

106 年中興化熱化反

Problem 1

【Solution】

(1) If there is one mixed reactor alone

By the design equation of mixed reactor,

$$V = \frac{F_R}{r_R} = \frac{v_0 C_{A0} x_A}{r_R}$$

By the rate equation,

$$r_R = 0.01 C_A C_R = 0.01 C_{A0}^2 (1 - x_A) x_A$$

Combined with the rate equation,

$$V = \frac{v_0 C_{A0} x_A}{0.01 C_{A0}^2 (1 - x_A) x_A}$$

$$\because F_R = v_0 C_{A0} x_A, \quad x_A = \frac{F_R}{v_0 C_{A0}} = \frac{1000}{v_0 C_{A0}}$$

$$V = \frac{v_0 C_{A0} \times \frac{1000}{v_0 C_{A0}}}{0.01 C_{A0}^2 (1 - \frac{1000}{v_0 C_{A0}}) \times \frac{1000}{v_0 C_{A0}}} = \frac{1000}{0.01 (C_{A0} - \frac{1000}{v_0}) \times \frac{1000}{v_0}}$$

$$V = \frac{1000}{0.01 (C_{A0} - \frac{1000}{v_0}) \times \frac{1000}{v_0}} = \frac{1000}{0.01 (100 - \frac{1000}{v_0}) \times \frac{1000}{v_0}} = \frac{1000 v_0^2}{0.01 (100 v_0 - 1000) \times 1000} = \frac{v_0^2}{(v_0 - 10)}$$

The total cost is,

$$C = 0.1 C_{A0} v_0 + 8 + \frac{0.01 v_0^2}{(v_0 - 10)} = 10 v_0 + 8 + \frac{0.01 v_0^2}{(v_0 - 10)}$$

To determine the volumetric flow rate when the cost is minimum, let,

$$\frac{dC}{dv_0} = 10 + 0.01 \left[\frac{2v_0(v_0 - 10) - v_0^2}{(v_0 - 10)^2} \right] = 0$$

$$10(v_0 - 10)^2 + 0.01 \times (v_0^2 - 10v_0) = 0$$

$$10.01 v_0^2 - 200.2 v_0 + 1000 = 0, \quad v_0 = 10.32, \quad 9.68 = 10.32 \text{ (L/hr)}$$

【Check if it's minimum】

$$\frac{d^2C}{dv_0^2} = 20.02v_0 - 200.2$$
$$\left. \frac{d^2C}{dv_0^2} \right|_{v_0=10.32} = 20.02 \times 10.32 - 200.2 = 6.32 > 0$$

The total cost is,

$$C = 10 \times 10.32 + 8 + \frac{0.01 \times (10.32)^2}{(10.32 - 10)} = 114.52 \text{ (dollars / hr)}$$

(2) If there is one mixed reactor and one separator, no A is recycled

此種情況體積流率與反應器體積與(1)相同，因沒有 A 回流，只是將產物再多利用分離單元分成純 A 與純 F，相比(1)來說還多了分離單元體積，成本勢必較高。

(3) If there is one mixed reactor and one separator, with A recycled

此種情況因有 A 回流，造成整體 A 進口流率為：

$$v_0' = v_0 + v_{\text{recycle}} > v_0$$

相比(1)來說進口流率體積較高，且又增加分離單元體積所造成之成本，因此成本比(1)高。

The reaction system with only one mixed reactor with no separator is the most economical, and the hourly cost is 114.52 (dollars/hr).

然而一般來說增加分離單元的好處在於，可以得到較純的產物(濃度較高)，並非增加莫耳流率。

Problem 2

【Solution】

For the reforming reaction, (calculated by the partial pressure of each species)

	CH_4	+	H_2O	\leftrightarrow	CO	+	$3H_2$
初	x		$5x$		0		0
反	$-y$		$-y$		$+y$		$+3y$
平	$x-y$		$5x-y$		y		$3y$
修正	$x-y$		$5x-y-z$		$y-z$		$3y+z$

For the shift reaction,

	CO	+	H_2O	\leftrightarrow	CO_2	+	H_2
初	y		$5x-y$		0		$3y$
反	$-z$		$-z$		$+z$		$+z$
平	$y-z$		$5x-y-z$		z		$3y+z$

(以此結果修正第一條反應式最終平衡結果)

$$P_{total} = P_{CH_4} + P_{H_2O} + P_{CO} + P_{H_2} + P_{CO_2}$$

$$x-y+5x-y-z+y-z+3y+z+z=6x+2y=20$$

$$y=10-3x \text{---(1)}$$

By the result of the reforming reaction,

$$K_p = \frac{(y-z)(3y+z)^3}{(x-y)(5x-y-z)} = 128 \text{---(2)}$$

By the result of the reforming reaction,

$$K_p = \frac{(z)(3y+z)}{(5x-y-z)(y-z)} = 1 \text{---(3)}$$

將 $y = 10 - 3x$ 代回(2)：

$$K_p = \frac{(10 - 3x - z)(30 - 9x + z)^3}{(x + 3x - 10)(5x - 10 + 3x - z)} = 128$$

$$K_p = \frac{(10 - 3x - z)(30 - 9x + z)^3}{(4x - 10)(8x - 10 - z)} = 128 \quad \text{--- (4)}$$

代回(3)

$$K_p = \frac{z(30 - 9x + z)}{(5x - 10 + 3x - z)(10 - 3x - z)} = 1$$

$$z = \frac{110x - 24x^2 - 100}{30 - 4x} \text{ 代回 reforming 之 } K_p :$$

$$x = 2.597, \quad z = 1.213$$

$$y = 10 - 3 \times 2.597 = 2.207$$

$$\left\{ \begin{array}{l} y_{CH_4} = \frac{x - y}{20} = \frac{2.597 - 2.207}{20} = 0.0195 \\ y_{H_2O} = \frac{5x - y - z}{20} = \frac{5 \times 2.597 - 2.207 - 1.213}{20} = 0.478 \\ y_{CO} = \frac{y - z}{20} = \frac{2.207 - 1.213}{20} = 0.0496 \\ y_{H_2} = \frac{3y + z}{20} = \frac{3 \times 2.207 + 1.213}{20} = 0.392 \\ y_{CO_2} = \frac{z}{20} = \frac{1.213}{20} = 0.061 \end{array} \right.$$

※本題不可將 reforming 反應後的結果未經修正就先代入 $K_p = 128$ 做初步計算，再利用計算後

之結果代入 shift 反應做第二步計算，比如：

$$K_p = \frac{(y)(3y)^3}{(x - y)(5x - y)} = 128$$

先算出 x, y ，再考慮第二步反應算 z ，則 $CO = y - z$

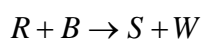
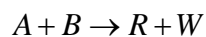
這是錯誤的解法，因為同時滿足兩個平衡的 CO 分壓是 $y - z$ (兩條反應在同一反應器下進行)，而非滿足 reforming 反應的分壓為 y ，滿足 shift 反應的分壓為 $y - z$ ；除非兩條反應分別在不同環境中進行，則可以在第一個反應器先考慮 reforming 的平衡，到第二個反應器 shift 反應才開始進行，此時再考慮下一步平衡反應。

Problem 3

【Solution】

令 $C_6H_5NH_2 = A$, $C_2H_5OH = B$, $C_6H_5NHC_2H_5 = R$, $C_6H_5N(C_2H_5)_2 = S$

$H_2O = W$, 則反應變為 :



(a)

$$\frac{k_2}{k_1} = \frac{k_2}{1.25k_2} = \frac{1}{1.25} = 0.8$$

$$\frac{-\Delta C_B}{C_{A0}} = \frac{-(0 - C_{B0})}{C_{A0}} = 1$$

對圖，可得：

$$\frac{C_R}{C_{A0}} = 0.4$$

$$\frac{C_{A0} - C_A}{C_{A0}} = 0.7 , \frac{C_A}{C_{A0}} = 0.3$$

$$\frac{C_S}{C_{A0}} = \frac{C_{B0} - (C_{A0} - C_A)}{C_{A0}} = 1 - (1 - 0.3) = 0.3$$

$$\frac{C_W}{C_{A0}} = 1$$

整理：

$\frac{C_A}{C_{A0}}$	$\frac{C_B}{C_{A0}}$	$\frac{C_R}{C_{A0}}$	$\frac{C_S}{C_{A0}}$	$\frac{C_W}{C_{A0}}$
0.3	0	0.4	0.3	1

(b)

By the design equation of mixed flow reactor,

$$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{B0} - C_B}{-r_B} = \frac{C_R}{r_R} = \frac{C_S}{r_S}$$

By the rate equation,

$$-r_A = k_1 C_A C_B$$

$$r_R = k_1 C_A C_B - k_2 C_R C_B$$

$$\frac{C_R}{k_1 C_A C_B - k_2 C_R C_B} = \frac{C_{A0} - C_A}{k_1 C_A C_B}$$

$$C_R = \frac{(C_{A0} - C_A) C_A}{C_A + \frac{k_1}{k_2} (C_{A0} - C_A)}$$

\therefore The conversion of A is 70%,

$$C_A = (1 - 0.7) C_{A0} = 0.3 C_{A0}$$

代入：

$$C_R = \frac{0.7 C_{A0} \times 0.3 C_{A0}}{0.3 C_{A0} + 1.25 \times 0.3 C_{A0}} = 0.311 C_{A0}$$

For C_S

$$\therefore C_{A0} + \cancel{C_{R0}} + \cancel{C_{S0}} = C_A + C_R + C_S$$

$$C_R + C_S = C_{A0} - C_A = 0.7 C_{A0}$$

$$C_S = 0.7 C_{A0} - C_R \text{ 代入得}$$

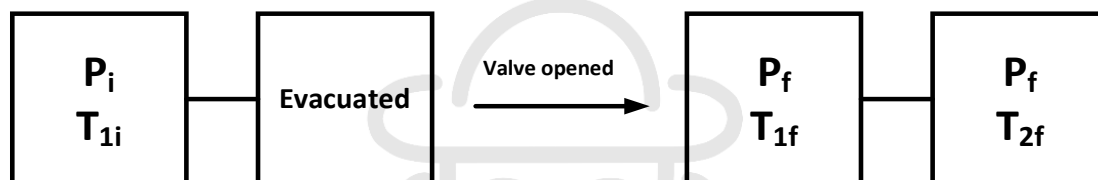
$$\frac{C_R}{C_S} = \frac{C_R}{0.7 C_{A0} - C_R} = \frac{0.311 C_{A0}}{0.7 C_{A0} - 0.311 C_{A0}} = \underline{\underline{0.8}}$$

※(b)小題不可直接用題目所附圖，因題目附圖為 batch or plug flow reactor 專用，mixed flow reactor 適用的圖可參考：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 191, Figure 8.14.，與題目附圖有些許差異。另外本題單純用算式計算的方式是令 A 的轉化率為 0.7(因無法得知 B 轉化率為 0.7 時 A 轉化率為多少)，然而若是可用題目附圖近似或題目有給 mixed flow 適用的圖，就可以將 0.7 視為 B 的轉化率，此時 $-\Delta C_B / C_{A0} = 1.4$ ，可自行嘗試做圖方法求出結果。
 本題改編自 Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 202, Problem 8.8.

