Chemistry 410B **Exam 1** **Fall 2016**

Solutions

1. **40 points.**

   (a) Identify the following parameters as intensive (**I**) or extensive (**E**):

   i. temperature $\boxed{\text{I}}$

   ii. entropy $\boxed{\text{E}}$

   iii. mass $\boxed{\text{E}}$

   (b) What is $\mathcal{P}(J=0)$ for HF at 298 K if $q_{\text{rot}} = 9.88$? **Solution:**

$$\mathcal{P}(J=0) = \frac{(2J+1)e^{-BJ(J+1)/(k_{\text{B}}T)}}{q_{\text{rot}}} = \frac{1}{9.88} = \boxed{0.101.}$$

   (c) Calculate the partition function of carbon dioxide at 400 K, based on the energies and degeneracies given in the table. **Solution:** Use $k_{\text{B}} = 0.6950\,\text{cm}^{-1}\,\text{K}^{-1}$ to calculate $g\exp[-\epsilon_{\text{vib}}/(k_{\text{B}}T)]$, and then add all the values up:

state	g	ϵ_{vib} (cm^{-1})	$g\exp[-\epsilon_{\text{vib}}/(k_{\text{B}}T)]$
(0,0,0)	1	0	1
(0,1,0)	2	667	0.182
(0,2,0)	3	1334	0.025
(1,1,0)	2	2000	0.002
total		$q =$	**1.21**

   (d) What is the number of equipartition degrees of freedom in sulfur hexafluoride (SF_6)

   i. when vibrations are *not* included? **Solution:** SF_6 is non-linear, so there are 3 translations and 3 rotations, so $N_{\text{ep}} = 3 + 3 = \boxed{6.}$

   ii. when vibrations *are* included? **Solution:** Now add $2 \times (3 \cdot 7 - 6) = 30$ vibrational contributions, so $N_{\text{ep}} = 3 + 3 + 30 = \boxed{36.}$

2. A system consists of N *distinguishable* particles is energized by M photons, each with energy ϵ_0. Each particle may absorb any number of photons, and many particles may absorb the same number of photons. (However, the photons are *not* distinguishable.)

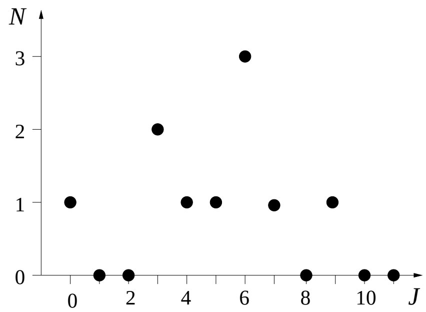
   (a) Write an expression for the ensemble size Ω in terms of the total energy $E = M\epsilon_0$. **Solution:** The number of ways of putting M photons into N particles is N^M, but then we divide by $M!$ because we don't care about the order in which the photons enter the system:

$$\Omega = \frac{N^M}{M!} = \boxed{\frac{N^{E/\epsilon_0}}{\left(\frac{E}{\epsilon_0}\right)!}.}$$

   (b) Find a usable expression for S assuming N and M are large. **Solution:** The warning to make the equation usable for large values is to remind us to use Stirling's approximation to make $\ln M!$ tractable:

$$S = k_{\text{B}}\ln\Omega = k_{\text{B}}\ln\frac{N^M}{M!} = k_{\text{B}}\left[M\ln N - M\ln M + M\right]$$
$$= Mk_{\text{B}}\left[\ln N - \ln M + 1\right] = Mk_{\text{B}}\left[\ln\left(\frac{N}{M}\right) + 1\right]$$

3. Based on the values shown in the plot below, estimate (a) the Gibbs entropy of the system in SI units and (b) the partition function at this temperature.



Solution: There are ten particles, so the probabilities $\mathcal{P}(J)$ are approximately the number of particles in state J divided by 10, so $J = 3$ appears to have a probability of roughly 2/10, $J = 6$ has a probability about 3/10, and 5 states have probability of about 1/10. We then use these values to estimate the Gibbs entropy:

(a) $$S = -Nk_\mathrm{B}\sum_{J=0}^{\infty}\mathcal{P}(J)\ln\mathcal{P}(J)$$

$$= -10(1.381\cdot 10^{-23}\,\mathrm{J\,K^{-1}})\left[(5)\frac{1}{10}\ln\left(\frac{1}{10}\right)+\frac{2}{10}\ln\left(\frac{2}{10}\right)+\frac{3}{10}\ln\left(\frac{3}{10}\right)\right] = \boxed{2.53\cdot 10^{-22}\,\mathrm{J\,K^{-1}}.}$$

(b) The partition function is roughly the number of occupied states at this temperature, Almost all of the particles in this plot are in states $J \leq 7$. Taking the $2J + 1$ degeneracy into account for J from 0 to 7, q is probably less than

$$1+3+5+7+9+11+13+15 = \boxed{64.}$$

We could also use the $J = 0$ population, which is 1/10 of the total population, to estimate q:

$$\mathcal{P}(J=0) = \frac{(2J+1)e^{-BJ(J+1)/(k_\mathrm{B}T)}}{q} = \frac{1}{q} \approx \frac{1}{10} \qquad q \approx \boxed{10.}$$

Because this result is based on only one particle, it is not very accurate, and almost certainly too low. A value of $q = 10$ would suggest that it is unlikely many of the particles would be found at $J > 4$ (because there are more than 10 states in $J \leq 4$), but most of the particles are at $J > 4$. Answers in this range would be accepted. The actual q in this simulation was equal to 30.

4. Consider neutrons bouncing on a surface in Earth's gravitational field. The potential energy is mgz, where $m = 1,675\cdot 10^{-27}\,\mathrm{kg}$, $g = 9.81\,\mathrm{m\,s^{-2}}$, and z is the height. Find an approximate equation for the average total energy per neutron as a function of the temperature. **Solution:**

$$\langle\epsilon\rangle = \left\langle\frac{m}{2}v_z^2\right\rangle + \langle mgz\rangle = \frac{m}{2}\left\langle v_z^2\right\rangle + mg\langle z\rangle$$

$$\frac{m}{2}\left\langle v_z^2\right\rangle = \tfrac{1}{2}k_\mathrm{B}T \qquad \text{by equipartition}$$

$$mg\langle z\rangle = mg\left[\frac{\int_0^\infty z\,e^{-mgz/(k_\mathrm{B}T)}\,dz}{\int_0^\infty e^{-mgz/(k_\mathrm{B}T)}\,dz}\right]$$

$$mg\langle z\rangle = mg\frac{\left[(1!)/(mg/(k_\mathrm{B}T))^2\right]}{\left[(0!)/(mg/(k_\mathrm{B}T))\right]} = mg\left(\frac{k_\mathrm{B}T}{mg}\right) = k_\mathrm{B}T \qquad \int_0^\infty x^n e^{-ax}dx = \frac{n!}{a^{n+1}}$$

$$\langle\epsilon\rangle = \tfrac{1}{2}k_\mathrm{B}T + k_\mathrm{B}T = \boxed{\tfrac{3}{2}k_\mathrm{B}T.}$$