

Part I

- (1) (35%) Performing a steady-state mole balance on species A as it enters, leaves, and reacts in a spherical shell of inner radius r and outer radius $r + \Delta r$ of the catalyst pellet, a governing equation in a dimensionless form is

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

B.C. 1: C_A is finite at $r = 0$

B.C. 2: $C_A = C_{As}$ at $r = R$

where $\varphi = C_A/C_{As}$, $\lambda = r/R$, $\Phi_n^2 = k_n R^2 S_a \rho_c C_{As}^{n-1} / D_e$, C_{As} is the concentration of A at the external surface of the catalyst pellet ($r=R$), the surface chemical reaction is of n th order in the gas-phase concentration of A within the pellet ($-r_A'' = k_n C_A^n$), S_a is the surface area of the catalyst per unit mass of catalyst, ρ_c is the density of catalyst, and D_e is the effective diffusivity.

- (a) For a first-order reaction, obtain an expression for the concentration profile within the catalyst pellet (hint: $y = \varphi \lambda$). What is the significance of Φ_n^2 ? (20%)
 (b) For a first-order reaction, obtain an expression for the internal effectiveness factor. What is the significance of the internal effectiveness factor? (15%)

- (2) (15%) Hydrogen (H_2) and toluene (abbreviated as T) are reacted over a solid catalyst to yield methane (abbreviated as M) and benzene (abbreviated as B). Assuming that toluene is adsorbed on the catalyst surface and then reacts with hydrogen in the gas phase to produce benzene adsorbed on the catalyst surface and methane in the gas phase. Benzene is then desorbed from the catalyst surface. Derive a reaction rate law for the catalytic reaction system in the presence of an inhibitor (I) when the surface chemical reaction is the rate-limiting step.

Part II.

- (3) (20%)

The exothermic reaction



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

%)

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

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(4) (20 %)

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 $k_1 = 0.15 \text{ h}^{-1}$

Elimination through gastrointestinal $k_2 = 0.6 \text{ h}^{-1}$

In the bloodstream:

Degradation of Tarzlon $k_3 = 0.1 \text{ mg}/\text{dm}^3 \cdot \text{h}$

Elimination through urine $k_4 = 0.2 \text{ h}^{-1}$

- (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 %)
- (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 %)
- (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 %)

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

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(5) (10 %)

Compound A undergoes a reversible isomerization reaction, $A \rightleftharpoons B$, over a supported metal catalyst. Under pertinent conditions, A and B are liquid, miscible, and of nearly identical density; the equilibrium constant for the reaction (in concentration units) is 5.8. In a *fixed-bed isothermal flow reactor* in which backmixing is negligible (i.e. plug flow), a feed of pure A undergoes a net conversion to B of 55%. The reaction is elementary. If a second, identical flow reactor at the same temperature is placed downstream from the first, what overall conversion of A would you expect if the reactors are directly connected in series.

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考試 時間	月 (星期)	日上午 下午第 節 晚間	份數	任課 教師
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國立臺灣科技大學

學年度第

學期

考試命題用紙

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考試科目: Advanced Chemical Reaction Engineering

研究所

大學部

工程在職進修

系班別:

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Part I.

1. An experimental rate measurement on the decomposition of A is made with a particular catalyst (see (10%) pertinent data listed below).

(a) Is it likely that film resistance to mass transfer influences the rate?

(b) Could this run have been made in the regime of strong pore diffusion?

Data:

For the spherical particle:

$$d_p = 2.4 \text{ mm or } L = \frac{R}{3} = 0.4 \text{ mm} = 4 \times 10^{-4} \text{ m cat}$$

$$D_e = 5 \times 10^{-5} \text{ m}^2/\text{s} \cdot \text{m cat (effective mass conductivity)}$$

For the gas film surrounding the pellet:

$$k_g = 300 \text{ m}^3/\text{s} \cdot \text{m}^2 \cdot \text{cat (mass transfer coefficient)}$$

For the reaction:

$$-r_{A, \text{obs}}'' = 10^5 \text{ mol}/\text{s} \cdot \text{g} \cdot \text{m}^2 \cdot \text{cat}$$

$$C_{A, g} = 20 \text{ mol}/\text{m}^3 \text{ (at 1 atm and } 336^\circ\text{C)}$$

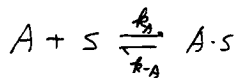
Assume that the reaction is first order.

