Chapter 19: The Kinetic Theory of Gases

The Avogadro constant (a.k.a. as Avogadro's number) is named after the early nineteenth century Italian scientist Amedeo Avogadro, who, in 1811, first proposed that the volume of a gas (at a given pressure and temperature) is proportional to the number of atoms or molecules regardless of the nature of the gas.

The French physicist Jean Perrin in 1909 proposed naming the constant in honor of Avogadro.[5] Perrin won the 1926 Nobel Prize in Physics, in a large part for his work in determining the Avogadro constant by several different methods.

The value of the Avogadro constant was first indicated by Johann Josef Loschmidt who, in 1865, estimated the average diameter of the molecules in air by a method that is equivalent to calculating the number of particles in a given volume of gas.

From Wikipedia

Avogadro's number

$$N_A = 6.02 \times 10^{23} \text{ *species / mol}$$

* atoms, molecules, sheep, red balloons…

Chapter 19:   The Kinetic Theory of Gases

Avogadro's number

$$N_A = 6.02 \times 10^{23} \text{ particles/mol}$$

Number of moles in a sample:

$$n = N_{samp}/N_A = m_{samp}/M$$

(number of items you have divided by the number of items in a mole, or mass of a sample divided by the atomic or molecular weight)

Universal Gas Constant

$$R = 8.31 \text{ J/mol} \cdot K$$

$$nR = N_{samp}k_B$$

Boltzmann constant

$$k_B = R/N_A = 1.38 \times 10^{-23} \text{ J/K}$$

Ideal Gases

At *low* gas densities, *all* gases can be treated as ideal gases. Ideal gases obey the relation:

$$pV = nRT \quad \text{(ideal gas law)}$$

Ideal gas molecules are non-interacting idealized points in space. (unlike these)

IF n is constant, then $\dfrac{p_i V_i}{T_i} = \dfrac{p_f V_f}{T_f} = nR$

p: **absolute** (not gauge) **pressure**.

V: **volume** of the gas

n: number of **moles** of gas present.

T: the **temperature** in **Kelvin**. It ***MUST*** be in Kelvin!

R: **gas constant** (same for all gases) $R = 8.31 \text{ J/mol} \cdot \text{K}$
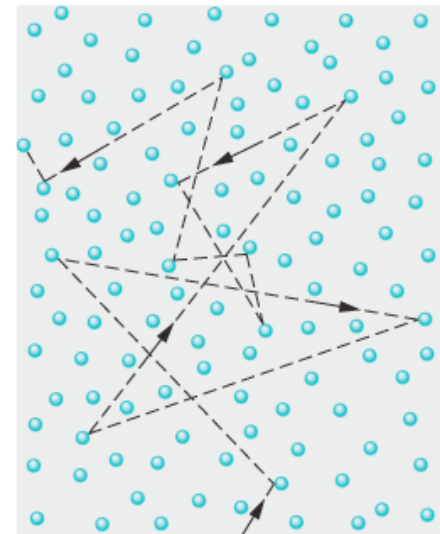
Ideal Gases

$$pV = nRT$$

Three variables in the ideal gas law (4 if you count n -- but let n be constant for now).

Some special cases

Pressure:

Isobaric -- constant pressure

Volume:

Isochoric (or isovolumic) -- constant volume

Temperature:

Isothermal -- constant temperature

Ideal Gases

$$\boxed{pV = nRT}$$

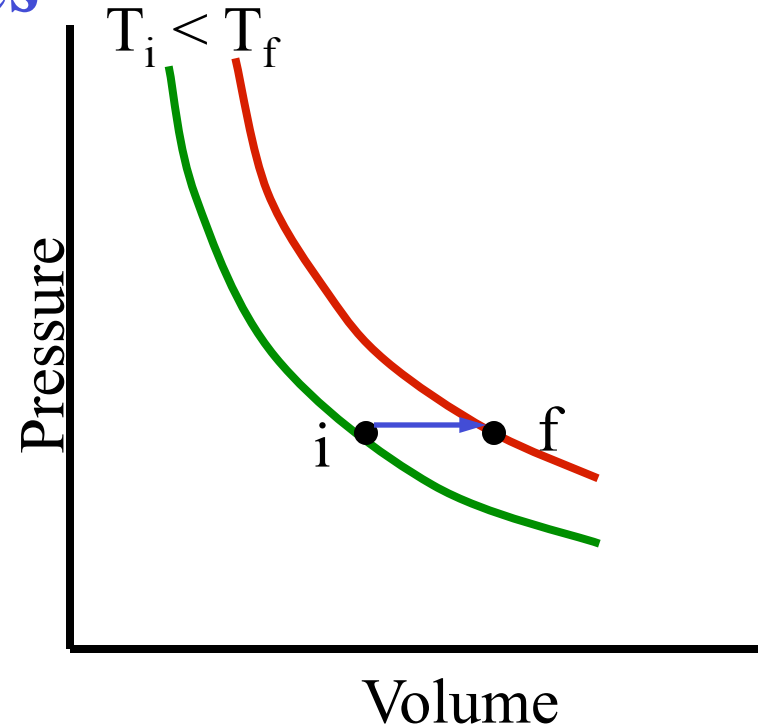For a fixed n, we have three variables in the ideal gas law

Consider special cases

Pressure:

Isobaric -- constant pressure

$T_i < T_f$

Pressure

Volume

$$W = \int_{V_i}^{V_f} p \, dV = p \int_{V_i}^{V_f} dV = p\left(V_f - V_i\right) = p\Delta V$$

V and T must be varying

Ideal Gases

$$\boxed{pV = nRT}$$

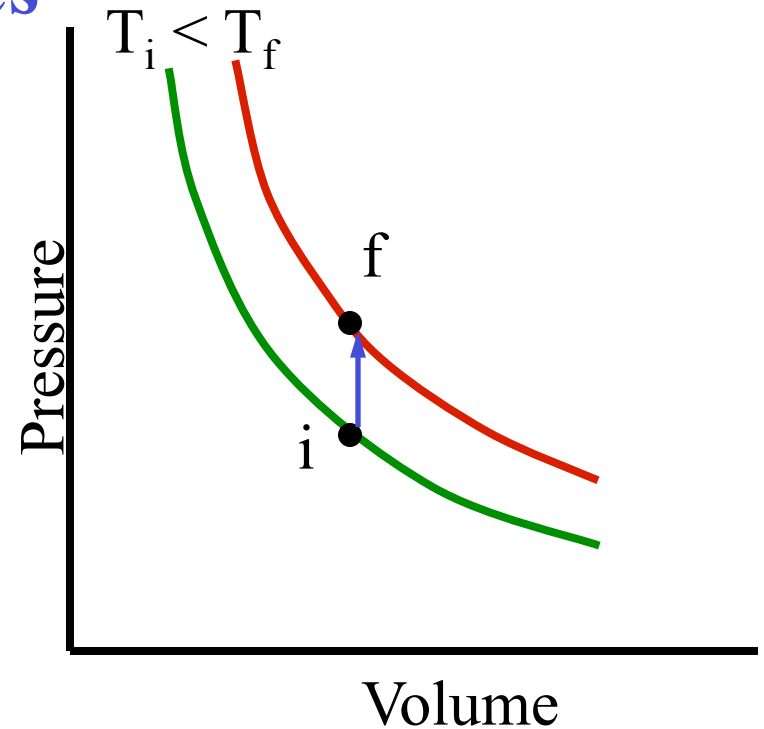Three variables in the ideal gas law (with n being constant).

