

Chapter 19

The Kinetic Theory of Gases

19.2 Avogadro's Number

One mole is the number of atoms in a 12 g sample of carbon-12.

The number of atoms or molecules in a mole is called *Avogadro's Number*, N_A .

$$\underline{N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \quad (\text{Avogadro's number})}$$

If n is the number of moles contained in a sample of any substance, N is the number of molecules, M_{sam} is the mass of the sample, and M is the molar mass, then

$$n = \frac{N}{N_A} \quad \longrightarrow \quad n = \frac{M_{sam}}{M} = \frac{M_{sam}}{mN_A} \quad \longrightarrow \quad M = mN_A$$

19.3: Ideal Gases

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

Here p is the absolute pressure, n is the number of moles of gas present, and T is its temperature in kelvins. R is the gas constant that has the same value for all gases.

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

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

Here, k is the Boltzmann constant, and N the number of molecules

$$k = \frac{R}{N_A} = \frac{8.31 \text{ J/mol} \cdot \text{K}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23} \text{ J/K}.$$

19.3: Ideal Gases; Work Done by an Ideal Gas at Constant Temperature

The expansion is along an isotherm (the gas has constant temperature).

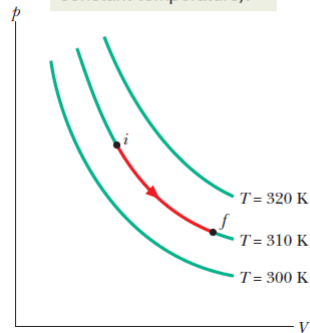


Fig. 19-2 Three isotherms on a p - V diagram. The path shown along the middle isotherm represents an isothermal expansion of a gas from an initial state i to a final state f . The path from f to i along the isotherm would represent the reverse process—that is, an isothermal compression.

$$W = \int_{V_i}^{V_f} p \, dV.$$

$$p = nRT \frac{1}{V} = (\text{a constant}) \frac{1}{V}.$$

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

$$= nRT \left[\ln V \right]_{V_i}^{V_f}.$$

$$W = nRT \ln \frac{V_f}{V_i} \quad (\text{ideal gas, isothermal process}).$$

19.3: Ideal Gases; Work Done at Constant Volume and Constant Pressure

W done by an ideal gas (or any other gas) during any process, such as a constant-volume process and a constant-pressure process.

If the volume of the gas is constant,

$$W = 0 \quad (\text{constant-volume process}).$$

If, instead, the volume changes while the pressure p of the gas is held constant,

$$W = p(V_f - V_i) = p \Delta V \quad (\text{constant-pressure process}).$$

Example, Ideal Gas Processes

A cylinder contains 12 L of oxygen at 20°C and 15 atm. The temperature is raised to 35°C, and the volume is reduced to 8.5 L. What is the final pressure of the gas in atmospheres? Assume that the gas is ideal.

KEY IDEA

Because the gas is ideal, we can use the ideal gas law to relate its parameters, both in the initial state i and in the final state f .

Calculations: From Eq. 19-5 we can write

$$p_i V_i = nRT_i \quad \text{and} \quad p_f V_f = nRT_f.$$

Dividing the second equation by the first equation and solving for p_f yields

$$p_f = \frac{p_i T_f V_i}{T_i V_f}. \quad (19-17)$$

Note here that if we converted the given initial and final volumes from liters to the proper units of cubic meters, the multiplying conversion factors would cancel out of Eq. 19-17. The same would be true for conversion factors that convert the pressures from atmospheres to the proper pascals. However, to convert the given temperatures to kelvins requires the addition of an amount that would not cancel and thus must be included. Hence, we must write

$$T_i = (273 + 20) \text{ K} = 293 \text{ K}$$

and $T_f = (273 + 35) \text{ K} = 308 \text{ K}.$

Inserting the given data into Eq. 19-17 then yields

$$p_f = \frac{(15 \text{ atm})(308 \text{ K})(12 \text{ L})}{(293 \text{ K})(8.5 \text{ L})} = 22 \text{ atm.} \quad (\text{Answer})$$

Example, Work done by an Ideal Gas

One mole of oxygen (assume it to be an ideal gas) expands at a constant temperature T of 310 K from an initial volume V_i of 12 L to a final volume V_f of 19 L. How much work is done by the gas during the expansion?

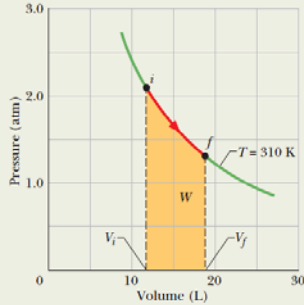


Fig. 19-3 The shaded area represents the work done by 1 mol of oxygen in expanding from V_i to V_f at a temperature T of 310 K.

