Chemistry 21b

Problem set # 8

Out: 07Mar2008
Due: 12Mar2008

1. From the equipartition of energy theorem, about which you'll learn more in Ch21c, the quantum mechanical formulation for a particle-in-a-box noted above can be related to $< \epsilon_{trans} > = \frac{3}{2}kT$.

   a. Assuming that $a = b = c = n$, find n for a nitrogen molecule at 298 K in a cube having $L_x = L_y = L_z = L = 0.2916$ m.

   b. Calculate $\epsilon_{trans}(1,1,1)$ and $\epsilon_{trans}(1,1,2)$ for N_2 in a cube with $L = 0.2916$ m. Compare $\Delta\epsilon_{trans}$ to $< \epsilon_{trans} >$ at 298 K.

   c. Calculate the value of the translational partition function for N_2 at 298 K in a 24.79 L container (the standard molar volume of an ideal gas under these conditions). What do the ratio q_{trans}/N_A (N_A = Avogadro's number) and the results above tell you about this system?

2. Show that for any microcanonical translational partition function of the form $f(T)V$, where $f(T)$ is any function of temperature, that the ideal gas equation of state is obtained.

3. Consider a system with evenly spaced energy levels $\epsilon_j = j\epsilon$, $j = 0, 1, 2, ...$, and N molecules. For $\beta = 1/kT$,

   a. What is the partition function and total energy for such a system in terms of the parition function? Use β and not $1/kT$ to keep derivatives simple, etc.

   b. Suppose the mean energy/molecule is $a\epsilon$. Show that the temperature is given by

   $$\beta = \frac{1}{\epsilon} \ln\left(1 + \frac{1}{a}\right) ,$$

   and evaluate the temperature for the case where a=1, ϵ=50 cm^{-1}.

   c. For the case where the mean energy/molecule is $a\epsilon$, what is the partition function q? Show that in this case the entropy of the system is given by

   $$S/k = (1 + a)\ln(1 + a) - a\ln(a)$$

   and evaluate this expression for a mean energy ϵ (that is, a=1).

4. Calculate the molar entropy (that is, calculate S in cal K^{-1} mole^{-1}) of N_2 at 25 °C and 1 atm pressure from the partition function involving translation, rotation, and vibration. The equilibrium separation of the nitrogen atoms is 1.095 Å and the vibrational frequency is 2330.7 cm^{-1}. Treat the molecular as a rigid rotor and harmonic oscillator, and use the equations from Maczek in Chapters 8 (translation), 10 (rotation), and 12 (vibration). Do the same for $H^{35}Cl$, where the line spacing in the far-infrared is 20.7 cm^{-1} and the center of the vibrational fundamental lies at 3.46 μm. Your answers should only differ by ∼2.5%. Why is the entropy so similar near room temperature and atmospheric pressure?

Responsible TA for Problem Set #8: Yao Sha (shayao@caltech.edu)