Chapter 10

Macroscopic to Microscopic-Gases and Kinetic Theory

Exercises in Chapter IO follow the two-part division of the white pages, establishing first the macroscopic foundations of the gas laws and then seeking a microscopic explanation. The resulting statistical theory, an inspired exploitation of ignorance, treats the gas as an enormously large collection of point particles in random motion. This reconciliation of chance and inevitability will be echoed later, in Chapter 14, when we identify entropy as the statistical driving force in all chemical processes.

The idealized nature of an ideal gas-its absence of interparticle interactions, its eradication of all chemical distinctions, its restriction to low densities-is implicit here throughout, acknowledged as a small price to pay for the universality of this simple model. "Real " gases, in which particles clearly do interact and clearly do take up space, appear in due course, in the very next chapter: And there, with the assumptions of the ideal gas relaxed, the intermolecular interactions introduced earlier in Chapter 9 are shown to engineer the gas-liquidphase transition. That change in state, in turn, gives us a prototypical example of dynamic equilibrium, which leads us into a three-chapter sequence on equilibrium and thermodynamics (Chapters 12 through 14).

The opening problems deal with the macroscopic variables of pressure and temperature, emphasizing basic characteristics andprovidingpractice in dimensional analysis. Soon after, beginning in Exercise 11, the focus turns to the gas laws themselves and eventually to the microscopic justifications of the kinetic theory

1. Pressure is the force exerted per unit area. The greater the force and the smaller the area, the higher the pressure. See *PoC*, pages 353-355 and 370-374.

(a) Each object has the same mass (1 kg) and hence the same weight in a local gravitational field. Since the weight arises from the gravitational force exerted on the

mass, the body with the smaller area on its bottom side-the smaller "footprint"—produces the greater pressure:

Object A: Area= $100 \text{ cm} \times 100 \text{ cm} = 1 \text{ mx } 1 \text{ m}= 1 \text{ m}^2$

Object B: Area= $1000 \text{ cm} \times 100 \text{ cm} = 10 \text{ m} \times 1 \text{ m} = 10 \text{ m}^2$

Object A distributes its 1 kilogram over 1 square meter, whereas object B distributes the same 1 kilogram over 10 square meters. The pressure generated by A is higher.

(b) Given the mass *(m),* area (A), and acceleration due to gravity *(g),* we obtain the pressure   directly:

$$P = \frac{\text{force}}{\text{area}} = \frac{mg}{A}$$

The pressure from object A is 9.81 newtons per square meter (assuming three significant figures):

$$P_A = \frac{1 \text{ kg x } 9.81 \text{ m s}^{-2}}{1 \text{ m}^2} = 9.81 \text{ N m}^{-2} = 9.81 \text{ Pa}$$

Acting over a tenfold greater area, object B imposes one-tenth the pressure of A:

$$P_B = \frac{1 \text{ kg x } 9.81 \text{ m s}^{-2}}{10 \text{ m}^2} = 0.981 \text{ N m}^{-2} = 0.981 \text{ Pa}$$

Recall from Chapter 1 (pages 18-20) that the SI unit of force, the newton, is derived from Newton's   second   law:

Force $=$ mass x acceleration $\sim$ kg m s^{-2} $\equiv$ N

2. Determined only by mass and gravitational acceleration, the force F developed in each orientation is the same:

$$F = mg = 1 \text{ kg} \times 9.81 \text{ m s}^{-2} = 9.81 \text{ N}$$

The corresponding pressure, however, depends on area:

$$P = \frac{F}{A}$$

Taking orientation (a), for instance, we find that the fixed force of 9.81 N is distributed over an area of 10 m^2 to produce a pressure of 0.98 1 Pa:

$$A = 1000 \text{ cm} \times 100 \text{ cm} = 10 \text{ m} \times 1 \text{ m} = 10 \text{ m}^2$$

$$P = \frac{F}{A} = \frac{9.81 \text{ N}}{10 \text{ m}^2} = 0.981 \text{ Pa}$$

Results for all three orientations are calculated below to three significant figures (consistent with the stated value of g):

	DIMENSIONS OF BASE (cm x cm)	AREA (m^2)	PRESSURE (Pa)
(a)	1000 x 100	10	0.981
(b)	1000 x 10	1	9.81
(c)	100 x 10	0.1	98.1

3. Atmospheric pressure denotes the force imposed on the earth's surface by a column of air, measured per unit area. The column, filled with molecules in motion, extends from the ground up to outer space.

To say that "atmospheric pressure is 101,325 pascals" is to say that the molecules contained in this column exert a net force of 101,325 newtons on I square meter of ground.

4. We are given the pressure exerted by a circular column of diameter **2r** and area πr^2,

$$P = \frac{F}{A} = 1.01325 \text{ x } 10^5 \text{ Pa} = 1.01325 \text{ x } 10^5 \text{ N m}^{-2}$$

$$2r = 1.00 \text{ cm}$$

$$A = \pi r^2 = \pi \left(1.500 \text{ cm x } \frac{1 \text{ m}}{100 \text{ cm}} \right)^2 = \pi \left(5.00 \text{ x } 10^{-3} \text{ m} \right)^2$$

from which we calculate the associated force:

$$F = PA = (1.01325 \text{ x } 10^5 \text{ N m}^{-2}) \pi \left(5.00 \times 10^{-3} \text{ m} \right)^2 = \textbf{7.96 N}$$

5. First, determine that a mass of 1 .OO kilogram has a weight of 9.81 newtons:

$$F = mg = 1.00 \text{ kg x } 9.81 \text{ m s}^{-2} = 9.81 \text{ kg m s}^{-2} = 9.81 \text{ N}$$

From the information given in the problem,

MASS   FORCE

$$1.00 \text{ kg} \equiv 2.21 \text{ lb}$$

we know also that 9.81 N (the force arising from 1 kg) is equal to 2.21 lb.
        With that, we use the unit-factor method to convert newtons into pounds and
square meters into square inches:

$$1.01325 \text{ x } 10^5 \text{ Pa x} \frac{1 \text{ N m}^{-2}}{\text{Pa}} \text{ x } \frac{2.21 \text{ lb}}{9.81 \text{ N}} \text{ x } \left(\frac{1 \text{ m}}{100 \text{ cm}} \text{ x } \frac{2.54 \text{ cm}}{\text{in}}\right)^2 = 14.7 \text{ lb in}^{-2}$$

6. Outside the tire, the air exerts a pressure of 14.7 lb in^{-2} pressing *inward (see* previous
exercise). Inside the tire, the compressed air must exert a balancing pressure of 14.7 lb in^{-2}
plus a net pressure of 30.0 lb in^{-2} pressing outward. The total pressure inside the tire is
therefore 44.7 lb in^{-2}:

$$14.7 \text{ lb } in^{-2} + 30.0 \text{ lb } in^{-2} = 44.7 \text{ lb } in^{-2}$$

7. A column of mercury, confined to an inverted tube sealed on one end, adjusts its
height when an opposing column of air presses down on the liquid outside. With a
vacuum space above it, the mercury reaches a level sufficient to balance the pressure
imposed by the air. At 1 atm and $0°C$, the increase in height is 760 millimeters.
        The height thus attained is orders of magnitude less than the many miles of air
overhead, because liquid mercury (13.6 g cm^{-3}) is far more dense than the mixed gases
that make up the atmosphere ($\approx$ 0.0013 g cm^{-3} at STP). See the next exercise.

8. Use the equation

$$P = \rho gh$$

derived in the problem, inserting the following numerical values to solve for the
density p:

$$P = 1.01325 \text{ x } 10^5 \text{ Pa} \quad \text{(pressure)}$$

$$g = 9.81 \text{ m s}^{-2} \quad \text{(acceleration due to gravity)}$$

$$h = 0.760 \text{ m} \quad \text{(change in height)}$$

The result is 13.6 g cm^{-3}:

$$\rho = \frac{P}{gh}$$

$$= \frac{1.01325 \times 10^5 \text{ kg m}^{-1}\text{ s}^{-2}}{(9.81 \text{ m s}^{-2})(0.760 \text{ m})}$$

$$= 1.36 \times 10^4 \text{ kg m}^{-3} \times \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3 \times \frac{1000 \text{ g}}{\text{kg}} = 13.6 \text{ g cm}^{-3}$$

Note that the newton and pascal are straightforwardly expressed in base SI units of mass, length, and time:

$$1 \text{ N} = 1 \text{ kg m s}^{-2}$$

$$1 \text{ Pa} = 1 \text{ N m}^{-2} = \left(1 \text{ kg m s}^{-2}\right)\left(\text{m}^{-2}\right) = 1 \text{ kg m}^{-1}\text{ s}^{-2}$$