Problem 4

【Solution】

(a)



By mole balance of the system,

$$\frac{P_i V_1}{RT_{1i}} + 0 = \frac{P_f V_1}{RT_{1f}} + \frac{P_f V_2}{RT_{2f}}$$

$$\frac{40}{200} = P_f \left(\frac{1}{T_{1f}} + \frac{1}{T_{2f}} \right)$$

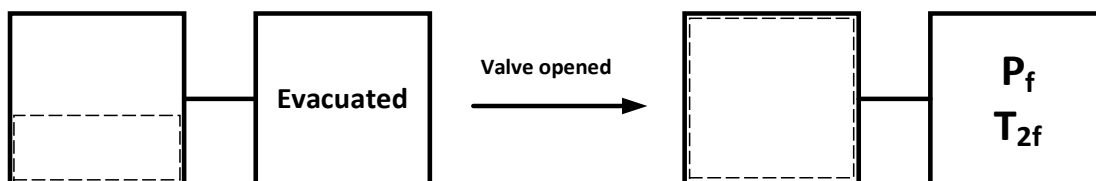
By energy balance of the system,

$$\frac{P_i V_f}{RT_{1i}} C_v T_{1i} + 0 = \frac{P_f V_1}{RT_{1f}} C_v T_{1f} + \frac{P_f V_2}{RT_{2f}} C_v T_{2f}$$

$$P_i = 2P_f, \quad \underline{\underline{P_f = \frac{40}{2} = 20 \text{ (bar)}}}$$

For T_{1f} , if we consider the portion of the gas remaining in the first tank as system,

the system can be assumed to undergo reversible, adiabatic expansion,



$$\left(\frac{T_{1f}}{T_{li}}\right)^{\frac{C_p^*}{R}} = \left(\frac{P_f}{P_i}\right), \quad \left(\frac{T_{1f}}{200}\right)^{\frac{24.9}{8.3}} = \left(\frac{20}{40}\right)$$

$$\underline{\underline{T_{1f} = 200 \times \left(\frac{1}{2}\right)^{\frac{1}{3}} = 158.74 \text{ (K)}}}$$

代回 mole balance,

$$\frac{40}{200} = 20 \left(\frac{1}{158.74} + \frac{1}{T_{2f}} \right), \quad \underline{\underline{T_{2f} = 270.24 \text{ (K)}}}$$

(b)



By mole balance of the system,

$$\frac{P_i V_1}{RT_{li}} + 0 + 0 = \frac{P_f V_1}{RT_{1f}} + \frac{P_f V_2}{RT_{2f}} + \frac{P_f V_3}{RT_{3f}}$$

The initial conditions and final pressure of 2 and 3 are the same, therefore,

$$T_{2f} = T_{3f}$$

$$\frac{40}{200} = P_f \left(\frac{1}{T_{1f}} + \frac{2}{T_{2f}} \right)$$

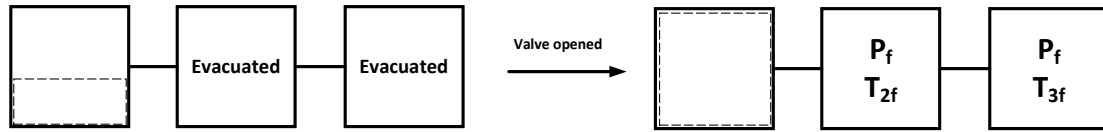
By energy balance of the system,

$$\frac{P_i V_f}{RT_{li}} C_v T_{li} + 0 = \frac{P_f V_1}{RT_{1f}} C_v T_{1f} + \frac{P_f V_2}{RT_{2f}} C_v T_{2f} + \frac{P_f V_3}{RT_{2f}} C_v T_{2f}$$

$$\underline{\underline{P_i = 3P_f, \quad P_f = \frac{40}{3} = 13.33 \text{ (bar)}}}$$

For T_{1f} , if we consider the portion of the gas remaining in the first tank as system,

the system can be assumed to undergo reversible, adiabatic expansion,



$$\left(\frac{T_{1f}}{T_{1i}}\right)^{\frac{C_p^*}{R}} = \left(\frac{P_f}{P_i}\right), \quad \left(\frac{T_{1f}}{200}\right)^{\frac{24.9}{8.3}} = \left(\frac{1}{3}\right)$$

$$T_{1f} = 200 \times \left(\frac{1}{3}\right)^{\frac{1}{3}} = 138.67 \text{ (K)}$$

$$\frac{40}{200} = 13.33 \times \left(\frac{1}{138.67} + \frac{2}{T_{2f}}\right)$$

$$T_{2f} = T_{3f} = 256.8 \text{ (K)}$$

(本題改編自：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

p 76~79, Illustration 3.4-5.)

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Problem 5**【Solution】**

(a)

By the triple-product rule,

$$\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -1$$

$$\left(\frac{\partial T}{\partial P}\right)_S = -\frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{V\alpha}{\left(\frac{C_P}{T}\right)} = \frac{V\alpha T}{C_P}$$

(b)

$$\frac{\kappa_S}{\kappa_T} = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$$

$$\left(\frac{\partial V}{\partial P}\right)_S = -\frac{\left(\frac{\partial S}{\partial P}\right)_V}{\left(\frac{\partial S}{\partial V}\right)_P}, \quad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{\left(\frac{\partial T}{\partial P}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_P}$$

$$\frac{\kappa_S}{\kappa_T} = \frac{\left(\frac{\partial S}{\partial P}\right)_V}{\left(\frac{\partial S}{\partial V}\right)_P} \times \frac{\left(\frac{\partial T}{\partial V}\right)_P}{\left(\frac{\partial T}{\partial P}\right)_V} = \frac{\left(\frac{\partial S}{\partial P}\right)_V}{\left(\frac{\partial S}{\partial V}\right)_P} \times \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{\left(\frac{\partial S}{\partial T}\right)_V}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{C_V}{C_P}$$

(本題改編自：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

P276, Problem 6.8.)

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Problem 1

【Solution】

(a)

$$-\frac{dp_A}{dt} = k_{A,gas} p_A^2 [=] atm / hr$$

$$k_{A,gas} [=] \left(\frac{atm}{hr} \cdot \frac{1}{atm^2} \right) [=] \underline{\underline{(atm \cdot hr)^{-1}}}$$

(b)

$$\frac{-dp_A}{dt} = \frac{-d(C_A RT)}{dt} = 3.66 p_A^2 = 3.66 (C_A RT)^2$$

$$\frac{-dC_A}{dt} = \underbrace{3.66(RT)}_{k_A} C_A^2$$

$$k_A' = \underbrace{3.66(0.082 \times 400)}_{(\frac{mol}{L})^{-1} \cdot hr^{-1}} \times \frac{1 hr}{3600 s} \times \frac{1 m^3}{1000 L} = \underline{\underline{3.33 \times 10^{-5} (m^3 / mole \cdot s)}}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 34, Problem 2.7.)

Problem 2

【Solution】

(a)

By the definition of equilibrium constant,

$$K_C = \frac{C_{Re}}{C_{Ae}} = \frac{C_{A0}(M + X_{Ae})}{C_{A0}(1 - X_{Ae})} = \underline{\underline{\frac{(M + X_{Ae})}{(1 - X_{Ae})}}}$$

(b)

$$-r_A = \frac{-dC_A}{dt} = C_{A0} \frac{dx_A}{dt} = k_1 C_A - k_2 C_R = k_1 C_{A0} [(1-x_A) - \frac{1}{K_C} (M+x_A)]$$

$$\frac{dx_A}{dt} = k_1 [(1 - \frac{M}{K_C}) - (1 + \frac{1}{K_C}) x_A] = k_1 [A + Bx_A]$$

$$\int_0^{x_A} \frac{1}{A + Bx_A} dx_A = \int_0^t k_1 dt$$

$$\frac{1}{B} \ln(\frac{A + Bx_A}{A}) = k_1 t, \quad \ln(\frac{A}{A + Bx_A}) = Bk_1 t$$

$$\ln[\frac{1 - \frac{M}{K_C}}{1 - \frac{M}{K_C} - (1 + \frac{1}{K_C}) x_A}] = (1 + \frac{1}{K_C}) k_1 t$$

$$\ln[\frac{1 - \frac{M}{K_C}}{1 - \frac{M}{K_C} - (1 + \frac{1}{K_C}) x_A}] = (1 + \frac{1}{K_C}) k_1 t$$

$$\text{For } 1 - \frac{M}{K_C} = 1 - \frac{M(1 - X_{Ae})}{(M + X_{Ae})} = \frac{M + X_{Ae} - M + MX_{Ae}}{M + X_{Ae}} = \frac{(M + 1)X_{Ae}}{M + X_{Ae}}$$

$$\text{For } 1 + \frac{1}{K_C} = 1 + \frac{(1 - X_{Ae})}{(M + X_{Ae})} = \frac{1 + X_{Ae} + M - X_{Ae}}{M + X_{Ae}} = \frac{M + 1}{M + X_{Ae}}$$

代回：

$$\ln[\frac{\frac{(M + 1)X_{Ae}}{M + X_{Ae}}}{\frac{(M + 1)X_{Ae}}{M + X_{Ae}} - \frac{(M + 1)x_A}{M + X_{Ae}}}] = \frac{(M + 1)x_A}{M + X_{Ae}} k_1 t$$

$$\ln[\frac{X_{Ae}}{X_{Ae} - x_A}] = \frac{(M + 1)x_A}{M + X_{Ae}} k_1 t$$

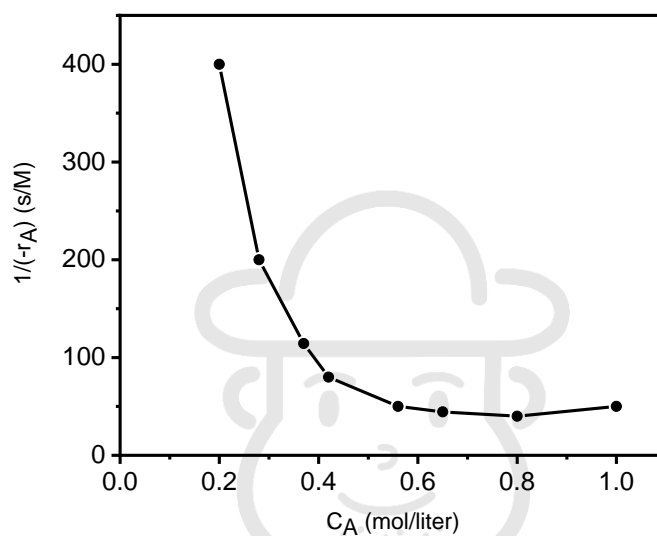
Problem 3

【Solution】

Assume the data are obtained in steady state runs of CSTR,

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

C_{Af}	1.00	0.80	0.65	0.56	0.42	0.37	0.28	0.20
$\frac{1}{-r_A}$	50	40	44.4	50	80	114.28	200	400



(a)

For PFR, by design equation,

$$V = v_0 \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} = \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A}$$

$$C_{A0} = 0.8 \text{ (M)}, \quad C_{Af} = C_{A0}(1 - x_A) = 0.8 \times (1 - 0.75) = 0.20 \text{ (M)}$$

By Simpson's rule,

$$V = \frac{0.15}{3} \left[\frac{1}{-r_A(0.2)} + \frac{4}{-r_A(0.35)} + \frac{2}{-r_A(0.5)} + \frac{4}{-r_A(0.65)} + \frac{1}{-r_A(0.80)} \right]$$
$$\approx \frac{0.15}{3} [400 + 4 \times 114.28 + 2 \times 50 + 4 \times 44.4 + 40] = \underline{\underline{58.73 \text{ (L)}}}$$

(b)

For CSTR, by design equation,

$$V = \frac{v_0(C_{A0} - C_{Af})}{-r_A}$$

$$C_{A0} = 0.8 \text{ (M)}, \quad C_{Af} = C_{A0}(1 - x_A) = 0.8 \times (1 - 0.75) = 0.20 \text{ (M)}$$

$$V = 1 \times (0.8 - 0.2) \times 40 = \underline{\underline{240 \text{ (L)}}}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 119, Problem 5.30.

