

## 21.10: Problems

1. Consider a system with three non-degenerate quantum states having energies  $\epsilon_1 = 0.9 kT$ ,  $\epsilon_2 = 1.0 kT$ , and  $\epsilon_3 = 1.1 kT$ . The system contains  $N = 3 \times 10^{10}$  molecules. Calculate the partition function and the number of molecules in each quantum state when the system is at equilibrium. This is the equilibrium population set  $\{N_1^*, N_2^*, N_3^*\}$ . Let  $W_{mp}$  be the number of microstates associated with the equilibrium population set. Consider the population set when  $10^{-5}$  of the molecules in  $\epsilon_2$  are moved to each of  $\epsilon_1$  and  $\epsilon_3$ . This is the population set  $\{N_1^* + 10^{-5} N_2^*, N_2^* - 2 \times 10^{-5} N_2^*, N_3^* + 10^{-5} N_2^*\}$ . Let  $W$  be the number of microstates associated with this non-equilibrium population set.

- What percentage of the molecules are moved in converting the first population set into the second?
  - How do the energies of these two populations sets differ from one another?
  - Find  $W_{mp}/W$ . Use Stirling's approximation and carry as many significant figures as your calculator will allow. You need at least six.
  - What does this calculation demonstrate?
2. Find the approximate number of energy levels for which  $\epsilon < kt$  for a molecule of molecular weight 40 in a box of volume  $10^{-6} \text{ m}^3$  at 300 K.
3. The partition function plays a central role in relating the probability of finding a molecule in a particular quantum state to the energy of that state. The energy levels available to a particle in a one-dimensional box are

$$\epsilon_n = \frac{n^2 h^2}{8m\ell^2}$$

where  $m$  is the mass of the particle and  $\ell$  is the length of the box. For molecular masses and boxes of macroscopic lengths, the factor  $h^2/8m\ell^2$  is a very small number. Consequently, the energy levels available to a molecule in such a box can be considered to be effectively continuous in the quantum number,  $n$ . That is, the partition function sum can be closely approximated by an integral in which the variable of integration,  $n$ , runs from 0 to  $\infty$ .

- Obtain a formula for the partition function of a particle in a one-dimensional box. Integral tables give

$$\int_0^\infty \exp(-an^2) dn = \sqrt{\pi/4a}$$

- The expected value of the energy of a molecule is given by

$$\langle \epsilon \rangle = kT^2 \left( \frac{\partial \ln z}{\partial T} \right)_V$$

What is  $\langle \epsilon \rangle$  for a particle in a box?

- The relationship between the partition function and the per-molecule Helmholtz free energy is  $A = -kT \ln z$ . For a molecule in a one-dimensional box, we have  $dA = -SdT - \rho d\ell$ , where  $\rho$  is the per-molecule "pressure" on the ends of the box and  $\ell$  is the length of the box. (The increment of work associated with changing the length of the box is  $dw = -\rho d\ell$ . In this relationship,  $d\ell$  is the incremental change in the length of the box and  $\rho$  is the one-dimensional "pressure" contribution from each molecule.  $\rho$  is, of course, just the force required to push the end of the box outward by a distance  $d\ell$ .  $\rho d\ell$  is the one-dimensional analog of  $PdV$ .) For the one-dimensional system, it follows that

$$\rho = - \left( \frac{\partial A}{\partial \ell} \right)_T$$

Use this information to find  $\rho$  for a molecule in a one-dimensional box.

- We can find  $\rho$  for a molecule in a one-dimensional box in another way. The per-molecule contribution to the pressure of a three-dimensional system is related to the energy-level probabilities,  $P_i$ , by

$$P_{\text{molecule}}^{\text{system}} = - \sum_{n=1}^{\infty} P_n \left( \frac{\partial \epsilon_n}{\partial V} \right)_T$$

By the same argument we use for the three-dimensional case, we find that the per-molecule contribution to the “pressure” inside a one-dimensional box is

$$\rho = - \sum_{n=1}^{\infty} P_n \left( \frac{\partial \epsilon_n}{\partial \ell} \right)_T$$

From the equation for the energy levels of a particle in a one dimensional box, find an equation for

$$\left( \frac{\partial \epsilon_n}{\partial \ell} \right)_T$$

(Hint: We can express this derivative as a simple multiple of  $\epsilon_n$ .)

(e) Using your result from part (d), show that the per molecule contribution,  $\rho$ , to the “one-dimensional pressure” of  $N$  molecules in a one-dimensional box is

$$\rho = 2 \langle \epsilon \rangle / \ell$$

(f) Use your results from parts (b) and (e) to express  $\rho$  as a function of  $k$ ,  $T$ , and  $\ell$ .

(g) Let  $\Pi$  be the pressure of a system of  $N$  molecules in a one-dimensional box. From your result in part (c) or part (f), give an equation for  $\Pi$ . Show how this equation is analogous to the ideal gas equation.

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