

## Notes

1. The statistical approach may also be used as an approximation in systems where the number of particles is not particularly large. For example, in Chapter 11 we will discuss briefly a statistical model of the atomic nucleus, a system containing only of the order of 100 particles.

2. Ludwig E. Boltzmann (1844–1906), Austrian physicist. His pioneering statistical interpretation of the second law of thermodynamics earned for him recognition as the founder of statistical mechanics. He explained theoretically the experimental observations of Josef Stefan, whom he served as an assistant while in college, that the quantity of radiation increases with the fourth power of the temperature. He eventually succeeded Stefan in the chair of physics at Vienna. A strong proponent of the atomic theory of matter, his suicide was apparently motivated in part by opposition to his views by others.

3. To avoid having to repeat this rather long phrase frequently, which will occur for  $E$  as well as  $v$ , we will hereafter use the expression “the number in  $dv_x$  at  $v_x$ ” or simply “the number in  $dv_x$ .”

4. Or refer to a table of integrals.

5. Historically, rotation about the  $z'$  axis of the dumbbell was ruled out by assuming either that the atoms are points and the moment of inertia about this axis is therefore zero (not true) or that the atoms are hard smooth spheres, in which case rotation about this axis cannot be changed by collisions and therefore does not participate in the exchange of energy (also not true). Either of these assumptions also rules out the possibility of rotation of a monatomic molecule.

6. Satyendra Nath Bose (1894–1974), Indian physicist. Following publication of his paper on the statistics of indistinguishable particles, which was translated into German for publication by Einstein himself, Bose spent two years in Europe, then returned to India to devote himself to teaching. Lacking a Ph.D., he was denied a professorship until a one-sentence postcard from Einstein was received at Dacca University in his support.

7. Enrico Fermi (1901–1954), Italian-American physicist. An exceedingly prolific scientist and intrepid amateur tennis player whose work encompassed solid-state, nuclear, and particle physics, he is perhaps best known as the “father” of the nuclear reactor. He was awarded the Nobel Prize in Physics in 1938 for his work in nuclear physics.

8. Paul A. M. Dirac (1902–1984), English physicist. His development of relativistic wave mechanics for spin- $\frac{1}{2}$  particles led to his prediction in 1930 of the existence of the positron. Its discovery by Anderson two years later resulted in Dirac’s being awarded (along with Schrödinger) the 1933 Nobel Prize in Physics. From 1932 until his retirement he occupied the Lucasian Chair of Mathematics at Cambridge University, which had been held 250 years earlier by Newton and most recently by Stephen Hawking.

9. Heike Kamerlingh Onnes (1853–1926), Dutch physicist. His success in liquefying helium enabled him to investigate the properties of other materials at liquid helium temperatures. This, in turn, led to his discovery of superconductivity in 1911. His work on the behavior of materials at low temperatures earned him the Nobel Prize in Physics in 1913.

10. J. C. McLennan, H. D. Smith, and J. O. Wilhelm, *Philosophical Magazine*, **14**, 161 (1932).

11. At very low temperatures liquid  $^4\text{He}$  does solidify at a pressure of about 25 atm, liquid  $^3\text{He}$  at about 30 atm.

12. Narrow channels that permit only the superfluid to pass are, of course, called *superleaks*.

13. These and many other properties are elegantly displayed in the film *Liquid Helium II: The Superfluid*. See the A. Leitner entry in the General References above.

14. In the thermodynamic equilibrium state their sample, rubidium, is a solid metal at room temperature.

15. Einstein used the Boltzmann distribution in its discrete form  $f_B(E) = \sum_{n=0}^{\infty} A e^{-E_n/kT}$ .

## Problems

## LEVEL I

## Section 8-1 Classical Statistics: A Review

8-1. (a) Calculate  $v_{\text{rms}}$  for  $\text{H}_2$  at  $T = 300$  K. (b) Calculate the temperature  $T$  for which  $v_{\text{rms}}$  for  $\text{H}_2$  equals the escape speed of 11.2 km/s.

8-2. (a) The ionization energy for hydrogen atoms is 13.6 eV. At what temperature is the average kinetic energy of translation equal to 13.6 eV? (b) What is the average kinetic energy of translation of hydrogen atoms at  $T = 10^7$  K, a typical temperature in the interior of the Sun?

**8-3.** The molar mass of oxygen gas ( $\text{O}_2$ ) is about 32 g/mol and that of hydrogen gas ( $\text{H}_2$ ) about 2 g/mol. Compute (a) the rms speed of  $\text{O}_2$  and (b) the rms speed of  $\text{H}_2$  when the temperature is  $0^\circ\text{C}$ .

**8-4.** Show that the SI units of  $(3RT/M)^{1/2}$  are m/s.

**8-5.** (a) Find the total kinetic energy of translation of 1 mole of  $\text{N}_2$  molecules at  $T = 273\text{ K}$ . (b) Would your answer be the same, greater, or less for 1 mole of He atoms at the same temperature? Justify your answer.

**8-6.** Use the Maxwell distribution of molecular speeds to calculate  $\langle v^2 \rangle$  for the molecules of a gas.

**8-7.** Neutrons in a nuclear reactor have a Maxwell speed distribution when they are in thermal equilibrium. Find  $\langle v \rangle$  and  $v_m$  for neutrons in thermal equilibrium at 300 K. Show that  $n(v)$  (Equation 8-8) has its maximum value at  $v = v_m = (2kT/m)^{1/2}$ .

**8-8.** A container holds 128 identical molecules whose speeds are distributed as follows:

No. of molecules	4	12	20	24	20	16	12	8	6	4
Speed range (m/s)	0.0–1.0	1.0–2.0	2.0–3.0	3.0–4.0	4.0–5.0	5.0–6.0	6.0–7.0	7.0–8.0	8.0–9.0	9.0–10.0

Graph these data and indicate on the graph  $v_m$ ,  $\langle v \rangle$ , and  $v_{\text{rms}}$ .

**8-9.** Show that the most probable speed  $v_m$  of the Maxwell distribution of speeds is given by Equation 8-9.

**8-10.** Compute the total translational kinetic energy of one liter of oxygen held at a pressure of one atmosphere and a temperature of  $20^\circ\text{C}$ .

**8-11.** From the absorption spectrum it is determined that about one out of  $10^6$  hydrogen atoms in a certain star is in the first excited state, 10.2 eV above the ground state (other excited states can be neglected). What is the temperature of the star? (Take the ratio of statistical weights to be 4, as in Example 8-2.)

**8-12.** The first excited rotational energy state of the  $\text{H}_2$  molecule ( $g_2 = 3$ ) is about  $4 \times 10^{-3}$  eV above the lowest energy state ( $g_1 = 1$ ). What is the ratio of the numbers of molecules in these two states at room temperature (300 K)?

**8-13.** A monatomic gas is confined to move in two dimensions so that the energy of an atom is  $E_k = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2$ . What are  $C_V$ ,  $C_P$ , and  $\gamma$  for this gas? ( $C_P$ , the heat capacity at constant pressure, is equal to  $C_V + nR$  and  $\gamma = C_P/C_V$ .)

**8-14.** Use the Dulong-Petit law that  $C_V = 3R$  for solids to calculate the specific heat  $c_v = C_V/M$  in cal/g for (a) aluminum,  $M = 27.0$  g/mol, (b) copper,  $M = 63.5$  g/mol, and (c) lead,  $M = 207$  g/mol, and compare your results with the values given in a handbook. (Include the handbook reference in your answer.)

**8-15.** Calculate the most probable kinetic energy  $E_m$  from the Maxwell distribution of kinetic energies (Equation 8-13).

**8-16.** (a) Show that the speed distribution function can be written  $n(v) = 4\pi^{-1/2}(v/v_m)^2 v_m^{-1} e^{-(v/v_m)^2}$ , where  $v_m$  is the most probable speed. Consider 1 mole of molecules and approximate  $dv$  by  $\Delta v = 0.01 v_m$ . Find the number of molecules with speeds in  $dv$  at (b)  $v = 0$ , (c)  $v = v_m$ , (d)  $v = 2v_m$ , and (e)  $v = 8v_m$ .

**8-17.** Consider a sample containing hydrogen atoms at 300 K. (a) Compute the number of atoms in the first ( $n = 2$ ) and second ( $n = 3$ ) excited states compared to those in the ground state ( $n = 1$ ). Include the effects of degeneracy in your calculations. (b) At what temperature would 1 percent of the atoms be in the  $n = 2$  state? (c) At the temperature found in (b), what fraction of the atoms will be in the  $n = 3$  state?

