

MOLECULES AND CONDENSED MATTER

42.1. IDENTIFY: The minimum energy the photon must have is the energy of the covalent bond.

SET UP: The energy of the photon is $E = \frac{hc}{\lambda}$. Visible light has wavelengths between 380 nm and 750 nm.

EXECUTE: The photon must have energy 4.48 eV. Solving for the wavelength gives

$$\lambda = \frac{hc}{E} = \frac{1.24 \times 10^{-6} \text{ eV} \cdot \text{m}}{4.48 \text{ eV}} = 277 \text{ nm}.$$

EVALUATE: This wavelength is shorter than the wavelengths of visible light so lies in the ultraviolet.

42.2. IDENTIFY and SET UP: $U = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$. The binding energy of the molecule is equal to U plus the ionization energy of K minus the electron affinity of Br.

EXECUTE: (a) $U = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = -5.0 \text{ eV}.$

(b) $-5.0 \text{ eV} + (4.3 \text{ eV} - 3.5 \text{ eV}) = -4.2 \text{ eV}.$

EVALUATE: We expect the magnitude of the binding energy to be somewhat less than this estimate. At this separation the two ions don't behave exactly like point charges and U is smaller in magnitude than our estimate. The experimental value for the binding energy is -4.0 eV , which is smaller in magnitude than our estimate.

42.3. IDENTIFY: The energy of the photon is equal to the energy difference between the $l=1$ and $l=2$ states. This energy determines its wavelength.

SET UP: The reduced mass of the molecule is $m_r = \frac{m_H m_H}{m_H + m_H} = \frac{1}{2} m_H$, its moment of inertia is $I = m_r r_0^2$,

the photon energy is $\Delta E = \frac{hc}{\lambda}$, and the energy of the state l is $E_l = l(l+1) \frac{\hbar^2}{2I}$.

EXECUTE: $I = m_r r_0^2 = \frac{1}{2} (1.67 \times 10^{-27} \text{ kg}) (0.074 \times 10^{-9} \text{ m})^2 = 4.57 \times 10^{-48} \text{ kg} \cdot \text{m}^2$. Using $E_l = l(l+1) \frac{\hbar^2}{2I}$,

the energy levels are $E_2 = 6 \frac{\hbar^2}{2I} = 6 \frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2(4.57 \times 10^{-48} \text{ kg} \cdot \text{m}^2)} = 6(1.218 \times 10^{-21} \text{ J}) = 7.307 \times 10^{-21} \text{ J}$ and

$E_1 = 2 \frac{\hbar^2}{2I} = 2(1.218 \times 10^{-21} \text{ J}) = 2.436 \times 10^{-21} \text{ J}$. $\Delta E = E_2 - E_1 = 4.87 \times 10^{-21} \text{ J}$. Using $\Delta E = \frac{hc}{\lambda}$ gives

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{4.871 \times 10^{-21} \text{ J}} = 4.08 \times 10^{-5} \text{ m} = 40.8 \text{ } \mu\text{m}.$$

EVALUATE: This wavelength is much longer than that of visible light.

42.4. IDENTIFY: The energy decrease of the molecule or atom is equal to the energy of the emitted photon. From this energy, we can calculate the wavelength of the photon.

SET UP: $\Delta E = \frac{hc}{\lambda}$. Use Figure 32.4 in the textbook to find out the region of the electromagnetic spectrum in which each wavelength lies.

(a) EXECUTE: $\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{0.198 \text{ eV}} = 6.26 \text{ } \mu\text{m}.$

EVALUATE: This radiation is in the infrared.

(b) EXECUTE: $\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{7.80 \text{ eV}} = 159 \text{ nm}.$

EVALUATE: This radiation is in the ultraviolet.

(c) EXECUTE: $\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{4.80 \times 10^{-3} \text{ eV}} = 0.258 \text{ mm}.$

EVALUATE: This radiation is in the microwave region.

42.5. IDENTIFY: The energy given to the photon comes from a transition between rotational states.

SET UP: The rotational energy of a molecule is $E = l(l+1)\frac{\hbar^2}{2I}$ and the energy of the photon is $E = hc/\lambda$.

EXECUTE: Use the energy formula, the energy difference between the $l = 3$ and $l = 1$ rotational levels of

the molecule is $\Delta E = \frac{\hbar^2}{2I}[3(3+1) - 1(1+1)] = \frac{5\hbar^2}{I}$. Since $\Delta E = hc/\lambda$, we get $hc/\lambda = 5\hbar^2/I$. Solving for I gives

$$I = \frac{5\hbar\lambda}{2\pi c} = \frac{5(1.055 \times 10^{-34} \text{ J} \cdot \text{s})(1.780 \text{ nm})}{2\pi(3.00 \times 10^8 \text{ m/s})} = 4.981 \times 10^{-52} \text{ kg} \cdot \text{m}^2.$$

Using $I = m_{\text{T}}r_0^2$, we can solve for r_0 :

$$r_0 = \sqrt{\frac{I(m_{\text{N}} + m_{\text{H}})}{m_{\text{N}}m_{\text{H}}}} = \sqrt{\frac{(4.981 \times 10^{-52} \text{ kg} \cdot \text{m}^2)(2.33 \times 10^{-26} \text{ kg} + 1.67 \times 10^{-27} \text{ kg})}{(2.33 \times 10^{-26} \text{ kg})(1.67 \times 10^{-27} \text{ kg})}} = 5.65 \times 10^{-13} \text{ m}.$$

EVALUATE: This separation is much smaller than the diameter of a typical atom and is not very realistic. But we are treating a *hypothetical* NH molecule.

42.6. IDENTIFY: The energy absorbed by the photon is equal to the energy difference between the two rotational states.

SET UP: The rotational energy of a molecule is $E_l = l(l+1)\frac{\hbar^2}{2I}$ and the energy of the photon is the energy

difference ΔE between the states, so $\Delta E = hc/\lambda$. The transition is from the $l = 3$ state to the $l = 4$ state.

EXECUTE: Using the rotational energy formula, the energy difference between the two states is

$$\Delta E = E_4 - E_3 = 4(4+1)\frac{\hbar^2}{2I} - 3(3+1)\frac{\hbar^2}{2I} = 4\frac{\hbar^2}{I}.$$

This is the energy absorbed by the photon, so $\Delta E = hc/\lambda$ gives $hc/\lambda = 4\hbar^2/I$. Solving for λ gives

$$\lambda = \pi^2 I c / h = \pi^2 (4.6 \times 10^{-48} \text{ kg} \cdot \text{m}^2) (3.00 \times 10^8 \text{ m/s}) / (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) = 2.05 \times 10^{-5} \text{ m} = 20.6 \text{ } \mu\text{m}, \text{ which rounds to } 21 \text{ } \mu\text{m}.$$

EVALUATE: Rotational energy changes are much less than transitions between n -shells, so the wavelengths involved are much longer for rotational transitions.

42.7. IDENTIFY and SET UP: The transition energy E and the frequency f of the absorbed photon are related by $E = hf$.

EXECUTE: The energy of the emitted photon is $1.01 \times 10^{-5} \text{ eV}$, and so its frequency and wavelength are

$$f = \frac{E}{h} = \frac{(1.01 \times 10^{-5} \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})} = 2.44 \text{ GHz} = 2440 \text{ MHz and}$$

$$\lambda = \frac{c}{f} = \frac{(3.00 \times 10^8 \text{ m/s})}{(2.44 \times 10^9 \text{ Hz})} = 0.123 \text{ m}.$$

EVALUATE: This frequency corresponds to that given for a microwave oven.

42.8. IDENTIFY: $I = m_1 r_1^2 + m_2 r_2^2$. Since the two atoms are identical, the center of mass is midway between them.

SET UP: Each atom has a mass m and is at a distance $L/2$ from the center of mass.

EXECUTE: The moment of inertia is $2(m)(L/2)^2 = mL^2/2 = 2.21 \times 10^{-44} \text{ kg} \cdot \text{m}^2$.

EVALUATE: $r_0 = L$ and $m_r = m/2$, so $I = m_r r_0^2$ gives the same result.

42.9. IDENTIFY and SET UP: Set $K = E_l$ from Example 42.2. Use $K = \frac{1}{2} I \omega^2$ to solve for ω and $v = r\omega$ to solve for v .

EXECUTE: (a) From Example 42.2, $E_l = 0.479 \text{ meV} = 7.674 \times 10^{-23} \text{ J}$ and $I = 1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2$.

$K = \frac{1}{2} I \omega^2$ and $K = E$ gives $\omega = \sqrt{2E_l/I} = 1.03 \times 10^{12} \text{ rad/s}$.

(b) $v_1 = r_1 \omega_1 = (0.0644 \times 10^{-9} \text{ m})(1.03 \times 10^{12} \text{ rad/s}) = 66.3 \text{ m/s}$ (carbon).

$v_2 = r_2 \omega_2 = (0.0484 \times 10^{-9} \text{ m})(1.03 \times 10^{12} \text{ rad/s}) = 49.8 \text{ m/s}$ (oxygen).

(c) $T = 2\pi/\omega = 6.10 \times 10^{-12} \text{ s}$.

EVALUATE: Even for fast rotation rates, $v \ll c$.

42.10. IDENTIFY: Calculate the energy difference between the $l = 0$ and $l = 1$ levels. Then equate this difference to $\frac{3}{2} kT$.

SET UP: The rotational energy of a molecule is $E_l = l(l+1) \frac{\hbar^2}{2I}$, and $\Delta E = \frac{3}{2} kT$.