KEY IDEA

Generally we find the work by integrating the gas pressure with respect to the gas volume, using Eq. 19-11. However, because the gas here is ideal and the expansion is isothermal, that integration leads to Eq. 19-14.

Calculation: Therefore, we can write

$$\begin{aligned} W &= nRT \ln \frac{V_f}{V_i} \\ &= (1 \text{ mol})(8.31 \text{ J/mol}\cdot\text{K})(310 \text{ K}) \ln \frac{19 \text{ L}}{12 \text{ L}} \\ &= 1180 \text{ J.} \end{aligned} \quad (\text{Answer})$$

The expansion is graphed in the p - V diagram of Fig. 19-3. The work done by the gas during the expansion is represented by the area beneath the curve if .

You can show that if the expansion is now reversed, with the gas undergoing an isothermal compression from 19 L to 12 L, the work done by the gas will be -1180 J . Thus, an external force would have to do 1180 J of work on the gas to compress it.

19.4: Pressure, Temperature, and RMS Speed

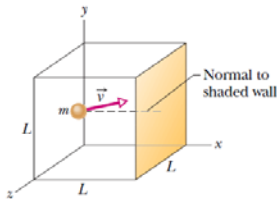


Fig. 19-4 A cubical box of edge length L , containing n moles of an ideal gas. A molecule of mass m and velocity \vec{v} is about to collide with the shaded wall of area L^2 . A normal to that wall is shown.

For a typical gas molecule, of mass m and velocity v , that is about to collide with the shaded wall, as shown, if the collision with the wall is elastic, the only component of its velocity that is changed is the x component.

$$\Delta p_x = (-mv_x) - (mv_x) = -2mv_x.$$

The only change in the particle's momentum is along the x axis:

Hence, the momentum Δp_x delivered to the wall by the molecule during the collision is $+2mv_x$.

The time Δt between collisions is the time the molecule takes to travel to the opposite wall and back again (a distance $2L$) at speed v_x . Therefore, Δt is equal to $2L/v_x$.

Therefore,
$$\frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}.$$

The pressure:
$$p = \frac{F_x}{L^2} = \frac{mv_x^2/L + mv_x^2/L + \dots + mv_x^2/L}{L^2} = \left(\frac{m}{L^3}\right)(v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2).$$

But,
$$v^2 = v_x^2 + v_y^2 + v_z^2.$$

Therefore,
$$p = \frac{nM(v^2)_{\text{avg}}}{3V} = \frac{nmN_A}{L^3}(v_x^2)_{\text{avg}} = \frac{nM(v_x^2)_{\text{avg}}}{V}.$$

With
$$\sqrt{(v^2)_{\text{avg}}} = v_{\text{rms}}$$

we finally have
$$p = \frac{nMv_{\text{rms}}^2}{3V}, \quad \text{and} \quad v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

19.4: RMS Speed

Table 19-1

Some RMS Speeds at Room Temperature ($T = 300 \text{ K}$)^a

Gas	Molar Mass (10^{-3} kg/mol)	v_{rms} (m/s)
Hydrogen (H_2)	2.02	1920
Helium (He)	4.0	1370
Water vapor (H_2O)	18.0	645
Nitrogen (N_2)	28.0	517
Oxygen (O_2)	32.0	483
Carbon dioxide (CO_2)	44.0	412
Sulfur dioxide (SO_2)	64.1	342

^aFor convenience, we often set room temperature equal to 300 K even though (at 27°C or 81°F) that represents a fairly warm room.

Example:

Sample Problem

Average and rms values

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

(a) What is the average value n_{avg} of these numbers?

Calculation: We find this from

$$n_{\text{avg}} = \frac{5 + 11 + 32 + 67 + 89}{5} = 40.8. \quad (\text{Answer})$$

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

Calculation: We find this from

$$n_{\text{rms}} = \sqrt{\frac{5^2 + 11^2 + 32^2 + 67^2 + 89^2}{5}} = 52.1. \quad (\text{Answer})$$

The rms value is greater than the average value because the larger numbers—being squared—are relatively more important in forming the rms value.