本題原題未提及數據是在哪種反應器中得到，因此為簡化計算，自行假設為 CSTR。)

Problem 4

【Solution】

(a)

For the reaction heat,

$$\Delta H_r = \Delta H_{r0} + \int_{T_0}^T \underbrace{\Delta C_p}_{C_{pA}=C_{pR}} dT = \Delta H_{r0}$$

For the equilibrium constant,

$$K_{298} = \exp[-\Delta G_{298}^\circ / RT] = \exp[14840 / (8.314 \times 298)] = 399.3$$

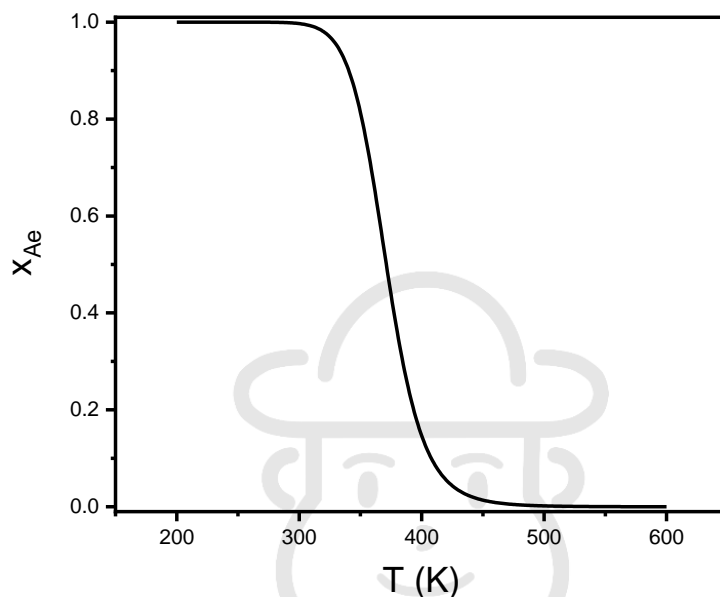
By Van't Hoff equation,

$$\frac{\ln K}{\ln K_{298}} = \frac{-\Delta H_r}{R} \left(\frac{1}{T} - \frac{1}{298} \right)$$
$$K = K_{298} e^{\frac{-\Delta H_r}{8.314} \left(\frac{1}{T} - \frac{1}{298} \right)} = 399.3 e^{\frac{-75300}{8.314} \left(\frac{1}{T} - \frac{1}{298} \right)} = 399.3 e^{9057 \left(\frac{1}{T} - \frac{1}{298} \right)}$$

For the relationship of conversion versus temperature, by the equilibrium relation,

$$K = \frac{C_{Re}}{C_{Ae}} = \frac{C_{A0}x_{Ae}}{C_{A0}(1-x_{Ae})} = \frac{x_{Ae}}{1-x_{Ae}}$$

$$x_{Ae} = \frac{K}{K+1} = \frac{399.3e^{9057(\frac{1}{T}-\frac{1}{298})}}{1+399.3e^{9057(\frac{1}{T}-\frac{1}{298})}}$$



(b)

$$x_{Ae} = 0.90 = \frac{399.3e^{9057(\frac{1}{T}-\frac{1}{298})}}{1+399.3e^{9057(\frac{1}{T}-\frac{1}{298})}}, T = 340.5 \text{ (K)}$$

The temperature of the reactor should be kept equal to or below 340.5K to obtain a conversion of 90% or higher.

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 213~215, Example 9.2.)

Problem 5

【Solution】

By energy balance on the each of the cylinder (open system, unsteady state):

$$\left[H + \frac{g}{g_c} z + \frac{1}{2g_c} v^2 \right]_{in} dn_{in} - \left[H + \frac{g}{g_c} z + \frac{1}{2g_c} v^2 \right]_{out} dn_{out} + \cancel{dQ} + \cancel{dW} = d \left[n \left(U + \frac{g}{g_c} z + \frac{1}{2g_c} v^2 \right) \right]_{sys}$$

$$H_{in} dn_{in} = d[nU]_{sys}, \quad H_{in} n_{in} = n_f U_f - n_i U_i$$

By mole balance of the each of the cylinder,

$$n_{in} = n_f - n_i = \frac{P_f V}{RT_f} - \frac{P_i V}{RT_i} \text{ 代入}$$

$$\left(\frac{P_f V}{RT_f} - \frac{P_i V}{RT_i} \right) C_p T_{in} = \frac{P_f V}{RT_f} C_v T_f - \frac{P_i V}{RT_i} C_v T_i$$

$$T_f = \frac{P_f}{\left(\frac{P_f - P_i}{T_{in}} \right) \left(\frac{C_v}{C_p} \right) + \frac{P_i}{T_i}}$$

For cylinder 1, $P_i = 0$

$$T_{f1} = \frac{P_f}{\left(\frac{P_f - P_i}{T_{in}} \right) \left(\frac{C_v}{C_v + R} \right) + \frac{P_i}{T_i}} = \frac{2}{\left(\frac{2-0}{120+273.15} \right) \left(\frac{29.3-8.314}{29.3} \right)} = \underline{\underline{548.9 \text{ (K)}}}$$

For cylinder 2, $P_i = 0.1 \text{ (MPa)}, T_i = 20 + 273.15 = 293.15 \text{ (K)}$

$$T_{f2} = \frac{P_f}{\left(\frac{P_f - P_i}{T_{in}} \right) \left(\frac{C_v}{C_v + R} \right) + \frac{P_i}{T_i}} = \frac{2}{\left(\frac{2-0.1}{120+273.15} \right) \left(\frac{29.3-8.314}{29.3} \right) + \frac{0.1}{20+273.15}} = \underline{\underline{525.9 \text{ (K)}}}$$

For cylinder 3, $P_i = 1 \text{ (MPa)}, T_i = 20 + 273.15 = 293.15 \text{ (K)}$

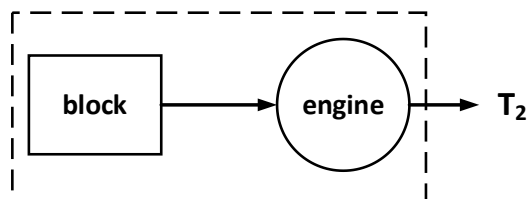
$$T_{f3} = \frac{P_f}{\left(\frac{P_f - P_i}{T_{in}} \right) \left(\frac{C_v}{C_v + R} \right) + \frac{P_i}{T_i}} = \frac{2}{\left(\frac{2-1}{120+273.15} \right) \left(\frac{29.3-8.314}{29.3} \right) + \frac{1}{20+273.15}} = \underline{\underline{382.2 \text{ (K)}}}$$

(本題改編自：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

p 95, Problem 3.19.)

Problem 6

【Solution】



By energy balance on the system (metal block + engine, closed system):

$$dU = dQ + dW \quad , \quad C_p dT = dQ + dW$$

solid, $C_v \approx C_p$

By entropy balance on the system,

$$\frac{dS}{dt} = \sum \frac{\dot{Q}}{T_2} + \underbrace{\dot{S}_{gen}}_{\text{maximum work}} \quad , \quad dQ = T_2 dS = T_2 \frac{C_p}{T} dT$$

$$C_p dT = T_2 \frac{C_p}{T} dT + dW$$

$$dW = C_p \left(1 - \frac{T_2}{T}\right) dT$$

$$W = \int_{T_1}^{T_2} C_p \left(1 - \frac{T_2}{T}\right) dT = C_p \left[(T_2 - T_1) - T_2 \ln \frac{T_2}{T_1} \right] = \underline{\underline{C_p T_2 \left[\left(1 - \frac{T_1}{T_2}\right) - \ln \frac{T_2}{T_1} \right]}}$$

(本題改編自：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

p 146, Problem 4.7.)

Problem 6

【Solution】

(a)

The Boyle temperature can be calculated as,

$$\frac{T_{Boyle} - 300}{400 - 300} = \frac{0 + 4.2}{9 + 4.2}, \quad \underline{\underline{T_{Boyle} = 331.8 \text{ (K)}}}$$

For inversion temperature, by definition,

$$\left(\frac{\partial T}{\partial P}\right)_H = 0$$

$$\therefore \left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial P}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_P = -1$$

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{[V - T\left(\frac{\partial V}{\partial T}\right)_P]}{C_P} = 0$$

For $V - T\left(\frac{\partial V}{\partial T}\right)_P$,

$$V - T\left(\frac{\partial V}{\partial T}\right)_P = \frac{RT}{P} + B - T\left(\frac{R}{P}\right) - T\left(\frac{dB}{dT}\right)_P = B - T\left(\frac{dB}{dT}\right)_P$$

代回：

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{[B - T\left(\frac{dB}{dT}\right)_P]}{C_P} = 0, \quad B - T\left(\frac{dB}{dT}\right)_P = 0$$

T (K)	87.5	112.5	137.5	175	225	275	350	450	550
$(\frac{dB}{dT})_P$	4.56	2.24	1.3	0.726	0.38	0.24	0.132	0.079	0.044
$B - T(\frac{dB}{dT})_P$	-616	-384	-266.5	-180.4	-111.2	-76.2	-43.8	-22.6	-5.1

T (K)	600	650
$(\frac{dB}{dT})_P$	0.0355	0.027
$B - T(\frac{dB}{dT})_P$	0	5.1

$$(\frac{dB}{dT})_{P,T=87.5K} = \frac{100-75}{-160-(-274)}, \quad B_{T=87.5K} = \frac{-160-(-274)}{2};$$

$$(\frac{dB}{dT})_{P,T=600K} = \frac{700-500}{24.0-16.9}, \quad B_{T=600K} = 21.3 \dots$$

The Boyle temperature is about 600 (K)

(b)

From the result of (a), we find,

$$(1) \quad T < T_{inversion}, \quad (\frac{\partial T}{\partial P})_H = -\frac{[B - T(\frac{dB}{dT})_P]}{C_P} > 0, \text{ so } P \downarrow, T \downarrow$$

$$(2) \quad T > T_{inversion}, \quad (\frac{\partial T}{\partial P})_H = -\frac{[B - T(\frac{dB}{dT})_P]}{C_P} < 0, \text{ so } P \downarrow, T \uparrow$$

(本題改編自：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

p 276, Problem 6.15.)

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Problem 1

【Solution】

By the design equation of MFR,

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

By the rate equation,

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

Combine,

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

At 300 K,

$$k_{1,300K} = 10^3 \exp\left[\frac{-4800}{1.987 \times 300}\right] = 0.318$$

$$K_{300K} = 10$$

$$100 = \frac{v_{A0}x_A}{k_1 \left[(1 - x_A) - \frac{x_A}{K} \right] \left(\frac{T_0}{T} \right)} = \frac{v_{A0} \times 0.6}{0.318 \times \left[(1 - 0.6) - \frac{0.6}{10} \right] \left(\frac{T_0}{300} \right)}$$
$$\frac{v_{A0}}{T_0} = 0.06$$

At 400 K,

$$k_{1,400K} = 10^3 \exp\left[\frac{-4800}{1.987 \times 400}\right] = 2.383$$

For K_{400K} , by Van't Hoff equation,

$$\frac{d \ln K}{dT} = \frac{\Delta H_r}{RT^2} = \frac{\Delta H_{r,300K} + \int_{300K}^T \Delta C_p dT}{RT^2} = \frac{\Delta H_{r,300K}}{RT^2} + \frac{5(T-300)}{RT^2} = \frac{\Delta H_{r,300K} - 300}{RT^2} + \frac{5}{RT}$$

$$\ln\left(\frac{K_T}{K_{300K}}\right) = \int_{300}^T \frac{\Delta H_{r,300K} - 1500}{RT^2} + \frac{5}{RT} dT = \frac{\Delta H_{r,300K} - 1500}{1.987} \left(\frac{1}{300} - \frac{1}{T}\right) + \frac{5}{1.987} \ln \frac{T}{300}$$

$$\ln\left(\frac{K_{400K}}{10}\right) = \frac{-4000 - 1500}{1.987} \left(\frac{1}{300} - \frac{1}{400}\right) + \frac{5}{1.987} \ln\left(\frac{400}{300}\right)$$

$$K_{400K} = 2.054$$

$$V = \frac{v_{A0} x_A}{k_1 \left[(1 - x_A) - \frac{x_A}{K} \right] \left(\frac{T_0}{T} \right)} = \frac{0.6}{2.383 \times \left[(1 - 0.6) - \frac{0.6}{2.054} \right] \left(\frac{1}{400} \right)} \times 0.06 = \underline{\underline{56.12 \text{ (L)}}}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 239, Example 9.12.)



