Chapter 9  Problem Solutions

1. At what temperature would one in a thousand of the atoms in a gas of atomic hydrogen be in the $n=2$ energy level?

   sol
   \[ g(\varepsilon_2) = 8, \quad g(\varepsilon_1) = 2 \]

   Then,
   \[ \frac{n(\varepsilon_2)}{n(\varepsilon_1)} = \frac{1}{1000} = 4e^{-(\varepsilon_2 - \varepsilon_1)/kT} = 4e^{3\varepsilon_1/kT} \]

   \[ T = \left( \frac{1}{k} \right) \frac{(3/4)(-\varepsilon_1)}{\ln 4000} = \frac{(3/4)(13.6 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV/K})(\ln 4000)} = 1.43 \times 10^4 \text{ K} \]

   where \( \varepsilon_2 = \varepsilon_1 / 4 \), and \( \varepsilon_1 = -13.6 \text{ eV} \)

3. The \( 3^2P_{1/2} \) first excited state in sodium is 2.093 eV above the \( 3^2S_{1/2} \) ground state. Find the ratio between the numbers of atoms in each state in sodium vapor at 1200 K. (see Example 7.6.)

   sol
   multiplicity of \( P \)-level : \( 2L+1 = 3 \), multiplicity of \( S \)-level : 1
   The ratio of the numbers of atoms in the states is then,
   \[ \left( \frac{3}{1} \right) \exp\left(-\frac{2.09 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/K})(1200 \text{ K})}\right) = 4.86 \times 10^{-9} \]
5. The moment of inertia of the $\text{H}_2$ molecule is $4.64 \times 10^{-48}$ kg·m$^2$. (a) Find the relative populations of the $J=0, 1, 2, 3,$ and 4 rotational states at 300 K. (b) can the populations of the $J=2$ and $J=3$ states ever be equal? If so, at what temperature does this occur?

(a) 

$$g(J) = 2J + 1, \quad \varepsilon_J = \frac{J(J+1)\hbar^2}{2I} \quad \varepsilon_{J=0} = 0$$

$$\frac{N(J)}{N(J=0)} = (2J + 1) \exp\left(-\frac{J(J+1)\hbar^2}{2IkT} \right) = (2J + 1) \left[ \exp\left(-\frac{\hbar^2}{2IkT} \right) \right]^{(J+1)\hbar^2}$$

$$= (2J + 1) \left[ \exp\left(-\frac{(1.06 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2(4.64 \times 10^{-48} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} \right) \right]^{(J+1)\hbar^2}$$

$$= (2J + 1)[0.749]^{(J+1)\hbar^2}$$

Applying this expression to $J=0, 1, 2, 3,$ and 4 gives, respectively, 1 exactly, 1.68, 0.880, 0.217, and 0.0275.

(b) Introduce the dimensionless parameter $x$. Then, for the populations of the $J=2$ and $J=3$ states to be equal,

$$5x^6 = 7x^{12}, \quad x^6 = \frac{5}{7} \quad \text{and} \quad 6 \ln x = \ln \frac{5}{7}$$

Using $\ln x = -\hbar^2 / 2IkT$ and $\ln(5/7) = -\ln(7/5)$ and solving for $T$,
\[
T = \frac{6 h^2}{2 I k \ln(7/5)}
\]
\[
= \frac{6(1.05 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2(4.64 \times 10^{-48} \text{ kg} \cdot \text{m}^2)(1.38 \times 10^{-23} \text{ J/K}) \ln(1.4)} = 1.55 \times 10^3 \text{ K}
\]

7. Find \( \bar{v} \) and \( v_{\text{rms}} \) for an assembly of two molecules, one with a speed of 1.00 m/s and the other with a speed of 3.00 m/s.

\[\text{sol} \]
\[
\bar{v} = \frac{1}{2}(1.00 + 3.00) = 2.00 \text{ (m/s)}
\]
\[
v_{\text{rms}} = \sqrt{\frac{1}{2}[1.00^2 + 3.00^2]} = 2.24 \text{ (m/s)}
\]

9. At what temperature will the average molecular kinetic energy in gaseous hydrogen equal the binding energy of a hydrogen atom?

