國立清華大學 104 學年度碩士班考試入學試題

系所班組別：化學工程學系碩士班

考試科目（代碼）：化工熱力學及化學反應工程(0902)

請在【答案卡】作答

Problem 1 (24 Points)

(1) (4%)Steam is expanded through a throttling valve from 1 MPa and 300 ^{o}C to 0.1 MPa adiabatically. Is the process

A. isenthalpic (constant enthalpy),
B. isentropic (constant entropy),
C. isobaric (constant pressure),
D. isothermal (constant temperature); or
E. none of the above?

(2) (4%)Steam is expanded through a reversible turbine from 1 MPa and 300 ^{o}C to 0.1 MPa adiabatically. Is the process

A. isenthalpic (constant enthalpy),
B. isentropic (constant entropy),
C. isobaric (constant pressure),
D. isothermal (constant temperature) or
E. none of the above?

(3) (4%)Steam is expanded through a turbine from 1 MPa and 300 ^{o}C to 0.1 MPa adiabatically. Is the process

A. isenthalpic (constant enthalpy),
B. isentropic (constant entropy),
C. isobaric (constant pressure),
D. isothermal (constant temperature) or
E. none of the above?

(4) (4%)An ideal gas is compressed reversibly by a compressor from 0.1 MPa 300 K to 0.5 MPa adiabatically. The constant volume heat capacity of the gas is 36 J/(mol-K). The universal gas constant is 8.314 J/(mol-K). What is the final temperature?

A. ~90 K,
B. ~352 K,
C. ~390 K,
D. ~1299 K, or
E. none of the above?

(5) (4%) An ideal gas is compressed by a polytropic compressor from 0.1 MPa 300 K to 0.5 MPa adiabatically. The constant volume heat capacity of the gas is 36 J/(mol-K). The universal gas constant is 8.314 J/(mol-K). How does the temperature T_{out}^{poly} compared to that obtained reversibly T_{out}^{rev}

A. $T_{out}^{poly} < T_{out}^{rev}$,
B. $T_{out}^{poly} = T_{out}^{rev}$,
C. $T_{out}^{poly} > T_{out}^{rev}$, or
D. we need the polytropic efficiency to determine the answer, or
E. even if we know the polytropic efficiency, we do not have enough information to determine the answer.

(6) (2%) Iron (III) sulfate, $Fe_2(SO_4)_3$, decomposes upon heating to make iron (III) oxide and sulfur trioxide by the following reaction: $Fe_2(SO_4)_3$ (s) $\rightleftharpoons$ Fe_2O_3 (s) + $3SO_3$ (g) Using the phase label given in the equilibrium reaction, how many degrees of freedom are there in this equilibrium? (A) 0 (B) 1 (C) 2 (D) 3

(7) (2%) Given the nonstandard concentrations for the following reaction, calculate the instantaneous voltage, E, of the Daniell cell: Zn + Cu^{2+} (0.0333M) $\rightarrow$ Zn^{2+} (0.0044M)+ Cu, where under the standard conditions, the standard voltage, E^0, is 1.104 V. Please assume that the molarity can be substituted for molality. (A) 0 (B) 1.104 (C) 1.130 (D) 1.237 V

以下各題請在【答案卷】作答

Problem 2 (8 Points)

A material (closed system) at constant pressure undergoes a reversible phase transition with temperature at $T=T_0$. Please indicate whether the following statements are ALWAYS TRUE, TRUE PART OF THE TIME, or NEVER TRUE?

(a) At the phase transition temperature, the high temperature phase has a higher volume than the low-temperature phase.

(b) At the phase transition temperature, the high temperature phase has a higher enthalpy than the low-temperature phase.

(c) At the phase transition temperature, the high temperature phase has a higher entropy than the low-temperature phase.

(d) At the phase transition temperature, the high temperature phase has a higher Gibbs free energy than the low-temperature phase.

Problem 3 (2 Points)

An oxide with stoichiometry $AO_{3-\delta}$ undergoes a polymorphic transition from a low-temperature alpha (α) phase to a high-temperature beta (β) phase at 500 °C when under normal atmospheric conditions ($pO_2 = 0.2$ atm). Calculate how much the transition temperature changes if the oxygen partial pressure is doubled.

