

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 The Boltzmann Distribution Law
- 21.6 Distribution of Molecular Speeds
- 21.7 Mean Free Path

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** Yes. As soon as the gases are mixed, they come to thermal equilibrium. Equation 21.4 predicts that the lighter helium atoms will on average have a greater speed than the heavier nitrogen molecules. Collisions between the different kinds of molecules gives each kind the same average kinetic energy of translation.
- Q21.4** If the average velocity were non-zero, then the bulk sample of gas would be moving in the direction of the average velocity. In a closed tank, this motion would result in a pressure difference within the tank that could not be sustained.
- Q21.5** The alcohol evaporates, absorbing energy from the skin to lower the skin temperature.
- Q21.6** Partially evacuating the container is equivalent to letting the remaining gas expand. This means that the gas does work, making its internal energy and hence its temperature decrease. The liquid in the container will eventually reach thermal equilibrium with the low pressure gas. This effect of an expanding gas decreasing in temperature is a key process in your refrigerator or air conditioner.
- Q21.7** Since the volume is fixed, the density of the cooled gas cannot change, so the mean free path does not change. The collision frequency decreases since each molecule of the gas has a lower average speed.
- Q21.8** The mean free path decreases as the density of the gas increases.
- Q21.9** The volume of the balloon will decrease. The pressure inside the balloon is nearly equal to the constant exterior atmospheric pressure. Then from $PV = nRT$, volume must decrease in proportion to the absolute temperature. Call the process isobaric contraction.

- Q21.10** 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.
- Q21.11** 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.
- Q21.12** A diatomic gas has more degrees of freedom—those of vibration and rotation—than a monatomic gas. The energy content per mole is proportional to the number of degrees of freedom.
- Q21.13**
- (a) Average molecular kinetic energy increases by a factor of 3.
 - (b) The rms speed increases by a factor of $\sqrt{3}$.
 - (c) Average momentum change increases by $\sqrt{3}$.
 - (d) Rate of collisions increases by a factor of $\sqrt{3}$ since the mean free path remains unchanged.
 - (e) Pressure increases by a factor of 3.
- Q21.14** They can, as this possibility is not contradicted by any of our descriptions of the motion of gases. If the vessel contains more than a few molecules, it is highly improbable that all will have the same speed. Collisions will make their speeds scatter according to the Boltzmann distribution law.
- Q21.15** Collisions between molecules are mediated by electrical interactions among their electrons. On an atomic level, collisions of billiard balls work the same way. Collisions between gas molecules are perfectly elastic. Collisions between macroscopic spheres can be very nearly elastic. So the hard-sphere model is very good. On the other hand, an atom is not ‘solid,’ but has small-mass electrons moving through empty space as they orbit the nucleus.
- Q21.16** 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 heat will be conducted into the now-cool parcel from the denser but warmer air below it.
- Q21.17** A more massive diatomic or polyatomic molecule will generally have a lower frequency of vibration. At room temperature, vibration has a higher probability of being excited than in a less massive molecule. The absorption of energy into vibration shows up in higher specific heats.

SOLUTIONS TO PROBLEMS

Section 21.1 Molecular Model of an Ideal Gas

P21.1
$$\bar{F} = Nm \frac{\Delta v}{\Delta t} = 500(5.00 \times 10^{-3} \text{ kg}) \frac{[8.00 \sin 45.0^\circ - (-8.00 \sin 45.0^\circ)] \text{ m/s}}{30.0 \text{ s}} = \boxed{0.943 \text{ N}}$$

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

P21.2
$$\bar{F} = \frac{(5.00 \times 10^{23}) \left[2(4.68 \times 10^{-26} \text{ kg})(300 \text{ m/s}) \right]}{1.00 \text{ s}} = 14.0 \text{ N}$$

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

P21.3 We first find the pressure exerted by the gas on the wall of the container.

$$P = \frac{NkT}{V} = \frac{3N_A k_B T}{V} = \frac{3RT}{V} = \frac{3(8.314 \text{ N} \cdot \text{m/mol} \cdot \text{K})(293 \text{ K})}{8.00 \times 10^{-3} \text{ m}^3} = 9.13 \times 10^5 \text{ Pa}$$

Thus, the force on one of the walls of the cubical container is

$$F = PA = (9.13 \times 10^5 \text{ Pa})(4.00 \times 10^{-2} \text{ m}^2) = \boxed{3.65 \times 10^4 \text{ N}}.$$

P21.4 Use Equation 21.2, $P = \frac{2N}{3V} \left(\frac{mv^2}{2} \right)$, so that

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

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

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

P21.5 $P = \frac{2}{3} \frac{N}{V} (\overline{KE})$ Equation 21.2

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

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

P21.6 One mole of helium contains Avogadro's number of molecules and has a mass of 4.00 g. Let us call m the mass of one atom, and we have

$$N_A m = 4.00 \text{ g/mol}$$

or
$$m = \frac{4.00 \text{ g/mol}}{6.02 \times 10^{23} \text{ molecules/mol}} = 6.64 \times 10^{-24} \text{ g/molecule}$$

$$m = \boxed{6.64 \times 10^{-27} \text{ kg}}$$

P21.7 (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 $m = \frac{4.00 \text{ g/mol}}{6.02 \times 10^{23} \text{ molecules/mol}} = 6.64 \times 10^{-24} \text{ g/molecule}$
 $m = 6.64 \times 10^{-27} \text{ kg/molecule}$

