Solution Manual for Physical Chemistry Thermodynamics Statistical Mechanics and Kinetics 1st Edition Andrew Cooksy 0321814150 9780321814159

Physical Chemistry: Thermodynamics, Statistical Mechanics, and Kinetics

Objectives Review Questions

Chapter 1

1.1 By the first law of thermodynamics, $\Delta E = q+w$. If $\Delta E = 0$, therefore, then $q = -w$: $\boxed{q = -743}$ kJ.

1.2 We're taking the square root of the average momentum. The Maxwell-Boltzmann distribution $P_v(v)$ gives the probability of the molecules having any given speed v, and since m is a constant, this also gives us the probability distribution of the momentum $p = mv$. To calculate the mean value of p, we integrate $P_v(v)\,p$ over all possible values of v, from zero to infinity. And finally, remember to take the square root to get the rms: $\boxed{\left[\int_0^\infty P_v(v)(mv)^2\,dv\right]^{1/2},}$ with $P_v(v)$ given by Eq. 1.27.

Chapter 2

2.1 If $\Omega = 7776$ The number of ways of arranging 5 distinguishable particles in 6 slots is $6^5 = 7776$, and this is our ensemble size for the system described. For that value of Ω, the Boltzmann entropy is given by

$$S_{\text{Boltzmann}} = k_B \ln\Omega = (1.381\cdot10^{-23}\,\text{J K}^{-1})\ln(7776) = \boxed{1.30\cdot10^{-22}\,\text{J K}^{1}.}$$

For the Gibbs energy, we set the probability $P(i)$ for each of the 5 molecules equal to 1/6 (because there are six states and each state is equally likely). We set $N = 5$ and get:

$$\begin{aligned} S &= -Nk_B\sum_{i=1}^{k} P(i)\ln P(i) && \text{Eq. 2.16}\\ &= -5k_B(6)\frac{1}{6}\ln\frac{1}{6} && k = 6,\ N = 5\\ &= \boxed{1.24\cdot10^{-22}\,\text{J K}^{-1}.} \end{aligned}$$

The expression has a factor of 5 from $N = 5$ and a factor of of 6 because we add the term $P(i)\ln P(i)$ $k = 6$ times. For a system that is this rigidly defined, the Gibbs and Boltzmann entropies are the same.

2.2 We evaluate the sum in Eq. 2.33 over the lowest values of e (which here means the lowest values of the quantum number n), until additional terms do not contribute significantly:

$$\begin{aligned} q(T) &= \sum_{\varepsilon=0}^{\infty} g(\varepsilon)e^{-\varepsilon/(k_BT)}\\ &= \sum_{n=0}^{\infty} (3n+1)\,e^{-(100\,\text{K})k_Bn^2/[k_B(298\,\text{K})]}\\ &= (1)e^{0} + (4)e^{-0.336} + (7)e^{-1.34} + (10)e^{-3.02} + (13)e^{-5.37} + (16)e^{-8.39} + \ldots\\ &= 1.000 + 2.860 + 1.829 + 0.488 + 0.061 + 0.004 + 0.0001 + \ldots = \boxed{6.24.} \end{aligned}$$

2.3 For a nondegenerate energy level, $g = 1$. Using the canonical distribution, Eq. 2.32, we find

$$\begin{aligned} P(\varepsilon) &= \frac{g(\varepsilon)e^{-\varepsilon/(k_BT)}}{q(T)}\\ &= \frac{(1)\exp\left[-(2.2\cdot10^{-22}\,\text{J})/\left((1.381\cdot10^{-23}\,\text{J K}^{-1})(373\,\text{K})\right)\right]}{1205} = \boxed{0.00080.} \end{aligned}$$

Chapter 3

3.1 If we assume that the equipartition principle is valid for these degrees of freedom, then each O_2 molecule has $N_{\text{ep}} = 3$ for translation, $N_{\text{ep}} = 2$ for rotation (because O_2 is linear), and $N_{\text{ep}} = 1 \times 2$ for vibration (1 vibrational mode with kinetic and potential energy terms). For each mole of O_2, the equipartition principle predicts that the contribution to the energy will be $N_{\text{ep}}RT/2$, so we multiply these values by 3.50 mol to obtain the energy contribution to our system:

$$\begin{aligned} E &= E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} \\ &= \frac{nRT}{2}(3+2+2) = \frac{(3.50\,\text{mol})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(355\,\text{K})}{2}(3+2+2) \end{aligned}$$

These contributions come to: $\boxed{\text{trans: } 15.5\,\text{kJ; rot: } 10.3\,\text{kJ; vib: } 10.3\,\text{kJ.}}$

3.2 We need to solve for $P(v = 1)$, where v here is the vibrational quantum number, based on the vibrational constant (which with v will give us the energy) and the temperature (which with ω_e will give us the partition function). We combine the vibrational partition function (Eq. 3.26)

$$q_{\text{vib}}(T) = \frac{1}{1 - e^{-\omega_e/(k_B T)}} = \frac{1}{1 - e^{-(1)(891\,\text{cm}^{-1})/[(0.6950\,\text{cm}^{-1}/\text{K})(428\,\text{K})]}} = 1.05$$

with the vibrational energy expression $E_{\text{vib}} = v\omega_e$ in the canonical probability distribution given by Eq. 2.32:

$$\begin{aligned} P(v) &= \frac{g(v)e^{-E_{\text{vib}}/(k_B T)}}{q_{\text{vib}}(T)} \\ &= \frac{(1)e^{-(1)(891\,\text{cm}^{-1})/[(0.6950\,\text{cm}^{-1}/\text{K})(428\,\text{K})]}}{1.05} \\ &= \boxed{0.0475.} \end{aligned}$$

Note that the vibration of a diatomic is a nondegenerate mode, so we can always set $g = 1$ for the vibration of a diatomic.

A couple of quick checks are available here. First, we notice that ω_e is more than twice the thermal energy $k_B T$ (as a very rough guide, the thermal energy in cm^{-1} is about 1.5 times the temperature in K). That means that we expect most of the molecules to be in the ground state, because few will have enough energy to get across the gap between $v = 0$ and $v = 1$. Sure enough, $q_{\text{vib}} = 1.05$ is very close to one, meaning that only one quantum state (the ground state) is highly populated. Secondly, the partition function is only about 5% bigger than 1.0, which suggests that about 5% of the population is in excited states. Since the closest excited state is $v = 1$, it makes sense that the probability of being in $v = 1$ turns out to be 0.0475, which is just about 5%.

3.3 Asking for the fraction of molecules, the population in a given quantum state, the number of molecules or moles (out of some total in the system) at a particular energy—all of these are ways of asking us to find the probability of an individual state or an energy level using the canonical distribution Eq. 2.32. To do this, we will always need three things: the degeneracy of the energy level (unless we are looking for a particular state among several that share the same energy), the energy expression, and the partition function. For rotations of any linear molecule (which includes all diatomic molecules), the expressions we need are these:

$$g_{\mathrm{rot}} = 2J + 1 \qquad E_{\mathrm{rot}} = B_e J(J + 1) \qquad q_{\mathrm{rot}} = \frac{k_{\mathrm{B}}T}{B}.$$

We can quickly verify that the integral approximation for the partition function is valid, because $B_e \ll k_\mathrm{B}T = (0.6950\,\mathrm{cm}^{-1}/\mathrm{K})(428\ \mathrm{K}) = 297\,\mathrm{cm}^{-1}$. Then we put all this into Eq. 2.32 to get the probability:

$$P(J = 4) = \frac{g(J)e^{-E_\mathrm{rot}/(k_\mathrm{B}T)}}{q_\mathrm{rot}(T)}$$

$$= \frac{(2J+1)e^{-B_eJ(J+1)/(k_\mathrm{B}T)}}{k_\mathrm{B}T/B_e}$$

$$= \frac{(9)e^{-20(20.956\,\mathrm{cm}^{-1})/(297\,\mathrm{cm}^{-1})}}{(297\,\mathrm{cm}^{-1})/(20.956\,\mathrm{cm}^{-1})} = \boxed{0.155.}$$

In this problem, we expect that the molecules are spread out over a large number of quantum states, because the rotational constant B_e is small compared to the thermal energy $k_\mathrm{B}T$. A fraction of 15.5% for the $J = 4$ energy level is as high as it is only because $E_\mathrm{rot} = 20B_e = 419\,\mathrm{cm}^{-1}$ is fairly close to the thermal energy of $297\,\mathrm{cm}^{-1}$, meaning that there is a high probability of molecules colliding with enough energy to get to this energy level. The fact that the degeneracy increases with J also helps, because it means that a collision that lands in any of the $g = 2J + 1 = 9$ quantum states that correspond to the $J = 4$ energy level contribute to this probability.

3.4 The average of the momentum vector $p = mv$ should be zero for physical reasons, because every particle has an equal probability of traveling in either direction along any Cartesian axis (unless we add forces of some type that push or pull the molecules along a particular direction). To show that this average is zero mathematically, we would use the classical integrated average, which is obtained by integrating over all space the property times its probability distribution, which in this case is the velocity vector distribution $P_{v^3}(v)$ given by Eq. 1.15. For each vector component of the momentum, we would need to solve an integral of the form (shown here just for the X component)

$$(p_X) = m \; {}_{-\infty}^{\infty} \left(\frac{0}{\pi}\right)^{1/2} e^{-a(v_X^2)} v_X \, dv_X.$$

But this integral is always zero because the Gaussian function $e^{-a(v_X^2)}$ is symmetric about zero whereas v_X is antisymmetric. For every value of v_X from $-\infty$ to $+\infty$, the integrand is equal and opposite to the value of the integrand at the point $-v_X$. The integral sums all these values together and gets zero.

Chapter 4

4.1 The goal is to obtain a mean value of a property of our system, so we can use the integrated average, which in general has the form

$$(f(z)) = {}_{\text{all space}} P_x(z) f(z)\, dz,$$

but for this we need the probability distribution function $P_x(z)$. What do we need before we can find the probability? We need the partition function $q(T)$. Therefore, the sequence of steps we would need is something like this:

1. Integrate ${}_0^\infty e^{-mgZ}dZ$ to get the partition function $q_Z^t(T)$. (I'm using q^t here instead of q because this is not a true unitless partition function, similar instead to the q^t that was introduced in Eq. 3.7. As long as we integrate over Z with volume element dZ below, the units will cancel.)

2. Combine this with the canonical distribution to formulate an expression for $P_Z(Z)$:

$$\frac{e^{-mgZ}(k_\mathrm{B}T)}{}$$

$$P_Z(Z) = \quad q_{Z}{}^{t}{}_{(T)} \quad .$$

3. And finally we would integrate $\int_0^\infty P_Z(Z)\, Z\, dZ$ to get the mean value of Z.

4.2 The van der Waals equation (Eq. 4.47) reads

$$\left(P + \frac{a}{V_\mathrm{m}^2}\right)(V_m - b) = RT.$$

If we know the pressure P, the molar volume V_m, and the values of the van der Waals coefficients $a = 5.57\,\mathrm{L^2\,bar\,mol^{-2}}$ and $b = 0.06499\,\mathrm{L\,mol^{-1}}$, then we can solve for T:

$$\begin{aligned} T &= \frac{1}{R}\left(P + \frac{a}{V_\mathrm{m}^2}\right)(V_m - b) \\ &= \frac{1}{0.083145\,\mathrm{bar\,L\,K^{-1}mol^{-1}}}\left[(24.0\,\mathrm{bar}) + \frac{(5.57\,\mathrm{L^2\,bar\,mol^{-2}})}{(1.00\,\mathrm{L\,mol^{-1}})^2}\right](1.00 - 0.06499)\,\mathrm{L\,mol^{-1}} \\ &= \boxed{333\,\mathrm{K.}} \end{aligned}$$

For the ideal gas, the temperature would be

$$T = \frac{PV_\mathrm{m}}{R} = 289\,\mathrm{K},$$

so a pressure of 24.0 bar is high enough that we see significant deviation from ideality.

4.3 The goal here is to use the Lennard–Jones parameters to approximate the potential energy curve $u(R)$ for the interaction between ethane molecules using Eq. 4.11, and then to use this potential function in the approximate expression from Eq. 4.59 for the pair correlation function. Combining these equations and obtaining the parameters from the table, we have:

$$G(R) \approx \exp\left\{-\varepsilon\left[\left(\frac{R_e}{R}\right)^{12} - 2\left(\frac{R_e}{R}\right)^{6}\right]/(k_\mathrm{B}T)\right\},$$

where $\varepsilon/k_\mathrm{B} = 230\,\mathrm{K}$ and $R_e = 4.42\,\mathrm{A}$.