**8-18.** Consider a sample of non-interacting lithium atoms (Li,  $Z = 3$ ) with the third (outer) electron in the  $3p$  state in a uniform 4.0 T magnetic field. (a) Determine the fraction of the atom in the  $m_l = +1, 0$ , and  $-1$  states at 300 K. (b) In the  $3p \rightarrow 2s$  transition, what will be the relative intensities of the three lines of the Zeeman effect?

### Section 8-2 Quantum Statistics

**8-19.** Find the number density  $N/V$  for electrons such that (a)  $e^{-\alpha} = 1$  and (b)  $e^{-\alpha} = 10^{-6}$ .

**8-20.** (a) Compute  $e^{-\alpha}$  from Equation 8-44 for  $O_2$  gas at standard conditions. (b) At what temperature is  $e^{-\alpha} = 1$  for  $O_2$ ?

**8-21.** Given three containers all at the same temperature, one filled with a gas of classical molecules, one with a fermion gas, and one with a boson gas, which will have the highest pressure? Which will have the lowest pressure? Support your answer.

**8-22.** (a) For  $T = 5800$  K, at what energy will the Bose-Einstein distribution function  $f_{BE}(E)$  equal one (for  $\alpha = 0$ )? (b) Still with  $\alpha = 0$ , to what value must the temperature change if  $f_{BE}(E) = 0.5$  for the energy in part (a)?

**8-23.** A container at 300 K contains  $H_2$  gas at a pressure of one atmosphere. At this temperature  $H_2$  obeys the Boltzmann distribution. To what temperature must the  $H_2$  gas be cooled before quantum effects become important and the use of the Boltzmann distribution is no longer appropriate? (*Hint:* Equate the de Broglie wavelength at the average energy to the average spacing between molecules, using the ideal gas law to compute the density.)

### Section 8-3 The Bose-Einstein Condensation

**8-24.** Compute  $N_0/N$  from Equation 8-52 for (a)  $T = 3T_c/4$ , (b)  $T = \frac{1}{2}T_c$ , (c)  $T = T_c/4$ , and (d)  $T = T_c/8$ .

**8-25.** Show that  $N_0 \approx 1/\alpha$  for small values of  $\alpha$  as asserted in the paragraph above Equation 8-52.

**8-26.** Like  ${}^4\text{He}$ , the most common form of neon,  ${}^{20}\text{Ne}$ , is a rare gas and the  ${}^{20}\text{Ne}$  atoms have zero spin and so are bosons. But unlike helium, neon does not become superfluid at low temperatures. Show that this is to be expected by computing neon's critical temperature and comparing it with the element's freezing point of 24.5 K.

### Section 8-4 The Photon Gas: An Application of Bose-Einstein Statistics

**8-27.** If the Sun were to become cooler (without changing its radius), the energy density at the surface would decrease according to Equation 8-56. Suppose the Sun's temperature were to decrease by 5 percent. Compute the fractional change in the rate at which solar energy arrives at Earth. (Assume that the Sun's surface is in equilibrium and radiates as a blackbody.)

**8-28.** Find the average energy of an oscillator at (a)  $T = 10hf/k$ , (b)  $T = hf/k$ , and (c)  $T = 0.1hf/k$ , and compare your results with those from the equipartition theorem.

**8-29.** (a) Show that the rule of Dulong-Petit follows directly from Einstein's specific heat formula (Equation 8-62) as  $T \rightarrow \infty$ . (b) Show that  $C_V \rightarrow 0$  as  $T \rightarrow 0$ .

**8-30.** Using Figure 8-13, compute the (approximate) frequency of atomic oscillations in silicon and in aluminum at 200 K.

**8-31.** Use Equation 8-62 to calculate the value of  $C_V$  for a solid at the Einstein temperature  $T_E = hf/k$ .

### Section 8-5 Properties of a Fermion Gas

**8-32.** Use Equation 8-69 to plot an accurate graph of  $n_{FD}(E)/V$  for electrons whose Fermi energy is 4.8 eV from  $E = 4.5$  eV to  $E = 5.1$  eV at  $T = 300$  K. Determine from the graph the number of electrons per unit volume just below the Fermi energy that can move to states just above the Fermi energy.

**8-33.** Consider a gas of electrons (fermions) and a gas of photons (bosons). Which has more states available at  $T = 1$  K? Explain why.

## LEVEL II

**8-34.** The molar heat capacity data given in Table 8-2 are taken from *AIP Handbook*, 2d ed. (McGraw-Hill, New York, 1963). Plot the data for these solids all on one graph and sketch in the curves  $C_V$  versus  $T$ . Estimate the Einstein temperature for each of the solids using the result of Problem 8-31.

**8-35.** Recalling that the Fermi-Dirac distribution function applies to all fermions, including protons and neutrons, each of which have spin  $\frac{1}{2}$ , consider a nucleus of  $^{22}\text{Ne}$  consisting of 10 protons and 12 neutrons. Protons are distinguishable from neutrons, so two of each particle (spin up, spin down) can be put into each energy state. Assuming that the radius of the  $^{22}\text{Ne}$  nucleus is  $3.1 \times 10^{-15}$  m, estimate the Fermi energy and the average energy of the nucleus in  $^{22}\text{Ne}$ . Express your results in MeV. Do the results seem reasonable?

**8-36.** What is the ground-state energy of 10 non-interacting bosons in a one-dimensional box of length  $L$ ?

**8-37.** Make a plot of  $f_{FD}(E)$  versus  $E$  for (a)  $T = 0.1T_F$  and (b)  $T = 0.5T_F$ , where  $T_F = E_F/k$ .

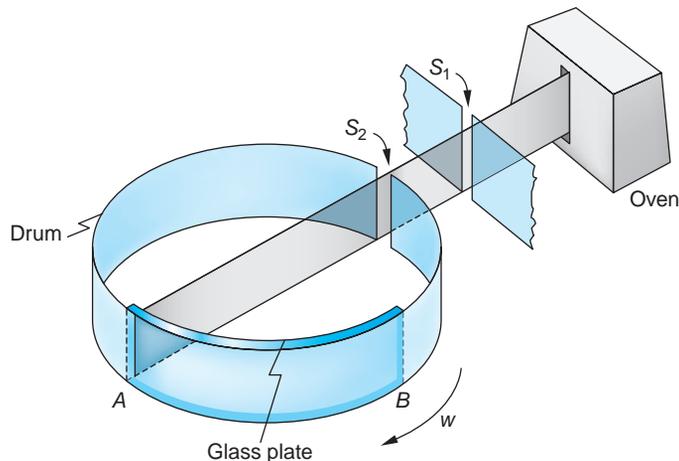
**8-38.** Compute the fraction of helium atoms in the superfluid state at (a)  $T = T_c/2$  and (b)  $T = T_c/4$ .

**8-39.** The depth of the potential well for free electrons in a metal can be accurately determined by observing that the photoelectric work function is the energy necessary to remove an electron at the top of the occupied states from the metal; an electron in such a state has the Fermi energy. Assuming each atom provides one free electron to the gas, compute the depth of the well for the free electrons in gold. The work function for gold is 4.8 eV.

**Table 8-2 Heat capacities in cal/mol · K for Au, diamond, Al, and Be**

T, K	Au	Diamond	Al	Be
20	0.77	0.00	0.05	0.003
50	3.41	0.005	0.91	0.04
70	4.39	0.016	1.85	0.12
100	5.12	0.059	3.12	0.43
150	5.62	0.24	4.43	1.36
200	5.84	0.56	5.16	2.41
250	5.96	0.99	5.56	3.30
300	6.07	1.46	5.82	3.93
400	6.18	2.45	6.13	4.77
500	6.28	3.24	6.42	5.26
600	6.40	3.85	6.72	5.59
800	6.65	4.66	7.31	6.07
1000	6.90	5.16	7.00	6.51

FIGURE 8-34 [Problem 8-40.]



**8-40.** An early method testing Maxwell's theoretical prediction for the distribution of molecular speeds is shown in Figure 8-34. In 1925 Otto Stern used a beam of  $\text{Bi}_2$  molecules emitted from an oven at 850 K. The beam defined by slit  $S_1$  was admitted into the interior of a rotating drum via slit  $S_2$  in the drum wall. The identical bunches of molecules thus formed struck and adhered to a curved glass plate fixed to the interior drum wall, the fastest molecules striking near A, which was opposite  $S_2$ , the slowest near B, and the others in between depending on their speeds. The density of the molecular deposits along the glass plate was measured with a densitometer. The density (proportional to the number of molecules) plotted against distance along the glass plate (dependent on  $v$ ) made possible determination of the speed distribution. If the drum is 10 cm in diameter and is rotating at 6250 rpm, (a) find the distance from A where molecules traveling at  $v_m$ ,  $\langle v \rangle$ , and  $v_{\text{rms}}$  will strike. (b) The plot in (a) must be corrected slightly in order to be compared with Maxwell's distribution equation. Why? (c) Would  $\text{N}_2$  molecules work as well as  $\text{Bi}_2$  molecules in this experiment? Why or why not?