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

P21.8 $v = \sqrt{\frac{3k_B T}{m}}$

$$\frac{v_{\text{O}}}{v_{\text{He}}} = \sqrt{\frac{M_{\text{He}}}{M_{\text{O}}}} = \sqrt{\frac{4.00}{32.0}} = \sqrt{\frac{1}{8.00}}$$

$$v_{\text{O}} = \frac{1350 \text{ m/s}}{\sqrt{8.00}} = \boxed{477 \text{ m/s}}$$

P21.9 (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) $\bar{K} = \frac{1}{2} m v_{\text{rms}}^2 = 8.76 \times 10^{-21} \text{ J}$

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

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

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

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

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

Substituting in (1) above,

we find for helium,

$$\boxed{v_{\text{rms}} = 1.62 \text{ km/s}}$$

and for argon,

$$\boxed{v_{\text{rms}} = 514 \text{ m/s}}$$

P21.10 (a) $PV = nRT = \frac{Nmv^2}{3}$

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

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

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

P21.11 (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 $\frac{E_{\text{trans}}}{V} = \boxed{\frac{3}{2} P}.$

Section 21.2 Molar Specific Heat of an Ideal Gas

P21.12 $E_{\text{int}} = \frac{3}{2}nRT$

$$\Delta E_{\text{int}} = \frac{3}{2}nR\Delta T = \frac{3}{2}(3.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(2.00 \text{ K}) = \boxed{74.8 \text{ J}}$$

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 The piston moves to keep pressure constant. Since $V = \frac{nRT}{P}$, then

$$\Delta V = \frac{nR\Delta T}{P} \text{ for a constant pressure process.}$$

$$Q = nC_P\Delta T = n(C_V + R)\Delta T \text{ so } \Delta T = \frac{Q}{n(C_V + R)} = \frac{Q}{n(5R/2 + R)} = \frac{2Q}{7nR}$$

and $\Delta V = \frac{nR}{P} \left(\frac{2Q}{7nR} \right) = \frac{2Q}{7P} = \frac{2}{7} \frac{QV}{nRT}$

$$\Delta V = \frac{2}{7} \frac{(4.40 \times 10^3 \text{ J})(5.00 \text{ L})}{(1.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})} = 2.52 \text{ L}$$

Thus, $V_f = V_i + \Delta V = 5.00 \text{ L} + 2.52 \text{ L} = \boxed{7.52 \text{ L}}$

P21.15 $n = 1.00 \text{ mol}$, $T_i = 300 \text{ K}$

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

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

- P21.16** (a) Consider heating 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) $U_g = mgy$

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

- *P21.17** (a) We assume that the bulb does not expand. Then this is a constant-volume heating process. The quantity of the gas is $n = \frac{P_i V}{RT_i}$. The energy input is $Q = \mathcal{P} \Delta t = nC_V \Delta T$ so

$$\Delta T = \frac{\mathcal{P} \Delta t}{nC_V} = \frac{\mathcal{P} \Delta t RT_i}{P_i V C_V}.$$

The final temperature is $T_f = T_i + \Delta T = T_i \left(1 + \frac{\mathcal{P} \Delta t R}{P_i V C_V} \right)$.

The final pressure is $P_f = P_i \frac{T_f}{T_i} = P_i \left(1 + \frac{\mathcal{P} \Delta t R}{P_i V C_V} \right)$.

- (b) $P_f = 1 \text{ atm} \left(1 + \frac{3.60 \text{ J/s} \cdot 8.314 \text{ J/mol} \cdot \text{K} \cdot 3 \text{ mol} \cdot \text{K}}{\text{s} \cdot \text{mol} \cdot \text{K} \cdot 1.013 \times 10^5 \text{ N} \cdot 4\pi(0.05 \text{ m})^3 \cdot 12.5 \text{ J}} \right) = \boxed{1.18 \text{ atm}}$

- P21.18** (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.

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

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

P21.19 Consider 800 cm^3 of (flavored) water at 90.0°C mixing with 200 cm^3 of diatomic ideal gas at 20.0°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°C .

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

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

$$(\Delta T)_w = - \frac{\left[(1.20 \times 10^{-3} \text{ g/cm}^3) (200 \text{ cm}^3) \right] (1.01 \text{ J/g} \cdot ^\circ\text{C}) (70.0^\circ\text{C})}{\left[(1.00 \text{ g/cm}^3) (800 \text{ cm}^3) \right] (4186 \text{ J/kg} \cdot ^\circ\text{C})}$$

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

The change of temperature for the water is between 10^{-3}°C and 10^{-2}°C .

P21.20
$$Q = (nC_P \Delta T)_{\text{isobaric}} + (nC_V \Delta T)_{\text{isovolumetric}}$$

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 $6T_i$.

