

106 年清大化熱化反

Problem 1

【Solution】

(a)

$$\Delta H_{mix}^{id} = 0$$

$$\Delta S_{mix}^{id} = -R(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta G_{mix}^{id} = RT(x_A \ln x_A + x_B \ln x_B)$$

(b)

$$G^E = RTx_Ax_B(0.4x_A + 0.2x_B)$$

$$\overline{G}_A = G_{A,pure} + \Delta \overline{G}_{A,mix} = G_{A,pure} + \Delta \overline{G}_A^E + \Delta \overline{G}_{A,mix}^{id}$$

$$\overline{G}_A^E = \left[\frac{\partial(nG^E)}{\partial n_A} \right]_{T,P,n_B} = RT(-0.4x_B^3 + 0.6x_B^2)$$

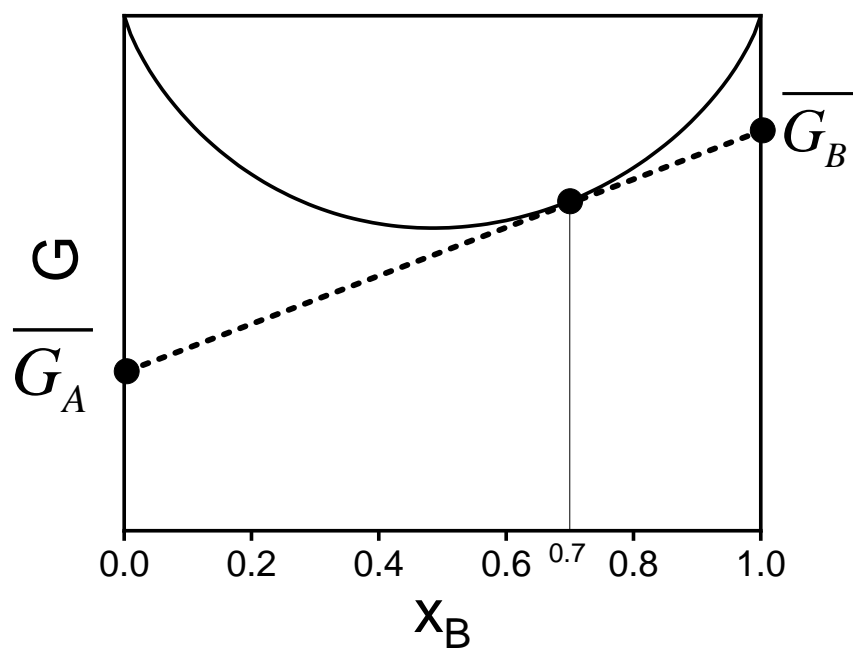
$$\overline{G}_A = G_{A,pure} + RT(-0.4x_B^3 + 0.6x_B^2 + \ln x_A) = G_{A,pure} + RT[-0.4x_B^3 + 0.6x_B^2 + \ln(1 - x_B)]$$

同理，

$$\overline{G}_B^E = \left[\frac{\partial(nG^E)}{\partial n_B} \right]_{T,P,n_A} = RT(-0.4x_B^3 + 1.2x_B^2 - 1.2x_B + 0.4)$$

$$\overline{G}_B = G_{B,pure} + RT(-0.4x_B^3 + 1.2x_B^2 - 1.2x_B + 0.4 + \ln x_B)$$

$$\text{則 } G = x_A \overline{G}_A + x_B \overline{G}_B \quad (\text{見下圖})$$

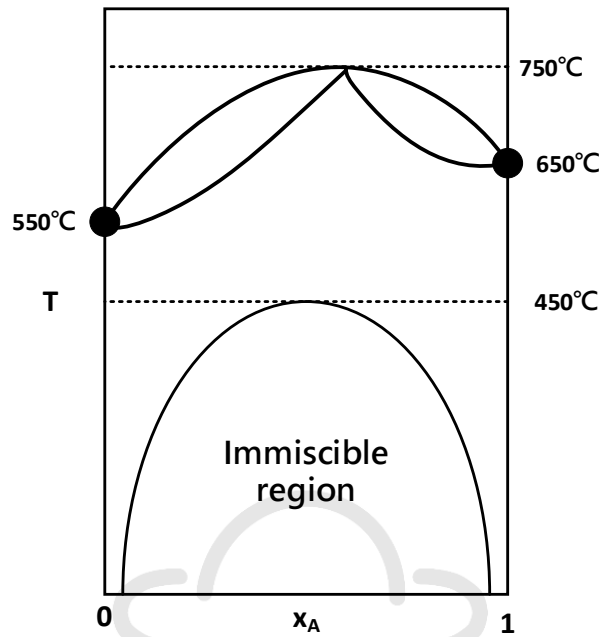


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Problem 2

【Solution】

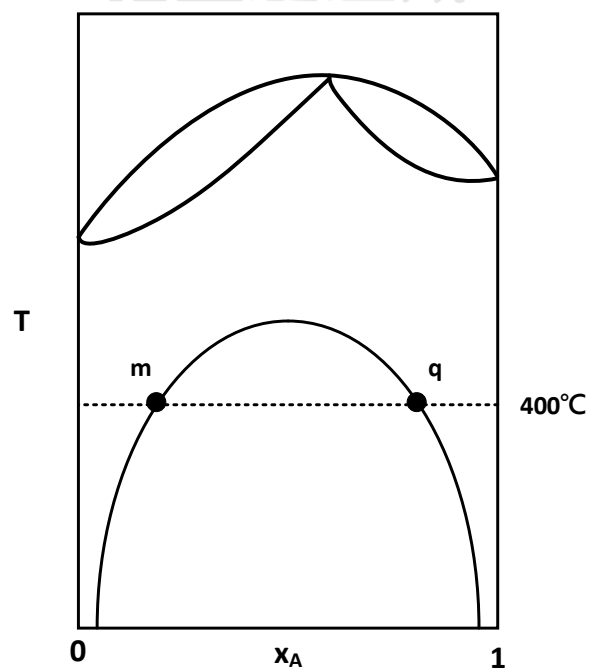
(a)



(b)

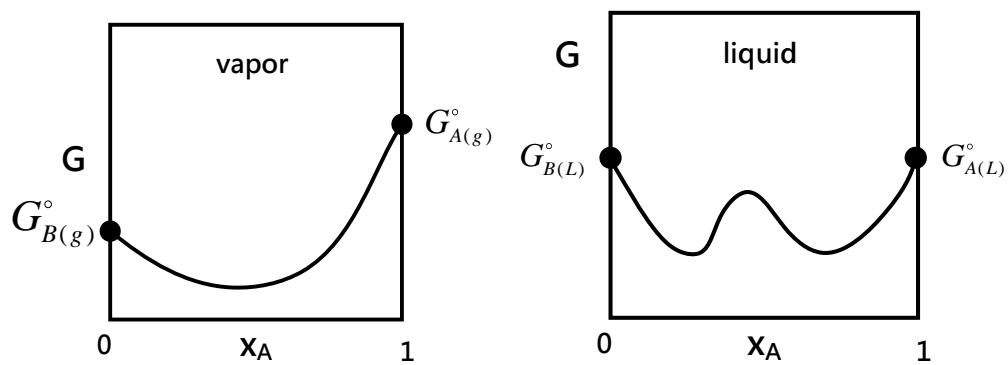
Assume : $\begin{cases} \text{gas phase} \rightarrow \text{ideal gas} \\ \text{liquid phase} \rightarrow \text{regular solution} \end{cases}$

@ 400°C

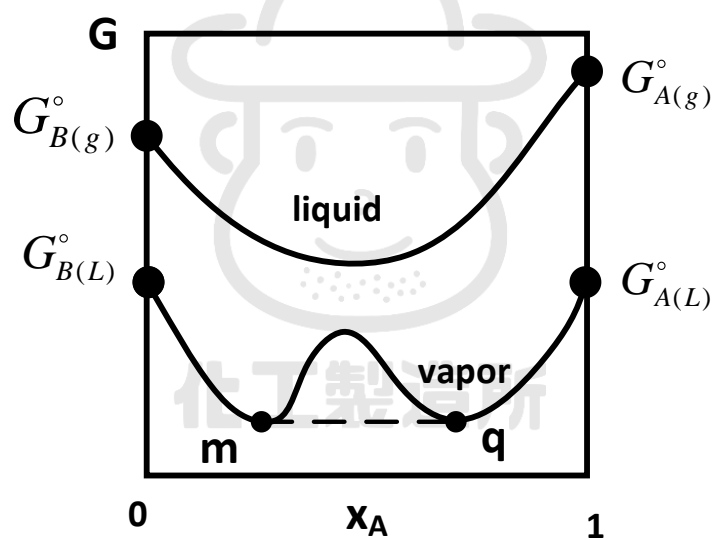


Set the standard states as : $G_{A(L)}^\circ = 0$ and $G_{B(L)}^\circ = 0$

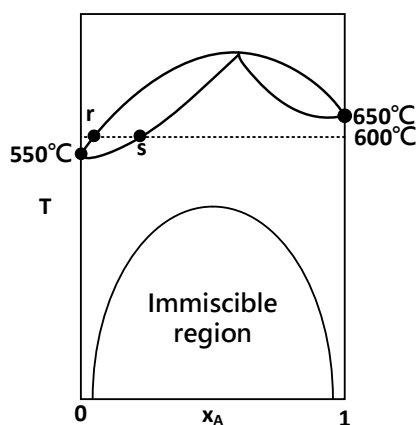
Assume $G_{A(g)}^\circ > G_{B(g)}^\circ$



合併：

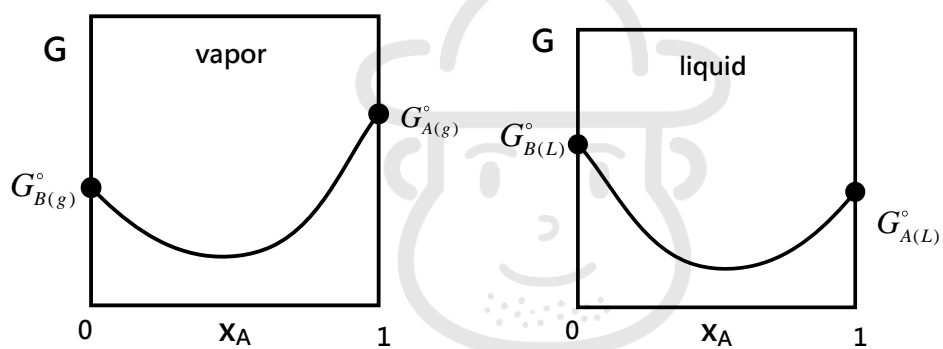


@600°C

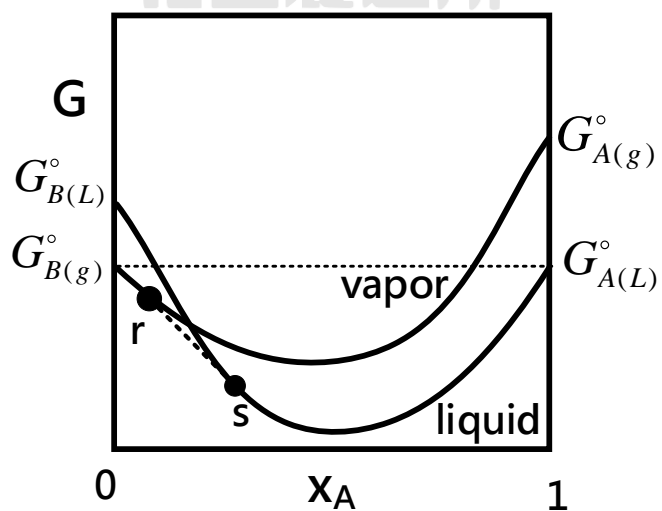


Set the standard states as : $G_{A(L)}^\circ = 0$ and $G_{B(g)}^\circ = 0$

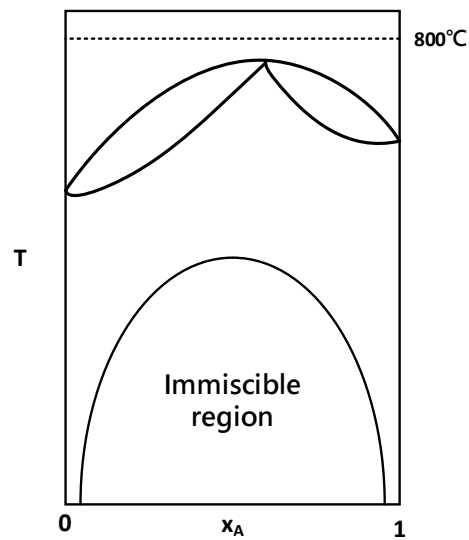
Assume $G_{A(g)}^\circ > G_{B(L)}^\circ$



合併：

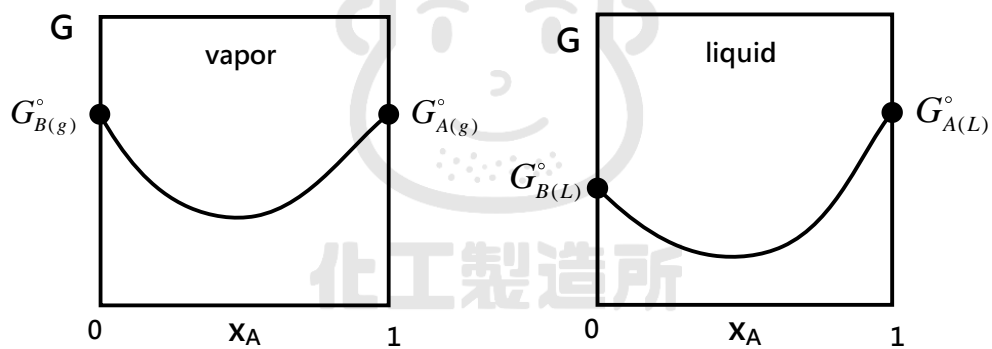


@800°C

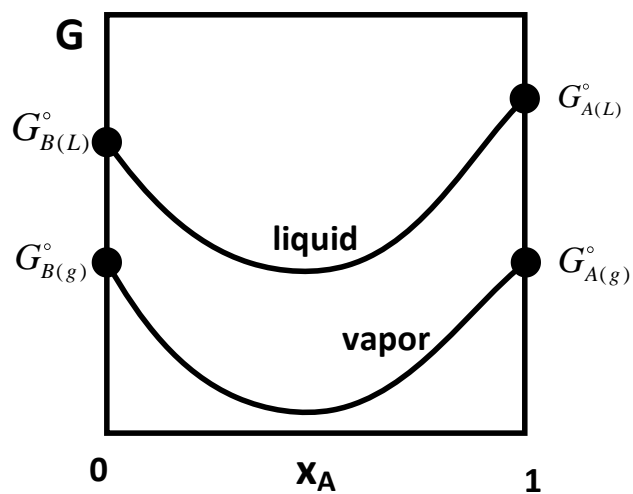


Set the standard states as : $G_{A(g)}^\circ = 0$ and $G_{B(g)}^\circ = 0$

Assume $G_{A(L)}^\circ > G_{B(L)}^\circ$



合併：



※關於此類相圖畫法可以參考清大材料系所開設之材料熱力學開放式課程

裡面有完整的介紹，相當不錯。而解題重點如下：

(1) 假設 solution model，通常為 ideal 或 regular solution

regular solution 與 ideal solution 只差在一個修正項，在大部分的情形下沒什麼差別，但像是這題因為有 miscibility gap 的產生，就不能使用 ideal solution 的假設，而 miscibility gap 的產生可用 regular solution 的修正項做說明，這個後面會提到。

(2) 訂好各個溫度下的標準態，以此題為例，純 A 的沸點為 650°C ，代表純 A 在 650°C 以上的穩定態為氣態，自由能應比液態低；反之，在 650°C 以下的穩定態為液態，自由能應比氣態低，因此細心的同學應該可以發現，在此題的三個溫度底下，液態 A、氣態 A 的自由能相對大小有所不同；同理，B 也是一樣的邏輯。

(3) 習慣上，我們可以根據上述的邏輯，訂出各相的標準態，做為參考原點 (注意是參考點，因為我們沒有方程式能夠算出絕對自由能)。以 600°C 來說，此時已超過 B 的沸點，因此純 B 之穩定態為氣態；而尚未達到 A 的熔點，因此純 A 的穩定態為液態。因此在 600°C 時，設定： $G_{A(L)}^{\circ} = 0$ 與 $G_{B(g)}^{\circ} = 0$ ，並且

$$G_{A(g)}^{\circ} > G_{A(L)}^{\circ} \text{、} G_{B(L)}^{\circ} > G_{B(g)}^{\circ} \text{。}$$

(4) 然而，以 400°C 為例，我們有時很難明確知道此種座標參考點的設定下 $G_{A(g)}^{\circ}$

與 $G_{B(g)}^{\circ}$ 到底誰高。一般來說，物質在溫度 T 經歷相變化時(固→液、液→氣等，

統一以 $\alpha \rightarrow \beta$ 表示)，其自由能變化 $\Delta G_{\alpha \rightarrow \beta}(T)$ 可由 ΔH 與 ΔS 得到：

$$\Delta H_{\alpha \rightarrow \beta}(T) = \Delta H_{\alpha \rightarrow \beta}^{\circ} + \int_{T_{\alpha \rightarrow \beta}}^T \Delta C_p dT$$

$$\Delta S_{\alpha \rightarrow \beta}(T) = \Delta S_{\alpha \rightarrow \beta}^{\circ} + \int_{T_{\alpha \rightarrow \beta}}^T \frac{\Delta C_p}{T} dT$$

$$\Delta G_{\alpha \rightarrow \beta}(T) = \Delta H_{\alpha \rightarrow \beta}^{\circ} - T \Delta S_{\alpha \rightarrow \beta}^{\circ}$$

然而，我們並未能單從此題知道所需要的參數，包含 $\Delta H_{\alpha \rightarrow \beta}^\circ$ 、 $\Delta S_{\alpha \rightarrow \beta}^\circ$ 以及 heat capacity 等。若假設相變化前後 heat capacity 改變幅度不大，此時可得到近似公式：

$$\Delta G_{\alpha \rightarrow \beta}(T) \approx \Delta H_{\alpha \rightarrow \beta}^\circ \left[\frac{T_{\alpha \rightarrow \beta} - T}{T_{\alpha \rightarrow \beta}} \right]$$

就算簡單許多，但還是不知道相變化熱(注意，並沒有相變化溫度高，相變化熱就一定高的必然)。因此以 400°C 來說， $G_{A(g)}^\circ > G_{B(g)}^\circ$ 是改以假設做進行，亦即假設

A 與 B 之 ΔH_{vap}° 差異不大，則：

$$\Delta G_{vap}(T) \approx \Delta H_{vap}^\circ \left[\frac{T_{vap} - T}{T_{vap}} \right] \approx \left[1 - \frac{T}{T_{vap}} \right], \quad T_{vap} \uparrow, \Delta G_{vap}(T) \uparrow$$

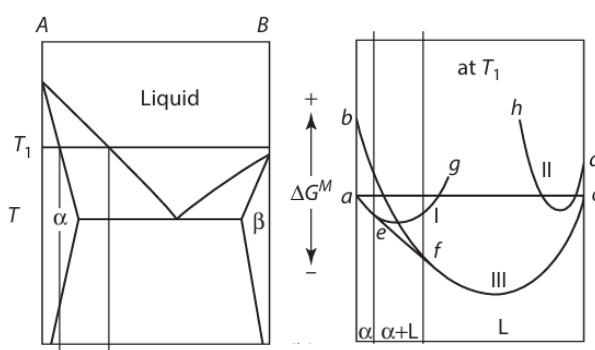
$$\text{因此本題 } T_{vap,A} > T_{vap,B}, \Delta G_{vap,A}(T) > \Delta G_{vap,B}(T), \quad G_{A(g)}^\circ > G_{B(g)}^\circ$$

(5)而在 600°C，根據慣例，因 600°C 時 A 在熔點以下、B 在熔點以上，因此 A 液態為穩定、且 B 氣態為穩定，因此設定標準態為：

$$G_{A(L)}^\circ = 0 \quad \text{and} \quad G_{B(g)}^\circ = 0$$

然而同樣有 $G_{A(g)}^\circ$ 與 $G_{B(L)}^\circ$ 誰高的問題，因此以(4)介紹的方式作假設。

(6)然而尚有不連過座標軸的畫法，例如 Gaskell 原文書給的範例：

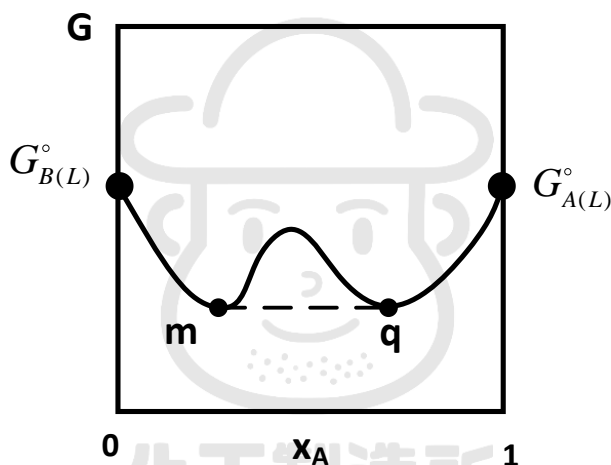


未延伸到底的部分代表比 standard state 高，只是不知道確切高多少。不過因為事實上上升上去的斜率會影響到最後相交於座標軸的高度，所以其實本來在資訊不

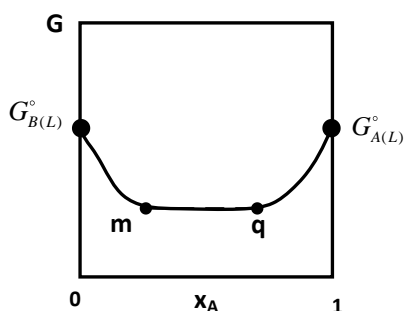
足的情況下畫此類相圖就有很多可以變化的空間，基本上本人在此認為考試最關鍵的核心還是在如何設定標準狀態、各相受溫度變化導致之高度變化關係、以及產生相平衡時需要作公切線這些比較核心的觀念。

(7)在繪製相圖時若是遇到有不同相平衡的出現，通常代表兩相的自由能曲線產生交點，可以參考 600°C 時的相圖，而有交點就代表可以往兩邊畫出公切線，一點在液態(s 點)、一點在氣態(r 點)，即代表相平衡的端點。

(8)在遇到有 miscibility gap 出現的區域，其 regular solution 的修正項會使得該相產生 W 型的曲線(如此題的 400°C)，其 W 型的最低兩點若畫出公切線就可以讓系統的自由能降至更低，如下：



代表若是組成落在 a 點，因為 m 與 q 的公切線可以使得自由能降至更低，因此組成在 m 與 q 之間的溶液，在條件允許的情況下，都能夠分成兩相，其等效自由能-溫度曲線如下：



(本題可參考：Gaskell, D.; Laughlin, D. *Introduction to Thermodynamics of Materials*, 6th Edition, 6th ed.; Ch10.)

【證明】達平衡之兩點間連線即可畫出共切線

以上頁 m 與 q 點為例，m 代表相態 m、q 代表相態 q

則：

$$\overline{\mu_1^m} = \overline{G_1^m} = G_m + x_2 \left. \frac{\partial G}{\partial x_1} \right|_m = G_m + (1-x_1) \left. \frac{\partial G}{\partial x_1} \right|_m$$

$$\overline{\mu_1^q} = \overline{G_1^q} = G_q + x_2 \left. \frac{\partial G}{\partial x_1} \right|_q = G_q + (1-x_1) \left. \frac{\partial G}{\partial x_1} \right|_q$$

At equilibrium, $\overline{\mu_1^q} = \overline{\mu_1^m}$

$$G_m + (1-x_1) \left. \frac{\partial G}{\partial x_1} \right|_m = G_q + (1-x_1) \left. \frac{\partial G}{\partial x_1} \right|_q$$

∵ 共切線， $\left. \frac{\partial G}{\partial x_1} \right|_m = \left. \frac{\partial G}{\partial x_1} \right|_q$ 代回

$$G_m + (1-x_1) \left. \frac{\partial G}{\partial x_1} \right|_m = G_q + (1-x_1) \left. \frac{\partial G}{\partial x_1} \right|_m$$

$$\frac{G_m - G_q}{x_1^m - x_1^q} = \left. \frac{\partial G}{\partial x_1} \right|_m = \left. \frac{\partial G}{\partial x_1} \right|_q$$

也即是說將 m 與 q 兩點連接，所得到之直線即是 m 與 q 點之公切線。

【補充】Regular solution

一般來說，regular solution 的性質有：

$$\begin{cases} V^{ex} = 0 \rightarrow \Delta V_{mix} = 0 \\ S^{ex} = 0 \rightarrow \Delta S_{mix} = -nR(x_1 \ln x_1 + x_2 \ln x_2) \end{cases}$$

且其混合自由能可被定義如下：

$$\frac{\Delta G_{mix}}{RT} = \frac{\Delta H_{mix}}{RT} - \frac{\Delta S_{mix}}{R} = \underbrace{\frac{\Omega_{AB}}{RT} x_A x_B}_{\Delta H_{mix}} + \underbrace{(x_A \ln x_A + x_B \ln x_B)}_{\Delta S_{mix}} = \alpha x_A x_B + (x_A \ln x_A + x_B \ln x_B)$$

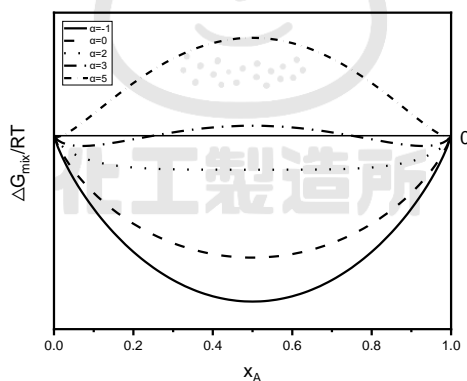
其中 Ω 為用於代表兩分子之間有作用力所產生之參數，定義為：

$$\Omega_{AB} \propto (2e_{AB} - e_{AA} - e_{BB})$$

AB間能量 AA間能量 BB間能量

$$\begin{cases} \Omega_{AB} > 0 \rightarrow AB\text{間能量} > AA\text{與}BB\text{平均，混合後較不穩定} \\ \Omega_{AB} = 0 \rightarrow AB\text{間能量} = AA\text{與}BB\text{平均，理想溶液} \\ \Omega_{AB} < 0 \rightarrow AB\text{間能量} < AA\text{與}BB\text{平均，混合後較穩定} \end{cases}$$

若我們將 $\frac{\Delta G_{mix}}{RT}$ 與 x_A 隨著不同 α 的值作圖，則可得結果如下：



可以發現，當 α 越高，代表混合後溶液越不穩定，甚至在曲線中段會有自由能大於 0 的情況發生，因此才會產生不互溶之相分離。而一般來說，若 α / RT 隨著溫度變高而越來越大，則會有最低臨界溫度(lower critical temperature)，代表溫度超過一個門檻以後則會產生相分離；若 α / RT 隨著溫度變高而越來越小，則會有最高臨界溫度(USCT)，代表溫度低過一定程度以後，才會產生相分離，如同此題條件。

Problem 3

【Solution】

(a)

For the reaction to be spontaneous,

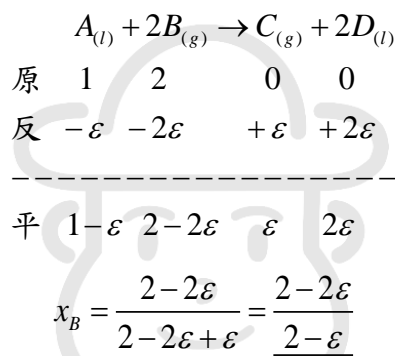
$$\Delta G_r = \Delta G_r^\circ + RT \ln \frac{P_C}{P_B^2}$$

反應初期沒有任何 C 或 D 存在，則 $P_C = 0$ 代入，

$$\Delta G_r = \Delta G_r^\circ + RT \ln 0 \rightarrow -\infty < 0$$

則反應將朝向產生 C 與 D 的方向走。

For mole fraction of B in the gas phase in terms of reaction coordinate,

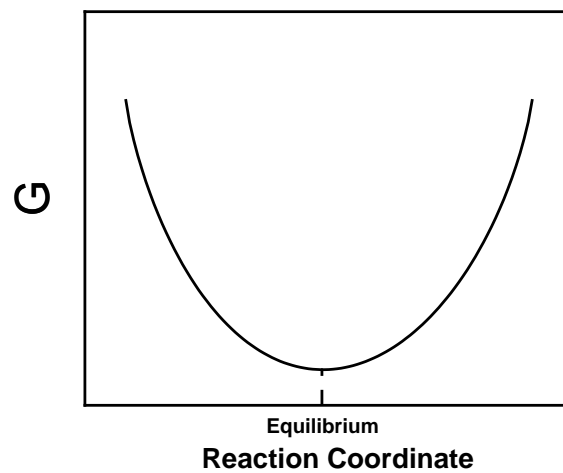


(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 484-488.)

(b)

達平衡時，應有 B 存在，否則不為平衡。

(c)



(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 489, Figure 13.1.)

(d)

見上圖，達平衡時， G' 將達到最小值

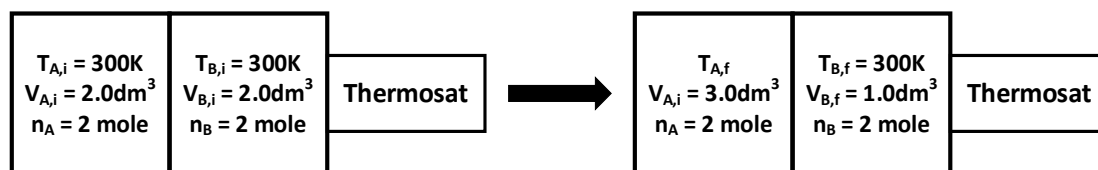
(e)

$$\sum \nu_i \mu_i = \sum \nu_i \bar{G}_i = \underline{\underline{\Delta G = 0}}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 490.)

Problem 4

【Solution】



(a)

$$\Delta S_B = n \left(\underbrace{C_V \ln \frac{T_{B,f}}{T_{B,i}}}_{\text{isothermal}} + R \ln \frac{V_{B,f}}{V_{B,i}} \right) = 2 \times 8.314 \ln \frac{1}{2} = \underline{\underline{-11.53 (J / K)}}$$

$$\Delta S_A = n \left(C_V \ln \frac{T_{A,f}}{T_{A,i}} + R \ln \frac{V_{A,f}}{V_{A,i}} \right)$$

For $T_{A,f}$, $\therefore P_{A,f} = P_{B,f}$

$$P_{A,f} = P_{B,f} = \frac{n_B R T_{B,f}}{V_{B,f}} = \frac{2 \times 0.082 \times 300}{1.0} = 49.2 \text{ atm}$$

則

$$T_{A,f} = \frac{P_{A,f} V_{A,f}}{n_A R} = \frac{49.2 \times 3.0}{2 \times 0.082} = 900K, \text{ 代回}$$

$$\Delta S_A = 2 \left(20 \ln \frac{900}{300} + 8.314 \ln \frac{3}{2} \right) = \underline{\underline{50.68 (J / K)}}$$

(b)

【原文書解答版本】

$$\Delta A_B = \cancel{\Delta U_B}_{\text{isothermal}} - T_B \Delta S_B = 0 - 300 \times (-11.53) = \underline{\underline{3459 (J)}}$$

$$\Delta A_A = \Delta U_A - \underbrace{\Delta(T_A S_A)}_{>0} = \underline{\underline{\text{indeterminate}}}$$

【另種看法】

$$\Delta A_A = \Delta U_A - \Delta(T_A S_A) = \Delta U_A - (T_{Af} S_{Af} - T_{Ai} S_{Ai})$$

$$\Delta A_A = \Delta U_A - [T_{Af} (S_{Ai} + \Delta S_A) - T_{Ai} S_{Ai}] = \Delta U_A - [(T_{Af} - T_{Ai}) S_{Ai} + T_{Af} \Delta S_A]$$

$$\Delta A_A = 2 \times 20 \times (900 - 300) - [(900 - 300) S_{Ai} + 900 \times 50.68]$$

$$\Delta A_A = -21612 - 600 S_{Ai} < 0$$

>0

(只有在 0K 下，物質絕對熵才有可能為 0)

(c)

【原文書解答版本】

$$\Delta G_B = \cancel{\Delta H_B}_{\text{isothermal}} - T_B \Delta S_B = 0 - 300 \times (-11.53) = \underline{\underline{3459 (J)}}$$

$$\Delta G_A = \Delta H_A - \underbrace{\Delta(T_A S_A)}_{>0} = \underline{\underline{\text{indeterminate}}}$$

【另種看法】

$$\Delta G_A = \Delta H_A - \Delta(T_A S_A) = \Delta H_A - (T_{Af} S_{Af} - T_{Ai} S_{Ai})$$

$$\Delta G_A = \Delta H_A - [T_{Af} (S_{Ai} + \Delta S_A) - T_{Ai} S_{Ai}] = \Delta H_A - [(T_{Af} - T_{Ai}) S_{Ai} + T_{Af} \Delta S_A]$$

$$\Delta G_A = 2 \times (20 + 8.314) \times (900 - 300) - [(900 - 300) S_{Ai} + 900 \times 50.68]$$

$$\Delta G_A = -11635.2 - 600 S_{Ai} < 0$$

>0

(只有在 0K 下，物質絕對熵才有可能為 0)

(d)

$$\Delta S_{total,sys} = \Delta S_A + \Delta S_B = 50.68 - 11.53 = \underline{\underline{39.15 \text{ (J / K)}}}$$

\therefore The process is reversible,

$$\Delta S_{total,sys} + \Delta S_{sur} = 0$$

$$\Delta S_{sur} = -\Delta S_{total,sys} = \underline{\underline{-39.15 \text{ (J / k)}}}$$

(本題改編自：Atkins, P.; De Paula, J.; Keeler, J. *Atkins' Physical Chemistry*, 9th ed.; p 132,

Problem 3.4.)



Problem 5

【Solution】

假設兩相(α 、 β 相)達相平衡，則關係如下：

$$dH^\alpha = C_p^\alpha dT + V^\alpha dP$$

$$dH^\beta = C_p^\beta dT + V^\beta dP$$

$$d(H^\alpha - H^\beta) = (C_p^\alpha - C_p^\beta)dT + (V^\alpha - V^\beta)dP$$

$$d(\Delta H) = \Delta C_p dT + \Delta V dP$$

By Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}, \quad dP = \frac{\Delta H}{T\Delta V} dT \text{ 代入上式}$$

$$d(\Delta H) = \Delta C_p dT + \frac{\Delta H}{T} dT$$

$$\frac{Td(\Delta H) - \Delta H dT}{T^2} = \frac{\Delta C_p}{T} dT$$

$$\underline{\underline{d\left(\frac{\Delta H}{T}\right) = \Delta C_p d \ln T}}$$

(本題改編自：Atkins, P.; De Paula, J.; Keeler, J. *Atkins' Physical Chemistry*, 9th ed.; p 155,

Problem 4.14.)