19.5: Translational Kinetic Energy

$$K_{\text{avg}} = \left(\frac{1}{2}mv^2\right)_{\text{avg}} = \frac{1}{2}m(v^2)_{\text{avg}} = \frac{1}{2}mv_{\text{rms}}^2,$$

$$K_{\text{avg}} = \left(\frac{1}{2}m\right) \frac{3RT}{M}.$$

$$K_{\text{avg}} = \frac{3RT}{2N_A}.$$

$$K_{\text{avg}} = \frac{3}{2}kT.$$

19.6: Mean Free Path

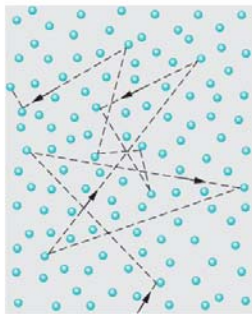


Fig. 19-5 A molecule traveling through a gas, colliding with other gas molecules in its path. Although the other molecules are shown as stationary, they are also moving in a similar fashion.

The mean free path, λ , is the average distance traversed by a molecule between collisions.

The expression for the mean free path does, in fact, turn out to be:

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 N/V} \quad (\text{mean free path}).$$

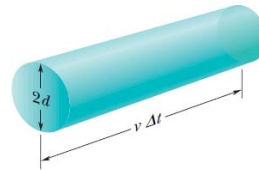


Fig. 19-7 In time Δt the moving molecule effectively sweeps out a cylinder of length $v \Delta t$ and radius d .

$$\begin{aligned} \lambda &= \frac{\text{length of path during } \Delta t}{\text{number of collisions in } \Delta t} \approx \frac{v \Delta t}{\pi d^2 v \Delta t N/V} \\ &= \frac{1}{\pi d^2 N/V}. \end{aligned}$$

Example, Mean Free Path, Average Speed, Collision Frequency:

(a) What is the mean free path λ for oxygen molecules at temperature $T = 300$ K and pressure $p = 1.0$ atm? Assume that the molecular diameter is $d = 290$ pm and the gas is ideal.

KEY IDEA

Each oxygen molecule moves among other *moving* oxygen molecules in a zigzag path due to the resulting collisions. Thus, we use Eq. 19-25 for the mean free path.

Calculation: We first need the number of molecules per unit volume, N/V . Because we assume the gas is ideal, we can use the ideal gas law of Eq. 19-9 ($pV = NkT$) to write $N/V = p/kT$. Substituting this into Eq. 19-25, we find

$$\begin{aligned}\lambda &= \frac{1}{\sqrt{2}\pi d^2 N/V} = \frac{kT}{\sqrt{2}\pi d^2 p} \\ &= \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{\sqrt{2}\pi(2.9 \times 10^{-10} \text{ m})^2(1.01 \times 10^5 \text{ Pa})} \\ &= 1.1 \times 10^{-7} \text{ m.} \quad (\text{Answer})\end{aligned}$$

This is about 380 molecular diameters.

(b) Assume the average speed of the oxygen molecules is $v = 450$ m/s. What is the average time t between successive

collisions for any given molecule? At what rate does the molecule collide; that is, what is the frequency f of its collisions?

KEY IDEAS

(1) Between collisions, the molecule travels, on average, the mean free path λ at speed v . (2) The average rate or frequency at which the collisions occur is the inverse of the time t between collisions.

Calculations: From the first key idea, the average time between collisions is

$$\begin{aligned}t &= \frac{\text{distance}}{\text{speed}} = \frac{\lambda}{v} = \frac{1.1 \times 10^{-7} \text{ m}}{450 \text{ m/s}} \\ &= 2.44 \times 10^{-10} \text{ s} \approx 0.24 \text{ ns.} \quad (\text{Answer})\end{aligned}$$

This tells us that, on average, any given oxygen molecule has less than a nanosecond between collisions.

From the second key idea, the collision frequency is

$$f = \frac{1}{t} = \frac{1}{2.44 \times 10^{-10} \text{ s}} = 4.1 \times 10^9 \text{ s}^{-1}. \quad (\text{Answer})$$

This tells us that, on average, any given oxygen molecule makes about 4 billion collisions per second.

19.7: The Distribution of Molecular Speeds

Maxwell's law of speed distribution

is:

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

Here M is the molar mass of the gas, R is the gas constant, T is the gas temperature, and v is the molecular speed. The quantity $P(v)$ is a probability distribution function: For any speed v , the product $P(v) dv$ is the fraction of molecules with speeds in the interval dv centered on speed v .

