

# 21

## The Kinetic Theory of Gases

### CHAPTER OUTLINE

- 21.1 Molecular Model of an Ideal Gas
- 21.2 Molar Specific Heat of an Ideal Gas
- 21.3 Adiabatic Processes for an Ideal Gas
- 21.4 The Equipartition of Energy
- 21.5 Distribution of Molecular Speeds

### ANSWERS TO QUESTIONS

**Q21.1** The molecules of all different kinds collide with the walls of the container, so molecules of all different kinds exert partial pressures that contribute to the total pressure. The molecules can be so small that they collide with one another relatively rarely and each kind exerts partial pressure as if the other kinds of molecules were absent. If the molecules collide with one another often, the collisions exactly conserve momentum and so do not affect the net force on the walls.

**Q21.2** The helium must have the higher rms speed. According to Equation (21.4), the gas with the smaller mass per atom must have the higher average speed-squared and thus the higher rms speed.

**Q21.3** The alcohol evaporates, absorbing energy from the skin to lower the skin temperature.

- \*Q21.4**
- (i) Statements a, d, and e are correct statements that describe the temperature increase of a gas.
  - (ii) Statement b is true if the molecules have any size at all, but molecular collisions with other molecules have nothing to do with temperature.
  - (iii) Statement c is incorrect. The molecular collisions are perfectly elastic. Temperature is determined by how fast molecules are moving through space, not by anything going on inside a molecule.

- \*Q21.5**
- (i) b. The volume of the balloon will decrease.
  - (ii) c. The pressure inside the balloon is nearly equal to the constant exterior atmospheric pressure. Snap the mouth of the balloon over an absolute pressure gauge to demonstrate this fact. Then from  $PV = nRT$ , volume must decrease in proportion to the absolute temperature. Call the process isobaric contraction.

**\*Q21.6** At 200 K,  $\frac{1}{2} m_0 v_{\text{rms0}}^2 = \frac{3}{2} k_B T_0$ . At the higher temperature,  $\frac{1}{2} m_0 (2v_{\text{rms0}})^2 = \frac{3}{2} k_B T$   
Then  $T = 4T_0 = 4(200 \text{ K}) = 800 \text{ K}$ . Answer (d).

**\*Q21.7** Answer  $c > a > b > e > d$ . The average vector velocity is zero in a sample macroscopically at rest. As adjacent equations in the text note, the asymmetric distribution of molecular speeds makes the average speed greater than the most probable speed, and the rms speed greater still. The most probable speed is  $(2RT/M)^{1/2}$  and the speed of sound is  $(\gamma RT/M)^{1/2}$ , necessarily smaller. Sound represents an organized disturbance superposed on the disorganized thermal motion of molecules, and moving at a lower speed.

- \*Q21.8** Answer (b). The two samples have the same temperature and molecular mass, and so the same rms molecular speed. These are all intrinsic quantities. The volume, number of moles, and sample mass are extrinsic quantities that vary independently, depending on the sample size.
- Q21.9** The dry air is more dense. Since the air and the water vapor are at the same temperature, they have the same kinetic energy per molecule. For a controlled experiment, the humid and dry air are at the same pressure, so the number of molecules per unit volume must be the same for both. The water molecule has a smaller molecular mass (18.0 u) than any of the gases that make up the air, so the humid air must have the smaller mass per unit volume.
- Q21.10** Suppose the balloon rises into air uniform in temperature. The air cannot be uniform in pressure because the lower layers support the weight of all the air above them. The rubber in a typical balloon is easy to stretch and stretches or contracts until interior and exterior pressures are nearly equal. So as the balloon rises it expands. This is an isothermal expansion, with  $P$  decreasing as  $V$  increases by the same factor in  $PV = nRT$ . If the rubber wall is very strong it will eventually contain the helium at higher pressure than the air outside but at the same density, so that the balloon will stop rising. More likely, the rubber will stretch and break, releasing the helium to keep rising and “boil out” of the Earth’s atmosphere.
- Q21.11** A diatomic gas has more degrees of freedom—those of molecular vibration and rotation—than a monatomic gas. The energy content per mole is proportional to the number of degrees of freedom.
- \*Q21.12** (i) Answer (b). Average molecular kinetic energy increases by a factor of 3.  
 (ii) Answer (c). The rms speed increases by a factor of  $\sqrt{3}$ .  
 (iii) Answer (c). Average momentum change increases by  $\sqrt{3}$ .  
 (iv) Answer (c). Rate of collisions increases by a factor of  $\sqrt{3}$  since the mean free path remains unchanged.  
 (v) Answer (b). Pressure increases by a factor of 3. This is the product of the answers to iii and iv.
- Q21.13** As a parcel of air is pushed upward, it moves into a region of lower pressure, so it expands and does work on its surroundings. Its fund of internal energy drops, and so does its temperature. As mentioned in the question, the low thermal conductivity of air means that very little energy will be conducted by heat into the now-cool parcel from the denser but warmer air below it.
- \*Q21.14** Answer (a), temperature 900 K. The area under the curve represents the number of molecules in the sample, which must be 100 000 as labeled. With a molecular mass larger than that of nitrogen by a factor of 3, and the same speed distribution, krypton will have  $(1/2)m_0v^2 = (3/2)k_B T$  average molecular kinetic energy larger by a factor of 3. Then its temperature must be higher by a factor of 3 than that of the sample of nitrogen at 300 K.

## SOLUTIONS TO PROBLEMS

## Section 21.1 Molecular Model of an Ideal Gas

**P21.1** Use  $1 \text{ u} = 1.66 \times 10^{-24} \text{ g}$

$$(a) \quad \text{For He, } m_0 = 4.00 \text{ u} \left( \frac{1.66 \times 10^{-24} \text{ g}}{1 \text{ u}} \right) = \boxed{6.64 \times 10^{-24} \text{ g}}$$

$$(b) \quad \text{For Fe, } m_0 = 55.9 \text{ u} \left( \frac{1.66 \times 10^{-24} \text{ g}}{1 \text{ u}} \right) = \boxed{9.29 \times 10^{-23} \text{ g}}$$

$$(c) \quad \text{For Pb, } m_0 = 207 \text{ u} \left( \frac{1.66 \times 10^{-24} \text{ g}}{1 \text{ u}} \right) = \boxed{3.44 \times 10^{-22} \text{ g}}$$

**\*P21.2** Because each mole of a chemical compound contains Avogadro's number of molecules, the number of molecules in a sample is  $N_A$  times the number of moles, as described by  $N = nN_A$ , and the molar mass is  $N_A$  times the molecular mass, as described by  $M = m_0N_A$ . The definition of the molar mass implies that the sample mass is the number of moles times the molar mass, as described by  $m = nM$ . Then the sample mass must also be the number of molecules times the molecular mass, according to  $m = nM = nN_A m_0 = Nm_0$ . The equations are true for chemical compounds in solid, liquid, and gaseous phases—this includes elements. We apply the equations also to air by interpreting  $M$  as the mass of Avogadro's number of the various molecules in the mixture.

$$\textbf{P21.3} \quad \bar{F} = Nm \frac{\Delta v}{\Delta t} = 500(5.00 \times 10^{-3} \text{ kg}) \frac{[8.00 \sin 45.0^\circ - (-8.00 \sin 45.0^\circ)] \text{ m/s}}{30.0 \text{ s}} = \boxed{0.943 \text{ N}}$$

$$P = \frac{\bar{F}}{A} = 1.57 \text{ N/m}^2 = \boxed{1.57 \text{ Pa}}$$

$$\textbf{P21.4} \quad \bar{F} = Nm_0 \frac{\Delta v}{\Delta t} = \frac{(5.00 \times 10^{23})[(4.68 \times 10^{-26} \text{ kg})2(300 \text{ m/s})]}{1.00 \text{ s}} = 14.0 \text{ N and}$$

$$P = \frac{\bar{F}}{A} = \frac{14.0 \text{ N}}{8.00 \times 10^{-4} \text{ m}^2} = \boxed{17.6 \text{ kPa}}$$

$$\textbf{*P21.5} \quad PV = \left( \frac{N}{N_A} \right) RT \text{ and } N = \frac{PVN_A}{RT} \text{ so that}$$

$$N = \frac{(1.00 \times 10^{-10})(133)(1.00)(6.02 \times 10^{23})}{(8.314)(300)} = \boxed{3.21 \times 10^{12} \text{ molecules}}$$

**P21.6** Use the equation describing the kinetic-theory account for pressure:  $P = \frac{2N}{3V} \left( \frac{m_0 v^2}{2} \right)$ . Then

$$K_{\text{av}} = \frac{m_0 v^2}{2} = \frac{3PV}{2N} \text{ where } N = nN_A = 2N_A$$

$$K_{\text{av}} = \frac{3PV}{2(2N_A)} = \frac{3(8.00 \text{ atm})(1.013 \times 10^5 \text{ Pa/atm})(5.00 \times 10^{-3} \text{ m}^3)}{2(2 \text{ mol})(6.02 \times 10^{23} \text{ molecules/mol})}$$

$$K_{\text{av}} = \boxed{5.05 \times 10^{-21} \text{ J/molecule}}$$

**P21.7**  $P = \frac{2}{3} \frac{N}{V} (\overline{KE})$  from the kinetic-theory account for pressure.

$$N = \frac{3}{2} \frac{PV}{(\overline{KE})} = \frac{3}{2} \frac{(1.20 \times 10^5)(4.00 \times 10^{-3})}{(3.60 \times 10^{-22})} = 2.00 \times 10^{24} \text{ molecules}$$

$$n = \frac{N}{N_A} = \frac{2.00 \times 10^{24} \text{ molecules}}{6.02 \times 10^{23} \text{ molecules/mol}} = \boxed{3.32 \text{ mol}}$$

**P21.8** (a)  $PV = nRT = \frac{Nm_0 v^2}{3}$

The total translational kinetic energy is  $\frac{Nm_0 v^2}{2} = E_{\text{trans}}$ :

$$E_{\text{trans}} = \frac{3}{2} PV = \frac{3}{2} (3.00 \times 1.013 \times 10^5)(5.00 \times 10^{-3}) = \boxed{2.28 \text{ kJ}}$$

(b)  $\frac{m_0 v^2}{2} = \frac{3k_B T}{2} = \frac{3RT}{2N_A} = \frac{3(8.314)(300)}{2(6.02 \times 10^{23})} = \boxed{6.21 \times 10^{-21} \text{ J}}$

**P21.9** (a)  $PV = Nk_B T$ :  $N = \frac{PV}{k_B T} = \frac{1.013 \times 10^5 \text{ Pa} \left[ \frac{4}{3} \pi (0.150 \text{ m})^3 \right]}{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})} = \boxed{3.54 \times 10^{23} \text{ atoms}}$

(b)  $\bar{K} = \frac{3}{2} k_B T = \frac{3}{2} (1.38 \times 10^{-23})(293) \text{ J} = \boxed{6.07 \times 10^{-21} \text{ J}}$

(c) For helium, the atomic mass is  $m_0 = \frac{4.00 \text{ g/mol}}{6.02 \times 10^{23} \text{ molecules/mol}} = 6.64 \times 10^{-24} \text{ g/molecule}$

$$m_0 = 6.64 \times 10^{-27} \text{ kg/molecule}$$

$$\frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T: \quad \therefore v_{\text{rms}} = \sqrt{\frac{3k_B T}{m_0}} = \boxed{1.35 \text{ km/s}}$$

**P21.10** (a)  $1 \text{ Pa} = (1 \text{ Pa}) \left( \frac{1 \text{ N/m}^2}{1 \text{ Pa}} \right) \left( \frac{1 \text{ J}}{1 \text{ N} \cdot \text{m}} \right) = \boxed{1 \text{ J/m}^3}$

(b) For a monatomic ideal gas,  $E_{\text{int}} = \frac{3}{2} nRT$

For any ideal gas, the energy of molecular translation is the same,  $E_{\text{trans}} = \frac{3}{2} nRT = \frac{3}{2} PV$

Thus, the energy per volume is  $\frac{E_{\text{trans}}}{V} = \boxed{\frac{3}{2} P}$

