Problem Set 2

Chemistry 448 Cynthia J. Jameson

- 1. Consider a system of 7 distinguishable particles distributed among the following energy levels: 0, ω , 2ω , 3ω only. What distributions are associated with a total energy 3ω of the system? Assuming equal accessibility of all the non-degenerate energy levels to all the particles, find the probabilities of each of these distributions. Suppose the energy levels are degenerate such that g_0 =1, g_1 = 2, g_2 = 3, and g_3 = 4. What are the distributions? What is the probability of each distribution? Which one is the most probable distribution?
- 2. In the land of Oz a die is a regular octahedron instead of a cube, with faces numbered 1 to 8. Find the number of possible outcomes of throwing a pair of dice. What is the normalized probability for the most probable throw?
- 3. Consider a mixed crystal containing N_A molecules of A and N_B molecules of B arranged randomly in the crystal lattice sites. Calculate the number of ways W in which the molecules can occupy the sites. If $N_A = N_B = N/2$, what is the number of ways W in which the molecules can occupy the sites? Now, use Stirling's approximation and find an approximate W. If $N_A = N_B = 2$, what is W? What is Stirling's approximate W? Why the discrepancy? For N = 100, how large is the discrepancy?

4. Given the nuclear spins

nucleus	spin I
¹ H	1/2
³⁵ Cl	3/2
³⁷ Cl	3/2
¹⁴ N	1
¹⁵ N	1/2
⁷ Li	3/2

Determine the degeneracy of the four lowest energy levels of a diatomic molecule with the following characteristics:

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molecule	electronic term symbol
H ³⁵ CI	$^{1}\Sigma$
³⁵ Cl ₂ ³⁵ Cl ³⁷ Cl	$^{1}\Sigma_{g}^{+}$
³⁵ Cl ³⁷ Cl	¹ _∑ +
¹⁴ N ₂	¹ Σ _g ⁺
¹⁵ N ₂	$^{1}\Sigma_{g}^{+}$
⁷ Li ₂	$^{1}\Sigma_{g}^{+}$
⁷ Li ₂	¹ Σ _u ⁺
³⁵ Cl ₂ ⁺	² ∏