Consider special cases

Volume:

Isochoric -- constant volume

$T_i < T_f$

$$W = \int_{V_i}^{V_f} p \, dV = \int_{V_i}^{V_i} p \, dV = 0 \quad \text{since the integral limts are equal}$$

P and T must be varying

Ideal Gases

$$pV = nRT$$

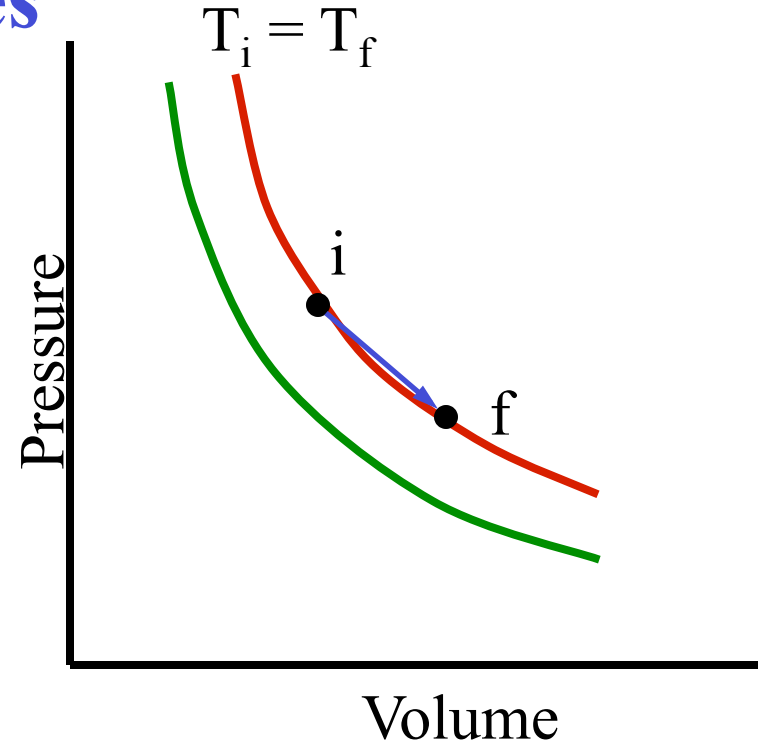Three variables in the ideal gas law (with n being constant).

Consider special cases

$T_i = T_f$

i

f

Pressure

Volume

P and V must be varying

Temperature:

Isothermal -- constant temperature

Gas expands from V_i to V_f, $\quad p = nRT/V$

$$W = \int_{V_i}^{V_f} p\,dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$= nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT[\ln V]_{V_i}^{V_f} = nRT \ln \frac{V_f}{V_i}$$

Summary of Work $\quad W = \int p\,dV$

Work done at **constant pressure**

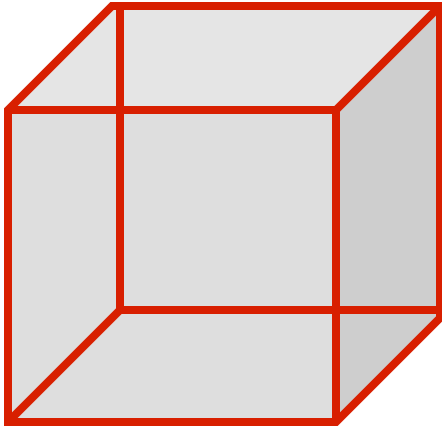$\quad$ p is constant, $\quad W = p\,(V_f - V_i) = p\,\Delta V$

Work done at **constant volume**

$\quad dV = 0, \quad$ so $\quad W = 0$

Work done by ideal gas at **constant temperature**

$$W = \int_{V_i}^{V_f} p\,dV = \int_{V_i}^{V_f} \frac{nRT}{V}\,dV = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT[\ln V]_{V_i}^{V_f} = nRT \ln \frac{V_f}{V_i}$$
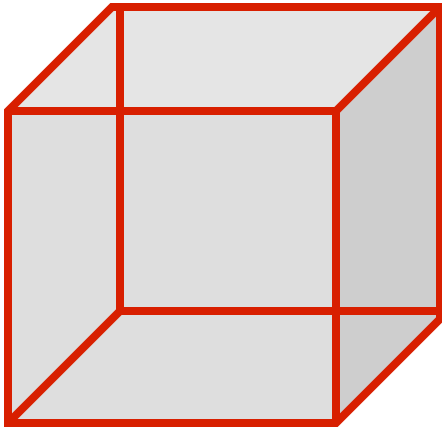
Sample Problem

Can one mole of an ideal gas at a temperature of 300K occupy a fixed volume of $10^{-2}\,m^3$ (ten liters) at one atmosphere ($1.01 \times 10^5 N/m^2$) of pressure?
Remember: $R = 8.31$ J/mol·K

1) yes.
2) No. The gas needs to be heated up to occupy that volume with that pressure.
3) No. The gas needs to be cooled down to occupy that volume with that pressure.
4) Depends on the type of ideal gas molecules.

Sample Problem

$$pV = nRT$$

$$pV = (1.01 \times 10^5 \text{N/m}^2)(10^{-2}\text{m}^3)$$
$$= 1010 \text{ N-m} = 1{,}010 \text{ J}$$

$$nRT = (1.0\text{mol})(8.31 \text{ J/mol} \cdot \text{K})(300\text{K})$$
$$= 2{,}493 \text{ J}$$

Can one mole of an ideal gas at a temperature of 300K occupy a fixed volume of 10^{-2}m^3 (ten liters) at one atmosphere (1.01×10^5N/m^2) of pressure? Remember: R = 8.31 J/mol·K

1) yes.
2) No. The gas needs to be heated up to occupy that volume with that pressure.
3) No. The gas needs to be cooled down to occupy that volume with that pressure.
4) Depends on the type of ideal gas mo

$$T = pV/nR$$
$$= 1010\text{J}/(1.0)(8.31) = 122 \text{ K}$$

Kinetic Theory of Gasses,
19-4:Pressure, Temperature and RMS Speed

What causes pressure?

All macroscopic (i.e., human scale) quantities must ultimately be explained on the **microscopic** scale.

Pressure

Consider n mols of ideal gas confined in cube of volume V (edge L) at a constant T…What is the connection between the pressure on the walls and the speed(s) of the molecules
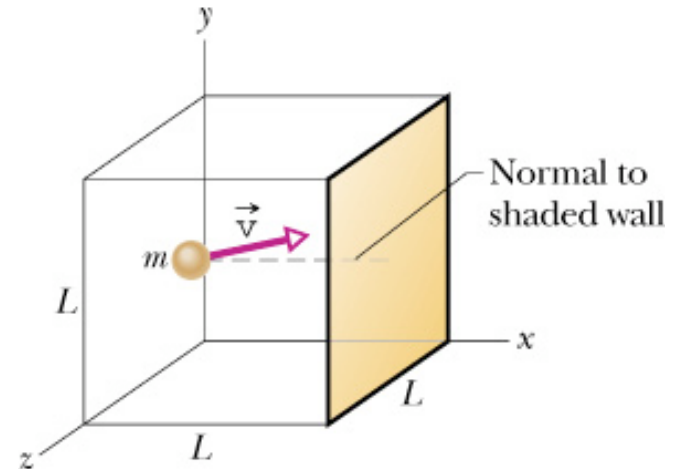
$\text{Pressure} = \dfrac{\text{Force}}{\text{Area}}$, but what is this force?

