

國立清華大學 107 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）

共 7 頁，第 1 頁 *請在【答案卷】作答

Problem 1 (10%)

Elements A and B have the same crystal structure, and the melting points of A and B at 1 atm. are at 200°C and 400°C , respectively. Both the solid and liquid phases of the binary A - B system are ideal solutions.

- What is the Gibbs energy of mixing of the liquid phase in the A - B binary system? What is the partial Gibbs energy of A of the liquid phase in the binary system? (4%)
- Draw a T - X (temperature-composition) phase diagram at 1 atm. of the binary A - B system from 0°C to 700°C , and mark all the phase regions. (3%)
- Draw the schematic G - X (Gibbs energy-composition) diagrams of the related phases of the binary A - B system at 300°C and 500°C . (3%)

Problem 2 (10%)

The vaporization points of elements A and B at 1 atm. are at 500°C and 800°C , respectively. The gas phase is an ideal gas. The excess Gibbs energy of the liquid

mixture at T and 1 atm is described by $\frac{G^E}{RT} = (-2.5x_B - 1.6x_A)x_Ax_B$.

- What is the partial Gibbs energy of B in the liquid phase of the binary A - B system? (3%)
- What is the expression of $\ln\gamma_B$ of the liquid phase at T and 1 atm.? (3%)
- What is Raoult's Law? Can the Raoult's law be applied to this system? Why or why not? (4%)

Problem 3 (20%)

Figure 1 shows the pressure-volume diagram of air (considered an ideal gas at these conditions with constant heat capacity, $C_p=7R/2$, $C_v=5R/2$, $R=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) be processed from State 1 to State 2 through 2 different mechanically reversible paths (processes).

- Please use this case to demonstrate that the work required (W) and heat transferred (Q) are path-dependent, and changes in enthalpy (ΔH) are function of state. (12%)
- Please calculate the change in entropy (ΔS) from state 1 and state 2. (5%)
- Please give a demonstration in detail to tell if the process could be spontaneous. (3%)

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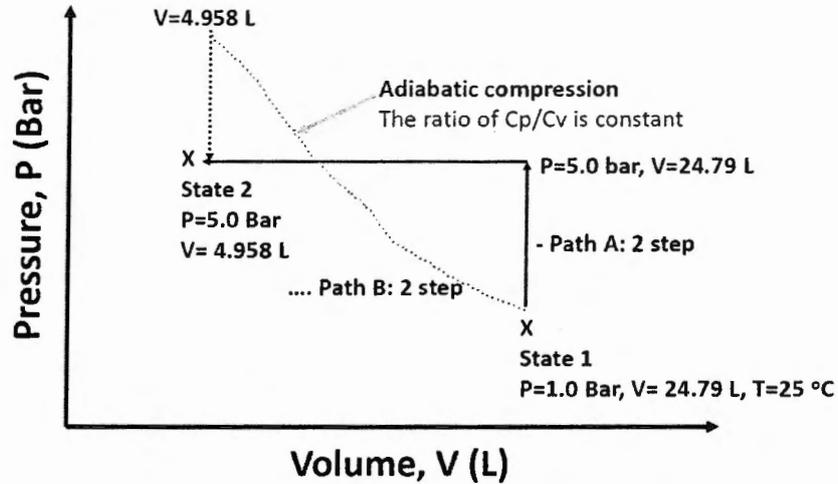
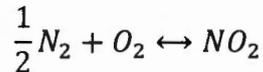
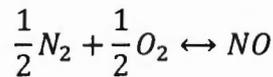


Figure 1.

