

# 106 年成大化反

## Problem 1

### **【Solution】**

(a)

$$\frac{k(T+10)}{k(T)} = \exp\left[\frac{-E_a}{R}\left(\frac{1}{T+10} - \frac{1}{T}\right)\right] = 2$$
$$\frac{-E_a}{R} = \frac{\ln 2}{\left(\frac{1}{T+10} - \frac{1}{T}\right)}, \quad E_a = \frac{R \ln 2}{\left(\frac{1}{T} - \frac{1}{T+10}\right)} \quad (\text{T is in K})$$

(b)

By Arrhenius law,

$$\ln k = \frac{-E_a}{RT} + \ln A$$

$$k = Ae^{\frac{-E_a}{RT}}$$

將題目所給數據代入：

$$\frac{k_{283K}}{k_{373K}} = \frac{0.005}{0.12} = \frac{e^{\frac{-E_a}{8.314 \times 283}}}{e^{\frac{-E_a}{8.314 \times 373}}}$$

$$\boxed{E_a = 30990.17 \text{ (J/mol)}}$$

For  $A$ ,

$$k_{283K} = Ae^{\frac{-30990.17}{8.314 \times 283}}, \quad \boxed{A = 2625.29 \text{ (min}^{-1}\text{)}}$$

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 133,

Problem 3-7B.)

## **Problem 2**

### **【Solution】**

For CSTR,

$$V = \frac{F_{A0}x_A}{-r_A}$$

For rate equation,

$$-r_A = kC_{A(CSTR)} = kC_{A0}(1 - x_{A(CSTR)})$$

$$\tau = \frac{C_{A0}x_{A(CSTR)}}{kC_{A0}(1 - x_{A(CSTR)})}, \quad k\tau = \frac{0.4}{1 - 0.4} = \frac{2}{3}$$

For PFR,

$$V = \int_0^{x_{A(PFR)}} \frac{F_{A0}dx_A}{-r_A}$$

代入 rate equation,

$$V = \int_0^{x_{A(PFR)}} \frac{F_{A0}dx_A}{kC_{A0}(1 - x_A)}$$

$$k\tau = \int_0^{x_{A(PFR)}} \frac{dx_A}{(1 - x_A)} = \frac{2}{3}, \quad \underline{\underline{x_{A(PFR)} = 0.486}} \quad (1^{\text{st}} \text{ reaction})$$

For 2<sup>nd</sup> reaction, 設  $x_{A(CSTR)} = 0.4$

$$\tau = \frac{C_{A0}x_{A(CSTR)}}{kC_{A0}^2(1 - x_{A(CSTR)})^2}, \quad kC_{A0}\tau = \frac{0.4}{(1 - 0.4)^2} = \frac{10}{9}$$

For PFR,

$$V = \int_0^{x_{A(PFR)}} \frac{F_{A0}dx_A}{kC_{A0}^2(1 - x_A)^2}$$

$$kC_{A0}\tau = \int_0^{x_{A(PFR)}} \frac{dx_A}{(1 - x_A)^2} = \frac{10}{9}, \quad \underline{\underline{x_{A(PFR)} = 0.526}}$$

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 239,

Problem 4-8B-(c).)

### Problem 3

#### 【Solution】

By energy-balance,

$$x_A = \frac{\sum_i \int_{T_{i0}}^T \theta_{i0} C_{pi} dT}{-[\Delta H_R(T_R) + \int_{T_R}^T \Delta C_p dT]}$$

$$\sum_i \int_{T_{i0}}^T \theta_{i0} C_{pi} dT = (80 \times 1 + 90 \times 2)(T - 500) = 260(T - 500)$$

$$-[\Delta H_R(T_R) + \int_{T_R}^T \Delta C_p dT] = -[12 \times 10^3 + (2 \times 85 - 90 - 80)(T - 300)] = -12 \times 10^3$$

$$-12 \times 10^3 x_A = 260(T - 500) \quad , \quad T = \frac{-12 \times 10^3}{260} x_A + 500$$

For rate constant, k,

$$k = 1.6 \times 10^{-6} \exp\left[\frac{15 \times 10^3}{1.987} \left(\frac{1}{300} - \frac{1}{T}\right)\right]$$

For equilibrium constant, K,

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad , \quad \ln \frac{K}{K_{300}} = \frac{12 \times 10^3}{1.987} \left(\frac{1}{300} - \frac{1}{T}\right) = \ln \frac{K}{0.0014}$$

(a)

For CSTR,

$$V = \frac{F_{A0} x_A}{-r_A}$$

For rate equation,

$$-r_A = k C_A C_B - k' C_C^2 = k C_{A0}^2 [(1 - x_A)(2 - x_A) - \frac{4}{K} x_A^2]$$

$$T = \frac{-12 \times 10^3}{260} \times 0.5 + 500 = 476.92(K)$$

$$k_{476.92} = 1.6 \times 10^{-6} \exp\left[\frac{15 \times 10^3}{1.987} \left(\frac{1}{300} - \frac{1}{476.92}\right)\right] = 0.0181$$

$$K_{476.92} = 0.0014 \exp\left[\frac{12 \times 10^3}{1.987} \left(\frac{1}{300} - \frac{1}{476.92}\right)\right] = 2.451$$

Combine,

$$V = \frac{F_{A0}x_A}{kC_{A0}^2[(1-x_A)(2-x_A) - \frac{4}{K}x_A^2]}$$

$$= \frac{100 \times 0.5}{0.0181 \times 10^2 [(1-0.5)(2-0.5) - \frac{4}{2.45} \times 0.5^2]} = \underline{\underline{80.66 \text{ (L)}}}$$

(b)

For PFR,

$$V = \int_0^{x_A} \frac{F_{A0} dx_A}{-r_A}$$

For rate equation,

$$-r_A = kC_A C_B - k' C_C^2 = kC_{A0}^2 [(1-x_A)(2-x_A) - \frac{4}{K}x_A^2]$$

$$= 1.6 \times 10^{-6} \exp\left[\frac{15 \times 10^3}{1.987} \left(\frac{1}{300} - \frac{1}{\frac{-12 \times 10^3}{260}x_A + 500}\right)\right] \times 10^2$$

$$\times \left[(1-x_A)(2-x_A) - \frac{4x_A^2}{0.0014 \exp\left[\frac{12 \times 10^3}{1.987} \left(\frac{1}{300} - \frac{1}{\frac{-12 \times 10^3}{260}x_A + 500}\right)\right]}\right]$$

By Simpson's rule, 令

$$1.6 \times 10^{-6} \exp\left[\frac{15 \times 10^3}{1.987} \left(\frac{1}{300} - \frac{1}{\frac{-12 \times 10^3}{260}x_A + 500}\right)\right] \times 10^2 = A$$

$$\left[(1-x_A)(2-x_A) - \frac{4x_A^2}{0.0014 \exp\left[\frac{12 \times 10^3}{1.987} \left(\frac{1}{300} - \frac{1}{\frac{-12 \times 10^3}{260}x_A + 500}\right)\right]}\right] = B$$

$x_A$	A	B	AB	$F_{A0}/AB$
0	3.7625	2.0000	7.5250	13.2890
0.125	3.1545	1.6243	5.1238	19.5167
0.25	2.6338	1.2369	3.2577	30.6962
0.375	2.1896	0.8184	1.7919	55.8055
0.5	1.8122	0.3421	0.6199	161.3268

$$V = \frac{0.125}{3} [13.2890 + 4 \times 19.5167 + 2 \times 30.6962 + 4 \times 55.8055 + 161.3268]$$

$$= \underline{\underline{22.39 \text{ (L)}}}$$

【補充】 利用 polymath 可數值解如下：

$x_A$	T (K)	V (L)	k ( $M^{-1} \min^{-1}$ )	K	$x_{Ae}$	$-r_A$ (M/min)	$F_{A0}/-r_A$ (L)
0	500	0	0.0376	4.397	0.681	7.525	13.28
0.10	495.3	1.562	0.0326	3,926	0.664	5.542	18.04
0.197	490.9	3.603	0.0284	3,517	0.646	3.996	25.02
0.3	486.2	6.816	0.0244	3.114	0.629	2.620	38.15
0.405	481.3	12.06	0.0209	2.752	0.610	1.489	67.13
0.5	476.9	21.89	0.0181	2.449	0.592	0.613	163.0
0.571	473.6	54.44	0.0162	2.244	0.579	0.0481	2079.8

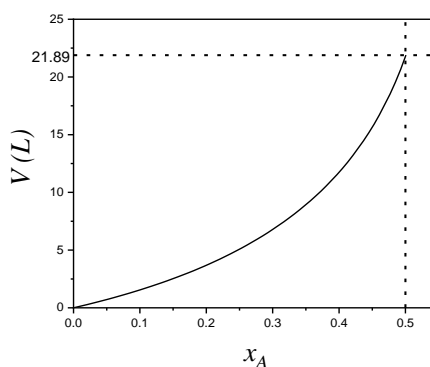
【補充】 利用 polymath 可作圖如下：

```
#To calculate the volume of PFR, we need its design equation, that is,
d(V)/dx_A = F_A0/(-r_A)

#The explicit equations or values are,
CA = CA0*(1-xA)
CB = CA0*(2-xA)
CC = CA0*(2-xA)
FA0 = 100
FB0 = 200
CA0 = 10
CB0 = 10*FB0/FA0
k = 1.6*10^4*exp(15000/(1.987*(1/300-1/T)))
K = 0.0014*exp(12000/(1.987*(1/300-1/T)))
T = -12000/260*xA+500
rA = -k*(CA*CB - (1/K)*(CC)^2)

#For additional information, define
g = 2*(4-K)
h = (9*K^2+8*K*(4-K))*0.5
xAe = (-3*K+h)/g
a = FA0/(-rA)

#Define the the guess initial value of V to obtain the true value, ranging from xA = 0~0.5
V(0) = 0
xA(0) = 0
xA(f) = 0.5
```



則線下面積根據數值解 = V=21.89 (L)

另外，若將  $x_A$  的範圍繼續延伸，並且對照  $x_{Ae}$  (熱力學平衡時之轉化率)，可知此反應最終將在  $x_A = x_{Ae} \approx 0.57$  達到熱力學與能量平衡，此時溫度為 473.6(K)附近(大致對照以上表格)。另外，在上方的 polymath 示範 code 中，額外定義了 g 與 h 兩個變數，其原因在於計算熱力學平衡轉化率與平衡常數關係，即：

$$K = \frac{C_{Ce}^2}{C_A C_B} = \frac{(2x_{Ae})^2}{(1-x_{Ae})(2-x_{Ae})}$$

展開並解出  $x_{Ae}$  的表達式為：

$$x_{Ae} = \frac{-3K + \sqrt{9K^2 + 8K(4-K)}}{2(4-K)} \begin{cases} g = 2(4-K) \\ h = \sqrt{9K^2 + 8K(4-K)} \end{cases}$$

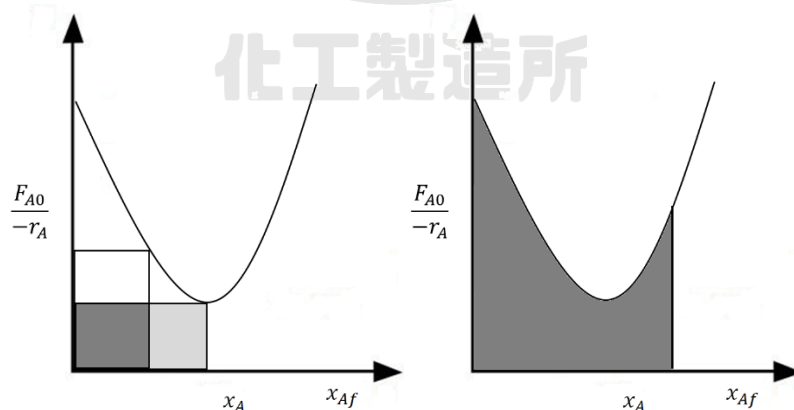
(c)

考慮一液相放熱反應，其速率定律式為：

$$-r_A = k(T)C_A^n$$

則此時速率有兩個因素來決定： $\begin{cases} k(T) \rightarrow \text{隨著反應放熱變大} \\ C_A^n \rightarrow \text{隨著反應進行而變小} \end{cases}$

此二因素互相拮抗的結果可由以下簡圖來表示，

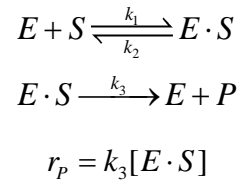


若考慮 CSTR(如左圖)，則在圖形的兩點可能會有相同的矩形面積，因此就會有多個 Steady State 的產生；然而 PFR 之轉化率是隨著反應器體積而隨之增加，並不會有相同面積的情形產生，是故沒有 multiple steady state 的生成。

((a)(b)小題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 490~495, Example 8-3.)

**Problem 4****【Solution】****(a)**

The Michaelis-Menten mechanism can be shown as,



By PSSH,

$$r_{E \cdot S} = k_1[E][S] - k_2[E \cdot S] - k_3[E \cdot S] = 0$$

$$[E \cdot S] = \frac{k_1[E][S]}{k_2 + k_3}$$

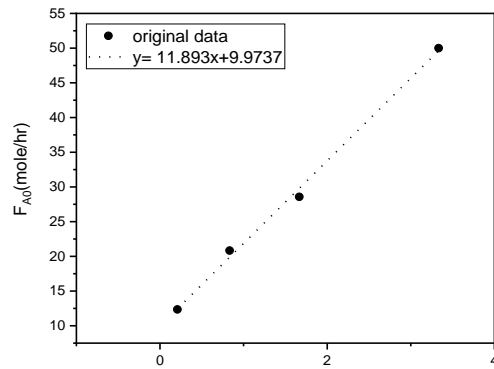
By enzyme balance,

$$\begin{aligned}
 [E]_0 &= [E] + [E \cdot S] = \left[ \frac{(k_2 + k_3)[E \cdot S]}{k_1[S]} + [E \cdot S] \right] \\
 &= \frac{(k_2 + k_3 + k_1[S])}{k_1[S]} [E \cdot S] \\
 r_p &= \frac{k_1 k_3 [S] [E]_0}{k_1 [S] + k_2 + k_3} = \frac{(k_3 [E]_0) [S]}{[S] + \frac{k_2 + k_3}{k_1}} = \frac{v_{\max} [S]}{[S] + K_M}
 \end{aligned}$$

**(b)**

$$\frac{1}{r_p} = \frac{K_M + [S]}{v_{\max} [S]} = \frac{K_M}{v_{\max}} \frac{1}{[S]} + \frac{1}{v_{\max}}$$

Plot  $\frac{1}{r_p} - \frac{1}{[S]}$  diagram,



$1/r_p$	12.34568	20.83333	28.57143	50
$1/[S]$	0.208333	0.833333	1.666667	3.333333

$$\left\{ \begin{array}{l} \text{slope} = \frac{K_M}{v_{\max}} = 11.893 \\ \text{intercept} = \frac{1}{v_{\max}} = 9.97 \end{array} \right. , \quad \left\{ \begin{array}{l} K_M = 1.192 \text{ mM} \\ v_{\max} = 0.100 (\text{mmol} / \text{min}) \end{array} \right.$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 401,

Example 7-3.)

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### Problem 5

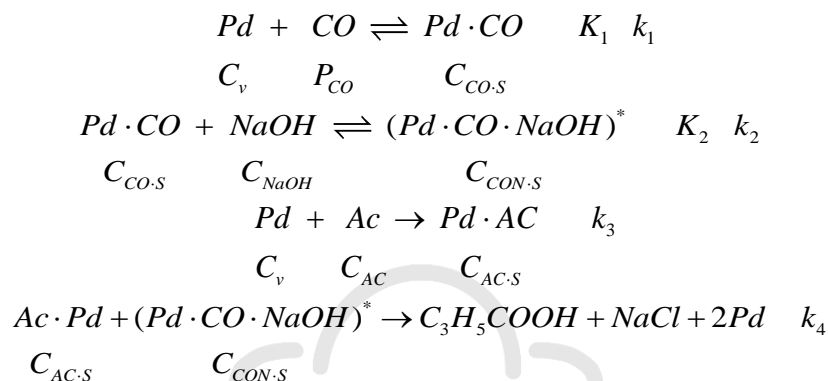
#### 【Solution】

By the rate law,

- (1) 分子有  $CO, Ac, NaOH \rightarrow$  表示 *rate determining step* 中有此三者參與  
(2) 分母有  $Ac \rightarrow$  表示  $Ac$  吸附於活性位上

$\Rightarrow$  推測 step 4 為 *rate determining step*

<討論是否合理>



$\therefore$  Step 4 is rate-determining,

$$\text{reaction rate, } r = k_4 C_{AC \cdot S} C_{CON \cdot S}$$

$$\text{For } C_{CO \cdot S}, \frac{-r_{CO}}{k_1} \approx 0 :$$

$$C_{CO \cdot S} = K_1 P_{CO} C_v$$

$$\text{For } C_{CON \cdot S}, \frac{-r_{CON}}{k_2} \approx 0 :$$

$$C_{CON \cdot S} = K_2 C_{CO \cdot S} C_{NaOH}$$

$$\text{For } C_{AC \cdot S}, :$$

$$-r_{AC} = k_3 C_v C_{AC}$$

The adsorption of  $Ac$  is irreversible, thus we can't obtain the relationship of  $C_{AC \cdot S}$  and other species. Therefore, there is at least no "one" rate-determining step from the mechanism.)

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 754,

COP10-LB. 在原文書示範中，有示範若第三部為決定步驟，則分母項將有  $CO$  與  $NaOH$  存在，也與假設不符，因此同樣也無法證明此機制有速率決定步驟的存在。)

### **Problem 6**

#### **【Solution】**

(a)(b)(d)

By the second figure, the reaction rate is proportional to the partial pressure of A and there seems no inverse relationship between the two value, so A is not adsorbed on the surface or the strength between the two is very weak ( $K_A \ll 1$ ).

(c)

By the third figure, the reaction rate is proportional to the partial pressure of B and as the figure shows, they have inversely relationship when  $P_B$  is very high, so B is on the reaction surface.

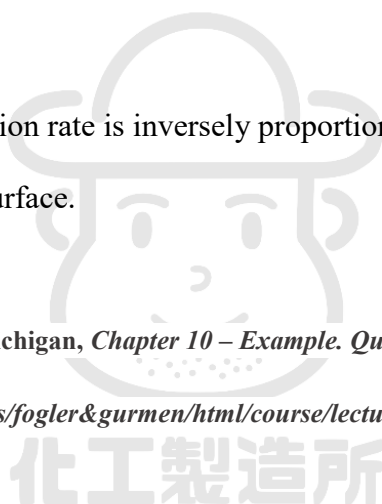
(e)

By the first figure, the reaction rate is inversely proportional to the partial pressure of C, so C is on the reaction surface.

**The answer is (d)**

(本題改編自：University of Michigan, Chapter 10 – Example. Question 2,

<http://www.umich.edu/~elements/fogler&gurmen/html/course/lectures/ten/test7.htm>.)

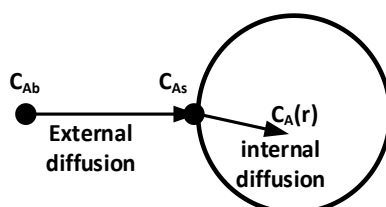


### **Problem 7**

#### **【Solution】**

**Ans : (d)**

Consider a heterogeneous reaction for a catalyst pellet, a several steps should be considered,



- (1) The mass transfer of the reactants from the bulk to the external surface of the catalyst, which is the external diffusion step.
- (2) The reactants then diffuse from the external surface into and through the pores within the catalyst, where the reaction only taking place on the surface of pore, which is the internal diffusion step.

Thiele Modulus is defined as,

$$\phi_n^2 \equiv \frac{\text{surface reaction rate}}{\text{diffusion rate}} = \frac{k_n R^2 C_{As}^{n-1}}{D_e}$$

For **large**  $\phi$ , **internal diffusion limits the rate of reaction**. So the surface reaction is rapid that the reactants are consumed very closed to the external surface, and very little penetrates into the internal region.

For **small**  $\phi$ , **surface reaction controls the rate of reaction**, with large amount of reactant diffuses through the interior of the catalyst without consumed.

(本题可参考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 835/p 837/  
p 814~815/p 821~823.)

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## Problem 1

Ans : (B)

(本题可参考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 38-40.

以及：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 30, Problem 1-8A.)

## Problem 2

Ans : (C)

(本题可参考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 12-14.

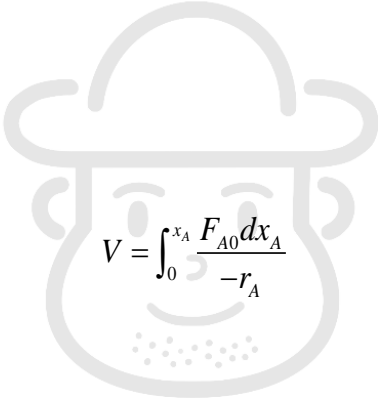
以及：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 30, Problem 1-8A.))

## Problem 3

Ans : (D)

### **【Solution】**

By design equation of PFR,


$$V = \int_0^{x_A} \frac{F_{A0} dx_A}{-r_A}$$

For the rate equation,

$$-r_A = \begin{cases} kC_{A0}^2(1-x_A)^2 \left(\frac{P}{P_0}\right)^2 & \text{gas phase} \\ kC_{A0}^2(1-x_A)^2 & \text{liquid phase} \end{cases}$$

Reaction rate of liquid phase reaction is independent of the partial pressure of the reactants, so the conversion will be the same.

Gas phase reaction rate is proportional to the partial pressure of the reactants; thus if the pressure decreases, the conversion will consequently be reduced.

### **Problem 4**

#### **【Solution】**

(a)

By Arrhenius Law,

$$\frac{k(100^\circ C)}{k(50^\circ C)} = \exp\left[\frac{-E_a}{R}\left(\frac{1}{T_{100}} - \frac{1}{T_{50}}\right)\right]$$
$$k(100^\circ C) = 10 \exp\left[\frac{-500}{8.314}\left(\frac{1}{373} - \frac{1}{323}\right)\right] = 10.25 \text{ (} M^{-2} \cdot s^{-1} \text{)}$$

$$-r_A = k C_A^2 C_B = 10.25 \times 3^2 \times 1.5 = 138.4 \text{ (} mol / dm^3 \cdot s \text{)}$$

(b)

$$-r_A = k C_A C_B^2 = 10.25 \times 3 \times 1.5^2 = 69.206 \text{ (} mol / L \cdot s \text{)}$$

(原題目給定之速率常數單位有誤，若為三級反應，則單位應為  $M^{-2} \cdot s = (mol / dm^3)^{-2} \cdot s$ )



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### **Problem 5**

#### **【Solution】**

令  $A = NH_3$  ,  $B = O_2$

For CSTR,

$$V = \frac{F_{A0}x_A}{-r_A}$$

For rate equation,

$$-r_A = kC_A C_B^{0.5} = \frac{kC_{A0}^{1.5}(1-x_A)(\theta_B - \frac{5}{4}x_A)^{0.5}}{(1+\varepsilon x_A)^{1.5}}$$

$$\theta_B = \frac{(1-0.15) \times \frac{1}{5}}{0.15} = \frac{17}{15}$$

$$\varepsilon = \delta y_{A0} = 0.25 \times 0.15 = 0.0375$$

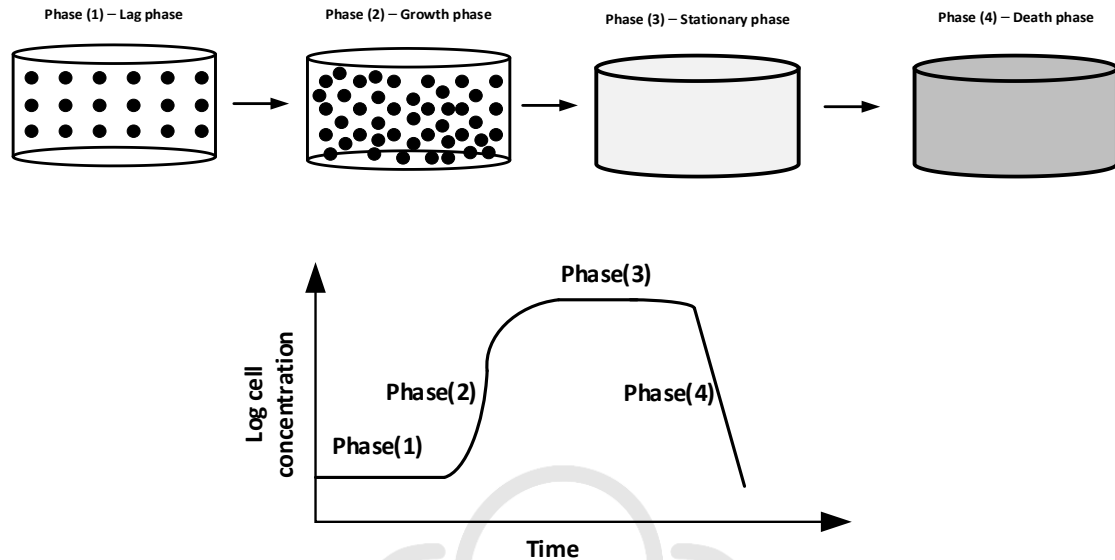
$$C_{A0} = \frac{P_{A0}}{RT} = \frac{9 \times 0.15}{0.082(276+273)} = 0.0299 \text{ (M)}$$

將 rate 與 design equations combine , 並代入各項數據 :

$$V = \frac{F_{A0}x_A}{\frac{kC_{A0}^{1.5}(1-x_A)(\theta_B - \frac{5}{4}x_A)^{0.5}}{(1+\varepsilon x_A)^{1.5}}} = \frac{2 \times 0.0299 \times 0.65}{\frac{0.1 \times 0.0299^{1.5}(1-0.65)(\frac{17}{15} - \frac{5}{4} \times 0.65)^{0.5}}{(1+0.0375 \times 0.65)^{1.5}}} = \underline{\underline{392.60 \text{ (L)}}}$$

**Problem 6**  
**【Solution】**

(a)



**Phase I (The lag phase)**：細胞剛存在於容器中，正在適應環境，因此生長速度較慢。

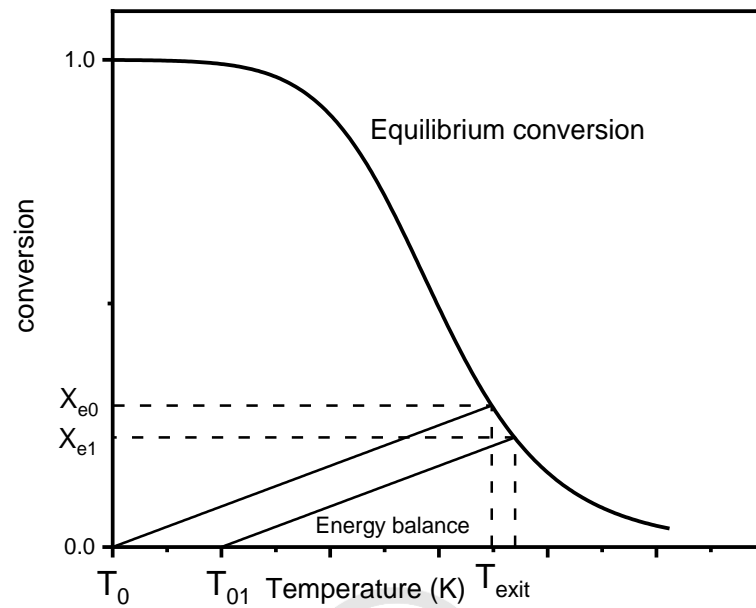
**Phase II (The exponential growth phase)**：容器中環境適中且養分充足，細胞能夠有效率利用養分快速生長，為指數生長期。

**Phase III (The stationary phase)**：細胞生長至一定極限後，即因開始缺乏部分養分而生長停滯，達到濃度最大值。

**Phase IV (The death phase)**：若環境久未改善與更新，則此嚴苛之環境將使細胞因養分不足以提供存活條件而開始大量死亡，且若細胞本身代謝之廢物無法排除，也會加劇細胞死亡速度，即進入消亡階段。

(本題原文說明可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 422~423.)

