國立勤益科技大學101學年度研究所碩士班招生筆試試題卷

所別：化工與材料工程系碩士班　　組別：化工科技

科目：化工動力學及熱力學

准考證號碼：□□□□□□□□□（考生自填）

考生注意事項：

一、考試時間100分鐘。

二、應考人不得自行攜帶電子計算器，一律由本校統一提供電子計算器。

三、試題作答均須詳列解答過程。

試題一：〈 25 分〉

請回答以下問題:

(1) 請解釋homogeneous與heterogeneous反應系統? 並說明在此兩種系統中影響其反應速率變因為何? (比較其異同)　10%

(2) 請解釋 elementary 與 nonelementary 反應? 各舉一例輔助說明之。5%

(3) 請寫出阿倫尼亞(Arrhenius)關係式, 解釋式中各變因? 並簡要說明如何利用此關係式求出反應活化能?　10%

試題二：〈 10 分〉

有一不可逆之反應 $A \rightarrow B$, 其反應速率常數為 k, 而其反應速率式可表示為

$$-r_A = k\, C_A^{\,n}$$

假設進行相關實驗得到以下資訊: (1)實驗 1: C_{A0} (反應物之起始濃度) = 0.5 M, $t_{1/2}$(半衰期) = 20 min; (2)實驗 2: C_{A0} = 1.0 M, $t_{1/2}$ = 10 min。請問此反應之階次(n)為何?

試題三：〈 15 分〉

有一液相反應

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

其中 $k_1 = 2$ liter/mol·min, $k_2 = 1$ liter/mol·min

在一體積為 10 升(liter)之連續攪拌反應器(continuous stirred tank reactor, CSTR)中進行反應。現有二相同體積流率之進料流進此反應器中，其中之一進料含 2 mol A/liter 反應物；而另一進料則含 0.6 mol B/liter。假設對限量反應成分(limiting component)而言，其轉化率為 80%，請問其體積流率為何? (假設在反應過程中，反應液之密度不變。)

試題四：〈 20 分〉

Steam flows at steady state through a converging, insulated nozzle, 25cm long and with an inlet diameter of 5cm. At the nozzle entrance, the temperature and pressure are 350ºC and 700kPa, and the velocity is 30m/sec. At the nozzle exit, the steam temperature and pressure are 200ºC and 350kPa. Property values are H_1 = 3164.3kJ/kg, V_1 = 405.71cm^3/g, H_2 = 2863.0kJ/kg, V_2 = 612.31cm^3/g. What is the velocity of the steam at the nozzle exit, and what is the exit diameter?

試題五：〈 15 分〉

Heat in the amount of 150 kJ is transferred directly from a hot reservoir at T_H = 550 K to two cooler reservoirs at T_1 = 350 K and T_2 = 250 K. The surroundings temperature is 300 K. If the heat transferred to the reservoir at T_1 is half that transferred to the reservoir at T_2, calculate: (a) The entropy generation in kJ/K. (b) The lost work.

試題六：〈 15 分〉

For a gas at a low pressure enough so that the virial expression may be truncated to Z = 1 + BP/RT, show that the equation for isothermal work in a reversible compression is RT ln (P_2/P_1) the same as for an ideal gas.

化工動力學及94之熱力學解答

試題一：（ 25 分）

請回答以下問題:

(1) 請解釋 homogeneous 與 heterogeneous 反應系統? 並說明在此兩種系統中影響其反應速率變因為何?(比較其異同) 10%

(2) 請解釋 elementary 與 nonelementary 反應? 各舉一例輔助說明之。5%

(3) 請寫出阿倫尼亞(Arrhenius)關係式, 解釋式中各變因? 並簡要說明如何利用此關係式求出反應活化能? 10%

(1) (a) 若反應物與產物以及觸媒等在反應系統中只有單一相，則稱之為 homogeneous 反應系統；而以上系統中若存有兩相(含)以上，則稱之為 heterogeneous 反應系統。