**8-41.** The speed distribution of molecules in a container is the Maxwell distribution  $v_m$ ,  $\langle v \rangle$ , and  $v_{\text{rms}}$ . The number with speed  $v$  that hit the wall in a given time is proportional to the speed  $v$  and to  $f(v)$ . Thus, if there is a very small hole in the wall (too small to have much effect on the distribution inside), the speed distribution of those that escape is  $F(v) \propto vf(v) \propto v^3 e^{-mv^2/2kT}$ . Show that the mean energy of those that escape is  $2kT$ .

### LEVEL III

**8-42.** This problem is related to the equipartition theorem. Consider a system in which the energy of a particle is given by  $E = Au^2$ , where  $A$  is a constant and  $u$  is any coordinate or momentum that can vary from  $-\infty$  to  $+\infty$ . (a) Write the probability of the particle having  $u$  in the range  $du$  and calculate the normalization constant  $C$  in terms of  $A$ . (b) Calculate the average energy  $\langle E \rangle = \langle Au^2 \rangle$  and show that  $\langle E \rangle = \frac{1}{2}kT$ .

**8-43.** Calculate the average value of the magnitude of  $v_x$  from the Maxwell distribution.

**8-44.** Show that  $f_{FD}(E) \rightarrow f_B(E)$  for  $E \gg E_F$ .

**8-45.** Carry out the integration indicated in Equation 8-43 to show that  $\alpha$  is given by Equation 8-44.

**8-46.** Consider a system of  $N$  particles that has only two possible energy states,  $E_1 = 0$  and  $E_2 = \epsilon$ . The distribution function is  $f_i = Ce^{-E_i/kT}$ . (a) What is  $C$  for this case?

(b) Compute the average energy  $\langle E \rangle$  and show that  $\langle E \rangle \rightarrow 0$  as  $T \rightarrow 0$  and  $\langle E \rangle \rightarrow \epsilon/2$  as  $T \rightarrow \infty$ . (c) Show that the heat capacity is

$$C_V = Nk \left( \frac{\epsilon}{kT} \right)^2 \frac{e^{-\epsilon/kT}}{(1 + e^{-\epsilon/kT})^2}$$

(d) Sketch  $C_V$  versus  $T$ .

**8-47.** If the assumptions leading to the Bose-Einstein distribution are modified so that the number of particles is not assumed constant, the resulting distribution has  $e^\alpha = 1$ . This distribution can be applied to a “gas” of photons. Consider the photons to be in a cubic box of side  $L$ . The momentum components of a photon are quantized by the standing-wave conditions  $k_x = n_1\pi/L$ ,  $k_y = n_2\pi/L$ ,  $k_z = n_3\pi/L$ , and  $k_z = n_3\pi/L$ , where  $p = \hbar(k_x^2 + k_y^2 + k_z^2)^{1/2}$  is the magnitude of the momentum. (a) Show that the energy of a photon can be written  $E = N(\hbar c\pi/L)$ , where  $N^2 = n_1^2 + n_2^2 + n_3^2$ . (b) Assuming two photons per space state because of the two possible polarizations, show that the number of states between  $N$  and  $N + dN$  is  $\pi N^2 dN$ . (c) Find the density of states and show that the number of photons in the energy interval  $dE$  is

$$n(E) dE = \frac{8\pi(L/hc)^3 E^2 dE}{e^{E/kT} - 1}$$

(d) The energy density in  $dE$  is given by  $u(E) dE = En(E) dE/L^3$ . Use this to obtain the Planck blackbody radiation formula for the energy density in  $d\lambda$ , where  $\lambda$  is the wavelength:

$$u(\lambda) = \frac{8\pi hc\lambda^{-5}}{e^{hc/\lambda kT} - 1}$$

## Notes

1. The term *orbital* is frequently used in molecular physics and in chemistry to refer to the space part of the electron wave functions, that is, the quantum numbers  $n$ ,  $\ell$ , and  $m_\ell$ . In molecular physics the electrons of interest are usually the outermost (valence) ones of the constituent atoms, which become associated with the entire molecule rather than their original atoms, so we speak of “molecular orbitals” as well as “atomic orbitals.”
2. Molecules whose atoms are identical, such as  $\text{H}_2$ , are sometimes called *homopolar* or *homonuclear*. Those whose atoms are not identical are called *heteropolar* or *heteronuclear*.
3.  $\text{C}_{60}$  and the other fullerenes are named after the philosopher and engineer R. Buckminster Fuller, who invented the architectural geodesic dome structure. Such domes, as Fuller pointed out, can be considered as networks of pentagons and hexagons.
4. Leonhard Euler (1707–1783), Swiss mathematician. Arguably the most prolific mathematician of all time, he published 866 papers during his lifetime and, despite having lost his sight in 1766 (in part due to his earlier observations of the Sun), he left so many manuscripts at his death that it took another 35 years to get them all published. He introduced the symbol  $e$  as the base of the natural logarithms and  $i$  as the square root of  $-1$ .
5. Johannes D. van der Waals (1837–1923), Dutch physicist. Largely self-taught, he became interested in the fact that the ideal gas law derived from kinetic theory does not hold exactly for real gases. This led him to question the assumption that no forces act between individual gas molecules except during collisions, which resulted in his development of an equation, the van der Waals equation, which more accurately describes real gases. He was awarded the 1910 Nobel Prize in Physics for his work.
6. This result is derived in most introductory physics books. See, for example, P. A. Tipler and G. Mosca, *Physics for Scientists and Engineers*, 6th ed., W. H. Freeman and Co., New York, 2008, page 671.
7. Terminology concerning the dipole-dipole forces is a bit confused. Some textbooks use *van der Waals* to describe all three types of dipole-dipole forces. We will follow the more common (and traditional) use, reserving *van der Waals* for the attractive force between induced dipoles only.
8. We use  $\nu$  (the Greek letter nu) here rather than  $n$  so as not to confuse the vibrational quantum number with the principal quantum number  $n$  for electronic energy levels.
9. The nitric oxide (NO) molecule is an exception due to its odd electron.
10. Also, the  $\ell \rightarrow \ell - 1$  group of lines are called the *P branch* and the  $\ell \rightarrow \ell + 1$  group the *R branch*.
11. Chandrasekhara V. Raman (1888–1970), Indian physicist. Graduating from college at the age of 16, like Einstein he became a civil servant and worked at science in his spare time. He had predicted that visible light should be inelastically scattered even before Heisenberg predicted it and before Compton had found the effect for x rays. He was awarded the 1930 Nobel Prize in Physics for his work, becoming the first Asian to be so recognized in the sciences.
12. There is also a Raman effect for the vibrational and electronic levels of molecules.
13. T. H. Maiman, “Stimulated Optical Radiation in Ruby,” *Nature*, **187**, 493 (1960).
14. The correction essentially accounts for the fact that, due to the finite line width, the energy density  $u(f)$  in the transition probability must include a narrow range of frequencies  $\Delta f$  rather than just the single frequency  $f$ .
15. Recall that the energy per unit volume  $u(f)$  times  $c$  is the intensity, for example,  $\text{W}/\text{m}^2$  in SI units.
16. A. Javan, W. B. Bennet, Jr., and D. R. Herriott, *Physical Review Letters*, **6**, 106 (1961).
17. W. Ketterle et al., *Science*, **301**, 1513 (2003).
18. To keep things in perspective, although the power of these pulsed lasers is extremely high, the duration of the pulses is very brief, so the total energy delivered in a single pulse is quite small, in the range of 5 J to 100 J.

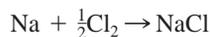
## Problems

### LEVEL I

#### Section 9-1 The Ionic Bond

- 9-1.** The dissociation energy is sometimes expressed in kilocalories per mole. (a) Find the relation between electron volts per molecule and kilocalories per mole. (b) Find the dissociation energy of molecular NaCl in kilocalories per mole. (c) The dissociation energy of the  $\text{Li}_2$  molecule is 106 kJ/mole. Find the value in eV per molecule.

**9-2.** The dissociation energy of  $\text{Cl}_2$  is 2.48 eV. Consider the formation of an NaCl molecule by the reaction



Is this reaction endothermic (requiring energy) or exothermic (giving off energy)? How much energy per molecule is required or given off?

**9-3.** Using the data in Table 9-1, compute the net energy required to transfer an electron between the following pairs of atoms: Cs to F, Li to I, and Rb to Br.

**9-4.** Using the data in Tables 9-1 and 9-2, estimate the dissociation energy of the three ionically bonded molecules CsI, NaF, and LiI. Your results are probably all higher than those in Table 9-2. Explain why.