(b)



(c)

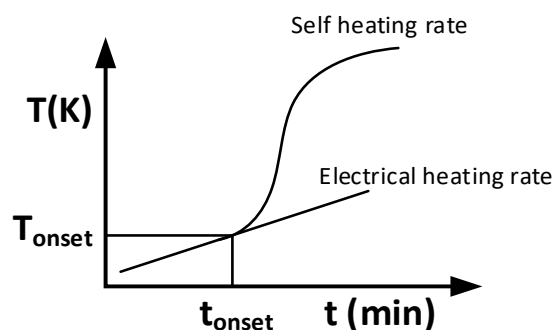
By the figure, if we want to increase the conversion of the reaction, we can lower the inlet temperature of the feed (進口溫度從  $T_{01}$  改為  $T_0$ ). Moreover, we can add some inert into the feed to increase the slope of the energy balance line.

((b)(c)小題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 513.)

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(d)



ARSST 系統是一個能夠測量溫度與時間變化，並用於估算反應相關理論常數的系統，即若我們將溫度與時間變化繪製於圖上，則其斜率就為反應系統的升溫速率。一般來說一放熱反應可以分為兩階段，即電熱升溫明顯階段(Electrical heating)與自我加熱明顯階段(Self heating)，其原因在於，在此種配置下，反應系統溫度主要由(1)外部電熱與(2)反應放熱所增加，在加熱初期，反應溫度不高的情況下，反應速率較慢，以至於就算有放熱，相較於電熱也不明顯，因此此時斜率主要由電熱控制，其速率稱為 electrical heating rate；而後，超過某一溫度時(即圖中之 onset)，反應放熱開始較為明顯，且因高溫又會加劇反應進行，放出更多熱，形成一種惡性循環而產生危險(即 thermal runaway)。此時，溫度上升之貢獻者就轉變為反應本身放熱(電熱本身也已關閉)。因此，超過 onset 溫度後之升溫速率稱為 Self-heating rate。而此系統不僅可以幫助我們預估反應隨加熱時間變化的情形，預防過熱危險以外，也可以用於推算反應固有資訊，比如反應熱、活化能以及頻率因子等。

(本小題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 605~607，有詳細之系統設計原理與各階段說明；而 p 608~613 之 Example 9-3 有推導各種數據的示範練習。)

### **Problem 7**

#### **【Solution】**

By energy balance,

$$x_A = \frac{\sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT - \frac{Q}{F_{A0}}}{-[\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT]}$$

$$\sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT = \int_{295}^T (146 + 75 + 79) dT = 300(T - 295)$$

$$Q = 1 \times 10^4 (305 - T)$$

$$F_{A0} = 91 \text{ (mol / h)}$$

$$\Delta H_R^\circ = -56800, \Delta C_p = (192 - 146 - 75) = -29$$

代入：

$$x_A = \frac{300(T - 295) + \frac{10^4(T - 305)}{91}}{-[-56800 - 29(T - 293)]} \text{----- (1)}$$

By mole balance,

$$V = \frac{F_{A0} x_A}{k C_{A0} (1 - x_A)}, \tau = \frac{x_A}{k (1 - x_A)}$$
$$x_A = \frac{k\tau}{1 + k\tau} = \frac{6.9 \times 10^{10} e^{\frac{-75000}{8.314T}} \times \frac{20}{25}}{1 + 6.9 \times 10^{10} e^{\frac{-75000}{8.314T}} \times \frac{20}{25}} \text{----- (2)}$$

令(1)與(2)式相等，則可以解其出口溫度，然而就算用 solve 功能，計算機可能也負荷不了，因此可以善用計算機有的 table 功能，(本人使用 fx-991EX)，代法如下

(1) 開啟 Table 功能，設定  $f(x)$  為 energy balance，溫度則為計算機之  $x$ ，因此輸入以下方程式，輸入完後按下=：

$$f(x) = \frac{300(x-295) + \frac{10^4(x-305)}{91}}{-[-56800 - 29(x-293)]}$$

(2) 按下等於後，出現輸入  $g(x)$  的提示，則輸入 mole balance 的式子

$$g(x) = \frac{6.9 \times 10^{10} e^{\frac{-75000}{8.314x}} \times \frac{20}{25}}{1 + 6.9 \times 10^{10} e^{\frac{-75000}{8.314x}} \times \frac{20}{25}}$$

(3) 同樣按下等於後，出現輸入要猜的  $x$  範圍與要切成幾等分，因題目設定 298 與 438K 之間，所以在 Start 輸入 298、End 輸入 438K，Step 則是每一次要增加多少下去代，這裡示範設為 20，則：

x	298	318	338	358	378	398	418	438
f(x)	0.002	0.145	0.284	0.421	0.5555	0.6871	~	~
g(x)	0.0039	0.0257	0.124	0.386	0.7046	0.8878	~	~

可以觀察到有塗色的兩個區間範圍內， $f(x)$  與  $g(x)$  有大小交換的趨勢，代表這兩個區域內都有可同時滿足質量平衡與能量平衡的解，因此需更細作查看，以下以 298K~318K 作為示範：

(4)按下 AC 退回原本輸入  $f(x)$  的畫面後(不用擔心剛剛輸入的函數會不見)，重新調整上下限為 298~318K，調整 step 為 5

x	298	303	308	313	318	323	328
f(x)	0.002	0.0381	0.0739	~	~	~	~
g(x)	0.0039	0.0064	0.0104	~	~	~	~

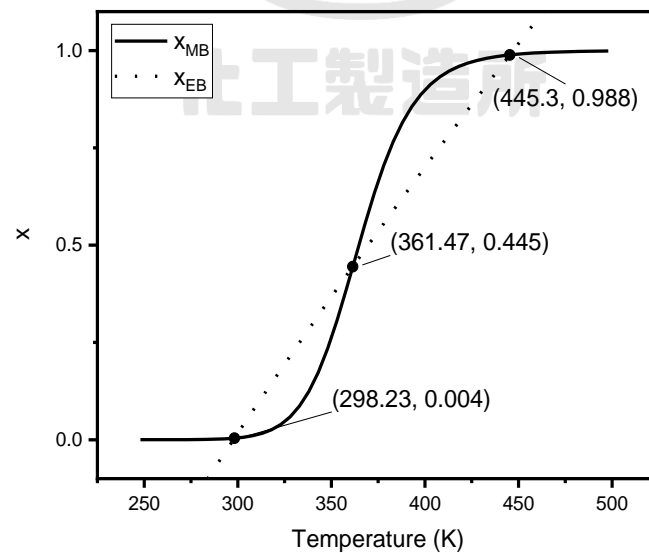
(5)調整上下限為 303~308，step 為 1

x	298	299	300	301	302	303
f(x)	0.002	0.0094	~	~	~	~
g(x)	0.0039	0.0043	~	~	~	~

接下來，可以再更細(step 設為 0.1 等等)，就不再多贅述，結果顯示大約 298.2 (K) 有一解，而高溫解為 361.5 (K)，因此 unstable steady state 溫度為 361.5 (K)

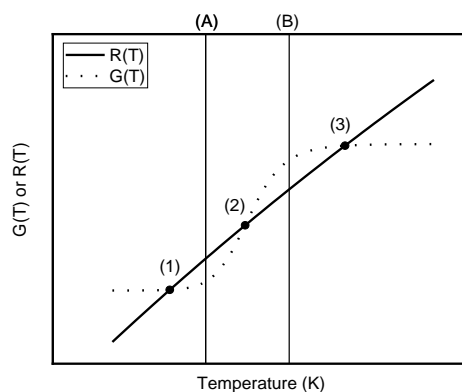
代回計算可得在此溫度下，轉化率  $x_A = 0.445$

※此題可繪圖如下：



一般來說，unstable steady state 的位置在原文書皆以  $G(T)$  與  $R(T)$  對溫度之關係說明，其原理

如下( $G(T)$ 代表熱產生項， $R(T)$ 代表熱移除項)：



首先，若系統溫度在(A)，則此時  $R(T) > G(T)$ ，代表熱移除速率快，溫度下移，因此往(1)移動後達到 steady state；若系統溫度在(B)，則此時  $G(T) > R(T)$ ，溫度上移，往(3)移動後達到 steady state，都沒有在(2)達到 steady state 的可能。而若是直接定溫度在(2)，此時雖然  $R(T)$  與  $G(T)$  產生交點，但微觀來說，任何反應系統並不是固定在同一個狀態就停止，假設此時有一微小的擾動使原先在(2)的系統溫度上移一點，就會因  $G(T) > R(T)$  而直接移動到(3)；反方向亦然。因此我們說(2)並不是穩定的狀態(儘管有交點)，而稱之為 unstable steady state。

另外，在計算機表格解中，我們發現 298K~438K 的範圍中，有兩個解，除了憑直覺回答 361.5(K) 並且作轉化率的計算作答之外(畢竟 298.2K 離 298K 很近)，可以用 unstable steady state 在  $R(T)$  與  $G(T)$  圖的關係，以及其與轉化率的關係來幫助判斷，以  $G(T)$  項來說，其定義為：

$$G(T) = (-\Delta H_{Rx}^\circ) X = (-\Delta H_{Rx}^\circ) x_{MB} \propto x_{MB}$$

exothermic, >0

以  $R(T)$  項來說，其定義為：

$$R(T) = C_{p0} (1 + \kappa)(T - T_c)$$

即為

$$x_{EB} = \frac{300(x-295) + \frac{10^4(x-305)}{91}}{-[-56800 - \underbrace{29(x-293)}_{\text{假設可略}}]} = \frac{300(x-295) + \frac{10^4(x-305)}{91}}{56800} \text{ 的分子項}$$

因此  $R(T) \propto x_{EB}$

根據上面段落，在 unstable steady state 的位置附近，有以下關係：

$T < T_{unstable}$ ， $R(T) > G(T)$ ，可想成  $x_{EB} > x_{MB}$

$T > T_{unstable}$ ， $G(T) > R(T)$ ，可想成  $x_{MB} > x_{EB}$

搭配在 361(K)與 362(K)這兩個溫度的數據，是否發現甚麼了呢？

T(K)	361	362
$x_{EB}$	0.441602	0.448355
$x_{MB}$	0.436718	0.453767

(※本題在做 Energy Balance 時因題目並未給定  $T_R$  之值，因此照原文書假設之  $T_R = 295K$  進行計算，特別注意。)

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.;

p 531, Example 8-9.

關於  $G(T)$ 、 $R(T)$  推導與其應用於判斷 steady state，可參考 FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 533~538, 非常推薦閱讀。)

### Problem 8

#### **【Solution】**

題目表格有誤：Set1 之速率應為 0.044

令  $A = Bu$  ,  $B = MEK$  ,  $C = H_2$

By set 1、5：

$r$  與  $B$  無關

→ 速率決定步驟反應不可逆，且不吸附或吸附弱

By set 4、6：

$r$  與  $C$  無關

→ 速率決定步驟反應不可逆，且不吸附或吸附弱

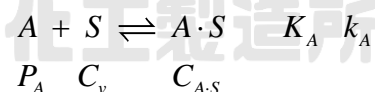
By set 2、4、5：

觀察到隨著  $A$  濃度上升，速率先升後降

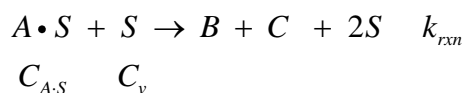
$$r \propto \frac{P_A}{(1 + P_A)^n}, n > 1$$

考慮題目為兩個生成物，假設為 Dual-Site mechanism,

Adsorption of A：



Surface reaction of A：



∴ Surface reaction is rate-determining,

$$\text{reaction rate, } r = k_{rxn} C_{A \cdot S} C_v$$

For  $C_{A,S}$ ,  $\frac{-r_A}{k_A} \approx 0$  :

$$C_{A,S} = K_A P_A C_v$$

By site balance,

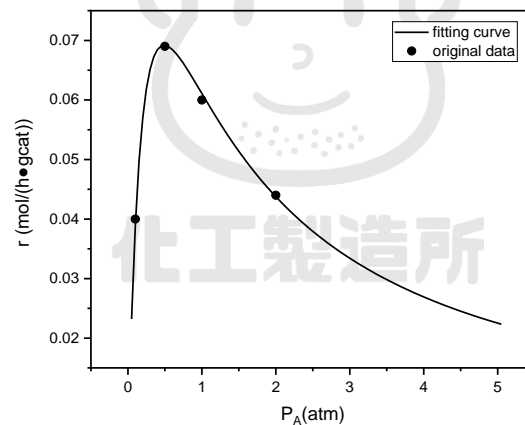
$$C_t = C_v(1 + K_A P_A)$$

代回 reaction rate 表示式，得：

$$r = \frac{k_{rxn} K_A P_A C_t^2}{(1 + K_A P_A)^2} = \frac{k K_A P_A}{(1 + K_A P_A)^2}$$

※本題也可以先假設 B 與 C 吸附於觸媒上再作脫附，而其吸引力非常弱，因此在分母之 B 與 C 之常數可被忽略，也可得到相同答案，即為原文書做法。

若進一步將速率表示式倒數(如同 105 年成大化反 Problem 4 的做法，則可得  $k = 0.277$  與  $K_A = 2.038$ )



(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 743,

Problem 10-9B.)



### **Problem 9**

#### **【Solution】**

For PBR,

$$F_A|_z - F_A|_{z+dz} + r_A'' a_c (A_c dz) = 0$$

$\therefore$  mass transfer limit,

$$-r_A'' = k_c (C_A - C_{As})$$

where  $C_{As}$  is the concentration on the catalyst surface

代入並同除  $dz \rightarrow 0$

$$\frac{-dF_A}{dz} - k_c a_c (C_A - C_{As}) A_c = 0$$

$\therefore C_A \gg C_{As}$  for mass-transfer-limiting reaction,

$$C_{A0} U A_c \frac{dx_A}{dz} - k_c a_c C_A A_c = 0$$

$$C_{A0} U \frac{dx_A}{dz} - k_c a_c C_{A0} (1 - x_A) = 0$$

$$\int_0^{x_A} \frac{dx_A}{1 - x_A} = \int_0^L \frac{k_c a_c}{U} dz, \quad \ln \frac{1}{1 - x_A} = \frac{k_c a_c}{U} L$$

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 789-790,

Example 11-4.)

# 108 年成大化反

## **Problem 1**

### **【Solution】**

(a)

For PFR,

$$V = \int_0^{x_A} \frac{F_{A0} dx_A}{-r_A}$$

For rate equation,

$$-r_A = kC_A^2 = kC_{A0}^2(1-x_A)^2 \quad (\text{liquid phase reaction})$$

$$C_{A0} = \frac{4}{2} = 2M, \quad F_{A0} = 2 \times (5+5) = 20 \text{ (mole/min)}$$

Combine the rate and design equations,

$$V = \int_0^{x_A} \frac{F_{A0} dx_A}{kC_{A0}^2(1-x_A)^2} = \int_0^{0.9} \frac{20 dx_A}{0.05 \times 2^2(1-x_A)^2} = \underline{\underline{900 \text{ (L)}}}$$

(b)

For CSTR,

$$V = \frac{F_{A0}x_A}{-r_A}$$

Combine the rate and design equations,

$$V = \frac{F_{A0}x_A}{kC_{A0}^2(1-x_A)^2} = \frac{20 \times 0.9}{0.05 \times 2^2(1-0.9)^2} = \underline{\underline{9000 \text{ (L)}}}$$

(c)

At T=350K, the rate constant would be,

$$k(350) = 0.05 \times \exp\left[\frac{-10 \times 10^3}{1.987} \left(\frac{1}{350} - \frac{1}{300}\right)\right] = 0.549$$

$$V = \frac{F_{A0}x_A}{kC_{A0}^2(1-x_A)^2} = \frac{20 \times 0.9}{0.549 \times 2^2(1-0.9)^2} = \underline{\underline{819.3 \text{ (L)}}}$$

(d)

By (a)(b) : Because the well-mixed condition in CSTR, so the concentration of reactants will be lower in CSTR than in PFR. Therefore, CSTR must offer more reaction volume than PFR to lengthen the residence time to achieve the same conversion.

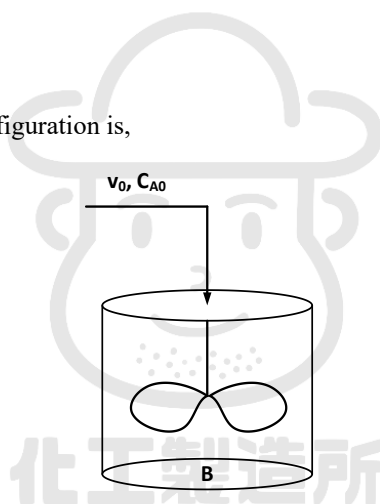
By (c) : The higher temperature will increase the reaction rate, so the reaction volume can be reduced and we can still reach the same conversion.

## **Problem 2**

### **【Solution】**

(a)

For a semi-batch reactor, the configuration is,



By mole balance of A,

$$N_A = F_{A0}t - N_{A0}x_A, \quad x_A = \frac{F_{A0}t - N_A}{N_{A0}}$$

**The conversion of A will change with the entering feed of A, and cannot be used to determine the concentrations of other species, so we calculate the conversion of B as a function of time otherwise.**

### **【Mole Balance Equations for calculation of concentrations】**

By overall mole balance of the semi-batch,

$$\rho v_0 = \rho \frac{dV}{dt}, \quad \underline{\underline{V = V_0 + v_0 t \text{ --- (1)}}}$$

For the concentration of B, by mole balance of B,

$$\frac{d(C_B V)}{dt} = r_B V, \quad V \frac{dC_B}{dt} + C_B \frac{dV}{dt} = r_B V$$

$$\frac{dC_B}{dt} = r_B - \frac{v_0}{V} C_B \quad \text{---(2)}$$

For the concentration of A, by mole balance of A,

$$\frac{d(C_A V)}{dt} = F_{A0} + r_A V = V \frac{dC_A}{dt} + C_A \frac{dV}{dt}$$

$$\frac{dC_A}{dt} = \frac{v_0(C_{A0} - C_A)}{V} + r_A \quad \text{---(3)}$$

In the same way, we can calculate the concentrations of C, D, E by,

$$\frac{dC_C}{dt} = r_C - \frac{v_0}{V} C_C \quad \text{---(4)}$$

$$\frac{dC_D}{dt} = r_D - \frac{v_0}{V} C_D \quad \text{---(5)}$$

$$\frac{dC_E}{dt} = r_E - \frac{v_0}{V} C_E \quad \text{---(6)}$$

For the calculation reaction rate, we use the rate laws,

**【Rate expressions for calculation of reaction rates】**

$$-r_A = -r_B = r_C = r_D = r_E = k(C_A C_B - \frac{1}{K_C} C_C C_D C_E) \quad \text{---(7)}$$

**【Definition of conversion for the calculation of itself】**

$$x_B = \frac{N_{B0} - N_B}{N_{B0}} = \frac{C_{B0} V_0 - C_B V}{C_{B0} V_0}$$

(b)

For B, its concentration is **monotonically decreasing** because it is only consumed by the reaction. The increase of the total volume is contributing its decrease, too.

For C, its concentration is **increasing initially**. But after a certain degree (like approaching equilibrium), **it may decrease** due to the increase of volume.

For A, its concentration should obtain by the rate of feed inlet and the reaction rate.

At the beginning of the reaction, the initial reaction rate would be,

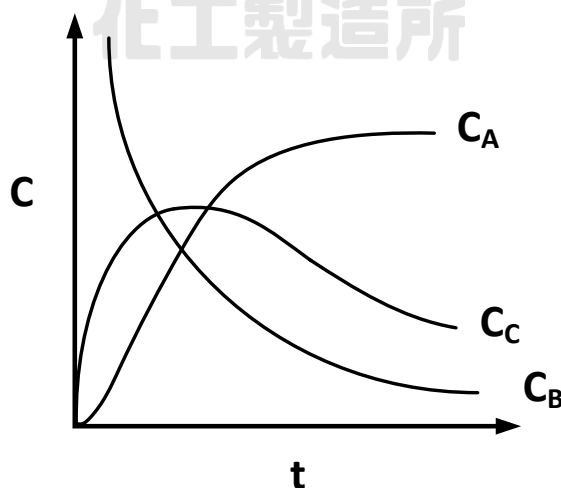
$$\begin{aligned} -r_A = C_{A0, \text{reactor}} C_{B0} &= \frac{F_{A0, \text{feed}}}{V_0} C_{B0} \approx \frac{2 \times 0.5}{2000} \times 1 \\ &= 5 \times 10^{-4} (M / hr) = \frac{5 \times 10^{-4} \times 2000}{3600} = 2.78 \times 10^{-4} (mol / min) \end{aligned}$$

Thus the rate of reaction is less than the rate of the feed

$$F_{A0} = 2 \times 0.5 = 1 (mole / min),$$

so the concentration of A **will increase with time, but approaching a final value because it has an inlet fixed at 2M.**

$$C_{A, \text{final}} \approx \lim_{V \rightarrow \infty} [2V / (2000 + V)] = 2$$



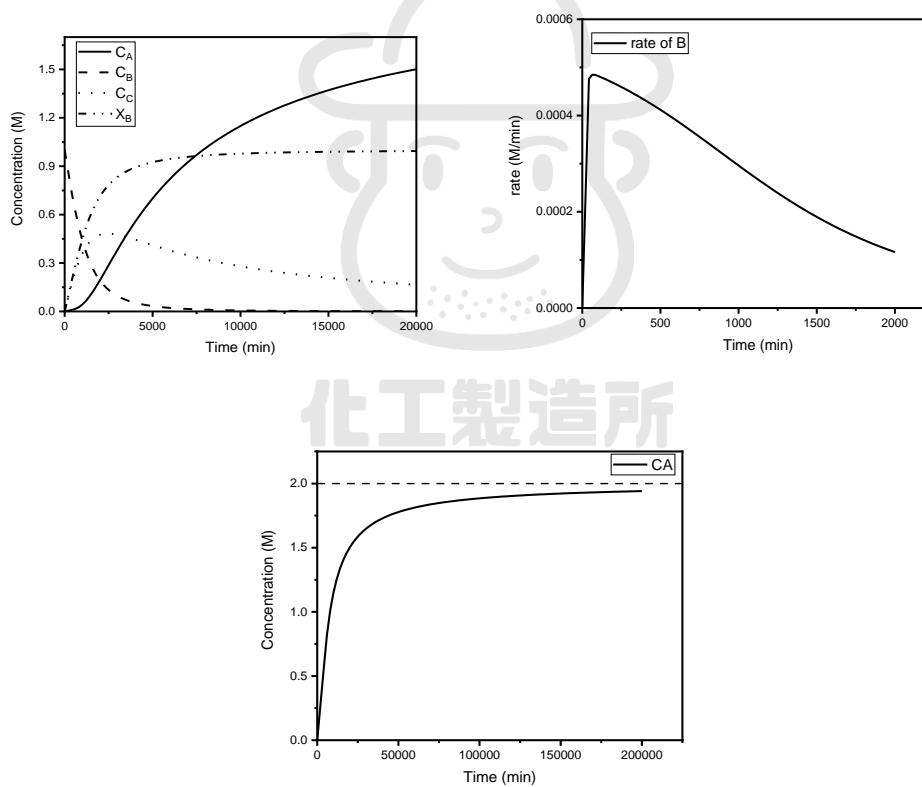
※補充，若使用 Polymath 做計算

```
#Differential equations
d(CA)/d(t) = v0*(CA0-CA)/V+rA
d(CB)/d(t) = rB-v0*CB/V
d(CC)/d(t) = rC-v0*CC/V
d(CD)/d(t) = rD-v0*CD/V
d(CE)/d(t) = rE-v0*CE/V

#explicit equations
k = 5/60 #change the unit of hr into min
Kc = 3
CA0 = 2 #feed concentration
CB0 = 1
V = V0+v0*t
V0 = 2000
v0 = 0.5
rA = -k*(CA*CB-((1/Kc)*CC*CD*CE))
rB = rA
rC = -rA
rD = -rA
rE = -rA
X = (CB0*V0-CB*V)/(CB0*V0)

#Initial values
CA(0) = 0 #No A in reactor when t=0
CB(0) = 1
CC(0) = 0
CD(0) = 0
CE(0) = 0

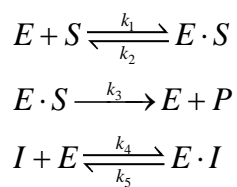
#Input the time range you want to calculate
t(0) = 0
t(f) = 20000
```



(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 217-224.)