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Problem 6**【Solution】****(a)**

For adiabatic, no shaft reactor, by energy balance,

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

$$0.45 = \frac{\int_{273+77}^T 1 \times 20 dT}{-[-20000 + \int_{273+27}^T (30 \times 1 - 20 \times 1) dT]}$$

$$\underline{\underline{T = 708.2 \text{ (K)}}}$$

(b)

For CSTR, by design equation,

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

For rate equation, (gas-phase, $\varepsilon = 0$)

$$-r_A = k_1 C_A - k_2 C_B = k_1 \left(C_A - \frac{1}{K} C_B \right) = k_1 C_{A0} \left(\frac{T_0}{T} \right) [(1 - X_A) - \frac{1}{K} X_A]$$

For $k_1(708.2K)$, by Arrhenius law,

$$\frac{k_1(273K)}{k_1(708.2K)} = \frac{0.001}{k_1(708.2K)} = \frac{e^{\frac{-10000}{1.987 \times 273}}}{e^{\frac{-10000}{1.987 \times 708.2}}}$$

$$k_1(708.2K) = 83.16 \text{ h}^{-1}$$

For $K(708.2K)$, by van't Hoff equation,

$$\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}}{RT^2} = \frac{\Delta H_R^\circ + \int_{300}^T \Delta C_p}{RT^2} = \frac{\Delta H_R^\circ}{RT^2} + \frac{10(T-300)}{RT^2}$$

$$\ln \frac{K(708.2)}{K(400)} = \int_{400}^{708.2} \frac{-20000}{1.987T^2} dT + \int_{400}^{708.2} \frac{10(T-300)}{1.987T^2} dT = -9.718$$

$$K(708.2) = 1.50$$

將數據代回，

$$V = \frac{F_{A0} X_A}{-r_A} = \frac{F_{A0} X_A}{k_1 C_{A0} \left(\frac{T_0}{T}\right) [(1 - X_A) - \frac{1}{K} X_A]}$$

$$V = \frac{10 \times 60 \times 0.45}{83.16 \times \frac{2.87}{0.082 \times (273 + 77)} \left(\frac{273 + 77}{708.2}\right) [(1 - 0.45) - \frac{1}{1.50} \times 0.45]} = \underline{\underline{261.9 \text{ (L)}}}$$



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Problem 7**【Solution】**

For PBR, by design equation,

$$W = \int_0^{X_P} \frac{F_{P0} dX_P}{-r_A}$$

For rate equation, (liquid-phase)

$$-r_P = k_1 C_P - k_2 C_Q = k_1 \left(C_P - \frac{1}{K} C_Q \right) = k_1 C_{P0} \left[(1 - X_P) - \frac{1}{K} X_P \right]$$

Combine,

$$W = \int_0^{X_A} \frac{F_{P0}}{k_1 C_{P0} \left[(1 - X_P) - \frac{1}{K} X_P \right]} dX_P, \text{ 代入數據}$$

$$W = \int_0^{0.55} \frac{F_{P0} dX_P}{k_1 C_{P0} \left[(1 - X_P) - \frac{1}{5.8} X_P \right]}$$

$$\frac{W k_1 C_{P0}}{F_{P0}} = 0.8829$$

For 2-nd PBR,

$$\frac{W k_1 C_{P0}}{F_{P0}} = 0.8829 = \int_{0.55}^{X_{P,2}} \frac{dX_P}{\left[(1 - X_P) - \frac{1}{5.8} X_P \right]}$$

$$\underline{\underline{X_{P,2} = 0.745}}$$

Problem 8

【Solution】

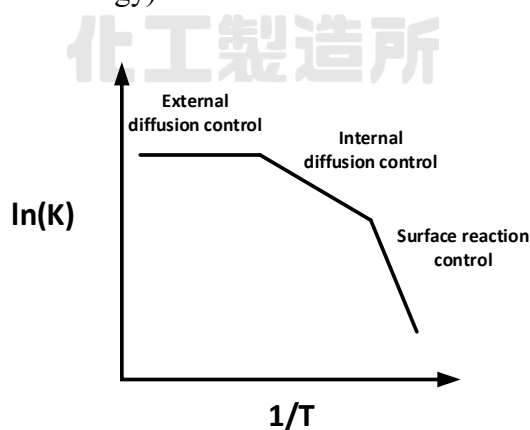
一般之觸媒化學反應可以分為 7 步驟：

- (1) 反應物於觸媒外部向內質傳
- (2) 反應物於觸媒內部向內質傳
- (3) 反應物吸附在觸媒上
- (4) 反應物發生表面反應產生產物
- (5) 產物脫附
- (6) 產物於觸媒內部向外質傳
- (7) 產物於觸媒外部向外質傳

其中，一般來說，反應速率可粗略分成三種機制來控制：

- (1) 外部質傳控制(external diffusion control)
- (2) 內部質傳控制(internal diffusion control)
- (3) 表面反應控制(surface reaction control)

此圖的三個斜率即代表在不同的溫度底下由不同的機制限制反應速率時的表觀活化能(apparent activation energy)



(本題可參考：Ertl, G.; Knözinger, H.; Schüth, F.; Weitkamp, J. *Handbook of Heterogeneous Catalysis*; p 2~3, Figure1.

以及：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 833~855.)

Problem 9

【Solution】

For rate equation, (gas-phase reaction, $\varepsilon = 0$)

$$-r_A = kC_A C_B = kC_{A0}(1 - X_A)C_{B0}$$

$$\begin{aligned} -r_A|_{X_A=0.5} &= k \frac{P_{A0}}{RT} (1 - X_A) \frac{P_{B0}}{RT} \\ &= 10^6 \times \frac{0.75(1-0.5)}{0.7302 \times (540 + 460)} \times \frac{0.25}{0.7302 \times 1000} = \underline{\underline{0.176(\text{lb-mole} / \text{s} \cdot \text{ft}^3)}} \end{aligned}$$

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 140,

Problem CDP3-FB.)



Problem 10**【Solution】**

For tubular reactor, design equation,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A}$$

For rate equation, (gas-phase reaction, $\varepsilon = 0$)

$$-r_A = k(T)C_A = k(T)C_{A0}(1 - X_A)$$

For $k(T)$, we need to know the activation energy, E_a

$$\frac{k(200^\circ\text{F})}{k(300^\circ\text{F})} = \frac{e^{\frac{-E_a}{1.987 \times (200+460)}}}{e^{\frac{-E_a}{1.987 \times (300+460)}}} = \frac{0.00152}{0.0740}$$

$$E_a = 38724 (\text{Btu} / \text{mole})$$

$$\frac{k(T)}{k(200^\circ\text{F})} = \frac{e^{\frac{-38724}{1.987(T+460)}}}{e^{\frac{-38724}{1.987(200+460)}}}, \quad k(T) = 0.00152 e^{\frac{38724}{1.987}(\frac{1}{T+460} - \frac{1}{660})} \quad \text{代回}$$

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A} = \int_0^{X_A} \frac{F_{A0} dX_A}{k(T)C_{A0}(1 - X_A)} = \int_0^{X_A} \frac{F_{A0} dX_A}{0.00152 e^{\frac{38724}{1.987}(\frac{1}{T+460} - \frac{1}{660})} C_{A0}(1 - X_A)}$$

$$V = 50 \times 40 \times \frac{\pi}{4} \left(\frac{0.75 \text{ in}}{12 \text{ in} / \text{ft}} \right)^2 = \int_0^{0.8} \frac{\frac{500/73}{3600} dX_A}{0.00152 e^{\frac{38724}{1.987}(\frac{1}{T+460} - \frac{1}{660})} \times \frac{100+14.7}{0.73(T+460)} (1 - X_A)}$$

$$\underline{\underline{T = 278^\circ\text{F}}}$$

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 241,

Problem 4-15A.)

107 年清大化熱化反

Problem 1

【Solution】

(a)

∵ The liquid phase is ideal solution

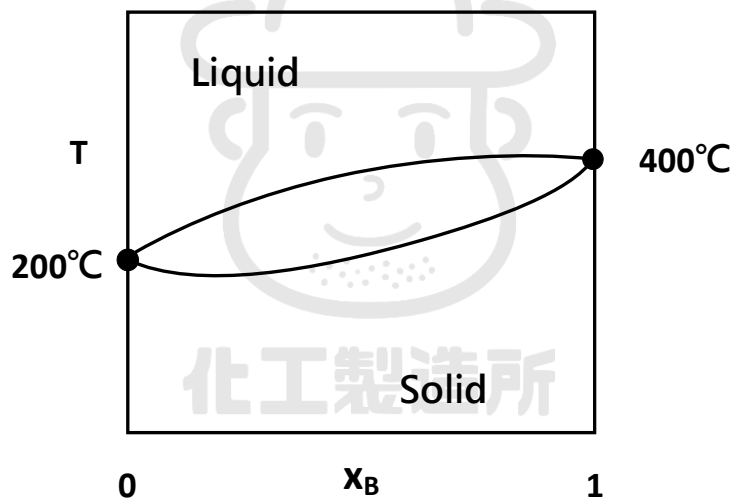
$$\underline{\underline{\Delta G_{mix}^{id} = RT(x_A \ln x_A + x_B \ln x_B)}}$$

For the partial Gibbs energy of A,

$$\overline{G}_A = G_{A,pure} + \overline{\Delta G_{mix,A}^{id}} = \underline{\underline{G_{A,pure} + RT \ln x_A}}$$

(b)

Because A and B have the same crystal structure,

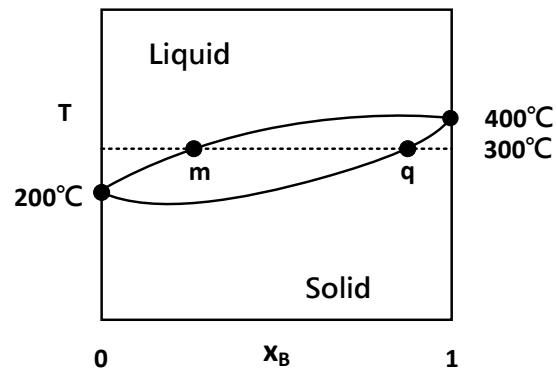


(自由能-組成相圖畫法可參考 106 年清大化熱化反 Problem 2 後解說。)

(c)

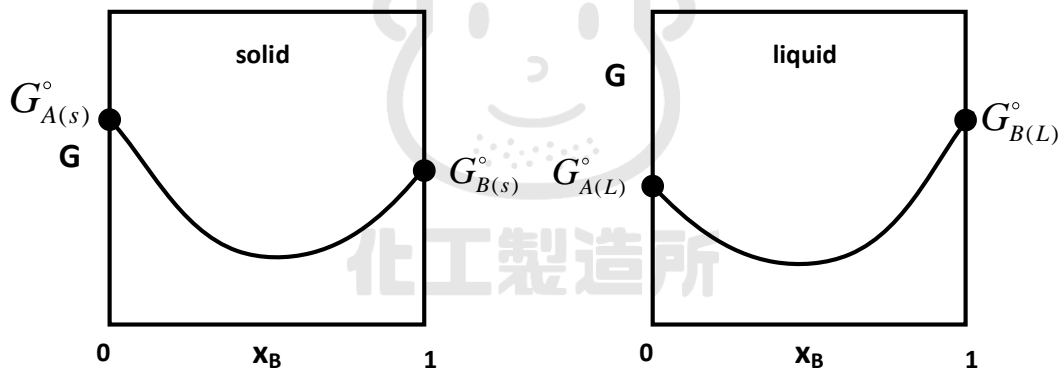
Assume $\begin{cases} \text{Liquid phase} \rightarrow \text{ideal solution} \\ \text{solid phase} \rightarrow \text{ideal solution} \end{cases}$

@300°C

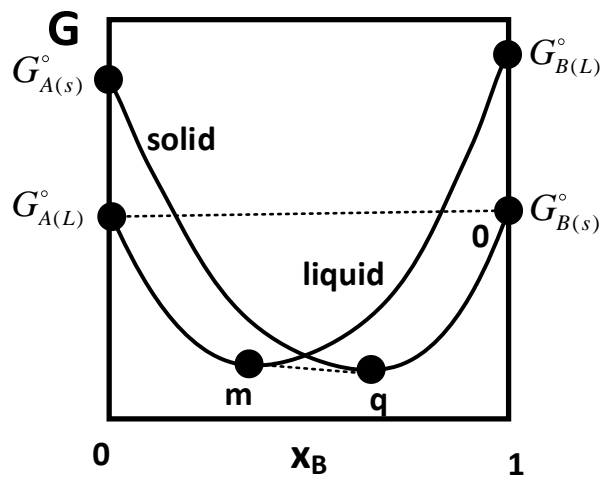


Set the standard states as : $G_{A(L)}^\circ = 0$ and $G_{B(s)}^\circ = 0$

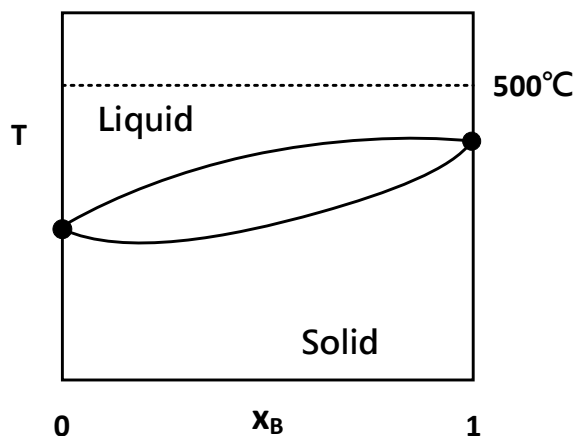
Assume $G_{A(s)}^\circ < G_{B(L)}^\circ$



合併：

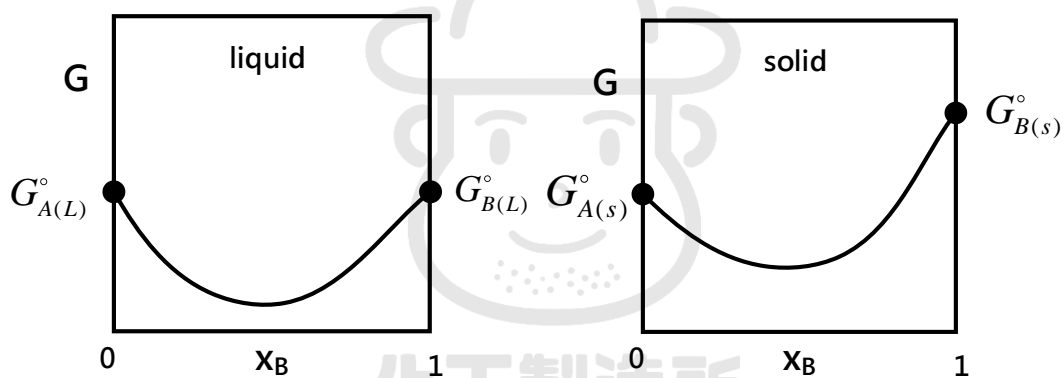


@500°C

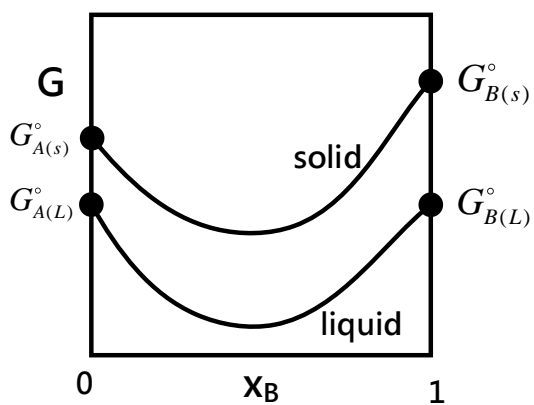


Set the standard states as : $G_{A(L)}^\circ = 0$ and $G_{B(L)}^\circ = 0$

Assume $G_{A(s)}^\circ < G_{B(s)}^\circ$



合併：



(本題可參考：Gaskell, D.; Laughlin, D. *Introduction to Thermodynamics of Materials*, 6th Edition, 6th ed.;Ch10.)

Problem 2

【Solution】

(a)

題目給定 excess property，則 $\overline{G}_B = G_{B,pure} + \Delta \overline{G}_{B,mix}^{id} + \overline{G}_B^{ex}$

For \overline{G}_B^{ex} ,

$$\overline{G}_B^{ex} = \left[\frac{\partial(nG^E)}{\partial n_B} \right]_{n_A, P, T} = RT(-3.4x_A^2x_B - 1.6x_A^3) \text{ 代回}$$

$$\begin{aligned}\overline{G}_B &= G_{B,pure} + RT \ln x_B + RT(-3.4x_A^2x_B - 1.6x_A^3) \\ &= \underline{\underline{G_{B,pure} + RT(-3.4x_A^2x_B - 1.6x_A^3 + \ln x_B)}}$$

(b)

$$\ln r_B = \frac{\overline{G}_B^{ex}}{RT} = \underline{\underline{-3.4x_A^2x_B - 1.6x_A^3}}$$

(c)

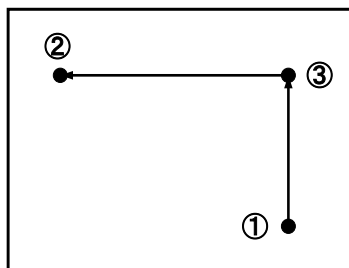
Raoult's 用於描述當氣相為 ideal gas、液相為 ideal solution 時之液氣平衡現象，此系統的液相兩成分之 activity coefficient 不為 1，因此無法使用 Raoult's law 來描述。

Problem 3

【Solution】

(a)

※Path A，設其路徑如下：



① to ③：

For T_3 , by ideal gas law,

$$\frac{P_1}{P_3} = \frac{T_1}{T_3} \quad (V \text{ is constant})$$
$$T_3 = \frac{T_1 P_3}{P_1} = \frac{298 \times 5.0}{1.0} = 1490 \text{ K}$$

則 Q 、 W 、 ΔH 可計算如下：

$$W_{13} = 0 \quad (V \text{ is constant})$$

$$Q_{13} = \Delta U_{13} = C_V \Delta T_{13} = \frac{5}{2} \times 8.314 (1490 - 298) = 24775.72 \text{ (J / mole)}$$

$$\Delta H_{13} = C_P \Delta T_{13} = \frac{7}{2} \times 8.314 (1490 - 298) = 34686.01 \text{ (J / mole)}$$

③ to ②：

For T_2 , by ideal gas law,

$$\frac{V_2}{V_3} = \frac{T_2}{T_3} \quad (P \text{ is constant})$$
$$T_2 = \frac{V_2 T_3}{V_3} = \frac{4.958 \times 1490}{24.79} = 298 \text{ K}$$

則 Q 、 W 、 ΔH 可計算如下：

$$W_{32} = -\int P dV = -P\Delta V = -5 \times (4.958 - 24.79) \times \frac{8.314}{0.08314} = 9916 \text{ (J / mole)}$$

$$\Delta U_{32} = C_V \Delta T_{32} = \frac{5}{2} \times 8.314(298 - 1490) = -24775.72 \text{ (J / mole)}$$

$$Q_{32} = \Delta U_{32} - W_{32} = -24775.72 - 9916 = -34691.72 \text{ (J / mole)}$$

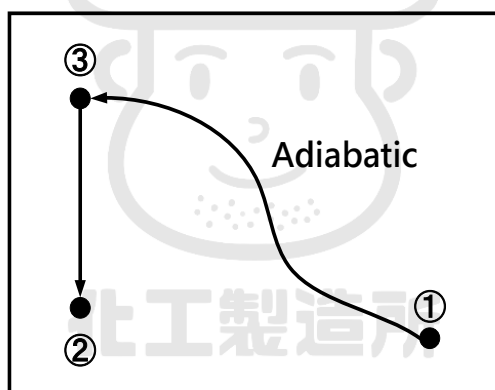
$$\Delta H_{32} = C_P \Delta T_{32} = \frac{7}{2} \times 8.314(298 - 1490) = -34686.01 \text{ (J / mole)}$$

$$W_A = W_{13} + W_{32} = 0 + 9916 = \underline{\underline{9916 \text{ (J / mole)}}}$$

$$Q_A = Q_{13} + Q_{32} = 24775.72 - 34691.72 = \underline{\underline{-9916 \text{ (J / mole)}}}$$

$$\Delta H_A = \Delta H_{13} + \Delta H_{32} = 34686.01 - 34686.01 = \underline{\underline{0 \text{ (J / mole)}}}$$

※Path B，設其路徑如下：



① to ③：

For T_3 , by adiabatic relation for ideal gas,

$$\frac{T_3}{T_1} = \left(\frac{V_1}{V_3}\right)^{\gamma-1}$$

$$\frac{T_3}{298} = \left(\frac{24.79}{4.958}\right)^{\frac{7}{5}-1}, \quad T_3 = 567.29 \text{ K}$$

則 Q 、 W 、 ΔH 可計算如下：

$$Q_{13} = 0 \text{ (adiabatic)}$$

$$\begin{aligned} W_{13} &= \int PdV = - \int \frac{PV_1^\gamma}{V^\gamma} dV = - \int \frac{(1.0 \times 24.79^{1.4})}{V^{1.4}} dV = - \int_{24.79}^{4.958} \frac{89.534}{V^{1.4}} dV \\ &= 56.00 \times \frac{8.314}{0.08314} = 5600 \text{ (J / mole)} \end{aligned}$$

$$\Delta H_{13} = C_p \Delta T_{13} = \frac{7}{2} \times 8.314 (567.29 - 298) = 7836.1 \text{ (J / mole)}$$

③ to ②：

Q 、 W 、 ΔH 可計算如下：

$$W_{32} = 0 \text{ (V is constant)}$$

$$Q_{32} = \Delta U_{32} = C_v \Delta T_{32} = \frac{5}{2} \times 8.314 (298 - 567.29) = -5597.19 \text{ (J / mole)}$$

$$\Delta H_{32} = C_p \Delta T_{32} = \frac{7}{2} \times 8.314 (298 - 567.29) = -7836.1 \text{ (J / mole)}$$

=>

$$W_B = W_{13} + W_{32} = 5600 + 0 = \underline{\underline{5600 \text{ (J / mole)}}}$$

$$Q_B = Q_{13} + Q_{32} = 0 - 5597.19 = \underline{\underline{-5597.19 \text{ (J / mole)}}}$$

$$\Delta H_B = \Delta H_{13} + \Delta H_{32} = 7836.1 - 7836.1 = \underline{\underline{0 \text{ (J / mole)}}}$$

將兩個 path 之 Q 、 W 、 ΔH 列表如下：

	Path A	Path B
Q	-9916	-5597.19 \approx -5600
W	9916	5600
ΔH	0	0

可知 Q 、 W 為 path function； ΔH 為 state function

(b)

∵ entropy is a state function,

$$\Delta S_A = \Delta S_B = \underbrace{C_p \ln \frac{T_2}{T_1}}_{T_1=T_2} - R \ln \frac{P_2}{P_1}$$

$$\Delta S_A = \Delta S_B = -8.314 \ln \frac{5}{1} = \underline{\underline{-13.38 \text{ (J / mole} \cdot \text{K)}}} \quad (\text{皆為 system})$$

(c)

For path A,

$$\begin{cases} \Delta S_{A,sur} = \frac{-Q_A}{T_{sur}} = \frac{9916}{298} = 33.27 \text{ (J / mole} \cdot \text{K)} \\ \Delta S_{B,sur} = \frac{-Q_B}{T_{sur}} = \frac{5600}{298} = 18.79 \text{ (J / mole} \cdot \text{K)} \end{cases} \quad (\text{假設保持室溫})$$

$\begin{cases} \Delta S_{A,total} = \Delta S_{A,sys} + \Delta S_{A,sur} = -13.38 + 33.27 = 19.89 \text{ (J / mole} \cdot \text{K)} \\ \Delta S_{B,total} = \Delta S_{B,sys} + \Delta S_{B,sur} = -13.38 + 18.79 = 6.51 \text{ (J / mole} \cdot \text{K)} \end{cases}$

不管 path A 或 B 之 ΔS_{total} 皆 > 0 ，皆可自發

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Problem 4

【Solution】

(a) @300K, $\log K_{eq} = -15.069$, $K_{eq} = e^{-15.069} = \underline{\underline{8.53 \times 10^{-16}}}$

(b) 題目題意不清，應改為 NO_2 ‘formation reaction’，(d)、(f) 小題同

@300K, $\log K_{eq} = -15.069 + 6.1126 = -8.9564$, $K_{eq} = e^{-8.9564} = \underline{\underline{1.105 \times 10^{-9}}}$

(c) @2000K, $\log K_{eq} = -1.6996$, $K_{eq} = e^{-1.6996} = \underline{\underline{0.01997}}$

(d) @2000K, $\log K_{eq} = -1.6996 - 2.4546 = -4.1542$, $K_{eq} = e^{-4.1542} = \underline{\underline{7.01 \times 10^{-5}}}$

(e) By (a), (c), $T \uparrow$, $K_{eq} \uparrow$, endothermic reaction

(f) By (b), (d), $T \uparrow$, $K_{eq} \uparrow$, endothermic reaction



Problem 5

【Solution】

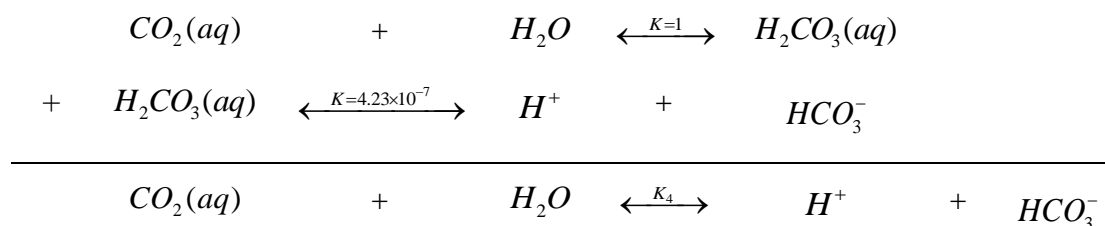
Assume the partial pressure of CO_2 is kept constant.

(a)

$$m_{CO_2} = \frac{P_{CO_2}}{H} = \frac{3.2 \times 10^{-4}}{26.3} = \underline{\underline{1.216 \times 10^{-5} (M)}}$$

(b)

題目有誤， K 非 1，假設為 K_4



$$K_4 = 1 \times 4.23 \times 10^{-7} = \underline{\underline{4.23 \times 10^{-7}}}$$

(c)

【法 1 - 電中性原理】：

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

$$[OH^-] = \frac{K_w}{[H^+]}$$

$$[HCO_3^-] = \frac{K_2[H_2CO_3]}{[H^+]} = \frac{K_2K_1[CO_2(aq)]}{[H^+]} = \frac{K_2K_1P_{CO_2}}{H[H^+]}$$

$$[CO_3^{2-}] = \frac{K_3[HCO_3^-]}{[H^+]} = \frac{K_3K_2K_1P_{CO_2}}{H[H^+]^2}$$

$$[H^+] = \frac{K_w}{[H^+]} + \frac{K_2K_1P_{CO_2}}{H[H^+]} + \underbrace{\frac{2K_3K_2K_1P_{CO_2}}{H[H^+]^2}}_{\text{negligible}}$$

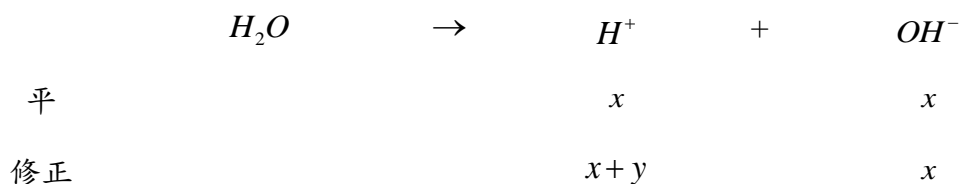
$$[H^+] = \frac{1 \times 10^{-14}}{[H^+]} + \frac{4.23 \times 10^{-7} \times 1 \times 3.2 \times 10^{-4}}{26.3[H^+]}$$

$$[H^+] = 2.271 \times 10^{-6} (M)$$

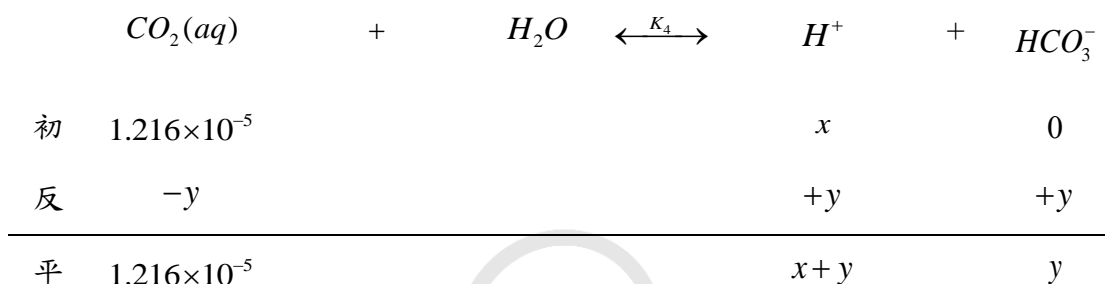
$$[HCO_3^-] = \frac{K_2K_1P_{CO_2}}{H[H^+]} = \frac{4.23 \times 10^{-7} \times 1 \times 3.2 \times 10^{-4}}{26.3 \times 2.27 \times 10^{-6}} = \underline{\underline{2.266 \times 10^{-6} (M)}}$$

【法 2 – 一般平衡】

水的解離：



$CO_2(aq)$ 的解離：



($CO_2(aq)$ 必須維持與 $CO_2(g)$ 的平衡，在 $CO_2(g)$ 分壓不變情況下，反應後 $CO_2(aq)$ 應維持定值。另外，水平衡的氫離子濃度必須修正，因為碳酸解離後，會影響水的解離。)

假設不考慮 $HCO_3^- \leftrightarrow CO_3^{2-}$ 的反應：

$$K_w = 10^{-14} = (x + y)x$$

$$K_4 = \frac{[H^+][HCO_3^-]}{[CO_2(aq)]} = \frac{(x + y)y}{1.216 \times 10^{-5}} = 4.23 \times 10^{-7}$$

相除：

$$\frac{10^{-14}}{4.23 \times 10^{-7}} = \frac{(x + y)x}{\frac{(x + y)y}{1.216 \times 10^{-5}}} = \frac{1.216 \times 10^{-5} x}{y}$$

$$x = 1.943 \times 10^{-3} y$$

代回 K_4

$$K_4 = \frac{(1.943 \times 10^{-3} y + y)y}{1.216 \times 10^{-5}} = 4.23 \times 10^{-7}, \quad \underline{\underline{y = 2.266 \times 10^{-6} (M)}}$$

(d)

$$[H^+] = 2.271 \times 10^{-6} \text{ (M)}$$

$$pH = -\log[H^+] = \underline{\underline{5.64}}$$

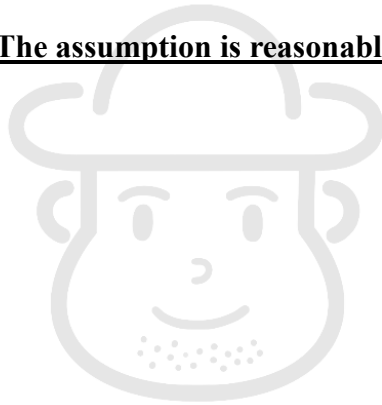
(e)

$$K_3 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

$$\frac{[HCO_3^-]}{[CO_3^{2-}]} = \frac{[H^+]}{K_{a2}} = \frac{2.271 \times 10^{-6}}{4.57 \times 10^{-11}} = \underline{\underline{49690}}$$

$$[HCO_3^-] \gg [CO_3^{2-}]$$

The assumption is reasonable.



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Problem 6

【Solution】

(a)

$$\psi = \frac{dC_s}{dC_R + dC_s + dC_T} = \frac{k_1 C_A}{k_0 + k_1 C_A + k_2 C_A^2} = \frac{0.2 C_A}{0.02 + 0.2 C_A + 0.5 C_A^2}$$

For ψ to be maximum, $\frac{d\psi}{dC_A} = 0$

$$\frac{0.016 - 0.4 C_A^2}{(C_A^2 + 0.4 C_A + 0.04)^2} = 0$$

$$0.016 - 0.4 C_A^2 = 0$$

$$\underline{\underline{C_A = 0.2 \text{ (M)}}}$$

For CSTR, design equation,

$$V = \frac{F_{A0} X_A}{-r_A} = \frac{v_0 C_{A0} X_A}{-r_A} = \frac{v_0 (C_{A0} - C_A)}{-r_A}$$

For rate equation,

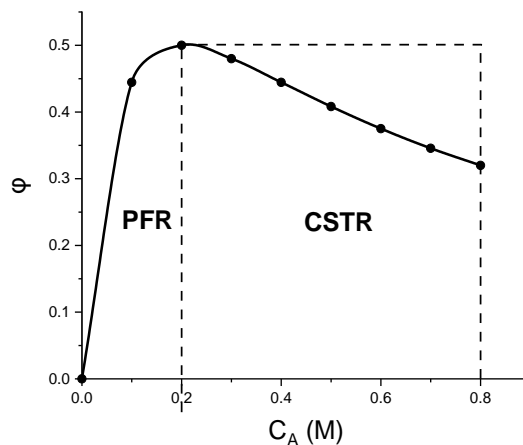
$$-r_A = k_0 + k_1 C_A + k_2 C_A^2 = 0.02 + 0.2 C_A + 0.5 C_A^2$$

Combine,

$$V = \frac{v_0 (C_{A0} - C_A)}{0.02 + 0.2 C_A + 0.5 C_A^2} = \frac{80(0.8 - 0.2)}{0.02 + 0.2 \times 0.2 + 0.5 \times 0.2^2} = \underline{\underline{600 \text{ (L)}}}$$

(b)

Plot $\psi - C_A$ diagram,



For, PFR,

$$C_{S,PFR} = \int_0^{0.2} \frac{0.2C_A}{0.02 + 0.2C_A + 0.5C_A^2} dC_A = \underline{\underline{0.077M}}$$

For, CSTR,

$$C_{S,CSTR} = 0.5(0.8 - 0.2) = 0.3M$$

則

$$C_{s,\max} = 0.077 + 0.3 = \underline{\underline{0.377 (M)}}$$

For volume of PFR, design equation,

$$\frac{V}{v_0} = \int_0^{0.2} \frac{dC_A}{-r_A}$$

For rate equation,

$$-r_A = 0.02 + 0.2C_A + 0.5C_A^2$$

Combine,

$$\frac{V}{v_0} = \int_0^{0.2} \frac{dC_A}{0.02 + 0.2C_A + 0.5C_A^2}$$

$$V = 5v_0 = 5 \times 80 = \underline{\underline{400 (L)}}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 166~167,

Problem 7.13~7.16.)

Problem 7

【Solution】

For PBR, design equation,

$$W = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A}$$

For rate equation,

$$-r_A = kC_A^2 = k \left[\frac{C_{A0}(1-X_A)}{(1+\varepsilon X_A)} \right]^2$$

$$\varepsilon = \delta y_{A0} = (3-1) \times 0.25 = 0.5$$

Combine,

$$W = \int_0^{X_A} \frac{F_{A0} dX_A}{k \left[\frac{C_{A0}(1-X_A)}{(1+0.5X_A)} \right]^2}$$

For X_A ,

$$C_A = \frac{C_{A0}(1-X_A)}{(1+0.5X_A)}$$

$$0.5 = \frac{2 \times (1-X_A)}{(1+0.5X_A)}, \quad X_A = 0.67 \text{ 代回}$$

$$3 = \int_0^{0.67} \frac{2 \times 1 dX_A}{k \left[\frac{2(1-X_A)}{(1+0.5X_A)} \right]^2}$$

$$k = 0.503 \text{ (m}^6 / \text{mole} \cdot \text{hr} \cdot (\text{kg} \cdot \text{cata}))$$

Rate equation,

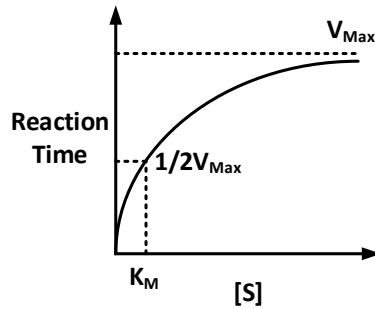
$$\underline{\underline{-r_A = 0.503 C_A^2 \text{ (mole / (hr} \cdot \text{kgcata))}}}$$

Problem 8

【Solution】

For Michaelis-Menten kinetics,

$$r = \frac{K_{cat}[E]_0[S]}{K_M + [S]}, \text{ 可繪圖如下:}$$



若[S]極小時， $r = \frac{K_{cat}}{K_M}[E]_0[S]$ ，則此時圖形接近直線，其斜率為 $\frac{K_{cat}}{K_M}[E]_0$

若已知 $[E]_0$ ，則可推得 $\frac{K_{cat}}{K_M}$

而在反應速率為 $\frac{V_{max}}{2}$ 時，濃度為 K_M ，代回上面結果可得 K_{cat}

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Problem 9

【Solution】

(a)

Enzyme 可將受質與其餘反應物吸附於其上，增加有效碰撞頻率，因而增加反應速率。

(b)

By the transition state theory, we have the relationship of rate constant with the activation of Gibbs energy,

$$k = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$

If the substrate is adsorbed by the enzyme, the formation of the structure will dispense energy into the surroundings, so the reaction rate will increase by enthalpic effect. However, the formation of the complex may lower the entropy, but can be compensated by the energy release or the structure distortion of the complex.