**9-5.** The equilibrium separation of the  $\text{Rb}^+$  and  $\text{Cl}^-$  ions in RbCl is about 0.267 nm. (a) Calculate the potential energy of attraction of the ions, assuming them to be point charges. (b) The ionization energy of rubidium is 4.18 eV, and the electron affinity of Cl is 3.62 eV. Find the dissociation energy, neglecting the energy of repulsion. (c) The measured dissociation energy is 4.37 eV. What is the energy due to repulsion of the ions?

**9-6.** Compute the Coulomb energy of the KBr molecule at the equilibrium separation. Use that result to compute the exclusion-principle repulsion at  $r_0$ .

**9-7.** If the exclusion-principle repulsion in Problem 9-6 is given by Equation 9-2, compute the coefficient  $A$  and the exponent  $n$ .

**9-8.** Compute the dissociation energy of molecular NaBr in kilocalories per mole.

**9-9.** Note in Table 9-2 that the equilibrium separation of the KBr and RbCl molecules is very nearly equal. Compute the exclusion-principle repulsion for these molecules.

### Section 9-2 The Covalent Bond

**9-10.** Hydrogen can bond covalently with many atoms besides those listed in Tables 9-3 and 9-5, including sulfur, tellurium, phosphorus, and antimony. What would you expect to be the chemical formula of the resulting molecules? (*Hint:* Use the table of electron configurations in Appendix C.)

**9-11.** What kind of bonding mechanism would you expect for (a) the KCl molecule, (b) the  $\text{O}_2$  molecule, and (c) the  $\text{CH}_4$  molecule?

**9-12.** The equilibrium separation of the atoms in the HF molecule is 0.0917 nm, and its measured electric dipole moment is  $6.40 \times 10^{-30} \text{ C} \cdot \text{m}$ . What percentage of the bonding is ionic?

**9-13.** The equilibrium separation of CsF is 0.2345 nm. If its bonding is 70 percent ionic, what should its measured electric dipole moment be?

**9-14.** Ionic bonding in the BaO molecule involves the transfer of two electrons from the Ba atom. If the equilibrium separation is 0.193 nm and the measured electric dipole moment is  $26.7 \times 10^{-30} \text{ C} \cdot \text{m}$ , to what extent is the bond actually ionic?

### Section 9-3 Other Bonding Mechanisms

**9-15.** Find three other elements with the same subshell electron configuration in the two outermost orbits as carbon. Would you expect the same kind of hybrid bonding for these elements as for carbon? Support your answer.

**9-16.** The dipole moment  $\mathbf{p}$  of the water molecule, illustrated in Figure 9-19, is actually the vector sum of two equal dipoles  $\mathbf{p}_1$  and  $\mathbf{p}_2$  directed from the oxygen atom to each of the hydrogen atoms. The measured value of the angle between the two hydrogen atoms is  $104.5^\circ$ , the O–H bond length is 0.0956 nm, and the magnitude of  $\mathbf{p}$  is  $6.46 \times 10^{-30} \text{ C} \cdot \text{m}$ . Compute the fraction of the electron charge that is transferred from each hydrogen to the oxygen.

**9-17.** The polarizability of Ne is  $1.1 \times 10^{-37} \text{ m} \cdot \text{C}^2/\text{N}$ . (a) At what separation would the dipole-dipole energy between a molecule of  $\text{H}_2\text{O}$  and an atom of Ne in the atmosphere

be sufficient to withstand collision with an  $\text{N}_2$  molecule moving with the average kinetic energy for  $T = 300 \text{ K}$ ? (b) At what separation does this energy occur for a typically bonded molecule? (c) On the basis of these results, do you expect  $\text{H}_2\text{O} - \text{Ne}$  bonds to be very likely? Explain your answer.

**9-18.** The hydrogen bonds linking the two helical strands of the DNA have bond strengths of about  $0.3 \text{ eV}$ , or approximately 15 percent of the strengths of the ionic/covalent bonds along the strands. (a) What is the wavelength of a photon with sufficient energy to break this bond? (b) In what part of the spectrum does this wavelength lie? (c) Since a significant intensity exists at this wavelength in the environment, why haven't all the DNA hydrogen bonds long since broken?

**9-19.** Would you expect the following molecules to be polar or nonpolar? Explain your answer in each case. (a)  $\text{NaCl}$ ; (b)  $\text{O}_2$ .

### Section 9-4 Molecular Spectra

**9-20.** The characteristic rotational energy  $E_{0r}$  for the  $\text{N}_2$  molecules is  $2.48 \times 10^{-4} \text{ eV}$ . From this, find the separation distance of the nitrogen atoms in  $\text{N}_2$ .

**9-21.** For the  $\text{O}_2$  molecule, the separation of the atoms is  $0.121 \text{ nm}$ . Calculate the characteristic rotational energy  $E_{0r} = \hbar^2/2I$  in eV.

**9-22.** The  $\text{CO}$  molecule undergoes a transition from the  $\nu = 1$  vibrational state to the  $\nu = 0$  state. (a) What is the wavelength of the emitted photon? (b) At what temperature would 1 percent of the  $\text{CO}$  molecules be in the  $\nu = 1$  vibrational state?

**9-23.** Using data from Table 9-8, (a) compute the vibrational energy of the  $\text{LiH}$  molecule in its lowest vibrational state. (b) Compute the reduced mass of  $\text{LiH}$ . (c) Determine the force constant for  $\text{LiH}$ . (d) From those results, compute an estimate of the  $\text{LiH}$  bond length and compare your result with the value in the table.

**9-24.** Calculate the reduced mass in unified mass units for (a)  $\text{H}_2$ , (b)  $\text{N}_2$ , (c)  $\text{CO}$ , and (d)  $\text{HCl}$ .

**9-25.** The characteristic rotational energy  $E_{0r} = \hbar^2/2I$  for  $\text{KCl}$  is  $1.43 \times 10^{-5} \text{ eV}$ . (a) Find the reduced mass for the  $\text{KCl}$  molecule. (b) Find the separation distance of the  $\text{K}^+$  and  $\text{Cl}^-$  ions.

**9-26.** Use the data from Table 9-8 to find the force constant for (a) the  $\text{H}^{35}\text{Cl}$  and (b) the  $\text{K}^{79}\text{Br}$  molecules.

**9-27.** The vibration frequency of the  $\text{NO}$  molecule is  $5.63 \times 10^{13} \text{ Hz}$ . Compute the force constant for  $\text{NO}$ .

**9-28.** The equilibrium separation of  $\text{HBr}$  is  $0.141 \text{ nm}$ . Treating the  $\text{Br}$  atom as fixed, compute the four lowest rotational energies of the  $\text{HBr}$  molecule and show them in a carefully sketched energy-level diagram.

**9-29.** The vibrational spectrum of  $\text{Li}_2$  consists of a series of equally spaced lines in the microwave region  $1.05 \times 10^{13} \text{ Hz}$  apart. Compute the equilibrium separation for  $\text{Li}_2$ .

**9-30.** Compute the difference in the rotational energy  $E_{0r}$  for  $\text{K}^{35}\text{Cl}$  and  $\text{K}^{37}\text{Cl}$ .

**9-31.** What type of bonding mechanism would you expect for (a)  $\text{NaF}$ , (b)  $\text{KBr}$ , (c)  $\text{N}_2$ , and (d)  $\text{Ne}$ ?

**9-32.** For  $\text{NaCl}$  compute (a) the energy in eV necessary to excite the first rotational state and (b) the wavelength and frequency of the photon emitted in the transition back to the ground state. (Assume that the molecule is in the electronic and vibrational ground states.)

### Section 9-5 Absorption, Stimulated Emission, and Scattering

**9-33.** The five lowest levels of a certain monatomic gas have the values  $E_1 = 0$ ,  $E_2 = 3.80 \text{ eV}$ ,  $E_3 = 4.30 \text{ eV}$ ,  $E_4 = 7.2 \text{ eV}$ , and  $E_5 = 7.5 \text{ eV}$ . (a) If the temperature is high enough that all levels are occupied and the gas is illuminated with light of wavelength  $2400 \text{ nm}$ , what transitions can occur? (b) Which of those found in part (a) will still occur if the temperature is so low that only the state  $E_1$  is occupied? (c) Repeat (a) and (b)

for light of 250 nm wavelength. (d) What wavelength of the incident light would stimulate emission from state  $E_4$ ?

**9-34.** A hydrogen discharge tube is operated at about 300 K in the laboratory in order to produce the Balmer series. Compute the ratio of the probability for spontaneous emission of the  $H_{\alpha}$  line to that for stimulated emission.