The total area under the distribution curve corresponds to the fraction of the molecules whose speeds lie between zero and infinity, and is equal to unity.

$$\int_0^{\infty} P(v) dv = 1.$$

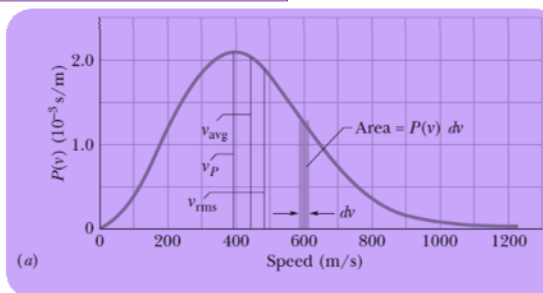


Fig. 19-8 (a) The Maxwell speed distribution for oxygen molecules at $T = 300$ K. The three characteristic speeds are marked.

19.7: Average, RMS, and Most Probable Speeds

The **average speed** v_{avg} of the molecules in a gas can be found in the following way:

Weigh each value of v in the distribution; that is, multiply it by the fraction $P(v) dv$ of molecules with speeds in a differential interval dv centered on v .

Then add up all these values of $v P(v) dv$.

The result is v_{avg} :

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

Therefore, $(v^2)_{\text{avg}} = \int_0^{\infty} v^2 P(v) dv$ leads to $(v^2)_{\text{avg}} = \frac{3RT}{M}$.

RMS speed: $v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$ (rms speed),

The **most probable speed** v_p is the speed at which $P(v)$ is maximum. To calculate v_p , we set $dP/dv = 0$ and then solve for v , thus obtaining:

$$v_p = \sqrt{\frac{2RT}{M}} \quad (\text{most probable speed}).$$

Example, Speed Distribution in a Gas:

A container is filled with oxygen gas maintained at room temperature (300 K). What fraction of the molecules have speeds in the interval 599 to 601 m/s? The molar mass M of oxygen is 0.0320 kg/mol.

KEY IDEAS

1. The speeds of the molecules are distributed over a wide range of values, with the distribution $P(v)$ of Eq. 19-27.
2. The fraction of molecules with speeds in a differential interval dv is $P(v) dv$.
3. For a larger interval, the fraction is found by integrating $P(v)$ over the interval.
4. However, the interval $\Delta v = 2$ m/s here is small compared to the speed $v = 600$ m/s on which it is centered.

Calculations: Because Δv is small, we can avoid the integration by approximating the fraction as

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

The function $P(v)$ is plotted in Fig. 19-8a. The total area between the curve and the horizontal axis represents the to-

tal fraction of molecules (unity). The area of the thin gold strip represents the fraction we seek.

To evaluate frac in parts, we can write

$$\text{frac} = (4\pi)(A)(v^2)(e^B)(\Delta v), \quad (19-36)$$

where

$$A = \left(\frac{M}{2\pi RT} \right)^{3/2} = \left(\frac{0.0320 \text{ kg/mol}}{(2\pi)(8.31 \text{ J/mol}\cdot\text{K})(300 \text{ K})} \right)^{3/2}$$

$$= 2.92 \times 10^{-9} \text{ s}^3/\text{m}^3$$

$$\text{and } B = -\frac{Mv^2}{2RT} = -\frac{(0.0320 \text{ kg/mol})(600 \text{ m/s})^2}{(2)(8.31 \text{ J/mol}\cdot\text{K})(300 \text{ K})}$$

$$= -2.31.$$

Substituting A and B into Eq. 19-36 yields

$$\text{frac} = (4\pi)(A)(v^2)(e^B)(\Delta v)$$

$$= (4\pi)(2.92 \times 10^{-9} \text{ s}^3/\text{m}^3)(600 \text{ m/s})^2(e^{-2.31})(2 \text{ m/s})$$

$$= 2.62 \times 10^{-3}. \quad (\text{Answer})$$

Thus, at room temperature, 0.262% of the oxygen molecules will have speeds that lie in the narrow range between 599 and 601 m/s. If the gold strip of Fig. 19-8a were drawn to the scale of this problem, it would be a very thin strip indeed.

Example, Different Speeds

The molar mass M of oxygen is 0.0320 kg/mol .

(a) What is the average speed v_{avg} of oxygen gas molecules at $T = 300 \text{ K}$?

Calculation: We end up with Eq. 19-31, which gives us

$$\begin{aligned} v_{\text{avg}} &= \sqrt{\frac{8RT}{\pi M}} \\ &= \sqrt{\frac{8(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{\pi(0.0320 \text{ kg/mol})}} \\ &= 445 \text{ m/s.} \end{aligned} \quad (\text{Answer})$$

This result is plotted in Fig. 19-8a.

(b) What is the root-mean-square speed v_{rms} at 300 K ?

