台灣科技大學化工系博士班「高等化工動力學」資格考試試題

2004/12/30

Part I

1. (16 points)

The carbonation of allyl chloride (AC) is carried out over the Pd catalyst:

$$CH_2CHCH_2Cl + CO + NaOH \xrightarrow{Pd} C_3H_5COOH + NaCl$$

The rate law determined experimentally is of the form

$$-r_{AC} = kC_{CO}C_{AC}C_{NaOH} / (1+K_{AC}C_{AC})^2$$

The reaction mechanism is believed to be

$$Pd + CO \equiv Pd \cdot CO \text{ (reversible)}$$

$$Pd \cdot CO + NaOH \equiv Pd \cdot CO \cdot NaOH \text{ (reversible)}$$

$$AC + Pd \dashrightarrow AC \cdot Pd$$

$$AC \cdot Pd + Pd \cdot CO \cdot NaOH \longrightarrow C_3H_5COOH + NaCl + 2\,Pd$$

where Pd · CO, Pd · CO · NaOH, and AC · Pd represent the adsorbed species. Comment on the validity of the proposed reaction mechanism.

2. (17 points)

Species A, which is present in dilute concentrations, is diffusing at steady state from the bulk fluid through a stagnant film of B of thickness δ to the external surface of the catalyst pellet. The concentration of A at the external boundary is C_{Ab} and at the external catalyst surface is C_{As}, with $C_{Ab} > C_{As}$. Because the thickness of the boundary layer next to the surface is small with regard to the diameter of the particle, we can neglect curvature and represent the diffusion in rectilinear coordinates. Derive expressions for the concentration profile and the flux of A to the surface.

3. (17 points)

For the irreversible first-order isomerization reaction A ———> B that

occurs on the surface of the pore walls within the spherical pellet of radius R, a steady-state mole balance on species A results in the following governing equation with two boundary conditions:

$$d^2\varphi/dr^2 + 2/\lambda\,(d\varphi/d\lambda) - \Phi_n^2\,\varphi^n = 0$$

B.C.: (i) $\lambda = 0$ $===>$ φ is finite and (ii) $\lambda = 1$ $===>$ $\varphi = 1$

where $\varphi = C_A/C_{As}$, C_A and C_{As} are the concentrations of A at r = r ($0 < r < R$) and r = R, respectively, $\lambda = r/R$, $\Phi_n^2 = k_n R^2 S_a \rho_c C_{As}^{n-1}/D_e$ is the square of the Thiele modulus, k_n is the reaction rate constant, S_a is the surface area of the catalyst per unit mass of catalyst, ρ_c is the density of the catalyst, and D_e is the effective diffusivity.

(a) What is the significance of Φ_n^2?

(b) With the aid of the transformation $y = \varphi\ \lambda$, derive an expression for the above ordinary differential equation.

(c) For the two reaction systems with the Thiele modulus equal to 1 and 30, respectively, which process (surface reaction or internal diffusion) is the rate-limiting step?

Part II.

4. (20 points)

The exothermic reaction

$$A \rightarrow B + C$$

was carried out adiabatically and the following data recorded:

X Conversion	0	0.2	0.4	0.5	0.6	0.8	0.9
$-r_A$ ($mol/dm^3.min$)	10	16.67	50	50	50	12.5	9.09

The entering molar flow rate of A was 300 mol/min.

(a) What is the PFR (Plug Flow Reactor) volume necessary to achieve 40% conversion? (10 points)

(b) What is the CSTR (Continuous Stirred Tank Reactor) volume necessary to achieve the same conversion as in (a)? (10 points)

Show All Your Work.

5. (20 points)

Tarzlon is a liquid antibiotic (抗生素) that is taken orally (口服) to treat infections (感染) of the spleen (脾臟). It is effective only if it can maintain a concentration in the blood-stream (based on volume of body fluid) above 0.4 mg per dm^3 of body fluid. Ideally, a concentration of 1.0 mg/dm^3 in the blood would like to be realized. However, if the concentration in the blood exceeds 1.5 mg/dm^3, harmful side effects can occur. Once the Tarzlon reaches the stomach (胃) it can proceed in two pathways, both of which are first order: (1) It can be absorbed into the bloodstream (血液) through the stomach walls; (2) it can pass out through the gastrointestinal tract (腹部的腸道) and not be absorbed into the blood. Both these processes are first order in Tarzlon concentration in the stomach. Once in the bloodstream, Tarzlon attacks bacterial cells (細菌的細胞) and is subsequently degraded by a zero-order process. Tarzlon can also be removed from the blood and excreted in urine (分泌於尿液) through a first-order process within the kidneys (腎臟). In the stomach:

Absorption into blood	$k_1 = 0.15\ h^{-1}$
Elimination through gastrointestine	$k_2 = 0.6\ h^{-1}$

