國立成功大學 106 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：0213，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. Judge the following statements are correct (O) or incorrect (×): **(15%)**
   (a) $\Delta S=0$ is always impossible for all irreversible processes (3%)
   (b) The spontaneous occurrence is impossible for a process with $\Delta H>0$ at constant T and P. (3%)
   (c) For a real gas, the temperature always decreases after adiabatic expansion. (3%)
   (d) For a binary solution, phase separation occurs only when positive deviation is large enough. (3%)
   (e) An ion with larger surface charge density has larger thickness of ionic atmosphere. (3%)

2. Answer the following questions: **(24%)**
   (a) For the adiabatic expansion of an ideal gas through a Joule-Thomson expansion, which of the quantities ΔU, ΔH, ΔS, ΔA, ΔG, q and w are equal to zero? (4%)
   (b) Explain the physically meanings of the terms $\frac{RT}{V_m - b}$ and $\frac{a}{V_m^2}$ for the van der Waals gas. (4%)
   (c) Explain what is Nernst potential (4%)
   (d) Transition-state theory is theoretically superior to the kinetic theory. Why? (4%)
   (e) Illustrate the fixed electric double layer and state what is zeta potential (4%)
   (f) Determine the number of degrees of freedom and suggest the required variables for the "bubble point surface". (4%)

3. A mole of nitrogen gas at 300 K and 10 bar is considered as an ideal gas.
   (a) Calculate the work done while expanding to 1 bar reversibly and adiabatically (5%);
   (b) Calculate the work done while expanding to 1 bar adiabatically against a constant pressure of 1 bar (5%);
   (c) Calculate the work while heating to 400 K at a constant pressure of 10 bar (5%)
   (d) Calculate ΔH_m while expanding to 1 bar adiabatically against a vacuum (3%). **(18%)**

4. The boiling point of water at 1 atm is 100°C. The molar volume of liquid water (18.78 cm^3/mol) and the heat of vaporization (about 125 J/mol) are considered to be unchanged in the ranges of temperature and pressure examined. (a) Estimate the boiling point of water at 0.92 atm according to the Clausius-Clapeyron equation. (5%) (b) Estimate the vapor pressure of water in a closed vessel at 100°C when N_2 gas is added until the total pressure is 20 atm if the vapor considered as an ideal gas. (5%) **(10%)**

5. The following data relate to the adsorption of nitrogen at 77 K on a 1.00-g sample of silica gel:

Pressure / kPa	10	50
Volume / cm^3 (0°C, 1atm)	150	250

At 77 K the saturation vapor pressure P_0 of nitrogen is 101.3 kPa. (a) Determine the equilibrium constant K and the volume required to form a monolayer V_0, according to the simplified BET equation ($\frac{PP_0}{V(P_0-P)}=\frac{1}{V_0K}+\frac{P}{V_0}$). (5%) (b) Estimate the surface area of the gel, taking the molecular area of nitrogen to be $1.62\times10^{-19}\ m^2$. (5%) **(10%)**

6. (a) For a first-order decomposition reaction in an aqueous medium, the rate constants are 450 and 700 min^{-1} at 290 and 310 K, respectively. Calculate the activation energy and preexponential factor according to the Arrhenius law. (8%)

(b) At 298K, the equilibrium constant for the reaction $CO(g)+H_2O(g)\Leftrightarrow CO_2(g)+H_2(g)$ is 1.0×10^{-5} and ΔS^0 is 41.8 J K^{-1} mol^{-1}. Calculate ΔG^0 and ΔH^0 at 298 K. (6%)

(c) For HCl at infinite dilution, the molar conductivities of H^+ and Cl^- ions at 25°C are 349.8 and 76.3 $S\ cm^2 mol^{-1}$, respectively. Calculate the transport number, mobility, and the speed under a potential gradient of 100 $V\ cm^{-1}$ for H^+ ions. (9%) **(23%)**