$\Delta H_{\alpha\text{-}\beta} = 8$ kJ/mol, $\delta_\alpha = 0.02$, $\delta_\beta = 0.01$.

Problem 4 (6 Points)

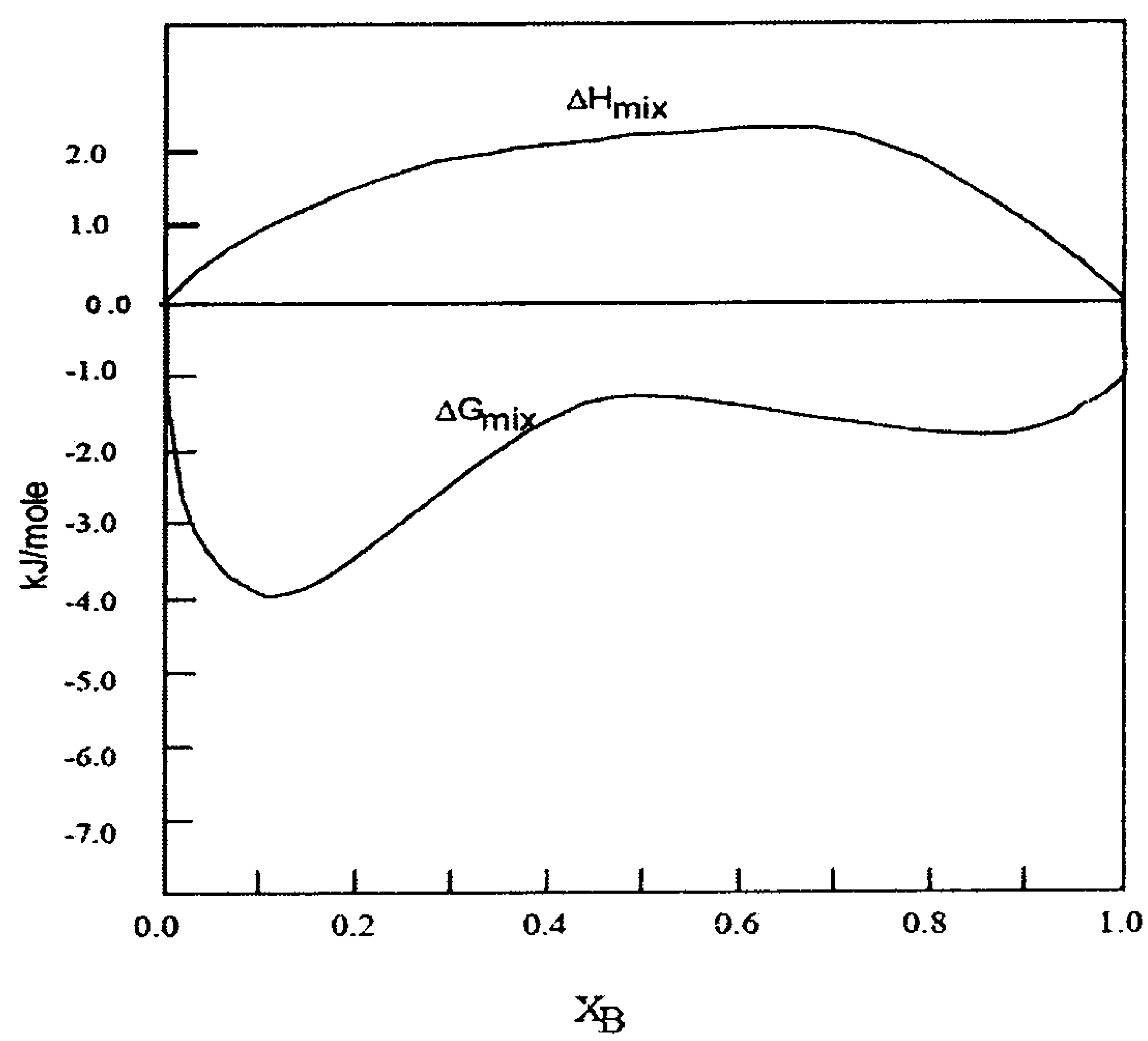
The curves below show the Gibbs free energy of mixing and enthalpy of mixing of an A-B solution at a temperature of 300K. The data is per mole of atoms in the solution. (e.g. one mole of A + one mole of B forms two moles of atoms in solution).