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108 年清大化熱化反

Problem 1

【Solution】

(a)

考慮一封閉活塞系統，其壓縮或膨脹所需做的功為 W 、所需吸與放之熱為 Q
則 internal energy

$$\Delta U = Q + W$$

(b)

考慮一開放活塞系統，其與封閉系統相比需多考慮流動功，是故其與 internal energy 之關係可經由此關係推得：

$$\Delta H = \Delta U + \Delta(PV)$$

(c)

考慮一封閉系統經過可逆絕熱壓縮/膨脹，則此程序為恆熵程序， $\Delta S = 0$

再考慮一封閉系統經過不可逆絕熱壓縮/膨脹，則此程序 $\Delta S \neq 0$

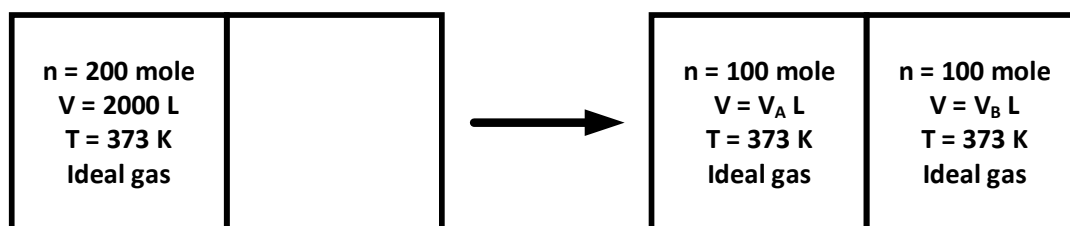
此兩者之差異可推得熵可用於預測依程序可不可逆

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Problem 2

【Solution】

假設此程序前後變化如下，即左右兩邊分子數相同，但壓力不一定平衡



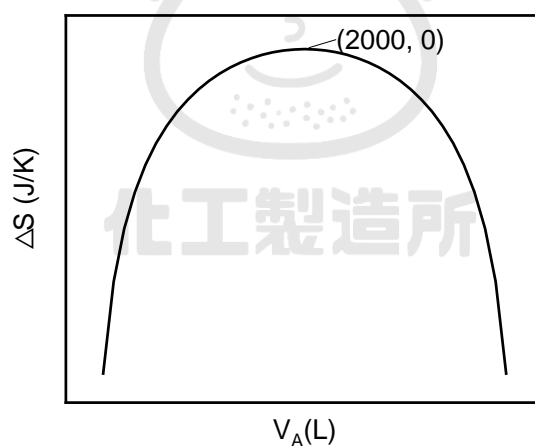
則此程序之 ΔS 為：

$$\Delta S = 100(\cancel{C_V \ln \frac{T_A}{T}} + R \ln \frac{V_A}{V}) + 100(\cancel{C_V \ln \frac{T_B}{T}} + R \ln \frac{V_B}{V})$$

$$\Delta S = 100(+8.314 \ln \frac{V_A}{2000}) + 100(8.314 \ln \frac{V_B}{2000}), \text{ 且 } V_A + V_B = 4000$$

$$\Delta S = 831.4 \ln \frac{V_A V_B}{4 \times 10^6} = 831.4 \ln \frac{V_A (4000 - V_A)}{4 \times 10^6}$$

Plot $\Delta S - V_A$ 圖



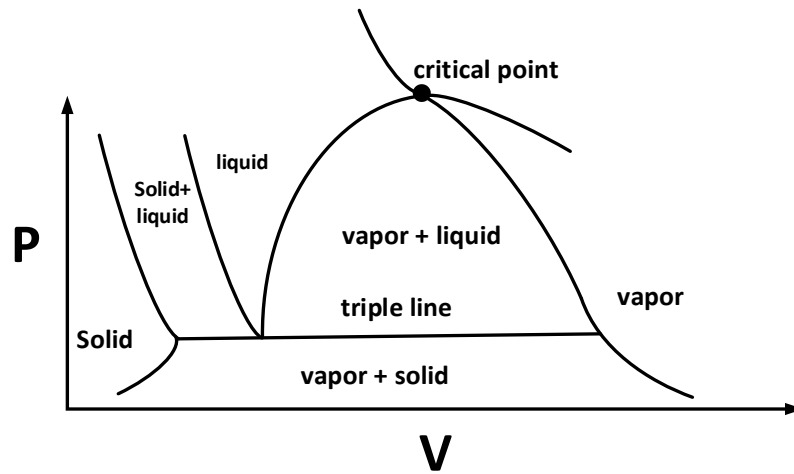
則根據上圖，若 A 與 B 達成平衡，則有 ΔS 最大值

且因為 $V_A = V_B$ 、 $n_A = n_B$ ， $T_A = T_B$ ，可推得平衡時 $P_A = P_B$

Problem 3

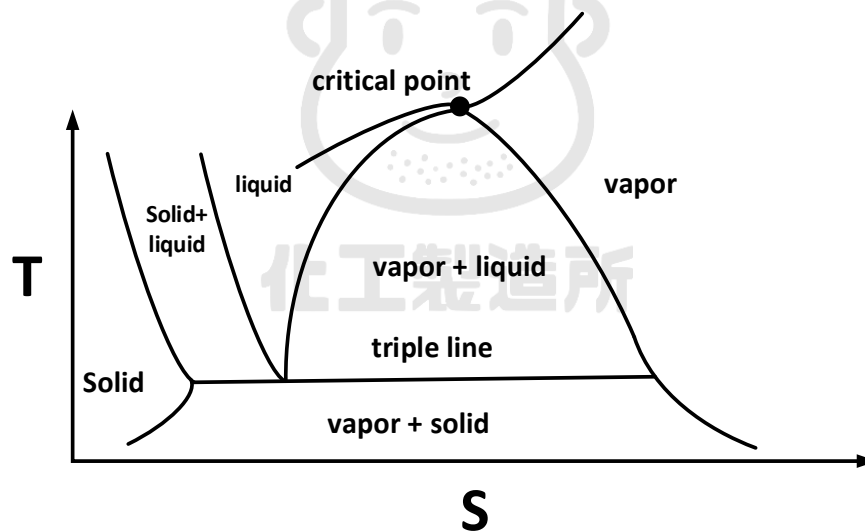
【Solution】

(a) P-V phase diagram



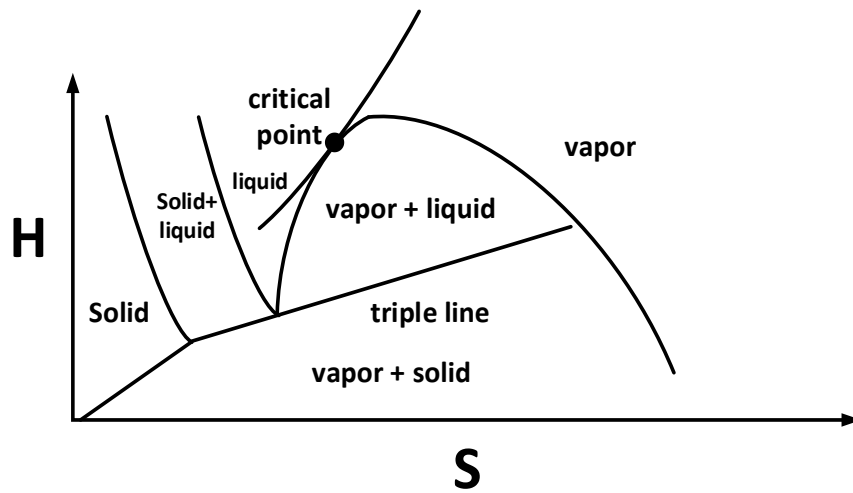
(本題可參考：Nag, P. *Basic And Applied Thermodynamics*, 1st ed, Section 9.1.)

(b) T-S phase diagram



(本題可參考：Nag, P. *Basic And Applied Thermodynamics*, 1st ed, Section 9.4.)

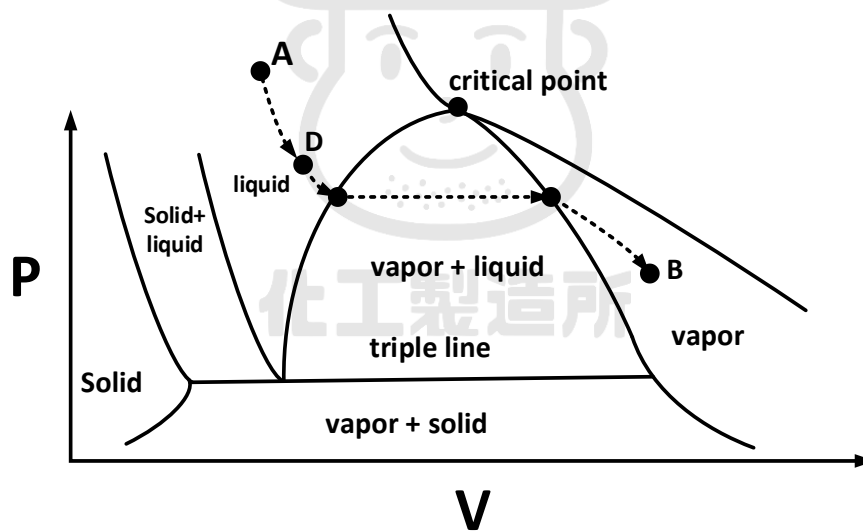
(c) H-S phase diagram



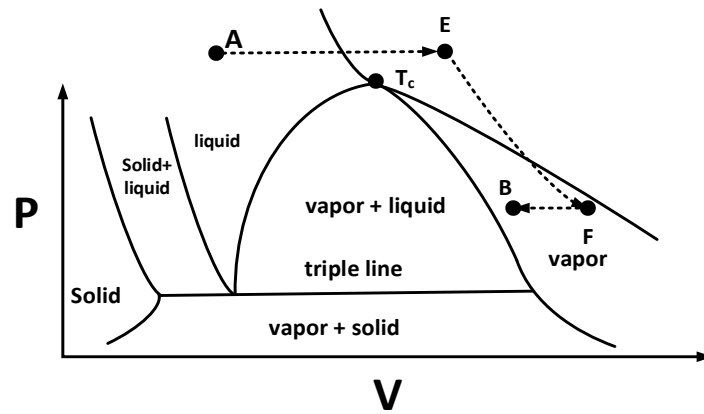
(本題可參考：Nag, P. *Basic And Applied Thermodynamics*, 1st ed, Section 9.5.)

(d) PV diagram

Path ADB

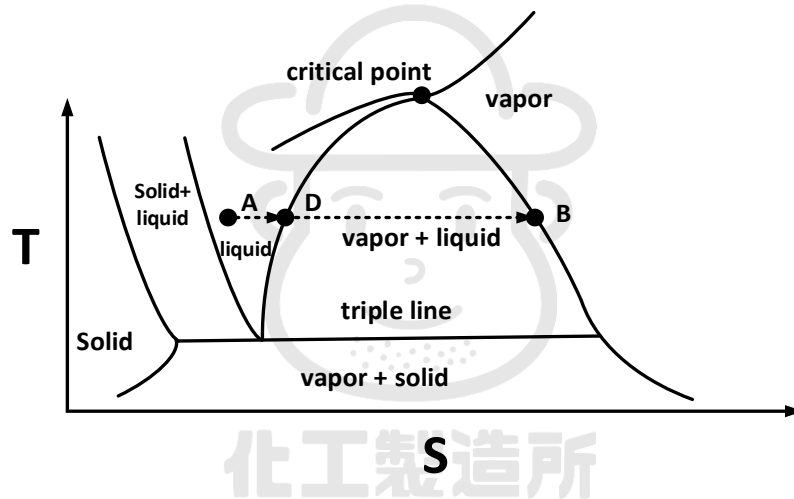


Path AEFB

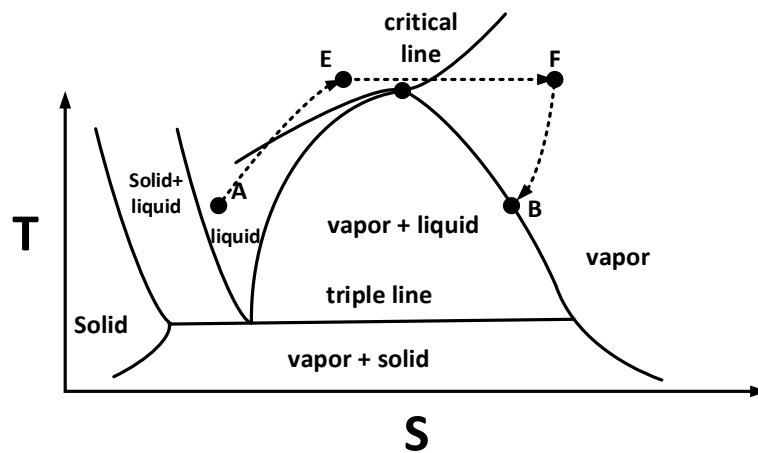


(e) TS diagram

Path ADB



Path AEFB



Problem 4

【Solution】

(a)

For ideal solution,

$$\underline{\underline{\Delta H_{mix}^{id} = 0}}$$

$$\underline{\underline{\Delta S_{mix}^{id} = -R(x_A \ln x_A + x_B \ln x_B)}}$$

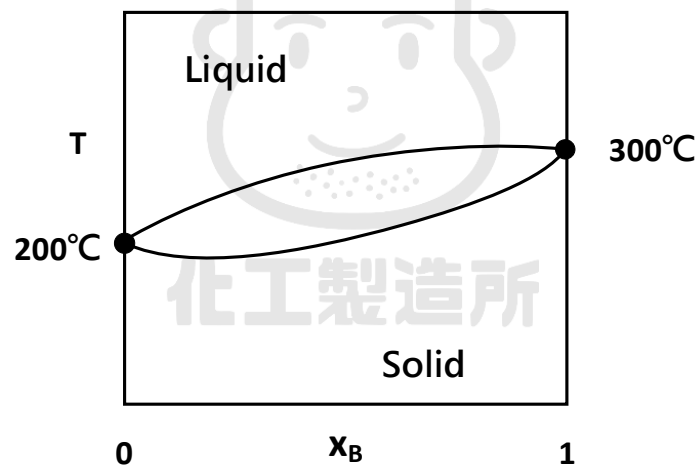
(b)

For ideal solution,

$$\underline{\underline{H^{ex} = H^{id} - H^{id} = 0}}$$

$$\underline{\underline{S^{ex} = S^{id} - S^{id} = 0}}$$

(c)



(自由能-組成相圖畫法可參考 106 年清大化熱化反 Problem 2 後解說。)

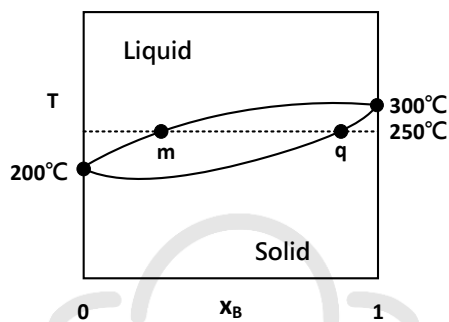
(d)

$$\overline{G}_A^S = G_A^0 + \Delta G_{mix,A} = \underline{\underline{G_A^0 + RT \ln x_A}}$$

(e)

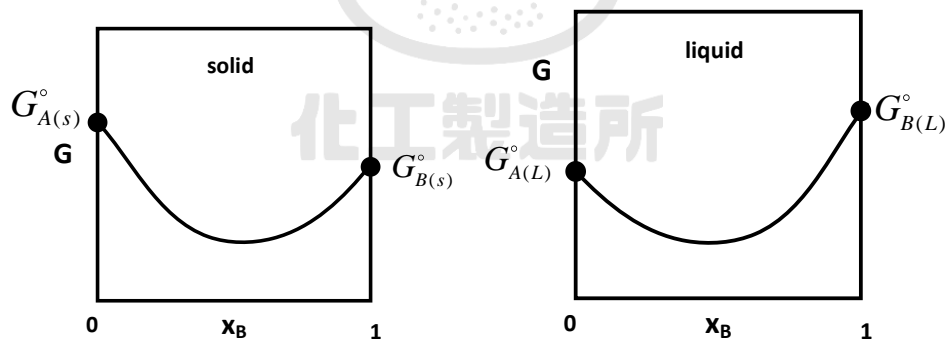
Assume $\begin{cases} \text{Liquid phase} \rightarrow \text{ideal solution} \\ \text{solid phase} \rightarrow \text{ideal solution} \end{cases}$

@250°C

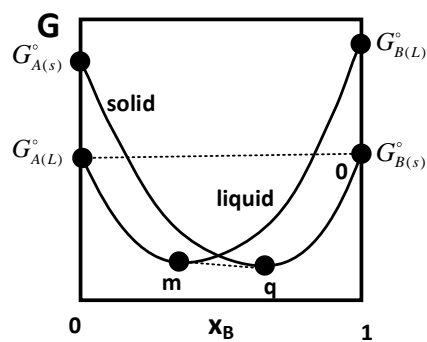


Set the standard states as : $G_{A(L)}^\circ = 0$ and $G_{B(s)}^\circ = 0$

Assume $G_{A(s)}^\circ < G_{B(L)}^\circ$



合併：



Problem 5

【Solution】

For regular liquid mixture,

$$\begin{aligned}\Delta \underline{S}_{mix} &= \Delta \underline{S}_{mix}^{id} = \underline{\underline{-R(x_A \ln x_A + x_B \ln x_B)}} \\ &= -8.314(0.6 \ln 0.6 + 0.4 \ln 0.4) \\ &= \underline{\underline{5.595 \text{ (J / K)}}}\end{aligned}$$

For $\Delta nH_{mix} = \Delta nG_{mix} + T\Delta nS_{mix}$

$$\begin{aligned}\Delta \underline{G}_{mix} &= \underline{G}^{ex} + \Delta \underline{G}_{mix}^{id} = RT(x_A x_B + x_A \ln x_A + x_B \ln x_B) \\ &= 8.314 \times 300 \times (0.6 \times 0.4 + 0.6 \ln 0.6 + 0.4 \ln 0.4) \\ &= -1080.02 \text{ (J / mole)} \\ \Delta \underline{H}_{mix} &= -1080.02 + 300 \times 5.595 = \underline{\underline{598.47 \text{ (J / mole)}}}\end{aligned}$$

Problem 6

【Solution】

$$\because \text{ideal liquid mixture} \Rightarrow y_i P = x_i P_i^{sat}$$

$$\Rightarrow P_A^{sat} = 0.708 \text{ bar}, P_B^{sat} = 0.0663 \text{ bar}$$

$$\Rightarrow y_A \times 0.5 = x_A \times 0.708 \text{---(1)}$$

$$y_B \times 0.5 = x_B \times 0.0663 \text{---(2)}$$

$$(1) + (2) : 0.5 = 0.708x_A + 0.0663(1 - x_A) \Rightarrow x_A = 0.675$$

$$y_A = 0.957$$

$$\Rightarrow \begin{cases} \text{liquid:} & \begin{cases} x_A = 0.675 \\ x_B = 0.325 \end{cases} \\ \text{gas:} & \begin{cases} y_A = 0.957 \\ y_B = 0.043 \end{cases} \end{cases}$$

(本題與 103 清大化熱化反 Problem 5-(b)雷同)

Problem 7

【Solution】

@dew point, $y_A = 0.95$

By Raoult's law,

$$y_A P = x_A P_A^{sat}$$

$$y_B P = x_B P_B^{sat}$$

$$0.95 \times 1 = x_A e^{10.4 - \left(\frac{26800}{RT}\right)} = x_A e^{10.4 - \left(\frac{26800}{8.314T}\right)}, \quad x_A = \frac{0.95}{e^{10.4 - \left(\frac{26800}{8.314T}\right)}}$$

$$0.05 \times 1 = x_B e^{11.4 - \left(\frac{35200}{RT}\right)} = x_B e^{11.4 - \left(\frac{35200}{8.314T}\right)}, \quad x_B = \frac{0.05}{e^{11.4 - \left(\frac{35200}{8.314T}\right)}}$$

上兩式相加，

$$1 = x_A + x_B = \frac{0.95}{e^{10.4 - \left(\frac{26800}{8.314T}\right)}} + \frac{0.05}{e^{11.4 - \left(\frac{35200}{8.314T}\right)}}$$

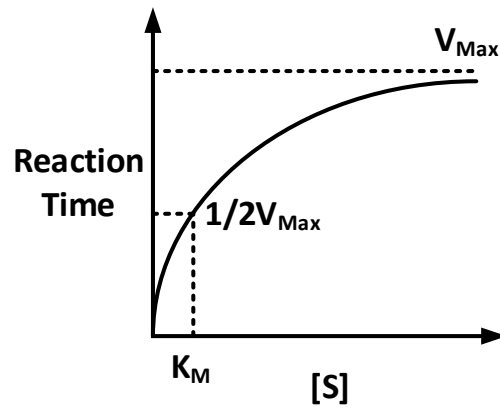
$$\underline{\underline{T = 319.9 \text{ (K)}}}$$

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Problem 8

【Solution】

(a)



(b)

\therefore

$$V_{\text{max}} = k_{\text{cat}} [E]_0 \propto [E]_0$$

$[E]_0$ 變兩倍， V_{max} 也變兩倍

(c)

K_M 只與酵素種類有關，因此若使用的是同種酵素，則 K_M 值不變。

(d)

因為可反應之酵素活性位有限，若反應受質濃度太高，也只能在相同活性位數量下反應，因此反應速率將會達到一最大值。

Problem 9

【Solution】

By figure (A),

$$\text{壓力小時， } -r_A \propto P_{total}^2 = P_A^2$$

壓力大時， $-r_A$ 趨近一定值，則分子分母同次，選(B)或(C)

By figure (B),

C 之分壓與 $-r_A$ 無關，選(C)

By figure (C)

B 之分壓與 $-r_A$ 成反比，(C)符合

Problem 10

【Solution】

(1)

Elementary reaction

$$\underline{\underline{Rate\ law = kC_A C_B^2}}$$

(2)

為 gas phase reaction,

$$C_A = \frac{C_{A0}(1-x)y}{(1+\varepsilon x)}$$

$$C_B = \frac{C_{A0}(2-2x)y}{(1+\varepsilon x)}$$

$$\varepsilon = (1-2-1) \times \frac{1}{3} = \frac{-2}{3}$$

(3)

A 與 B 濃度關係錯誤：

$$\theta_B = \frac{C_{B0}}{C_{A0}} = 2$$

(4)

y 的表示法錯誤：

$$\because \varepsilon \neq 0$$

$$\frac{dy}{dW} = \frac{-\alpha}{2y}(1 + \varepsilon x)$$

(本題(4)可參考 FOGLER, *H. Elements of Chemical Reaction Engineering*, 4th ed.; p 180.)

(本題出自於：<http://umich.edu/~elements/course/lectures/four/whats4p.htm>)



109 年清大化熱化反

Problem 1

【Solution】

The Van der Waals equation is,

$$(P + \frac{a'}{V^2})(V - b') = RT \text{ or}$$

$$(P + a \frac{n^2}{V^2})(V - nb) = nRT$$

\Rightarrow The answer is (E)

Problem 2

【Solution】

(2)

(A)

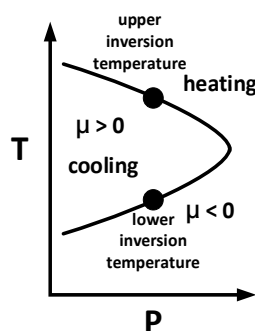
For ideal gas H is a function only of T

$$\Rightarrow \mu \equiv (\frac{\partial T}{\partial P})_H = 0$$

(\because H is constant, T is constant)

(B)

There are two types of inversion temperature



$$\left\{ \begin{array}{l} \text{upper inversion temperature:} \\ \text{lower inversion temperature:} \end{array} \right. \left\{ \begin{array}{l} \text{above: } \mu < 0 \\ \text{below: } \mu > 0 \\ \text{above: } \mu > 0 \\ \text{below: } \mu < 0 \end{array} \right.$$

(C)

For liquid undergoing Joule-Thomson expansion,

\therefore isenthalpic process

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

$$C_p dT + [V - T\left(\frac{\partial V}{\partial T}\right)_P] dP = 0$$

$$C_p dT + V\left[1 - \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P\right] dP = 0$$

\therefore liquid is usually nearly incompressible,

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \beta \approx 0 \text{ 代回}$$

$$C_p dT + V\left[1 - \frac{T}{V}\cancel{\left(\frac{\partial V}{\partial T}\right)_P}\right] dP = C_p dT + V dP = 0$$

$\therefore P \downarrow$ (expansion), $dP < 0$

$$dT = \frac{-V dP}{C_p} > 0, \quad T \uparrow$$

$$P \downarrow, T \uparrow \Rightarrow \mu = \left(\frac{\partial T}{\partial P}\right)_H < 0$$

\Rightarrow the answer is (c)

(本題可參考：Atkins, P.; De Paula, J.; Keeler, J. *Atkins' Physical Chemistry*, 9th ed.; p 81~83.)

(3)

Consider the degree of freedoms for molecular motions on heat capacities,

$$C_V \approx \left(\frac{n_{\text{translational}}}{2} + \frac{n_{\text{rotational}}}{2} + n_{\text{vibrational}} \right) R$$

At ambient temperature, the relation simplifies to,

$$C_V \approx \left(\frac{n_{\text{translational}}}{2} + \frac{n_{\text{rotational}}}{2} \right) R$$

For gaseous species, assume ideal gas behavior,

$$C_P \approx \left(\frac{n_{\text{translational}}}{2} + \frac{n_{\text{rotational}}}{2} + 1 \right) R$$

(A) He 與 Ar 皆為單原子分子， $n_{\text{translational}} = 3$ ， $n_{\text{rotational}} = 0$ 代入：

$$C_P = \left(\frac{3}{2} + 1 \right) R = \underline{\underline{20.78 \text{ (J / mol} \cdot \text{K)}}}$$

(B)(C) N₂, CO, H₂, O₂ 皆為線性雙原子分子，應差不多：

$n_{\text{translational}} = 3$ ， $n_{\text{rotational}} = 2$ 代入：

$$C_P = \left(\frac{3}{2} + \frac{2}{2} + 1 \right) R = \underline{\underline{29.10 \text{ (J / mol} \cdot \text{K)}}}$$

(D) NH₃ 與 CH₄ 皆為非線性多原子分子：

$n_{\text{translational}} = 3$ ， $n_{\text{rotational}} = 3$ 代入：

$$C_P = \left(\frac{3}{2} + \frac{3}{2} + 1 \right) R = \underline{\underline{33.26 \text{ (J / mol} \cdot \text{K)}}} \text{ , } \Rightarrow \underline{\underline{\text{The answer is (E)}}$$

The real C_p data (in J / K · mol):

He_(g) : 20.786

Ar_(g) : 20.786

H_{2(g)} : 28.824

N_{2(g)} : 29.125

O_{2(g)} : 29.355

CO_(g) : 29.14

NH_{3(g)} : 35.06

CH_{4(g)} : 35.31

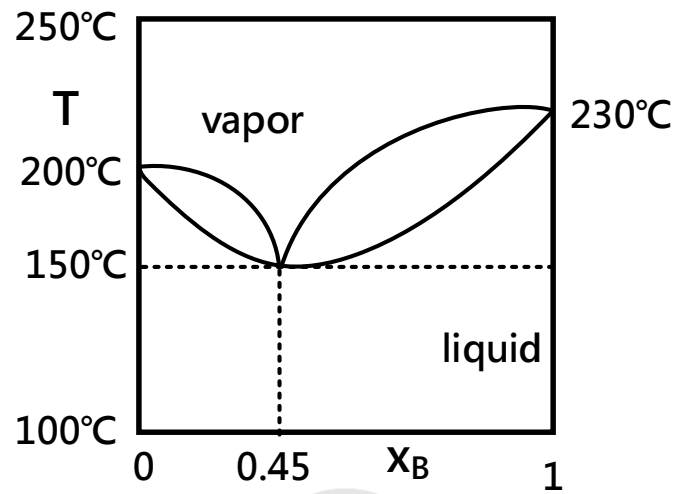
(資料來源：Atkins, P.; De Paula, J.; Keeler, J. *Atkins' Physical Chemistry*, 9th ed.; p 918~924.)

可以發現估算的數值與真實數值並沒有差很多，此題在選項上(C)的兩組是相差最多的，不過尚在估算的範圍內，所以我認為還是選(E)，端看同學選擇。

Problem 3

【Solution】

(a)



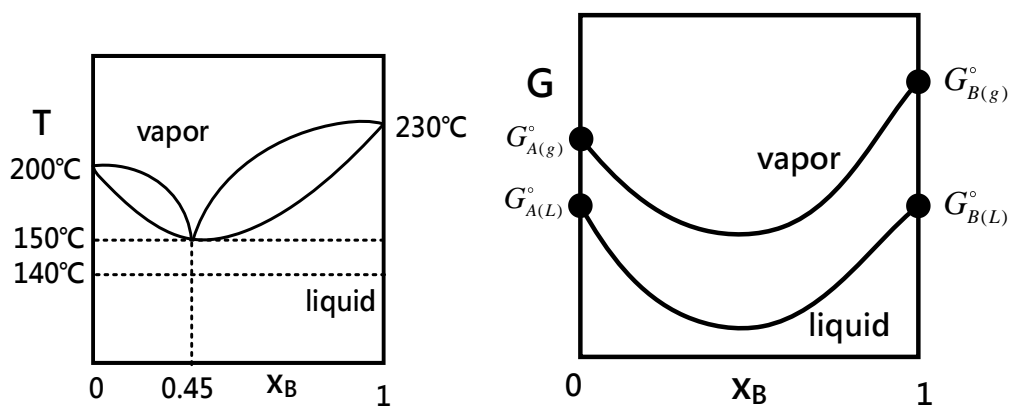
(b)

Assume : $\begin{cases} \text{liquid phase} \rightarrow \text{regular solution} \\ \text{vapor phase} \rightarrow \text{ideal gas} \end{cases}$

@At 140°C

Set the standard states as : $G_{A(L)}^{\circ} = 0$ and $G_{B(L)}^{\circ} = 0$

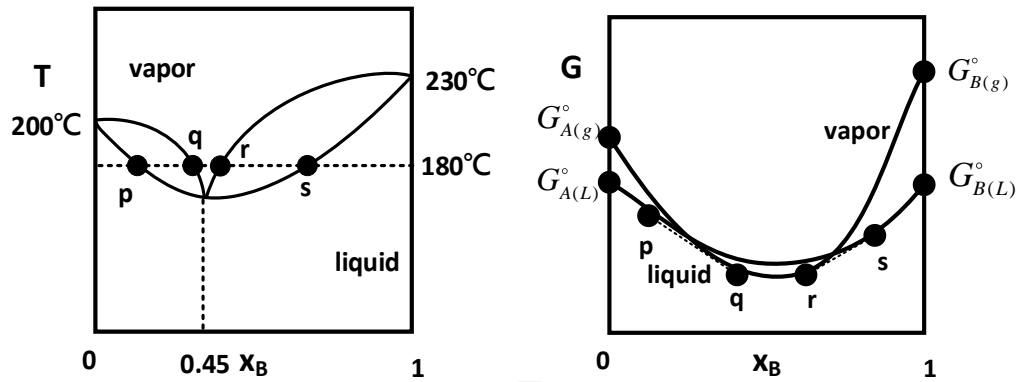
Assume $G_{A(g)}^{\circ} < G_{B(g)}^{\circ}$



@At 180°C

Set the standard states as : $G_{A(L)}^\circ = 0$ and $G_{B(L)}^\circ = 0$

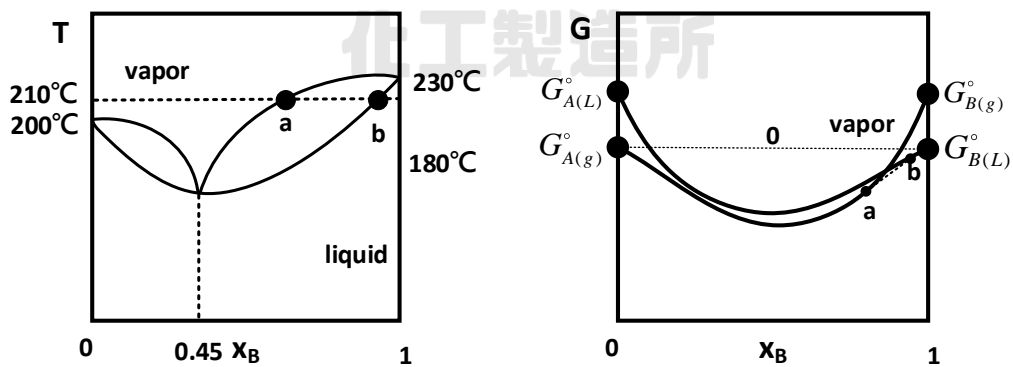
Assume $G_{A(g)}^\circ < G_{B(g)}^\circ$



@At 210°C

Set the standard states as : $G_{A(g)}^\circ = 0$ and $G_{B(L)}^\circ = 0$

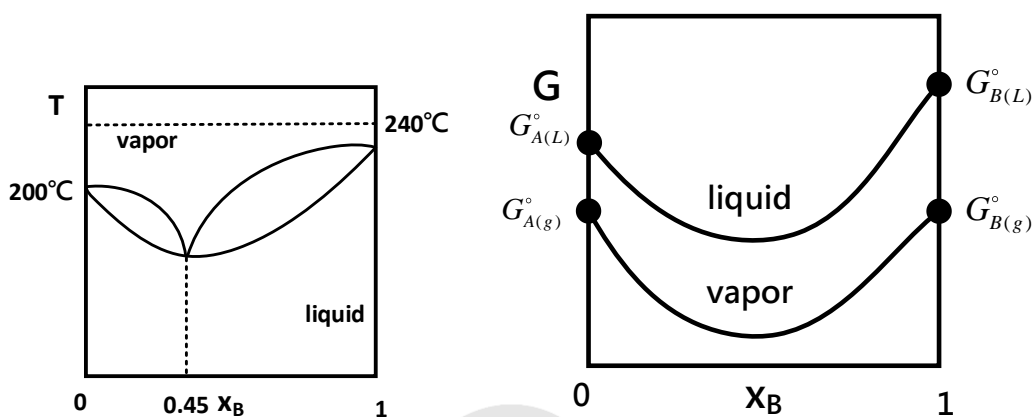
Assume $G_{A(g)}^\circ < G_{B(L)}^\circ$



@At 240°C

Set the standard states as : $G_{A(g)}^\circ = 0$ and $G_{B(g)}^\circ = 0$

Assume $G_{A(L)}^\circ < G_{B(L)}^\circ$



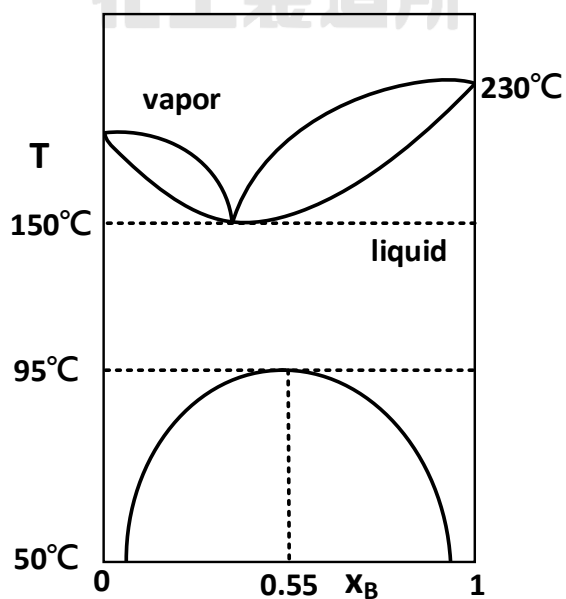
(相圖畫法可參考 106 年清大化熱化反 Problem 2 後解說。)

(本題可參考：Gaskell, D.; Laughlin, D. *Introduction to Thermodynamics of Materials*, 6th Edition, 6th ed.; Ch10.)

