國立成功大學 104 學年度碩士班招生考試試題

系所組別：化學工程學系乙組

考試科目：物理化學

考試日期：0211，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: **(29%)**

(a) Explain the main differences between Langmuir isotherm and Freundlich isotherm. (4%)

(b) Does the vaporization of water at 1 atm and 100°C approach a reversible process? Why? (4%)

(c) Determine the numbers of degrees of freedom and suggest the required variables for a closed system with $CaCO_3(s)$, $CaO(s)$, $CO_2(g)$, and $Ar(g)$ in equilibrium at 25C. (4%)

(d) An ideal gas undergoes an isothermal expansion process from 10 bar to 1 bar at 300 K, what kinds of energies decrease in this system? (4%)

(e) Compare the entropy values of H_2, CO, N_2O, CO_2, Ar at the absolute zero temperature based on the statistical probability. (5%)

(f) What is relaxation time for a first-order reaction? (4%)

(g) Describe the effect of charge number on the thickness of ionic atmosphere. (4%)

2. One mole of ideal monatomic gas at 300 K and 1 bar is expanded to 0.1 bar adiabatically against an evacuated chamber, calculate the changes of internal energy (ΔU) (4%), entropy (ΔS) (4%), and Gibbs energy (ΔG) (4%). **(12%)**

3. If both ammonia and hydrogen can be adsorbed on the surface of Pt catalyst, (a) derive the adsorption isotherm of ammonia in the presence of hydrogen in terms of θ_A, K_A, K_H, P_A and P_H where θ is the fraction of the surface covered by adsorbed molecules, K is equilibrium constant, P is pressure, and the subscripts A and H denote ammonia and hydrogen, respectively. (8%); (b) derive the rate expression for the decomposition of ammonia into nitrogen and hydrogen ($2\,NH_3 = N_2 + 3\,H_2$) on a Pt catalyst if the adsorption of nitrogen is negligible. (5%) **(13%)**

4. Consider the cell $Ag\,|\,AgCl(s)\,|\,HCl(m_1)\,\vdots\,HCl(m_2)\,|\,AgCl(s)\,|\,Ag$ in which the solutions are separated by a membrane that is permeable to both H^+ and Cl^- ions. The ratio of the speeds with which these ions pass through the membrane is the ratio of their transport numbers, t_+ and t_-. (a) Write the half-cell reactions and cell reaction. (6%); (b) Derive the expression for the electromotive force (emf) of this cell (6%). (c) If the emf is 0.0190 V when m_1=0.01 m and m_2=0.10 m, what are the transport numbers of H^+ and Cl^- ions? (4%) **(16%)**

5. An enzyme reaction can be expressed as $E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + Z$, in which E is enzyme, S is substrate, ES is the complex of E and S, Z is product, and k_1, k_{-1}, and k_2 denote the rate constants,

(a) derive the Michaelis-Menten equation by steady-state treatment (8%); and

(b) prove that the activation energy *Ea* at any temperature is given by

$$Ea = \frac{k_{-1}(E_1 + E_2 - E_{-1}) + k_2 E_1}{k_{-1} + k_2}$$

, where E_1, E_{-1}, E_2 denote the activation energies for the rate constants k_1, k_{-1}, k_2, respectively. (8%) **(16%)**

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6. For a gas system that PV work is the only type of work involved, (a) show that

$$Cp - Cv = [P + (\frac{\partial U}{\partial V})_T](\frac{\partial V}{\partial T})_P$$ (6%); and (b) show that

$$C_P - C_V = \frac{nR}{1 - \frac{2na(V-nb)^2}{RTV^3}}$$ for a van der Waals gas (i.e., $(P + \frac{n^2 a}{V^2})(V - nb) = nRT$) (8%) **(14%)**