

※ 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:

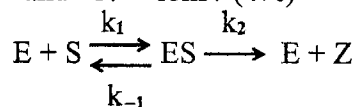
**(29%)**

- (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  $\text{CaCO}_3(\text{s})$ ,  $\text{CaO}(\text{s})$ ,  $\text{CO}_2(\text{g})$ , and  $\text{Ar}(\text{g})$  in equilibrium at 25°C. (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  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{Ar}$  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 ( $\Delta U$ ) (4%), entropy ( $\Delta S$ ) (4%), and Gibbs energy ( $\Delta G$ ) (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  $\theta_A$ ,  $K_A$ ,  $K_H$ ,  $P_A$  and  $P_H$  where  $\theta$  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 ( $2 \text{NH}_3 = \text{N}_2 + 3 \text{H}_2$ ) on a Pt catalyst if the adsorption of nitrogen is negligible. (5%) **(13%)**

4. Consider the cell  $\text{Ag} | \text{AgCl}(\text{s}) | \text{HCl}(m_1) :: \text{HCl}(m_2) | \text{AgCl}(\text{s}) | \text{Ag}$  in which the solutions are separated by a membrane that is permeable to both  $\text{H}^+$  and  $\text{Cl}^-$  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  $\text{H}^+$  and  $\text{Cl}^-$  ions? (4%) **(16%)**



5. An enzyme reaction can be expressed as  $\text{E} + \text{S} \xrightleftharpoons[k_{-1}]{k_1} \text{ES} \xrightarrow{k_2} \text{E} + \text{Z}$ , 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  $E_a$  at any temperature is given by

$$E_a = \frac{k_{-1}(E_1 + E_2 - E_{-1}) + k_2 E_1}{k_{-1} + k_2}, \text{ where } E_1, E_{-1}, E_2 \text{ denote the activation energies for the rate}$$

constants  $k_1, k_{-1}, k_2$ , respectively. (8%)

**(16%)**

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

$$C_p - C_v = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P \quad (6\%); \text{ and (b) show that}$$

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