國　立　清　華　大　學　命　題　紙

九十二學年度＿＿化學工程學＿＿系（所）＿＿＿＿＿組碩士班研究生招生考試

科目＿化工熱力學及化學反應工程＿科號＿1202＿共＿4＿頁第＿1＿頁 *請在試卷【答案卷】內作答

Problem 1 (20%)

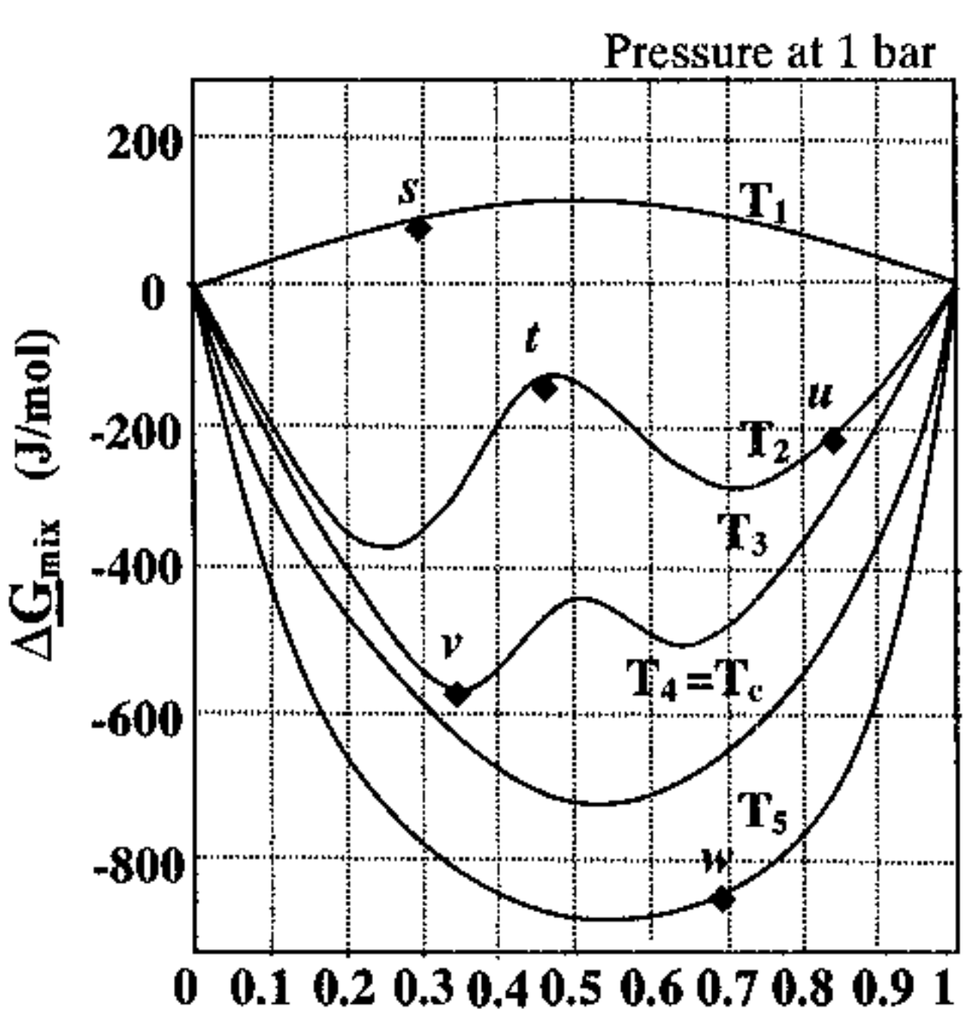
You are assigned to study the phase behavior of liquid mixture of A and B components. The only available information is the diagram of Gibbs free energy change on mixing (i.e., the plot of ΔG_{mix} versus fA) at different temperatures where temperature **T1 <T2 <T3 <T4 <T5** and **T4** is the critical solution temperature. The initial state for these mixtures is indicated in the diagram. Please answer the following questions:

a. What is the degree of freedom and the final composition(s) for the mixture at each indicated state? Please also specify the fraction of each phase while the mixture becomes a two-phase system. Finally, construct the phase diagram of T versus molar fraction regarding the phase diagram. (12%)

b. What are the thermodynamic conditions for the mixture to reach two-phase equilibrium system? What are the criteria for the formation of stable two-phase equilibrium system?
(Hint: Describe your answer by using Gibbs free energy change on mixing!) (4%)

c. Please determine the partial molar Gibbs free energy of A and B components for v mixture. The molar Gibbs free energy for pure A and B are 100 J/mol and 50 J/mol, respectively. (2%)

d. Please justify the enthalpy of mixing (i.e., zero, endothermic or exothermic reaction), and explain your answer. (2%)