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

P21.21 In the isovolumetric process $A \rightarrow B$, $W = 0$ and $Q = nC_V \Delta T = 500 \text{ J}$

$$500 \text{ J} = n \left(\frac{3R}{2} \right) (T_B - T_A) \text{ or } T_B = T_A + \frac{2(500 \text{ J})}{3nR}$$

$$T_B = 300 \text{ K} + \frac{2(500 \text{ J})}{3(1.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})} = 340 \text{ K}$$

In the isobaric process $B \rightarrow C$,

$$Q = nC_P \Delta T = \frac{5nR}{2} (T_C - T_B) = -500 \text{ J}.$$

Thus,

(a)
$$T_C = T_B - \frac{2(500 \text{ J})}{5nR} = 340 \text{ K} - \frac{1000 \text{ J}}{5(1.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})} = \boxed{316 \text{ K}}$$

(b) The work done on the gas during the isobaric process is

$$W_{BC} = -P_B \Delta V = -nR(T_C - T_B) = -(1.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(316 \text{ K} - 340 \text{ K})$$

or
$$W_{BC} = +200 \text{ J}$$

The work done on the gas in the isovolumetric process is zero, so in total

$$W_{\text{on gas}} = \boxed{+200 \text{ J}}.$$

- *P21.22** (a) At any point in the heating process, $P_i = kV_i$ and $P = kV = \frac{P_i}{V_i}V = \frac{nRT_i}{V_i^2}V$. At the end,

$$P_f = \frac{nRT_i}{V_i^2}2V_i = 2P_i \text{ and } T_f = \frac{P_f V_f}{nR} = \frac{2P_i 2V_i}{nR} = \boxed{4T_i}.$$

- (b) The work input is $W = -\int_i^f P dV = -\int_{V_i}^{2V_i} \frac{nRT_i}{V_i^2} V dV = -\frac{nRT_i}{V_i^2} \frac{V^2}{2} \bigg|_{V_i}^{2V_i} = -\frac{nRT_i}{2V_i^2} (4V_i^2 - V_i^2) = -\frac{3}{2}nRT_i$.

The change in internal energy, is $\Delta E_{\text{int}} = nC_V \Delta T = n \frac{5}{2} R (4T_i - T_i) = +\frac{15}{2} nRT_i$. The heat input is $Q = \Delta E_{\text{int}} - W = \frac{18}{2} nRT_i = \boxed{9(1 \text{ mol})RT_i}$.

- P21.23** (a) The heat required to produce a temperature change is

$$Q = n_1 C_1 \Delta T + n_2 C_2 \Delta T$$

The number of molecules is $N_1 + N_2$, so the number of "moles of the mixture" is $n_1 + n_2$ and $Q = (n_1 + n_2)C\Delta T$,

$$\text{so } C = \boxed{\frac{n_1 C_1 + n_2 C_2}{n_1 + n_2}}.$$

- (b) $Q = \sum_{i=1}^m n_i C_i \Delta T = \left(\sum_{i=1}^m n_i \right) C \Delta T$

$$C = \boxed{\frac{\sum_{i=1}^m n_i C_i}{\sum_{i=1}^m n_i}}$$

Section 21.3 Adiabatic Processes for an Ideal Gas

- P21.24** (a) $P_i V_i^\gamma = P_f V_f^\gamma$ so $\frac{V_f}{V_i} = \left(\frac{P_i}{P_f} \right)^{1/\gamma} = \left(\frac{1.00}{20.0} \right)^{5/7} = \boxed{0.118}$

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

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

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

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

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

P21.25 (a) $P_i V_i^\gamma = P_f V_f^\gamma$
 $P_f = P_i \left(\frac{V_i}{V_f} \right)^\gamma = 5.00 \text{ atm} \left(\frac{12.0}{30.0} \right)^{1.40} = \boxed{1.39 \text{ atm}}$

(b) $T_i = \frac{P_i V_i}{nR} = \frac{5.00 (1.013 \times 10^5 \text{ Pa}) (12.0 \times 10^{-3} \text{ m}^3)}{2.00 \text{ mol} (8.314 \text{ J/mol} \cdot \text{K})} = \boxed{365 \text{ K}}$
 $T_f = \frac{P_f V_f}{nR} = \frac{1.39 (1.013 \times 10^5 \text{ Pa}) (30.0 \times 10^{-3} \text{ m}^3)}{2.00 \text{ mol} (8.314 \text{ J/mol} \cdot \text{K})} = \boxed{253 \text{ K}}$

(c) The process is adiabatic: $\boxed{Q = 0}$
 $\gamma = 1.40 = \frac{C_P}{C_V} = \frac{R + C_V}{C_V}, C_V = \frac{5}{2} R$
 $\Delta E_{\text{int}} = n C_V \Delta T = 2.00 \text{ mol} \left(\frac{5}{2} (8.314 \text{ J/mol} \cdot \text{K}) \right) (253 \text{ K} - 365 \text{ K}) = \boxed{-4.66 \text{ kJ}}$
 $W = \Delta E_{\text{int}} - Q = -4.66 \text{ kJ} - 0 = \boxed{-4.66 \text{ kJ}}$

P21.26 $V_i = \pi \left(\frac{2.50 \times 10^{-2} \text{ m}}{2} \right)^2 0.500 \text{ m} = 2.45 \times 10^{-4} \text{ m}^3$

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) $P_i V_i^\gamma = P_f V_f^\gamma$
 $V_f = V_i \left(\frac{P_i}{P_f} \right)^{1/\gamma} = 2.45 \times 10^{-4} \text{ m}^3 \left(\frac{101.3}{901.3} \right)^{5/7}$
 $V_f = \boxed{5.15 \times 10^{-5} \text{ m}^3}$