EXECUTE: $\Delta E = E_1 - E_0 = 1(1+1) \frac{\hbar^2}{2I} - 0 = \frac{3}{2} kT$. Solving for T gives

$$T = \frac{2\hbar^2}{3kI} = \frac{2(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{3(1.38 \times 10^{-23} \text{ J/K})(4.6 \times 10^{-48} \text{ kg} \cdot \text{m}^2)} = 117 \text{ K, which rounds to } 120 \text{ K.}$$

EVALUATE: This temperature is well below room temperature ($\approx 300 \text{ K}$), so at room temperature colliding molecules will easily have enough energy to excite electrons to the $l = 1$ level.

42.11. IDENTIFY and SET UP: The energy of a rotational level with quantum number l is $E_l = l(l+1)\hbar^2/2I$.

$I = m_r r^2$, with the reduced mass m_r given by $m_r = \frac{m_1 m_2}{m_1 + m_2}$. Calculate I and ΔE and then use $\Delta E = hc/\lambda$ to find λ .

EXECUTE: (a) $m_r = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_{\text{Li}} m_{\text{H}}}{m_{\text{Li}} + m_{\text{H}}} = \frac{(1.17 \times 10^{-26} \text{ kg})(1.67 \times 10^{-27} \text{ kg})}{1.17 \times 10^{-26} \text{ kg} + 1.67 \times 10^{-27} \text{ kg}} = 1.461 \times 10^{-27} \text{ kg}$.

$I = m_r r^2 = (1.461 \times 10^{-27} \text{ kg})(0.159 \times 10^{-9} \text{ m})^2 = 3.694 \times 10^{-47} \text{ kg} \cdot \text{m}^2$.

$$l = 3: E = 3(4) \left(\frac{\hbar^2}{2I} \right) = 6 \left(\frac{\hbar^2}{I} \right).$$

$$l = 4: E = 4(5) \left(\frac{\hbar^2}{2I} \right) = 10 \left(\frac{\hbar^2}{I} \right).$$

$$\Delta E = E_4 - E_3 = 4 \left(\frac{\hbar^2}{I} \right) = 4 \left(\frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{3.694 \times 10^{-47} \text{ kg} \cdot \text{m}^2} \right) = 1.20 \times 10^{-21} \text{ J} = 7.49 \times 10^{-3} \text{ eV}.$$

$$\text{(b) } \Delta E = hc/\lambda \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV})(2.998 \times 10^8 \text{ m/s})}{7.49 \times 10^{-3} \text{ eV}} = 166 \text{ } \mu\text{m}.$$

EVALUATE: LiH has a smaller reduced mass than CO and λ is somewhat smaller here than the λ calculated for CO in Example 42.2.

42.12. IDENTIFY: For a $n \rightarrow n-1$ vibrational transition, $\Delta E = \hbar \sqrt{\frac{k'}{m_r}}$. ΔE is related to λ of the photon by $\Delta E = \frac{hc}{\lambda}$.

SET UP: $m_r = \frac{m_{\text{Na}} m_{\text{Cl}}}{m_{\text{Na}} + m_{\text{Cl}}}$.

EXECUTE: $\Delta E = \frac{hc}{\lambda} = \hbar \sqrt{k'/m_r}$, and solving for k' , $k' = \left(\frac{2\pi c}{\lambda}\right)^2 m_r = 205 \text{ N/m}$.

EVALUATE: The value of k' we calculated for NaCl is comparable to that of a fairly stiff lab spring.

42.13. IDENTIFY: The vibrational energy of the molecule is related to its force constant and reduced mass, while the rotational energy depends on its moment of inertia, which in turn depends on the reduced mass.

SET UP: The vibrational energy is $E_n = (n + \frac{1}{2})\hbar\omega = (n + \frac{1}{2})\hbar \sqrt{\frac{k'}{m_r}}$ and the rotational energy is

$$E_l = l(l+1) \frac{\hbar^2}{2I}.$$

EXECUTE: For a vibrational transition, we have $\Delta E_v = \hbar \sqrt{\frac{k'}{m_r}}$, so we first need to find m_r . The energy

for a rotational transition is $\Delta E_R = \frac{\hbar^2}{2I} [2(2+1) - 1(1+1)] = \frac{2\hbar^2}{I}$. Solving for I and using the fact that

$I = m_r r_0^2$, we have $m_r r_0^2 = \frac{2\hbar^2}{\Delta E_R}$, which gives

$$m_r = \frac{2\hbar^2}{r_0^2 \Delta E_R} = \frac{2(1.055 \times 10^{-34} \text{ J} \cdot \text{s})(6.583 \times 10^{-16} \text{ eV} \cdot \text{s})}{(0.8860 \times 10^{-9} \text{ m})^2 (8.841 \times 10^{-4} \text{ eV})} = 2.0014 \times 10^{-28} \text{ kg}.$$

Now look at the vibrational transition to find the force constant.

$$\Delta E_v = \hbar \sqrt{\frac{k'}{m_r}} \Rightarrow k' = \frac{m_r (\Delta E_v)^2}{\hbar^2} = \frac{(2.0014 \times 10^{-28} \text{ kg})(0.2560 \text{ eV})^2}{(6.583 \times 10^{-16} \text{ eV} \cdot \text{s})^2} = 30.27 \text{ N/m}.$$

EVALUATE: This would be a rather weak spring in the laboratory.

42.14. IDENTIFY: Find ΔE for the transition and compute λ from $\Delta E = hc/\lambda$.

SET UP: From Example 42.2, $E_l = l(l+1) \frac{\hbar^2}{2I}$, with $\frac{\hbar^2}{2I} = 0.2395 \times 10^{-3} \text{ eV}$. $\Delta E = 0.2690 \text{ eV}$ is the spacing between vibrational levels. Thus $E_n = (n + \frac{1}{2})\hbar\omega$, with $\hbar\omega = 0.2690 \text{ eV}$. The total vibrational and

rotational energy is $E = E_n + E_l = (n + \frac{1}{2})\hbar\omega + l(l+1) \frac{\hbar^2}{2I}$.

EXECUTE: (a) $n = 0 \rightarrow n = 1$ and $l = 2 \rightarrow l = 3$.

For $n = 0, l = 2$, $E_i = \frac{1}{2}\hbar\omega + 6\left(\frac{\hbar^2}{2I}\right)$.

For $n = 1, l = 3$, $E_f = \frac{3}{2}\hbar\omega + 12\left(\frac{\hbar^2}{2I}\right)$.

$$\Delta E = E_f - E_i = \hbar\omega + 6\left(\frac{\hbar^2}{2I}\right) = 0.2690 \text{ eV} + 6(0.2395 \times 10^{-3} \text{ eV}) = 0.2704 \text{ eV}.$$

$$\frac{hc}{\lambda} = \Delta E \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{0.2704 \text{ eV}} = 4.586 \times 10^{-6} \text{ m} = 4.586 \mu\text{m}.$$

(b) $n = 0 \rightarrow n = 1$ and $l = 3 \rightarrow l = 2$.

$$\text{For } n = 0, l = 3, E_i = \frac{1}{2}\hbar\omega + 12\left(\frac{\hbar^2}{2I}\right).$$

$$\text{For } n = 1, l = 2, E_f = \frac{3}{2}\hbar\omega + 6\left(\frac{\hbar^2}{2I}\right).$$

$$\Delta E = E_f - E_i = \hbar\omega - 6\left(\frac{\hbar^2}{2I}\right) = 0.2690 \text{ eV} - 6(0.2395 \times 10^{-3} \text{ eV}) = 0.2676 \text{ eV}.$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{0.2676 \text{ eV}} = 4.634 \times 10^{-6} \text{ m} = 4.634 \mu\text{m}.$$

(c) $n = 0 \rightarrow n = 1$ and $l = 4 \rightarrow l = 3$.

$$\text{For } n = 0, l = 4, E_i = \frac{1}{2}\hbar\omega + 20\left(\frac{\hbar^2}{2I}\right).$$

$$\text{For } n = 1, l = 3, E_f = \frac{3}{2}\hbar\omega + 12\left(\frac{\hbar^2}{2I}\right).$$

$$\Delta E = E_f - E_i = \hbar\omega - 8\left(\frac{\hbar^2}{2I}\right) = 0.2690 \text{ eV} - 8(0.2395 \times 10^{-3} \text{ eV}) = 0.2671 \text{ eV}.$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{0.2671 \text{ eV}} = 4.643 \times 10^{-6} \text{ m} = 4.643 \mu\text{m}.$$

EVALUATE: All three transitions are for $n = 0 \rightarrow n = 1$. The spacing between vibrational levels is larger than the spacing between rotational levels, so the difference in λ for the various rotational transitions is small. When the transition is to a larger l , $\Delta E > \hbar\omega$ and when the transition is to a smaller l , $\Delta E < \hbar\omega$.

42.15. IDENTIFY and SET UP: Find the volume occupied by each atom. The density is the average mass of Na and Cl divided by this volume.

EXECUTE: Each atom occupies a cube with side length 0.282 nm. Therefore, the volume occupied by each atom is $V = (0.282 \times 10^{-9} \text{ m})^3 = 2.24 \times 10^{-29} \text{ m}^3$. In NaCl there are equal numbers of Na and Cl atoms, so the average mass of the atoms in the crystal is

$$m = \frac{1}{2}(m_{\text{Na}} + m_{\text{Cl}}) = \frac{1}{2}(3.82 \times 10^{-26} \text{ kg} + 5.89 \times 10^{-26} \text{ kg}) = 4.855 \times 10^{-26} \text{ kg}.$$

$$\text{The density then is } \rho = \frac{m}{V} = \frac{4.855 \times 10^{-26} \text{ kg}}{2.24 \times 10^{-29} \text{ m}^3} = 2.17 \times 10^3 \text{ kg/m}^3.$$

EVALUATE: The density of water is $1.00 \times 10^3 \text{ kg/m}^3$, so our result is reasonable.