**9-35.** Determine the ratio of the number of molecules in the  $v = 1$  state to the number in the  $v = 0$  state for a sample of  $O_2$  molecules at 273 K. Repeat the calculation for 77 K. (Ignore rotational motion.)

**9-36.** The nuclei in the  $F_2$  molecule are separated by 0.14 nm. (a) Compute the energy separations and sketch an energy-level diagram for the lowest four rotational levels with  $v = 0$ . (b) What are the wavelengths of possible transitions between these levels?

### Section 9-6 Lasers and Masers

**9-37.** A pulse from a ruby laser has an average power of 10 MW and lasts 1.5 ns. (a) What is the total energy of the pulse? (b) How many photons are emitted in this pulse?

**9-38.** A helium-neon laser emits light of wavelength 632.8 nm and has a power output of 4 mW. How many photons are emitted per second by this laser?

**9-39.** A laser beam is aimed at the Moon from a distance  $3.84 \times 10^8$  m away. The angular spread of the beam is given by the diffraction formula (Rayleigh's criterion),  $\sin \theta = 1.22\lambda/D$ , where  $D$  is the diameter of the laser tube or rod. (a) Calculate the size of the beam on the Moon for  $D = 10$  cm and  $\lambda = 600$  nm. (b) Repeat the calculation if the laser beam is projected toward the Moon through a 1.0-m-diameter telescope.

**9-40.** A particular atom has two energy levels with a transition wavelength of 420 nm. At 297 K there are  $2.5 \times 10^{21}$  atoms in the lower state. (a) How many atoms are in the upper state? (b) Suppose that  $1.8 \times 10^{21}$  of the atoms in the lower state are pumped to the upper state. How much energy could this system release in a single laser pulse?

### LEVEL II

**9-41.** (a) Calculate the electrostatic potential energy of  $Na^+$  and  $Cl^-$  ions at their equilibrium separation distance of 0.24 nm, assuming the ions to be point charges. (b) What is the energy of repulsion at this separation? (c) Assume that the energy of repulsion is given by Equation 9-2. From Figure 9-2b, this energy equals  $ke^2/r$  at about  $r = 0.14$  nm. Use this and your answer to part (b) to calculate  $n$  and  $A$ . (Although this calculation is not very accurate, the energy of repulsion does vary much more rapidly with  $r$  than does the energy of attraction.)

**9-42.** The angular width of a ruby laser beam is determined by Rayleigh's criterion (see Problem 9-39). For this laser the diameter of the ruby rod is 1.0 cm and  $\lambda = 694.3$  nm. (a) What is the diameter of the spot projected by the ruby laser at a distance of 1.0 km? (b) If the laser is emitting  $10^{18}$  photons/s, what is the power deposited per square centimeter on the target at 1.0 km?

**9-43.** The equilibrium separation of the  $K^+$  and  $Cl^-$  ions in KCl is about 0.267 nm. (a) Calculate the potential energy of attraction of the ions assuming them to be point charges at this separation. (b) The ionization energy of potassium is 4.34 eV and the electron affinity of chlorine is 3.61 eV. Find the dissociation energy for KCl, neglecting any energy of repulsion (see Figure 9-2a). (c) The measured dissociation energy is 4.40 eV. What is the energy due to repulsion of the ions at the equilibrium separation?

**9-44.** Use the equilibrium separation for the  $K^+$  and  $Cl^-$  ions given in Problem 9-43 and the reduced mass of KCl to calculate the characteristic rotational energy  $E_{0r}$  of KCl.

**9-45.** In this problem, you are to find how the van der Waals force between a polar and a nonpolar molecule depends on the distance between the molecules. Let the dipole moment of the polar molecule be in the  $x$  direction and the nonpolar molecule be a distance  $x$  away. (a) How does the electric field due to an electric dipole depend on the distance  $x$ ? (b) Use

the facts that the potential energy of an electric dipole of moment  $\mathbf{p}$  in an electric field  $\mathbf{E}$  is  $U = -\mathbf{p} \cdot \mathbf{E}$  and that the induced dipole moment of the nonpolar molecule is proportional to  $\mathbf{E}$  to find how the potential energy of interaction of the two molecules depends on separation distance. (c) Using  $F_x = -dU/dx$ , find the  $x$  dependence of the force between the two molecules.

**9-46.** The force constant of the covalent bond in the  $\text{H}_2$  molecule is 580 N/m. Determine the energies of the lowest four vibrational levels of the  $\text{H}_2$ , HD, and  $\text{D}_2$  molecules. Compute the wavelengths of photons emitted in transitions between adjacent states for each of these molecules.

**9-47.** The microwave spectrum of CO has lines at 0.86 mm, 1.29 mm, and 2.59 mm. (a) Compute the photon energies and carefully sketch the energy-level diagram that corresponds. What molecular motion produces these lines? (b) Compute the equilibrium separation (bond length) of CO.

**9-48.** Carefully draw a potential energy curve for a diatomic molecule (like Figure 9-2b) and indicate the mean values of  $r$  for two vibrational levels. Show that because of the asymmetry of the curve,  $r_{\text{av}}$  increases with increasing vibrational energy and therefore solids expand when heated.

**9-49.** A sample of HCl is illuminated with light of wavelength 435.8 nm. (a) Compute the wavelengths of the four lines in the rotational Raman spectrum that are closest to that of the incident light. (b) Compare the difference in their frequencies with the corresponding lines in Figure 9-30.

**9-50.** Use data from Table 9-8 to compute the first excited vibrational and the first excited rotational states of (a) the  $\text{Li}_2$  and (b) the  $\text{K}^{79}\text{Br}$  molecules.

**9-51.** Calculate the effective force constant for HCl from its reduced mass and the fundamental vibrational frequency obtained from Figure 9-30.

**9-52.** Notice in Figure 9-33d that the level  $E_2$  in  $\text{Cr}^{3+}$  is a doublet, the pair of states being separated by only 0.0036 eV. (a) Assume that all of the  $\text{Cr}^{3+}$  ions in a certain laser are in the three states  $E_1$  and  $E_2$  (doublet) and compute the relative populations of these levels. (b) If only the lower state of the  $E_2$  doublet can produce laser light but both levels must be pumped together, determine the pumping power necessary for laser action to occur. The density of states (degeneracy) of level  $E_1$  is 4 and for each of the  $E_2$  levels is 2.

**9-53.** The central frequency for the absorption band of HCl shown in Figure 9-30 is at  $f = 8.66 \times 10^{13}$  Hz, and the absorption peaks are separated by about  $\Delta f = 6 \times 10^6$  Hz. Using this information, find (a) the lowest (zero-point) vibrational energy for HCl, (b) the moment of inertia of HCl, and (c) the equilibrium separation of the atoms.

### LEVEL III

**9-54.** The potential energy between two atoms in a molecule can often be described rather well by the Lenard-Jones potential, which can be written

$$U(r) = U_0 \left[ \left( \frac{a}{r} \right)^{12} - 2 \left( \frac{a}{r} \right)^6 \right]$$

where  $U_0$  and  $a$  are constants. (a) Find the interatomic separation  $r_0$  in terms of  $a$  for which the potential energy is minimum. (b) Find the corresponding value of  $U_{\text{min}}$ . (c) Use Figure 9-8b to obtain numerical values for  $r_0$  and  $U_0$  for the  $\text{H}_2$  molecule. Express your answer in nanometers and electron volts. (d) Make a plot of the potential energy  $U(r)$  versus the internuclear separation  $r$  for the  $\text{H}_2$  molecule. Plot each term separately, together with the total  $U(r)$ .

**9-55.** (a) Find the exclusion-principle repulsion for NaCl. (b) Use Equation 9-2 to find  $A$  and  $n$ .

**9-56.** Show that the  $\text{H}^+ - \text{H}^-$  system cannot be ionically bonded. (Hint: Show that  $U(r)$  has no negative minimum.)

**9-57.** (a) Calculate the fractional difference  $\Delta\mu/\mu$  for the reduced masses of the  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  molecules. (b) Show that the mixture of isotopes in HCl leads to a fractional difference in the frequency of a transition from one rotational state to another given by  $\Delta f/f = -\Delta\mu/\mu$ . (c) Compute  $\Delta f/f$  and compare your result with Figure 9-30.

**9-58.** For a molecule such as CO, which has a permanent electric dipole moment, radiative transitions obeying the selection rule  $\Delta\ell = \pm 1$  between two rotational energy levels of the same vibrational energy state are allowed; that is, the selection rule  $\Delta\nu = \pm 1$  does not hold. (a) Find the moment of inertia of CO for which  $r_0 = 0.113$  nm, and calculate the characteristic rotational energy  $E_{0r}$  in electron volts. (b) Make an energy-level diagram for the rotational levels for  $\ell = 0$  to  $\ell = 5$  for some vibrational level. Label the energies in electron volts, starting with  $E = 0$  for  $\ell = 0$ . (c) Indicate on your diagram transitions that obey  $\Delta\ell = -1$  and calculate the energy of the photons emitted. (d) Find the wavelength of the photon emitted for each transition in (c). In what region of the electromagnetic spectrum are these photons?