(b) $P_f V_f = nRT_f$
 $T_f = T_i \frac{P_f V_f}{P_i V_i} = T_i \frac{P_f}{P_i} \left(\frac{P_i}{P_f} \right)^{1/\gamma} = T_i \left(\frac{P_i}{P_f} \right)^{(1/\gamma - 1)}$
 $T_f = 300 \text{ K} \left(\frac{101.3}{901.3} \right)^{(5/7 - 1)} = \boxed{560 \text{ K}}$

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

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

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

continued on next page

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

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

$$53.9 \text{ J} = (9.97 \times 10^{-3} \text{ mol}) \frac{5}{2} (8.314 \text{ J/mol} \cdot \text{K})(T_{ff} - 300 \text{ K}) \\ + (53.3 \times 10^{-3} \text{ kg})(448 \text{ J/kg} \cdot \text{K})(T_{ff} - 300 \text{ K})$$

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

$$T_{ff} - 300 \text{ K} = \boxed{2.24 \text{ K}}$$

P21.27 $\frac{T_f}{T_i} = \left(\frac{V_i}{V_f} \right)^{\gamma-1} = \left(\frac{1}{2} \right)^{0.400}$

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

***P21.28** (a) In $P_i V_i^\gamma = P_f V_f^\gamma$ we have $P_f = P_i \left(\frac{V_i}{V_f} \right)^\gamma$

$$P_f = P_i \left(\frac{0.720 \text{ m}^3}{0.240 \text{ m}^3} \right)^{1.40} = 4.66 P_i$$

$$\text{Then } \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \quad T_f = T_i \frac{P_f V_f}{P_i V_i} = T_i (4.66) \frac{1}{3} = 1.55$$

The factor of increase in temperature is the same as the factor of increase in internal energy, according to $E_{\text{int}} = nC_V T$. Then $\frac{E_{\text{int},f}}{E_{\text{int},i}} = \boxed{1.55}$.

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

$$2 = \left(\frac{0.720 \text{ m}^3}{V_f} \right)^{0.40}$$

$$\frac{0.720 \text{ m}^3}{V_f} = 2^{1/0.4} = 2^{2.5} = 5.66$$

$$V_f = \frac{0.720 \text{ m}^3}{5.66} = \boxed{0.127 \text{ m}^3}$$

P21.29 (a) See the diagram at the right.

$$\begin{aligned}
 (b) \quad P_B V_B^\gamma &= P_C V_C^\gamma \\
 3P_i V_i^\gamma &= P_i V_C^\gamma \\
 V_C &= (3^{1/\gamma}) V_i = (3^{5/7}) V_i = 2.19 V_i \\
 V_C &= 2.19(4.00 \text{ L}) = \boxed{8.77 \text{ L}}
 \end{aligned}$$

$$\begin{aligned}
 (c) \quad P_B V_B &= nRT_B = 3P_i V_i = 3nRT_i \\
 T_B &= 3T_i = 3(300 \text{ K}) = \boxed{900 \text{ K}}
 \end{aligned}$$

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

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

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

$$P_C V_C = nRT_C = P_i(2.19V_i) = (2.19)nRT_i$$

$$\text{so } T_C = 2.19T_i$$

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

For the whole cycle,

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

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

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

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

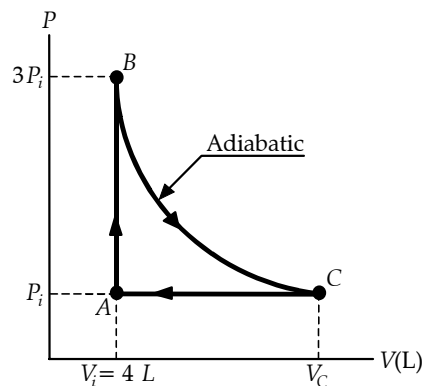


FIG. P21.29

P21.30 (a) See the diagram at the right.

$$\begin{aligned}
 (b) \quad P_B V_B^\gamma &= P_C V_C^\gamma \\
 3P_i V_i^\gamma &= P_i V_C^\gamma \\
 V_C &= 3^{1/\gamma} V_i = 3^{5/7} V_i = \boxed{2.19 V_i}
 \end{aligned}$$

$$\begin{aligned}
 (c) \quad P_B V_B &= nRT_B = 3P_i V_i = 3nRT_i \\
 T_B &= \boxed{3T_i}
 \end{aligned}$$

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

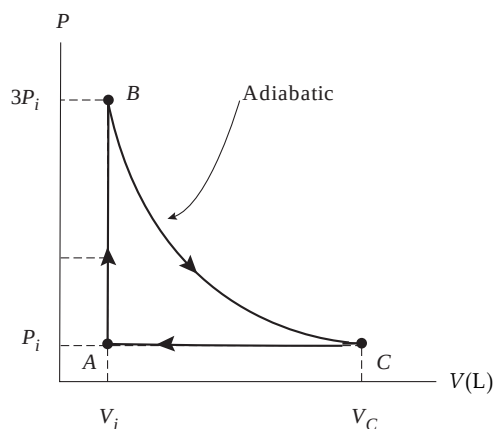


FIG. P21.30

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(e) 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

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

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

For the whole cycle,

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

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

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

P21.31 (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, $W_{ab'} = 5.00 \text{ mol}(8.314 \text{ J/mol}\cdot\text{K})(293 \text{ K})\ln(10.0)$