42.16. IDENTIFY and SET UP: For an average spacing a , the density is $\rho = m/a^3$, where m is the average of the ionic masses.

$$\text{EXECUTE: (a) } a^3 = \frac{m}{\rho} = \frac{(6.49 \times 10^{-26} \text{ kg} + 1.33 \times 10^{-25} \text{ kg})/2}{(2.75 \times 10^3 \text{ kg/m}^3)} = 3.60 \times 10^{-29} \text{ m}^3, \text{ and}$$

$$a = 3.30 \times 10^{-10} \text{ m} = 0.330 \text{ nm}.$$

EVALUATE: (b) Exercise 42.15 says that the average spacing for NaCl is 0.282 nm. The larger (higher atomic number) atoms have the larger spacing.

42.17. IDENTIFY: The energy gap is the energy of the maximum-wavelength photon.

SET UP: The energy difference is equal to the energy of the photon, so $\Delta E = hc/\lambda$.

EXECUTE: (a) Using the photon wavelength to find the energy difference gives

$$\Delta E = hc/\lambda = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})/(1.11 \times 10^{-6} \text{ m}) = 1.12 \text{ eV}.$$

(b) A wavelength of $1.11 \mu\text{m} = 1110 \text{ nm}$ is in the infrared, shorter than that of visible light.

EVALUATE: Since visible photons have more than enough energy to excite electrons from the valence to the conduction band, visible light will be absorbed, which makes silicon opaque.

- 42.18. IDENTIFY and SET UP:** $\Delta E = \frac{hc}{\lambda}$, where ΔE is the band gap.

EXECUTE: (a) $\lambda = \frac{hc}{\Delta E} = 2.27 \times 10^{-7} \text{ m} = 227 \text{ nm}$, in the ultraviolet.

EVALUATE: (b) Visible light lacks enough energy to excite the electrons into the conduction band, so visible light passes through the diamond unabsorbed.

(c) Impurities can lower the gap energy making it easier for the material to absorb shorter wavelength visible light. This allows longer wavelength visible light to pass through, giving the diamond color.

- 42.19. IDENTIFY and SET UP:** The energy ΔE deposited when a photon with wavelength λ is absorbed is

$$\Delta E = \frac{hc}{\lambda}.$$

EXECUTE: $\Delta E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{9.31 \times 10^{-13} \text{ m}} = 2.14 \times 10^{-13} \text{ J} = 1.34 \times 10^6 \text{ eV}$. So the number

of electrons that can be excited to the conduction band is $n = \frac{1.34 \times 10^6 \text{ eV}}{1.12 \text{ eV}} = 1.20 \times 10^6$ electrons.

EVALUATE: A photon of wavelength

$$\lambda = \frac{hc}{\Delta E} = \frac{(4.13 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{1.12 \text{ eV}} = 1.11 \times 10^{-6} \text{ m} = 1110 \text{ nm}$$
 can excite one electron. This

photon is in the infrared.

- 42.20. IDENTIFY:** Set $\frac{3}{2}kT = \frac{1}{2}mv_{\text{rms}}^2$.

SET UP: $k = 1.38 \times 10^{-23} \text{ J/K}$. $m = 9.11 \times 10^{-31} \text{ kg}$. $T = 300 \text{ K}$.

EXECUTE: $v_{\text{rms}} = \sqrt{3kT/m} = 1.17 \times 10^5 \text{ m/s}$, which is essentially what was found in Example 42.8.

EVALUATE: Temperature plays a very small role in determining the properties of electrons in metals. Instead, the average energies and corresponding speeds are determined almost exclusively by the exclusion principle.

- 42.21. IDENTIFY:** The density of states is given by $g(E) = \frac{(2m)^{3/2}V}{2\pi^2\hbar^3} E^{1/2}$.

SET UP: $m = 9.11 \times 10^{-31} \text{ kg}$, the mass of an electron.

EXECUTE: $g(E) = \frac{(2m)^{3/2}V}{2\pi^2\hbar^3} E^{1/2} = \frac{[2(9.11 \times 10^{-31} \text{ kg})]^{3/2}(1.0 \times 10^{-6} \text{ m}^3)(5.0 \text{ eV})^{1/2}(1.60 \times 10^{-19} \text{ J/eV})^{1/2}}{2\pi^2(1.054 \times 10^{-34} \text{ J} \cdot \text{s})^3}$.

$$g(E) = (9.5 \times 10^{40} \text{ states/J})(1.60 \times 10^{-19} \text{ J/eV}) = 1.5 \times 10^{22} \text{ states/eV}.$$

EVALUATE: For a metal the density of states expressed as states/eV is very large.

- 42.22. IDENTIFY:** At absolute zero, the average free-electron energy is $E_{\text{av}} = \frac{3}{5}E_{\text{F}}$. The speed v is related to E_{av}

$$\text{by } \frac{1}{2}mv^2 = E_{\text{av}}.$$

SET UP: $k = 1.38 \times 10^{-23} \text{ J/K}$.

EXECUTE: (a) $E_{\text{av}} = \frac{3}{5}E_{\text{F}} = 1.94 \text{ eV}$.

$$(b) v = \sqrt{2E_{\text{av}}/m} = \sqrt{\frac{2(1.94 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{9.11 \times 10^{-31} \text{ kg}}} = 8.25 \times 10^5 \text{ m/s}.$$

$$(c) \frac{E_{\text{F}}}{k} = \frac{(3.23 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}{(1.38 \times 10^{-23} \text{ J/K})} = 3.74 \times 10^4 \text{ K}.$$

EVALUATE: The Fermi energy of sodium is less than that of copper. Therefore, the values of E_{av} and v we have calculated for sodium are less than those calculated for copper in Example 42.7.

42.23. IDENTIFY and SET UP: The electron contribution to the molar heat capacity at constant volume of a metal

$$\text{is } C_V = \left(\frac{\pi^2 kT}{2E_F} \right) R.$$

$$\text{EXECUTE: (a) } C_V = \frac{\pi^2 (1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})}{2(5.48 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV})} R = 0.0233R.$$

(b) The electron contribution found in part (a) is $0.0233R = 0.194 \text{ J/mol} \cdot \text{K}$. This is $0.194/25.3 = 7.67 \times 10^{-3} = 0.767\%$ of the total C_V .

EVALUATE: (c) Only a small fraction of C_V is due to the electrons. Most of C_V is due to the vibrational motion of the ions.

42.24. IDENTIFY and SET UP: The probability $f(E)$ that a state with energy E is occupied is given by the

$$\text{Fermi-Dirac distribution } f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}, \text{ where } E_F \text{ is the Fermi energy. In this case, } E = 2E_F = 2(kT_F).$$

$$\text{EXECUTE: } f(2E_F) = \frac{1}{e^{(2E_F-E_F)/kT_F} + 1} = \frac{1}{e^{E_F/kT_F} + 1} = \frac{1}{e^{kT_F/kT_F} + 1} = \frac{1}{e + 1} = 0.269.$$

EVALUATE: A probability of $0.269 \approx 27\%$ is about 1 in 4. As E increases, the probability gets smaller.

42.25. IDENTIFY: The probability is given by the Fermi-Dirac distribution.

$$\text{SET UP: The Fermi-Dirac distribution is } f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}.$$

EXECUTE: We calculate the value of $f(E)$, where $E = 8.520 \text{ eV}$, $E_F = 8.500 \text{ eV}$,

$k = 1.38 \times 10^{-23} \text{ J/K} = 8.625 \times 10^{-5} \text{ eV/K}$, and $T = 20^\circ\text{C} = 293 \text{ K}$. The result is $f(E) = 0.312 = 31.2\%$.

EVALUATE: Since the energy is close to the Fermi energy, the probability is quite high that the state is occupied by an electron.

42.26. IDENTIFY and SET UP: Follow the procedure of Example 42.9. Evaluate $f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$ for

$E - E_F = E_g/2$, where E_g is the band gap.

EXECUTE: (a) The probabilities are 1.78×10^{-7} , 2.37×10^{-6} , and 1.51×10^{-5} .

(b) It can be shown that the Fermi-Dirac distribution, $f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$, has the property that

$f(E_F - E) = 1 - f(E)$, and so the probability that a state at the top of the valence band is occupied is the same as the probability that a state of the bottom of the conduction band is filled (this result depends on having the Fermi energy in the middle of the gap). Therefore, the probabilities at each T are the same as in part (a).

EVALUATE: The probabilities increase with temperature.

42.27. IDENTIFY: Use the Fermi-Dirac distribution $f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$. Solve for $E - E_F$.

$$\text{SET UP: } e^{(E-E_F)/kT} = \frac{1}{f(E)} - 1.$$

The problem states that $f(E) = 4.4 \times 10^{-4}$ for E at the bottom of the conduction band.

$$\text{EXECUTE: } e^{(E-E_F)/kT} = \frac{1}{4.4 \times 10^{-4}} - 1 = 2.272 \times 10^3.$$

$$E - E_F = kT \ln(2.272 \times 10^3) = (1.3807 \times 10^{-23} \text{ J/T})(300 \text{ K}) \ln(2.272 \times 10^3) = 3.201 \times 10^{-20} \text{ J} = 0.20 \text{ eV}.$$

$E_F = E - 0.20 \text{ eV}$; the Fermi level is 0.20 eV below the bottom of the conduction band.

EVALUATE: The energy gap between the Fermi level and bottom of the conduction band is large compared to kT at $T = 300 \text{ K}$ and as a result $f(E)$ is small.

42.28. IDENTIFY: The wavelength of the photon to be detected depends on its energy.

SET UP: $\Delta E = \frac{hc}{\lambda}$.

EXECUTE: (a) $\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{0.67 \text{ eV}} = 1.9 \text{ } \mu\text{m}.$

(b) $\lambda = (1.9 \text{ } \mu\text{m}) \left(\frac{0.67 \text{ eV}}{1.12 \text{ eV}} \right) = 1.1 \text{ } \mu\text{m}.$

EVALUATE: Both of these photons are in the infrared.

