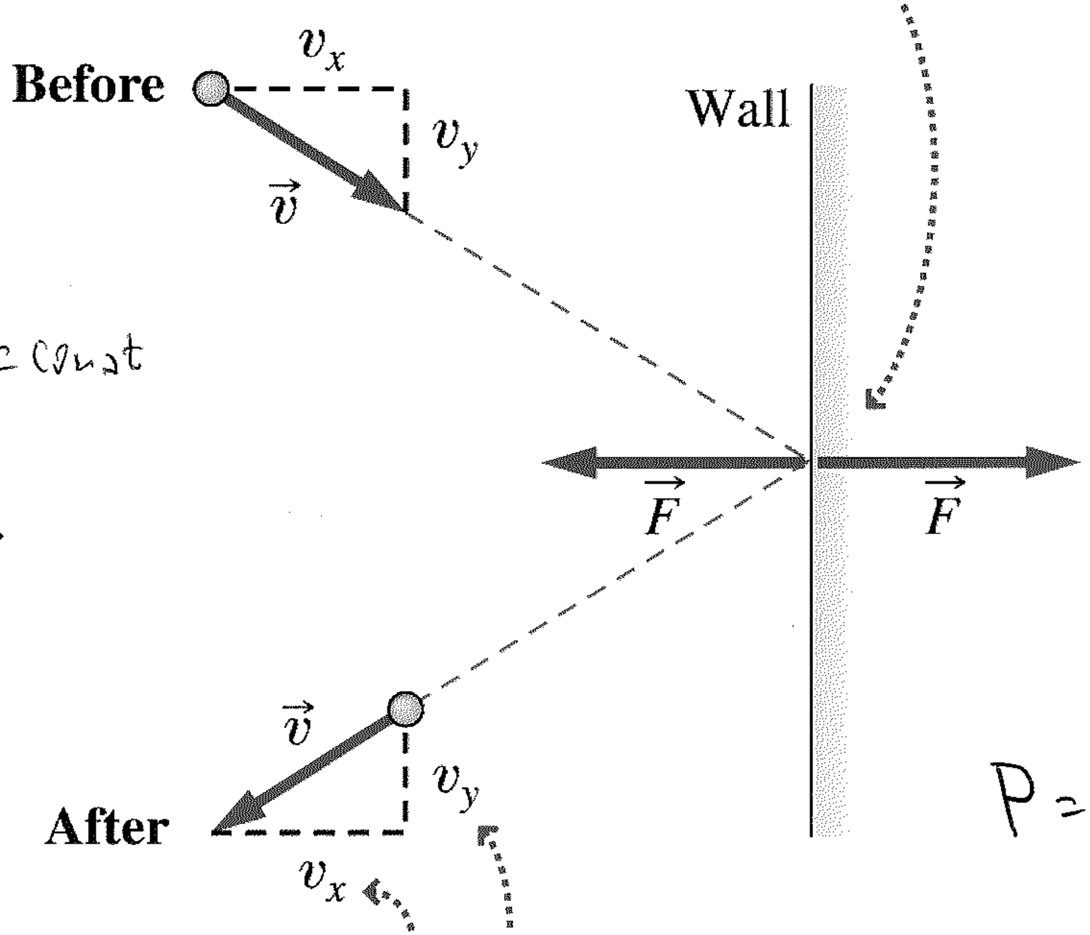


Figure 12.10

When a molecule collides elastically with a container wall, the molecule and wall exert forces on each other.



The force exerted on the molecule reverses the sign of the *x*-component of the velocity but does not change the *y*-component.