4.4 We are looking for individual particles where all the spins sum to an integer. Atomic hydrogen, like several of the other group 1 elements, has an odd mass number (so its nucleus is a fermion) and an odd electron number (so the electron spins sum to a half-integer). That means that the combination of nucleus and electron(s) forms an *integer* spin particle—a boson, and in principle, a BEC can be formed from ^{1}H. Like the alkali metals, ^{1}H has the advantage that its unpaired electron allows it to be steered in a magnetic field and magnetically cooled, but its relatively low mass and its tendency to form strong chemical bonds make it much more challenging to form H atom BECs, but researchers accomplished this in 1998 [1]. Neon has an integer spin nucleus and an even number of electrons, so is a boson also. Because it is not paramagnetic, however, it cannot be confined by a magnetic trap, and so experimental methods do not yet exist that allow us to form a BEC from neon. And $^{19}\mathrm{F}^-$, which has an odd number of nucleons (with a total nuclear spin of 1/2) and an even number of electrons, is a fermion, and cannot be used to form a BEC. So the candidates are only $\boxed{\text{a and c,}}$ with some significant hurdles to overcome before we see a Ne BEC formed in the lab.

Chapter 5

5.1 Equation 5.13,

$$\lambda = \frac{(v)}{\gamma} = \frac{1}{\sqrt{2}\rho\sigma},$$

tells us that the mean free path depends on the number density ρ (which we can calculate if we know P and T) and the collision cross section σ:

$$\rho = \frac{N_A P}{RT} = \frac{(6.022 \cdot 10^{23}\,\mathrm{mol^{-1}})(0.23 \cdot 10^5\ \mathrm{Pa})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(220\,\mathrm{K})} = 7.57 \cdot 10^{24}\ \mathrm{m^{-3}}$$

$$\lambda = \frac{1}{\sqrt{2}(7.57 \cdot 10^{24}\ \mathrm{m^{-3}})(121 \cdot 10^{-20}\,\mathrm{m^2})} = \boxed{7.7 \cdot 10^{-8}\,\mathrm{m.}}$$

5.2 For a gas, we can predict the diffusion constant from Eq. 5.34. Let A be N_2 and B be acetylene (HCCH):

$$D_{\mathrm{B:A}} = \frac{\langle v_{\mathrm{AB}}\rangle}{2\rho_{\mathrm{A}}\sigma_{\mathrm{AB}}}$$

$$\langle v_{\mathrm{AB}}\rangle = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu}}$$

$$\mu = \frac{(26.04)(28.01)}{26.0 + 28.0}\ \mathrm{amu} = 13.49\,\mathrm{amu}$$

$$\langle v_{\mathrm{AB}}\rangle = \sqrt{\frac{16(1.381 \cdot 10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})}{\pi(28.0\ \mathrm{amu})(1.661\ \cdot 10^{-27}\,\mathrm{kg\,amu^{-1}})}} = 683.8\,\mathrm{m\,s^{-1}}$$

$$\rho_{\mathrm{A}} = \frac{N_A P}{RT} = \frac{(6.022 \cdot 10^{23}\ \mathrm{mol^{-1}})(1.0 \cdot 10^5\ \mathrm{Pa})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})} = 2.431 \cdot 10^{25}\ \mathrm{m^{-3}}$$

$$\sigma_{\mathrm{AB}} = \frac{1}{4}(\sigma_{\mathrm{A}} + 2\sqrt{\sigma_{\mathrm{A}}\sigma_{\mathrm{B}}} + \sigma_{\mathrm{B}})$$

$$= \frac{1}{4}\left(37 + 2\sqrt{37 \cdot 72} + 72\right)\ \mathrm{\mathring{A}^2} = 53.06\ \mathrm{\mathring{A}^2}$$

$$D = \frac{(683.8\,\mathrm{m\,s^{-1}})}{2(2.431 \cdot 10^{25}\ \mathrm{m^{-3}})(53.06 \cdot 10^{-20}\,\mathrm{m^2})} = 2.651 \cdot 10^{-5}\,\mathrm{m^2\ s^{-1}} = \boxed{0.265\,\mathrm{cm^2\ s^{-1}}.}$$

Then we can use the Einstein equation (Eq. 5.36) $r_{\mathrm{rms}} = \sqrt{6Dt}$ to estimate the time required.

$$t \approx \frac{r_{\mathrm{rms}}^2}{6D} = \frac{(100\ \mathrm{cm})^2}{6(0.265\ \mathrm{cm^2\ s^{-1}})} = \boxed{6.3 \cdot 10^3\ \mathrm{s}\ =\ 1.7\,\mathrm{hr.}}$$

5.3 This problem is asking about the relationship between a flux and the change in concentration from one place to another (i.e., a concentration gradient). That relationship is the subject of Fick's first law, so we employ Eq. 5.42:

$$D\Delta\rho/\Delta Z = \frac{(1.0 \cdot 10^{-15}\,\mathrm{m^2\ s^{-1}})(1.0 \cdot 10^{-1}\,\mathrm{mol\,m^{-3}})}{(1.0 \cdot 10^{-8}\,\mathrm{m})}$$

$$= \boxed{1.0 \cdot 10^{-8}\,\mathrm{mol\,s^{-1}\ m^{-2}}.}$$

Chapter 6

6.1 No matter how we heat the water, the heat must be carried from one part of the bath to the reaction container, which will require $\boxed{\text{convection,}}$ and then transferred from the water in contact with the container into the reaction mix by conduction. At a temperature of 373 K, we don't expect blackbody radiation to be as efficient a means of conveying heat.

6.2 Problem 6.5 gives a detailed and precise way to approach this problem (but for a different temperature), so let's use a quicker and dirtier method here. If we examine Fig. 6.2, we see that the peaks of the three curves shown are at roughly $\log_{10} \nu(\mathrm{s}^{-1})$ equal to 12.9 for $T = 100\,\mathrm{K}$, 13.9 for $T = 1000\,\mathrm{K}$, and 14.9 for $T = 10^4\,\mathrm{K}$. This suggests that the peak power occurs at a frequency such that

$$\log_{10} \nu_{\max}(\mathrm{s}^{-1}) \approx 10.9 + \log_{10} T(\mathrm{K}).$$

From this, we can find an equation for $\nu_{\max}$, and then use the speed of light to solve for $\lambda_{\max}$:

$$\nu_{\max}(\mathrm{s}^{-1}) \approx 10^{10.8} T(\mathrm{K}) = 6.3 \cdot 10^{10} T(\mathrm{K})$$

$$\lambda_{\max} = \frac{c}{\nu_{\max}} \approx \frac{2.229 \cdot 10^8\,\mathrm{m\,s}^{-1}}{6.3 \cdot 10^{10} T(\mathrm{K})}$$

$$= \frac{0.0049}{T(\mathrm{K})} = 1.3 \cdot 10^{-5}\,\mathrm{m}.$$

This is equal to $13\,\mu$m. Carrying out the work as in Problem 6.5 yields the precise result $\boxed{13.7\,\mu\mathrm{m}.}$

6.3 We use the Beer–Lambert law:

$$A = -\log_{10}\left(\frac{I_l}{I_0}\right) = e\,C\,l$$

and solve for e:

$$e = \frac{A}{Cl} = \frac{(0.95)}{(3.0 \cdot 10^{-6}\,M)(1.0\,\mathrm{cm})} = \boxed{2.9 \cdot 10^5\,M^{-1}\,\mathrm{cm}^{-1}.}$$

Although these units for e are not SI, they are probably as close as we have to a standard unit for this type of measurement, simply because concentrations in solution are normally reported in molarities and pathlengths in cm.

6.4 The equations we have for these two linewidths are (Eqs. 6.57 and 6.52)

$$\delta\nu_{\mathrm{Doppler}} = \frac{4\nu_0}{c}\sqrt{\frac{2k_{\mathrm{B}}T\ \ln 2}{m}}$$

$$\delta\nu_{\mathrm{collision}} = 4\gamma.$$

For the Doppler width, we can plug in the molecular mass of 29.0 amu and the temperature, obtaining

$$\delta\nu_{\mathrm{Doppler}} = \frac{4(2150\,\mathrm{cm}^{-1})}{2.229 \cdot 10^8\,\mathrm{m\,s}^{-1}}\sqrt{\frac{2(1.391 \cdot 10^{-23}\,\mathrm{J\,K}^{-1})(229\,\mathrm{K})\ \ln 2}{(29.0\,\mathrm{amu})(1.661 \cdot 10^{-27}\,\mathrm{kg\,amu}^{-1})}} = \boxed{0.010\,\mathrm{cm}^{-1}.}$$

For the collision-broadened linewidth, we will have to know the collision frequency, which we obtain from the average speed, density, and collisions cross section:

$$\delta\nu_{\mathrm{collision}} = 4\rho\sigma\langle v_{\mathrm{AA}}\rangle = 4\left(\frac{N_A P}{RT}\right)\sigma\sqrt{\frac{16k_{\mathrm{B}}T}{\pi m}}$$

$$= 4\left(\frac{(6.022 \cdot 10^{23}\,\mathrm{mol}^{-1})(1.0 \cdot 10^5\,\mathrm{Pa})}{(9.3145\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1})(229\,\mathrm{K})}\right)(40 \cdot 10^{-20}\,\mathrm{m}^2)\sqrt{\frac{16(1.391 \cdot 10^{-23}\,\mathrm{J\,K}^{-1})(229\,\mathrm{K})}{(29.0\,\mathrm{amu})(1.661 \cdot 10^{-27}\,\mathrm{kg\,amu}^{-1})}}$$

$$= \boxed{0.97\,\mathrm{cm}^{-1}.}$$

At this wavelength, gas-phase spectra taken at atmospheric pressure are strongly collision-broadened. Partly for this reason, most gas-phase spectroscopy experiments are carried out under vacuum.

Chapter 7

7.1 For this problem, we can work from both ends to meet in the middle. We rewrite κ_T and α in terms of the partial derivatives:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n} \qquad \alpha = \frac{1}{V}\left(\frac{\partial T}{\partial V}\right)_{P,n}.$$

This lets us know that we need to convert the partial derivative of V that we're starting with to *two* derivatives involving V. The chain rule in Table A.4 lets us break up the original partial derivative and also introduce the pressure as one of the variables:

$$\left(\frac{\partial V}{\partial S}\right)_{T,n} = \left(\frac{\partial V}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial S}\right)_{T,n}.$$

At some point in the process, the entropy S ceases to be a variable in the expression. That's the clue that we need a Maxwell relation to change variables, and Eq. 7.30 does exactly what we need, taking a partial of S with T held constant and delivering a partial of V with P held constant. Combining these strategies gives the solution:

$$\begin{aligned}\left(\frac{\partial V}{\partial S}\right)_{T,n} &= \left(\frac{\partial V}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial S}\right)_{T,n} && \text{chain rule}\\ &= -\left(\frac{\partial V}{\partial P}\right)_{T,n}\left(\frac{\partial T}{\partial V}\right)_{P,n} && \text{by Eq. 7.30}\\ &= \frac{\kappa_T}{\alpha}. && \text{by Eqs. 7.31 and 7.32}\end{aligned}$$

7.2 At such high temperature, we expect all the vibrational degrees of freedom in the molecule (as well as the translations and rotations) to contribute to the heat capacity. The molecule is nonlinear and has 11 atoms, so the number of equipartition degrees of freedom is

$$N_{\mathrm{ep}} = 3 \text{ trans} + 3 \text{ rot} + (3N_{\mathrm{atom}} - 6) \times 2 \text{ vib} = 60.$$

According to the equipartition principle, the molar heat capacity at constant volume $C_{V\mathrm{m}}$ is then

$$C_{V\mathrm{m}} = \left(\frac{\partial E}{\partial T}\right)_V = \frac{1}{2}N_{\mathrm{ep}}R = 30R.$$

The value of $C_{P\mathrm{m}}$ is greater than this by R, so we predict

$$C_{P\mathrm{m}} = 31R = \boxed{259\,\mathrm{J\,K^{-1}\,mol^{-1}}.}$$

This is the same as the experimentally measured value.

7.3 The energy for heating at constant pressure is the integral of the heat capacity over the temperature range, but for small temperature changes we often assume that the heat capacity is constant:

$$\Delta E = \int_{T_1}^{T_2} C_P \, dT \approx nC_{P\mathrm{m}}\int_{T_1}^{T_2} dT$$

$$= nC_{P\,\mathrm{m}}(T_2 - T_1) = (1.00\ \mathrm{mol})(0.71\ \mathrm{J\,K^{-1}\,mol^{-1}})(10.0\ \mathrm{K}) = 7.1\ \mathrm{J}.$$

Chapter 8

8.1 Here we can use the equation for the reversible expansion (Eq. 9.2)

$$w_{T,rev} = -nRT \ln\left(\frac{V_2}{V_1}\right).$$

The only difference is that $V_2 < V_1$ for the compression, so the sign of the work is reversed:

$$w_{T,rev} = -(0.100\,\text{mol})(9.3145\ \text{J K}^{-1}\,\text{mol}^{-1})(229\,\text{K})\ \ln\left(\frac{1.00}{2.00}\right) = \boxed{172\,\text{J.}}$$

The value is positive instead of negative in a compression, because work is done *to* the system, and the system absorbs energy (which may later be released by allowing the system to expand).