Relate force to impulse and associated change in momentum with collisions.

$$\vec{F} \equiv \frac{d\vec{p}}{dt} \implies d\vec{p} = \vec{F}dt$$

Here we are talking about momentum (a vector)…!

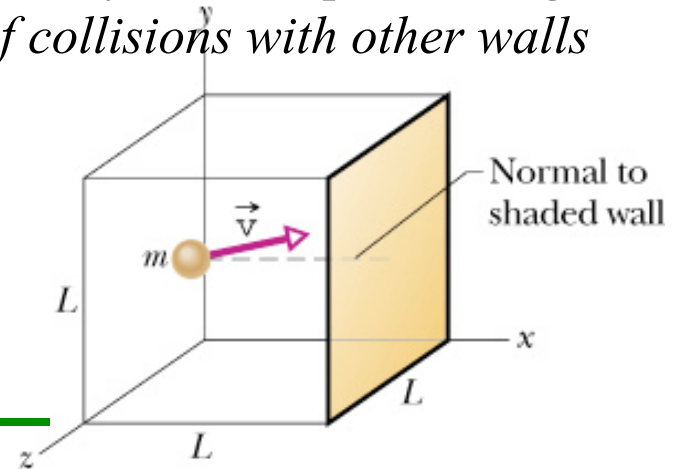$$\Delta p_x = p_f - p_i = (-mv_x) - (mv_x) = -2mv_x$$

(This is the momentum delivered to the wall by the particle)

Take Δt to be the time between collisions (with the wall, in the +/- x direction). It will have traveled 2L in that time with speed v_x.

Holds for x component, regardless of collisions with other walls

$$F_x = \frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L / v_x} = \frac{mv_x^2}{L}$$

For one particle

For many identical particles, allowing for different v_x ...

The pressure on wall of area L^2 will be:

$$p = \frac{F_x}{L^2} = \frac{mv_{x1}^2 / L + mv_{x2}^2 / L + \ldots + mv_{xN}^2 / L}{L^2}$$

$$= \left(\frac{m}{L^3}\right)\left(v_{x1}^2 + v_{x2}^2 + \ldots + v_{xN}^2\right)$$

Where N is the # of particles in the box

Since there are N molecules in the box, $N = nN_A$ and N is usually a *very* big number, we can use the average speed instead of the actual speeds.
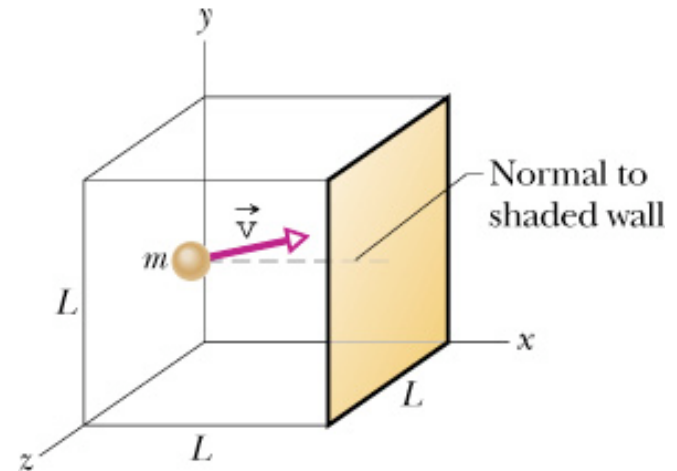
$$p = \frac{F_x}{L^2} = \frac{mv_{x1}^2/L + mv_{x2}^2/L + \ldots + mv_{xN}^2/L}{L^2}$$

$$= \left(\frac{m}{L^3}\right)\left(v_{x1}^2 + v_{x2}^2 + \ldots + v_{xN}^2\right)$$

$$= \left(\frac{m}{L^3}\right)\left(v_x^2\right)_{avg}$$

The volume of the box is L^3, so

$$p = \frac{m\,nN_A}{V}\left(v_x^2\right)_{avg}$$

v_{rms}

Since there are 3 dimensions, $v_x^2 + v_y^2 + v_z^2 = v^2$ and each dimension is equivalent, $v_x^2 = v_y^2 = v_z^2 \Rightarrow v^2 = 3v_x^2$

$$p = \frac{m\,n\,N_A}{V}\left(v_x^2\right)_{avg} = \frac{m\,n\,N_A}{V}\left(\frac{1}{3}v^2\right)_{avg} = \frac{m\,n\,N_A}{3V}\left(v^2\right)_{avg}$$

$\left(v^2\right)_{avg}$ is the average of the squared speed -- which makes the speed the (square) **root** of the **mean** (average) **squared** speed -- i.e., root-mean-squared speed, v_{rms}.

$$\sqrt{\left(v^2\right)_{avg}} = v_{rms}$$

Rearrange $\quad p = \dfrac{m\,n\,N_A}{3V}\left(v_{rms}^2\right) \Rightarrow \quad v_{rms} = \sqrt{\dfrac{3pV}{n\,m\,N_A}}$

gas temperature

mN_A is the mass of a mol of gas particles, i.e. the molar mass M of the gas…using the ideal gas law $pV = nRT$:

$$v_{rms} = \sqrt{\frac{3pV}{n\,mN_A}} = \sqrt{\frac{3nRT}{n\,M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_BT}{m}}$$

Since $k_B N_A = R$ and $M = mN_A$

Remember: M and m have units of kgs

Thus, the characteristic speed of the gas molecules is related to the temperature of the gas!

Here are some speeds at 300 K:

Gas	v_{rms} (m/s)
Hydrogen	1920
Helium	1370
N_2	517
escape speed$_{Earth}$	1120

Kinetic Energies

Average kinetic energy:

$$K_{avg} = \tfrac{1}{2}m\left(v^2\right)_{avg} = \tfrac{1}{2}mv^2_{rms}$$

$$= \left(\tfrac{1}{2}m\right)\frac{3RT}{M} = \left(\tfrac{1}{2}\right)\frac{3RT}{M/m} = \frac{3RT}{2N_A} = \left(\frac{3}{2}\right)\left(\frac{R}{N_A}\right)T = \tfrac{3}{2}kT$$
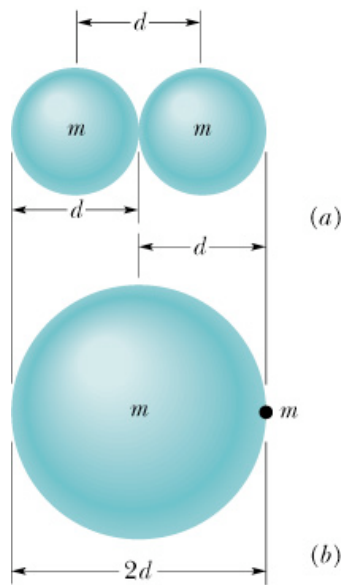
Kinetic energy only depends on the gas's temperature!

