

國立成功大學

113學年度碩士班招生考試試題

編 號： 74

系 所： 化學工程學系

科 目： 化學反應工程

日 期： 0201

節 次： 第 3 節

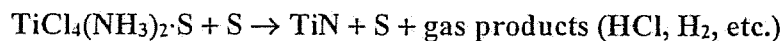
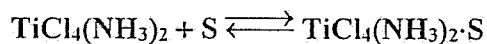
備 註： 可使用計算機

※ 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. Titanium nitride (TiN) films are used in decorative coatings as well as in wear-resistant tools. Titanium nitride films were formed by CVD from a mixture of TiCl_4 , NH_3 , H_2 and Ar. The following observations can be made from the experiment:

- The rate of deposition is independent of Ar and H_2 .
- At low partial pressures of both TiCl_4 and NH_3 , the deposition rate appears to be first-order in TiCl_4 and second-order in NH_3 .
- At high partial pressures of NH_3 , the rate varies inversely with TiCl_4 .

The following mechanism has been suggested for the reaction:



It is believed that the gas-phase reaction to form the complex $\text{TiCl}_4(\text{NH}_3)_2$ is in equilibrium.

- a. (8%) Determine the rate expression for the suggested mechanism.
- b. (5%) Discuss if the rate expression obtained in (a) agree with each experimental observation?
- c. (5%) Determine the reaction rate parameters from the data given below.

$r_{\text{Dep}} \times 10^8$	15	10	6	8.5	16
(mol TiN/cm ² ·min)					
P_{NH_3} (mT)	79	79	79	60	100
P_{TiCl_4} (mT)	1	3	10	2.3	2.3

2. (6%) What is the **physical meaning** of the internal effective factor (η) for spherical catalyst pellets and why its magnitude is between 0 and 1?
 (6%) For a first-order reaction in a spherical catalyst, what is the relationship between the internal effective factor (η) and the thiele modulus (ϕ_n)?
 (3%) When the thiele modulus (ϕ_n) is large, we can say the reaction is **internal diffusion-limited**. Is it true or not? Please explain the reason.

3. For reactions involving enzymes (biocatalysts), Michaelis-Menten kinetics that considers Pseudo Steady State Hypothesis (PSSH) is widely used to describe the relationship between the substrate and enzyme reaction as:



where E is the enzyme, S is the substrate, ES is the enzyme-substrate complex, and P is the desired product. In your textbooks, it is often stated that “the reaction of $E + S \rightleftharpoons ES$ is reversible and very fast” and “the reaction of $ES \rightarrow E + P$ is irreversible and very slow compared to the first reaction.”

- a、(8%) However, it is important to really understand if the assumptions are reasonable and valid instead of accepting them unquestioningly. Could you please explain why the first reaction can be considered reversible and fast, while the second reaction is deemed irreversible and slow? You may want to consider the nature of an enzyme or a catalyst.
- b、(8%) Based on your response to question (a), could you draw a Gibbs free energy diagram plotting the energy changes for both reactions on a single graph? Please include E , S , ES , and P on your diagram to visually represent the energy variations associated with these two reactions. Be careful of the relative energy changes. You may want to double-check that your graph matches your response to question (a).
4. Consider a non-isothermal batch reactor filled initially with an inert solvent and reactant A, undergoing an exothermic reaction $A \rightarrow B$ characterized by zero-order kinetics. Please ensure that you thoroughly examine all parts of this question and provide a clear rationale for your answers. Answers without justification/reasoning receive no credit.
- a、(8%) Please derive an analytical expression for the reactor temperature T as a function of time t before reactant A is completely depleted in the reactor.
- b、(6%) After a certain time, all reactant A will be consumed. Please derive an analytical expression for the reactor temperature T as a function of time t after reactant A has been all consumed in the reactor.
- c、(4%) What will be the temperature of the reactor after a very long time based on your answer in (b)?

Additional Information:

Zero-order rate constant k ($\text{mol}/\text{m}^3 \text{ s}$)

$k = C_1 + C_2 \cdot T$, where C_1 and C_2 are constants independent of T (T = reactor temperature (K))

(Note: Instead of the usual Arrhenius expression involving exponentials, the k above has been linearized in the temperature window of interest using a Taylor series expansion)

U = overall heat transfer coefficient ($\text{W}/(\text{m}^2 \cdot \text{K})$)

A = heat transfer area available in reactor (m^2)

T_a = ambient temperature (K)

ΔH_{rxn}^0 = standard-state enthalpy changes of reaction per mole of A reacted (< 0)

V = reactor volume (m^3)

C_p = same molar heat capacity for all species in reactor including inert solvent ($\text{J}/(\text{mol} \cdot \text{K})$)

N_{A0} = initial amount of A filled to reactor (moles)

N_S = amount of inert solvent charged to reactor (moles)

T_0 = reactor temperature at $t=0$ (K)

T_{max} = reactor temperature when all the species A are depleted

5. Calculate the ratio of the volumes of a CSTR and a PFR (V_{ST}/V_{PF}) required to achieve a fractional conversion of 0.5 for the reactant A with an identical feed rate for each reactor, if the liquid-phase reaction $A \rightarrow \text{products}$ is:

a、(6%) first-order with respect to A (please find the value of V_{ST}/V_{PF} ?)

b、(7%) second-order with respect to A (please find the value of V_{ST}/V_{PF} ?)

6. (20%) A 5-liter CSTR is used to carry out a liquid-phase reaction $A \rightarrow 2R$. Reactant A is fed to the reactor at a concentration of 1 mol/liter. We intend to find the kinetic parameters for this reaction by conducting experiments at different conditions. The experimental results are summarized as follows.

Run No.	Feed Rate (cm^3/sec)	Reaction Temperature ($^{\circ}\text{C}$)	Concentration of R in Output (mol/liter)
1	2	13	1.8
2	15	13	1.5
3	15	84	1.8

Please find the reaction order and activation energy for this reaction. [$R = 8.314 \text{ J}/(\text{mol K})$]