系所組別：化學工程學系乙組

考試科目：物理化學 考試日期：0222，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. Answer the following questions: **(22%)**

(a) Explain the supersaturation phenomenon in the condensation process according to the Kelvin equation. (4%)

(b) The solubility of $AgCl$ in water at 25°C is $1.274\times10^{-5}\ mol\ dm^{-3}$. Calculate the solubility of $AgCl$ in a mixed solution of 0.01M $Mg(NO_3)_2$ and 0.01M $Al(NO_3)_3$ according to the Debye-Hückel Limiting Law. (6%)

(c) Is fractional crystallization more difficult than fractional distillation in practical application? Why? (4%)

(d) How to break the azeotrope? (4%)

(e) A lower consolute temperature was observed for the water-triethylamine system. Explain the temperature effect on the solubility. (4%)

2. Judge the following statements are correct (O) or incorrect (×): **(15%)**

(a) For a cyclic process containing some irreversible processes, $\Delta S > 0$. (3%)

(b) The addition of nitrogen gas into a closed vessel containing water will suppress the vapor pressure of water. (3%)

(c) According to the 3rd law of thermodynamics, the entropies of all species are equal to zero. (3%)

(d) For an ideal solution, the interactions among all molecules are negligible. (3%)

(e) For the expansion of a gas, the work done on the surroundings via an irreversible process is lower than that via a reversible process. The lost work will convert into heat and lead to the increase of system temperature. (3%)

3. The boiling point of benzene is 80.1°C at 1 atm. (a) Estimate the enthalpy of vaporization of benzene according to Trouton's rule (5%); (b) Estimate the vapor pressure of benzene at 25°C according to Clausius-Clapeyron equation, assuming the enthalpy of vaporization remains constant at 25-80.1°C. (7%) **(12%)**

4. The standard Gibbs energies of formation ($\Delta_f G°$) for Cu^{2+} and Zn^{2+} ions at 25°C and 1 bar are 65.49 and -147.06 kJ/mol, respectively. (a) Calculate the $\Delta_r G°$ of the reaction $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$ (5%); (b) Construct an electrochemical cell based on the above reaction to convert the chemical energy into electric energy. Illustrate its configuration (indicating the positive and negative electrodes) (5%) and calculate its standard electromotive force (3%). **(13%)**

(背面仍有題目,請繼續作答)

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5. Joule-Thomson coefficient is defined as $\mu_{JT} = (\partial T/\partial P)_H$, show that

(a) $\mu_{JT} = \dfrac{T(\partial V_m/\partial T)_P - V_m}{C_{P,m}}$ (i.e., V_m: molar volume, $C_{p,m}$: molar heat capacity at constant P) (6%)

(b) for a van der Waals gas, $\mu_{JT} \approx \dfrac{(2a/RT) - b}{C_{P,m}}$ (7%)

(c) Assuming N_2 gas is a van der Waals gas (i.e., a=0.1408 Pa m^6 mol^{-2}, b=0.0391×10^{-3} m^3 mol^{-1}), estimate ΔH for the isothermal compression of 1.0 mole of N_2 gas at 300 K from 10 bar to 1 bar. (7%)

(20%)

6. Consider first order parallel reactions $A \xrightarrow{k_1} 2B$ *and* $A \xrightarrow{k_2} C$

The initial concentration of A is $[A]_0$. Neither B or C are present initially.

(a) Derive the expressions for the variations of [A] and [B] with time. (6%)

(b) $[A]_0$=0.12 $mol\ dm^{-3}$, $k_1 = 100\ s^{-1}$, and $k_2 = 50\ s^{-1}$. Calculate the half-life of A (3%) and the final concentration ratio of B to C. (3%).

(c) Derive the expression of the activation energy E for the disappearance of A in terms of k_1 , k_2 , and the activation energies E_1 and E_2 for the two paths (6%) **(18%)**