CHAPTER 18: Kinetic Theory of Gases

Responses to Questions

- 2. The change in temperature when a gas is compressed or when it expands against a piston is due to the increase or decrease in the average speed of the molecules. The increase or decrease in speed comes about when the gas molecules collide elastically with the moving piston. In the case of compression, the piston is moving toward the molecules. The net result is an increase in the momentum of the gas molecules. When the gas expands, the piston is moving away from the gas molecules. In this case the net result of collisions between the molecules and the piston is a decrease in the momentum of the molecules. (See Section 9-5.)
- 12. (a)If the pressure is doubled while the volume is held constant, the temperature also doubles. v_{rms} is proportional to the square root of temperature, so it will increase by a factor of the square root of two.
 - (*b*)The average velocity is also proportional to the square root of the temperature, so it will increase by a factor of the square root of two as well.
- 13. Evaporation. Only molecules in a liquid that are traveling fast enough will be able to escape the surface of the liquid and evaporate.
- 14. No. Boiling occurs when the saturated vapor pressure and the external pressure are equal. At that point bubbles will be able to form in the liquid. For water at 100°C, the saturated vapor pressure is 1 atm. If the external pressure is also 1 atm, then the water will boil at 100°C. If the water is at 100°C and the external pressure is greater than 1 atm (such as in a pressure cooker), the saturated vapor pressure will still be 1 atm, but bubbles will not be able to form and the water will not boil because the external pressure is higher. The saturated vapor pressure does not depend on the external pressure, but the temperature of boiling does.
- 16. On a hot day, cooling occurs through evaporation of perspiration. If the day is hot and *dry*, then the partial pressure of water vapor in the air will be low and evaporation will readily occur, since the saturated vapor pressure for water will be higher than the external pressure. If the day is hot and *humid*, then the partial pressure of water vapor in the air will be much higher and the air will be holding all or nearly all the water vapor it can. In this case evaporation will not occur as readily, resulting in less cooling.
- 21. (a) A pressure cooker, by definition, increases the pressure on what is inside it. An increased pressure yields a higher boiling point. The water in which the food is usually prepared will boil at a higher temperature than normal, thereby cooking the food faster. (b) At high altitudes, the atmospheric pressure is less than it is at sea level. If atmospheric pressure decreases, the boiling point of water will decrease. Boiling occurs at a lower temperature. Food (including pasta and rice) will need to cook longer at this lower temperature to be properly prepared. (c) It is actually easier to boil water at higher altitude, because it boils at a lower temperature.

Solutions to Problems

2. The rms speed is given by Eq. 18-5, $v_{\rm rms} = \sqrt{3kT/m}$. Helium has an atomic mass of 4.0.

$$v_{\rm rms} = \sqrt{3kT/m} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(6000 \text{ K})}{4.0(1.66 \times 10^{-27} \text{ kg})}} = 6116 \text{ m/s} \approx \boxed{6 \times 10^3 \text{ m/s}}$$

3. The rms speed is given by Eq. 18-5, $v_{\rm rms} = \sqrt{3kT/m}$. The temperature must be in Kelvins.

$$\frac{(v_{\rm rms})_2}{(v_{\rm rms})_1} = \frac{\sqrt{3kT_2/m}}{\sqrt{3kT_1/m}} = \sqrt{\frac{T_2}{T_1}} = \sqrt{\frac{453 \text{ K}}{273 \text{ K}}} = \boxed{1.29}$$

6. (a) The average molecular kinetic energy is $\frac{3}{2}kT$, so the total kinetic energy for a mole would be Avogadro's number times $\frac{3}{2}kT$.

$$K = N_0 \left(\frac{3}{2} kT\right) = \frac{3}{2} RT = \frac{3}{2} \left(8.314 \text{ J/molgK}\right) \left(273 \text{ K} + 15 \text{ K}\right) = \boxed{3740 \text{ J}}$$

(b) $K = \frac{1}{2} mv^2 = 3704 \text{ J} \rightarrow v = \sqrt{\frac{2(3740 \text{ J})}{65 \text{ kg}}} = \boxed{11 \text{ m/s}}$

7.

