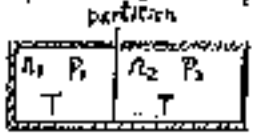
甲. 化工熱力學部份 (50%)

(18%) 1. n_1 (mol) of an ideal gas at pressure P_1 and temperature T is in one compartment of an insulated container. In an adjoining compartment, separated by a partition, is n_2 (mol) of an ideal gas at pressure P_2 and temperature T.



When the partition is removed:

(a) Calculate the final pressure P of the mixture.

(b) Calculate the entropy change when the gases are identical.

(c) Calculate the entropy change when the gases are different.

(d) What is minimum amount of work required to separate the mixture in (c) into two different gases, each at temperature T and pressure P.

(10%) 2. A thick-walled insulated metal chamber contains n_1 (mol) of helium at high pressure P_1. It is connected through a valve with a large, almost empty gasholder in which the pressure is maintained at a constant value P', very nearly atmospheric. The valve is opened slightly, and the helium flows slowly and adiabatically into the gasholder until the pressures on the two sides of the valve are equalized. Prove that

$$n_2/n_1 = (U_1 - H')/(U_2 - H')$$

where n_2 = number of moles of helium left in the chamber,
U_1 = initial molar internal energy of helium in the chamber,
U_2 = final molar internal energy of helium in the chamber,
H' = molar enthalpy of helium in the gasholder

(14%) 3. Two identical bodies each have heat capacities of $C_v = a/T$, where a = constant. Their initial temperature are T_1 and T_2, with $T_2 > T_1$. The two bodies are to be brought into thermal equilibrium with each other (maintain both volumes constant) while delivering work to the surroundings.

(a) Derive an expression for the work delivered in terms of T_1, T_2, and the final temperature T_f.

(b) What is T_f in terms of T_1 and T_2 if no work is delivered?

(c) What is T_f in terms of T_1 and T_2 if the maximum work is delivered?

(d) What is the maximum work delivered if $T_2 = 2T_1$?

(8%) 4. At 25 °C and atmospheric pressure the excess volumes of binary liquid mixtures of species 1 and 2 are given by the equation

$$V^E = x_1x_2(30x_1 + 20x_2)$$

where V is in cm^3mol^{-1}. At these conditions, the molar volumes are: $V_1 = 100$ and $V_2 = 90$ cm^3mol^{-1}. Determine the partial molar volumes $\overline{V}_1$ and $\overline{V}_2$ in a mixture containing 30 mol% of species 1 at the given conditions.

(背面仍有題目,請繼續作答)

乙. 化學反應工程部份(50%)

1. A + B ⇔ C + D 是以固體觸媒催化，它可能之反應機構有下列三種(S 代表活性座)：

(a) $A + S \Leftrightarrow A{\cdot}S$
$A{\cdot}S + B \Leftrightarrow C{\cdot}S + D$
$C{\cdot}S \Leftrightarrow C + S$

(b) $A + S \Leftrightarrow A{\cdot}S$
$B + S \Leftrightarrow B{\cdot}S$
$A{\cdot}S + B{\cdot}S \Leftrightarrow C{\cdot}S + D{\cdot}S$
$C{\cdot}S \Leftrightarrow C + S$
$D{\cdot}S \Leftrightarrow D + S$

(c) $B + S \Leftrightarrow B{\cdot}S$
$B{\cdot}S + A \Leftrightarrow C{\cdot}S + D$
$C{\cdot}S \Leftrightarrow C + S$

(1)請問要用什麼方法才能判定上列那一種反應機構較為正確？(3%)
(2)假定該反應機構為(a)，如何判定每一步驟是否為可逆？(3%)

2. 填充床反應器中
(1)當觸媒粒內擴散對反應速率有顯著影響時，實驗所求出之活化能比實際反應的活化能大或小？何故？(3%)
(2)觸媒粒徑大小對壓降有何影響？(2%)
(3)觸媒粒徑大小對對薄膜擴散有何影響？(2%)

3. 以固體觸媒催化苯的氫化反應，可採用二相反應器或三相反應器。
(1)請問採用三相反應器有何優點？(2%)
(2) Trickle bed reactor (一種三相反應器)與 Packed bed reactor (一種二相反應器)互相比較，所使用的觸媒與反應器設施有何顯著的不同？(2%)

4. 以純 B 在一個管狀反應器內進行 B → C 反應，此反應僅在管內壁進行，其反應速率表達式 $-r_B = AkC_B$
A 為反應面積，反應速率常數 k 為 0.7cm/min。入口處流量 10 mole/min，流速 50 liter/min，B 的擴散系數 10^{-5} cm²/sec，擴散層厚度為 1mm。
(1)試問此速反應控制或為擴散控制的反應？(3%)
(2)試建立非穩定狀態下(unsteady state)的質量平衡微分方程式。(6%)
(3)穩定狀態下(unsteady state)，B 濃度與反應器體積的關係為何？(3%)

5. 試舉兩個提高反應器系統轉換率的方法（須敘明所需條件）。(4%)

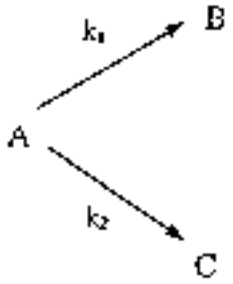
6. The thermal decomposition of ethane to ethylene, methane, butane, and hydrogen is believed to follow the sequence below:

$$C_2H_6 \xrightarrow{k_1} 2\,CH_3\bullet$$
$$CH_3\bullet + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5\bullet$$
$$C_2H_5\bullet \xrightarrow{k_3} C_2H_4 + H\bullet$$
$$H\bullet + C_2H_6 \xrightarrow{k_4} H_2 + C_2H_5\bullet$$
$$2\,C_2H_5\bullet \xrightarrow{k_5} C_4H_{10}$$

Derive a rate law for the rate of formation of ethylene. (11%)

(背面仍有題目,請繼續作答)

7. For a parallel reaction



$r_B = k_1 C_A$, $r_C = k_2 C_C^2$

to have the same conversion of A,

(1) which one of the following reactors shall you choose to maximize the selectivity of B? (3%)

(2) which one will you use to maximize the selectivity of C? (3%)

The reactors considered include a plug-flow reactor, a recycled plug flow reactor, a completely-stirred tank reactor (CSTR), and two CSTR reactors in series.