\[\text{sol} \]
For a monatomic hydrogen, the kinetic energy is all translational and \( \bar{KE} = \frac{3}{2} kT \)
solving for \( T \) with \( \bar{KE} = -E_1 \)
\[
T = \frac{2}{3} \left( -\frac{E_1}{k} \right) = \frac{(2/3)(13.6 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV/K})} = 1.05 \times 10^5 \text{ K}
\]
11. Find the width due to the Doppler effect of the 656.3-nm spectral line emitted by a gas of atomic hydrogen at 500 K.

\[ \Delta \lambda = 2 \lambda \frac{\sqrt{3kT/m}}{c} \]

\[ = 2(656.3 \times 10^{-9} \text{ m}) \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(500 \text{ K})}{(1.67 \times 10^{-27} \text{ kg})}} \]

\[ = 1.54 \times 10^{-11} \text{ m} = 15.4 \text{ pm} \]

13. Verify that the average value of \( 1/v \) for an ideal-gas molecule is \( \sqrt{2m/\pi kT} \).

[Note : \( \int_{0}^{\infty} ve^{-av^2} dv = 1/(2a) \)]

The average value of \( 1/v \) is

\[ \langle \frac{1}{v} \rangle = \frac{1}{N} \int_{0}^{\infty} \frac{1}{v} n(v) dv \]

\[ = \frac{1}{N} 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} \int_{0}^{\infty} ve^{-mv^2/2kT} dv \]

\[ = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \left( \frac{kT}{m} \right) = \sqrt{\frac{2m}{\pi kT}} = 2 \frac{1}{\langle v \rangle} \]
17. How many independent standing waves with wavelengths between 95 and 10.5 mm can
occur in a cubical cavity 1 m on a side? How many with wavelengths between 99.5 and 100.5
mm? (Hint: First show that $g(\lambda) d\lambda = 8\pi L^3 \frac{d\lambda}{\lambda^4}$.)

\[
g(\lambda) d\lambda = g(\nu) d\nu = \frac{8\pi L^3}{c^3} \left( \frac{c}{\lambda} \right)^2 \frac{c}{\lambda^2} d\lambda = \frac{8\pi L^3}{\lambda^4} d\lambda
\]

Therefore the number of standing waves between 9.5 mm and 10.5 mm is

\[
g(\lambda) d\lambda = \frac{8\pi (1 \text{ m})^3}{(1.0 \text{ mm})^4} = 2.5 \times 10^6
\]

Similarly, the number of waves between 99.5 mm and 100.5 mm is $2.5 \times 10^2$, lower by a
factor of $10^4$.

19. A thermograph measures the rate at which each small portion of a person's skin emits
infrared radiation. To verify that a small difference in skin temperature means a significant
difference in radiation rate, find the percentage difference between the total radiation from skin
at 34°C and at 35°C.
By the Stefan-Boltzmann law, the total energy density is proportional to the fourth power of the absolute temperature of the cavity walls, as

\[ R = \sigma T^4 \]

The percentage difference is

\[ \frac{\sigma T_1^4 - \sigma T_2^4}{\sigma T_1^4} = \frac{T_1^4 - T_2^4}{T_1^4} = 1 - \left( \frac{T_2}{T_1} \right)^4 = 1 - \left( \frac{307 \, \text{K}}{308 \, \text{K}} \right) = 0.013 = 1.3\% \]

For temperature variations this small, the fractional variation may be approximated by

\[ \frac{\Delta R}{R} = \frac{\Delta(T^4)}{T^4} = 3\frac{T^3 \Delta T}{T^4} = 3 \frac{\Delta T}{T} = 3 \frac{1 \, \text{K}}{308 \, \text{K}} = 0.013 \]

21. At what rate would solar energy arrive at the earth if the solar surface had a temperature 10 percent lower than it is?

Lowering the Kelvin temperature by a given fraction will lower the radiation by a factor equal to the fourth power of the ratio of the temperatures. Using 1.4 kW/m² as the rate at which the sun’s energy arrives at the surface of the earth

\[ (1.4 \, \text{kW/m}^2)(0.90)^4 = 0.92 \, \text{kW/m}^2 \, (= \, 66\%) \]
23. An object is at a temperature of 400°C. At what temperature would it radiate energy twice as fast?

\[ T = \text{solution} \]

To radiate at twice the rate, the fourth power of the Kelvin temperature would need to double. Thus,

\[ 2[(400 + 273) \text{ K}]^4 = T^4 \quad T = 673 \times 2^{1/4} \text{ K} = 800 \text{ K}(527^\circ \text{C}) \]