Problem 4 (10%)

Consider the reactions



- What is the equilibrium constant of NO formation reaction at 300 K? (1%)
- What is the equilibrium constant of NO_2 reaction at 300 K? (2%)
- What is the equilibrium constant of NO formation reaction at 2000 K (1%)
- What is the equilibrium constant of NO_2 reaction at 2000 K (2%)
- Is the NO formation reaction endothermic or exothermic? (2%)
- Is the NO formation reaction endothermic or exothermic? (2%)

The following data are given

$T^{-1}[K^{-1}]$	$\log_{10}(K_{eq})$	
	$\frac{1}{2} N_2 + \frac{1}{2} O_2 \leftrightarrow NO$	$NO + \frac{1}{2} O_2 \leftrightarrow NO_2$
0.00050	-1.6996	-2.4546
0.00333	-15.069	6.1126

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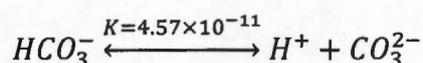
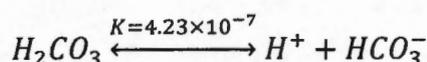
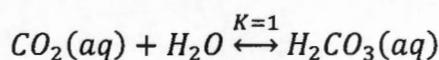
共 7 頁，第 3 頁 *請在【答案卷】作答

Problem 5 (10%)

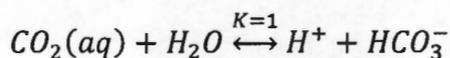
Calculate the pH of a rain drop at 298 K with an atmospheric partial pressure of CO_2 equal to $3.2 \times 10^{-4} \text{ atm}$. The Henry's law coefficient of CO_2 in water:

$$\frac{P_{CO_2}}{m_{CO_2(aq)}} = H = 26.3 \frac{\text{atm}}{M}$$

The equilibrium constants of the following reactions are



- (a) What is the equilibrium concentration of $CO_2(aq)$ formation reaction at 298 K? (2%)
(b) What is the equilibrium constant of the reaction at 298 K (2%)



- (c) What is the equilibrium concentration of HCO_3^- in the solution if we assume that the dissociation of HCO_3^- into CO_3^{2-} is negligible? (2%)
(d) What is the pH of the solution if we assume that the dissociation of HCO_3^- into CO_3^{2-} is negligible? (2%)
(e) What is the ratio of concentrations HCO_3^- to CO_3^{2-} given the answers in (c) and (d)? Is the assumption that the dissociation of HCO_3^- into CO_3^{2-} is negligible a reasonable one? (2%)

Problem 6 (10%)

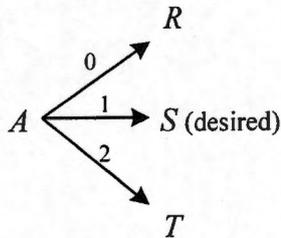
In the following elementary reactions, reactant A decomposes by three simultaneously reactions to form three products, one that is desired, S , and two that are undesired, R and T .

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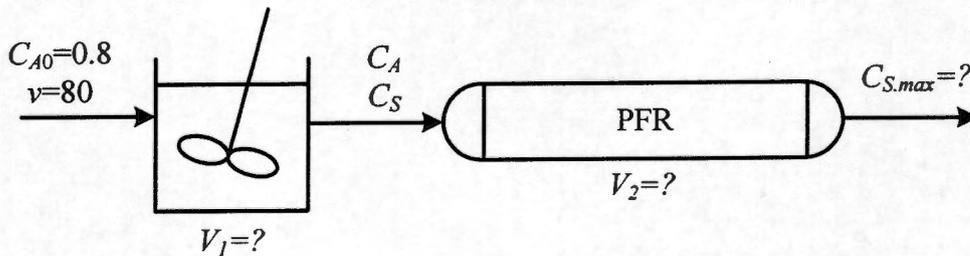


$$r_R = k_0, k_0 = 0.02 \frac{\text{mol}}{\text{liter} \cdot \text{min}}$$

$$r_S = k_1 C_A, k_1 = 0.2 \frac{1}{\text{min}}$$

$$r_T = k_2 C_A^2, k_2 = 0.5 \frac{\text{liter}}{\text{mol} \cdot \text{min}}$$

- (a) You have to use a CSTR to maximize the fraction yield of S under the condition that $C_{A0} = 0.8 \text{ mole liter}^{-1}$ and a volumetric flow rate, $v = 80 \text{ liter min}^{-1}$. Determine the volume of CSTR. (5%)
- (b) We now wish to maximize the production rate of S by adding a PFR after the CSTR system. Determine $C_{S,max}$ obtainable and the reactor volumes of PFR. (5%)



