

Physical Chemistry
Thermodynamics, Statistical Mechanics, and Kinetics

Solutions Manual

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Objectives Review Questions

Chapter 1

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

1.2 We're taking the square root of the average momentum. The Maxwell-Boltzmann distribution $\mathcal{P}_v(v)$ 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 $\mathcal{P}_v(v)p$ over all possible values of v , from zero to infinity. And finally, remember to take the square root to get the rms: $\left[\int_0^\infty \mathcal{P}_v(v)(mv)^2 dv \right]^{1/2}$, with $\mathcal{P}_v(v)$ 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

$$S_{\text{Boltzmann}} = k_B \ln \Omega = (1.381 \cdot 10^{-23} \text{ J K}^{-1}) \ln(7776) = 1.30 \cdot 10^{-22} \text{ J K}^{-1}.$$

For the Gibbs energy, we set the probability $\mathcal{P}(i)$ 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:

$$\begin{aligned} S &= -Nk_B \sum_{i=1}^k \mathcal{P}(i) \ln \mathcal{P}(i) && \text{Eq. 2.16} \\ &= -5k_B(6) \frac{1}{6} \ln \frac{1}{6} && k = 6, N = 5 \\ &= 1.24 \cdot 10^{-22} \text{ J K}^{-1}. \end{aligned}$$

The expression has a factor of 5 from $N = 5$ and a factor of 6 because we add the term $\mathcal{P}(i) \ln \mathcal{P}(i)$ $k = 6$ 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 ϵ (which here means the lowest values of the quantum number n), until additional terms do not contribute significantly:

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

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

$$\begin{aligned}\mathcal{P}(\varepsilon) &= \frac{g(\varepsilon)e^{-\varepsilon/(k_B T)}}{q(T)} \\ &= \frac{(1) \exp \left\{ -(2.2 \cdot 10^{-22} \text{ J}) / [(1.381 \cdot 10^{-23} \text{ J K}^{-1})(373 \text{ K})] \right\}}{1205} = \boxed{0.00080.}\end{aligned}$$

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: trans: 15.5 kJ; rot: 10.3 kJ; vib: 10.3 kJ.

3.2 We need to solve for $\mathcal{P}(v = 1)$, 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:

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

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:

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

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

$$\begin{aligned} \mathcal{P}(J = 4) &= \frac{g(J)e^{-E_{\text{rot}}/(k_B T)}}{q_{\text{rot}}(T)} \\ &= \frac{(2J + 1)e^{-B_e J(J+1)/(k_B T)}}{k_B T/B_e} \\ &= \frac{(9)e^{-20(20.956 \text{ cm}^{-1})/(297 \text{ cm}^{-1})}}{(297 \text{ cm}^{-1})/(20.956 \text{ cm}^{-1})} = \boxed{0.155}. \end{aligned}$$

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 $k_B T$. A fraction of 15.5% for the $J = 4$ energy level is as high as it is only because $E_{\text{rot}} = 20B_e = 419 \text{ cm}^{-1}$ is fairly close to the thermal energy of 297 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 $\vec{p} = m\vec{v}$ 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 $\mathcal{P}_{v^3}(\vec{v})$ 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)

$$\langle p_X \rangle = m \int_{-\infty}^{\infty} \left(\frac{a}{\pi} \right)^{1/2} e^{-a(v_X^2)} v_X dv_X.$$

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

$$\langle f(x) \rangle = \int_{\text{all space}} \mathcal{P}_x(x) f(x) dx,$$

but for this we need the probability distribution function $\mathcal{P}_x(x)$. 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 $\int_0^\infty e^{-mgZ} dZ$ to get the partition function $q_Z'(T)$. (I'm using q' here instead of q because this is not a true unitless partition function, similar instead to the q' 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 $\mathcal{P}_Z(Z)$:

$$\mathcal{P}_Z(Z) = \frac{e^{-mgZ}(k_B T)}{qZ'(T)}.$$

3. And finally we would integrate $\int_0^\infty \mathcal{P}_Z(Z) Z dZ$ to get the mean value of Z .

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

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

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

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

For the ideal gas, the temperature would be

$$T = \frac{PV_m}{R} = 289 \text{ K},$$

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:

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

where $\varepsilon/k_B = 230 \text{ K}$ and $R_e = 4.42 \text{ Å}$.

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 ^1H . Like the alkali metals, ^1H 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 $^{19}\text{F}^-$, 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 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,

$$\lambda = \frac{\langle v \rangle}{\gamma} = \frac{1}{\sqrt{2}\rho\sigma},$$

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 :

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

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

5.2 For a gas, we can predict the diffusion constant from Eq. 5.34. Let A be N₂ and B be acetylene (HCCH):

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

$$\langle v_{AB} \rangle = \sqrt{\frac{8k_B T}{\pi \mu}}$$

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

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

$$\rho_A = \frac{\mathcal{N}_A P}{RT} = \frac{(6.022 \cdot 10^{23} \text{ mol}^{-1})(1.0 \cdot 10^5 \text{ Pa})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 2.431 \cdot 10^{25} \text{ m}^{-3}$$

$$\sigma_{AB} = \frac{1}{4}(\sigma_A + 2\sqrt{\sigma_A \sigma_B} + \sigma_B)$$

$$= \frac{1}{4}(37 + 2\sqrt{37 \cdot 72} + 72) \text{ \AA}^2 = 53.06 \text{ \AA}^2$$

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

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

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

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:

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

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

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 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.