9. Use the equation

$$P = \rho gh$$

developed in the previous exercise to solve for h, the height of the barometric column:

$$h = \frac{P}{\rho g}$$

Expressing ρ, P, and g in base SI units of mass (kg), length (m), and time (s),

$$\rho = \frac{1.00 \text{ g}}{\text{mL}} \times \frac{1 \text{ mL}}{\text{cm}^3} \times \left(\frac{100 \text{ cm}}{\text{m}}\right)^3 \times \frac{1 \text{ kg}}{1000 \text{ g}} = 1.00 \times 10^3 \text{ kg m}^{-3}$$

$$P = 1.00 \text{ atm} \times \frac{1.01325 \times 10^5 \text{ Pa}}{\text{atm}} \times \frac{1 \text{ N m}^{-2}}{\text{Pa}} \times \frac{1 \text{ kg m s}^{-2}}{\text{N}} = 1.01325 \times 10^5 \text{ kg m}^{-1}\text{ s}^{-2}$$

$$g = 9.81 \text{ m s}^{-2}$$

we have only to convert finally from meters into feet:

$$h = \frac{P}{\rho g} = \frac{1.01325 \times 10^5 \text{ kg m}^{-1}\text{ s}^{-2}}{(1.00 \times 10^3 \text{ kg m}^{-3})(9.81 \text{ m s}^{-2})} \times \frac{100 \text{ cm}}{\text{m}} \times \frac{1 \text{ in}}{2.54 \text{ cm}} \times \frac{1 \text{ ft}}{12 \text{ in}} = 33.9 \text{ ft}$$

10. The relevant conversion factors are between **pascals** and atmospheres and between atmospheres and **torr**:

$$1.01325 \times 10^5 \text{ Pa} = 1 \text{ atm} = 760 \text{ torr (definition)}$$

(a) $0.816 \text{ atm} \times \dfrac{760 \text{ torr}}{\text{atm}} = 620. \text{ torr}$

(b) $712.3 \text{ torr} \times \dfrac{1 \text{ atm}}{760 \text{ torr}} = 0.9372 \text{ atm}$

(c) $712.3 \text{ torr} \times \dfrac{1 \text{ atm}}{760 \text{ torr}} \times \dfrac{1.01325 \times 10^5 \text{ Pa}}{\text{atm}} \times \dfrac{1 \text{ kPa}}{1000 \text{ Pa}} = 94.97 \text{ kPa}$

(d) $24.32 \text{ atm} \times \dfrac{1.01325 \times 10^5 \text{ Pa}}{\text{atm}} \times \dfrac{1 \text{ kPa}}{1000 \text{ Pa}} = 2464 \text{ kPa}$

(e) $7659.1 \text{ Pa} \times \dfrac{1 \text{ atm}}{1.01325 \times 10^5 \text{ Pa}} = 0.075589 \text{ atm}$

(f) $7659.1 \text{ Pa} \times \dfrac{1 \text{ atm}}{1.01325 \times 10^5 \text{ Pa}} \times \dfrac{760 \text{ torr}}{\text{atm}} = 57.448 \text{ torr}$

The macroscopic formulation of Boyle's law is discussed on pages 355-362 of PoC *and illustrated in Examples 1 O-l and I O-2.*

11. Boyle's law states that

$$P_1V_1 = P_2V_2 \quad \text{(fixed } n, T)$$

and   hence

$$V_2 = V_1 \frac{P_1}{P_2}$$

We are given the following data:

$$P_1 = 1 \text{ atm} \qquad V_1 = 1 \text{ L}$$

(a) The gas is compressed isothermally into a smaller volume at higher pressure, $P_2 = 10$ atm. A 1 O-fold increase in pressure causes a 1 O-fold decrease in volume:

$$V_2 = V_1 \frac{P_1}{P_2} = 1 \, \text{L} \times \frac{1 \, \text{atm}}{10 \, \text{atm}} = 0.1 \, \text{L}$$

(b) Similar, with $P_2 = 100$ atm. A 100-fold increase in pressure causes a 100-fold decrease in volume:

$$V_2 = V_1 \frac{P_1}{P_2} = 1 \, \text{L} \times \frac{1\text{atm}}{100 \, \text{atm}} = 0.01 \, \text{L}$$

(c) The gas expands into a larger volume when pressure is reduced to $P_2 = 0.1$ atm. The 1 O-fold decrease in pressure causes a 1 O-fold increase in volume:

$$V_2 = V_1 \frac{P_1}{P_2} = 1 \, \text{L} \times \frac{1 \, \text{atm}}{0.1 \, \text{atm}} = 10 \, \text{L}$$

(d) Similar, with $P_2 = 0.01$ atm. A 100-fold decrease in pressure causes a 100-fold increase in volume:

$$V_2 = V_1 \frac{P_1}{P_2} = 1 \, \text{L} \times \frac{1 \, \text{atm}}{0.01 \, \text{atm}} = 100 \, \text{L}$$

12. Boyle's law applies, since temperature is constant ($T = 273$ K at STP) and the amount of gas is constant ($n = 1$ mol):

$$P_1 V_1 = P_2 V_2 \quad (\text{fixed } n, \, T)$$

Given values of three variables,

$$P_1 = 1 \, \text{atm} = 760 \, \text{torr} \qquad V_1 = 22.4 \, \text{L}$$
$$P_2 = 616 \, \text{torr} \qquad V_2 = ?$$

we solve for the fourth:

$$V_2 = V_1 \frac{P_1}{P_2} = \mathbf{22.4} \, \text{L} \times \frac{760 \, \text{torr}}{616 \, \text{torr}} = 27.6 \, \text{L}$$

Note the substitution of 760 torr for 1 atm (P_1), necessary for dimensional consistency if P_2 is stated in torr. Equally acceptable would be to use $P_1 = 1$ atm while converting P_2 into atmospheres as well:

$$P_2 = 616 \, \text{torr} \times \frac{1 \, \text{atm}}{760 \, \text{torr}} = 0.8 \, 11 \, \text{atm}$$

13. Boyle's law is again applicable, since both the amount of gas and the temperature remain unchanged:

$$P_1V_1 = P_2V_2 \quad \text{(fixed } n, T\text{)}$$

Given the two volumes,

$$V_1 = 435.1 \text{ mL} \qquad V_2 = 172.9 \text{ mL}$$

we solve for the ratio of pressures:

$$\frac{P_2}{P_1} = \frac{V_1}{V_2} = \frac{435.1 \text{ mL}}{172.9 \text{ mL}} = 2.516$$

The pressure is increased by a factor of approximately 2.5, in inverse proportion to the fractional change in volume. If we squeeze the gas, it occupies less space.

14. Another application of Boyle's law, similar to the preceding exercise. Given three of the pressure-volume variables,

$$P_1 = 1.0 \text{ atm} \qquad V_1 = 1.0 \text{ L}$$
$$P_2 = 54.6 \text{ atm} \qquad V_2 = ?$$

we solve for the fourth:

$$P_1V_1 = P_2V_2 \quad \text{(fixed } n, T\text{)}$$

$$V_2 = V_1 \frac{P_1}{P_2} = 1.0 \text{ L x} \frac{1.0 \text{ atm}}{54.6 \text{ atm}} = 0.018 \text{ L}$$

See pages 362-365 and Example 1 0-3 in PoC *for relevant material on the Kelvin scale and Charles 's law. Temperature conversions are also mentioned on page 32 and in Table C-4 of Appendix C (page A64).*

15. Use the relationships

$$T_K = \frac{1 \text{ K}}{1 °\text{C}} \left(t_C \right) + 273.15 \text{ K}$$

$$t_C = \frac{1 °\text{C}}{1 \text{ K}} \left(T_K - 273.15 \text{ K} \right)$$

to convert between temperature in kelvins (T_K) and temperature in degrees Celsius (t_C).

The two scales differ in their zero points, but the magnitude of a degree is the same in each. The number of decimal places is determined by the least significant digit:

(a) $t_C = 0.0°C$: $T_K = (0.0 + 273.15)$ K = 273.2 K

(b) $T_K = 0$ K: $t_C = (0 - 273.15)°C = -273°C$

(c) $T_K = 3\ 15.75$ K: $t_C = (315.75 - 273.15)°C = 42.60°C$

(d) $t_C = -123.6°C$: $T_K = (-123.6 + 273.15)$ K = 149.6 K

16. The Celsius and Fahrenheit scales differ both in their zero points and in their definition of a degree:

$$t_F = \frac{9\,°F}{5\,°C}\left(t_C\right) + 32\,°F$$

$$t_C = \frac{5\,°C}{9\,°F}\left(t_F - 32\,°F\right)$$

Zero on the Celsius scale (the freezing point of water) corresponds to $32°F$, and the Celsius degree is larger than the Fahrenheit degree by a factor of $\frac{9}{5}$:

(a) $t_C = 342.45°C$: $t_F = \left[\frac{9}{5}(342.45) + 32\right]°F = 648.41°F$

(b) $t_F = 98.6°F$: $t_C = \frac{5}{9}(98.6 - 32)"\ C = 37.0"\ C$ (body   temperature)

(c) $t_C = -10.6°C$: $t_F = \left[\frac{9}{5}(-10.6) + 32\right]°F = 12.9°F$

(d) $t_F = -40.0°F$: $t_C = \frac{5}{9}(-40.0 - 32)°C = -40.0°C$

The two scales coincide at -40 degrees.

17. Charles's **law** is **valid** at constant **pressure and** amount:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{fixed } n, P)$$

Given two temperatures and the initial volume,

$$V_1 = 1.00 \text{ L} \qquad T_1 = (0 + 273.15) \text{ K} = 273 \text{ K}$$
$$V_2 = ? \qquad T_2 = (-50 + 273.15) \text{ K} = 223 \text{ K}$$

we solve for the final volume:

$$V_2 = V_1 \frac{T_2}{T_1} = 1.00 \text{ L} \times \frac{223 \text{ K}}{273 \text{ K}} = 0.817 \text{ L}$$

A fixed amount of gas shrinks in order to maintain a constant pressure as the temperature falls.