**Problem 3****【Solution】****(a)**

For competitive inhibition between S and I, the mechanism is,

**(b)**

$$r_p = k_3[E \cdot S]$$

By PSSH,

$$r_{E \cdot S} = k_1[E][S] - k_2[E \cdot S] - k_3[E \cdot S] = 0, \quad [E \cdot S] = \frac{k_1[E][S]}{k_2 + k_3}$$

$$r_{E \cdot I} = k_4[E][I] - k_5[E \cdot I] = 0, \quad [E \cdot I] = \frac{k_4}{k_5}[E][I]$$

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By enzyme balance,

$$\begin{aligned}
 [E]_0 &= [E] + [E \cdot S] + [E \cdot I] \\
 &= \frac{k_1 + k_2}{k_1[S]} [E \cdot S] + [E \cdot S] + \frac{k_4(k_2 + k_3)[I]}{k_1 k_5[S]} [E \cdot S] \\
 &= [E \cdot S] \left[ \frac{k_5(k_2 + k_3) + k_4(k_2 + k_3)[I] + k_1 k_5[S]}{k_1 k_5[S]} \right] \\
 &= [E \cdot S] \left[ \frac{\left(\frac{k_2 + k_3}{k_1}\right) + \frac{k_4}{k_5} \left(\frac{k_2 + k_3}{k_1}\right)[I] + [S]}{[S]} \right] \\
 &= [E \cdot S] \left[ \frac{K_M + \frac{K_M[I]}{K_I} + [S]}{[S]} \right] \\
 [E \cdot S] &= \frac{[E]_0[S]}{K_M + \frac{K_M[I]}{K_I} + [S]} \\
 r_p &= \frac{k_3[E]_0[S]}{K_M + \frac{K_M[I]}{K_I} + [S]} = \frac{v_{\max}[S]}{K_M \left(1 + \frac{[I]}{K_I}\right) + [S]} \begin{cases} K_M = \frac{k_2 + k_3}{k_1} \\ K_I = \frac{k_5}{k_4} \end{cases}
 \end{aligned}$$

(c) Ans : (B)

將(b)小題結果取倒數，

$$\frac{1}{r_p} = \frac{1}{v_{\max}} + \frac{1}{[S]} \frac{K_M}{v_{\max}} \left(1 + \frac{[I]}{K_I}\right) \quad (\text{Lineweaver-Burk plot})$$

將  $\frac{1}{r_p}$  對  $\frac{1}{[S]}$  作圖，則斜率為  $\frac{K_M}{v_{\max}} \left(1 + \frac{[I]}{K_I}\right)$ ，可分為兩種情況：

$$\begin{cases} \text{with inhibition} \rightarrow \frac{K_M}{v_{\max}} \left(1 + \frac{[I]}{K_I}\right) \\ \text{without inhibition} \rightarrow \frac{K_M}{v_{\max}} \end{cases}$$

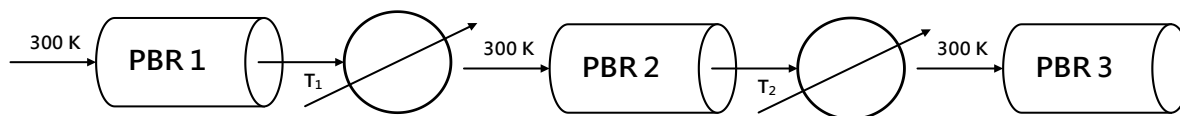
而 A 與 B 的斜率相比，(A)的斜率較大、(B)的斜率較小，可推得(B)應該較沒有 inhibition 的傾向，此題選(B)



(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 410-412.)

#### Problem 4

#### 【Solution】



By energy balance,

$$x_A = \frac{\sum_i \int_{T_{i0}}^T \theta_{pi} C_{pi} dT}{-[\Delta H_{rxn}^\circ(T_R) + \int_{T_R}^T \Delta C_p dT]}$$

$$\sum_i \int_{T_{i0}}^T \theta_{pi} C_{pi} dT = (1 \times 25 + 1 \times 25)(T - 300) = 50(T - 300)$$

$$\Delta H_{rxn}^\circ(T_R) + \int_{T_R}^T \Delta C_p dT = -30000 (\text{cal/mol})$$

$$x_{A,EB} = \frac{50(T - 300)}{30000}$$

By thermodynamics,

$$\frac{d \ln K}{dT} = \frac{\Delta H_R}{RT^2}$$

$$\ln \frac{K(T)}{K(323)} = \frac{\Delta H_R}{R} \left( \frac{1}{323} - \frac{1}{T} \right)$$

$$K(T) = 500000 \exp \left[ -15098.13 \left( \frac{1}{323} - \frac{1}{T} \right) \right]$$

$$\therefore K(T) = \frac{C_C C_D}{C_A C_B} = \frac{C_{A0}^2 x_{Ae}^2}{C_{A0}^2 (1 - x_{Ae})^2} = \frac{x_{Ae}^2}{(1 - x_{Ae})^2}, \quad x_{Ae} = \frac{\sqrt{K}}{1 + \sqrt{K}}$$

$$\text{聯立 } \frac{50(T - 300)}{30000} = \frac{\sqrt{K}}{1 + \sqrt{K}} = \frac{1}{\frac{1}{\sqrt{K}} + 1} = \frac{1}{\frac{1}{\sqrt{500000 \exp \left[ -15098.13 \left( \frac{1}{323} - \frac{1}{T} \right) \right]} + 1}}$$

$T(K)$	440	450	460	470	480	490
$x_{A,EB}$	0.233333	0.25	0.266667	0.283333	0.3	0.316667
$x_{Ae}$	0.585751	0.491292	0.401426	0.321105	0.252879	0.197138

$$\begin{cases} T=474.267 \text{ (K)} \\ x_{Ae1} = 0.29 \end{cases}$$

For 2<sup>nd</sup> CSTR, the energy balance equation will be,

$$x_{A2} = \frac{50(T-300)}{30000} + 0.29 = \frac{1}{\frac{1}{\sqrt{K}} + 1}$$

$T(K)$	420	430	440	450	460	470
$x_{A2,EB}$	0.49	0.506667	0.523333	0.54	0.556667	0.573333
$x_{Ae}$	0.761955	0.678182	0.585751	0.491292	0.401426	0.321105

$$\begin{cases} T_2 = 445.6 \text{ (K)} \\ x_{Ae2} = 0.533 \end{cases}$$

For 3<sup>rd</sup> CSTR, the energy balance equation will be,

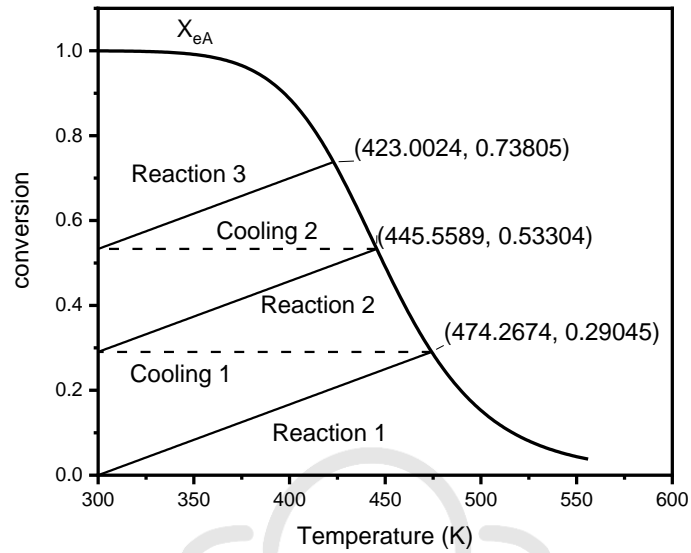
$$x_{A2} = \frac{50(T-300)}{30000} + 0.53 = \frac{1}{\frac{1}{\sqrt{K}} + 1}$$

$T(K)$	390	400	410	420	430	440
$x_{A2,EB}$	0.68	0.696667	0.713333	0.73	0.746667	0.763333
$x_{Ae}$	0.927307	0.887167	0.832272	0.761955	0.678182	0.585751

$$\begin{cases} T_3 = 423 \text{ (K)} \\ x_{Ae3} = 0.738 \end{cases}$$

【補充】

若將此過程畫在  $x_A - T$  diagram 上，則其軌跡為：



(本題題目參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 577,

Problem 8.13<sub>a</sub>.)

本題作法參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 517,

Example 8-7.)

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### Problem 5

#### **【Solution】**

(a)

By set 5~8 (low concentration of CO) :

$$rate \propto P_{CO}$$

By set 11、12 (high concentration of CO, rate decreases) :

$$rate \propto \frac{1}{(1 + K_{CO}P_{CO} + \dots)^2}$$

By set 1~4 :

$$rate \propto P_{O_2}^{\frac{1}{2}}$$

Rate law,

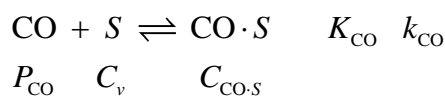
$$r = \frac{kP_{O_2}^{\frac{1}{2}}P_{CO}}{(1 + KP_{CO})^2}$$

(b)

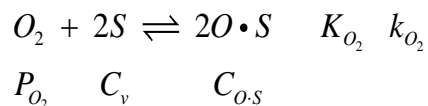
The  $\frac{1}{2}$  order of  $O_2$  indicates the dissociative adsorption, and thus the following

mechanism is proposed,

Adsorption of CO :

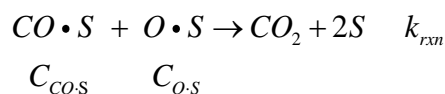


Dissociative adsorption of  $O_2$  :



Surface reaction :

Desorption of B :



Assume surface reaction is rate-determining,

$$\text{reaction rate, } r = k_{rxn} C_{CO.S} C_{O.S}$$

$$\text{For } C_{CO.S}, \frac{-r_{CO}}{k_{CO}} \approx 0 :$$

$$C_{CO.S} = K_{CO} P_{CO} C_v$$

$$\text{For } C_{O.S}, \frac{-r_O}{k_O} \approx 0 :$$

$$C_{O.S} = \sqrt{K_{O_2} P_{O_2}} C_v$$

By site balance,

$$C_t = C_v (1 + K_{CO} P_{CO} + \sqrt{K_{O_2} P_{O_2}})$$

代入 reaction rate 表示式，得：

$$r = \frac{k_{rxn} K_{CO} P_{CO} \sqrt{K_{O_2} P_{O_2}} C_t^2}{(1 + K_{CO} P_{CO} + \sqrt{K_{O_2} P_{O_2}})^2}$$

The oxygen may be weakly adsorbed, so

$$\sqrt{K_{O_2} P_{O_2}} \ll 1$$

$$r \approx \frac{k_{rxn} K_{CO} P_{CO} \sqrt{K_{O_2} P_{O_2}} C_t^2}{(1 + K_{CO} P_{CO})^2} = \frac{k_{rxn}' K_{CO} P_{CO} \sqrt{K_{O_2} P_{O_2}}}{(1 + K_{CO} P_{CO})^2}$$

(本題可參考：University of Michigan, Chapter 10 Self Test,

<http://umich.edu/~elements/course/lectures/ten/test8.htm>)

### **Problem 6**

#### **【Solution】**

For internal mass-transfer limiting reactions, the Thiele modulus is very large, and the corresponding effectiveness factor will be

$$\begin{aligned}\eta &\simeq \frac{3}{\phi_1} = \frac{3}{R} \sqrt{\frac{D_e}{k_1}} \\ -r_A &= \frac{\text{Actual reaction rate}}{\text{Reaction rate at } C_{As}} \times (\text{Reaction rate at } C_{As}) \\ &= \eta(-r_{As}) = \eta(k_1 C_{As}) \\ &= \frac{3}{R} \sqrt{D_e k_1} C_{As} = \frac{3}{R} \sqrt{D_e S_a \rho_c k''} C_{As}\end{aligned}$$

If the effective diffusion coefficient is obeying Arrhenius law, then

$$D_e = D_0 e^{\frac{-E_a}{RT}}$$

$$\left\{ \begin{array}{l} d_p = 2R \downarrow, -r_A \uparrow \\ U \text{ is not related to the reaction rate} \\ T \uparrow, -r_A \uparrow \end{array} \right.$$

(本題題目參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 827-831.)

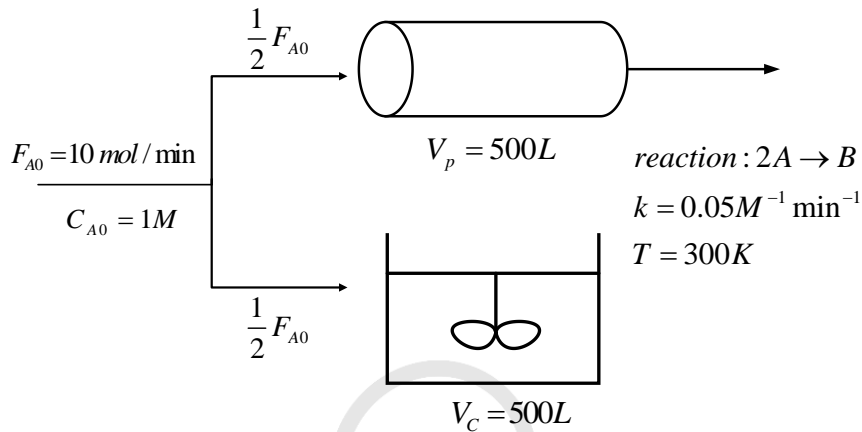
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# 109 年成大化反

## Problem 1

### 【Solution】

(1)



For PFR:

$$\text{design equation: } V_p = \int_0^{X_{Ap}} \frac{F_{A0,p} dx}{-r_A}, F_{A0,p} = \frac{1}{2} F_{A0}$$

$$\text{rate equation: } -r_A = kC_A^2 = kC_{A0}^2(1 - X_A)^2, (V = \text{constant})$$

Combine:

$$V_p = \int_0^{X_{Ap}} \frac{\frac{1}{2} F_{A0}}{kC_{A0}^2(1 - X_A)^2} dX_A$$

$$500 = \int_0^{X_{Ap}} \frac{5dX_A}{0.05 \times 1^2 \times (1 - X_A)^2} \Rightarrow \underline{\underline{X_{Ap} = 0.833}}$$

For CSTR:

$$\text{design equation: } V_c = \frac{F_{A0,C} X_{AC}}{-r_A}$$

$$\text{rate equation: } -r_A = kC_A^2 = kC_{A0}^2(1 - X_{AC})^2, (V = \text{constant})$$

Combine:

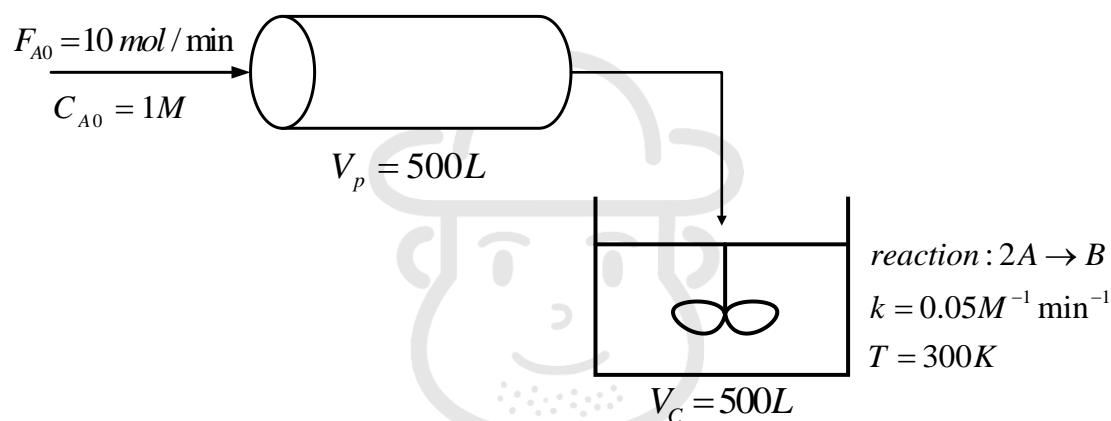
$$V_C = \frac{\frac{1}{2} F_{A0} X_{AC}}{k C_{A0}^2 (1 - X_{AC})^2}$$

$$500 = \frac{5 X_{AC}}{0.05 \times 1^2 \times (1 - X_{AC})^2} \Rightarrow \underline{\underline{X_{AC} = 0.642}}$$

$$\Rightarrow \text{exit conversion} = \frac{F_{A0} - [F_{Ap} + F_{AC}]}{F_{A0}} = \frac{F_{A0} - [\frac{1}{2} F_{A0} (1 - 0.833) + \frac{1}{2} F_{A0} (1 - 0.642)]}{F_{A0}}$$

$$\Rightarrow \underline{\underline{X_A = 0.7375}}$$

(2)



For PFR, combine design and rate equations,

$$V_P = \int_0^{X_{Ap}} \frac{F_{A0} dX_A}{k C_{A0}^2 (1 - X_A)^2}$$

$$\Rightarrow 500 = \int_0^{X_{Ap}} \frac{10 dX_A}{0.05 \times 1^2 \times (1 - X_A)^2} \Rightarrow X_{Ap} = 0.7143$$

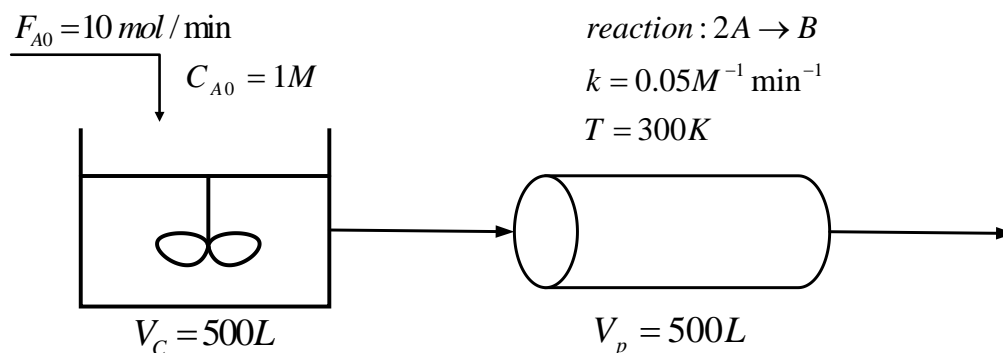
For CSTR, combine design and rate equations

$$V_C = \frac{F_{A0} (X_{AC} - 0.7143)}{k C_{A0}^2 (1 - X_A)^2}$$

$$\Rightarrow 500 = \frac{10 (X_{AC} - 0.7143)}{0.05 \times 1^2 \times (1 - X_{AC})^2} \Rightarrow \underline{\underline{X_{AC} = 0.807}}$$



(3)



For CSTR, combine design and rate equations,

$$V_C = \frac{F_{A0} X_{AC}}{k C_{A0}^2 (1 - X_{AC})^2}$$
$$500 = \frac{10 X_{AC}}{0.05 \times 1^2 \times (1 - X_{AC})^2} \Rightarrow \underline{\underline{X_{AC} = 0.537}}$$

For PFR, combine design and rate equation,

$$V_P = \int_{0.537}^{X_{Ap}} \frac{F_{A0} dX_A}{k C_{A0}^2 (1 - X_A)^2}$$
$$500 = \int_{0.537}^{X_{Ap}} \frac{10 dX_A}{0.05 \times 1^2 \times (1 - X_A)^2} \Rightarrow \underline{\underline{X_{Ap} = 0.785}}$$

(4)

Compare the results for (2) and (3), we can find that the exit conversion is larger when the feed first reacted in PFR and CSTR afterward.

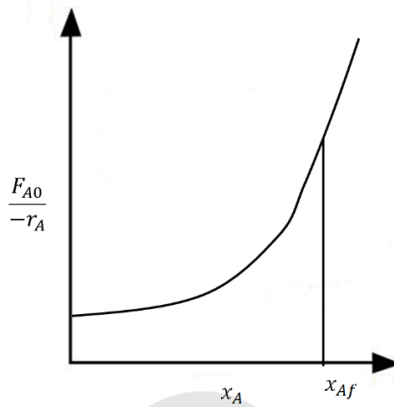
For a second-order reaction, it is better to react with the configuration in problem (2) than (3).

## Problem 2

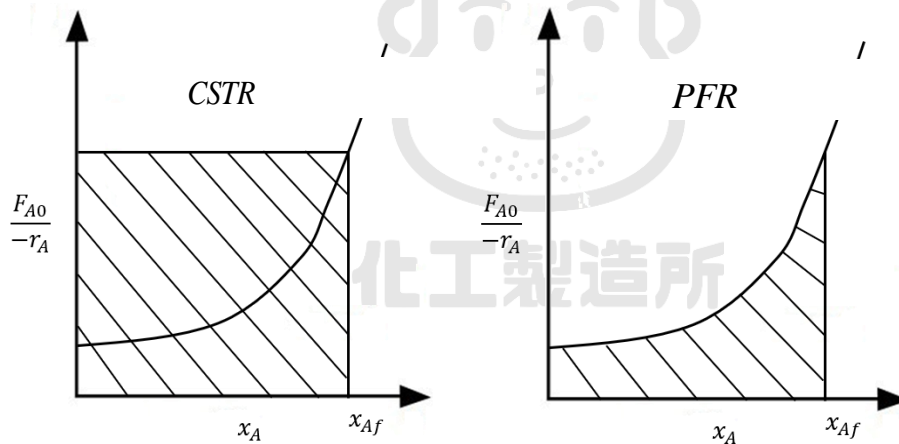
### 【Solution】

(a)

For a second-order reaction, the  $\left(\frac{F_{A0}}{-r_A}\right)$  vs.  $X_A$  plot is shown as,

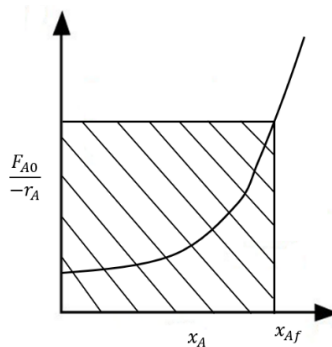


For CSTR and PFR, the required volume to achieve certain conversion can be shown as following respectively,

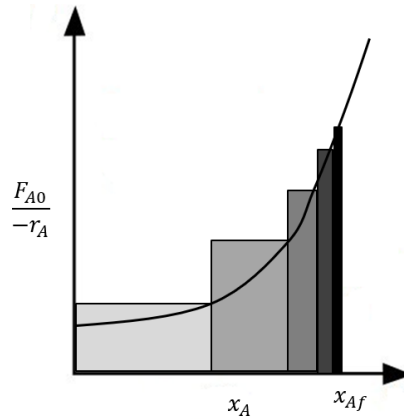


(b)

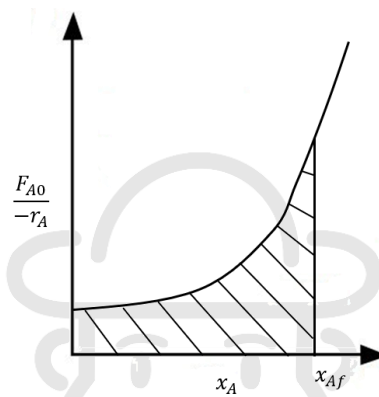
對於 CSTR, 其反應器體積可被圖解為



若將無限個 CSTR 串聯，則



可近似於：



即可當成PFR

### **Problem 3**

#### **【Solution】**

For enzyme reaction in a batch reactor,

$$\frac{-1}{V} \frac{dN_s}{dt} = \frac{-dC_s}{dt} = -r_s = \frac{v_{\max} C_s}{K_M + C_s}$$

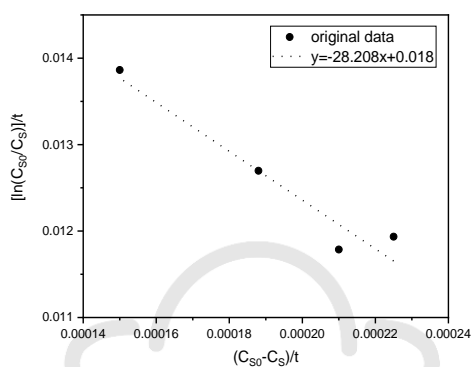
$$\int_{C_{s0}}^{C_s} \left[ \frac{K_M}{C_s} + 1 \right] dC_s = \int_0^t v_{\max} dt$$

$$\Rightarrow K_M \ln \frac{C_s}{C_{s0}} + C_s - C_{s0} = -v_{\max} t$$

$$\Rightarrow \frac{1}{t} \ln \frac{C_{s0}}{C_s} = -\frac{C_{s0} - C_s}{K_M t} + \frac{v_{\max}}{K_M}$$

Plot  $\frac{1}{t} \ln \frac{C_{s0}}{C_s} - \frac{C_{s0} - C_s}{t}$  圖

$\frac{1}{t} \ln \frac{C_{s0}}{C_s}$	0.011934	0.011786	0.012697	0.013863
$\frac{C_{s0} - C_s}{t}$	0.000225	0.00021	0.000188	0.00015



$$\text{slope} = \frac{-1}{K_M} = -28.208 \Rightarrow K_M = 0.03545M$$

$$\text{intercept} = 0.018 = \frac{v_{\max}}{K_M}$$

$$\Rightarrow v_{\max} = 0.018 \times 0.03545$$

$$= 6.381 \times 10^{-4} (M \cdot \text{min}^{-1})$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 460, Problem 7.11B.)