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Problem 2

【Solution】

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 maximum concentration of B,

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

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

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

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

$$\tau = \frac{V}{v_0} = \frac{V}{1000 \times \frac{1}{60}} = \frac{1}{\sqrt{0.2 \times 0.2}} = \frac{1}{0.2}, \quad V = 83.33 \text{ (L)}$$

$$C_{B, \max} = \frac{k_1 C_{A0}}{(\sqrt{k_1} + \sqrt{k_2})^2} = \frac{0.2 \times 1}{(\sqrt{0.2} + \sqrt{0.2})^2} = 0.25 \text{ (mole / L)}$$

Problem 3

【Solution】

(1)

	P	\leftrightarrow	$3A$
Initial	100		0
Reaction	$-x$		$+3x$
Final	$100 - x$		$3x$

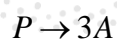
$$P_T = 100 - x + 3x = 100 + 2x$$

The fraction of paradihyde decomposed is $x_p = \frac{x}{100} = \frac{P_T - 100}{2 \times 100}$

Time (hr)	0	1	2	3	4	∞
P_{total}	100	173	218	248	266	300
x_p	0	0.365	0.59	0.74	0.83	1

(2)

$\because t \rightarrow \infty$, $x_p = 1$, the reaction is irreversible,



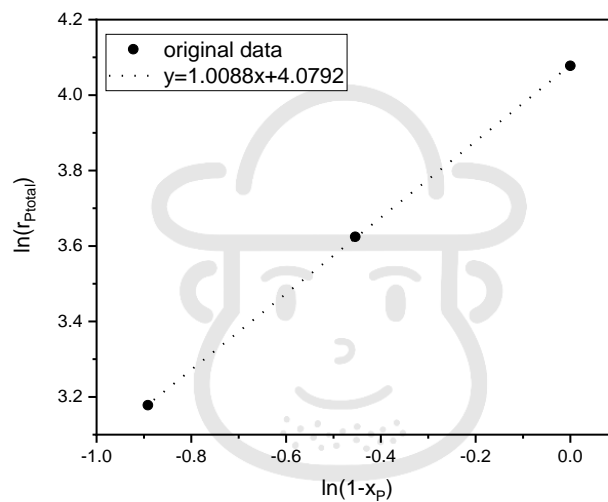
By the rate expression $-r_p = \frac{-dP_p}{dt} = kP_p^n = k[P_{p0}(1-x_p)]^n = \frac{1}{2} \frac{dP_{total}}{dt} = \frac{1}{2} r_{P_{total}}$

$$\frac{1}{2} r_{P_{total}} = k[P_{p0}(1-x_p)]^n$$

$$\ln(r_{P_{total}}) = \ln(k) + n \ln P_{p0} + n \ln(1-x_p) + \ln(2)$$

Plot $\ln(r_{p_{total}}) - \ln(1+2x_p)$:

Time (hr)	1	2	3
$r_{p_{total}}$	59	37.5	24
$\ln(r_{p_{total}})$	4.077	3.624	3.178
x_p	0	0.365	0.59
$\ln(1-x_p)$	0	-0.454	-0.892



By the slope of the regression line, **the reaction is first-order**

(3)

For the reaction constant,

$$\text{intercept} = \ln(k) + n \ln P_{p0} + \ln(2) = \ln(k) + \ln(100) + \ln(2)$$

$$4.0792 = \ln(k) + \ln(100) + \ln(2) \quad , \quad \underline{\underline{k = 0.295 \text{ (hr}^{-1}\text{)}}}$$

(4)

By Eyring equation,

$$k = \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}}$$

$$\frac{1}{60 \times 60} = \frac{1.38 \times 10^{-23} \times (260 + 273.15)}{6.626 \times 10^{-34}} \times e^{\frac{-\Delta G^\ddagger}{8.314 \times (260 + 273.15)}}$$

$$\Delta G^\ddagger = 169445.4 \text{ (J / mol)}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = \Delta H^\ddagger = 169445.4 \text{ (J / mol)}$$

∴ The reaction is unimolecular-reaction (反應物係數為 1)

$$E_a = \Delta H^\ddagger + RT = 169445.4 + 8.314 \times (260 + 273.15) = \underline{\underline{173878.0 \text{ (J / mol)}}}$$

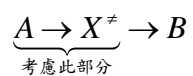
For the specific rate at 280°C, by Arrhenius equation,

$$\frac{k_{280}}{k_{260}} = e^{\frac{E_a}{R} \left(\frac{1}{280 + 273.15} - \frac{1}{260 + 273.15} \right)}$$

$$\frac{k_{280}}{1} = e^{\frac{173878.0}{8.314} \left(\frac{1}{280 + 273.15} - \frac{1}{260 + 273.15} \right)}, \quad k = \underline{\underline{4.13 \text{ (hr}^{-1}\text{)}}}$$

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※Transition-State theory 是以反應物→活化複合體的觀點所推導之理論，若考慮一 unimolecular reaction，則：



$$E_a = \Delta H^{\ddagger} - P\Delta V^{\ddagger} + RT$$

(1) Unimolecular reaction ($A \rightarrow X^{\ddagger}$), $P\Delta V^{\ddagger} = (\Delta n)RT = 0$

$$E_a = \Delta H^{\ddagger} + RT$$

(2) Reaction in solution, $P\Delta V^{\ddagger} \approx 0$

$$E_a = \Delta H^{\ddagger} + RT$$

(3) Bimolecular reaction ($A + B \rightarrow X^{\ddagger}$), $P\Delta V^{\ddagger} = (\Delta n)RT = RT$

$$E_a = \Delta H^{\ddagger} + 2RT$$

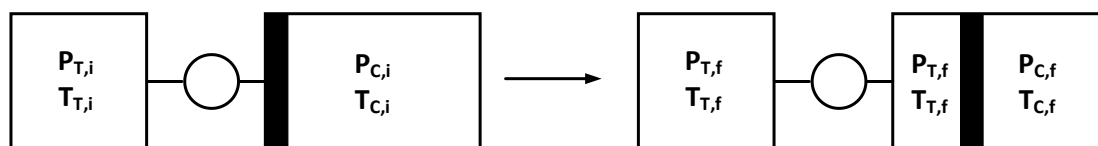
(本小題可參考：Laidler, K.; Meiser, J.; Sanctuary, B. *Physical Chemistry*, 4th ed.; p 392~393.)

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Problem 4

【Solution】

(a)



By total energy balance of nitrogen,

$$\Delta U = \cancel{Q} + \cancel{W}$$

(tank+cylinder 一起看，系統不對外做功)

$$\underbrace{\frac{P_{T,i} V_{T,i}}{RT_{T,i}} C_V^* T_{T,i}}_{n_{T,i}} + \underbrace{\frac{P_{C,i} V_{C,i}}{RT_{C,i}} C_V^* T_{C,i}}_{n_{C,i}} = \frac{P_{T,f} V_{T,f}}{RT_{T,f}} C_V^* T_{T,f} + \frac{P_{C, \text{left}, f} V_{C, \text{left}, f}}{RT_{C, \text{left}, f}} C_V^* T_{C, f} + \frac{P_{C, \text{right}, f} V_{C, \text{right}, f}}{RT_{C, \text{right}, f}} C_V^* T_{C, f}$$

$$P_{T,i} V_{T,i} + P_{C,i} V_{C,i} = P_{T,f} V_{T,f} + P_{C, \text{left}, f} V_{C, \text{left}, f} + P_{C, \text{right}, f} V_{C, \text{right}, f}$$

$$P_{T,i} V_{T,i} + P_{C,i} V_{C,i} = P_{T,f} (V_{T,f} + V_{C, \text{left}, f} + V_{C, \text{right}, f})$$

$$V_{T,i} = 0.25 \text{ (m}^3\text{)}, V_{C,i} = 0.5 \text{ (m}^3\text{)}, V_{T,f} + V_{C, \text{left}, f} + V_{C, \text{right}, f} = 0.25 + 0.5 = 0.75 \text{ (m}^3\text{)}$$

$$P_{T,i} = 0.4 \text{ (MPa)}, P_{C,i} = 0.1 \text{ (MPa)} \text{ 代入:}$$

$$0.4 \times 0.25 + 0.1 \times 0.5 = P_{T,f} \times 0.75, \quad \underline{\underline{P_{T,f} = 0.2 \text{ (MPa)}}}$$

For the right part of the cylinder, it is undergone adiabatic, reversible compression,

$$\left(\frac{T_{C, \text{right}, f}}{T_{C,i}} \right) = \left(\frac{P_{C, \text{right}, f}}{P_{C,i}} \right)^{\frac{R}{C_p}}$$

$$\left(\frac{T_{C, \text{right}, f}}{15 + 273.15} \right) = \left(\frac{0.2}{0.1} \right)^{\frac{8.314}{29.3}}, \quad \underline{\underline{T_{C,f} = 350.8 \text{ (K)}}}$$

By mole balance on the right of the tank,

$$\frac{P_{C,i} V_{C,i}}{RT_{C,i}} = \frac{P_{C, \text{right}, f} V_{C, \text{right}, f}}{RT_{C, \text{right}, f}}, \quad \frac{0.1 \times 0.5}{15 + 273.15} = \frac{0.2 V_{C, \text{right}, f}}{350.8}$$

$$V_{C, \text{right}, f} = 0.304 \text{ (m}^3\text{)}$$

$$V_{T,f} + V_{C, \text{left}, f} = 0.25 + 0.5 - 0.304 = 0.446 \text{ (m}^3\text{)}$$

By mole balance on the (tank + left of the cylinder),

$$\frac{P_{T,i} V_{T,i}}{RT_{T,i}} + 0 = \frac{P_{T,f} V_{T,f}}{RT_{T,f}} + \frac{P_{C,left,f} V_{C,left,f}}{RT_{C,left,f}} = P_{T,f} \left(\frac{V_{T,f} + V_{C,left,f}}{RT_{T,f}} \right)$$

$$(T_{T,f} = T_{C,left,f})$$

$$\frac{0.4 \times 0.25}{200 + 273.15} = 0.2 \times \left(\frac{0.446}{T_{T,f}} \right), \quad \underline{\underline{T_{T,f} = 421.7 \text{ (K)}}}$$

整理：

$$\boxed{P_{equalized} = 0.2 \text{ (MPa)}}$$

$$\boxed{T_{T,f} = 421.7 \text{ (K)}}$$

$$\boxed{T_{C,left,f} = T_{T,f} = 421.7 \text{ (K)}}$$

$$\boxed{T_{C,right,f} = T_{C,f} = 350.8 \text{ (K)}}$$

(b)

As the same results of (a),

$$\underline{\underline{V_{C,right,f} = 0.304 \text{ (m}^3\text{)}}}$$

$$V_{T,f} + V_{C,left,f} = 0.446 \text{ (m}^3\text{)}, \quad V_{C,left,f} = 0.446 - 0.25 = \underline{\underline{0.196 \text{ (m}^3\text{)}}}$$

(c)

By entropy balance on the whole system,

$$\Delta S = \sum \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

$$\dot{S}_{gen} = \Delta S$$

$$= n_{T,f} \left(C_p^* \ln \frac{T_{T,f}}{T_{T,i}} - R \ln \frac{P_{T,f}}{P_{T,i}} \right) + n_{C,left,f} \left(C_p^* \ln \frac{T_{C,left,f}}{T_{C,left,i}} - R \ln \frac{P_{C,left,f}}{P_{C,left,i}} \right) + n_{C,right,f} \left(C_p^* \ln \frac{T_{C,right,f}}{T_{C,right,i}} - R \ln \frac{P_{C,right,f}}{P_{C,right,i}} \right)$$

$$= n_{T,i} \left(C_p^* \ln \frac{T_{T,f}}{T_{T,i}} - R \ln \frac{P_{T,f}}{P_{T,i}} \right) + n_{C,right,f} \left(C_p^* \ln \frac{T_{C,right,f}}{T_{C,right,i}} - R \ln \frac{P_{C,right,f}}{P_{C,right,i}} \right)$$

(若考慮過程之後在 cylinder 左端之氮氣，其初始狀態與在 Tank 的氣體相同，而末狀態溫度與壓力也與留在 Tank 中的氮氣相同，故可合併)

$$n_{C, \text{left}, f} = \frac{P_{C, \text{left}, f} V_{C, \text{left}, f}}{RT_{C, \text{left}, f}} = \frac{0.2 \times 10^6 \times 0.196}{8.314 \times 421.7} = 11.16 \text{ (mole)}$$

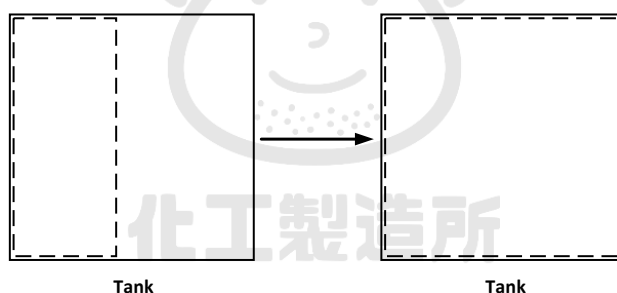
$$n_{T, i} = \frac{P_{T, i} V_{T, i}}{RT_{T, i}} = \frac{0.4 \times 10^6 \times 0.25}{8.314(200 + 273.15)} = 25.42 \text{ (mole)}$$

$$\begin{aligned} \dot{S}_{gen} = \Delta S &= 25.42 \left(29.3 \ln \frac{421.7}{200 + 273.15} - 8.314 \ln \frac{0.2}{0.4} \right) + 20.87 \left(29.3 \ln \frac{350.8}{15 + 273.15} - 8.314 \ln \frac{0.2}{0.1} \right) \\ &= \underline{\underline{60.80 \text{ (J / K)}}} \end{aligned}$$