In the bloodstream:

Degradation of Tarzon	$k_3 = 0.1$ mg/dm^3.h
Elimination through urine	$k_4 = 0.2\ h^{-1}$

(a) Write down all of the reaction schemes involving the Tarzlon in the stomach (denoted by A) and the Tarzlon in the blood (denoted by B). (4 points)

(b) Derive two differential equations (including initial conditions) describing the variation of the Tarzlon in the stomach, whose concentration can be denoted by C_A, and the Tarzlon in the blood , whose concentration can be denoted by C_B, as a function of time when 1 dose (i.e. one liquid capsule) of Tarzlon is taken. (10 points)

(c) Solve the ODEs in (b) and obtain C_B as a function of time. Sketch $C_B(t)$ vs. time curve from t = 0 to t = 6 hr using the calculated values of C_B at t = 0, 2, 4, and 6 hr. (6 points)

Additional information: One dose of Tarzlon is 250 mg. in liquid form: Volume of body fluid = 40 dm^3.

Show All Your Work.

6. (10 points)

Cyclohexanol was passed over a catalyst to form cyclohexene and water:

cyclohexanol → cyclohexene + water

A → B + H

The following data were obtained.

Run	Reaction Rate ($mol/dm^3.s$) x 10^5	Partial Pressure of Cyclohexanol (P_A)	Partial Pressure of Cyclohexene (P_B)	Partial Pressure of Steam (H_2O) (P_H)
1	3.3	1	1	1
2	1.05	5	1	1
3	0.565	10	1	1
4	1.826	2	5	1
5	1.49	2	10	1
6	1.36	3	0	5
7	1.08	3	0	10
8	0.862	1	10	10
9	0	0	5	8
10	1.37	3	3	3

It is suspected that the reaction may involve a dual-site mechanism, but it is not known for certain. It is believed that the adsorption equilibrium constant for cyclohexanol is around 1 and is roughly one or two orders of magnitude greater than the adsorption equilibriums for the other compounds. Using these data, suggest a rate law and mechanism consistent with the data above.

Hint: For the reaction C $\rightarrow$ D, the surface reaction with a dual-site mechanism can be expressed as CS + S = DS + S, where S is the vacant site, and CS and DS are the species C and D adsorbed on the site S, respectively.

Show All Your Work.

Qualify Exam.

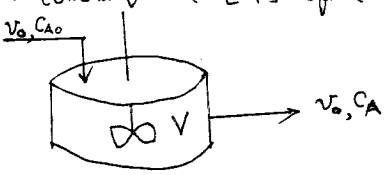
考試時間	月 日上午 下午第 節 (星期) 晚間	份數		任課教師	

國立臺灣科技大學 93 學年度第 學期 考試命題用紙 第 頁共 頁

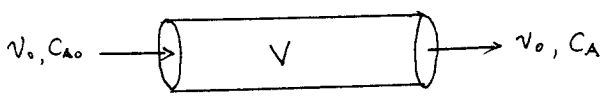
考試科目：Advanced Chemical Reaction Engineering ☐研究所 ☐大學部 ☐工程在職進修 系班別： First page

1. (10%) In a CSTR, the rate of disappearance of A, $-r_A = 1.25\times10^{-3}$ mol/dm^3·s, is evaluated and the conversion is that of the exit stream of the reactor, 80%. If the volume of this CSTR is 277.4 dm^3 and the entering molar flow rate is 0.867 mol/s, what is the conversion of A that has been achieved in the previous process before entering this CSTR? This CSTR is assumed to be operated under steady state and constant density.

2. (20%) A second-order liquid-phase reaction is being carried out in a CSTR, as shown in the following figure. Please derive the equation in which the conversion, X, is expressed in terms of Da, $Da = \tau k C_{A0}$. This CSTR is assumed to be operated under steady state and constant density. Here, k is the reaction rate constant and τ is equal to V/v_0.



3. (20%) A second-order liquid-phase reaction is being carried out in a plug flow tubular reactor as shown in the following figure. Please derive the equation in which the volume of the reactor, V, is expressed in terms of exit conversion X and other parameters. Here, k is the reaction rate constant. This plug flow tubular reactor is assumed to be operated under steady state and constant density.



4. (20%) A_2 molecule is adsorbed on the adsorbent surface and then decompases. The adsorption equation is shown as follows

$$A_2 + 2S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2A\cdot S \qquad (1)$$

where S is the active site for adsorption. Please derive the expression for $C_{A\cdot S}$, i.e. $C_{A\cdot S} = f(C_{A_2})$.