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

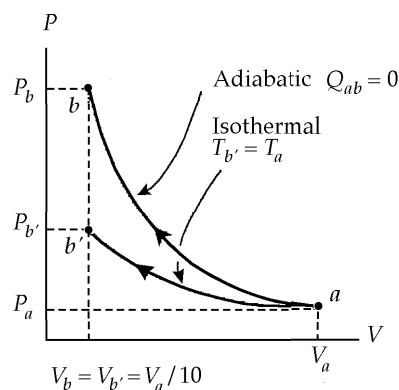


FIG. P21.31

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

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

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

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

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

continued on next page

(c) For the isothermal process, we have

$$P_b V_b = P_a V_a.$$

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

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

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

P21.32 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 $Q = 0$

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

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

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

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

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

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

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

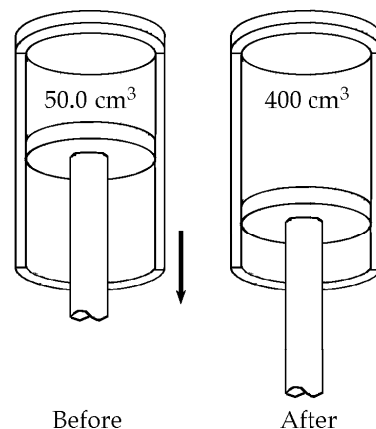


FIG. P21.32

Section 21.4 The Equipartition of Energy

P21.33 The 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

$$nC_V = n\left(\frac{7}{2}R\right) = \boxed{58.2 \text{ J/K}}$$

$$\text{and } nC_P = n\left(\frac{9}{2}R\right) = \boxed{74.8 \text{ J/K}}$$

P21.34 (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) $\gamma = \frac{C_P}{C_V} = \frac{f+2}{f}$

P21.35 Rotational Kinetic Energy $= \frac{1}{2} I \omega^2$

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

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

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

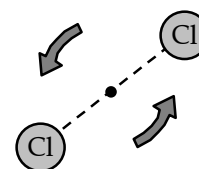


FIG. P21.35

Section 21.5 The Boltzmann Distribution Law

Section 21.6 Distribution of Molecular Speeds

- P21.36** (a) The ratio of the number at higher energy to the number at lower energy is $e^{-\Delta E/k_B T}$ where ΔE 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°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

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

P21.37 (a) $v_{\text{av}} = \frac{\sum n_i v_i}{N} = \frac{1}{15} [1(2) + 2(3) + 3(5) + 4(7) + 3(9) + 2(12)] = \boxed{6.80 \text{ m/s}}$

(b) $(v^2)_{\text{av}} = \frac{\sum n_i v_i^2}{N} = 54.9 \text{ m}^2/\text{s}^2$
 so $v_{\text{rms}} = \sqrt{(v^2)_{\text{av}}} = \sqrt{54.9} = \boxed{7.41 \text{ m/s}}$

(c) $v_{\text{mp}} = \boxed{7.00 \text{ m/s}}$

P21.38 (a) $\frac{V_{\text{rms}, 35}}{V_{\text{rms}, 37}} = \frac{\sqrt{\frac{3RT}{M_{35}}}}{\sqrt{\frac{3RT}{M_{37}}}} = \left(\frac{37.0 \text{ g/mol}}{35.0 \text{ g/mol}} \right)^{1/2} = \boxed{1.03}$

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

P21.39 In the Maxwell Boltzmann speed distribution function take $\frac{dN_v}{dv} = 0$ to find

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

and solve for v to find the most probable speed.

Reject as solutions $v = 0$ and $v = \infty$

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

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

P21.40 The most probable speed is $v_{\text{mp}} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2(1.38 \times 10^{-23} \text{ J/K})(4.20 \text{ K})}{6.64 \times 10^{-27} \text{ kg}}} = \boxed{132 \text{ m/s}}$.

P21.41 (a) From $v_{\text{av}} = \sqrt{\frac{8k_B T}{\pi m}}$

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

P21.42 At 0°C , $\frac{1}{2}mv_{\text{rms}0}^2 = \frac{3}{2}k_B T_0$

At the higher temperature, $\frac{1}{2}m(2v_{\text{rms}0})^2 = \frac{3}{2}k_B T$

$T = 4T_0 = 4(273 \text{ K}) = 1092 \text{ K} = \boxed{819^\circ\text{C}}$.

- *P21.43** (a) From the Boltzmann distribution law, the number density of molecules with gravitational energy mgy is $n_0 e^{-mgy/k_B T}$. These are the molecules with height y , so this is the number per volume at height y as a function of y .