**P21.11** (a)  $\bar{K} = \frac{3}{2} k_B T = \frac{3}{2} (1.38 \times 10^{-23} \text{ J/K})(423 \text{ K}) = \boxed{8.76 \times 10^{-21} \text{ J}}$

(b)  $\bar{K} = \frac{1}{2} m_0 v_{rms}^2 = 8.76 \times 10^{-21} \text{ J}$

so 
$$v_{rms} = \sqrt{\frac{1.75 \times 10^{-20} \text{ J}}{m}} \quad (1)$$

For helium, 
$$m_0 = \frac{4.00 \text{ g/mol}}{6.02 \times 10^{23} \text{ molecules/mol}} = 6.64 \times 10^{-24} \text{ g/molecule}$$

$$m_0 = 6.64 \times 10^{-27} \text{ kg/molecule}$$

Similarly for argon, 
$$m_0 = \frac{39.9 \text{ g/mol}}{6.02 \times 10^{23} \text{ molecules/mol}} = 6.63 \times 10^{-23} \text{ g/molecule}$$

$$m_0 = 6.63 \times 10^{-26} \text{ kg/molecule}$$

Substituting in (1) above, we find for helium, 
$$v_{rms} = 1.62 \text{ km/s}$$

and for argon, 
$$v_{rms} = 514 \text{ m/s}$$

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## Section 21.2 Molar Specific Heat of an Ideal Gas

**P21.12**  $n = 1.00 \text{ mol}$ ,  $T_i = 300 \text{ K}$

(b) Since  $V = \text{constant}$ ,  $W = \boxed{0}$

(a)  $\Delta E_{\text{int}} = Q + W = 209 \text{ J} + 0 = \boxed{209 \text{ J}}$

(c)  $\Delta E_{\text{int}} = nC_V \Delta T = n \left( \frac{3}{2} R \right) \Delta T$

so 
$$\Delta T = \frac{2\Delta E_{\text{int}}}{3nR} = \frac{2(209 \text{ J})}{3(1.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})} = 16.8 \text{ K}$$

$$T = T_i + \Delta T = 300 \text{ K} + 16.8 \text{ K} = \boxed{317 \text{ K}}$$

**P21.13** We use the tabulated values for  $C_p$  and  $C_v$

(a)  $Q = nC_p \Delta T = 1.00 \text{ mol}(28.8 \text{ J/mol} \cdot \text{K})(420 - 300) \text{ K} = \boxed{3.46 \text{ kJ}}$

(b)  $\Delta E_{\text{int}} = nC_v \Delta T = 1.00 \text{ mol}(20.4 \text{ J/mol} \cdot \text{K})(120 \text{ K}) = \boxed{2.45 \text{ kJ}}$

(c)  $W = -Q + \Delta E_{\text{int}} = -3.46 \text{ kJ} + 2.45 \text{ kJ} = \boxed{-1.01 \text{ kJ}}$

- P21.14** (a) Consider warming it at constant pressure. Oxygen and nitrogen are diatomic, so  $C_p = \frac{7R}{2}$

$$Q = nC_p\Delta T = \frac{7}{2}nR\Delta T = \frac{7}{2}\left(\frac{PV}{T}\right)\Delta T$$

$$Q = \frac{7}{2} \frac{(1.013 \times 10^5 \text{ N/m}^2)(100 \text{ m}^3)}{300 \text{ K}} (1.00 \text{ K}) = \boxed{118 \text{ kJ}}$$

- (b)  $U_g = mgy$

$$m = \frac{U_g}{gy} = \frac{1.18 \times 10^5 \text{ J}}{(9.80 \text{ m/s}^2) 2.00 \text{ m}} = \boxed{6.03 \times 10^3 \text{ kg}}$$

- P21.15** Consider  $800 \text{ cm}^3$  of (flavored) water at  $90.0^\circ\text{C}$  mixing with  $200 \text{ cm}^3$  of diatomic ideal gas at  $20.0^\circ\text{C}$ :

$$Q_{\text{cold}} = -Q_{\text{hot}}$$

or  $m_{\text{air}}c_{p,\text{air}}(T_f - T_{i,\text{air}}) = -m_w c_w (\Delta T)_w$

$$(\Delta T)_w = \frac{-m_{\text{air}}c_{p,\text{air}}(T_f - T_{i,\text{air}})}{m_w c_w} = \frac{-(\rho V)_{\text{air}} c_{p,\text{air}} (90.0^\circ\text{C} - 20.0^\circ\text{C})}{(\rho_w V_w) c_w}$$

where we have anticipated that the final temperature of the mixture will be close to  $90.0^\circ\text{C}$ .

The molar specific heat of air is  $C_{p,\text{air}} = \frac{7}{2}R$

So the specific heat per gram is  $c_{p,\text{air}} = \frac{7}{2}\left(\frac{R}{M}\right) = \frac{7}{2}(8.314 \text{ J/mol} \cdot \text{K})\left(\frac{1.00 \text{ mol}}{28.9 \text{ g}}\right) = 1.01 \text{ J/g} \cdot ^\circ\text{C}$

$$(\Delta T)_w = -\frac{[(1.20 \times 10^{-3} \text{ g/cm}^3)(200 \text{ cm}^3)](1.01 \text{ J/g} \cdot ^\circ\text{C})(70.0^\circ\text{C})}{[(1.00 \text{ g/cm}^3)(800 \text{ cm}^3)](4.186 \text{ J/kg} \cdot ^\circ\text{C})}$$

or  $(\Delta T)_w \approx -5.05 \times 10^{-3}^\circ\text{C}$

The change of temperature for the water is  $\boxed{\text{between } 10^{-3}^\circ\text{C} \text{ and } 10^{-2}^\circ\text{C}}$ .

- P21.16** (a)  $C_v = \frac{5}{2}R = \frac{5}{2}(8.314 \text{ J/mol} \cdot \text{K})\left(\frac{1.00 \text{ mol}}{0.0289 \text{ kg}}\right) = 719 \text{ J/kg} \cdot \text{K} = \boxed{0.719 \text{ kJ/kg} \cdot \text{K}}$

(b)  $m = Mn = M\left(\frac{PV}{RT}\right)$

$$m = (0.0289 \text{ kg/mol})\left(\frac{200 \times 10^3 \text{ Pa}(0.350 \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}\right) = \boxed{0.811 \text{ kg}}$$

- (c) We consider a constant volume process where no work is done.

$$Q = mC_v\Delta T = 0.811 \text{ kg}(0.719 \text{ kJ/kg} \cdot \text{K})(700 \text{ K} - 300 \text{ K}) = \boxed{233 \text{ kJ}}$$

- (d) We now consider a constant pressure process where the internal energy of the gas is increased and work is done.

$$Q = mC_p\Delta T = m(C_v + R)\Delta T = m\left(\frac{7R}{2}\right)\Delta T = m\left(\frac{7C_v}{5}\right)\Delta T$$

$$Q = 0.811 \text{ kg}\left[\frac{7}{5}(0.719 \text{ kJ/kg} \cdot \text{K})\right](400 \text{ K}) = \boxed{327 \text{ kJ}}$$

$$\text{P21.17} \quad Q = (nC_p \Delta T)_{\text{isobaric}} + (nC_v \Delta T)_{\text{isovolumetric}}$$

In the isobaric process,  $V$  doubles so  $T$  must double, to  $2T_i$ .

In the isovolumetric process,  $P$  triples so  $T$  changes from  $2T_i$  to  $6T_i$ .

$$Q = n \left( \frac{7}{2} R \right) (2T_i - T_i) + n \left( \frac{5}{2} R \right) (6T_i - 2T_i) = 13.5nRT_i = \boxed{13.5PV}$$

### Section 21.3 Adiabatic Processes for an Ideal Gas

$$\text{P21.18} \quad (a) \quad P_i V_i^\gamma = P_f V_f^\gamma \quad \text{so} \quad \frac{V_f}{V_i} = \left( \frac{P_i}{P_f} \right)^{1/\gamma} = \left( \frac{1.00}{20.0} \right)^{5/7} = \boxed{0.118}$$

$$(b) \quad \frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i} = \left( \frac{P_f}{P_i} \right) \left( \frac{V_f}{V_i} \right) = (20.0)(0.118) \quad \frac{T_f}{T_i} = \boxed{2.35}$$

$$(c) \quad \text{Since the process is adiabatic,} \quad \boxed{Q = 0}$$

$$\text{Since } \gamma = 1.40 = \frac{C_p}{C_v} = \frac{R + C_v}{C_v}, \quad C_v = \frac{5}{2} R \text{ and } \Delta T = 2.35T_i - T_i = 1.35T_i$$

$$\Delta E_{\text{int}} = nC_v \Delta T = (0.0160 \text{ mol}) \left( \frac{5}{2} \right) (8.314 \text{ J/mol} \cdot \text{K}) [1.35(300 \text{ K})] = \boxed{135 \text{ J}}$$

$$\text{and} \quad W = -Q + \Delta E_{\text{int}} = 0 + 135 \text{ J} = \boxed{+135 \text{ J}}.$$

$$\text{P21.19} \quad (a) \quad P_i V_i^\gamma = P_f V_f^\gamma$$

$$P_f = P_i \left( \frac{V_i}{V_f} \right)^\gamma = 5.00 \text{ atm} \left( \frac{12.0}{30.0} \right)^{1.40} = \boxed{1.39 \text{ atm}}$$

$$(b) \quad T_i = \frac{P_i V_i}{nR} = \frac{5.00 (1.013 \times 10^5 \text{ Pa}) (12.0 \times 10^{-3} \text{ m}^3)}{2.00 \text{ mol} (8.314 \text{ J/mol} \cdot \text{K})} = \boxed{366 \text{ K}}$$

$$T_f = \frac{P_f V_f}{nR} = \frac{1.39 (1.013 \times 10^5 \text{ Pa}) (30.0 \times 10^{-3} \text{ m}^3)}{2.00 \text{ mol} (8.314 \text{ J/mol} \cdot \text{K})} = \boxed{253 \text{ K}}$$

$$(c) \quad \text{The process is adiabatic:} \quad \boxed{Q = 0}$$

$$\gamma = 1.40 = \frac{C_p}{C_v} = \frac{R + C_v}{C_v}, \quad C_v = \frac{5}{2} R$$

$$\Delta E_{\text{int}} = nC_v \Delta T = 2.00 \text{ mol} \left( \frac{5}{2} (8.314 \text{ J/mol} \cdot \text{K}) \right) (253 \text{ K} - 366 \text{ K}) = \boxed{-4.66 \text{ kJ}}$$

$$W = \Delta E_{\text{int}} - Q = -4.66 \text{ kJ} - 0 = \boxed{-4.66 \text{ kJ}}$$

$$\mathbf{P21.20} \quad V_i = \pi \left( \frac{2.50 \times 10^{-2} \text{ m}}{2} \right)^2 0.500 \text{ m} = 2.45 \times 10^{-4} \text{ m}^3$$