(a) Calculate the heat that needs to be added or subtracted to a system in which 1/2 mole of A at 300K is mixed with 1/2 mole of B at 300K, and the system comes to equilibrium at 300K.

(b) Calculate the heat evolved/absorbed when a system with $x_B= 0.3$ is reacted with a system with $x_B= 0.7$, to form a system with $x_B= 0.5$ at constant temperature of 300K. State your answer per mol of system formed.

(c) What is the partial molar entropy of A (relative to the entropy of pure A) in a mixture with $x_B= 0.1$ at 300K? Show clearly how you obtain this result.

(接上頁)



Problem 5 (10 Points)

Oxygen reduction is a common reaction in electrochemical systems. In general, the catalysts of oxygen reduction in aqueous electrolytes ($P_{O2} = 1\,atm$) are designed for the 4-electron or 2-electron transfer reactions which can be expressed as following two reactions:

$$O_{2(g)} + 4H^+{}_{(aq)} + 4e \leftrightarrow 2H_2O_{(l)} \qquad E_1 = 1.23 - 0.0592\ pH \qquad \text{(unit: V)}$$

$$O_{2(g)} + 2H^+_{(aq)} + 2e \leftrightarrow H_2O_{2(aq)} \qquad E_2 = 0.68 - 0.0592\ pH \qquad \text{(unit: V)}$$

However, H_2O_2 is an active intermediate which may be further reduced to water.

(a) (2%) What is the electrochemical reaction of H_2O_2 reduction to water?

(b) (5%) What is the equilibrium potential of H_2O_2 reduction to water if pH of the aqueous electrolyte is equal to 3?

(c) (3%) Since the equilibrium potential of H^+/H_2 ($P_{H2} = 1\,atm$) with its electrochemical reaction can be expressed as: $2H^+_{(aq)} + 2e \leftrightarrow H_{2(g)}$ $E_3 = 0 - 0.0592pH$ (unit: V), what is the maximum cell voltage if a fuel cell employs pure H_2 and O_2 (at 1 atm for both gases) as the sources for electricity generation?

Problem 6 (10 Points)

An irreversible liquid phase reaction in 3 isothermal CSTRs of different sizes in series at 70°C obeys the following rate law:

$$A \rightarrow D \qquad -r_A = \frac{33C_A}{65 + 0.5C_A^2} \quad \text{in mole/(dm}^3\cdot\text{min)}$$

The volumes of first, second and third reactors are equal to 0.1, 0.1, and 0.2 m^3, respectively. The volume flow rate of the feed stream is equal to 50 dm^3/min and the initial concentration of A is equal to 2 M.

(a) (8%) What are the exit concentrations of A for the three CSTRs?

(b) (2%) What is the conversion of this irreversible reaction in such 3 CSTRs of different sizes in series?

Problem 7 (10 Points)

The reaction rate equation in terms of the reactant X of the irreversible reaction

$$X + 2Y \rightarrow Z$$

has been determined to be

$$-r_x = \frac{1.82[X][Y]^2}{1 + 2[Y]}$$

(a) (2%) Please show the rate equation in terms of the reactant Y.

(b) (2%) Is the reaction an elementary reaction? Please tell your reasons.

(c) (6%) John proposed a mechanism for the reaction as

$$X + Y \underset{k_2}{\overset{k_1}{\rightleftarrows}} XY^*$$

$$XY^* + Y \underset{k_4}{\overset{k_3}{\rightleftarrows}} Z$$

Please verify if the mechanism proposed by John is possibly correct.