25. At what rate does radiation escape from a hole 10 cm\(^2\) in area in the wall of a furnace whose interior is at 700°C?

\[ P = \text{solution} \]

The power radiated per unit area with unit emissivity in the wall is \( P = \sigma T^4 \). Then the power radiated for the hole in the wall is

\[ P' = \sigma T^4 A = (5.67 \times 10^{-8} \text{ W/(m}^2 \cdot \text{K}^4)) (973 \text{ K})^4 (10 \times 10^{-4} \text{ m}^2) = 51 \text{ W} \]

27. Find the surface area of a blackbody that radiates 100 kW when its temperature is 500°C. If the blackbody is a sphere, what is its radius?

\[ A = \text{solution} \]

The radiated power of the blackbody (assuming unit emissivity) is

\[ P = Ae\sigma T^4 \quad A = \frac{P}{e\sigma T^4} = \frac{100 \times 10^3 \text{ W}}{(1)(5.67 \times 10^{-8} \text{ W/(m}^2 \cdot \text{K}^4))((500 + 273) \text{K})^4} \]

\[ = 4.94 \times 10^{-2} \text{ m}^2 = 494 \text{ cm}^2 \]
The radius of a sphere with this surface area is, then,
\[ A = 4\pi r^2 \quad r = \sqrt{\frac{A}{4\pi}} = 6.27\, \text{cm} \]

31. The brightest part of the spectrum of the star Sirius is located at a wavelength of about 290 nm. What is the surface temperature of Sirius?

From the Wien’s displacement law, the surface temperature of Sirius is
\[ T = \frac{2.898 \times 10^{-3}\, \text{m} \cdot \text{K}}{\lambda_{\text{max}}} = \frac{2.898 \times 10^{-3}\, \text{m} \cdot \text{K}}{290 \times 10^{-9}\, \text{m}} = 1.0 \times 10^4\, \text{K} \]

33. A gas cloud in our galaxy emits radiation at a rate of 1.0 \times 10^{27}\, \text{W}. The radiation has its maximum intensity at a wavelength of 10 \mu m. If the cloud is spherical and radiates like a blackbody, find its surface temperature and its diameter.

From the Wien’s displacement law, the surface temperature of the cloud is
\[ T = \frac{2.898 \times 10^{-3}\, \text{m} \cdot \text{K}}{10 \times 10^{-6}\, \text{m}} = 2.9 \times 10^2\, \text{K} = 290\, \text{K} = 17^\circ\, \text{C} \]

Assuming unit emissivity, the radiation rate is
\[ R = \sigma T^4 = \frac{P}{A} = \frac{P}{\pi D^2} \]
where \( D \) is the cloud’s diameter. Solving for \( D \),
\[ D = \sqrt{\frac{P}{\pi \sigma T^4}} = \left( \frac{1.0 \times 10^{27}\, \text{W}}{\pi (5.67 \times 10^{-8}\, \text{W/m}^2 \cdot \text{K}^4)(290\, \text{K})^4} \right)^{1/2} = 8.9 \times 10^{11}\, \text{m} \]
35. Find the specific heat at constant volume of 1.00 cm$^3$ of radiation in thermal equilibrium at 1000 K.

The specific heat at constant volume is then

$$c_V = \frac{\partial U}{\partial T} = \frac{16\sigma}{c} T^3 V$$

$$= \frac{16(5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4)}{2.998 \times 10^8 \text{ m/s}} (1000\text{K})^3 (1.0 \times 10^{-6} \text{ m}^3)$$

$$= 3.03 \times 10^{-12} \text{ J/K}$$

37. Show that the median energy in a free-electron gas at $T=0$ is equal to $\varepsilon_F/2^{2/3} = 0.630\varepsilon_F$.

