

Problem Set 10

P1

- a) In this case, the number of coin tosses is equal to the number of units (N), and each unit can exist in one of two states: heads (H) or tails (T). Since the number of microstates is equal to the weight (W):

$$W = \frac{N!}{H!T!}$$

- b) For this case, $N = 1000$, $H = 500$, and $T = 500$. Substituting into the above expression for W :

$$W = \frac{N!}{H!T!} = \frac{1000!}{(500!)^2}$$

The factorials that require evaluation are generally too large to determine on a calculator; therefore, evaluation of W is performed using Sterling's approximation:

$$\begin{aligned}\ln W &= \ln(1000!) - 2 \ln(500!) \\ &= 1000 \ln(1000) - 1000 - 2[500 \ln(500) - 500] \\ &= 1000 \ln(1000) - 1000 \ln(500) = 1000 \ln(2) \\ &= 693\end{aligned}$$

Therefore, $W = \exp(693)$.

- c) Proceeding as in part (b), but with $H = 400$ and $T = 600$:

$$\begin{aligned}\ln W &= \ln(1000!) - \ln(400!) - \ln(600!) \\ &= 1000 \ln(1000) - 1000 - 400 \ln(400) + 400 - 600 \ln(600) + 600 \\ &= 1000 \ln(1000) - 400 \ln(400) - 600 \ln(600) \\ &= 673\end{aligned}$$

Therefore, $W = \exp(673)$. Comparing the answers to parts (b) and (c), the $H = 500$, $T = 500$ outcome is approximately $\exp(20)$ or 4.85×10^8 times more likely than the $H = 400$, $T = 600$ outcome.

P5

In a two-level system, $N = n_0 + n_1$ where n_0 is the number of particles in the lowest energy state, and n_1 is the number of particles in the excited energy state. Using this definition:

$$W = \frac{N!}{n_0!n_1!} = \frac{N!}{(N - n_1)!n_1!}$$

P8

- a) According to the energy-level diagram, there is one state at $\epsilon = 0$ and one state at $\epsilon = 300 \text{ cm}^{-1}$. Therefore:

$$0.15 = p_1 = \frac{e^{-\beta\epsilon_1}}{q} = \frac{e^{-\beta(300 \text{ cm}^{-1})}}{1 + e^{-\beta(300 \text{ cm}^{-1})}}$$

$$0.15 + 0.15 \left(e^{-\beta(300 \text{ cm}^{-1})} \right) = e^{-\beta(300 \text{ cm}^{-1})}$$

$$0.15 = 0.85 \left(e^{-\beta(300 \text{ cm}^{-1})} \right)$$

$$0.176 = e^{-\beta(300 \text{ cm}^{-1})}$$

$$1.74 = \beta(300 \text{ cm}^{-1}) = \left(\frac{1}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(T)} \right) (300 \text{ cm}^{-1})$$

$$T = 248 \text{ K}$$

- b) According to the energy-level diagram, there is one state at $\epsilon = 0$ and two states at $\epsilon = 300 \text{ cm}^{-1}$. Therefore:

$$0.15 = p_1 = \frac{2e^{-\beta\epsilon_1}}{q} = \frac{2e^{-\beta(300 \text{ cm}^{-1})}}{1 + 2e^{-\beta(300 \text{ cm}^{-1})}}$$

$$0.15 + 0.30 \left(e^{-\beta(300 \text{ cm}^{-1})} \right) = 2e^{-\beta(300 \text{ cm}^{-1})}$$

$$0.15 = 1.70 \left(e^{-\beta(300 \text{ cm}^{-1})} \right)$$

$$0.088 = e^{-\beta(300 \text{ cm}^{-1})}$$

$$2.43 = \beta(300 \text{ cm}^{-1}) = \left(\frac{1}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(T)} \right) (300 \text{ cm}^{-1})$$

$$T = 178 \text{ K}$$

The temperature at which $p_1 = 0.15$ is lower for case b since the presence of two states at the higher energy provides more opportunity for the system to populate the higher energy state.