#### Problem 4

#### 【Solution】

By energy balance,  $in - out + gen = \cancel{acc}$

$$F_{A0} \sum \theta_i C_{P_i} (T - T_0) + \Delta H_R (T_R) F_{A0} X_A + UA(T - T_a) = 0$$

$$\underbrace{C_{PA}(T - T_0) + \frac{UA(T - T_a)}{F_{A0}}}_{R(T)} = \underbrace{-\Delta H_R^o X_A}_{G(T)} \quad (\Delta C_{P_i} = 0)$$

For  $Q_{gen} : G(T) = \Delta H_R^o X_A$

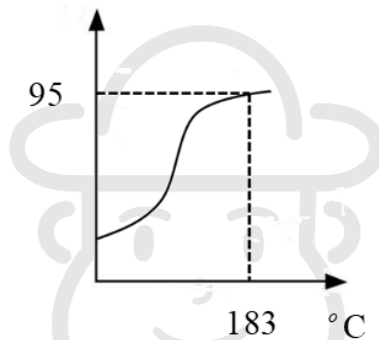
$$X_A = \frac{G(T)}{\Delta H_R^o} = \frac{G(T)}{100} = \frac{G(T)}{100} \quad (1)$$

For  $R(T)$ :

$$\begin{aligned} R(T) &= C_{pA}(T - T_0) + \frac{UA(T - T_a)}{F_{A0}} = 2(T - T_0) + \frac{1}{0.5} \times (T - 100) \\ &= 4T - 2T_0 - 200 \quad (2) \end{aligned}$$

(a)

$$X_A = 0.95 = \frac{G(T)}{100} \Rightarrow G(T) = 95$$



對照圖，此時 reactor temperature  $\approx 183^\circ C$

代入(2)：

$$R(T) = 4 \times 183 - 2T_0 - 200 = 95$$

$$\Rightarrow \underline{\underline{T_0 = 218.5^\circ C}}$$

(b)

$$\underline{\underline{183^\circ C}}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 580,

Problem 8.19C.)

**Problem 5****【Solution】**

(1)

At low pressure,  $rate \propto P_{VTIPO}^2$ .At high pressure,  $rate \approx \text{constant}$ 

Assume :

$$r = \frac{kP_{VTIPO}^2}{1 + KP_{VTIPO}^2}, \quad \frac{1}{r} = \frac{1}{kP_{VTIPO}^2} + \frac{K}{k}$$

Plot  $\frac{1}{r} - \frac{1}{P_{VTIPO}^2}$  diagram,(i)  $T = 120^\circ C$ 

$\frac{1}{r}$	250	66.67	40	25	14.7	12.5	10.53	10
$\frac{1}{P_{VTIPO}^2}$	100	25	11.11	4	1.563	1	0.444	0.25

$$\begin{cases} \text{slope} = \frac{1}{k} = 2.3855 \Rightarrow k = 0.419 \\ \text{intercept} = \frac{K}{k} = 10.924 \Rightarrow K = 4.579 \end{cases}$$

(ii)  $T = 200^\circ C$ 

$\frac{1}{r}$	35.714	2.222	0.556	0.357	0.139
$\frac{1}{P_{VTIPO}^2}$	400	25	6.25	4	1.5625

$$\begin{cases} \text{slope} = \frac{1}{k} = 0.0893 \Rightarrow k = 11.20 \\ \text{intercept} = \frac{K}{k} = -0.0032 \Rightarrow K = -0.0358 \end{cases}$$

(2)

By Arrhenius law,

$$\ln \frac{k_{120}}{k_{200}} = \frac{-E}{R} \left( \frac{1}{120 + 273} - \frac{1}{200 + 273} \right)$$

$$\ln \frac{0.419}{11.20} = \frac{-E}{1.987} \left( \frac{1}{393} - \frac{1}{473} \right)$$

$$\underline{\underline{E = 15170 \text{ cal/mol}}}$$

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 745,

Problem 10.13A.)



### **Problem 6**

#### **【Solution】**

First, the molar rate of mass transfer from the bulk fluid to the external surface is,

$$\text{Molar rate} = (\text{Molar flux}) \cdot (\text{External surface area})$$

$$M_A = W_{Ar} \cdot a_c \cdot \Delta V \quad (1)$$

, where  $a_c$  is the external surface area per unit reactor volume.

Secondly, the molar rate of mass transfer to the surface is equal to the net rate of reaction on and within the pellet

$$M_A = -r_A'' (\text{External} + \text{Internal}) \text{ area}$$

$$M_A = -r_A'' (a_c \Delta V + S_a \rho_b \Delta V) \quad (2) \quad \left\{ \begin{array}{l} S_a = \frac{\text{Internal area}}{\text{Mass of pellet}} \\ \rho_b = \frac{\text{Mass of pellet}}{\text{Reactor volume}} \end{array} \right.$$

Combine eq. (1) and (2):

$$M_A = W_{Ar} a_c \Delta V = -r_A'' (a_c \Delta V + S_a \rho_b \Delta V)$$

$$W_{Ar} a_c = -r_A'' (a_c + S_a \rho_b)$$

For most catalyst, *internal area*  $\gg$  *external area*,  $S_a \rho_b \gg a_c$

$$W_{Ar} a_c = -r_A'' S_a \rho_b$$



$$\therefore W_{Ar} = k_c (C_{Ab} - C_{AS})$$

$$-r_A'' = -r_{AS}'' \eta = \eta k_1'' C_{AS}, \text{ where } \eta = \frac{\text{Actual reaction rate}}{\text{Reaction rate at surface}}$$

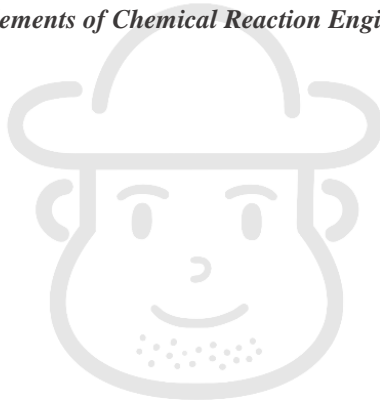
$$k_c a_c (C_{Ab} - C_{AS}) = \eta k_1'' C_{AS} S_a \rho_b$$

$$C_{AS} = \frac{k_c a_c C_{Ab}}{k_c a_c + \eta k_1'' S_a \rho_b} \Rightarrow -r_A'' = \frac{\eta k_1'' k_c a_c C_{Ab}}{k_c a_c + \eta k_1'' S_a \rho_b}$$

$$-r_A'' = \frac{\eta}{1 + \frac{\eta k_1'' S_a \rho_b}{k_c a_c}} k_1'' C_{Ab}$$

$$\text{define, } \Omega = \frac{\eta}{1 + \frac{\eta k_1'' S_a \rho_b}{k_c a_c}} = \frac{\text{actual reaction rate}}{\text{rate when entire surface exposed to bulk condition}}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 835-838.)



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## Problem 1

### **【Solution】**

(a)

Ergun equation 描述了壓降隨行進過程變化的關係，其簡化形式為：

$$\frac{dP}{dz} = -\beta_0 \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

又因行進距離  $z$  與接觸的總觸媒質量成正比，因此：

$$\frac{dP}{dW} \propto \frac{dP}{dz} \propto \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}} = -\frac{\alpha}{2} \frac{T}{T_0} \frac{P_0}{P/P_0} \frac{F_T}{F_{T0}}$$

令  $y = \frac{P}{P_0}$ ，則上式可整理為：

$$\frac{dy}{dW} = -\frac{\alpha}{2y} \frac{T}{T_0} \frac{F_T}{F_{T0}} = \frac{-\alpha}{2y} \frac{T}{T_0} (1 + \varepsilon x)$$

If

(1) Isothermal  $\Rightarrow T = T_0$

(2)  $\varepsilon = 0$

$$\frac{dy}{dW} = \frac{-\alpha}{2y}$$

$$\int_1^y 2y dy = \int_0^W -\alpha W dW$$

$$\underline{\underline{y = \frac{P}{P_0} = (1 - \alpha W)^{\frac{1}{2}}}}$$

(本題因非討論 Ergun equation 的推導與化簡方式，因此採用快速說明的方式帶過，只著重在怎麼得到題目的方程式形式。其原始形式與相關後續推導化簡請參考 FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 175~182，有較完整的觀念)

(b)

For PBR, design equation,

$$dW = \frac{F_{A0} dx_A}{-r_A}$$

Rate equation,

$$\begin{aligned} -r_A &= kC_A^2 = kC_{A0}^2(1-x_A)^2\left(\frac{P}{P_0}\right)^2 \\ &= kC_{A0}^2(1-x_A)^2(1-\alpha W) \end{aligned}$$

Combine,

$$dW = \frac{F_{A0} dx_A}{kC_{A0}^2(1-x_A)^2(1-\alpha W)}$$

For  $F_{A0}$ ,

$$F_B = \frac{1}{2} F_{A0} x_A$$

$$\frac{120}{60} = \frac{1}{2} F_{A0} \times 0.8, \quad F_{A0} = 5 \text{ (mol / min)}$$

$$\int_0^W (1-0.01W) dW = \int_0^{0.8} \frac{5 dx_A}{9.5 \times \left[ \frac{10}{0.082 \times (200 + 273.15)} \right]^2 (1-x_A)^2}, \quad \underline{\underline{W = 39.487 \text{ (g)}}}$$

## Problem 2

### 【Solution】

Let reaction rate,

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

假設  $n = 0, 1, 2$  並積分可得：

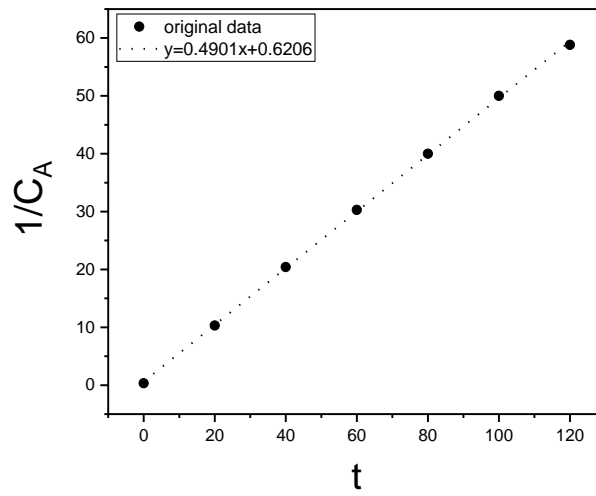
$$\begin{cases} n=0 \rightarrow (C_{A0} - C_A) = kt \\ n=1 \rightarrow \ln \frac{C_{A0}}{C_A} = kt \\ n=2 \rightarrow \frac{1}{C_A} - \frac{1}{C_{A0}} = kt \end{cases}$$

分別將數據轉化為  $\ln C_A - t$  與  $\frac{1}{C_A} - t$  關係，若前者為線性關係，則  $n = 1$ ；若後者為線性關係，則  $n = 2$  (在此不考慮 0 級，因為題目所給之  $C_{A0} - t$  數據非線性)

$t$	0	20	40	60	80	100	120
$C_A$	3.000	0.097	0.049	0.033	0.025	0.020	0.017
$\ln(C_A)$	$\infty$	2.995	3.689	4.094	4.382	4.605	4.787
$\frac{1}{C_A}$	0.333	10.309	20.408	30.303	40	50	58.823

可觀察到  $\frac{1}{C_A} - t$  較接近線性關係，因此 reaction order,  $\boxed{n=2}$ ，

並且可畫出回歸直線推求其他數據：



For k,

$$k = \text{slope} = 0.490 \left( \frac{\text{dm}^3}{\text{mol} \cdot \text{min}} \right)$$

For half life of A, let  $C_A = \frac{1}{2} C_{A0}$ ,

$$\frac{2}{C_{A0}} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} = 0.490 t_{1/2}$$

$$t_{1/2} = \frac{1}{0.490 C_{A0}} = \frac{1}{0.490 \times 3} = 0.680 \text{ (min)}$$

### **Problem 3**

#### **【Solution】**

(a)

缺少產生溫度 T

By energy balance,

$$x_A = \frac{\sum_i \int_{T_{i0}}^T \theta_{i0} C_{pi} dT}{-[\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT]}$$

For  $\sum_i \int_{T_{i0}}^T \theta_{i0} C_{pi} dT$ ,

$$\sum_i \int_{T_{i0}}^T \theta_{i0} C_{pi} dT = [40 \times 1 + 25 \times 0 + 15 \times 0](T - 450) = 40(T - 450)$$

For  $-\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT$

$$-\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT = -[(-50 - 40 + 70) \times 10^3 + \int_{273}^T [25 + 15 - 40] dT] = 20000$$

$$0.8 = \frac{40(T - 450)}{20000}, \quad T = 850(K)$$

For catalyst weight, by design equation,

$$W = \frac{F_{A0} x_A}{-r_A} = \frac{F_{A0} x_A}{k C_{A0} \left[ \frac{(1-x_A)}{(1+x_A)} \right] \left[ \frac{T_0}{T} \right]} = \frac{v_{A0} x_A}{k \left[ \frac{(1-x_A)}{(1+x_A)} \right] \left[ \frac{T_0}{T} \right]} \quad (\text{no pressure drop})$$

$$W = \frac{20 \times 0.8}{0.133 e^{\frac{31.4 \times 10^3}{8.314} \left[ \frac{1}{450} - \frac{1}{850} \right]} \left( \frac{1-0.8}{1+0.8} \right) \left( \frac{450}{850} \right)} = \underline{\underline{39.395 \text{ (kg)}}}$$

(b)

For PBR, the result of energy balance is still valid,

$$T = 850 \text{ (K)}$$

For the catalyst weight, by mole balance,

$$W = \int_0^{x_A} \frac{F_{A0} dx_A}{k C_{A0} \left( \frac{1-x_A}{1+x_A} \right) \left( \frac{T_0}{T} \right)} = \int_0^{x_A} \frac{20 dx_A}{0.133 e^{\frac{31.4 \times 10^3}{8.314} \left( \frac{1}{450} - \frac{1}{T} \right)} \left( \frac{1-x_A}{1+x_A} \right) \left( \frac{T_0}{T} \right)}$$

令

$$T = 450 + 500x_A \text{ 代入}$$

$$W = \int_0^{0.8} \frac{20 dx_A}{0.133 e^{\frac{31.4 \times 10^3}{8.314} \left( \frac{1}{450} - \frac{1}{450+500x_A} \right)} \left( \frac{1-x_A}{1+x_A} \right) \left( \frac{450}{450+500x_A} \right)} = \underline{\underline{43.137 \text{ (kg)}}}$$

此小題若是太難積分 (計算機跑不出來)

答案可由 Simpson's three-eight rule 得到

令

$$0.133 e^{\frac{31.4 \times 10^3}{8.314} \left( \frac{1}{450} - \frac{1}{450+500x_A} \right)} \left( \frac{1-x_A}{1+x_A} \right) \left( \frac{450}{450+500x_A} \right) = A$$

$x_A$	0	0.266667	0.533333	0.8
$T$	450	583.3333	716.6667	850
$k$	0.13300	0.90570	3.02073	6.90433
$(1-x_A)/(1+x_A)$	1	0.578947	0.304348	0.111111
$(T_0/T)$	1	0.771429	0.627907	0.529412
$A$	0.133	0.404499	0.577268	0.406137
$1/A$	7.518796	2.472193	1.732299	2.462222

$$W = \frac{3}{8} \times \frac{0.8}{3} [7.518 + 3 \times 2.472 + 3 \times 1.732 + 2.462] \times 20 = \underline{\underline{45.19 \text{ (kg)}}}$$

※利用 polymath 可作圖如下：

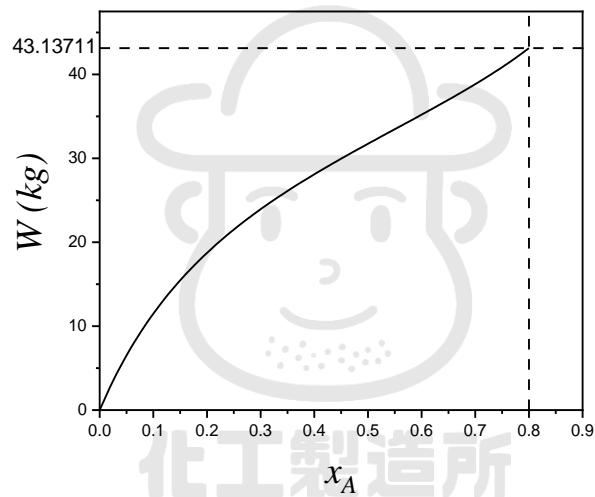
```
#To calculate the catalyst weight of PBR, we need its design equation, that is,
d(W)/d(xA) = v0/(-rA)

#The explicit equations or values are,
CA = (1-xA)/(1+xA)*(T0/T)
v0 = 20
k = 0.133*exp(31.4*10^3/8.314*(1/450-1/T))
T = T0+500*xA
T0 = 450
rA = -k*CA

#Define the the guess initial value of V to obtain the true value, ranging from xA = 0~0.8|
W(0) = 0
xA(0)=0
xA(f) =0.8
```

※注意此題直接利用  $F_{A0} / C_{A0} = v_0$  比較好做(題目有給)，因此在程式輸入上 design equation 直

接將  $F_{A0}$  取代為  $v_0$ ，並且 rate equation 部分就不輸入  $C_{A0}$ 。





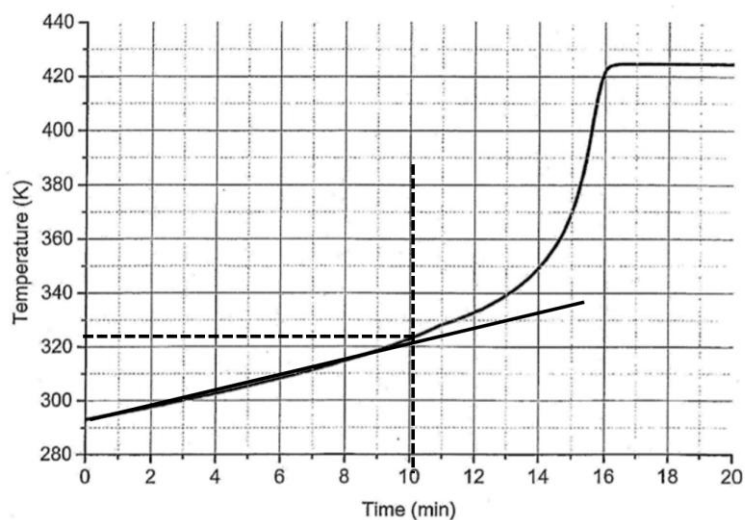
### Problem 4

#### 【Solution】

(a) @  $T_{onset}$

$$\dot{T}_s > \dot{T}_E \quad (\text{初始直線斜率})$$

如圖



$$\underline{T_{onset} = 325 \text{ (K)}}$$

(b)

The heat of reaction for such an nearly adiabatic operation can be found based the adiabatic temperature rise **when the reaction is completed**. Therefore, by energy balance,

$$x = \sum_i \theta_i C_{pi} \left[ \frac{(T - T_0)}{(\Delta H_{Rx}^\circ)} \right] = 1 \quad (\Delta C_p \approx 0)$$

$$-\Delta H_{Rx}^\circ = (C_{pA} + \theta_B C_{pB})(T_f - T_{onset}) = (187.9 + 3 \times 75.4)(425 - 325) = 41410 \text{ (J / mol)}$$

$$\underline{\underline{\Delta H_{Rx}^\circ = -41410 \text{ (J / mol)}}}$$

(關於 ARSST 的概念，於 107 成大化反 Problem 6(d)已有做簡易說明。本題實際解題可參考：

FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 608~611, Example 9.3.)

### **Problem 5**

#### **【Solution】**

(a)

For A, by data (1)(3)(6)(7)

$$\begin{cases} \text{low } C_A, r_A \downarrow \\ \text{high } C_A, r_A \uparrow \text{ 且趨於定值} \end{cases}$$

$$rate \propto \frac{P_A}{1 + K_A P_A \dots}$$

For B, by data (2)(7)

$C_B \uparrow, r \uparrow$  , 且直接正比

$$rate \propto P_B$$

For C, by data (4)(5)(8)

$$C_C \uparrow, r \downarrow$$

$$rate \propto \frac{1}{1 + K_C P_C \dots}$$

Rate law,

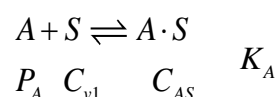
$$r = \frac{k P_A P_B}{(1 + K_A P_A + K_C P_C)}$$

(b)

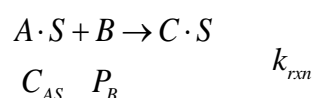
(1) 分子有 A 與 B，速率決定步驟應有 A 與 B 參與

(2) 且分母 A 與 C 項，分開，應為 Dual-site mechanism，且  $S_1 \neq S_2$

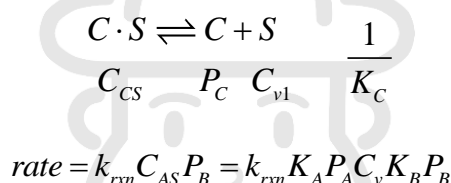
Adsorption of A



Surface reaction, (假設為 rate-determining step)



Desorption of C,



For  $C_v$ , by site balance,

$$C_t = C_v + C_{AS} + C_{CS} = C_v (1 + K_A P_A + K_C P_C)$$

代回

$$rate = \frac{k_{rxn} K_A P_A P_B C_t}{(1 + K_A P_A + K_C P_C)} = \frac{k P_A P_B}{(1 + K_A P_A + K_C P_C)}$$

(本題改編自：University of Michigan, Chapter 10 – Example CD10-1,

<http://websites.umich.edu/~essen/html/10chap/html/excd10-1.htm>)

本題有些許瑕疵，於 Run 4 時 B 分壓為 30 大氣壓，然而速率卻非 Run 2 (B 為 10 大氣壓) 的 3 倍，造成判斷易出錯。另外，此題網站上有進一步推求各類速率與吸附常數，最終速率定律式結果為：

$$rate = \frac{4.76 P_A P_B}{1 + 8.23 P_A + 2.38 P_C}$$

將 Run 4 資料代入可得速率為 10.2，也非題目所給之 6.8

### **Problem 6**

#### **【Solution】**

(a)

For infinite loading rate,

$$a = 1$$

$$W = \int_0^{x_A} \frac{F_{A0} dx_A}{-r_A}$$

For rate equation,

$$-r_A = k C_A C_B = k C_{A0}^2 (1 - x_A)^2$$

$$W = \int_0^{x_A} \frac{F_{A0} dx_A}{k C_{A0}^2 (1 - x_A)^2}$$
$$5 = \int_0^{x_A} \frac{1.0 \times 0.2 dx_A}{1.0 \times 0.2^2 (1 - x_A)^2}, \quad \underline{\underline{x_A = 0.5}}$$

(b)

*decay rate law* :

$$\frac{-da}{dt} = k_D = 0.2$$

若要計算觸媒效率與時間之關係，則：

在位置為  $z$  時，氣體反應物從進口到  $z$  時共接觸到  $W$  克重的觸媒反應物

而新鮮觸媒從進口處走到  $z$  時，其所需要之時間為(全程皆與反應物接觸)：

$$t = \frac{W}{U_s}, \quad dt = \frac{dW}{U_s}$$

$$U_s = \text{catalyst feed rate (kg / s)}$$

而觸媒效率對時間之關係為遵守 *decay rate law* :

$$\frac{-da}{dt} = -U_s \frac{da}{dW} = k_d$$

$$\int_1^a da = \frac{-k_d}{U_s} \int_0^W dW, \quad a = 1 - \frac{k_d}{U_s} W$$

代回：

$$dW = \int_0^{x_A} \frac{F_{A0} dx_A}{k(1 - \frac{k_d}{U_s} W) C_{A0}^2 (1 - x_A)^2}$$

$$\int_0^W (1 - \frac{k_d}{U_s}) dW = \int_0^{x_A} \frac{F_{A0} dx_A}{k C_{A0}^2 (1 - x_A)^2}$$

$$W - \frac{k_d W^2}{2U_s} = \int_0^{x_A} \frac{F_{A0} dx_A}{k C_{A0}^2 (1 - x_A)^2}$$

$$5 - \frac{0.2 \times 5^2}{2U_s} = \int_0^{0.4} \frac{1.0 \times 0.2}{1.0 \times 0.2^2 (1 - x_A)^2} dx_A$$

$$\underline{\underline{U_s = 1.5 \text{ (kg / s)}}}$$

(c)

$$a = 1 - \frac{k_d W}{U_s} = 0$$

$$1 - \frac{0.2 \times 5}{U_s} = 0, \quad \underline{\underline{U_s = 1 \text{ (kg / s)}}}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 749,

Problem 10-19B.。為 103 年成大化反 Problem 4 之同系列題組，詳細之反應器介紹參考該年詳

解。)

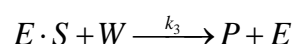
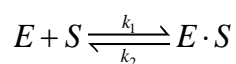
# 111 年成大化反

## Problem 1

### **【Solution】**

(a)

If we consider the following reaction mechanism,



Michaelis-Menten constant is defined as,

$$K_M = \frac{k_3[W] + k_2}{k_1}$$

and the reaction rate is,

$$-r_s = \frac{V_{\max}[S]}{K_M + [S]}$$

When  $K_M = [S]$ ,  $-r_s = \frac{V_{\max}}{2}$ , so the Michaelis-Menten constant equals to the substrate concentration where the rate of the reaction is one-half the maximum rate.