(c)

No, the solution of A and B will form azeotrope, which is not observed for ideal solution.

(d)

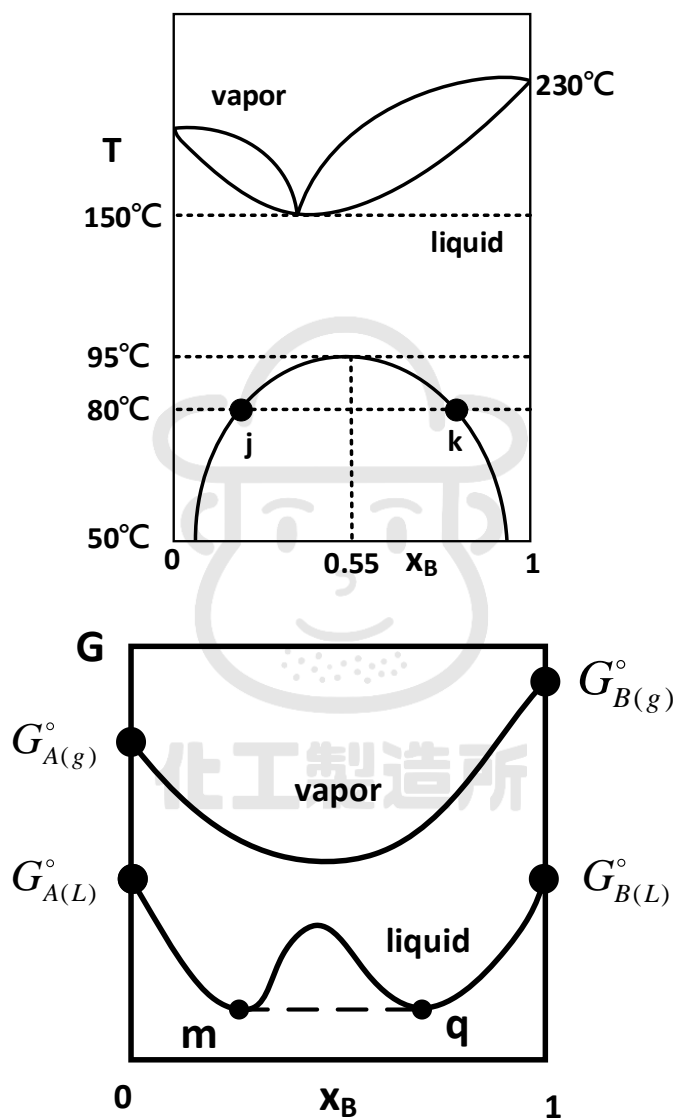


(e)

At 80°C

Set the standard states as : $G_{A(L)}^\circ = 0$ and $G_{B(L)}^\circ = 0$

Assume $G_{A(g)}^\circ < G_{B(g)}^\circ$



(相圖畫法可參考 106 年清大化熱化反 Problem 2 後解說。)

(本小題只要畫 liquid phase，不過就順便把 vapor phase 也畫一下。)

(本題可參考：Gaskell, D.; Laughlin, D. *Introduction to Thermodynamics of*

Materials, 6th Edition, 6th ed.; Ch10.)

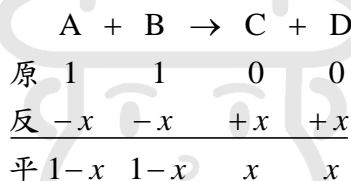
Problem 4**【Solution】****(a)**

$$\begin{aligned}\Delta G_{298}^{\circ} &= (\Delta G_{298,D}^{\circ} + \Delta G_{298,C}^{\circ}) - (\Delta G_{298,B}^{\circ} - \Delta G_{298,A}^{\circ}) \\ &= (-237129 - 332200) - (-174780 - 389900) = \underline{\underline{-4649 \text{ J}}}\end{aligned}$$

(b)

$$\text{By } \Delta G_{298}^{\circ} = -RT \ln K \Rightarrow -4649 = -8.314 \times 298.15 \ln K$$

$$\Rightarrow \underline{\underline{K = 6.524}}$$

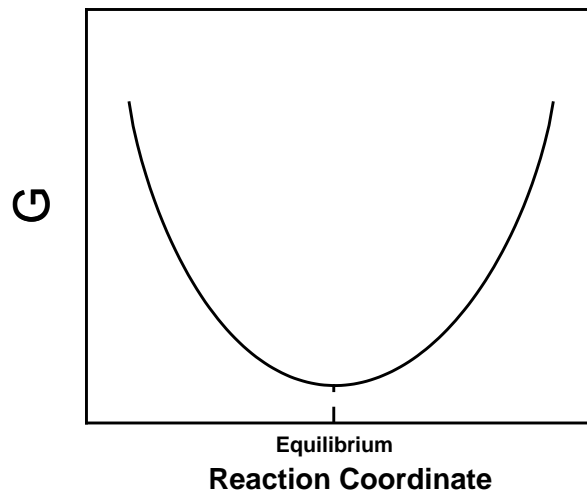
(c)

$$\Rightarrow K = \frac{C_C C_D}{C_A C_B} = \frac{\left(\frac{x}{V}\right)^2}{\left(\frac{1-x}{V}\right)^2} = \left(\frac{x}{1-x}\right)^2 = 6.524$$

$$\Rightarrow x = 0.7186$$

$$\Rightarrow \text{mole fraction of } C = \frac{x}{(1-x) + (1-x) + x + x} = \frac{x}{2} = \underline{\underline{0.359}}$$

(d)



(e)

At lowest Gibbs free energy, the system reaches equilibrium

$$\begin{cases} x_A = \frac{1-x}{2} = 0.141 = x_B \\ \underline{\underline{x_C = x_D = 0.359}} \end{cases}$$

(本題與 101 年清大 Problem 3 相同，與 106 年清大 Problem 6 相似)

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Problem 5

【Solution】

(a)

$$n_T = \frac{P_T V}{RT} = \frac{7.02 \times 2}{0.082 \times (1000 + 273)} = \underline{\underline{0.1345 \text{ moles}}}$$

(b)

Reaction:	$\text{CH}_{4(g)}$	\rightarrow	$\text{C}_{(s)}$	+	$2\text{H}_{2(g)}$
原	$\frac{0.1 \times 0.082 \times (1000 + 273)}{2}$		0		0
反	$-x$		$+x$		$+2x$
平	$5.219 - x$		x		$2x$

$$\text{且 } P_T = P_{\text{CH}_4} + P_{\text{H}_2} = 5.219 - x + 2x = 7.02$$

$$\Rightarrow x = 1.80$$

$$\Rightarrow \text{mole}_{\text{CH}_4, \text{reacted}} = \frac{xV}{RT} = \frac{1.80 \times 2}{0.082 \times (1000 + 273)} = \underline{\underline{0.03448 \text{ (moles)}}}$$

(c)

$$K_a = \frac{a_{\text{H}_2}^2}{a_{\text{CH}_4}} = \frac{\left(\frac{y_{\text{H}_2} P}{1}\right)^2}{\left(\frac{y_{\text{CH}_4} P}{1}\right)} = \frac{P_{\text{H}_2}^2}{P_{\text{CH}_4}} = \frac{(2x)^2}{5.219 - x} = \frac{(2 \times 1.80)^2}{5.219 - 1.80} = \underline{\underline{3.79}}$$

(本題可參考：Sandler, S. Chemical, Biochemical and Engineering Thermodynamics, 5th ed.;

p 744/ Illustration 13.1-1.)

(d)

$$\text{Define } Q = \frac{(P_{\text{H}_2})^2}{P_{\text{CH}_4}} = \frac{(5 \times 0.58)^2}{[5 \times (1 - 0.58)]} = 4.005 > K_a$$

\Rightarrow 反應將由右往左走，然而一開始並無 $\text{C}_{(s)}$ 存在，因此槽內組成維持相同且無

$\text{C}_{(s)}$ 被生成

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical*

Engineering Thermodynamics, 7th ed.; p 539, Problem 13.32/13.34.)

Problem 6

【Solution】

(a)

Consider the dimensionless group, vessel distribution number:

$$\frac{D}{uL} : \begin{cases} D: \text{longitudinal dispersion} \\ u: \text{velocity of the flow} \\ L: \text{characteristic length} \end{cases}$$

$$\Rightarrow \begin{cases} \frac{D}{uL} \rightarrow 0, \text{negligible dispersion, like PFR} \\ \frac{D}{uL} \rightarrow \infty, \text{large dispersion, like CSTR} \end{cases}$$

For RTD 1: the dispersion is not as obvious as RTD 2 \Rightarrow PFR

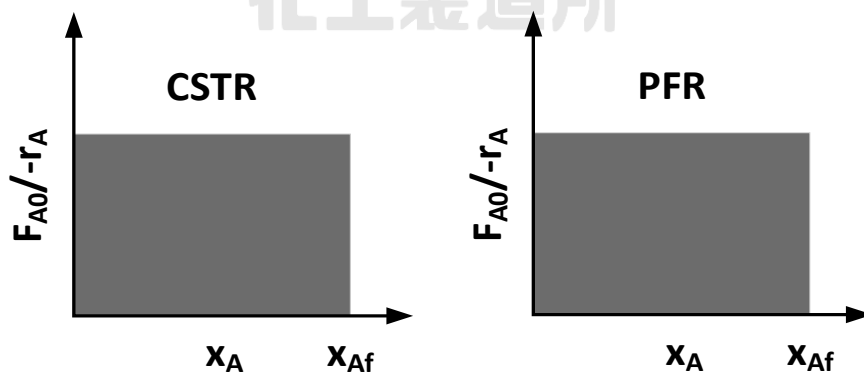
$$\text{and RTD 2 is CSTR: } \begin{cases} \text{RTD 1} \Rightarrow \text{PFR} \\ \text{RTD 2} \Rightarrow \text{CSTR} \end{cases}$$

(CSTR 因為 well mixed 性質，因此濃度分布較廣)

(本題可參考：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 295~297.)

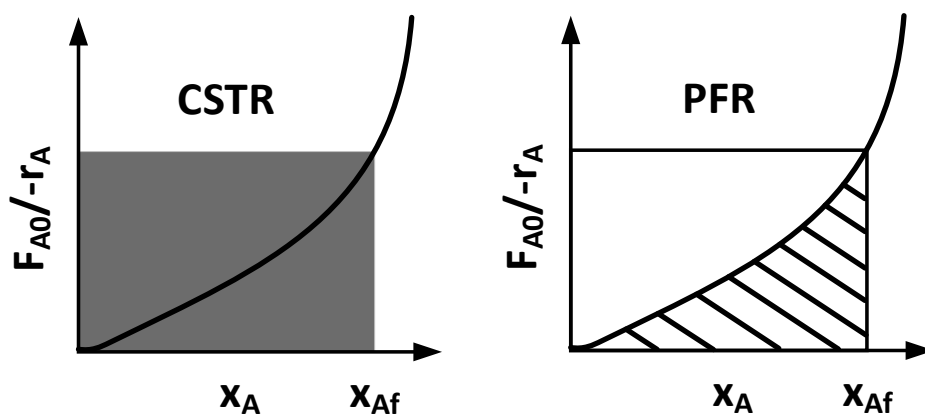
(b)

For 0th-order reaction:



$$\Rightarrow \underline{\underline{x_{Af, CSTR} = x_{Af, PFR}}}$$

For first-order reaction:



$$\Rightarrow \underline{x_{Af, PFR} > x_{Af, CSTR}}$$

(c)

Reactor (1) will maximize the yield of B because PFR will maintain at high concentration of A and thus increase the rate of production of B.

(關於 series reaction 在 CSTR 與 PFR 中最大濃度的探討，可以參考：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 171~178。不同形式之連鎖反應在兩種反應器中的濃度變化可參考社團補充檔案 – series reaction。)

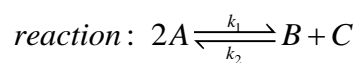
(d)

Reactor (2) will maximize the selectivity of B to C because the production of C depends on a higher-order of concentration of A, so we choose CSTR-type reactor.

(本小題可參考：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 153.)

Problem 7**【Solution】**

令 diphenyl = B, pure benzene = A, hydrogen = C



(a)

$$K_{eq} = \frac{C_{Be} C_{Ce}}{C_{Ae}^2} = \frac{(C_{A0} \cdot \frac{1}{2} x_{Ae})^2}{C_{A0}^2 (1 - x_{Ae})^2} = 0.3 \Rightarrow \underline{\underline{x_{Ae} = 0.523}}$$

(b)

For CSTR,

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

For rate equation,

$$\begin{aligned} -r_A &= k_1 C_A^2 - k_2 C_B C_C = k_1 C_{A0}^2 \left[\left(\frac{1 - x_A}{1 + \varepsilon x_A} \right)^2 - \frac{1}{K} \left(\frac{\frac{1}{2} x_A}{1 + \varepsilon x_A} \right)^2 \right], \quad \varepsilon = 0 \\ &= k_1 C_{A0}^2 \left[(1 - x_A)^2 - \frac{x_A^2}{4K} \right] \end{aligned}$$

$$\begin{cases} k_1 = 1800 \text{ ft}^3 / \text{lbmol} \cdot \text{s} \\ C_{A0} = \frac{P_{A0}}{RT} = \frac{5}{0.73 \times (760 + 273) \times 1.8} = 0.0037 \text{ mol} / \text{ft}^3 \\ x_A = 0.523 \times 0.98 = 0.5125 \\ K = 0.3 \end{cases} \quad \text{代入}$$

$$\Rightarrow V = \frac{10 / 60 \times 0.5125}{1800 \times 0.0037^2 [(1 - 0.5125)^2 - \frac{0.5125^2}{4 \times 0.3}]} = \underline{\underline{184.61 \text{ ft}^3}}$$

Problem 8

【Solution】

(a)

$$\text{令 } \begin{cases} A = NO \\ B = O_2 \\ C = NO_2 \end{cases} \Rightarrow 2A + B \rightarrow 2C$$

By the unit of rate constant, the rate law is

$$-r_A = kP_A^2P_B = \frac{-dP_A}{dt}$$

\therefore The source of oxygen is air

$$P_B \approx P_{B0} = 0.21 = 2.1 \times 10^5 (\text{ppm})$$

$$\Rightarrow \int_{P_{A0}}^{P_A} \frac{-dP_A}{P_A^2} = 2.1 \times 10^5 \int_0^t k dt$$

$$\Rightarrow \left(\frac{1}{P_A} - \frac{1}{P_{A0}} \right) = 2.1 \times 10^5 \times kt$$

$$P_{A0} = 3000, P_A = 1500, k = 1.4 \times 10^{-9} \text{ 代入}$$

$$\Rightarrow \left(\frac{1}{1500} - \frac{1}{3000} \right) = 2.1 \times 10^5 \times 1.4 \times 10^{-9} t$$

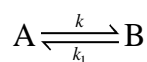
$$\Rightarrow \underline{\underline{t = 1.134 \text{ min}}}$$

(b)

$$P_{A0} = 1, P_A = 0.5 \text{ 代入}$$

$$\Rightarrow \left(\frac{1}{0.5} - \frac{1}{1} \right) = 2.1 \times 10^5 \times 1.4 \times 10^{-9} t$$

$$\Rightarrow \underline{\underline{t = 3401.36 \text{ min}}}$$

Problem 9**【Solution】**

By energy balance,

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

$$\text{for } \sum_i \int_{T_{i0}}^T \theta_{i0} C_{P_i} dT = \int_{T_{i0}}^T (141 + \frac{0.1}{0.9} \times 161) dT = 158.89(T - 330)$$

$$-[\Delta H_R(T_R) + \int_{T_R}^T \Delta C_P dT] = -[-6900 + \int_{273+25}^T (141-141) dT] = 6900$$

$$\Rightarrow 0.4 = \frac{158.89(T - 330)}{6900} \Rightarrow T = 347.37 \text{ (K)}$$

By design equation of CSTR,

$$V = \frac{F_{A0} x_A}{-r_A} = \frac{F_{A0} x_A}{k C_A - k_1 C_B} = \frac{F_{A0} x_A}{k C_{A0} [(1 - x_A) - \frac{1}{K} x_A]}$$

For $k_{(T=347.37)}$

$$\Rightarrow k_{347.37} = 31.1 \exp\left[\frac{-65.7 \times 10^3}{8.314} \left(\frac{1}{347.37} - \frac{1}{360}\right)\right] = 14.00 \text{ h}^{-1}$$

For $K_{(347.37)}$

$$\Rightarrow K_{347.37} = 3.03 \times \exp\left[\frac{-6900}{8.314} \left(\frac{1}{273+60} - \frac{1}{347.37}\right)\right] = 2.73$$

$$\Rightarrow V = \frac{163 \times 0.9 \times 0.4}{14.00 \times 9.3 \left[(1 - 0.4) - \frac{0.4}{2.73}\right]} = 0.994 \text{ (dm}^3\text{)}$$

Problem 10

【Solution】

Decay rate law,

$$\begin{aligned}r_d &= \frac{-da}{dt} = k_d a^2 \\ \Rightarrow \int_1^a \frac{-da}{a^2} &= \int_0^t k_d dt \\ \Rightarrow \frac{1}{a} - 1 &= k_d t \Rightarrow a = \frac{1}{1 + k_d t}\end{aligned}$$

For x_A , by design equation of batch

$$\begin{aligned}-r_A &= \frac{-1}{W} \frac{dN_A}{dt} = \frac{N_{A0}}{W} \frac{dx_A}{dt} = \frac{k'}{1 + k_d t} C_A = \frac{k'}{1 + k_d t} C_{A0} (1 - x_A) = \frac{k'}{1 + k_d t} \frac{N_{A0}}{V} (1 - x_A) \\ \frac{dx_A}{dt} &= \frac{W}{V} k' a(t) (1 - x_A), \text{ 令 } \frac{W}{V} k' = k \\ \Rightarrow \int_0^{x_A} \frac{dx_A}{1 - x_A} &= \int_0^t \frac{k}{1 + k_d t} dt \\ \Rightarrow \ln \frac{1}{1 - x_A} &= \frac{k}{k_d} \ln \frac{1 + k_d t}{1} \\ \Rightarrow 1 - x_A &= \frac{1}{(1 + k_d t)^{\left(\frac{k}{k_d}\right)}} \\ \Rightarrow x_A &= 1 - \frac{1}{(1 + k_d t)^{\left(\frac{k}{k_d}\right)}}\end{aligned}$$

※此題的指數項擺的是 k'/k_d ，然而原文書上證明是將 k' 與 W 、 V 合併成為

k ，因此結果有所不同，在此採用的解法為原文書上解法。

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 711,

Example 10-5.)

110 年清大化熱化反

Problem 1

【Solution】

By energy balance,

$$\Delta H + \underbrace{\frac{\Delta v^2}{2g_c} + \frac{g}{g_c} \Delta z}_{\text{negligible}} = \cancel{\emptyset} + \cancel{W}_{\text{adiabatic, no shaft work}}$$

$$\Delta H = 0 \text{ (isenthalpic process)}$$

1. Ans : (A)

【Solution】

\because isenthalpic process

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

$$C_p dT + [V - T\left(\frac{\partial V}{\partial T}\right)_P] dP = 0$$

$$C_p dT + V\left[1 - \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P\right] dP = 0$$

\because incompressible liquid

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \beta = 0 \text{ 代回}$$

$$C_p dT + V\left[1 - \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P\right] dP = C_p dT + V dP = 0$$

$\because P_1 > P_2$, $dP < 0$

$$dT = \frac{-V dP}{C_p} > 0 \text{ , } \underline{\underline{T_1 < T_2}}$$

※此題所用到之 incompressible liquid 性質為根據化熱 Smith 原文書所定義(第 7 版 p 68)

以 Smith 原文書的觀點來說，若一個流體滿足 incompressible liquid 的假設，則

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = 0, \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = 0$$

然而在另一本化熱原文書 Sandler，其對於 incompressible liquid 之定義只有

$$\left(\frac{\partial V}{\partial P} \right)_T = 0 \quad (\text{第五版 p 67})$$

在這裡所採用的是 Smith 的定義，而若是以 Sandler 的定義來寫則 $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \neq 0$

但液體之 β 一般來說都很微小($10^{-4} \sim 10^{-6}$)，也可能可以忽略不計而得相同的結果。

2. Ans : (A)

【Solution】

$$\because dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV, \quad dU = C_V dT$$

$$\because T_1 < T_2, \quad \underline{\underline{U_1 < U_2}}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 206, Example 6.2.)

※本題因考慮到題目是給溫度與壓力變化求其大小關係，同學也可採用 $U(T, P)$ 的方式作答：

$$dU = \left(\frac{\partial U}{\partial T} \right)_P dT + \left(\frac{\partial U}{\partial P} \right)_T dP$$

$\because U = H - PV$ 代入：

$$dU = \underbrace{\left(\frac{\partial H}{\partial T} \right)_P}_{C_P} dT - \cancel{V \left(\frac{\partial P}{\partial T} \right)_P dT} - \underbrace{P \left(\frac{\partial V}{\partial T} \right)_P}_{\text{incompressible}} dT + \left(\frac{\partial H}{\partial P} \right)_T dP - \underbrace{V \left(\frac{\partial P}{\partial P} \right)_T}_1 dP - \underbrace{P \left(\frac{\partial V}{\partial P} \right)_T}_{\text{incompressible}} dP$$

$$\left(\frac{\partial H}{\partial P} \right)_T dP = \underbrace{V dP - T \left(\frac{\partial V}{\partial T} \right)_P dP}_{\text{incompressible}} \text{ 代入}$$

$$dU = C_P dT + V dP - V dP = C_P dT$$

$$T_2 > T_1, \quad dT > 0, \quad \underline{\underline{dU > 0}}$$

事實上，根據 Smith 第七版 p.206, Example 6.2 最後的推導結論，對於 incompressible fluid,

$$\boxed{C_P = C_V = C}, \text{ 也可從此證明出。}$$

3. Ans : (C)

【Solution】

$$\Delta H = 0 \text{ , } \underline{\underline{H_1 = H_2}}$$

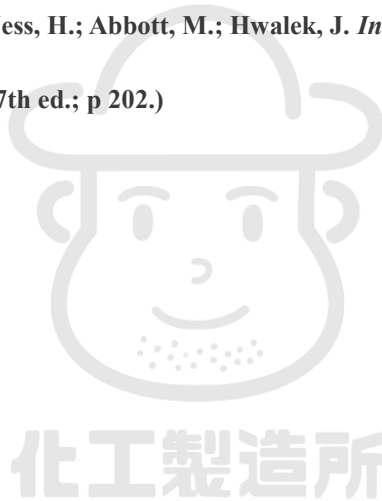
4. Ans : (A)

【Solution】

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \\ &= \frac{C_p}{T} dT - \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{\text{incompressible liquid}} dP \end{aligned}$$

$$\therefore dT > 0 \text{ , } dS > 0 \text{ , } \underline{\underline{S_2 > S_1}}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 202.)



5. Ans : (B)

【Solution】

By entropy balance,

$$\frac{dS}{dt} = \sum_i \dot{M}_k \hat{S}_k + \cancel{\sum \frac{\dot{Q}}{T}}_{adiabatic} + \dot{S}_{gen}$$
$$\dot{S}_{gen} = -\sum_i \dot{M}_k \hat{S}_k = \dot{M} \underbrace{(S_2 - S_1)}_{>0} > 0$$

The process is irreversible

6. Ans : (C)

【Solution】

For ideal gas,

$$dH = C_p(T)dT = 0, \quad \underline{T_1 = T_2}$$

7. Ans : (C)

【Solution】

For ideal gas,

$$T_1 = T_2, \quad \underline{U_1(T) = U_2(T)}$$

8. Ans : (C)

【Solution】

$$T_1 = T_2, \quad H_1 = H_2$$

9. Ans : (A)

【Solution】

$$S_2 - S_1 = \underbrace{\dot{n} C_p \ln \frac{T_2}{T_1}}_{T_2 > T_1} - \underbrace{\dot{n} R \ln \frac{P_2}{P_1}}_{P_2 < P_1} = -\dot{n} R \ln \frac{P_2}{P_1} > 0$$

$$\underline{\underline{S_2 > S_1}}$$

10. **Ans : (B)**

【Solution】

By entropy balance,

$$\frac{dS}{dt} = \sum_i \dot{M}_k \hat{S}_k + \sum_{\text{adiabatic}} \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

$$\dot{S}_{gen} = -\sum_i \dot{M}_k \hat{S}_k = \dot{n}(S_2 - S_1) = (S_2 - S_1) > 0$$

The process is **irreversible**

Problem 2

【Solution】

11. **Ans : (C)**

【Solution】

Define selectivity : $S_{R/S} = \frac{k_1 C_A^2}{k_2 C_A} = \frac{k_{01}}{k_{02}} e^{\frac{-(80-120)}{RT}} C_A$

$$\begin{cases} \text{concentration: } C_A \uparrow, S_{R/S} \uparrow \\ \text{temperature: } T \downarrow, S_{R/S} \uparrow \end{cases}$$

The reaction should be conducted at **low temperature in a PFR**

12. **Ans : (B)**

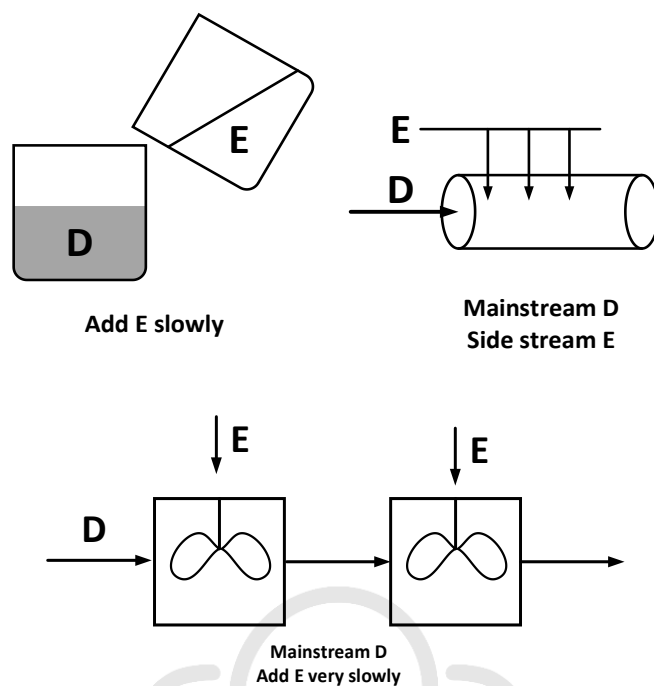
【Solution】

Define selectivity,

$$S_{F/G} = \frac{k_1 C_D C_E^{0.3}}{k_2 C_D C_E^{1.8}} = \frac{k_1}{k_2} C_D^{0.5} C_E^{-1.5}$$

$$C_D \uparrow, C_E \downarrow, S_{F/G} \uparrow$$

The desirable contacting schemes may be,



13. **Ans : (C)**

【Solution】

For fractional yield,

$$\varphi = \frac{dC_B}{-dC_A} = \frac{k_1 C_A - k_2 C_B}{k_1 C_A} = 1 - \frac{k_2 C_B}{k_1 C_A}$$

$\frac{k_2}{k_1} \uparrow, \varphi \downarrow$

14. **Ans : (D)**

【Solution】

$$\varphi = \frac{dC_R}{-dC_A} = \frac{k C_A^{1.5} C_B^{0.8}}{k C_A^{1.5} C_B^{0.8} + k C_A^{0.5} C_B^{1.7}} = \frac{1}{1 + C_A^{-1} C_B^{0.9}}$$

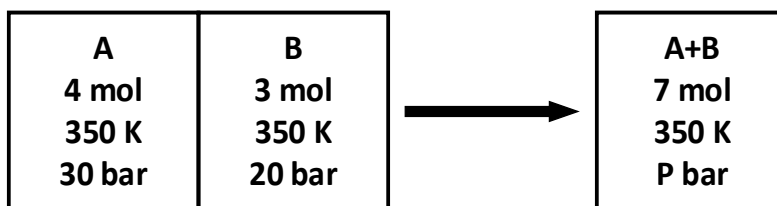
$$C_A \uparrow, C_B \downarrow, \varphi \uparrow$$

15. **Ans : (B)**

Problem 3

【Solution】

(a)



∵ A and B are ideal gases,

$$\Delta T = 0, \quad \underline{\underline{\Delta H = 0}}$$

For entropy change, by entropy balance,

$$\Delta S = \underbrace{nC_p \ln \frac{T_f}{T_i}}_{T_f = T_i = 350\text{ K}} - nR \ln \frac{P_f}{P_i} = -nR \ln \frac{P_f}{P_i}$$

For P_f

$$V_A + V_B = V_{total}, \quad \frac{n_A \cancel{RT_A}}{P_A} + \frac{n_B \cancel{RT_B}}{P_B} = \frac{(n_A + n_B) \cancel{RT}}{P_f}$$

$$\frac{4}{30} + \frac{3}{20} = \frac{4+3}{P_f}, \quad P_f = 24.7(\text{bar}) \text{ 代回}$$

$$\Delta S = -(n_A R \ln \frac{P_{f,A}}{P_{i,A}} + n_B R \ln \frac{P_{f,B}}{P_{i,B}}) = -8.314(4 \ln \frac{24.7 \times \frac{4}{7}}{30} + 3 \ln \frac{24.7 \times \frac{3}{7}}{20})$$

$$= \underline{\underline{40.93(J / K)}}$$

$$\Delta G = \Delta H - T\Delta S = 0 - 350 \times 40.93 = \underline{\underline{-14325.6 (J)}}$$

(b)

$$\begin{aligned} H &= 600x_C + 400x_D + x_Cx_D(40x_C + 20x_D) \\ &= 600x_C + 400(1-x_C) + x_C(1-x_C)[40x_C + 20(1-x_C)] \\ &= -20x_C^3 + 220x_C + 400 \end{aligned}$$

$$H_{C,pure} = H|_{x_C=1} = 600(J/mol)$$

$$\begin{aligned} \overline{H}_C &= H + x_D \frac{dH}{dx_C} \\ &= -20x_C^3 + 220x_C + 400 + (1-x_C)(-60x_C^2 + 220) \\ &= 40x_C^3 - 60x_C^2 + 620(J/mol) \end{aligned}$$

$$\because H_{C,pure} \neq \overline{H}_C, \text{ The solution isn't ideal}$$



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Problem 4

【Solution】

(a)

【看法(1)】

$$F = C - P + 2 - E - r$$

$$F = 2 - 2 + 2 - 0 - 1 = 1$$

where $r = \text{sepcial constraint} = 1$

because of the addition relation that when azeotropic mixture is formed,

$$x_i = y_i$$

【看法(2)】

因為題目限定 101.3kPa，且在此張相圖上壓力為固定，因此此時：

$$F = C - P + 1 - E - r$$

$$F = 2 - 2 + 1 - 0 - 1 = 0$$

where $r = \text{sepcial constraint} = 1$

because of the addition relation that when azeotropic mixture is formed,

$$x_i = y_i$$

此時自由度為 0，在相圖上為一個固定點

※本題題目問法有兩種看法，一種為當“兩物質形成共沸物時，共沸物的自由度為何”，一種為“相圖上”共沸點的自由度為何。前者情況因為壓力溫度皆沒有固定，因此自由度為 1，也就是給定溫度或壓力以後，共沸點才固定在那個點上；後者情況是固定在這張相圖上，共沸點的自由度為何，因為有明確的位置，所以自由度為 0，與上述討論相符。

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. Introduction to Chemical Engineering Thermodynamics, 7th ed.; p 515~516, Example 13.11.)

(b)

The liquid phase isn't an ideal solution because it forms azeotrope.

