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 115 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. 提早交卷者不可攜出試題，請將試題連同答案卷(卡)交予監考人員，攜出將以違規論處。當節考試結束後試題將置於講台，可自行取回，本試場不負保管責任。
7. 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%)

(a) (3%) Draw a *P-V* (pressure-volume) diagram of a pure substance. Mark on the diagram the phase regions, the critical point, and the triple-point line.

(b) (3%) Draw an *H-S* (enthalpy-entropy) diagram of a pure substance. Mark on the diagram the phase regions, the critical point, and the triple-point line.

(c) (2%) There is a pure substance with a vaporization point of 100 °C at 1 atm. Draw a schematic *G-T* (Gibbs free energy–temperature) diagram of the liquid phase and the vapor phase at 1 atm over a temperature range from 50 °C to 150 °C.

(d) (2%) For the same substance as in (c), draw a schematic *H–T* (enthalpy–temperature) diagram of the liquid phase and the vapor phase at 1 atm over the temperature range from 50 °C to 150 °C.

Problem 2 (10%)

A binary *A–B* system at 1 atm over the temperature range from 200 °C to 800 °C has two liquid phases and one vapor phase. The vapor phase and the two liquid phases are in equilibrium at 400 °C. The solubility of both liquid phases is maximum at 400 °C and occurs at A–20.0 at.% B and A–85.0 at.% B.

(a) (4%) Draw a schematic T–X_B (temperature–composition of component *B*) phase diagram for the binary *A–B* system at 1 atm over the temperature range from 200 °C to 800 °C.

(b) (3%) Draw a schematic G-X_B (Gibbs free energy–composition of component *B*) diagram at 300 °C of both the vapor phase and the liquid phase.

(c) (3%) Draw a μ_B - X_B (Chemical potential of component *B*–composition of component *B*) diagram at 300 °C of the liquid phase.

Problem 3 (10%)

A volume V_1 tank (tank 1) containing air with Cp* = a J/(mol K) at temperature T_1 K and pressure P_1 bar is

(a) (4%) Pumped to P_2 bar using a pressurized motor with the air at temperature T_0 K and Pressure P_0 bar. The air is an ideal gas and this is an adiabatic process. What is the final temperature of the gas in tank 1?

(b) (4%) Vented to another tank with volume $3V_1$ (tank 2) until the pressure drops to P_2 bar. Assume that the air is an ideal gas and this is an adiabatic and reversible process. What is the final temperature of gas in tank 1?

(c) (2%) Following question (2), if tank 2 is not evacuated, the tank contains same air

at temperature T_3 K and pressure P_3 bar. Will the final temperature in tank 2 increase or decrease?

Problem 4 (10%)

A gas turbine in a small electric power plant is designed to accept 100 mol/hr of gas at 1000 kPa bar and 500°C, and exhaust the gas at 100 kPa. Assume that the gas turbine is adiabatic and has been well designed (so that the entropy generation rate ~ 0), please compute the exit temperature and the power generated by the turbine.

(a) (4%) Assume that it is an ideal gas with $Cp^* = 30$ J/(mol K).

(b) (6%) The gas is a non-ideal gas with $Cp = 29 + 0.003T$ J/(mol K) and the equation of state is $P(\underline{V} - b)=RT$ where $b= 4.0 \times 10^{-5}$ (m^3/mol).

Problem 5 (20%)

A liquid-phase, electroless deposition of Cu from Cu^{2+} follows the reaction:

$$Cu^{2+}_{(aq)} + HCHO_{(aq)} + 2OH^- \rightarrow Cu_{(s)} + HCOO^-_{(aq)} + H_2O_{(l)} + H_{2(g)}$$