P10

a) The total energy is equal to the sum of energy associated with a given level times the number of particles in that level. We will leave the energy in units of

e/k when performing the sum, then multiply the result by k after summation to convert the answer to joules. For set A:

$$\begin{aligned} E &= \sum_n \epsilon_n a_n = \epsilon_0 a_0 + \epsilon_1 a_1 + \epsilon_2 a_2 + \epsilon_3 a_3 \\ &= (0 \text{ K})(33) + (100 \text{ K})(33) + (200 \text{ K})(33) + (300 \text{ K})(33) \\ &= (4400 \text{ K})(1.38 \times 10^{-23} \text{ J K}^{-1}) = 6.07 \times 10^{-20} \text{ J} \end{aligned}$$

Repeating this calculation for Sets B and C reveals that all three sets contain the same energy.

b) The most probable distribution of energy will be that distribution with the greatest weight. Calculating the weight associated with the distributions for each set reveals that set C is the most probable:

$$\begin{aligned} W_A &= \frac{N!}{\prod_n a_n!} = \frac{N!}{a_0! a_1! a_2! a_3!} = \frac{60!}{(33!)(15!)(7!)(5!)} = 1.21 \times 10^{27} \\ W_B &= \frac{N!}{\prod_n a_n!} = \frac{60!}{(31!)(17!)(9!)(3!)} = 1.31 \times 10^{27} \\ W_C &= \frac{N!}{\prod_n a_n!} = \frac{60!}{(32!)(16!)(8!)(4!)} = 1.56 \times 10^{27} \end{aligned}$$

- c) The occupation numbers corresponding to the Boltzmann distribution are given by:

$$a_i = Np_i = \frac{Ne^{-\beta\epsilon_i}}{q}$$

The ratio of any two occupation numbers for a set of non-degenerate energy levels is given by:

$$\frac{a_i}{a_j} = e^{-\beta(\epsilon_i - \epsilon_j)} = e^{-\left(\frac{\epsilon_i - \epsilon_j}{k}\right)\frac{1}{T}}$$

The above expression suggests that the ratio of occupation numbers can be used to determine the temperature. For set C, comparing the occupation numbers for level 2 and level 0 results in:

$$\begin{aligned} \frac{a_2}{a_0} &= e^{-\left(\frac{\epsilon_2 - \epsilon_0}{k}\right)\frac{1}{T}} \\ \frac{8}{32} &= e^{-\left(\frac{200 \text{ cm}^{-1} - 0 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)\frac{1}{T}} \\ T &= 144 \text{ K} \end{aligned}$$

Repeating the same calculation for level 3 and level 0:

$$\begin{aligned} \frac{a_3}{a_0} &= e^{-\left(\frac{\epsilon_3 - \epsilon_0}{k}\right)\frac{1}{T}} \\ \frac{4}{32} &= e^{-\left(\frac{300 \text{ cm}^{-1} - 0 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right)\frac{1}{T}} \\ T &= 144 \text{ K} \end{aligned}$$

The distribution of energy in set C is in accord with the Boltzmann distribution.

P12

The probability of occupying a specific energy level is given by:

$$p_i = \frac{e^{-\beta \epsilon_i}}{q} = \frac{e^{-\beta \epsilon_i}}{e^{-\beta \epsilon_0} + e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2}} = \frac{e^{-\beta \epsilon_i}}{1 + e^{-(100 \text{ K}/T)} + e^{-(200 \text{ K}/T)}}$$

At 50 K, the probability of occupying the ground ($i = 0$), and the first two excited states ($i = 1$ and 2, respectively) is:

$$p_{0,50 \text{ K}} = \frac{e^{-\beta \epsilon_0}}{q} = \frac{1}{1 + e^{-2} + e^{-4}} = 0.867$$

$$p_{1,50 \text{ K}} = \frac{e^{-\beta \epsilon_1}}{q} = \frac{e^{-2}}{1 + e^{-2} + e^{-4}} = 0.117$$

$$p_{2,50 \text{ K}} = \frac{e^{-\beta \epsilon_2}}{q} = \frac{e^{-4}}{1 + e^{-2} + e^{-4}} = 0.016$$

Performing this calculation for 500 K and 5000 K yields the following:

i	p_i (50 K)	p_i (500 K)	p_i (5000 K)
0	0.867	0.402	0.340
1	0.117	0.329	0.333
2	0.016	0.269	0.327

The high-temperature limit for the probability is where each state has an equal probability of being populated, or 1/3 in this example for three, non-degenerate energy levels.

P13

The ratio of any two occupation numbers for a set of non-degenerate energy levels is given by:

$$\frac{a_i}{a_j} = e^{-\beta(\epsilon_i - \epsilon_j)} = e^{-\left(\frac{\epsilon_i - \epsilon_j}{k}\right) \frac{1}{T}}$$

The above expression suggests that the ratio of occupation numbers can be used to determine the temperature. The ratio of a_1 to a_0 is $1/8$. Using this information and the separation between energy levels, the temperature is:

$$\begin{aligned} \frac{a_1}{a_0} &= e^{-\left(\frac{\epsilon_1 - \epsilon_0}{k}\right) \frac{1}{T}} \\ \frac{1}{8} &= e^{-\left(\frac{6000 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}}\right) \frac{1}{T}} \\ T &= 4150 \text{ K} \end{aligned}$$