The quantity of air we find from  $P_i V_i = nRT_i$

$$n = \frac{P_i V_i}{RT_i} = \frac{(1.013 \times 10^5 \text{ Pa})(2.45 \times 10^{-4} \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}$$

$$n = 9.97 \times 10^{-3} \text{ mol}$$

Adiabatic compression:  $P_f = 101.3 \text{ kPa} + 800 \text{ kPa} = 901.3 \text{ kPa}$

$$(a) \quad P_i V_i^\gamma = P_f V_f^\gamma$$

$$V_f = V_i \left( \frac{P_i}{P_f} \right)^{1/\gamma} = 2.45 \times 10^{-4} \text{ m}^3 \left( \frac{101.3}{901.3} \right)^{5/7}$$

$$V_f = \boxed{5.15 \times 10^{-5} \text{ m}^3}$$

$$(b) \quad P_f V_f = nRT_f$$

$$T_f = T_i \frac{P_f V_f}{P_i V_i} = T_i \frac{P_f}{P_i} \left( \frac{P_i}{P_f} \right)^{1/\gamma} = T_i \left( \frac{P_i}{P_f} \right)^{(1/\gamma - 1)}$$

$$T_f = 300 \text{ K} \left( \frac{101.3}{901.3} \right)^{(5/7 - 1)} = \boxed{560 \text{ K}}$$

$$(c) \quad \text{The work put into the gas in compressing it is } \Delta E_{\text{int}} = nC_V \Delta T$$

$$W = (9.97 \times 10^{-3} \text{ mol}) \frac{5}{2} (8.314 \text{ J/mol} \cdot \text{K})(560 - 300) \text{ K}$$

$$W = 53.9 \text{ J}$$

Now imagine this energy being shared with the inner wall as the gas is held at constant volume. The pump wall has outer diameter 25.0 mm + 2.00 mm + 2.00 mm = 29.0 mm, and volume

$$\left[ \pi (14.5 \times 10^{-3} \text{ m})^2 - \pi (12.5 \times 10^{-3} \text{ m})^2 \right] 4.00 \times 10^{-2} \text{ m} = 6.79 \times 10^{-6} \text{ m}^3 \text{ and mass}$$

$$\rho V = (7.86 \times 10^3 \text{ kg/m}^3)(6.79 \times 10^{-6} \text{ m}^3) = 53.3 \text{ g}$$

The overall warming process is described by

$$53.9 \text{ J} = nC_V \Delta T + mc \Delta T$$

$$53.9 \text{ J} = (9.97 \times 10^{-3} \text{ mol}) \frac{5}{2} (8.314 \text{ J/mol} \cdot \text{K})(T_f - 300 \text{ K})$$

$$+ (53.3 \times 10^{-3} \text{ kg})(448 \text{ J/kg} \cdot \text{K})(T_f - 300 \text{ K})$$

$$53.9 \text{ J} = (0.207 \text{ J/K} + 23.9 \text{ J/K})(T_f - 300 \text{ K})$$

$$T_f - 300 \text{ K} = \boxed{2.24 \text{ K}}$$

$$\mathbf{P21.21} \quad \frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\gamma - 1} = \left( \frac{1}{2} \right)^{0.400}$$

$$\text{If } T_i = 300 \text{ K, then } T_f = \boxed{227 \text{ K}}.$$



**P21.22** We suppose the air plus burnt gasoline behaves like a diatomic ideal gas. We find its final absolute pressure:

$$21.0 \text{ atm} (50.0 \text{ cm}^3)^{7/5} = P_f (400 \text{ cm}^3)^{7/5}$$

$$P_f = 21.0 \text{ atm} \left( \frac{1}{8} \right)^{7/5} = 1.14 \text{ atm}$$

Now  $Q = 0$

$$\text{and } W = \Delta E_{\text{int}} = nC_V(T_f - T_i)$$

$$\therefore W = \frac{5}{2} nRT_f - \frac{5}{2} nRT_i = \frac{5}{2} (P_f V_f - P_i V_i)$$

$$W = \frac{5}{2} [1.14 \text{ atm} (400 \text{ cm}^3) - 21.0 \text{ atm} (50.0 \text{ cm}^3)] \left( \frac{1.013 \times 10^5 \text{ N/m}^2}{1 \text{ atm}} \right) (10^{-6} \text{ m}^3/\text{cm}^3)$$

$$W = -150 \text{ J}$$

The output work is  $-W = +150 \text{ J}$

$$\text{The time for this stroke is } \frac{1}{4} \left( \frac{1 \text{ min}}{2500} \right) \left( \frac{60 \text{ s}}{1 \text{ min}} \right) = 6.00 \times 10^{-3} \text{ s}$$

$$\mathcal{P} = \frac{-W}{\Delta t} = \frac{150 \text{ J}}{6.00 \times 10^{-3} \text{ s}} = \boxed{25.0 \text{ kW}}$$

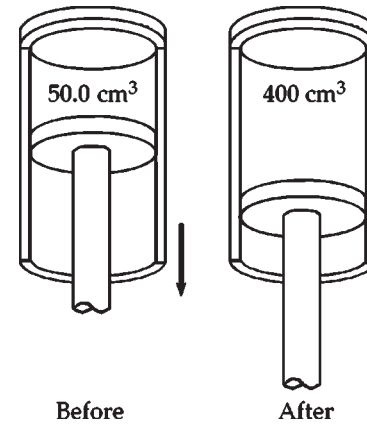


FIG. P21.22

**P21.23** (a) See the diagram at the right.

$$(b) \quad P_B V_B^\gamma = P_C V_C^\gamma$$

$$3P_i V_i^\gamma = P_i V_C^\gamma$$

$$V_C = (3^{1/\gamma}) V_i = (3^{5/7}) V_i = 2.19 V_i$$

$$V_C = 2.19 (4.00 \text{ L}) = \boxed{8.77 \text{ L}}$$

$$(c) \quad P_B V_B = nRT_B = 3P_i V_i = 3nRT_i$$

$$T_B = 3T_i = 3(300 \text{ K}) = \boxed{900 \text{ K}}$$

$$(d) \quad \text{After one whole cycle, } T_A = T_i = \boxed{300 \text{ K}}.$$

$$(e) \quad \text{In } AB, Q_{AB} = nC_V \Delta T = n \left( \frac{5}{2} R \right) (3T_i - T_i) = (5.00) nRT_i$$

$Q_{BC} = 0$  as this process is adiabatic

$$P_C V_C = nRT_C = P_i (2.19 V_i) = (2.19) nRT_i \quad \text{so} \quad T_C = 2.19 T_i$$

$$Q_{CA} = nC_P \Delta T = n \left( \frac{7}{2} R \right) (T_i - 2.19 T_i) = (-4.17) nRT_i$$

For the whole cycle,

$$Q_{ABCA} = Q_{AB} + Q_{BC} + Q_{CA} = (5.00 - 4.17) nRT_i = (0.829) nRT_i$$

$$(\Delta E_{\text{int}})_{ABCA} = 0 = Q_{ABCA} + W_{ABCA}$$

$$W_{ABCA} = -Q_{ABCA} = -(0.829) nRT_i = -(0.829) P_i V_i$$

$$W_{ABCA} = -(0.829) (1.013 \times 10^5 \text{ Pa}) (4.00 \times 10^{-3} \text{ m}^3) = \boxed{-336 \text{ J}}$$

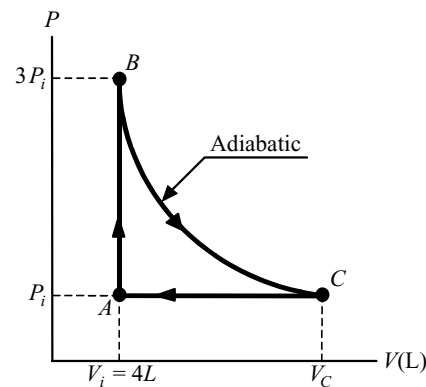


FIG. P21.23

**P21.24** (a) See the diagram at the right.

$$(b) P_B V_B^\gamma = P_C V_C^\gamma$$

$$3P_i V_i^\gamma = P_i V_C^\gamma$$

$$V_C = 3^{1/\gamma} V_i = 3^{5/7} V_i = \boxed{2.19 V_i}$$

$$(c) P_B V_B = nRT_B = 3P_i V_i = 3nRT_i$$

$$T_B = \boxed{3T_i}$$

$$(d) \text{ After one whole cycle, } T_A = \boxed{T_i}$$

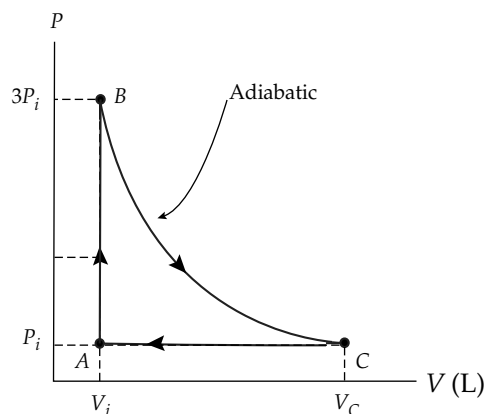


FIG. P21.24

$$(e) \text{ In } AB, Q_{AB} = nC_V \Delta T = n\left(\frac{5}{2}R\right)(3T_i - T_i) = (5.00)nRT_i$$

$Q_{BC} = 0$  as this process is adiabatic

$$P_C V_C = nRT_C = P_i (2.19 V_i) = 2.19 nRT_i \quad \text{so} \quad T_C = 2.19 T_i$$

$$Q_{CA} = nC_P \Delta T = n\left(\frac{7}{2}R\right)(T_i - 2.19 T_i) = -4.17 nRT_i$$

For the whole cycle,

$$Q_{ABCA} = Q_{AB} + Q_{BC} + Q_{CA} = (5.00 - 4.17)nRT_i = 0.830 nRT_i$$

$$(\Delta E_{\text{int}})_{ABCA} = 0 = Q_{ABCA} + W_{ABCA}$$

$$W_{ABCA} = -Q_{ABCA} = -0.830 nRT_i = \boxed{-0.830 P_i V_i}$$

**P21.25** (a) The work done *on* the gas is

$$W_{ab} = - \int_{V_a}^{V_b} P dV$$

For the isothermal process,

$$W_{ab'} = -nRT_a \int_{V_a}^{V_{b'}} \left(\frac{1}{V}\right) dV$$

$$W_{ab'} = -nRT_a \ln\left(\frac{V_{b'}}{V_a}\right) = nRT \ln\left(\frac{V_a}{V_{b'}}\right)$$

Thus,

$$W_{ab'} = 5.00 \text{ mol} (8.314 \text{ J/mol} \cdot \text{K}) (293 \text{ K}) \ln(10.0)$$

$$W_{ab'} = \boxed{28.0 \text{ kJ}}$$

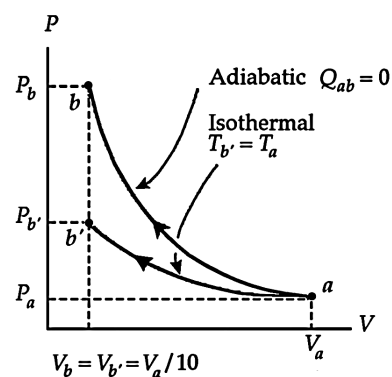


FIG. P21.25

*continued on next page*

- (b) For the adiabatic process, we must first find the final temperature,  $T_b$ . Since air consists primarily of diatomic molecules, we shall use

$$\gamma_{\text{air}} = 1.40 \quad \text{and} \quad C_{V, \text{air}} = \frac{5R}{2} = \frac{5(8.314)}{2} = 20.8 \text{ J/mol} \cdot \text{K}$$

Then, for the adiabatic process

$$T_b = T_a \left( \frac{V_a}{V_b} \right)^{\gamma-1} = 293 \text{ K} (10.0)^{0.400} = 736 \text{ K}$$

Thus, the work done on the gas during the adiabatic process is

$$W_{ab} (-Q + \Delta E_{\text{int}})_{ab} = (-0 + nC_V \Delta T)_{ab} = nC_V (T_b - T_a)$$

$$\text{or} \quad W_{ab} = 5.00 \text{ mol} (20.8 \text{ J/mol} \cdot \text{K}) (736 - 293) \text{ K} = \boxed{46.0 \text{ kJ}}$$

- (c) For the isothermal process, we have

$$P_b V_b = P_a V_a$$

Thus

$$P_b = P_a \left( \frac{V_a}{V_b} \right) = 1.00 \text{ atm} (10.0) = \boxed{10.0 \text{ atm}}$$

For the adiabatic process, we have  $P_b V_b^\gamma = P_a V_a^\gamma$

Thus

$$P_b = P_a \left( \frac{V_a}{V_b} \right)^\gamma = 1.00 \text{ atm} (10.0)^{1.40} = \boxed{25.1 \text{ atm}}$$

## Section 21.4 The Equipartition of Energy

**P21.26** (1)  $E_{\text{int}} = Nf \left( \frac{k_B T}{2} \right) = f \left( \frac{nRT}{2} \right)$

(2)  $C_V = \frac{1}{n} \left( \frac{dE_{\text{int}}}{dT} \right) = \frac{1}{2} fR$

(3)  $C_P = C_V + R = \frac{1}{2} (f + 2)R$

(4)  $\gamma = \frac{C_P}{C_V} = \frac{f + 2}{f}$

*continued on next page*

**P21.27** The sample's total heat capacity at constant volume is  $nC_v$ . An ideal gas of diatomic molecules has three degrees of freedom for translation in the  $x$ ,  $y$ , and  $z$  directions. If we take the  $y$  axis along the axis of a molecule, then outside forces cannot excite rotation about this axis, since they have no lever arms. Collisions will set the molecule spinning only about the  $x$  and  $z$  axes.