Equations:

$$M_w = \frac{(-r_{A, \text{obs}}'') L^2}{D_e C_{A, g}}$$

$$\frac{\text{observed rate}}{\text{rate if film resistance controls}} = \frac{k_{\text{obs}}'' V_p}{k_g S_{\text{ext}}} = \frac{(-r_{A, \text{obs}}'') (\pi d_p^3/6)}{k_g (\pi d_p^2)}$$

2. The adsorption of A on a site S is represented by (20%)



and the conceptual model is depicted in Fig. 1.

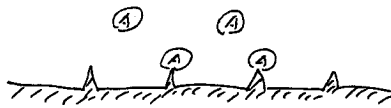


Fig. 1

Please derive the Langmuir isotherm.

$$C_{A \cdot S} = \frac{K_A P_A C_t}{1 + K_A P_A}$$

Use the following symbols

$C_{A \cdot S}$ = concentration of sites occupied by molecule A

C_t = total concentration of sites

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第二頁共 頁

考試科目: Advanced Chemical Reaction Engineering

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系班別:

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C_v = concentration of vacant sites
 k_{A1} = attach rate constant
 k_{-A} = detatch rate constant
 B_A = adsorption equilibrium constant, k_{A1}/k_{-A}
 P_A = partial pressure of A
 r_{Ad} = net rate of adsorption

3. The first-order isomerization $A \rightarrow B$ is being carried out isothermally in a batch reactor on (20%) a catalyst that is decaying as a result of aging. Derive an equation for conversion x_A as a function of time.

Equations:

- Design equation for a batch reactor $N_{A0} \frac{dx}{dt} = -r'_A W$
- Decay law for second-order decay by sintering $a(t) = \frac{1}{1+k_d t}$

Chemical Reaction Engineering- Part II

4. The gas phase reaction: $N_2 + 3H_2 \rightarrow 2NH_3$
 is to be carried out isothermally. The molar feed is 40% H_2 and 60% N_2 , at a pressure of 16.4 atm and 227 °C.
 (a) Please construct a complete stoichiometric table. (10%)
 (b) Please calculate the concentration of ammonia and hydrogen when the conversion of H_2 is 60%. (10%)

5. The elementary gas phase reaction



is carried out isothermally at 127 °C in a packed bed reactor in the presence of pressure drop. The relationship between pressure (P) and catalyst weight (W) can be expressed as

$$P = P_0 (1 - \alpha W)^{1/2} \quad \text{with } \alpha = 0.02/\text{g cat.}; P_0 = 10 \text{ atm}$$

The following parameters are given

$$k = 6.0 \text{ dm}^6/(\text{mol}\cdot\text{s}\cdot\text{g cat.}) \text{ at } 27 \text{ }^\circ\text{C}; C_{A0} = 0.2 \text{ mol/dm}^3; v_0 = 1 \text{ dm}^3/\text{s};$$

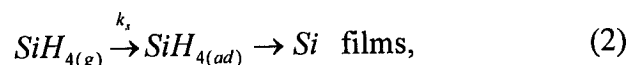
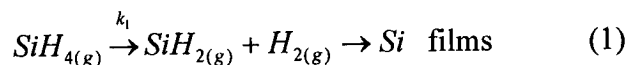
Please calculate the catalyst weight necessary to achieve 60% conversion in a packed-bed reactor. (20%)

6. (a) Please derive a general mole balance equation for a reactor system. (5%)
 (b) Please give the conditions or assumptions to get the reactor design equation of a plug flow reactor (PFR) in terms of conversion. (5%)

