國立清華大學 106 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（1002）

 *請在【答案卷】作答

Problem 1

A binary *A-B* liquid solution is at constant temperature *T* and pressure *P*, and the Gibbs energies of pure liquid *A* and *B* are G_A^0 and G_B^0, respectively.

(a) If the solution is an ideal solution, what are the enthalpy change of mixing, entropy change of mixing and Gibbs energy change of mixing? (5%)

(b) If the solution is not an ideal solution, and its excess Gibbs energy is given by the following equation: $G^E/RT = X_A X_B(0.4X_A + 0.2X_B)$. Draw a schematic Gibbs energy-composition diagram, and indicate on the diagram the values of the partial Gibbs energy, $\overline{G_A}$ and $\overline{G_B}$, at $X_B = 0.7$. (5%)

Problem 2

At 1 atm, the vaporization point of species A is at 650°C and that of species B is at 550°C. The binary *A-B* system has an azeotrope at 750°C and $X_B = 0.4$. The two speies A and B are completely soluble in each other in the liquid phase when thw temperature is higher than 450°C. A liquid miscibility gap appears when the temperature is lower than 450°C.

(a) Draw the temperature-composition *A-B* phase diagram at 1 atm with temperature ranging from 300°C to 900°C. (5%)

(b) Draw schematic Gibbs energy-composition diagrams at 400°C, 600°C and 800°C, showing both the Gibb energy curves of the liquid phase and vapor phase. (5%)

Problem 3

One mole of liquid *A* is reacted with two moles of gas *B* to Produce gas *C* and liquid *D* in a closed system at *T* and *P* according to the reaction: $A_{(\ell)} + 2B_{(g)} = C_{(g)} + 2D_{(\ell)}$.

The reaction coordinate, $\mathcal{E}$, is defined as $d\mathcal{E}_i = \frac{dn_i}{\mathcal{V}_i}$, where $\mathcal{V}_i$ is the stoichiometric number and dn_i is the changes in numbers of moles.

(a) If the Gibbs energy change of reaction, $\Delta G^0 = G^0_{C(g)} + 2G^0_{D(\ell)} - G^0_{A(\ell)} - 2G^0_{B(g)}$, is negative, will the reaction proseed to produce *C* and *D*? What is the mole fraction of *B* in the gas phase in terms of reaction coordinate? (2%)

(b) When the system is in equilibrium, is there any *B* in the system? Why? (2%)

(c) Draw a schematic diagram showing the total Gibbs energy, G^t, of the above-mentioned system in relation to the reaction coordinate. (2%)

(d) What is the condition for the system in equilibrium regarding the value of G^t? (2%)

(e) The chemical potential of species *i* is μ_i. What is the criterion of chemical reaction equilibrium of $\sum_i \nu_i \mu_i$? (2%)

Problem 4

Consider a perfect gas contained in a cylinder and separately by a frictionless adiabatic piston into two sections A and B. All changes in B is isothermal; that is, a thermostat surroundings B to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially, $T_A = T_B = 300K,\ V_A = V_B = 2.0dm^3$. Energy is supplied as heat to Section A and the piston moves to the right reversibly until the final volume of Section B is 1.00dm^3. $C_{v,m} = 20JK^{-1}mol^{-1}$

Calculate

(a) $\Delta S_A\ and\ \Delta S_B$ (2.5%)

(b) $\Delta A_A\ and\ \Delta A_B$ (2.5%)

(c) $\Delta G_A\ and\ \Delta G_B$ (2.5%)

(d) ΔS of total system and its surroundings (2.5%)

If numerical values cannot be obtained, indicate whether the values should be positive, negative, or zero or are indeterminate from the information given.

Problem 5

The change in enthalpy is given by $\mathrm{d}H = C_p dT + Vdp$. The Clapeyron equation relates dp and dT at equilibrium, and so in combination the two equations can be used to find how the enthalpy changes along a phase boundary as the temperature changes and the two phases remain in equilibrium. Show that $\mathrm{d}(\Delta H/T) = \Delta C_p \mathrm{dln}T$ (10%)

Problem 6

The elementary reversible gas-phase reaction $A \Leftrightarrow B$ is to be carried out adiabatically to achieve 45% conversion of A. Pure A is fed to the reactor at a rate of 10 mol/min at a pressure of 2.87 atm and a temperature of 77 °C. Shaft work is neglected. Calculate

(A) the temperature of the exit stream (5%)

(B) the reactor volume for a CSTR (5%)