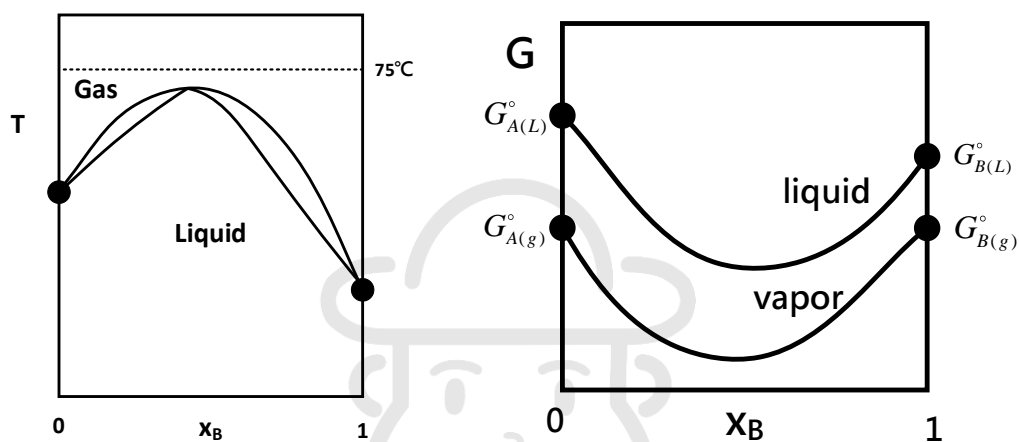
(c)

Assume : $\begin{cases} \text{liquid phase} \rightarrow \text{non-ideal solution} \\ \text{vapor phase} \rightarrow \text{ideal gas} \end{cases}$

Set the standard states as : $G_{A(g)}^\circ = 0$ and $G_{B(g)}^\circ = 0$

Assume $G_{A(L)}^\circ > G_{B(L)}^\circ$

@75°C

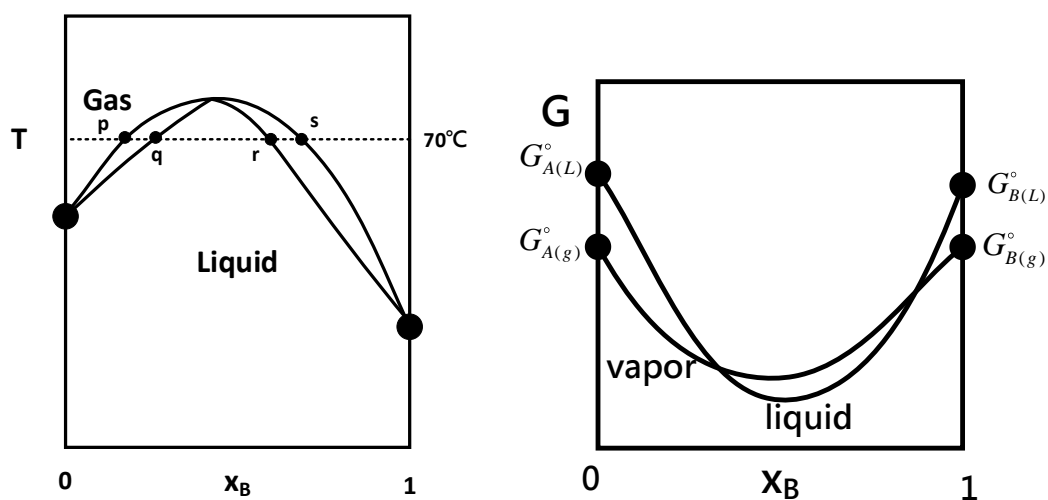


(d)

@70°C

Set the standard states as : $G_{A(g)}^\circ = 0$ and $G_{B(g)}^\circ = 0$

Assume $G_{A(L)}^\circ > G_{B(L)}^\circ$

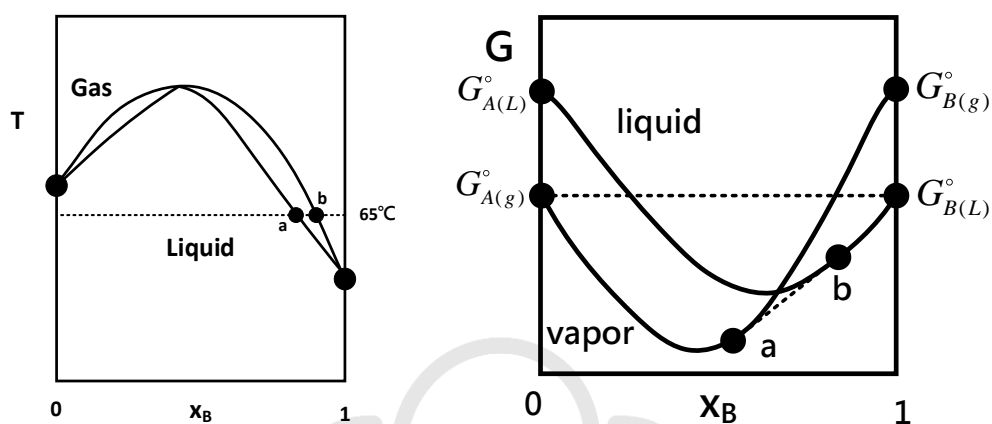


(e)

@65°C

Set the standard states as : $G_{A(L)}^\circ = 0$ and $G_{B(g)}^\circ = 0$

Assume $G_{A(g)}^\circ > G_{B(L)}^\circ$



Problem 5

【Solution】

Let,

$$k_1 = k_{01} e^{\frac{-E_{a1}}{RT}}, \quad k_2 = k_{02} e^{\frac{-E_{a2}}{RT}}$$

$$K = \frac{k_1}{k_2} = \frac{k_{01}}{k_{02}} e^{\frac{-(E_{a1}-E_{a2})}{RT}} = A e^{\frac{-(E_{a1}-E_{a2})}{RT}} = \exp\left[\frac{-\Delta G^\circ}{RT}\right]$$

$$\therefore H_i^\circ = -RT^2 \frac{d\left(\frac{G^\circ}{RT}\right)}{dT}$$

$$\Delta H_i^\circ = -RT^2 \frac{d\left(\frac{\Delta G^\circ}{RT}\right)}{dT}, \quad \frac{d\left(\frac{\Delta G^\circ}{RT}\right)}{dT} = \frac{-\Delta H^\circ}{RT^2}$$

$$\frac{\Delta G^\circ}{RT} = \frac{\Delta H^\circ}{RT} + C \text{ 代回}$$

$$K = \exp\left[\frac{-\Delta G^\circ}{RT}\right] = \exp\left[\frac{-\Delta H^\circ}{RT} - C\right] = B \exp\left[\frac{-\Delta H^\circ}{RT}\right] = A \exp\left[\frac{-(E_{a1} - E_{a2})}{RT}\right]$$

$$\underline{\underline{\Delta H^\circ = E_{a1} - E_{a2}}}$$

Problem 6

【Solution】

Rate equation,

$$-r_p = kC_p C_Q = kC_p^2 = kC_{p0}^2 (1 - x_p)^2$$

Design equation of CSTR,

$$V = \frac{F_{p0}(x_{p,out} - x_{p,in})}{-r_p} = \frac{F_{p0}(x_{p,out} - x_{p,in})}{kC_{p0}^2 (1 - x_{p,out})^2}$$

$$\tau = \frac{(x_{p,out} - x_{p,in})}{kC_{p0} (1 - x_{p,out})^2}$$

$$x_{p,in} = x_{p,out} - kC_{p0} (1 - x_{p,out})^2 \tau$$

For the three CSTRs,

$$x_{p2} = 0.75 - 3.5 \times 1.2 (1 - 0.75)^2 \tau = 0.75 - 0.2625 \tau$$

$$\begin{aligned} x_{p1} &= x_{p2} - 3.5 \times 1.2 (1 - x_{p2})^2 \tau \\ &= 0.75 - 0.2625 \tau - 4.2 (1 - 0.75 + 0.2625 \tau)^2 \tau \\ &= 0.75 - 0.2625 \tau - 4.2 \tau (0.25 + 0.2625 \tau)^2 \end{aligned}$$

$$\begin{aligned} x_{p0} &= x_{p1} - 3.5 \times 1.2 (1 - x_{p1})^2 \tau \\ &= [0.75 - 0.2625 \tau - 4.2 \tau (0.25 + 0.2625 \tau)^2] - 4.2 \tau \{1 - [0.75 - 0.2625 \tau - 4.2 \tau (0.25 + 0.2625 \tau)^2]\}^2 \\ &= 0 \end{aligned}$$

$$\tau = 0.3754 = \frac{F_{p0}}{v_{p0}} = \frac{9300}{3} \cdot \frac{1}{v_{p0}} \quad , \quad \underline{\underline{v_{p0} = 8257.7 (L/h)}}$$

$$x_{p2} = 0.75 - 0.2625 \times 0.3754 = \underline{\underline{0.6514}}$$

$$x_{p1} = 0.6514 - 3.5 \times 1.2 (1 - 0.6514)^2 \times 0.3754 = \underline{\underline{0.4599}}$$

Problem 7

【Solution】

Rate equation,

$$-r_A = ka(t)C_A = a(t)kC_{A0}(1-x_A)$$

Design equation,

$$r_A W = \frac{dN_A}{dt} = N_{A0} \frac{-dx_A}{dt}$$

Combine,

$$N_{A0} \frac{dx_A}{dt} = (-r_A W) = a(t)kC_{A0}(1-x_A)W$$

$$\frac{dx_A}{dt} = a(t) \frac{kW}{V} (1-x_A)$$

For $a(t)$, \because first-order decay rate law

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

$$a(t) = e^{-k_d t} \text{ 代回}$$

$$\frac{dx_A}{dt} = e^{-k_d t} \frac{kW}{V} (1-x_A)$$

$$\int_0^{x_A} \frac{dx_A}{1-x_A} = \frac{kW}{V} \int_0^t e^{-k_d t} dt$$

$$\int_0^{x_A} \frac{dx_A}{1-x_A} = \frac{0.2 \times 1}{1} \int_0^{10} e^{-0.1t} dt, \quad \underline{\underline{x_A = 0.717}}$$

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

p 711~712, Example 10-5, 為 109 清大化熱化反 Problem 10 之應用題)

(本題出自：<http://www.umich.edu/~elements/fogler&gurmen/html/course/lectures/ten/test23-1.htm>)

Problem 8

【Solution】

By energy balance,

$$\frac{dT}{dt} = \frac{-\sum F_i C_{pi}(T - T_{i0}) + (-H_{Rx}^\circ)(-r_A V)}{\sum N_i C_{pi}} = 0$$

(注意這裡題目給錯式子， $\sum F_i C_{pi}(T - T_{i0})$ 前應該有負號)

$$-\sum F_i C_{pi}(T - T_{i0}) + (-H_{Rx}^\circ)(-r_A V) = 0$$

For $(-r_A V)$, by design equation (batch),

$$-r_A V = \frac{-dN_A}{dt} = k C_A V = k N_A$$

$$\int_{N_{A0}}^{N_A} \frac{dN_A}{N_A} = -\int_0^t k dt, \quad N_A = N_{A0} e^{-kt} \text{ 代回}$$

$$-F_C C_{pC}(T - T_{C0}) + (\Delta H_{Rx}^\circ)(k N_{A0} e^{-kt}) = 0$$

$$-0.5 F_C (100 - 80) + (25000)(1.2 \times 10^{-4} \times 50 \times 0.5 e^{-2 \times 3600 \times 1.2 \times 10^{-4}}) = 0$$

$$\underline{\underline{F_C = 3.16 \text{ (lb / s)}}}$$

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

p 636, Problem 9-6B.)

(本題之正確能量守恆方程式可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*,

4th ed.; p 593.)

111 年清大化熱化反

題號	答案	題號	答案	題號	答案	題號	答案
1	(C)	6	(A)	11	(B)	16	(B)
2	(A)	7	(A)	12	(D)	17	(C)
3	(C)	8	-	13	(C)		
4	(D)	9	(A)	14	(B)		
5	(E)	10	(A)	15	(B)		

Problem 1

1. 2.

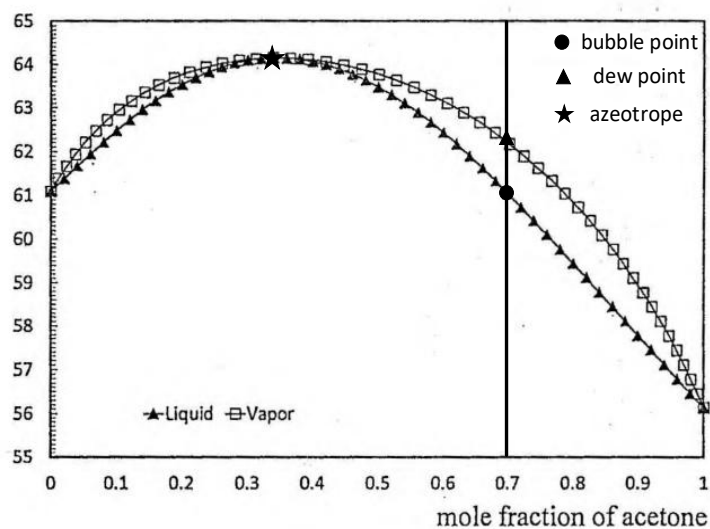
【Solution】

When the mole fraction of acetone is 0, it represents pure chloroform, whose boiling point is approximately, by the figure, 61°C

When the mole fraction of acetone is 1, which is pure acetone, the boiling point is about 56°C.

3. 4. 5.

【Solution】



Problem 2

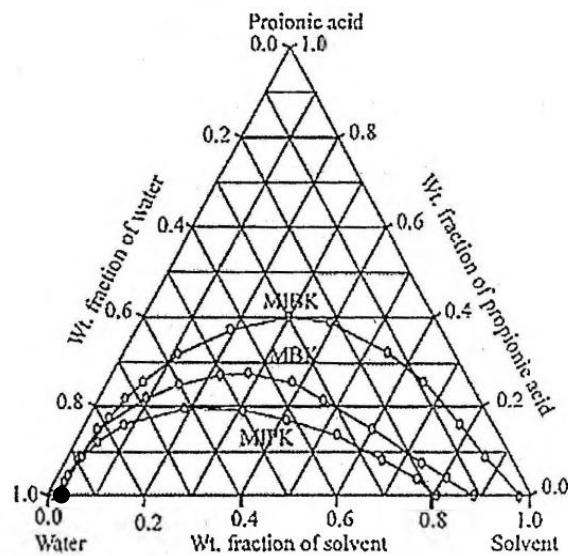
6. 7.

【Solution】

第 6 與 7 小題題意不清，將其改為：

(6) What is the solubility of MIBK in water?

(7) What is the solubility of MBK in water?

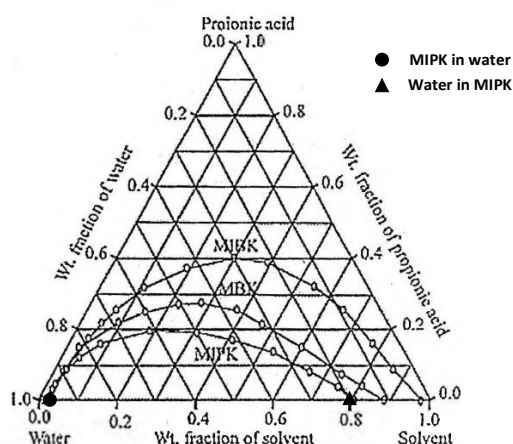


對 MIBK 而言，在水中慢慢滴加 MIBK，則最終達到圖中圓點就會形成相分離，此時 MIBK 分率為 0.01。(如圖中圓點)

對 MBK 而言，在水中慢慢滴加 MBK，則最終達到圖中圓點就會形成相分離，此時 MBK 分率為 0.01。(如圖中圓點)

8. 9.

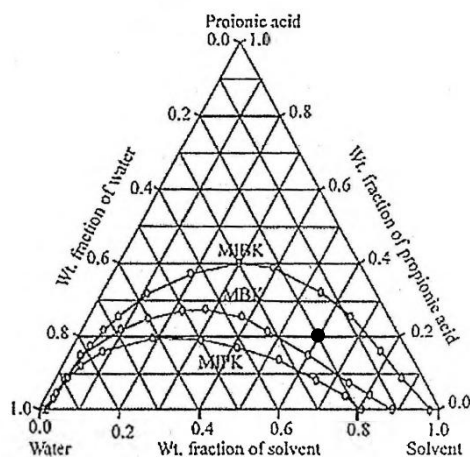
【Solution】



對 MIPK 而言，在 MIPK 中慢慢滴加水，則最終達到圖中三角形點就會形成相分離，此時 MIPK 分率為 0.8，水分率為 0.2。(如圖中三角形點)，此題無答案
對水而言，在水中慢慢滴加 MIPK，則最終達到圖中圓形點就會形成相分離，此時 MIPK 分率為 0.01，水分率為 0.99。(如圖中圓形點)

10.

【Solution】



對於 MBK 與 MIPK 兩系統而言，圓點在相分離區域外，因此形成均勻單一相
對於 MIBK 而言，圓點在相分離區域內，因此形成兩相

Problem 3

11.

【Solution】

於圖中可看出，當轉化率接近 0.8 時，就已呈現漸進線的特徵，因此可推測平衡轉化率大約為 0.8

12.

【Solution】

By the design equation of CSTR,

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

然而題目並未給出可用於計算之 $-r_A$ 數據，無法得知 flow rate

13.

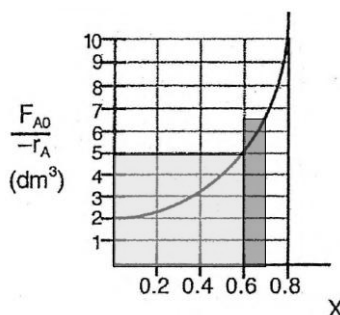
【Solution】

將配置變為兩個體積變為一半的反應器並聯，且個別 flow rate 也變為一半，則轉化率將不變

14.

【Solution】

由題目給的資訊作圖，第一個反應器出口轉化率為 0.6；假設末轉化率為 0.7，則可做圖如下：



此時第二個反應器體積 $> 0.6 \text{ dm}^3$ ，然而轉化率卻 < 0.8 ，因此在題目的配置下，其轉化率一定 < 0.8

Problem 4

15.

【Solution】

By mole balance of species A, $in - out + gen = \cancel{accu}$

$$F_{A0} - F_A + \int^V r_A dV = 0, \quad r_A < 0$$

By mole balance of species B, $in - out + gen = \cancel{accu}$

$$F_{B0} - F_B + \int^V r_B dV = 0, \quad r_B < 0$$

By mole balance of species C, $in - out + gen = \cancel{accu}$

$$0 - F_C + \int^V r_C dV = 0$$

The relationship of the flow rate,

$$F_{A0} = F_{B0}$$

$$F_A = F_B$$

(係數、進料流率相同)

The relationship of the reaction rate,

$$-2r_A = -2r_B = r_C$$

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16.

【Solution】

For PFR, design equation,

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

For rate expression,

$$-r_A = kC_A = \frac{kC_{A0}(1-x_A)}{(1+\varepsilon x_A)} \quad (\text{gas phase elementary reaction})$$

Combine,

$$V = \int_0^{x_A} \frac{F_{A0} dx_A}{kC_{A0} \frac{(1-x_A)}{(1+\varepsilon x_A)}} = \int_0^{x_A} \frac{v_0(1+\varepsilon x_A) dx_A}{k(1-x_A)} = \frac{v_0}{k} [(1+\varepsilon) \ln\left(\frac{1}{1-x_A}\right) - \varepsilon x_A]$$

$$V = \frac{v_0}{k} [(1+\varepsilon) \ln\left(\frac{1}{1-x_A}\right) - \varepsilon x_A]$$

將 $\ln\left(\frac{1}{1-x_A}\right)$ 泰勒展開得：

$$\ln\left(\frac{1}{1-x_A}\right) = x_A + \frac{x_A^2}{2} + \frac{x_A^3}{3} + \dots$$

因轉化率 $x_A \leq 1$ ，保留前二項

$$\ln\left(\frac{1}{1-x_A}\right) \approx x_A + \frac{x_A^2}{2}$$

代回：

$$V = \frac{v_0}{k} [(1+\varepsilon)\left(x_A + \frac{x_A^2}{2}\right) - \varepsilon x_A] = \frac{v_0}{k} \left[x_A + (1+\varepsilon)\left(\frac{x_A^2}{2}\right)\right]$$

If the concentration of R decreases, ε will be smaller, as a result, the conversion will increase with the same entering volumetric flow rate.

17.

【Solution】

對於 batch 或 PFR，其設計方程式皆為：

$$\frac{-dC_A}{dt} \text{ or } \frac{-dC_A}{d\tau} = -r_A$$

因此若是有相同的 space time，其最後算出來的轉化率就會相同。

Problem 5

【Solution】

(a)

After the equilibrium is reached, the volume ratio of A to B is the same as the mole ratio of A to B,

$$\frac{V_{A,f}}{V_{B,f}} = \frac{n_A}{n_B} = \frac{\left(\frac{P_{A,i} V_{A,i}}{RT_{A,i}}\right)}{\left(\frac{P_{B,i} V_{B,i}}{RT_{B,i}}\right)} = \frac{\left(\frac{20 \times 1}{273.15 + 250}\right)}{\left(\frac{10 \times 5}{273.15 + 700}\right)} = 0.74$$

The volume of A becomes, (截面積一樣，用長度表示)

$$(5+1) \times \frac{0.74}{0.74+1} = 2.56 \text{ (m)}$$

The piston moves by,

$$2.56 - 1 = \underline{\underline{1.56 \text{ (m)}}}$$

(b)(c)

By energy balance,

$$n_A C_V T_{A,i} + n_B C_V T_{B,i} = (n_A + n_B) C_V T_f$$

$$P_{A,i} V_{A,i} + P_{B,i} V_{B,i} = P_f V_f$$

$$20 \times 1 + 10 \times 5 = P_f \times 6, \quad \underline{\underline{P_f = 11.67 \text{ (bar)}}}$$

For the temperature at equilibrium, by mole balance,

$$\frac{P_{A,i}V_{A,i}}{RT_{A,i}} + \frac{P_{B,i}V_{B,i}}{RT_{B,i}} = \frac{P_fV_f}{RT_f}$$
$$\frac{20 \times 1}{273.15 + 250} + \frac{10 \times 5}{273.15 + 700} = \frac{11.67 \times 6}{T + 273.15}, \quad T = \underline{\underline{508.24 \text{ (}^\circ\text{C)}}}$$

(本題改編自原文書習題：Milo D. Koretsky, *Engineering and Chemical Thermodynamics*,
2nd ed.; Problem 3.33.)



Problem 6

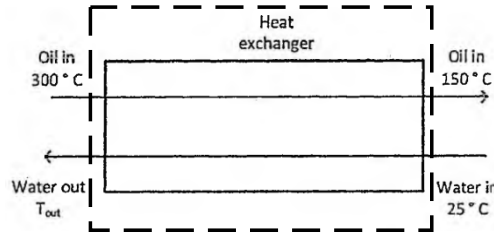
【Solution】

By energy balance,

$$q = \dot{m}_o C_{p,o} (T_{i,o} - T_{o,o}) = \dot{m}_w C_{p,w} (T_{o,w} - T_{i,w})$$

$$5 \times 2.5 \times (300 - 150) = 10 \times 4.2 \times (T_{o,w} - 25) \quad , \quad T_{out} = T_{o,w} = \underline{\underline{69.6 \text{ (}^\circ\text{C)}}}$$

By entropy balance on the heat exchanger,



$$\frac{dS}{dt} = \sum_i \dot{M}_k \hat{S}_k + \sum \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

s.s. no heat transfer

$$\dot{S}_{gen} = -\sum_i \dot{M}_k \hat{S}_k = -[\dot{m}_o (S_{o,in} - S_{o,out}) + \dot{m}_w (S_{w,in} - S_{w,out})]$$

$$= -(\dot{m}_o \int_{T_{o,o}}^{T_{i,o}} \frac{C_{p,o}}{T} dT + \dot{m}_w \int_{T_{o,w}}^{T_{i,w}} \frac{C_{p,w}}{T} dT) = \dot{m}_o C_{p,o} \ln \frac{T_{o,o}}{T_{i,o}} + \dot{m}_w C_{p,w} \ln \frac{T_{o,w}}{T_{i,w}}$$

$$= 5 \times 2.5 \ln \left(\frac{150 + 273.15}{300 + 273.15} \right) + 10 \times 4.2 \ln \left(\frac{47.1 + 273.15}{25 + 273.15} \right) = \underline{\underline{2.07 \text{ (kJ / K} \cdot \text{min)}}}$$

$$\dot{S}_{gen} > 0 \quad , \quad \underline{\underline{\text{The process is irreversible}}}$$

Problem 7

【Solution】

Define the reactivity ratio,

$$S_{B/XY} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2}$$

To find the maximum C_A when $S_{B/XY}$ reaches its maximum, let

$$\frac{dS_{B/XY}}{dC_A} = \frac{k_2(k_1 + k_3 C_A^2) - 2k_3 k_2 C_A^2}{(k_1 + k_3 C_A^2)^2} = 0$$

$$C_A = \sqrt{\frac{k_1}{k_3}} = \sqrt{\frac{0.0001}{0.008}} = 0.112 \text{ (mol / dm}^3\text{)}$$

To find the volume of CSTR, by the design equation of CSTR,

$$V = \frac{F_{A0} x_A}{-r_A} = \frac{v_0 (C_{A0} - C_A)}{-r_A}$$

By the rate expression,

$$-r_A = k_1 + k_2 C_A + k_3 C_A^2$$

Combine,

$$V = \frac{v_0 (C_{A0} - C_A)}{k_1 + k_2 C_A + k_3 C_A^2} = \frac{2.0 \times (0.4 - 0.112)}{0.0001 + 0.0015 \times 0.112 + 0.008 \times 0.112^2} = \underline{\underline{1567.5 \text{ (dm}^3\text{)}}}$$

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 312~314,

Example 6-2.)

Problem 8

【Solution】

$t_{1/10}$ 並非固定，因此非 1 次反應

Assume the rate law,

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

移項並積分：

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

$$C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt$$

At $t_{1/10}$, $\frac{C_A}{C_{A0}} = \frac{1}{10}$ 代入：

$$\left(\frac{1}{10} C_{A0}\right)^{1-n} - C_{A0}^{1-n} = (n-1)kt_{1/10} = \left[\left(\frac{1}{10}\right)^{1-n} - 1\right]C_{A0}^{1-n}$$

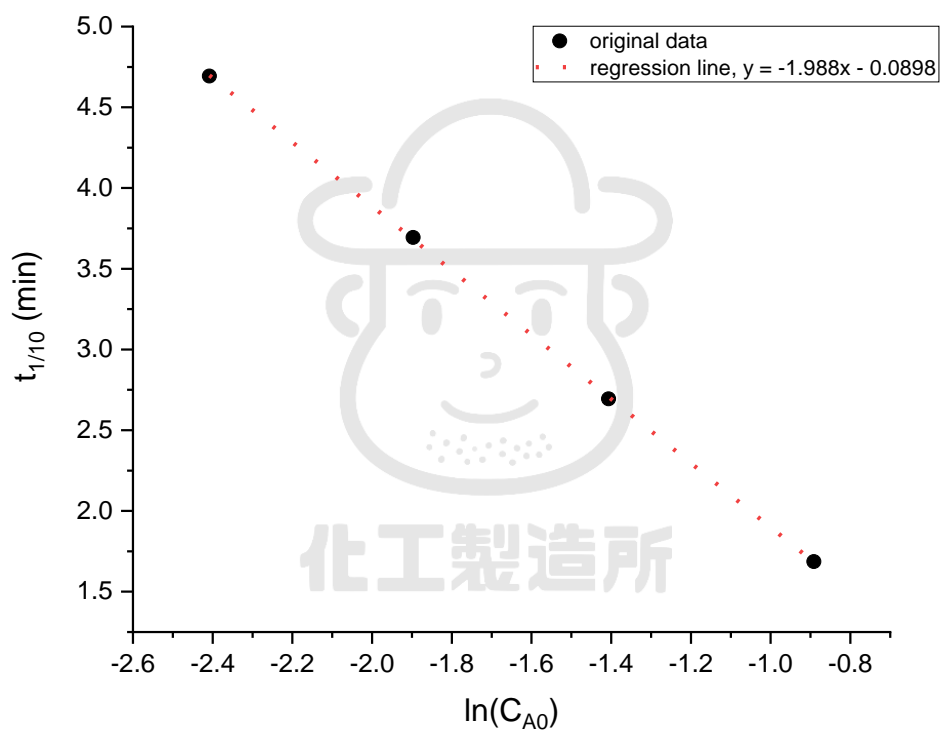
兩邊同取 ln

$$\ln t_{1/10} = \ln\left[\frac{10^{n-1} - 1}{(n-1)k}\right] + (1-n)\ln C_{A0}$$

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Plot $\ln t_{1/10} - \ln C_{A0}$

Run	1	2	3	4
C_{A0}	0.090	0.150	0.245	0.41
$\ln C_{A0}$	-2.408	-1.897	-1.406	-0.892
$t_{1/10}$	109.2	40.2	14.8	5.4
$\ln t_{1/10}$	4.693	3.694	2.695	1.686



$$(1-n) = -1.988, \quad \underline{\underline{n = 2.988 \approx 3}}$$

Problem 9

【Solution】

(a) For a typical single reaction, $a > 0$. Therefore, CSTR is not preferred because the reactant concentration may be very low, thus increasing the volume of the reactor needed.

(b)

If $a_2 > a_1$, CSTR is preferred because the reactant concentration is low to restrict the production of the byproducts.

If $a_2 < a_1$, batch reactor and PFR may be suitable because they keep the concentration of reactant high, favoring the production of the product.

(本小題可參考：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 153.)

(c)

For a series reaction, batch reaction or PFR will always produce higher $C_{product, max}$ than mixed flow reactor because they can maintain a sufficient high concentration of A to maximize the production of product.

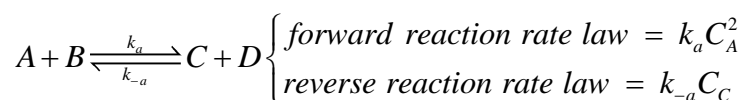
(關於 series reaction 在 CSTR 與 PFR 中最大濃度的探討，可以參考：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 171~178。不同形式之連鎖反應在兩種反應器中的濃度變化可參考社團補充檔案 – series reaction。)

Problem 10

【Solution】

(a)

Reaction,



$$K = \frac{k_a}{k_{-a}} = \frac{C_C}{C_A^2} = \frac{C_{A0} x_{Ae}}{C_{A0}^2 (1 - x_{Ae})^2}$$

$$\frac{x_{Ae}}{C_{A0} (1 - x_{Ae})^2} = \frac{0.002688}{0.004644} = \frac{x_{Ae}}{8.33(1 - x_{Ae})^2}, \quad \underline{\underline{x_{Ae} = 0.637}}$$

(b)

To produce 10 tons of C per day, the mole flow rate of A entering can be calculated as,

$$F_C = F_{A0} x_{Ae, reactor}$$
$$F_{A0} = \frac{F_C}{x_{Ae, reactor}} = \frac{10 \times 10^3}{0.637 \times 0.95} = 0.130 \text{ (kmol / min)}$$

For CSTR, design equation,

$$V = \frac{F_{A0} x_{Ae, reactor}}{-r_A}$$

For the rate law,

$$-r_A = k_a C_A^2 - k_{-a} C_C = k_a C_{A0}^2 (1 - x_{Ae, reactor})^2 - k_{-a} C_{A0} x_{Ae, reactor}$$

Combine,

$$V = \frac{F_{A0} x_{Ae, reactor}}{k_a C_{A0}^2 (1 - x_{Ae, reactor})^2 - k_{-a} C_{A0} x_{Ae, reactor}}$$
$$= \frac{0.130 \times 0.637 \times 0.95}{0.002688 \times 8.33^2 (1 - 0.637 \times 0.95)^2 - 0.004644 \times 8.33 \times 0.637 \times 0.95} = \underline{\underline{13.74 \text{ (m}^3\text{)}}}$$

(c)

For PFR, design equation,

$$V = \int_0^{x_{Ae, reactor}} \frac{F_{A0} dx_A}{-r_A}$$

For the rate law,

$$-r_A = k_a C_A^2 - k_{-a} C_C = k_a C_{A0}^2 (1 - x_A)^2 - k_{-a} C_{A0} x_A$$

Combine,

$$\begin{aligned} V &= \int_0^{x_{Ae, reactor}} \frac{F_{A0} dx_A}{k_a C_{A0}^2 (1 - x_A)^2 - k_{-a} C_{A0} x_A} \\ \tau &= \int_0^{x_{Ae, reactor}} \frac{C_{A0} dx_A}{k_a C_{A0}^2 (1 - x_A)^2 - k_{-a} C_{A0} x_A} \\ \tau &= \int_0^{x_{Ae, reactor}} \frac{dx_A}{k_a C_{A0} (1 - x_A)^2 - k_{-a} x_A} \\ &= \int_0^{0.637 \times 0.95} \frac{dx_A}{0.002688 \times 8.33 (1 - x_A)^2 - 0.004644 x_A} = \underline{\underline{119.98 \text{ (min)}}} \end{aligned}$$

For the reactor volume of PFR, we have

$$V = \tau v_0 = \tau \frac{F_{A0}}{C_{A0}} = 119.98 \times \frac{0.130}{8.33} = \underline{\underline{1.88 \text{ (m}^3\text{)}}}$$

$$\underline{\underline{V_{PFR} < V_{CSTR}}}$$

112 年清大化熱化反

Problem 1

【Solution】

(1) For the entropy change of gas,

$$\Delta S_1 = \cancel{nC_p \ln \frac{T_2}{T_1}} - nR \ln \frac{P_2}{P_1} = -1 \times 8.314 \ln \frac{6.5}{4} = -4.036 \text{ (J / K)}$$

isothermal

For the entropy change of the reservoir,

$$\Delta S_2 = \frac{-Q_{sys}}{T_{sur}}$$

For Q_{sys} , by the 1st law of thermodynamics on the gas,

$$\Delta U = Q + W_{irre} = 0$$

(isothermal process for ideal gas)

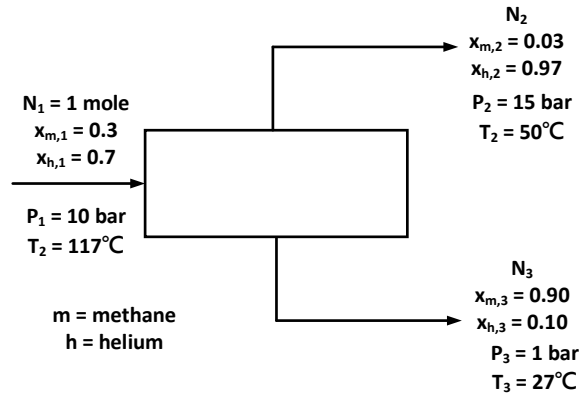
$$\begin{aligned} Q = -W_{irre} &= 1.2 \int_{V_1}^{V_2} P dV = 1.2 \int_{V_1}^{V_2} \frac{nRT}{V} dV = 1.2nRT \ln \frac{V_2}{V_1} \\ &= 1.2nRT \ln \frac{P_1}{P_2} = 1.2 \times 1 \times 8.314 \times (100 + 273.15) \ln \frac{4}{6.5} = -1807.47 \text{ (J)} \end{aligned}$$

$$\Delta S_2 = \frac{1807.47}{25 + 273.15} = 6.062 \text{ (J / K)}$$

$$\Delta S^{total} = -4.036 + 6.062 = \underline{\underline{2.026 \text{ (J / K)}}}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 144, Problem 5.26.)

(2)



By mole balance of the helium and methane,

$$1 \times 0.3 = 0.03N_2 + 0.90N_3$$

$$1 \times 0.7 = 0.97N_2 + 0.10N_3$$

$$N_2 = 0.690 \text{ (mole)} , N_3 = 0.310 \text{ (mole)}$$

By entropy balance on the stream,

$$\Delta S_{\text{sys}} = \sum_1^n N_k S_k + \frac{Q}{T} + S_{\text{gen}}$$

steady state
 adiabatic

$$\begin{aligned}
 S_{\text{gen}} &= -\sum_1^n N_k S_k = N_2 S_2 + N_3 S_3 - N_1 S_1 \\
 &= N_2 \{x_{m,2} [C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_{2,m}}{P_{1,m}}] + x_{h,2} [C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_{2,h}}{P_{1,h}}]\} \\
 &\quad + N_3 \{x_{m,3} [C_P \ln \frac{T_3}{T_1} - R \ln \frac{P_{3,m}}{P_{1,m}}] + x_{h,3} [C_P \ln \frac{T_3}{T_1} - R \ln \frac{P_{3,h}}{P_{1,h}}]\}
 \end{aligned}$$

$$\begin{aligned}
 S_{\text{gen}} &= 0.69 \times 8.314 \left[0.03 \times \left(\frac{9}{2} \ln \frac{273.15 + 50}{273.15 + 117} - \ln \frac{15 \times 0.03}{10 \times 0.3} \right) + 0.97 \times \left(\frac{5}{2} \ln \frac{273.15 + 50}{273.15 + 117} - \ln \frac{15 \times 0.97}{10 \times 0.7} \right) \right] \\
 &\quad + 0.31 \times 8.314 \left[0.9 \times \left(\frac{9}{2} \ln \frac{273.15 + 27}{273.15 + 117} - \ln \frac{1 \times 0.9}{10 \times 0.3} \right) + 0.1 \times \left(\frac{5}{2} \ln \frac{273.15 + 50}{273.15 + 117} - \ln \frac{1 \times 0.1}{10 \times 0.7} \right) \right]
 \end{aligned}$$

$$S_{\text{gen}} = -5.530 \text{ (J / K)} < 0$$

Which indicates the process violates the second law of thermodynamics.

For the total change of entropy, by consider entropy balance on surroundings,

$$\Delta S_{sur} = -\sum_1^n N_k S_k + \frac{Q}{\cancel{T_{sur}^{adiabatic}}} = -\sum_1^n N_k S_k = S_{gen}$$

$$\Delta S_{total} = \cancel{\Delta S_{sys}^{steady state}} + \Delta S_{sur} = S_{gen} = \underline{\underline{-5.530 \text{ (J / K)}}}$$

Which also indicates the process is impossible.