- (a) If the molecules do not vibrate, they have five degrees of freedom. Random collisions put equal amounts of energy  $\frac{1}{2}k_B T$  into all five kinds of motion. The average energy of one molecule is  $\frac{5}{2}k_B T$ . The internal energy of the two-mole sample is

$$N\left(\frac{5}{2}k_B T\right) = nN_A\left(\frac{5}{2}k_B T\right) = n\left(\frac{5}{2}R\right)T = nC_v T$$

The molar heat capacity is  $C_v = \frac{5}{2}R$  and the sample's heat capacity is

$$nC_v = n\left(\frac{5}{2}R\right) = 2 \text{ mol} \left(\frac{5}{2}(8.314 \text{ J/mol} \cdot \text{K})\right)$$

$$\boxed{nC_v = 41.6 \text{ J/K}}$$

For the heat capacity at constant pressure we have

$$nC_p = n(C_v + R) = n\left(\frac{5}{2}R + R\right) = \frac{7}{2}nR = 2 \text{ mol} \left(\frac{7}{2}(8.314 \text{ J/mol} \cdot \text{K})\right)$$

$$\boxed{nC_p = 58.2 \text{ J/K}}$$

- (b) In vibration with the center of mass fixed, both atoms are always moving in opposite directions with equal speeds. Vibration adds two more degrees of freedom for two more terms in the molecular energy, for kinetic and for elastic potential energy. We have

$$nC_v = n\left(\frac{7}{2}R\right) = \boxed{58.2 \text{ J/K}} \quad \text{and} \quad nC_p = n\left(\frac{9}{2}R\right) = \boxed{74.8 \text{ J/K}}$$

**P21.28** Rotational Kinetic Energy =  $\frac{1}{2}I\omega^2$

$$I = 2m_0 r^2, \quad m_0 = 35.0 \times 1.67 \times 10^{-27} \text{ kg}, \quad r = 10^{-10} \text{ m}$$

$$I = 1.17 \times 10^{-45} \text{ kg} \cdot \text{m}^2 \quad \omega = 2.00 \times 10^{12} \text{ s}^{-1}$$

$$\therefore K_{\text{rot}} = \frac{1}{2}I\omega^2 = \boxed{2.33 \times 10^{-21} \text{ J}}$$

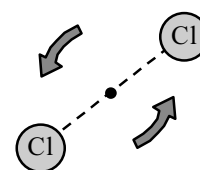


FIG. P21.28

**\*P21.29** Sulfur dioxide is the gas with the greatest molecular mass of those listed. If the effective spring constants for various chemical bonds are comparable,  $\text{SO}_2$  can then be expected to have low frequencies of atomic vibration. Vibration can be excited at lower temperature than for the other gases. Some vibration may be going on at 300 K. With more degrees of freedom for molecular motion, the material has higher specific heat.

- \*P21.30** (a) The energy of one molecule can be represented as  
 $(1/2)m_0v_x^2 + (1/2)m_0v_y^2 + (1/2)m_0v_z^2 + (1/2)I\omega_x^2 + (1/2)I\omega_z^2$   
 Its average value is  $(1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T = (5/2)k_B T$   
 The energy of one mole is obtained by multiplying by Avogadro's number,  $E_{int}/n = (5/2)RT$   
 And the molar heat capacity at constant volume is  $E_{int}/nT = \boxed{(5/2)R}$
- (b) The energy of one molecule can be represented as  
 $(1/2)m_0v_x^2 + (1/2)m_0v_y^2 + (1/2)m_0v_z^2 + (1/2)I\omega_x^2 + (1/2)I\omega_z^2 + (1/2)I\omega_y^2$   
 Its average value is  $(1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T = 3k_B T$   
 The energy of one mole is obtained by multiplying by Avogadro's number,  $E_{int}/n = 3RT$   
 And the molar heat capacity at constant volume is  $E_{int}/nT = \boxed{3R}$
- (c) Let the modes of vibration be denoted by 1 and 2. The energy of one molecule can be represented as  
 $0.5m_0[v_x^2 + v_y^2 + v_z^2] + 0.5I\omega_x^2 + 0.5I\omega_z^2 + [0.5\mu v_{rel}^2 + 0.5kx^2]_1 + [0.5\mu v_{rel}^2 + 0.5kx^2]_2$   
 Its average value is  
 $(3/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T = (9/2)k_B T$   
 The energy of one mole is obtained by multiplying by Avogadro's number,  $E_{int}/n = (9/2)RT$   
 And the molar heat capacity at constant volume is  $E_{int}/nT = \boxed{(9/2)R}$
- (d) The energy of one molecule can be represented as  
 $0.5m_0[v_x^2 + v_y^2 + v_z^2] + 0.5I\omega_x^2 + 0.5I\omega_z^2 + 0.5I\omega_y^2 + [0.5\mu v_{rel}^2 + 0.5kx^2]_1 + [0.5\mu v_{rel}^2 + 0.5kx^2]_2$   
 Its average value is  $(3/2)k_B T + (3/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T = (5)k_B T$   
 The energy of one mole is obtained by multiplying by Avogadro's number,  $E_{int}/n = 5RT$   
 And the molar heat capacity at constant volume is  $E_{int}/nT = \boxed{5R}$
- (e) Measure the constant-volume specific heat of the gas as a function of temperature and look for plateaus on the graph, as shown in Figure 21.7. If the first jump goes from  $\frac{3}{2}R$  to  $\frac{5}{2}R$ , the molecules can be diagnosed as linear. If the first jump goes from  $\frac{3}{2}R$  to  $3R$ , the molecules must be nonlinear. The tabulated data at one temperature are insufficient for the determination. At room temperature some of the heavier molecules appear to be vibrating.

## Section 21.5 Distribution of Molecular Speeds

- P21.31** (a)  $v_{av} = \frac{\sum n_i v_i}{N} = \frac{1}{15} [1(2) + 2(3) + 3(5) + 4(7) + 3(9) + 2(12)] = \boxed{6.80 \text{ m/s}}$
- (b)  $(v^2)_{av} = \frac{\sum n_i v_i^2}{N} = 54.9 \text{ m}^2/\text{s}^2$   
 so  $v_{rms} = \sqrt{(v^2)_{av}} = \sqrt{54.9} = \boxed{7.41 \text{ m/s}}$
- (c)  $v_{mp} = \boxed{7.00 \text{ m/s}}$

- P21.32** (a) The ratio of the number at higher energy to the number at lower energy is  $e^{-\Delta E/k_B T}$  where  $\Delta E$  is the energy difference. Here,

$$\Delta E = (10.2 \text{ eV}) \left( \frac{1.60 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) = 1.63 \times 10^{-18} \text{ J}$$

and at  $0^\circ\text{C}$ ,

$$k_B T = (1.38 \times 10^{-23} \text{ J/K})(273 \text{ K}) = 3.77 \times 10^{-21} \text{ J}$$

Since this is much less than the excitation energy, nearly all the atoms will be in the ground state and the number excited is

$$(2.70 \times 10^{25}) \exp \left( \frac{-1.63 \times 10^{-18} \text{ J}}{3.77 \times 10^{-21} \text{ J}} \right) = (2.70 \times 10^{25}) e^{-433}$$

This number is much less than one, so almost all of the time no atom is excited.

- (b) At  $10\,000^\circ\text{C}$ ,

$$k_B T = (1.38 \times 10^{-23} \text{ J/K}) 10\,273 \text{ K} = 1.42 \times 10^{-19} \text{ J}$$

The number excited is

$$(2.70 \times 10^{25}) \exp \left( \frac{-1.63 \times 10^{-18} \text{ J}}{1.42 \times 10^{-19} \text{ J}} \right) = (2.70 \times 10^{25}) e^{-11.5} = \boxed{2.70 \times 10^{20}}$$

- P21.33** In the Maxwell Boltzmann speed distribution function take  $\frac{dN_v}{dv} = 0$  to find

$$4\pi N \left( \frac{m_0}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{m_0 v^2}{2k_B T} \right) \left( 2v - \frac{2m_0 v^3}{2k_B T} \right) = 0$$

and solve for  $v$  to find the most probable speed.

Reject as solutions  $v = 0$  and  $v = \infty$ . They describe minimally probable speeds.

Retain only  $2 - \frac{m_0 v^2}{k_B T} = 0$

Then  $v_{\text{mp}} = \sqrt{\frac{2k_B T}{m_0}}$

**P21.34** (a)  $\frac{V_{\text{rms}, 35}}{V_{\text{rms}, 37}} = \frac{\sqrt{3RT/M_{35}}}{\sqrt{3RT/M_{37}}} = \left( \frac{37.0 \text{ g/mol}}{35.0 \text{ g/mol}} \right)^{1/2} = \boxed{1.03}$

- (b) The lighter atom,  $^{35}\text{Cl}$ , moves faster.

**P21.35** (a) From  $v_{\text{av}} = \sqrt{\frac{8k_B T}{\pi m_0}}$

we find the temperature as  $T = \frac{\pi (6.64 \times 10^{-27} \text{ kg}) (1.12 \times 10^4 \text{ m/s})^2}{8 (1.38 \times 10^{-23} \text{ J/mol} \cdot \text{K})} = \boxed{2.37 \times 10^4 \text{ K}}$

(b)  $T = \frac{\pi (6.64 \times 10^{-27} \text{ kg}) (2.37 \times 10^3 \text{ m/s})^2}{8 (1.38 \times 10^{-23} \text{ J/mol} \cdot \text{K})} = \boxed{1.06 \times 10^3 \text{ K}}$

**\*P21.36** For a molecule of diatomic nitrogen the mass is

$$m_0 = M/N_A = (28.0 \times 10^{-3} \text{ kg/mol}) / (6.02 \times 10^{23} \text{ molecules/mol}) = 4.65 \times 10^{-26} \text{ kg/molecule}$$

$$(a) \quad v_{mp} = \sqrt{\frac{2k_B T}{m_0}} = \sqrt{\frac{2(1.38 \times 10^{-23} \text{ J/molecule} \cdot \text{K})(900 \text{ K})}{4.65 \times 10^{-26} \text{ kg/molecule}}} = \boxed{731 \text{ m/s}}$$

$$(b) \quad v_{avg} = \sqrt{\frac{8k_B T}{\pi m_0}} = \sqrt{\frac{8(1.38 \times 10^{-23} \text{ J/molecule} \cdot \text{K})(900 \text{ K})}{\pi \cdot 4.65 \times 10^{-26} \text{ kg/molecule}}} = \boxed{825 \text{ m/s}}$$

$$(c) \quad v_{rms} = \sqrt{\frac{3k_B T}{m_0}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/molecule} \cdot \text{K})(900 \text{ K})}{4.65 \times 10^{-26} \text{ kg/molecule}}} = \boxed{895 \text{ m/s}}$$

(d) The graph appears to be drawn correctly within about 10 m/s.