42.29. IDENTIFY: Knowing the saturation current of a p - n junction at a given temperature, we want to find the current at that temperature for various voltages.

SET UP: $I = I_S(e^{eV/kT} - 1).$

EXECUTE: (a) (i) For $V = 1.00 \text{ mV}$, $\frac{eV}{kT} = \frac{(1.602 \times 10^{-19} \text{ C})(1.00 \times 10^{-3} \text{ V})}{(1.381 \times 10^{-23} \text{ J/K})(290 \text{ K})} = 0.0400.$

$I = (0.500 \text{ mA})(e^{0.0400} - 1) = 0.0204 \text{ mA}.$

(ii) For $V = -1.00 \text{ mV}$, $\frac{eV}{kT} = -0.0400$. $I = (0.500 \text{ mA})(e^{-0.0400} - 1) = -0.0196 \text{ mA}.$

(iii) For $V = 100 \text{ mV}$, $\frac{eV}{kT} = 4.00$. $I = (0.500 \text{ mA})(e^{4.00} - 1) = 26.8 \text{ mA}.$

(iv) For $V = -100 \text{ mV}$, $\frac{eV}{kT} = -4.00$. $I = (0.500 \text{ mA})(e^{-4.00} - 1) = -0.491 \text{ mA}.$

EVALUATE: (b) For small V , between $\pm 1.00 \text{ mV}$, $R = V/I$ is approximately constant and the diode obeys Ohm's law to a good approximation. For larger V the deviation from Ohm's law is substantial.

42.30. IDENTIFY: The current depends on the voltage across the diode and its temperature, so the resistance also depends on these quantities.

SET UP: The current is $I = I_S(e^{eV/kT} - 1)$ and the resistance is $R = V/I$.

EXECUTE: (a) The resistance is $R = \frac{V}{I} = \frac{V}{I_S(e^{eV/kT} - 1)}$. The exponent is

$\frac{eV}{kT} = \frac{e(0.0850 \text{ V})}{(8.625 \times 10^{-5} \text{ eV/K})(293 \text{ K})} = 3.3635$, giving $R = \frac{85.0 \text{ mV}}{(0.950 \text{ mA})(e^{3.3635} - 1)} = 3.21 \text{ } \Omega.$

(b) In this case, the exponent is $\frac{eV}{kT} = \frac{e(-0.050 \text{ V})}{(8.625 \times 10^{-5} \text{ eV/K})(293 \text{ K})} = -1.979$

which gives $R = \frac{-50.0 \text{ mV}}{(0.950 \text{ mA})(e^{-1.979} - 1)} = 61.1 \text{ } \Omega.$

EVALUATE: Reversing the voltage can make a considerable change in the resistance of a diode.

42.31. IDENTIFY and SET UP: The voltage-current relation is given by $I = I_S(e^{eV/kT} - 1)$. Use the current for $V = +15.0 \text{ mV}$ to solve for the constant I_S .

EXECUTE: (a) Find I_S : $V = +15.0 \times 10^{-3} \text{ V}$ gives $I = 9.25 \times 10^{-3} \text{ A}.$

$\frac{eV}{kT} = \frac{(1.602 \times 10^{-19} \text{ C})(15.0 \times 10^{-3} \text{ V})}{(1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.5800.$

$I_S = \frac{I}{e^{eV/kT} - 1} = \frac{9.25 \times 10^{-3} \text{ A}}{e^{0.5800} - 1} = 1.177 \times 10^{-2} = 11.77 \text{ mA}.$

Then can calculate I for $V = 10.0 \text{ mV}$: $\frac{eV}{kT} = \frac{(1.602 \times 10^{-19} \text{ C})(10.0 \times 10^{-3} \text{ V})}{(1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.3867.$

$I = I_S(e^{eV/kT} - 1) = (11.77 \text{ mA})(e^{0.3867} - 1) = 5.56 \text{ mA}.$

(b) $\frac{eV}{kT}$ has the same magnitude as in part (a) but now V is negative so $\frac{eV}{kT}$ is negative.

$$V = -15.0 \text{ mV}: \frac{eV}{kT} = -0.5800 \text{ and } I = I_s(e^{eV/kT} - 1) = (11.77 \text{ mA})(e^{-0.5800} - 1) = -5.18 \text{ mA.}$$

$$V = -10.0 \text{ mV}: \frac{eV}{kT} = -0.3867 \text{ and } I = I_s(e^{eV/kT} - 1) = (11.77 \text{ mA})(e^{-0.3867} - 1) = -3.77 \text{ mA.}$$

EVALUATE: There is a directional asymmetry in the current, with a forward-bias voltage producing more current than a reverse-bias voltage of the same magnitude, but the voltage is small enough for the asymmetry not be pronounced.

42.32. IDENTIFY: Apply the equation $I = I_s(e^{eV/kT} - 1)$.

SET UP: $I_s = 6.40 \text{ mA}$. $\ln e^x = x$.

EXECUTE: (a) Solving $I = I_s(e^{eV/kT} - 1)$ for the voltage as a function of current gives

$$V = \frac{kT}{e} \ln \left(\frac{I}{I_s} + 1 \right) = \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{1.602 \times 10^{-19} \text{ C}} \ln \left(\frac{40.0 \text{ mA}}{6.40 \text{ mA}} + 1 \right) = 0.0512 \text{ V} = 51.2 \text{ mV.}$$

(b) Using the result from part (a), the quantity $e^{eV/kT} = 7.242$, so for a reverse-bias voltage of the same magnitude, $I = I_s(e^{-eV/kT} - 1) = (6.40 \text{ mA}) \left(\frac{1}{7.242} - 1 \right) = -5.52 \text{ mA}$.

EVALUATE: The reverse bias current for a given magnitude of voltage is much less than the forward bias current.

42.33. IDENTIFY: During the transition, the molecule emits a photon of light having energy equal to the energy difference between the two vibrational states of the molecule.

SET UP: The vibrational energy is $E_n = (n + \frac{1}{2})\hbar\omega = (n + \frac{1}{2})\hbar\sqrt{\frac{k'}{m_r}}$.

EXECUTE: (a) The energy difference between two adjacent energy states is $\Delta E = \hbar\sqrt{\frac{k'}{m_r}}$, and this is the energy of the photon, so $\Delta E = hc/\lambda$. Equating these two expressions for ΔE and solving for k' , we have

$$k' = m_r \left(\frac{\Delta E}{\hbar} \right)^2 = \frac{m_H m_O}{m_H + m_O} \left(\frac{\Delta E}{\hbar} \right)^2, \text{ and using } \frac{\Delta E}{\hbar} = \frac{hc/\lambda}{\hbar} = \frac{2\pi c}{\lambda} \text{ with the appropriate numbers gives us}$$

$$k' = \frac{(1.67 \times 10^{-27} \text{ kg})(2.656 \times 10^{-26} \text{ kg}) \left[\frac{2\pi(3.00 \times 10^8 \text{ m/s})}{2.39 \times 10^{-6} \text{ m}} \right]^2}{1.67 \times 10^{-27} \text{ kg} + 2.656 \times 10^{-26} \text{ kg}} = 977 \text{ N/m.}$$

(b) $f = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k'}{m_r}} = \frac{1}{2\pi} \sqrt{\frac{k'}{m_H m_O}} \sqrt{\frac{m_H m_O}{m_H + m_O}}$. Substituting the appropriate numbers gives us

$$f = \frac{1}{2\pi} \sqrt{\frac{977 \text{ N/m}}{\left(\frac{(1.67 \times 10^{-27} \text{ kg})(2.656 \times 10^{-26} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 2.656 \times 10^{-26} \text{ kg}} \right)}} = 1.25 \times 10^{14} \text{ Hz.}$$

EVALUATE: The frequency is close to, but not quite in, the visible range.

42.34. IDENTIFY and SET UP: $E_l = l(l+1)\frac{\hbar^2}{2I}$. ΔE for the molecule is related to λ for the photon by $\Delta E = \frac{hc}{\lambda}$.

EXECUTE: $E_2 = 3\frac{\hbar^2}{I}$ and $E_1 = \frac{\hbar^2}{I}$, so $\Delta E = \frac{2\hbar^2}{I}$. Using $\lambda = 54.3 \mu\text{m}$, we get

$$I = \frac{2\hbar^2}{\Delta E} = \frac{h\lambda}{2\pi^2 c} = 6.08 \times 10^{-48} \text{ kg} \cdot \text{m}^2.$$

EVALUATE: The I we calculated is approximately a factor of 24 times smaller than I calculated for the CO molecule in Example 42.2.

- 42.35. IDENTIFY and SET UP:** From Chapter 21, the electric dipole moment is $p = qd$, where the dipole consists of charges $\pm q$ separated by distance d .

EXECUTE: (a) Point charges $+e$ and $-e$ separated by distance d , so

$$p = ed = (1.602 \times 10^{-19} \text{ C})(0.24 \times 10^{-9} \text{ m}) = 3.8 \times 10^{-29} \text{ C} \cdot \text{m}.$$

$$(b) \quad p = qd \quad \text{so} \quad q = \frac{p}{d} = \frac{3.0 \times 10^{-29} \text{ C} \cdot \text{m}}{0.24 \times 10^{-9} \text{ m}} = 1.3 \times 10^{-19} \text{ C}.$$

$$(c) \quad \frac{q}{e} = \frac{1.3 \times 10^{-19} \text{ C}}{1.602 \times 10^{-19} \text{ C}} = 0.81.$$

$$(d) \quad q = \frac{p}{d} = \frac{1.5 \times 10^{-30} \text{ C} \cdot \text{m}}{0.16 \times 10^{-9} \text{ m}} = 9.37 \times 10^{-21} \text{ C}.$$

$$\frac{q}{e} = \frac{9.37 \times 10^{-21} \text{ C}}{1.602 \times 10^{-19} \text{ C}} = 0.058.$$

EVALUATE: The fractional ionic character for the bond in HI is much less than the fractional ionic character for the bond in NaCl. The bond in HI is mostly covalent and not very ionic.

