Problem Set 3
Chemistry 448
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1. The nuclear masses of ^6Li and ^7Li are 6.017034 amu and 7.018232 amu, respectively, and their corresponding terrestial abundances are 7.52% and 92.48%. The ^2P electronic state has an excitation energy of 14,904 cm^{-1} above the ground state, and the ^2D state is excited by 27,206 cm^{-1} above the ground state. Calculate the partition function and the entropy of Li at 1000 K and 1500 K.

2. The molecule Li_2 has an equilibrium internuclear distance of 2.672×10^{-8} cm and a fundamental vibration frequency of 351.43 cm^{-1}. The excited electronic states known are, respectively,

excited electronic state	excitation energy
$^1\Sigma_u^+$	14,068 cm^{-1}
$^1\Pi_u$	20,439 cm^{-1}
$^1\Sigma_u^+$	30,558 cm^{-1}

The ground state is $^1\Sigma_g^+$. Calculate the partition function and the entropy of Li_2 at 1000 K and 1500 K.

3. The vapor pressure of lithium at 1000 K is 0.782 mm Hg. The dissociation energy D_0 of Li_2 has been independently determined to be 1.08 ± 0.05 eV. Calculate the ΔS for the dissociation. Using the partition functions you have calculated, determine the fraction of molecules in the vapor which are Li_2 molecules. Show that the thermodynamic ($\Delta G^0 = -RT \ln K$) approach yields the same result.

4. What is the equilibrium constant for the homogeneous gas phase reaction:

$$^6Li + {}^7Li \leftrightarrow \; {}^6Li^7Li + {}^7Li$$

at 1000 K?

5. In Doklady Akademii Nauk USSR 128, 977 (1959), evidence is presented for the existence of a molecule Be_2 in high intensity in the vapor at equilibrium with crystalline Be. According to the authors of this article, the ratio of Be_2 : Be is ca. 10:1 at 1528 K. The vapor pressure of Be is 1.3×10^{-2} mm Hg at 1528 K. Some information about the Be atom: The nuclear mass of Be is 9.015060 amu (it is mono-isotopic). Excited electronic states are ^3P (21, 957 cm^{-1}) and ^1P (42,565 cm^{-1}) and the ground state is $^1S_0$. The molecular parameters of Be_2 are not known, but by analogy with similar molecules we may estimate $\omega_e \sim 800$ cm^{-1} and $r_e = 1.95 \times 10^{-8}$ cm. If we further assume no low-lying electronic energy states for Be_2, what value of D_0 for Be_2 is implied by the experimental results of the Russian workers? Is this a reasonable value, based on your knowledge of molecular bonding?

6. Suppose that a molecule could exist in either of two energy levels, ε_1 and ε_2, with degeneracies g_1 and g_2. Derive expressions for E, S, A, and C_V for N molecules of the

substance. Taking cognizance of the numbers of molecules, N_1 and N_2 in each of the two states, show that the heat capacity will be

$$C_V = \{N_1N_2/NkT^2\} [\varepsilon_2-\varepsilon_1]^2.$$

7. Assuming that 75% of the atoms of chlorine have mass number 35 and 25% have mass number 37, what fraction of the molecules of chlorine will have masses 70, 72, and 74, if pairs of atoms are taken at random?

8. Consider the equilibrium

$$I_{2(g)} \leftrightarrow 2I_{(g)}$$

(a) Set up an expression for the equilibrium constant for this reaction, using the following data: the bond energy, ΔE_0, is equal to 35.603 kcal; the moment of inertia of the I_2 molecule is equal to $750.2\text{x}10^{-40}$ g cm^2; the vibrational frequency of the diatomic molecule is 213.67 cm^{-1}; the molecule has an electronic degeneracy equal to unity, but the atom, in a $^2P_{3/2}$ state, has a degeneracy equal to 4.

(b) Calculate numerical values for K_p, and compare them with the following experimental results:

temperature	K_p observed
800 C	$1.14\text{x}10^{-2}$ atm
1000 C	$1.65\text{x}10^{-1}$ atm
1200 C	1.23 atm

9. Estimate the standard Gibbs energy change in calories for the following reaction at 25 C:

$$Cl_{2(g)} + Br_{2(g)} \leftrightarrow 2BrCl_{(g)}$$

The value of ΔE_0 for this reaction can be taken as the heat of reaction, -0.387 kcal (using what approximation?). As for the effect of rotation, use for the covalent radii of Br and Cl the values 1.14 Å and 0.99 Å, respectively, from which the moments of inertia can be calculated. {Be sure to use the appropriate reduced masses, such as $m_{Br}m_{Cl}/[m_{Br}+m_{Cl}]$ for the molecule BrCl.} Finally you may neglect any vibrational excitation (or assume that such effects cancel). Compare your answer with the accepted value of -1.211 kcal.