$E = \text{const}$

$\frac{\Delta p}{\Delta t} = F \neq 0$

p – momentum

P – pressure

Elastic $\rightarrow E_k = \text{const}$

$\Delta\vec{p} \neq 0$

$\frac{\Delta\vec{p}}{\Delta t} \neq 0 \neq \vec{F}$

$\vec{p} = m\vec{v}$

$P = \frac{Nm\overline{v^2}}{3V}$

$V_{RMS} = \sqrt{\overline{V^2}}$

From $P = N \frac{m\overline{V^2}}{3V}$; $\overline{V^2} = \frac{1}{N}\sum_i V_i^2$; $V_{rms} = \sqrt{\overline{V^2}}$

$P.V = N \frac{m\overline{V^2}}{3}$ $\cancel{N}\frac{m\overline{V^2}}{3} = \cancel{N} K_B T$

$P.V = N K_B T$

$PV = nRT = NRT/N_A$

$\frac{R}{N_A} = K_B = 1{,}38 \times 10^{-23}\ J/K$

$\longrightarrow m\overline{V^2} = 3 K_B T$ $\times \frac{1}{2}$

$\overline{K} = \frac{1}{2} m\overline{V^2}$ → one ~~molecule~~ atom

$$\boxed{\overline{K} = \frac{3}{2} K_B T\ [K]}$$

Thermal energy $E_{TR} = N.\overline{K}$

$= \frac{3}{2} N K_B T$

Sample Problem 19-3

Here are five numbers: 5, 11, 32, 67, and 89.

(a) What is the average value of these numbers?

$$n_{avg} = \frac{5+11+32+67+89}{5} = 40.8$$

(b) What is the *rms* value n_{rms} of these numbers?

$$n_{rms} = \sqrt{\underbrace{\frac{5^2+11^2+32^2+67^2+89^2}{5}}_{\overline{V^2}}} = 52.1$$

Find the average kinetic energy of a molecule of ideal gas at 654 K. The value of Boltzmann's constant $k_B = 1.38 \times 10^{-23}$ J/K.

By definition the average kinetic energy of a molecule is $\bar{K} = (3/2) .K_B .T$

Therefore, in our case, $\bar{K} = (3/2) . (1.38 \times 10^{-23}) .(654) = 1.35 \times 10^{-20}$ J

Find the thermal energy of 3.5 mol of monoatomic gas at 293 K and 1. Note the molar gas constant $R = 8.315$ J/(mol.K)

By definition $E_{th} = (3/2).N.k_B.T$

where $N = N_A.n$

Here "N_A" is so-called Avogardro's number and "n" – number of moles.

Also, $k_B = R/N_A$, therefore $E_{th} = (3/2).N.k_B.T = (3/2).(N_A .n)(R/N_A) .T$