$$K_{avg} = \tfrac{1}{2}m\,v^2_{rms} = \tfrac{3}{2}kT$$

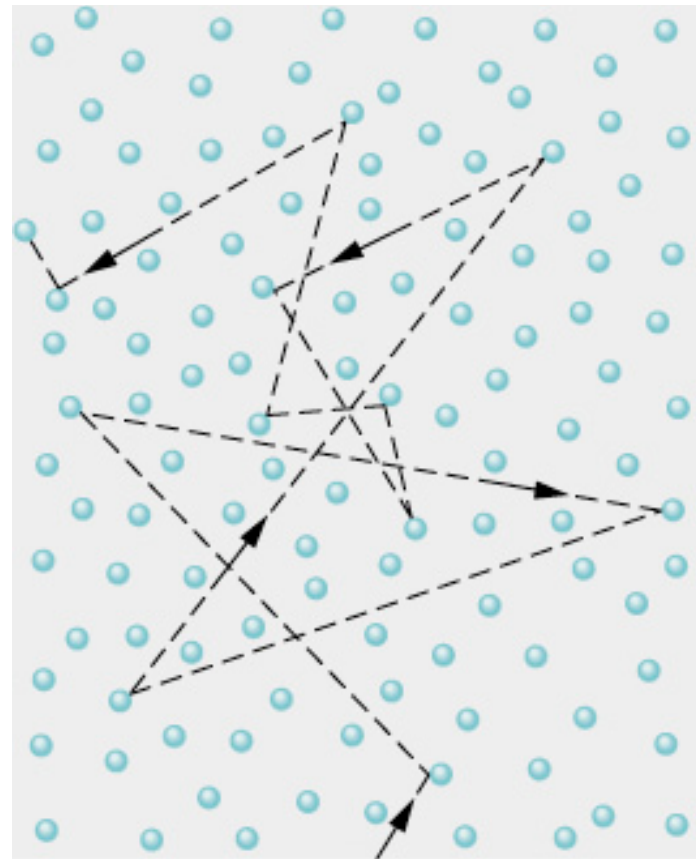The "3" comes from the three dimensions: x, y, and z!

Mean Free path

Now consider that the molecules have some size… the mean-free-path λ between collisions with other molecules is:

λ is proportional to V, inversely proportional to N and d²

$$\lambda = \frac{1}{\sqrt{2}\,\pi d^2\,N/V}$$

Molecular sizes

A simple (but somewhat inaccurate) calculation of λ

As our single molecule zigzags through the gas, it sweeps out a short cylinder of cross-sectional area πd^2 between successive collisions. If we watch this molecule for a time interval Δt, it moves a distance $v\Delta t$, where v is its assumed speed. Thus, if we align all the short cylinders swept out in interval Δt, we form a composite cylinder (Fig. 19-7) of length $v\Delta t$ and volume $(\pi d^2)(v\Delta t)$. The number of collisions that occur in time Δt is then equal to the number of (point) molecules that lie within this cylinder.
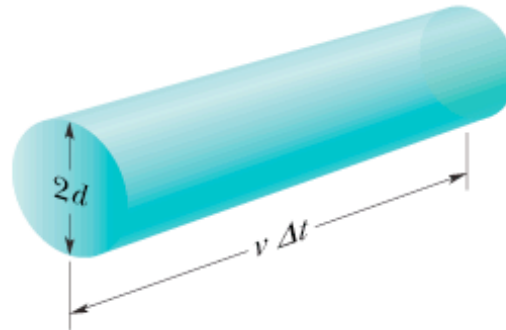
FIGURE 19-7 In time Δt the moving molecule effectively sweeps out a cylinder of length $v\Delta T$ and radius d.

Since N/V is the number of molecules per unit volume, the number of molecules in the cylinder is N/V times the volume of the cylinder, or $(N/V)(\pi d^2 v\Delta t)$. This is also the number of collisions in time Δt. The mean free path is the length of the path (and of the cylinder) divided by this number:

$$\lambda = \frac{\text{length of path during } \Delta t}{\text{number of collisions in } \Delta t} \approx \frac{v\Delta t}{\pi d^2 v\Delta t\, N/V}$$

$$= \frac{1}{\pi d^2 N/V} . \qquad\qquad (19\text{-}26)$$

Real world values for λ:

The mean free path of air molecules at sea level is about $0.1\,\mu$m. At an altitude of 100 km, the density of air has dropped to such an extent that the mean free path rises to about 16 cm. At 300 km, the mean free path is about 20 km. A problem faced by those who would study the physics and chemistry of the upper atmosphere in the laboratory is the unavailability of containers large enough to hold gas samples that simulate upper atmospheric conditions. Yet studies of the concentrations of Freon, carbon dioxide, and ozone in the upper atmosphere are of vital public concern.

We know V_{rms}, but there is a distribution of speeds

We know V_{rms}, but there is a distribution of speeds

But.... not all the molecules are going at that speed.
Some are going *faster* and some slooooower than v_{rms}.

A gas molecule interacting
with neighboring molecules
is like you trying to get to the
concession stand during a
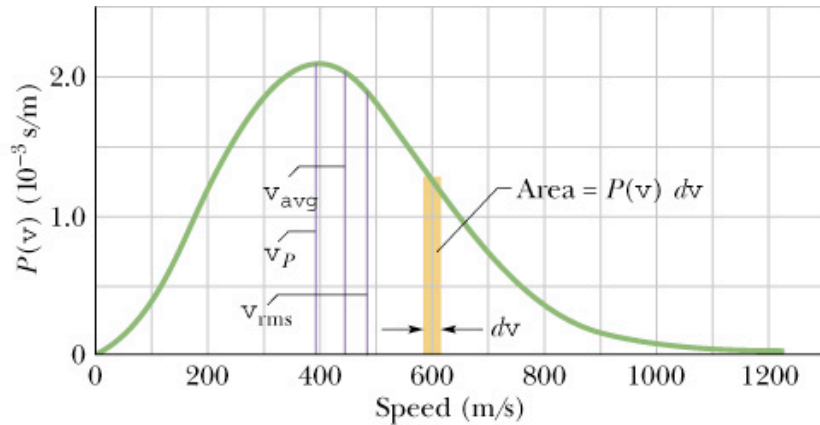rock concert!
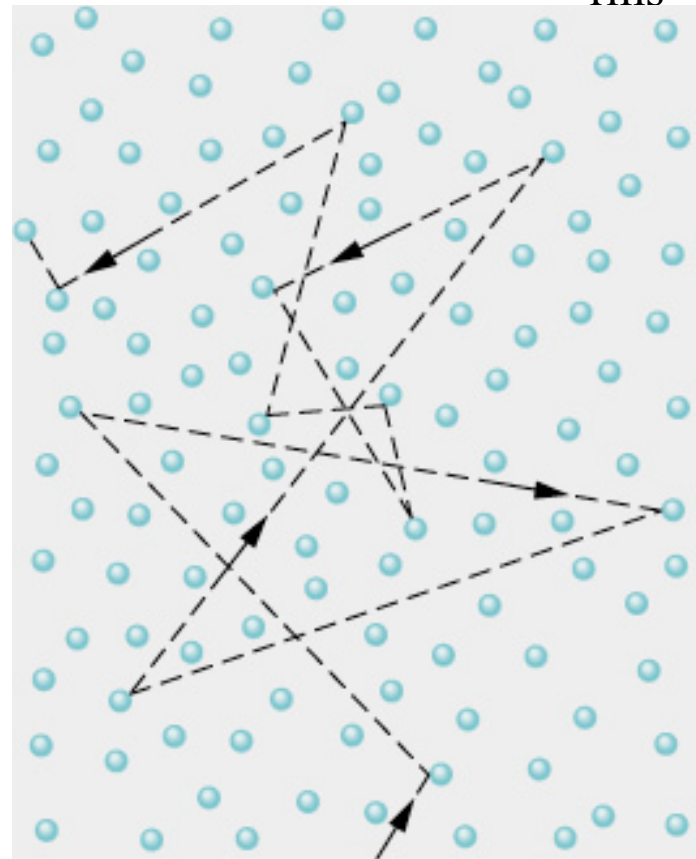
Maxwell-Boltzmann Distribution

Define a probability distribution function P(v)….

