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 112 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。

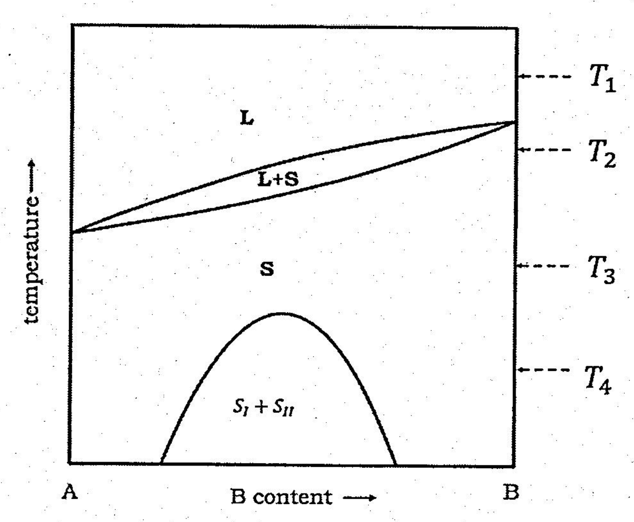
Problem 1 (20%)

1. One mole of an ideal gas is compressed isothermally but irreversibly at 100 °C from 4 to 6.5 bar in a piston/cylinder device. The work required is 20% greater than the work of a reversible isothermal compression. The heat transferred from the gas during the compression flows to a heat reservoir at 25 °C. Calculate the entropy changes of the gas, the heat reservoir, and ΔS^{total}. ***(10%)***

2. A design for purifying helium consists of an adiabatic process that splits a helium stream containing 30 mole percent methane into two products streams, one containing 97 mole percent helium, and the other 90 mole percent methane. The feed enters at 10 bar and 117 °C; the methane-rich product leaves at 1 bar and 27 °C; the helium-rich product leaves at 50 °C and 15 bar. Moreover, work is produced by the process. Assuming helium an ideal gas with Cp = (5/2)R and methane an ideal gas with Cp = (9/2)R. Calculate the total entropy change of the process on the basis of 1 mol of feed. Does the process violate the second law? ***(10%)***

Problem 2 (20%)

3. The figure shown below is a *T-X* (Temperature-composition) phase diagram of an *A-B* binary system. There is one liquid phase, **L**. At higher temperature, there is only one solid phase, **S**. At lower temperature, there is a miscibility gap and there are two solid phases, the A-rich S_I, and the B-rich S_{II}. Draw schematic $\Delta G - X$ (Gibbs free energy-composition) diagrams of both liquid and solid phases at T_1, T_2, T_3 and T_4. ***(10%)***



Temperature-composition phase diagram

4.(a) The Gibbs free energy of pure liquid A and pure liquid B are $\Delta G_A^{o,Liquid}$ and $\Delta G_B^{o,Liquid}$, respectively. The liquid phase is an ideal solution phase. What is the Gibbs free energy of liquid phase at temperature T and at composition X_B^{Liquid}? ***(5%)***

(b) Is the solid phase an ideal solution according to the attached figure shown above? Why? ***(5%)***

Problem 3 (20%)

5. An irreversible, liquid phase, series reaction is expected to be operated in single isothermal continuous stirred-tank reactor (CSTR; system I) or in two isothermal CSTRs connected in series (system II). The series reaction (see below) obeys the elementary rate law:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Where the rate constants of A → B and B → C are equal to k_1 and k_2, respectively. In these two systems, there are no B and C initially (i.e., $C_{B0} = 0$; $C_{C0} = 0$), and the initial concentration of A is C_{A0}. Please show that the maximum concentration of B obtained at the optimal space time (i.e., $\tau_{B,max}$) in system I is always higher than the concentration of B obtained in system II with any space time of the two CSTRs connected in series. ***(10%)***

6. A liquid phase, irreversible reaction (A → B) follows an elementary rate law. The reaction rate constant is equal to k with an activation energy of 50 kJ/mol. The initial concentration of A (C_{A0}) is equal to 2 mol/dm^3. The conversion ratio in an isothermal CSTR under steady state was 0.25 when the reaction was conducted at 25°C. For the same reactor under steady state and the same entrance flow conditions, what will be the reaction temperature if the conversion ratio reaches a value of 0.5? ***(10%)***

Problem 4 (20%)

7. The liquid phase reaction

Triphenyl methyl chloride (A) + Methanol (B) → Products

was carried out in a batch reactor at 25 °C in a solution of benzene and pyridine in an excess of methanol (C_{B0} = 0.5 mol/dm^3). Pyridine reacts with HCl, which then precipitates as pyridine hydrochloride thereby making the reaction irreversible. The reaction is second order in triphenyl methyl chloride and first order in methanol. The concentration of triphenyl methyl chloride (C_A) was measured as a function of time (t) shown below：

t (min)	0	50	100	150	200	250	300
C_A (mol/dm^3)	0.05	0.038	0.0306	0.0256	0.0222	0.0195	0.0174

Please determine the rate constant k of this liquid phase reaction. *(10%)*

8. Nitrogen pentoxide reacts with nitric oxide in the gas phase according to the stoichiometric equation:

$$N_2O_5 + NO \leftrightarrow 3NO_2$$

The following mechanism has been proposed.

$$N_2O_5 \overset{k_1}{\rightarrow} NO_2 + NO_3$$

$$NO_2 + NO_3 \overset{k_2}{\leftarrow} N_2O_5$$

$$NO + NO_3 \overset{k_3}{\rightarrow} 2NO_2$$

We can assume that the steady-state approximation can be applied to NO_3. Please derive the equation for the rate of consumption of N_2O_5. *(10%)*

Problem 5 (20%)

9. Compound A undergoes a reversible isomerization reaction as follows:

$$A \leftrightarrow B.$$

The equilibrium constant of the above reaction is 5.8.

Here, an isothermal plug flow reactor (PFR) is employed for this reaction, where a feed of pure A undergoes a net conversion to B of 55%. The reaction is elementary.

If a second identical PFR at the same temperature is placed downstream from the first one, what overall conversion of A will you expect in the following two scenarios?

(a) The second PFR is directly connected in series. ***(10%)***

(b) The products from the first PFR are separated by appropriate processing and only unconverted A is fed into second PFR. ***(10%)***