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

- *P21.44** (a) We calculate

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

Using Table B.6 in the appendix

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

$$\text{Then } \bar{y} = \frac{\int_0^\infty y e^{-mgy/k_B T} dy}{\int_0^\infty e^{-mgy/k_B T} dy} = \frac{(k_B T/mg)^2}{k_B T/mg} = \frac{k_B T}{mg}.$$

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

Section 21.7 Mean Free Path

- P21.45** (a) $PV = \left(\frac{N}{N_A} \right) RT$ and $N = \frac{PV N_A}{RT}$ so that

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

$$\text{(b)} \quad \ell = \frac{1}{n_V \pi d^2 2^{1/2}} = \frac{V}{N \pi d^2 2^{1/2}} = \frac{1.00 \text{ m}^3}{(3.21 \times 10^{12} \text{ molecules}) \pi (3.00 \times 10^{-10} \text{ m})^2 (2)^{1/2}}$$

$$\ell = \boxed{779 \text{ km}}$$

$$\text{(c)} \quad f = \frac{v}{\ell} = \boxed{6.42 \times 10^{-4} \text{ s}^{-1}}$$

P21.46 The average molecular speed is

$$v = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8k_B N_A T}{\pi N_A m}}$$

$$v = \sqrt{\frac{8RT}{\pi M}}$$

$$v = \sqrt{\frac{8(8.314 \text{ J/mol} \cdot \text{K})3.00 \text{ K}}{\pi(2.016 \times 10^{-3} \text{ kg/mol})}}$$

$$v = 178 \text{ m/s}$$

(a) The mean free path is

$$\ell = \frac{1}{\sqrt{2}\pi d^2 n_V} = \frac{1}{\sqrt{2}\pi(0.200 \times 10^{-9} \text{ m})^2 \text{ 1/m}^3}$$

$$\ell = \boxed{5.63 \times 10^{18} \text{ m}}$$

The mean free time is

$$\frac{\ell}{v} = \frac{5.63 \times 10^{18} \text{ m}}{178 \text{ m/s}} = 3.17 \times 10^{16} \text{ s} = \boxed{1.00 \times 10^9 \text{ yr}}.$$

(b) Now n_V is 10^6 times larger, to make ℓ smaller by 10^6 times:

$$\ell = \boxed{5.63 \times 10^{12} \text{ m}}.$$

$$\text{Thus, } \frac{\ell}{v} = 3.17 \times 10^{10} \text{ s} = \boxed{1.00 \times 10^3 \text{ yr}}.$$

P21.47 From Equation 21.30, $\ell = \frac{1}{\sqrt{2}\pi d^2 n_V}$

For an ideal gas, $n_V = \frac{N}{V} = \frac{P}{k_B T}$

Therefore, $\ell = \frac{k_B T}{\sqrt{2}\pi d^2 P}$, as required.

P21.48 $\ell = \left[\sqrt{2}\pi d^2 n_V \right]^{-1}$ $n_V = \frac{P}{k_B T}$

$$d = 3.60 \times 10^{-10} \text{ m} \quad n_V = \frac{1.013 \times 10^5}{(1.38 \times 10^{-23})(293)} = 2.51 \times 10^{25} / \text{m}^3$$

$$\therefore \ell = 6.93 \times 10^{-8} \text{ m, or about } \boxed{193 \text{ molecular diameters}}.$$

P21.49 Using $P = n_V k_B T$, Equation 21.30 becomes $\ell = \frac{k_B T}{\sqrt{2\pi} P d^2}$ (1)

$$(a) \quad \ell = \frac{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{\sqrt{2\pi}(1.013 \times 10^5 \text{ Pa})(3.10 \times 10^{-10} \text{ m})^2} = \boxed{9.36 \times 10^{-8} \text{ m}}$$

(b) Equation (1) shows that $P_1 \ell_1 = P_2 \ell_2$. Taking $P_1 \ell_1$ from (a) and with $\ell_2 = 1.00 \text{ m}$, we find

$$P_2 = \frac{(1.00 \text{ atm})(9.36 \times 10^{-8} \text{ m})}{1.00 \text{ m}} = \boxed{9.36 \times 10^{-8} \text{ atm}}.$$

(c) For $\ell_3 = 3.10 \times 10^{-10} \text{ m}$, we have

$$P_3 = \frac{(1.00 \text{ atm})(9.36 \times 10^{-8} \text{ m})}{3.10 \times 10^{-10} \text{ m}} = \boxed{302 \text{ atm}}.$$

Additional Problems

P21.50 (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) $\frac{1}{2} m_0 v^2 = \frac{3}{2} k_B T = \frac{3}{2} (1.38 \times 10^{-23} \text{ J/K})(293 \text{ K}) = \boxed{6.07 \times 10^{-21} \text{ J/molecule}}$

(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) $E_{\text{int}} = nC_V T = n\left(\frac{5}{2} R\right) T = \frac{5}{2} PV$

$$E_{\text{int}} = \frac{5}{2} (1.013 \times 10^5 \text{ Pa})(31.5 \text{ m}^3) = \boxed{7.98 \text{ MJ}}$$

P21.51 (a) $P_f = \boxed{100 \text{ kPa}}$ $T_f = \boxed{400 \text{ K}}$

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

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

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

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

(b) $T_f = \boxed{400 \text{ K}}$ $V_f = V_i = \frac{nRT_i}{P_i} = \frac{2.00 \text{ mol}(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{100 \times 10^3 \text{ Pa}} = 0.0499 \text{ m}^3 = \boxed{49.9 \text{ L}}$

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

$$\Delta E_{\text{int}} = \boxed{5.82 \text{ kJ}} \text{ as in part (a)} \quad Q = \Delta E_{\text{int}} - W = 5.82 \text{ kJ} - 0 = \boxed{5.82 \text{ kJ}}$$

(c) $P_f = \boxed{120 \text{ kPa}}$ $T_f = \boxed{300 \text{ K}}$

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

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

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

$$Q = \Delta E_{\text{int}} - W = 0 - 910 \text{ J} = \boxed{-909 \text{ J}}$$

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

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

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

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

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

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

- P21.52** (a) The average speed v_{av} is just the weighted average of all the speeds.