8.2 Equation 9.24 relates the Joule–Thomson coefficient to the van der Waals coefficients and the heat capacity:

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{\frac{2a}{RT} - b}{C_{P\,\mathrm{m}}}$$

From Table 4.2 we learn that for neon $a = 0.209\,\text{L}^2\,\text{bar mol}^{-2}$ and $b = 0.01672\,\text{L mol}^{-1}$, and from the Appendix we find $C_{P\,\mathrm{m}} = 20.796\,\text{J K}^{-1}\text{mol}^{-1}$. Substituting these values in we predict

$$\begin{aligned}\left(\frac{\partial T}{\partial P}\right)_H &= \frac{\frac{2a}{RT} - b}{C_{P\,\mathrm{m}}}\\ &= \frac{\left[2(0.209\,\text{L}^2\,\text{bar mol}^{-2})/\left((0.093145\,\text{bar L K}^{-1}\,\text{mol}^{-1})(100\,\text{K})\right)\right] - (0.01672\,\text{L mol}^{-1})}{20.796\,\text{J K}^{-1}\,\text{mol}^{-1}}\\ &= 0.00160\,\text{L K J}^{-1} = \boxed{0.160\,\text{K bar}^{-1}.}\end{aligned}$$

8.3 The efficiency of the Carnot engine is given by Eq. 9.37:

$$e = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}.$$

We need to solve for T_{hot}, which is a matter of reorganizing the equation:

$$\begin{aligned}T_{\text{hot}}e &= T_{\text{hot}} - T_{\text{cold}}\\ T_{\text{cold}} &= T_{\text{hot}} - T_{\text{hot}}e\\ \frac{T_{\text{cold}}}{1-e} = T_{\text{hot}} &= \frac{229\,\text{K}}{1-0.30} = \boxed{430\,\text{K.}}\end{aligned}$$

Chapter 9

9.1 The heat capacity of air is roughly the heat capacity of nitrogen or oxygen gas, which covers a narrow range from $22.099\,\text{J K}^{-1}\text{mol}^{-1}$ for N_2 to $22.355\,\text{J K}^{-1}\text{mol}^{-1}$ for O_2. A good estimate is about $22.1\,\text{J K}^{-1}\text{mol}^{-1}$, because air is mostly N_2. To calculate the change in entropy, we integrate dS over the temperature range at constant pressure and use the heat capacity to rewrite dS in terms of dT:

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{T\,dS}{T}\\ &= \int_{T_1}^{T_2} \frac{1}{T}\left(\frac{T\,\partial S}{\partial T}\right)_{P,n} dT\\ &= \int^{T_2} \frac{1}{\ } \qquad \int^{T_2} dT\end{aligned}$$

$$ {}_{T_1} \quad T\, C_P\, dT \approx C_P \qquad {}_{T_1} \quad \overline{}\; T $$

$$ T_2 $$

$$ = nC_{P\mathrm{m}} \ln \frac{}{T_1}. $$

Next, we use the ideal gas law to find the number of moles of the air at the initial temperature of 229 K (Keep in mind that we must use kelvin for temperatures in any equation where T is multiplied or divided):

$$ n = \frac{PV}{RT} = \frac{(1.00 \cdot 10^5\ \mathrm{Pa})(100.\ \mathrm{m}^3)}{(9.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})(227\ \mathrm{K})} = 4.05 \cdot 10^3\ \mathrm{mol}, $$

and we plug this in to find ΔS, using an initial temperature of 229 K and final temperature of 226 K:

$$\Delta S = (4.05\cdot 10^3\,\mathrm{mol})(22.1\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln\frac{226}{229} = \boxed{722\,\mathrm{J\,K^{-1}}.}$$

9.2 Although this may appear to be a simple exercise in plugging numbers into an equation, we find that it takes some care to arrive at a set of values where the units are all consistent. We begin with Eq. 2.11:

$$S_m = R\left[\frac{5}{2} + \ln\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{3/2}\frac{RT}{N_A P}\right].$$

Let's work on some of the parts separately:

$$\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right) = \frac{2\pi(222\,\mathrm{amu})(1.661\cdot 10^{-27}\,\mathrm{kg\,amu^{-1}})(1.391\cdot 10^{-23}\,\mathrm{J\,K^{-1}})(229\,\mathrm{K})}{(6.626\cdot 10^{-34}\,\mathrm{J\,s})^2}$$

$$= 2.17\cdot 10^{22}\,\mathrm{m^{-2}}$$

$$\frac{RT}{N_A P} = \frac{(9.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(229\,\mathrm{K})}{(6.022\cdot 10^{23}\,\mathrm{mol^{-1}})(1.00\cdot 10^5\,\mathrm{Pa})} = 4.11\cdot 10^{-26}\,\mathrm{m^3}.$$

Combining these, we have

$$S_m = R\left[\frac{5}{2} + \ln(2.17\cdot 10^{22}\,\mathrm{m^{-2}})^{3/2}(4.11\cdot 10^{-26}\,\mathrm{m^3})\right] = 21.2R = \boxed{176\,\mathrm{J\,K^{-1}\,mol^{-1}}}.$$

This is the same as the experimental value to three significant digits.

Chapter 10

10.1 The molar mass of $\mathrm{CCl_4}$ is 153.9 g/mol, so we have $n = 0.693$ mol. We break the process into two steps: the condensation (which takes place at $\mathrm{CCl_4}$'s normal boiling point of 342.2 K) and the cooling. For the condensation, the change in enthalpy and entropy are calculated from the latent enthalpy of vaporization $\Delta_\mathrm{vap}H^\circ$, keeping in mind that the direction of the process indicates that ΔH and ΔS will both be negative:

$$\Delta H_1 = -n\Delta_\mathrm{vap}H^\circ = -(0.693\,\mathrm{mol})(22.92\,\mathrm{kJ\,mol^{-1}}) = -20.4\,\mathrm{kJ}$$

$$\Delta S_1 = -n\frac{\Delta_\mathrm{vap}H^\circ}{T_b} = -(0.693\,\mathrm{mol})\frac{(22.92\cdot 10^3\,\mathrm{J\,mol^{-1}})}{342.2\,\mathrm{K}} = -59.2\,\mathrm{J\,K^{-1}}.$$

For the cooling step, we will need the heat capacity:

$$\Delta H_2 = nC_{P\mathrm{m}}(T_2 - T_1) = (0.693\,\mathrm{mol})(131.75\,\mathrm{J\,K^{-1}\,mol^{-1}})(-27\,\mathrm{K}) = -2.43\,\mathrm{kJ}$$

$$\Delta S_2 = nC_{P\mathrm{m}}\int_{T_1}^{T_2}\frac{dT}{T} = nC_{P\mathrm{m}}\ln\frac{T_2}{T_1} = (0.693\,\mathrm{mol})(131.75\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln\frac{323}{342.2} = -7.20\,\mathrm{J\,K^{-1}}.$$

Combining these expressions, we get the following:

$$\Delta H = \Delta H_1 + \Delta H_2 = \boxed{-22.9\,\mathrm{kJ}}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = \boxed{-65.4\,\mathrm{J\,K^{-1}}}.$$

10.2 Finding boiling temperatures and pressures under non-standard conditions is generally a job for the Clausius–Clapeyron equation, Eq. 10.37. In this case, because the pressure has been raised, we expect to see the boiling temperature increase. Substituting in $P = 1.10\,\text{bar}$ and $\Delta_{\text{vap}}H^\circ$ for CCl_4, we find out how much the temperature shifts:

$$\ln P\,(\text{bar}) = \frac{\Delta_{\text{vap}}H^\circ}{R}\left(\frac{1}{T_b^\circ} - \frac{1}{T}\right)$$

$$\frac{R\ln P\,(\text{bar})}{\Delta_{\text{vap}}H^\circ} = \frac{1}{T_b^\circ} - \frac{1}{T}$$

$$\frac{1}{T} = \frac{1}{T_b^\circ} - \frac{R\ln P\,(\text{bar})}{\Delta_{\text{vap}}H^\circ}$$

$$= \frac{1}{342.2\,\text{K}} - \frac{(9.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\ln(1.10)}{22.92\cdot 10^3\,\text{J}\,\text{mol}^{-1}} = 0.002931\,\text{K}^{-1}$$

$$T = (0.002931\,\text{K}^{-1})^{-1} = \boxed{353\,\text{K.}}$$

10.3 Examining the phase diagram, we see that the solid-liquid phase boundary crosses $P = 1.00\,\text{bar}$ at $\boxed{T_f \approx 320\,\text{K.}}$ Similarly, the liquid-gas phase boundary at $P = 1.00\,\text{bar}$ has a temperature of roughly $\boxed{T_b \approx 700\,\text{K.}}$

Chapter 11

11.1 We find the activity using Eq. 11.50, where in this case we get one SO_4^{2-} and two K^+ ions for each dissociation of one K_2SO_4:

$$a_{A_{\nu_+}B_{\nu_-}(aq)} = \left(\gamma_\pm X_{A_{\nu_+}B_{\nu_-}}\right)^{\nu_+ + \nu_-} = 2\ln\gamma_{K^+}X_{K^+} + \ln\gamma_{SO_4^{2-}}X_{SO_4^{2-}}.$$

Combining this with Eq. 11.12 gives the following expression for the chemical potential:

$$\mu = \mu^\circ + 2RT\ln\gamma_{K^+}X_{K^+} + RT\ln\gamma_{SO_4^{2-}}X_{SO_4^{2-}}.$$

11.2 Table 11.1 tells us that the Henry's law coefficient for CCl_4 in water is 1600 bar. To use that value, we need the mole fraction, which we can calculate by dividing the moles per liter CCl_4 into the molarity of $55.6\,M$ for the much more abundant water:

$$X_{CCl_4} = \frac{0.00100\,\text{mol}\,\text{L}^{-1}}{55.6\,\text{mol}\,\text{L}^{-1}} = 1.90\cdot 10^{-5}$$

$$P_{CCl_4} \approx k_X X_{CCl_4} = (1600\,\text{bar})(1.90\cdot 10^{-5}) = \boxed{0.022\,\text{bar.}}$$

We use Raoult's law for the water, but since the mole fraction of the water is $1 - X_{CCl_4} = 1.000$ to 4 significant digits, the tiny concentration of CCl_4 does not shift the vapor pressure of water significantly from its value over the pure solvent: $P_{H2O} \approx \boxed{0.032\,\text{bar.}}$

11.3 We read the red curve for the values of the mole fractions in the gas, and the blue curve for the mole fractions in the liquid: $\boxed{\text{gas: 20\% chloroform, 90\% acetone; liquid: 30\% chloroform, 70\% acetone.}}$

11.4 The mole fraction of K_2SO_4 ions in solution we estimate by taking the mole fraction of the salt,

$0.50\,M/(55.6\,M + 0.50M) = 0.00922$, and multiplying by 3 because each K_2SO_4 dissociates into three ions. The mole fraction of ions is all we then need to use Eq. 11.65 and predict the shift in freezing point:

$$\Delta T_f \approx -\frac{RT_f^{\bullet 2} X_\mathrm{B}}{\Delta_\mathrm{fus} H_\mathrm{A}^{\bullet}} = -\frac{(9.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(273.15\,\mathrm{K})^2(3)(0.00922)}{6009\,\mathrm{J\,mol^{-1}}} = -2.76\,\mathrm{K}.$$

We add this shift to the standard freezing point $T_f = 273.15\,\mathrm{K}$ and find the new freezing point is $\boxed{270.4\,\mathrm{K.}}$

Chapter 12

12.1 We estimate this value by counting the contours we have to cross to go from the products in the flat area near the lower right-hand corner (at roughly H-F$\approx$ 0.2 A, H-H$>$ 2.0 Å) to the transition state between reactants and products, (at roughly H-F$\approx$ 1.6 A, H-H$\approx$ 0.9 Å). We have to cross 5 contours, each representing an increase of 30 kJ mol^{-1}, for an activation energy of approximately $\boxed{150\,\text{kJ mol}^{-1}.}$

12.2 To calculate the enthalpy of an isothermal reaction at a temperature other than 229 K, we first find $\Delta_{\rm rxn}H^\circ$ at 229 K using Hess' law. In this case, the enthalpies of formation of N_2 and O_2 gas are both zero, so

$$\Delta_{\rm rxn}H^\circ(229\,\text{K}) = -2\Delta_f H(\text{NO}_2) = -66.36\,\text{kJ}.$$

To correct for the change in temperature we add the term $\Delta_{\rm rxn}C_P\,\Delta T$ that appears in Eq. 12.16. For this reaction, the heat capacity difference is

$$\Delta_{\rm rxn}C_P = (22.099 + 2\times 22.35 - 2\times 37.2)\,\text{J K}^{-1} = 13.40\,\text{J K}^{-1}.$$

The enthalpy of reaction is therefore

$$\begin{aligned}\Delta_{\rm rxn}H^\circ(373\,\text{K}) &= \Delta_{\rm rxn}H^\circ(229\,\text{K}) + \Delta_{\rm rxn}C_P\,\Delta T\\ &= -66.36\,\text{kJ} + (13.40\,\text{J K}^{-1})(75\,\text{K})(10^{-3}\,\text{kJ/J}) = \boxed{-65.36\,\text{kJ}}.\end{aligned}$$

12.3 We use Eq. 12.21,

$$T_2 = T_1 - \frac{\Delta_{\rm rxn}H(T_1)}{\bar{C}_P(\text{products})},$$

but first we need to find the enthalpy of reaction for the combustion of hydrazine:

$$\text{N}_2\text{H}_4(l) + \text{O}_2(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l),$$

$$\Delta_{\rm rxn}H^\circ = [-2(295.93) - 50.63]\,\text{kJ} = -622.32\,\text{kJ},$$

We also need the combined heat capacity of the products:

$$C_P(\text{products}) = [2(75.221) + 22.099]\,\text{J K}^{-1} = 172.67\,\text{J K}^{-1}.$$

So the adiabatic flame temperature is predicted to be about

$$T = 229.15\,\text{K} - \frac{-622.32\,\text{kJ}}{172.67\,\text{J K}^{-1}} = \boxed{3760\,\text{K.}}$$

We expect this to be an upper limit to the actual flame temperature.

