

國立台灣科技大學九十八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

(總分為 100 分)

PART I 化工熱力學 (50%)

1. "A reaction that results in more order in the system ($\Delta S_{\text{system}} < 0$) can never be spontaneous." Is the above statement correct or incorrect? Without explanation you will receive no points. (5)
2. An ideal gas is contained in a rigid tank of volume V initially at P_1 and T_1 . Heat is supplied to the contents until a pressure P_2 . The gas can escape as the pressure reaches P_2 , which is the set pressure of the relief valve on the tank.
 - (a) Derive an expression for the heat transfer in terms of V , P_1 and P_2 during the change from P_1 to P_2 . (5)
 - (b) Derive an expression for the heat transfer in terms of V , T and P_2 when gas start to escape from the tank. (10)
3. (a) Use the Clayperon equation, $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$, to calculate the pressure (in kPa) at which ice would melt at -5°C . Data: ice melts at 273.15 K at 101.3 kPa, $\Delta H_{\text{fusion}} = 6.01 \text{ kJ/mol}$, the density of ice is 920 kg/m^3 , the density of liquid water is 997 kg/m^3 , and the molar mass of water is 18.02 g/mol . (10)
 - (b) Assume an ice skater weighs 60 kg, and she uses skates that have a length of 30 cm. What should be the width of her skates to make ice melt at -5°C ? Describe in details what happen to the ice during her ice skating. (5)
4. Calculate the heat exchange of (i) one mole of a gas following the equation of state of $P(V - b) = RT$, and (ii) one mole of Ni during (a) a reversible process of isothermal change in pressure from 1 atm to 1000 atm at 300 K and (b) a sudden release of pressure from 1000 atm, 300 K back to 1 atm. (Hint: Find the thermodynamic relationship of reversible heat.) The needed data for the gas: $b = 0.04 \text{ m}^3/\text{kmol}$ and $C_p = 35.56 \text{ J/mol/K}$, and for Ni: $C_p = 16.99 + 2.95 \cdot 10^{-2} T$ in J/mol/K , density = 8.9 g/cm^3 , MW = 58.7 g/mol , $\alpha_p = 40 \cdot 10^{-6} \text{ K}^{-1}$, and $\kappa_T = 1.5 \cdot 10^{-6} \text{ atm}^{-1}$. (15)

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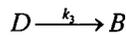
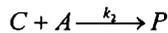
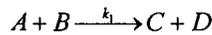
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PART II 化工動力學 (50%)

- (1) The catalytic liquid-phase reactions in an isothermal batch reactor are shown as following. In the beginning, the values of C_A , C_B , C_C and C_D are C_{A0} , C_{B0} , 0 and 0, respectively.



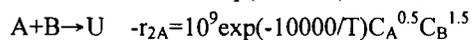
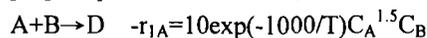
Where k_3 is very large and $k_2 \gg k_1$. All reactions are elementary and please express the conversion of A species by time, rate constant and C_B . (10%)

- (2) The homogeneous gas decomposition of phosphine, $4 \text{PH}_3(\text{g}) \rightarrow \text{P}_4(\text{g}) + 6 \text{H}_2(\text{g})$, proceeds isothermally at 649°C with a rate constant of 10 hr^{-1} .
- (a) What size plug-flow reactor (PFR) operating at 460 kPa can produce 70% conversion of a pure feed consisting of 40 mol/h of pure phosphine? (10%)
- (b) What is the size of continuous-stirred tank reactor (CSTR) in the same operating conditions for 80% conversion? (10%)

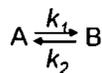
Hint: gas constant (R) = $8.3 \text{ Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$,

$$\int_b^a \frac{1+ax}{1-x} = (1+a) \ln \frac{1}{1-x} - ax$$

- (3) Make your sketches to get maximum selectivity of product D. Please describe the proper operation conditions, such as temperature, concentration. (5%)



- (4) The following liquid-phase reaction is carried out in an **adiabatic** CSTR without shaft work.



Please calculate the reactor volume necessary to achieve 90% conversion. The formula obtained from energy balance of reactor temperature and conversion is: $T(K) = T_0 + 40 X$.

Additional information:

Feed = 300 kmol/h at 330K, $C_{A0} = 20 \text{ M}$, $C_{B0} = 0$,

E (activation energy) = 60000 J/mol, k_1 (rate constant at 360K) = 30 h^{-1} ,

K_c (concentration equilibrium constant at 330 K) = 3

ΔH_{Rxn} (Heat of reaction at 298K) = $-7000 \text{ J/mol}\cdot\text{A}$, $R = 8.3 \text{ J/mol}\cdot\text{K}$

Van't - Hoff Relationship $\frac{d \ln K_c}{dT} = \frac{\Delta H_{Rxn}(T)}{RT^2}$ (15%)

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