(※本題出自 MIT 化工熱力學課程網站之練習題，為 Problem set H 第 26 題，原題網址：

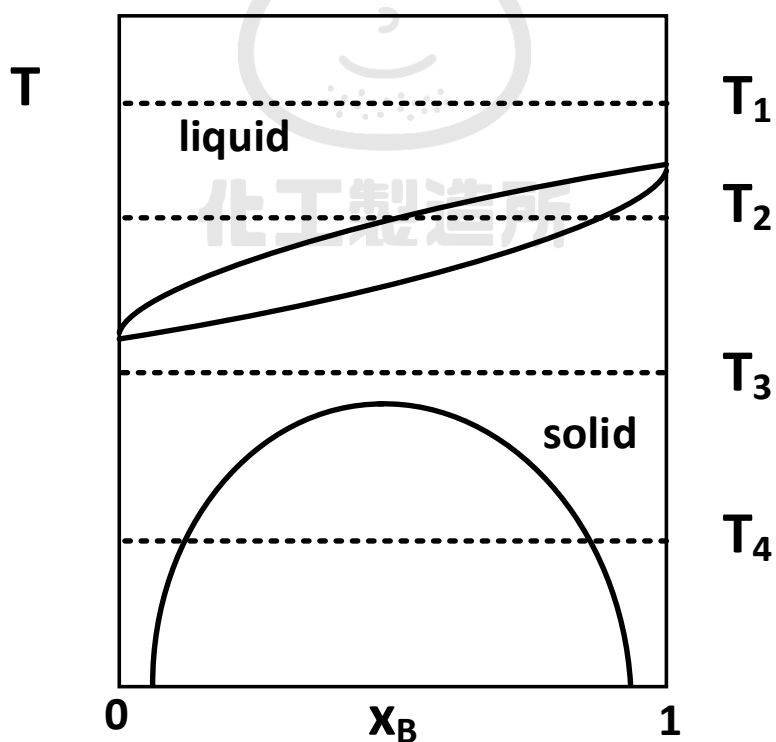
<http://web.mit.edu/10.213/www/problemsets.shtml>)

Problem 2

【Solution】

(3)

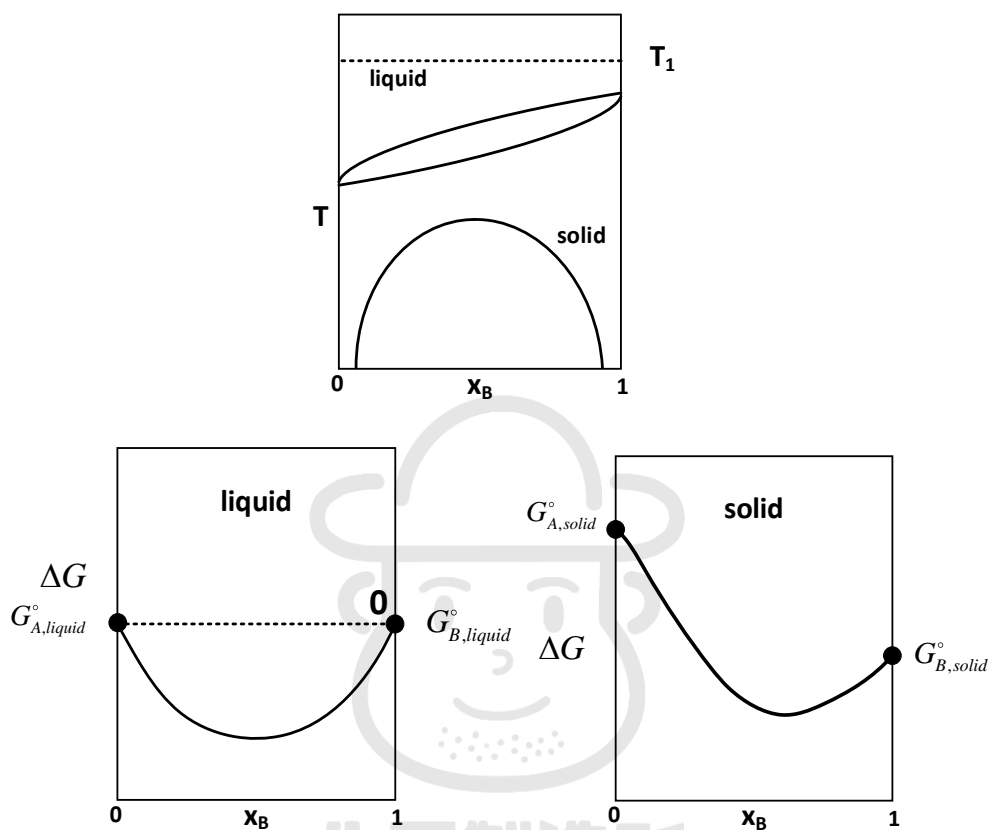
Assume : $\begin{cases} \text{solid} \rightarrow \text{regular solution} \\ \text{liquid phase} \rightarrow \text{ideal solution} \end{cases}$



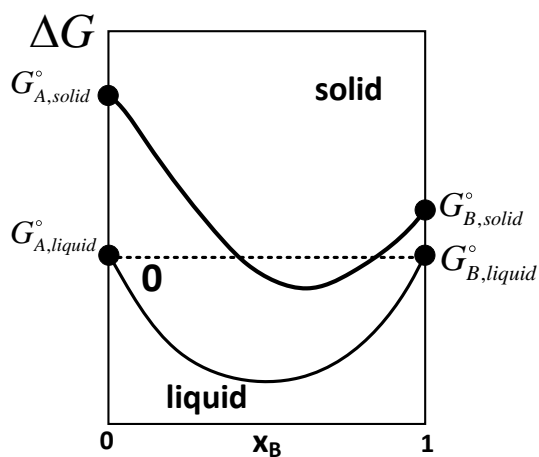
@At T_1

Set the standard states as : $G_{A,liquid}^\circ = 0$ and $G_{B,liquid}^\circ = 0$

Assume : $G_{B,solid}^\circ > G_{A,solid}^\circ$



Combine,



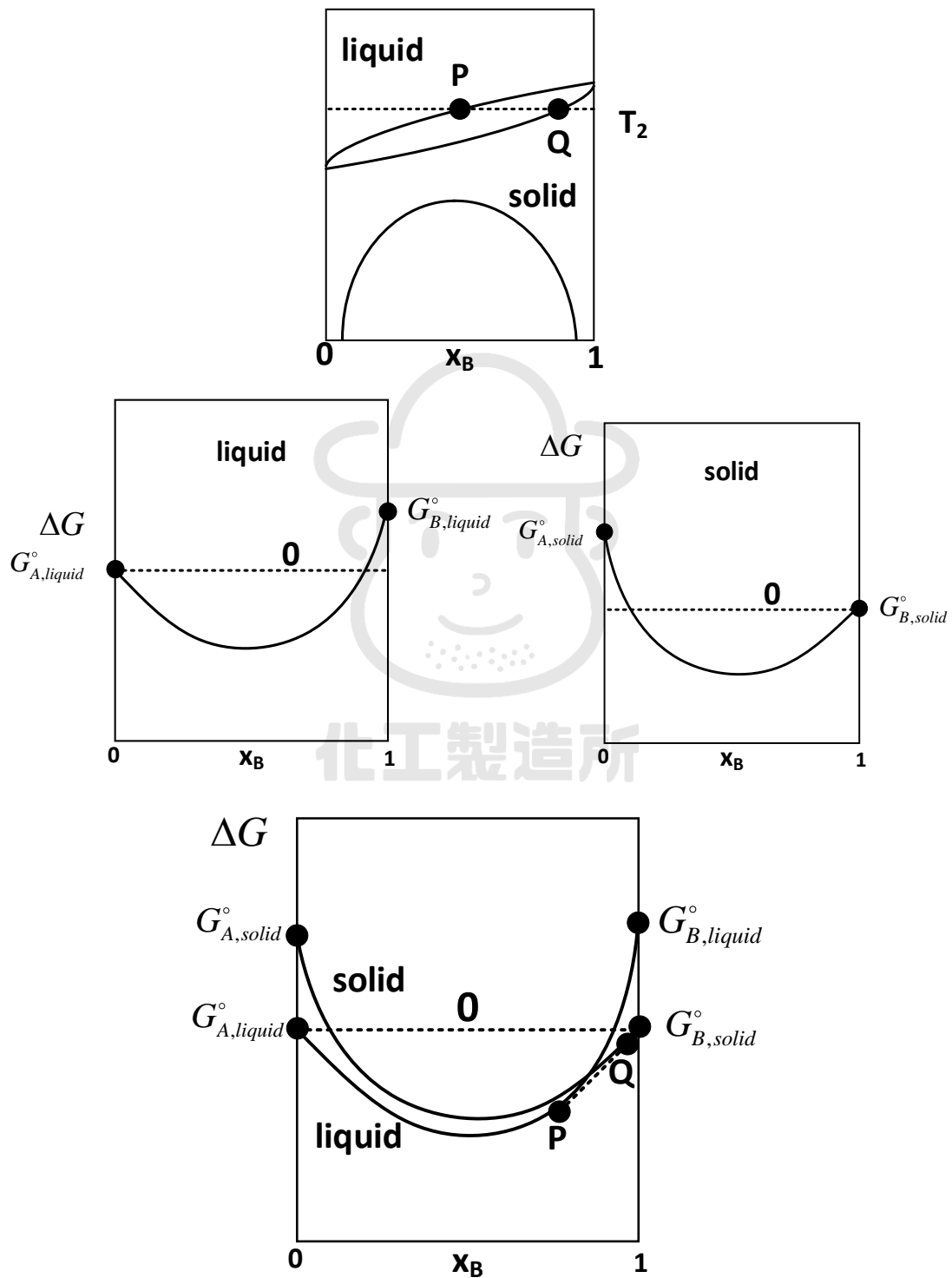
其中， $G_{A,solid}^\circ = G_{A,solid}^\circ - \underbrace{G_{A,standard}^\circ}_0 = \Delta G_{A,solid}^\circ$ ，因此在合適的參考態選擇下，

$\Delta G = G$ ，與一般 $G-X$ 畫法無異，而就算有差，也只是上下移動關係。

@At T_2

Set the standard states as : $G_{A,liquid}^\circ = 0$ and $G_{B,solid}^\circ = 0$

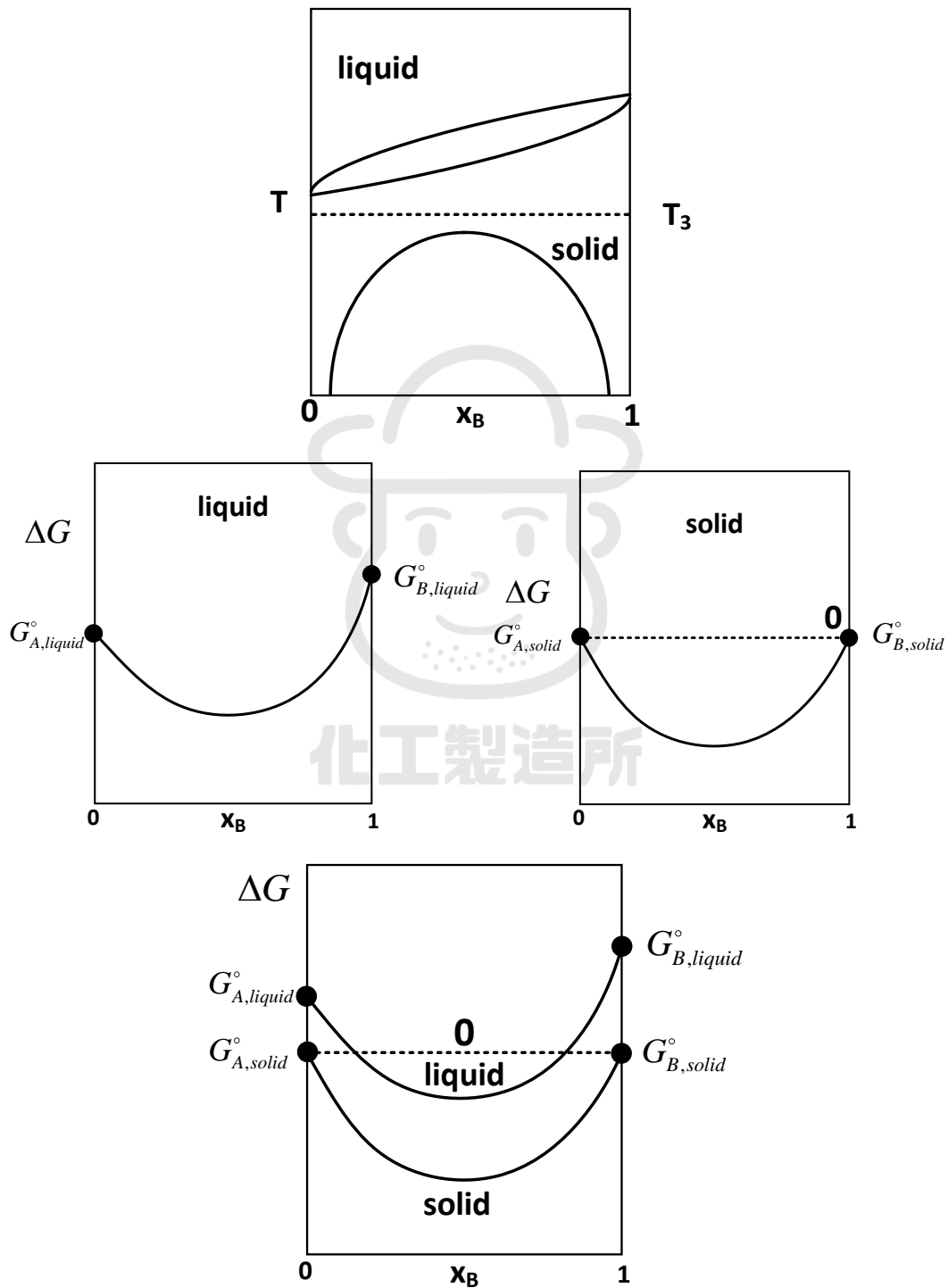
Assume : $G_{B,liquid}^\circ > G_{A,solid}^\circ$



@At T_3

Set the standard states as : $G_{A,solid}^\circ = 0$ and $G_{B,solid}^\circ = 0$

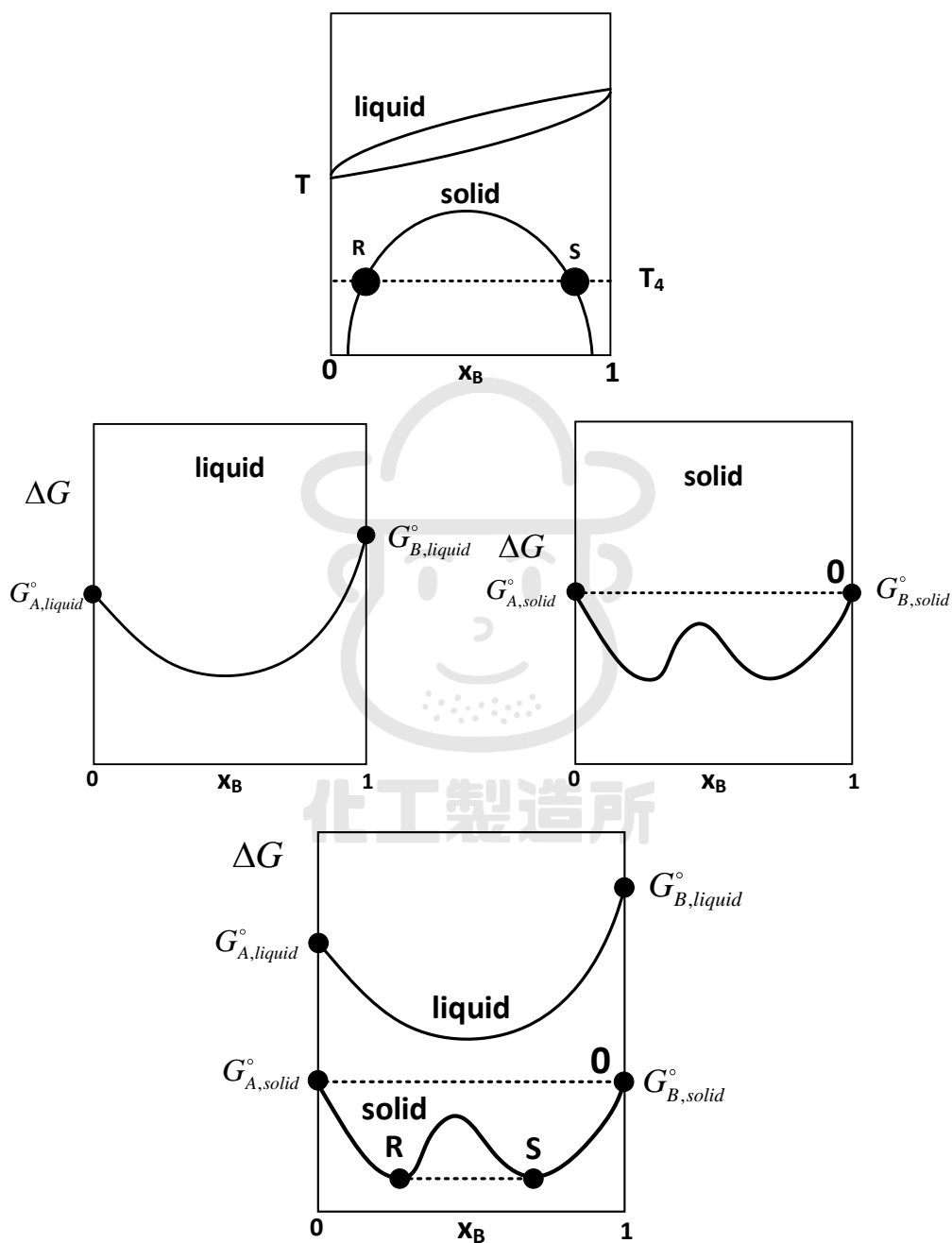
Assume : $G_{B,liquid}^\circ > G_{A,liquid}^\circ$



@At T_4

Set the standard states as : $G_{A,solid}^\circ = 0$ and $G_{B,solid}^\circ = 0$

Assume : $G_{B,liquid}^\circ > G_{A,liquid}^\circ$



(自由能-組成相圖畫法可參考 106 年清大化熱化反 Problem 2 後解說。)

關於選擇不同 reference standard state 對圖形的影響，可參考：Gaskell, D.; Laughlin, D.

Introduction to Thermodynamics of Materials, 6th Edition, 6th ed.; p 335.

(4)

(a)

If A and B form an ideal solution, the Gibbs free energy can be calculated as,

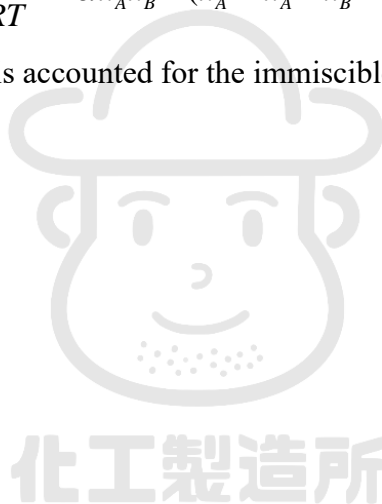
$$\underline{G_{ideal} = x_A \Delta G_{A,liquid}^{\circ} + x_B \Delta G_{B,liquid}^{\circ} + RT[x_A \ln x_A + x_B \ln x_B]}$$

(假設參考態的自由能定義為 0)

(b) By the figure shown above, the liquid phase is not an ideal solution because it would form a miscibility gap under certain conditions. Instead, the liquid phase can be described by the regular solution model, which can be expressed as,

$$\frac{\Delta G_{mix}}{RT} = \alpha x_A x_B + (x_A \ln x_A + x_B \ln x_B)$$

where the $\alpha x_A x_B$ term is accounted for the immiscible behavior of the solution.



Problem 3

【Solution】

(5)

(結論：此題目目前沒有好的正解，討論請看以下)

For one CSTR with optimal space time,

By the design of CSTR,

$$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{A0} - C_A}{k_1 C_A}, \quad C_A = \frac{C_{A0}}{1 + k_1 \tau}$$
$$\tau = \frac{C_B}{k_1 C_A - k_2 C_B}$$
$$C_B = \frac{k_1 C_A}{1 + k_2 \tau} = \frac{k_1 \tau C_{A0}}{(1 + k_1 \tau)(1 + k_2 \tau)}$$

To determine the optimal space time,

$$\frac{dC_B}{d\tau} = \frac{k_1 C_{A0}(1 + k_1 \tau)(1 + k_2 \tau) - k_1 \tau C_{A0}[(k_1)(1 + k_2 \tau) + k_2(1 + k_1 \tau)]}{[(1 + k_1 \tau)(1 + k_2 \tau)]^2} = 0$$

$$k_1 C_{A0}(1 + k_1 \tau)(1 + k_2 \tau) - k_1 \tau C_{A0}[(k_1)(1 + k_2 \tau) + k_2(1 + k_1 \tau)] = 0$$

$$k_1 k_2 \tau^2 = 1, \quad \tau = \frac{1}{\sqrt{k_1 k_2}}$$

$$C_{B, \max} = C_{A0} \left[\frac{\frac{k_1}{\sqrt{k_1 k_2}}}{\left(1 + \frac{k_1}{\sqrt{k_1 k_2}}\right) \left(1 + \frac{k_2}{\sqrt{k_1 k_2}}\right)} \right] = \frac{k_1 C_{A0}}{(\sqrt{k_1} + \sqrt{k_2})^2}$$

For two CSTR with any space time in series, the first CSTR would give,

$$\tau_1 = \frac{C_{A0} - C_{A1}}{k_1 C_{A1}}, \quad C_{A1} = \frac{C_{A0}}{1 + k_1 \tau_1}$$

$$\tau_1 = \frac{C_{B1}}{k_1 C_{A1} - k_2 C_{B1}}, \quad C_{B1} = \frac{\tau_1 k_1 C_{A1}}{1 + \tau_1 k_2} = \frac{\tau_1 k_1 C_{A0}}{(1 + k_1 \tau_1)(1 + k_2 \tau_1)}$$

The second CSTR would give,

$$\tau_2 = \frac{C_{A1} - C_{A2}}{k_1 C_{A2}}, \quad C_{A2} = \frac{C_{A1}}{1 + k_1 \tau_2} = \frac{C_{A0}}{(1 + k_1 \tau_1)(1 + k_1 \tau_2)}$$

$$\tau_2 = \frac{C_{B2} - C_{B1}}{k_1 C_{A2} - k_2 C_{B2}}$$

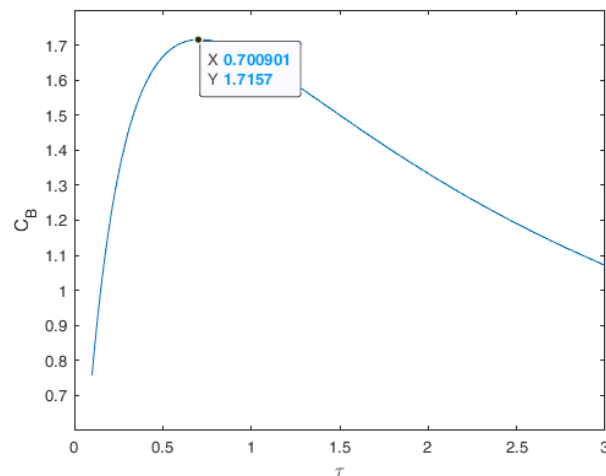
$$C_{B2} = \frac{k_1 \tau_2 C_{A2} + C_{B1}}{1 + k_2 \tau_2} = \frac{\left[\frac{k_1 \tau_2 C_{A0}}{(1 + k_1 \tau_1)(1 + k_1 \tau_2)} \right] + \frac{\tau_1 k_1 C_{A0}}{(1 + k_1 \tau_1)(1 + k_2 \tau_1)}}{1 + k_2 \tau_2}$$

若以不同 (τ_1, τ_2) 作為變數利用 matlab 做 C_{B2} 的計算：

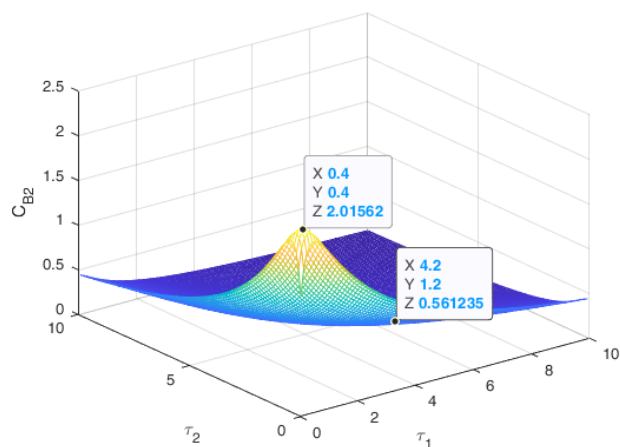
【Case①】 $C_{A0} = 10$, $k_1 = 1$, $k_2 = 2$

則在單一具有 optimal 體積的 CSTR 中，其最大濃度可計算為：

$$C_{B,\max} = \frac{1 \times 10}{(\sqrt{1} + \sqrt{2})^2} = 1.716$$



若在兩個串連的 CSTR 中，利用代值做圖可得到結果如下：



(X 為 τ_1 ，Y 為 τ_2 ，Z 為計算之 C_{B2})

若重複利用 polymath 做圖的數據檢驗：

```
#Calculation of exit concentration of the species
f(CA1) = (tau1)*(-rA1)-(CA0-CA1)
f(CB1) = tau1*(rB1)-(CB1)
f(CA2) = (tau2)*(-rA2)-(CA1-CA2)
f(CB2) = tau2*(rB2)-(CB2-CB1)

#Explicit values
CA0 = 10
k1 = 1
k2 = 2
tau1 = 0.4
tau2 = 0.4
rA1 = -k1*CA1
rA2 = -k1*CA2
rB1 = k1*CA1-k2*CB1
rB2 = k1*CA2-k2*CB2

#Guess the initial values
CA1(0) = 10
CB1(0) = 0
CA2(0) = 5
CB2(0) = 1
```

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	CA1	7.142857	1.523E-09	10.
2	CA2	5.102041	-5.438E-11	5.
3	CB1	1.587302	-1.744E-09	0
4	CB2	2.015621	2.225E-09	1.

```
#Calculation of exit concentration of the species
f(CA1) = (tau1)*(-rA1)-(CA0-CA1)
f(CB1) = tau1*(rB1)-(CB1)
f(CA2) = (tau2)*(-rA2)-(CA1-CA2)
f(CB2) = tau2*(rB2)-(CB2-CB1)

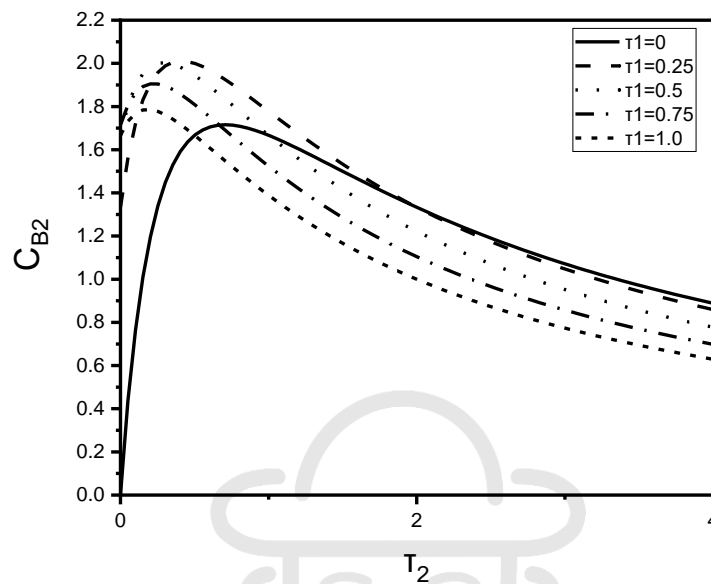
#Explicit values
CA0 = 10
k1 = 1
k2 = 2
tau1 = 4.2
tau2 = 1.2
rA1 = -k1*CA1
rA2 = -k1*CA2
rB1 = k1*CA1-k2*CB1
rB2 = k1*CA2-k2*CB2

#Guess the initial values
CA1(0) = 10
CB1(0) = 0
CA2(0) = 5
CB2(0) = 1
```

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	CA1	1.923077	5.739E-09	10.
2	CA2	0.8741259	-4.397E-09	5.
3	CB1	0.8592471	1.679E-08	0
4	CB2	0.5612348	6.481E-09	1.

最後，利用不同之固定 τ_1 情況下，繪製出相對應的 $C_{B2}-\tau_2$ 圖，也可以很明顯看到，在單一 CSTR 情況下(即 $\tau_1=0$ ，實線)所得到之 C_{B2} 最大值還是有可能小於兩台 CSTR 串聯所可以得到之最大值。)



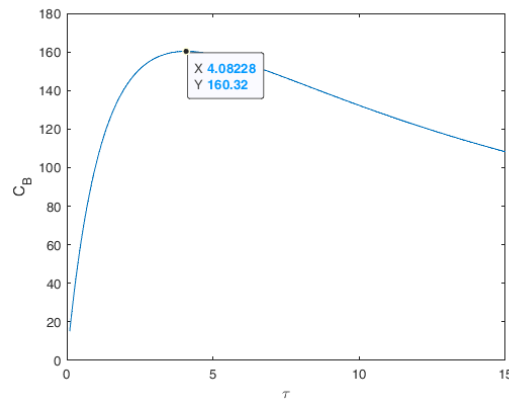
也就是兩台 CSTR 串聯的情況下，有可能達到比單一最佳 CSTR 更高的 C_B ，與此題命題不合。若覺得怕怕的可以按照我所設的參數手算，會有同樣的結果。以下嘗試改變參數，再做同樣的討論。

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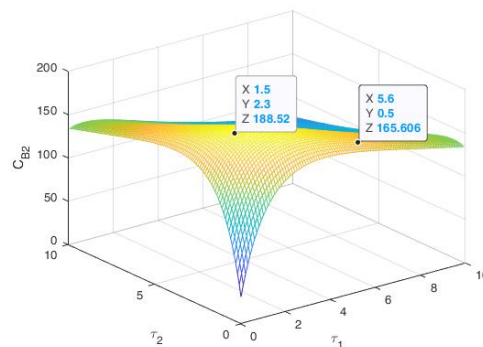
【Case②】 $C_{A0} = 529$, $k_1 = 0.3$, $k_2 = 0.2$

則在單一具有 optimal 體積的 CSTR 中，其最大濃度可計算為：

$$C_{B,\max} = \frac{0.3 \times 529}{(\sqrt{0.3} + \sqrt{0.2})^2} = 160.319$$



若在兩個串連的 CSTR 中，利用代值做圖可得到結果如下：



(X 為 τ_1 , Y 為 τ_2 , Z 為計算之 C_{B2})

若重複利用 polymath 做圖的數據檢驗：

```
#Calculation of exit concentration of the species
f(CA1) = (tau1)*(-rA1)-(CA0-CA1)
f(CB1) = tau1*(rB1)-(CB1)
f(CA2) = (tau2)*(-rA2)-(CA1-CA2)
f(CB2) = tau2*(rB2)-(CB2-CB1)

#Explicit values
CA0 = 529
k1 = 0.3
k2 = 0.2
tau1 = 1.5
tau2 = 2.3
rA1 = -k1*CA1
rA2 = -k1*CA2
rB1 = k1*CA1-k2*CB1
rB2 = k1*CA2-k2*CB2

#Guess the initial values
CA1(0) = 529
CB1(0) = 0
CA2(0) = 5
CB2(0) = 1
```

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	CA1	364.8276	2.842E-14	529.
2	CA2	215.8743	-2.842E-14	5.
3	CB1	126.2865	0	0
4	CB2	188.5204	0	1.

```

#Calculation of exit concentration of the species
f(CA1) = (tau1)*(rA1)-(CA0-CA1)
f(CB1) = tau1*(rB1)-(CB1)
f(CA2) = (tau2)*(rA2)-(CA1-CA2)
f(CB2) = tau2*(rB2)-(CB2-CB1)

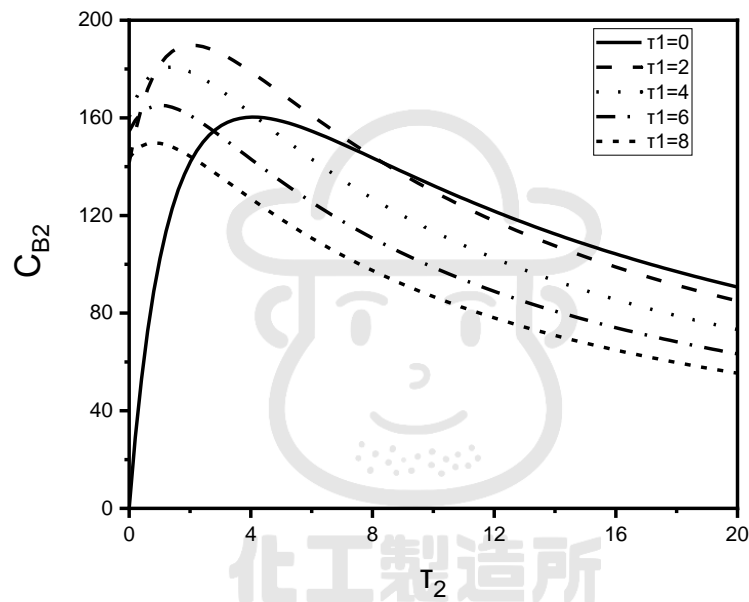
#Explicit values
CA0 = 529
k1 = 0.3
k2 = 0.2
tau1 = 5.6
tau2 = 0.5
rA1 = -k1*CA1
rA2 = -k1*CA2
rB1 = k1*CA1-k2*CB1
rB2 = k1*CA2-k2*CB2

#Guess the initial values
CA1(0) = 529
CB1(0) = 0
CA2(0) = 5
CB2(0) = 1

```

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	CA1	197.3881	0	529.
2	CA2	171.6418	1.066E-14	5.
3	CB1	156.4207	-5.684E-14	0
4	CB2	165.6064	1.421E-14	1.