**P21.37** (a) From the Boltzmann distribution law, the number density of molecules with gravitational energy  $m_0 g y$  is  $n_0 e^{-m_0 g y / k_B T}$ . These are the molecules with height  $y$ , so this is the number per volume at height  $y$  as a function of  $y$ .

$$\begin{aligned} (b) \quad \frac{n(y)}{n_0} &= e^{-m_0 g y / k_B T} = e^{-M g y / N_A k_B T} = e^{-M g y / R T} \\ &= e^{-(28.9 \times 10^{-3} \text{ kg/mol})(9.8 \text{ m/s}^2)(11 \times 10^3 \text{ m}) / (8.314 \text{ J/mol} \cdot \text{K})(293 \text{ K})} \\ &= e^{-1.279} = \boxed{0.278} \end{aligned}$$

**P21.38** (a) We calculate

$$\begin{aligned} \int_0^\infty e^{-m_0 g y / k_B T} dy &= \int_{y=0}^\infty e^{-m_0 g y / k_B T} \left( -\frac{m_0 g dy}{k_B T} \right) \left( -\frac{k_B T}{m_0 g} \right) \\ &= -\frac{k_B T}{m_0 g} e^{-m_0 g y / k_B T} \bigg|_0^\infty = -\frac{k_B T}{m_0 g} (0 - 1) = \frac{k_B T}{m_0 g} \end{aligned}$$

Using Table B.6 in the appendix,

$$\int_0^\infty y e^{-m_0 g y / k_B T} dy = \frac{1!}{(m_0 g / k_B T)^2} = \left( \frac{k_B T}{m_0 g} \right)^2$$

Then

$$\bar{y} = \frac{\int_0^\infty y e^{-m_0 g y / k_B T} dy}{\int_0^\infty e^{-m_0 g y / k_B T} dy} = \frac{(k_B T / m_0 g)^2}{k_B T / m_0 g} = \frac{k_B T}{m_0 g}$$

$$(b) \quad \bar{y} = \frac{k_B T}{(M/N_A)g} = \frac{RT}{Mg} = \frac{8.314 \text{ J } 283 \text{ K s}^2}{\text{mol} \cdot \text{K } 28.9 \times 10^{-3} \text{ kg } 9.8 \text{ m}} = \boxed{8.31 \times 10^3 \text{ m}}$$

## Additional Problems

**P21.39** (a)  $P_f = 100 \text{ kPa}$        $T_f = 400 \text{ K}$

$$V_f = \frac{nRT_f}{P_f} = \frac{2.00 \text{ mol}(8.314 \text{ J/mol} \cdot \text{K})(400 \text{ K})}{100 \times 10^3 \text{ Pa}} = 0.0665 \text{ m}^3 = 66.5 \text{ L}$$

$$\Delta E_{\text{int}} = (3.50)nR\Delta T = 3.50(2.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(100 \text{ K}) = 5.82 \text{ kJ}$$

$$W = -P\Delta V = -nR\Delta T = -(2.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(100 \text{ K}) = -1.66 \text{ kJ}$$

$$Q = \Delta E_{\text{int}} - W = 5.82 \text{ kJ} + 1.66 \text{ kJ} = 7.48 \text{ kJ}$$

(b)  $T_f = 400 \text{ K}$

$$V_f = V_i = \frac{nRT_i}{P_i} = \frac{2.00 \text{ mol}(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{100 \times 10^3 \text{ Pa}} = 0.0499 \text{ m}^3 = 49.9 \text{ L}$$

$$P_f = P_i \left( \frac{T_f}{T_i} \right) = 100 \text{ kPa} \left( \frac{400 \text{ K}}{300 \text{ K}} \right) = 133 \text{ kPa} \quad W = -\int P dV = 0 \text{ since } V = \text{constant}$$

$$\Delta E_{\text{int}} = 5.82 \text{ kJ} \text{ as in part (a)}$$

$$Q = \Delta E_{\text{int}} - W = 5.82 \text{ kJ} - 0 = 5.82 \text{ kJ}$$

(c)  $P_f = 120 \text{ kPa}$

$$T_f = 300 \text{ K}$$

$$V_f = V_i \left( \frac{P_i}{P_f} \right) = 49.9 \text{ L} \left( \frac{100 \text{ kPa}}{120 \text{ kPa}} \right) = 41.6 \text{ L} \quad \Delta E_{\text{int}} = (3.50)nR\Delta T = 0 \text{ since } T = \text{constant}$$

$$W = -\int P dV = -nRT_i \int_{V_i}^{V_f} \frac{dV}{V} = -nRT_i \ln \left( \frac{V_f}{V_i} \right) = -nRT_i \ln \left( \frac{P_i}{P_f} \right)$$

$$W = -(2.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K}) \ln \left( \frac{100 \text{ kPa}}{120 \text{ kPa}} \right) = +909 \text{ J}$$

$$Q = \Delta E_{\text{int}} - W = 0 - 909 \text{ J} = -909 \text{ J}$$

(d)  $P_f = 120 \text{ kPa}$        $\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = \frac{3.50R + R}{3.50R} = \frac{4.50}{3.50} = \frac{9}{7}$

$$P_f V_f^\gamma = P_i V_i^\gamma \quad \text{so} \quad V_f = V_i \left( \frac{P_i}{P_f} \right)^{1/\gamma} = 49.9 \text{ L} \left( \frac{100 \text{ kPa}}{120 \text{ kPa}} \right)^{7/9} = 43.3 \text{ L}$$

$$T_f = T_i \left( \frac{P_f V_f}{P_i V_i} \right) = 300 \text{ K} \left( \frac{120 \text{ kPa}}{100 \text{ kPa}} \right) \left( \frac{43.3 \text{ L}}{49.9 \text{ L}} \right) = 312 \text{ K}$$

$$\Delta E_{\text{int}} = (3.50)nR\Delta T = 3.50(2.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(12.4 \text{ K}) = 722 \text{ J}$$

$$Q = 0 \text{ (adiabatic process)}$$

$$W = -Q + \Delta E_{\text{int}} = 0 + 722 \text{ J} = +722 \text{ J}$$



- \*P21.40** (a)  $n = \frac{PV}{RT} = \frac{(1.013 \times 10^5 \text{ Pa})(4.20 \text{ m} \times 3.00 \text{ m} \times 2.50 \text{ m})}{(8.314 \text{ J/mol} \cdot \text{K})(293 \text{ K})} = 1.31 \times 10^3 \text{ mol}$   
 $N = nN_A = (1.31 \times 10^3 \text{ mol})(6.02 \times 10^{23} \text{ molecules/mol})$   
 $N = \boxed{7.89 \times 10^{26} \text{ molecules}}$
- (b)  $m = nM = (1.31 \times 10^3 \text{ mol})(0.0289 \text{ kg/mol}) = \boxed{37.9 \text{ kg}}$
- (c)  $\frac{1}{2}m_0v^2 = \frac{3}{2}k_B T = \frac{3}{2}(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K}) = \boxed{6.07 \times 10^{-21} \text{ J/molecule}}$
- (d) For one molecule,  
 $m_0 = \frac{M}{N_A} = \frac{0.0289 \text{ kg/mol}}{6.02 \times 10^{23} \text{ molecules/mol}} = 4.80 \times 10^{-26} \text{ kg/molecule}$   
 $v_{\text{rms}} = \sqrt{\frac{2(6.07 \times 10^{-21} \text{ J/molecule})}{4.80 \times 10^{-26} \text{ kg/molecule}}} = \boxed{503 \text{ m/s}}$
- (e), (f)  $E_{\text{int}} = nC_V T = n\left(\frac{5}{2}R\right)T = \frac{5}{2}PV$   
 $E_{\text{int}} = \frac{5}{2}(1.013 \times 10^5 \text{ Pa})(31.5 \text{ m}^3) = \boxed{7.98 \text{ MJ}}$

The smaller mass of warmer air at 25°C contains the same internal energy as the cooler air. When the furnace operates, air expands and leaves the room.

- \*P21.41** For a pure metallic element, one atom is one molecule. Its energy can be represented as  $(1/2)m_0v_x^2 + (1/2)m_0v_y^2 + (1/2)m_0v_z^2 + (1/2)k_x x^2 + (1/2)k_y y^2 + (1/2)k_z z^2$   
 Its average value is  $(1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T + (1/2)k_B T = 3k_B T$   
 The energy of one mole is obtained by multiplying by Avogadro's number,  $E_{\text{int}}/n = 3RT$   
 And the molar heat capacity at constant volume is  $E_{\text{int}}/nT = \boxed{3R}$

- (b)  $3(8.314 \text{ J/mole} \cdot \text{K}) = 3 \times 8.314 \text{ J}/[55.845 \times 10^{-3} \text{ kg}] \cdot \text{K} = 447 \text{ J/kg} \cdot \text{K} =$   
 $\boxed{447 \text{ J/kg} \cdot ^\circ\text{C}}.$  This agrees with the tabulated value of 448 J/kg·°C within 0.3%.
- (c)  $3(8.314 \text{ J/mole} \cdot \text{K}) = 3 \times 8.314 \text{ J}/[197 \times 10^{-3} \text{ kg}] \cdot \text{K} = 127 \text{ J/kg} \cdot \text{K} =$   
 $\boxed{127 \text{ J/kg} \cdot ^\circ\text{C}}.$  This agrees with the tabulated value of 129 J/kg·°C within 2%.

- P21.42** (a) The average speed  $v_{\text{avg}}$  is just the weighted average of all the speeds.

$$v_{\text{avg}} = \frac{[2(v) + 3(2v) + 5(3v) + 4(4v) + 3(5v) + 2(6v) + 1(7v)]}{(2 + 3 + 5 + 4 + 3 + 2 + 1)} = \boxed{3.65v}$$

- (b) First find the average of the square of the speeds,

$$(v^2)_{\text{avg}} = \frac{[2(v)^2 + 3(2v)^2 + 5(3v)^2 + 4(4v)^2 + 3(5v)^2 + 2(6v)^2 + 1(7v)^2]}{2 + 3 + 5 + 4 + 3 + 2 + 1} = 15.95v^2$$

$$\text{The root-mean square speed is then } v_{\text{rms}} = \sqrt{(v_{\text{avg}})^2} = \boxed{3.99v}$$

- (c) The most probable speed is the one that most of the particles have;  
 i.e., five particles have speed  $\boxed{3.00v}$ .

continued on next page

$$(d) \quad PV = \frac{1}{3} N m_0 v_{\text{av}}^2$$

Therefore,

$$P = \frac{20}{3} \left[ \frac{m_0 (15.95)^2 v^2}{V} \right] = \boxed{106 \left( \frac{m_0 v^2}{V} \right)}$$

(e) The average kinetic energy for each particle is

$$\bar{K} = \frac{1}{2} m_0 v_{\text{av}}^2 = \frac{1}{2} m_0 (15.95 v^2) = \boxed{7.98 m_0 v^2}$$

$$\text{*P21.43 (a) } PV^\gamma = k. \text{ So } W = - \int_i^f P dV = -k \int_{V_i}^{V_f} \frac{dV}{V^\gamma} = \left. \frac{-kV^{1-\gamma}}{1-\gamma} \right|_{V_i}^{V_f}$$

For  $k$  we can substitute  $P_i V_i^\gamma$  and also  $P_f V_f^\gamma$  to have

$$W = - \frac{P_f V_f^\gamma V_f^{1-\gamma} - P_i V_i^\gamma V_i^{1-\gamma}}{1-\gamma} = \frac{P_f V_f - P_i V_i}{\gamma - 1}$$

(b)  $dE_{\text{int}} = dQ + dW$  and  $dQ = 0$  for an adiabatic process.

Therefore,

$$W = +\Delta E_{\text{int}} = nC_V (T_f - T_i)$$

To show consistency between these two equations, consider that  $\gamma = \frac{C_p}{C_V}$  and  $C_p - C_V = R$ .