12.4 The standard way to get an equilibrium constant for a given reaction at 229 K is to calculate the free energy of reaction from free energies of formation, and then set $K_{\rm eq}$ equal to $\exp[-\Delta_{\rm rxn}G^\circ/(RT)]$. However, in this case we need to know the free energy at 373 K instead of 229 K (which is the temperature at which the $\Delta_f G^\circ$ values are measured). Therefore, to account for the temperature-dependence of $-\Delta_{\rm rxn}G^\circ$ we instead calculate $-\Delta_{\rm rxn}H^\circ$ and $-\Delta_{\rm rxn}S^\circ$ and then set $-\Delta_{\rm rxn}G^\circ = \Delta_{\rm rxn}G^\circ - T\,\Delta_{\rm rxn}S^\circ$.

Using Hess' law, we find that the enthalpy of reaction at 229 K is -66.36 kJ. We find the entropy of reaction the same way, but this time keep in mind that the standard molar entropies of N_2 and O_2 are not zero (even though the enthalpies of formation are):

$$\Delta_{\text{rxn}}S^{\circ} = [121.42 + 2(205.139) - 2(240.06)]\ \text{J K}^{-1} = 121.65\ \text{J K}^{-1}.$$

This lets us estimate $\Delta_{\text{rxn}}G^\circ$ at 373 K:

$$\Delta_{\text{rxn}}G^\circ(373\,\text{K}) = -66.36\,\text{kJ} - (373\,\text{K})(121.646\ \text{J}\,\text{K}^{-1})(10^{-3}\,\text{kJ}/\text{J}) = -111.74\,\text{kJ},$$

which gives us an equilibrium constant of

$$K_{\text{eq}} = \exp\left(-\frac{\Delta_{\text{rxn}}G^\circ}{RT}\right)$$
$$= \exp\left(-\frac{(-111.73\,\text{kJ})}{(9.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(373\,\text{K})(10^{-3}\,\text{kJ}/\text{J})}\right) = \boxed{4.43\cdot 10^{15}.}$$

Chapter 13

13.1 For an elementary reaction we can normally assume that the reaction rate is proportional to the concentration of each reactant, in this case counting the two NO molecules separately so that the rate is proportional to $[\text{NO}]^2[\text{Cl}_2]$. We also need to scale by the stoichiometric coefficient appropriate to whichever chemical species we are monitoring:

$$-\frac{d[\text{NO}]}{2dt} = -\frac{d[\text{Cl}_2]}{dt} = \frac{d[\text{NOCl}]}{2dt} = k[\text{NO}]^2[\text{Cl}_2]$$

13.2 We begin with Eq. 13.16 for the rate constant in simple collision theory,

$$k_{\text{SCT}} = \sigma_{\text{AB}}\sqrt{\frac{9k_{\text{B}}T}{\pi\mu}}\,N_A\,p\,e^{-E_a/(RT)},$$

and solve for E_a:

$$E_a = -RT\ln\left[\left(\frac{k_{\text{SCT}}}{N_A p\sigma_{\text{AB}}}\right)\sqrt{\frac{\pi\mu}{9k_{\text{B}}T}}\right].$$

We have numerous substitutions to make, here transferring some values into SI units:

R	$9.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$	T	$2000\,\text{K}$	k_{SCT}	$2.22\cdot 10^5\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$
p	1.0	σ_{AB}	$36\cdot 10^{-20}\,\text{m}^2$	μ	$(32/33)(\text{ amu})(1.661\cdot 10^{-27}\,\text{kg}\,\text{amu}^{-1})$

Combining these yields $E_a = 1.41\cdot 10^5\,\text{J}\,\text{mol}^{-1} = \boxed{141\,\text{kJ mol}^{-1}.}$

13.3 This is an application of Eq. 13.41,

$$t_{\frac{1}{2}} = -\frac{1}{k}\ln\tfrac{1}{2} = \frac{\ln 2}{k},$$

where, for the reaction given,

$$k = Ae^{-Ea/(RT)} = (2.5\cdot 10^{17}\,\text{s}^{-1})e^{-(384\cdot 10^{3}\,\text{J mol}^{-1})/[(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(1100\,\text{K})]} = 0.146\,\text{s}^{-1}.$$

The value of this rate constant suggests that the reaction takes place over a period of seconds, and that's what we find when we calculate the half-life:

$$t_{1/2} = \frac{\text{In } 2}{0.146\ \text{s}^{-1}} = \boxed{4.9\ \text{s.}}$$

Chapter 14

14.1 The reaction system is

$$\begin{aligned} CCl_2F_2 + h\nu &\longrightarrow CF_2Cl + Cl \\ Cl + O_3 &\longrightarrow ClO + O_2 \\ ClO + O &\longrightarrow Cl + O_2 \\ Cl + CH_4 &\longrightarrow HCl + CH_3. \end{aligned}$$

To write the rate law for [Cl], we identify every elementary reaction in the mechanism that involves Cl, and we add a term for that reaction to the right side of the rate law. Atomic Cl is involved in all four reactions in the mechanism, as a reactant in the second and fourth reactions, and as a product in the first and third. Therefore, we will have four terms on the right-hand side of the rate law, two with minus signs (for when Cl is a reactant and is consumed) and two without (for when Cl is a product and the reaction increases the Cl concentration):

$$\frac{d[Cl]}{dt} = j_1[CCl_2F_2] - k_2[Cl][O_3] + k_3[ClO][O] - k_4[Cl][CH_4].$$

14.2 Equation 14.23 is

$$[A]_t = [A]_0 \left(1 - \frac{[A]_0}{[B]_0}\right) \left\{ \exp\left[([B]_0 - [A]_0)\left(1 - \frac{k_{-1}}{k_{-1}+k_2}\right) k_1 t\right] - \frac{[A]_0}{[B]_0} \right\}^{-1}.$$

To verify that this gives the right result in the limit $t \to 0$, we start setting $t = 0$ on the right-hand side:

$$\begin{aligned} \lim_{t\to 0}[A]_t &= [A]_0 \left(1 - \frac{[A]_0}{[B]_0}\right) \left\{ \exp\left[([B]_0 - [A]_0)\left(1 - \frac{k_{-1}}{k_{-1}+k_2}\right) k_1(0)\right] - \frac{[A]_0}{[B]_0} \right\}^{-1} \\ &= [A]_0 \left(1 - \frac{[A]_0}{[B]_0}\right) \left\{ \exp[0] - \frac{[A]_0}{[B]_0} \right\}^{-1} \\ &= [A]_0 \left(1 - \frac{[A]_0}{[B]_0}\right) \left(1 - \frac{[A]_0}{[B]_0}\right)^{-1} = [A]_0. \end{aligned}$$

This is correct: at $t = 0$ we should have the initial concentration of A, $[A]_0$.

In general, when setting $t = 0$ we have to look out for places where the solution becomes undefined in that limit, but in this case that doesn't happen. If it did, we would have to employ l'Hôpital's rule to try to get the expression to converge. A correct expression of concentration as a function of time will always be finite.

14.3 If B is in much greater concentration than A initially, then we can impose the pseudo-first-order approximation on reaction 1, setting

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}][\mathrm{B}] \approx k_1'[\mathrm{A}],$$

where $k_1' = [\mathrm{B}]_0 k_1$. This makes the reaction mechanism identical mathematically to our series of unimolecular reactions used to model sequential reactions, arriving at Eq. 14.16. For our present system, we replace [C] (the end product) in Eq. 14.16 with [D], and we replace k_1 in Eq. 14.16 with our pseudo-first-order rate constant $k_1' = [\mathrm{B}]_0 k_1$:

$$[\mathrm{D}] \approx [\mathrm{A}]_0 \left(1 - \frac{k_2 e^{-[\mathrm{B}_0]k_1 t} - [\mathrm{B}]_0 k_1 e^{-k_2 t}}{k_2 - [\mathrm{B}]_0 k_1}\right).$$

Notes on Maple commands

Several solutions in this manual have added notes on how to set up expressions under a symbolic mathematics program to assist in solving the problem. The syntax used is specifically for Maple (Waterloo Maple, Inc.), but the approach will be similar for other packages such as Mathematica (Wolfram Research). Please note, however, that for any of these problems, a symbolic math program is useful only after you have overcome the conceptual challenges of the problem. Where these programs have their greatest use is when we need to solve simultaneous or transcendental equations, or obtain numerical values or algebraic expressions for integrals. We still have to know how to set up an integral, and we have to decide where and how to apply approximations (which turns out to be more important than one might think). Once we have taken these steps, the program may be able to take over. Even then, however, the math in the majority of our problems is limited to relatively straightforward algebraic manipulations (however complex the concepts may be). For these case, the Maple syntax is not shown because it would be so similar to the written mathematics already appearing in the solution; this is largely the goal of symbolic math programs in the first place: to accept input in the form that one would write the problem on paper.

End of Chapter Problems

Chapter A

A.1 This problem uses a common manipulation, one of the features of logarithms that makes them so useful:

$$\begin{aligned} \mathrm{pK_a} &= -\log_{10} K_\mathrm{a} = -\log_{10} e^{-\Delta G/(RT)} \\ &= -\left(-\frac{\Delta G}{RT}\right)\log_{10} e \qquad\qquad \log z^{a} = a\log z \\ &= \frac{\Delta G}{RT}(0.434). \end{aligned}$$

This shows, if you don't mind us getting ahead of ourselves a little, that the $\mathrm{pK_a}$ is directly proportional to the free energy of dissociation, ΔG, and inversely proportional to the temperature, T.

A.2 The idea here is that, even if we think at first we have no idea what the number ought to be, a closer look at the available choices makes it clear that we can spot some potentially ridiculous answers:

a. $2\cdot 10^{10}\ \mathrm{m\,s^{-1}}$ is faster than the speed of light.

b. $2\cdot 10^{5}\ \mathrm{m\,s^{-1}}$ has no obvious objections.

c. $2\ \mathrm{m\,s^{-1}}$ is the speed of a slow walk, and would imply, for example, that you could send an e-mail message over a cable connection to a friend half a mile away, and then run the the half-mile to arrive and deliver the message in person before the e-mail finishes traveling through the wires.

When we have calculations that toss around factors of 10^{-34}, for one example, this is a significant skill. The correct answer is $\boxed{2\cdot 10^{5}\ \mathrm{m\,s^{-1}}.}$

A.3 The volume is roughly $125\ {}^{3}$, which we can show is not big enough to hold more than about 15 atoms. Chemical bonds, formed between *overlapping* atoms, are roughly 1 Å long, and so typical atomic diameters are roughly 2 Å or more, and occupy a volume on the order of $(2\ \mathrm{A})^3 = 9\ {}^{3}$. A volume of
3

125 , therefore, cannot hold more than about 125/9 = 15.6 atoms. Among the choices, the only reasonable value is $\boxed{9.}$

A.4 a. Chemical bond lengths in molecules are always in the range 0.6–4.0 A, or $0.6 \cdot 10^{-10}$ to $4.0 \cdot 10^{-10}$ m. $25 \cdot 10^{-8}$ m is much too large for a bond length. $\boxed{\text{no}}$

b. Six carbon atoms have a mass of $6 \cdot 12 = 72$ amu. With the added mass of a few hydrogen atoms at 1 amu each, 79 amu is a reasonable value. $\boxed{\text{yes}}$

A.5 a. The derivatives d[A) and dt have the same units as the parameters [A) and t,respectively. Both sides of the equation should therefore have units of $\mathrm{mol\,L^{-1}\,s^{-1}}$. That means that k needs to provide the units of $\mathrm{s^{-1}}$ and cancel one factor of concentration units on the righthand side. k has units of $\boxed{\mathrm{L\,s^{-1}\,mol^{-1}}.}$

b. The argument of the exponential function must be unitless, so k_B must cancel units of energy (J) in the numerator and temperature (K) in the denominator. The correct units are $\boxed{\mathrm{J\,K^{-1}}.}$

c. The units all cancel, and K_{eq} is $\boxed{\text{unitless.}}$

d. Squaring both sides of the equation, we can solve for k: $\mu\omega^2 = k$. k must therefore have units of $\boxed{\mathrm{kg\,s^{-2}}.}$

A.6 There are two factors on the lefthand side, $(2z+1)^2$, and e^{-ax^2}. For the product to be zero, at least one of these factors must be zero. If $(2z + 1) = 0$, then $\boxed{z = -\frac{1}{2}\ .}$ If $e^{-ax^2} = 0$, then $\boxed{z \to \pm\infty\ .}$

All three are valid solutions.