…with area (integral) equal to 1.
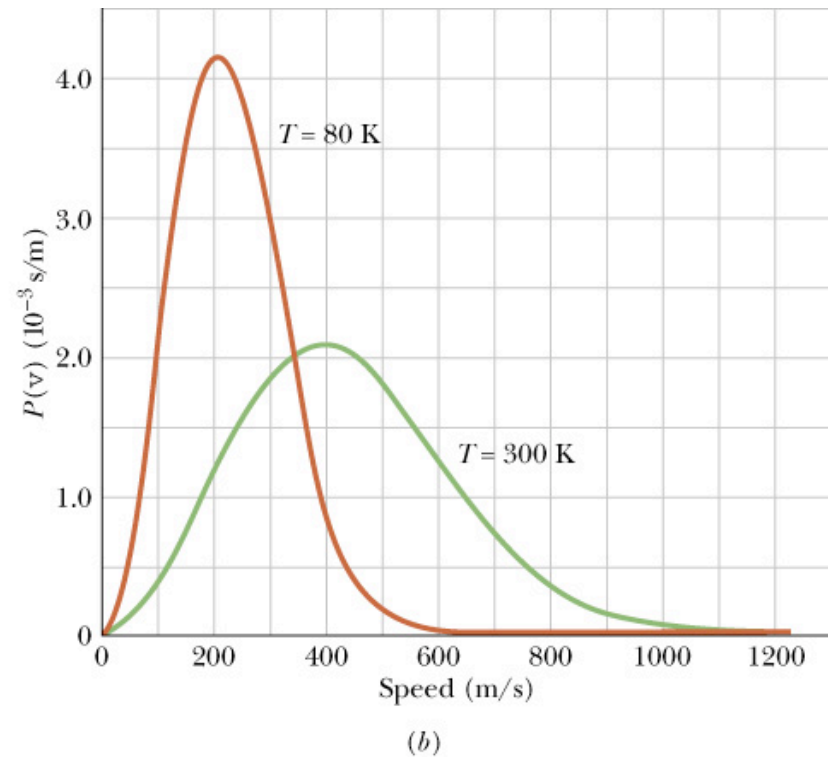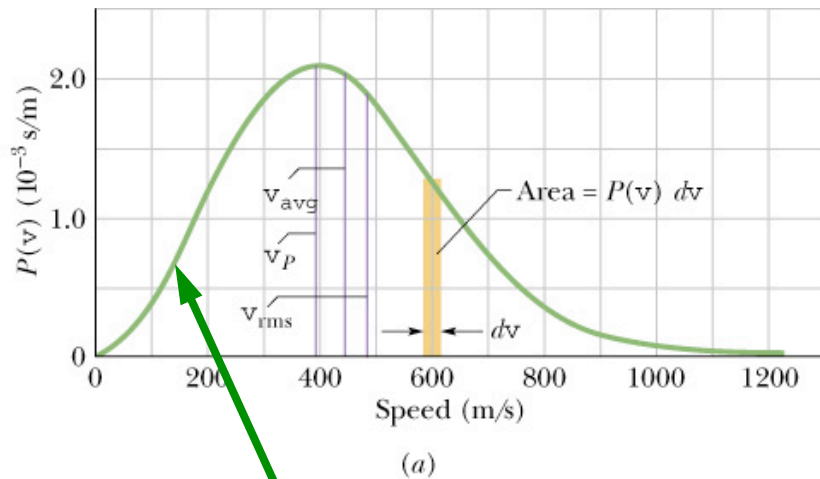
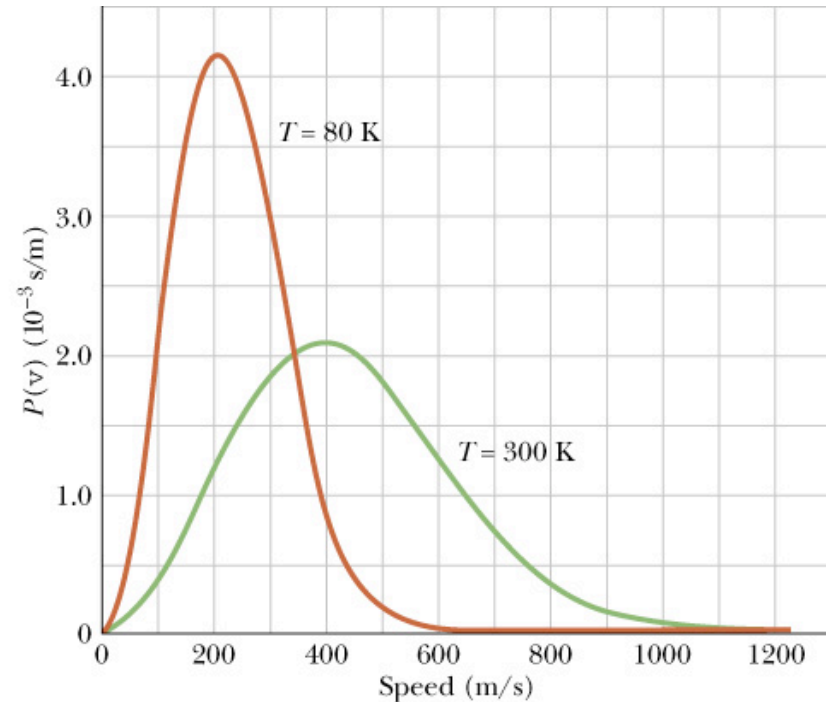$$P(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

P(v) is the Maxwell-Boltzmann Probability function
P(v) dv is *dimensionless (just a number in range 0 to 1)*

Maxwell-Boltzmann Distribution

(a)

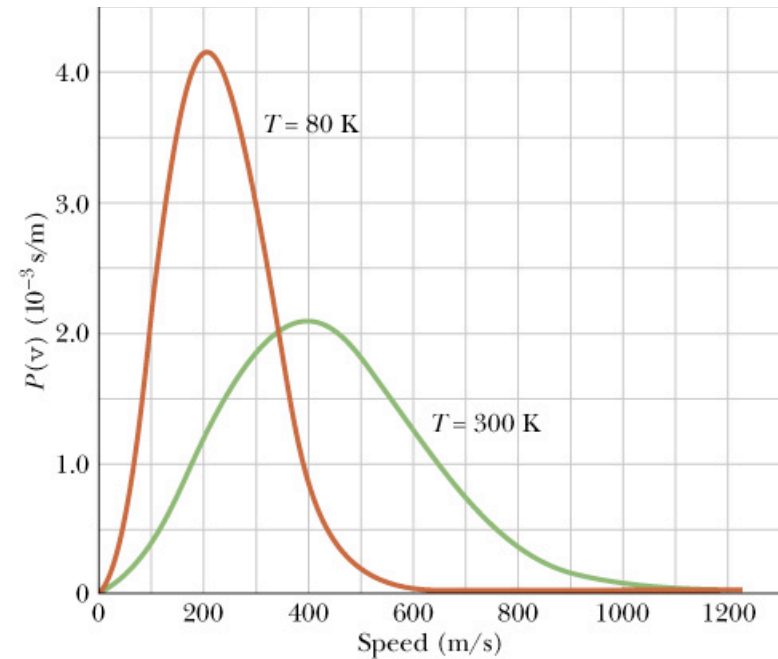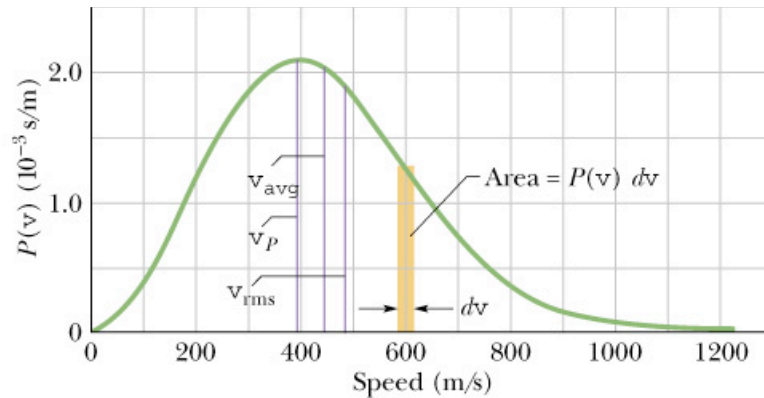$$P(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

