國立臺灣大學97學年度碩士班招生考試試題

Part I. Physical Chemistry

Procedures for all calculations and the units of the final results must be given.

1. The molar Gibbs free energy of a certain gas is given by $G_m = a + bP + RT \ln P$, where a, b are constants, T is the absolute temperature, and P is the pressure (in atm). *One mol of this gas at 300 K is compressed isothermally and reversibly from 1 atm to* 5 atm. Answer the following questions. ($R = 8.31\ J \cdot K^{-1} \cdot mol^{-1}$) 10%

(a) Find the equation of state for the gas.

(b) Find the change in entropy of this process.

(c) Find the change in enthalpy of this process.

(d) Find the change in internal energy of this process.

(e) Find the work done in this process

2. The vapor pressures P (in atm) at various absolute temperature T for the solid and liquid states of the same material are given by $\ln P = 2 - 600/T$ and $\ln P = 1 - 360/T$, respectively. Answer the following questions. 10%

(a) Find the temperature and pressure at the triple point of this material.

(b) Find the normal boiling point of this material.

(c) Estimate the enthalpy of sublimation of this material.

(d) Estimate the entropy of sublimation of this material.

3. The energy of an electron in a hydrogen atom is given by $-B/n^2$, where B is 2.18×10^{-18} J. The three 4p orbials of a hydrogen atom are $4p_{+1}$, $4p_0$, and $4p_{-1}$, where the subscripts indicate the values of m_l. Another common designation of the 4p orbitals are given by: $4p_x = \frac{1}{\sqrt{2}}(4p_{+1} + 4p_{-1})$, $4p_y = \frac{1}{\sqrt{2}}(4p_{+1} - 4p_{-1})$, and $4p_z = 4p_0$. Answer the following questions. ($h = 6.625 \times 10^{-34}$ J·s) 15%

(a) What is the energy of an electron in a $4p_x$ orbital?

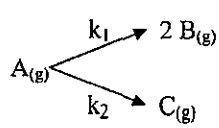
(b) What is the total orbital angular momentum of an electron in a $4p_y$ orbital?

(c) What is the z-component of the orbital angular momentum of an electron in a $4p_z$ orbital?

(d) Find the wavelength (in nm) of light emitted from the electronic transition of $4p_x$ to 3s.

(e) Show that $\hat{L}_z(4p_x) = \frac{h}{2\pi}(4p_y)$, where $\hat{L}_z$ is the operator for the z-component of the orbital angular momentum.

4. Suppose that the gaseous molecule $A_{(g)}$ can undergo two first-order, parallel reactions at 500 K to form the products $B_{(g)}$, and $C_{(g)}$ as shown in the following diagram:



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Initially, one mole of pure A(g) was enclosed in a sealed vessel at 500 K. After 5 hours of reaction at fixed volume and temperature, the total pressure of the system was 1.1 atm and the partial pressure of A(g) and $C_{(g)}$ were 0.5 atm, and 0.4 atm, respectively. Answer the following questions. 15%

(a) Find the volume of the vessel.

(b) Find the half-life for the disappearance of $A_{(g)}$.

(c) Find the values of k_1 and k_2.

(d) Calculate the initial rate for the formation of B(g)..

Part II. Analytical Chemistry 50%

A. Briefly answer the following questions (total 20%, 2% each)

1. Round the answer with the correct number of digits: $50.000 + (4.500 \times 10^2) - (5.0000 \times 10^3) = -4500.000$
2. Round the answer with the correct number of digits: $log(5.50 \times 10^5) = 5.740362689$
3. *Clearly* **list (do not** do the calculations) how you derive the standard deviation for $\frac{4.00(\pm 0.02) \times 0.0050(\pm 0.0005)}{2.00(\pm 0.04)} = 0.0100(\pm ?)$
4. Considering the solubility case of AgCl, species such as AgCl(*aq*), $AgCl_2^-$ and $AgCl_3^{2-}$ also contribute to the total solubility. Please list *all* the species in the saturated AgCl(*s*) solution containing excess Cl^-.
5. In the above AgCl case, please write down an equation to express the solubility of AgCl(*s*) as a function of $[Cl^-]$. Use K_{sp} and either stepwise formation constants, K_i, or overall formation constants, β_i.
6. Write the mass balance equation for a saturated solution of $Mg(OH)_2$ (i.e., introducing solid $Mg(OH)_2$ into pure water). Given: $Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$; $Mg^{2+} + OH^- \rightleftharpoons Mg(OH)^+$; $H_2O \rightleftharpoons H^+ + OH^-$
7. Under what experimental conditions is an auxiliary complexing agent used in EDTA titration?
8. Generally speaking, which of the following detector requires the longest time to collect a UV/Vis spectrum? (PMT, PDA, or CCD)
9. Which term(s) in the van Deemter equation become(s) smaller when a faster linear flow rate is applied?
10. UV detectors are common and relatively inexpensive detector for capillary electrophoresis. However, the limits of detection for CE-UV are not very good. Please give a simple explanation.

B. Essay questions (total 30%, 15% each)

1. The calcium content of a person's urine was determined on two different days. The results were 238 (± 8) mg/L (n = 4) and 255 (± 10) mg/L (n = 5). Based on null hypothesis, the two values are significantly different.
   1a. Please use this example to explain the meaning of null hypothesis. (Both your knowledge and **writing** will be graded.)
   1b. Should or should not the data be pooled for the statistical analysis? Why so?
2. Propose a method to analyze the metal contents of a rock. It is required to determine iron, calcium, and cobalt *simultaneously* in one run. Please emphasize the answer on how the *sampling* and *sample preparation* should be carried out, and on the reason why your *analytical method* can solve the problem. (Grading will be based on how reasonable your proposal is and how well your writing is.)

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