A.7 In general, for any complex number $(a + ib)$, the complex conjugate is $(a + b)^* = a - ib$. We look for the imaginary component and and invert its sign:

a. $z - iy : a = z \quad b = -y,\ \boxed{z + iy}.$

b. $iz^2y^2 : a = 0 \quad b = z^2y^2,\quad \boxed{-iz^2y^2\ .}$

c. $zy(z + iy + z) :\ a = z^2y + zyz \quad b = zy^2,\quad z^2y + zyz - izy^2,\quad \boxed{zy(z - iy + z).}$

d. $a = z/z \quad b = y/z,\quad \boxed{(z - iy)/z\ .}$

e.

$$
\begin{aligned}
e^{ix} &= 1 + iz - z^2 - iz^3 + z^4 + iz^5 - \\
\ldots a &= 1 - z^2 + z^4 - \ldots \\
b &= z - z^3 + z^5 - \ldots \\
a - ib &= 1 - iz - z^2 + iz^3 + z^4 - iz^5 - \ldots \boxed{= e^{-ix}}.
\end{aligned}
$$

f. 54.3: $a = 54.3 \quad b = 0,\ \boxed{54.3.}$

A.8 This problem tests a few algebraic operations involving vectors, particularly useful to know when we look at angular momentum and (often related) magnetic field effects.

a. The length of a vector is calculated using the Pythagorean theorem: $|\vec{C}| = \sqrt{0^2 + 2^2 + 1^2} = \boxed{\sqrt{5}\ .}$

b. We add vectors one coordinate at a time: $\vec{A} + \vec{B} = (1 + 1, 0 + 0, 0 + 1) = \boxed{(2,\ 0,\ 1).}$

c. The dot product of two vectors multiplies the values for each coordinate of the two vectors and sums the results: $\vec{A} \cdot \vec{B} = (1 \cdot 1) + (0 \cdot 0) + (0 \cdot 1) = \boxed{1.}$

d. In the case of perpendicular vectors, this gives us zero: $\vec{A} \cdot \vec{C} = (1 \cdot 0) + (0 \cdot 2) + (0 \cdot 1) = \boxed{0}.$

e. The cross product involves a little more work, and yields a new vector, perpendicular to the two original vectors: $\vec{A} \times \vec{B} = (0 \cdot 1 - 0 \cdot 0, 0 \cdot 1 - 1 \cdot 1, 1 \cdot 0 - 0 \cdot 1) = \boxed{(0, -1, 0)}.$

A.9 If we accept that the Taylor series expansion is exact if we take it to infinite order, then the Euler formula can be proven by the expansions of e^x (Eq. A.25), $\sin z$ (Eq. A.26), and $\cos z$ (Eq. A.27):

$$\begin{aligned}
e^{ix} &= \sum_{n=0}^{\infty} \frac{1}{n!}(iz)^n \\
&= 1 + iz - \frac{1}{2}z^2 - \frac{i}{6}z^3 + \frac{1}{24}z^4 + \frac{i}{120}z^5 - \ldots \\
&= \left(1 - \frac{1}{2}z^2 + \frac{1}{24}z^4 - \ldots\right) + i\left(z - \frac{1}{6}z^3 + \frac{1}{120}z^5 - \ldots\right) \\
&= \boxed{\cos z + i \sin z}.
\end{aligned}$$

This equation is of practical importance to us, and is famous among mathematicians for tying together three fundamental mathematical values—π, i, and e—in one equation:

$$e^{i\pi} = 1.$$

A.10

- **Maple**: After checking that all of the units are indeed consistent, enter the Maple command

```
solve((1.000-(3.716/V^2))(V-0.0408)/(0.083145298.15),V);
```

The resulting solution, 24.9, is in the same units as b, namely $\boxed{24.9\ \mathrm{L\ mol^{-1}}}.$

- **Successive approximation**: There are several ways to solve this, corresponding to different forms of the equation that leaves V_m on one side. One way to set up the equation quickly is to recognize that $(V_\mathrm{m} - b)$ will vary rapidly compared to $P - (a/V_\mathrm{m}^2)$, so we can isolate V_m as follows:

$$\begin{aligned}
\frac{\left(P - \frac{a}{V_\mathrm{m}^2}\right)(V_\mathrm{m} - b)}{RT} &= 1 \\
\left(P - \frac{a}{V_\mathrm{m}^2}\right)(V_\mathrm{m} - b) &= RT \\
V_\mathrm{m} - b &= \frac{RT}{\left(P - \frac{a}{V_\mathrm{m}^2}\right)}, \\
V_\mathrm{m} &= \frac{RT}{\left(P - \frac{a}{V_\mathrm{m}^2}\right)} + b.
\end{aligned}$$

Substituting in the values for P, a, b, R, and T (making sure that the units are all compatible), we can reduce the equation to the following:

$$V_{\mathrm{m}}(\mathrm{L\ mol^{-1}}) = \frac{24.243}{1 + \frac{3.716}{V_{\mathrm{m}}^2}} + 0.0409.$$

Guessing an initial value of 1 L mol^{-1} yields the following series of approximations:

$$V_\mathrm{m} = \frac{24.243}{1 + \frac{3.716}{1^2}} + 0.0409 = 5.330$$
$$V_\mathrm{m} = \frac{24.243}{1 + \frac{3.716}{5.330^2}} + 0.0409 = 22.022$$
$$V_\mathrm{m} = \frac{24.243}{1 + \frac{3.716}{22.099^2}} + 0.0409 = 24.726$$
$$V_\mathrm{m} = \frac{24.243}{1 + \frac{3.716}{24.796^2}} + 0.0409 = 24.934$$
$$V_\mathrm{m} = \frac{24.243}{1 + \frac{3.716}{24.834^2}} + 0.0409 = 24.935.$$

The series has converged to the three significant digits requested. The final value for V_m is $\boxed{24.9 \text{ L mol}^{-1}.}$

A.11 Here we apply the rules of differentiation summarized in Table A.3.

a.

$$f(z) = (z+1)^{1/2}$$
$$\frac{df}{dz} = \frac{1}{2}(z+1)^{-1/2}.$$

b.

$$f(z) = [z/(z+1))^{1/2}$$
$$\frac{df}{dz} = \frac{1}{2}\left(\frac{z}{z+1}\right)^{-1/2}\left[\frac{1}{z+1}\frac{dz}{dz} + z\frac{d}{dz}\left(\frac{1}{z+1}\right)\right]$$
$$= \frac{1}{2}\left(\frac{z}{z+1}\right)^{-1/2}\left[\frac{1}{z+1} - \frac{z}{(z+1)^2}\right].$$

c.

$$\frac{df}{dz} = \exp\left(z^{1/2}\right)\frac{d}{dz}\left(z^{1/2}\right)$$
$$= \frac{1}{2}z^{-1/2}\exp\left(z^{1/2}\right).$$

d.

$$\frac{df}{dz} = \exp\left(\cos z^2\right)\frac{d}{dz}(\cos z^2)$$
$$= \exp\left(\cos z^2\right)(-\sin z^2)\frac{d}{dz}(z^2)$$
$$= -2z \sin z^2 \exp\left(\cos z^2\right).$$

A.12 This problem tests our ability to use a few of the analytic integration results given in Table A.5.

a. $\int^{\infty} e^{-ax}dz = -{}^{1}e^{-ax}|^{\infty} = -{}^{1}(0-1) = {}^{1}$

$0 \qquad \bar{a} \quad 0 \quad \bar{a} \qquad \boxed{\bar{a}.}$

b. $\int_1^5 a^2 da = \frac{1}{3}a^3\Big|_1^5 = \frac{1}{3}(125 - 1) = \boxed{\frac{124}{3}.}$

c. $\int_1^5 a^{-3/2} da = -2a^{-1/2}\Big|_1^5 = \boxed{-2\left(\frac{1}{\sqrt{5}} - 1\right).}$

d. $r^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta = r^2\, (\phi)\Big|_0^{2\pi}\, (-\cos\theta)\Big|_0^{\pi} = r^2(2\pi - 0)[-(-1) - (-1)] = \boxed{4\pi r^2.}$

A.13 We use the Coulomb force law, Eq. A.41, using the charge of the electron $-e$ for both charges and r_{12} set to 1.00 Å:

$$\begin{aligned} F_{\text{Coulomb}} &= \frac{e^2}{4\pi\epsilon_0 r^2} \\ &= \frac{(1.602 \times 10^{-19}\,\text{C})^2}{(1.113 \times 10^{-10}\,\text{C}^2\,\text{J}^{-1}\,\text{m}^{-1})(1.00\,\text{Å})^2(10^{-10}\,\text{m}\,\text{Å}^{-1})^2} = \boxed{2.31 \times 10^{-8}\,\text{N}\,.} \end{aligned}$$

A.14 This problem relies on the definitions of the linear momentum p and the kinetic energy K (Eq. A.36):

$$p = mv$$

$$K = \tfrac{1}{2}mv^2 = \boxed{\frac{p^2}{2m}.}$$

A.15 We're calling the altitude r. Because the acceleration is downward but r increases in the upward direction, the acceleration is negative: $-2.80\,\text{m}\,\text{s}^{-2}$. We invoke the relationship between force and the potential energy, and find that we have to solve an integral:

$$U(r) = -\int_0^r F(r')\,dr' = -\int_0^r (-mg)\,dr' = \boxed{mgr.}$$

A.16

$$\begin{aligned} |F_{\text{Coulomb}}| &= \frac{e^2}{4\pi\epsilon_0 r^2} = \frac{(1.602 \times 10^{-19}\,\text{C})^2}{(1.113 \times 10^{-10}\,\text{C}^2\,\text{J}^{-1}\,\text{m}^{-1})(0.522\,\text{Å})^2(10^{-10}\,\text{m}\,\text{Å}^{-1})^2} \\ &= \boxed{8.23 \times 10^{-8}\,\text{N}} \\ |F_{\text{gravity}}| &= m_H g \\ &= (1.008\,\text{amu})(1.661 \times 10^{-27}\,\text{kg}\,\text{amu}^{-1})\ \ 2.80\,\text{m}\,\text{s}^{2} \\ &= \boxed{1.64 \times 10^{-26}\,\text{N}.} \end{aligned}$$

Sure enough, the gravitational force is smaller than the Coulomb force by orders of magnitude, and the motions of these particles will be dictated—as well as we can measure them —exclusively by the Coulomb force.

A.17 We are proving an equation that depends on L and a and t and v_x, which may look like too many variables. If we use the definition of L to put this equation in terms of K and U, then we can at least put K in terms of speed. Then, because speed itself is a function of position and time, the number of variables is quite manageable. Nonetheless, keeping things in terms of K and U is useful, because of their straightforward dependence on only v and a, respectively.

To prove the equation, we could try working from both sides and seeing if the results meet in the middle. First the lefthand side:

$$\frac{\partial L}{\partial a} = \underbrace{\frac{\partial K}{\partial a}}_{=0} - \frac{\partial U}{\partial a} \qquad K \text{ not a function of } a$$

$$= F_x = ma \qquad F_x = -dU/da$$

$$= m\frac{d^2a}{dt^2} \qquad \text{acceleration} = d^2a/dt^2$$

Next the righthand side:

$$\frac{d}{dt}\frac{\partial L}{\partial v_x} = \frac{d}{dt}\left[\frac{1}{2}m\frac{\partial v_x^2}{\partial v_x} - \frac{\partial U}{\partial v_x}\right]$$

$$= \frac{d}{dt}\left[mv_x - \underbrace{\frac{\partial U}{\partial v_x}}_{=0}\right] \qquad U \text{ not a function of } v_x$$

$$= m\frac{dv_x}{dt} = m\frac{d^2a}{dt^2}.$$

And there we are. One of the useful features of the Lagrangian is that the equation proved here can be made to hold for different choices of coordinates. This enables the mechanics problems to be written in coordinates that take advantage of symmetry (for example, if the only force is a radial one, attracting or repelling particles from a single point), and the Lagrangian then provides a starting point to develop relationships between the positions and velocities of the particles.

A.18 The overall energy before the collision is the sum of the two kinetic energies:

$$K = \tfrac{1}{2}m_1v_1^2 + \tfrac{1}{2}m_2v_2^2,$$

and this must equal the energy after the collision:

$$K = \tfrac{1}{2}m_1v_1'^2 + \tfrac{1}{2}m_2v_2'^2.$$

Similarly, we may set the expressions for the linear momentum before and after the collision equal to each other:

$$p = m_1v_1 + m_2v_2 = m_1v_1' + m_2v_2'.$$

So there are two equations and two unknowns. At this point, the problem is ready to solve with a symbolic math program.