This irreversible reaction is an autocatalytic reaction with a rate law: $r_{Cu} = k_{Cu}C_{Cu}C_{HCHO}$ where k_{Cu}, C_{Cu}, and C_{HCHO} correspond to the rate constant, Cu^{2+} concentration, and HCHO concentration, respectively. In order to get the advantage of this autocatalytic reaction, the surfaces of the polyimide substrates were initially coated with a very uniform monolayer of metallic Cu atoms by an atomic layer deposition instrument. The batch reactor volume of deposition bath is 10 L, the total exposed surface area of the polyimide substrates in each batch is 1600 cm^2, the density of metallic Cu is 9 g/cm^3, the atomic weight of Cu is 63 g/mol, and the Avogadro constant is 6×10^{23}. If the electroless deposition is conducted at 50 °C and the turnover frequency of this autocatalytic reaction on metallic Cu atoms is 10/s at 50 °C when the equal molar concentration of Cu^{2+} and HCHO in the deposition bath is 2 M.

(a) (10%) Please estimate the deposition rate of metallic Cu in nm/min at 50 °C if both the initial concentrations of Cu^{2+} and HCHO are equal to 2 M.

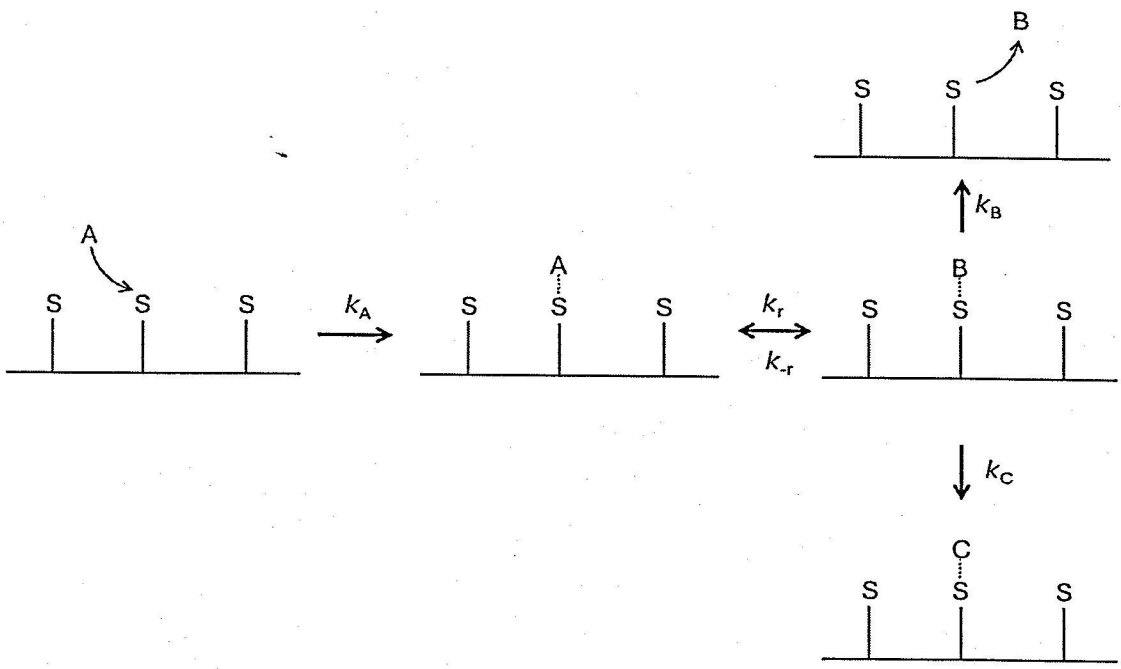
(b) (6%) Based on the above deposition settings, when does the operator need to add concentrated Cu^{2+} and HCHO into the deposition bath to reach the initial concentrations if the deposition rate of metallic Cu cannot be lower than 3/4 of the initial deposition rate?

(c) (4%) If the average thickness of Cu electroless-deposited onto the polyimide substrates in each deposition batch is 1 μm, how many deposition batches can be done between each addition of concentrated Cu^{2+} and HCHO into the deposition

bath to reach the initial concentrations?

