

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

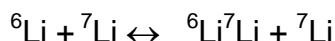
2. The molecule Li_2 has an equilibrium internuclear distance of $2.672 \times 10^{-8}\text{ cm}$ and a fundamental vibration frequency of 351.43 cm^{-1} . The excited electronic states known are, respectively,

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

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 $1.08 \pm 0.05\text{ eV}$. 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:



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 $\text{Be}_2 : \text{Be}$ is ca. 10:1 at 1528 K. The vapor pressure of Be is $1.3 \times 10^{-2}\text{ mm Hg}$ 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 ${}^3\text{P}$ ($21,957\text{ cm}^{-1}$) and ${}^1\text{P}$ ($42,565\text{ cm}^{-1}$) and the ground state is ${}^1\text{S}_0$. The molecular parameters of Be_2 are not known, but by analogy with similar molecules we may estimate $\omega_e \sim 800\text{ cm}^{-1}$ and $r_e = 1.95 \times 10^{-8}\text{ cm}$. 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

$$C_V = \{N_1 N_2 / N k T^2\} [\varepsilon_2 - \varepsilon_1]^2.$$

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

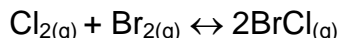


(a) Set up an expression for the equilibrium constant for this reaction, using the following data: the bond energy, ΔE_0 , is equal to 35.603 kcal; the moment of inertia of the I_2 molecule is equal to 750.2×10^{-40} g cm²; the vibrational frequency of the diatomic molecule is 213.67 cm⁻¹; the molecule 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	1.14×10^{-2} atm
1000 C	1.65×10^{-1} atm
1200 C	1.23 atm

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



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.