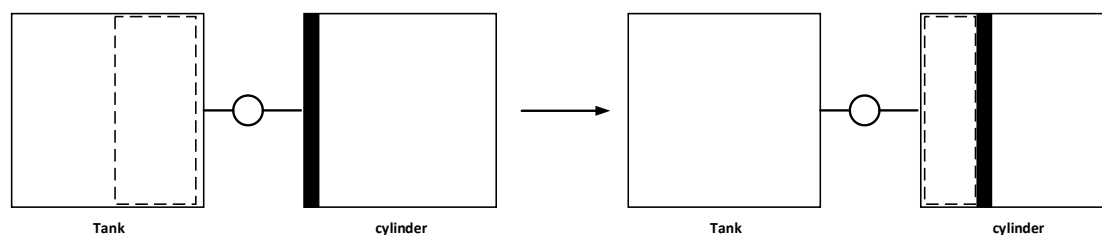
※事實上可不必計算 cylinder 右邊之 entropy generation，因其經歷之過程為”可逆”壓縮，結果為 0，或若考慮誤差，則應非常接近 0

$$20.87 \left(29.3 \ln \frac{350.8}{15 + 273.15} - 8.314 \ln \frac{0.2}{0.1} \right) = 0$$

而(a)小題中，只有過程後”留在”Tank 中的氣體做為系統時，過程才為可逆膨脹，即：



若系統改為過程後”移動至 cylinder 左半部”之氣體，則其示意圖為：



則氣體離開 Tank 後，將進入 cylinder 左半部，會經過兩個程序：

(1) 壓力改變，直至壓力與 cylinder 左半部已有的氣體壓力相同

(2) 溫度改變，直至溫度與 cylinder 左半部已有的氣體溫度相同

而在第(2)步驟中，明顯代表剛進入 cylinder 之氣體與已存在於 cylinder 之氣體溫度不相同，而產生溫度梯度，因此過程不可逆。總結來說，不可直接將”Tank + cylinder 左半部分”之氣體當作系統，利用可逆絕熱程序的公式算出其溫度。

而此題改編自 Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

p 150, Problem 4.41，並未有 Tank 與左半 cylinder 溫度相同的條件。因此，在時間較本題短的情況下，Tank、左半 cylinder、右半 cylinder 溫度皆不相同。

而相關概念可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

p 130~131, Illustration 4.5-2.)

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Problem 5

【Solution】

By Gibbs-Duhem equation,

$$x_1 d \ln r_1 + x_2 d \ln r_2 = 0$$

$$(1-x_2)d(Ax_2^2+Bx_2^3+Cx_2^4)+x_2d \ln r_2=0$$

$$x_2 d \ln r_2 = (x_2-1)(2Ax_2+3Bx_2^2+4Cx_2^3)dx_2$$

$$d \ln r_2 = (x_2-1)(2A+3Bx_2+4Cx_2^2)dx_2 = [(-2A)+(2A-3B)x_2+(3B-4C)x_2^2+4Cx_2^3]dx_2$$

$$\int_{\ln r_2=0}^{\ln r_2} d \ln r_2 = \int_{x_2=1}^{x_2} [(-2A)+(2A-3B)x_2+(3B-4C)x_2^2+4Cx_2^3]dx_2$$

$$\ln r_2 = \frac{-2A(x_2-1) + \frac{2A-3B}{2}(x_2^2-1) + \frac{(3B-4C)}{3}(x_2^3-1) + C(x_2^4-1)}{}$$

若繼續整理成較好看的形式：

$x_2 = 1 - x_1$ 代入：

$$\begin{aligned} \ln r_2 &= -2A(1-x_1-1) + \frac{2A-3B}{2}[(1-x_1)^2-1] + \frac{(3B-4C)}{3}[(1-x_1)^3-1] + C[(1-x_1)^4-1] \\ &= 2Ax_1 + \frac{2A-3B}{2}(-2x_1+x_1^2) + \frac{(3B-4C)}{3}(-3x_1+3x_1^2-x_1^3) + C(-4x_1+6x_1^2-4x_1^3+x_1^4) \\ &= \underline{\underline{(A+\frac{3B}{2}-2C)x_1^2 - (B+\frac{8}{3}C)x_1^3 + Cx_1^4}} \end{aligned}$$

(本題改編自 Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

p 459, Illustration 9.5-3.)

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Problem 1

【Solution】

Assume the process obeys Arrhenius law,

$$rate \propto k \propto \frac{1}{time}$$

$$\frac{(\frac{1}{15})}{(\frac{1}{30 \times 60})} = e^{\frac{-E_a}{8.314} (\frac{1}{273.15+74} - \frac{1}{273.15+63})}$$

$$\underline{\underline{E_a = 4.22 \times 10^5 \text{ (J / mole)}}}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 29, Example 2.3.)



Problem 2

【Solution】

For gaseous system,

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

$$\varepsilon_A = \delta y_{A0} = \left(\frac{6-3-1}{1}\right) \times \left(\frac{100}{100+200+100}\right) = \frac{1}{2}$$

$$40 = \frac{100(1 - X_A)}{(1 + \frac{1}{2} X_A)}, \quad \underline{\underline{X_A = 0.5}}$$

For C_B ,

$$C_B = \frac{C_{A0}(\theta_B - 3X_A)}{(1 + \varepsilon_A X_A)} = \frac{C_{B0}(1 - X_B)}{(1 + \varepsilon_B X_B)}$$

$$C_B = \frac{100\left(\frac{200}{100} - 3 \times 0.5\right)}{(1 + \frac{1}{2} \times 0.5)} = \underline{\underline{40}}$$

For X_B ,

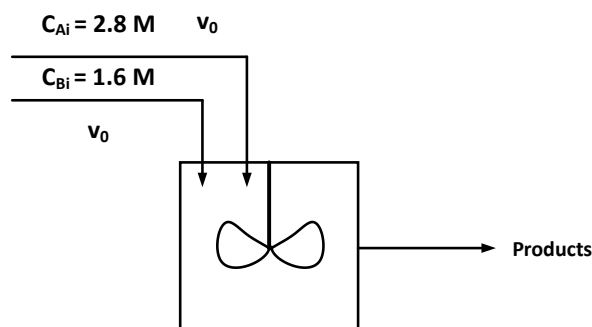
$$\varepsilon_B = \delta y_{B0} = \left(\frac{6-3-1}{3}\right) \times \frac{200}{100+200+100} = \frac{1}{3}$$

$$40 = \frac{200(1 - X_B)}{(1 + \frac{1}{3} X_B)}, \quad \underline{\underline{X_B = 0.75}}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 88~89, Example 4.1.)

Problem 3

【Solution】



\therefore The reaction is $A + 2B \xrightleftharpoons[k_2]{k_1} R$, and $C_{Bi} < C_{Ai}$, the limiting component is B.

By the design equation of mixed flow-reactor,

$$V = \frac{v_1 C_{B0} x_B}{-r_B}$$

$$v_1 = v_0 + v_0 = 2v_0$$

By the rate equation,

$$-r_B = -2r_A = 25C_A C_B^2 - 3C_R = 25C_{B0}^3(\theta_A - 0.5x_B)(1 - x_B)^2 - 3 \times 0.5C_{B0}x_B$$

$$C_{B0} = \frac{C_{Bi}}{2} = 0.8 \text{ (M)}, \quad \theta_A = \frac{2.8}{1.6} = 1.75$$

Combine,

$$V = \frac{v_1 C_{B0} x_B}{25C_{B0}^3(1.75 - 0.5x_B)(1 - x_B)^2 - 3 \times 0.5C_{B0}x_B}$$

$$V = \frac{v_1 x_B}{25C_{B0}^2(1.75 - 0.5x_B)(1 - x_B)^2 - 3 \times 0.5x_B}$$

$$6 = \frac{v_1 \times 0.75}{25 \times 0.8^2(1.75 - 0.5 \times 0.75)(1 - 0.75)^2 - 3 \times 0.5 \times 0.75}$$

$$v_1 = 2 \text{ (L/min)}, \quad v_0 = \frac{v_1}{2} = 1 \text{ (L/min)}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 99~100, Example 5.3.)

Problem 4

【Solution】

For the gaseous parallel reactions, $\varepsilon = 0$.

By the design equation of CSTR,

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

By the rate equation,

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

Combine,

$$V = \frac{F_{A0}x_A}{-r_A} = \frac{F_{A0}x_A}{k_1 C_A^2 + k_2 C_A} = \frac{F_{A0}x_A}{k_1 C_{A0}^2 (1-x_A)^2 + k_2 C_{A0} (1-x_A)}$$
$$V = \frac{10 \times 1 \times 0.6}{2 \times 1^2 (1-0.6)^2 + 1 \times 1 (1-0.6)} = \underline{\underline{8.33 \text{ (dm}^3\text{)}}}$$

For the overall selectivity of B,

$$S_{B/C} = \frac{F_B}{F_C} = \frac{r_B V}{r_C V} = \frac{k_1 C_A^2}{k_2 C_A} = \frac{k_1 C_A}{k_2} = \frac{2}{1} C_{A0} (1-x_A) = \frac{2}{1} \times 1 \times (1-0.6) = \underline{\underline{0.8}}$$

※Selectivity 可分為兩種：

(1) Instantaneous selectivity

$$S_{B/C} = \frac{\text{rate of formation of B}}{\text{rate of formation of C}} = \frac{r_B}{r_C}$$

(2) Overall selectivity

$$S_{B/C} = \frac{\text{exit molar flow rate of B}}{\text{exit molar flow rate of C}} = \frac{F_B}{F_C}$$

雖然在此題兩者相同，然而實際上有所差別

可參考：FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 307~309.

Problem 5

【Solution】

(a)

Start from $S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

For $\left(\frac{\partial S}{\partial T}\right)_V$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{\left(\frac{\partial U}{\partial T}\right)_V}{\left(\frac{\partial U}{\partial S}\right)_T} = \frac{C_V}{T}$$

For $\left(\frac{\partial S}{\partial V}\right)_T$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_V}{T} \left(\frac{dT}{dT}\right)_P + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

As the same manner, let $S = S(T, P)$,

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP, \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\frac{C_P}{T} = \frac{C_V}{T} \left(\frac{dT}{dT}\right)_P + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P, \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

將 $\left(\frac{\partial P}{\partial T}\right)_V$ 做代換：

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$$

$$\frac{C_P}{T} = \frac{C_V}{T} - \left(\frac{\partial P}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2 = \frac{C_V}{T} - \frac{(V\alpha)^2}{(-\kappa_T V)} = \frac{C_V}{T} + \frac{\alpha^2 V}{\kappa_T}$$

$$C_P - C_V = \frac{T\alpha^2 V}{\kappa_T}$$

(b)

For ideal gas, $PV = RT$,

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{PV}$$
$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left(\frac{-RT}{P^2} \right) = \frac{RT}{P^2 V}$$

代回：

$$C_P - C_V = \frac{T \alpha^2 V}{\kappa_T} = \frac{T \left(\frac{R}{PV} \right)^2 V}{\left(\frac{RT}{P^2 V} \right)} = R$$

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

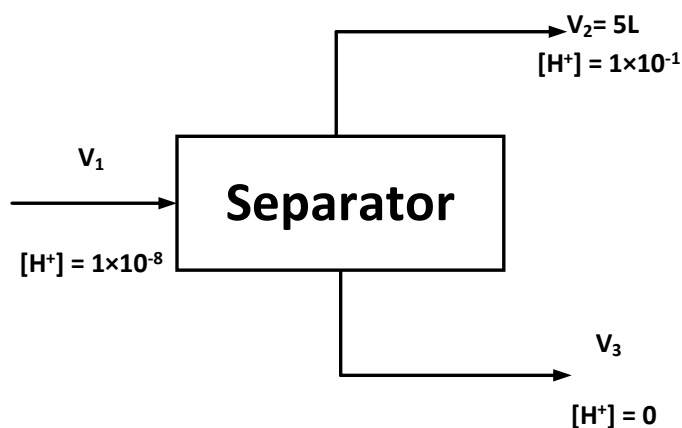
p 211~214, Illustration 6.2-2/6.2-3.)