The mean (average) speed is as follows.

$$v_{\text{avg}} = \frac{6.0 + 2.0 + 4.0 + 6.0 + 0.0 + 4.0 + 1.0 + 8.0 + 5.0 + 3.0 + 7.0 + 8.0}{12} = \frac{54.0}{12} = \boxed{4.5}.$$

The rms speed is the square root of the mean (average) of the squares of the speeds.

$$v_{\rm rms} = \sqrt{\frac{6.0^2 + 2.0^2 + 4.0^2 + 6.0^2 + 0.0^2 + 4.0^2 + 1.0^2 + 8.0^2 + 5.0^2 + 3.0^2 + 7.0^2 + 8.0^2}{12}}$$
$$= \sqrt{\frac{320}{12}} = \boxed{5.2}$$

9. From the ideal gas law, PV = nRT, if the volume and amount of gas are held constant, the temperature is proportional to the pressure, $PV = nRT \rightarrow P = \frac{nR}{V}T = (\text{constant})T$. Thus the temperature will be tripled. Since the rms speed is proportional to the square root of the temperature, $v_{\text{rms}} = \sqrt{3kT/m} = (\text{constant})\sqrt{T}$, v_{rms} will be multiplied by a factor of $\sqrt{3} \approx 1.73$.

11. The rms speed is given by Eq. 18-5,
$$v_{\rm rms} = \sqrt{3kT/m}$$
.

$$\frac{(v_{\rm rms})_2}{(v_{\rm rms})_1} = \frac{\sqrt{3kT/m_2}}{\sqrt{3kT/m_1}} \rightarrow \frac{(v_{\rm rms})_2}{(v_{\rm rms})_1} = \sqrt{\frac{m_1}{m_2}}$$

14. Assume that oxygen is an ideal gas, and that each molecule occupies the same cubical volume of I^{3} . Find the volume per molecule from the ideal gas law, and then the side length of that cubical molecular volume will be an estimate of the average distance between molecules.

$$PV = NkT \rightarrow \frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(273 \text{ K})}{1.01 \times 10^5 \text{ Pa}} = 3.73 \times 10^{-26} \text{ m}^3/\text{molecule}$$
$$I = \left(\frac{kT}{P}\right)^{1/3} = \left(\frac{(1.38 \times 10^{-23} \text{ J/K})(273 \text{ K})}{1.01 \times 10^5 \text{ Pa}}\right)^{1/3} = \boxed{3.34 \times 10^{-9} \text{ m}}$$

19. In the Maxwell distribution, Eq. 18-6, we see that the mass and temperature always occur as a ratio. Thus if the mass has been doubled, doubling the temperature will keep the velocity distribution constant.

21. (a) We find the rms speed by taking the square root of the average squared speed.

$$v_{\rm rms} = \sqrt{\frac{1}{N} \sum_{i} n_{i} v_{i}^{2}} = \sqrt{\frac{1}{15,200}} \begin{bmatrix} 1600 (220 \,\text{m/s})^{2} + 4100 (440 \,\text{m/s})^{2} + 4700 (660 \,\text{m/s})^{2} \\ +3100 (880 \,\text{m/s})^{2} + 1300 (1100 \,\text{m/s})^{2} + 400 (1320 \,\text{m/s})^{2} \end{bmatrix}$$

$$= 706.6 \,\text{m/s} \approx \boxed{710 \,\text{m/s}}$$

(b) The temperature is related to the rms speed by Eq. 18-5.