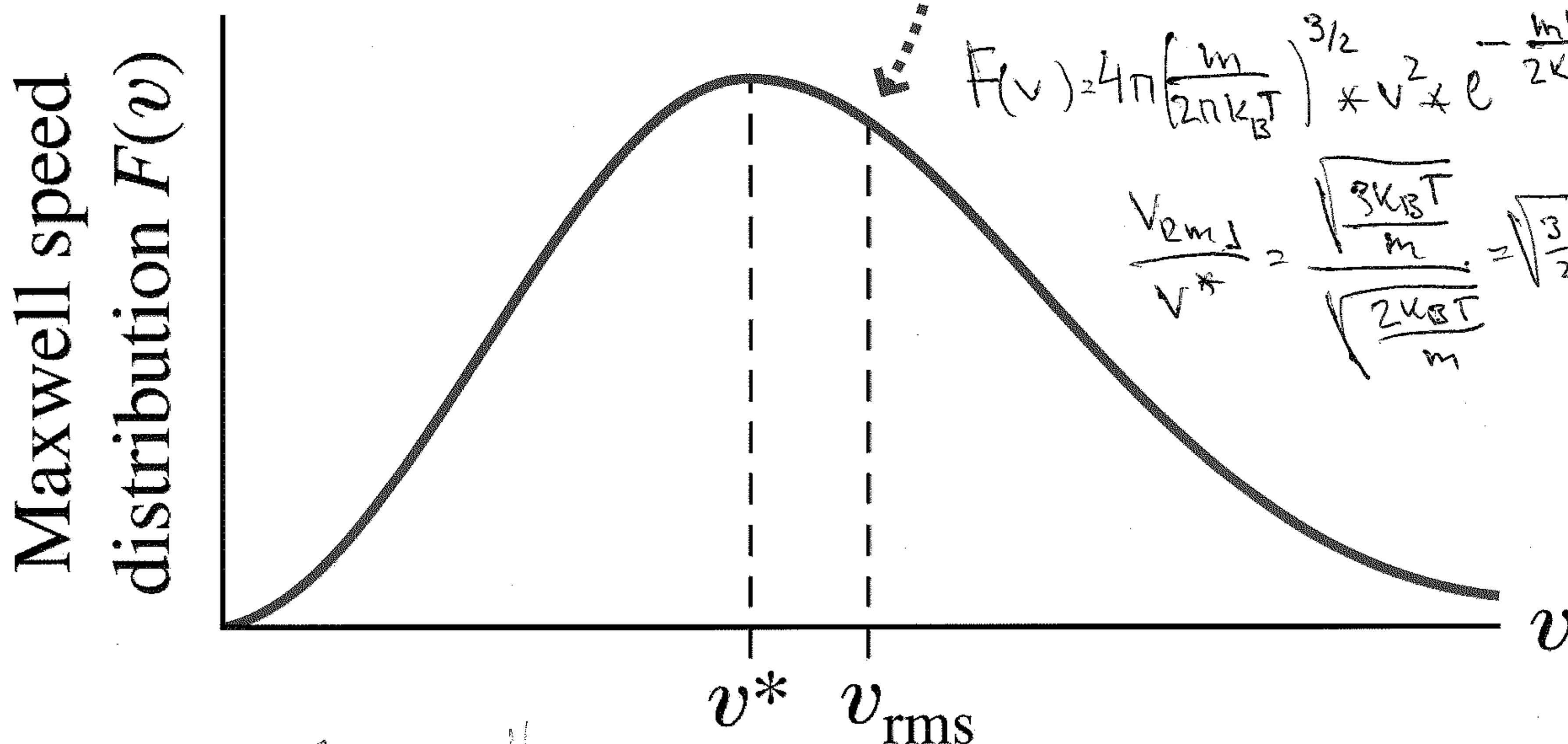
$= (3/2).n. R .T$

In our case $E_{th} = (3/2).(3.5). (8.315).(293) = 12.8$ kJ

Figure 12.11

Distribution of molecular speeds

v_{rms} is larger than the most probable speed v^*.



$$F(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} * v^2 * e^{-\frac{mv^2}{2k_BT}}$$

$$\frac{V_{rms}}{v^*} = \frac{\sqrt{\frac{3k_BT}{m}}}{\sqrt{\frac{2k_BT}{m}}} = \sqrt{\frac{3}{2}} = 1.225$$