Problem 2 (20%)

A block of metal (10kG, MW=100, water insoluble, c_P=1 kJ/kG , T=400K) is thrown into a lake containing 1,800,000 kG water (MW=18, c_P=1 kJ/kG , T=300K) and comes to equilibrium. Calculate:

1. The enthalpy change of the metal

2. The entropy change of the metal

3. The enthalpy change of the water

4. The entropy change of the water

5. The total enthalpy change

6. The total entropy change

A block of water soluble compound (10kG, MW=100, c_P=1 kJ/kG , T=300K) is thrown into a pool containing 1,800,000 kG water (MW=18, c_P=1 kJ/kG , T=300K) and dissolves completely. Calculate:

7. The entropy change of the compound

8. The entropy change of the water

9. The total entropy change

Which process is more irreversible?

Given

R=8.314 J/(mol-K)

log(300/400) = -0.2877

log(0.000001) = -13.805

log(0.999999) = -1.e-6

Problem 3 (20%)

For the gaseous reaction $H_2 + Br_2 = 2HBr$, the following mechanism has been proposed:

$Br_2 \xrightarrow{k_1} 2Br^{\bullet}$ (initiation)

$Br^{\bullet} + H_2 \xrightarrow{k_2} H^{\bullet} + HBr$

$H^{\bullet} + Br_2 \xrightarrow{k_3} Br^{\bullet} + HBr$

$H^{\bullet} + HBr \xrightarrow{k_4} H_2 + Br^{\bullet}$

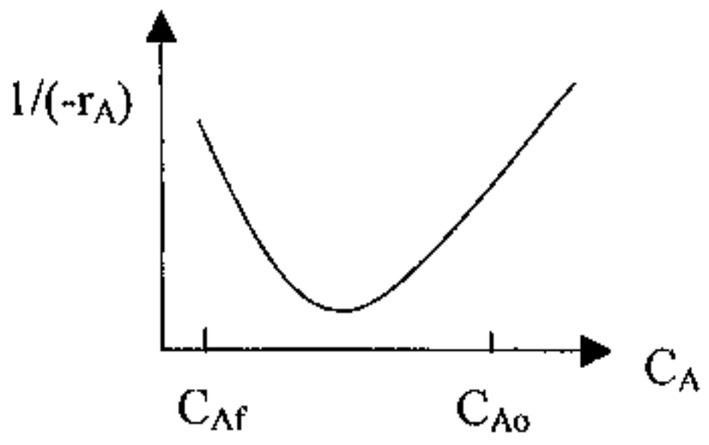
$2\,Br^{\bullet} \xrightarrow{k_5} Br_2$ (termination)

Show that this mechanism leads to the rate equation of

$$r = \frac{dC_{HBr}}{dt} = \frac{k_2 C_{H2} C_{Br2}^{1/2}}{1 + k_i C_{HBr} / C_{Br2}}$$

You should define the symbols and write down every step for your derivation.

Problem 4 (20%)



For a reaction with reaction rate curve as shown (C_A is the concentration of reactant, $-r_A$ is the reaction rate), the volumetric flow rate (v_o), the initial and final reactant concentrations, C_{Ao} and C_{Af}, are known.

Describe and sketch how you are going to minimize the size of reactor(s) if you are using

(i) 1 PFR with recycle (also determine the recycle flow rate) (8%)

(ii) 2 CSTR (different sizes) in series (8%)

(iii) 1 PFR and 1 CSTR (4%)

You only need to explain by graphical method and write down the equations for calculation, but no numbers are required. Use notations of your choice if necessary.

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Problem 5 (20%)

Consider a liquid phase reaction

$$A \xrightarrow{k_1} B, \quad r_1 = k_1 C_A$$

$$A \xrightarrow{k_2} C, \quad r_2 = k_2 C_A^2$$

(a) Will a PER give a smaller reactor size and a better selectivity of B than a CSTR for the same conversion? (5%)

(b) Find an expression for space time (θ_m) in a CSTR in term of k_1, k_2, C_{A0} and C_A. (5%)

(c) Find space time, selectivity of B (S_B) in a CSTR at 90% conversion of A with $C_{A0} = 2$ moles/liter, $k_1 = 4hr^{-1}$ and $k_2 = 1hr^{-1}$ (mole/liter)$^{-1}$. (10%)