(b)

Distribution of speeds is broader and faster at higher T

What is the average speed?

$$v_{avg} = \int_0^\infty v\, P(v)\, dv$$

Maxwell-Boltzmann Distribution

$$P(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

Thus, $v_{avg} = \int_0^\infty v\, P(v)\, dv = \sqrt{\frac{8RT}{\pi M}}$

and $(v^2)_{avg} = \int_0^\infty v^2\, P(v)\, dv = \frac{3RT}{M}$

and $v_{rms} = \sqrt{(v^2)_{avg}} = \sqrt{\frac{3RT}{M}}$

Recognizing the Integral is of the form

$$\int_0^\infty x^{2n+1} e^{-ax^2}\, dx = \frac{n!}{2a^{n+1}} \quad (a > 0)$$

Ditto...

$$\int_0^\infty x^{2n} e^{-ax^2}\, dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$$

Molar specific heat of an ideal gas

Molar specific heat:

$$Q = c \, n \, (\, T_f - T_i \,)$$

The specific heat c is a value that depends on the ability of a substance to **absorb energy**. As such, c depends on both the type of material and whether the process is a constant volume process or a constant pressure process.
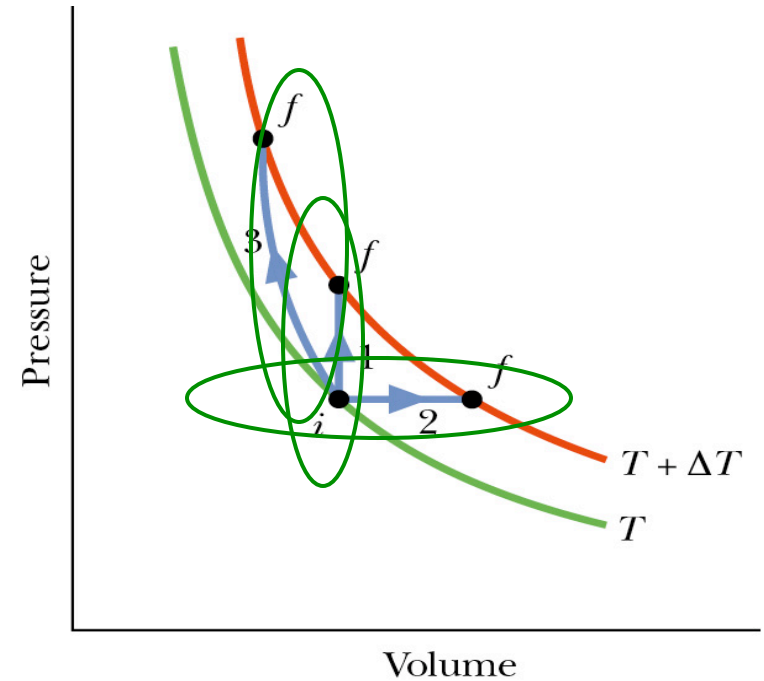
1) Constant-volume process

2) Constant-pressure process

3) Arbitrary process

Molar specific heat of an ideal gas

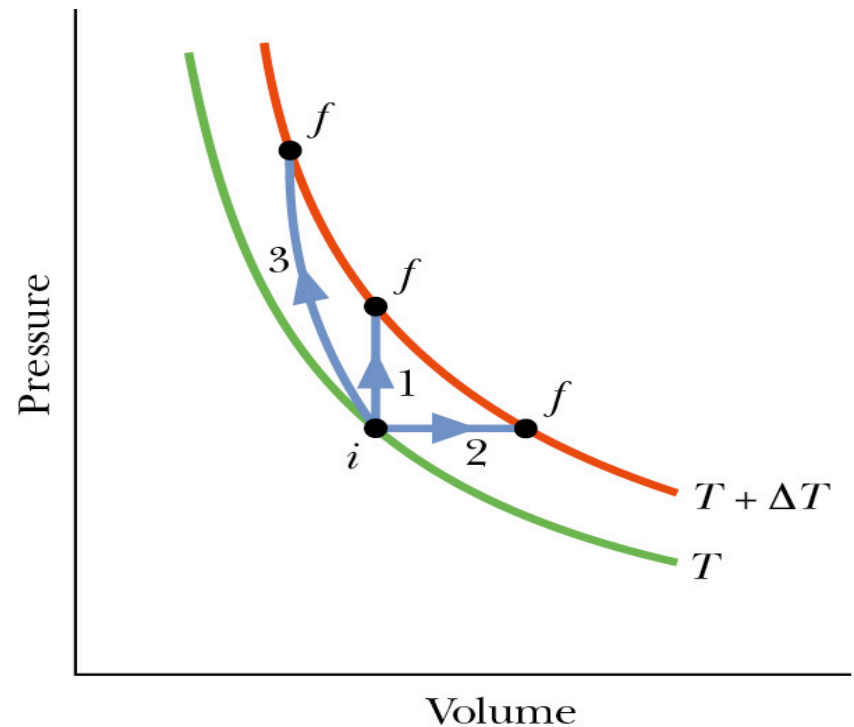**Molar specific heat at constant volume: C_V**

$Q = n\, C_V\, \Delta T$ (constant V process) since V = constant, so
$W = 0$, so $\Delta E_{int} = Q - W = n\, C_V\, \Delta T$ or $E_{int} = n\, C_V\, \Delta T$

For ideal gas, the change in internal energy depends only on the change in gas temperature.

Molar specific heat at constant pressure: C_p

$Q = n\, C_p \Delta T$ (constant Pressure process)

$\Delta E_{int} = Q - W,$

since p = constant, $W = p\Delta V = nR\Delta T$

$\Delta E_{int} = n\, C_p \Delta T - nR\Delta T = n(C_p - R)\Delta T$

But ΔE_{int} is the same for all processes

ΔE_{int} constant volume $= n\, C_V\, \Delta T$

Therefore, $nC_V\Delta T = n(C_p - R)\Delta T$

$$\boxed{C_V = C_p - R}$$

Adiabatic expansion of an ideal gas.

For an adiabatic process, $Q = 0$.