Problem 7 (10%)

A second-order reaction $A \rightarrow 3R$ is studied in a plug flow reactor which contains 3 kg of catalyst. A gas containing 25% of A and a molar concentration of $2 \text{ mol} \cdot \text{m}^{-3}$ and 75% inerts is fed at $1 \text{ m}^3 \cdot \text{hr}^{-1}$ to the reactor. The output composition from the reactor system is measured to be $0.5 \text{ mol} \cdot \text{m}^{-3}$. Find the rate equation for the decomposition of A . Be sure to give the units of rate equation and rate constant in your final expression.

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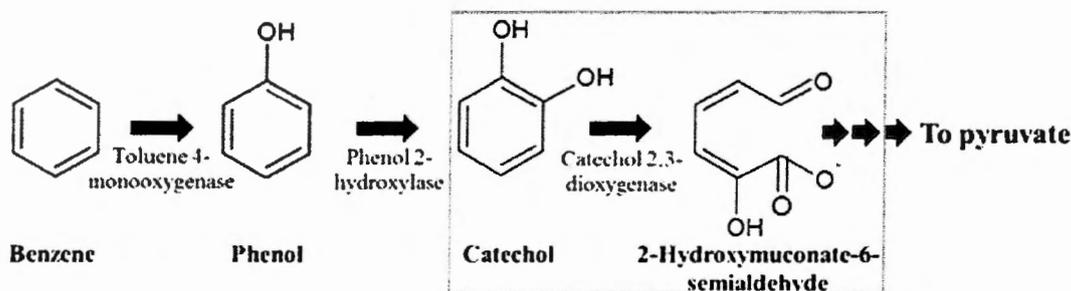
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Problem 8 (10%)

Benzene is a widely used industrial feedstock. The majority of the entire benzene production is processed into ethylbenzene, a precursor to styrene, which is used to make polymers and plastics like polystyrene. However, benzene is very toxic. As benzene is common in gasoline and hydrocarbon fuels are used everywhere, human exposure to benzene is a global health problem. Benzene targets liver, kidney, lung, heart and the brain and can cause chromosomal damage. Benzene causes cancer in animals including humans. The American Petroleum Institute (API) stated that "it is generally considered that the only absolutely safe concentration for benzene is zero". There is no safe exposure level; even tiny amounts can cause harm. Therefore, degradation of benzene into non-hazardous chemical during waste water treatment is very essential.

Evolved for millions of years, many soil bacteria are able to catabolize a wide variety of natural and man-made aromatic compounds, including benzene, into environmental-friendly metabolites. The oxidative catabolism of aromatic compounds by these bacteria generally requires the formation of dihydroxy aromatic intermediates such as catechol, followed by a ring-opening reaction which is often the rate limiting step in the degradation of benzene.



You work in a sewage treatment facility and recently discovered a new "catechol 2,3-dioxygenase" enzyme in the soil bacteria isolated from your backyard and are eager to check if this new enzyme works efficiently at converting catechol into 2-hydroxymuconate-6-semialdehyde. From literature search, you know that this new enzyme follows the Michaelis-Menten kinetics behavior, which can be represented by the schematics below (E = enzyme, S = substrate, ES = substrate-enzyme complex, P = product) and obeys the "initial rate" assumption, the "rate-limiting" assumption, and

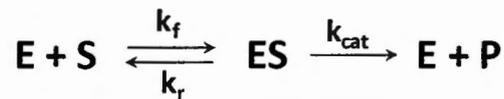
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the “pseudo-steady state” assumption. You know in the Michaelis-Menten kinetics, the catalytic efficiency of an enzyme is determined by two constants, the rate constant or turnover number “ K_{cat} ” (unit = time^{-1}) and the Michaelis constant “ K_m ” (the substrate concentration at which half of maximum velocity is reached).



You would like to design an experiment to determine the value of K_{cat} and K_m .

