

2008 Spring Semester Advanced Physical Chemistry Qualify Exam

Gas constant $R=0.082$ L-atm/mole-K= 8.314 J/K-mole

Faraday constant $F=96,487$ coulomb

1. (10%) The following data were obtained for the equilibrium of $2\text{NO}_2(\text{g}) = \text{N}_2\text{O}_4(\text{g})$

T (K)	P_{NO_2} (torr)	$P_{\text{N}_2\text{O}_4}$ (torr)
298	46	23
305	68	30

Calculate the standard enthalpy and standard free energy of reaction at 298K, (standard pressure $P^\circ = 1$ bar = 750.062 torr)

2. (10%) The normal boiling point (at 1 atm) of diethyl ether is 34.50C, and its enthalpy of evaporation is 26.69 kJ/mole. Determine the vapor pressure (in atm) of diethyl ether at 250°C via the Clausius-Clapeyron equation.

3. (10%) The standard emf of the cell $\text{Ag} | \text{AgI}(\text{s}) | \text{AgI}(\text{aq}) | \text{Ag}$ at 25°C is 0.9509V, and the electrochemical reaction is $\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}(\text{s})$

Please calculate the $\log K_{\text{sp}}$, where K_{sp} is the solubility product of AgI

4. (10%) At body temperature of 37°C, the potassium concentration inside the nerve cell is 20 times of the potassium concentration outside. Assume ion activity is proportional to its concentration, calculate the electrical potential difference across the cell membrane.

5. (10%) How much time is needed to deposit 0.1 μm thick nickel film on a 0.03 m² metal electrode by passing 4 Ampere current through a $\text{Ni}(\text{NO}_3)_2$ solution. The atomic weight of Ni is 58.69, and its density is 8.9 g/cm³.

6. (15%) Consider the molecule CH_3Cl . (a) What point group does the molecule belong to? (b) What symmetries do the molecule have? (c) How many normal modes of vibration does the molecule have? What are they? (d) Which of the vibrational modes are IR active? Why? (e) Which of the vibrational modes are Raman active? Why?

7. (10%) Calculate σ_d in magnetic resonance for a hydrogenic atom with

atomic number Z .

8. (10%) Calculate the proportion of I_2 molecules in their ground, first excited and second excited vibrational states at 25°C , starting from evaluation the partition function. (The vibrational wavenumber is 214.6cm^{-1})

9. (15%) (a) The standard molar entropy of graphite at 298K, 410K and 498K is 5.69, 9.03 and 11.63 J/K-mol. If 1.00 mole graphite at 298K is surrounded by thermal insulation and placed next to 1.00mole insulated graphite at 498K, how many configurations are there altogether for the combined but independent system? (b) If the same two samples are now placed in thermal contact and brought to thermal equilibrium, the final temperature will be 410K without volume change. Why the final temperature is not the average? How many configurations are there now in the combined system? (c) Demonstrate that this process is spontaneous.