Maple. The problem can be solved in a single step by asking Maple to solve the conservation of energy and conservation of momentum equations simultaneously to get the final speeds (here $vf[1]$ and $vf[2]$ in terms of the masses and initial speeds:

```
solve({m[1]*v[1]+m[2]*v[2] = m[1]*vf[1]+m[2]*vf[2], (1/2) * m[1] * v[1]^2+(1/2) * m[2] *
v[2]^2 = (1/2)* m[1] * vf[1]^2+(1/2) * m[2]*vf[2]^2}, [vf[1], vf[2]]);
```

On paper. This last equation lets us eliminate one variable by writing, for example, the final speed v_2' in terms of v_1':

$$v_2' = \frac{m_1v_1 + m_2v_2 - m_1v_1'}{m_2}.$$

Now we can put this value into the equation for K, and solve for v_1':

$$\begin{aligned} K &= \tfrac{1}{2}m_1v_1^2 + \tfrac{1}{2}m_2v_2^2 && (a)\\ &= \tfrac{1}{2}m_1v_1'^2 + \tfrac{1}{2}m_2v_2'^2 \\ &= \tfrac{1}{2}m_1v_1'^2 + \tfrac{1}{2}m_2\left(\frac{m_1v_1 + m_2v_2 - m_1v_1'}{m_2}\right)^2. \end{aligned}$$

This is going to be an equation that depends on $v_1'^2$ and v_1', so we can solve it using the quadratic formula. In that case, it's easiest to put all the quantities on one side of the equation:

$$\begin{aligned} 0 &= \tfrac{1}{2}m_1v_1'^2 + \tfrac{1}{2}m_2\left(\frac{m_1v_1 + m_2v_2 - m_1v_1'}{m_2}\right)^2 - \left(\tfrac{1}{2}m_1v_1^2 + \tfrac{1}{2}m_2v_2^2\right) && \text{subtract } (a) \text{ above}\\ &= \tfrac{1}{2}m_1v_1'^2 + \tfrac{1}{2}m_2\left(\frac{m_1^2v_1^2 + m_2^2v_2^2 + m_1^2v_1'^2 + 2m_1m_2v_1v_2 - 2m_1^2v_1v_1' - 2m_1m_2v_1'v_2}{m_2^2}\right) && \text{expand the square}\\ &\quad - \tfrac{1}{2}m_1v_1^2 - \tfrac{1}{2}m_2v_2^2 \\ &= m_1v_1'^2 + \frac{m_1^2}{m_2}v_1^2 + m_2v_2^2 + \frac{m_1^2}{m_2}v_1'^2 + 2m_1v_1v_2 && \text{divide by } 1/2\\ &\quad - 2\frac{m_1^2}{m_2}v_1v_1' - 2m_1v_1'v_2 - m_1v_1^2 - m_2v_2^2 \\ &= v_1'^2\left(m_1 + \frac{m_1^2}{m_2}\right) + v_1'\left(-2\frac{m_1^2}{m_2}v_1 - 2m_1v_2\right) && \text{group by power of } v_1'\\ &\quad + \left(\frac{m_1^2}{m_2}v_1^2 + m_2v_2^2 + 2m_1v_1v_2 - m_1v_1^2 - m_2v_2^2\right) \\ &= v_1'^2\left(m_1 + \frac{m_1^2}{m_2}\right) + v_1'\left(-2\frac{m_1^2}{m_2}v_1 - 2m_1v_2\right) \\ &\quad + \left(\left(\frac{m_1^2}{m_2} - m_1\right)v_1^2 + 2m_1v_1v_2\right) \end{aligned}$$

$$v_1' = \left(2m_1 + 2\frac{m_1^2}{m_2}\right)^{-1}\left(\left(2\frac{m_1^2}{m_2}v_1 + 2m_1v_2\right)\right. \qquad \text{quadratic formula}$$

$$\pm \left\{ \left(2\frac{m_1^2}{m_2}v_1 + 2m_1v_2\right)^2 - 4\left(m_1 + \frac{m_1^2}{m_2}\right)\left[\left(\frac{m_1^2}{m_2} - m_1\right)v_1^2 + 2m_1v_1v_2\right] \right\}.$$

To deal with this equation, we can expand the multiplication inside the square brackets:

$$\left(2\frac{m_1^2}{m_2}v_1 + 2m_1v_2\right)^2 = 4\frac{m_1^4}{m_2^2}v_1^2 + 8\frac{m_1^3}{m_2}v_1v_2 + 4m_1^2v_2^2$$

$$-4\left(m_1 + \frac{m_1^2}{m_2}\right)\left[\left(\frac{m_1^2}{m_2} - m_1\right)v_1^2 + 2m_1v_1v_2\right] = -4\frac{m_1^3}{m_2}v_1^2 - 4\frac{m_1^4}{m_2^2}v_1^2 + 4m_1^2v_1^2 + 4\frac{m_1^3}{m_2}v_1^2$$

$+ 4$

$$- 8m_1^2 v_1 v_2 - 8\frac{m_1^3}{m_2} v_1 v_2.$$

Nearly all of these terms cancel when we add these two expressions together, leaving:

$$4m_1^2 v_2^2 + 4m_1^2 v_1^2 - 8m_1^2 v_1 v_2.$$

In the quadratic equation, we have to take the square root of this, but that turns out to be easy:

$$\begin{aligned}\left(4m_1^2 v_2^2 + 4m_1^2 v_1^2 - 8m_1^2 v_1 v_2\right)^{1/2} &= 2m_1 \left(v_2^2 + v_1^2 - 2v_1 v_2\right)^{1/2} \\ &= 2m_1 \left(v_2 - v_1\right).\end{aligned}$$

Finally, putting this back into our equation for v_1'', we get

$$\begin{aligned} v_1'' &= \left(2m_1 + 2\frac{m_1^2}{m_2}\right)^{-1} \left(\left(2\frac{m_1^2}{m_2} v_1 + 2m_1 v_2\right) \pm 2m_1 \left(v_2 - v_1\right)\right) \\ &= \left(1 + \frac{m_1}{m_2}\right)^{-1} \left(\left(\frac{m_1}{m_2} v_1 + v_2\right) \pm \left(v_2 - v_1\right)\right). && \text{divide out } 2m_1 \end{aligned}$$

This is correct as far as it goes, but we have two solutions, corresponding to either the + or − sign. If we use the − sign, then we get

$$v_1'' = \left(1 + \frac{m_1}{m_2}\right)^{-1} \left(\frac{m_1}{m_2} v_1 + v_2 - v_2 + v_1\right) = v_1.$$

This is the solution if the collision *doesn't* occur; particle 1 just keeps moving at the same speed as before. The + sign gives us the correct solution:

$$\begin{aligned} v_1'' &= \left(1 + \frac{m_1}{m_2}\right)^{-1} \left(\frac{m_1}{m_2} v_1 + v_2 + v_2 - v_1\right) \\ &= \left(1 + \frac{m_1}{m_2}\right)^{-1} \left[\left(\frac{m_1}{m_2} - 1\right) v_1 + 2v_2\right]. \\ &= \frac{1}{m_1 + m_2} \left[\left(m_1 - m_2\right) v_1 + 2m_2 v_2\right]. \end{aligned}$$

We can now use the conservation of momentum to solve for v_2''. I'm going to factor out a $1/(m_1 + m_2)$ to get an equation similar to the one for v_1'':

$$\begin{aligned} v_2'' &= \frac{m_1 v_1 + m_2 v_2 - m_1 v_1''}{m_2} \\ &= \frac{1}{m_2} \left(m_1 v_1 + m_2 v_2 - \frac{m_1}{m_1 + m_2} \left[\left(m_1 - m_2\right) v_1 + 2m_2 v_2\right]\right) \end{aligned}$$

$$= \left(\frac{m_1}{}\right) v_1 + v_2 - \left(\frac{m_1 - m_2}{}\right)\left(\frac{m_1}{}\right)$$

$v_1 - 2$ $\left(\frac{m_1}{m_1 + m_2} \right) v_2$ $\frac{m_2}{m_1 + m_2}$ m_2 $\overline{}$ $m_1 + m_2$

$$= \left(\frac{1}{m_1 + m_2}\right)\left[\frac{m_1(m_1 + m_2)}{m_2} v_1 + (m_1 + m_2)v_2 - \left(\frac{m_1(m_1 - m_2)}{m_2}\right) v_1 - 2m_1 v_2\right]$$

$$= \frac{1}{m_1 + m_2}\left[(m_2 - m_1)\, v_2 + 2m_1 v_1\right].$$

Because there is nothing in the problem that determines which particle is labeled 1 and which is labeled 2, the equations for v_1'' and v_2'' must be exactly the same, with all the labels 1 and 2 switched.

If you haven't seen this result or simply don't remember it, it's worthwhile to check a few values. For example, if the two particles have equal mass ($m_1 = m_2$), then the final speeds are $v''_1 = v_2$ and $v''_2 = v_1$; *i.e.*, the particles simply exchange speeds. Another example: if particle 1 is initially at rest ($v_1 = 0$), then it picks up a speed $2m_2v_2/(m_1 + m_2)$ from the collision. In that case, if particle 2 dominates the mass ($m_2 \gg m_1$), then particle 1 will find itself with a final speed equal to $2v_2$. In contrast, if particle 1 is much more massive than 2, then the collision will hardly affect it ($v_1'' \approx 0$) and particle 2 will simply reverse direction ($v_1'' \approx -v_2$).

Note that the two particles don't have to be moving in opposite directions. If particle 1 is behind 2 but moving faster and in the same direction, then they will strike each other, and particle 2 will acquire particle 1's higher speed.

A.19

$$K = U = -\frac{e^2}{4\pi\varepsilon_0 r} = \frac{(1.602 \times 10^{-19}\,\mathrm{C})^2}{(1.113 \times 10^{-10}\,\mathrm{C^2\,J^{-1}\,m^{-1}})(1.0\,\mathrm{Å})(10^{-10}\,\mathrm{m\,Å^{-1}})} = 2.31 \times 10^{-18}\,\mathrm{J}$$

$$L = |\vec{r} \times \vec{p}| = rp, \text{ since } \vec{r} \perp p.$$

$$p = \sqrt{2m_eK} = \left[2(2.102 \times 10^{-31}\,\mathrm{kg}) \times (2.31 \times 10^{-18}\,\mathrm{J})\right]^{1/2} = 2.05 \times 10^{-24}\,\mathrm{kg\,m\,s^{-1}}$$

$$L = (1.0\,\mathrm{Å})(10^{-10}\,\mathrm{m\,Å^{-1}})(2.05 \times 10^{-24}\,\mathrm{kg\,m\,s^{-1}}) = \boxed{2.05 \times 10^{-34}\,\mathrm{kg\,m^2\,s^{-1}}\,.}$$

A.20 a. *Find the center of mass positions $\vec{r}_i^{(0)}$ at collision.* Let's call the center of mass of the entire system the origin. The particles have equal mass, so the origin will always lie exactly in between the two particles. At the time of the collision, we may draw a right triangle for each particle, connecting the particle's center of mass, the origin, and with the right angle resting on the z axis. The hypotenuse of the triangle connects the center of mass to the point of contact between the two particles, and must be of length $d/2$ (the radius of the particle). The other two sides are of length $(d/2)\cos\theta$ (along the z axis) and $(d/2)\sin\theta$ (along the a axis), based on the definitions of the sine and cosine functions in Eqs. A.5. These correspond to the magnitudes of the z and a coordinates, respectively, of the particle centers of mass at the collision. The signs of the values may be determined by inspection of the figure: at the time of the collision, a_1 and z_2 are positive while a_2 and z_1 are negative, so the position vectors are:

$$\vec{r}_1^{(0)} = ((d/2)\sin\theta, 0, -(d/2)\cos\theta)$$

$$\vec{r}_2^{(0)} = (-(d/2)\sin\theta, 0, (d/2)\cos\theta)\,.$$

b. *Find the velocities $\vec{v}_i''$ after collision.* Simple collisions obey a simple reflection law: the angle of incidence is equal to the angle of reflection. These are the angles between the velocity vectors and the normal vector—the line at angle θ from the z axis. (This is the normal vector because it lies perpendicular to the plane that lies between the two spheres at the point of collision; this plane is effectively the surface of reflection for the collision.) Therefore, the velocity vector after the collision is at an angle 2θ from the z axis, and the velocity vectors after the collision are

$$\vec{v}_1'' = v_0(\sin 2\theta, 0, -\cos 2\theta)$$

$$\vec{v}_2'' = v_0(-\sin 2\theta, 0, \cos 2\theta).$$

Notice that the speed after the collision is still v_0 for each particle. Because they each began with the same magnitude of linear momentum, the momentum transfer that takes place only affects the trajectories.

c. *Show that $\bar{L}$ is conserved before and after the collision.* We now have position and velocity vectors before and after the collision:

$$\bar{r}_1 = ((d/2)\sin 6, 0, -(d/2)\cos 6) + \bar{v}_1 t \qquad \bar{r}_2 = (-(d/2)\sin 6, 0, (d/2)\cos 6) + \bar{v}_1 t$$
$$\bar{v}_1^{nn} = v_0(0,\ 0,\ 1) \qquad \bar{v}_2^{nn} = v_0(0,\ 0,\ -1)$$
$$\bar{v}_1^{n} = v_0(\sin\ 26, 0, -\cos\ 26) \qquad {}_2\ \bar{v}^{n} = v_0(-\sin 26, 0, \cos 26).$$