Therefore,  $\frac{1}{\gamma - 1} = \frac{C_V}{R}$

Using this, the result found in part (a) becomes  $W = (P_f V_f - P_i V_i) \frac{C_V}{R}$

Also, for an ideal gas  $\frac{PV}{R} = nT$  so that  $W = nC_V (T_f - T_i)$ , as found in part (b).

$$\text{P21.44 (a) } W = nC_V (T_f - T_i)$$

$$-2500 \text{ J} = 1 \text{ mol} \left( \frac{3}{2} \right) 8.314 \text{ J/mol} \cdot \text{K} (T_f - 500 \text{ K})$$

$$T_f = \boxed{300 \text{ K}}$$

$$(b) \quad P_i V_i^\gamma = P_f V_f^\gamma$$

$$P_i \left( \frac{nRT_i}{P_i} \right)^\gamma = P_f \left( \frac{nRT_f}{P_f} \right)^\gamma \quad T_i^\gamma P_i^{1-\gamma} = T_f^\gamma P_f^{1-\gamma}$$

$$\frac{T_i^{\gamma/(\gamma-1)}}{P_i} = \frac{T_f^{\gamma/(\gamma-1)}}{P_f} \quad P_f = P_i \left( \frac{T_f}{T_i} \right)^{\gamma/(\gamma-1)}$$

$$P_f = P_i \left( \frac{T_f}{T_i} \right)^{(5/3)(3/2)} = 3.60 \text{ atm} \left( \frac{300}{500} \right)^{5/2} = \boxed{1.00 \text{ atm}}$$

**P21.45** Let the subscripts '1' and '2' refer to the hot and cold compartments, respectively. The pressure is higher in the hot compartment, therefore the hot compartment expands and the cold compartment contracts. The work done by the adiabatically expanding gas is equal and opposite to the work done by the adiabatically compressed gas.

$$\frac{nR}{\gamma-1}(T_{1i} - T_{1f}) = -\frac{nR}{\gamma-1}(T_{2i} - T_{2f})$$

Therefore

$$T_{1f} + T_{2f} = T_{1i} + T_{2i} = 800 \text{ K} \quad (1)$$

Consider the adiabatic changes of the gases.

$$P_{1i}V_{1i}^\gamma = P_{1f}V_{1f}^\gamma \quad \text{and} \quad P_{2i}V_{2i}^\gamma = P_{2f}V_{2f}^\gamma$$

$$\therefore \frac{P_{1i}V_{1i}^\gamma}{P_{2i}V_{2i}^\gamma} = \frac{P_{1f}V_{1f}^\gamma}{P_{2f}V_{2f}^\gamma}$$

$$\therefore \frac{P_{1i}}{P_{2i}} = \left(\frac{V_{1f}}{V_{2f}}\right)^\gamma, \text{ since } V_{1i} = V_{2i} \text{ and } P_{1f} = P_{2f}$$

$$\therefore \frac{nRT_{1i}/V_{1i}}{nRT_{2i}/V_{2i}} = \left(\frac{nRT_{1f}/P_{1f}}{nRT_{2f}/P_{2f}}\right)^\gamma, \text{ using the ideal gas law}$$

$$\therefore \frac{T_{1i}}{T_{2i}} = \left(\frac{T_{1f}}{T_{2f}}\right)^\gamma, \text{ since } V_{1i} = V_{2i} \text{ and } P_{1f} = P_{2f}$$

$$\therefore \frac{T_{1f}}{T_{2f}} = \left(\frac{T_{1i}}{T_{2i}}\right)^{1/\gamma} = \left(\frac{550 \text{ K}}{250 \text{ K}}\right)^{1/1.4} = 1.756 \quad (2)$$

Solving equations (1) and (2) simultaneously gives  $T_{1f} = 510 \text{ K}, T_{2f} = 290 \text{ K}$

**P21.46** The net work done by the gas on the bullet becomes the bullet's kinetic energy:

$$\frac{1}{2}mv^2 = \frac{1}{2}1.1 \times 10^{-3} \text{ kg}(120 \text{ m/s})^2 = 7.92 \text{ J}$$

The air in front of the bullet does work

$$P\Delta V = (1.013 \times 10^5 \text{ N/m}^2)(-0.5 \text{ m})(0.03 \times 10^{-4} \text{ m}^2) = -0.152 \text{ J}$$

The hot gas behind the bullet then must do output work  $+W$  in  $+W - 0.152 \text{ J} = 7.92 \text{ J}$   
 $W = 8.07 \text{ J}$ . The input work on the hot gas is  $-8.07 \text{ J}$

$$\frac{1}{\gamma-1}(P_f V_f - P_i V_i) = -8.07 \text{ J}$$

$$\text{Also} \quad P_f V_f^\gamma = P_i V_i^\gamma \quad P_f = P_i \left(\frac{V_i}{V_f}\right)^\gamma$$

$$\text{So} \quad -8.07 \text{ J} = \frac{1}{0.40} P_i \left[ V_f \left(\frac{V_i}{V_f}\right)^\gamma - V_i \right]$$

$$\text{And} \quad V_f = 12 \text{ cm}^3 + 50 \text{ cm} \cdot 0.03 \text{ cm}^2 = 13.5 \text{ cm}^3$$

$$\text{Then} \quad P_i = \frac{-8.07 \text{ J}(0.40)10^6 \text{ cm}^3/\text{m}^3}{[13.5 \text{ cm}^3(12/13.5)^{1.40} - 12 \text{ cm}^3]} = \boxed{5.85 \times 10^6 \text{ Pa}} = 57.7 \text{ atm}$$

- P21.47** The pressure of the gas in the lungs of the diver must be the same as the absolute pressure of the water at this depth of 50.0 meters. This is:

$$P = P_0 + \rho gh = 1.00 \text{ atm} + (1.03 \times 10^3 \text{ kg/m}^3)(9.80 \text{ m/s}^2)(50.0 \text{ m})$$

$$\text{or } P = 1.00 \text{ atm} + 5.05 \times 10^5 \text{ Pa} \left( \frac{1.00 \text{ atm}}{1.013 \times 10^5 \text{ Pa}} \right) = 5.98 \text{ atm}$$

If the partial pressure due to the oxygen in the gas mixture is to be 1.00 atmosphere (or the fraction  $\frac{1}{5.98}$  of the total pressure) oxygen molecules should make up only  $\frac{1}{5.98}$  of the total number of molecules. This will be true if 1.00 mole of oxygen is used for every 4.98 mole of helium. The ratio by weight is then

$$\frac{(4.98 \text{ mol He})(4.003 \text{ g/mol He})}{(1.00 \text{ mol O}_2)(2 \times 15.999 \text{ g/mol O}_2)} = \boxed{0.623}$$

- P21.48** (a) Maxwell's speed distribution function is

$$N_v = 4\pi N \left( \frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0 v^2 / 2k_B T}$$

With

$$N = 1.00 \times 10^4,$$

$$m_0 = \frac{M}{N_A} = \frac{0.032 \text{ kg}}{6.02 \times 10^{23}} = 5.32 \times 10^{-26} \text{ kg}$$

$$T = 500 \text{ K}$$

$$\text{and } k_B = 1.38 \times 10^{-23} \text{ J/molecule} \cdot \text{K}$$

$$\text{this becomes } N_v = (1.71 \times 10^{-4}) v^2 e^{-(3.85 \times 10^{-6}) v^2}$$

To the right is a plot of this function for the range  $0 \leq v \leq 1500 \text{ m/s}$ .

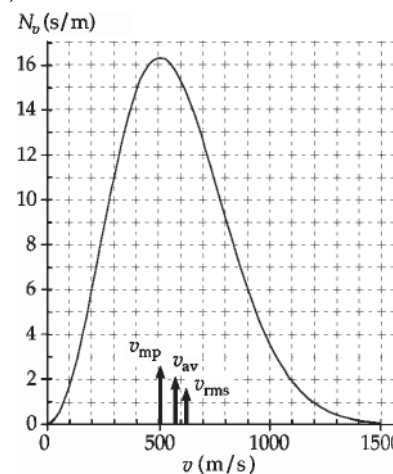


FIG. P21.48(a)

- (b) The most probable speed occurs where  $N_v$  is a maximum.

$$\text{From the graph, } \boxed{v_{mp} \approx 510 \text{ m/s}}$$

$$(c) \quad v_{av} = \sqrt{\frac{8k_B T}{\pi m_0}} = \sqrt{\frac{8(1.38 \times 10^{-23})(500)}{\pi(5.32 \times 10^{-26})}} = \boxed{575 \text{ m/s}}$$

Also,

$$v_{rms} = \sqrt{\frac{3k_B T}{m_0}} = \sqrt{\frac{3(1.38 \times 10^{-23})(500)}{5.32 \times 10^{-26}}} = \boxed{624 \text{ m/s}}$$

- (d) The fraction of particles in the range  $300 \text{ m/s} \leq v \leq 600 \text{ m/s}$

$$\text{is } \frac{\int_{300}^{600} N_v dv}{N}$$

where

$$N = 10^4$$

and the integral of  $N_v$  is read from the graph as the area under the curve. This is approximately  $(11 + 16.5 + 16.5 + 15)(1/4)(300) = 4400$  and the fraction is 0.44 or  $\boxed{44\%}$ .

- P21.49** (a) Since pressure increases as volume decreases (and vice versa),

$$\frac{dV}{dP} < 0 \quad \text{and} \quad -\frac{1}{V} \left[ \frac{dV}{dP} \right] > 0$$

- (b) For an ideal gas,  $V = \frac{nRT}{P}$  and  $\kappa_1 = -\frac{1}{V} \frac{d}{dP} \left( \frac{nRT}{P} \right)$

If the compression is isothermal,  $T$  is constant and

$$\kappa_1 = -\frac{nRT}{V} \left( -\frac{1}{P^2} \right) = \frac{1}{P}$$

- (c) For an adiabatic compression,  $PV^\gamma = C$  (where  $C$  is a constant) and

$$\kappa_2 = -\frac{1}{V} \frac{d}{dP} \left( \frac{C}{P} \right)^{1/\gamma} = \frac{1}{V} \left( \frac{1}{\gamma} \right) \frac{C^{1/\gamma}}{P^{(1/\gamma)+1}} = \frac{P^{1/\gamma}}{\gamma P^{1/\gamma+1}} = \frac{1}{\gamma P}$$

- (d)  $\kappa_1 = \frac{1}{P} = \frac{1}{(2.00 \text{ atm})} = \boxed{0.500 \text{ atm}^{-1}}$

$\gamma = \frac{C_P}{C_V}$  and for a monatomic ideal gas,  $\gamma = \frac{5}{3}$ , so that

$$\kappa_2 = \frac{1}{\gamma P} = \frac{1}{\frac{5}{3}(2.00 \text{ atm})} = \boxed{0.300 \text{ atm}^{-1}}$$

- \*P21.50** (a) The speed of sound is  $v = \sqrt{\frac{B}{\rho}}$  where  $B = -V \frac{dP}{dV}$   
According to Problem 49, in an adiabatic process, this is  $B = \frac{1}{\kappa_2} = \gamma P$

Also,

$$\rho = \frac{m_s}{V} = \frac{nM}{V} = \frac{(nRT)M}{V(RT)} = \frac{PM}{RT}$$

where  $m_s$  is the sample mass. Then, the speed of sound in the ideal gas is

$$v = \sqrt{\frac{B}{\rho}} = \sqrt{\gamma P \left( \frac{RT}{PM} \right)} = \sqrt{\frac{\gamma RT}{M}}$$

- (b)  $v = \sqrt{\frac{1.40(8.314 \text{ J/mol} \cdot \text{K})(293 \text{ K})}{0.0289 \text{ kg/mol}}} = \boxed{344 \text{ m/s}}$

This agrees within 0.2% with the 343 m/s listed in Table 17.1.

- (c) We use  $k_B = \frac{R}{N_A}$  and  $M = m_0 N_A$ :  $v = \sqrt{\frac{\gamma RT}{M}} = \sqrt{\frac{\gamma k_B N_A T}{m_0 N_A}} = \sqrt{\frac{\gamma k_B T}{m_0}}$

The most probable molecular speed is  $\sqrt{\frac{2k_B T}{m_0}}$ , the average speed is  $\sqrt{\frac{8k_B T}{\pi m_0}}$ ,

and the rms speed is  $\sqrt{\frac{3k_B T}{m_0}}$ .

The speed of sound is somewhat less than each measure of molecular speed. Sound propagation is orderly motion overlaid on the disorder of molecular motion.

**\*P21.51** (a) The latent heat of evaporation per molecule is

$$2430 \frac{\text{J}}{\text{g}} = 2430 \frac{\text{J}}{\text{g}} \left( \frac{18.0 \text{ g}}{1 \text{ mol}} \right) \left( \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ molecule}} \right) = \boxed{7.27 \times 10^{-20} \text{ J/molecule}}$$

If the molecule has just broken free, we assume that it possesses the energy as translational kinetic energy.