(b) 此兩反應系統中之共同變因：① 溫度，② 壓力；③ 系統中各組成濃度。

不同：在 heterogeneous 反應系統中，因有兩相或以上，故物質會通過相邊界時，存在有質傳變因，此與 homogeneous 系統不同。

(2) elementary 反應：反應式所示即為真實反應途徑：

Ex: $A + B \xrightarrow{k} R$

⇒ 反應速率 $-r_A = k C_A C_B$

Nonelementary 反應：反應式所寫之並非真實之反應途徑(機構)，式中各係數亦非真正之分子反應階次。Ex: $H_2 + Br_2 \to 2HBr$

⇒ $r_{HBr} = \dfrac{k_1[H_2][Br_2]^{1/2}}{k_2 + [HBr]/[Br_2]}$

(3) Arrhenius 關係式：

(a) $k = Ae^{-E_a/RT}$

(b) 可以改變反應溫度，求出各溫度下之反應速率及其反應速率常數(k)，再利用 $\ln k = \ln A - \frac{E_a}{R}\frac{1}{T}$ 關係式，以 $\ln k$ 對 $\frac{1}{T}$ 作圖，所得斜線中之斜率即為 $-\frac{E_a}{R}$，因此而求得其活化能(E_a)。

試題二：〈 10 分〉

有一不可逆之反應 $A \rightarrow B$, 其反應速率常數為 k, 而其反應速率式可表示為

$$-r_A = k C_A^n$$

假設進行相關實驗得到以下資訊: (1)實驗 1: C_{A0} (反應物之起始濃度) = 0.5 M, $t_{1/2}$(半衰期) = 20 min; (2)實驗 2: C_{A0} = 1.0 M, $t_{1/2}$ = 10 min。請問此反應之階次(n)為何?

$$-r_A = -\frac{dC_A}{dt} = k C_A^n$$

$$\Rightarrow -\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^n} = \int_0^t k\, dt$$

$$\Rightarrow -\frac{1}{1-n} C_A^{1-n} \Big|_{C_{A0}}^{C_A} = k t \Big|_0^t$$

$$\Rightarrow \frac{1}{n-1}\left[C_A^{1-n} - C_{A0}^{1-n}\right] = k t$$

$$\Rightarrow C_A^{1-n} - C_{A0}^{1-n} = (n-1) k t$$

當 $t = t_{1/2} \Rightarrow C_A = \frac{1}{2} C_{A0}$ 代入上式得

$$\Rightarrow t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)} C_{A0}^{1-n}$$

$$\Rightarrow \ln t_{1/2} = \ln\left(\frac{2^{n-1} - 1}{k(n-1)}\right) + (1-n) \ln C_{A0}$$

$$\therefore \ln \frac{t_{1/2}}{t'_{1/2}} = (1-n) \ln \frac{C_{A0}}{C'_{A0}}$$

$$\Rightarrow (1-n) = \frac{\ln(t_{1/2}/t'_{1/2})}{\ln(C_{A0}/C'_{A0})}$$

$$n = 1 - \frac{\ln(t_{1/2}/t'_{1/2})}{\ln(C_{A0}/C'_{A0})} = 1 - \frac{\ln(20/10)}{\ln(0.5/1.0)} = 1 - (-1)$$

$$= 2$$

試題三：〈 15 分〉

有一液相反應

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D \qquad \text{其中 } k_1 = 2 \text{ liter/mol·min}, k_2 = 1$$

liter/mol·min

在一體積為 10 升(liter)之連續攪拌反應器(continuous stirred tank reactor, CSTR)中進行反應。現有二相同體積流率之進料流進此反應器中，其中之一進料含 2 mol A/liter 反應物；而另一進料則含 0.6 mol B/liter。假設對限量反應成分(limiting component)而言，其轉化率為 80%，請問其體積流率為何？(假設在反應過程中，反應液之密度不變。)

