2009.Physical Chemistry

Part I

1. The melting point of naphthalene is 80.2℃, vapor pressure of its liquid is 10 torr at 85.8℃, 40 torr at 119.3℃, use Clausius-Clapeyron equation to calculate:
   (a) $\triangle H_{vaporization}$ in kJ/mole (10%)
   (b) Normal boiling point (10%)
   (c) $\triangle S_{vaporization}$ at b.p. (10%)

2. At 25℃ , the half potentials for the battery $Ag \mid Ag^+ \mid Br^- \mid AgBr_{(s)} \mid Ag$ are listed below, please calculate the solubility product constant for AgBr (10%)
   $AgBr_{(s)} + e^- \rightarrow Ag + Br^-$ $E^o = +0.0711$ V
   $Ag^+ + e^- \rightarrow Ag$ $E^o = -0.7989$ V

3. The degree of dissociation of the reaction $N_2O_4(g) = 2\,NO_2(g)$ at 25°C and 1 bar is 18.56%, find the $\triangle G^o$ for this reaction. (10%)

Qualify - Advanced Physical Chemistry

Part II

1. Answer the following questions: (8pts)
   (1) One of the excited states of the Carbon molecule (C_2) has the **valence electron configuration** $1\sigma_g^2 1\sigma_u^2 1\pi_u^3 1\pi_g^1$. Give the multiplicity and parity of the term.
   (2) Which of the following transitions is electric-dipole allowed? Use **group theory** to justify it. (i) $\pi^* \leftarrow \pi$ in ethane, (ii) $\pi^* \leftarrow n$ in a carbonyl group

2. (1) Write an expression for the partition function of an HCl molecule treated as a **rigid rotor**. (2) At what temperature would the population of the 1st excited state of **rotational** level of HCl molecule be 1/e times its population of the ground state? (3) What about the temperature for the **vibrational** state of HCl molecule of the same condition as (2)? (16pts)

3. Consider a system of the unique particles having only three non-degenerate energy levels separated by an energy which is equal to the value of kT at 25.0K. Answer the following questions: (16pts)
   (1) The ratio of populations in the states at 1.0K, 25.0K and 100K
   (2) The molecular partition function at 25.0K
   (3) The molar energy at 25.0K
   (4) The molar heat capacity at 25.0K

4. Justify that the relation between equilibrium constant K and the standard molar partition function partition function $q^{\oplus}_{J,m}$ is $K = \left\{ \prod_J \left(\frac{q^{\oplus}_{J,m}}{N_A} \right)^{\nu_J} \right\} e^{-\Delta_r E_o / RT}$. (10pts)