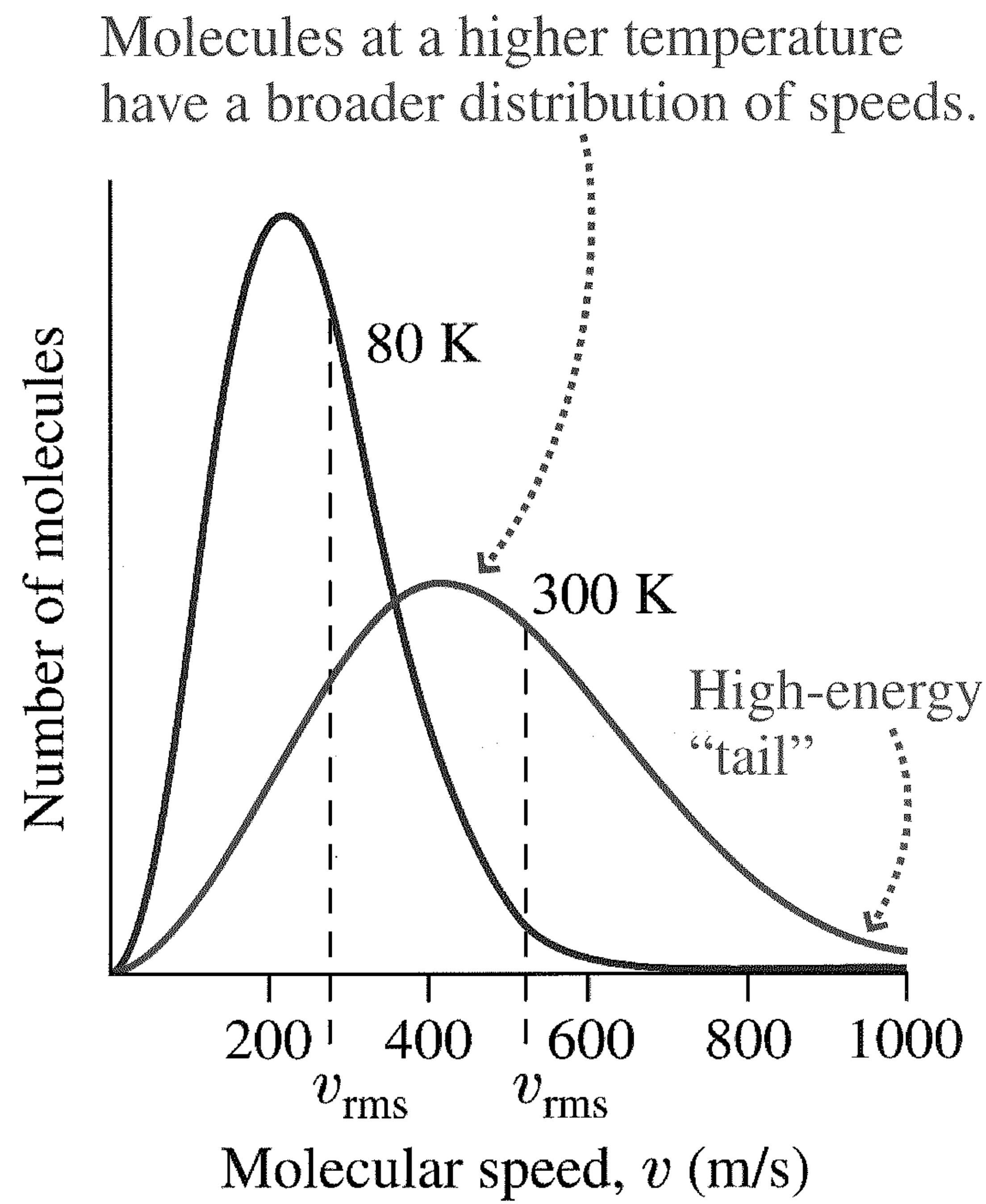
$V_{rms} = \sqrt{\frac{3k_BT}{m}}$

from $\frac{1}{2}m\overline{V^2} = \overline{K} = \frac{3}{2}k_BT$

$V^* = \sqrt{2k_BT/m}$, m - molecule mass

most probable speed

Figure 12.12



Molecules at a higher temperature
have a broader distribution of speeds.
Number of molecules
80 K
300 K
High-energy
"tail"
200
400
600
800
1000
v_{rms}
v_{rms}
Molecular speed, v (m/s)

At what temperature would the average thermal/most probable speed of oxygen molecules be 33 m/s ? The mass of O_2 molecule is 5.312 x10^{-26} kg.

Average thermal/most probable speed is $v^* = \sqrt{2k_BT/m}$.