- 42.36. IDENTIFY:** The electric potential energy U , the binding energy E_B , the electron affinity E_A , and the ionization energy E_I , where E_B , E_A , and E_I are positive and U is negative, are related by

$$E_B = -U + E_A - E_I.$$

SET UP: For two point charges q_1 and q_2 separated by a distance r , the electric potential energy is given

$$\text{by } U = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}.$$

EXECUTE: The electrical potential energy is $U = -5.13 \text{ eV}$, and $r = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{U} = 2.8 \times 10^{-10} \text{ m}$.

EVALUATE: We have neglected the kinetic energy of the ions in the molecule. Also, it is an approximation to treat the two ions as point charges.

- 42.37. (a) IDENTIFY:** $E(\text{Na}) + E(\text{Cl}) = E(\text{Na}^+) + E(\text{Cl}^-) + U(r)$. Solving for $U(r)$ gives

$$U(r) = -[E(\text{Na}^+) - E(\text{Na})] + [E(\text{Cl}) - E(\text{Cl}^-)].$$

SET UP: $[E(\text{Na}^+) - E(\text{Na})]$ is the ionization energy of Na, the energy required to remove one electron, and is equal to 5.1 eV. $[E(\text{Cl}) - E(\text{Cl}^-)]$ is the electron affinity of Cl, the magnitude of the decrease in energy when an electron is attached to a neutral Cl atom, and is equal to 3.6 eV.

EXECUTE: $U = -5.1 \text{ eV} + 3.6 \text{ eV} = -1.5 \text{ eV} = -2.4 \times 10^{-19} \text{ J}$, and $-\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = -2.4 \times 10^{-19} \text{ J}$.

$$r = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{2.4 \times 10^{-19} \text{ J}} = (8.988 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \frac{(1.602 \times 10^{-19} \text{ C})^2}{2.4 \times 10^{-19} \text{ J}} = 9.6 \times 10^{-10} \text{ m} = 0.96 \text{ nm}.$$

(b) IDENTIFY and SET UP: The ionization energy of K is 4.3 eV and the electron affinity of Br is 3.5 eV.

Thus $U = -4.3 \text{ eV} + 3.5 \text{ eV} = -0.8 \text{ eV} = -1.28 \times 10^{-19} \text{ J}$, and $-\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = -1.28 \times 10^{-19} \text{ J}$.

$$\text{EXECUTE: } r = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{e^2}{1.28 \times 10^{-19} \text{ J}} = (8.988 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \frac{(1.602 \times 10^{-19} \text{ C})^2}{1.28 \times 10^{-19} \text{ J}}$$

$$= 1.8 \times 10^{-9} \text{ m} = 1.8 \text{ nm}.$$

EVALUATE: K has a smaller ionization energy than Na and the electron affinities of Cl and Br are very similar, so it takes less energy to make $\text{K}^+ + \text{Br}^-$ from $\text{K} + \text{Br}$ than to make $\text{Na}^+ + \text{Cl}^-$ from $\text{Na} + \text{Cl}$. Thus, the stabilization distance is larger for KBr than for NaCl.

42.38. IDENTIFY and SET UP: For an $l \rightarrow l-1$ transition, the frequency of the emitted photon is

$$f = \frac{\Delta E}{h} = \frac{\Delta E}{2\pi\hbar} = \frac{l\hbar}{2\pi I}, \text{ so } \Delta E = \frac{l\hbar^2}{I}. \quad I = m_r r_0^2. \quad m_r = \frac{(3.82 \times 10^{-26} \text{ kg})(3.15 \times 10^{-26} \text{ kg})}{3.82 \times 10^{-26} \text{ kg} + 3.15 \times 10^{-26} \text{ kg}} = 1.726 \times 10^{-26} \text{ kg}.$$

EXECUTE: $I = \frac{\hbar^2 l}{\Delta E} = \frac{\hbar l \lambda}{4\pi^2 c} = 6.43 \times 10^{-46} \text{ kg} \cdot \text{m}^2$ and from $I = m_r r_0^2$ the separation is

$$r_0 = \sqrt{\frac{I}{m_r}} = 0.193 \text{ nm}.$$

EVALUATE: Section 42.1 says $r_0 = 0.24 \text{ nm}$ for NaCl. Our result for NaF is smaller than this. This makes sense, since F is a smaller atom than Cl.

42.39. IDENTIFY: $E_{\text{ex}} = \frac{L^2}{2I} = \frac{\hbar^2 l(l+1)}{2I}$. $E_g = 0$ ($l=0$), and there is an additional multiplicative factor of $2l+1$ because for each l state there are really $(2l+1)$ m_l -states with the same energy.

SET UP: From Example 42.2, $I = 1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2$ for CO.

EXECUTE: (a) $\frac{n_l}{n_0} = (2l+1)e^{-\hbar^2 l(l+1)/(2IkT)}$.

$$\text{(b) (i)} \quad E_{l=1} = \frac{\hbar^2(1)(1+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)} = 7.67 \times 10^{-23} \text{ J}. \quad \frac{E_{l=1}}{kT} = \frac{7.67 \times 10^{-23} \text{ J}}{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.0185.$$

$$(2l+1) = 3, \text{ so } \frac{n_{l=1}}{n_0} = (3)e^{-0.0185} = 2.95.$$

$$\text{(ii)} \quad \frac{E_{l=2}}{kT} = \frac{\hbar^2(2)(2+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 0.0556. \quad (2l+1) = 5, \text{ so}$$

$$\frac{n_{l=1}}{n_0} = (5)(e^{-0.0556}) = 4.73.$$

$$\text{(iii)} \quad \frac{E_{l=10}}{kT} = \frac{\hbar^2(10)(10+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 1.02.$$

$$(2l+1) = 21, \text{ so } \frac{n_{l=10}}{n_0} = (21)(e^{-1.02}) = 7.57.$$

$$\text{(iv)} \quad \frac{E_{l=20}}{kT} = \frac{\hbar^2(20)(20+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 3.90. \quad (2l+1) = 41, \text{ so}$$

$$\frac{n_{l=20}}{n_0} = (41)e^{-3.90} = 0.833.$$

$$\text{(v)} \quad \frac{E_{l=50}}{kT} = \frac{\hbar^2(50)(50+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} = 23.7. \quad (2l+1) = 101, \text{ so}$$

$$\frac{n_{l=50}}{n_0} = (101)e^{-23.7} = 5.38 \times 10^{-9}.$$

EVALUATE: (c) There is a competing effect between the $(2l+1)$ term and the decaying exponential. The $2l+1$ term dominates for small l , while the exponential term dominates for large l .

42.40. IDENTIFY: The ratio n_l/n_0 will be largest when its derivative with respect to l is zero.

SET UP: From Problem 42.39, we know that $n_l/n_0 = (2l+1)e^{-\hbar^2 l(l+1)/(2IkT)}$. Set $\frac{\partial(n_l/n_0)}{\partial l} = 0$ and solve for l .

$$\text{EXECUTE: (a)} \quad \frac{\partial}{\partial l} \left[(2l+1)e^{-\hbar^2 l(l+1)/(2IkT)} \right] = 2e^{-\hbar^2 l(l+1)/(2IkT)} - \frac{(2l+1)^2 \hbar^2}{2IkT} e^{-\hbar^2 l(l+1)/(2IkT)} = 0.$$

The exponentials cannot be zero, so

$$2 - \frac{(2l+1)^2 \hbar^2}{2IkT} = 0 \rightarrow l_{\max} = \frac{\sqrt{IkT}}{\hbar} - \frac{1}{2}.$$

(b) Using $I = 1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2$ for CO from Example 42.2 gives

$$l_{\max} = \frac{\sqrt{(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}}{1.055 \times 10^{-34} \text{ J} \cdot \text{s}} - \frac{1}{2} = 6.84 \approx 7.$$

EVALUATE: Since $l_{\max} \propto \sqrt{I}$, it would have a different value for molecules other than CO.

42.41. IDENTIFY and SET UP: $E_l = l(l+1)\hbar^2/2I$, so E_l and the transition energy ΔE depend on I . Different isotopic molecules have different I .