$pV^\Upsilon = $ a constant

$\Upsilon = C_p/C_V$ treat Υ as a constant that depends on the type of the gas molecules.
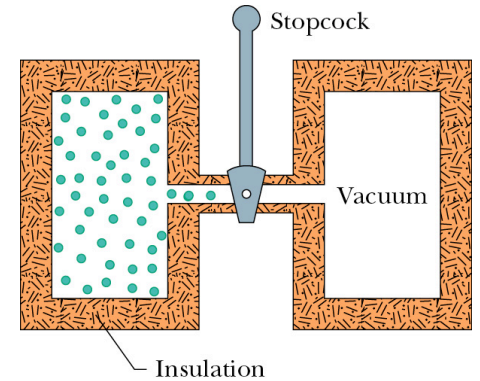
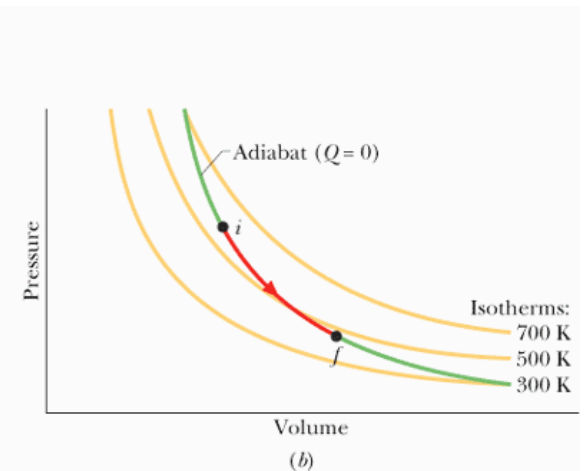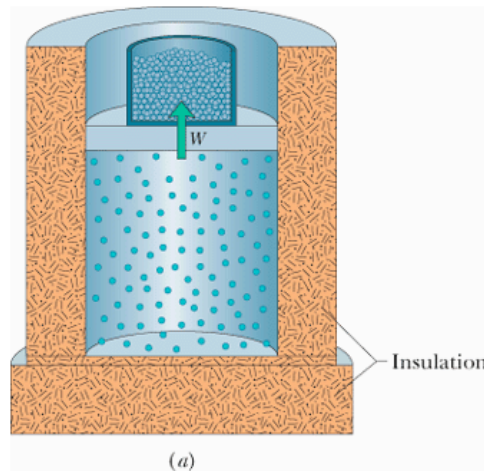Rapid processes, or even slow ones if the system is well insulated

Free expansions (when mass is removed)

$Q = W = 0$,

So $\Delta E_{int} = 0$,

Therefore $T_i = T_f$

or $P_i V_i = P_f V_f$

Derivation of pV$^\gamma$ = constant

Suppose that you remove some shot from the piston of Fig. 19-15a, allowing the ideal gas to push the piston and the remaining shot upward and thus to increase the volume by a differential amount dV. Since the volume change is tiny, we may assume that the pressure p of the gas on the piston is constant during the change. This assumption allows us to say that the work dW done by the gas during the volume increase is equal to $p\, dV$. From Eq. 18-27, the first law of thermodynamics can then be written as

$$dE_{\text{int}} = Q - p \quad dV . \tag{19-57}$$

Since the gas is thermally insulated (and thus the expansion is adiabatic), we substitute 0 for Q. Then we use Eq. 19-45 to substitute $nC_V\, dT$ for dE_{int}. With these substitutions, and after some rearranging, we have

$$n\, dT = - \left(\frac{p}{C_V}\right) dV . \tag{19-58}$$

Now from the ideal gas law ($pV = nRT$) we have

$$p\, dV + V\, dp = nR\, dT . \tag{19-59}$$

Replacing R with its equal, $C_p - C_V$, in Eq. 19-59 yields

$$n\, dT = \frac{p\, dV + V\, dp}{C_p - C_V} . \tag{19-60}$$

Equating Eqs. 19-58 and 19-60 and rearranging then give

$$\frac{dp}{p} + \left(\frac{C_p}{C_V}\right)\frac{dV}{V} = 0 .$$

Replacing the ratio of the molar specific heats with γ and integrating (see integral 5 in Appendix E) yield

$$\ln p + \gamma \ln V = a\, \text{constant} .$$

Rewriting the left side as $\ln pV^\gamma$ and then taking the antilog of both sides, we find

$$pV^\gamma = a\, \text{constant} . \tag{19-61}$$

Isobaric --- constant pressure process

$$Q = n\, C_p \Delta T, \qquad W = p\, \Delta V$$

Isothermal --- constant temperature process

$$\Delta E_{int} = 0, \qquad Q = W = nRT\, \ln(V_f/V_i)$$

Isochoric process --- constant volume process

$$Q = \Delta E_{int} = n\, C_V\, \Delta T, \qquad W = 0$$

Adiabatic expansion of an ideal gas

$$Q = 0, \quad pV^\gamma = a \text{ constant}$$

$$\boxed{\begin{aligned} &\Delta E_{int} = Q - W \\ &\text{for all processes.} \end{aligned}}$$

Free expansion

$$Q = W = 0 \implies \Delta E_{int} = 0, \implies T_i = T_f \implies p_i V_i = p_f V_f$$
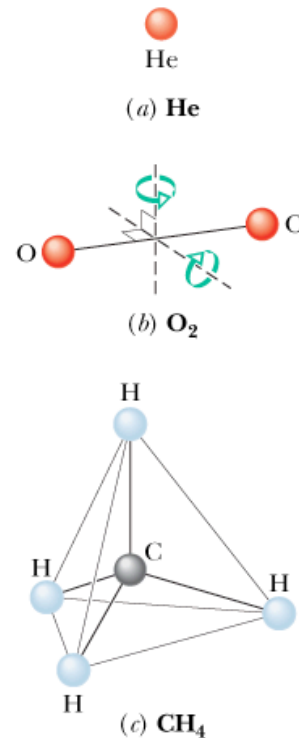
FIGURE 19-13 Models of molecules as used in kinetic theory: (a) helium, a typical monatomic molecule; (b) oxygen, a typical diatomic molecule; and (c) methane, a typical polyatomic molecule. The spheres represent atoms, and the lines between them represent bonds. Two rotation axes are shown for the oxygen molecule.

To keep account of the various ways in which energy can be stored in a gas, James Clerk Maxwell introduced the theorem of the **equipartition of energy:**

Every kind of molecule has a certain number f of *degrees of freedom,* which are independent ways in which the molecule can store energy. Each such degree of freedom has associated with it—on average—an energy of $\frac{1}{2}kT$ per molecule (or $\frac{1}{2}RT$ per mole).

Degrees of Freedom

Particles can absorb energy depending on their structure.
A degree of freedom is a way that a particle can move.

All particles can move in x-, y-, and z-directions.

→ 3 degrees of freedom

diatomic molecules (N_2, O_2, etc.) have two rotatational energies.

→ 2 more degrees of freedom

polyatomic molecules (CH_4, SiO_2 etc.) have three rotational energies.

→ 3 more degrees of freedom

Degrees of Freedom

Particles can absorb energy depending on their structure.
A degree of freedom is the way the particle can move.

Molecule	Translational	Rotational	Total	C_V
monotomic	3	0	3	3/2
diatomic	3	2	5	5/2
polyatomic	3	3	6	6/2 = 3

Each degree of freedom contributes 1/2R to the C_V.

monotomic $\Delta E_{int} = \dfrac{3}{2} nR\Delta T$

diatomic $\Delta E_{int} = \dfrac{5}{2} nR\Delta T$

polyatomic $\Delta E_{int} = 3nR\Delta T$

Degrees of Freedom

Particles can absorb energy depending on their structure. A degree of freedom is the way the particle can move.