Therefore, $(v^*)^2 = 2k_BT/m$ and so $T = (v^*)^2 \times m(O_2) / (2 \times k_B)$

$= (33\ \text{m/s})^2 \times 5.312 \times 10^{-26}\ \text{kg} / (2 \times 1.38 \times 10^{-23}\ \text{J/K})$

$= 2.1$ K

$V_{rms}(H_2) = ?$ at $0°C$ $(273K)$ and $(2*273K)$

65. **ORGANIZE AND PLAN** (a) We use the equation for the rms speed as $v_{rms} = \sqrt{\frac{3\,k_B T}{m}}$, where we find the mass of one H_2 molecule by dividing by Avogadro's number, N_A. For part (b), we repeat the calculation for the higher temperature.

$H \to 1*10^{-3}\ \frac{kg}{mol}$

$H_2 \to 2*10^{-3}\ \frac{kg}{mol}$

SOLVE

(a)

$$v_{rms} = \sqrt{\frac{3k_B T}{(M/N_A)}} = \sqrt{\frac{3\,(1.38\times10^{-23}\ J\,K^{-1})\times(273.15\ K)}{(2.02\times10^{-3}\ kg\,mol^{-1}/6.022\times10^{23}\ mol^{-1})}} = 1836.1\ m/s^{-1}$$

$m = \frac{M}{N_A}$

(b)

$$v_{rms} = \sqrt{\frac{3\,k_B T}{(M/N_A)}} = \sqrt{\frac{3\,(1.38\times10^{-23}\ J\,K^{-1})\times(546.0\ K)}{(2.02\times10^{-3}\ kg\,mol^{-1}/6.022\times10^{23}\ mol^{-1})}} = 2595.9\ m/s^{-1}$$

REFLECT The rms speed increases with the square root of the increase in temperature.

$$\frac{1}{\cancel{2}} m \overline{V^2} = \frac{3}{\cancel{2}} k_B T$$

$$\overline{V^2} = \frac{3k_B T}{m} \quad \sqrt[2]{\ }$$

$$V_{rms} = \sqrt{\overline{V^2}} = \sqrt{\frac{3k_B T}{m}}$$

$$M(H_2) = M(H) + M(H)$$
$$= 1.01*10^{-3} + 1.01*10^{-3}\ [kg.mol^{-1}]$$

$$m = \frac{M}{N_A}$$

$= 44 \times 10^{-3} \frac{kg}{mol}$

$Molar(CO_2) = 12+16+16 = 44 \, g/mol \; ; \; V_{rms} = 652 \frac{m}{s} \,|\, T = ?$

70. ORGANIZE AND PLAN We use the equation for the rms speed and solve for temperature.

SOLVE $v_{rms} = \sqrt{\frac{3k_B T}{(M/N_A)}}$, $V^2_{rms} = \frac{3k_B T}{(M/N_A)} \rightarrow T = \frac{(M/N_A) \cdot V^2_{rms}}{3k_B}$

$$T = \frac{(M/N_A)\, v_{rms}^2}{3k_B} = \frac{(44\times10^{-3}\ \text{kg mol}^{-1}/6.022\times10^{23}\ \text{mol}^{-1})\times(652\ \text{m s}^{-1})}{3\times\ (1.38\times10^{-23}\ \text{J K}^{-1})} = 750.3\ \text{K}$$

Venus

$$\frac{1}{2} m \overline{V^2} = \frac{3}{2} k_B T$$

$$V_{rms} = \sqrt[2]{\overline{V}^2} = \sqrt[2]{\frac{3k_B T}{m}} = \sqrt[2]{\frac{3k_B T}{(M/N_A)}}$$

$$T = \frac{(M/N_A) \times V^2_{rms}}{3k_B}$$

Figure 12.13

Diffusion

The molecules move randomly, but the density difference means that more molecules move from the high- to the low-density region than vice versa, until the density difference is erased.

