國立台灣科技大學九十五學年度碩士班招生試題

系所組別： 化學工程系碩士班

科　　目： 化工熱力學與動力學

總分 100 分

Part I. 化工熱力學（50%）

1. It is possible to cool liquid water (subcooled liquid water) below its freezing point of 273.15 K without the formation of ice, if care is taken to prevent nucleation. One kilogram of subcooled liquid water at 261.15 K is contained in a well-insulated vessel. Nucleation of ice is induced by the introduction of a spot of dust, and a spontaneous crystallization process follows. If the heat capacity of liquid water C_p = 4.185 kJ/kg・K and can be assumed constant over the small temperature range, please answer the following questions.
   (a) The introduction of dust induces formation of some ice at 273.15 K, where the heat of fusion is 334 kJ/kg. Find the final state (composition) of the water.
   (b) Calculate the entropy change of the water, the surroundings, and the total entropy change. Is it a spontaneous process? (15%)

2. Due to the shortage of solar cell grade polysilicon (SOG-Si), a chemical plant that utilizes the so called Siemens process is planned now for the eager demand from solar cell industry. The Siemens process starts with the transformation of metal Si powders to gaseous trichlorosilane ($SiHCl_3$) by reaction with HCl in a fluidized bed system (See Fig. 1). HCl gas is supplied from a huge gas tank under normal state, and is compressed to 1.5 atm and 60℃ by a compressor, then heated to 600 ℃ by a heater. The gas stream then is introduced into the fluidized bed to meet with Si powders at a superficial velocity of 4 m/s. The cross-sectional area of bed is 1.0 m^2.
   (a) How many moles of HCl do we need per second?
   (b) From $H = H(T, P)$, $dH = TdS + VdP$ and one of the Maxwell's equations, please derive an expression for dH as a function of T and P in terms of measurable properties. Also show the form of dH when ideal gas behavior is assumed.
   (c) Find the work rate needed for the compressor to compress adiabatically and reversibly.
   (d) How much heat must each mole of HCl absorb in the heater, in kJ/mol?
   (e) If we use electrical heaters for the heating job, and if the local electricity costs NT1.83 dollar/kW・hr, what would be cost of electricity for a 24hr run? (molecular weight of HCl = 36.46 g/mol, its heat capacity in the ideal gas state $C_P^{ig}/R = 3.512$, R = 8.314 J/mol・K) (20%)

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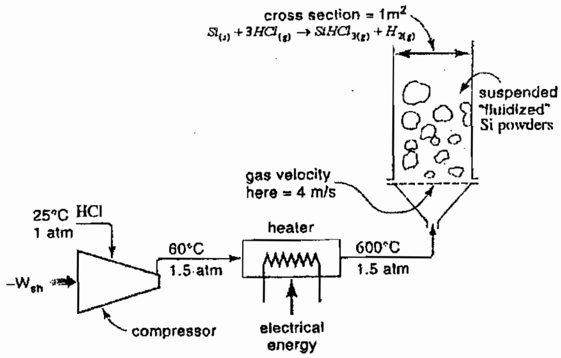

Fig. 1 The first part of Siemens process

3. (a) Start from the Gibbs free energy for an ideal mixture $G = \sum_i \mu_i n_i = \sum_i \bar{G}_i n_i$, where μ_i is the chemical potential of species i in the mixture and can be expressed as a function of the fugacity f_i in the mixture as $\mu_i = \mu_i^* + RT \ln f_i$ (μ_i^* is an integration constant), to show the change in free energy on mixing.

(b) What is the ideal entropy change on mixing at constant T and P?

(15%)

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Part II. 化工動力學 (50%)

4. Please choose the proper equations for the following items, respectively. You may only write down the alphabets and the numbers. (16%)

Items:

(a) Second order reaction

(b) Space time

(c) First order reaction

(d) Ideal batch reactor

(e) Ideal continuous-stirred tank reactor

(f) Plug flow reactor

(g) Thiele modulus

(h) Michaelis-Menten rate equation

Equations:

(1) $-r_A = k\dfrac{C_{E0}C_A}{C_M + C_A}$

(2) $\dfrac{1}{C_A} - \dfrac{1}{C_{A0}} = kt$

(3) $-\ln\dfrac{C_A}{C_{A0}} = kt$

(4) $\tau = \dfrac{C_{A0}x_A}{(-r_A)}$

(5) $t = -\int_{C_{A0}}^{C_A} \dfrac{dC_A}{(-r_A)}$

(6) $\phi_n^2 = \dfrac{k_n S_a \rho_c R^2 C_{As}^{n-1}}{De}$

(7) $\tau = \dfrac{C_{A0}V}{F_{A0}}$

(8) $\tau = -\int_{C_{A0}}^{C_A} \dfrac{dC_A}{(-r_A)}$

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5. In 1906, Walker investigated the following reaction

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

in a batch reactor at 25℃ by commencing with equal concentrations (0.01 mol/l) of ethyl acetate and sodium hydroxide and obtained the following results:

t(min)	0	5	9	13	20	25	33	37
mol NaOH/l	0.01	0.00755	0.00633	0.00541	0.00434	0.00385	0.00320	0.00296

On the basis of these data, determine the order of the reaction and evaluate the rate constant. (18%)

6. An elementary and reversible reaction

$$2C_6H_6 \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} C_{12}H_{10} + H_2$$

or symbolically,

$$2A \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} B + C$$

is to be carried out in an ideal continuous stirred tank reactor(with a benzene feed of 10 lb mol/min) at 760℃. The feed is to be pure benzene in the gas phase at a total pressure of 5 atm (C_{A0} =0.0037 lb mol/ft^3). The reaction rate constant is $k = 1,800\ ft^3/lb\ mol \cdot s$, the concentration equilibrium constant is $K_C = 0.3$ and the equilibrium conversion is Xe = 0.52. Calculate the reactor volume needed to achieve 98 % of the equilibrium conversion of benzene. (16%)