A. Write the expression for the molecular partition function *q*. $q = 1 + 3e^{-2\varepsilon} + 9e^{-4\varepsilon}$

B. What are the values of q at $T \rightarrow 0$ and at $T \rightarrow \infty$? q=1 at $T \rightarrow 0$ and 13 at $T \rightarrow \infty$

C. You found that at T=200 K all three energy levels are equally populated. Determine the value of ε .

By equating the populations of all three levels, we get $1 = 3e^{-2\epsilon\beta} = 9e^{-4\epsilon\beta}$. Let's solve the first equation, i.e. equate the populations of levels ϵ_1 and ϵ_0 :

$$3e^{-2\epsilon\beta} = 1 \Rightarrow e^{-2\epsilon\beta} = 3^{-1} \Rightarrow 2\epsilon\beta = \ln 3 \Rightarrow \epsilon = \frac{k_B T}{2} \ln 3 = 1.516 \ 10^{-21} \text{ J}$$

Because $9e^{-4\epsilon\beta} = (3e^{-2\epsilon\beta})^2$, this solution will also satisfy the equation $9e^{-4\epsilon\beta} = 1$. Alternatively, the same result will be obtained from equating the populations of levels ϵ_2 and ϵ_0 : $9e^{-4\epsilon\beta} = 1 \Rightarrow e^{-4\epsilon\beta} = 9^{-1} \Rightarrow e^{-2\epsilon\beta} = 3^{-1}$; or ϵ_2 and ϵ_1 : $9e^{-4\epsilon\beta} = 3e^{-2\epsilon\beta} \Rightarrow e^{-2\epsilon\beta} = 3^{-1}$.

D. Calculate the total energy of the system at this temperature.

There are several ways to calculate the total energy. Here is one of them. Using equation

$$E = -N \frac{d}{d\beta} \ln q$$
 and the expression for q from Q.1, we get

$$E = N_A \varepsilon \frac{6e^{-2\varepsilon\beta} + 36e^{-4\varepsilon\beta}}{q} = 2N_A \varepsilon \frac{3e^{-2\varepsilon\beta} + 18e^{-4\varepsilon\beta}}{1 + 3e^{-2\varepsilon\beta} + 9e^{-4\varepsilon\beta}} = 2N_A \varepsilon \frac{1+2}{1+1+1} = 2 \times N_A \varepsilon = 1825 \text{ J},$$

where N_A is the Avogadro number (recall we have 1 mole of particles).

You can also reason that because all three levels are equally populated, the average energy (per particle) should be $\langle \epsilon \rangle = (0 + 2\epsilon + 4\epsilon)/3 = 2\epsilon$. Therefore, the total energy is simply N_A×2 ϵ .

E. Calculate the entropy of the system at this temperature.

 $S = \frac{E}{T} + R \ln q = \frac{E}{T} + R \ln (3) = (9.1268 + 9.1268) \text{ J/K} = 18.25 \text{ J/K} \text{ (note that at this temperature } q=3).$

Problem 2. Compare the molecular partition functions of N_2 and CO molecules at the same temperature (300 K), volume (V), and pressure. Which molecule has the larger value of the molecular partition function, or perhaps they are equal? Consider the total molecular partition function as a product of the partition functions associated with various types of motions/states that we studied in this course: translational, rotational, vibrational, nuclear spin. For simplicity, ignore the contributions from the electronic states and electron spins. Assume the highest isotopic abundance for the nuclei, i.e. ^{12}C , ^{14}N , ^{16}O . Some relevant characteristics of these molecules can be found in Table 8.3 of the *Quantum Chemistry and Spectroscopy* textbook. Compare the partition functions associated with the same type of motion for the two molecules: are they equal or not, and if not – by what factor do they differ? Then combine your results to compare the total partition functions of the molecules.

(*Hints*: think how the partition function associated with each type of motion depends on the physical characteristics of the molecule. You can but don't need to calculate all these individual partition functions for each molecule – it might be simpler to calculate their ratio between the two molecules.)

1. <u>Translational motion</u>. Because both molecules have the same total mass, and are at the same conditions, their translational partition functions will be the same: $q_{transl,N_2} = q_{transl,CO}$

2. <u>Rotational motion</u>. The rotational partition function depends on the bond length *r*, reduced mass μ , and the symmetry factor of the molecule σ (assuming the temperature is the same). In high-T approximation (which you need to verify, i.e. show that $hcB << k_BT$ holds!),

$$q_{rot} = \frac{1}{hcB\beta\sigma} = \frac{kT}{hcB\sigma} = A \frac{\mu r^2}{\sigma}$$
 where A includes all the factors/constants that are the same for

both molecules. Thus, $q_{rot,N_2} = q_{rot,CO} \times \frac{\mu_{N_2}}{\mu_{CO}} \left(\frac{r_{N_2}}{r_{CO}}\right)^2 \frac{\sigma_{CO}}{\sigma_{N_2}}$. Because N₂ molecule is symmetric with

respect to a 180° flip, while CO isn't, $\sigma_{N2}=2$ and $\sigma_{CO}=1$. Substituting the relevant numbers into this equation gives:

$$q_{rot,N_2} = q_{rot,CO} \times \frac{7}{6.8571} \left(\frac{109.8}{112.8}\right)^2 \frac{1}{2} = q_{rot,CO} \times 1.0208 \times 0.9475 \times \frac{1}{2} = 0.4836 \ q_{rot,CO} \ . \ \text{Note that, as}$$

you can see from here, the difference is dominated by the symmetry factor. The bond lengths and reduced masses are not much different, and so are their contributions.

3. <u>Vibrational motion</u>. Assuming that the vibrations in both molecules can be described using the harmonic oscillator model, the general expression for the molecular partition is $q_{vibr} = \frac{1}{1 - e^{-hv\beta}}$. Using the data from the Table we get $hv_{N2}=4.6803 \times 10^{-20}$ J = 11.3 k_BT and $hv_{CO}=4.3096 \times 10^{-20}$ J = 10.4 k_BT – in both cases exp(-hv β) <<1, therefore to a good precision $q_{vib,N_2} = q_{vib,CO}$. This reflects the fact that at room temperature the ground level is predominantly populated, and the first excited vibrational level is very weakly populated.

4. <u>Nuclear spin</u>. If we ignore the contributions from the electronic states and electron spins (electron spins are paired), the only remaining motion/degree of freedom associated with these molecules is related to their nuclear spins. As we discussed in class, the naturally abundant isotopes of the nuclei involved are ¹⁴N (spin I=1) and ¹²C (spin I=0), and ¹⁶O (spin I=0). The problem doesn't specify the strength of the magnetic field. However, even if a magnetic field

was applied, the difference between the energy levels of a nuclear spin is many orders of magnitude smaller than the k_BT (at room temperature). This means that the nuclear-spin partition function is simply equal the number of available spin states for a given spin, i.e. 2I+1. For ¹⁴N it's 3 for each nucleus, making it $q_{nuc,N_2} = 3 \times 3 = 9$ for ¹⁴N₂. For ¹²C¹⁶O it's 1 for each nucleus,

which means $q_{nuc,CO} = 1$. Therefore, $q_{nuc,N_2} = 9 \times q_{nuc,CO}$.

5. Putting all these results together:

 $q_{N_2} = q_{trans,N_2} \times q_{rot,N_2} \times q_{virb,N_2} \times q_{nuc,N_2} = q_{trans,CO} \times q_{rot,CO} \times q_{virb,CO} \times q_{nuc,CO} \approx 0.4836 \times 9q_{CO} \approx 4.35q_{CO}$. Thus, the molecular partition function of N₂ is greater than that of CO.