EXECUTE: (a) Calculate I for Na^{35}Cl :

$$m_r = \frac{m_{\text{Na}}m_{\text{Cl}}}{m_{\text{Na}} + m_{\text{Cl}}} = \frac{(3.8176 \times 10^{-26} \text{ kg})(5.8068 \times 10^{-26} \text{ kg})}{3.8176 \times 10^{-26} \text{ kg} + 5.8068 \times 10^{-26} \text{ kg}} = 2.303 \times 10^{-26} \text{ kg}.$$

$$I = m_r r^2 = (2.303 \times 10^{-26} \text{ kg})(0.2361 \times 10^{-9} \text{ m})^2 = 1.284 \times 10^{-45} \text{ kg} \cdot \text{m}^2.$$

$l = 2 \rightarrow l = 1$ transition:

$$\Delta E = E_2 - E_1 = (6 - 2) \left(\frac{\hbar^2}{2I} \right) = \frac{2\hbar^2}{I} = \frac{2(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{1.284 \times 10^{-45} \text{ kg} \cdot \text{m}^2} = 1.734 \times 10^{-23} \text{ J}.$$

$$\Delta E = \frac{hc}{\lambda} \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{1.734 \times 10^{-23} \text{ J}} = 1.146 \times 10^{-2} \text{ m} = 1.146 \text{ cm}.$$

$l = 1 \rightarrow l = 0$ transition:

$$\Delta E = E_1 - E_0 = (2 - 0) \left(\frac{\hbar^2}{2I} \right) = \frac{\hbar^2}{I} = \frac{1}{2}(1.734 \times 10^{-23} \text{ J}) = 8.67 \times 10^{-24} \text{ J}.$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{8.67 \times 10^{-24} \text{ J}} = 2.291 \text{ cm}.$$

(b) Calculate I for Na^{37}Cl : $m_r = \frac{m_{\text{Na}}m_{\text{Cl}}}{m_{\text{Na}} + m_{\text{Cl}}} = \frac{(3.8176 \times 10^{-26} \text{ kg})(6.1384 \times 10^{-26} \text{ kg})}{3.8176 \times 10^{-26} \text{ kg} + 6.1384 \times 10^{-26} \text{ kg}} = 2.354 \times 10^{-26} \text{ kg}.$

$$I = m_r r^2 = (2.354 \times 10^{-26} \text{ kg})(0.2361 \times 10^{-9} \text{ m})^2 = 1.312 \times 10^{-45} \text{ kg} \cdot \text{m}^2.$$

$l = 2 \rightarrow l = 1$ transition:

$$\Delta E = \frac{2\hbar^2}{I} = \frac{2(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{1.312 \times 10^{-45} \text{ kg} \cdot \text{m}^2} = 1.697 \times 10^{-23} \text{ J}.$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{1.697 \times 10^{-23} \text{ J}} = 1.171 \times 10^{-2} \text{ m} = 1.171 \text{ cm}.$$

$l = 1 \rightarrow l = 0$ transition:

$$\Delta E = \frac{\hbar^2}{I} = \frac{1}{2}(1.697 \times 10^{-23} \text{ J}) = 8.485 \times 10^{-24} \text{ J}.$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{8.485 \times 10^{-24} \text{ J}} = 2.341 \text{ cm}.$$

The differences in the wavelengths for the two isotopes are:

$$l = 2 \rightarrow l = 1 \text{ transition: } 1.171 \text{ cm} - 1.146 \text{ cm} = 0.025 \text{ cm}$$

$$l = 1 \rightarrow l = 0 \text{ transition: } 2.341 \text{ cm} - 2.291 \text{ cm} = 0.050 \text{ cm}.$$

EVALUATE: Replacing ^{35}Cl by ^{37}Cl increases I , decreases ΔE and increases λ . The effect on λ is small but measurable.

42.42. IDENTIFY: The rotational energy levels are given by $E_l = l(l+1)\frac{\hbar^2}{2I}$. The transition energy ΔE for the

molecule and λ for the photon are related by $\Delta E = \frac{hc}{\lambda}$.

SET UP: From Example 42.2, $I_{\text{CO}} = 1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2$.

EXECUTE: (a) $E_{l=1} = \frac{\hbar^2 l(l+1)}{2I} = \frac{(1.054 \times 10^{-34} \text{ J} \cdot \text{s})^2 (1)(1+1)}{2(1.449 \times 10^{-46} \text{ kg} \cdot \text{m}^2)} = 7.67 \times 10^{-23} \text{ J}$. $E_{l=0} = 0$.

$$\Delta E = 7.67 \times 10^{-23} \text{ J} = 4.79 \times 10^{-4} \text{ eV}. \quad \lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(7.67 \times 10^{-23} \text{ J})} =$$

$$2.59 \times 10^{-3} \text{ m} = 2.59 \text{ mm}.$$

EVALUATE: (b) Let's compare the value of kT when $T = 20 \text{ K}$ to that of ΔE for the $l=1 \rightarrow l=0$ rotational transition: $kT = (1.38 \times 10^{-23} \text{ J/K})(20 \text{ K}) = 2.76 \times 10^{-22} \text{ J}$.

$\Delta E = 7.67 \times 10^{-23} \text{ J}$ (from part (a)). So $\frac{kT}{\Delta E} = 3.60$. Therefore, although T is quite small, there is still plenty of energy to excite CO molecules into the first rotational level. This allows astronomers to detect the 2.59 mm wavelength radiation from such molecular clouds.

42.43. IDENTIFY: The vibrational energy levels are given by $E_n = (n + \frac{1}{2}) \hbar \sqrt{\frac{k'}{m_r}}$. The zero-point energy is

$$E_0 = \frac{1}{2} \hbar \sqrt{\frac{2k'}{m_{\text{H}}}}.$$

SET UP: For H_2 , $m_r = \frac{m_{\text{H}}}{2}$.

EXECUTE: $E_0 = \frac{1}{2} (1.054 \times 10^{-34} \text{ J} \cdot \text{s}) \sqrt{\frac{2(576 \text{ N/m})}{1.67 \times 10^{-27} \text{ kg}}} = 4.38 \times 10^{-20} \text{ J} = 0.274 \text{ eV}$.

EVALUATE: This is much less than the magnitude of the H_2 bond energy.

42.44. IDENTIFY: $\Delta E = hf = \hbar \sqrt{\frac{k'}{m_r}}$.

SET UP: $m_r = \frac{m_{\text{O}} m_{\text{H}}}{m_{\text{O}} + m_{\text{H}}} = 1.57 \times 10^{-27} \text{ kg}$.

EXECUTE: The vibration frequency is $f = \frac{\Delta E}{h} = 1.12 \times 10^{14} \text{ Hz}$. The force constant is

$$k' = (2\pi f)^2 m_r = 777 \text{ N/m}.$$

EVALUATE: This would be a fairly stiff spring in an ordinary physics lab.

42.45. IDENTIFY and SET UP: Use $I = m_r r_0^2$ to calculate I . The energy levels are given by

$$E_{nl} = l(l+1) \left(\frac{\hbar^2}{2I} \right) + (n + \frac{1}{2}) \hbar \sqrt{\frac{k'}{m_r}}. \quad \text{The transition energy } \Delta E \text{ is related to the photon wavelength by}$$

$$\Delta E = hc/\lambda.$$

EXECUTE: (a) $m_r = \frac{m_{\text{H}} m_{\text{I}}}{m_{\text{H}} + m_{\text{I}}} = \frac{(1.67 \times 10^{-27} \text{ kg})(2.11 \times 10^{-25} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 2.11 \times 10^{-25} \text{ kg}} = 1.657 \times 10^{-27} \text{ kg}$.

$$I = m_r r_0^2 = (1.657 \times 10^{-27} \text{ kg})(0.160 \times 10^{-9} \text{ m})^2 = 4.24 \times 10^{-47} \text{ kg} \cdot \text{m}^2.$$

(b) The energy levels are $E_{nl} = l(l+1)\left(\frac{\hbar^2}{2I}\right) + (n + \frac{1}{2})\hbar\sqrt{\frac{k'}{m_r}}$.

$$\sqrt{\frac{k'}{m}} = \omega = 2\pi f \text{ so } E_{nl} = l(l+1)\left(\frac{\hbar^2}{2I}\right) + (n + \frac{1}{2})hf.$$

(i) Transition $n = 1 \rightarrow n = 0, l = 1 \rightarrow l = 0$:

$$\Delta E = (2 - 0)\left(\frac{\hbar^2}{2I}\right) + (1 + \frac{1}{2} - \frac{1}{2})hf = \frac{\hbar^2}{I} + hf.$$

$$\Delta E = \frac{hc}{\lambda} \text{ so } \lambda = \frac{hc}{\Delta E} = \frac{hc}{(\hbar^2/I) + hf} = \frac{c}{(\hbar/2\pi I) + f}.$$

$$\frac{\hbar}{2\pi I} = \frac{1.055 \times 10^{-34} \text{ J} \cdot \text{s}}{2\pi(4.24 \times 10^{-47} \text{ kg} \cdot \text{m}^2)} = 3.960 \times 10^{11} \text{ Hz}.$$

$$\lambda = \frac{c}{(\hbar/2\pi I) + f} = \frac{2.998 \times 10^8 \text{ m/s}}{3.960 \times 10^{11} \text{ Hz} + 6.93 \times 10^{13} \text{ Hz}} = 4.30 \mu\text{m}.$$

(ii) Transition $n = 1 \rightarrow n = 0, l = 2 \rightarrow l = 1$:

$$\Delta E = (6 - 2)\left(\frac{\hbar^2}{2I}\right) + hf = \frac{2\hbar^2}{I} + hf.$$

$$\lambda = \frac{c}{2(\hbar/2\pi I) + f} = \frac{2.998 \times 10^8 \text{ m/s}}{2(3.960 \times 10^{11} \text{ Hz}) + 6.93 \times 10^{13} \text{ Hz}} = 4.28 \mu\text{m}.$$

(iii) Transition $n = 2 \rightarrow n = 1, l = 2 \rightarrow l = 3$:

$$\Delta E = (6 - 12)\left(\frac{\hbar^2}{2I}\right) + hf = -\frac{3\hbar^2}{I} + hf.$$

$$\lambda = \frac{c}{-3(\hbar/2\pi I) + f} = \frac{2.998 \times 10^8 \text{ m/s}}{-3(3.960 \times 10^{11} \text{ Hz}) + 6.93 \times 10^{13} \text{ Hz}} = 4.40 \mu\text{m}.$$

EVALUATE: The vibrational energy change for the $n = 1 \rightarrow n = 0$ transition is the same as for the $n = 2 \rightarrow n = 1$ transition. The rotational energies are much smaller than the vibrational energies, so the wavelengths for all three transitions don't differ much.

42.46. IDENTIFY: The frequency is proportional to the reciprocal of the square root of the reduced mass. The transition energy ΔE and the wavelength of the light emitted are related by $\Delta E = \frac{hc}{\lambda}$.

SET UP: $f_0 = 1.24 \times 10^{14} \text{ Hz}$.