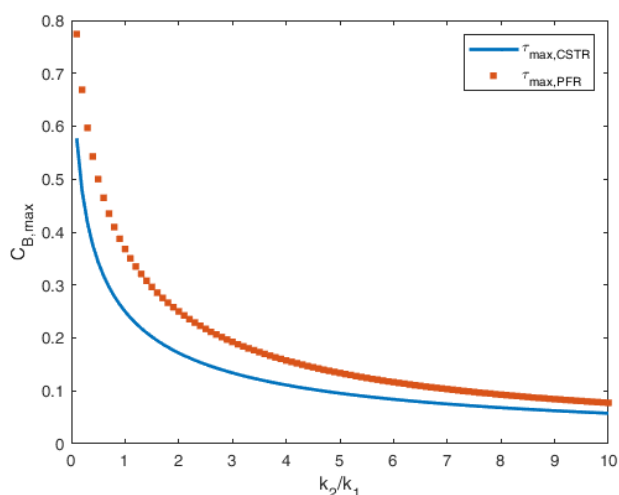
同樣，利用不同之固定 τ_1 情況下，繪製出相對應的 $C_{B2}-\tau_2$ 圖，也可以明顯看出，在單一 CSTR 情況下(即 $\tau_1=0$ ，實線)所得到之 C_{B2} 最大值還是有可能小於兩台 CSTR 串聯所可以得到之最大值。)

之所以會有這樣的現象，個人認為可以參考 Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 171~178.。原文書提及在同樣的連鎖反應下，PFR 所能夠得到的最大 B 濃度(方程式可參考 174 頁)為：

$$\frac{C_{B,\max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2-k_1}}$$

此值在任何 $\frac{k_2}{k_1}$ 下皆大於單個具有最佳滯留時間之 CSTR。

又此題兩個 CSTR 串聯的情形，雖然並不是無限小，然而也許能夠當作比單個 CSTR 更接近 PFR(無限多個無限小的 CSTR 串聯，等同於 PFR，”類似”)，因此可能達到比單個具有最佳滯留時間設計之 CSTR 更大的中間產物濃度。



綜上所述，本人認為此題目前沒有合適的解法，因以數據模擬來看，此題所需證明的性質不存在。

(6)

For CSTR, by design equation,

$$\tau = \frac{C_{A0}x_A}{-r_A}$$

For the reaction rate law,

$$-r_A = kC_A = kC_A(1-x_A)$$

Combine,

$$\tau = \frac{C_{A0}x_A}{kC_{A0}(1-x_A)}$$

Because the space time and the initial concentration of the reactions under different temperature are the same,

$$\frac{\cancel{C_{A0}}x_{A,25}}{\cancel{k_0}e^{\frac{Ea}{RT_{25}}} \cdot \cancel{C_{A0}}(1-x_{A,25})} = \frac{\cancel{C_{A0}}x_{A,T}}{\cancel{k_0}e^{\frac{Ea}{RT}} \cdot \cancel{C_{A0}}(1-x_{A,T})}$$
$$\frac{0.25}{e^{\frac{50 \times 10^3}{8.314 \times (273.15 + 25)}} \cdot (1 - 0.25)} = \frac{0.5}{e^{\frac{50 \times 10^3}{8.314 \times T}} \cdot (1 - 0.5)}$$
$$\underline{\underline{T = 315.3 \text{ (K)}}}$$

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Problem 4

【Solution】

(7)

For batch reactor, the design equation,

$$\frac{dC_A}{dt} = r_A$$

For rate equation,

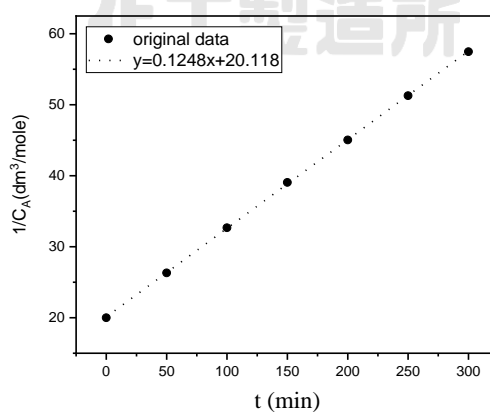
$$r_A = -kC_A^2C_B \approx -kC_A^2C_{B0}^{\text{excess}}$$

Combine,

$$\frac{dC_A}{dt} = -kC_A^2C_{B0}, \quad \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = -\int_0^t kC_{B0}dt$$
$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kC_{B0}t$$

Plot $1/C_A - t$ diagram,

t (min)	0	50	100	150	200	250	300
C_A (mol / dm ³)	0.05	0.038	0.0306	0.0256	0.0222	0.0195	0.0174
$1/C_A$ (dm ³ / mol)	20	26.315	32.679	39.062	45.045	51.282	57.471

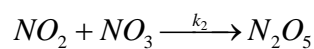


$$\text{slope} = kC_{B0} = 0.1248$$

$$k = \frac{0.1248}{C_{B0}} = \frac{0.1248}{0.5} = \underline{\underline{0.2496 \text{ (M}^{-1} / \text{min)}}}$$

(8)

第二條反應式有誤，應改為：



Define,

$$-r_{N_2O_5} = k_1[N_2O_5] \quad (\text{第一條反應式})$$

$$r_{N_2O_5} = k_2[NO_2][NO_3] \quad (\text{第二條反應式})$$

$$-r_{NO} = k_3[NO][NO_3] \quad (\text{第三條反應式})$$

則：

$$r_{N_2O_5} = -k_1[N_2O_5] + k_2[NO_2][NO_3]$$

By steady state assumption on NO_3 ,

$$r_{NO_3} = k_1[N_2O_5] - k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0$$

$$[NO_3] = \frac{k_1[N_2O_5]}{k_2[NO_2] + k_3[NO]}$$

代回：

$$\begin{aligned} r_{N_2O_5} &= -k_1[N_2O_5] + \frac{k_1[N_2O_5]k_2[NO_2]}{k_2[NO_2] + k_3[NO]} = k_1[N_2O_5] \left(\frac{k_2[NO_2]}{k_2[NO_2] + k_3[NO]} - 1 \right) \\ &= \underline{\underline{\frac{-k_1k_3[N_2O_5][NO]}{k_2[NO_2] + k_3[NO]}}} \end{aligned}$$

Problem 5**【Solution】****(9)****(a)**

For PFR, the design equation,

$$\tau = \int_0^{x_A} \frac{C_{A0} dx_A}{-r_A}$$

For the rate law,

$$-r_A = k(C_A - \frac{1}{K} C_B) = kC_{A0}[(1-x_A) - \frac{1}{K} x_A]$$

Combine,

$$\tau = \int_0^{x_A} \frac{C_{A0} dx_A}{kC_{A0}[(1-x_A) - \frac{1}{K} x_A]}, \quad \tau k = \int_0^{x_A} \frac{dx_A}{[(1-x_A) - \frac{1}{K} x_A]}$$

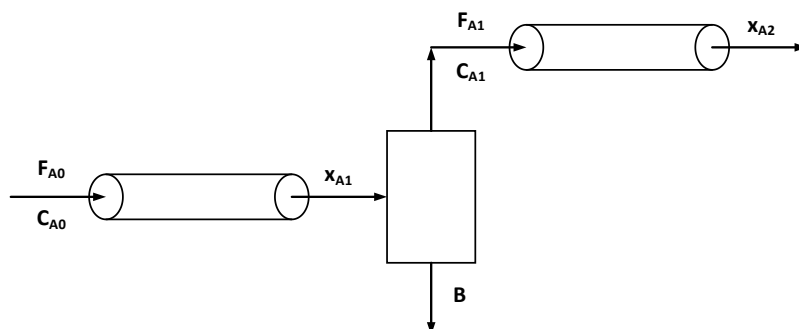
Because the second PFR is directly connected to the first, their conversions are all based on the initial concentration of the inlet stream,

$$\tau k = \int_0^{0.55} \frac{dx_A}{[(1-x_A) - \frac{1}{K} x_A]} = \int_{0.55}^{x_A} \frac{dx_A}{[(1-x_A) - \frac{1}{K} x_A]}$$

$$\int_0^{0.55} \frac{dx_A}{[(1-x_A) - \frac{1}{5.8} x_A]} = \int_{0.55}^{x_A} \frac{dx_A}{[(1-x_A) - \frac{1}{5.8} x_A]}$$

$$0.8829 = \int_{0.55}^{x_A} \frac{dx_A}{[(1-x_A) - \frac{1}{5.8} x_A]}, \quad \underline{\underline{x_A = 0.745}}$$

(b) If the stream into the second PFR is purified before entering the second,



For F_{A1} , $F_{A1} = F_{A0}(1 - x_{A1}) = (1 - 0.55)F_{A0} = 0.45F_{A0}$

For C_{A1} , because it's pure, $C_{A1} = C_{A0}$

$$\tau = \int_0^{0.55} \frac{C_{A0} dx_A}{kC_{A0}[(1 - x_A) - \frac{x_A}{5.8}]} = 0.45C_{A0} \int_0^{x_{A2}} \frac{dx_A}{kC_{A0}[(1 - x_A) - \frac{x_A}{5.8}]}$$

$$x_{A2} = 0.767$$

The total conversion based on the inlet of the first PFR is,

$$x_A = \frac{C_{A0} - C_{A1}(1 - x_{A2})}{C_{A0}} = \frac{C_{A0} - C_{A0}(1 - x_{A1})(1 - x_{A2})}{C_{A0}} = \frac{C_{A0} - C_{A0}(1 - 0.55)(1 - 0.767)}{C_{A0}} = \underline{\underline{0.895}}$$

(本題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 241,

Problem 4-13B.)

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Problem 1

【Solution】

(A) For the α phase,

$$G^E = \underbrace{\Delta G^\alpha - \sum x_i G_i}_{\Delta \bar{G}_{mix}} - RT \sum x_i \ln x_i = 400(1 - x_B^\alpha) x_B^\alpha \neq 0$$

The α phase is not an ideal solution.

(B) The partial Gibbs energy of B in the α phase is,

$$\bar{G}_B^\alpha = \Delta G^\alpha + (1 - x_B^\alpha) \frac{d\Delta G^\alpha}{dx_B^\alpha}$$

$$(1 - x_B^\alpha) \frac{d\Delta G^\alpha}{dx_B^\alpha} = (1 - x_B^\alpha)(-G_A^{0,\alpha} + G_B^{0,\alpha}) + (1 - x_B^\alpha)RT[\ln(x_B^\alpha) - \ln(1 - x_B^\alpha)] + (1 - x_B^\alpha)400(-2x_B^\alpha + 1)$$

$$(1 - x_B^\alpha) \frac{d\Delta G^\alpha}{dx_B^\alpha} = G_B^{0,\alpha}(1 - x_B^\alpha) - G_A^{0,\alpha}(1 - x_B^\alpha) + (1 - x_B^\alpha)RT[\ln(x_B^\alpha) - \ln(1 - x_B^\alpha)] + (1 - x_B^\alpha)400(-2x_B^\alpha + 1)$$

代回：

$$\bar{G}_B^\alpha = \Delta G^\alpha + (1 - x_B^\alpha) \frac{d\Delta G^\alpha}{dx_B^\alpha} = \underline{\underline{G_B^{0,\alpha} + RT \ln x_B^\alpha + 400(1 - x_B^\alpha)^2}}$$

Problem 2

【Solution】

(A) The gibbs free energy changes during a reaction is,

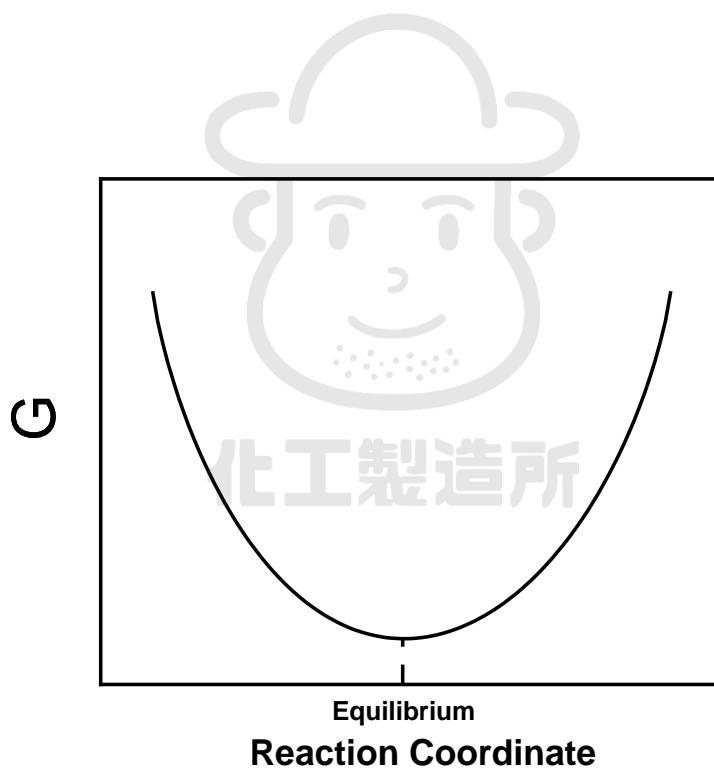
$$\Delta G_{298K} = \Delta G_{298K}^{\circ} + RT \ln(Q)$$

Where Q is the reaction quocient defined as,

$$Q = \frac{(a_{SO_3})}{(a_{O_2})^{1/2}(a_{SO_2})} = \frac{(P_{SO_3})}{(P_{O_2})^{1/2}(P_{SO_2})}$$

Therefore, whether the reaction proceeds toward RHS (right-hand-side) or LHS (left-hand-side) **depends on the reaction quocient calculated by the species.**

(B)



Problem 3

【Solution】

(A)

By the design equation of PFR,

$$d\tau = \int_0^{x_A} \frac{C_{A0}}{-r_A} dx_A = \int_{C_A}^{C_{A0}} \frac{1}{-r_A} dC_A$$

By the rate equation of the reaction,

$$-r_A = kC_A C_B$$

By mass balance,

$$C_{A0} + C_{B0} = C_A + C_B$$

$$C_B = C_{A0} + C_{B0} - C_A = 1 - C_A$$

代入：

$$-r_A = kC_A C_B = kC_A (1 - C_A)$$

合併：

$$\tau = \int_{C_A}^{C_{A0}} \frac{1}{-r_A} dC_A = \int_{0.1}^{0.99} \frac{1}{kC_A (1 - C_A)} dC_A = \int_{0.1}^{0.99} \frac{1}{C_A (1 - C_A)} dC_A = \underline{\underline{6.79 \text{ (min)}}}$$

(B)

To achieve a recycle stream mimicing a CSTR, **the recycle ratio should be infinity.**

At 5°C, the space time of the CSTR is,

$$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{A0} - C_A}{kC_A (1 - C_A)} = \frac{0.99 - 0.1}{1 \times 0.1 \times (1 - 0.1)} = \underline{\underline{9.89 \text{ (min)}}}$$

At 15°C, by Arrhenius' law,

$$\frac{k_{15}}{k_5} = \exp\left[\frac{-E_A}{R} \left(\frac{1}{273.15 + 15} - \frac{1}{273.15 + 5}\right)\right] = \exp\left[\frac{-46 \times 10^3}{8.314} \left(\frac{1}{273.15 + 15} - \frac{1}{273.15 + 5}\right)\right]$$

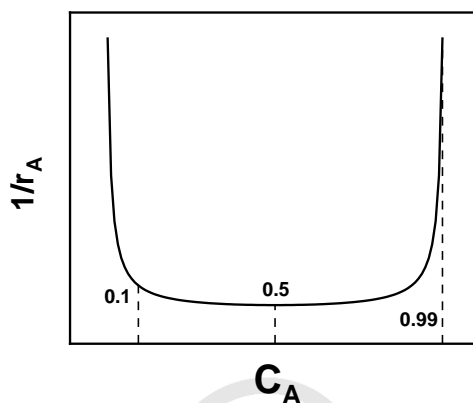
$$k_{15} = 1.99 \text{ (L/mol} \cdot \text{min)}$$

$$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{A0} - C_A}{kC_A (1 - C_A)} = \frac{0.99 - 0.1}{1.99 \times 0.1 \times (1 - 0.1)} = \underline{\underline{4.96 \text{ (min)}}}$$

(C)

The Levenspiel plot of the reaction is,

$$\frac{1}{-r_A} = \frac{1}{kC_A(1-C_A)}$$



According to the plot, the first reactor should be a CSTR ($R \rightarrow \infty$) with a exit concentration of $C_A = 0.5$ (mol / L). The space time is,

$$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{A0} - C_A}{kC_A(1-C_A)} = \frac{0.99 - 0.5}{1 \times 0.5 \times (1 - 0.5)} = 1.96 \text{ (min)}$$

The second reactor should be PFR ($R = 0$) with a exit concentration of

$C_A = 0.1$ (mol / L). The space time is,

$$\tau = \int_{C_A}^{C_{A0}} \frac{1}{-r_A} dC_A = \int_{0.1}^{0.50} \frac{1}{kC_A(1-C_A)} dC_A = \int_{0.1}^{0.50} \frac{1}{C_A(1-C_A)} dC_A = 2.197 \text{ (min)}$$

The total space time required is,

$$\underline{\underline{\tau_{PFR} + \tau_{CSTR} = 4.157 \text{ (min)}}}$$

Problem 4**【Solution】**

(A)

For the volume of the batch reactor, by the design equation of batch reactor,

$$\frac{dN_A}{dt} = r_A V, \quad \frac{dC_A}{dt} = r_A$$

For r_A , by the rate expression,

$$r_A = -k_1 C_A + k_{-1} C_B$$

Combine, the relationship of the volume of the batch reactor and the concentration of

A can be expressed as following,

$$\frac{dC_A}{dt} = (-k_1 C_A + k_{-1} C_B)$$

For the relationship between the reactor volume and the amount of B, C, D

$$\frac{dC_B}{dt} = r_B = (k_1 C_A - k_{-1} C_B - k_2 C_B)$$

$$\frac{dC_C}{dt} = r_C = (k_2 C_B - k_3 C_C + k_{-3} C_D)$$

$$\frac{dC_D}{dt} = r_D = (k_3 C_C - k_{-3} C_D)$$

(B)

將此 ODE 組矩陣化，令 $\bar{C} = \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix}$ ，且此矩陣滿足：

$$\frac{d\bar{C}}{dt} = A\bar{C}$$
$$A = \begin{bmatrix} -k_1 & k_{-1} & 0 & 0 \\ k_1 & -k_{-1}-k_2 & 0 & 0 \\ 0 & k_2 & -k_3 & k_{-3} \\ 0 & 0 & k_3 & -k_{-3} \end{bmatrix} = \begin{bmatrix} -3 & \frac{8}{3} & 0 & 0 \\ 3 & -10 & 0 & 0 \\ 0 & \frac{22}{3} & -2 & 3 \\ 0 & 0 & 2 & -3 \end{bmatrix}$$

將矩陣對角化，令：

$$\det(A - \lambda I) = 0$$
$$\det(A - \lambda I) = \begin{vmatrix} -3-\lambda & \frac{8}{3} & 0 & 0 \\ 3 & -10-\lambda & 0 & 0 \\ 0 & \frac{22}{3} & -2-\lambda & 3 \\ 0 & 0 & 2 & -3-\lambda \end{vmatrix} = 0$$

將第一二行做比例計算，令：

$$\frac{-3-\lambda}{3} = \frac{8}{3(-10-\lambda)}, \quad \boxed{\lambda = -2, -11} \quad (\text{即為兩個根})$$

剩餘二根由行列式之 $\det(A)$ 與 $\text{trace}(A)$ 計算：

$$\text{trace}(A) = -3 - 10 - 2 - 3 = -2 - 11 + \lambda_3 + \lambda_4, \quad \lambda_3 + \lambda_4 = -5$$

$$\det(A) = 0 = (-2) \times (-11) \times \lambda_3 \lambda_4, \quad \lambda_3 \lambda_4 = 0$$

$$\text{則 } \boxed{\lambda_3 = 0}, \quad \boxed{\lambda_4 = -5}$$

令 $\lambda_1 = -2$ 代入 $(A - \lambda I)\bar{C}_1 = 0$:

$$\begin{bmatrix} -1 & \frac{8}{3} & 0 & 0 \\ 3 & -8 & 0 & 0 \\ 0 & \frac{22}{3} & 0 & 3 \\ 0 & 0 & 2 & -1 \end{bmatrix} \bar{C}_1 = 0, \quad \bar{C}_1 = \begin{bmatrix} -24 \\ -9 \\ 11 \\ 22 \end{bmatrix}$$

令 $\lambda_2 = 0$ 代入 $(A - \lambda I)\bar{C}_2 = 0$:

$$\begin{bmatrix} -3 & \frac{8}{3} & 0 & 0 \\ 3 & -10 & 0 & 0 \\ 0 & \frac{22}{3} & -2 & 3 \\ 0 & 0 & 2 & -3 \end{bmatrix} \bar{C}_2 = 0, \quad \bar{C}_2 = \begin{bmatrix} 0 \\ 0 \\ 3 \\ 2 \end{bmatrix}$$

令 $\lambda_3 = -11$ 代入 $(A - \lambda I)\bar{C}_3 = 0$:

$$\begin{bmatrix} 8 & \frac{8}{3} & 0 & 0 \\ 3 & 1 & 0 & 0 \\ 0 & \frac{22}{3} & 9 & 3 \\ 0 & 0 & 2 & 8 \end{bmatrix} \bar{C}_3 = 0, \quad \bar{C}_3 = \begin{bmatrix} -3 \\ 9 \\ -8 \\ 2 \end{bmatrix}$$

令 $\lambda_4 = -5$ 代入 $(A - \lambda I)\bar{C}_4 = 0$:

$$\begin{bmatrix} 2 & \frac{8}{3} & 0 & 0 \\ 3 & -5 & 0 & 0 \\ 0 & \frac{22}{3} & 3 & 3 \\ 0 & 0 & 2 & 2 \end{bmatrix} \bar{C}_4 = 0, \quad \bar{C}_4 = \begin{bmatrix} 0 \\ 0 \\ 1 \\ -1 \end{bmatrix}$$

則此方程式的解為：

$$\bar{C} = \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix} = C_1 \begin{bmatrix} -24 \\ -9 \\ 11 \\ 22 \end{bmatrix} e^{-2t} + C_2 \begin{bmatrix} 0 \\ 0 \\ 3 \\ 2 \end{bmatrix} + C_3 \begin{bmatrix} -3 \\ 9 \\ -8 \\ 2 \end{bmatrix} e^{-11t} + C_4 \begin{bmatrix} 0 \\ 0 \\ 1 \\ -1 \end{bmatrix} e^{-5t}$$

即：

$$\begin{cases} C_A = -24C_1e^{-2t} - 3C_3e^{-11t} \\ C_B = -9C_1e^{-2t} + 9C_3e^{-11t} \\ C_C = 11C_1e^{-2t} + 3C_2 - 8C_3e^{-11t} + C_4e^{-5t} \\ C_D = 22C_1e^{-2t} + 2C_2 + 2C_3e^{-11t} - C_4e^{-5t} \end{cases}, \begin{cases} t=0, C_A = C_{A0} \\ t=0, C_B = 0 \\ t=0, C_C = 0 \\ t=0, C_D = 0 \end{cases}$$

將四個邊界條件代入解係數，得：

$$\begin{cases} C_A = -24C_1e^{-2t} - 3C_3e^{-11t} \\ C_B = -9C_1e^{-2t} + 9C_3e^{-11t} \\ C_C = 11C_1e^{-2t} + 3C_2 - 8C_3e^{-11t} + C_4e^{-5t} \\ C_D = 22C_1e^{-2t} + 2C_2 + 2C_3e^{-11t} - C_4e^{-5t} \end{cases}, \begin{cases} C_1 = -\frac{1}{27}C_{A0} \\ C_2 = \frac{1}{5}C_{A0} \\ C_3 = -\frac{1}{27}C_{A0} \\ C_4 = -\frac{22}{45}C_{A0} \end{cases}$$

(圖在下頁最後面)

(C)

令

$$\frac{d(C_C - C_D)}{dt} = 0$$

得：

$$\frac{d}{dt} C_{A0} \left[\left(\frac{11}{27}e^{-2t} + \frac{1}{5} + \frac{10}{27}e^{-11t} + 2 \times \frac{22}{455}e^{-5t} \right) \right] = 0$$

$$\text{得 } t = 0.589 \text{ (min)}, \max(C_C - C_D) = 137.68 \text{ (mM)}$$

※本題亦有可能須計算 C_C / C_D 的比例最大值，然而其最大值發生在反應初使階段，亦即 C_C 剛有濃度，但 C_D 尚未開始產生，但需要逼近 $t \rightarrow 0$ ，找不到一個明確的時間，而 C_C / C_D 可以找到最小值，也就是發生在接近平衡的時候，此時 $t \rightarrow \infty$ ，可計算 $C_C / C_D = k_{-3} / k_3 = 3/2 = \underline{\underline{1.5}}$

(D)

令

$$\frac{d(C_B)}{dt} = 0$$

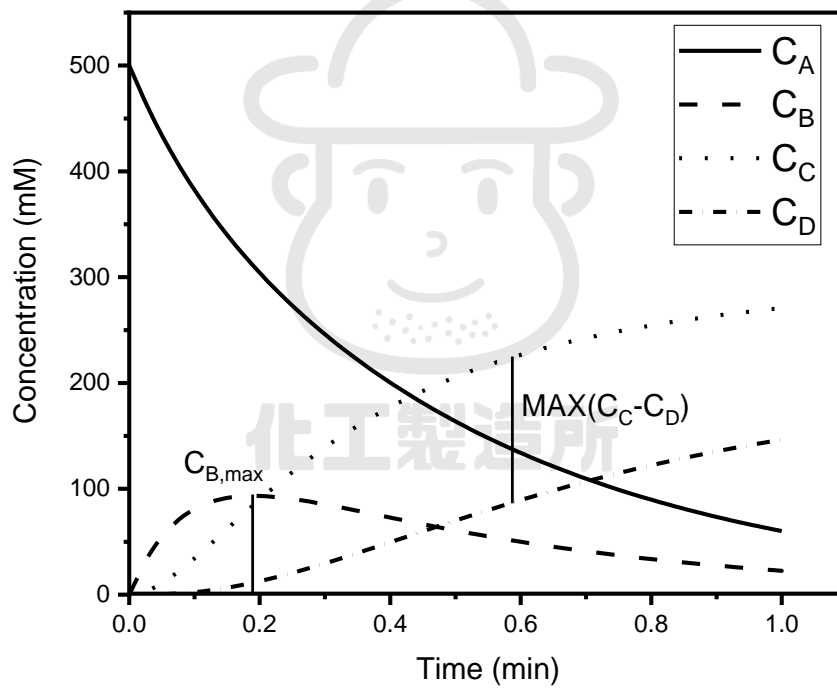
得：

$$\frac{d}{dt} \left(\frac{1}{3} e^{-2t} - \frac{1}{3} e^{-11t} \right) = 0$$

$$\text{得 } t = 0.189 \text{ (min)}$$

此時

$$C_{B,\max} = 500 \times \left(\frac{1}{3} e^{-2 \times 0.189} - \frac{1}{3} e^{-11 \times 0.189} \right) = \underline{\underline{93.36 \text{ (mM)}}}$$



```

#To calculate the volume of the batch reactor, we need the following defferential equations,
d(CA)/d(t) = rA
d(CB)/d(t) = rB
d(CC)/d(t) = rC
d(CD)/d(t) = rD

#Difine the rate equation
rA = -k1*CA+k2*CB
rB = k1*CA-k2*CB-k3*CB
rC = k3*CB-k4*CC+k5*CD
rD = k4*CC-k5*CD

#The parameters or conditions we need or values are,
k1 = 3
k2 = 8/3
k3 = 22/3
k4 = 2
k5 = 3
CA(0) = 500
CB(0) = 0
CC(0) = 0
CD(0) = 0

#To complete the calculation, we need
p = CA+CB+CC+CD
d = CC-CD

#The range of time we want to know
t(0) = 0
t(f) = 1

```



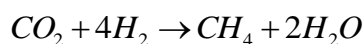
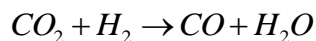
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Problem 5

【Solution】

(A)

Reactions:



【Production of CO】

The reaction enthalpy of the production of CO is,

$$H_{f,H_2O} + H_{f,CO} - H_{f,CO_2} = -241.83 - 110.53 - (-393.51) = 41.45 \text{ (kJ / mol)}$$

The reaction entropy of the production of CO is,

$$S_{H_2O} + S_{CO} - S_{CO_2} - S_{H_2} = 188.84 + 197.6 - 213.8 - 130.68 = 41.96 \text{ (J / mol} \cdot \text{K)}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 41.45 \times 10^3 - (500 + 273.15) \times 41.96 = 9008.6 \text{ (J / mol)}$$

For the equilibrium constant, we have,

$$\Delta G^\circ = -RT \ln K$$

$$9008.6 = -8.314 \times (500 + 273.15) \ln(K_{500})$$

$$\underline{\underline{K_{500} = 0.246}}$$

For the equilibrium constant at 700°C, by the relationship (assume the reaction enthalpy is independent of temperature),

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

$$\ln \frac{K_{700}}{K_{500}} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{700 + 273.15} - \frac{1}{500 + 273.15} \right)$$

$$\ln \frac{K_{700}}{0.246} = -\frac{41.45 \times 10^3}{8.314} \left(\frac{1}{700 + 273.15} - \frac{1}{500 + 273.15} \right)$$

$$\underline{\underline{K_{700} = 0.925}}$$

【Production of CH₄】

The reaction enthalpy of the production of CH₄ is,

$$2H_{f,H_2O} + H_{f,CH_4} - H_{f,CO_2} = -2 \times 241.83 - 74.8 - (-393.51) = -164.95 \text{ (kJ / mol)}$$

The reaction entropy of the production of CH₄ is,

$$2S_{H_2O} + S_{CH_4} - S_{CO_2} - 4S_{H_2} = 2 \times 188.84 + 186.25 - 213.8 - 4 \times 130.68 = -172.6 \text{ (J / mol} \cdot \text{K)}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -164.95 \times 10^3 - (500 + 273.15) \times (-172.6) = -31504.3 \text{ (J / mol)}$$

For the equilibrium constant, we have,

$$\Delta G^\circ = -RT \ln K$$

$$-31504.3 = -8.314 \times (500 + 273.15) \ln K$$

$$\underline{\underline{K_{500} = 134.4}}$$

For the equilibrium constant at 700°C, by the relationship (assume the reaction enthalpy is independent of temperature),

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

$$\ln \frac{K_{700}}{K_{500}} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{700 + 273.15} - \frac{1}{500 + 273.15} \right)$$

$$\ln \frac{K_{700}}{134.4} = -\frac{-164.95 \times 10^3}{8.314} \left(\frac{1}{700 + 273.15} - \frac{1}{500 + 273.15} \right)$$

$$\underline{\underline{K_{700} = 0.689}}$$

(B)

【Production of CO】

At 500°C, assume there are n moles of CO_2 and H_2 initially,

$$K_{500} = \frac{x_{\text{CO}} x_{\text{H}_2\text{O}}}{x_{\text{CO}_2} x_{\text{H}_2}} = \frac{(nX)^2}{[n(1-X)]^2} = \frac{X^2}{(1-X)^2} = 4.06$$

$$\underline{\underline{X = 0.668}}$$

At 700°C, assume there are n moles of CO_2 and H_2 initially,

$$K_{700} = \frac{x_{\text{CO}} x_{\text{H}_2\text{O}}}{x_{\text{CO}_2} x_{\text{H}_2}} = \frac{(nX)^2}{[n(1-X)]^2} = \frac{X^2}{(1-X)^2} = 15.28$$

$$\underline{\underline{X = 0.796}}$$

【Production of CH_4 】

At 500°C, assume there are n moles of CO_2 and H_2 initially,

$$K_{700} = \frac{x_{\text{CH}_4} x_{\text{H}_2\text{O}}^2}{x_{\text{CO}_2} x_{\text{H}_2}^4} = \frac{(nX)[n(2X)]^2}{n(1-X)[n(1-4X)]^4} = \frac{X(2X)^2}{n^2(1-X)(1-4X)^4} = 134.4$$

If $n = 1$,

$$\underline{\underline{X = 0.215}}$$

At 700°C, assume there are n moles of CO_2 and H_2 initially,

$$K_{700} = \frac{x_{\text{CH}_4} x_{\text{H}_2\text{O}}^2}{x_{\text{CO}_2} x_{\text{H}_2}^4} = \frac{(nX)[n(2X)]^2}{n(1-X)[n(1-4X)]^4} = \frac{X(2X)^2}{n^2(1-X)(1-4X)^4} = 0.689$$

If $n = 1$,

$$\underline{\underline{X = 0.152}}$$

(C)

According to Le Chatelier's principle (勒沙特列原理), if all the species are in gaseous state,

【Production of CO】

$\Delta n = 0$, the equilibrium conversion is independent of pressure

【Production of CH₄】

$\Delta n = -2$, the equilibrium conversion will increase upon the increase of pressure.

Problem 6

【Solution】

(A)

By employing the pseudo-steady-state assumption, we hypothesize that the reaction intermediate in a specific reaction will endure for an exceedingly short duration, reacting practically as swiftly as it is generated.