Calculation: We end up with Eq. 19-34, which gives us

$$\begin{aligned} v_{\text{rms}} &= \sqrt{\frac{3RT}{M}} \\ &= \sqrt{\frac{3(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{0.0320 \text{ kg/mol}}} \\ &= 483 \text{ m/s.} \end{aligned} \quad (\text{Answer})$$

This result, plotted in Fig. 19-8a, is greater than v_{avg} because the greater speed values influence the calculation more when we integrate the v^2 values than when we integrate the v values.

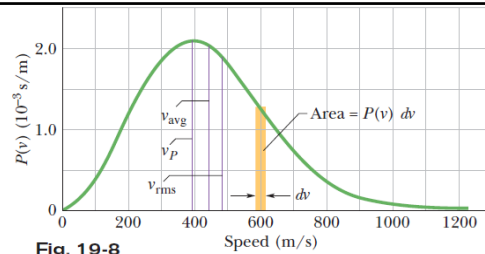


Fig. 19-8

(c) What is the most probable speed v_p at 300 K ?

$$\begin{aligned} v_p &= \sqrt{\frac{2RT}{M}} \\ &= \sqrt{\frac{2(8.31 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{0.0320 \text{ kg/mol}}} \\ &= 395 \text{ m/s.} \end{aligned} \quad (\text{Answer})$$

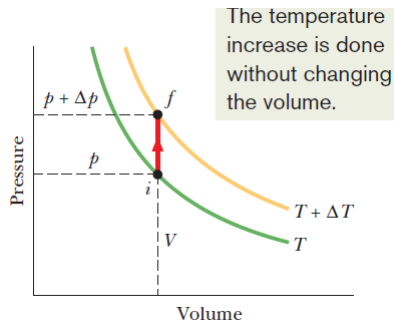
This result is also plotted in Fig. 19-8a.

19.8: Molar Specific Heat of Ideal Gases: Internal Energy

The internal energy E_{int} of an ideal gas is a function of the gas temperature only; it does not depend on any other variable.

$$E_{\text{int}} = \frac{3}{2}nRT \quad (\text{monatomic ideal gas}).$$

19.8: Molar Specific Heat at Constant Volume



$$Q = nC_V \Delta T \quad (\text{constant volume}),$$

where C_V is a constant called the **molar specific heat at constant volume**.

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

Therefore, $\Delta E_{\text{int}} = nC_V \Delta T - W$.

With the volume held constant, the gas cannot expand and thus cannot do any work.

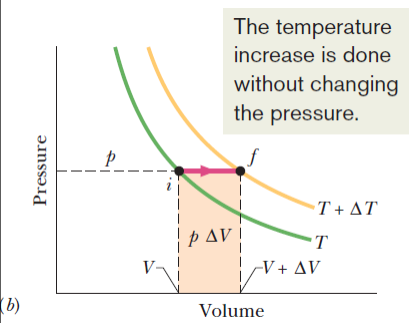
Therefore, $C_V = \frac{\Delta E_{\text{int}}}{n \Delta T}$

$$\Delta E_{\text{int}} = \frac{3}{2} n R \Delta T. \quad \longrightarrow \quad C_V = \frac{3}{2} R = 12.5 \text{ J/mol} \cdot \text{K} \quad (\text{monatomic gas}).$$

When a confined ideal gas undergoes temperature change ΔT , the resulting change in its internal energy is $\Delta E_{\text{int}} = nC_V \Delta T$ (ideal gas, any process).

A change in the internal energy E_{int} of a confined ideal gas depends on only the change in the temperature, not on what type of process produces the change.

19.8: Molar Specific Heat at Constant Pressure



$$Q = nC_p \Delta T \quad (\text{constant pressure}),$$

where C_p is a constant called the molar specific heat at constant pressure. This C_p is greater than the molar specific heat at constant volume C_V .

We also have: $\Delta E_{\text{int}} = Q - W$.

And $W = p \Delta V$

$$W = p \Delta V = nR \Delta T.$$

Therefore, $C_V = C_p - R$

$$\downarrow$$

$$C_p = C_V + R.$$

19.8: Molar Specific Heats

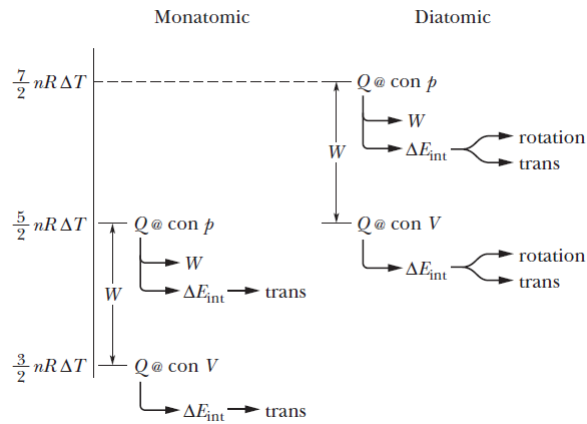


Fig. 19-12 The relative values of Q for a monatomic gas (left side) and a diatomic gas undergoing a constant-volume process (labeled “*con V*”) and a constant-pressure process (labeled “*con p*”). The transfer of the energy into work W and internal energy (E_{int}) is noted.