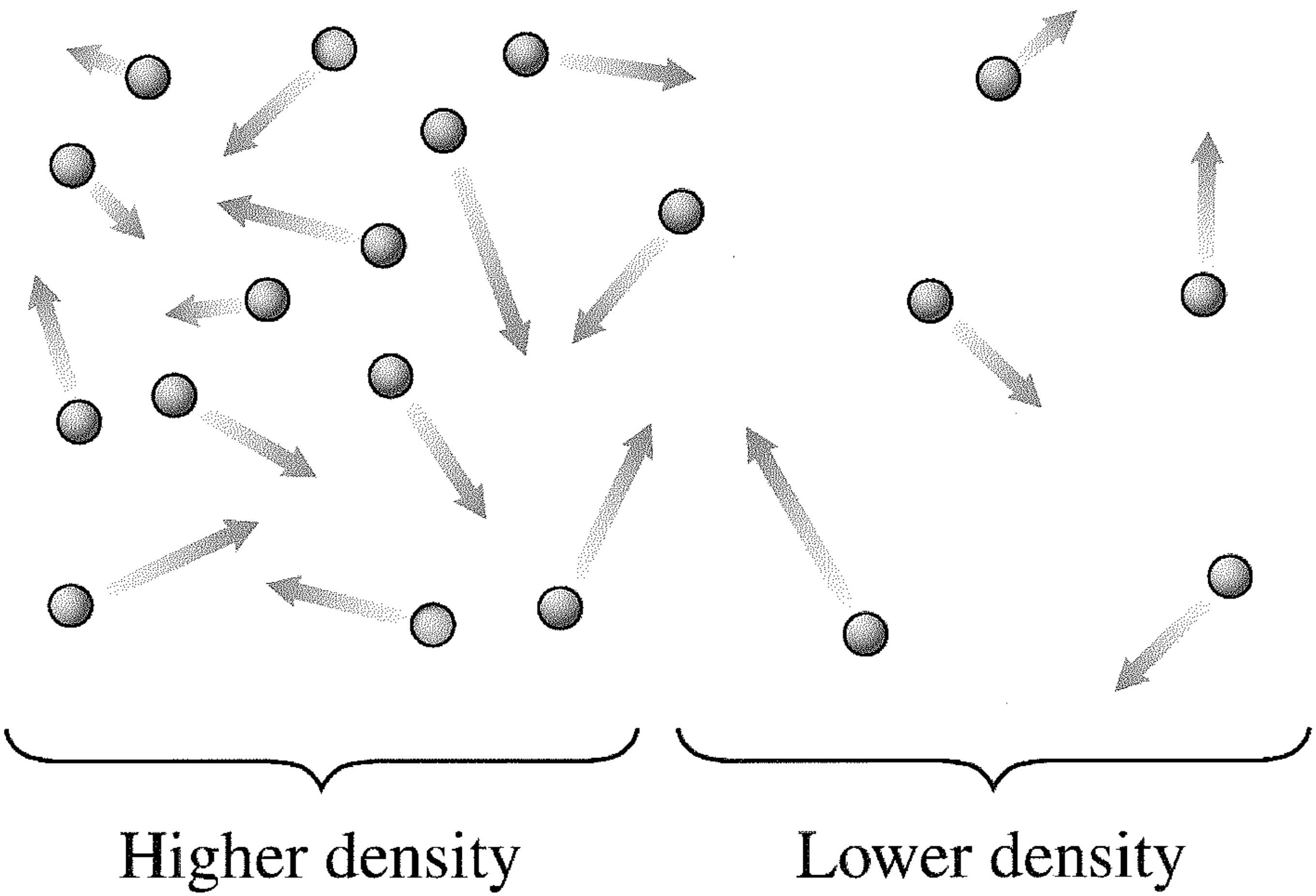