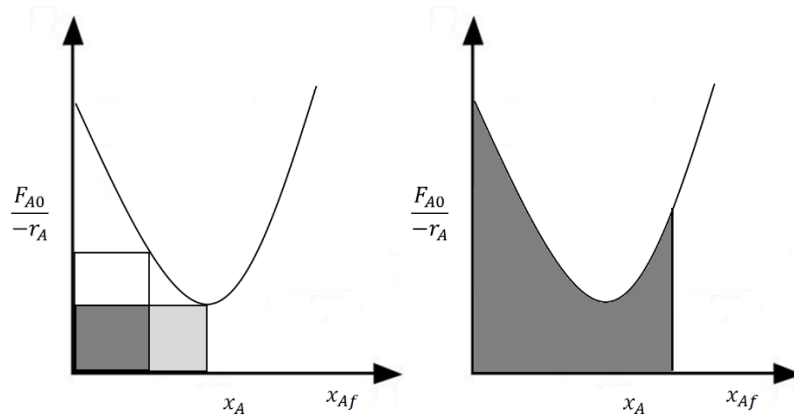
(b)

考慮一液相放熱反應，其速率定律式為：

$$-r_A = k(T)C_A^n$$

則此時速率有兩個因素來決定： $\begin{cases} k(T) \rightarrow \text{隨著反應放熱變大} \\ C_A^n \rightarrow \text{隨著反應進行而變小} \end{cases}$

此二因素互相拮抗的結果可由以下簡圖來表示，



若考慮 CSTR(如左圖)，則在圖形的兩點可能會有相同的矩形面積，因此就會有多個 Steady State 的產生；然而 PFR 之轉化率是隨著反應器體積而隨之增加的，並不會有相同面積的情形產生，是故沒有 multiple steady state 的生成。

(c)  $\frac{dN}{dt} \neq 0$ 、 $\frac{dT}{dt} \neq 0$ 、 $\frac{dS}{dt} \neq 0$

(d)

The Advanced Reaction System Screening Tool (ARSST) is based on the idea that reactants are placed and sealed in a calorimeter which is electrically heated as the temperature and pressure are monitored. In such configuration, we can determine the heat of reaction and the heating rate, enabling us to find the onset temperature, where the heat of reaction increases more rapidly than the electrically heating rate.

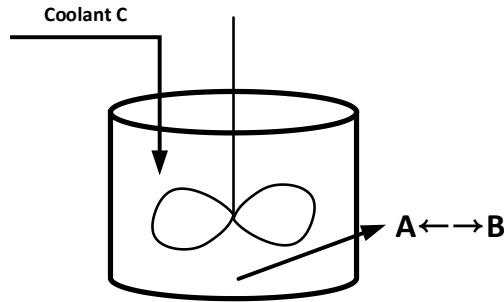
The ARSST offers us a way to determine the **reaction activation energies, frequency factors, and the heat of reaction.**

(關於 ARSST 的概念，於 107 成大化反 Problem 6(d) 已有做說明。而本題可參考：FOGLER,

H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 605~612.)

## **Problem 2**

**【Solution】**



The reaction is carried out at a semi-batch reactor, by energy balance,

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum F_{i0} C_{Pi} (T - T_{i0}) - [\Delta H_{Rx}] (-r_A V)}{\sum N_i C_{Pi}} = 0$$

$T = \text{constant}$

$$F_{C0} C_{P,C} (T - T_{C0}) = -\Delta H_{Rx} (-r_A V)$$

For  $(-r_A V)$ , by mole balance of A in the reactor,

$$\frac{dN_A}{dt} = r_A V$$

For the rate expression,

$$r_A = -k_f C_A + k_b C_B$$

$$\begin{aligned} \frac{dN_A}{dt} &= (-k_f C_A + k_b C_B) V = -k_f N_A + k_b N_B \\ &= -k_f N_A + k_b (N_{A0} - N_A) = k_b N_{A0} - (k_f + k_b) N_A = B - A N_A \end{aligned}$$

For  $N_A$ ,

$$\int_{N_{A0}}^{N_A} \frac{dN_A}{B - A N_A} = \int_0^t dt, \quad -\frac{1}{A} \ln\left(\frac{A N_A - B}{A N_{A0} - B}\right) = t$$

$$N_A = \frac{\exp[-At](A N_{A0} - B) + B}{A}$$

$$r_A V = \frac{dN_A}{dt} = \exp[-At](B - A N_{A0})$$

代回：

$$F_{C0} C_{P,C} (T - T_{C0}) = -\Delta H_{Rx} (-r_A V) = -\Delta H_{Rx} \exp[-At](A N_{A0} - B)$$



$$F_{C0}C_{P,C}(T-T_{C0}) = -\Delta H_{Rx} \exp[-At](AN_{A0} - B) = -\Delta H_{Rx} \exp[-At]k_f N_{A0}$$

$$F_{C0} \times 0.5(150 - 100) = 25000 \times e^{(1.2 \times 10^{-4} + 1.5 \times 10^{-4}) \times 3600} \times 1.2 \times 10^{-4} \times 1 \times 50$$

$$\underline{\underline{F_{C0} = 15.86 \text{ (lb mol / s)}}}$$

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 636, P9-6B)

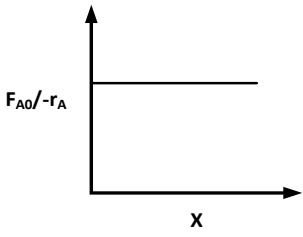
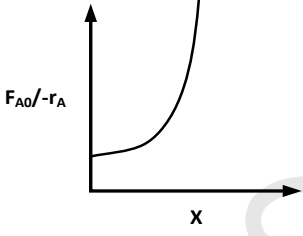
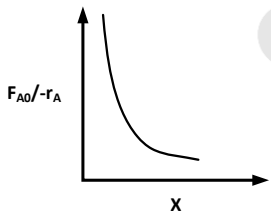
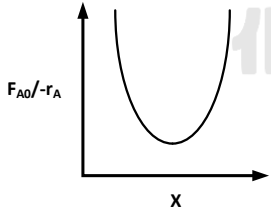
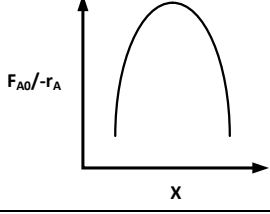


化工製造所

### Problem 3

#### 【Solution】

本題並未附上 Levenspiel plot，自行假設幾種情形：

Levenspiel plot 情形	反應器類型
	任何反應器皆可
	PFR 較適合
	CSTR 較適合
	先 CSTR 到最低點，再 PFR
	先 PFR 到最高點，再 CSTR

**Problem 4****【Solution】**

For the volume of PFR, by the design equation of PFR,

$$\frac{dF_A}{dV} = r_A$$

For  $-r_A$ , by the rate expression,

$$r_A = -\frac{7}{5}k_{1C}C_A^3C_B^2 - \frac{3}{4}k_{2E}C_A C_C^2$$

Combine, the relationship of the volume of the PFR and the concentration of A can be expressed as following,

$$\frac{dF_A}{dV} = -\frac{7}{5}k_{1C}C_A^3C_B^2 - \frac{3}{4}k_{2E}C_A C_C^2$$

For the relationship between the reactor volume and the molar flow rate of B,

$$\frac{dF_B}{dV} = r_B = -\frac{3}{5}r_{1C} - \frac{1}{2}r_{3D}$$

As for C, D, E, and F

$$\frac{dF_C}{dV} = r_C = r_{1C} - \frac{1}{4}r_{2E} \quad (C)$$

$$\frac{dF_D}{dV} = r_D = \frac{2}{5}r_{1C} + r_{3E} \quad (D)$$

$$\frac{dF_E}{dV} = r_E = r_{2E} + \frac{1}{4}r_{3D} \quad (E)$$

$$\frac{dF_F}{dV} = r_F = -\frac{3}{2}r_{3D} \quad (F)$$

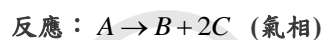
To solve the relationship of  $F_i$  and  $V$ , we may need:

- (1) The temperature of the system to calculate the rate constants of each of the reaction.
- (2) The temperature and pressure of the system to calculate the concentration of the species,  $C_{i0}$ , to insert them into the rate equations.
- (3) The initial values of  $F_i$ , that is  $F_{i0}$ , initially in the system.

Then we can set a variety of values of  $V$  to obtain the corresponding  $F_i$ .

(本題須注意題目已有定義各個速率表示式所代表的物質種類，因此要考慮係數以及正負號)

【補充】若我們自行假設一個較簡單的題目：



且於固定 400K、10 atim 下進行反應，速率常數為  $k = 0.043 \text{ min}^{-1}$ ，A 進料速率為 2.5 mol/min

則根據速率定律式，我們可以寫出：

$$r_A = -kC_A = -kC_{A0} \left( \frac{1-x_A}{1+2x_A} \right) \quad (\varepsilon = \delta y_{A0} = (2+1-1) \times 1 = 2)$$

$$r_B = kC_A = kC_{A0} \left( \frac{1-x_A}{1+2x_A} \right)$$

$$r_C = 2kC_A = 2kC_{A0} \left( \frac{1-x_A}{1+2x_A} \right)$$

且根據 PFR 設計方程式：

$$\frac{dF_A}{dV} = r_A, \quad \frac{dF_B}{dV} = r_B, \quad \frac{dF_C}{dV} = r_C$$

則可使用 polymath 作圖如下：

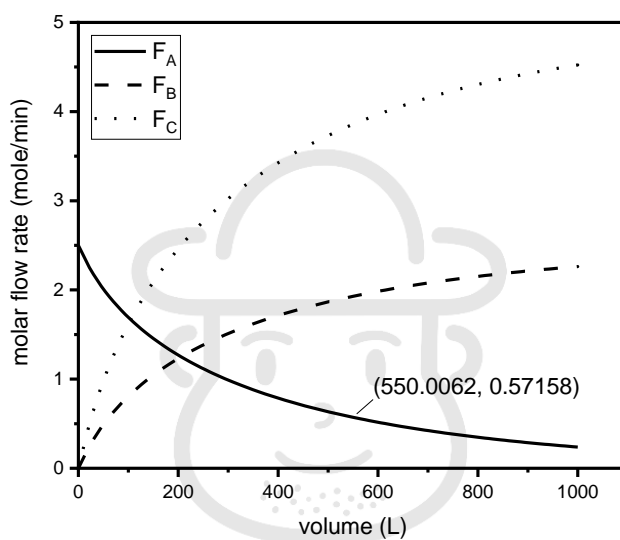
```
#To calculate the volume of PFR, we need the following differential equations,
d(FA)/d(V) = rA
d(FB)/d(V) = rB
d(FC)/d(V) = rC

#Define the rate equation
rA = -k*CA0*(1-x)/(1+e*x)
rB = -rA
rC = -2*rA

#The parameters or conditions we need or values are,
k = 0.043
FA0 = 2.5
CA0 = 10/0.082/400
FA(0) = 2.5
FB(0) = 0
FC(0) = 0

#To complete the calculation, we need
e = 2+1.1
x = (FA0-FA)/FA0

#The range of volume we want to know
V(0) = 0
V(f) = 1000
```



驗算圖中的點：By design equation,

$$V = \int_0^{x_A} \frac{F_{A0} dx_A}{-r_A} = \int_0^{x_A} \frac{F_{A0} dx_A}{k C_{A0} \frac{(1-x_A)}{(1+2x_A)}}$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{10}{0.082 \times 400} = 0.305 \text{ (mol / L)}$$

代回：

$$550 = \int_0^{x_A} \frac{2.5 dx_A}{0.043 \times 0.305 \frac{(1-x_A)}{(1+2x_A)}}, \quad x_A = 0.771$$

則此時：

$$F_A = F_{A0} (1-x_A) = 2.5(1-0.771) = 0.571, \text{ 符合作圖結果。}$$

### **Problem 5**

#### **【Solution】**

(1)

For PFR, by design equation,

$$V_1 = \int_0^{x_A} \frac{F_{A0,1} dx_A}{-r_{A,1}}$$

By the rate expression,

$$-r_{A,1} = k_{A,1} C_A = k_{A,1} C_{A0,1} \frac{(1-x_A)}{(1+\varepsilon x_A)}, \quad \varepsilon = \delta y_{A0} = \frac{2+1-1}{1} \times 1 = 2$$

Combine,

$$V_1 = \int_0^{x_A} \frac{F_{A0,1} (1+\varepsilon x_A) dx_A}{k_{A,1} C_{A0,1} (1-x_A)} = \frac{v_{0,1}}{k_{A,1}} \int_0^{0.8} \frac{(1+2x_A) dx_A}{(1-x_A)} = 3.228 \frac{v_{0,1}}{k_{A,1}}$$

For CSTR, by design equation,  $\varepsilon = \delta y_{A0} = \frac{2+1-1}{1} \times 0.25 = 0.5$

$$V_2 = \frac{F_{A0,2} x_A (1+\varepsilon x_A)}{k_{A,2} C_{A0,2} (1-x_A)} = \frac{v_{0,2}}{k_{A,2}} \times \frac{0.8(1+0.5 \times 0.8)}{1-0.8} = 5.6 \frac{v_{0,2}}{k_{A,2}}$$

$$\frac{V_1}{V_2} = \frac{3.228 \frac{v_{0,1}}{k_{A,1}}}{5.6 \frac{v_{0,2}}{k_{A,2}}} = \frac{3.228 v_{0,1}}{5.6 v_{0,2}} e^{\frac{-E_a}{R} (\frac{1}{T_2} - \frac{1}{T_1})}$$

將數據代入：

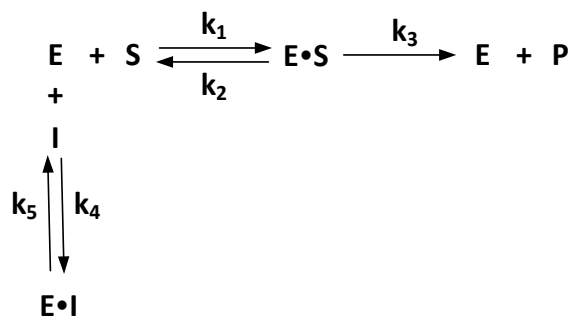
$$\frac{35}{30} = \frac{3.228 \times 5}{5.6 \times 6} e^{\frac{-E_a}{8.314} (\frac{1}{320} - \frac{1}{290})}, \quad \underline{\underline{E_a = 22819.0 \text{ (J/mol)}}}$$

### Problem 6

#### **【Solution】**

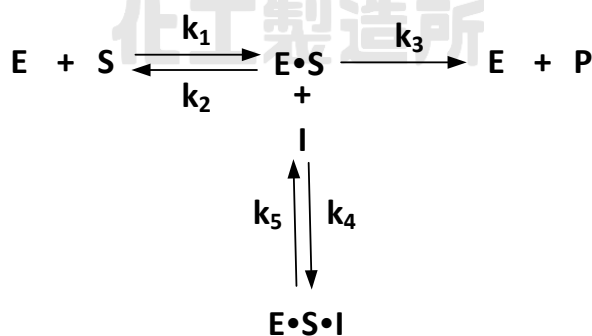
**【Case 1】 Competitive inhibition**：substrate 與 inhibitor 性質、幾何形狀相

似，因此相互競爭 enzyme 的接合位。



$$r_P = \frac{V_{\max} [S]}{S + K_M \left(1 + \frac{[I]}{K_I}\right)} \quad \left\{ \begin{array}{l} V_{\max} = k_3 [E]_0 \\ K_M = \frac{k_2 + k_3}{k_1} \\ K_I = \frac{k_5}{k_4} \end{array} \right.$$

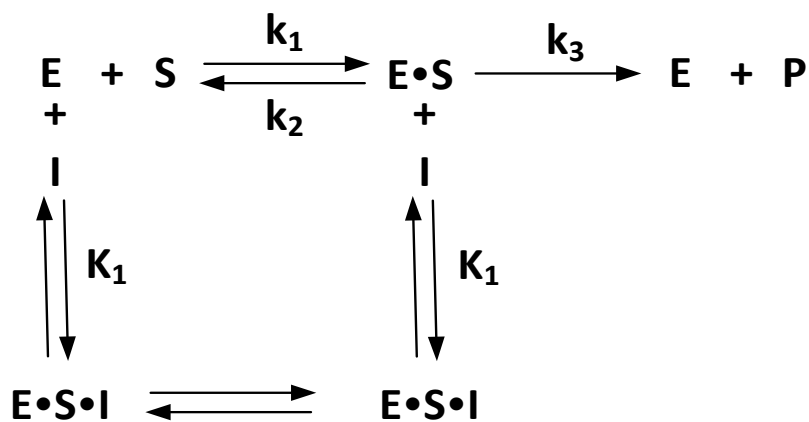
**【Case 2】 Uncompetitive inhibition**：inhibitor 與 enzyme 本身無親和性，而是 enzyme 與 substrate 接合後，inhibitor 才與 enzyme-substrate 複合物接合，因此導致其與 inhibitor 接合而使整體反應失效。



$$r_P = \frac{V_{\max} [S]}{K_M + [S] \left(1 + \frac{[I]}{K_I}\right)} \quad \left\{ \begin{array}{l} V_{\max} = k_3 [E]_0 \\ K_M = \frac{k_2 + k_3}{k_1} \\ K_I = \frac{k_5}{k_4} \end{array} \right.$$

**【Case 3】 Noncompetitive inhibition (Mixed inhibition)**：inhibitor 與 substrate 皆

可與 enzyme 接合，且兩者接合位互不相同，然而一旦 inhibitor 與 enzyme 接合，則同樣使得酵素失活。



$$r_p = \frac{V_{\max} [S]}{(K_M + [S]) \left(1 + \frac{[I]}{K_I}\right)}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 409~416

詳細方程式推導過程可參考：

<http://websites.umich.edu/~essen/html/course/lectures/nine/index.htm#sec2>)

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### **Problem 7**

#### **【Solution】**

(a) By the design equation of CSTR,

$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{F_B}{r_B} = \frac{F_C}{r_C}$$

Combine with the rate expression,

$$V = \frac{F_{A0} - F_A}{k_1 C_A} = \frac{F_B}{k_1 C_A - k_2 C_B} = \frac{F_C}{k_2 C_B}$$

∴ The ratio of  $C_B / C_C$  is 10%, and 50% of A is converted,

$$F_A = 0.5 F_{A0}, \quad F_B = \frac{1}{1+10} F_A = \frac{1}{11} F_A, \quad F_C = \frac{10}{11} F_A$$

代入：

$$\frac{F_{A0} - 0.5 F_{A0}}{k_1 C_A} = \frac{F_C}{k_2 C_B}, \quad \frac{F_{A0} - 0.5 F_{A0}}{k_1 C_A \cdot v} = \frac{F_C}{k_2 C_B \cdot v}$$

$$\frac{1}{k_1} = \frac{10}{k_2}, \quad \frac{1}{2 \times 10^9 e^{\frac{-31000}{1.987 \times T}}} = \frac{10}{1 \times 10^{11} e^{\frac{-40000}{1.987 T}}}$$

$$\underline{\underline{T = 2814.3 \text{ (R)}}}$$

(b) By the design equation of CSTR,

$$V = \frac{F_{A0} - F_A}{k_1 C_A} = \frac{\cancel{F_{A0}} - \cancel{F_A}}{k_1 \frac{\cancel{F_A}}{v_0 \left( \frac{T}{T_0} \right)}} = \frac{1}{2 \times 10^9 e^{\frac{-31000}{1.987 \times 2814.3}} \times \frac{1}{7.85 \times \frac{2814.3}{(400 + 460)}}} = \underline{\underline{3.28 \times 10^{-6} \text{ (ft}^3\text{)}}}$$

(c)

By energy balance,

$$Q - \dot{W} - F_{A0} \sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT + \underbrace{\sum_i V r_{ij} \Delta H_{rxn,ij}}_{\text{reaction heat}} = 0$$

$$UA(T_a - T) - F_{A0} C_{PA}(T - T_0) + V[(\Delta H_{R1A})(r_{1A}) + (\Delta H_{R2B})(r_{2B})] = 0$$

For  $r_{1A}$ , 假設  $k_1$  為根據 A 的消耗量定義：

$$r_{1A} = -k_1 C_A = -k_1 \frac{F_A}{v_0} \left( \frac{T_0}{T} \right) = -2 \times 10^9 e^{\frac{-31000}{1.987 \times 2814.3}} \times \frac{0.05 \times 0.5}{7.85} \times \frac{400 + 460}{2814.3} = -7614.9$$

For  $r_{2B}$ , 假設  $k_2$  為根據 B 的消耗量定義：

$$r_{2B} = -k_2 C_B = -k_2 \frac{F_B}{v_0} \left( \frac{T_0}{T} \right) = -1 \times 10^{11} e^{\frac{-40000}{1.987 \times 2814.3}} \times \frac{1}{7.85} \times 0.5 \times 0.05 \times \frac{400 + 460}{2814.3} = -6922.6$$

代回：

$$\begin{aligned} & \frac{400}{3600} \times A(350 + 460 - 2814.3) - 0.05 \times 25(2814.3 - 860) \\ & + 3.28 \times 10^{-6} \times (-15000 \times 7614.9 - 20000 \times 6922.6) = 0 \\ & \underline{\underline{A = -14.69 \text{ (ft}^2\text{)}}} \end{aligned}$$

※本題出題有瑕疵，出自：

<http://websites.umich.edu/~elements/08chap/html/p8-31.htm>

原題之  $C_B / C_C$  比例為 10，而非題目所給之 10%

將條件改為 10 後，(a) 小題可算出出口溫度為  $T = 728.82 \text{ (R)} = 268.82 \text{ (}^\circ\text{F)}$

(b) 小題可算出 CSTR 體積為  $6.59 \text{ (ft}^3\text{)}$

(c) 小題則為  $28.4 \text{ (ft}^2\text{)}$

下接正確解答：

(a) By the design equation of CSTR,

$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{F_B}{r_B} = \frac{F_C}{r_C}$$

Combine with the rate expression,

$$V = \frac{F_{A0} - F_A}{k_1 C_A} = \frac{F_B}{k_1 C_A - k_2 C_B} = \frac{F_C}{k_2 C_B}$$

$\therefore$  The ratio of  $C_B / C_C$  is 10, and 50% of A is converted,

$$F_A = 0.5 F_{A0}, \quad F_B = \frac{10}{1+10} F_A = \frac{10}{11} F_A, \quad F_C = \frac{1}{11} F_A$$

代入：

$$\frac{F_{A0} - 0.5 F_{A0}}{k_1 C_A} = \frac{F_C}{k_2 C_B}, \quad \frac{F_{A0} - 0.5 F_{A0}}{k_1 C_A \cdot v_{F_A}} = \frac{F_C}{k_2 C_B \cdot v_{F_B}}$$

$$\frac{1}{k_1} = \frac{0.1}{k_2}, \quad \frac{1}{2 \times 10^9 e^{\frac{-31000}{1.987 \times T}}} = \frac{0.1}{1 \times 10^{11} e^{\frac{-40000}{1.987 T}}}$$

$$T = 728.82 \text{ (R)} = \underline{\underline{268.82 \text{ (}^\circ\text{F)}}}$$

(b) By the design equation of CSTR,

$$V = \frac{F_{A0} - F_A}{k_1 C_A} = \frac{\cancel{F_{A0}} - \cancel{F_A}}{k_1 \frac{\cancel{F_A}}{v_0 \left( \frac{T}{T_0} \right)}} = \frac{1}{2 \times 10^9 e^{\frac{-31000}{1.987 \times 728.82}} \times \frac{860}{7.85 \times 728.82}} = \underline{\underline{6.59 \text{ (ft}^3\text{)}}}$$

(c)

By energy balance,

$$Q - \dot{W} - F_{A0} \sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT + \underbrace{\sum_i V r_{ij} \Delta H_{rxn,ij}}_{\text{reaction heat}} = 0$$

$$UA(T_a - T) - F_{A0} C_{PA}(T - T_0) + V[(\Delta H_{R1A})(r_{1A}) + (\Delta H_{R2B})(r_{2B})] = 0$$

For  $r_{1A}$ , 假設  $k_1$  為根據 A 的消耗量定義：

$$r_{1A} = -k_1 C_A = -k_1 \frac{F_A}{v_0} \left( \frac{T_0}{T} \right) = -2 \times 10^9 e^{\frac{-31000}{1.987 \times 728.82}} \times \frac{0.05 \times 0.5}{7.85} \times \frac{400 + 460}{728.82} = -0.00379$$

For  $r_{2B}$ , 假設  $k_2$  為根據 B 的消耗量定義：

$$r_{2B} = -k_2 C_B = -k_2 \frac{F_B}{v_0} \left( \frac{T_0}{T} \right) = -1 \times 10^{11} e^{\frac{-40000}{1.987 \times 728.82}} \times \frac{10}{11} \times \frac{0.5 \times 0.05}{7.85} \times \frac{400 + 460}{728.82} = -0.00034$$