Remember always to use absolute temperature (K) when solving these gas-law problems, never Celsius or Fahrenheit temperatures. The conversion from °C to K is shown explicitly above.

18. A fixed amount of gas (here, one mole) obeys Charles's law when its volume is changed under constant pressure:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{fixed } n, P)$$

Told that the volume doubles,

$$\frac{V_2}{V_1} = 2$$

and that the constant-pressure process begins at STP,

$$P_1 = 1 \text{ atm} \qquad T_1 = 273 \text{ K}$$

we solve for the final temperature. T_2:

$$T_2 = T_1 \frac{V_2}{V_1} = 273 \text{ K} \times 2 = 546 \text{ K}$$

The volume scales in direct proportion to the absolute (Kelvin) temperature.

19. The key words "fixed amount" and "constant pressure" tell us, once again, to implement Charles's law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{(fixed } n, P)$$

Converting temperature from °C into K,

$$V_1 = ? \qquad\qquad T_1 = (400 + 273.15) \text{ K} = 673 \text{ K}$$

$$V_2 = 2.38 \text{ L} \qquad T_2 = (500 + 273.15) \text{ K} = 773 \text{ K}$$

we determine the original volume:

$$V_1 = V_2 \frac{T_1}{T_2} = 2.38 \text{ L} \times \frac{673 \text{ K}}{773 \text{ K}} = 2.07 \text{ L}$$

The gas expands upon heating.

20. Use the same method as in the preceding exercise:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{(fixed } n, P)$$

$$V_1 = ? \qquad\qquad T_1 = 400 \text{ K}$$

$$V_2 = 344 \text{ cm}^3 \qquad T_2 = 300 \text{ K}$$

$$V_1 = V_2 \frac{T_1}{T_2} = 344 \text{ cm}^3 \, x \, \frac{400 \text{ K}}{300 \text{ K}} = 459 \text{ cm}^3$$

A fixed amount of gas shrinks in volume as the temperature decreases.

Avogadro 's law, implicit in the next group of exercises, states that equal volumes of gases contain equal numbers ofparticles at constant pressure and temperature (PoC, *pages 3 6 5 - 3 6 6) .*

All of the individual gas laws-Boyle 's law, Charles 's law, Avogadro 's law-come together in the ideal gas equation of state, PV = nRT. For discussion and sample problems, see pages 366-369 and also Examples 10-4 through I O-7.

21. The equation of state

$$PV=nRT$$

holds for any gas **obeying** the ideal gas law, regardless of its particular chemical makeup, Solving for the number of moles and particles in 22.4 L at STP,

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(22.4 \text{ L})}{(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(273 \text{ K})}$$

$$= 1.00 \text{ mol} \times \frac{6.02 \times 10^{23} \text{ particles}}{\text{mol}} = 6.02 \times 10^{23} \text{ particles}$$

we thereby confirm the computation done on page 367 of *PoC*: One mole of *any* ideal gas occupies 22.4 L at STP.

(a) $22.4 \text{ L } CO_2 \equiv 6.02 \times 10^{23}$ molecules CO_2

(b) $22.4 \text{ L } N_2 \equiv 6.02 \times 10^{23}$ molecules N_2

(c) $22.4 \text{ L } O_2 \equiv 6.02 \times 10^{23}$ molecules O_2

(d) $22.4 \text{ L air} \equiv 6.02 \times 10^{23}$ molecules (mostly N_2 and O_2, with small amounts of Ar, CO_2, and other substances)

22. We can always *use* $PV = nRT$ to solve for n, the number of moles:

$$n = \frac{PV}{RT}$$

A number of shortcuts, however, can simplify or eliminate most of the explicit numerical calculations, as demonstrated below.

(a) Since one mole of any ideal gas occupies 22.4 L at STP, we expect to find 6.02×10^{23} atoms of helium under these same conditions. See page 367 of *PoC* and also Exercise 2 1.

(b) The pressure is doubled (from I .OO atm to 2.00 atrn), but the temperature remains the same (273 K):

$$n = \frac{PV}{RT} = \frac{(2.00 \text{ atm})(22.4 \text{ L})}{(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(273 \text{ K})}$$

$$= 2.00 \text{ mol} \times \frac{6,02 \times 10^{23} \text{ atoms}}{\text{mol}} = 1.20 \times 10^{24} \text{ atoms}$$

An alternative method is simply to use the result "1 .OO mol $\equiv$ 22.4 L at STP" and apply correction factors for nonstandard temperature and pressure.

1. Nonstandard temperature: $P = 1$ atm, $V = 22.4$ L, $T \neq 273$ K. With pressure and volume fixed, the number of moles goes up and down in inverse proportion to the temperature:

$$nT = \frac{PV}{R} = \text{constant} \quad \text{(fixed } P, V)$$

At higher temperatures, the gas laws demand that fewer particles occupy the same volume at the same pressure. At lower temperatures, more particles are needed to maintain standard pressure and volume.

2. Nonstandard pressure: $P \neq 1$ atm, $V = 22.4$ L, $T = 273$ K. At fixed volume and temperature, the number of moles scales in direct proportion to the pressure:

$$\frac{n}{P} = \frac{V}{RT} = \text{constant} \quad \text{(fixed } V, T)$$

If P is greater than 1 atm, then a larger quantity of matter $(n > 1$ mol$)$ must be compressed into the same 22.4 L at 273 K. If P is less than 1 atm, then n is less than 1 mol as well.

Thus at 273 K and 2.00 atm-higher than standard pressure-we have only to correct the standard amount (1 .OO mol) by a pressure ratio greater than 1:

$$1.00 \text{ mol} \times \frac{2.00 \text{ atm}}{1.00 \text{ atm}} = 2.00 \text{ mol}$$

value at STP and 22.4 L   value at 2.00 atm and 273 K

correction for increased pressure

Either way, we arrive at the same result-but with the shortcut we avoid explicit use of the universal gas constant, *R.*

(c) Similar. If 1 .OO mol occupies 22.4 L at STP (P = 1 .OO atm, T = 273 K), then only 0.500 mol can occupy the same 22.4 L at half the pressure (0.500 atm):

$$n = 0.500 \text{ mol} = 3.01 \text{ x } 10^{23} \text{ atoms}$$

Alternatively, we may solve the equation

$$n = \frac{PV}{RT}$$

to get the same result. Substitute the values P = 0.500 atm, V = 22.4 L, T = 273 K, and R = 0.08206 atm L $\text{mol}^{-1} \text{K}^{-1}$.

(d) At temperatures higher than standard, the gas would normally expand into a larger volume. Prevented from doing so, the system must fill the fixed volume of 22.4 L with less than one mole of substance:

$$1.00 \text{ mol x } \frac{273 \text{ K}}{546 \text{ K}} = 0.500 \text{ mol} = 3.01 \text{ x } 10^{23} \text{ atoms}$$

The correction factor has a value less than 1.

(e) The same method yields n = 2.00 mol when the temperature is cut to half its standard value. Now the correction factor is greater than 1:

$$1.00 \text{ mol x } \frac{273 \text{ K}}{136.5 \text{ K}} = 2.00 \text{ mol} = 1.20 \text{ x } 10^{24} \text{ atoms}$$

23. The same reasoning applies both here and in Exercise 22. Given values of P, V, and T, *we* can solve the equation

$$PV = nRT$$

for the number of moles (n) and thence the number of particles (N):

$$n = \frac{PV}{RT} \qquad \left(R = 0.08206 \text{ atm L } \text{mol}^{-1} \text{K}^{-1}\right)$$

$$N = nN_0 = nx \frac{6.02 \text{ x } 10^{23} \text{ particles}}{\text{mol}} \qquad \left(N_0 = \text{Avogadro' s number}\right)$$

Or, if we choose, we may begin with the molar volume

$$22.4 \text{ L} \equiv 1.00 \text{ mol} = 6.02 \times 10^{23} \text{ particles at STP} \quad (P = 1.00 \text{ atm}, \; T = 273 \text{ K})$$

and **apply** correction factors to transform the standard state (P_1, V_1, T_1, n_1) into the actual state (P_2, V_2, T_2, n_2):

$$P_1 = 1.00 \text{ atm} \quad V_1 = 22.4 \text{ L} \quad T_1 = 273 \text{ K} \quad n_1 = 1.00 \text{ mol}$$

$$n_2 = n_1 \times \frac{P_2}{4} \times \frac{V_2}{V_1} \times \frac{T_1}{T_2}$$

Each of the correction factors is derived from the ideal **gas** law, $PV = nRT$, conveniently expressed in the following form:

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

Consider three cases:

1. At constant volume and temperature, the amount of gas is directly proportional to pressure:

$$\frac{n}{P} = \frac{V}{RT} = \text{constant} \quad \text{(fixed } V, T)$$

For pressures P_2 greater than 1.00 atm, the ratio P_2/P_1 is greater than 1. For pressures less than 1.00 atm, the ratio is less than 1.

