20.15: Problems

1. Three non-degenerate energy levels are available to a set of five distinguishable molecules, $\{A,\ B,\ C,\ D,\ E\}$. The energies of these levels are 1, 2, and 3, in arbitrary units. Find all of the population sets that are possible in this system. For each population set, find the system energy, E, and the number of microstates, W. For each system energy, E, list the associated population sets and the total number of microstates. How many population sets are there? What is W_{max}? If this system is isolated with $E=10$, how many population sets are possible? What is Ω_E for $E=10$?

2. For the particle in a box, the allowed energies are proportional to the squares of the successive integers. What population sets are possible for the distinguishable molecules, $\{A,\ B,\ C,\ D,\ E\}$, if they can occupy three quantum states whose energies are 1, 4, and 9? For each population set, find the system energy, E, and the number of microstates. For each system energy, E, list the associated population sets and the total number of microstates. How many population sets are there? What is W_{max}? If this system is isolated with $E=24$, how many population sets are possible? What is Ω_E for $E=24$?

3. Consider the results you obtained in problem 2. In general, when the allowed energies are proportional to the squares of successive integers, how many population sets do you think will be associated with each system energy?

4.

(a) Compare W for the population set $\{3,3,3\}$ to W for the population set $\{2,5,2\}$. The energy levels are non-degenerate.

(b) Consider an N-molecule system that has a finite number, M, of quantum states. Show that W is (at least locally) a maximum when $N_1=N_2=\cdots=N_M=N/M$. (Hint: Let $U=N/M$, and assume that N can be chosen so that U is an integer. Let

$$W_U=N!/\left[U!U!\prod_{i=1}^{i=M-2}U!\right]$$

and let

$$W_O=N!/\left[(U+1)!\,(U-1)!\prod_{i=1}^{i=M-2}U!\right]$$

Show that $W_O/W_U<1$.)

5. The energy levels available to isomer A are $\epsilon_0=1$, $\epsilon_2=2$, and $\epsilon_4=3$, in arbitrary units. The energy levels available to isomer B are $\epsilon_1=2$, $\epsilon_3=3$, and $\epsilon_5=4$. The energy levels are non-degenerate.

(a) A system contains five molecules. The energy of the system is 10. List the population sets that are consistent with $N=5$ and $E=10$. Find W for each of these population sets. What are $W^{max}_{A,B}$, W^{max}_A, and W^{max}_B? What is the total number of microstates, $=\Omega_{A,B}$, available to the system in all of the cases in which A and B molecules are present? What is the ratio $\Omega_{A,B}/W^{max}_{A,B}$?

(b) Repeat this analysis for a system that contains six molecules and whose energy is 12.

(c) Would the ratio $\Omega_{A,B}/W^{max}_{A,B}$ be larger or smaller for a system with $N=50$ and $E=100$?

(d) What would happen to this ratio if the number of molecules became very large, while the average energy per molecule remained the same?

6. In Section 20.11, we assume that all of the energy levels available to an isomeric pair of molecules have the same degeneracy. We then argue that the thermodynamic probabilities of a mixture of the isomers must be greater than the thermodynamic probability of either pure isomer: $W^{max}_{A,B}>W^{max}_A$ and $W^{max}_{A,B}>W^{max}_B$. Implicitly, we assume that many energy levels are multiply occupied: $N_i>1$ for many energy levels ϵ_i. Now consider the case that $g_i>1$ for most ϵ_i, but that nearly all energy levels are either unoccupied or contain only one molecule: $N_i=0$ or $N_i=1$. Show that under this assumption also, we must have $W^{max}_{A,B}>W^{max}_A$ and $W^{max}_{A,B}>W^{max}_B$.

Notes

[1] The statistical-mechanical procedures that have been developed for finding the energy levels available to a molecule express molecular energies as the difference between the molecule energy and the energy that its constituent atoms have when they are motionless. This is usually effected in two steps. The molecular energy levels are first expressed relative to the energy of the molecule's own lowest energy state. The energy released when the molecules is formed in its lowest energy state from the isolated

constituent atoms is then added. The energy of each level is then equal to the work done on the component atoms when they are brought together from infinite separation to form the molecule in that energy level. (Since energy is released in the formation of a stable molecule, the work done on the atoms and the energy of the resulting molecule are less than zero.) In our present discussion, we suppose that we can solve the Schrödinger equation to find the energies of the allowed quantum states. This corresponds to choosing the isolated constituent electrons and nuclei as the zero of energy for both isomers.