EXECUTE: (a) In terms of the atomic masses, the frequency of the isotope with the deuterium atom is

$$f = f_0 \left(\frac{m_F m_H / (m_H + m_F)}{m_F m_D / (m_D + m_F)} \right)^{1/2} = f_0 \left(\frac{1 + (m_F/m_D)}{1 + (m_F/m_H)} \right)^{1/2}. \text{ Using } f_0 \text{ and the given masses, } f = 8.99 \times 10^{13} \text{ Hz}.$$

(b) For the molecule, $\Delta E = hf$. $hf = \frac{hc}{\lambda}$, so $\lambda = \frac{c}{f} = \frac{3.00 \times 10^8 \text{ m/s}}{8.99 \times 10^{13} \text{ Hz}} = 3.34 \times 10^{-6} \text{ m} = 3340 \text{ nm}$. This

wavelength is in the infrared.

EVALUATE: The vibrational frequency of the molecule equals the frequency of the light that is emitted.

42.47. IDENTIFY: E_{F0} is given by $E_{F0} = \frac{3^{2/3} \pi^{4/3} \hbar^2 n^{2/3}}{2m}$. Since potassium is a metal and E does not change

much with T for metals, we approximate E_F by E_{F0} , so $E_F = \frac{3^{2/3} \pi^{4/3} \hbar^2 n^{2/3}}{2m}$.

SET UP: The number of atoms per m^3 is ρ/m . If each atom contributes one free electron, the electron concentration is $n = \frac{\rho}{m} = \frac{851 \text{ kg/m}^3}{6.49 \times 10^{-26} \text{ kg}} = 1.31 \times 10^{28} \text{ electrons/m}^3$.

EXECUTE: $E_F = \frac{3^{2/3} \pi^{4/3} (1.054 \times 10^{-34} \text{ J} \cdot \text{s})^2 (1.31 \times 10^{28} / \text{m}^3)^{2/3}}{2(9.11 \times 10^{-31} \text{ kg})} = 3.24 \times 10^{-19} \text{ J} = 2.03 \text{ eV}.$

EVALUATE: The E_F we calculated for potassium is about a factor of three smaller than the E_F for copper that was calculated in Example 42.7.

42.48. IDENTIFY and SET UP: At r where U_{tot} is a minimum, $\frac{d}{dr}U_{\text{tot}} = 0$.

EXECUTE: (a) $\frac{d}{dr}U_{\text{tot}} = \frac{\alpha e^2}{4\pi\epsilon_0} \frac{1}{r^2} - 8A \frac{1}{r^9}$. Setting this equal to zero when $r = r_0$ gives $r_0^7 = \frac{8A4\pi\epsilon_0}{\alpha e^2}$ and

so $U_{\text{tot}} = \frac{\alpha e^2}{4\pi\epsilon_0} \left(-\frac{1}{r} + \frac{r_0^7}{8r^8} \right)$. At $r = r_0$, $U_{\text{tot}} = -\frac{7\alpha e^2}{32\pi\epsilon_0 r_0} = -1.26 \times 10^{-18} \text{ J} = -7.85 \text{ eV}.$

(b) To remove a Na^+Cl^- ion pair from the crystal requires 7.85 eV. When neutral Na and Cl atoms are formed from the Na^+ and Cl^- atoms there is a net release of energy $-5.14 \text{ eV} + 3.61 \text{ eV} = -1.53 \text{ eV}$, so the net energy required to remove a neutral Na Cl pair from the crystal is $7.85 \text{ eV} - 1.53 \text{ eV} = 6.32 \text{ eV}.$

EVALUATE: Our calculation is in good agreement with the experimental value.

42.49. IDENTIFY and SET UP: Use the description of the bcc lattice in Figure 42.11c in the textbook to calculate the number of atoms per unit cell and then the number of atoms per unit volume.

EXECUTE: (a) Each unit cell has one atom at its center and 8 atoms at its corners that are each shared by 8 other unit cells. So there are $1 + 8/8 = 2$ atoms per unit cell.

$$\frac{n}{V} = \frac{2}{(0.35 \times 10^{-9} \text{ m})^3} = 4.66 \times 10^{-8} \text{ atoms/m}^3.$$

(b) $E_{F0} = \frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \left(\frac{N}{V} \right)^{2/3}.$

In this equation N/V is the number of free electrons per m^3 . But the problem says to assume one free electron per atom, so this is the same as n/V calculated in part (a).

$m = 9.109 \times 10^{-31} \text{ kg}$ (the electron mass), so $E_{F0} = 7.563 \times 10^{-19} \text{ J} = 4.7 \text{ eV}.$

EVALUATE: Our result for metallic lithium is similar to that calculated for copper in Example 42.7.

42.50. (a) IDENTIFY: The rotational energy levels are given by $E_l = l(l+1) \frac{\hbar^2}{2I}$. The photon wavelength λ is

related to the transition energy of the atom by $\Delta E = \frac{hc}{\lambda}.$

SET UP: For emission, $\Delta l = -1$. For such a transition, from state l to state $l-1$, we have

$\Delta E_l = [l(l+1) - (l-1)l] \frac{\hbar^2}{2I} = \frac{l\hbar^2}{I}.$ The difference in transition energies for adjacent lines in the spectrum is

$\Delta E = \Delta E_l - \Delta E_{l-1} = \frac{\hbar^2}{I}.$

EXECUTE: The transition energies corresponding to the observed wavelengths are $3.29 \times 10^{-21} \text{ J}$, $2.87 \times 10^{-21} \text{ J}$, $2.47 \times 10^{-21} \text{ J}$, $2.06 \times 10^{-21} \text{ J}$, and $1.65 \times 10^{-21} \text{ J}$. The average spacing of these energies is

$0.410 \times 10^{-21} \text{ J}$. Then, $\frac{\hbar^2}{I} = 0.410 \times 10^{-21} \text{ J}$, from which $I = 2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2.$

EVALUATE: With $\frac{\hbar^2}{I} = 0.410 \times 10^{-21} \text{ J}$ and $\Delta E_l = \frac{l\hbar^2}{I}$, we find that these wavelengths correspond to transitions from levels 8, 7, 6, 5, and 4 to the respective next lower levels.

(b) IDENTIFY: Each transition is from the level l to the level $l-1$. The rotational energies are given by $E_l = l(l+1)\frac{\hbar^2}{2I}$. The transition energy is related to the photon wavelength by $\Delta E = hc/\lambda$.

SET UP: $E_l = l(l+1)\hbar^2/2I$, so $\Delta E = E_l - E_{l-1} = [l(l+1) - l(l-1)]\left(\frac{\hbar^2}{2I}\right) = l\left(\frac{\hbar^2}{I}\right)$.

EXECUTE: $l\left(\frac{\hbar^2}{I}\right) = \frac{\hbar^2}{\lambda}$.

$$l = \frac{2\pi c I}{\hbar \lambda} = \frac{2\pi(2.998 \times 10^8 \text{ m/s})(2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2)}{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})\lambda} = \frac{4.843 \times 10^{-4} \text{ m}}{\lambda}.$$

$$\text{For } \lambda = 60.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{60.4 \times 10^{-6} \text{ m}} = 8.$$

$$\text{For } \lambda = 69.0 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{69.0 \times 10^{-6} \text{ m}} = 7.$$

$$\text{For } \lambda = 80.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{80.4 \times 10^{-6} \text{ m}} = 6.$$

$$\text{For } \lambda = 96.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{96.4 \times 10^{-6} \text{ m}} = 5.$$

$$\text{For } \lambda = 120.4 \mu\text{m}, l = \frac{4.843 \times 10^{-4} \text{ m}}{120.4 \times 10^{-6} \text{ m}} = 4.$$

EVALUATE: In each case l is an integer, as it must be.

(c) IDENTIFY: The rotational energies of a molecule depend on its moment of inertia, which in turn depends on the separation between the atoms in the molecule.

SET UP: Part (a) gives $I = 2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2$. $I = m_r r^2$. Calculate m_r and solve for r .

$$\text{EXECUTE: } m_r = \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} = \frac{(1.67 \times 10^{-27} \text{ kg})(5.81 \times 10^{-26} \text{ kg})}{1.67 \times 10^{-27} \text{ kg} + 5.81 \times 10^{-26} \text{ kg}} = 1.623 \times 10^{-27} \text{ kg}.$$

$$r = \sqrt{\frac{I}{m_r}} = \sqrt{\frac{2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2}{1.623 \times 10^{-27} \text{ kg}}} = 1.29 \times 10^{-10} \text{ m} = 0.129 \text{ nm}.$$

EVALUATE: This is a typical atomic separation for a diatomic molecule; see Example 42.2 for the corresponding distance for CO.

(d) IDENTIFY and SET UP: The longest λ implies the smallest ΔE , and this is for the transition from $l=1$ to $l=0$.

$$\text{EXECUTE: } \Delta E = l\left(\frac{\hbar^2}{I}\right) = (1)\frac{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2.71 \times 10^{-47} \text{ kg} \cdot \text{m}^2} = 4.099 \times 10^{-22} \text{ J}.$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{4.099 \times 10^{-22} \text{ J}} = 4.85 \times 10^{-4} \text{ m} = 485 \mu\text{m}.$$

EVALUATE: This is longer than any wavelengths in part (b).

42.51. IDENTIFY and SET UP: The occupation probability $f(E)$ is $f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$.

EXECUTE: (a) Figure 42.51 shows the graph of E versus $\ln\{[1/f(E)] - 1\}$ for the data given in the problem. The slope of the best-fit straight line is 0.445 eV, and the y -intercept is 1.80 eV.

