Problem set 11

Due May 28, 2025

1. Calculate the mole fractions of lithium (Li) atoms in the first and in the second excited state at its boiling temperature ($t = 1330°\text{C}$). The degeneracy of the ground electronic state (term ${}^2S_{1/2}$) is $\omega_\circ = 2$, while the degeneracies and the excitation energies of the first and the second excited states (terms ${}^2P_{1/2}$ and ${}^2P_{3/2}$, respectively), are $\omega_1 = 2$, $\Delta\epsilon_1 =$ 1.85 eV and $\omega_2 = 4$, $\Delta\epsilon_2 = 1.85$ eV, respectively.

2. Calculate the translational and electronic contributions to the energy and to the heat capacity of 1 mol of atomic tin (Sn) gas at T=2000 K. The degeneration of the ground state is $\omega_\circ = 1$ and the degeneration and the relative energy of the first excited state are $\omega_1 = 3$ and $\Delta\varepsilon_1 =$ 20 kcal/mol, respectively. The second and higher excited states can be ignored. What percentage of the total energy and total heat capacity makes the electronic contribution at 2000 K?

   Hint: Determine the characteristic vibrational temperature first and use the expressions for vibrational energy and heat capacity that contain that characteristic temperature.

3. Calculate the characteristic vibrational (Θ_ν) and rotational (Θ_r) temperatures of nitrogen monooxide ${}^{14}\text{N}{}^{16}\text{O}$ and determine the percentage of molecules at (i) the first excited vibration state and (ii) the 10th excited rotational state at (a) $T = 298$ K and (b) $T = 1000$ K. The equilibrium bond length of the molecule is $d_\circ = 1.15$ Å and the force constant of the N-O bond is $k_d = 1570$ N/m.

4. Calculate the translational, rotational, vibrational, and electronic contributions to (i) energy and (ii) heat capacity of 1 mole of gaseous iodine (${}^{127}\text{I}_2$) at $T = 308$ K. The dissociation energy of the iodine molecule corrected to add zero-point vibrational energy is $D_\circ = 35.6$ kcal/mol, the force constant of the I–I bond is $k_d = 170$ N/m, and high-temperature approximation can be used to compute the translational and rotational contributions to energy and heat capacity.

   Hint: Determine the characteristic vibrational temperature first and use the expressions for vibrational energy and heat capacity that contain that characteristic temperature.

Energy conversion: 1 kcal/mol = 4184 J/mol; 1 eV = 96490.5 J/mol
Universal gas constant: $R = 8.3145$ J/(mol×K)