注意：考試開始鈴響前，不得翻閱試題，
並不得書寫、畫記、作答。

國立清華大學 113 學年度碩士班考試入學試題

系所班組別：化學工程學系

科目代碼：0902

考試科目：化工熱力學及化學反應工程

—作答注意事項—

1. 請核對答案卷（卡）上之准考證號、科目名稱是否正確。
2. 考試開始後，請於作答前先翻閱整份試題，是否有污損或試題印刷不清，得舉手請監試人員處理，但不得要求解釋題意。
3. 考生限在答案卷上標記「▼ 由此開始作答」區內作答，且不可書寫姓名、准考證號或與作答無關之其他文字或符號。
4. 答案卷用盡不得要求加頁。
5. 答案卷可用任何書寫工具作答，惟為方便閱卷辨識，請儘量使用藍色或黑色書寫；答案卡限用 2B 鉛筆畫記；如畫記不清（含未依範例畫記）致光學閱讀機無法辨識答案者，其後果一律由考生自行負責。
6. 其他應考規則、違規處理及扣分方式，請自行詳閱准考證明上「國立清華大學試場規則及違規處理辦法」，無法因本試題封面作答注意事項中未列明而稱未知悉。

國立清華大學 113 學年度碩士班考試入學試題

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考試科目（代碼）：化工熱力學及化學反應工程（0902）

Problem 1 (10%)

An *A-B* binary α phase is a solution phase. At temperature T and 1 atm, the Gibbs energy of the α phase is:

$$\Delta G^{\alpha} = (1 - x_B^{\alpha})G_A^{o,\alpha} + x_B^{\alpha}G_B^{o,\alpha} + RT[(1 - x_B^{\alpha})\,ln(1 - x_B^{\alpha}) + x_B^{\alpha}lnx_B^{\alpha}] + 400(1 - x_B^{\alpha})x_B^{\alpha}.$$

$G_A^{o,\alpha}$ and $G_B^{o,\alpha}$ are the standard Gibbs free energies at temperature T and 1 atm of pure A and B, respectively. x_B^{α} is the mole fraction of component B in the α solution phase.

(A). Is the α phase an ideal solution? Why or why not? **(4%)**

(B). What is the partial Gibbs free energy of B in the α phase, $\bar{G}_B^{\alpha}$? **(6%)**

Problem 2 (10%)

The Gibbs energy of the gas-phase oxidation at 25°C of SO_2 to SO_3

$$SO_2 + \frac{1}{2}O_2 \leftrightarrow SO_3$$

$\Delta G_{298\ K}^{0}$, is -70866 J/mol.

(A). Does the reaction proceed to the right-hand side or to the left-hand side? *i.e.*, does SO_2 oxidize to form SO_3, or does SO_3 decompose to form SO_2 and oxygen? Why? **(4%)**

(B). A variable ε called the reaction coordinate, is defined as $\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \frac{dn_3}{\nu_3} = d\varepsilon$. It characterizes the extent to which a reaction has taken place. n is the number of moles, and ν is the stoichiometric number for a species. Draw a schematic plot of the total Gibbs energy as a function of the reaction coordinate, a G-ε diagram, and illustrate this plot. **(6%)**

Problem 3 (20%)

A liquid-phase, auto-catalytic reaction consists of the following elementary mechanism:

$$A + B \xrightarrow{k} 2B$$

where the rate of A disappearance is:

$$-r_A = kC_AC_B$$

k = 1.0 L/mol·min (at 5 °C; obey the Arrhenius' Law)

The above auto-catalytic reaction is conducted in an isothermal plug flow reactor (PFR) with a recycle stream (see the attached figure), where R is the ratio of the molar flow rate of the recycle stream to the exit stream (stream e), *i.e.*,

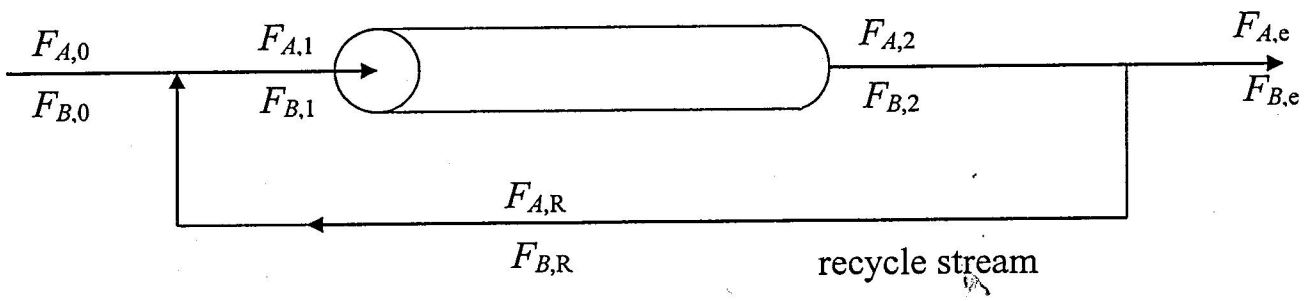
$$R = \frac{F_{total,R}}{F_{total,e}} = \frac{F_{A,R}}{F_{A,e}} = \frac{F_{B,R}}{F_{B,e}}$$

The feed concentrations of A (C_{A0}) and B (C_{B0}) are 0.99 mol/L and 0.01 mol/L, respectively. The desired exit concentrations of A (C_{Ae}) and B (C_{Be}) are 0.1 mol/L and 0.9 mol/L, respectively.