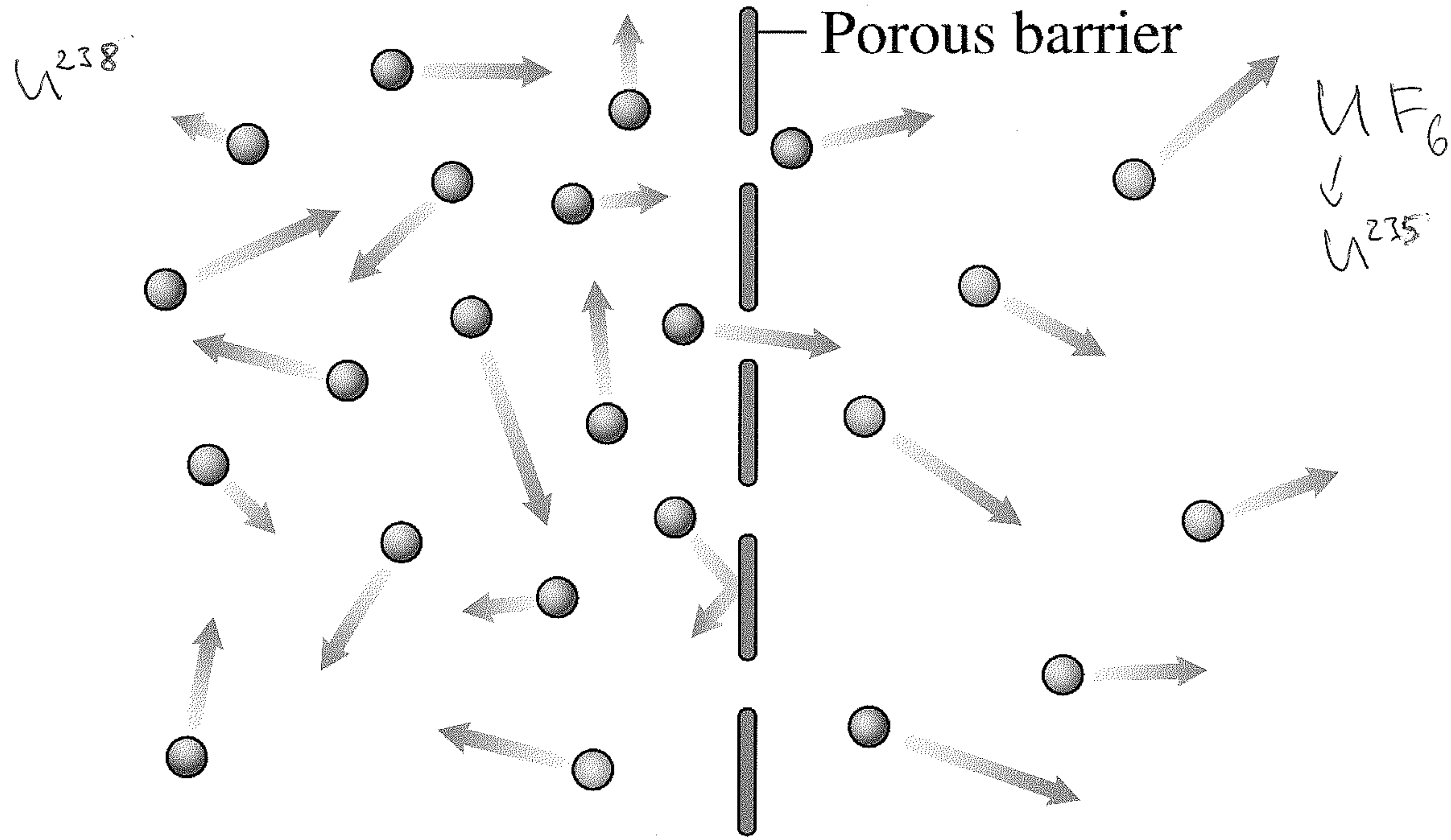