2007 反應工程資格考

簡答與計算題

1. A study of the chemical vapor deposition (CVD) of silica from silane (SiH_4) showed the following mechanism.

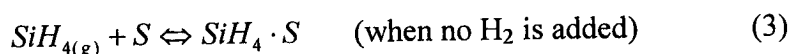


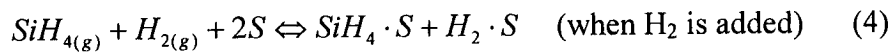
where Eq. (1) is the gas-phase decomposition of SiH_4 and Eq.(2) is the direct surface reaction of SiH_4 on wafer substrates, and the activation energy for k_1 (~50 kcal/mol) is larger than that for k_s (~20 kcal/mol). The recent Si based IC process for 12 inch wafers applies rapid thermal processing (RTP) as a single wafer alternative approach to batch furnaces as shown in Fig. (1). The use of IR lamps for wafer heating allows rapid temperature cycling and short time wafer processing. Since only wafer surface is heated, RTP-CVD reactor belongs to cold-wall type CVD reactor. However, there still has some possibility for gas-phase reaction to occur for SiH_4 may decompose within the thermal boundary layer above the wafer surface. The film growth mechanism of SiH_4 -CVD as illustrated in Fig. 1(c) is quite complex but can be categorized into two reaction pathways, i.e., the gas-phase and the surface reactions. Note that consecutive gas-phase reaction of SiH_4 with the gas-phase decomposed SiH_2 is easily to occur to form high order silanes ($\text{Si}_n\text{H}_{2n+2}$) which results in particle formation in the reactor.

Question 1: The overall reaction rate law for SiH_4 can be expressed as $-r_{\text{SiH}_4} = kC^{\alpha}_{\text{SiH}_4}$,

where k is the reaction rate constant, α is a concentration dependent factor and both gas-phase and surface reactions contribute to the film growth. Using first-order reaction approximation, the surface reaction rate constant k_s can be expressed by $k_s = (V/S)k$, where V/S is the volume-to-surface ratio of the reaction zone, and k is the gas-phase reaction rate constant in s^{-1} . What reaction conditions would you choose to minimize the gas-phase reaction path? (Hints: Please consider conditions such as reaction temperature, reactant concentration, reactant stream volumetric flow rate, reactor total pressure (adding inert gas or not), etc.)

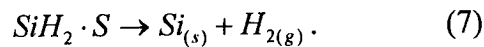
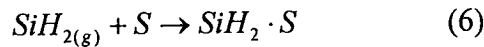
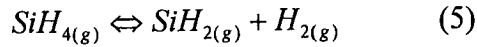
Question 2: Experiments demonstrated that adding H_2 gas will retard the direct surface reaction path of SiH_4 . Neglecting gas-phase reaction path and consider only the surface reaction of SiH_4 only. Firstly SiH_4 will adsorb on the substrate, followed by a series of surface reactions to form Si films. The adsorption reactions can be written as





Please derive the adsorption isotherms for $C_{\text{SiH}_4 \cdot S}$ for the two situations to show the effect of H_2 addition.

Question 3: A recent study showed that at moderate pressures (several Torr), the main film forming path is as follows.



According to the film growth scheme, please derive the rate of deposition as a function of SiH_4 and H_2 partial concentrations. (30%)

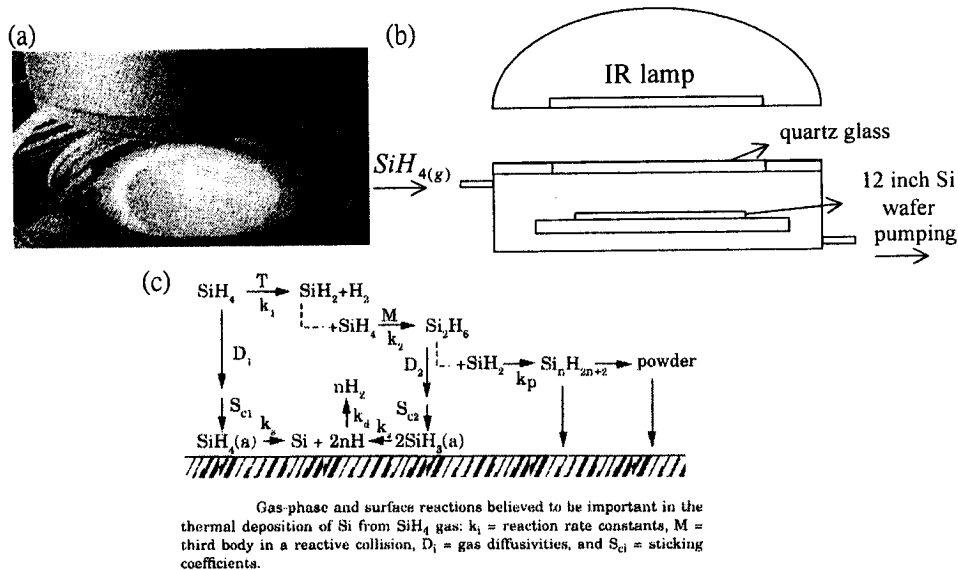
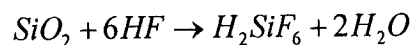