Example, Monatomic Gas:

A bubble of 5.00 mol of helium is submerged at a certain depth in liquid water when the water (and thus the helium) undergoes a temperature increase ΔT of 20.0 C° at constant pressure. As a result, the bubble expands. The helium is monatomic and ideal.

(a) How much energy is added to the helium as heat during the increase and expansion?

Calculations: Because the pressure p is held constant during the addition of energy, we use the molar specific heat at constant pressure C_p and Eq. 19-46,

$$Q = nC_p \Delta T, \quad (19-50)$$

to find Q . To evaluate C_p we go to Eq. 19-49, which tells us that for any ideal gas, $C_p = C_V + R$. Then from Eq. 19-43, we know that for any *monatomic* gas (like the helium here), $C_V = \frac{3}{2}R$. Thus, Eq. 19-50 gives us

$$\begin{aligned} Q &= n(C_V + R) \Delta T = n\left(\frac{3}{2}R + R\right) \Delta T = n\left(\frac{5}{2}R\right) \Delta T \\ &= (5.00 \text{ mol})(2.5)(8.31 \text{ J/mol} \cdot \text{K})(20.0 \text{ C}^\circ) \\ &= 2077.5 \text{ J} \approx 2080 \text{ J}. \quad (\text{Answer}) \end{aligned}$$

(b) What is the change ΔE_{int} in the internal energy of the helium during the temperature increase?

Calculation: We can now easily find the constant-volume change ΔE_{int} with Eq. 19-45:

$$\begin{aligned} \Delta E_{int} &= nC_V \Delta T = n\left(\frac{3}{2}R\right) \Delta T \\ &= (5.00 \text{ mol})(1.5)(8.31 \text{ J/mol} \cdot \text{K})(20.0 \text{ C}^\circ) \\ &= 1246.5 \text{ J} \approx 1250 \text{ J}. \quad (\text{Answer}) \end{aligned}$$

(c) How much work W is done by the helium as it expands against the pressure of the surrounding water during the temperature increase?

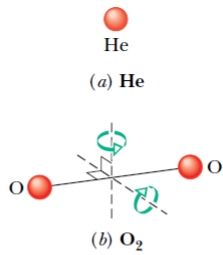
Calculation: We end up with

$$\begin{aligned} W &= nR \Delta T \\ &= (5.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(20.0 \text{ C}^\circ) \\ &= 831 \text{ J}. \quad (\text{Answer}) \end{aligned}$$

Another way: Because we happen to know Q and ΔE_{int} , we can work this problem another way: We can account for the energy changes of the gas with the first law of thermodynamics, writing

$$\begin{aligned} W &= Q - \Delta E_{int} = 2077.5 \text{ J} - 1246.5 \text{ J} \\ &= 831 \text{ J}. \quad (\text{Answer}) \end{aligned}$$

19.9: Degrees of Freedom and Molar Specific Heats



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 $\frac{1}{2}RT$ permole).

$$C_V = \left(\frac{f}{2}\right)R = 4.16f \text{ J/mol} \cdot \text{K},$$

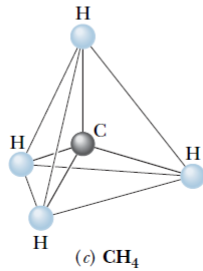


Fig. 19-13 Models of molecules as used in kinetic theory: (a) helium, a typical monatomic molecule; (b) oxygen, a typical diatomic molecule; and (c) methane, a typical polyatomic molecule. The spheres represent atoms, and the lines between them represent bonds. Two rotation axes are shown for the oxygen molecule.

19.9: Degrees of Freedom and Molar Specific Heats

Table 19-3

Degrees of Freedom for Various Molecules

Molecule	Example	Degrees of Freedom			Predicted Molar Specific Heats	
		Translational	Rotational	Total (f)	C_V (Eq. 19-51)	$C_p = C_V + R$
Monatomic	He	3	0	3	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic	O ₂	3	2	5	$\frac{5}{2}R$	$\frac{7}{2}R$
Polyatomic	CH ₄	3	3	6	$3R$	$4R$

Example, Diatomic Gas:

We transfer 1000 J as heat Q to a diatomic gas, allowing the gas to expand with the pressure held constant. The gas molecules each rotate around an internal axis 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)?