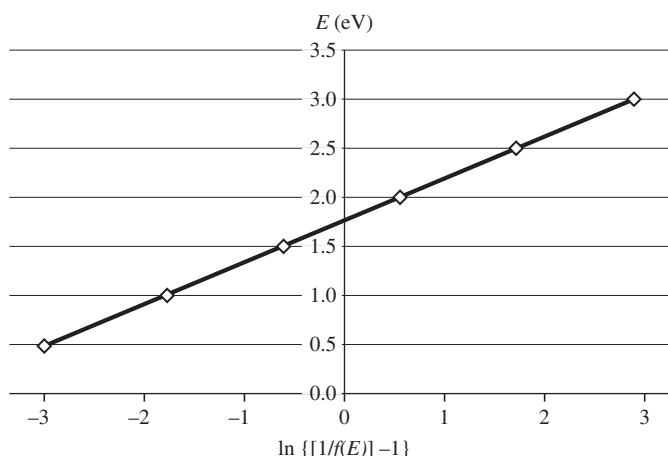


Figure 42.51

(b) Solve the $f(E)$ equation for E , giving $e^{(E-E_F)/kT} = 1/f(E) - 1$. Now take natural logarithms of both side of the equation, giving $(E - E_F)/kT = \ln\{[1/f(E)] - 1\}$, which gives $E = kT \ln\{[1/f(E)] - 1\} + E_F$.

From this we see that a graph of E versus $\ln\{[1/f(E)] - 1\}$ should be a straight line having a slope equal to kT and a y -intercept equal to E_F . From our graph, we get $E_F = y\text{-intercept} = 1.80 \text{ eV}$.

The slope is equal to kT , so $T = (\text{slope})/k = (0.445 \text{ eV})/(1.38 \times 10^{-23} \text{ J/K}) = (7.129 \times 10^{-20} \text{ J})/(1.38 \times 10^{-23} \text{ J/K}) = 5170 \text{ K}$.

EVALUATE: In Example 42.7, the Fermi energy for copper was found to be 7.03 eV, so our result of 1.80 eV seems plausible.

- 42.52. IDENTIFY and SET UP:** We assume that the equation $I = I_S(e^{eV/kT} - 1)$ applies for this p - n junction. Use the given information for I and V to calculate the saturation current I_S and the temperature T for the junction.

EXECUTE: Put the numbers given in the problem into the equation for the current.

$$0.407 \text{ mA} = I_S(e^{(1.60 \times 10^{-19} \text{ C})(0.00500 \text{ V})/(1.38 \times 10^{-23} \text{ J/K})T} - 1) = I_S(e^{(57.97 \text{ K})/T} - 1).$$

$$-0.338 \text{ mA} = I_S(e^{(1.60 \times 10^{-19} \text{ C})(-0.00500 \text{ V})/(1.38 \times 10^{-23} \text{ J/K})T} - 1) = I_S(e^{(-57.97 \text{ K})/T} - 1).$$

$$\text{Dividing the two equations gives } \frac{0.407}{0.338} = \frac{(e^{(57.97 \text{ K})/T} - 1)}{(e^{(-57.97 \text{ K})/T} - 1)}.$$

$$\text{Cross-multiplying and simplifying gives } e^{(57.97 \text{ K})/T} - 2.204 + 1.204e^{-(57.97 \text{ K})/T} = 0.$$

$$\text{Letting } x = e^{(57.97 \text{ K})/T}, \text{ this equation becomes } x - 2.204 + 1.204x^{-1} = 0.$$

$$\text{Multiplying by } x \text{ gives the quadratic equation } x^2 - 2.204x + 1.204 = 0.$$

The two solutions are $x = 1.00$ or $x = 1.204$. The $x = 1.00$ solution would require $T = \infty$, which is not physically possible, so $x = 1.204$ is the solution to use. This gives $1.204 = e^{(57.97 \text{ K})/T}$. Taking natural logarithms of both sides gives $\ln(1.204) = (57.97 \text{ K})/T$, so $T = (57.97 \text{ K})/\ln(1.204) = 312 \text{ K}$.

$$\text{The saturation current is } I_S = \frac{I}{e^{eV/kT} - 1} = \frac{0.407 \text{ mA}}{e^{(1.60 \times 10^{-19} \text{ C})(0.00500 \text{ V})/[(1.38 \times 10^{-23} \text{ J/K})(312 \text{ K})]} - 1} = 1.99 \text{ mA}.$$

EVALUATE: 312 K = 39°C = 102°F, which is quite a bit warmer than room temperature ($\approx 20^\circ\text{C}$). A current of about 2 mA is not unusual in laboratory apparatus.

- 42.53. IDENTIFY and SET UP:** $p = -\frac{dE_{\text{tot}}}{dV}$. Relate E_{tot} to E_{F0} and evaluate the derivative.

$$\text{EXECUTE: (a) } \frac{dE_{\text{tot}}}{dV} = \frac{3}{5} \left(\frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \right) N^{5/3} \left(-\frac{2}{3} V^{-5/3} \right), \text{ so } p = \left(\frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} \right) \left(\frac{N}{V} \right)^{5/3}, \text{ as was to be shown.}$$

(b) $N/V = 8.45 \times 10^{28} \text{ m}^{-3}$.

$$p = \left(\frac{3^{2/3} \pi^{4/3} (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{5(9.109 \times 10^{-31} \text{ kg})} \right) (8.45 \times 10^{28} \text{ m}^{-3})^{5/3} = 3.81 \times 10^{10} \text{ Pa} = 3.76 \times 10^5 \text{ atm}.$$

EVALUATE: (c) Normal atmospheric pressure is about 10^5 Pa , so these pressures are extremely large. The electrons are held in the metal by the attractive force exerted on them by the copper ions.

42.54. IDENTIFY and SET UP: From Problem 42.53, $p = \frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} \left(\frac{N}{V} \right)^{5/3}$. Use this expression to calculate dp/dV .

EXECUTE: (a) $B = -V \frac{dp}{dV} = -V \left[\frac{5}{3} \cdot \frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} \cdot \left(\frac{N}{V} \right)^{2/3} \left(\frac{-N}{V^2} \right) \right] = \frac{5}{3} p$.

(b) $\frac{N}{V} = 8.45 \times 10^{28} \text{ m}^{-3}$. $B = \frac{5}{3} \cdot \frac{3^{2/3} \pi^{4/3} \hbar^2}{5m} (8.45 \times 10^{28} \text{ m}^{-3})^{5/3} = 6.33 \times 10^{10} \text{ Pa}$.

EVALUATE: (c) The fraction of B due to the free electrons is $\frac{6.33 \times 10^{10} \text{ Pa}}{1.4 \times 10^{11} \text{ Pa}} = 0.45$. The copper ions

themselves make up the remaining fraction.

42.55. IDENTIFY and SET UP: Follow the steps specified in the problem.

EXECUTE: (a) $E_{F0} = \frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \left(\frac{N}{V} \right)^{2/3}$. Let $E_{F0} = \frac{1}{100} mc^2$.

$$\left(\frac{N}{V} \right) = \left[\frac{2m^2 c^2}{(100) 3^{2/3} \pi^{4/3} \hbar^2} \right]^{3/2} = \frac{2^{3/2} m^3 c^3}{100^{3/2} 3 \pi^2 \hbar^3} = \frac{2^{3/2} m^3 c^3}{3000 \pi^2 \hbar^3} = 1.67 \times 10^{33} \text{ m}^{-3}.$$

(b) $\frac{8.45 \times 10^{28} \text{ m}^{-3}}{1.67 \times 10^{33} \text{ m}^{-3}} = 5.06 \times 10^{-5}$. Since the real concentration of electrons in copper is less than one part

in 10^{-4} of the concentration where relativistic effects are important, it is safe to ignore relativistic effects for most applications.

(c) The number of electrons is $N_e = \frac{6(2 \times 10^{30} \text{ kg})}{1.99 \times 10^{-26} \text{ kg}} = 6.03 \times 10^{56}$. The concentration is

$$\frac{N_e}{V} = \frac{6.03 \times 10^{56}}{\frac{4}{3} \pi (6.00 \times 10^6 \text{ m})^3} = 6.66 \times 10^{35} \text{ m}^{-3}.$$

EVALUATE: (d) Comparing this to the result from part (a) $\frac{6.66 \times 10^{35} \text{ m}^{-3}}{1.67 \times 10^{33} \text{ m}^{-3}} \cong 400$ so relativistic effects

will be very important.

42.56. IDENTIFY and SET UP: The sensitivity is defined as $\Delta V / \Delta T$.

EXECUTE: From the graph shown with the introduction, we see that for a current of 0.1 A (100 mA), the voltage at 25°C is about 0.75 V, and at 150°C it is about 0.55 V. Therefore the sensitivity is

$$\frac{\Delta V}{\Delta T} = \frac{0.55 \text{ V} - 0.75 \text{ V}}{150^\circ\text{C} - 25^\circ\text{C}} = -1.6 \text{ mV}/^\circ\text{C} \approx -2.0 \text{ mV}/^\circ\text{C}. \text{ Therefore choice (d) is correct.}$$

EVALUATE: If the temperature changes by 10°C , V changes by about 20 mV, which can be significant.

42.57. IDENTIFY and SET UP: As the temperature increases, the electrons gain energy.

EXECUTE: As T increases, more electrons gain enough energy to jump into the conduction band, so for a given voltage, more current will flow at a higher temperature than at a lower temperature. Therefore choice (b) is correct.

EVALUATE: For ordinary resistors, increasing their temperature increases their resistance, so less current would flow.

42.58. IDENTIFY and SET UP: On the graph shown with the introduction, draw a vertical line between the two curves. This line represents a constant voltage.

EXECUTE: For V greater than about 0.2 V, the current at 150°C is greater than at 25°C. So increasing the temperature at a constant voltage increases the current, which makes choice (b) correct.

EVALUATE: This result is consistent with what we found in Passage Problem 42.57.