PRINCE OF SONGKLA UNIVERSITY FACULTY OF ENGINEERING

Midterm Examination: Semester I Academic Year: 2004

Date: August 5, 2004 Time: 9:00-12:00

Subject: 230-620 Advanced Engineering Room: Chemical

Kinetics and Chemical Reactor Design engineering's Meeting

Room

อนุญาตให้นำเอกสารและเครื่องคำนวณทุกชนิดเข้าห้องสอบได้

ทุจริตในการสอบโทษขั้นต่ำคือปรับตกในรายวิชาที่ทุจริตและพักการศึกษา 1 ภาคการศึกษา

Please do all 6 questions, including bonus. Show all your work to receive full or partial credit. Total score is 120.

| Question # | Total Score | Score |
|------------|--------------------|-------|
| 1 | 20 | |
| 2 | 15 | |
| 3 | 15 | |
| 4 | 20 | |
| 5 | 25 | |
| 6 | 25 | |
| Total | 120 | |

สุกฤทธิรา (บุญเรื่อง) รัตนวิไล ผู้ออกข้อสอบ

Macro kinetics

1. The irreversible reaction

$$2A + B \xrightarrow{\kappa} A_2B$$

has been studied kinetically, and the rate of formation of product has been found to be well corrected by the following rate equation:

$$r_{A_2B} = \frac{0.72C_A^2C_B}{1 + 2C_A}$$

What reaction mechanism is suggested by this rate expression if the chemistry of the reactions that the intermediate consists of an association of reactant molecules and that a chain reaction does not occur? (20 points)

Micro kinetics and Catalysis

2. CO reacts with H₂O over Fe₂O₃ catalyst to form H₂ and CO₂. The rate has been found to agree with the experimental data and is shown below.

$$CO + H_2O \xrightarrow{\kappa} H_2 + CO_2$$

$$-r_{CO}' = \frac{k_1 P_{CO} P_{H_2O} - k_2 P_{H_2} P_{CO_2}}{\left(1 + k_3 P_{CO} + k_4 P_{H_2O} + k_5 P_{CO_2} + k_6 P_{H_2}\right)^2}$$

Propose an adsorption surface reaction-desorption mechanism (micro-kinetics) and specify the rate-limiting step that will explain rate law. (15 points)

3. The pyrolysis of acetaldehyde is believed to take place according to the following sequence (15 points):

CH₃CHO
$$\xrightarrow{\kappa_1} CH_3 \cdot + CHO \cdot$$
CH₃ · + CH₃CHO
$$\xrightarrow{\kappa_2} CH_3 \cdot + CO + CH_4$$
CHO · + CH₃CHO
$$\xrightarrow{\kappa_3} CH_3 \cdot + 2CO + H_2$$
2CH₃ · C₂H₆

- a. Derive the rate expression for the rate of disappearance of acetaldehyde
- b. Under what conditions does it reduce to

$$-r_{\text{CH3CHO}} = k[\text{CH}_3\text{CHO}]^{3/2}$$

Conceptual knowledge

- **4.** Answer the following questions in THAI LANGUAGE based on your understanding: **(5 points for each question)**
 - a. What are promoters and inhibitors?
 - b. What is homopolyner and copolymer? And also classified types of the copolymer.
 - c. What is the most common types of reversible inhabitation occurring in enzymatic reaction please explain and also compare among each type by using graph [graph plots between $(-1/r_s)$ and (1/S), S = substrate]
 - d. What are the advantages and disadvantages of recirculation transport reactor?

Rate data

5. Initial rate data of the following reaction are in table 1. (25 points)

$$H_2 + Br_2 \xrightarrow{\kappa} 2HBr$$

Using some of the data explore the kinetics of a reaction only for

- a. Over all order of reaction
- b. Reaction order with respect to individual reactants

Table 1 Initial rate data

| [H ₂]o, mol/l | [Br ₂]o, mol/l | $(-r_{H2})x10^3$ |
|---------------------------|----------------------------|------------------|
| 0.900 | 0.900 | 10.9 |
| 0.675 | 0.675 | 8.19 |
| 0.450 | 0.450 | 4.465 |
| 0.225 | 0.225 | 1.76 |
| 0.5637 | 0.2947 | 4.48 |
| 0.3103 | 0.5064 | 3.28 |
| 0.2881 | 0.1517 | 1.65 |
| 0.1552 | 0.2554 | 1.267 |