(b) Consider one gram of these molecules:  $K = (1/2)mv^2$

$$2430 \text{ J} = (1/2)(10^{-3} \text{ kg}) v^2 \quad v = (4\,860\,000 \text{ m}^2/\text{s}^2)^{1/2} = \boxed{2.20 \times 10^3 \text{ m/s}}$$

(c) The total translational kinetic energy of an ideal gas is  $(3/2)nRT$ , so we have

$$(2430 \text{ J/g})(18.0 \text{ g/mol}) = (3/2)(1 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})T \quad T = \boxed{3.51 \times 10^3 \text{ K}}$$

The evaporating molecules are exceptional, at the high-speed tail of the distribution of molecular speeds. The average speed of molecules in the liquid and in the vapor is appropriate just to room temperature.

**\*P21.52** (a) Let  $d = 2r$  represent the diameter of the particle. Its mass is

$$m = \rho V = \rho \frac{4}{3} \pi r^3 = \rho \frac{4}{3} \pi \left( \frac{d}{2} \right)^3 = \frac{\rho \pi d^3}{6}. \text{ Then } \frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} kT \text{ gives } \frac{\rho \pi d^3}{6} v_{\text{rms}}^2 = 3kT \text{ so}$$

$$v_{\text{rms}} = \left( \frac{18kT}{\rho \pi d^3} \right)^{1/2} = \left( \frac{18 \times 1.38 \times 10^{-23} \text{ J/K} \times 293 \text{ K}}{1000 \text{ kg/m}^3 \pi} \right)^{1/2} d^{-3/2} = \boxed{4.81 \times 10^{-12} \text{ m}^{5/2} \text{s}^{-1} d^{-3/2}}$$

(b)  $v = d/t \quad [4.81 \times 10^{-12} \text{ m}^{5/2}/\text{s}] d^{-3/2} = d/t$

$$t = \frac{d}{[4.81 \times 10^{-12} \text{ m}^{5/2}/\text{s}] d^{-3/2}} = \boxed{2.08 \times 10^{11} \text{ s} \cdot \text{m}^{-5/2} d^{5/2}}$$

(c)  $v_{\text{rms}} = \left( \frac{18kT}{\rho \pi d^3} \right)^{1/2} = \left( \frac{18(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{(1000 \text{ kg/m}^3) \pi (3 \times 10^{-6} \text{ m})^3} \right)^{1/2} = \boxed{9.26 \times 10^{-4} \text{ m/s}}$

$$v = \frac{x}{t} \quad t = \frac{x}{v} = \frac{3 \times 10^{-6} \text{ m}}{9.26 \times 10^{-4} \text{ m/s}} = \boxed{3.24 \text{ ms}}$$

(d)  $70 \text{ kg} = 1000 \text{ kg/m}^3 \frac{\pi d^3}{6} \quad d = 0.511 \text{ m}$

$$v_{\text{rms}} = \left( \frac{18kT}{\rho \pi d^3} \right)^{1/2} = \left( \frac{18(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{(1000 \text{ kg/m}^3) \pi (0.511 \text{ m})^3} \right)^{1/2} = \boxed{1.32 \times 10^{-11} \text{ m/s}}$$

$$t = \frac{0.511 \text{ m}}{1.32 \times 10^{-11} \text{ m/s}} = \boxed{3.88 \times 10^{10} \text{ s}} = 1\,230 \text{ yr} \quad \text{This motion is too slow to observe.}$$

(e)  $\left( \frac{18kT}{\rho \pi d^3} \right)^{1/2} = \frac{d}{1 \text{ s}} \quad \frac{18kT}{\rho \pi} = \frac{d^5}{1 \text{ s}^2}$

$$d = \left( \frac{18(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})(1 \text{ s}^2)}{(1000 \text{ kg/m}^3) \pi} \right)^{1/5} = \boxed{2.97 \times 10^{-5} \text{ m}}$$

(f) Brownian motion is best observed with pollen grains, smoke particles, or latex spheres smaller than this  $29.7\text{-}\mu\text{m}$  size. Then they can jitter about convincingly, showing relatively large accelerations several times per second. A simple rule is to use the smallest particles that you can clearly see with some particular microscopic technique.

**P21.53**  $n = \frac{m}{M} = \frac{1.20 \text{ kg}}{0.0289 \text{ kg/mol}} = 41.5 \text{ mol}$

(a)  $V_i = \frac{nRT_i}{P_i} = \frac{(41.5 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{200 \times 10^3 \text{ Pa}} = \boxed{0.514 \text{ m}^3}$

(b)  $\frac{P_f}{P_i} = \frac{\sqrt{V_f}}{\sqrt{V_i}}$  so  $V_f = V_i \left( \frac{P_f}{P_i} \right)^2 = (0.514 \text{ m}^3) \left( \frac{400}{200} \right)^2 = \boxed{2.06 \text{ m}^3}$

(c)  $T_f = \frac{P_f V_f}{nR} = \frac{(400 \times 10^3 \text{ Pa})(2.06 \text{ m}^3)}{(41.5 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})} = \boxed{2.38 \times 10^3 \text{ K}}$

(d)  $W = - \int_{V_i}^{V_f} P dV = -C \int_{V_i}^{V_f} V^{1/2} dV = - \left( \frac{P_i}{V_i^{1/2}} \right) \frac{2V^{3/2}}{3} \Big|_{V_i}^{V_f} = - \frac{2}{3} \left( \frac{P_i}{V_i^{1/2}} \right) (V_f^{3/2} - V_i^{3/2})$   
 $W = - \frac{2}{3} \left( \frac{200 \times 10^3 \text{ Pa}}{\sqrt{0.514 \text{ m}^3}} \right) \left[ (2.06 \text{ m}^3)^{3/2} - (0.514 \text{ m}^3)^{3/2} \right] = \boxed{-4.80 \times 10^5 \text{ J}}$

(e)  $\Delta E_{\text{int}} = nC_v \Delta T = (41.5 \text{ mol}) \left[ \frac{5}{2} (8.314 \text{ J/mol} \cdot \text{K}) \right] (2.38 \times 10^3 - 298) \text{ K}$

$$\Delta E_{\text{int}} = 1.80 \times 10^6 \text{ J}$$

$$Q = \Delta E_{\text{int}} - W = 1.80 \times 10^6 \text{ J} + 4.80 \times 10^5 \text{ J} = 2.28 \times 10^6 \text{ J} = \boxed{2.28 \text{ MJ}}$$

**P21.54** The ball loses energy  $\frac{1}{2} m v_i^2 - \frac{1}{2} m v_f^2 = \frac{1}{2} (0.142 \text{ kg}) [(47.2)^2 - (42.5)^2] \text{ m}^2/\text{s}^2 = 29.9 \text{ J}$

The air volume is  $V = \pi (0.0370 \text{ m})^2 (19.4 \text{ m}) = 0.0834 \text{ m}^3$

and its quantity is  $n = \frac{PV}{RT} = \frac{1.013 \times 10^5 \text{ Pa} (0.0834 \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K}) (293 \text{ K})} = 3.47 \text{ mol}$

The air absorbs energy as if it were warmed over a stove according to  $Q = nC_p \Delta T$

So

$$\Delta T = \frac{Q}{nC_p} = \frac{29.9 \text{ J}}{3.47 \text{ mol} \left( \frac{7}{2} \right) (8.314 \text{ J/mol} \cdot \text{K})} = \boxed{0.296^\circ \text{C}}$$

**P21.55**  $N_v(v) = 4\pi N \left( \frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(\frac{-m_0 v^2}{2k_B T}\right)$  where  $\exp(x)$  represents  $e^x$

Note that  $v_{\text{mp}} = \left( \frac{2k_B T}{m_0} \right)^{1/2}$

Thus,  $N_v(v) = 4\pi N \left( \frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{(-v^2/v_{\text{mp}}^2)}$

And  $\frac{N_v(v)}{N_v(v_{\text{mp}})} = \left( \frac{v}{v_{\text{mp}}} \right)^2 e^{(1-v^2/v_{\text{mp}}^2)}$

For  $v = \frac{v_{\text{mp}}}{50}$

$$\frac{N_v(v)}{N_v(v_{\text{mp}})} = \left( \frac{1}{50} \right)^2 e^{[1-(1/50)^2]} = 1.09 \times 10^{-3}$$

The other values are computed similarly, with the following results:

$\frac{v}{v_{\text{mp}}}$	$\frac{N_v(v)}{N_v(v_{\text{mp}})}$
$\frac{1}{50}$	$1.09 \times 10^{-3}$
$\frac{1}{10}$	$2.69 \times 10^{-2}$
$\frac{1}{2}$	0.529
1	1.00
2	0.199
10	$1.01 \times 10^{-41}$
50	$1.25 \times 10^{-1082}$

To find the last value, we note:

$$(50)^2 e^{1-2.500} = 2500 e^{-2.499}$$

$$10^{\log 2500} e^{(\ln 10)(-2.499/\ln 10)} = 10^{\log 2500} 10^{-2.499/\ln 10} = 10^{\log 2500 - 2.499/\ln 10} = 10^{-1.081904} = 10^{0.096} \times 10^{-1082}$$

- P21.56** (a) The effect of high angular speed is like the effect of a very high gravitational field on an atmosphere. The result is: The larger-mass molecules settle to the outside while the region at smaller  $r$  has a higher concentration of low-mass molecules.
- (b) Consider a single kind of molecules, all of mass  $m_0$ . To cause the centripetal acceleration of the molecules between  $r$  and  $r + dr$ , the pressure must increase outward according to  $\sum F_r = m_0 a_r$ . Thus,

$$PA - (P + dP)A = -(nm_0 A dr)(r\omega^2)$$

where  $n$  is the number of molecules per unit volume and  $A$  is the area of any cylindrical surface. This reduces to  $dP = nm_0 \omega^2 r dr$ .

But also  $P = nk_B T$ , so  $dP = k_B T dn$ . Therefore, the equation becomes

$$\frac{dn}{n} = \frac{m_0 \omega^2}{k_B T} r dr \quad \text{giving} \quad \int_{n_0}^n \frac{dn}{n} = \frac{m_0 \omega^2}{k_B T} \int_0^r r dr \quad \text{or} \quad \ln(n) \Big|_{n_0}^n = \frac{m_0 \omega^2}{k_B T} \left( \frac{r^2}{2} \right) \Big|_0^r$$

$$\ln\left(\frac{n}{n_0}\right) = \frac{m_0 \omega^2}{2k_B T} r^2 \quad \text{and solving for } n \text{ gives} \quad \boxed{n = n_0 e^{m_0 r^2 \omega^2 / 2k_B T}}$$



**P21.57** First find  $v_{\text{av}}^2$  as  $v_{\text{av}}^2 = \frac{1}{N} \int_0^\infty v^2 N_v dv$ . Let  $a = \frac{m_0}{2k_B T}$

Then,

$$v_{\text{av}}^2 = \frac{[4N\pi^{-1/2}a^{3/2}]}{N} \int_0^\infty v^4 e^{-av^2} dv = [4a^{3/2}\pi^{-1/2}] \frac{3}{8a^2} \sqrt{\frac{\pi}{a}} = \frac{3k_B T}{m}$$

The root-mean square speed is then  $v_{\text{rms}} = \sqrt{v_{\text{av}}^2} = \sqrt{\frac{3k_B T}{m_0}}$

To find the average speed, we have

$$v_{\text{av}} = \frac{1}{N} \int_0^\infty v N_v dv = \frac{(4Na^{3/2}\pi^{-1/2})}{N} \int_0^\infty v^3 e^{-av^2} dv = \frac{4a^{3/2}\pi^{-1/2}}{2a^2} = \sqrt{\frac{8k_B T}{\pi m_0}}$$

**P21.58** We want to evaluate  $\frac{dP}{dV}$  for the function implied by  $PV = nRT = \text{constant}$ , and also for the different function implied by  $PV^\gamma = \text{constant}$ . We can use implicit differentiation:

From  $PV = \text{constant}$   $P \frac{dV}{dV} + V \frac{dP}{dV} = 0$   $\left(\frac{dP}{dV}\right)_{\text{isotherm}} = -\frac{P}{V}$

From  $PV^\gamma = \text{constant}$   $P\gamma V^{\gamma-1} + V^\gamma \frac{dP}{dV} = 0$   $\left(\frac{dP}{dV}\right)_{\text{adiabat}} = -\frac{\gamma P}{V}$

Therefore,  $\left(\frac{dP}{dV}\right)_{\text{adiabat}} = \gamma \left(\frac{dP}{dV}\right)_{\text{isotherm}}$

The theorem is proved.