Problem 6

【Solution】

(a)



Assume the gastric juice is water-based, and constant density throughout.

By mole balance on the HCl (gastric juice = HCl + water),

$$V_1 \times 1 \times 10^{-8} = 5 \times 1 \times 10^{-1} + V_3 \times 0, \quad V_1 = 5 \times 10^7 \text{ (L)}$$

$$V_3 = V_1 - V_2 = 5 \times 10^7 - 5 \approx 5 \times 10^7 \text{ (L)}$$

For the calculation of minimum work required,

by energy balance,

$$U_2 - U_1 = Q + W_s - (P_2 V_2 - P_1 V_1), \quad P_2 = P_1 (\text{constant } P)$$

By entropy balance,

$$\Delta S_{\text{sys}} = \frac{Q}{T} + \underbrace{S_{\text{gen}}}_{\text{minimum work}} = S_2 - S_1$$

$Q = T(S_2 - S_1)$ 代回(定温):

$$U_2 - U_1 = TS_2 - TS_1 + W_s - P_2 V_2 - P_1 V_1$$

$$W_s = (U_2 + P_2 V_2 - TS_2) - (U_1 + P_1 V_1 - TS_1) = G_2 - G_1, \quad W_{\min} = -\Delta G_{\text{mix}}^{\text{id}}$$

$$W_{\min} = -RT[n_1(x_{a1} \ln x_{a1} + x_{w1} \ln x_{w1}) + n_2(x_{a2} \ln x_{a2} + x_{w2} \ln x_{w2}) + \underbrace{n_3(x_{a3} \ln x_{a3} + x_{w3} \ln x_{w3})}_{\text{pure water}}]$$

($x_{a,i}$ = mole fraction of acid in i)

For n_2, x_{a2}, x_{w2}

$$n_{a2} = [H^+]_2 V_2 = 0.1 \times 5 = 0.5 \text{ mol}$$

$$n_{w2} = \frac{\rho_2 V_2 - n_{a2} M_{HCl}}{18} = \frac{1 \times 5 \times 10^3 - 0.5 \times 36.5}{18} = 276.76 \text{ (mol)}$$

$$n_2 = n_{a2} + n_{w2} = 276.76 + 0.5 = 277.26 \text{ (mol)}$$

$$x_{a2} = \frac{n_{a2}}{n_2} = \frac{0.5}{277.26} = 1.8 \times 10^{-3}$$

$$x_{w2} = \frac{n_{w2}}{n_2} = \frac{276.76}{277.26} = 0.9982$$

代回：

$$\begin{aligned} W_{\min,2} &= -RT[n_2(x_{a2} \ln x_{a2} + x_{w2} \ln x_{w2})] \\ &= -8.314 \times (273.15 + 37) [277.26(1.8 \times 10^{-3} \ln 1.8 \times 10^{-3} + 0.9982 \ln 0.9982)] \\ &= 9434.04 \text{ (J)} \end{aligned}$$

For n_1, x_{a1}, x_{w1}

$$n_{a1} = [H^+]_1 V_1 = 1 \times 10^{-8} \times 5 \times 10^7 = 0.5 \text{ mol}$$

$$n_{w1} = \frac{\rho_1 V_1 - n_{a1} M_{HCl}}{18} = \frac{1 \times 5 \times 10^7 \times 10^3 - 0.5 \times 36.5}{18} = 2.76 \times 10^9 \text{ (mol)}$$

$$n_1 = n_{a1} + n_{w1} = 2.76 \times 10^9 + 0.5 \approx 2.76 \times 10^9 \text{ (mol)}$$

$$x_{a1} = \frac{n_{a1}}{n_1} = \frac{0.5}{2.76 \times 10^9} = 1.8 \times 10^{-10}$$

$$x_{w1} = 1 - x_{a1} = 0.99999999982$$

$$\begin{aligned}
 W_{\min,1} &= -RT[n_1(x_{a1} \ln x_{a1} + x_{w1} \ln x_{w1})] \\
 &= -8.314 \times (273.15 + 37)[2.76 \times 10^9 (1.8 \times 10^{-10} \ln 1.8 \times 10^{-10} + 0.99999999982 \ln 0.99999999982)] \\
 &= 30218.5 \text{ (J)}
 \end{aligned}$$

$$W_{\min} = W_{\min,1} + W_{\min,2} = 9434.04 + 30218.5 = \underline{\underline{39652.5 \text{ (J)}}}$$

Problem 7

【Solution】

(a)

$$\because G^{ex} = H^{ex} - TS^{ex}$$

$$S^{ex} = -\left(\frac{\partial G}{\partial T}\right)_{P, x_i} = 3x_A x_B$$

$$H^{ex} = G^{ex} + TS^{ex} = (4500 - 3T)x_A x_B + T(3x_A x_B) = \underline{\underline{4500x_A x_B \text{ (J/mol)}}}$$

(b)

The result is the same as (a),

$$S^{ex} = -\left(\frac{\partial G}{\partial T}\right)_{P, x_i} = \underline{\underline{3x_A x_B}}$$

※觀察題目：

$$G^{ex} = H^{ex} - TS^{ex} = \underbrace{4500x_A x_B}_{H^{ex}} - T \underbrace{(3x_A x_B)}_{S^{ex}}$$

(c)

$$\underline{\underline{C_P^{ex} = \left(\frac{\partial H^{ex}}{\partial T}\right)_P = 0}}$$

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一、熱力學

Problem 1

【Solution】

(a) False

For general case,

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

(b) False

By entropy balance of surrounding,

$$\Delta S_{sur} = -\sum_1^n N_k S_k + \frac{Q}{T_{sur}^{adiabatic}} = -\sum_1^n N_k S_k \neq 0$$

(c) True

For ideal engines,

$$\eta = 1 - \frac{T_C}{T_H}$$

(d) True

For expansion into a vacuum,

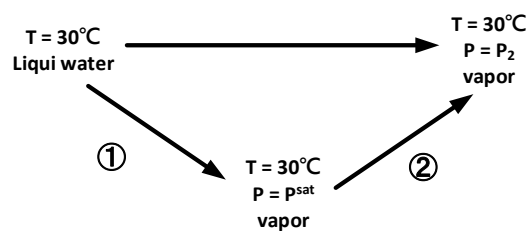
$$W = -\cancel{P}dV = 0$$

(e) False

This relation is valid when the mixture is ideal, and only for volume and enthalpy, whose volume and enthalpy of mixing are zero.

Problem 2

【Solution】



(a)

$$\Delta H = \Delta H_1 + \underbrace{\Delta H_2}_{\text{ideal gas, isothermal}} = n\Delta H_{\text{vap}}$$

$$\Delta H_{\text{vap}} = 2431 \text{ (J / g)} = 2431 \times 18 = 43758 \text{ (J / mol)}$$

$$\Delta H = n\Delta H_{\text{vap}} = 2 \times 43758 = \underline{\underline{87516 \text{ (J)}}}$$

(b)

$$\Delta S = \Delta S_1 + \Delta S_2 = n\left(\frac{\Delta H_{\text{vap}}}{T} - R \ln \frac{P_2}{P^{\text{sat}}}\right)$$

$$\Delta S = 2 \times \left(\frac{43758}{30 + 273.15} - 8.314 \ln \frac{10^{-4}}{4.25}\right) = \underline{\underline{465.897 \text{ (J / K)}}}$$

(c)

$$\Delta G = \Delta H - T\Delta S = 87516 - 465.897(30 + 273.15) = \underline{\underline{-53720.9 \text{ (J)}}}$$

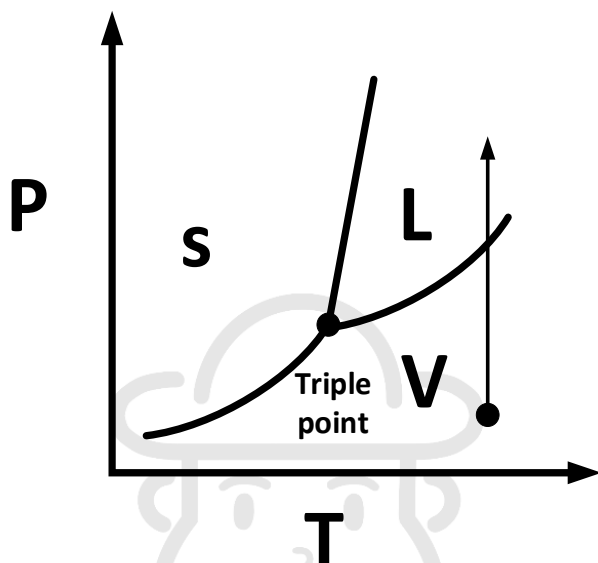
Problem 3

【Solution】

For this incompressible compound, the triple point is,

$$P^{sat} = 10^{5.223 - \frac{2146}{T}} = P^{sub} = \frac{10^{-9}}{T}, \quad T = 131.3(K) = -141.8(^{\circ}C)$$

因此，此物質於 25°C 下，應該在該物質三相點的右邊



若要決定該物質在 25°C 與 35 bar 下的 fugacity，需要知道其狀態。按圖來說，可能為液體或固體。若是固體，則需要知道其液氣轉變的壓力為多少，以及其液體與固體的密度，然而：

(1) 根據 Clausius-Clapeyron equation,

$$\frac{d \ln P^{sat}}{dT} = \frac{d(2.303 \log_{10} P^{sat})}{dT} = \frac{2.303 \times 2146}{T^2} = \frac{\Delta H^{vap}}{RT^2}$$

$$\Delta H^{vap} = 2.303 \times 2146 \times 8.314 = 41089 \text{ (J / mol)}$$

若知道 $\frac{d \ln P^{sub}}{dT}$ ，就可推得 ΔH^{sub} ，並且回推 ΔH^{fus} ：

$$\Delta H^{fus} = \Delta H^{sub} - \Delta H^{vap}$$

就可以此估算液-固共存線的相關資訊，進而求出固體 fugacity

然而題目所給之 P^{sub} 並非 Antoine equation 形式，無法估算

(2) 題目也未給液體與固體的莫爾體積相關資訊，因此也未能求出精確 fugacity

因此，假設該物質在 25°C 與 35 bar 的條件下為液態，相對於理想氣體，其 fugacity 可被計算為：

$$\begin{aligned} RT \ln\left(\frac{f^L}{P}\right) &= \int_0^{P^{vap(T)}} \left(\underline{V} - \frac{RT}{P}\right) dP + \cancel{RT \Delta(\ln \frac{f}{P})_{\text{相轉換}}} + \int_{P^{vap(T)}}^P \left(\underline{V}^L - \frac{RT}{P}\right) dP \\ &= RT \ln\left(\frac{f}{P}\right)_{sat, T} + \int_{P^{vap(T)}}^P \underline{V}^L dP - RT \int_{P^{vap(T)}}^P \frac{1}{P} dP \\ &= RT \ln\left(\frac{f}{P}\right)_{sat, T} + \int_{P^{vap(T)}}^P \underline{V}^L dP - RT \ln\left(\frac{P}{P^{vap(T)}}\right) \end{aligned}$$

因此：

$$f^L = P^{vap(T)} \left(\frac{f}{P}\right)_{sat, T} \exp\left[\frac{\int_{P^{vap(T)}}^P \underline{V}^L dP}{RT}\right] \approx P^{vap(T)} \left(\frac{f}{P}\right)_{sat, T} \exp\left[\frac{V^L(P - P^{vap})}{RT}\right]$$

又因為

$$P^{sat} = P^{vap} = 10^{\frac{5.223 - \frac{2146}{273.15 + 25}}{}} = 0.0106 \text{ (bar)} \ll 1 \text{ bar}$$

因此：

$$\begin{aligned} f^L &= P^{vap} \underbrace{\left(\frac{f}{P}\right)_{sat, T}}_{P^{sat} \text{ very low} \approx 1} \exp\left[\frac{V^L(P - P^{vap})}{RT}\right] \approx P^{vap} \exp\left[\frac{V^L(P - P^{vap})}{RT}\right] \\ f^L &= P^{vap} \exp\left[\frac{V^L(P - P^{vap})}{RT}\right] = 0.0106 \times \exp\left[\frac{\frac{205.85}{1.27} \times 10^{-6} (35 - 0.0106) \times 10^5}{8.314 \times (273.15 + 25)}\right] = \underline{\underline{0.0133 \text{ (bar)}}} \end{aligned}$$

