2009. Physical Chemistry

Part I

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

2. At 25°C, the half potentials for the battery $\text{Ag} \mid \text{Ag}^+ \mid \text{Br}^- \mid \text{AgBr(s)} \mid \text{Ag}$ are listed below, please calculate the solubility product constant for AgBr (10%)
   \[
   \begin{align*}
   \text{AgBr(s)} + e^- & \rightarrow \text{Ag} + \text{Br}^- & E^0 &= +0.0711 \text{ V} \\
   \text{Ag}^+ + e^- & \rightarrow \text{Ag} & E^0 &= -0.7989 \text{ V}
   \end{align*}
   \]

3. The degree of dissociation of the reaction $\text{N}_2\text{O}_4(g) = 2 \text{NO}_2(g)$ at 25°C and 1 bar is 18.56%, find the $\Delta G^0$ for this reaction. (10%)
Part II

1. Answer the following questions: (8pts)

   (1) One of the excited states of the Carbon molecule \( (\text{C}_2) \) has the valence electron configuration \( 1\sigma_g^21\sigma_u^21\pi_u^31\pi_g^1 \). 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 250K. 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 250K
   (3) The molar energy at 250K
   (4) The molar heat capacity at 250K

4. Justify that the relation between equilibrium constant \( K \) and the standard molar partition function \( q^0_{J,m} \) is

\[
K = \left\{ \prod_j \left( \frac{q^0_{J,m}}{N_A} \right)^{\nu_j} \right\} e^{-\Delta F_{m}/RT} \]

(10pts)