Problem 6 (10%)

In heterogeneous catalysis, the reactants are first adsorbed on the catalytic sites on the catalyst surface and then undergo chemical transformation to form products and side products that will either desorb from the surface or poison the surface. Suppose the chemical transformation of a reactant A to product B and side product C is carried out as illustrated in the following scheme:



Where S is the catalytic sites on the catalyst surface.

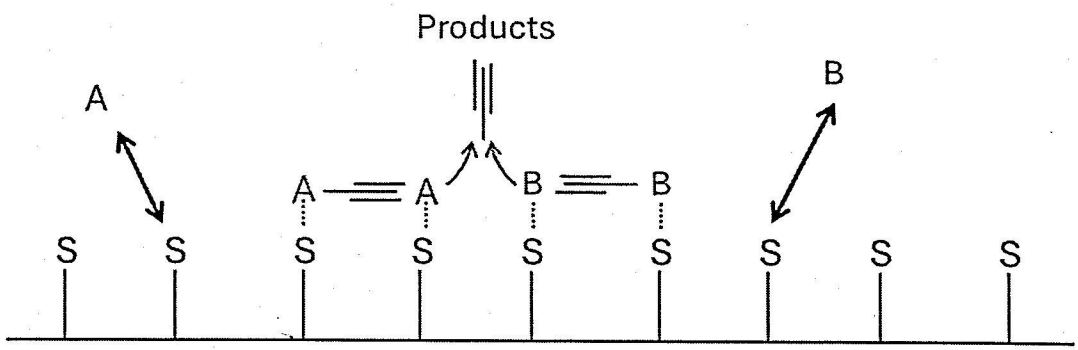
(a) (1%) Write down the rate equation for each species, namely species A, B, S, AS, BS, and CS, in the form of d[A]/dt =.

(b) (2%) Suppose reactant A is in excess, how does this simplify the problem.

(c) (7%) Suppose the rate constants are provided as the following:
$k_A = 60.5\ M^{-1}h^{-1}$; $k_r = 24\ h^{-1}$; $k_{-r}=10\ h^{-1}$; $k_B = 30\ h^{-1}$; $k_c=3\ h^{-1}$
Please solve the system of ODEs and plot the concentrations of all species (including the reactant, surface species, and products) as a function of time under the assumption that reactant A is in excess while being kept at a concentration of 2 M, and the concentration of catalytic sites on a clean catalyst surface is 1 M. (You may draw approximate curves as long as they are physically reasonable; however, you must clearly indicate the steady-state concentration(s) on each plot.)

Problem 7 (10%)

For the following surface reaction having reversible adsorption/desorption of reactants A and B on the active sites S, followed by the irreversible reaction of adsorbed A and B to form the products that instantaneously desorbs:



(a) (2%) Write down the adsorption and chemical reactions that are occurring on the catalyst surface.

(b) (2%) The rate constants for adsorption/desorption are k_A/k_{-A} and k_B/k_{-B} for A and B respectively. The rate constant for the chemical reaction to form the products is k_r. Write down the rate of product formation as a function of the coverage of adsorbed A (θ_A) and B (θ_B) on the catalyst surface.

(c) (4%) Apply the steady-state approximation to the adsorbed A and B, please derive θ_A and θ_B as functions of θ_E (coverage of empty sites). Then, under the assumption that the reaction between adsorbed A and B to form products is the rate-limiting step, please derive the rate of product formation as a function of measurable quantities like the bulk concentration of A (C_A), B (C_B) and surface site S (C_S).

(d) (2%) What is the reaction order for reactant A and B if the adsorption of B on the surface is very low and the bulk concentration of reactant A is very high?

Problem 8(20%)

A gas phase reaction, A → 2R, is carried out in a tubular plug flow reactor at T = 45 °C and P_t = 4.75 atm. The feed consists of 50 mol% A and 50 mol% inert at a rate of 4000 kg/h. The molecular weights of A and inert are 30 and 15, respectively, and the rate coefficient is k = 2000 h^{-1}. Determine the reactor size for 35% conversion of A.