∵為等體積進料，且密度不變

∴ $C_{A0} = 1$ mol/ℓ；$C_{B0} = 0.3$ mol/ℓ；$C_{C0} = C_{D0} = 0$

∵ 80% 轉化率 (以 B 而言)，所以在 CSTR 中各成分之濃度為：

$C_A = 1.0 - 0.3 \times 0.8 = 0.76$ (mol/ℓ)

$C_B = 0.3 - 0.3 \times 0.8 = 0.06$ (mol/ℓ)

$C_C = 0.3 \times 0.8 = 0.24$ (mol/ℓ)

$C_D = 0.3 \times 0.8 = 0.24$ (mol/ℓ)

$\Rightarrow -r_A = -r_B = k_1 C_A C_B - k_{-1} C_C C_D$

$= 2 \times 0.76 \times 0.06 - 1 \times 0.24 \times 0.24 = 0.0336$ mol/ℓ·min

對 CSTR 而言：

$$\frac{V}{v} = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{B0} - C_B}{-r_B}$$ (其中 V 為體積，v 為體積流率)

$$\Rightarrow v = \frac{V(-r_A)}{C_{A0} - C_A} = \frac{10 \times 0.0336}{1.0 - 0.76} = 1.4 \text{ (ℓ/min)} \#$$

試題四：〈 20 分〉

Steam flows at steady state through a converging, insulated nozzle, 25cm long and with an inlet diameter of 5cm. At the nozzle entrance, the temperature and pressure are 350°C and 700kPa, and the velocity is 30m/sec. At the nozzle exit, the steam temperature and pressure are 200°C and 350kPa. Property values are H_1 = 3164.3kJ/kg, V_1 = 405.71cm^3/g, H_2 = 2863.0kJ/kg, V_2 = 612.31cm^3/g. What is the velocity of the steam at the nozzle exit, and what is the exit diameter?

$$(2863 - 3164.3)\ \text{kJ/kg} \times \frac{1000\ \text{J}}{1\ \text{kJ}} + \frac{\bar{u}_2^2 - 30^2}{2\times 1} = 0 \Rightarrow \bar{u}_2 = 226.85\ \text{m/sec}$$

$$\frac{P_1^2 \bar{u}_1}{V_1} = \frac{P_2^2 \bar{u}_2}{V_2} \rightarrow \frac{5^2 \times 30}{405.71} = \frac{D_2^2 \times 226.85}{612.31}$$

$\therefore D_2 = 1.2\ \text{cm} = 0.012\ \text{m}$.

試題五：〈 15 分〉

Heat in the amount of 150 kJ is transferred directly from a hot reservoir at T_H = 550 K to two cooler reservoirs at T_1 = 350 K and T_2 = 250 K. The surroundings temperature is 300 K. If the heat transferred to the reservoir at T_1 is half that transferred to the reservoir at T_2, calculate: (a) The entropy generation in kJ/K. (b) The lost work.

(a) $\frac{-150}{550} + \frac{50}{350} + \frac{100}{250} = S_g = 0.29$

(b) $W_{lost} = 0.29 \times 300 = 87\ \text{kJ}$

試題六：〈 15 分〉

For a gas at a low pressure enough so that the virial expression may be truncated to Z = 1 + BP/RT, show that the equation for isothermal work in a reversible compression is RT ln (P_2/P_1) the same as for an ideal gas.

$$\frac{PV}{RT} = Z = 1 + \frac{BP}{RT} \rightarrow PV = RT + BP \rightarrow (V-B)P = RT$$

$$\rightarrow P = \frac{RT}{V-B}$$

$$W = -\int_{V_1}^{V_2} P\,dV = \int_{V_1}^{V_2} \frac{-RT}{V-B}\,dV = -RT \ln \frac{V_2 - B}{V_1 - B} = -RT \ln \frac{RT/V_1 - B}{RT/V_2 - B}$$

$$= -RT \ln \frac{P_1}{P_2} = RT \ln \frac{P_2}{P_1}$$