國立雲林科技大學
九十學年度研究所碩士班入學考試試題

系所：化工所
科目：化工動力學

1. The irreversible reaction $2A + B = A_2B$ has been studied kinetically, and the rate of formation of product has been found to be well correlated by the following rate equation: $r_{A_2B} = 0.72\, C_A^2\, C_B\, /\, (1+2\, C_A)$. The two reaction mechanisms suggested are as follows:

Model 1:
$$2A \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} A_2^*$$
$$A_2^* + B \xrightarrow{k_2} A_2B$$

Model 2:
$$A + B \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} AB^*$$
$$AB^* + A \xrightarrow{k_2} A_2B$$

Use the steady-state approximation for the intermediates to derive the rate equation for each model and decide which model is appropriate. (12%)

2. The results of a irreversible liquid phase reaction, expressed as $A + B \rightarrow C + D$, at 139℃ in a well-mixed batch reactor are shown in the following table:

Time, min	13	34	59	120
Conversion of A, %	11.2	25.7	36.7	55.2

The reaction begins with equimolar amount (0.1 g mol/liter) of species A and B as the reactants. The two rate equations suggested are as follows:

First-order: $-r_A = -\dfrac{dC_A}{dt} = k_1 C_A$ or **Second-order:** $-r_A = -\dfrac{dC_A}{dt} = k_2 C_A C_B$

Use the integral method to determine which rate equation is preferred and also calculate its reaction rate constant. (18%)

3. An aqueous reaction, $A + B \rightarrow$ products, with the first–order rate equation

$$-r_A = 0.158\, C_A,\ \text{g mol/(cm}^3\text{)(min)}$$

is considered. The feed rate to be treated is 500 cm^3/min of solution, with the concentration of species A of 1.5×10^{-4} g mol/cm^3. Assuming volume does not change with reaction, derive the design equation and calculate the conversion of species A of each of the following arrangements:

(a) One continuous stirred tank reactor (5 liters).
(b) Two continuous stirred tank reactors in series (each 2.5 liters).
(c) One plug flow reactor (5 liters).
(d) One continuous stirred tank reactor followed by one plug flow reactor (each 2.5 liters). (20%)

4. (25分)

Write the mole balance equations to be solved for the liquid-phase reaction set

$$\begin{tikzcd} A \arrow[r, "k_1"] \arrow[d, "k_3"] & B \arrow[r, "k_2"] \arrow[d, "k_4"] & D \\ C & E \arrow[r, "k_5"] & F \end{tikzcd}$$

assuming all reactions are elementary and irreversible

(a) in a plug-flow reactor (PFR) operated at steady state. (8分)

(b) in a continuous-stirred tank reactor (CSTR) operated at steady state. (8分)

(c) solve equations in (a) for $C_A(\tau)$ and $C_B(\tau)$. (9分)

(τ is the space time; the initial concentration of A is C_{A0})

5. (15分)

We wish to produce B in the liquid-phase reaction $A \xrightarrow{k_1} B$ in a CSTR operated at steady state at $v_0 = 4$ liter/min with $C_{A0} = 2$ moles/liter. However, we find that there is a second reaction $A \xrightarrow{k_2} C$, which can also occur. We find that both reactions are first order and irreversible with $k_1 = 0.5\ \text{min}^{-1}$ and $k_2 = 0.1\ \text{min}^{-1}$. Find the space time ($\tau$), reactor volume (V) and concentration of B (C_B) for 90% conversion of A.

6. (10分)

Parallel reactions as follows:

$2A \longrightarrow R$, undesired, $r_R = k_1 C_A^2$
$A + B \longrightarrow S$, desired, $r_S = k_2 C_A C_B$
$2B \longrightarrow T$, undesired, $r_T = k_3 C_B^2$

Find what ratio of C_A to C_B should be maintained in a CSTR so as to maximize the instantaneous fractional yield of desired product S ,i.e., Y_S.