※假設該物質在 25°C 與 35 bar 的條件下為固態，相對於理想氣體，其 fugacity 可被計算為：

$$\begin{aligned} RT \ln\left(\frac{f^S}{P}\right) &= \underbrace{\int_0^{P^{vap(T)}} \left(\underline{V} - \frac{RT}{P}\right) dP}_{\phi^{sat} \sim 1} + \cancel{RT \Delta(\ln \frac{f}{P})_{\text{氣-液相轉換}}} + \int_{P^{vap(T)}}^{P^{fus(T)}} \left(\underline{V}^L - \frac{RT}{P}\right) dP + \cancel{RT \Delta(\ln \frac{f}{P})_{\text{液-固相轉換}}} + \int_{P^{fus(T)}}^P \left(\underline{V}^S - \frac{RT}{P}\right) dP \\ RT \ln\left(\frac{f^S}{P}\right) &\approx \int_{P^{vap(T)}}^{P^{fus(T)}} \left(\underline{V}^L - \frac{RT}{P}\right) dP + \int_{P^{fus(T)}}^P \left(\underline{V}^S - \frac{RT}{P}\right) dP \\ f^S &= \underline{\underline{P^{vap(T)} \exp\left[\frac{V^L(P^{fus(T)} - P^{vap(T)})}{RT}\right] \exp\left[\frac{V^S(P - P^{fus(T)})}{RT}\right]}} \end{aligned}$$

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

p.320~322, Illustration 7.4-8 與 7.4-9；為利用 sublimation 做固體計算的題目。)

Problem 4

【Solution】

(a)

For property M ,

$$d(nM) = \left[\frac{\partial(nM)}{\partial P} \right]_{T,n} dP + \left[\frac{\partial(nM)}{\partial T} \right]_{P,n} dT + \sum_i \left[\frac{\partial(nM)}{\partial n_i} \right]_{P,T,n_j} dn_i$$

$$d(nM) = n \left(\frac{\partial M}{\partial P} \right)_{T,x} dP + n \left(\frac{\partial M}{\partial T} \right)_{P,x} dT + \sum_i \bar{M}_i dn_i$$

$$\because dn_i = d(nx_i) = x_i dn + n dx_i, \quad d(nM) = ndM + Mdn$$

$$ndM + Mdn = n \left(\frac{\partial M}{\partial P} \right)_{T,x} dP + n \left(\frac{\partial M}{\partial T} \right)_{P,x} dT + \sum_i \bar{M}_i (x_i dn + n dx_i)$$

$$\underbrace{n \left[dM - \left(\frac{\partial M}{\partial P} \right)_{T,x} dP - \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i \bar{M}_i dx_i \right]}_0 + \underbrace{[Mdn - \sum_i x_i \bar{M}_i] dn}_0 = 0$$

$$dM - \left(\frac{\partial M}{\partial P} \right)_{T,x} dP - \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i \bar{M}_i dx_i = 0$$

$$\because M = \sum_i x_i \bar{M}_i, \quad dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i$$

$$\sum_i x_i d\bar{M}_i + \sum_i \cancel{\bar{M}_i dx_i} - \left(\frac{\partial M}{\partial P} \right)_{T,x} dP - \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i \cancel{\bar{M}_i dx_i} = 0$$

$$\left(\frac{\partial M}{\partial P} \right)_{T,x} dP + \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i x_i d\bar{M}_i = 0$$

At constant T, P,

$$\boxed{\sum_i x_i d\bar{M}_i = 0}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering*

Thermodynamics, 7th ed.; p 383~385.)

(b)

By Gibbs-Duhem equation,

$$\sum_i x_i d\bar{M}_i = x_1 d\bar{G}_1 + x_2 d\bar{G}_2 = 0$$

$$x_1 d \ln P_1 + x_2 d \ln P_2 = 0$$

If component 2 follows Henry's law,

$$P_2 = k_2 x_2$$

$$x_1 d \ln P_1 + x_2 d \ln(k_2 x_2) = 0$$

$$x_1 d \ln P_1 + x_2 \frac{dx_2}{x_2} = 0$$

$$x_1 d \ln P_1 = -dx_2 = dx_1$$

$$\int_{\ln P_1}^{\ln P_1^{sat}} d \ln P_1 = -dx_2 = \int_{x_1}^1 \frac{dx_1}{x_1}$$

$$\ln \frac{P_1^{sat}}{P_1} = \ln \frac{1}{x_1}, \quad \underline{\underline{P_1 = P_1^{sat} x_1}}$$

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二、動力學

Problem 1

【Solution】

(a)

$$-r_A = k_1 C_A C_B$$

$$-r_B = k_1 C_A C_B + k_2 C_R C_B$$

$$r_R = k_1 C_A C_B - k_2 C_R C_B$$

$$r_S = k_2 C_R C_B$$

(b)

For PFR,

$$d\tau = -\frac{dC_A}{-r_A} = \frac{dC_R}{r_R}, \quad \frac{dC_R}{dC_A} = -\frac{r_R}{-r_A} = \frac{k_2 C_R C_B - k_1 C_A C_B}{k_1 C_A C_B} = \frac{k_2}{k_1 C_A} C_R - 1$$

$$dC_R - \left(\frac{k_2}{k_1 C_A} C_R\right) dC_A = -dC_A$$

Let $I = \exp^{-\int \frac{k_2}{k_1 C_A} dC_A} = (C_A)^{\frac{-k_2}{k_1}}$ 乘入：

$$d[C_R C_A^{\frac{-k_2}{k_1}}] = -C_A^{\frac{-k_2}{k_1}} dC_A$$

$$C_R C_A^{\frac{-k_2}{k_1}} = -\frac{1}{-\frac{k_2}{k_1} + 1} C_A^{\frac{-k_2}{k_1} + 1} + C = \frac{k_1}{k_2 - k_1} C_A^{\frac{-k_2}{k_1} + 1} + C$$

$$C_R = \frac{k_1}{k_2 - k_1} C_A + C C_A^{\frac{k_2}{k_1}}$$

$$\because C_A = C_{A0}, C_R = 0$$

$$0 = \frac{k_1}{k_2 - k_1} C_{A0} + C C_{A0}^{\frac{k_2}{k_1}}, \quad \frac{k_1}{k_1 - k_2} C_{A0}^{1 - \frac{k_2}{k_1}} = C$$

$$C_R = \frac{k_1}{k_2 - k_1} C_A + \frac{k_1}{k_1 - k_2} C_{A0}^{1 - \frac{k_2}{k_1}} C_A^{\frac{k_2}{k_1}}, \quad \frac{C_R}{C_{A0}} = \frac{k_1}{k_2 - k_1} \left[\frac{C_A}{C_{A0}} - \left(\frac{C_A}{C_{A0}} \right)^{\frac{k_2}{k_1}} \right]$$

For CSTR,

$$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{C_R}{r_R}$$

$$\frac{C_{A0} - C_A}{k_1 C_A C_B} = \frac{C_R}{k_1 C_A C_B - k_2 C_R C_B}$$

$$C_{A0}(k_1 C_A C_B - k_2 C_R C_B) - C_A(k_1 C_A C_B - k_2 C_R C_B) = k_1 C_A C_B C_R$$

$$C_R(k_1 C_A C_B - k_2 C_A C_B + k_2 C_{A0} C_B) = k_1 C_{A0} C_A C_B - k_1 C_A^2 C_B$$

$$\frac{C_R}{C_{A0}} = \frac{k_1 C_A C_B - \frac{k_1 C_A^2 C_B}{C_{A0}}}{(k_1 C_A C_B - k_2 C_A C_B + k_2 C_B C_{A0})} = \frac{k_1 C_{A0} C_A - k_1 C_A^2}{k_1 C_A C_{A0} - k_2 C_A C_{A0} + k_2 C_{A0}^2}$$

(c)

For the maximum intermediate product of C_R of PFR,

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_2 - k_1} \left[\frac{C_A}{C_{A0}} - \left(\frac{C_A}{C_{A0}} \right)^{\frac{k_2}{k_1}} \right]$$

$$\frac{d\left(\frac{C_R}{C_{A0}}\right)}{dC_A} = \frac{k_1}{k_2 - k_1} \left[\frac{1}{C_{A0}} - \frac{k_2}{k_1} \left(\frac{C_A}{C_{A0}} \right)^{\frac{k_2}{k_1} - 1} \right] = 0$$

$$\left(\frac{C_A}{C_{A0}} \right)^{\frac{k_2}{k_1} - 1} = \frac{k_1}{k_2}, \quad \left(\frac{C_A}{C_{A0}} \right)^{\frac{k_2}{k_1}} = \frac{k_1 C_A}{k_2 C_{A0}} \text{ 代入:}$$

$$\frac{C_{R, \max, PFR}}{C_{A0}} = \frac{k_1}{k_2 - k_1} \left[\frac{C_A}{C_{A0}} - \frac{k_1 C_A}{k_2 C_{A0}} \right] = \frac{k_1}{k_2 - k_1} \left[\frac{(k_2 - k_1) C_A}{k_2 C_{A0}} \right] = \frac{k_1 C_A}{k_2 C_{A0}}$$

For the maximum intermediate product of C_R of CSTR,

$$\frac{C_R}{C_{A0}} = \frac{k_1 C_{A0} C_A - k_1 C_A^2}{k_1 C_A C_{A0} - k_2 C_A C_{A0} + k_2 C_{A0}^2}$$

$$\frac{d(\frac{C_R}{C_{A0}})}{dC_A} = \frac{(k_1 C_{A0} - 2k_1 C_A)(k_1 C_A C_{A0} - k_2 C_A C_{A0} + k_2 C_{A0}^2) - (k_1 C_{A0} - k_2 C_{A0})(k_1 C_{A0} C_A - k_1 C_A^2)}{[(k_1 C_A C_{A0} - k_2 C_A C_{A0} + k_2 C_{A0}^2)]^2} = 0$$

$$(k_1 C_{A0} - 2k_1 C_A)(k_1 C_A C_{A0} - k_2 C_A C_{A0} + k_2 C_{A0}^2) - (k_1 C_{A0} - k_2 C_{A0})(k_1 C_{A0} C_A - k_1 C_A^2) = 0$$

$$(-2k_1^2 C_{A0} + 2k_1 k_2 C_{A0} + k_1 C_{A0} - k_1 k_2 C_{A0}) C_A^2$$

$$+ (k_1^2 C_{A0}^2 - k_1 k_2 C_{A0}^2 - 2k_1 k_2 C_{A0}^2 - k_1^2 C_{A0}^2 + k_1 k_2 C_{A0}^2) C_A + k_1 k_2 C_{A0}^3 = 0$$

$$(k_1 k_2 - k_1^2) C_A^2 - (2k_1 k_2 C_{A0}) C_A + k_1 k_2 C_{A0}^2 = 0$$

$$C_A = \frac{2k_1 k_2 C_{A0} \pm \sqrt{4k_1^2 k_2^2 C_{A0}^2 - 4k_1 k_2 C_{A0}^2 (k_1 k_2 - k_1^2)}}{2(k_1 k_2 - k_1^2)} = \frac{2k_1 k_2 C_{A0} \pm \sqrt{4k_1^3 k_2 C_{A0}^2}}{2(k_1 k_2 - k_1^2)}$$

$$C_A = \frac{k_1 k_2 \pm \sqrt{k_1^3 k_2}}{(k_1 k_2 - k_1^2)} C_{A0} = \frac{k_2 \pm \sqrt{k_1 k_2}}{(k_2 - k_1)} C_{A0} = \frac{k_2 - \sqrt{k_1 k_2}}{(k_2 - k_1)} C_{A0}$$

$$(\frac{k_2 + \sqrt{k_1 k_2}}{(k_2 - k_1)} C_{A0} > C_{A0} \text{ 不合})$$

Also,

$$\frac{k_2 - \sqrt{k_1 k_2}}{(k_2 - k_1)} C_{A0} = \frac{\sqrt{k_2}(\sqrt{k_2} - \sqrt{k_1})}{(\sqrt{k_2} - \sqrt{k_1})(\sqrt{k_2} + \sqrt{k_1})} C_{A0} = \frac{\sqrt{k_2}}{(\sqrt{k_2} + \sqrt{k_1})} C_{A0}$$