**9-59.** An  $\text{H}_2$  in its ground electronic, vibrational, and rotational state absorbs a photon of frequency  $1.356 \times 10^{14}$  Hz, undergoing a transition to the  $\nu = 1$ ,  $\ell = 1$  state while remaining in the electronic ground state. It then undergoes a transition to the  $\nu = 0$ ,  $\ell = 2$  state, emitting a photon of frequency  $1.246 \times 10^{14}$  Hz. (a) Compute the moment of inertia of the  $\text{H}_2$  molecule about an axis through the center of mass. (b) Determine the vibrational frequency and  $r_0$  for  $\text{H}_2$  and compare these with the values in Table 9-8.

## General References

The following general references are written at a level appropriate for the readers of this book.

- Anderson, B., *Fundamentals of Semiconductor Devices*, McGraw-Hill, New York, 2005.
- Blatt, F., *Modern Physics*, McGraw-Hill, New York, 1992.
- Eisberg, R., and R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles*, 2d ed., Wiley, New York, 1985.

- Fermi, E., *Molecules, Crystals, and Quantum Statistics* (trans. M. Ferro-Luzzi), W. A. Benjamin, New York, 1966.
- Holden, A., *The Nature of Solids*, Columbia University Press, 1968. An excellent nonmathematical treatment of the properties of solids.
- Kittel, C., *Introduction to Solid State Physics*, 8th ed., Wiley, New York, 2005.
- Shockley, W., *Electrons and Holes in Semiconductors*, Van Nostrand, Princeton, NJ, 1950.

## Notes

1. The constant  $n$  is often called the Born exponent.
2. Carbon also has a fourth solid form, charcoal, which has no well-defined crystalline structure.
3. Notice that this view of the metal fits the definition of a plasma set forth in the opening paragraph of the chapter. Though not usually thought of in that way, metals are indeed low-temperature plasmas.
4. Felix Bloch (1905–1983), Swiss-American physicist. He devised a method for measuring atomic magnetic fields in liquids and solids that led to the development of nuclear magnetic resonance (NMR) spectroscopy and earned for him a share (with E. M. Purcell) of the 1952 Nobel Prize in Physics. He was the first director-general of CERN, the European Organization for Nuclear Research.
5. The graph of the energy bands and gaps of Figure 10-19b results from a simplified version of the conditional equation connecting  $k$ ,  $k'$ , and  $\alpha$  in which  $b \rightarrow 0$  and  $U_0 \rightarrow \infty$ . In that limit the lattice spacing is  $a$  rather than  $a + b$ , as in Figure 10-18.
6. This mixing, called hybridization, was discussed in Section 9-2.
7. See, for example, Section 25-5 in P. Tipler and G. Mosca, *Physics for Scientists and Engineers*, 6th ed. (W. H. Freeman and Co., New York, 2008.)
8. The fact that the radius of the bound electron is several times the equilibrium spacing of the atoms helps justify our tacit assumption that the fifth electron “sees” a uniform dielectric constant in the crystal.
9. Klaus von Klitzing (b. 1943), German physicist. He received the 1985 Nobel Prize in Physics for this discovery.
10. Daniel C. Tsui (b. 1939), Chinese-American physicist. He received the 1998 Nobel Prize in Physics with H. L. Stormer and R. B. Laughlin for their discovery.

11. William B. Shockley (1910–1989), John Bardeen (1908–1991), and Walter H. Brattain (1902–1987), American physicists. Shockley discovered that doped germanium crystals were excellent rectifiers and subsequently the three Bell Laboratories colleagues discovered that two such “solid-state rectifiers” combined would amplify current. The discovery of this device, the transistor, earned them the 1956 Nobel Prize in Physics.
12. Actually, the field decreases exponentially across the surface, reaching zero at a depth of about 10 nm.
13. Isotopes are atoms with the same atomic number  $Z$  but different atomic mass numbers  $A$ . Isotopes will be discussed in Chapter 11.
14. John Bardeen (1908–1991), Leon N. Cooper (b. 1930), and J. Robert Schrieffer (b. 1931), American physicists. Developed at the University of Illinois, the BCS theory earned the collaborators the 1972 Nobel Prize in Physics and Bardeen became the only person thus far to win two physics Nobel Prizes (see note 11).
15. This may make it seem like the Cooper pair is a boson and superconductivity another example of Bose-Einstein condensation (see Section 8-3); however, the large size of the Cooper pair (see Example 10-13) means that many pairs overlap and that the symmetry of the pair with respect to an exchange of electrons must also take into account exchanges involving electrons in different pairs. The result is that the Cooper pair is neither a pure boson nor a pure fermion.
16. Brian D. Josephson (b. 1940), Welsh physicist. For this discovery, made while he was still a graduate student, he shared the 1973 Nobel Prize in Physics with L. Esaki and I. Giaever. Bardeen had strongly opposed Josephson’s tunneling prediction until experiments, led by those of Giaever (also done while he was a graduate student), confirmed tunneling by Cooper pairs.

## Problems

### LEVEL I

#### Section 10-1 The Structure of Solids

- 10-1.** Find the value of  $n$  in Equation 10-6 that gives the measured dissociation energy of 741 kJ/mol for LiCl, which has the same structure as NaCl and for which  $r_0 = 0.257$  nm.

**10-2.** Calculate the distance  $r_0$  between the  $K^+$  and  $Cl^-$  ions in KCl, assuming that each ion occupies a cubic volume of side  $r_0$ . The molar mass of KCl is 74.55 g/mol and its density is 1.984 g/cm<sup>3</sup>.

**10-3.** The distance between the  $Li^+$  and  $Cl^-$  ions in LiCl is 0.257 nm. Use this and the molecular mass of LiCl (42.4 g/mol) to compute the density of LiCl.

**10-4.** The crystal structure of KCl is the same as that of NaCl. (a) Calculate the electrostatic potential energy of attraction of KCl, assuming that  $r_0$  is 0.314 nm. (b) Assuming that  $n = 9$  in Equation 10-6, calculate the dissociation energy in eV per ion pair and in kcal/mol. (c) The measured dissociation energy is 165.5 kcal/mol. Use this to determine  $n$  in Equation 10-6.

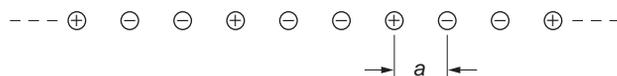
**10-5.** The observed dissociation energy of solid LiBr is 788 kJ/mol. Compute the cohesive energy of LiBr and compare the result with the value in Table 10-1. (Ionization energies for Li and Br are in Table 9-1.)

**10-6.** The density of NaCl (an fcc crystal) is 2.16 g/cm<sup>3</sup>. Find the distance between ions that are nearest neighbors.

**10-7.** The separation of nearest-neighbor ions in the KCl crystal (an fcc structure) is 0.315 nm. Use this information to determine the density of KCl.

**10-8.** Using the data for ionic and metallic crystals from Table 10-1, (a) graph cohesive energy versus melting point and put the best straight line through the points. (b) Determine the cohesive energies of cobalt, silver, and sodium, whose melting temperatures are 1495°C, 962°C, and 98°C, respectively. (The measured values are cobalt 4.43 eV, silver 2.97 eV, and sodium 1.13 eV.)

**10-9.** Figure 10-56 shows a one-dimensional ionic lattice consisting of doubly charged positive ions and twice as many singly charged negative ions. Compute the Madelung constant for this “crystal” to within 1 percent.



**FIGURE 10-56** Problem 10-9.

## Section 10-2 Classical Theory of Conduction

**10-10.** (a) Given a mean free path  $\lambda = 0.4$  nm and a mean speed  $\langle v \rangle = 1.17 \times 10^5$  m/s for the current flow in copper at a temperature of 300 K, calculate the classical value for the resistivity  $\rho$  of copper. (b) The classical model suggests that the mean free path is temperature independent and that  $\langle v \rangle$  depends on temperature. From this model, what would  $\rho$  be at 100 K?

**10-11.** Find (a) the current density and (b) the drift velocity if there is a current of 1 mA in a No. 14 copper wire. (The diameter of No. 14 wire, which is often used in household wiring, is 0.064 in = 0.163 cm.)

**10-12.** A measure of the density of the free-electron gas in a metal is the distance  $r_s$ , which is defined as the radius of the sphere whose volume equals the volume per conduction electron. (a) Show that  $r_s = (3/4\pi n_a)^{1/3}$ , where  $n_a$  is the free-electron number density. (b) Calculate  $r_s$  for copper in nanometers.