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系所：化工所
科目：化工熱力學

1. One mole of an ideal gas originally confined in a vessel at 350 K and 5 Mpa is allowed to expand through a valve into an evacuated vessel whose volume is 9 times that of the first. The system is thermally and mechanically insulated from the surroundings. Sufficient time has elapsed and the valve is left open so that the temperatures of the two vessels have come to equilibrium. What are the values of W, Q, $\triangle U$, $\triangle H$, $\triangle S$ for this process？（25 points）

2. Find the final temperature if the combustion of hydrogen gas

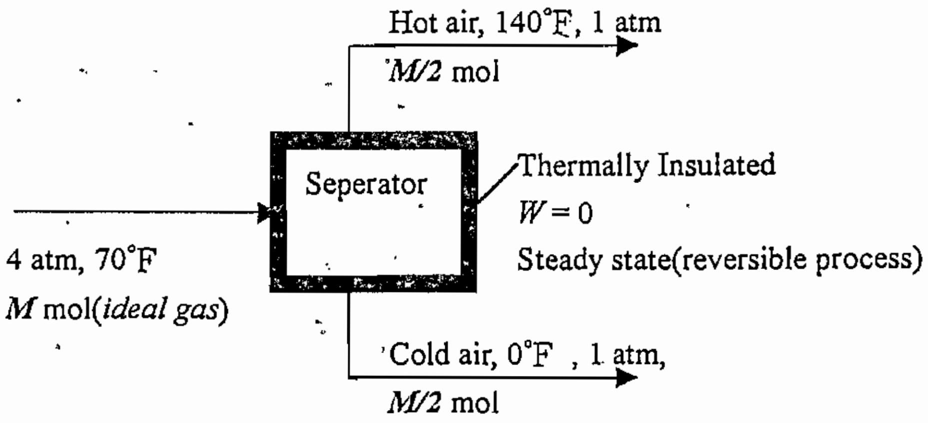
$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

is carried out adiabatically at constant pressure, beginning at 298.15 K. Assume that a stoichiometric mixture is present before the reaction and the reaction proceeds to completion. Assume that the heat capacity of water vapor is constant and equal to its value at 2000K. Assume that the value of H at 298.15 K can be used over the range of temperature encountered.（15 point）

	$\overline{C}_P^\circ$	$\overline{S}^\circ$	$\overline{H}^\circ - \overline{H}_{298}^\circ$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
T/K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
			$H_2O(g)$		
0	0.000	0.000	−9.904	−238.921	−238.921
298	33.590	188.834	0.000	−241.826	−228.582
500	35.226	206.534	6.925	−243.826	−219.051
1000	41.268	232.738	26.000	−247.857	−192.590
2000	51.180	264.769	72.790	−251.575	−135.528
3000	55.748	286.504	126.549	−253.024	−77.163

3. It is desired to lower temperature of m moles of a finite material body (molar heat capacity，$C_{p,m}$) from T_1 to T_2 by the operation of a refrigerator which discards heat to the surrounding at temperature T_0 (Assume the surrounding is large enough to maintain temperature at T_0). Determine the minimum work, W_{min} required. (20 points)

4. An engineer claims to have invented a steady flow device that will take air at 4atm and 70°F and separate it into two streams of equal mass：one at 1atm and 0°F and the second at 1atm and 140°F. He claims that his device operates adiabatically and does not require or produce work. Is such a device possible？ Please make your judgement according to the 2nd law of thermodynamics. (20 points)



5. Calculate the Gibbs energy change of mixing（ΔG_{mix}）, the entropy change of mixing (ΔS_{mix}), the enthalpy change of mixing (ΔH_{mix}), and the volume change of mixing（ΔV_{mix}） for a solution of 1.200 mol of benzene and 1.300 mol of toluene at 20.00°C. Assume the solution to be ideal. (10 points)

6. Give explanation or definition for the following terms: (10 points)
   - (a) fugacity（2 points）
   - (b) Partial molar quantity（2 points）
   - (c) Criteria of equilibrium at constant temperature and constant pressure（2 points）
   - (d) Explain earthquake phenomena according to thermodynamics laws. (4 points)

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系所：化工所
科目：單元操作與輸送現象

1. Consider the system pictured in Fig. 1, in which the cylindrical rod is being moved with velocity v. The rod and the cylinder are coaxial. Find
   (a) the steady-state velocity distribution (15%)
   (b) the volume rate of flow (5%).

   (hint: $\int x \ln x dx = \frac{1}{2}x^2 \ln x - \frac{1}{4}x^2 + C$)

2. For heterogeneous catalytic reaction, porous catalysts are usually applied to this purpose due to their high surface area. However, there is a mass transport problem in those macro- and micro-pores of those catalysts. Considering a single cylindrical pore of length L, with reactant A diffusing into the pore as shown in Fig. 2a,
   (a) show that the concentration of reactant A within the pore is

$$\frac{C_A}{C_{A_S}} = \frac{\cosh[m(L-x)]}{\cosh(mL)}$$

   where C_{As} is outside surface concentration of the catalyst, $m = [2k''/(D \cdot r)]^{1/2} = (k/D)^{1/2}$, k" and k are the rate constants in m/s and in 1/s, respectively, since k×(Volume) = k"×(Surface area), D is the diffusivity in m^2/s. (10%)
   (b) If the catalyst is a pellet with flat plate form as shown in Fig. 2b, show that there is similar concentration distribution equation.