At $T=0$, all states with energy less than the Fermi energy $\varepsilon_F$ are occupied, and all states with energy above the Fermi energy are empty. For $0 \leq \varepsilon \leq \varepsilon_F$, the electron energy distribution is proportional to $\sqrt{\varepsilon}$. The median energy is that energy for which there are many occupied states below the median as there are above. The median energy $\varepsilon_M$ is then the energy such that

$$\int_0^{\varepsilon_M} \sqrt{\varepsilon} \, d\varepsilon = \frac{1}{2} \int_0^{\varepsilon_F} \sqrt{\varepsilon} \, d\varepsilon$$
Evaluating the integrals,
\[ \frac{2}{3}(\varepsilon_M)^{3/2} = \frac{1}{3}(\varepsilon_F)^{3/2}, \quad \text{or} \quad \varepsilon_M = (\frac{1}{2})^{3/2} \varepsilon_F = 0.63 \varepsilon_F \]

39. The Fermi energy in silver is 5.51 eV. (a) What is the average energy of the free electrons in silver at 0 K? (b) What temperature is necessary for the average molecular energy in an ideal gas to have this value? (c) What is the speed of an electron with this energy?

\[ \text{sol} \]
(a) The average energy at \( T=0 \) K is \( \overline{\varepsilon_0} = \frac{3}{5} \varepsilon_F = 3.31 \text{ eV} \)

(b) Setting \((3/2)kT=(3/5)e_F\) and solving for \( T \),
\[ T = \frac{2 \varepsilon_F}{5k} = \frac{2}{5} \frac{5.51 \text{ eV}}{8.62 \times 10^{-5} \text{ eV/K}} = 2.56 \times 10^4 \text{ K} \]

(c) The speed in terms of the kinetic energy is
\[ v = \sqrt{\frac{2KE}{m}} = \sqrt{\frac{6\varepsilon_F}{5m}} = \sqrt{\frac{6(5.51 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV})}{5(9.11 \times 10^{-31} \text{ kg})}} = 1.08 \times 10^6 \text{ m/s} \]

43. Show that, if the average occupancy of a state of energy \( \varepsilon_F+\Delta\varepsilon \) is \( f_1 \) at any temperature, then the average occupancy of a state of energy \( \varepsilon_F-\Delta\varepsilon \) is \( f_2=1-f_1 \). (This is the reason for the symmetry of the curves in Fig.9.10 about \( \varepsilon_F \).)
Using the Fermi-Dirac distribution function

\[
\begin{align*}
    f_1 &= f_{FD}(\varepsilon_F + \Delta\varepsilon) = \frac{1}{e^{\Delta\varepsilon / kT} + 1} \\
    f_2 &= f_{FD}(\varepsilon_F - \Delta\varepsilon) = \frac{1}{e^{-\Delta\varepsilon / kT} + 1} \\
    f_1 + f_2 &= \frac{1}{e^{\Delta\varepsilon / kT} + 1} + \frac{1}{e^{-\Delta\varepsilon / kT} + 1} = 1
\end{align*}
\]

45. The density of zinc is 7.13 g/cm³ and its atomic mass is 65.4 u. The electronic structure of zinc is given in Table 7.4, and the effective mass of an electron in zinc is 0.85 \( m_e \). Calculate the Fermi energy in zinc.

Zinc in its ground state has two electrons in 4s subshell and completely filled K, L, and M shells. Thus, there are two free electrons per atom. The number of atoms per unit volume is the ratio of the mass density \( \rho_{Zn} \) to the mass per atom \( m_{Zn} \). Then,

\[
\varepsilon_F = \frac{\hbar^2}{2m^*} \left( \frac{3(2) \rho_{Zn}}{8\pi m_{Zn}} \right)^{2/3}
\]

\[
= \left( \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2(0.85)(9.11 \times 10^{-31} \text{ kg})} \right) \left( \frac{3(2)(7.13 \times 10^3 \text{ kg/m}^3)}{8\pi (65.4 \text{u})(1.66 \times 10^{-27} \text{ kg/u})} \right)^{2/3}
\]

\[
= 1.78 \times 10^{-18} \text{ J} = 11 \text{ eV}
\]
47. Find the number of electron states per electronvolt at \( \varepsilon = \varepsilon_F/2 \) in a 1.00-g sample of copper at O K. Are we justified in considering the electron energy distribution as continuous in a metal?

\[ n(\varepsilon) = \frac{3N}{2} (\varepsilon_F)^{-3/2} \sqrt{\varepsilon} \]

At \( \varepsilon = \varepsilon_F/2 \),
\[ n\left(\frac{\varepsilon_F}{2}\right) = \frac{3}{\sqrt{8} \varepsilon_F} N \]

