國　立　清　華　大　學　命　題　紙

98 學年度__化學工程學__系（所）_____組碩士班入學考試

科目__化工熱力學及化學反應工程__ 科目代碼__0702__共_3_頁第_1_頁 *請在【答案卷卡】內作答

1. (I)(a) The van der Waals equation of state is the first practical cubic equation of state: P = RT/(V-b) – a/V^2; Please derive expressions for parameters of a and b in terms of critical constants, i.e. Tc, and Pc. (7%)

   (b) Please also show that the critical compressibility for components following this equation of state is Zc = 3/8 (3%)

   (II)(a) Please derive the following equation: $dH = Cp\,dT + [V - T(\partial V/\partial T)_P]\,dP$ (4%)

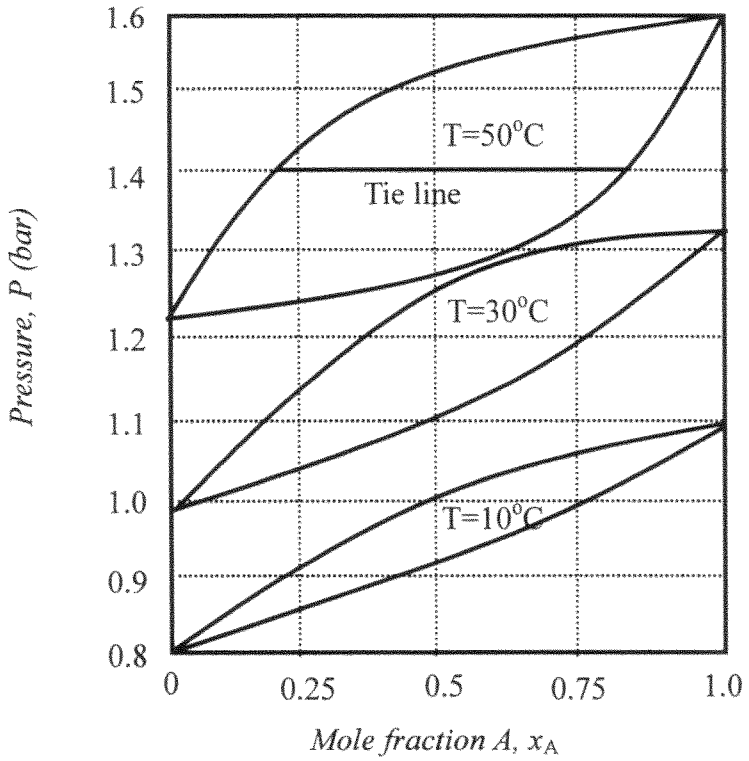
   (b) Please calculate the enthalpy change for liquid water from 1 bar, 25°C to 1000 bar, 50°C based on the data given in the following table (6%).

T (°C)	P (bar)	Cp (J/mol-°K)	V (cm3/mol)	β (°K^{-1})
25	1	75.305	18.071	256 x 10^{-6}
25	1000	--	18.012	366 x 10^{-6}
50	1	75.314	18.234	458 x 10^{-6}
50	1000	--	18.174	568 x 10^{-6}

2. (I)(a) What is the mathematic definition of partial molar property $\overline{M}_i$ of property M of species *i* in solution at constant *T* (temperature) and *P* (pressure). (b) Write down the Gibbs/Duhem equation at constant *T* and *P*. (c) The enthalpy of a binary liquid system of species A and B at fixed *T* and *P* is represented by the equation: $H(J/mol) = 600x_A + 400x_B + x_A x_B(20x_A + 40x_B)$. Determine the numerical value of partial enthalpy $\overline{H}_B$ at $x_B = 0.6$. (10%)

   (II)The vaporization points of species A and B at 1 bar are at 50 and 110°C, respectively. Both the gas and liquid phases of the binary A-B system are ideal solutions. (a) What is the Gibbs free energy of mixing of the vapor phase? (b) What is the excess Gibbs free energy of mixing of the vapor phase? (c) Draw a schematic *T-x* (temperature-composition) phase diagram of the binary A-B system at 1 bar. The temperature range is from 0 to 200°C. (d) Draw a schematic μ_B-x_B (chemical potential of B- composition of B) diagram at 70°C and 1 bar. (10%)

3.(I) You are assigned to design a process for the transferring of a gas mixture of A and B components containing 50 molar % A at 30°C. All the information you have is a plot of pressure versus molar % A (x_A) as shown below.



(a). What is the pressure condition required if you would like to transfer the mixture under liquid state? (2%)

(b). What is the pressure condition required in order to bring the liquid mixture at (a) back to gas state? (2%)

(c). What can you do if you need to decrease the required pressure for the transferring of the liquid mixture at (a) according to the phase diagram? (2%)

(d). Please predict the final equilibrium state of the mixture if you control the final pressure at 1.2 bar? List the final composition(s) and the corresponding state(s) as well as the fraction of the phase(s). (4%)

(e). What can you do if you have to separate these two components from the liquid mixture at (a)? Which temperature should be the best for the separation? (2%)

(II) (a)Please calculate the equilibrium extent of decomposition of A as a result of the chemical reaction A(g) = 2B(g) at standard state. Assume that the gas phase is ideal. Known that the Gibbs energies of formation for A and B are 100 and 50 kJ/mol at standard state. (2%)

(b)If pure A is diluted with C and keep the condition at standard state and the initial mole fraction of A in the mixture before dissociation begins is 0.3, what are the mole fractions of A and B present at equilibrium? (2%)

(c)If this reaction is exothermic, what will happen for the equilibrium extent while the reaction temperature increases and why? (2%)

(d)If this reaction is carried out at higher pressure, what will happen for the equilibrium extent and why? (2%)

4.(I)The rate equation of the following irreversible reaction

$2A+B \rightarrow A_2B$ is $rA_2B=\frac{k_2 C_A^2 C_B}{1+k_1 C_A}$

What reaction mechanism is suggested by this rate expression if the chemistry of the reaction suggests that the intermediate consists of an association of reactant molecules? (10%)

(II)Propylene and chlorine react to give allyl chloride,

(1) $C_3H_6+Cl_2 \rightarrow CH_2=CH\text{-}CH_2Cl+HCl$ and 1,2,-dichlcropropane,

(2) $C_3H_6+Cl_2 \rightarrow CH_2Cl\text{-}CHCl\text{-}CH_3$

The rate laws for reaction (1)and (2) are

$$-r_1=206{,}000 \exp\left(-\frac{7610}{T}\right)p_p p_c$$

$$-r_2=11.7\exp\left(-\frac{1920}{T}\right) p_p p_c \qquad (T \text{ is in kelvin})$$

Where p_p and p_c are partial pressures of propylene and chlorine, respectively. Consider two types of reactors, a CSTR and a plug flow reactor, and two temperatures for constant-temperature operation, 350°C and 450°C. Which combination of temperature and reactor type will give the largest production of allyl chloride? Why? (10%)

5. (a) Describe the features of ideal batch, plug flow and mixed flow reactors. In other words, indicate the assumptions you make when you use these ideal reactors. (6%)

(b) For a mixed flow reactor, derive the design equations, starting from the mole balance. (4%)

(c) A liquid phase reaction $A+B \Leftrightarrow R+S$ (forward rate constant k_1=7 *l*/mol· min, reverse rate constant k_2= 3 l/mol·min) is carried out in a mixed flow reactor (V=120 l). If A and B are fed to the reactor at identical volumetric flow rate v_o, C_{Ao}=2.8 mol/l and C_{Bo}=1.6 mol/l before mixing, find v_o if the conversion of B is expected to reach 75%. (10%)