2. At constant pressure and temperature, the number of moles is directly proportional to volume:

$$\frac{n}{V} = \frac{P}{RT} = \text{constant} \quad \text{(fixed } P, T)$$

For volumes V_2 greater than 22.4 L, the ratio V_2/V_1 is greater than 1. For volumes less than 22.4 L, the ratio is less than 1.

3. At constant pressure and volume, the amount of gas is inversely proportional to temperature:

$$nT = \frac{PV}{R} = \text{constant} \quad \text{(fixed } P, V)$$

For temperatures T_2 greater than 273 K, the ratio T_1/T_2 is **less** than 1. For temperatures less than 273 K, the ratio is greater than 1.

Note that the calculations required in this exercise are simpler than in the general case, since we need only compare a nonstandard volume, V_2, with the standard molar volume of 22.4 L. Pressure and temperature remain fixed at their standard values of 1.OO atm and 273 K, respectively. The key expression then reduces to

$$n_2 = n_1 \; x \; \frac{V_2}{v_,}$$

See also Example 1 O-4 in *PoC* (beginning on page R10.8).

(a) Knowing that $n = 1.00$ mol and $V = 22.4$ L at STP *(P = 1.OO atm, T = 273 K)*, we have our answer automatically. All ideal gases behave the same way:

$$1.OO \text{ mol} = 6.02 \text{ x } 10^{23} \text{ molecules CO}$$

For confirmation, substitute *P, V,* and *T* explicitly into the ideal gas equation and solve for *n,* the number of moles:

$$n = \frac{PV}{RT} - \frac{(1.00 \text{ atm})(22.4 \text{ L})}{(0.08206 \text{ atm L mol}^{-1}\text{K}^{-1})(273 \text{ K})} = 1.00 \text{ mol}$$

(b) A volume of 44.8 L contains exactly double the standard amount at STP:

$$n_2 = n_1 \; x \; \frac{V_2}{V_1} = 1.00 \text{ mol x } \frac{44.8 \text{ L}}{22.4 \text{ L}} = 2.00 \text{ mol}$$

$$2.00 \text{ mol} = 1.20 \times 10^{24} \text{ molecules CO}$$

(c) If a volume of 22.4 L contains 1.OO mol at STP, then a volume of 11.2 L contains exactly half the number of moles under the same conditions:

$$n_2 = n, \; x \; \frac{V_2}{V_1} = 1.00 \text{ mol } x \; \frac{11.2 \text{ L}}{22 \text{ 4 L}} - 0500 \text{ mol}$$

$$0.500 \text{ mol} = 3.01 \text{ x } 10^{23} \text{ molecules CO}$$

24. Plug in the numbers and solve:

$$R = \frac{PV}{nT} - \frac{(1.00 \text{ atm})(22.4 \text{ L})}{(1.00 \text{ mol})(273 \text{ K})} = 0.0821 \text{ atm L mol}^{-1}\text{K}^{-1}$$

The result is accurate to three significant figures.

25. A straightforward application of the unit-factor method.

(a) Convert atmospheres into torr:

$$R = \frac{0.0821 \text{ atm L}}{\text{mol K}} \times \frac{760 \text{ torr}}{\text{atm}} = 62.4 \text{ torr L mol}^{-1} \text{K}^{-1}$$

(b) Convert atmospheres into pascals and liters into cubic meters:

$$R = \frac{0.08206 \text{ atm L}}{\text{mol K}} \times \frac{1.01325 \times 10^5 \text{ Pa}}{\text{atm}} \times \frac{1000 \text{ cm}^3}{L} \times \left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^3$$

$$= 8.31 \text{ Pa m}^3 \text{ mol}^{-1} \text{K}^{-1} \quad (3 \text{ sig fig})$$

Note that we carry along a fourth digit in *R* before rounding off at the end.

(c) Since the pascal is defined as 1 newton per square meter,

$$1 \text{ Pa} = 1 \text{ N m}^{-2}$$

the factor of pressure x volume in (b) has equivalent units of joules:

$$\text{Pa m}^3 = \text{N m}^{-2} \text{ m}^3 = \text{N m} = \text{J}$$

The numerical value of *R* is identical to that calculated just above:

$$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

26. Given *P, T,* and *n,* we use the ideal gas equation of state *(PV= nRT)* to solve for *V*:

$$V = \frac{nRT}{P}$$

(a) Make sure that the units of *P, V, T,* and *R* are consistent. Here we need to convert torr into atmospheres and degrees Celsius into kelvins:

$$P = 589.1 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.7751 \text{ atm}$$

$$T = (312.4 + 273.15) \text{ K} = 585.6 \text{ K}$$

$$n = 3.28 \text{ mol}$$

$$V = \frac{nRT}{P} = \frac{(3.28 \text{ mol})(0.08206 \text{ atm L mol}^{-1}\text{K}^{-1})(585.6 \text{ K})}{0.7751 \text{ atm}} = 203 \text{ L}$$

(b) The pressure of any ideal gas,

$$P_1 = \frac{nRT_1}{V_1}$$

remains the same if both temperature and volume are halved:

$$P_2 = \frac{nR(T_1/2)}{V_1/2} = \frac{nRT_1}{V_1} = P_1$$

27. Use the relationship

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (\text{fixed } n, V)$$

while remembering to convert temperatures from degrees Fahrenheit into kelvins:

	°F	°C	K
	↓	↓	↓
$P_1 = 1.00$ atm	$T_1 = 400°F = \frac{5}{9}(400 - 32)°C = (204.44 + 273.15)\ K = 477.6\ K$		
$P_2 = \ ?$	$T_2 = 800°F = \frac{5}{9}(800 - 32)°C = (426.67 + 273.15)\ K = 699.8\ K$		

With sufficient data in hand, we then solve for P_2:

$$P_2 = P_1 x \frac{T_2}{T_1} = 1.00\ \text{atm}\ x\frac{699.8\ K}{\mathbf{477.6\ K}} = 1.47\ \text{atm}$$

Pressure increases in direct proportion to the *absolute* temperature, not the Celsius temperature and not the Fahrenheit temperature. Measured in degrees Fahrenheit, T_2 is twice the value of T_1. Measured in kelvins, however-the only temperature scale that is relevant to these problems-the increase is only 47%.

28. Use the ideal gas law, $PV = nRT$.

(a) Given the pressure, volume, and temperature,

$$P = 2.944\ \text{atm} \qquad V = 12.56\ \text{L} \qquad T = 298.2\ K$$

we solve straightforwardly for *n:*

$$n = \frac{PV}{RT} = \frac{(2.944 \text{ atm})(12.56 \text{ L})}{(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(298.2 \text{ K})} = 1.511 \text{ mol}$$

(b) The temperature of any ideal gas,

$$T_1 = \frac{PV_1}{nR}$$

is halved if the volume is halved at constant pressure:

$$T_2 = \frac{P(V_1/2)}{nR} = \frac{1}{2}\frac{PV_1}{nR} = \frac{T_1}{2}$$

Exercises 29 through 32 deal with Dalton 's law of partial pressures, described on pages 368-369 of PoC. *See also Example 1 O-7, beginning on page R1 0. Il.*

29. Before N_2 is added, we know that the vessel contains 1 .OO mol O_2. The stated volume of 22.4 L happens to be the molar volume of any ideal gas at STP, as shown on page 367 of *PoC* and demonstrated further in Exercises 21 through 24.

Subsequent addition of 1 .OO mol N_2 therefore gives us a total of 2.00 mol gas particles at a temperature of 405 K,

$$n_{tot} = 2.00 \text{ mol} \qquad T = 405 \text{ K} \qquad V = 22.4 \text{ L}$$

and we have enough information to solve for the new pressure:

$$PV = n_{tot} RT$$

$$P = \frac{n_{tot} RT}{V} = \frac{(2.00 \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(405 \text{ K})}{22.4 \text{ L}} = 2.97 \text{ atm}$$

30. For a review of *limiting reactant,* see pages 69-71 in *PoC* and also Example 2-7 (beginning on page R2.15). Exercises 44 through 47 in Chapter 2 provide additional practice in determining stoichiometric limits.

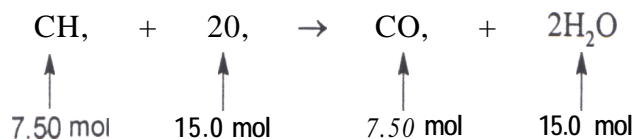(a) First, calculate the molar amounts of CH_4 and O_2:

$$160. \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.043 \text{ g CH}_4} = 9.97 \text{ mol CH}_4$$

$$480. \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{31.9988 \text{ g O}_2} = 15.0 \text{ mol O}_2$$

The available 15.0 moles of oxygen react completely with 7.50 moles of methane,

$$15.0 \text{ mol } O_2 \times \frac{1 \text{ mol } CH_4}{2 \text{ mol } O_2} = 7.50 \text{ mol } CH_4$$

producing 7.50 moles of carbon dioxide and 15.0 moles of water:

$$CH_4 \quad + \quad 2O_2 \quad \rightarrow \quad CO_2 \quad + \quad 2H_2O$$

$$7.50 \text{ mol} \qquad 15.0 \text{ mol} \qquad 7.50 \text{ mol} \qquad 15.0 \text{ mol}$$

A total of 2.47 mol CH_4 remains unreacted, left over from the 9.97 mol present at the start. All of the oxygen is consumed.