External diffusion

- **6.** A₂ diffuses at steady state from a bulk solution to a catalytic surface, where it dissociates instantaneously to form 2A. Species A then diffuses back into the bulk solution, which contains only A and A₂. **(25 points)**
 - a. From a differential mole balance on A_2 , derive a differential equation in terms of W_{A2} . State the appropriate boundary conditions.
 - b. After determining the proper relationship between W_{A2} and W_{A} , use expression for a molar flux to substitute for W_{A2} in the differential equation derived in Part (a)
 - c. Obtain concentration profile for A₂.

Solution Problem #4

a. Promoter as a substance added during the preparation on a catalyst which improves activity or selectivity or stabilizes the catalytic agent so as to prolong its life.

Inhibitor is the opposite of a promoter. When added in small amounts during catalyst manufacture, it lessens activity, stability, or selectivity. Inhibitors are useful for reducing the activity of a catalyst for an undesirable side reaction.

b.

- Homopolymer คือ polymer ซึ่งในโช่มีหน่วยที่ซ้ำๆกันเพียงชนิดเดียวเท่านั้น เช่น polyrthylene, polystyrene
- 2. Copolymer คือ polymer ซึ่งในโซ่มีหน่วยที่ซ้ำๆกัน 2 ชนิด หรือมากกว่า 2 ชนิด

Copolymer ที่มีหน่วยที่ซ้ำๆกัน 2 ชนิด อาจแบ่งตามลักษณะการจัดเรียงโมเลกูลของหน่วยที่ซ้ำๆกัน ออกได้เป็น

- 1. Alternating copolymer -A-B-A-B-A-B-A-B-A-
- 2. Block copolymer -A-A-A-B-B-B-B-A-A-

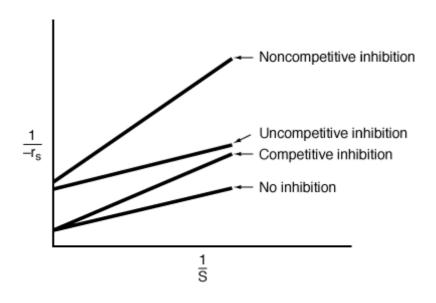
c.

The **three most common types** of reversible inhibition occurring in enzymatic reactions

- **I.** Competitive inhibition: the substrate and inhibitor are usually similar molecules that compete for the same site on the enzyme.
- **II. Uncompetitive Inhibition**: the inhibitor deactivates the enzyme-substrate complex by attaching itself to both the substrate and enzyme molecules of the complex.
- **III. Noncompetitive Inhibition:** Enzymes containing at least two different types of sites. The inhibitor attaches the only one type of site and the substrate only to the other.

Graph

- 1. In *competitive inhibition* the slope increases with increasing inhibitor concentration while the intercept remains fixed.
- 2. In *uncompetitive inhibition* the *y*-intercept increases with increasing inhibitor concentration while the slope remains fixed.
- 3. In *noncompetitive inhibition* both the intercept and slope will increase with observe the following relationships: increasing inhibitor concentration.



d. ข้อดี

- ให้ คอนเวอร์ชันสูง
- ประหยัดตัวเร่งใหม่ที่ใช้
- มีการสัมผัสกันของตั้งเร่งและสารป้อนดีมาก
- สามารถศึกษาในระดับห้องปฏิบัติการแล้วนำไป
- ประยุกต์ใช้ ได้ง่ายเนื่องจากมีความคล้ายคลึงกัน และมีข้อมูลทางจลนพลศาสตร์ที่น่าเชื่อถือ

ข้อเสีย

- ใช้กลไกที่ยุ่งยากกว่า STTR
- มีค่าใช้จ่ายเกี่ยวกับ โครงสร้างและการติดตั้งที่สูงกว่า STTR โดยจะมีส่วนของ recircutating pump หรือ recirculating jet เพิ่มขึ้น
- อาจพบปัญหาเกี่ยวกับการใหล เช่น มีการอุดตัน