$$v_{\rm rms} = \sqrt{\frac{3kT}{m}} \rightarrow T = \frac{mv_{\rm rms}^2}{3k} = \frac{(2.00 \times 10^{-26} \,\text{kg})(706.6 \,\text{m/s})^2}{3(1.38 \times 10^{-23} \,\text{J/K})} = 241.2 \,\text{K} \approx 240 \,\text{K}$$

(c) Find the average speed, and then use a result from Example 18-5.

$$\overline{v} = \frac{1}{N} \sum_{i} n_{i} v_{i} = \frac{1}{15,200} \begin{bmatrix} 1600(220 \text{ m/s}) + 4100(440 \text{ m/s}) + 4700(660 \text{ m/s}) \\ +3100(880 \text{ m/s}) + 1300(1100 \text{ m/s}) + 400(1320 \text{ m/s}) \end{bmatrix}$$
$$= 654.2 \text{ m/s} \approx \boxed{650 \text{ m/s}}$$
$$\overline{v} = \sqrt{\frac{8}{\pi} \frac{kT}{m}} \rightarrow T = \frac{\pi m \overline{v}^{2}}{8k} = \frac{\pi (2.00 \times 10^{-26} \text{ kg})(654.2 \text{ m/s})^{2}}{8(1.38 \times 10^{-23} \text{ J/K})} = 243.6 \text{ K} \approx \boxed{240 \text{ K}}$$

Yes, the temperatures are consistent.

22. (a) Show that $\int_{0}^{\infty} f(v) dv = N$. We use a change of variable, and we make use of an integral

from Appendix B-5; specifically,
$$\int_{0}^{\infty} x^{2} e^{-ax^{2}} dx = \sqrt{\frac{\pi}{16a^{3}}}.$$
$$\int_{0}^{\infty} f(v) dv = \int_{0}^{\infty} 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^{2} e^{-\frac{1}{2}\frac{mv^{2}}{kT}} dv$$
$$x = \sqrt{\frac{mv^{2}}{2kT}} \rightarrow x^{2} = \frac{mv^{2}}{2kT} \rightarrow v^{2} = \frac{2kT}{m}x^{2} \rightarrow v = \sqrt{\frac{2kT}{m}}x \rightarrow dv = \sqrt{\frac{2kT}{m}} dx$$
$$\int_{0}^{\infty} 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^{2} e^{-\frac{1}{2}\frac{mv^{2}}{kT}} dv = \int_{0}^{\infty} 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{2kT}{m} x^{2} e^{-x^{2}} \sqrt{\frac{2kT}{m}} dx$$
$$= 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{2kT}{m} \sqrt{\frac{2kT}{m}} \int_{0}^{\infty} x^{2} e^{-x^{2}} dx = 4\pi N \left(\frac{1}{\pi}\right)^{3/2} \frac{\sqrt{\pi}}{4} = N$$

(b) Show that $\int_{0}^{\infty} v^{2} f(v) dv / N = \frac{3kT}{m}$. We use the same change of variable as above, and we

make use of an integral from Appendix B-5; specifically, $\int_{0}^{\infty} x^{4} e^{-ax^{2}} dx = \frac{3}{8}\sqrt{\pi}.$

$$\int_{0}^{\infty} v^{2} f(v) dv = \int_{0}^{\infty} 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^{4} e^{-\frac{1mv^{2}}{2kT}} dv$$

$$x = \sqrt{\frac{mv^{2}}{2kT}} \rightarrow x^{2} = \frac{mv^{2}}{2kT} \rightarrow v^{2} = \frac{2kT}{m} x^{2} \rightarrow v = \sqrt{\frac{2kT}{m}} x \rightarrow dv = \sqrt{\frac{2kT}{m}} dx$$

$$\int_{0}^{\infty} 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^{4} e^{-\frac{1mv^{2}}{2kT}} dv = \int_{0}^{\infty} 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{4k^{2}T^{2}}{m^{2}} x^{4} e^{-x^{2}} \sqrt{\frac{2kT}{m}} dx$$

$$= 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{4k^{2}T^{2}}{m^{2}} \sqrt{\frac{2kT}{m}} \int_{0}^{\infty} x^{4} e^{-x^{2}} dx = N \frac{3kT}{m} \rightarrow$$

$$\int_{0}^{\infty} v^{2} f(v) dv = N \frac{3kT}{m} \rightarrow \int_{0}^{\infty} v^{2} f(v) dv / N = \frac{3kT}{m}$$