5. (15%) Irreversible gas-solid reaction

$$aA(g) + S(s) \longrightarrow \text{product} \qquad (2)$$

can be interpreted by a "shrinking core model". Solid S is a spherical pellet and the chemical reaction is first order with respect to gas concentration while zero order with respect to solid concentration

$$-r_A = a\,k_s\,C'_{As}\,C_{S0}$$
$$-r_S = k_s\,C'_{As}\,C_{S0}$$

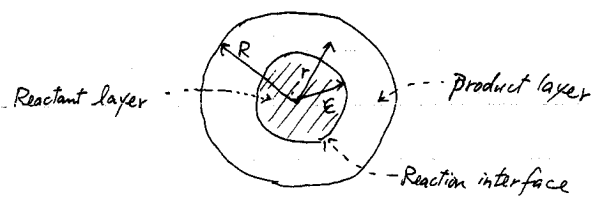
Please write out

(1) balance equation for gas A

(2) two boundary conditions

(3) balance equation for solid S

(4) initial condition



Use following notations in your equations.

D_e' = effective diffusivity

C'_{As} = concentration of gas A on product layer

C_S = concentration of solid S

C_{S0} = concentration of solid S at $t=0$

k_s = chemical reaction rate constant

k_g = mass transfer coefficient

C^s_{As} = concentration of gas A on pellet surface

t = reaction time

6. A first order gas reaction, $A(g) \xrightarrow{\text{solid catalyst}} B(g)$ takes place on the pore surface of a spherical porous catalyst. Gas A is diffused into the catalyst sphere from bulk gas outside the catalyst. Mass transfer resistance in the gas film outside of the catalyst can be neglected and the concentration of gas A on the external surface of a catalyst can be considered as a constant, $C_{As} = 1\times10^{-3}\ mol\cdot cm^{-3}$ (1 atm, 400°C). The ~~overall~~ reaction rate under the conditions of the external surface is $-r_A'' = 1\times10^{-9}\ mol\cdot s^{-1}\cdot cm^{-2}cat.$ Specific surface area and density of the catalyst are $S_a = 100\ m^2\cdot g^{-1}$ and $\rho_c = 1\ g\cdot cm^{-3}$, respectively. Effective diffusivity is $D_e = 1\times10^{-2}\ cm^2\cdot s^{-1}$. Please calculate the range of catalyst diameter, when the system is in the region of chemical reaction control. $\phi \equiv R\sqrt{\frac{k_1\rho_c S_a}{D_e}}$

$$\eta = \frac{3}{\phi^2}(\phi\coth\phi - 1)$$

命題請勿超出線外

93

台灣科技大學化工系博士班「高等化工動力學」資格考試試題

2004/12/30

Part I

1. (16 points)

The carbonation of allyl chloride (AC) is carried out over the Pd catalyst:

$$CH_2CHCH_2Cl + CO + NaOH \xrightarrow{Pd} C_3H_5COOH + NaCl$$

The rate law determined experimentally is of the form

$$-r_{AC} = kC_{CO}C_{AC}C_{NaOH} / (1+K_{AC}C_{AC})^2$$

The reaction mechanism is believed to be

$$Pd + CO \equiv Pd \cdot CO \text{ (reversible)}$$

$$Pd \cdot CO + NaOH \equiv Pd \cdot CO \cdot NaOH \text{ (reversible)}$$

$$AC + Pd \longrightarrow AC \cdot Pd$$

$$AC \cdot Pd + Pd \cdot CO \cdot NaOH \longrightarrow C_3H_5COOH + NaCl + 2\,Pd$$

where Pd · CO, Pd · CO · NaOH, and AC · Pd represent the adsorbed species. Comment on the validity of the proposed reaction mechanism.

2. (17 points)

Species A, which is present in dilute concentrations, is diffusing at steady state from the bulk fluid through a stagnant film of B of thickness δ to the external surface of the catalyst pellet. The concentration of A at the external boundary is C_{Ab} and at the external catalyst surface is C_{As}, with $C_{Ab} > C_{As}$. Because the thickness of the boundary layer next to the surface is small with regard to the diameter of the particle, we can neglect curvature and represent the diffusion in rectilinear coordinates. Derive expressions for the concentration profile and the flux of A to the surface.

3. (17 points)

For the irreversible first-order isomerization reaction A ———> B that

occurs on the surface of the pore walls within the spherical pellet of radius R, a steady-state mole balance on species A results in the following governing equation with two boundary conditions:

$$d^2\varphi/dr^2 + 2/\lambda\,(d\varphi/d\lambda) - \Phi_n^2\varphi^n = 0$$

B.C.: (i) $\lambda = 0$ $===>$ φ is finite and (ii) $\lambda = 1$ $===>$ $\varphi = 1$

where $\varphi = C_A/C_{As}$, C_A and C_{As} are the concentrations of A at r = r ($0 < r < R$) and r = R, respectively, $\lambda = r/R$, $\Phi_n^2 = k_n R^2 S_a \rho_c C_{As}^{n-1}/D_e$ is the square of the Thiele modulus, k_n is the reaction rate constant, S_a is the surface area of the catalyst per unit mass of catalyst, ρ_c is the density of the catalyst, and D_e is the effective diffusivity.

