Problem set 9

Due May 12, 2026

1. Calculate the fractions of cerium (Ce) atoms in the first and in the second excited states at $t = 3257°\text{C}$ (the boiling point of this metal). The degeneracy of the ground electronic state (term $^1G_4$) is $\omega_\circ = 9$, while the degeneracies and the excitation energies of the first and the second excited states (terms $^3F_2$ and $^3P_3$, respectively), are $\omega_1 = 5$, $\Delta\epsilon_1 = 2.74$ kJ/mol and $\omega_2 = 7$, $\Delta\epsilon_2 = 19.9$ kJ/mol, respectively. It is assumed that the populations of the higher excited states are negligible at this temperature.

2. Calculate the translational and electronic contributions to the energy and to the heat capacity and the relative electronic contributions to the energy and heat capacity of 1 mol of gaseous cerium at the boiling point temperature of this metal. The electronic excitation energies and state degeneracies are listed in the text of Problem 1. Assume that only the first excited state contributes to thermodynamic averages.

3. Calculate the characteristic vibrational (Θ_ν) and rotational (Θ_r) temperatures of the dichlorine molecule composed of alternating isotopes $^{35}Cl^{37}Cl$. Based on these values and assuming the high-temperature approximation (Boltzmann statistics), plot the distributions (note that they are defined on positive integers) and cumulative distributions at (a) $T = 298$ K and (b) $T = 1000$ K (determine the range of state numbers so that a distribution is negligible outside the plot). The equilibrium length and force constant of the Cl-Cl bond are $d_\circ = 1.99$ Å and $k_d = 320$ N/m, respectively.

4. Calculate the translational, rotational, vibrational, and electronic contributions to (i) energy and (ii) heat capacity of 1 mole of gaseous $^{35}Cl_2$ at $T = 800$ K assuming the high-temperature approximation (Boltzmann statistics). The dissociation energy of the dichlorine molecule corrected to add zero-point vibrational energy is $D_\circ = 57.6$ kcal/mol and the force constant of the Cl-Cl bond is given in the text of Problem 3.

   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)