- (a) From Fig. 18-5, water is vapor when the pressure is 0.01 atm and the temperature is 90°C.
 (b) From Fig. 18-5, water is solid when the pressure is 0.01 atm and the temperature is -20°C.
- 27. From Table 18-2, the saturated vapor pressure at 30°C is 4240 Pa. Since the relative humidity is 85%, the partial pressure of water is as follows.

$$P_{\text{water}} = 0.85 P_{\text{saturated}} = 0.85 (4240 \text{ Pa}) = |3600 \text{ Pa}|$$

- 29. At the boiling temperature, the external air pressure equals the saturated vapor pressure. Thus from Table 18-2, for 80°C the saturated air pressure is 355 torr or $4.73 \times 10^4 \text{ Pa}$ or 0.466 atm.
- 30. From Table 18-2, if the temperature is 25°C, the saturated vapor pressure is 23.8 torr. If the relative humidity is 75%, then the partial pressure of water is 75% of the saturated vapor pressure, or 17.85 torr. The dew point is the temperature at which the saturated vapor pressure is 17.85 torr, and from Table 18-2 that is between 20°C and 25°C. Since there is no entry for 17.85 torr, the temperature can be estimated by a linear interpolation. Between 20°C and 25°C, the temperature change per torr is as follows:

$$\frac{(25-20)C^{\circ}}{(23.8-17.5) \text{ torr}} = 0.7937 C^{\circ}/\text{torr}$$

Thus the temperature corresponding to 17.85 torr is

 $20^{\circ}\text{C} + [(17.85 - 17.5) \text{ torr}](0.7937 \text{ C}^{\circ}/\text{ torr}) = 20.28^{\circ}\text{C} \approx \boxed{20^{\circ}\text{C}}.$

31. At the boiling temperature, the air pressure equals the saturated vapor pressure. The pressure of 0.75 atm is equal to 7.60×10^4 Pa. From Table 18-2, the temperature is between 90°C and 100°C. Since there is no entry for 7.60×10^4 Pa, the temperature can be estimated by a linear interpolation. Between 90°C and 100°C, the temperature change per Pa is as follows:

$$\frac{(100-90)C^{\circ}}{(10.1-7.01)\times10^{4}Pa} = 3.236\times10^{-4} C^{\circ}/Pa.$$

Thus the temperature corresponding to 7.60×10^4 Pa is

$$90^{\circ}\text{C} + \left[(7.60 - 7.01) \times 10^{4} \text{Pa} \right] (3.236 \times 10^{-4} \text{ C}^{\circ}/\text{Pa}) = 91.9^{\circ}\text{C} \approx \boxed{92^{\circ}\text{C}}.$$

32. The volume, temperature, and pressure of the water vapor are known. We use the ideal gas law to calculate the mass. The pressure must be interpolated from Table 18-2. Between 20°C and 25°C, the pressure change per temperature change per C° is as follows.

$$\frac{(3170 - 2330) \operatorname{Pa}}{(25 - 20) \operatorname{C}^{\circ}} = 168 \operatorname{Pa}/\operatorname{C}^{\circ}$$

Thus the saturated vapor pressure at 20° C is $2330 \text{ Pa} + (168 \text{ Pa}/\text{C}^{\circ})4\text{C}^{\circ} = 3000 \text{ Pa}$.