The number of atoms is the mass divided by the mass per atom,
\[ N = \frac{(1.00 \times 10^{-3} \text{ kg})}{(63.55 \text{ u})(1.66 \times 10^{-27} \text{ kg/u})} = 9.48 \times 10^{21} \]

with the atomic mass of copper from the front endpapers and \( \varepsilon_F = 7.04 \text{ eV} \). The number of states per electronvolt is
\[ n\left(\frac{\varepsilon_F}{2}\right) = \frac{3}{\sqrt{8}} \frac{9.48 \times 10^{21}}{7.04 \text{ eV}} = 1.43 \times 10^{21} \text{ states/eV} \]

and the distribution may certainly be considered to be continuous.
49. The Bose-Einstein and Fermi-Dirac distribution functions both reduce to the Maxwell-Boltzmann function when \( e^\alpha \frac{e}{kT} \gg 1 \). For energies in the neighborhood of \( kT \), this approximation holds if \( e^\alpha \gg 1 \). Helium atoms have spin 0 and so obey Bose-Einstein statistics.

Verify that \( f(e)=1/e^\alpha e^{e/kT} \approx A e^{-e/kT} \) is valid for He at STP (20°C and atmospheric pressure, when the volume of 1 kmol of any gas is 22.4 m³) by showing that \( f(A) \ll 1 \) under these circumstances.

To do this, use Eq(9.55) for \( g(e) \) with a coefficient of 4 instead of 8 since a He atom does not have the two spin states of an electron, and employing the approximation, find \( A \) from the normalization condition \( n(e) d\epsilon = N \), where \( N \) is the total number of atoms in the sample. (A kilomole of He contains Avogadro’s number \( N_o \) atoms, the atomic mass of He is 4.00 u and

\[
\int_0^\infty \frac{\sqrt{x e^{-\alpha \epsilon}}} {\alpha / 2} dx = \sqrt{\pi / \alpha / 2a}
\]

Using the approximation \( f(e)=A e^{e/kT} \), and a factor of 4 instead of 8 in Equation (9.55), Equation (9.57) becomes

\[
n(e) d\epsilon = g(e) f(e) d\epsilon = A 4/\sqrt{2\pi} \frac{V_m^{3/2}}{h^3} \sqrt{\epsilon} e^{-e/kT} d\epsilon
\]

Integrating over all energies,

\[
N = \int_0^\infty n(e) d\epsilon = A 4\sqrt{2\pi} \frac{V_m^{3/2}}{h^3} \int_0^\infty \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon
\]
The integral is that given in the problem with \( x = \varepsilon \) and \( \alpha = kT \),

\[
\int_0^\infty \sqrt{\varepsilon} e^{-\varepsilon/kT} d\varepsilon = \frac{\sqrt{\pi} (kT)^{3/2}}{2}, \quad \text{so that}
\]

\[
N = A4\sqrt{2\pi} \frac{V m^{3/2} \sqrt{\pi} (kT)^{3}}{h^3} = A \frac{V}{h^3} (2\pi mkT)^{3/2}
\]

Solving for \( A \),

\[
A = \frac{N}{V} h^3 (2\pi mkT)^{-3/2}
\]

Using the given numerical values,

\[
A = \frac{6.022 \times 10^{26} \text{ kmol}^{-1}}{22.4 \text{ kg/kmol}} \times (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^3 \times [2\pi (4.00 \text{ u})(1.66 \times 10^{-27} \text{ kg/u})(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})]^{-3/2}
\]

\[
= 3.56 \times 10^{-6},
\]

which is much less than one.
51. The Fermi-Dirac distribution function for the free electrons in a metal cannot be approximated by the Maxwell-Boltzmann function at STP for energies in the neighborhood of $kT$. Verify this by using the method of Exercise 49 to show that $A>1$ in copper if $f(\varepsilon) \approx A \exp(\varepsilon/kT)$. As calculated in Sec. 9.9 $N/V = 8.48 \times 10^{28}$ electrons/m$^3$ for copper. Note that Eq. (9.55) must be used unchanged here.

\[
A = \frac{1}{2V} \frac{N}{V} h^3 (2\pi n_e kT)^{-3/2}
\]

\[
= \frac{1}{2} (8.48 \times 10^{26} \text{ m}^{-3})(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^3 [2\pi(9.11 \times 10^{-31})(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})]^{-3/2}
\]

\[
= 3.50 \times 10^3.
\]

Which is much greater than one, and so the Fermi-Dirac distribution cannot be approximated by a Maxwell-Boltzmann distribution.