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

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

We next find ΔE_{int} from Eq. 19-45, substituting the molar specific heat $C_V (= \frac{5}{2}R)$ for a constant-volume process and using the same ΔT . Because we are dealing with a diatomic gas, let's call this change $\Delta E_{\text{int, dia}}$. Equation 19-45 gives us

$$\begin{aligned} \Delta E_{\text{int, dia}} &= nC_V \Delta T = n\left(\frac{5}{2}R\right)\left(\frac{Q}{\frac{7}{2}nR}\right) = \frac{5}{7}Q \\ &= 0.71428Q = 714.3 \text{ J.} \end{aligned} \quad (\text{Answer})$$

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, as the gas pushes the walls of its container outward.

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 $\Delta E_{\text{int, mon}}$, 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,

$$\Delta E_{\text{int, mon}} = n\left(\frac{3}{2}R\right)\Delta T.$$

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

$$\begin{aligned} \Delta E_{\text{int, mon}} &= n\left(\frac{3}{2}R\right)\left(\frac{Q}{\frac{7}{2}nR}\right) = \frac{3}{7}Q \\ &= 0.42857Q = 428.6 \text{ J.} \end{aligned}$$

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 $\Delta E_{\text{int, dia}}$ (that is, the additional 285.7 J) goes into the rotational motion of the molecules. Thus, for the diatomic gas,

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

19.10: A Hint of Quantum Theory

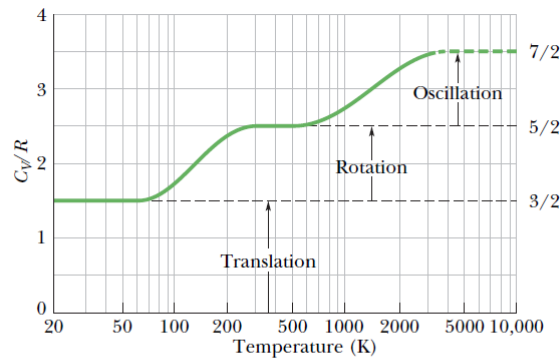


Fig. 19-14 C_V/R versus temperature for (diatomic) hydrogen gas. Because rotational and oscillatory motions begin at certain energies, only translation is possible at very low temperatures. As the temperature increases, rotational motion can begin. At still higher temperatures, oscillatory motion can begin.

19.11: The Adiabatic Expansion of an Ideal Gas

Starting from: $dE_{\text{int}} = Q - p dV$.

And using the result for E_{int} , we get: $n dT = -\left(\frac{p}{C_V}\right) dV$.

From the ideal gas law, $p dV + V dp = nR dT$.

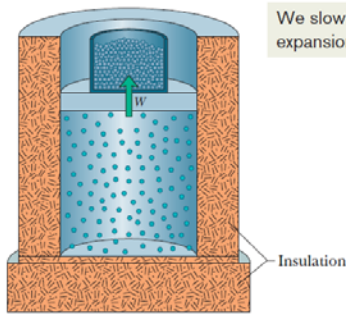
Also, since $C_p - C_V = R$, $n dT = \frac{p dV + V dp}{C_p - C_V}$

Using the above relations, we get: $\frac{dp}{p} + \left(\frac{C_p}{C_V}\right) \frac{dV}{V} = 0$.

Using $\gamma = C_p/C_V$, and integrating, we get: $\ln p + \gamma \ln V = \text{a constant}$.

Finally we obtain: $pV^\gamma = \text{a constant}$ (adiabatic process),

19.11: The Adiabatic Expansion of an Ideal Gas



We slowly remove lead shot, allowing an expansion without any heat transfer.

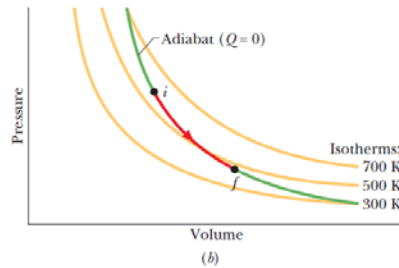


Fig. 19-15 (a) The volume of an ideal gas is increased by removing mass from the piston. The process is adiabatic ($Q = 0$). (b) The process proceeds from i to f along an adiabat on a p - V diagram.

$$pV^\gamma = \text{a constant} \quad (\text{adiabatic process}),$$

$$p_i V_i^\gamma = p_f V_f^\gamma \quad (\text{adiabatic process}).$$

$$\left(\frac{nRT}{V}\right) V^\gamma = \text{a constant}.$$

$$TV^{\gamma-1} = \text{a constant} \quad (\text{adiabatic process})$$

19.11: The Adiabatic Expansion of an Ideal Gas, Free Expansion

A free expansion of a gas is an adiabatic process with no work or change in internal energy. Thus, a free expansion differs from the adiabatic process described earlier, in which work is done and the internal energy changes.