Additional data:

specific reaction rate at 0°C: 0.001 h^{-1} (first order)

activation energy: 10,000 cal/mol

heat of reaction at 27°C: -20,000 cal/mol A

equilibrium constant at 127°C: 25,000

Heat capacity of A=20 cal/mol·K

Heat capacity of B=30 cal/mol·K

國立清華大學 106 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（1002）

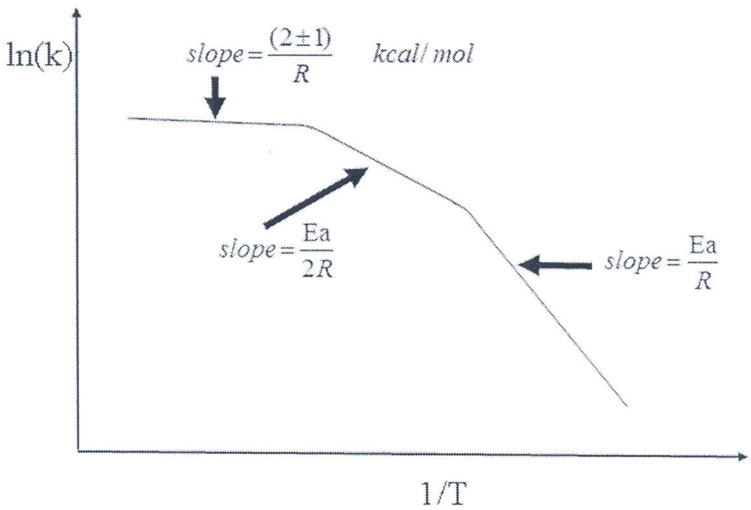
　　*請在【答案卷】作答

Problem 7

A liquid-phase, reversible, elementary reaction, P $\Leftrightarrow$ Q, is conducted in a catalytic packed bed reactor where P and Q are miscible and of nearly identical density. The equilibrium constant for this reaction, K, is 5.8 at 227°C meanwhile the fixed bed reactor is operated isothermally at 227°C without any backmixing effects. When pure P was fed into this reactor, 55% of the net conversion to Q was obtained. What will be the conversion if two such identical packed bed reactors are operated isothermally in series at 227°C? (10%)

Problem 8

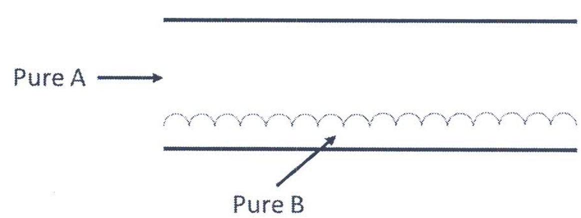
There are generally 7 basic steps for converting reactants to products via a heterogeneous catalytic mechanism. The figure shows the dependence of the natural logarithm of reaction rate constants for a heterogeneous, gas-phase, catalytic reaction on a highly porous catalyst upon the reciprocal of absolute temperature (i.e., ln(k) vs. 1/T). The value of Ea is similar to the activation energy of common chemical reactions. Please briefly explain why we obtain such a plot where three activation energy values are obtained for this gas-solid catalytic process with varying the reaction temperature. (10%)



Problem 9

The elementary reaction: $A_{(g)}+B_{(l)} \rightarrow C_{(g)}$
is taking place only in the gas-phase of a square duct. The feed to the duct consists of a gas stream of pure A and a liquid stream of pure B. The flowing liquid B covers the bottom of the duct and evaporates into the gas-phase, maintaining its equilibrium vapor pressure throughout the system. The gas-phase flows in plug flow. Ignore the volume occupied by liquid B, what is the rate of reaction, $-r_a$, when the conversion is 50%? (10%)

Additional Information:
Total pressure (constant): 1 atm
Rate constant, $k=10^6$ ft^3/lbmol*s
Temperature in the reactor (constant): 540°F
Vapor pressure of B at 540°F: 0.25 atm
Inlet flow rate of A: 1.5 lbmol/s



Problem 10

It is desired to carry out the gaseous reaction A→B in an existing tubular reactor consisting of 50 parallel tubes 40 ft long with a 0.75-in inside diameter. Bench-scale experiments have given the reaction rate constant for this first order reaction as 0.00152 s^{-1} at 200°F and 0.0740 s^{-1} at 300°F. At what temperature should the reactor be operated to give a conversion of A of 80%, with a feed rate of 500 lb/h of pure A and an operating pressure of 100 psig? A has a molecular weight of 73. Assuming perfect gas and irreversible reaction. (10%)

Constants and conversion factors for problem 9 & 10

1. °R= °F+460
2. gas constant $R=\frac{0.73ft^3\times atm}{lbmol\times {}^oR}=\frac{8.314kpa\times dm^3}{mol\times K}=\frac{0.73ft^3\times atm}{lbmol\times {}^oR}=\frac{1.987Btu}{lbmol\times {}^oR}=\frac{0.082dm^3\times atm}{mol\times K}$
3. 1 atm=14.7 psia