Oxygen, which reacts 2: 1 with methane, is therefore the limiting reactant. Methane is present in excess.

(b) See above: 7.50 mol CO_2 and 15.0 mol H_2O are produced in a stoichiometric reaction between 7.50 mol CH_4 and 15.0 mol O_2.

(c) Dalton's law of partial pressures allows us to treat the different molecules as generic particles. Each mole of particles-regardless of chemical identity-contributes equally to the total amount:

$$n_{tot} = n_{CH_4} + n_{CO_2} + n_{H_2O}$$

$$= 2.47 \text{ mol } + 7.50 \text{ mol } + 15.0 \text{ mol}$$

$$= 24.97 \text{ mol}$$

Given the volume and temperature,

$$v = 1.00 \text{ L} \qquad T = (125 + 273.15) \text{ K} = 398 \text{ K}$$

we then determine the collective pressure of the gaseous mixture:

$$P = \frac{n_{tot} RT}{v} = \frac{(24.97 \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(398 \text{ K})}{1.00 \text{ L}} = 816 \text{ atm}$$

Note that we carry along one extra digit in n_{tot} before rounding off finally to three significant figures.

31. Don't be fooled by the equal *gram* amounts. Calculate, instead, the total number of moles,

$$n_{tot} = n_{CO_2} + n_{H_2O} + n_{CH_4}$$

$$= 2.00 \text{ g c o,} \times \frac{1 \text{ mol CO,}}{44.010 \text{ g c o,}} + 2.00 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}}$$

$$+ 2.00 \text{ g CH,} \times \frac{1 \text{ mol CH,}}{16.043 \text{ g CH,}}$$

$$= 0.28113 \text{ mol}$$

and then use the ideal gas equation to establish the temperature:

$$P = 10.0 \text{ atm} \qquad v = 1.00 \text{ L} \qquad n_{tot} = 0.28 \ 113 \text{ mol (before round-off)}$$

$$T = \frac{PV}{n_{tot} R} = \frac{(10.0 \text{ atm})(1.00 \text{ L})}{(0.28 \ 113 \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})} = 433 \text{ K}$$

To avoid round-off error, we retain two nonsignificant digits in the intermediate value n_{tot}.

32. Another application of Dalton's law of partial pressures. For additional practice with mole fractions, see Exercises 25 through 28 in Chapter 9.

(a) From the known total pressure of 1.17 atm,

$$P_{tot} = P_{N_2} + P_{He} = 1.17 \text{ atm}$$

we determine the partial pressure of He and the mole fractions of both N_2 and He:

$$P_{He} = P_{tot} - P_{N_2} = 1.17 \text{ atm} - 1.00 \text{ atm} = 0.17 \text{ atm}$$

$$X_{N_2} = \frac{P_{N_2}}{P_{tot}} = \frac{1.00 \text{ atm}}{1.17 \text{ atm}} = 0.855 \ (0.8547 \text{ before round-off})$$

$$X_{He} = \frac{P_{He}}{P_{tot}} = 1 - X_{N_2} = 0.145 \quad (0.1453 \text{ before round-off})$$

(b) With values of P_{tot}, V, and T in hand,

$$P_{tot} = 1.17 \text{ atm} \quad V = 1.00 \text{ L} \quad T = 285 \text{ K}$$

we first calculate the total number of moles, n_{tot}, by solving the ideal gas equation:

$$P_{tot}V = n_{tot} RT$$

$$n_{tot} = \frac{P_{tot}V}{RT} = \frac{(1.17 \text{ atm})(1.00 \text{ L})}{(0.08206 \text{ atm L mol}^{-1} \text{K}^{-1})(285 \text{ K})} = 0.0500 \text{ mol}$$

The amount of each component then follows directly from the definition of mole fraction:

$$n_{N2} = X_{N_2} n_{tot} = 0.8547 \text{ x } 0.0500 \text{ mol} = 0.0427 \text{ mol N}_2$$

$$n_{He} = X_{He} n_{tot} = 0.1453 \text{ x } 0.0500 \text{ mol} = 0.0073 \text{ mol He}$$

The final results are significant through the fourth decimal place.

Calculations involving molar density and molar mass are described on page 367 of **PoC** *and demonstrated numerically in Examples 1 O-5 and I O-6 (beginning on page* **R1** *0.10).*

33. Given the pressure and temperature,

$$P = 2.50 \text{ atm} \qquad T = (-10.0 + 273.15) \text{ K} = 263.2 \text{ K}$$

we solve for the molar density $(p = n/V)$:

$$PV = nRT$$

$$\rho = \frac{n}{V} = \frac{P}{RT} = \frac{2.50 \text{ atm}}{(0.08206 \text{ atm L mol}^{-1}\text{K}^{-1})(263.2 \text{ K})} = 0.116 \text{ mol L}^{-1}$$

34. Let m_{tot} denote the total mass of Cl_2 gas (in grams), and let m denote its molar mass $(70.906 \text{ g mol}^{-1})$:

$$n = \frac{m_{tot}}{m} = \frac{PV}{RT}$$

Solving for m_{tot}, we have our answer:

$$m_{tot} = \frac{mPV}{RT} = \frac{(70.906 \text{ g Cl, mol}^{-1})\left(976 \text{ torr x}\frac{1 \text{ atm}}{760 \text{ torr}}\right)(3.00 \text{ L})}{(0.08206 \text{ atm L mol}^{-1} \text{K}^{-1})(48.6 + 273.15) \text{ K}} = 10.3 \text{ g Cl,}$$

35. We write the number of moles as

$$n = \frac{m_{\cdot tot}}{m} = \frac{PV}{RT}$$

where m_{tot} represents the total mass of the sample (in grams) and m is the molar mass (in grams per mole). We then rearrange the equation to isolate m:

$$m = \frac{m_{tot} RT}{PV} = \frac{(2.14 \text{ g})(0.08206 \text{ atm L mol}^{-1}\text{K}^{-1})(273 \text{ K})}{(1.00 \text{ atm})(1.50 \text{ L})} = 32.0 \text{ g mol}^{-1}$$

The diatomic gas, X_2, is oxygen: O_2, with a standard molar mass of 32.00 g mol^{-1}.

36. Use the same method as in the previous exercise to compute the molar mass:

$$m = \frac{m_{tot} RT}{PV} = \frac{(34.84 \text{ g})(0.08206 \text{ atm L mol}^{-1}\text{K}^{-1})(273 \text{ K})}{(1.00 \text{ atm})(17.7 \text{ L})} = 441 \text{ g mol}^{-1}$$

Next, determine the empirical formula from the elemental composition by mass. Assume 100 grams:

$$81.7 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g c}} = 6.80 \text{ mol C}$$

$$18.3 \text{ g H} \times \frac{1 \text{ mol H}}{1.00794 \text{ g H}} = 18.2 \text{ mol H} \quad (18.16 \text{ before round-off})$$

Reduced to smallest integers, the molar ratio

$$C_{6.80}H_{18\ 16} \rightarrow C_{1.00}H_{2.67} \rightarrow C_3H_8$$

yields an empirical formula of C_3H_8 and a formula weight of 44.1 g. The molecular formula is therefore C_3H_8, consistent with the molar mass calculated above.

We turn now to the kinetic theory of the ideal gas, covered in Section I O-3 of PoC. See Examples 1 O-8 through 1 0-11 for sample problems.

37. The total translational kinetic energy of an ideal gas (excluding vibrational, rotational, or any other degrees of freedom) is proportional only to temperature and amount:

$$E_k = \frac{3}{2} nRT$$

The value per mole is the same for each gas at a given temperature:

$$E_k(150 \text{ K}) = \frac{3}{2}nRT = \frac{3}{2}(1.00 \text{ mol})(8.3\,145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(150 \text{ K}) = 1.87 \text{ kJ}$$

$$E_k(300 \text{ K}) = \frac{3}{2}nRT = \frac{3}{2}(1.00 \text{ mol})(8.3\,145 \times 1\,0^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(300 \text{ K}) = 3.74 \text{ kJ}$$

$$E_k(450 \text{ K}) = \frac{3}{2}nRT = \frac{3}{2}(1.00 \text{ mol})(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(450 \text{ K}) = 5.61 \text{ kJ}$$

So long as we maintain that our gas is "ideal," we treat it as a collection of point particles with no distinctive chemical identity:

TOTAL TRANSLATIONAL KINETIC ENERGY (kJ mol^{-1})

	150K	300 K	450 K
(a) H_2	1.87	3.74	5.61
(b) He	1.87	3.74	5.61
(c) Ne	1.87	3.74	5.61
(d) Ar	1.87	3.74	5.61

See pages 369-376 in *PoC* and also Examples 10-8 and 10-9 (starting on page R1 0.12).