In a free expansion, a gas is in equilibrium only at its initial and final points; thus, we can plot only those points, but not the expansion itself, on a p - V diagram.

Since $E_{int} = 0$, the temperature of the final state must be that of the initial state. Thus, the initial and final points on a p - V diagram must be on the same isotherm, and we have

$$T_i = T_f \quad (\text{free expansion})$$

Also, if the gas is ideal, $p_i V_i = p_f V_f$ (free expansion).

Example, Adiabatic Expansion:

Initially, 1 mol of oxygen (assumed to be an ideal gas) has temperature 310 K and volume 12 L. We will allow it to expand to volume 19 L.

(a) What would be the final temperature if the gas expands adiabatically? Oxygen (O_2) is diatomic and here has rotation but not oscillation.

KEY IDEAS

1. When a gas expands against the pressure of its environment, it must do work.
2. When the process is adiabatic (no energy is transferred as heat), then the energy required for the work can come only from the internal energy of the gas.
3. Because the internal energy decreases, the temperature T must also decrease.

Calculations: We can relate the initial and final temperatures and volumes with Eq. 19-56:

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}. \quad (19-64)$$

Because the molecules are diatomic and have rotation but not oscillation, we can take the molar specific heats from Table 19-3. Thus,

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40.$$

Solving Eq. 19-64 for T_f and inserting known data then yield

$$\begin{aligned} T_f &= \frac{T_i V_i^{\gamma-1}}{V_f^{\gamma-1}} = \frac{(310 \text{ K})(12 \text{ L})^{1.40-1}}{(19 \text{ L})^{1.40-1}} \\ &= (310 \text{ K})\left(\frac{12}{19}\right)^{0.40} = 258 \text{ K}. \quad (\text{Answer}) \end{aligned}$$

(b) What would be the final temperature and pressure if, instead, the gas expands freely to the new volume, from an initial pressure of 2.0 Pa?

KEY IDEA

The temperature does not change in a free expansion because there is nothing to change the kinetic energy of the molecules.

Calculation: Thus, the temperature is

$$T_f = T_i = 310 \text{ K}. \quad (\text{Answer})$$

We find the new pressure using Eq. 19-63, which gives us

$$p_f = p_i \frac{V_i}{V_f} = (2.0 \text{ Pa}) \frac{12 \text{ L}}{19 \text{ L}} = 1.3 \text{ Pa}. \quad (\text{Answer})$$

Four Gas Processes for an Ideal Gas

Problem-Solving Tactics

A Graphical Summary of Four Gas Processes

In this chapter we have discussed four special processes that an ideal gas can undergo. An example of each (for a monatomic ideal gas) is shown in Fig. 19-16, and some associated characteristics are given in Table 19-4, including two process names (isobaric and isochoric) that we have not used but that you might see in other courses.

CHECKPOINT 5

Rank paths 1, 2, and 3 in Fig. 19-16 according to the energy transfer to the gas as heat, greatest first.

Fig. 19-16

A p - V diagram representing four special processes for an ideal monatomic gas.

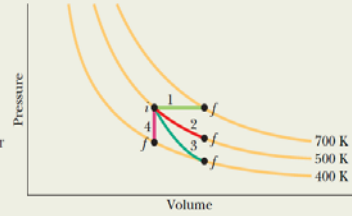


Table 19-4

Four Special Processes

Path in Fig. 19-16	Constant Quantity	Process Type	Some Special Results
			$(\Delta E_{\text{int}} = Q - W \text{ and } \Delta E_{\text{int}} = nC_V \Delta T \text{ for all paths})$
1	p	Isobaric	$Q = nC_p \Delta T; W = p \Delta V$
2	T	Isothermal	$Q = W = nRT \ln(V_f/V_i); \Delta E_{\text{int}} = 0$
3	$pV^\gamma, TV^{\gamma-1}$	Adiabatic	$Q = 0; W = -\Delta E_{\text{int}}$
4	V	Isochoric	$Q = \Delta E_{\text{int}} = nC_V \Delta T; W = 0$