代回：

$$\begin{aligned} & \frac{400}{3600} \times A(350 + 460 - 728.82) - 0.05 \times 25(728.82 - 860) \\ & + 6.59 \times (-15000 \times 0.00379 - 20000 \times 0.00034) = 0 \\ & \underline{\underline{A = 28.4 \text{ (ft}^2\text{)}}} \end{aligned}$$

※注意此題題意定義反應熱為每產生 1 mole C 可吸收 20000 Btu 的能量，以"原文書的公式"來說需要先將其轉換成以 B 的消耗來看。不過剛好產生 1 mole C 同時消耗 1 mole B，因此此題反應 2 的反應熱為消耗 1 mole B，吸收 20000 Btu 的能量。

本題關於 multiple reaction 的能量平衡說明，請參考 105 成大化反 Problem 3 講解。

※若是不想背公式的同學，也可參考其能量平衡意義來作答，以較為常見的能量平衡來說：

$$Q - \dot{W} - F_{A0} \sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT - \sum_i F_{i0} X_{i,reacted} \Delta H_{rxn,ij} = 0$$

其中  $\sum_i F_{i0} X_{i,reacted} \Delta H_{rxn,ij}$  本就是反應莫爾數×莫耳反應熱，因此將其先展開：

$$Q - \dot{W} - F_{A0} \sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT - (F_{A0} - F_A) \Delta H_{rxn,1A} - F_C \Delta H_{rxn,2C} = 0$$

其中  $(F_{A0} - F_A)$  就是反應中 A 反應掉的莫爾流量、 $F_C$  就是反應中 C 產生的莫爾流量  
根據(a)小題結果，我們知道：

$$F_{A0} - F_A = 0.5F_{A0} \quad , \quad F_C = \frac{1}{11}F_A = \frac{0.5}{11}F_{A0}$$

代回：

$$Q - \dot{W} - F_{A0} \sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT - 0.5F_{A0} \Delta H_{rxn,1A} - \frac{0.5}{11}F_{A0} \Delta H_{rxn,2C} = 0$$

因此：

$$\frac{400}{3600} \times A(350 + 460 - 728.82) - 0.05 \times 25(728.82 - 860) - 0.05 \times 0.5 \times 15000 - \frac{0.05}{11} \times 0.5 \times 20000 = 0$$

$$\underline{\underline{A = 28.4 \text{ (ft}^2\text{)}}}$$



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# 112 年成大化反

## Problem 1

### **【Solution】**

By the decay rate law (zero-order),

$$-\frac{da}{dt} = k_d, \quad -\int_1^a da = \int_0^t k_d dt$$

$$a = 1 - k_d t = 1 - 0.05t$$

**【Check the maximum reaction time】**

$$a = 1 - 0.05t = 0, \quad t = 20 \text{ (min)}$$

(代表 20 分鐘後觸媒就失去活性，剩下的 20 分鐘對轉化率沒有影響)

By the design equation of batch reactor with catalyst,

$$N_{B0} \frac{dx_B}{dt} = -r_B W a$$

By the rate equation,

$$-r_B = k' C_B^2 = k' C_{B0}^2 (1 - x_B)^2$$

Combine,

$$-N_{B0} \frac{dx_B}{dt} = k' C_{B0}^2 (1 - x_B)^2 W a = k' \frac{N_{B0}^2}{V^2} (1 - x_B)^2 W a$$

$$\int_0^{x_B} \frac{dx_B}{(1 - x_B)^2} = k' \frac{N_{B0} W}{V^2} \int_0^t a dt$$

$$\int_0^{x_B} \frac{dx_B}{(1 - x_B)^2} = k' \frac{N_{B0} W}{V^2} \int_0^t (1 - 0.05t) dt$$

$$\int_0^{x_B} \frac{dx_B}{(1 - x_B)^2} = 0.01 \times \frac{10 \times 1}{(1)^2} \int_0^{20} (1 - 0.05t) dt$$

$$\underline{\underline{x_B = 0.5}}$$

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 755,

CDP10-WB)

## Problem 2

### 【Solution】

(a)

令：

$$\text{第一條反應式： } r_{R^*} = k_I[CFC_s]$$

$$\text{第二條反應式： } r_{O_2} = k_1[O_3][R^*]$$

$$\text{第三條反應式： } r_{O_2} = k_2[O_3][O]$$

$$\text{第四條反應式： } r_{CFC_s} = k_D[R^*]^2$$

則：

$$-r_{O_3} = k_1[O_3][R^*] + \frac{1}{2}k_2[O_3][O]$$

By pseudo-steady state assumptions,

$$r_{R^*} = k_I[CFC_s] - k_1[O_3][R^*] + k_1[O_3][R^*] - 2k_D[R^*]^2 = 0, \quad [R^*] = \sqrt{\frac{k_I[CFC_s]}{2k_D}}$$

$$r_{O_2} = k_1[O_3][R^*] - \frac{1}{2}k_2[O_3][O] = 0$$

$$[O] = \frac{2k_1[R^*]}{k_2} = \frac{2k_1}{k_2} \sqrt{\frac{k_I[CFC_s]}{2k_D}}$$

代回：

$$-r_{O_3} = k_1[O_3] \sqrt{\frac{k_I[CFC_s]}{2k_D}} + \frac{1}{2}k_2[O_3] \frac{2k_1}{k_2} \sqrt{\frac{k_I[CFC_s]}{2k_D}} = \underline{\underline{2k_1[O_3] \sqrt{\frac{k_I[CFC_s]}{2k_D}}}}$$

(b)

$$r_{O_2} = k_1[O_3][R^*] + k_2[O_3][O]$$

$$r_{O_2} = k_1[O_3] \sqrt{\frac{k_I[CFC_s]}{2k_D}} + k_2[O_3] \frac{2k_1}{k_2} \sqrt{\frac{k_I[CFC_s]}{2k_D}} = \underline{\underline{3k_1[O_3] \sqrt{\frac{k_I[CFC_s]}{2k_D}}}}$$

### Problem 3

#### 【Solution】

$$\phi_n^2 = \frac{k_n R^2 C_{As}^{n-1}}{D_e} = \frac{k_n R C_{As}^n}{\left[\frac{D_e C_{As}}{R}\right]} = \frac{\text{surface reaction rate}}{\text{diffusion rate}}$$

To derive the Thiele modulus, from mass balance,

$$W_{Ar}(4\pi r^2)\Big|_r - W_{Ar}(4\pi r^2)\Big|_{r+dr} + r_A' \rho_c (4\pi r^2) dr = 0$$

$$\begin{cases} r_A' = \text{reaction rate / unit weight of catalyst} \\ \rho_c = \text{weight of catalyst / volume} \end{cases}$$

同除  $4\pi dr \rightarrow 0$

$$\frac{d(W_{Ar} r^2)}{dr} - r_A' \rho_c r^2 = 0$$

將  $W_{Ar} = -D_e \frac{dC_A}{dr}$  代入：

$$\frac{d}{dr} \left( r^2 D_e \frac{dC_A}{dr} \right) + r_A' \rho_c r^2 = 0$$

$$r_A' \rho_c = \text{reaction rate / volume} = -k_n C_A^n$$

$$\frac{d}{dr} \left( r^2 D_e \frac{dC_A}{dr} \right) - k_n C_A^n r^2 = 0$$

微分：

$$D_e \left( 2r \frac{dC_A}{dr} + r^2 \frac{d^2 C_A}{dr^2} \right) - k_n C_A^n r^2 = 0$$

$$\frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{dC_A}{dr} - \frac{k_n C_A^n}{D_e} = 0$$

無因次化方程式：

$$\Psi = \frac{C_A}{C_{As}}, \quad \lambda = \frac{r}{R}$$

$$\frac{C_{As}}{R^2} \frac{d^2 \Psi}{d\lambda^2} + \frac{2C_{As}}{R^2} \frac{1}{\lambda} \frac{d\Psi}{d\lambda} - C_{As}^n \frac{k_n \Psi^n}{D_e} = 0$$



整理：

$$\frac{d^2\Psi}{d\lambda^2} + \frac{2}{\lambda} \frac{d\Psi}{d\lambda} - \frac{k_n C_{As}^{n-1} R^2}{D_e} \Psi^n = 0$$

令

$$\phi_n^2 = \sqrt{\frac{k_n C_{As}^{n-1} R^2}{D_e}}$$

※若 Thiele modulus  $\gg 1$ ，則

$$\frac{k_n C_{As}^{n-1} R^2}{D_e} \Psi^n \approx 0 \text{ (實際非零，想成非常小)}$$

$C_A$  is small

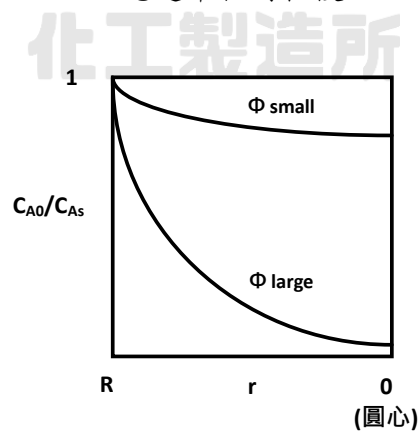
代表內部反應非常快，擴散進來的 A 很快就被消耗到很小。

若 Thiele modulus  $\ll 1$ ，則

$$\frac{d^2\Psi}{d\lambda^2} + \frac{2}{\lambda} \frac{d\Psi}{d\lambda} \approx 0 \text{ (實際非零，想成非常小)}$$

代表擴散梯度非常小，即  $C_A \approx C_{As}$

因反應速率相對較慢。



(本題推導可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 817~821,

Thiele modulus 大小與濃度-觸媒位置之關係可參考 p 823。)

### **Problem 4**

#### **【Solution】**

(a)

For CSTR with n-order reaction,

$$Da = \frac{\text{rate of reaction at entrance}}{\text{Entering flow rate of A}} = \frac{-r_{A0}V}{F_{A0}} = \frac{kC_{A0}^n V}{F_{A0}}$$

By the design equation of CSTR,

$$V = \frac{F_{A0}x_A}{-r_A} = \frac{F_{A0}x_A}{kC_A^n} = \frac{F_{A0}x_A}{kC_{A0}^n(1-x_A)^n}$$
$$\frac{kC_{A0}^n V}{F_{A0}} = Da = \frac{x_A}{(1-x_A)^n}$$

將圖上數據代入(取  $x_A = 0.35$  ,  $Da \approx 0.225$  , 圖中虛線)

$$0.225 = \frac{0.35}{(1-0.35)^n} , \underline{\underline{n \approx -1}}$$

Therefore, the rate expression is,

$$\underline{\underline{-r_A = kC_A^{-1}}}$$

因濃度與反應速率成反比關係，因此 PFR 反應物濃度較高的特性將造成在同樣轉化率下，其所需反應器體積較 CSTR 高。根據 Damköhler number 定義：

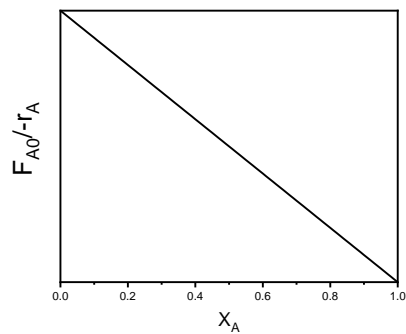
$$Da = \frac{-r_{A0}V}{F_{A0}} \propto V , \text{ 因此 PFR 在高轉化率下，其 } Da \text{ 數值就較高。}$$

(b)

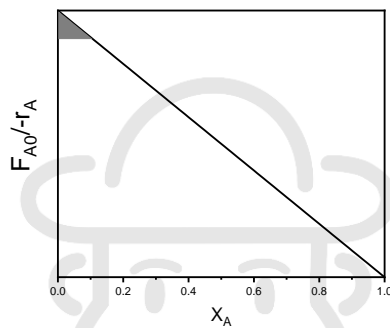
To plot a Levenspiel plot, we need,

$$\frac{F_{A0}}{-r_A} = \frac{F_{A0}}{k[C_{A0}(1-x_A)]^{-1}} = \frac{F_{A0}C_{A0}(1-x_A)}{k}$$

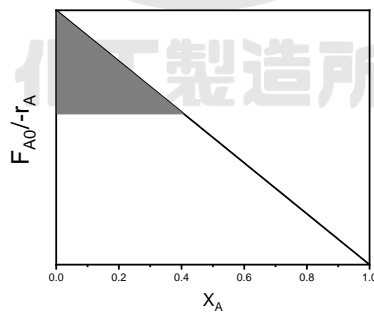
Plot  $\frac{F_{A0}}{-r_A} - x_A$ ,



※轉化率低時，PFR 所需體積與 CSTR 差異



轉化率高時，PFR 所需體積與 CSTR 差異



因此在高轉化率下，其  $x_A - Da$  關係才會有較大偏差。

(Damköhler number 定義可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 158。)

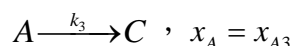
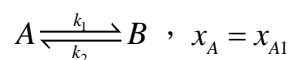
### Problem 5

#### 【Solution】

(a)

※此題  $T_f$  改為 480.93 (K) 做計算，假設 steady state

If we separate the reactions into two individual reactions,



By energy balance,

$$Q - \dot{W} - F_{A0} \sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT - \sum_i F_{A0} \Delta H_{rxn, iA} x_{Ai} = 0$$

$$UA(T_a - T) - \sum_i \int_{T_{i0}}^T F_{A0} \theta_i C_{pi} dT - \sum_i F_{A0} \Delta H_{rxn, iA} x_{Ai} = 0$$

$$UA(T_a - T) - F_{A0} \int_{T_{i0}}^T (C_{PA} + C_{PB}) dT - F_{A0} [(\Delta H_{R1} + \int_{T_R}^T \Delta C_{P1} dT) x_{A1} + (\Delta H_{R3} + \int_{T_R}^T \Delta C_{P3} dT) x_{A3}] = 0$$

$$1600(500 - 480.93) - 1 \times (100 + 100)(480.93 - 330) - 1 \times (-1800x_{A1} - 1100x_{A3}) = 0$$

$$1800x_{A1} + 1100x_{A3} = -326$$

By design equation,

$$W = \frac{F_{A0} x_{A3}}{r_C} = \frac{F_{A0} x_{A3}}{k_3 C_A} = \frac{F_{A0} x_{A3}}{k_3 C_{A0} (1 - x_{A1} - x_{A3}) \left(\frac{T_0}{T}\right)}$$

$$100 = \frac{1 \times x_{A3}}{0.005 e^{4.6(1 - \frac{460}{480.93})} \times 1(1 - x_{A1} - x_{A3}) \left(\frac{330}{480.93}\right)}$$

$$0.419(1 - x_{A1} - x_{A3}) = x_{A3}$$

$$0.419x_{A1} + 1.419x_{A3} = 0.419 \quad \begin{cases} x_{A1} = -0.441 \\ x_{A2} = 0.425 \end{cases}$$

※此題 mixed flow fluidized bed reactor 應為一般 CSTR 配置，只不過反應器內有觸媒才可反應。

若用 PBR 觀念去做，則要解微分式，在原文書中一般以數值 polymath 數值解進行，於考試當中

不太可能寫出正解。

$$C_A = C_{A0}(1 - x_{A1} - x_{A2})\left(\frac{T_0}{T}\right) = 1 \times (1 + 0.441 - 0.425)\left(\frac{330}{480.93}\right) = 0.697 \text{ (mol / dm}^3\text{)}$$

$$C_B = C_{A0}(1 + x_{A1})\left(\frac{T_0}{T}\right) = 1 \times (1 - 0.441)\left(\frac{330}{480.93}\right) = 0.383 \text{ (mol / dm}^3\text{)}$$

$$C_C = C_{A0}x_{A2}\left(\frac{T_0}{T}\right) = 1 \times 0.425\left(\frac{330}{480.93}\right) = 0.292 \text{ (mol / dm}^3\text{)}$$

In a sequence arranged from largest to smallest,

$$\underline{\underline{C_A > C_B > C_C}}$$

(0.697)    (0.383)    (0.292)

※此題解出  $x_{A1} < 0$  代表 A 與 B 平衡是向 A 的方向移動，因為 A 反應成 C 的反應不可逆，對 A

與 B 的平衡來說 A 會漸漸變少，因此 B 必須向左反應才有達到平衡的可能。

※另外，此題原本給定之 outlet temperature 並無法同時滿足能量平衡與物質平衡，若將此題利用 polymath 算出，則得：

```
#Calculation of exit concentration of the species
f(Ca) = W*(ra1-ra2)-(v0*Ca0-v*Ca)
f(Cb) = W*(rb)-(v*Cb-v0*Cb0)
f(Cc) = W*(rc)-v*Cc

#Energy balance
f(T) = Ua*(Ta-T)-FA0*(cpa+cpb)*(T-T0)+W*(ra1*dHa1+ra2*dHa3)

#Explicit values
Ca0 = 1
Cb0 = 1
v = v0*(T/T0)
v0 = 2/2
T0 = 330
Ua = 1600
Ta = 500
FA0 = 1
cpa = 100
cpb = 100
W = 100
k1 = 0.5*exp(2-640/T)
k3 = 0.005*exp(4.6*(1-460/T))
Kc = 10*exp(4.8*(430/T-1.5))
ra1 = -k1*(Ca-1/Kc*Cb)
ra2 = -k3*Ca
rb = -1*(ra1)
rc = -1*(ra2)
dHa1 = -1800
dHa3 = -1100
xA3 = Cc*v/FA0
xA = (FA0-(Ca*v))/FA0

#Guess the initial values
Ca(0) = 1
Cb(0) = 1
Cc(0) = 0
T(0) = 330
```

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	Ca	0.6972064	-4.717E-14	1.
2	Cb	0.3829207	-4.741E-14	1.
3	Cc	0.2922157	1.11E-16	0
4	T	480.9294	-1.164E-10	330.

這裡的能量平衡利用

$$Q - \dot{W} - F_{A0} \sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT + \underbrace{\sum_i W_{r,i} \Delta H_{rxn,i}}_{\text{reaction heat}} = 0$$

列式算出，可不必定義轉化率，直接用濃度做計算。

若以原題給定之出口溫度(400 K)利用 polymath 做計算並算出相對應的轉化率，則無合理解：

```

#Calculation of conversions by mass balance and energy balance
f(xA1) = 1600*(500-T)-(200)*(T-330)+1800*xA1+1100*xA3
f(xA3) = W-FA0*xA3/(k3*Ca0*(1-xA1-xA3)*(T0/T))

#Explicit values
Ca0 = 1
Cb0 = 1
v = v0*(T/T0)
v0 = 2/2
T0 = 330
Ua = 1600
Ta = 500
FA0 = 1
W = 100
k1 = 0.5*exp(2-640/T)
k3 = 0.005*exp(4.6*(1-460/T))
Kc = 10*exp(4.8*(430/T-1.5))
T = 400

#Guess the initial values
xA1(0) = 1
xA3(0) = 1

```

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	xA1	-90.72001	7.276E-12	1.
2	xA3	15.72366	-1.705E-13	1.

在同樣配置下，改變出口溫度為 480.93 (K)，則結果為：

```

#Calculation of conversions by mass balance and energy balance
f(xA1) = 1600*(500-T)-(200)*(T-330)+1800*xA1+1100*xA3
f(xA3) = W-FA0*xA3/(k3*Ca0*(1-xA1-xA3)*(T0/T))

#Explicit values
Ca0 = 1
Cb0 = 1
v = v0*(T/T0)
v0 = 2/2
T0 = 330
Ua = 1600
Ta = 500
FA0 = 1
W = 100
k1 = 0.5*exp(2-640/T)
k3 = 0.005*exp(4.6*(1-460/T))
Kc = 10*exp(4.8*(430/T-1.5))
T = 480.9293

#Guess the initial values
xA1(0) = 1
xA3(0) = 1

```

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	xA1	-0.4419647	1.137E-13	1.
2	xA3	0.4258696	-8.723E-11	1.

不過，若維持題目所給之 400K 做計算，則也有可能在 undteady state 的假設下進行計算，只不過此時依舊需要先解溫度-時間微分式，再利用質量平衡解濃度-時間微分關係，在原文書依舊使用 polymath 做計算，於考試中不太實際。

(b)

以 AB 平衡的觀點來說：

$$K_c = 10e^{4.8\left(\frac{430}{T} - 1.5\right)}$$

溫度降低， $K_c$  越高，代表平衡越向 B 的產生方向

以 A 變 C 的反應來說：

$$k_3 = 0.005e^{4.6\left(1 - \frac{460}{T}\right)}$$

溫度越低， $k_3$  越低，代表 A 反應成 C 的速率越低

綜上所述，若要盡可能產生最多 B，溫度應該越低越好。

(此題改編自：FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 584, Problem 8-25c, 原題反應器為 PBR，需利用 polymath 數值解。)



## Problem 6

### 【Solution】

※一般而言，氣體於反應過程中的壓力變化，可由理想氣體方程式看出：

$$P \propto \frac{F_r T}{v}, \text{ 抑或同學常記的 } v \propto \frac{F_r T}{P}$$

基礎上，壓力不僅只與反應所剩的莫爾數有關，也與溫度、體積等參數有關，抑或是單純可由外力控制，例如在恆壓反應器中，不論總莫耳數增加或減少，壓力依舊可維持恆壓。又就算假設此題條件可由壓力與莫爾數直接正比推出，也並不知道各條反應進行的程度，以至於無法做精確的計算(例如題目說 A 轉化率為 0.3，然而這並沒有透露多少被反應式 1 消耗掉，多少被 2 消耗掉)。因此，本題改採用別的可能影響壓降的參數做說明。在 Folger 原文書的討論上，氣體反應可以分為在一般 pipe (例如 PFR) 以及填充床(PBR)進行兩種情況，其壓降的產生機制與結果也大不相同：

#### (1) PBR

因 PBR 本身具有固體顆粒觸媒床當作氣體流過的阻礙，因此其壓降可由 Ergun equation 做描述，其淨結果為：

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1+\varepsilon x) \frac{T}{T_0} \begin{cases} y = P/P_0 (\text{壓降}) \\ \alpha = \text{係數} \end{cases}$$

由方程式不論莫爾數是否變化，氣體經過 PBR 本來就會產生壓降，而莫爾數變化的結果，會導致壓降的程度不同，亦即：

$$\begin{cases} \varepsilon < 0 \rightarrow \left| \frac{dy}{dW} \right| \downarrow, \text{壓降較小} \\ \varepsilon > 0 \rightarrow \left| \frac{dy}{dW} \right| \uparrow, \text{壓降較大} \end{cases}$$

(注意， $\varepsilon > 0$  不代表壓力就會上升，甚至於在 PBR 中反而壓降更明顯)

(細部的 Ergun equation 推導，請自行參考 FOLGER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 175~181。)

(後續還有)



## (2) PFR

假設一般 PFR 視為單純的 pipe，則通常來說，氣體因產生較少摩擦損耗，則不太考慮流體流過的壓降，除非是在通道過小以及流速過快的情況，則：

$$\frac{dP}{dL} = -G \frac{du}{dL} - \frac{2fG^2}{\rho D} \begin{cases} g = \text{average velocity} \\ G = \text{mass velocity} = \rho u \end{cases}$$

經過近似以後，其可表示為：

$$\frac{P}{P_0} \approx (1 - \alpha_p V)^{1/2}$$

而本題是發生在 PFR 類的反應器，在不考慮特殊情況下，其壓降應該非常微小，因此：

$$P_T \sim P_{T0}$$

因此對於總濃度：

$$C_{T0} = \frac{P_{T0}}{RT} \xrightarrow{\text{after reaction}} C_T = \frac{P_T}{RT}$$

$$C_T = C_{T0}$$

亦即單就反應器設計來說，假設損耗摩擦很小，PFR 類反應器其總壓與總濃度應該不變。

抑或也可回答具有壓降，且總濃度變小，然而此因損耗摩擦本來就會導致的壓降，單就莫爾數

變化我們無從得知確切下降多少。

(細部的觀念推導，請自行參考 FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 182。)

### **Problem 7**

#### **【Solution】**

By the equilibrium relation,

$$K_C = \frac{C_{Be} C_{Ce}}{C_{Ae}}$$

For  $C_{Ae}$ ,

$$C_{Ae} = \frac{C_{A0}(1-x_{Ae})}{(1+\varepsilon x_{Ae})\left(\frac{T}{T_0}\right)} = \frac{C_{A0}(1-x_{Ae})}{(1+\varepsilon x_{Ae})} \left(\frac{T}{T_0}\right)$$

$$\text{with } \varepsilon = \delta y_{A0} = \frac{1+1-1}{1} \times 1 = 1$$

$$C_{Ae} = \frac{C_{A0}(1-x_{Ae})}{(1+\varepsilon x_{Ae})\left(\frac{T}{T_0}\right)} = \frac{C_{A0}(1-x_{Ae})}{(1+x_{Ae})} \left(\frac{T}{T_0}\right)$$

For  $C_{Be}$  and  $C_{Ce}$ ,

$$C_{Be} = C_{Ce} = \frac{C_{A0}x_{Ae}}{(1+x_{Ae})\left(\frac{T}{T_0}\right)}$$

Therefore, the equilibrium relation is,

$$K_C = \frac{C_{Be} C_{Ce}}{C_{Ae}} = \frac{\left[\frac{C_{A0}x_{Ae}}{(1+x_{Ae})\left(\frac{T}{T_0}\right)}\right]^2}{\frac{C_{A0}(1-x_{Ae})}{(1+x_{Ae})} \left(\frac{T}{T_0}\right)} = \frac{C_{A0}x_{Ae}^2}{(1+x_{Ae})(1-x_{Ae})\left(\frac{T}{T_0}\right)} = \frac{C_{A0}x_{Ae}^2}{(1-x_{Ae}^2)\left(\frac{T}{T_0}\right)}$$

$$\frac{x_{Ae}^2}{(1-x_{Ae}^2)} = \frac{K_C \left(\frac{T}{T_0}\right)}{C_{A0}}, \quad x_{Ae}^2 = \frac{K_C \left(\frac{T}{T_0}\right)}{C_{A0}} - \frac{K_C \left(\frac{T}{T_0}\right)}{C_{A0}} x_{Ae}^2$$

$$x_{Ae} = \sqrt{\frac{\frac{K_C T}{C_{A0} T_0}}{1 + \frac{K_C T}{C_{A0} T_0}}} = \sqrt{\frac{K_C T}{C_{A0} T_0 + K_C T}}$$