Please describe briefly what type of data you need to collect experimentally in order to find “ K_{cat} ” and “ K_m ”. Please write your answer in the boxes provided below and answer with short descriptive phrases such as “measure... as a function of ...”, “decreasing... to measure...” etc.

- (a) To determine “ K_{cat} ”, what experimental data should you collect? (5%)
- (b) To determine “ K_m ”, what experimental data should you collect? (5%)

Problem 9 (10%)

Enzymes are biological catalysts found in our bodies to carry out biochemical reactions for a diverse range of metabolic purposes. Enzymes are essentially amino acid polymers known to accelerate chemical reactions at mild condition by binding to the substrates thus allowing the occurrence of many reactions in human body without harsh temperature or pressure. To give you an example, OMP decarboxylase is known for being an extraordinarily efficient enzyme in our body capable of accelerating the reaction rate of nucleotide synthesis by a factor of 10^{17} . To put this in perspective, the reaction would take 78 million years in the absence of enzyme, but only takes 18 milliseconds when it is enzyme catalyzed.

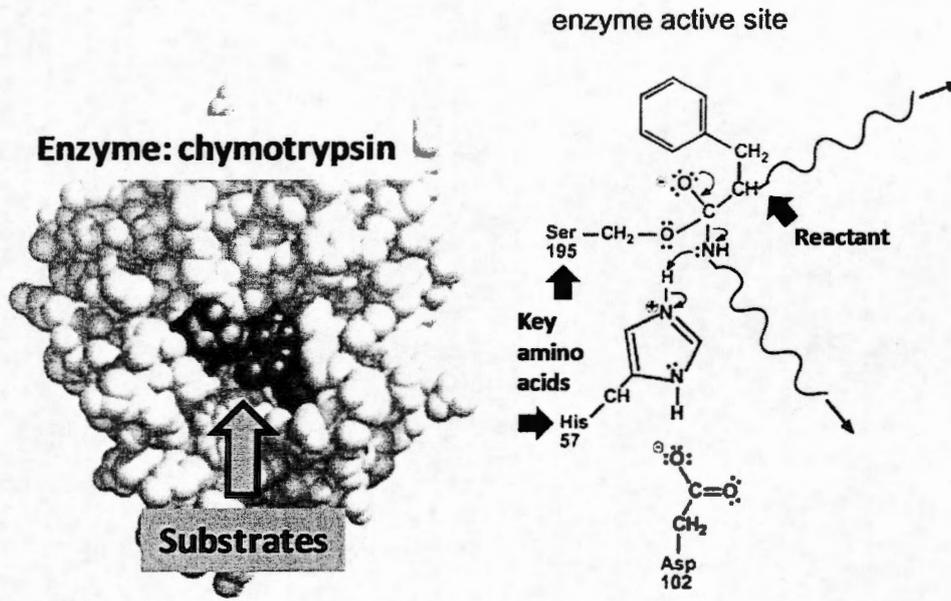
To give you a better idea about enzyme catalysis, please see the figure below about chymotrypsin, a digestive enzyme in our pancreas responsible for breaking down proteins. As illustrated by this model enzyme schematic below, enzyme catalyzes chemical reactions by binding to the reacting substrate (left picture, 3D molecular simulation) and interacting with the reactants via key amino acid residues in the active site (right picture).

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Whether the chemical reactions are catalyzed by enzymes or not, the Arrhenius' equation, which describes the temperature dependence of reaction rates, holds.

$$k = A e^{-E_a/RT}$$

where k is the rate constant at T

E_a is the activation energy

R is the energy gas constant

T is the Kelvin temperature

A is the collision frequency factor

Based on the Arrhenius' equation, please explain using short phrases in the box below

- How does the enzyme accelerate the rate of a reaction at mild condition? (5%)
- How does the enzyme achieve the effect in part (A) in terms of its catalytic behavior and mechanism? *Hint: the type of enzymatic behavior leading to entropic and/or enthalpic effect which increases the reaction kinetics. (5%)