

國立成功大學

111學年度碩士班招生考試試題

編 號： 79

系 所： 化學工程學系

科 目： 物理化學

日 期： 0219

節 次： 第 3 節

備 註： 可使用計算機

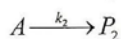
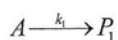
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※ 考生請注意：本試題可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

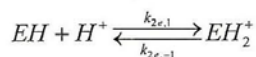
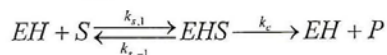
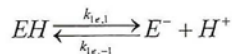
Useful constants:  $F=96485 \text{ C mol}^{-1}$ ,  $R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

1. Answer the following questions: (15%)

- a. What is the meaning of “state functions” in thermodynamics? Please provide some examples for state functions. (5%)
- b. Often in organic synthesis, the desired product is selectively synthesized through kinetic control. For example, the following reactions of reactant A lead to two different products,  $P_1$  and  $P_2$ . The activation energy for the reaction to  $P_1$  is greater than that of  $P_2$ . Will the ratio of product concentrations,  $[P_1]/[P_2]$ , increase or decrease if the temperature is raised? (5%)



- c. For some binary mixtures, positive or negative deviation from Raoult’s law occurs. Please provide some potential reasons for this phenomenon. (5%)
2. A mixture contains 0.330 mol fraction of toluene in benzene. The vapor pressure of benzene in the mixture is 6.677 kPa at 298 K. On the other hand, toluene exhibits a vapor pressure of 1.214 kPa in the mixture. Calculate the activity and activity coefficients for toluene in the above solution. The vapor pressures of pure benzene and pure toluene at 298 K are 9.657 kPa and 3.572 kPa, respectively. (10%)
3. The catalytic activity of enzymes often depends on the pH of the medium in which it operates. One way to account for this behavior is to propose that the enzyme-substrate complex is active only in specific protonation states as the following mechanism:



Derive a modified Michaelis-Menten equation based on the mechanism above. Please use the following equilibrium constants in your final expression. (20%)

$$K_{1e} = \frac{k_{1e,1}}{k_{1e,-1}} \quad K_{2e} = \frac{k_{2e,1}}{k_{2e,-1}} \quad K_m = \frac{k_{s,-1} + k_c}{k_{s,1}}$$

4. A Carnot engine involves the following process: (25%)

- (1) Reversible isothermal expansion at 1000 K from A to B. 150 kJ of heat is absorbed.
- (2) Reversible adiabatic expansion from B to C.
- (3) Reversible isothermal compression at 200 K from C to D.
- (4) Reversible adiabatic compression from D to A.
  - a. Plot the above process in a pressure-volume diagram. (5%)
  - b. What is the thermodynamic efficiency of the engine? (5%)
  - c. How much work is done in the process? (5%)
  - d. What is the overall entropy change for the entire cycle? (5%)
  - e. What is the change in Gibbs energy in step 1? (5%)

5. Suppose it is known that ozone ( $O_3$ ) adsorbs on a particular surface in accord with a Langmuir isotherm. How could you use the pressure dependence of the fractional coverage to distinguish between adsorption (1) without dissociation, and (2) with dissociation into  $O+O+O$ ? (10%)

6. Hexavalent chromium, Cr(VI), is a common compound for textile dyes, coating, and steel production. However, Cr(VI) is highly toxic and carcinogenic. Removal of Cr(VI) from wastewater is a key environmental issue. One common strategy is to use the redox reaction of Cr(VI) with Fe(II). Consider the following half-reactions:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O, \quad E^{\circ} = 1.33 \text{ V at pH} = 0$$

$$6Fe^{3+} + 6e^- \rightarrow 6Fe^{2+}, \quad E^{\circ} = 0.771 \text{ V at pH} = 0$$

(20%)

- a. Write the net reaction that converts  $Cr_2O_7^{2-}$  into  $Cr^{3+}$  using  $Fe^{3+}/Fe^{2+}$ , and calculate the emf at the standard state. (5%)
- b. The pH dependence of the net reaction can be expressed as the following: (5%)
 
$$E = E^{\circ'} + a \times \text{pH}$$

$$\text{where } E^{\circ'} = E^{\circ} - \frac{RT}{zF} \ln \frac{[Cr^{3+}]^2 [Fe^{3+}]^6}{[Cr_2O_7^{2-}] [Fe^{2+}]^6}$$

Determine the parameter "a" that relates pH to emf at 25 °C. Note:  $\ln(x) = 2.303 \times \log(x)$
- c. It is now obvious the reaction is spontaneous at acidic pH. Determine the pH that the reaction becomes "Not spontaneous". For simplicity, you may assume other electrolytes are at the standard state concentration. (5%)
- d. It is highly desirable to remove Cr(VI) at neutral pH. This can be achieved by stabilizing  $Fe^{3+}$  with small ligand molecules. For example, we can use the complexation of iron with ethylenediaminetetraacetic acid (EDTA).
 
$$[Fe(EDTA)]^- + e^- \rightarrow [Fe(EDTA)]^{2-}, \quad E^{\circ} = 0.08 \text{ V at pH} = 0$$

If we introduce enough EDTA to the wastewater, will this redox reaction become spontaneous at the pH you determined in part c? Make a brief calculation to explain your result. (5%)