For  $K_C$ , by Van't Hoff equation,

$$\begin{aligned}\frac{d \ln K_C}{dT} &= \frac{\Delta H_R}{RT^2} = \frac{\Delta H_R(T_R) + \int_{T_R}^T \Delta C_p dT}{RT^2} \\ &= \frac{\Delta H_R(T_R)}{RT^2} + \frac{\int_{T_R}^T (C_{pB} + C_{pC} - C_{pA}) dT}{RT^2} = \frac{\Delta H_R(T_R)}{RT^2} + \frac{\Delta C_p (T - T_R)}{RT^2} = \frac{\Delta H_R(T_R) - \Delta C_p T_R}{RT^2} + \frac{\Delta C_p}{RT} \\ \ln\left(\frac{K_{C,T_f}}{K_{C,T_0}}\right) &= \int_{T_0}^{T_f} \left[ \frac{\Delta H_R(T_R) - \Delta C_p T_R}{RT^2} + \frac{\Delta C_p}{RT} \right] dT = \frac{\Delta H_R(T_R) - \Delta C_p T_R}{R} \left( \frac{1}{T_0} - \frac{1}{T_f} \right) + \frac{\Delta C_p}{R} \ln \frac{T_f}{T_0} \\ K_{C,T_f} &= K_{C,T_0} \exp \left[ \frac{\Delta H_R(T_R) - \Delta C_p T_R}{R} \left( \frac{1}{T_0} - \frac{1}{T_f} \right) + \frac{\Delta C_p}{R} \ln \frac{T_f}{T_0} \right]\end{aligned}$$

代入  $x_{Ae} = \sqrt{\frac{K_C T}{C_{A0} T_0 + K_C T}}$  即可整理出  $x_{Ae, TB}(T_f)$

By energy balance,

$$\phi - \mathcal{W} - F_{A0} \sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT - \sum_i F_{A0} \Delta H_{rxn, iA} x_{Ai} = 0$$

$$x_{A, EB} = \frac{\sum_i \int_{T_{i0}}^T \theta_i C_{pi} dT}{-\Delta H_R} = \frac{C_{pA} (T_f - T_0)}{-[\Delta H_R(T_R) + \int_{T_R}^{T_f} \Delta C_p dT]} = \frac{C_{pA} (T_f - T_0)}{-[\Delta H_R(T_R) + \Delta C_p (T_f - T_R)]}$$

將  $x_{Ae, TB}$  與  $x_{A, EB}$  求交點，即可得到同時滿足熱力學平衡與能量平衡之

$x_{Ae, TB} = x_{A, EB} = x_{Ae}$  與其相對應溫度  $T_f$ ，接續代回下式即可求出  $C_{Ae}$ 。

$$C_{Ae} = \frac{C_{A0}(1 - x_{Ae})}{(1 + x_{Ae})} \left( \frac{T_f}{T_0} \right)$$

然而若題目意思為只回答熱力學平衡與溫度之關係，則應回答  $C_{Ae, TB}$  即可。

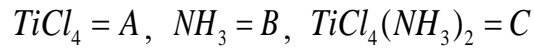
# 113 年成大化反

## Problem 1

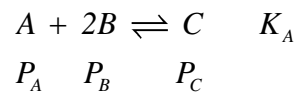
### **【Solution】**

(a)

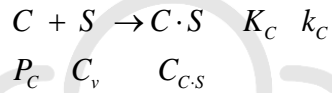
Denote the species as,



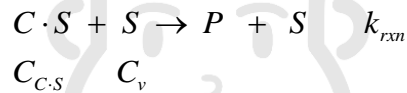
Complex formation reaction,



Adsorption of C :



Surface reaction :



Assume surface reaction is rate-determining,

$$\text{reaction rate, } r = k_{rxn} C_{C \cdot S} C_v$$

For  $C_{C \cdot S}$ ,  $\frac{-r_C}{k_C} \approx 0$  :

$$C_{C \cdot S} = K_C P_C C_v$$

By site balance,

$$C_t = C_v (1 + K_C P_C)$$

代回 reaction rate 表示式，得：

$$r = \frac{k_{rxn} K_C P_C C_t^2}{(1 + K_C P_C)^2}$$

因題目給的分壓由  $A$  與  $B$  來表示，因此將  $P_C$  換成與  $P_A$  與  $P_B$  有關的式子，根據 complex formation 的平衡式：

$$P_C = K_A P_A P_B^2$$

代回：

$$r = \frac{k_{rxn} K_C K_A P_A P_B^2 C_t^2}{(1 + K_C K_A P_A P_B^2)^2} = \frac{K_1 P_A P_B^2}{(1 + K_2 P_A P_B^2)^2}$$

(b)

Run 1,2,3：

在高  $NH_3$  分壓下，速率與  $TiCl_4$  呈現負相關，吻合。

Run 4,5：

在低  $TiCl_4$  分壓下，速率與  $NH_3$  呈現正相關，吻合

(c)

$$r = \frac{K_1 P_A P_B^2}{(1 + K_2 P_A P_B^2)^2}$$

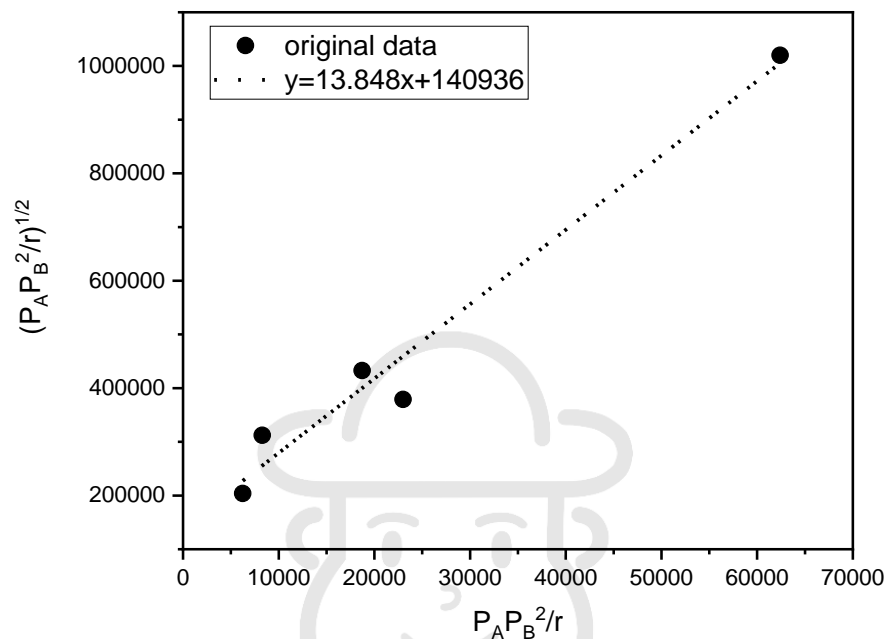
倒數並取根號：

$$\sqrt{\frac{1}{r}} = \frac{(1 + K_2 P_A P_B^2)}{\sqrt{K_1 P_A P_B}} = \frac{1}{\sqrt{K_1 P_A P_B}} + \frac{K_2 P_A P_B^2}{\sqrt{K_1 P_A P_B}}$$

$$\sqrt{\frac{P_A P_B^2}{r}} = \frac{(1 + K_2 P_A P_B^2)}{\sqrt{K_1 P_A P_B}} = \frac{1}{\sqrt{K_1}} + \frac{K_2 P_A P_B^2}{\sqrt{K_1}}$$

做  $\sqrt{\frac{P_A P_B^2}{r}} - P_A P_B^2$  關係圖：

$\sqrt{P_A P_B^2 / r}$	203977.1	432700.8	1019886	312108.6	379143.8
$P_A P_B^2$	6241	18723	62410	8280	23000



$$\begin{cases} K_1 = \frac{1}{(\text{intercept})^2} = 5.034 \times 10^{-11} \text{ (mol / cm}^2 \cdot \text{min} \cdot \text{mT}^3) \\ K_2 = \text{slope} \times \sqrt{K_1} = 13.848 \sqrt{5.034 \times 10^{-11}} = 9.82 \times 10^{-5} \text{ (1 / mT}^3) \end{cases}$$

(本題可參考：University of Michigan, *Chapter 10 Additional Homework Problems*,

<https://websites.umich.edu/~elements/10chap/html/cdp10-fb.htm>)

## **Problem 2**

### **【Solution】**

(a)

$$\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions}}$$

因為真實反應速率可由質傳或反應速率控制，因此最高不會超過整體充滿外界飽和濃度之假設所得到的反應速率。

(b)

For a first-order reaction in a spherical catalyst, the internal effective factor is,

$$\eta = \frac{3}{\phi_1^2} (\phi_1 \coth \phi_1 - 1)$$

(c)

The physical meaning of Thiele modulus is,

$$\phi = \frac{\text{surface reaction rate}}{\text{diffusion rate}}$$

**If the Thiele modulus is large, it implies that the diffusion rate is slower compared to the surface reaction rate, indicating that the reaction is limited by diffusion.**

((a)(b)小題可參考：FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 827~829.

(c)小題可參考：FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 820~821.)

### **Problem 3**

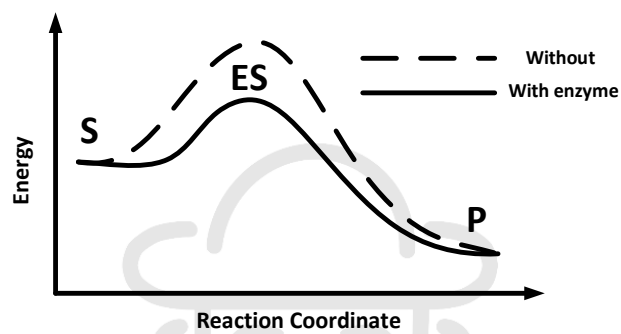
#### **【Solution】**

(a)

(1) 因為酵素觸媒具有專一性，只能催化一種反應，因此若是催化  $S \rightarrow P$ ，自然就不會催化反向反應。

(2) 觸媒可以降低整體反應所需要之活化能，又若形成中間體的活化能較低，自然就不需考慮產物往回走的平衡。

(b)



(本小題可參考：FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 394.)

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**Problem 4****【Solution】**

(a)

By the unsteady-state energy balance,

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^n F_i H_i \Big|_{in} - \sum_{i=1}^n F_i H_i \Big|_{out} = \frac{dE_{sys}}{dt}$$

$$E_{sys} = \sum_{i=1}^n N_i E_i = \sum_{i=1}^n N_i U_i = \sum_{i=1}^n N_i (H_i - PV_i) = \sum_{i=1}^n N_i H_i - \underbrace{P \sum_{i=1}^n N_i V_i}_{PV}$$

代入：

$$\dot{Q} - \dot{W}_s + \sum_{i=1}^n F_{i0} H_{i0} \Big|_{in} - \sum_{i=1}^n F_i H_i \Big|_{out} = \left[ \sum_{i=1}^n N_i \frac{dH_i}{dt} + \sum_{i=1}^n H_i \frac{dN_i}{dt} \right]_{sys}$$

(variation of PV is neglected)

$$\because H_i = H^\circ(T_R) + \int_{T_R}^T C_{P,i} dT, \quad \frac{dH_i}{dt} = C_{P,i} \frac{dT}{dt} \text{ 代入：}$$

$$\dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i = \sum N_i C_{P,i} \frac{dT}{dt} + \sum H_i \frac{dN_i}{dt}$$

For the mole balance on species I, we have,

$$\frac{dN_i}{dt} = -v_i r_A V + F_{i0} - F_i$$

$$\dot{Q} - \dot{W}_s + \sum F_{i0} H_{i0} - \sum F_i H_i = \sum N_i C_{P,i} \frac{dT}{dt} + \sum v_i H_i (-r_A V) + \sum F_{i0} H_i - \sum F_i H_i$$

Rearrange,

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s + \sum F_{i0} (H_i - H_{i0}) + (-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{P,i}}$$

$$(\sum v_i H_i = \Delta H_{Rx})$$

For a batch reactor without inlet stream and shaft work,

$$\frac{dT}{dt} = \frac{\dot{Q} + (-\Delta H_{Rx})(-r_A V)}{\sum N_i C_{Pi}} = \frac{UA(T_a - T) - [\Delta H_{Rx} + \cancel{\Delta C_p(T - T_R)}](kV)}{N_A C_p + N_B C_p + N_I C_p}$$

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \Delta H_{Rx}[(C_1 + C_2 T)V]}{N_{A0}(\sum \theta_i C_p)}$$

積分：

$$\int_{T_0}^T \frac{dT}{(UAT_a - \Delta H_{Rx} C_1 V) - (UA + \Delta H_{Rx} C_2 V)T} = \int_0^t \frac{dt}{N_{A0}(\sum \theta_i C_p)}$$

$$(UA + \Delta H_{Rx} C_2 V) \ln \left[ \frac{(UAT_a - \Delta H_{Rx} C_1 V) - (UA + \Delta H_{Rx} C_2 V)T_0}{(UAT_a - \Delta H_{Rx} C_1 V) - (UA + \Delta H_{Rx} C_2 V)T} \right] = N_{A0}(\sum \theta_i C_p)t$$


---

(b)

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \cancel{\Delta H_{Rx}[(C_1 + C_2 T)V]}}{(N_B + N_S)C_p} = \frac{UA(T_a - T)}{N_{A0}C_p(1 + \theta_s)}$$

$$\int_{T_{\max}}^T \frac{dT}{UA(T_a - T)} = \int_0^t \frac{dt}{N_{A0}C_p(1 + \theta_s)}$$

$$UA \ln \left[ \frac{(T_a - T_{\max})}{(T_a - T)} \right] = \frac{t}{N_{A0}C_p(1 + \theta_s)}$$


---

(c)

After a very long time,  $t \rightarrow \infty$

$$T = T_a - \exp\left[\frac{-t}{UAN_{A0}C_p(1 + \theta_s)}\right](T_a - T_{\max}) \approx \underline{T_a}$$

(本小題可參考：FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 591~595.)

**Problem 5****【Solution】****(a)**

For the rate equation of the reaction,

$$-r_A = kC_A = kC_{A0}(1-x_A)$$

For the design equation of CSTR,

$$V_{CSTR} = \frac{F_{A0}x_A}{-r_A} = \frac{F_{A0}x_A}{kC_{A0}(1-x_A)}$$

For the design equation of PFR,

$$V_{PFR} = \int_0^{x_A} \frac{F_{A0}}{-r_A} dx_A = \int_0^{x_A} \frac{F_{A0}}{kC_{A0}(1-x_A)} dx_A$$

The ratio is calculated as,

$$\frac{V_{CSTR}}{V_{PFR}} = \frac{\frac{F_{A0}x_A}{kC_{A0}(1-x_A)}}{\int_0^{x_A} \frac{F_{A0}}{kC_{A0}(1-x_A)} dx_A} = \frac{\frac{0.5}{(1-0.5)}}{\int_0^{0.5} \frac{1}{(1-x_A)} dx_A} = \underline{\underline{1.44}}$$

**(b)**

For the rate equation of the reaction,

$$-r_A = kC_A^2 = kC_{A0}^2(1-x_A)^2$$

For the design equation of CSTR,

$$V_{CSTR} = \frac{F_{A0}x_A}{-r_A} = \frac{F_{A0}x_A}{kC_{A0}^2(1-x_A)^2}$$

For the design equation of PFR,

$$V_{PFR} = \int_0^{x_A} \frac{F_{A0}}{-r_A} dx_A = \int_0^{x_A} \frac{F_{A0}}{kC_{A0}^2(1-x_A)^2} dx_A$$

The ratio is calculated as,

$$\frac{V_{CSTR}}{V_{PFR}} = \frac{\frac{F_{A0}x_A}{kC_{A0}^2(1-x_A)^2}}{\int_0^{x_A} \frac{F_{A0}}{kC_{A0}^2(1-x_A)^2} dx_A} = \frac{\frac{0.5}{(1-0.5)^2}}{\int_0^{0.5} \frac{1}{(1-x_A)^2} dx_A} = \underline{\underline{2}}$$

### **Problem 6**

#### **【Solution】**

By the design equation of CSTR,

$$V = \frac{F_{A0}x_A}{-r_A} = \frac{v_0 C_{A0}x_A}{-r_A} = \frac{v_0 C_{A0}x_A}{kC_A^n} = \frac{v_0 x_A}{kC_{A0}^{n-1}(1-x_A)^n}$$

For  $x_{A,run1}$

$$C_R = C_{A0} \cdot 2x_{A,run1} = 2 \times 1 \times x_{A,run1} = 1.8, \quad x_{A,run1} = 0.9$$

For  $x_{A,run2}$

$$C_R = C_{A0} \cdot 2x_{A,run2} = 2 \times 1 \times x_{A,run2} = 1.5, \quad x_{A,run2} = 0.75$$

代入：

$$V_1 = V_2$$
$$\frac{2 \times 0.9}{kC_{A0}^{n-1}(1-0.9)^n} = \frac{15 \times 0.75}{kC_{A0}^{n-1}(1-0.75)^n}, \quad \underline{\underline{n=2}}$$

For the activation energy,

by run 2,3 ,

$$V = \frac{v_0 x_A}{kC_{A0}^{n-1}(1-x_A)^n} \propto \frac{x_A}{k(1-x_A)^2}$$

$$V_2 = V_3$$

$$\frac{0.75}{k_{13}(1-0.75)^2} = \frac{0.9}{k_{84}(1-0.9)^2}$$

$$\frac{k_{13}}{k_{84}} = 0.133 = \exp\left[\frac{-E_a}{8.314} \left(\frac{1}{273.15+13} - \frac{1}{273.15+84}\right)\right]$$

$$\underline{\underline{E_a = 24112.94 \text{ (J / mol)}}}$$

# 114 年成大化反

## Problem 1

### **【Solution】**

(a)

For the reaction,

	A	→	5R	I
Initial	0.8		0	0.2
Reacted	-x		+5x	0.2
Final	0.8-x		5x	0.2

The final pressure is 1.8 atm, which gives,

$$0.8 - x + 5x + 0.2 = 1.8 \quad , \quad x = 0.2 \text{ (atm)}$$

Therefore, we know in 2 min of reaction, A reacts 0.2 (atm),

$$k = \frac{0.2}{2} = 0.1 \text{ (atm / min)} = \frac{0.1}{0.082 \times (273 + 27)} = \underline{\underline{0.0040 \text{ (M / min)}}}$$

(b)

After the reaction for 5 min, the total pressure is,

$$P_T = 0.8 - 5 \times 0.1 + 5 \times 5 \times 0.1 + 0.2 = \underline{\underline{3 \text{ (atm)}}}$$

And the partial pressure of A is,

$$P_A = 0.8 - 5 \times 0.1 = \underline{\underline{0.3 \text{ (atm)}}}$$

## **Problem 2**

### **【Solution】**

(a)

By the design equation of CSTR (assume constant V),

$$\tau = \frac{C_{A,in} - C_{A,out}}{-r_A}$$

The rate equation is,

$$-r_A = kC_A$$

Combine,

$$\tau = \frac{C_{A,in} - C_{A,out}}{kC_{A,out}}, \quad C_{A,out} = \frac{C_{A,in}}{1 + k\tau}$$

(For single CSTR)

For the 2<sup>nd</sup> CSTR,

$$C_{A,out,2} = \frac{C_{A,in,2}}{1 + k\tau} = \frac{C_{A,out}}{1 + k\tau} = \frac{C_{A,in}}{(1 + k\tau)^2}$$

In the same way,

$$C_{A,out,5} = \frac{C_{A,in}}{(1 + k\tau)^5}, \quad \frac{C_{A,out,5}}{C_{A,in}} = \frac{1}{(1 + k\tau)^5} = \frac{1}{(1 + 0.158 \times \frac{1800}{582})^5} = 0.137$$

The conversion can be calculated as,

$$\frac{C_{A,in} - C_{A,out,5}}{C_{A,in}} = \frac{1 - 0.137}{1} = \underline{\underline{0.863}}$$

(b)

For the case where the reaction carried out in a single CSTR,

$$\tau = \frac{C_{A,in} - C_{A,out}}{kC_{A,out}} = \frac{C_{A,in} \times 0.863}{0.158 \times C_{A,in} (1 - 0.863)} = \frac{0.863}{0.158 \times (1 - 0.863)} = 39.73 \text{ (min)}$$

The volume needed is,

$$V = v\tau = 582 \times 39.73 = \underline{\underline{23117 \text{ (cm}^3\text{)}}}$$

### **Problem 3**

#### **【Solution】**

(a)

Assume the rate equations,

$$-r_{AB} = k_1[AB]$$

$$r_X = k_2[A^*][AB]$$

$$r_Y = k_3[AB^*]$$

$$r_Z = k_4[A^*]^2$$

For the formation rate of Z,

$$r_Z = k_4[A^*]^2$$

By pseudo-steady-state treatment,

$$r_{A^*} = k_1[AB] - k_2[A^*][AB] + k_3[AB^*] - 2k_4[A^*]^2 = 0$$

$$r_{AB^*} = k_2[A^*][AB] - k_3[AB^*] = 0$$

二式相加

$$r_{A^*} = k_1[AB] - 2k_4[A^*]^2 = 0, \quad k_4[A^*]^2 = \frac{k_1}{2}[AB]$$

代回：

$$r_Z = \frac{d[Z]}{dt} = \frac{k_1}{2}[AB]$$

For  $[AB]$ , we have,

$$r_{AB} = -\frac{d[AB]}{dt} = k_1[AB] + k_2[A^*][AB]$$

$\because k_4 \gg k_2$  and  $k_4, k_3 \gg k_1$ , it is reasonable to assume the RDS is the 1<sup>st</sup> equation,

$$-\frac{d[AB]}{dt} \approx k_1[AB], \quad -\int_{C_{AB,0}}^{C_{AB}} \frac{d[AB]}{[AB]} = \int_0^t k_1 dt, \quad C_{AB} = C_{AB,0} e^{-k_1 t}$$

代回：

$$r_Z = \frac{d[Z]}{dt} = \frac{k_1}{2} [AB] = \frac{k_1}{2} C_{AB,0} e^{-k_1 t}$$

$$\int_0^{C_Z} d[Z] = \frac{k_1}{2} C_{AB,0} \int_0^t e^{-k_1 t} dt$$

$$\underline{\underline{C_Z = \frac{1}{2} C_{AB,0} (1 - e^{-k_1 t})}}$$

(b)

The selectivity of Z to Y is,

$$S_{Z/Y} = \frac{r_Z}{r_Y} = \frac{k_4 [A^*]^2}{k_3 [AB^*]} = \frac{k_4 [A^*]^2}{k_2 [A^*] [AB]} = \frac{k_4 [A^*]}{k_2 [AB]} = \frac{k_4 \sqrt{\frac{k_1}{2k_4} [AB]}}{k_2 [AB]} = \underline{\underline{\frac{\sqrt{2k_1 k_4} [AB]}{2k_2 [AB]}}}$$

$$(\text{note } r_{AB^*} = k_2 [A^*] [AB] - k_3 [AB^*] = 0, \quad k_3 [AB^*] = k_2 [A^*] [AB])$$

(c)

At every instance, the instantaneous yield of Z relative to the conversion of AB is,

$$Y_Z = \frac{d[Z]}{d[AB]} = \frac{k_4 [A^*]^2}{k_1 [AB] + k_2 [A^*] [AB]} = \frac{\frac{k_1}{2} [AB]}{k_1 [AB] + k_2 \sqrt{\frac{k_1}{2k_4} [AB] [AB]}} \propto \frac{k_1}{2k_1 + k_2 \sqrt{\frac{2k_1}{k_4} [AB]}} \propto \frac{1}{\sqrt{[AB]}}$$

Therefore, keeping [AB] low can promote the yield of Z, **CSTR is preferred**.