**10-13.** Calculate the number density of free electrons in (a) Ag ( $\rho = 10.5$  g/cm<sup>3</sup>) and (b) Au ( $\rho = 19.3$  g/cm<sup>3</sup>), assuming one free electron per atom, and compare your results with the values listed in Table 10-3.

**10-14.** Calculate the number density of free electrons for (a) Mg ( $\rho = 1.74$  g/cm<sup>3</sup>) and (b) Zn ( $\rho = 7.1$  g/cm<sup>3</sup>), assuming two free electrons per atom, and compare your results with the values listed in Table 10-3.

**10-15.** (a) Using  $\lambda = 0.37$  nm and  $\langle v \rangle = 1.08 \times 10^5$  m/s at  $T = 300$  K, calculate  $\sigma$  and  $\rho$  for copper from Equations 10-13. Using the same value of  $\lambda$ , find  $\sigma$  and  $\rho$  at (b)  $T = 200$  K and (c)  $T = 100$  K.

### Section 10-3 Free-Electron Gas in Metals

- 10-16.** Find the average energy of the electrons at  $T = 0$  K in (a) copper ( $E_F = 7.06$  eV) and (b) Li ( $E_F = 4.77$  eV).
- 10-17.** Calculate the Fermi energy for magnesium in a long, very thin wire.
- 10-18.** Compute (a) the Fermi energy and (b) the Fermi temperature for silver and for iron and compare your results with the corresponding values in Table 10-3.
- 10-19.** Show that for  $T = 300$  K, about 0.1 percent of the free electrons in metallic silver have an energy greater than  $E_F$ .

### Section 10-4 Quantum Theory of Conduction

- 10-20.** What is the Fermi speed, that is, the speed of a conduction electron whose energy is equal to the Fermi energy  $E_F$ , for (a) Na, (b) Au, and (c) Sn? (See Table 10-3.)
- 10-21.** The resistivities of Na, Au, and Sn at  $T = 273$  K are  $4.2 \mu\Omega \cdot \text{cm}$ ,  $2.04 \mu\Omega \cdot \text{cm}$ , and  $10.6 \mu\Omega \cdot \text{cm}$ , respectively. Use these values and the Fermi speeds calculated in Problem 10-20 to find the mean free paths  $\lambda$  for the conduction electrons in these elements.
- 10-22.** At what temperature is the heat capacity due to the electron gas in copper equal to 10 percent of that due to lattice vibrations?
- 10-23.** Use Equation 10-29 with  $\alpha = \pi^2/4$  to calculate the average energy of an electron in copper at  $T = 300$  K. Compare your result with the average energy at  $T = 0$  and the classical result of  $(3/2)kT$ .
- 10-24.** Compute the maximum fractional contribution to the heat capacity of solid iron that can be made by the electrons.

### Section 10-5 Magnetism in Solids

- 10-25.** The magnetic polarization  $P$  of any material is defined as  $P = (\rho_+ - \rho_-)/\rho$ . Compute the high-temperature polarization of a paramagnetic solid at  $T = 200$  K in a magnetic field of 2.0 T.
- 10-26.** Show that the magnetic susceptibility  $\chi$  is a dimensionless quantity.

### Section 10-6 Band Theory of Solids

- 10-27.** (a) The energy gap between the valence band and the conduction band in silicon is 1.14 eV at room temperature. What is the wavelength of a photon that will excite an electron from the top of the valence band to the bottom of the conduction band? Do the same calculation for (b) germanium, for which the energy gap is 0.72 eV, and (c) for diamond, for which the energy gap is 7.0 eV.
- 10-28.** (a) The energy-band gap in germanium is 0.72 eV. What wavelength range of visible light will be transmitted by a germanium crystal? (Think about it carefully!) (b) Now consider a crystal of an insulator whose energy-band gap is 3.6 eV. What wavelength range of visible light will this crystal transmit? (c) Justify each of your answers to (a) and (b).
- 10-29.** A photon of wavelength  $3.35 \mu\text{m}$  has just enough energy to raise an electron from the valence band to the conduction band in a lead sulfide crystal. (a) Find the energy gap between these bands in lead sulfide. (b) Find the temperature  $T$  for which  $kT$  equals this energy gap.
- 10-30.** Consider a small silicon crystal measuring 100 nm on each side. (a) Compute the total number  $N$  of silicon atoms in the crystal. (The density of silicon is  $2.33 \text{ g/cm}^3$ .) (b) If the conduction band in silicon is 13 eV wide and recalling that there are  $4N$  states in this band, compute an approximate value for the energy spacing between adjacent conduction-band states for the crystal.

### Section 10-7 Impurity Semiconductors

**10-31.** Arsenic has five valence electrons. If arsenic is used as a dopant in silicon, compute (a) the ionization energy and (b) the orbit radius of the fifth arsenic electron. The effective mass for electrons in silicon is  $0.2 m_e$ . (c) What is the ratio of the ionization energy of the fifth electron to the energy gap in silicon?

**10-32.** Gallium has three valence electrons. If gallium is used to dope germanium, compute (a) the ionization energy of the hole and (b) the orbit radius of the hole. The effective mass of holes in germanium is  $0.34 m_e$ .

**10-33.** What type of semiconductor is obtained if silicon is doped with (a) aluminum and (b) phosphorus? (See Appendix C for the electron configurations of these elements.)

**10-34.** The donor energy levels in an  $n$ -type semiconductor are  $0.01$  eV below the conduction band. Find the temperature for which  $kT = 0.01$  eV.

**10-35.** A strip of tin is  $10$  mm wide and  $0.2$  mm thick. When a current of  $20$  A is established in the strip and a uniform magnetic field of  $0.25$  T is oriented perpendicular to the plane of the strip, a Hall voltage of  $2.20$   $\mu$ V is measured across the width of the strip. Compute (a) the density of charge carriers in tin and (b) the average number of charge carriers contributed by each tin atom. The density of tin is  $5.75 \times 10^3$  kg/m<sup>3</sup> and its molecular mass is  $118.7$ .

### Section 10-8 Semiconductor Junctions and Devices

**10-36.** For a temperature of  $300$  K, use Equation 10-49 to find the bias voltage  $V_b$  for which the exponential term has the value (a)  $10$  and (b)  $0.1$ .

**10-37.** For what value of bias voltage  $V_b$  does the exponential in Equation 10-49 have the value (a)  $5$  and (b)  $0.5$  for  $T = 200$  K?

**10-38.** Compute the fractional change in the current through a  $pn$  junction diode when the forward bias is changed from  $+0.1$  V to  $+0.2$  V.

**10-39.** For  $T = 300$  K, use Equation 10-49 to find the bias voltage  $V_b$  for which the exponential term had the value (a)  $10$  and (b)  $0.1$ .

**10-40.** When light of wavelength no larger than  $484$  nm illuminates a CdS solar cell, the cell produces electric current. Determine the energy gap in CdS.

### Section 10-9 Superconductivity

**10-41.** Three naturally occurring isotopes of lead are  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ . Using the value of  $\alpha$  from Table 10-7 and the isotopic masses from Appendix A, compute the critical temperatures of these isotopes.

**10-42.** Compute (a) the superconducting energy gap for indium and (b) the wavelength of a photon that could just break up a Cooper pair in indium at  $T = 0$  K.

**10-43.** (a) Use Equation 10-56 to calculate the superconducting energy gap for tin and compare your result with the measured value of  $6 \times 10^{-4}$  eV. (b) Use the measured value to calculate the wavelength of a photon having sufficient energy to break up a Cooper pair in tin at  $T = 0$  K.

**10-44.** Use the BCS curve in Figure 10-53 to estimate the energy gaps in (a) tin, (b) niobium, (c) aluminum, and (d) zinc, all at  $T = 0.5T_c$ .

**10-45.** Expressing the temperature  $T$  as a fraction of the critical temperature  $T_c$ , according to BCS theory at what temperature is (a)  $B_c(T) = 0.1B_c(0)$ , (b)  $B_c(T) = 0.5B_c(0)$ , (c)  $B_c(T) = 0.9B_c(0)$ ?

### LEVEL II

**10-46.** Approximating atoms in an fcc crystal as hard spheres of radius  $r$  with  $a$  being the length of each side of the unit cube, what fraction of the volume of the cube (and hence the crystal) is occupied by atoms?

**10-47.** Estimate the fraction of free electrons in copper that are in excited states above the Fermi energy at (a) room temperature of 300 K and (b) 1000 K.

