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 114 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 ：1002

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 (10%)

Consider a binary *A-B* system in vapor/liquid equilibrium. At a constant pressure of 1 atm, the boiling point of *A* is 300°C, and that of *B* is 400°C. The vapor phase is an ideal solution. The Gibbs energies of pure *A* and pure *B* in the vapor phase are $\Delta G_A^{o,gas}$ and $\Delta G_B^{o,gas}$, respectively.

(a) (2%) What is the enthalpy change of mixing of the vapor phase?

(b) (2%) What is the Gibbs energy change of mixing of the vapor phase?

(c) (3%) What is the partial Gibbs energy of *A*, $\bar{G}_A^{gas}$, in the vapor phase?

(d) (3%) The *A-B* binary system is an isomorphous system. It has an azeotrope at 220 °C and 60.0at.%A-40.0at.%B. Draw a binary *A-B* temperature-composition (*T-x*) phase diagram with a temperature range from 100 °C to 600 °C, and label all the phase regions.

Problem 2 (10%)

Consider a binary *A-B* system in liquid/solid equilibrium. At a constant pressure of 1 atm, the melting point of *A* is 300 °C, and that of *B* is 400 °C. The *A-B* binary system is isomorphous at higher temperatures, and at temperatures lower than 220 °C exhibits a miscibility gap with a critical concentration at 60 at.%A-40 at.% B.

(a) (3%) Draw a binary *A-B* temperature-composition (*T-x*) phase diagram with a temperature range from 100°C to 600 °C, and label all the phase regions.

(b) (2%) Draw a schematic Gibbs energy–composition (*G-x*) diagram showing both the liquid phase and the solid phase at 350 °C.

(c) (3%) Draw a schematic Gibbs energy–composition (*G-x*) diagram showing both the liquid phase and the solid phase at 200 °C.

(d) (2%) Is the solid solution an ideal solution? Why or why not?

Problem 3 (20%)

In thermodynamics, the isothermal compressibility quantifies the instantaneous relative change in volume of a material in response to a change in pressure. Mathematically, isothermal compressibility β is expressed as:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

where V, p, and T are volume, pressure, and temperature, respectively.

(a) (5%) Derive the expression of β for the ideal gas as a function of p.

(b) (10%) A liquid **A** exhibits a constant isothermal compressibility β over a pressure range from p_1 to p_2. Show that the reversible isothermal work w required to compress liquid **A** from an initial volume V_1, (at a pressure p_1) to a final volume V_2 (at a pressure p_2) is given by:

$$w = -p_1(V_2 - V_1) + \frac{V_1}{\beta}\left(\frac{V_2}{V_1} ln\frac{V_2}{V_1} - \frac{V_2}{V_1} + 1\right)$$

(c) (5%) Following (b), it can be shown that if β is small (incompressible fluid), the w can be approximated as:

$$w \approx \frac{\beta V_1}{2}(P_2^2 - P_1^2)$$

Using this equation, calculate the work required to compress one mole of liquid **A** reversibly and isothermally from 1 bar to 10 bar at 300 K. Take the value of β to be 10^{-5} bar^{-1} and the molar volume to be 10^{-1} L/mol at 300 K.

Problem 4 (10%)

Assuming platinum (Pt) oxidation and dissolution impedes the durability of hydrogen fuel cells, especially under very low electrode loading. Modeling Pt oxidation and dissolution in a fuel cell cathode is therefore very important. Assuming the oxidation and dissolution of Pt follows the reactions below

$$Pt + H_2O \xrightarrow{k_1} PtO + 2H^+ + 2e^-$$

$$PtO + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} PtO_2 + 2H^+ + 2e^-$$

$$PtO + 2H^+ \xrightarrow{k_3} Pt^{2+} + H_2O$$

where $k_1 = 1$, $k_2 = 3$, $k_{-2} = 5$, and $k_3 = 4$.

As a chemical engineer, you are expected to use the provided information to model the oxidation and dissolution of Pt over time.

(a) (3%) List down the differential equations to model the dynamic changes of Pt-containing species.

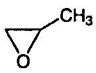
(b) (7%) The Pt on the electrode was originally pure metallic. Assuming that water, protons, and electrons are in excess, how does the content of PtO change with time?

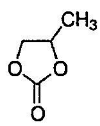
(Please derive the PtO content as a function of time)

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 conversion of CO_2 and propylene oxide (PO) into propylene carbonate (PC) is a route considered by many chemical companies.

Species	Formation Enthalpy (kJ/mol)	Entropy at 1 bar (J/mol/K)
$CO_{2(g)}$	-393.51	213.8
$PO_{(g)}$	-94.68	287.4
$PC_{(l)}$	-613	218.6
$H_2O_{(l)}$	-285.83	69.95

PO: 

PC: 

(a) (5%) Calculate the equilibrium constant of the reaction of CO_2 and PO to form PC at 180 °C.

(b) (5%) Calculate the equilibrium conversion at 180 °C if the reactor is initially fed with a CO_2-to-PO ratio of 1.

Problem 6 (20%)

The elementary irreversible gas phase reaction 2A→B is carried out in a constant volume batch reactor where 50 % conversion is achieved in 1 hour. Pure A is charged to the reactor at an initial concentration of 0.2 mol/dm^3. If the same reaction is carried out in a CSTR, what volume would be necessary to achieve 50 % conversion for a feed molar flow rate of 500 mol/h and an entering concentration of A of 0.2 mol/dm^3?

Problem 7 (20%)

(20%) A mixture containing 28% SO_2 and 72% air (comprising 21% O_2 and 79% N_2) is introduced into a flow reactor, where it undergoes gas-phase oxidation under constant isothermal and isobaric conditions.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

(a) (10%) Please show the concentrations SO_2, SO_3, O_2, and N_2 as functions of conversion for the case when the total pressure is 1485 kPa and the temperature is constant at 500 K.

(b) (10%) Please create a plot showing the concentrations of SO_2, SO_3, O_2, and N_2 as functions of conversion (X = 0, 0.25, 0.5, and 1).