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

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

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

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

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

- (d) $PV = \frac{1}{3}Nmv_{\text{av}}^2$

$$\text{Therefore, } P = \frac{20}{3} \frac{[m(15.95)v^2]}{V} = \boxed{106 \left(\frac{mv^2}{V} \right)}.$$

- (e) The average kinetic energy for each particle is

$$\bar{K} = \frac{1}{2}mv_{\text{av}}^2 = \frac{1}{2}m(15.95v^2) = \boxed{7.98mv^2}.$$

- P21.53** (a) $PV^\gamma = k$. So, $W = -\int_i^f P dV = -k \int_i^f \frac{dV}{V^\gamma} = \frac{P_f V_f - P_i V_i}{\gamma - 1}$

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

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

To show consistency between these 2 equations, consider that $\gamma = \frac{C_p}{C_V}$ and $C_p - C_V = R$.

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

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 $W = nC_V(T_f - T_i)$.

***P21.54** (a) $W = nC_V(T_f - T_i)$

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

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

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

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

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

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

***P21.55** 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.

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

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

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

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

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

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

Solving equations (1) and (2) simultaneously gives

$$\boxed{T_{1f} = 510 \text{ K}, T_{2f} = 290 \text{ K}}.$$

***P21.56** The work done by the gas on the bullet becomes its 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 work on the gas is

$$\frac{1}{\gamma - 1}(P_f V_f - P_i V_i) = -7.92 \text{ J}.$$

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

So $-7.92 \text{ J} = \frac{1}{0.40} P_i \left[V_f \left(\frac{V_i}{V_f} \right)^\gamma - V_i \right]$.

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

Then $P_i = \frac{-7.92 \text{ J}(0.40)10^6 \text{ cm}^3/\text{m}^3}{\left[13.5 \text{ cm}^3 \left(\frac{12}{13.5} \right)^{1.40} - 12 \text{ cm}^3 \right]} = \boxed{5.74 \times 10^6 \text{ Pa}} = 56.6 \text{ atm}.$

P21.57 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:

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

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

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

P21.58 (a) Maxwell's speed distribution function is

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

With

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

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

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

and

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

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 $0 \leq v \leq 1500 \text{ m/s}$.

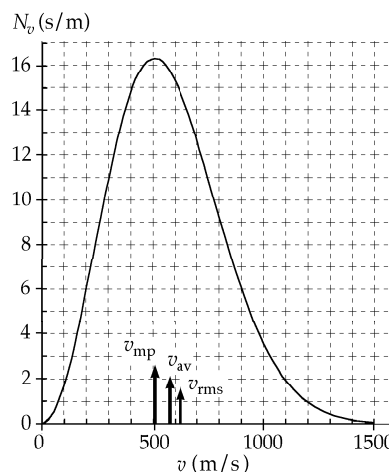


FIG. P21.58(a)

continued on next page

624 The Kinetic Theory of Gases

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

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

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

Also,

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

- (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 4 400 and the fraction is 0.44 or 44% .

- P21.59** (a) Since pressure increases as volume decreases (and vice versa),

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

- (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

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

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

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

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

P21.60 (a) The speed of sound is $v = \sqrt{\frac{B}{\rho}}$ where $B = -V \frac{dP}{dV}$.

According to Problem 59, 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 nearly agrees with the 343 m/s listed in Table 17.1.

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

The most probable molecular speed is $\sqrt{\frac{2k_B T}{m}}$,

the average speed is $\sqrt{\frac{8k_B T}{\pi m}}$, and the rms speed is $\sqrt{\frac{3k_B T}{m}}$.

All are somewhat larger than the speed of sound.

P21.61 $n = \frac{m}{M} = \frac{1.20 \text{ kg}}{0.0289 \text{ kg/mol}} = 41.5 \text{ mol}$

(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) $W = - \int_{V_i}^{V_f} P dV = -C \int_{V_i}^{V_f} V^{1/2} dV = - \left(\frac{P_i}{V_i^{1/2}} \right) \frac{2V^{3/2}}{3} \bigg|_{V_i}^{V_f} = - \frac{2}{3} \left(\frac{P_i}{V_i^{1/2}} \right) (V_f^{3/2} - V_i^{3/2})$

$W = - \frac{2}{3} \left(\frac{200 \times 10^3 \text{ Pa}}{\sqrt{0.514 \text{ m}^3}} \right) \left[(2.06 \text{ m}^3)^{3/2} - (0.514 \text{ m}^3)^{3/2} \right] = \boxed{-4.80 \times 10^5 \text{ J}}$

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

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

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

P21.62 The ball loses energy $\frac{1}{2}mv_i^2 - \frac{1}{2}mv_f^2 = \frac{1}{2}(0.142 \text{ kg})[(47.2)^2 - (42.5)^2] \text{ m}^2/\text{s}^2 = 29.9 \text{ J}$

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 according to

$$Q = nC_p \Delta T$$

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

P21.63 $N_v(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2k_B T} \right)$

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

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

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:

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

To find the last value, note:

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

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

- P21.64** (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 . To cause the centripetal acceleration of the molecules between r and $r + dr$, the pressure must increase outward according to $\sum F_r = ma_r$. Thus,

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

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

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

$$\frac{dn}{n} = \frac{m\omega^2}{k_B T} r dr \text{ giving } \int_{n_0}^n \frac{dn}{n} = \frac{m\omega^2}{k_B T} \int_0^r r dr \text{ or}$$

$$\ln(n) \Big|_{n_0}^n = \frac{m\omega^2}{k_B T} \left(\frac{r^2}{2} \right) \Big|_0^r$$

$$\ln\left(\frac{n}{n_0}\right) = \frac{m\omega^2}{2k_B T} r^2 \text{ and solving for } n: \boxed{n = n_0 e^{mr^2\omega^2/2k_B T}}.$$

- P21.65** First find v_{av}^2 as $v_{av}^2 = \frac{1}{N} \int_0^\infty v^2 N_v dv$. Let $a = \frac{m}{2k_B T}$.

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

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

To find the average speed, we have

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

- *P21.66** 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:

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

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

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

The theorem is proved.

P21.67 (a) $n = \frac{PV}{RT} = \frac{(1.013 \times 10^5 \text{ Pa})(5.00 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})} = \boxed{0.203 \text{ mol}}$

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

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

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

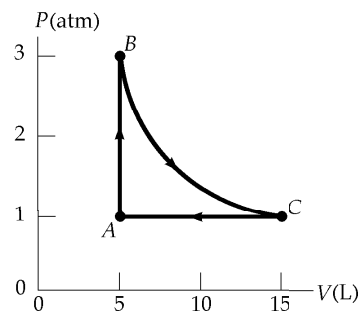


FIG. P21.67

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

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

(d)

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

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

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

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

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

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

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

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

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

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

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

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

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

P21.68 (a) $(10\,000\text{ g})\left(\frac{1.00\text{ mol}}{18.0\text{ g}}\right)\left(\frac{6.02 \times 10^{23}\text{ molecules}}{1.00\text{ mol}}\right) = \boxed{3.34 \times 10^{26}\text{ molecules}}$

- (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 $\boxed{27\text{ days}}$, 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:

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

P21.69 (a) For escape, $\frac{1}{2}mv^2 = \frac{GmM}{R_E}$. Since the free-fall acceleration at the surface is $g = \frac{GM}{R_E^2}$, this can also be written as: $\frac{1}{2}mv^2 = \frac{GmM}{R_E} = \boxed{mgR_E}$.

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

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

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

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

P21.70 (a) For sodium atoms (with a molar mass $M = 32.0\text{ g/mol}$)

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

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

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

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

ANSWERS TO EVEN PROBLEMS

P21.2	17.6 kPa	P21.42	819°C
P21.4	5.05×10^{-21} J/molecule	P21.44	(a) see the solution; (b) 8.31 km
P21.6	6.64×10^{-27} kg	P21.46	(a) 5.63×10^{18} m; 1.00×10^9 yr; (b) 5.63×10^{12} m; 1.00×10^3 yr
P21.8	477 m/s	P21.48	193 molecular diameters
P21.10	(a) 2.28 kJ; (b) 6.21×10^{-21} J	P21.50	(a) 7.89×10^{26} molecules; (b) 37.9 kg; (c) 6.07×10^{-21} J/molecule; (d) 503 m/s; (e) 7.98 MJ; (f) 7.98 MJ
P21.12	74.8 J	P21.52	(a) $3.65v$; (b) $3.99v$; (c) $3.00v$; (d) $106 \left(\frac{mv^2}{V} \right)$; (e) $7.98mv^2$
P21.14	7.52 L	P21.54	(a) 300 K; (b) 1.00 atm
P21.16	(a) 118 kJ; (b) 6.03×10^3 kg	P21.56	5.74×10^6 Pa
P21.18	(a) 719 J/kg·K; (b) 0.811 kg; (c) 233 kJ; (d) 327 kJ	P21.58	(a) see the solution; (b) 5.1×10^2 m/s; (c) $v_{av} = 575$ m/s; $v_{rms} = 624$ m/s; (d) 44%
P21.20	13.5PV	P21.60	(a) see the solution; (b) 344 m/s nearly agreeing with the tabulated value; (c) see the solution; somewhat smaller than each
P21.22	(a) $4T_i$; (b) $9(1 \text{ mol})RT_i$	P21.62	0.296°C
P21.24	(a) 0.118; (b) 2.35; (c) 0; 135 J; 135 J	P21.64	see the solution
P21.26	(a) 5.15×10^{-5} m ³ ; (b) 560 K; (c) 2.24 K	P21.66	see the solution
P21.28	(a) 1.55; (b) 0.127 m^3	P21.68	(a) 3.34×10^{26} molecules; (b) during the 27th day; (c) 2.53×10^6 molecules
P21.30	(a) see the solution; (b) $2.19V_i$; (c) $3T_i$; (d) T_i ; (e) $-0.830P_iV_i$	P21.70	(a) 0.510 m/s; (b) 20 ms
P21.32	25.0 kW		
P21.34	see the solution		
P21.36	(a) No atom, almost all the time; (b) 2.70×10^{20}		
P21.38	(a) 1.03; (b) ^{35}Cl		
P21.40	132 m/s		