**10-48.** A one-dimensional model of an ionic crystal consists of a line of alternating positive and negative ions with distance  $r_0$  between adjacent ions. (a) Show that the potential energy of attraction of one ion in the line is

$$V = -\frac{2ke^2}{r_0} \left( 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \dots \right)$$

(b) Using the result that

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

show that the Madelung constant for this one-dimensional model is  $\alpha = 2 \ln 2 = 1.386$ .

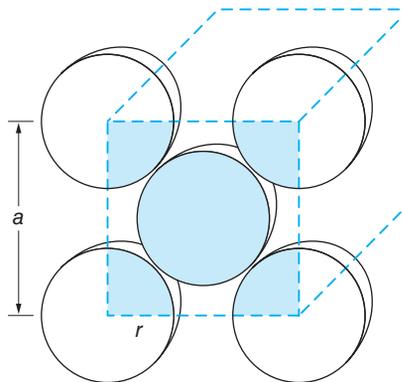
**10-49.** Estimate the Fermi energy of zinc from its electronic molar heat capacity of  $(3.74 \times 10^{-4} \text{ J/mol} \cdot \text{K})T$ .

**10-50.** The density of the electron states in a metal can be written  $g(E) = AE^{\frac{1}{2}}$ , where  $A$  is a constant and  $E$  is measured from the bottom of the conduction band. (a) Show that the total number of states is  $(2/3)A(E_F)^{3/2}$ . (b) About what fraction of the conduction electrons is within  $kT$  of the Fermi energy? (c) Evaluate this fraction for copper at  $T = 300 \text{ K}$ .

**10-51.** High-purity germanium (HPGe) crystals are used as detectors for x rays and gamma rays. On interacting with the crystal, incoming photons produce electron-hole pairs, exciting many electrons across the 0.72 eV energy gap into the conduction band. The decay of the radioisotope  $^{60}\text{Co}$  results in the emission of two gamma rays with energies 1.17 MeV and 1.33 MeV (see Chapter 11). (a) Compute the numbers of electrons  $N_1$  and  $N_2$  excited across the energy gap by each of the two gamma rays. (b) The numbers  $N_1$  and  $N_2$  are subject to statistical fluctuations of  $\pm\sqrt{N_1}$  and  $\pm\sqrt{N_2}$ . Compute the fractional uncertainties in  $N_1$  and  $N_2$ . (c) Compute the corresponding fractional uncertainties in the energies of the two gamma rays. This is a measure of the energy resolution of the HPGe crystal.

**10-52.** A doped  $n$ -type silicon sample with  $10^{16}$  electrons per cubic centimeter in the conduction band has a resistivity of  $5 \times 10^{-3} \Omega \cdot \text{m}$  at 300 K. Find the mean free path of the electrons, using  $0.2 m_e$  for the effective mass of the electron. Compare your result with the mean free path of electrons in copper at 300 K.

**10-53.** Crystallographers and materials scientists use the density of a metallic sample to infer its likely crystal structure. The density of copper (Cu) is  $8.96 \text{ g/cm}^3$  and its atomic radius is 0.128 nm. Is the copper crystal more likely to be face-centered cubic or body-centered cubic? (See Figure 10-57.)



**FIGURE 10-57** Problem 10-53.

**10-54.** A “good” silicon diode has a current-voltage characteristic given by

$$I = I_0(e^{eV_b/kT} - 1)$$

Let  $kT = 0.025$  eV (room temperature) and the saturation current  $I_0 = 1$  nA. (a) Show that for small reverse-bias voltages, the resistance is  $25$  M $\Omega$ . (*Hint:* Do a Taylor expansion of the exponential function, or use your calculator and enter small values for  $V_b$ .) (b) Find the dc resistance for a reverse bias of  $0.5$  V. (c) Find the dc resistance for a  $0.5$  V forward bias. What is the current in this case? (d) Calculate the ac resistance  $dV/dI$  for a  $0.5$  V forward bias.

**10-55.** The relative binding of the extra electron in the arsenic atom that replaces an atom in silicon or germanium can be understood from a calculation of the first Bohr orbit of this electron in these materials. Four of arsenic’s outer electrons form covalent bonds, so the fifth electron “sees” a singularly charged center of attraction. This model is a modified hydrogen atom. In the Bohr model of the hydrogen atom, the electron moves in free space at a radius  $a_0$  given by

$$a_0 = \frac{\epsilon_0 h^2}{\pi m_e e^2}$$

When an electron moves in a crystal, we can approximate the effect of the other atoms by replacing  $\epsilon_0$  with  $\kappa\epsilon_0$  and  $m_e$  with an effective mass for the electron. For silicon  $\kappa$  is 12 and the effective mass is about  $0.2m_e$ , and for germanium  $\kappa$  is 16 and the effective mass is about  $0.1m_e$ . Estimate the Bohr radii for the outer electron as it orbits the impurity arsenic atom in silicon and germanium.

**10-56.** InSb is a semiconductor. The energy gap  $E_g$  between its valence and conduction bands is  $0.23$  eV, and its dielectric constant  $\kappa = 18$ . In the InSb crystal the electron’s effective mass  $m^* = 0.015m_e$ . (a) Compute the ionization energy for an electron donor in InSb. (b) What is the radius of the ground-state orbit? (c) At approximately what donor concentration will the orbits of adjacent donor atoms begin to overlap?

**10-57.** The mean free path of an electron in a metal depends on both the lattice oscillations of the metal ions and those of any impurity ions according to  $1/\lambda = 1/\lambda_m + 1/\lambda_i$ . The resistivity of pure copper is increased by about  $1.2 \times 10^{-8}$   $\Omega \cdot \text{m}$  by the addition of 1 percent (by number of atoms) of a certain impurity dispersed evenly throughout the metal. (a) Estimate  $\lambda_i$  from this information. (b) The impurity atoms are “seen” by the electrons to have an effective diameter  $d$ . Estimate the scattering cross section  $d^2$  from Equation 10-12, where  $d = 2r$ .

### Level III

**10-58.** When arsenic is used to dope silicon, the fifth arsenic electron and the  $\text{As}^+$  ion act like a hydrogen atom system, except that the potential function  $V(r)$  and the electron mass must be modified as described in Section 10-7 to account for the crystal lattice. With these modifications, (a) solve the Schrödinger equation, using the solution in Chapter 7 as a guide. (b) Obtain Equation 10-43, and (c) sketch a properly scaled energy-level diagram for the fifth electron for  $n = 1$  through 5.

**10-59.** The quantity  $\kappa$  is the force constant for a “spring” consisting of a line of alternating positive and negative ions. If these ions are displaced slightly from their equilibrium separation  $r_0$ , they will vibrate with a frequency

$$f = \frac{1}{2\pi} \sqrt{\frac{K}{m}}$$

(a) Use the values of  $\alpha$ ,  $n$ , and  $r_0$  for NaCl and the reduced mass for the NaCl molecule to calculate this frequency. (b) Calculate the wavelength of electromagnetic radiation corresponding to this frequency, and compare your result with the characteristic strong infrared absorption bands in the region of about  $\lambda = 61$   $\mu\text{m}$  that are observed for NaCl.

**10-60.** Consider a model for a metal in which the lattice of positive ions forms a container for a classical electron gas with  $n$  electrons per unit volume. In equilibrium, the average electron velocity is zero, but the application of an electric field produces an acceleration of the electrons. If we use a relaxation time  $\tau$  to account for the electron-lattice collisions, then we have the equation

$$m \frac{dv}{dt} + \frac{m}{\tau} v = -eE$$

(a) Solve the equation for the drift velocity in the direction of the applied electric field.  
 (b) Verify that Ohm's law is valid, and find the resistivity as a function of  $n$ ,  $e$ ,  $m$ , and the relaxation time  $\tau$ .

**10-61.** Imagine a cubic crystal like NaCl, with a negative charge at the center of a Cartesian coordinate system with scale units equal to the interatomic distance. (a) Show that an ion at a position  $r$  units along the  $x$  axis,  $s$  units along the  $y$  axis, and  $t$  units along the  $z$  axis has a charge of  $e(-1)^r \cdot (-1)^s \cdot (-1)^t = e(-1)^{r+s+t}$ , where  $e$  is the electron charge. (b) Using Equation 10-2 as a guide, calculate the Madelung constant for a cube 2 units on a side. Do the same for cubes of sides 4, 6, 8, 10, 12, 16, and 20 units. (You will probably want to use a computer spreadsheet to write a program to do the calculations for the larger cubes.) Are your answers approaching the value  $\alpha = 1.7476$ ?

**10-62.** (a) Show that for a paramagnetic solid with electron energies given by Equation 10-33, the magnetization per unit volume  $M$  is given by

$$M = \mu\rho \tanh(\mu B/kT)$$

(b) For  $\mu B \ll kT$  show that the susceptibility is given by Equation 10-35.