**\*P21.59** (a)  $n = \frac{PV}{RT} = \frac{(1.013 \times 10^5 \text{ Pa})(5.00 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}$   
 $= 0.203 \text{ mol}$

(b)  $T_B = T_A \left(\frac{P_B}{P_A}\right) = 300 \text{ K} \left(\frac{3.00}{1.00}\right) = 900 \text{ K}$

$T_C = T_B = 900 \text{ K}$

$V_C = V_A \left(\frac{T_C}{T_A}\right) = 5.00 \text{ L} \left(\frac{900}{300}\right) = 15.0 \text{ L}$

(c)  $E_{\text{int}, A} = \frac{3}{2} nRT_A = \frac{3}{2} (0.203 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K}) = 760 \text{ J}$

$E_{\text{int}, B} = E_{\text{int}, C} = \frac{3}{2} nRT_B = \frac{3}{2} (0.203 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(900 \text{ K}) = 2.28 \text{ kJ}$

(d)

	$P$ (atm)	$V$ (L)	$T$ (K)	$E_{\text{int}}$ (kJ)
A	1.00	5.00	300	0.760
B	3.00	5.00	900	2.28
C	1.00	15.00	900	2.28

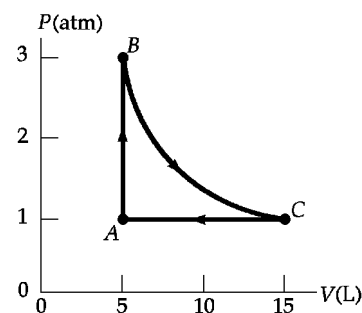


FIG. P21.59

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- (e) For the process  $AB$ , lock the piston in place and put the cylinder into an oven at 900 K. For  $BC$ , keep the sample in the oven while gradually letting the gas expand to lift a load on the piston as far as it can. For  $CA$ , carry the cylinder back into the room at 300 K and let the gas cool without touching the piston.

(f) For  $AB$ :  $W = 0$   $\Delta E_{\text{int}} = E_{\text{int}, B} - E_{\text{int}, A} = (2.28 - 0.760) \text{ kJ} = 1.52 \text{ kJ}$

$$Q = \Delta E_{\text{int}} - W = 1.52 \text{ kJ}$$

For  $BC$ :  $\Delta E_{\text{int}} = 0$ ,  $W = -nRT_B \ln\left(\frac{V_C}{V_B}\right)$

$$W = -(0.203 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(900 \text{ K}) \ln(3.00) = -1.67 \text{ kJ}$$

$$Q = \Delta E_{\text{int}} - W = 1.67 \text{ kJ}$$

For  $CA$ :  $\Delta E_{\text{int}} = E_{\text{int}, A} - E_{\text{int}, C} = (0.760 - 2.28) \text{ kJ} = -1.52 \text{ kJ}$

$$W = -P\Delta V = -nR\Delta T = -(0.203 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(-600 \text{ K}) = 1.01 \text{ kJ}$$

$$Q = \Delta E_{\text{int}} - W = -1.52 \text{ kJ} - 1.01 \text{ kJ} = -2.53 \text{ kJ}$$

- (g) We add the amounts of energy for each process to find them for the whole cycle.

$$Q_{ABCA} = +1.52 \text{ kJ} + 1.67 \text{ kJ} - 2.53 \text{ kJ} = 0.656 \text{ kJ}$$

$$W_{ABCA} = 0 - 1.67 \text{ kJ} + 1.01 \text{ kJ} = -0.656 \text{ kJ}$$

$$(\Delta E_{\text{int}})_{ABCA} = +1.52 \text{ kJ} + 0 - 1.52 \text{ kJ} = 0$$

**P21.60** (a)  $(10\,000 \text{ g}) \left( \frac{1.00 \text{ mol}}{18.0 \text{ g}} \right) \left( \frac{6.02 \times 10^{23} \text{ molecules}}{1.00 \text{ mol}} \right) = 3.34 \times 10^{26} \text{ molecules}$

- (b) After one day,  $10^{-1}$  of the original molecules would remain. After two days, the fraction would be  $10^{-2}$ , and so on. After 26 days, only 3 of the original molecules would likely remain, and after 27 days, likely none.

(c) The soup is this fraction of the hydrosphere:  $\left( \frac{10.0 \text{ kg}}{1.32 \times 10^{21} \text{ kg}} \right)$

Therefore, today's soup likely contains this fraction of the original molecules. The number of original molecules likely in the pot again today is:

$$\left( \frac{10.0 \text{ kg}}{1.32 \times 10^{21} \text{ kg}} \right) (3.34 \times 10^{26} \text{ molecules}) = 2.53 \times 10^6 \text{ molecules}$$

**P21.61** (a) For escape,  $\frac{1}{2} m_0 v^2 = \frac{Gm_0 M}{R_E}$ . Since the free-fall acceleration at the surface is  $g = \frac{GM}{R_E^2}$ , this

can also be written as:

$$\frac{1}{2} m_0 v^2 = \frac{Gm_0 M}{R_E} = m_0 g R_E$$

continued on next page

- (b) For
- $O_2$
- , the mass of one molecule is

$$m_0 = \frac{0.0320 \text{ kg/mol}}{6.02 \times 10^{23} \text{ molecules/mol}} = 5.32 \times 10^{-26} \text{ kg/molecule}$$

Then, if  $m_0 g R_E = 10 \left( \frac{3k_B T}{2} \right)$ , the temperature is

$$T = \frac{m_0 g R_E}{15k_B} = \frac{(5.32 \times 10^{-26} \text{ kg})(9.80 \text{ m/s}^2)(6.37 \times 10^6 \text{ m})}{15(1.38 \times 10^{-23} \text{ J/mol} \cdot \text{K})} = \boxed{1.60 \times 10^4 \text{ K}}$$

- P21.62**
- (a) For sodium atoms (with a molar mass
- $M = 32.0 \text{ g/mol}$
- )

$$\frac{1}{2} m_0 v^2 = \frac{3}{2} k_B T$$

$$\frac{1}{2} \left( \frac{M}{N_A} \right) v^2 = \frac{3}{2} k_B T$$

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J/mol} \cdot \text{K})(2.40 \times 10^{-4} \text{ K})}{23.0 \times 10^{-3} \text{ kg}}} = \boxed{0.510 \text{ m/s}}$$

$$(b) \quad t = \frac{d}{v_{\text{rms}}} = \frac{0.010 \text{ m}}{0.510 \text{ m/s}} = \boxed{20 \text{ ms}}$$

**ANSWERS TO EVEN PROBLEMS**

**P21.2** Because each mole of a chemical compound contains Avogadro's number of molecules, the number of molecules in a sample is  $N_A$  times the number of moles, as described by  $N = nN_A$ , and the molar mass is  $N_A$  times the molecular mass, as described by  $M = m_0 N_A$ . The definition of the molar mass implies that the sample mass is the number of moles times the molar mass, as described by  $m = nM$ . Then the sample mass must also be the number of molecules times the molecular mass, according to  $m = nM = nN_A m_0 = Nm_0$ . The equations are true for chemical compounds in solid, liquid, and gaseous phases—this includes elements. We apply the equations also to air by interpreting  $M$  as the mass of Avogadro's number of the various molecules in the mixture.

**P21.4** 17.6 kPa**P21.6**  $5.05 \times 10^{-21} \text{ J/molecule}$ **P21.8** (a) 2.28 kJ (b)  $6.21 \times 10^{-21} \text{ J}$ **P21.10** see the solution**P21.12** (a) 209 J (b) 0 (c) 317 K**P21.14** (a) 118 kJ (b)  $6.03 \times 10^3 \text{ kg}$ **P21.16** (a) 719 J/kg·K (b) 0.811 kg (c) 233 kJ (d) 327 kJ**P21.18** (a) 0.118 (b) 2.35 (c) 0; +135 J; +135 J**P21.20** (a)  $5.15 \times 10^{-5} \text{ m}^3$  (b) 560 K (c) 2.24 K**P21.22** 25.0 kW**P21.24** (a) see the solution (b)  $2.19 V_i$  (c)  $3T_i$  (d)  $T_i$  (e)  $-0.830P_i V_i$

**P21.26** see the solution

**P21.28**  $2.33 \times 10^{-21} \text{ J}$

**P21.30** (a)  $5R/2$  (b)  $3R$  (c)  $9R/2$  (d)  $5R$  (e) Measure the constant-volume specific heat of the gas as a function of temperature and look for plateaus on the graph, as shown in Figure 21.7. If the first jump goes from  $\frac{3}{2}R$  to  $\frac{5}{2}R$ , the molecules can be diagnosed as linear. If the first jump goes from  $\frac{3}{2}R$  to  $3R$ , the molecules must be nonlinear. The tabulated data at one temperature are insufficient for the determination. At room temperature some of the heavier molecules appear to be vibrating.

**P21.32** (a) No atom, almost all the time (b)  $2.70 \times 10^{20}$

**P21.34** (a) 1.03 (b)  $^{35}\text{Cl}$

**P21.36** (a) 731 m/s (b) 825 m/s (c) 895 m/s (d) The graph appears to be drawn correctly within about 10 m/s.

**P21.38** (a) see the solution (b) 8.31 km

**P21.40** (a)  $7.89 \times 10^{26}$  molecules (b) 37.9 kg (c)  $6.07 \times 10^{-21} \text{ J/molecule}$  (d) 503 m/s (e) 7.98 MJ (f) 7.98 MJ The smaller mass of warmer air contains the same internal energy as the cooler air. When the furnace operates, air expands and leaves the room.

**P21.42** (a)  $3.65v$  (b)  $3.99v$  (c)  $3.00v$  (d)  $106 \left( \frac{m_0 v^2}{V} \right)$  (e)  $7.98 m_0 v^2$

**P21.44** (a) 300 K (b) 1.00 atm

**P21.46** 5.85 MPa

**P21.48** (a) see the solution (b)  $5.1 \times 10^2 \text{ m/s}$  (c)  $v_{\text{av}} = 575 \text{ m/s}$ ;  $v_{\text{rms}} = 624 \text{ m/s}$  (d) 44%

**P21.50** (a) see the solution (b) 344 m/s, in good agreement with Table 17.1 (c) The speed of sound is somewhat less than each measure of molecular speed. Sound propagation is orderly motion overlaid on the disorder of molecular motion.

**P21.52** (a)  $[18 k_B T / \pi \rho d^3]^{1/2} = [4.81 \times 10^{-12} \text{ m}^{5/2}/\text{s}] d^{-3/2}$  (b)  $[2.08 \times 10^{11} \text{ s} \cdot \text{m}^{-5/2}] d^{5/2}$  (c) 0.926 mm/s and 3.24 ms (d)  $1.32 \times 10^{-11} \text{ m/s}$  and  $3.88 \times 10^{10} \text{ s}$  (e)  $29.7 \mu\text{m}$  (f) It is good to use the smallest particles that you can clearly see with some particular microscopic technique.

**P21.54**  $0.296^\circ\text{C}$

**P21.56** (a) The effect of high angular speed is like the effect of a very high gravitational field on an atmosphere. The result is that the larger-mass molecules settle to the outside while the region at smaller  $r$  has a higher concentration of low-mass molecules. (b) see the solution

**P21.58** see the solution

**P21.60** (a)  $3.34 \times 10^{26}$  molecules (b) during the 27th day (c)  $2.53 \times 10^6$  molecules

**P21.62** (a) 0.510 m/s (b) 20 ms