(B)

【Mechanism 1】

$$r_{A_2B} = k_C[A_2^*][B]$$

By PSSH,

$$r_{A_2^*} = k_A[A]^2 - k_B[A_2^*] - k_C[A_2^*][B] = 0$$

$$[A_2^*] = \frac{k_A[A]^2}{k_B + k_C[B]}$$

代回：

$$r_{A_2B} = \frac{k_A k_C [A]^2 [B]}{k_B + k_C [B]} = \frac{k_2 [A]^2 [B]}{1 + k_1 [B]}$$

形式與題幹不符，此 mechanism 不合理

【Mechanism 2】

$$r_{A_2B} = k_C[AB^*][A]$$

By PSSH,

$$r_{AB^*} = k_A[A][B] - k_B[AB^*] - k_C[AB^*][A] = 0$$

$$[AB^*] = \frac{k_A[A][B]}{k_B + k_C[A]}$$

代入：

$$r_{A_2B} = \frac{k_A k_C [A]^2 [B]}{k_B + k_C [A]} = \frac{k_1 [A]^2 [B]}{1 + k_2 [A]}$$

形式與題幹相符，此 mechanism 合理

Problem 6

【Solution】

(A)

$$dW = -PdV$$

For the van der Waals equation of state,

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

代入：

$$dW = -PdV = -\left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right)dV$$

$$W = \int_{V_1}^{V_2} -\left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right)dV = nRT \ln\left(\frac{V_1 - nb}{V_2 - nb}\right) + an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$W = 3 \times 8.314 \times 300 \ln\left(\frac{1 - 3 \times 0.04267}{3 - 3 \times 0.04267}\right) + 3.640 \times 3^2 \left(\frac{1}{1} - \frac{1}{3}\right) \times 100$$

$$(1 \text{ bar} \cdot L = 100J)$$

$$\underline{\underline{W = -6735.13 (J)}}$$

(B)

$$Z = \frac{\int_{V_1}^{V_2} Z dV}{V_2 - V_1}$$

For the van der Waals equation of state,

$$Z = \frac{PV}{nRT} = \frac{V}{V - nb} - \frac{an}{RTV}$$

代回：

$$Z = \frac{\int_{V_1}^{V_2} Z dV}{V_2 - V_1} = \frac{\int_{V_1}^{V_2} \left(\frac{V}{V - nb} - \frac{an}{RTV} \right) dV}{V_2 - V_1} = \frac{V_2 - V_1 + nb \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - \frac{an}{RT} \ln \frac{V_2}{V_1}}{V_2 - V_1}$$
$$Z = \frac{V_2 - V_1 + nb \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - \frac{an}{RT} \ln \frac{V_2}{V_1}}{V_2 - V_1} = \frac{3 - 1 + 3 \times 0.04267 \ln\left(\frac{3 - 3 \times 0.04267}{1 - 3 \times 0.04267}\right) - \frac{3.640 \times 3}{0.08314 \times 300} \ln \frac{3}{1}}{3 - 1}$$
$$\underline{\underline{Z = 0.83579}}$$

(此題採用積分平均的方式算出，然而因題目並沒有限定要怎麼平均，因此也可能可以由算術平均方式算出)

(C)

(a) H_2

(b) ideal gas

(c) CH_4

(d) CO_2

分子間作用力越大，越偏離理想氣體行為。

114 年清大化熱化反

Problem 1

【Solution】

(a) \because The vapor phase is an ideal solution,

$$\Delta H_{mix} = 0$$

(b) \because The vapor phase is an ideal solution,

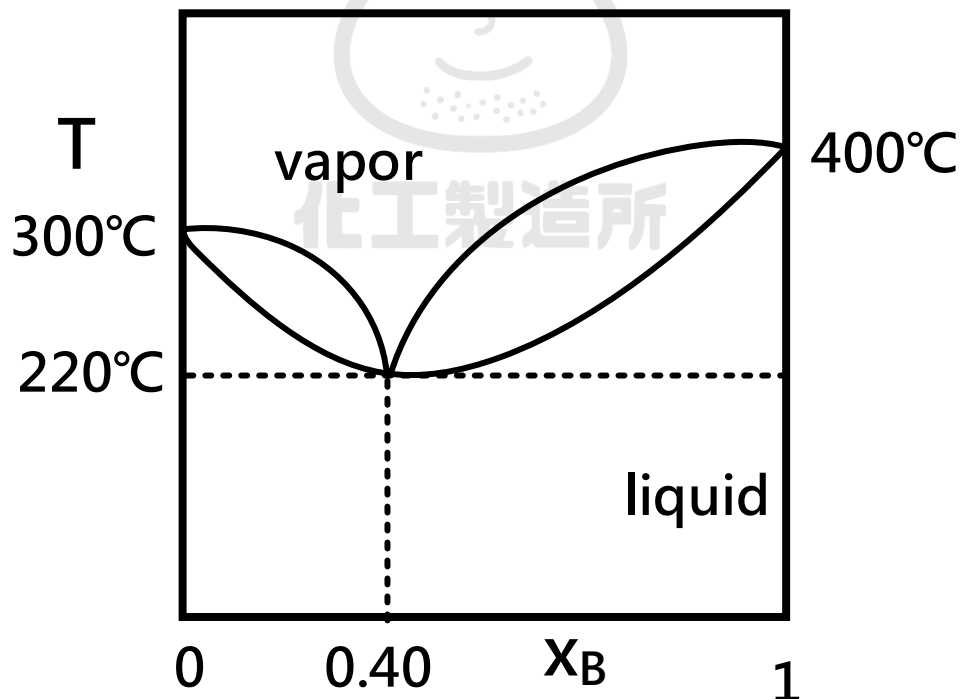
$$\Delta G_{mix} = RT(x_A \ln x_A + x_B \ln x_B)$$

(c) The partial Gibbs energy of A in the vapor phase is,

$$\bar{G}_A^{gas} = \Delta G_A^{gas} + RT \ln x_A$$

(設參考態自由能定義為 0)

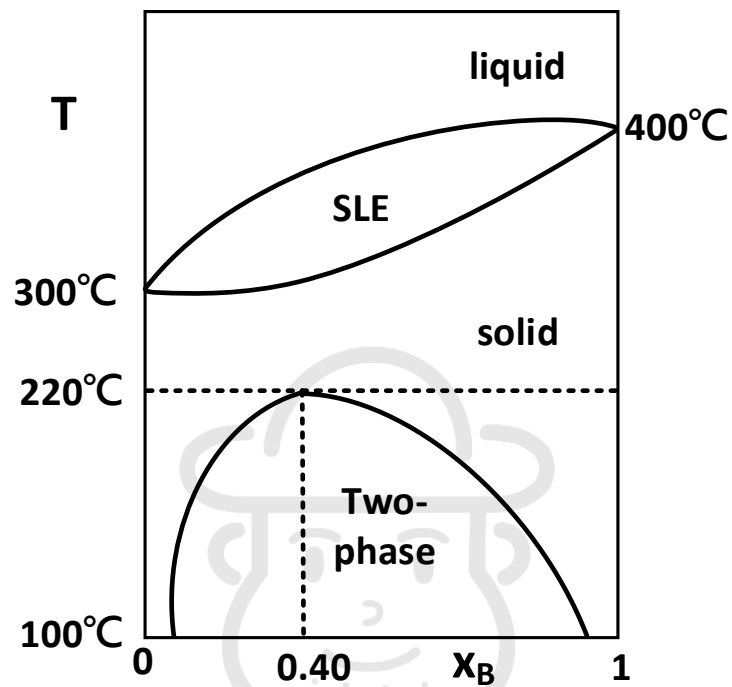
(d) Isomorphous 通常用於形容在一個固液溶液系統當中，其固體與液體相都為共溶溶液的情況，此小題應意指其氣相與液相都為均勻混合物。



Problem 2

【Solution】

(a) Isomorphous 的定義為兩成分原子具有相似之尺寸大小與晶格結構，因此其在固體與液體為共溶的情況。然而此題之 isomorphous 行為只在 220°C 以下，因此此題之相圖即為：



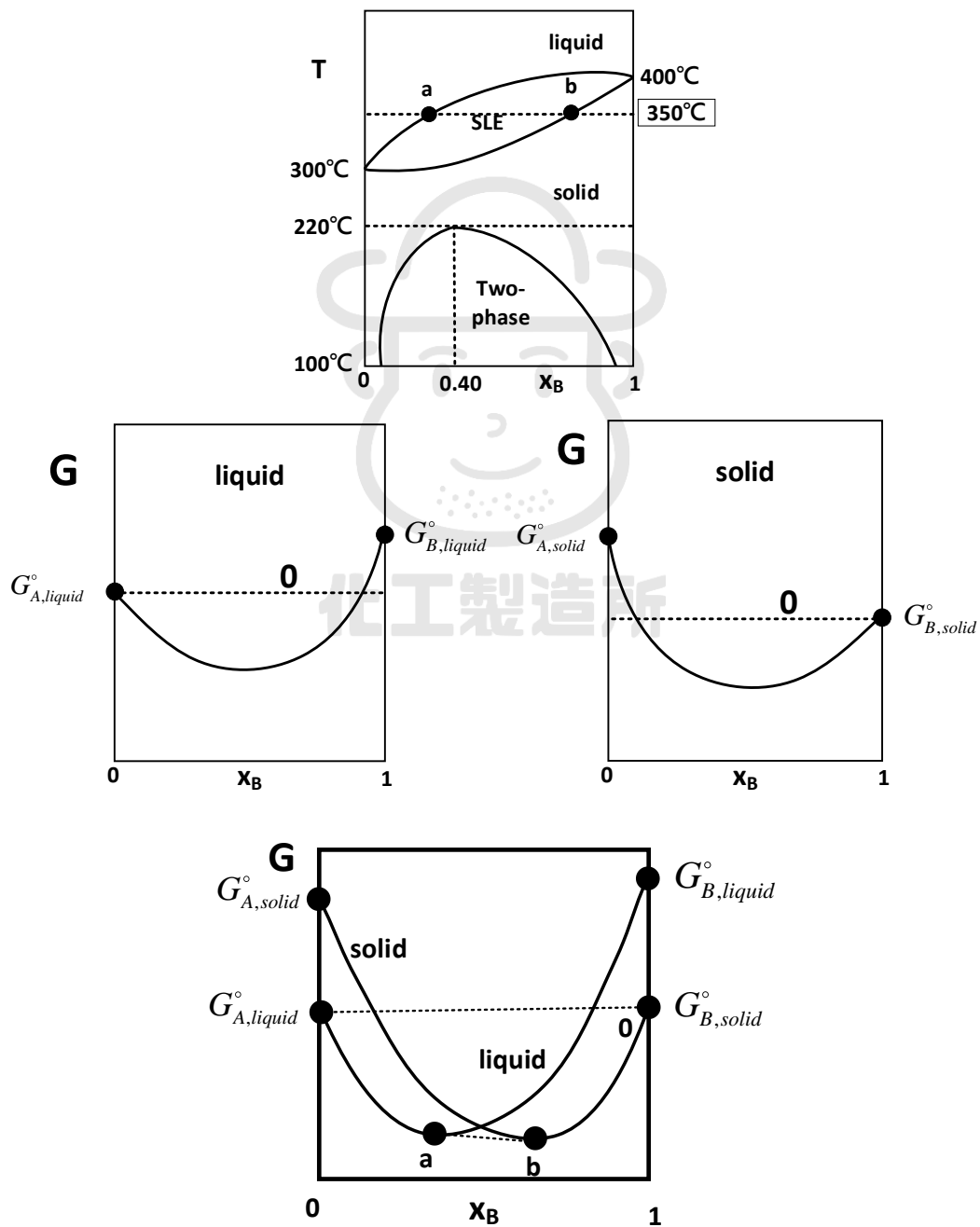
(b)

Assume : $\begin{cases} \text{solid} \rightarrow \text{regular solution} \\ \text{liquid phase} \rightarrow \text{ideal solution} \end{cases}$

@At 350°C

Set the standard states as : $G_{A,\text{liquid}}^\circ = 0$ and $G_{B,\text{solid}}^\circ = 0$

Assume : $G_{B,\text{liquid}}^\circ > G_{A,\text{solid}}^\circ$

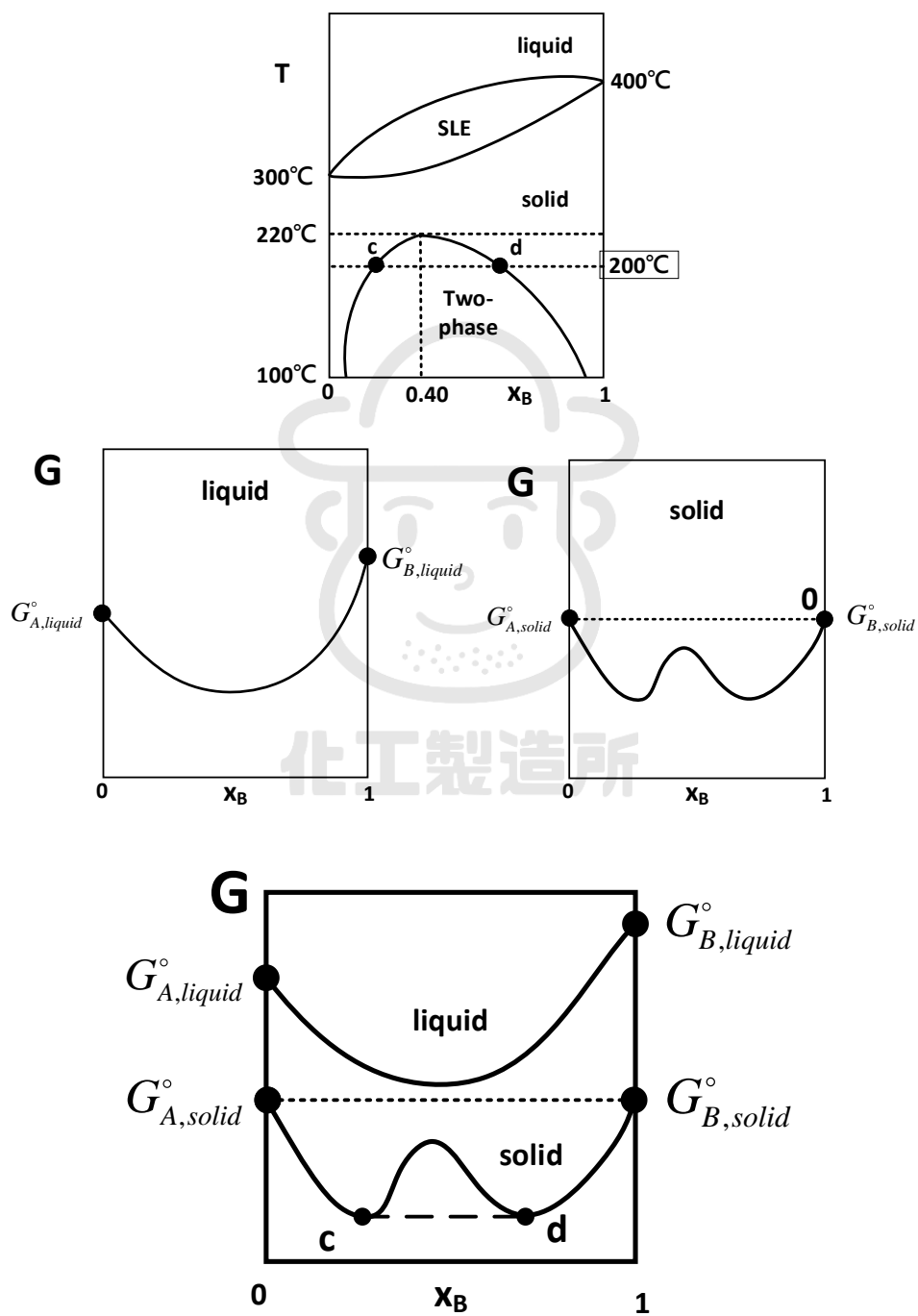


(c)

@At 200°C

Set the standard states as : $G_{A,solid}^\circ = 0$ and $G_{B,solid}^\circ = 0$

Assume : $G_{B,liquid}^\circ > G_{A,liquid}^\circ$



(自由能-組成相圖畫法可參考 106 年清大化熱化反 Problem 2 後解說。)

(d)

The liquid phase is not ideal solution because it would form a miscibility gap under certain condition. Instead, the liquid phase can be described by regular solution model, which can be expressed as,

$$\frac{\Delta G_{mix}}{RT} = \alpha x_A x_B + (x_A \ln x_A + x_B \ln x_B)$$

where the $\alpha x_A x_B$ term is accounted for the immiscible behavior of the solution.



Problem 3

【Solution】

(a)

For ideal gas per unit mole,

$$PV = RT \quad , \quad V = \frac{RT}{P}$$

代入：

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{P}{RT} \left[-\frac{RT}{P^2} \right] = \underline{\underline{\frac{1}{P}}}$$

(b)

For the fluid undergoing isothermal work,

$$w = -\int_{V_1}^{V_2} p dV$$

For constant β ,

$$\begin{aligned} \beta &= -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad , \quad dp = -\frac{1}{\beta V} dV \\ \int_{p_1}^p dp &= -\frac{1}{\beta} \int_{V_1}^V \frac{1}{V} dV \quad , \quad p = -\frac{1}{\beta} \ln \frac{V}{V_1} + p_1 \end{aligned}$$

代回：

$$w = -\int_{V_1}^{V_2} p_1 + \frac{1}{\beta} \int_{V_1}^{V_2} \ln \frac{V}{V_1} dV = -p_1(V_2 - V_1) + \frac{1}{\beta} \int_{V_1}^{V_2} \ln \frac{V}{V_1} dV$$

For $\int_{V_1}^{V_2} \ln \frac{V}{V_1} dV$, by integration by parts (IBP),

$$\int_{V_1}^{V_2} \ln \frac{V}{V_1} dV = V \ln \frac{V}{V_1} \Big|_{V_1}^{V_2} - \int_{V_1}^{V_2} V d \ln \frac{V}{V_1} = V_2 \ln \frac{V_2}{V_1} - \int_{V_1}^{V_2} dV = V_2 \ln \frac{V_2}{V_1} - V_2 + V_1$$

代回：

$$w = -p_1(V_2 - V_1) + \frac{1}{\beta} \int_{V_1}^{V_2} \ln \frac{V}{V_1} dV = -p_1(V_2 - V_1) + \frac{1}{\beta} V_2 \ln \frac{V_2}{V_1} - V_2 + V_1$$

$$\underline{\underline{w = -p_1(V_2 - V_1) + \frac{V_1}{\beta} \left[\frac{V_2}{V_1} \ln \frac{V_2}{V_1} - \frac{V_2}{V_1} + 1 \right]}}$$

(c)

根據此方程式，將數據代入：

$$\begin{aligned}w &= \frac{\beta V_1}{2}(p_2^2 - p_1^2) = \frac{1 \times 10^{-5} \times 0.1}{2}(10^2 - 1^2) = 4.95 \times 10^{-5} (\text{bar} \cdot \text{L}) \\&= 4.95 \times 10^{-5} \times \frac{10^5 \text{ Pa}}{1 \text{ bar}} \times \frac{10^{-3} \text{ m}^3}{1 \text{ L}} = \underline{\underline{4.95 \times 10^{-3} (\text{J})}}\end{aligned}$$

※在此簡單證明一下(雖然題目沒有要求)：

$$w = -p_1(V_2 - V_1) + \frac{V_1}{\beta} \left[\frac{V_2}{V_1} \ln \frac{V_2}{V_1} - \frac{V_2}{V_1} + 1 \right]$$

根據 β 定義：

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \approx -\frac{1}{V_1} \left(\frac{V_2 - V_1}{p_2 - p_1} \right), \quad V_2 - V_1 = -\beta V_1(p_2 - p_1)$$

$$\frac{V_2}{V_1} - 1 = -\beta(p_2 - p_1), \quad \frac{V_2}{V_1} = 1 - \beta(p_2 - p_1) = 1 - \varepsilon$$

(其中 $\varepsilon = \beta(p_2 - p_1) \ll 1$ ，因為體積變化不大)

對 $\ln\left(\frac{V_2}{V_1}\right) = \ln(1 - \varepsilon)$ 做泰勒展開：

$$\begin{aligned}\ln(1-x) &= -\sum_{k=1}^{\infty} \frac{x^k}{k} = -x - \frac{1}{2}x^2 - \dots \\ \ln(1-\varepsilon) &\approx -\varepsilon - \frac{1}{2}\varepsilon^2\end{aligned}$$

代回：

$$\frac{V_1}{\beta} \left\{ -(1-\varepsilon) \left[\varepsilon + \frac{1}{2}\varepsilon^2 \right] - (1-\varepsilon) + 1 \right\} = \frac{V_1}{\beta} \left\{ \cancel{-\varepsilon} - \frac{1}{2}\varepsilon^2 + \varepsilon^2 + \underbrace{\frac{1}{2}\varepsilon^3}_{\varepsilon \ll 1} + \cancel{\varepsilon} \right\} \approx \frac{1}{2} \frac{V_1}{\beta} \varepsilon^2$$

代回：

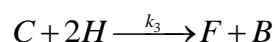
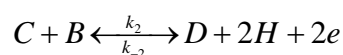
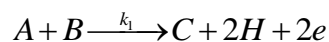
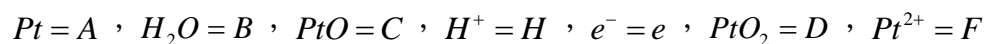
$$w = -p_1(V_2 - V_1) + \frac{V_1}{\beta} \left[\frac{V_2}{V_1} \ln \frac{V_2}{V_1} - \frac{V_2}{V_1} + 1 \right] \approx -p_1(V_2 - V_1) + \frac{1}{2} \beta V_1 (p_2 - p_1)^2$$

$$\begin{aligned}w &= p_1[\beta V_1(p_2 - p_1)] + \frac{1}{2} \beta V_1 (p_2 - p_1)^2 = \beta V_1 (p_2 - p_1) \left[p_1 + \frac{1}{2}(p_2 - p_1) \right] \\&= \frac{1}{2} \beta V_1 (p_2 - p_1) [(p_2 + p_1)] = \underline{\underline{\frac{\beta V_1}{2} (p_2^2 - p_1^2) }}\end{aligned}$$

Problem 4

【Solution】

將題目所給的反應式做簡寫，令：



(a)

The differential equation needed to model the dynamic changes of Pt-containing species

(A, C, D, F) are, (假設各條反應式之反應常數皆基於係數為 1 之反應物做定義)

$$\frac{dC_A}{dt} = -k_1 C_A C_B$$

$$\frac{dC_C}{dt} = k_1 C_A C_B - k_2 C_C C_B + k_{-2} C_D C_H^2 C_e^2 - k_3 C_C C_H^2$$

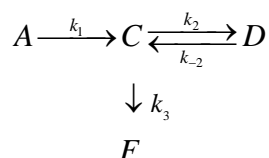
$$\frac{dC_D}{dt} = k_2 C_C C_B - k_{-2} C_D C_H^2 C_e^2$$

$$\frac{dC_F}{dt} = k_3 C_C C_H^2$$

(b)

【定性想法】

我們可以將此方程式簡化為以下路徑(因 B, H, e 皆過量，所以視為不影響反應)：



此為稍微複雜一點的連鎖反應，但對 C 來說，其濃度變化應也呈現如同一般連鎖反應中間產物之先上升後下降的濃度趨勢。

【定量算法】

Assume water (B), protons (H), and electrons (e) are in excess, the differential equations become,

$$\begin{aligned}\frac{dC_A}{dt} &= -k_1 C_A C_B \approx -k_1' C_A \\ \frac{dC_C}{dt} &\approx k_1' C_A - k_2' C_C + k_{-2}' C_D - k_3' C_C \\ \frac{dC_D}{dt} &\approx k_2' C_C - k_{-2}' C_D \\ \frac{dC_F}{dt} &\approx k_3' C_C\end{aligned}$$

然而因題目未給定此些過量反應物之濃度，因此以 $k_i = k_i'$ 做近似，例如 $k_1 = k_1'$

將此 ODE 組矩陣化，令 $\bar{C} = \begin{bmatrix} C_A \\ C_C \\ C_D \\ C_F \end{bmatrix}$ ，且此矩陣滿足：

$$\frac{d\bar{C}}{dt} = A\bar{C}$$

$$A = \begin{bmatrix} -k_1 & 0 & 0 & 0 \\ k_1 & -k_2 - k_3 & k_{-2} & 0 \\ 0 & k_2 & -k_{-2} & 0 \\ 0 & k_3 & 0 & 0 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 1 & -7 & 5 & 0 \\ 0 & 3 & -5 & 0 \\ 0 & 4 & 0 & 0 \end{bmatrix}$$

將矩陣對角化，令：

$$\det(A - \lambda I) = 0$$

$$\det(A - \lambda I) = \begin{vmatrix} -1-\lambda & 0 & 0 & 0 \\ 1 & -7-\lambda & 5 & 0 \\ 0 & 3 & -5-\lambda & 0 \\ 0 & 4 & 0 & -\lambda \end{vmatrix} = 0$$

觀察原本的矩陣，有一行本就為 0，因此必有一特徵值為 0

若將 $-1-\lambda$ 令為 0，則第一列皆為 0，則此行列式也必為 0

因此**必有一特徵值為-1**

剩餘之特徵值，可由第四行展開行列式做計算：

$$\det(A-\lambda I) = -\lambda \begin{vmatrix} -1-\lambda & 0 & 0 \\ 1 & -7-\lambda & 5 \\ 0 & 3 & -5-\lambda \end{vmatrix} = 0$$

$$\det(A-\lambda I) = -\lambda[(-1-\lambda)(-7-\lambda)(-5-\lambda) - (-1-\lambda) \times 15] = 0$$

$$\det(A-\lambda I) = -\lambda(-1-\lambda)[\lambda^2 + 12\lambda + 20] = 0$$

(λ 與 $(-1-\lambda)$ 暗示之二根前面已經算過)

$$\text{則解 } \lambda^2 + 12\lambda + 20, \quad \boxed{\lambda = -2, -10}$$

令 $\lambda_1 = -2$ 代入 $(A-\lambda I)\bar{C}_1 = 0$ ：

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 1 & -5 & 5 & 0 \\ 0 & 3 & -3 & 0 \\ 0 & 4 & 0 & 2 \end{bmatrix} \bar{C}_1 = 0, \quad \bar{C}_1 = \begin{bmatrix} 0 \\ 1 \\ 1 \\ -2 \end{bmatrix}$$

令 $\lambda_2 = -10$ 代入 $(A-\lambda I)\bar{C}_2 = 0$ ：

$$\begin{bmatrix} 9 & 0 & 0 & 0 \\ 1 & 3 & 5 & 0 \\ 0 & 3 & 5 & 0 \\ 0 & 4 & 0 & 10 \end{bmatrix} \bar{C}_2 = 0, \quad \bar{C}_2 = \begin{bmatrix} 0 \\ -5 \\ 3 \\ 2 \end{bmatrix}$$

令 $\lambda_3 = -1$ 代入 $(A-\lambda I)\bar{C}_3 = 0$ ：

$$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 1 & -6 & 5 & 0 \\ 0 & 3 & -4 & 0 \\ 0 & 4 & 0 & 1 \end{bmatrix} \bar{C}_3 = 0, \quad \bar{C}_3 = \begin{bmatrix} 9 \\ 4 \\ 3 \\ -16 \end{bmatrix}$$

令 $\lambda_4 = 0$ 代入 $(A-\lambda I)\bar{C}_4 = 0$ ：

$$\begin{bmatrix} -1 & 0 & 0 & 0 \\ 1 & -7 & 5 & 0 \\ 0 & 3 & -5 & 0 \\ 0 & 4 & 0 & 0 \end{bmatrix} \bar{C}_4 = 0, \quad \bar{C}_4 = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

則此方程式的解為：

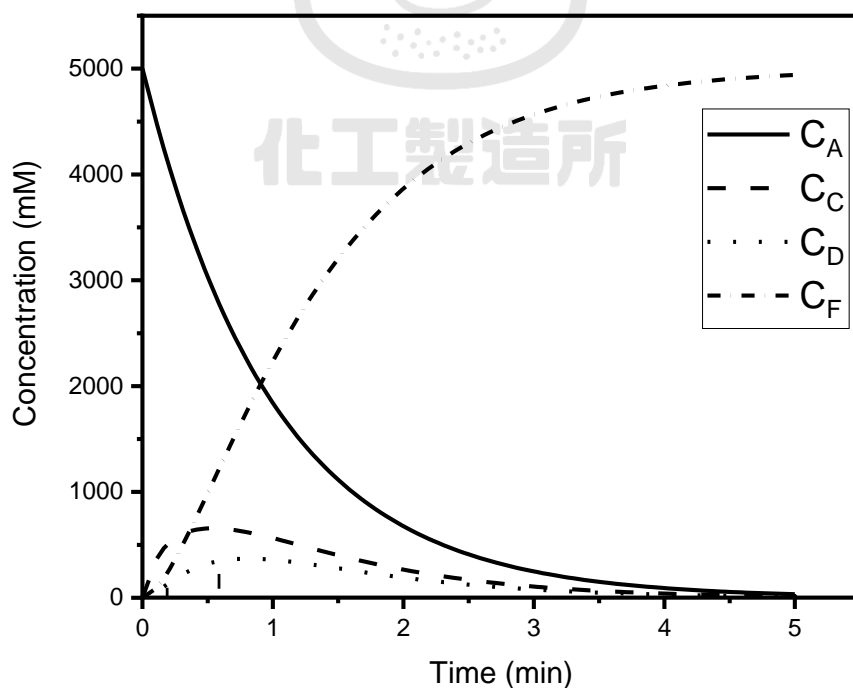
$$\bar{C} = \begin{bmatrix} C_A \\ C_C \\ C_D \\ C_F \end{bmatrix} = C_1 \begin{bmatrix} 0 \\ 1 \\ 1 \\ -2 \end{bmatrix} e^{-2t} + C_2 \begin{bmatrix} 0 \\ -5 \\ 3 \\ 2 \end{bmatrix} e^{-10t} + C_3 \begin{bmatrix} 9 \\ 4 \\ 3 \\ -16 \end{bmatrix} e^{-t} + C_4 \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

即：

$$\begin{cases} C_A = 9C_3 e^{-t} \\ C_C = C_1 e^{-2t} - 5C_2 e^{-10t} + 4C_3 e^{-t} \\ C_D = C_1 e^{-2t} + 3C_2 e^{-10t} + 3C_3 e^{-t} \\ C_F = -2C_1 e^{-2t} + 2C_2 e^{-10t} - 16C_3 e^{-t} + C_4 \end{cases}, \begin{cases} t=0, C_A = C_{A0} \\ t=0, C_C = 0 \\ t=0, C_D = 0 \\ t=0, C_F = 0 \end{cases}$$

將四個邊界條件代入解係數，得：

$$\begin{cases} C_A = 9C_3 e^{-t} \\ C_C = C_1 e^{-2t} - 5C_2 e^{-10t} + 4C_3 e^{-t} \\ C_D = C_1 e^{-2t} + 3C_2 e^{-10t} + 3C_3 e^{-t} \\ C_F = -2C_1 e^{-2t} + 2C_2 e^{-10t} - 16C_3 e^{-t} + C_4 \end{cases}, \begin{cases} C_1 = -\frac{3}{8}C_{A0} \\ C_2 = \frac{1}{72}C_{A0} \\ C_3 = \frac{1}{9}C_{A0} \\ C_4 = C_{A0} \end{cases}$$



這裡畫圖上假設 $C_{A0} = 5000$ ，考試時應該示意即可


```

#To calculate the volume of the batch reactor, we need the following differential equations,
d(CA)/d(t) = rA
d(CC)/d(t) = rC
d(CD)/d(t) = rD
d(CF)/d(t) = rF

#Define the rate equation
rA = -k1*CA
rC = k1*CA-k2*CC+k3*CD-k4*CC
rD = k2*CC-k3*CD
rF = k4*CC

#The parameters or conditions we need or values are,
k1 = 1
k2 = 3
k3 = 5
k4 = 4

CA(0) = 5000
CC(0) = 0
CD(0) = 0
CF(0) = 0

#To complete the calculation, we need
p = CA+CC+CD+CF

#The range of time we want to know
t(0) = 0
t(f) = 5

```

本題與 112 年清大化熱化反 Problem 4 相似，基本上都遵照一般鏈鎖反應的濃度變化進程。

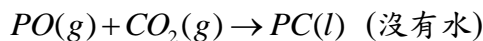


Problem 5

【Solution】

(a)

Reactions:



The reaction enthalpy is then,

$$H_{f,PC} - H_{f,CO_2} - H_{f,PO} = -613 - (-393.51) - (-94.68) = -124.81 \text{ (kJ / mol)}$$

The reaction entropy of the production of CO is,

$$S_{PC} - S_{CO_2} - S_{PO} = 218.6 - 213.8 - 287.4 = -282.6 \text{ (J / mol} \cdot \text{K)}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -124.81 \times 10^3 - (180 + 273.15) \times (-282.6) = 3250.2 \text{ (J / mol)}$$

For the equilibrium constant, we have,

$$\Delta G^\circ = -RT \ln K, \quad 3250.2 = -8.314 \times (180 + 273.15) \ln(K), \quad \underline{\underline{K = 0.422}}$$

(b)

※本題按原先給的條件不足，無法作實際的運算，因氣相反應與壓力有關，在題目未給壓力的情況下，無法得到一個明確的數值。即使題目假設為 1 bar，則此時按照題目給的進料條件，

$P_{CO_2} = P_{PO} = 0.5 \text{ (bar)}$ ，則其反應商數可計算為：

$$Q = \frac{1}{P_{CO_2} P_{PO}} = \frac{1}{0.5 \times 0.5} = 4 > K$$

則反應不會向右走，就沒有轉化率可做計算。

假設初始壓力為 10 bar，則 $P_{CO_2,i} = P_{PO,i} = 5 \text{ bar}$

$$K = \frac{1}{P_{CO_2} P_{PO}} = \frac{1}{(5-x)^2} = 0.422, \quad x = 3.46$$

$$\text{則轉化率為 } \frac{3.46}{5} = \underline{\underline{0.692}}$$

Problem 6

【Solution】

For the reaction carrying with a constant-volume batch reactor, by the design equation,

$$-\frac{dN_A}{dt} = -r_A V, \quad C_{A0} \frac{dx_A}{dt} = -r_A$$

By the rate expression,

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

Combine,

$$\begin{aligned} \frac{dx_A}{dt} &= kC_{A0}(1-x_A)^2 \\ \int_0^{0.5} \frac{1}{(1-x_A)^2} dx_A &= \int_0^1 kC_{A0} dt \\ k &= \frac{1}{\int_0^{0.5} \frac{1}{(1-x_A)^2} dx_A \times \int_0^1 0.2 dt} = 5 \text{ (M}^{-1}\text{hr}^{-1}\text{)} \end{aligned}$$

For the reaction carried out at CSTR,

$$V = \frac{F_{A0}x_A}{-r_A} = \frac{F_{A0}x_A}{kC_A^2} = \frac{F_{A0}x_A}{kC_{A0}^2 \left(\frac{1-x_A}{1+\varepsilon x_A} \right)^2}, \quad \varepsilon = \delta y_{A0} = \left(\frac{1-2}{2} \right) \times 1 = -0.5$$

$$V = \frac{F_{A0}x_A}{kC_{A0}^2 \left(\frac{1-x_A}{1-0.5x_A} \right)^2} = \frac{500 \times 0.5}{5 \times 0.2^2 \left(\frac{1-0.5}{1-0.5 \times 0.5} \right)^2} = \underline{\underline{2812.3(\text{dm}^3)}}$$

Problem 7

【Solution】

(a) For the gas-phase reaction at constant pressure and temperature,

$$C_{SO_2} = C_{SO_2,0} \left(\frac{1-X}{1+\varepsilon X} \right)$$

$$\varepsilon = \delta y_{SO_2,0} = \frac{2-1-2}{2} \times 0.28 = -0.5 \times 0.28 = -0.14$$

$$C_{SO_2} = C_{SO_2,0} \left(\frac{1-X}{1-0.14X} \right) = \frac{P_{SO_2,0}}{RT} \left(\frac{1-X}{1-0.14X} \right) = \frac{1485 \times 10^3 \times 0.28}{8.314 \times 500} \left(\frac{1-X}{1-0.14X} \right) = \underline{\underline{100 \left(\frac{1-X}{1-0.14X} \right)}}$$

同理：

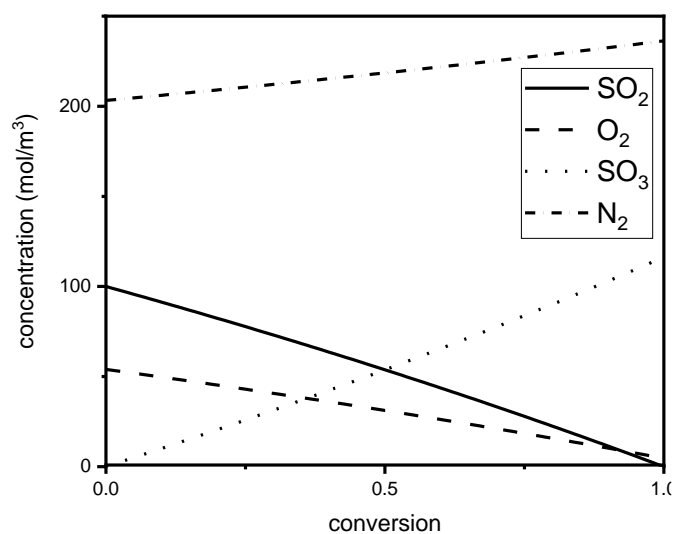
$$C_{O_2} = C_{SO_2,0} \left(\frac{\theta_{O_2} - 0.5X}{1-0.14X} \right) = \frac{P_{SO_2,0}}{RT} \left(\frac{\theta_{O_2} - 0.5X}{1-0.14X} \right) = 100 \left(\frac{\frac{0.72 \times 0.21}{0.28} - 0.5X}{1-0.14X} \right) = \underline{\underline{100 \left(\frac{0.54 - 0.5X}{1-0.14X} \right)}}$$

$$C_{SO_3} = C_{SO_2,0} \left(\frac{X}{1-0.14X} \right) = \frac{P_{SO_2,0}}{RT} \left(\frac{0.5X}{1-0.14X} \right) = \underline{\underline{100 \left(\frac{X}{1-0.14X} \right)}}$$

$$\begin{aligned} C_{N_2} &= C_{T0} - C_{SO_2} - C_{O_2} - C_{SO_3} \\ &= \frac{1485 \times 1000}{8.314 \times 500} - 100 \left[\left(\frac{1-X}{1-0.14X} \right) + \left(\frac{0.54-0.5X}{1-0.14X} \right) + \left(\frac{X}{1-0.14X} \right) \right] = \underline{\underline{357.22 - \left[\frac{100(-0.5X+1.54)}{1-0.14X} \right]}} \end{aligned}$$

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(b)



Convserion	C_{SO_2}	C_{O_2}	C_{SO_3}	C_{N_2}	C_{Total}
0	100	54	0	203.22	357.22
0.25	77.72021	43.00518	25.90674	210.5879	357.22
0.5	53.76344	31.1828	53.76344	218.5103	357.22
1	0	4.651163	116.2791	236.2898	357.22

(提供同學驗算)

※基本上，因每一個濃度項的分母 $(1-0.14X)$ 其最低不過 $1-0.14=0.86$ ，因此其所造成的非線性現象比較沒有這麼明顯，因此考試如果要粗略的畫圖，可以以線性變化的方式去思考。