38. Use the same method as in the previous exercise, this time explicitly calculating the number of moles *(n)* corresponding to each mass in grams:

$$E_k = \frac{3}{2}nRT$$

Take, for example, a sample containing 1.008 g H_2:

$$E_k(150 \text{ K}) = \frac{3}{2}\left(1.008 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.016 \text{ g } H_2}\right)(8.3145 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1})(150 \text{ K})$$

$$= \$0.5000 \text{ mol})(8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(150 \text{ K})$$

$$= 0.935 \text{ kJ}$$

Values below are reported to three significant figures:

TOTAL TRANSLATIONAL KINETIC ENERGY (kJ)

	n (mol)	150 K	300 K	450 K
(a)	0.5000	0.935	1.87	2.81
(b)	1.000	1.87	3.74	5.61
(c)	2.000	3.74	7.48	11.2
(d)	3.000	5.61	11.2	16.8
(e)	4.000	7.48	15.0	22.4

39. Take a system of N particles, and express the number of moles as a fraction of Avogadro's number, N_0:

$$n = \frac{N}{N_0}$$

The translational kinetic energy for n moles

$$E_k = \frac{3}{2} nRT$$

then becomes

$$E_k = \frac{3}{2}\left(\frac{N}{N_0}\right)RT = \frac{3}{2} N\left(\frac{R}{N_0}\right)T = \frac{3}{2} N k_B T$$

by which we define the Boltzmann constant, k_B:

$$k_B = \frac{R}{N_0} = \frac{8.314510 \text{ J mol}^{-1} \text{ K}^{-1}}{6.0221367 \times 10^{23} \text{ mol}^{-1}} = 1.380658 \times 10^{-23} \text{ J K}^{-1}$$

The average kinetic energy *per particle*

$$\langle \varepsilon_k \rangle = \frac{E_k}{N} = \frac{3}{2}\frac{N k_B T}{N} - \frac{3}{-2} k_B T$$

is therefore an intensive property, independent of the size of the sample (see *PoC*, pages 7-8 and 468-469). Its value depends only on the temperature, not the number of particles:

$$\langle \varepsilon_k (150 \text{ K}) \rangle = \$1.38066 \sim 10^{-23} \text{ J K}^{-1}(150 \text{ K}) = 3.11 \times 10^{-21} \text{ J}$$

$$\langle \varepsilon_k (300 \text{ K}) \rangle = \frac{3}{2}(1.38066 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K}) = 6.21 \times 10^{-21} \text{ J}$$

$$\langle \varepsilon_k (450 \text{ K}) \rangle = \$1.38066 \times 10^{-23} \text{ J K}^{-1}(450 \text{ K}) = 9.32 \times 10^{-21} \text{ J}$$

These energies per particle, $\frac{3}{2}k_B T$, are all the same at a given temperature, regardless of the gram amounts involved:

AVERAGE TRANSLATIONAL KINETIC ENERGY PER PARTICLE (J)

	n (mol)	150K	300 K	450 K
(a)	0.5000	3.11×10^{-21}	6.21×10^{-21}	9.32×10^{-21}
(b)	1.000	3.11×10^{-21}	6.21×10^{-21}	9.32×10^{-21}
(c)	2.000	3.11×10^{-21}	6.21×10^{-21}	9.32×10^{-21}
(d)	3.000	3.11×10^{-21}	6.21×10^{-21}	9.32×10^{-21}
(e)	4.000	3.11×10^{-21}	6.21×10^{-21}	9.32×10^{-21}

A similar derivation is provided on pages 379-380 of *PoC*.

40. See pages 374-378 and Example 10-10 in *PoC* for a treatment of root-mean-square speed. Additional commentary is provided in the solution to Exercise 43.

(a) To compute v_{rms} for H_2, substitute the molar mass

$$m = 2.016 \text{ g mol}^{-1} = 0.002016 \text{ kg mol}^{-1}$$

into the defining equation:

$$v_{rms} = \sqrt{\frac{3RT}{m}}$$

Values at the three requested temperatures are calculated on the opposite page:

$$v_{rms}(150\ K) = \sqrt{\frac{3(8.3145\ kg\ m^2\ s^{-2}\ mol^{-1}\ K^{-1})(150\ K)}{0.002016\ kg\ mol^{-1}}} = 1.36 \times 10^3\ m\ s^{-1}$$

$$v_{rms}(300\ K) = \sqrt{\frac{3(8.3145\ kg\ m^2\ s^{-2}\ mol^{-1}\ K^{-1})(300\ K)}{0.002016\ kg\ mol^{-1}}} = 1.93 \times 10^3\ m\ s^{-1}$$

$$v_{rms}(450\ K) = \sqrt{\frac{3(8.3145\ kg\ m^2\ s^{-2}\ mol^{-1}\ K^{-1})(450\ K)}{0.002016\ kg\ mol^{-1}}} = 2.36 \times 10^3\ m\ s^{-1}$$

(b) The root-mean-square speed is proportional to $T^{1/2}$, the square root of the absolute temperature. **It** does not vary linearly with T.

41. Use the same general method as in Exercise 37, taking care to convert grams into moles. As an example, consider the calculation for 19.97 g Ar (one-half mole) at 150 K:

$$E_k = \frac{3}{2}nRT$$

$$E_k(150\ K) = \frac{3}{2}\left(19.97\ g\ Ar \times \frac{1\ mol\ Ar}{39.948\ g\ Ar}\right)(8.3145 \times 10^{-3}\ kJ\ mol^{-1}\ K^{-1})(150\ K)$$

$$= 0.935\ kJ$$

A full set of values is tabulated below. Note that the original mass in (c) should be 79.90 g:

TOTAL TRANSLATIONAL KINETIC ENERGY (kJ)

	n (mol)	150 K	300 K	450 K
(a)	0.500	0.935	1.87	2.81
(b)	1.000	1.87	3.74	5.61
(c)	2.000	3.74	7.48	11.2
(d)	3.000	5.61	11.2	16.8
(e)	4.000	7.48	15.0	22.4

The numbers are the same as for H_2 (Exercise 38), as they would be for the translational energy of any ideal gas in the same amount. Molecular mass does not enter into the expression that determines the kinetic energy:

$$E_k = \frac{3}{2}nRT$$

Realize, though, that the *total* energy of Hz-inclusive of rotational and vibrational

degrees of freedom absent in monatomic systems-is indeed different from the total energy of argon, but the translational contribution is identical for both gases.

42. The average translational kinetic energy per particle depends only on temperature:

$$\langle \varepsilon_k \rangle = \frac{3}{2} k_B T$$

Use the same procedure as in Exercise 39 to obtain the results in the following table:

AVERAGE TRANSLATIONAL KINETIC ENERGY PER PARTICLE (J)

	n (mol)	150K	300 K	450 K
(a)	0.500	3.11 x 10^{-21}	6.21 x 10^{-21}	9.32 x 10^{-21}
(b)	1 .000	3.11 x 10^{-21}	6.21 x 10^{-21}	9.32 x 10^{-21}
(c)	2.000	3.11 x 10^{-21}	6.21 x 10^{-21}	9.32 x 10^{-21}
(d)	3.000	3.11 x 10^{-21}	6.21 x 10^{-21}	9.32 x 10^{-21}
(e)	4.000	3.11 x 10^{-21}	6.21 x 10^{-21}	9.32 x 10^{-21}

The values, independent of molecular mass, are the same as for H_2. See also Exercise 41.

43. The formula for root-mean-square speed is

$$v_{rms} = \sqrt{\frac{3RT}{m}}$$

where m is the molar mass (in kg mol^{-1}), R is the universal gas constant (in J mol^{-1} K^{-1}), and T is the absolute temperature (in K).

Recalling that a joule is a unit of work (force x distance),

$$1 \text{ J} = 1 \text{ N m} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

we quickly verify that v_{rms} has the expected units of m s^{-1}:

$$v_{rms} \propto \sqrt{\frac{RT}{m}} \sim \sqrt{\frac{\left(\text{J mol}^{-1} \text{ K}^{-1}\right) \text{K}}{\text{kg mol}^{-1}}} \sim \sqrt{\frac{\text{kg m}^2 \text{ s}^{-2}}{\text{kg}}} \sim \sqrt{\text{m}^2 \text{ s}^{-2}} \sim \text{m s}^{-1}$$

Be careful to express the molar mass m in kilograms, thereby matching the base SI unit implicit in R.

See pages 374-378 in *PoC, as* well as Example 10- 10 (beginning on page R1 0.13).

(a) To calculate v_{rms} for Ar, substitute the molar mass

$$m = 39.948 \text{ g mol}^{-1} = 0.039948 \text{ kg mol}^{-1}$$

into the defining equation:

$$v_{rms} = \sqrt{\frac{3RT}{m}}$$

Values at the three requested temperatures are calculated below:

$$v_{rms}(150 \text{ K}) = \sqrt[3]{\frac{(8.3\,145 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1})(150 \text{ K})}{0.039948 \text{ kg mol}^{-1}}} = 3.06 \times 10^2 \text{ m s}^{-1}$$

$$v_{rms}(300 \text{ K}) = \sqrt{\frac{3(8.3\,145 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{0.039948 \text{ kg mol}^{-1}}} = 4.33 \times 10^2 \text{ m s}^{-1}$$

$$v_{rms}(450 \text{ K}) = \sqrt{\frac{3(8.3145 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1})(450 \text{ K})}{0.039948 \text{ kg mol}^{-1}}} = 5.30 \times 10^2 \text{ m s}^{-1}$$

(b) Argon atoms, more massive than hydrogen molecules, move slower at a given temperature-although the average kinetic energy is identical for both. The root-mean-square speeds differ in inverse proportion to the square roots of the molecular masses:

$$\frac{v_{rms}(\text{Ar})}{v_{rms}(\text{H}_2)} = \sqrt{\frac{m_{H2}}{m_{Ar}}} = \sqrt{\frac{2.016}{39.948}} = 0.225$$

Endowed with the same average energy at each temperature,

$$\langle \varepsilon_k \rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_B T$$

the two particles therefore develop different speeds. The one with a lower mass is able to translate more of its energy into velocity.