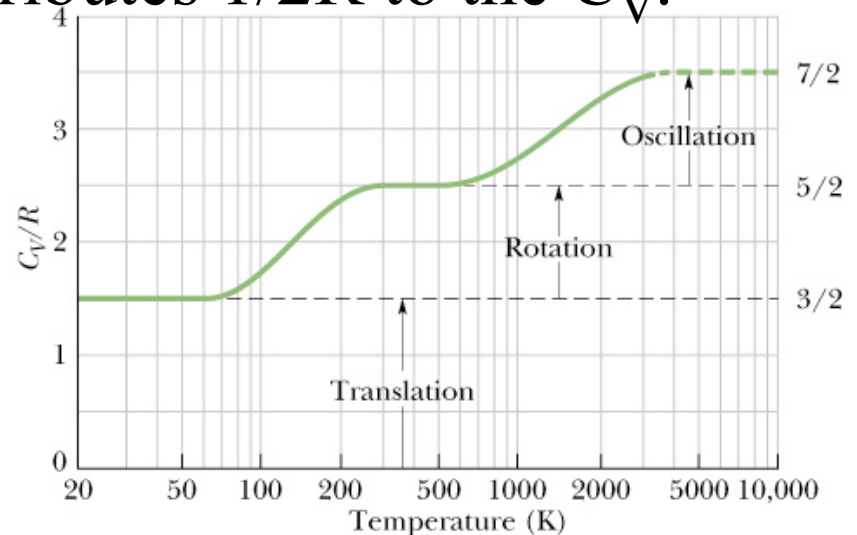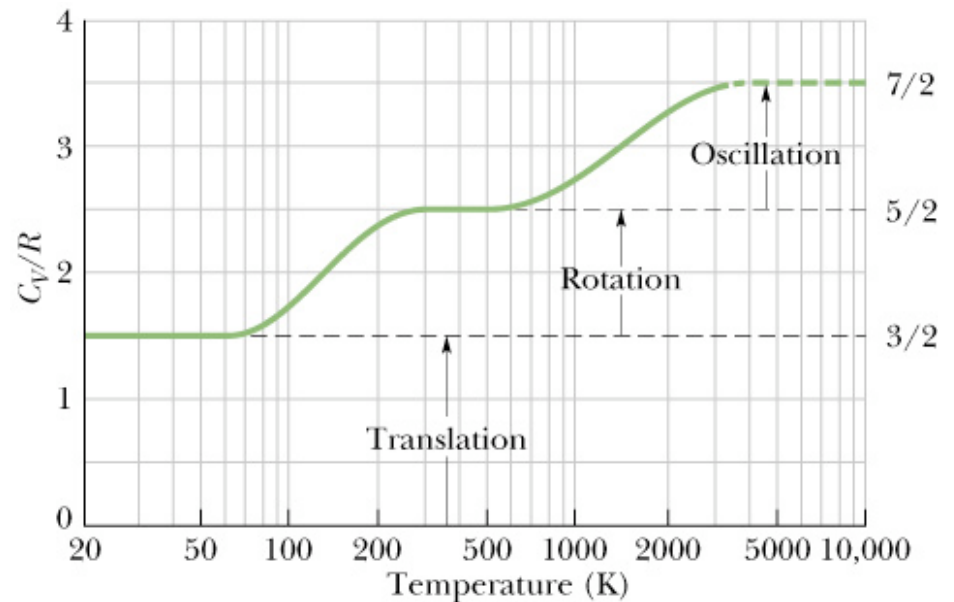diatomic $\quad \Delta E_{int} = \dfrac{5}{2} nR\Delta T$

New degrees of freedom are accessed as temperature is increased

Sample Problem 19-8 Build your skill

We transfer 1000 J to a diatomic gas, allowing it to expand with the pressure held constant. The gas molecules rotate but do not oscillate. How much of the 1000 J goes into the increase of the gas's internal energy? Of that amount, how much goes into ΔK_{tran} (the kinetic energy of the translational motion of the molecules) and ΔK_{rot} (the kinetic energy of their rotational motion)?

KEY IDEAS

1. The transfer of energy as heat Q to a gas under constant pressure is related to the resulting temperature increase ΔT via Eq. 19-46 (
$Q = nC_p\Delta T$).

2. Because the gas is diatomic with molecules undergoing rotation but not oscillation, the molar specific heat is, from Fig. 19-12 and Table 19-3,
$C_p = \frac{7}{2}R.$

3. The increase ΔE_{int} in the internal energy is the same as would occur with a constant-volume process resulting in the same ΔT. Thus, from Eq. 19-45, $\Delta E_{int} = nC_v\Delta T.$ From Fig. 19-12 and Table 19-3, we see that $C_v = \frac{5}{2}R.$

4. For the same n and ΔT, ΔE_{int} is greater for a diatomic gas than a monatomic gas because additional energy is required for rotation.

Increase in E_{int}: Let's first get the temperature change ΔT due to the transfer of energy as heat. From Eq. 19-46, substituting $\frac{7}{2}R$ for C_p, we have

$$\Delta T = \frac{Q}{\frac{7}{2}nR} . \qquad (19\text{-}52)$$

We next find ΔE_{int} from Eq. 19-45, substituting the molar specific heat $C_v\left(=\frac{5}{2}R\right)$ for a constant-volume process and using the same ΔT.

Because we are dealing with a diatomic gas, let's call this change $\Delta E_{int, dia}$. Equation 19-45 gives us

$$\Delta E_{int, dia} = nC_v\Delta T = n\frac{5}{2}R\left(\frac{Q}{\frac{7}{2}nR}\right) = \frac{5}{2}Q \qquad \text{(Answer)}$$

$$= 0.71428Q = 714.3\text{J} .$$

In words, about 71% of the energy transferred to the gas goes into the internal energy. The rest goes into the work required to increase the volume of the gas

Increases in K: If we were to increase the temperature of a *monatomic* gas (with the same value of *n*) by the amount given in Eq. 19-52, the internal energy would change by a smaller amount, call it $\Delta E_{int, \, mon}$, because rotational motion is not involved. To calculate that smaller amount, we still use Eq. 19-45 but now we substitute the value of C_V for a monatomic gas—namely, $C_V = \frac{3}{2}R$. So,

$$\Delta E_{int, \, mon} = n\frac{3}{2}R\Delta T.$$

Substituting for ΔT from Eq. 19-52 leads us to

$$\Delta E_{int, \, mon} = n\frac{3}{2}R\left(\frac{Q}{n\frac{7}{2}R}\right) = \frac{3}{7}Q$$

$$= 0.42857Q = 428.6 \, \text{J}.$$

For the monatomic gas, all this energy would go into the kinetic energy of the translational motion of the atoms. The important point here is that for a diatomic gas with the same values of *n* and ΔT, the same amount of energy goes into the kinetic energy of the translational motion of the molecules. The rest of $\Delta E_{int, \, dia}$ (that is, the additional 285.7 J) goes into the rotational motion of the molecules. Thus, for the diatomic gas,

$$\Delta K_{trans} = 428.6 \, \text{J} \quad \text{and} \quad \Delta K_{rot} = 285.7 \, \text{J}. \qquad \text{(Answer)}$$