$$\frac{C_A}{C_{A_S}} = \frac{\cosh(\Phi x)}{\cosh(\Phi L)}$$

   where $\Phi = (k'\rho/D)^{1/2}$, k' is the rate constant in $m^3/(kg \cdot s)$, ρ is the catalyst density in kg/m^3. (10%)

3. Consider the wall initially at uniform temperature T_0, its surface temperature is T_s for $t > 0$. Assume the temperature in the wall of the

form

$$T = A + B\sin Cx$$

The normalized temperature distribution is $\dfrac{T - T_0}{T_s - T_0} = \phi\left(\dfrac{x}{\delta}\right)$. Derive

the form of $\phi\left(\dfrac{x}{\delta}\right)$. (20%)

4. A heated sphere of radius R is suspended in a large, motionless body of fluid. It is desired to study the heat conduction in the fluid surrounding the sphere. It is assumed in this problem that free convection effects can be neglected.
   (a) Derive the temperature profile equation that can describe the temperature T in the surrounding fluid as a function of r, the distance from the center of the sphere. The thermal conductivity of the fluid k is constant. (10%)

   (hint: $r = R$, $T = T_R$ and $r = \infty$, $T = T_\infty$)

   (b) From the temperature profile, obtain an expression for the heat flux at surface. Equate this result to the heat flux written as "Newton's law of cooling" and show that a dimensionless heat transfer coefficient (known as the "Nusselt number") is given by

   $$Nu = (h \cdot D/k) = 2$$

   in which D is the sphere diameter. (10%)

5. The process is to operate isothermally at 300K and pressure 101.3 kPa. To absorb 90% of the acetone in a gas containing 1.0 mol% acetone in air in a countercurrent stage tower. The total inlet gas flow to the tower is 30 kgmol/hr, and the total inlet pure water flow to be used to absorb the acetone is 90 kgmol/hr. The equilibrium relation for the acetone (*A*) in the gas-liquid is $y_A = 2.53x_A$.
   (a) Derive the operating line in this tower. (10%)

(b) Using the Kremser analytical equation, determine the number of theoretical states required for this separation. (10%)

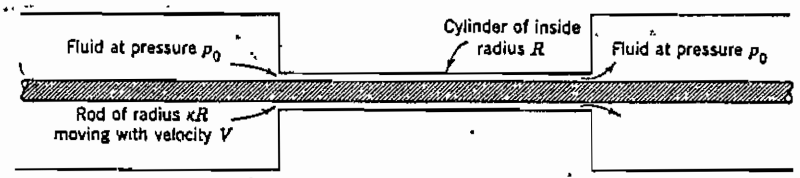

Fig 1 Annular flow with inner cylinder moving axially.

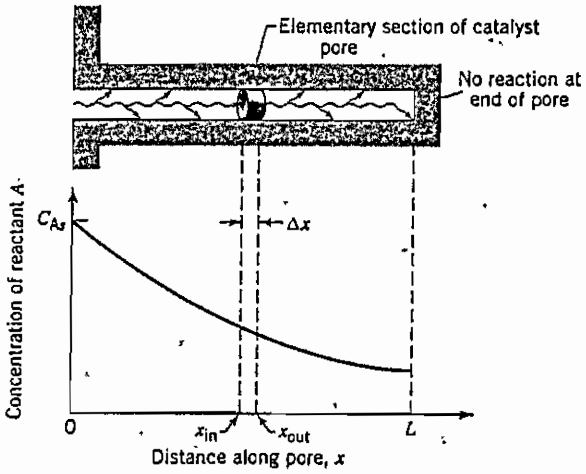

Figure 2a Representation of a cylindrical catalyst pore.

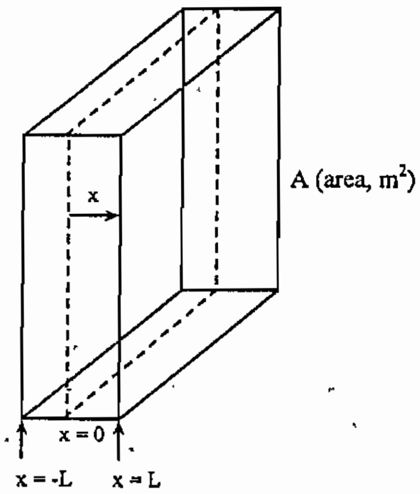

Fig. 2b