(A). At 5 °C, please determine the space time of this PFR with a recycle stream to achieve the desired exit concentrations when this reactor achieves a PFR. **(4%)**

(B). At 5 °C, this PFR with a recycle stream mimics a continuous stirred-tank reactor (CSTR) at a certain condition. How is it achieved? **(3%)**
What is the space time of this CSTR-like reactor to reach the desired exit concentration? **(3%)**
What is the space time when this CSTR-like reactor is operated at 15 °C? **(3%)**
Assuming the activation energy of this auto-catalytic reaction is 46 kJ/mol.

(C). Having two PFRs with a recycle stream attached to each reactor, how can the two reactors be connected in series to achieve the shortest space time? **(3%)**
Determine the corresponding shortest space time if both reactors are operated at 5 °C. **(4%)**



Problem 4 (10%)

In a batch reactor, the following reaction is carried out:

$$A \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} B \xrightarrow{k_2} C \underset{k_{-3}}{\overset{k_3}{\longleftrightarrow}} D$$

Where $k_1 = 3\ min^{-1}$; $k_{-1} = 8/3\ min^{-1}$; $k_2 = 22/3\ min^{-1}$; $k_3 = 2\ min^{-1}$; $k_{-3} = 3\ min^{-1}$

Here, C is the desired product and D is the isomer of C. This means that D and C are typically very difficult to separate, leading to high separation cost if the formation of D is not well controlled. As a chemical engineer, you are expected to use the provided information to model the composition of the reactant mixture as a function of time. Then, the optimum reaction time that leads to the highest C/D ratio can be determined without carrying out try-and-error type experiments that are both time-consuming and cost-ineffective.

(A). List down the rate equations that model the reaction system. **(2%)**

(B). The reactor is initially fed with 500 mM pure A. Solve and plot the concentration profile of each species, which are functions of time. **(4%)**

(C). What is the maximum difference between the concentration of C and D and when does it occur? **(2%)**

(D). If B is the desired product, what is the maximum concentration one can obtain and when does it occur? **(2%)**

Problem 5 (10%)

Carbon capture and utilization is an attractive way of providing economic incentives to drive efforts in converting waste CO_2 into value-added chemicals. The hydrogenation of CO_2 by green hydrogen may be a practical route to convert CO_2 into various products. Under low pressure, the primary products are usually carbon monoxide (CO) or methane (CH_4). As a chemical engineer, you are expected to use the provided thermodynamic data to calculate the equilibrium conversion of CO_2 towards CO and CH_4.

Species (gas phase)	Formation Enthalpy (kJ/mol)	Entropy at 1 bar (J/mol/K)
CO_2	-393.51	213.8
CO	-110.53	197.6
CH_4	-74.8	186.25
H_2	-	130.68
H_2O	-241.83	188.84

(A). Calculate the equilibrium constants of the hydrogenation reaction of CO_2 to CO and CO_2 to CH_4 individually at 500°C and 700°C. **(4%)**

(B). Calculate the equilibrium conversion of the hydrogenation reaction of CO_2 to CO and CO_2 to CH_4 individually at 500°C and 700°C if the reactor is initially fed with equal molars of CO_2 and H_2. **(4%)**

(C). If the pressure inside the reactor is increased from 1 bar to 10 bars, please qualitatively describe how the equilibrium conversion of CO_2 will change for the hydrogenation towards CO and CH_4. **(2%)**

Problem 6 (20%)

For an irreversible reaction:

$$2A + B \rightarrow A_2B$$

The reaction rate is:

$$r_{A_2B} = \frac{k_2 C_A^2 C_B}{1 + k_1 C_A}$$

The chemistry of the reaction suggests that the intermediate consists of an association of reactant molecules. In other words, the whole reaction is actually composed of multiple elementary steps involving the formation and consumption of key reaction intermediates. The pseudo-steady-state assumption applies to the intermediate in this case.

(A). What is the pseudo-steady-state assumption? **(5%)**

(B). For the two proposed reaction mechanisms listed below, which one is to accurately describe the irreversible reaction listed above? The pseudo-steady-state assumption applies to the intermediate in this case. **(15%; Derivation must be presented in details to get full credit)**

Mechanism 1:
$A + A \leftrightarrow A_2^*$
$A_2^* + B \rightarrow A_2B$

Mechanism 2:
$A + B \leftrightarrow AB^*$
$AB^* + A \rightarrow A_2B$

Problem 7 (20%)

The van der Waals equation (see equation below), coined after the Dutch physicist Johannes Diderik van der Waals, expands upon the ideal gas law by incorporating the influences of intermolecular interactions and the finite size of gas molecules.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

(A). Calculate the work (in J) done by 3 mole of CO_2 gas (a=3.640 L^2bar/mol^2, b=0.04267 L/mol) following an isothermal reversible expansion from 1 liter to 3 liter at 300 K. **(5%)**

(B). The compressibility factor describes the deviation of a real gas from ideal gas behavior. It is usually a function of pressure for a real gas. Following question 7(A), calculate the average compressibility factor ($\bar{Z}$) over the reversible expansion process for CO_2. **(10%)**

(C). The figure below depicts the compressibility factor curves across a range of pressure for four gases: ideal gas, CO_2, H_2, and methane. Identify the respective gas for each curve. Only with all correct answers will you receive a score. **(5 %)**