$$PV = nRT \rightarrow n = \frac{PV}{RT} = \frac{(0.65)(3000 \,\text{Pa})(5.0 \,\text{m})(6.0 \,\text{m})(2.4 \,\text{m})}{(8.314 \,\text{J/molgK})(273.15 \,\text{K} + 24.0 \,\text{K})} = 56.8 \,\text{mol}$$
$$m_{\text{H}_{2}\text{O}} = (56.8 \,\text{mol})(0.018 \,\text{kg/mol}) = \boxed{1.0 \,\text{kg}}$$

40. For one mole of gas, the "lost" volume (the volume occupied by the molecules) is the value of *b*. We assume spherical molecules.

$$b = N_0 \frac{4}{3} \pi \left(\frac{1}{2} d\right)^3 \rightarrow d = 2 \left(\frac{3b}{4\pi N_0}\right)^{1/3} = 2 \left(\frac{3(3.2 \times 10^{-5} \text{ m}^3/\text{mol})}{4\pi (6.02 \times 10^{23} \text{ molecules/mol})}\right)^{1/3} = 4.7 \times 10^{-10} \text{ m}$$

41. (*a*) Use the van der Waals equation.

$$P = \frac{RT}{(V/n) - b} - \frac{a}{(V/n)^2}$$

= $\frac{(8.314 \text{ J/molgK})(273 \text{ K})}{(0.70 \times 10^{-3} \text{ m}^3/\text{mol}) - (3.2 \times 10^{-5} \text{ m}^3/\text{mol})} - \frac{0.13 \text{ m/s}}{(0.70 \times 10^{-3} \text{ m}^3/\text{mol})^2} = \overline{[3.1 \times 10^6 \text{ Pa}]}$
(b) Use the ideal gas law.
$$PV = nRT \quad \rightarrow \quad P = \frac{nRT}{V} = \frac{(1.0 \text{ mol})(8.314 \text{ J/molgK})(273 \text{ K})}{0.70 \times 10^{-3} \text{ m}^3} = \overline{[3.2 \times 10^6 \text{ Pa}]}$$

48. The mean free path is given by Eq. 18-10b. Combine this with the ideal gas law to find the mean free path-diameter relationship.

$$PV = NkT \rightarrow \frac{N}{V} = \frac{P}{kT} ; I_{\rm M} = \frac{1}{4\pi\sqrt{2}r^2(N/V)} = \frac{kT}{4\pi\sqrt{2}\left(\frac{1}{2}d\right)^2 P} \rightarrow d = \sqrt{\frac{kT}{\sqrt{2}\pi I_{\rm M}P}}$$

(a) $d = \sqrt{\frac{kT}{\sqrt{2}\pi I_{\rm M}P}} = \sqrt{\frac{\left(1.38 \times 10^{-23} \,\text{J/K}\right)\left(273 \,\text{K}\right)}{\sqrt{2}\pi \left(5.6 \times 10^{-8} \,\text{m}\right)\left(1.013 \times 10^5 \,\text{Pa}\right)}} = \boxed{3.9 \times 10^{-10} \,\text{m}}$

(b)
$$d = \sqrt{\frac{kT}{\sqrt{2}\pi I_{\rm M}P}} = \sqrt{\frac{\left(1.38 \times 10^{-23} \,{\rm J/K}\right)\left(273 \,{\rm K}\right)}{\sqrt{2}\pi \left(25 \times 10^{-8} \,{\rm m}\right)\left(1.013 \times 10^{5} \,{\rm Pa}\right)}} = \boxed{1.8 \times 10^{-10} \,{\rm m}}$$

53. We use the equation derived in Eq. 18-9.

$$t = \frac{\overline{C}}{\Delta C} \frac{(\Delta x)^2}{D} = \frac{1}{2} \frac{(1.0 \text{ m})^2}{(4 \times 10^{-5} \text{ m}^2/\text{s})} = 12,500 \text{ s} \approx \boxed{3.5 \text{ h}}$$

Because this time is so long, we see that convection is much more important than diffusion.