44. Translational kinetic energy is partitioned as $\frac{1}{2}nRT$ or, equivalently, $\frac{1}{2}Nk_B T$ in each of the three dimensions. Thus we expect the following relationship to govern a two-dimensional system:

$$E_{k,\,2D} = 2 \times \tfrac{1}{2}nRT = nRT = Nk_B T$$

(a) Two-dimensional translational energy is equal to RT per mole ($n = 1$):

$$E_{k, 2D}(150 \text{ K}) = (1.00 \text{ mol})(8.3 \text{ 145 x } 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(150 \text{ K}) = 1.25 \text{ kJ}$$

$$E_{k, 2D}(300 \text{ K}) = (1.00 \text{ mol})(8.3 \text{ 145 x } 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(300 \text{ K}) = 2.49 \text{ kJ}$$

$$E_{k, 2D}(450 \text{ K}) = (1.00 \text{ mol})(8.3 \text{ 145 x } 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(450 \text{ K}) = 3.74 \text{ kJ}$$

(b) Two-dimensional translational energy is equal to $k_B T$ per atom (N $= 1$):

$$\langle \varepsilon_{k, 2D}(150 \text{ K}) \rangle = (1.38066 \text{ x } 10^{-23} \text{ J K}^{-1})(150 \text{ K}) = 2.07 \text{ x } 10^{-21} \text{ J}$$

$$\langle \varepsilon_{k, 2D}(300 \text{ K}) \rangle = (1.38066 \text{ x } 10^{-23} \text{ J K}^{-1})(300 \text{ K}) = 4.14 \text{ x } 10^{-21} \text{ J}$$

$$\langle \varepsilon_{k, 2D}(450 \text{ K}) \rangle = (1.38066 \text{ x } 10^{-23} \text{ J K}^{-1})(450 \text{ K}) = 6.21 \text{ x } 10^{-21} \text{ J}$$

(c) With only two degrees of translational freedom, we have a different kinetic energy and consequently a different equation for root-mean-square speed:

$$E_{k, 2D} = RT = \frac{1}{2} m \langle v_{2D}^2 \rangle \qquad \text{(per mole)}$$

$$v_{\text{rms, 2D}} = \sqrt{\langle v_{2D}^2 \rangle} = \sqrt{\frac{2RT}{m}}$$

The two-dimensional values are smaller relative to the three-dimensional values by a factor of $(2/3)^{1/2}$:

T (K)	$v_{\text{rms, 2D}}$ (m s^{-1})
150	2.50 x 10^2
300	3.53 x 10^2
450	4.33 x 10^2

See Exercise 43.

(d) All values differ to the extent that the total translational energy per mole is RT, not $\frac{3}{2}RT$.

45. Use the expression for root-mean-square **speed,**

$$v_{rms} = \sqrt{\frac{3RT}{m}}$$

to evaluate each set of conditions. Note that v_{rms} depends only on the temperature and molar mass.

(a) Both systems have the same value of v_{rms}, since the same molecule is moving at the same temperature. The system at higher pressure contains *more* molecules in the same volume, but the average speed per particle is unaffected.

(b) Same reasoning as in (a). A change in volume has no effect on v_{rms}, provided that the two temperatures are the same.

(c) Argon, less massive than xenon, has the higher root-mean-square speed at any given temperature.

(d) Krypton at 1000 K has a higher v_{rms} than carbon dioxide at 500 K, but only slightly:

$$\frac{v_{rms}(Kr)}{v_{rms}(CO_2)} = \sqrt{\frac{\dfrac{1000 \ K}{83.80 \ g \ mol^{-1}}}{\dfrac{500 \ K}{44.01 \ g \ mol^{-1}}}} = \frac{3.45}{3.37} = 1.02$$

The difference is approximately 2%.

As temperature goes up, the extra thermal energy allows the heavier Kr atom to move faster. Krypton at 952 K has the same root-mean-square speed as CO_2 at 500 K; krypton at 1000 K has a modest advantage, despite its higher mass.

46. Graham's law $(PoC,$ page 379) asserts that the effusion rate varies inversely with the square root of molecular mass:

$$\frac{Rate_,}{Rate_B} = \sqrt{\frac{m_B}{m_A}}$$

(a) $H_2,$ with half the mass of He, effuses approximately 40% faster:

$$\frac{Rate_{H_2}}{Rate_{He}} = \sqrt{\frac{m_{He}}{m_{H_2}}} \approx \sqrt{\frac{4}{2}} \approx 1.4$$

(b) CO_2 (44.010 g mol^{-1}) and C_3H_8 (44.097 g mol^{-1}) have nearly the same masses. Their rates of effusion differ only negligibly, by less than 0.1%.

(c) N_2 has a mass of $\approx$ 28. C_2H_6 has a mass of $\approx$ 30. N_2 effuses approximately 3.5% faster:

$$\frac{Rate_{N_2}}{Rate_{C_2H_6}} = \sqrt{\frac{m_{C_2H_6}}{m_{N_2}}} \approx \sqrt{\frac{30}{28}} \approx 1.035$$

(d) N_2 (28.013 g mol^{-1}) has virtually the same mass as CO (28.010 g mol^{-1}). Effusion rates for the two molecules are effectively identical, the difference amounting to little more than 1 part in 20,000.

(e) Slightly less massive than molecular nitrogen, HCN effuses at a rate approximately 1.8%   higher:

$$\frac{Rate_{HCN}}{Rate_{N_2}} = \sqrt{\frac{m_{N_2}}{m_{HCN}}} \approx \sqrt{\frac{28}{27}} \approx 1.018$$

47. See the discussion of thermal energy on pages 379-384 of *PoC*.

(a) Particles moving in three dimensions acquire translational thermal energy equal to $\frac{3}{2}RT$ per mole. Equating this quantity with the dissociation energy of H_2, we obtain a temperature of approximately 35,000 K:

$$\frac{3}{2}RT = 436 \text{ kJ mol}^{-1} \times \frac{1000 \text{ J}}{kJ} = 4.36 \times 10^5 \text{ J mol}^{-1}$$

$$T = \frac{2(4.36 \times 10^5 \text{ J mol}^{-1})}{3(8.3145 \text{ J mol}^{-1} K^{-1})} = 3.50 \times 10^4 \text{ K}$$

Another acceptable estimate is to take *RT* as a rough measure of molar thermal energy, in recognition of its appearance in the Boltzmann factor, $\exp(-E_k/RT)$. Doing so, we obtain a corresponding temperature of over 50,000 K:

$$T = \frac{4.36 \times 10^5 \text{ J mol}^{-1}}{8.3 \text{ } 145 \text{ J mol}^{-1} K^{-1}} = 5.24 \times 10^4 \text{ K}$$

Hot, either way.

(b) H_2 is highly unlikely to dissociate thermally at 273 K, where $\frac{3}{2}RT$ (equal to 3.40 kJ mol^{-1}) is over two orders of magnitude less than the bond energy.

48. The Maxwell-Boltzmann distribution for a particle with mass *m,*

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

or, equivalently, for a particle with molar mass $\mathcal{m},$

$$F(v) = 4\pi \left(\frac{\mathcal{m}}{2\pi RT}\right)^{3/2} v^2 \exp\left(-\frac{\mathcal{m}v^2}{2RT}\right)$$

is discussed on pages 3 84-39 1 and R10.5 of *PoC*, as well as in Example 10- 11. Each value $F(v)$ Av gives the probability that a particle will have a speed between v and v + Av, where Av is infinitesimally small.