※數值解如下：設  $k_1 = 0.05$ ， $k_2 = 1$ ， $k_3 = 300$ ， $k_4 = 500$

```
#To calculate the volume of PFR, we need the following differential equations: # Calculation of conversions by mass balance
d(CAB)/dt = rAB-rX
d(CA)/dt = -rAB-rX+rY-2*rZ #CA=CA*
d(CABB)/dt = rX-rY #ABB=AB*
d(CX)/dt = rX
d(CY)/dt = rY
d(CZ)/dt = rZ

#Define the rate equations:
rAB = -k1*CAB
rX = k2*CA*CAB
rY = k3*CABB
rZ = k4*(CA)^2

#Parameters and conditions:
CAB(0) = 1000
k1 = 0.05
k2 = 1
k3 = 300
k4 = 500
CA(0)=0
CABB(0)=0
CX(0) = 0
CY(0) = 0
CZ(0) = 0
t(0) = 0

#Volume range:
t(f) = 50

f(CAB) = CAB0 - CAB + (tau * (rAB-rX))
f(CA) = CA - (tau * (-rAB - rX + rY - 2*rZ))
f(CABB) = CABB - (tau * (rX - rY))
f(CX) = CX - (tau * rX)
f(CY) = CY - (tau * rY)
f(CZ) = CZ - (tau * rZ)

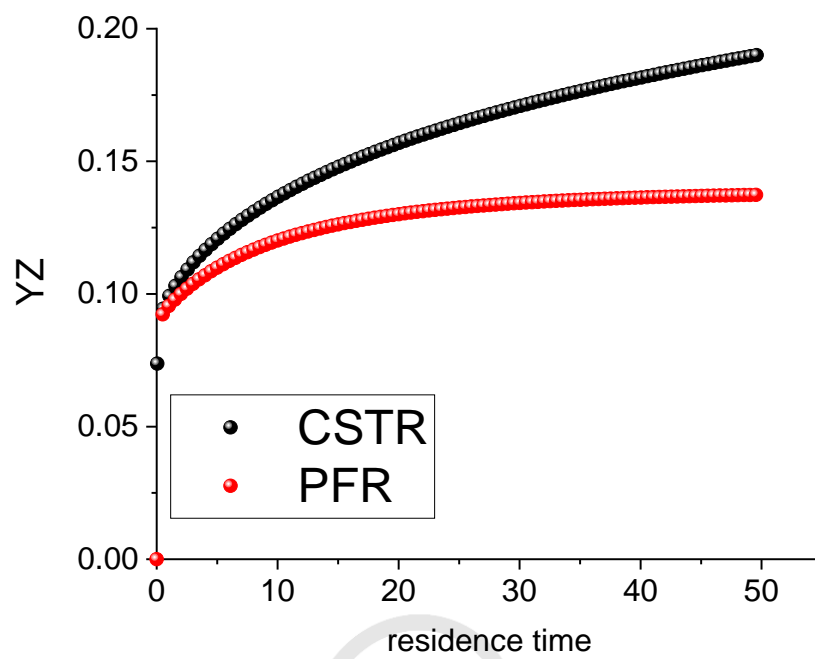
# Reaction rate equations
rAB = -k1 * CAB
rX = k2 * CA * CAB
rY = k3 * CABB
rZ = k4 * (CA)^2

# Explicit values
CAB0 = 1000
CA0 = 0
CABB0 = 0
CX0 = 0
CY0 = 0
CZ0 = 0
tau = 50

# Rate constants
k1 = 0.05
k2 = 1
k3 = 300
k4 = 500

# Guess the initial values
CAB(0) = 1000
CA(0) = 0
CABB(0) = 0
CX(0) = 0
CY(0) = 0
CZ(0) = 0
```





$Y_Z$  由  $\frac{[Z]}{[AB]_0 - [AB]}$  計算出

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**Problem 4****【Solution】****(a)**

For the effectiveness factor,

$$\varepsilon = \frac{6}{d_p} \sqrt{\frac{2D_e}{(n+1)kC_A^{n-1}}} = \frac{6}{4 \times 10^{-3}} \sqrt{\frac{2 \times 3 \times 10^{-8}}{(2+1) \times 10 \times (1 \times 0.5)^1}} = 0.095$$

The design equation is,

$$W = \frac{F_{A0}x_A}{-r_A}$$

The rate equation is,

$$-r_A = kC_A^2\varepsilon$$

Combine,

$$W = \frac{F_{A0}x_A}{-r_A} = \frac{F_{A0}x_A}{kC_A^2\varepsilon} = \frac{10 \times 0.5}{10 \times (1 \times 0.5)^2 \times 0.095} = \underline{\underline{21.1 \text{ (kg)}}}$$

**(b)**Assume at such condition,  $\varepsilon \sim 1$ 

$$W = \frac{F_{A0}x_A}{-r_A} = \frac{F_{A0}x_A}{kC_A^2\varepsilon} = \frac{10 \times 0.5}{10 \times (1 \times 0.5)^2 \times 1} = \underline{\underline{2 \text{ (kg)}}}$$

## Problem 5

### 【Solution】

#### (a) (A)(E)(G)(K)

首先定義曲線為  $G(T)$ ，直線為  $R(T)$

Point 1 高溫一點， $G > R$ ，低溫一點， $R > G \Rightarrow$  unstable

Point 2 高溫一點， $R > G$ ，低溫一點， $G > R \Rightarrow$  stable

Point 3 高溫一點， $G > R$ ，低溫一點， $R > G \Rightarrow$  unstable

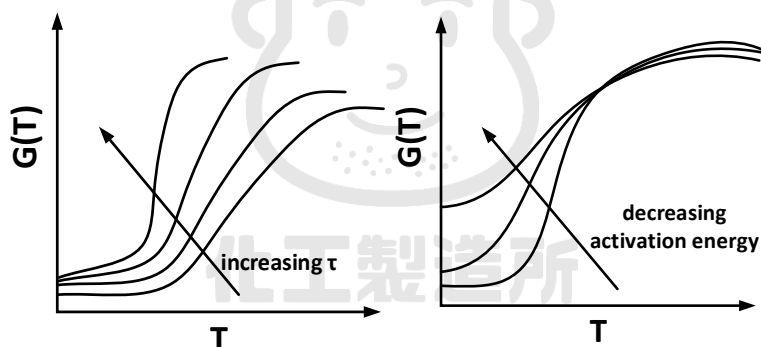
Point 4 高溫一點， $R > G$ ，低溫一點， $G > R \Rightarrow$  stable

(本小題可參考：FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 538~540.)

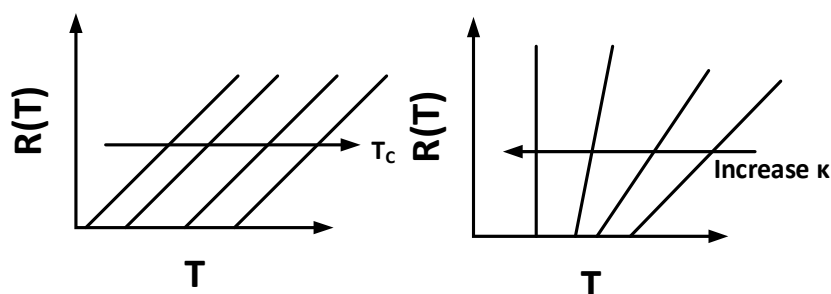
#### (b) (I)

以一般放熱反應來說，若不可逆，則：

$$\text{For } G(T) = (-\Delta H_{R_x}^\circ) \left( \frac{\tau A e^{-E/RT}}{1 + \tau A e^{-E/RT}} \right)$$

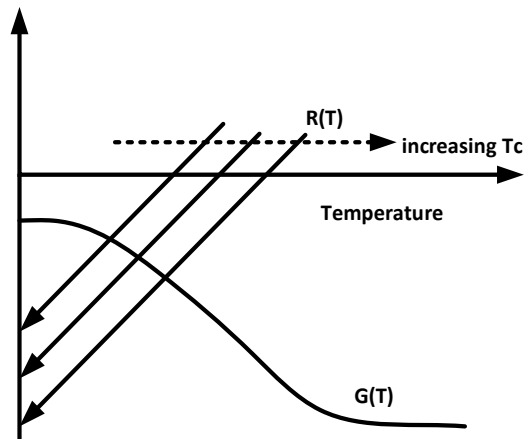


$$\text{For } R(T) = C_{P0}(1 + \kappa)(T - T_c), \quad \kappa = \frac{UA}{C_{P0}F_{A0}}, \quad T_c = \frac{T_0 + \kappa T_a}{1 + \kappa}$$



(此些圖可參考：FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 533~536.)

然而若為 irreversible endothermic reaction，則其  $R(T)$  與  $G(T)$  圖：



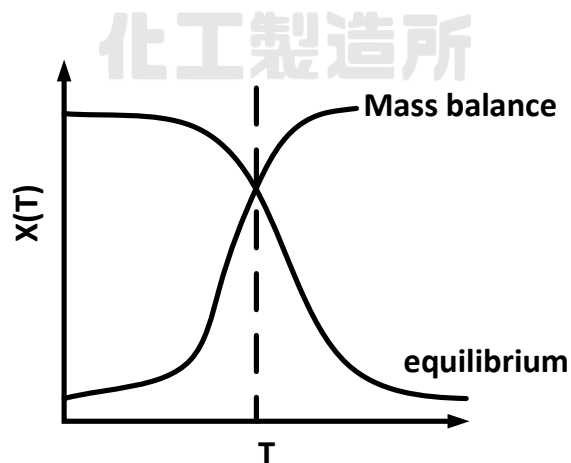
此圖交點即為 steady state point，不管參數怎麼改變，只可能有一個 steady state point。

(本題可參考 Fogler 之 self test，網址為：

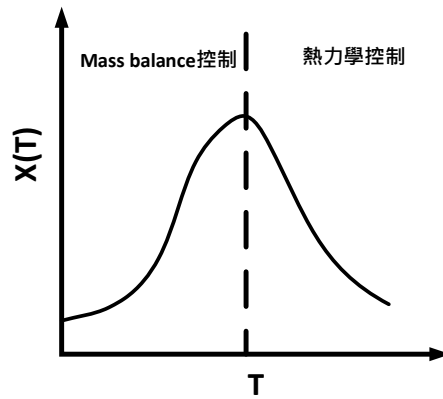
<http://websites.umich.edu/~elements/course/lectures/eight/test9.htm#solution>)

(c) (A)(B)(C)(D)(E)(F)(G)(H)

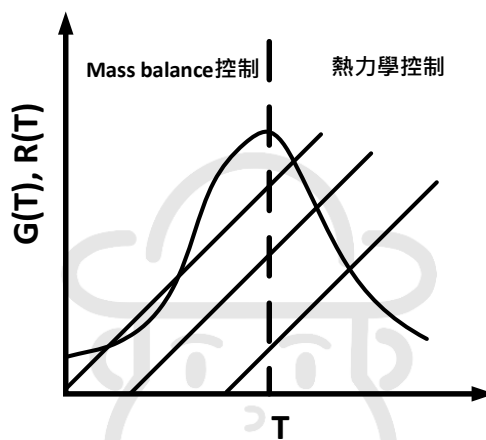
若反應改為可逆放熱反應，則需要考慮熱力學平衡轉化率對整體反應轉化率的限制，即：



然而，可以發現，在虛線以右，質量平衡所得的轉化率(mass balance，以不可逆來示範)將大於熱力學平衡轉化率(equilibrium)。因任何反應都不可能突破其熱力學限制，因此實際的可逆放熱反應轉化率-溫度曲線，應為：



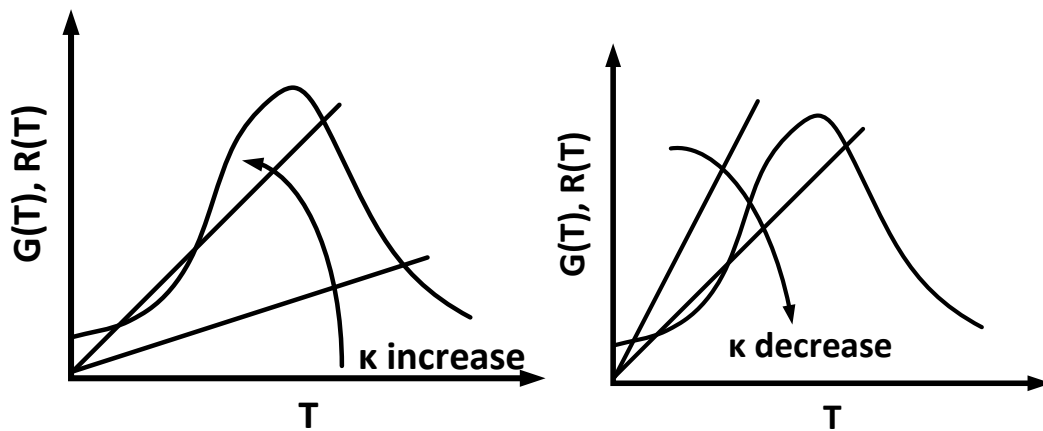
按此邏輯，可將此狀況下之  $G(T)$  與  $R(T)$  關係繪製如下：



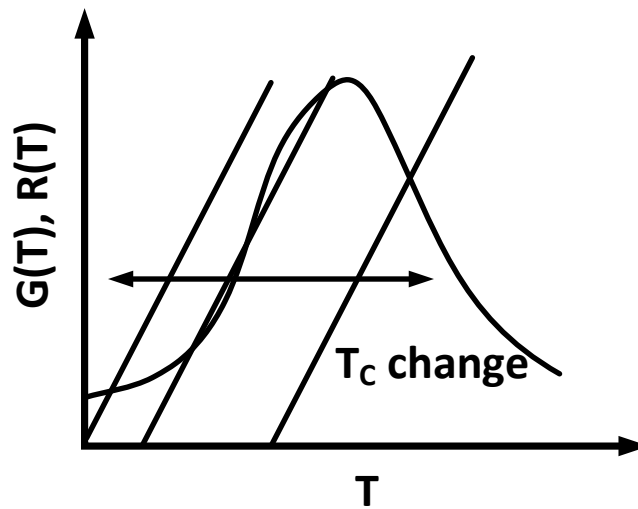
(關於可逆平衡的討論可參考：Levenspiel, O. Chemical Reaction Engineering, 3rd ed.; p226~229.)

可能有助於 multiple steady state 的操作討論：

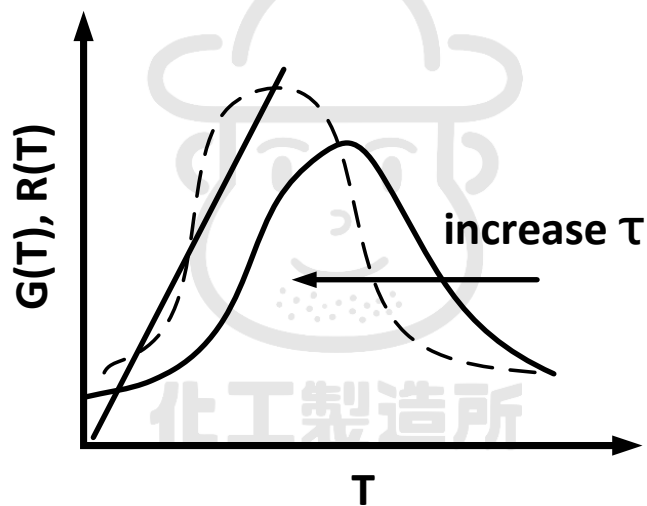
(1)  $\kappa$  增加或減小，都有可能，增加：(A)(G)；減小：(D)(H) (皆為增加  $F_{A0}$ )



(2)  $T_c$  增加或減小，都有可能，增加：(B)；減小：(C)



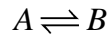
(3) 增加  $\tau$  與  $E$  都有可能，(E)(F)



※不過此種討論方法其實有點吹毛求疵，因為一定能夠找到可行的組合，使得原先只有一個穩態，變為多個穩態。然而有些繪製的方式初始的穩態轉化率都很低，可能不符合實際情況。但在解答上，依舊以只要可行，就選該選項的方式作答。

※reversible exothermic 的轉化率-溫度關係，可以由 Fogler 第四版的課後習題 P.8-18B 來討論 (p. 579)，題目如下：

The elementary reversible liquid-phase reaction,



takes place in a CSTR with a heat exchange. Pure A enters the reactor.

*The additional information:*

$$UA = 3600 \text{ cal} / \text{min} \cdot K, E / R = 20000K$$

$$C_{PA} = C_{PB} = 40 \text{ cal} / \text{mol} \cdot K, V = 10 \text{ dm}^3$$

$$\Delta H_{Rx} = -80000 \text{ cal} / \text{mol} \cdot A, v_0 = 10 \text{ dm}^3$$

$$K_{eq} = 100 \text{ at } 400K, F_{A0} = 10 \text{ mol} / \text{min}$$

$$k = 1 \text{ min}^{-1} @ 400K, T_a = 310K, T_0 = 310K$$

For the conversion-temperature relationship, we have the design equation of CSTR,

$$\tau = \frac{C_{A0}x_A}{-r_A} = \frac{C_{A0}x_A}{kC_{A0}(1-x_A-\frac{x_A}{K})}, x_A = \frac{\tau k}{1 + \tau k(1 + \frac{1}{K})}$$

By van't Hoff equation,

$$K = K_{400K} \exp\left[\frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] = 100 \exp\left[\frac{80000}{1.987}\left(\frac{1}{T} - \frac{1}{400}\right)\right]$$

And the rate constant is,

$$k = k_{400K} \exp\left[\frac{-Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] = \exp\left[-20000\left(\frac{1}{T} - \frac{1}{400}\right)\right]$$

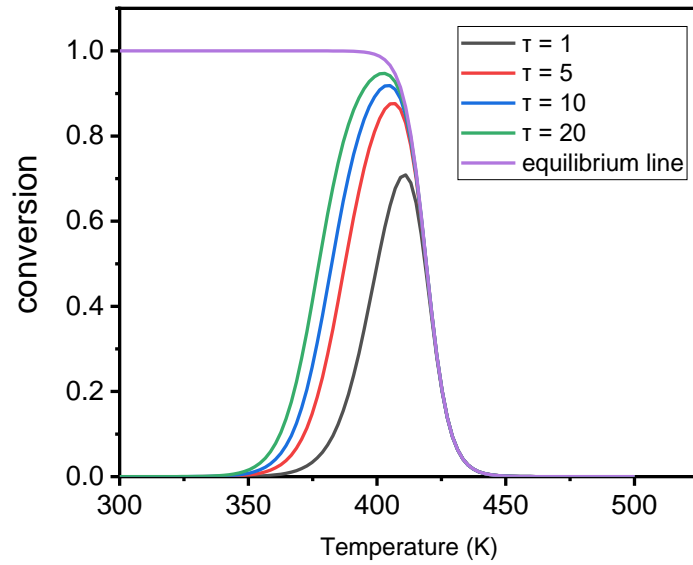
代回：

$$x_A = \frac{\tau \exp\left[-20000\left(\frac{1}{T} - \frac{1}{400}\right)\right]}{1 + \tau \exp\left[-20000\left(\frac{1}{T} - \frac{1}{400}\right)\right] \left(1 + \frac{1}{100 \exp\left[\frac{80000}{1.987}\left(\frac{1}{T} - \frac{1}{400}\right)\right]}\right)}$$

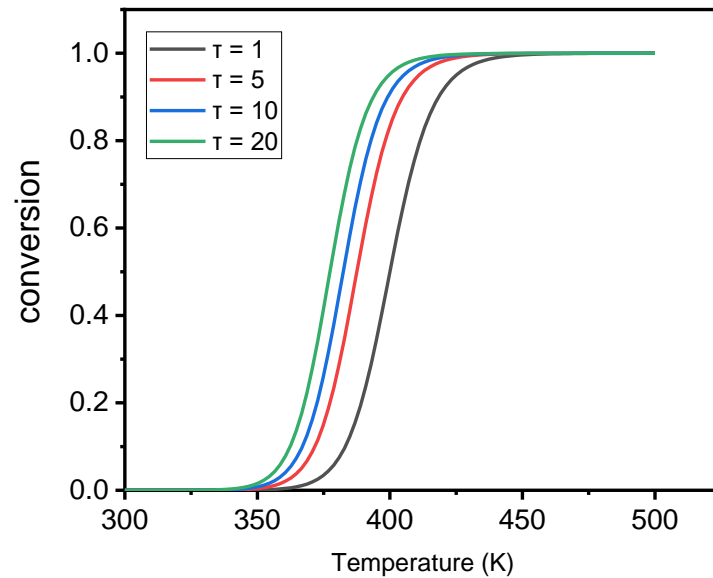
【改變  $\tau$ 】

若設定  $\tau = 1, 5, 10, 20$

(1) 可逆情況



(2) 不可逆情況(事實上，可逆吸熱反應也長這樣，因為吸熱反應平衡轉化率也會隨溫度變高，就不會受到平衡限制，會受限制的只在低轉化率部分，但不影響圖形的整體形狀。)

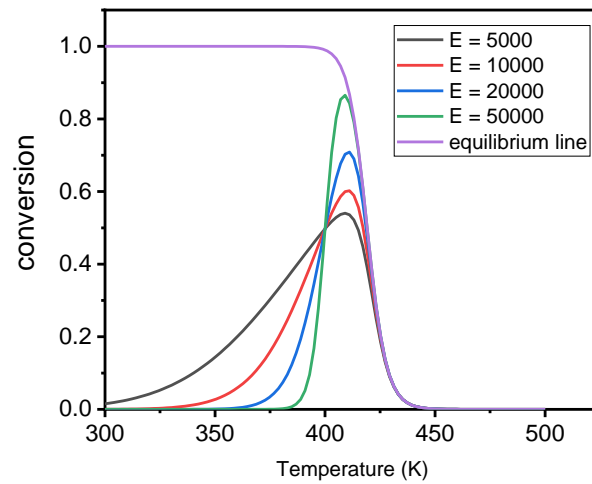




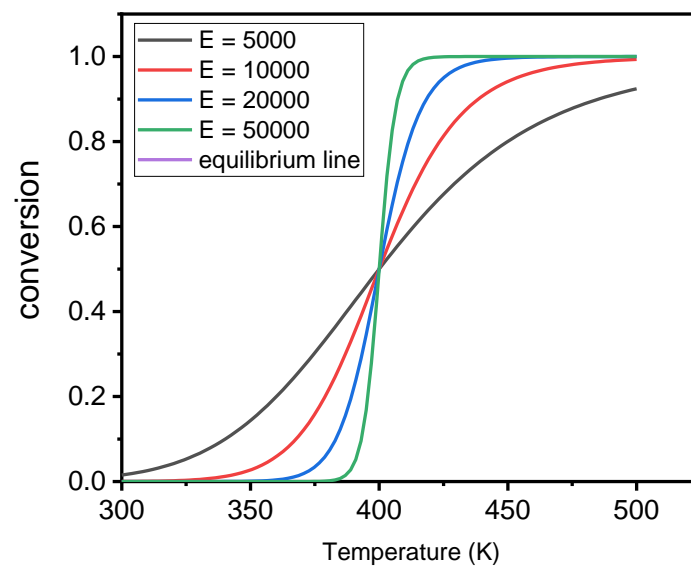
【改變  $E$ 】

若設定  $E = 5000, 10000, 20000, 50000$

(1) 可逆情況



(2) 不可逆情況(或可逆吸熱)



### 【改變 coolant rate】

按熱交換項的原式來說(可參考 Fogler 第四版 p 522~523)：

$$Q = m_c C_{Pc} \{ (T_a - T) [1 - \exp(\frac{-UA}{m_c C_{Pc}})] \}$$

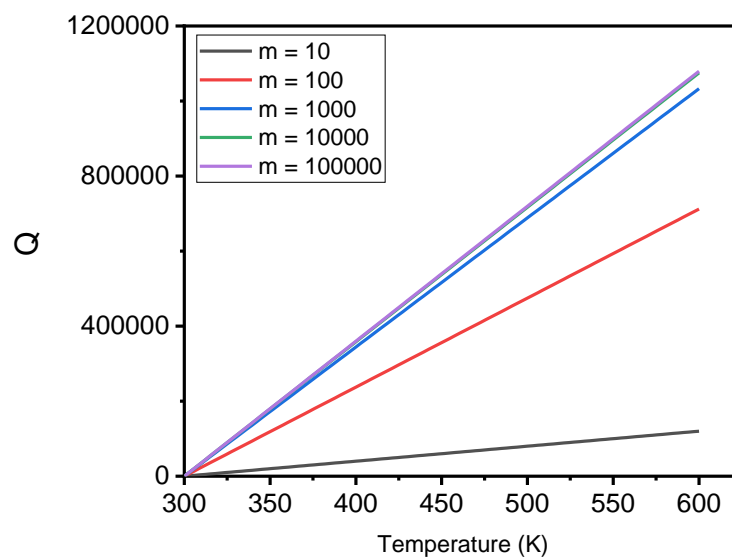
有些複雜，不過原文書一般當作 coolant rate 很大，因此 exponential 項極小，根據泰勒展開：

$$e^{-x} = 1 - x + \frac{1}{2}x^2 - \frac{1}{6}x^3 + \dots \approx 1 - x$$

代回：

$$Q \approx m_c C_{Pc} \{ (T_a - T) [1 - (1 - \frac{UA}{m_c C_{Pc}})] \} = UA(T_a - T)$$

這才得到原文書比較常用的熱交換項形式，一般是看不出 coolant rate 的影響，當然可能可以用 coolant rate 變多，熱交換變好的想法下去想，只是就沒這麼直接。然而若是考慮原本的方程式，按照不同 coolant rate 對溫度作圖，可得：



基本上，綠色(m = 10000)與紫色(m = 100000)幾乎沒有分別。然而在低流量下，依舊可以看到隨著 m 越大，斜率越高，基本上可以當作跟 K 一樣的影響。

### **Problem 6**

#### **【Solution】**

(a)

題意為從反應開始到冷卻系統故障的瞬間( $t_s$ )與冷卻系統故障的時長( $t_d$ )之間的關係。一般來說，在此高度放熱的系統，反應初期至中段因為反應物濃度尚高，因此若是在此區間發生故障(也就是 $t_s = 0 \sim$ 反應中間)，冷卻系統停機不能太久(也就是 $t_d$ 要越小越好)，因此符合此條件者為**(B)(E)**。

(b)

**Ans : (A)(B)(C)(E)(F)**

(A) 反應後期反應物濃度較少，較有機會預防熱失控。

(B) 反應溫度降低，雖然可能降低反應速率，但以延長反應時間的方式，預防短期大量放熱，可以。

(C) 添加惰性物質，可以稀釋反應物濃度，可以。

(D) **無法**，因  $\text{NH}_3$  濃度的降低，反而會增加 ONCB 的反應物濃度(按題意，此反應為 ONCB 的一級反應。)

(E) 縮短停機時間，可以避免在失控以前重新冷卻。

(F) 將反應物分批加入，有助於降低在每個瞬間的反應物濃度，可以。