P15

The resonance frequency can be converted to energy as follows:

$$\Delta E = \frac{\text{freq.}}{c} = \frac{1.445 \times 10^7 \text{ s}^{-1}}{3.00 \times 10^{10} \text{ cm s}^{-1}} = 4.82 \times 10^{-4} \text{ cm}^{-1}$$

With this energy gap, the partition function becomes:

$$q = \sum_n e^{-\beta \epsilon_n} = e^{-\beta \epsilon_-} + e^{-\beta \epsilon_0} + e^{-\beta \epsilon_+} = e^{-\left(\frac{-4.82 \times 10^{-4} \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(298 \text{ K})}\right)} + 1 + e^{-\left(\frac{4.82 \times 10^{-4} \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(298 \text{ K})}\right)} \cong 3.00$$

With the partition function, the occupation numbers are readily determined:

$$a_- = \frac{e^{-\beta \epsilon_-}}{q} = \frac{e^{-\left(\frac{-4.82 \times 10^{-4} \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(298 \text{ K})}\right)}}{3.00} = \frac{1.00000233}{3.00} = 0.333334$$

$$a_0 = \frac{e^{-\beta \epsilon_0}}{q} = \frac{1}{3.00} = 0.333333$$

$$a_+ = \frac{e^{-\beta \epsilon_+}}{q} = \frac{e^{-\left(\frac{4.82 \times 10^{-4} \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(298 \text{ K})}\right)}}{3.00} = \frac{0.999998}{3.00} = 0.333333$$

P17

Since the energy level spacings are larger for Cl_2 relative to I_2 , we would expect the temperature at which $a_1/a_0 = 0.5$ to be greater for Cl_2 .

$$\frac{a_1}{a_0} = \frac{1}{2} = e^{-\beta(\epsilon_1 - \epsilon_0)} = e^{-\beta(525 \text{ cm}^{-1})}$$

$$0.5 = e^{-\left(\frac{525 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(T)}\right)}$$

$$0.693 = \frac{525 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K})(T)}$$

$$T = 1090 \text{ K}$$

P18

For Cl₂ at 300 K:

$$q = \frac{1}{1 - e^{-\beta h c \nu}} = \frac{1}{1 - e^{\frac{-(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ cm s}^{-1})(525 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}}} = 1.087$$

$$p_1 = \frac{e^{-\beta \epsilon_1}}{q} = \frac{e^{-\beta h c \nu}}{q} = \frac{e^{\frac{-(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ cm s}^{-1})(525 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}}}{1.087} = 0.074$$

For Cl₂ at 1000 K:

$$q = \frac{1}{1 - e^{-\beta h c \nu}} = \frac{1}{1 - e^{\frac{-(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ cm s}^{-1})(525 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}}} = 1.885$$

$$p_1 = \frac{e^{-\beta \epsilon_1}}{q} = \frac{e^{-\beta h c \nu}}{q} = \frac{e^{\frac{-(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ cm s}^{-1})(525 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}}}{1.885} = 0.249$$

To determine the temperatures at which F₂ has equivalent populations in the first vibrational excited state, we first reduce the expression for p_1 as follows:

$$p_1 = \frac{e^{-\beta \epsilon_1}}{q} = \frac{e^{-\beta h c \nu}}{\left(\frac{1}{1 - e^{-\beta h c \nu}}\right)} = e^{-\beta h c \nu} (1 - e^{-\beta h c \nu})$$

$$p_1 = 0.074 = e^{-\beta h c (917 \text{ cm}^{-1})} - e^{-2\beta h c (917 \text{ cm}^{-1})} = e^{-1319 \text{ K}/T} - e^{-2(1319 \text{ K})/T}$$

$$0 = -0.074 + e^{-1319 \text{ K}/T} - e^{-2(1319 \text{ K})/T}$$

$$T = 524 \text{ K}$$

Repeating this calculation to determine at which temperature p_1 will be equal to the Cl₂ case at 1000 K:

$$p_1 = 0.249 = e^{-\beta h c (917 \text{ cm}^{-1})} - e^{-2\beta h c (917 \text{ cm}^{-1})} = e^{-1319 \text{ K}/T} - e^{-2(1319 \text{ K})/T}$$

$$0 = -0.249 + e^{-1319 \text{ K}/T} - e^{-2(1319 \text{ K})/T}$$

$$T = 1742 \text{ K}$$

P19

$$\frac{a_1}{a_0} = \frac{1}{5} = e^{-\beta \Delta E}$$

$$0.2 = e^{-\frac{1.30 \times 10^{-4}}{(1.38 \times 10^{-23} \text{ J K}^{-1})}(T)}$$

$$T = 5.85 \times 10^4 \text{ K}$$