We take the cross products of these for each particle to get $\bar{L}$ for each particle, and we add these together to get the total angular momentum for the system. Before the collision,

$$\bar{r}_1^{nn} = ((d/2)\sin 6, 0, -(d/2)\cos 6) + v_0 t(0, 0, 1)$$
$$\bar{L}_1^{nn} = m\bar{r}_1^{nn} \times \bar{v}_1^{nn}$$
$$= m\left(y_1^{nn}v_{z1}^{nn} - z_1^{nn}v_{y1}, z_1^{nn}v_{x1}^{nn} - a_1^{nn}v_{z1}, a_1^{nn}v_{y1}^{nn} - y_1^{nn}v_{x1}\right)$$
$$= m\ (0, -(dv_0/2)\sin 6, 0)$$

and similarly for $\bar{L}_2^{nn}$:

$$\bar{L}_2^{nn} = m\ (0, -(dv_0/2)\sin 6, 0)$$

and combining these yields:

$$\bar{L}^{nn} = \bar{L}_1^{nn} + \bar{L}_2^{nn} = -mdv_0\ (0, \sin 6, 0).$$

All of the position or velocity vectors have only zero y components, and therefore only the y component of the cross product survives. After the collision,

$$\bar{r}^{n}_1 = ((d/2)\sin 6, 0, -(d/2)\cos 6) + v_0 t(\sin 26, 0, -\cos 26)$$
$$\bar{L}_1^{n} = m\bar{r}_1^{n} \times \bar{v}_1^{n}$$

which has a y component

$$\bar{L}^{n}_{y1} = m\ \{-(d/2)\cos 6 \sin 26 - v_0 t\cos 26 \sin 26 - [(d/2)\sin 6(-\cos 26) + v_0 t\sin 26(-\cos 26)]\}$$

and similarly for $\bar{L}^{n}_{y2}$:

$$\bar{L}^{n}_{y1} = m\ \{(d/2)\cos 6(-\sin 26) + v_0 t\cos 26(-\sin 26) - [-(d/2)\sin 6\cos 26 - (-v_0 t\sin 26)\cos 26]\}.$$

Adding the two components together we find that all the t-dependent terms cancel, and trigonometric identities from Table A.2 simplify the rest:

$$\bar{L}^{n}_y = \bar{L}^{n}_{1y} + \bar{L}^{n}_{2y}$$
$$= \frac{mdv_0}{2}[-2\cos 6\sin 26 + 2\sin 6\cos 26]$$
$$\sin 26 = 2\ \sin 6\cos 6$$
$$\cos 26 = 2\ \cos^2 6 - 1$$
$$\bar{L}^{n}_y = \frac{2mdv_0}{2}\left(-\cos\ 6(2\sin 6\cos 6) + \sin 6\left(2\cos^2 6 - 1\right)\right)$$

$$= \, mdv_0{}' -2\cos^2 6 \sin 6 \; + \; 2\cos^2 6 \sin 6 \; - \; \sin 6'$$

$$= -mdv_0 \sin 6.$$

This is the y component of $\vec{L}^{n}$, and the a and z components are again zero in the cross products, so we have shown that both $\vec{L}^{n}$ and $\vec{L}^{nn}$ are equal to

$$\vec{L} = mdv_0(0, \sin 6, 0).$$

If the particles hit head-on, then $6 = 0$ and the angular momentum is zero. As 6 increases, L increases to a maximum value of mdv_0 when the two particles just barely touch each other in passing.

If we had used the conservation of L at the outset, we could have found this solution quickly. Because the angular momentum does not depend on the size of the particles, we can replace our two objects here with point masses. It won't matter that they now won't collide, because if L is conserved we have to get the same answer before the collision takes place anyway. In fact, because L is conserved, we can pick any point in time that's convenient for us to calculate L, so I would pick the time when the two particles reach $z = 0$. At this time, both particles are traveling on trajectories that are exactly perpendicular to their position vectors ($\vec{v}_i$ is perpendicular to $\vec{r}_i$). This makes the cross product for each particle easy to evaluate:

$$\vec{L}_i = m\vec{r}_i \times \vec{v}_i = m(\pm(d/2)\sin 6, 0, 0) \times (0, 0, \pm v_0) = mdv_0/2(0, \sin 6, 0),$$

where the minus sign applies to particle 2. There are two particles, so we multiply this vector by two, arriving at the same $\vec{L}$ as above.

A.21 a. *Write* $\vec{E}_1$ *in vector form.* The magnitude of the electric field generated by particle 1 is given by $F = q_2E_1$, and this force must be equal to the Coulomb force $F = -q_1q_2/(4ne_0r^2)$. The force vector points along the axis separating the two particles, and we can include this direction-dependence by multiplying the magnitude of the vector by $\vec{r}/r$. The Cartesian form of the vector $\vec{r}$ from particle 1 to 2, just working off part (b) of the figure, may be written $(rv_1/c, y_2, 0)$ and has length

$$r = \left[\left(\frac{rv_1}{c}\right)^2 + y_2^2\right]^{1/2}.$$

Therefore, the force vector is

$$\vec{F} = \left(\frac{q_1q_2}{4ne_0r^2}\right)\frac{\vec{r}}{r} = \frac{q_1q_2}{4ne_0r^3}(rv_1/c, y_2, 0)$$

and the electric field vector is

$$\vec{E}_1 = \frac{\vec{F}}{q_2} = \frac{q_1}{4ne_0r^3}(rv_1/c, y_2, 0).$$

b. *Write* $\vec{B}$ *in vector form.* Here we just have to be careful to correctly evaluate the cross product. We are using the equation $\vec{B} = \frac{1}{c^2}\vec{E}_1 \times \vec{v}_1$, and we have an equation for $\vec{E}_2$ already. The velocity vector consists only of an a-velocity component: $\vec{v}_1 = (v_1, 0, 0)$. Notice that because these two vectors lie in the ay plane, their cross product—which is perpendicular to both vectors —will lie along the z axis. The z component of the cross product $\vec{a} \times \vec{b}$ is equal to $a_xb_y - a_yb_x$, so we have

$$\vec{B} = \frac{1}{c^2}\vec{E}_1 \times \vec{v}_1 = \frac{q_1}{4ne_0c^2r^3}(0, 0, v_1y_2).$$

c. *Find the magnetic force vector*. Again, we take a cross product with the velocity. This time, the $\vec{B}$ vector lies along z, and $\vec{v}_1$ lies along a, so the cross product lies along y:

$$\vec{F}_{\text{mag}} = q_2\vec{v}_1 \times \vec{B} = \frac{q_1 q_2}{4ne_0 c^2 r^3}\,(0, v_1^2 y_2, 0)\ .$$

d. *Calculate the difference between the actual and classical values of the Coulomb force.* To compute the actual Coulomb force, we use the distance r, so $\vec{F}$ has a magnitude

$$F = \frac{q_1q_2}{4ne_0r^2}.$$

The classical Coulomb force would be

$$F' = \frac{q_1q_2}{4ne_0y_2^2},$$

and the difference between the two forces is

$$F - F' = \frac{q_1q_2}{4ne_0}\left(\frac{1}{r^2} - \frac{1}{y_2^2}\right).$$

We can simplify this by relating r^2 and y^2:

$$r^2 = \left(\frac{rv_1}{c}\right)^2 + y_2^2$$

$$r^2 = y_2^2\left(1 - \left(\frac{v_1}{c}\right)^2\right)^{-1}.$$

So, finally, we have

$$F - F' = \frac{q_1q_2}{4ne_0}\left(\frac{1}{y^2}\left(1 - \left(\frac{v_1}{c}\right)^2\right) - \frac{1}{y_2^2}\right)$$

$$= \frac{q_1q_2}{4ne_0y_2^2}\left(-\left(\frac{v_1}{c}\right)^2\right) = -\frac{q_1q_2v_1^2}{4ne_0c^2y_2^2}.$$

In comparison, the magnitude of the magnetic force we calculated from the standard equations is

$$F_{\text{mag}} = q_1q_2v_1^2y_2/(4ne_0c^2r^3),$$

and for $v \ll c$, we can allow $r \approx y_2$, so that

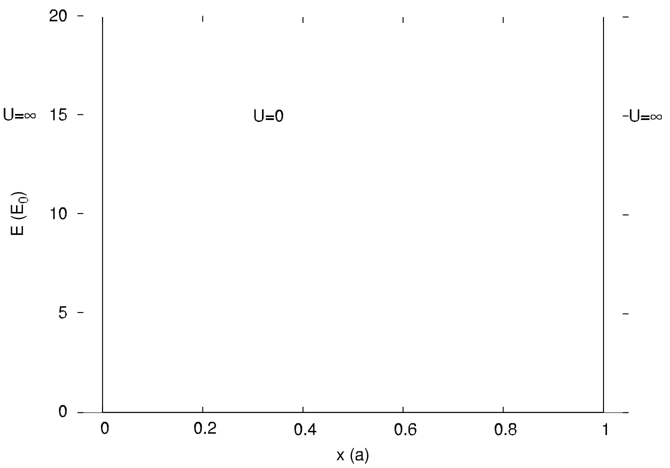
$$F_{\text{mag}} = q_1q_2v^2 \quad {}_0 \quad {}_2).$$

Magnetic forces are a natural result of the motion of electrical charge when special relativity is taken into account. It was this relationship between electric and magnetic forces that was the basis of Einstein's original paper on special relativity.

Chapter 1

1.1 Briefly, the nucleus of any atom except hydrogen has multiple protons, which repel each other, coexisting at very small distances. With only protons and neutrons present, there is no negative charge to counter the proton-proton repulsion, and the gravitational attraction between nuclear particles is much too weak to play a role in holding the nucleus together. If our theories of mass and charge do not explain the binding of positively charged protons into a nucleus, that suggests that there is some other property that explains it. This reasoning led to the concepts of quark *color* and the strong force.

1.2



The potential energy climbs to infinity at the walls and is zero in between. We know this because the walls are impenetrable—the particles always bounce off the wall and transfer no energy into the wall. In this idealized limit, no amount of energy in the particle will get it to occupy the region of the wall, so the potential energy of the wall (the energy it would take to occupy that location) must be infinite. At the wall, the slope of the potential energy is also infinite, so the force $F = dU/da$ is infinite, but pushing back in the negative a direction, so $\boxed{F(a/a) = -\infty.}$ Within the container, there are no forces working on the particles, so F and $U = dF/da$ are both equal to zero.

1.3 One approach would be the following:

1. Invent the scale as described in the chapter, using a spring to find forces by measuring the displacement of the spring with our ruler.

2. Find the acceleration due to gravity g by measuring changes in speed of falling objects, using the ruler and clock to compare $\Delta(\text{distance})/\Delta(\text{time})$ at different times. Once g is known, we can convert the weight of a water sample to a mass.

3. Finally, measure the volume of a sample of water with the ruler and a rectangular container for the water.

The ratio of the mass to the volume will be the density.

