國立成功大學 109 學年度碩士班招生考試試題

系　　所：化學工程學系

考試科目：物理化學

考試日期：0210，節次：3

※ 考生請注意：本試題可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

1. A diatomic ideal gas is at 300 K and 1 bar initially. Calculate w, ΔH, ΔS, and ΔG after adiabatic free expansion until the volume is doubled. **(16%)**

2. A cell Cu(s) | $CuCl_2(0.01\ mol\ kg^{-1})$ | AgCl(s) |Ag is constructed. It is known that the standard electrode potentials of Cu and AgCl at 298K are as follows:

   $Cu^{2+} + 2e^- \rightarrow Cu(s)$ $\qquad E° = 0.3419\ V$

   $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ $\qquad E° = 0.22233\ V$

   (a) Write the cell reaction (3%) and give the standard electromotive force ($E°$) (3%); (b) Estimate the mean ionic activity coefficient of Cu^{2+} and Cl^- ions using Debye-Hückel limiting law (4%) (c) Calculate the electromotive force (E) (4%) and the reaction Gibbs energy (ΔG) (3%) of the cell. **(17%)**

3. Derive the following relationships:

   (a) Prove that $\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$ (8%); (b) $\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$ (8%) **(16%)**

4. Suppose that a reaction of stoichiometry A + 2B = 2Y + 2Z is believed to occur according to the mechanism

   $$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2X$$

   $$X + B \xrightarrow{k_2} Y + Z$$

   (a) If the first step reaches the equilibrium very rapidly as compared to the second step, derive the expression for the rate of formation of the product Y. (8%)

   (b) Derive the expression for the activation energy (E_a) of the above rate expression in terms of E_1, E_{-1}, E_2, which denote the activation energies for the rate constants k_1, k_{-1}, k_2, respectively.(8%) **(16%)**

5. The equation of state for a van der Waals gas is $(P + \frac{a}{V_m^2})(V_m - b) = RT$,

   (a) prove that $a = 3P_cV_c^2$ and $b = \frac{V_c}{3}$, in which P_c, V_c, T_c are the critical P, V, T, respectively. (8%);

   (b) derive the reduced equation of state and describe the law of correspondence state (8%). **(16%)**

6. Answer the following questions: **(19%)**

   (a) Determine the number of degrees of freedom and suggest the required variables for an aqueous solution

of potassium chloride and sodium chloride at 1 atm. (4%)

(b) The combustion of $C_2H_5OH_{(l)}$ in a bomb calorimeter produces about 1364 $kJ\,mol^{-1}$ at 25°C. Calculate ΔH_m for the combustion reaction at 25°C: $C_2H_5OH_{(l)} + 3O_{2(g)} = 2CO_{2(g)} + 3H_2O_{(l)}$ (4%)

(c) Suppose that a refrigerator cools to 250 K and discharges heat at 300 K. If the refrigerator operates with an efficiency of the 25% of the maximum theoretical coefficient of performance (COP), how much work would be required to freeze 18 kg of water ($\Delta_f H \approx -6.0 kJmol^{-1}$) (4%)

(d) The molar conductivities at infinite dilution ($\Lambda°$) of KCl, KI, and NaCl are 149.79, 150.31, and 126.39 Scm^2mol^{-1}. Calculate the $\Lambda°$ of NaI. (4%)

(e) The main difference between Langmuir adsorption isotherm and BET adsorption isotherm. (3%)

------ END ----