(a) What is the significance of Φ_n^2?

(b) With the aid of the transformation $y = \varphi\ \lambda$, derive an expression for the above ordinary differential equation.

(c) For the two reaction systems with the Thiele modulus equal to 1 and 30, respectively, which process (surface reaction or internal diffusion) is the rate-limiting step?

Part II.

4. (20 points)

The exothermic reaction

$$A \rightarrow B + C$$

was carried out adiabatically and the following data recorded:

X Conversion	0	0.2	0.4	0.5	0.6	0.8	0.9
$-r_A$ (mol/dm^3.min)	10	16.67	50	50	50	12.5	9.09

The entering molar flow rate of A was 300 mol/min.

(a) What is the PFR (Plug Flow Reactor) volume necessary to achieve 40% conversion? (10 points)

(b) What is the CSTR (Continuous Stirred Tank Reactor) volume necessary to achieve the same conversion as in (a)? (10 points)

Show All Your Work.

5. (20 points)

Tarzlon is a liquid antibiotic (抗生素) that is taken orally (口服) to treat infections (感染) of the spleen (脾臟). It is effective only if it can maintain a concentration in the blood-stream (based on volume of body fluid) above 0.4 mg per dm^3 of body fluid. Ideally, a concentration of 1.0 mg/dm^3 in the blood would like to be realized. However, if the concentration in the blood exceeds 1.5 mg/dm^3, harmful side effects can occur. Once the Tarzlon reaches the stomach (胃) it can proceed in two pathways, both of which are first order: (1) It can be absorbed into the bloodstream (血液) through the stomach walls; (2) it can pass out through the gastrointestinal tract (腹部的腸道) and not be absorbed into the blood. Both these processes are first order in Tarzlon concentration in the stomach. Once in the bloodstream, Tarzlon attacks bacterial cells (細菌的細胞) and is subsequently degraded by a zero-order process. Tarzlon can also be removed from the blood and excreted in urine (分泌於尿液) through a first-order process within the kidneys (腎臟). In the stomach:

Absorption into blood	$k_1 = 0.15\ h^{-1}$
Elimination through gastrointestine	$k_2 = 0.6\ h^{-1}$

In the bloodstream:

Degradation of Tarzon	$k_3 = 0.1$ mg/dm^3.h
Elimination through urine	$k_4 = 0.2\ h^{-1}$

(a) Write down all of the reaction schemes involving the Tarzlon in the stomach (denoted by A) and the Tarzlon in the blood (denoted by B). (4 points)

(b) Derive two differential equations (including initial conditions) describing the variation of the Tarzlon in the stomach, whose concentration can be denoted by C_A, and the Tarzlon in the blood , whose concentration can be denoted by C_B, as a function of time when 1 dose (i.e. one liquid capsule) of Tarzlon is taken. (10 points)

(c) Solve the ODEs in (b) and obtain C_B as a function of time. Sketch $C_B(t)$ vs. time curve from t = 0 to t = 6 hr using the calculated values of C_B at t = 0, 2, 4, and 6 hr. (6 points)

Additional information: One dose of Tarzlon is 250 mg. in liquid form: Volume of body fluid = 40 dm^3.

Show All Your Work.

6. (10 points)

Cyclohexanol was passed over a catalyst to form cyclohexene and water:

cyclohexanol → cyclohexene + water

A → B + H

The following data were obtained.

Run	Reaction Rate ($mol/dm^3.s$) x 10^5	Partial Pressure of Cyclohexanol (P_A)	Partial Pressure of Cyclohexene (P_B)	Partial Pressure of Steam (H_2O) (P_H)
1	3.3	1	1	1
2	1.05	5	1	1
3	0.565	10	1	1
4	1.826	2	5	1
5	1.49	2	10	1
6	1.36	3	0	5
7	1.08	3	0	10
8	0.862	1	10	10
9	0	0	5	8
10	1.37	3	3	3

It is suspected that the reaction may involve a dual-site mechanism, but it is not known for certain. It is believed that the adsorption equilibrium constant for cyclohexanol is around 1 and is roughly one or two orders of magnitude greater than the adsorption equilibriums for the other compounds. Using these data, suggest a rate law and mechanism consistent with the data above.

Hint: For the reaction C $\rightarrow$ D, the surface reaction with a dual-site mechanism can be expressed as CS + S = DS + S, where S is the vacant site, and CS and DS are the species C and D adsorbed on the site S, respectively.

Show All Your Work.