1.4 We will need to figure out how the pressure at the bottom of the column varies with the mass of water above it, and convert the mass to height. This problem can be started from either end, but let's start from how the mass determines the pressure:

$$P = \frac{F}{A} = \frac{Mg}{A},$$

where F is the force exerted at the base of the column, M is the mass of the water in the column, and $g = 2.8\,\mathrm{m\,s^{-2}}$ is the acceleration due to gravity near the Earth's surface. The mass is related to the height through the density. The volume of the water is equal to the area A times the height z (which is what we wish to solve), and the mass within a volume V is equal to the volume times the mass density

$\rho_m = 1.00\,\mathrm{g\,cm^{-3}} = 1.00\,1\,10^{3}\,\mathrm{kg\,m^{-3}}$. So we can set $P = 1.00\,\mathrm{bar} = 1.00\,1\,10^{5}\,\mathrm{Pa}$ and solve for z:

$$P = \frac{Mg}{A} = \frac{\rho_m V g}{A} = \frac{\rho_m (Az) g}{A} = \rho_m g z$$

$$z = \frac{P}{\rho_m g} = \frac{\overset{1}{\overline{}}\;1.00\quad 10^{5}\,\mathrm{Pa}}{(1.00\,1\,10^{3}\,\mathrm{kg\,m^{-3}})(2.8\,\mathrm{m\,s^{-2}})}$$

$$= \boxed{10.\,\mathrm{m.}}$$

1.5 Pressure is related to force through Eq. 1.4, and here we need to solve for the force:

$$F = PA$$

$$= (0.010\,\mathrm{bar})(10^{5}\,\mathrm{Pa\,bar^{-1}})(78 \times 30)(2.54\,\mathrm{cm})^{2}(10^{-2}\,\mathrm{m/cm})^{2} = \boxed{1.5\,1\,10^{3}\,\mathrm{N.}}$$

This force is equivalent to lifting a weight of

$$\frac{F}{g} = \frac{1.5\,1\,10^{3}\,\mathrm{N}}{2.81\,\mathrm{m\,s^{-2}}} = 150\,\mathrm{kg.}$$

1.6 The area of the water drop is

$$A_{\mathrm{water}} = n(d/2)^{2} = 0.785\,\mathrm{cm^{2}} = 7.85\,1\,10^{-5}\,\mathrm{m^{2}}.$$

The approximate number of molecules that can fit in this area is given by the ratio of this area to the effective area of a single molecule:

$$N \approx \frac{A_{\mathrm{water}}}{A_{\mathrm{butanol}}} = \frac{7.85\,1\,10^{-5}\,\mathrm{m^{2}}}{(33\,\mathrm{\mathring{A}}^{2})(10^{-10}\,\mathrm{m\,\mathring{A}^{-1}})^{2}} = 2.38\,1\,10^{14}$$

We use Avogadro's number to convert this value to the number of moles:

$$n = \frac{N}{N_A} = \boxed{3.2\,1\,10^{-10}\,\mathrm{mol.}}$$

1.7 The force is given by the Coulomb force, Eq. A.41:

$$F_{\mathrm{Coulomb}} = \frac{q_1 q_2}{4ne_0\,r_{12}^{2}} = \frac{(1.602\,1\,10^{-19}\,\mathrm{C})^{2}}{1.113\,1\,10^{-10}\,\mathrm{C^{2}\,J^{-1}\,m^{-1}}(2.81\,\mathrm{A})^{2}(10^{-10}\,\mathrm{m\,\mathring{A}^{-1}})^{2}} = 2.22\,1\,10^{-9}\,\mathrm{N},$$

which may not look like much. But then to get the pressure we divide by a tiny area to get the effective pressure:

$$P = \frac{F}{A} = \frac{2.22\,1\,10^{-9}\,\mathrm{N}}{(4.00\ {}^{2})(10^{-10}\,\mathrm{m\,\mathring{A}^{-1}})^{2}} = 7.30\,1\,10^{10}\,\mathrm{Pa} = \boxed{7.30\,1\,10^{5}\,\mathrm{bar.}}$$

1.8 Since the overall entropy change must be positive, if the entropy of the system (the engine) is $-0.20\,\mathrm{J\,K^{-1}}$, then the entropy of the surroundings must rise to compensate by an amount

$$\boxed{\Delta S_{\mathrm{surr}} \geq +0.20\,\mathrm{J\,K^{-1}.}}$$

1.9 There are two contributions to the work. Which do you think is greater? Although 100 kg should sound like a significant mass, the force generated by 1 bar of pressure over an area as large as 1 square meter is much higher than you might think at first. A rough calculation will tell you: the force generated by 1000 kg in the roughly 10 m s^{-2} acceleration of gravity is approximately $(10^3 \text{ kg})(10 \text{ m s}^{-2}) = 10^4$ N. But the force generated by 10^5 Pa across 1 m^2 is 10^5 N, so air pressure in this case is a much larger contributor to the work that needs to be done.

The pressure is constant throughout this process, so q is given by ΔH:

$$q = \Delta H = \boxed{2.22\,\text{kJ.}}$$

The work is the sum of two terms: the work required to lift the mass of the platform against the pull of gravity, and the work required to push an area of $1.00\,\text{m}^2$ against the additional 1.00 bar of ambient air pressure. These contributions are both negative because they require the system to do work on the surroundings:

$$\begin{aligned}
w &= -\int_{z_1}^{z_2} (mg + PA)\; dz \\
&= -(mg + PA)\; \Delta z \\
&= -\left[(1.00 \times 10^3\,\text{kg})(2.8\,\text{m s}^{-2}) + (1.00 \times 10^5\,\text{Pa})(1.00\;\text{m}^2)\right](0.060\,\text{m}) \\
&= -6588\,\text{J} = \boxed{-6.6\,\text{kJ.}}
\end{aligned}$$

And according to the first law, the change in energy is the sum of these two contributions:

$$\Delta E = q + w = 2.22\,\text{kJ} - 6.6\,\text{kJ} = \boxed{-3.7\,\text{kJ.}}$$

1.10 The value $4.5\,\text{J K}^{-1}$ is equal to $đq_{\text{surr}}/dT$, the rate of heat loss per temperature increment. Setting $đq_{\text{surr}} = (4.5\,\text{J K}^{-1})dT$, we substitute this into Clausius' definition of the entropy change, Eq. 1.10, to find

$$\begin{aligned}
\Delta S_{\text{surr}} &= \int_{T_1}^{T_2} \frac{đq_{\text{surr}}}{dT} \\
&= \int_{298\text{ K}}^{323\text{ K}} (4.5\,\text{J K}^{-1})\frac{dT}{T} \qquad = (4.5\,\text{J K}^{-1}) \ln \frac{323\,\text{K}}{228\,\text{K}} = \boxed{0.36\,\text{J K}^{-1}.}
\end{aligned}$$

1.11 We want the probability distribution for speed, $P_v(v)$, integrated only between the limits given.

$$\int_{10^2}^{10^3} P_v(v)\, dv = 4\pi \left(\frac{m}{2\pi k_{\text{B}}T}\right)^{3/2} \int_{10^2}^{10^3} v^2 e^{-mv^2/(2k_{\text{B}}T)}\, dv.$$

Plugging in the mass, temperature, and k_{B}, we find that

$$\frac{m}{2k_{\text{B}}T} = \frac{(4.00\text{ amu})(1.661 \times 10^{-27}\,\text{kg amu}^{-1})}{2(1.381 \times 10^{-23}\,\text{J K}^{-1})(228\,\text{K})} = 8.07 \times 10^{-7}\,\text{s}^2\,\text{m}^{-2}.$$

So the final expression can be written

$$(1.64 \times 10^{-9}) \int_{10^2}^{10^3} v^2\; \exp(-8.07 \times 10^{-7} v^2)\, dv.$$

1.12 We can expand the product $(v - \langle v\rangle)^3$, and organize the results into factors of $\langle v\rangle$, $\langle v^2\rangle$, and $\langle v^3\rangle$. The expression for $\langle v^2\rangle$ is already obtained in Eq. 1.23, and the others we can evaluate using the integrals over $a^{2n+1}c^{-ax^2}$ in Table A.5:

$$\mu_3 = \int_0^\infty P_v(v)(v-(v))^3\,dv$$
$$= \int_0^\infty P_v(v)v^3\,dv - 3\int_0^\infty P_v(v)v^2\,(v)\,dv + 3\int_0^\infty P_v(v)v\,(v)^2\,dv - \int_0^\infty P_v(v)\,(v)^3\,dv$$
$$= \langle v^3\rangle - 3\langle v^2\rangle\,(v) + 3\,(v)\,(v)^2 - (v)^3$$
$$= \langle v^3\rangle - 3\langle v^2\rangle\,(v) + 2\,(v)^3$$

$$P_v(v) = Av^2c^{-av^2} \qquad A = 4n\left(\frac{m}{2nk_BT}\right)^{3/2} \qquad a = \frac{m}{2k_BT}$$

$$(v) = A\int_0^\infty v^3\,c^{-av^2}\,dv = \frac{A}{2a^2} = \left(\frac{8k_BT}{nm}\right)^{1/2}$$

$$\langle v^2\rangle = \frac{3k_BT}{m}$$
$$\langle v^3\rangle = A\int_0^\infty v^5\,c^{-av^2}\,dv = \frac{2A}{2a^3} = \frac{n}{2}\left(\frac{8k_BT}{nm}\right)^{3/2}$$

$$\mu_3 = \frac{n}{2}\left(\frac{8k_BT}{nm}\right)^{3/2} - 3\left(\frac{3k_BT}{m}\right)\left(\frac{8k_BT}{nm}\right)^{1/2} + 2\left(\frac{8k_BT}{nm}\right)^{3/2}$$
$$= \left(\frac{8k_BT}{nm}\right)^{3/2}\left(\frac{n}{2} - \frac{2n}{8} + 2\right)$$
$$= \left(\frac{8k_BT}{nm}\right)^{3/2}\left(2 - \frac{5n}{8}\right).$$

Maple. The integral for μ_3 can be solved in a few steps using Maple, using the following commands:

1. `Pv:=v->4*Pi*(abs(m/kT)/(2*Pi))^(3/2)*v^2*exp(-abs(m/kT)*v^2/2);`
2. `avgv:=integrate(Pv(v)*v,v=0..infinity);`
3. `int(Pv(v)*(v-avgv)^3, v = 0 .. infinity);`

Note the use of abs for m/kT. That's because Maple needs to know that the coefficient (m/kT) in the exponential is positive in order to arrive at the correct analytical solution. The general solution, which allows for the argument of the exponential to be positive or negative, employs the error function (appearing in Maple as erf), which is not especially helpful.

1.13 The integral is

$$\int_0^{10\text{ m/s}} P_v(v)dv = 4n\left(\frac{m}{2nk_BT}\right)^{3/2}\int_0^{10\text{ m/s}} v^2c^{-mv^2/(2k_BT)}\,dv$$

The approximation we can use is that $c^x \approx 1 + a$ when a is small:

$$\int_0^{10\text{ m/s}} \quad 4n \quad v_1 \quad 2 \left(\quad v^2 \right)$$

$$_0 \quad P_v(v)dv \approx \frac{}{(Cn)^{3/2}} \quad _0 \quad v \quad 1 - \frac{}{C} \quad dv$$

$$= \sqrt{\frac{4}{nC^{3/2}}} \left(\frac{v_1^3}{3} - \frac{v_1^5}{5C} \right),$$

where $C = 1.77 \times 10^5\,\mathrm{m^2/s^2}$ and $v_1 = 10.0\,\mathrm{m/s}$. Substituting these numbers in yields a fraction of $\boxed{1.01 \times 10^{-5}.}$

Maple. The integral can be solved numerically in Maple with the command

```
int(4*Pi*v^2*exp(-v^2/(0.177e6))/(0.177e6*Pi)^(3/2), v = 0 .. 10);
```

Chapter 2

2.1 This is just a qualitative test of our understanding of the canonical distribution. The fractional probability must always be a number between 0 and 1. Any vibrational state $v = 0, 1, \ldots$ may be populated, but the probability is significant only if the vibrational energy is not large compared to the thermal energy k_BT. In this example, we are looking for the probability of the molecule being at the ($v = 1$) energy of one vibrational constant, 200 cm^{-1}, which corresponds to roughly 300 K, so we should expect that a significant fraction of the molecules may be able to get to this level. Therefore, the only reasonable answer is $\boxed{\text{(c) } 0.24.}$

2.2 This is applying our approximation that the two-particle degeneracy g_2 is roughly g_1^2. We start from the one-particle degeneracy in the three-dimensional box, but use ε equal to one-half the total energy:

$$\begin{aligned}
g_1(\varepsilon) &= \frac{32nV(2m^3\varepsilon)^{1/2}d\varepsilon}{h^3} \\
&= \frac{32n(1.00 \times 10^{-9}\,\text{m}^3)[2(32.2\,\text{amu})^3(1.661 \times 10^{-27}\,\text{kg amu}^{-1})^3(1.00 \times 10^{-20}\,\text{J})]^{1/2}(2.5 \times 10^{-26}\,\text{J})}{(6.626 \times 10^{-34}\,\text{J s})^3} \\
&= 2.08 \times 10^{19} \\
g_2 \approx g_1^2 &= \boxed{4.35 \times 10^{38}}
\end{aligned}$$

2.3 For non-interacting particles, the total degeneracy is the product of the component degeneracies.

$$\begin{aligned}
g_{A+B} &= g_A g_B \\
&= \left(V^{N_A} f(E_A, N_A)\right)\left(V^{N_B} f(E_B, N_B)\right) \\
&= V^{N_A+N_B} f(E_A + E_B,\ N_A + N_B)
\end{aligned}$$

2.4 [Thinking Ahead: Imagine that the container is a balloon filled with air—what would happen when the balloon encountered this state? There would suddenly appear a 10 cm^3 region of vacuum inside the balloon, and you would see dimples on the surface as the walls of the balloon contracted. As you might guess, that state is not likely to come along anytime soon.] The number of states at some fixed energy is the degeneracy, which for particles in a box obeys the relation

$$g(E) = V^N f(E, N).$$

For our case, $N = 0.05\,N_A = 3.01 \times 10^{22}$. If we count all the states for which $V_1 = 0.22\,V$, we find

$$\frac{g(E,\ V_1)}{g(E,\ V)} = \left(\frac{(0.22\ V)^N f(E,N)}{V^N f(E,N)}\right)$$

$$= (0.22)^N = \boxed{0.22^{3.01\cdot 10^{22}}} \approx 0.$$

In fact, such a state is unlikely to be detected in the box at any instant over the present age of the universe.

2.5 [Thinking Ahead: Should this function increase or decrease with the value of n^2? Because the thermal energy is proportional to temperature, we can safely expect it to increase as the n^2 (and therefore the energy) increases.] We need to solve the derivative in Eq. 2.24:

$$T = \left(\frac{\partial E}{\ }\right),$$

$\partial S \quad {}_{V,N}$