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Problem 8 (10 Points)

The kinetics of the reaction

$$A + B \rightarrow P$$

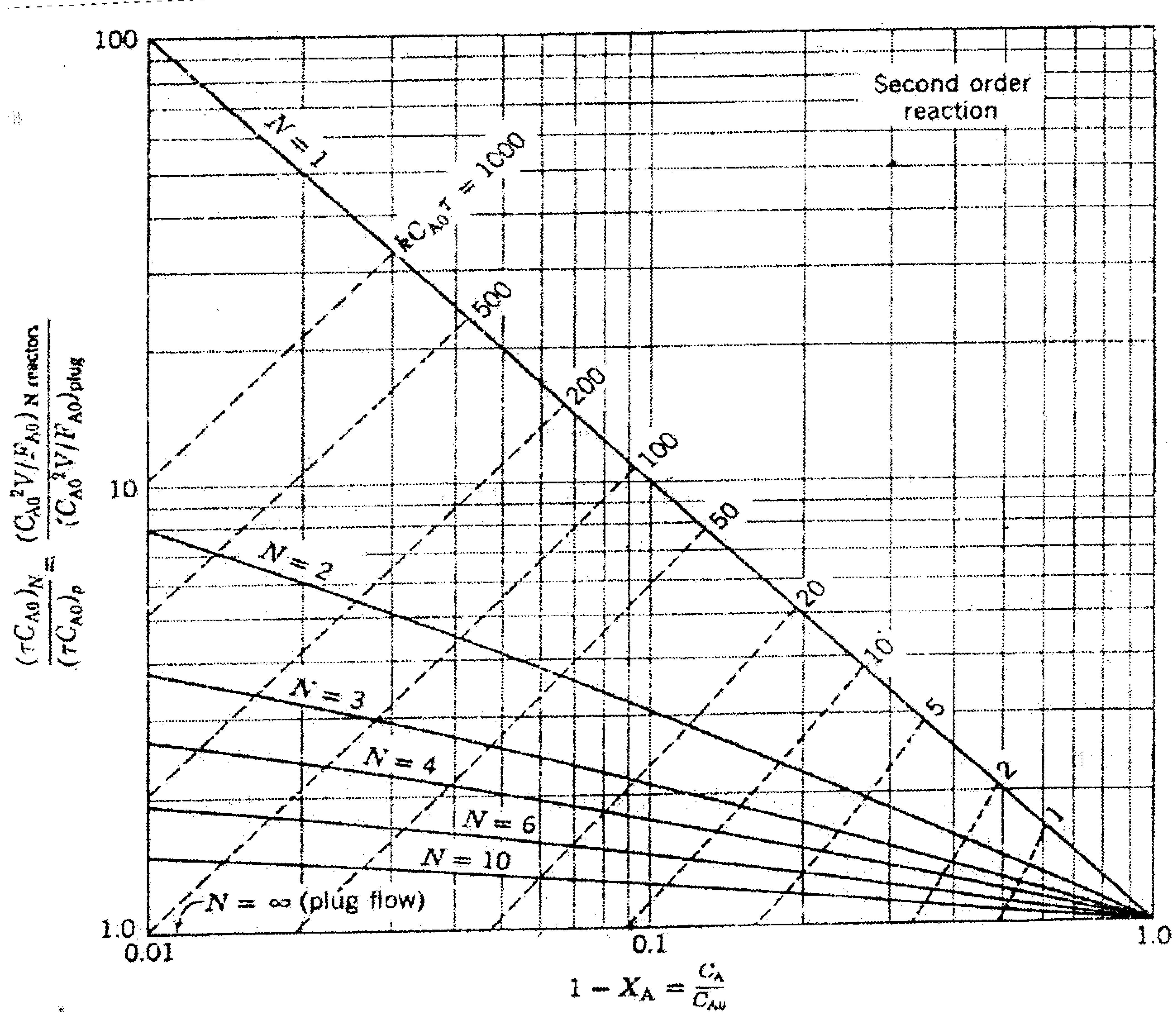
being taken place in an experimental plug-flow reactor is

$$-r_x = 9000\,[A][B]\,(L\,mol^{-1}\,h^{-1})$$

(a) (4%) Please determine the reactor size with the conditions of
Volumetric feed rate = 0.05 L min^{-1}
Concentration of reactants in feed, [A] = [B] = 0.02 mol L^{-1}
Expected conversion for A is 0.95.

(b) (4%) How could the conversion for A be increased to 0.98?

(c) (2%)If the reactor is changed to be a back-mixed reactor in the same size given in problem (a), what is the conversion for A?