Figure 12.14

Figure 12.15

Faster molecules encounter the barrier more often than slower ones and therefore pass through it more frequently.



 $\updownarrow$ 12.5 m ; $\rho_{H_2O} = 1030\ kg/m^3$ | $V = ?$ at surface
air bubble ~ 25 cm^3 | $T = 20°C$

61. ORGANIZE AND PLAN We use the definition of the hydrostatic pressure, the pressure at a certain depth, inserted into the ideal gas law, and we can calculate the amount air exhaled by the diver. Then, we use this result to calculate the volume of the bubble at the surface using the ideal gas law. We assume a water temperature of 20°C.

SOLVE With the definition of the hydrostatic pressure, $P = \rho gh$, where g, r, and h are the density of water, the gravitational constant, ~~and the dep~~th, we can calculate number of moles of air exhaled at 12.5 m:

$\boxed{PV = nRT}$ || $P_{H_2O} = \rho g h$
$P \cdot V = n \cdot R \cdot T$

$$n = \frac{PV}{RT} = \frac{(\rho gh + P_0)\ V}{RT}$$

$$n = \frac{\left[(1030\ \text{kg m}^3)\times(9.81\ \text{m/s}^2)\times(12.5\ \text{m}) + (101325\ \text{Pa})\right]\times(0.000\ 025\ \text{m}^3)}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})\times(293.15\ \text{K})} = 2.33\times10^{-3}\ \text{mol}$$

Using the number of moles, the volume at the surface is then:

25 cm^3 ?

$$V = \frac{nRT}{P} = \frac{(2.33\times10^{-3}\ \text{mol})\times(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\times(293.15\ \text{K})}{(101325\ \text{Pa})} = 5.61\times10^{-5}\ \text{m}^3 = 56.1\ \text{cm}^3$$

$1\ m^3 = (100\ cm)(100\ cm)(100\ cm) =$

$= 1 \times 10^6\ cm^3$

$1\ cm^3 = 10^{-6}\ m^3$

$V = 2.12 \times 10^5\ m^3 \rightarrow H_2 \qquad \frac{m(H_2)}{m(He)} = ?$

63. **ORGANIZE AND PLAN** We use the ideal gas law combined with the definition of molecular mass. To obtain the same buoyancy with He as with H_2, the blimp has to have the same volume, since the mass of the replaced air volume is providing the force to keep the blimp in the air.

SOLVE

(a)

ϕH_2

$$n = \frac{PV}{RT} = \frac{m}{M} \rightarrow m = \frac{P.V.M}{R.T}$$

The mass of H_2 in the Hindenburg is:

$\rightarrow \frac{N}{m^2}$

$$m(H_2) = \frac{MPV}{RT} = \frac{(2.02 \times 10^{-3}\ \text{kg mol}^{-1}) \times (101325\ \text{Pa}) \times (2.12 \times 10^5\ m^3)}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}) \times (293.15\ \text{K})} = 17803.4\ \text{kg}$$

$\times J \quad N \cdot m$

The mass of He with the same buoyancy:

$\rightarrow He$

$$m(\text{He}) = \frac{MPV}{RT} = \frac{(4.00 \times 10^{-3}\ \text{kg mol}^{-1}) \times (101325\ \text{Pa}) \times (2.12 \times 10^5\ m^3)}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}) \times (293.15\ \text{K})} = 35254.3\ \text{kg}$$

The mass of the H_2 in the Hindenburg is less.

(b) The mass of H_2 under the different conditions is:

$$m(H_2) = \frac{MPV}{RT} = \frac{(2.02 \times 10^{-3}\ \text{kg mol}^{-1}) \times (1.05 \times 10^5\ \text{Pa}) \times (2.12 \times 10^5\ m^3)}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}) \times (283.15\ \text{K})} = 19098.4\ \text{kg} = 1.9 \times 10^4\ \text{kg}$$

REFLECT LZ 129 *Hindenburg* (Deutsche Luftschiff Zeppelin #129; Registration: D-LZ 129) was a large German commercial passenger-carrying rigid airship, the lead ship of the *Hindenburg* class, the largest flying machines of any kind (by dimension) ever built. The airship flew from March 1936 until destroyed by fire 14 months later on May 6, 1937, at the end of the first North American transatlantic journey of its second season of service. Thirty-six people died in the accident, which occurred while landing at Lakehurst Naval Air Station in Manchester Township, New Jersey.