Fig. 1 (a) photo of a RTP-CVD reactor, (b) schematics of RTP-CVD system, (c) reaction mechanism of SiH_4 -CVD

2. Microelectronic devices are formed by first forming SiO_2 on a Si wafer by CVD (Fig. 2).

This procedure is followed by coating the SiO_2 with a photoresist. The pattern of the electronic circuit is then placed on the photoresist and the sample is irradiated with UV light. If the photoresist is a positive type, the sections that were irradiated with dissolve in the appropriate solvent, and those sections not irradiated will protect the SiO_2 from further treatment. The wafer is then exposed to strong acids, such as HF, which etch the exposed SiO_2 . It is extremely important to know the kinetics of the reaction so that the proper depth of the channel can be achieved. The dissolution reaction is



Question 1: From the following initial rate data, determine the rate law. Also estimate the etching rate at 1 wt% of HF.

Etching rate (nm/min)	60	200	600	1000	1400
HF (wt %)	8	20	33	40	48

Question 2: A total of 1000 thin wafer chips are to be placed in 0.5 dm³ of 20% HF. If a spiral channel 10 μm wide and 10 m in length were to be etched to a depth of 50 μm on both sides of each wafer, how long should the chips be left in the solution? Assume that the solution is well mixed. (20%)

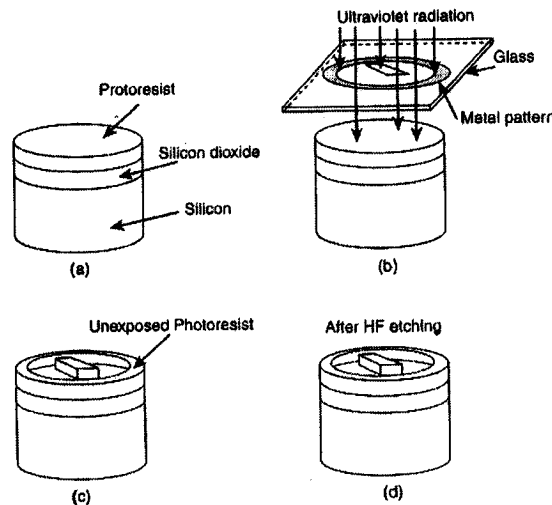


Fig. 2 Semiconductor etching

3. The hydrogenation of ethylene (A) to ethane (B) catalyzed by copper has been studied in a differential reactor. The data show that the rate may be expressed as follows

$$-r_A = \frac{kP_A P_{H_2}}{1 + K_A P_A + K_B P_B}$$

Propose a reaction mechanism and show that the mechanism is consistent with the rate expression. (15%)

4. The dehydrogenation of butane was carried out at atmospheric pressure using a spherical chromia-alumina catalyst of 0.32 cm diameter. The experimental data suggested a first-order rate constant of 0.94 cm³/s·g-cat. Assuming the diffusion in the pores of the catalyst is of Knudsen type and has a value of 3.97x10⁻² cm²/s, estimate the effectiveness factor for the catalyst.

Additional information:

void volume of the catalyst: 0.21 cm³/g-cat

tortuosity of the pores: 3.0

density of the catalyst: 2.5 g/cm³

(20%)

5. A second-order reaction, $A \rightarrow B$, was carried out at 500 K over a spherical catalyst of 0.2 dm diameter. It was known that the intrinsic rate constant was $1.8 \text{ dm}^3/\text{mol}\cdot\text{s}$. The mass-transfer coefficient through the external gas-film of the catalyst was 0.2 dm/s. If the concentration of A at the catalyst surface is $0.098 \text{ mol}/\text{dm}^3$ when the partial pressure of A in the gas phase is 4.1 atm, determine the effectiveness factor, η . (15%)