Problem 9 (10 Points)

A sample of serum albumin particles stored in a batch container undergoes the irreversible aggregation process and also the conformation change. The storage conditions are 1 atm, 20 °C with a good humidity control. We assume that the total liquid volume in the sample is constant.

(a) (5%) It is known that the aggregation process of serum albumin is complicated, involving multiple reactions: serum albumin with different number of monomers per particle (e.g., monomers, dimers, trimers) can collide with each other. Every collision results in a loss of one total particle count (for example, once two individual monomers of serum albumin collide to form a dimer serum albumin, the total number of particles should be decreased from 2 to 1).

Hence the aggregation of serum albumin is following a second-order reaction simplified as: $-\frac{dC_{total}}{dt} = k_r C_{total}^2$, where C_{total} is the total number concentration of serum albumin particles (including monomers, dimers, trimers, etc.). k_r is the aggregate rate constant.

We assume k_r to be the same for all types of serum albumin here and the molecular mass of a monomer serum albumin is uniform (≈ 70,000 g/mol). The initial number concentration of the serum albumin is $10^8/cm^3$.

What are the k_r and the half-life of this serum albumin product? Data of C_{total} versus the storage time, t, are shown in the Table below.

(b) (5%) In addition to the aggregation process, we observe a certain extent of conformation change from N-form to L-form following a first-order reaction:

N-form serum albumin ⇔ L-form serum albumin

We assume the conformation change is reversible and is independent of the aggregation discussed previously. The variation in temperature is negligible. Based on the data shown in the Table below, **please describe the sample quantitatively after a 40-hr reaction** (i.e., in terms of the percentage of serum albumin in N-form and L-form). (接下頁)

(接上頁)

t (hr)	C_{total} (#/cm^3)	Percentages in N-form (%)
0	$1*10^8$	100
1	$8.3*10^7$	98
2	$7.1*10^7$	96
3	$6.2*10^7$	94.5
4	$5.6*10^7$	92.5
Infinity	1	50

Problem 10 (10 Points)

To minimize the CO pollution from the exhausted gases of the scooters, we are designing a catalytic reactor composed of multiple tube-shape, plug-flow reactors. The idea is to convert CO into CO_2 at the gas-solid interface using an irreversible catalytic reaction: CO + O*S $\Rightarrow$ CO_2 + S, where S is the binding site of a solid catalyst. The design of one reactor is 30 cm in length and 2.5 cm in diameter packed with solid, metallic catalysts having a large surface area. To satisfy the requirements of this specific scooter, the removal rate of CO should beat 0.01 kg/min.

Before connecting to this tube-shape catalytic reactor, the initial concentration of CO ($C_{CO,0}$) is 3 mol/m^3 and initial concentration of O_2 ($C_{O2,0}$) is 10 mol/m^3. Even though the reaction is exothermic, we assume the variations in temperature and pressure along the reactors are negligible.

The targeted concentration of CO existing the reactors is set at 0.03 mol/m^3. **Due to the limited space inside the scooter and the requirement of a high conversion rate, we need to use multiple tube reactors with connection in parallel.**

The following table shows the data obtained by using <u>one catalytic reactor</u> (before connecting in parallel). R_{CO2} is the rate of CO_2 generation. C_{CO} and C_{O2} are the measured concentrations of CO and O_2, respectively.

(接下頁)

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R_{CO_2} [mol/(m^3*s)]	C_{CO} (mol/m^3)	C_{O2} (mol/m^3)
0.21	0.10	0.20
0.39	0.20	0.20
0.58	0.30	0.20
0.81	0.40	0.20
1.01	0.50	0.20
2.10	1.00	0.20
2.05	1.00	0.40
2.04	1.00	0.60
2.01	1.00	0.80
2.12	1.00	1.00

(a) (5%) Based on the data in the Table and the information described above, please suggest a rate law (in terms of $C_{CO,0}$ and the conversion ratio of CO, X_{CO}) and calculate the rate constant that is suitable for describing this catalytic reaction. Presumably the correlation is still suitable at a higher C_{CO} and C_{O2}.

(b) (5%) In order to implement the design by using multiple reactors connecting in parallel: how many reactors are required? (i.e., to reduce C_{CO} from 3 mol/m^3 to be 0.03 mol/m^3)