The peak of the distribution-the most probable speed, v_{MP}—occurs at

$$v_{MP} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{\mathcal{m}}}$$

whereas the root-mean-square speed occurs 22.5% higher:

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{\mathcal{m}}}$$

Root-mean-square speeds for He ($\mathcal{m} = 4.0026$ g mol^{-1}) are determined in the same way as in Exercise 43:

$$v_{rms}(50\ K) = \sqrt{\frac{3\left(8.3145\ kg\ m^2\ s^{-2}\ mol^{-1}\ K^{-1}\right)(50\ K)}{0.0040026\ kg\ mol^{-1}}} = 5.58 \times 10^2\ m\ s^{-1}$$

$$v_{rms}(300\ K) = \sqrt{\frac{3\left(8.3\ 145\ kg\ m^2\ s^{-2}\ mol^{-1}\ K^{-1}\right)(300\ K)}{0.0040026\ kg\ mol^{-1}}} = 1\ 37 \times 10^3\ m\ s^{-1}$$

$$v_{rms}(600\ K) = \sqrt{\frac{3\left(8.3145\ kg\ m^2\ s^{-2}\ mol^{-1}\ K^{-1}\right)(600\ K)}{0.0040026\ kg\ mol^{-1}}} = 1.93 \times 10^3\ m\ s^{-1}$$

See Figure 10.1 for plots of the distribution at these three temperatures.
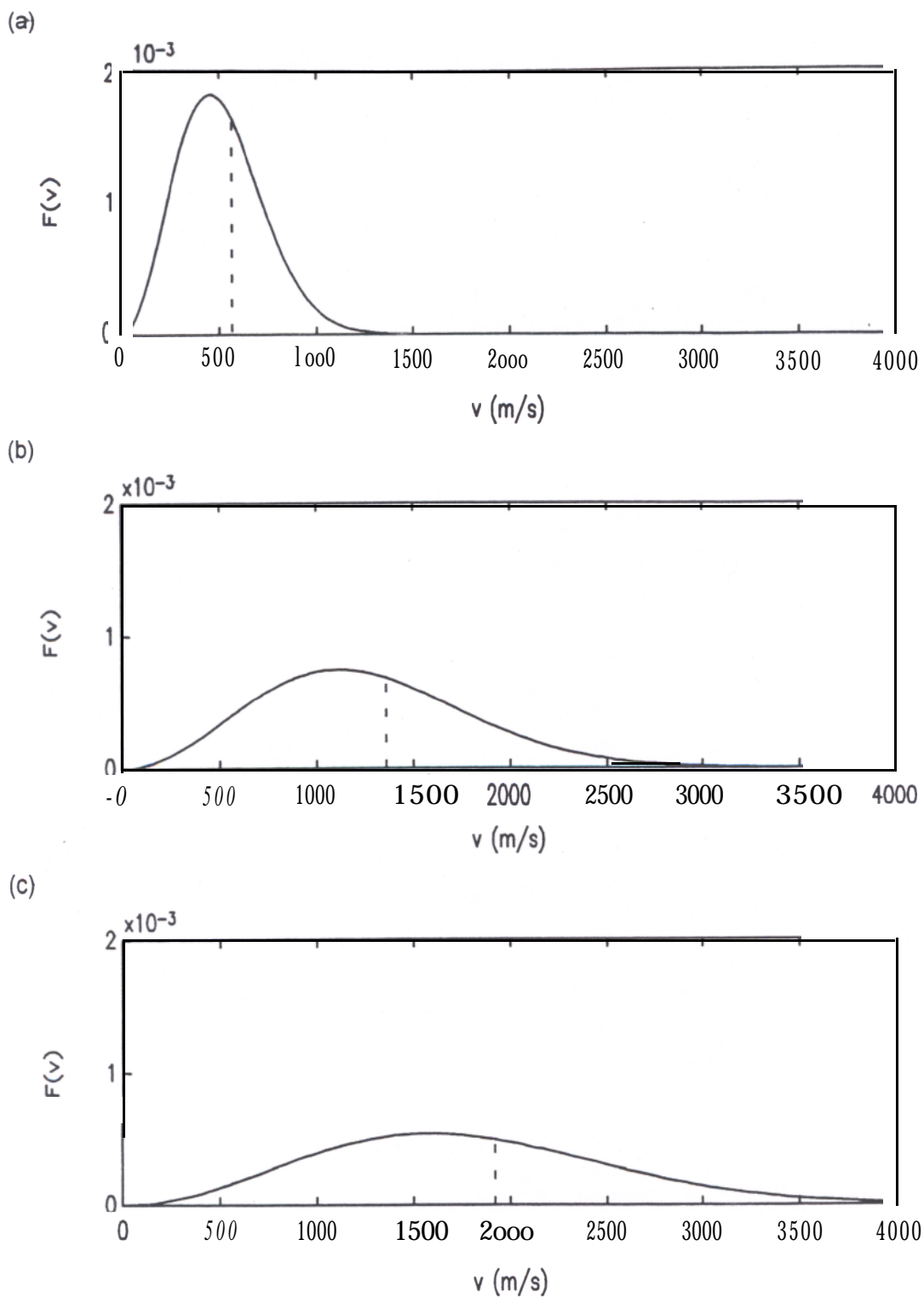
(a)

(b)

(c)

FIGURE 10.1   Normalized   Maxwell-Boltzmann   distribution   for   helium   at   three   temperatures.   The
root-mean-square speed is indicated by a dashed vertical line in each panel.   (a) 50 K. (b) 300 K.
(c) 600 K.

49. Use the formula

$$v_{rms} = \sqrt{\frac{3RT}{m}}$$

to calculate the root-mean-square speed at the stated temperature, as worked out explicitly in Exercise 48. Then study Figure 10.1 to determine where the given values of F(v) lie relative to the reference value, $F(v_{rms})$.

(a) The root-mean-square speed for helium is approximately 560 m s^{-1} at 50 K:

$$v_{rms} = \sqrt{\frac{3RT}{m}} = \sqrt{\frac{3(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(50 \text{ K})}{4.0026 \times 10^{-3} \text{ kg mol}^{-1}}} = 558 \text{ m s}^{-1}$$

A speed of 500 m s^{-1} is roughly 10% less than v_{rms}. The corresponding value of F falls near the peak of the Maxwell-Boltzmann distribution, and therefore 500 m s^{-1} is a more probable speed than 50 m s^{-1}—which lies close to the origin. See Figure 10.1(a).

(b) Both the distribution and root-mean-square speed are the same as in part (a). A speed of 1000 m s^{-1} falls far to the right of v_{rms} (equal to 560 m s^{-1}), making the lower value (v = 500 m s^{-1}) more probable. The curve decreases monotonically for speeds greater than v_{rms}.

(c) Directly proportional to $\sqrt{T}$, the root-mean-square speed increases from approximately 560 m s^{-1} to 1370 m s^{-1} when the temperature goes from 50 K to 300 K. A speed of 1500 m s^{-1}, about 10% greater than v_{rms}, is more likely than a speed of 50 m s^{-1} (which falls far to the left of the peak in Figure lo-lb).

(d) The root-mean-square speed is the same as in part (c), and the reasoning is the same as in part (b): A speed of 1500 m s^{-1} is only 10% greater than v_{rms} and hence more probable than a speed of 2000 m s^{-1}.

(e) With v_{rms} increasing to 1930 m s^{-1} at 600 K, a speed of 2000 m s^{-1} is closer to the root-mean-square value (and consequently more likely to occur) than a speed of 1000 m s^{-1}. See Figure 10.1 (c).

(f) Similar to (b) and (d): The lower speed, 2000 m s^{-1}, is closer to v_{rms} and thus more probable than a speed of 4000 m s^{-1}.

50. Start with the Maxwell-Boltzmann distribution,

$$F(v) = Kv^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$$

where K is a proportionality constant and m is the mass of a single particle. The ratio of $F(v)$ at two speeds is therefore

$$\frac{F(v_2)}{W_{,)}} = \left(\frac{v_2}{v_1}\right)^2 \exp\left[-\frac{m}{2k_B T}\cdot\left(v_2^2 - v_1^2\right)\right]$$

Its value is independent of K.

Next, noting that m/k_B is the same ratio as m/R, we equivalently write

$$\frac{F(v_2)}{F(v_1)} = \left(\frac{v_2}{v_1}\right)^2 \exp\left[-\frac{m}{2RT}\left(v_2^2 - v_1^2\right)\right]$$

and express the given speeds in terms of v_{rms} and a scaling factor x:

$$v_1 = v_{rms}$$

$$v_2 = xv_{rms}$$

Insertion of these general forms into the equation for $F(v_2)/F(v_1)$ yields

$$\frac{F(v_2)}{F(v_1)} \equiv \left(\frac{xv_{rms}}{v_{rms}}\right)^2 \exp\left[-\frac{mv_{rms}^2}{2RT}\left(x^2 - 1\right)\right]$$

By definition, however, we know that

$$v_{rms}^2 = \frac{3RT}{m}$$

and hence

$$\frac{F(v_2)}{F(v_1)} = x^2 \exp\left[-\frac{3}{2}\left(x^2 - 1\right)\right]$$

This is the expression we now evaluate by substituting the dimensionless variable x:

$$x = \frac{v_2}{v_{rms}}$$

(a) For $x = 0.1$:

$$\frac{F(v_2)}{F(v_1)} = 0.1^2 \exp\left[-\frac{3}{2}\left(0.1^2 - 1\right)\right] = 0.0441 \approx \frac{44{,}100}{1{,}000{,}000}$$

(b) For $x = 0.9$:

$$\frac{F(v_2)}{F(v_1)} = 0.9^2 \exp\left[-\frac{3}{2}\left(0.9^2 - 1\right)\right] = 1.077 \approx \frac{1{,}077{,}000}{1{,}000{,}000}$$

(c) For $x = 2$:

$$\frac{F(v_2)}{F(v_1)} = 2^2 \exp\left[-\frac{3}{2}\left(2^2 - 1\right)\right] = 0.0444 \approx \frac{44{,}400}{1{,}000{,}000}$$

(d) For $x = 3$:

$$\frac{F(v_2)}{F(v_1)} = 3^2 \exp\left[-\frac{3}{2}\left(3^2 - 1\right)\right] = 0.000055 \approx \frac{55}{1{,}000{,}000}$$

Note that the ratios are independent of m and T.