$$\frac{C_{R, \max, CSTR}}{C_{A0}} = \frac{k_1 C_{A0} C_A - k_1 C_A^2}{k_1 C_A C_{A0} - k_2 C_A C_{A0} + k_2 C_{A0}^2} = \frac{k_1 C_{A0}^2 \frac{\sqrt{k_2}}{(\sqrt{k_2} + \sqrt{k_1})} - k_1 C_{A0}^2 [\frac{\sqrt{k_2}}{(\sqrt{k_2} + \sqrt{k_1})}]^2}{k_1 [\frac{\sqrt{k_2}}{(\sqrt{k_2} + \sqrt{k_1})}] C_{A0}^2 - k_2 [\frac{\sqrt{k_2}}{(\sqrt{k_2} + \sqrt{k_1})}] C_{A0}^2 + k_2 C_{A0}^2}$$

$$\frac{C_{R, \max, CSTR}}{C_{A0}} = \frac{k_1 \sqrt{k_2}(\sqrt{k_2} + \sqrt{k_1}) - k_1 k_2}{k_1 \sqrt{k_2}(\sqrt{k_2} + \sqrt{k_1}) - k_2 \sqrt{k_2}(\sqrt{k_2} + \sqrt{k_1}) + k_2(\sqrt{k_2} + \sqrt{k_1})^2}$$

$$\frac{C_{R,\max,CSTR}}{C_{A0}} = \frac{\cancel{k_1 k_2} + k_1 \sqrt{k_1 k_2} - \cancel{k_1 k_2}}{k_1 k_2 + k_1 \sqrt{k_1 k_2} - \cancel{k_2^2} - k_2 \sqrt{k_1 k_2} + \cancel{k_2^2} + k_2 k_1 + 2k_2 \sqrt{k_2 k_1}} = \frac{k_1 \sqrt{k_1 k_2}}{2k_1 k_2 + k_1 \sqrt{k_1 k_2} + k_2 \sqrt{k_1 k_2}}$$

$$\frac{C_{R,\max,CSTR}}{C_{A0}} = \frac{k_1 \sqrt{k_1 k_2}}{2k_1 k_2 + k_1 \sqrt{k_1 k_2} + k_2 \sqrt{k_1 k_2}} = \frac{k_1}{2\sqrt{k_1 k_2} + k_1 + k_2} = \frac{k_1}{(\sqrt{k_1} + \sqrt{k_2})^2}$$

According to the results, for PFR, the maximum concentration of R is related to the exit concentration of A,

$$C_{R,\max} = \frac{k_1 C_A}{k_2 C_{A0}}, \quad C_A \downarrow, C_{R,\max} \downarrow$$

For CSTR, the maximum concentration of R is independent of the concentration of A, only depending on the kinetic parameters.



Problem 2

【Solution】

For PBR, the design equation is,

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

By the rate equation,

$$-r_A = 96C_A = \frac{96C_{A0}(1-x_A)}{(1+\varepsilon x_A)}$$

$$\varepsilon = \delta y_{A0} = \frac{2+1-1}{1} \times 0.8 = 1.6$$

Combine,

$$dW = \int_0^{x_A} \frac{F_{A0} dx_A}{\frac{96C_{A0}(1-x_A)}{(1+1.6x_A)}} = \int_0^{x_A} \frac{F_{A0}(1+1.6x_A)dx_A}{96C_{A0}(1-x_A)}$$

$$\text{For } C_{A0} = \frac{P_{A0}}{RT} = \frac{2 \times 1.013 \times 10^5 \times 0.8}{8.314 \times (273.15 + 110)} = 50.9 \text{ (mol / m}^3\text{)}$$

$$W = \int_0^{0.50} \frac{1500 \times (1+1.6x_A)}{96 \times 50.9(1-x_A)} dx_A = \underline{\underline{0.308 \text{ (kg)}}}$$

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Problem 3

【Solution】

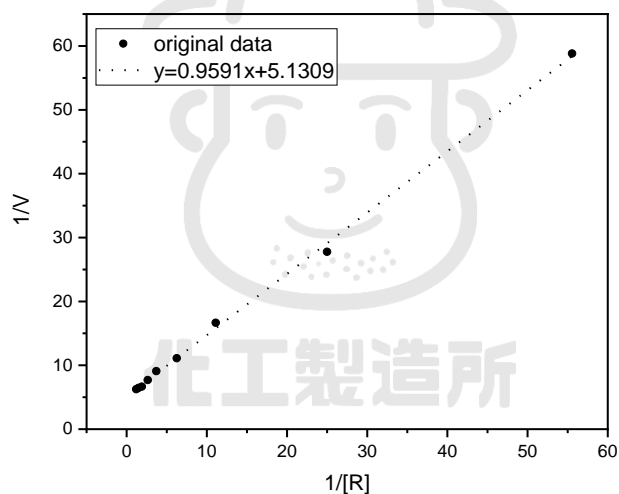
Rearrange the rate equation,

$$\frac{1}{V} = \frac{K_m}{V_{\max}[R]} + \frac{1}{V_{\max}}$$

Plot $\frac{1}{V} - \frac{1}{[R]}$

Time	1	2	3	4	5	6	7	8	9
1/[R]	1.19	1.47	1.89	2.63	3.70	6.25	11.1	25	55.6
1/V	6.25	6.45	6.67	7.69	9.09	11.1	16.7	27.8	58.8

$$(V_{t=1} = \frac{[R]_{t=2} - [R]_{t=0}}{2}, V_{t=2} = \frac{[R]_{t=3} - [R]_{t=1}}{2} \dots)$$



$$\begin{cases} \text{slope} = 0.9591 = \frac{K_m}{V_{\max}} \\ \text{intercept} = \frac{1}{V_{\max}} = 5.1309 \end{cases}$$

$$\begin{cases} V_{\max} = 0.195 \text{ (mmol / (L} \cdot \text{hr))} = 3.25 \times 10^{-6} \text{ (mol / (L} \cdot \text{s))} \\ K_m = 0.187 \text{ (mmol / L)} = 1.87 \times 10^{-4} \text{ (mol / L)} \end{cases}$$

111 年中興化熱化反

Problem 1

【Solution】

Assume the process obeys Arrhenius law,

$$rate \propto k \propto \frac{1}{time}$$

$$\frac{(\frac{1}{30})}{(\frac{1}{30 \times 60})} = e^{\frac{-E_a}{8.314} (\frac{1}{273.15+80} - \frac{1}{273.15+63})}$$

$$\underline{\underline{E_a = 2.38 \times 10^5 \text{ (J / mole)}}}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 29, Example 2.3.)

與 109 年中興化熱化反 Problem 1 雷同)

Problem 2

【Solution】

For gaseous system,

$$C_A = \frac{C_{A0}(1 - X_A)}{(1 + \varepsilon_A X_A)} \left(\frac{T_0 \pi}{T \pi_0} \right)$$

$$\varepsilon_A = \delta y_{A0} = \left(\frac{2-1-1}{1} \right) \times \left(\frac{100}{100+200} \right) = 0$$

$$20 = 100(1 - X_A) \left(\frac{400 \times 3}{300 \times 4} \right), \quad \underline{\underline{X_A = 0.8}}$$

For C_B ,

$$C_B = C_{A0}(\theta_B - X_A) \left(\frac{T_0 \pi}{T \pi_0} \right) = C_{B0}(1 - X_B) \left(\frac{T_0 \pi}{T \pi_0} \right)$$

$$C_B = 100 \times \left(\frac{200}{100} - 0.8 \right) \left(\frac{400 \times 3}{300 \times 4} \right) = \underline{\underline{120 \text{ (mmol / L)}}}$$

For X_B ,

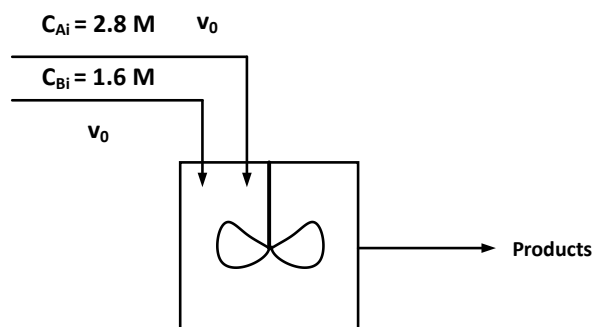
$$120 = 200(1 - X_B) \left(\frac{400 \times 3}{300 \times 4} \right), \quad \underline{\underline{X_B = 0.8}}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 88~89, Example 4.1.)

與 109 年中興化熱化反 Problem 2 雷同。)

Problem 3

【Solution】



\therefore The reaction is $A + 2B \xrightleftharpoons[k_2]{k_1} R$, and $C_{Bi} < C_{Ai}$, the limiting component is B.

By the design equation of mixed flow-reactor,

$$V = \frac{v_1 C_{B0} (1 - x_B)}{-r_B}$$

$$v_1 = v_0 + v_0 = 2v_0$$

By the rate equation,

$$-r_B = -2r_A = 25C_A C_B^2 - 3C_R = 25C_{B0}^3 (\theta_A - 0.5x_B)(1 - x_B)^2 - 3 \times 0.5C_{B0} x_B$$

$$C_{B0} = \frac{C_{Bi}}{2} = 0.8 \text{ (M)}, \quad \theta_A = \frac{2.8}{1.6} = 1.75$$

Combine,

$$V = \frac{v_1 C_{B0} (1 - x_B)}{25C_{B0}^3 (1.75 - 0.5x_B)(1 - x_B)^2 - 3 \times 0.5C_{B0} x_B}$$

$$V = \frac{v_1 (1 - x_B)}{25C_{B0}^2 (1.75 - 0.5x_B)(1 - x_B)^2 - 3 \times 0.5x_B}$$

$$6 = \frac{v_1 (1 - 0.75)}{25 \times 0.8^2 (1.75 - 0.5 \times 0.75)(1 - 0.75)^2 - 3 \times 0.5 \times 0.75}$$

$$v_1 = 6 \text{ (L/min)}, \quad v_0 = \frac{v_1}{2} = 3 \text{ (L/min)}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 99~100, Example 5.3.

與 109 年中興化熱化反 Problem 3 雷同。)

Problem 4**【Solution】**

By the design equation of CSTR,

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

By the rate equation,

$$-r_A = kC_A = \frac{kC_{A0}(1-x_A)}{(1+\varepsilon x_A)}$$

$$\varepsilon = \delta y_{A0} = \frac{2+1-1}{1} \times 0.6 = 1.2$$

Combine,

$$V = \frac{F_{A0}(1+1.2x_A)x_A}{kC_{A0}(1-x_A)}$$
$$500 = \frac{400(1+1.2x_A)x_A}{0.2 \times 4(1-x_A)}, \quad \underline{\underline{x_A = 0.4}}$$

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Problem 5

【Solution】

By the first law of thermodynamics,

$$\Delta H + \frac{\cancel{g}}{\cancel{g_c}} \cancel{\Delta z} + \frac{1}{2g_c} \Delta v^2 = \cancel{\phi}_{insulated} + W$$

horizontal pipe

$$\Delta(v^2) = 2g_c(-\Delta H + W)$$

$$\Delta(v^2) = 2 \times [-1 \times C_p(T_f - T_i) + W] = 2 \times [1.1 \times (25 + 30) - 0.55 \times 10^3] = \underline{\underline{-979 \text{ (m}^2/\text{s}^2\text{)}}}$$

Which is,

$$v_{inlet}^2 - v_{outlet}^2 = 979 \text{ (m}^2/\text{s}^2\text{)}$$

$$\underline{\underline{v_{inlet} = \sqrt{v_{outlet}^2 + 979 \text{ (m}^2/\text{s}^2\text{)}}}}$$

(本題改編自：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 54, Example 2.16.)

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Problem 6

【Solution】

For a length change in a rubber material, the energy balance is given by,

$$dU = TdS + FdL = C_L dT$$

(長度變化會造成能量變化，形式與 $work = force \times length\ change$ 相同)

$$dS = \frac{C_L}{T} dT - \frac{F}{T} dL$$

將 $F = \alpha(L - L_0)T$ 代入：

$$\underline{\underline{dS = \frac{C_L}{T} dT - \alpha(T - T_0)dL}}$$

(以 entropy 的觀點來說，溫度上升，亂度變大；若材料被拉伸，橡膠高分子排列雜亂無章逐漸朝向拉伸方向排列有序，造成亂度下降，以數學模型來則是 $dL > 0$ ，造成亂度下降。此結果將導致會有一個阻力抵抗拉伸應變，可用於推導楊氏係數、剪切模數等材料特性常數。)

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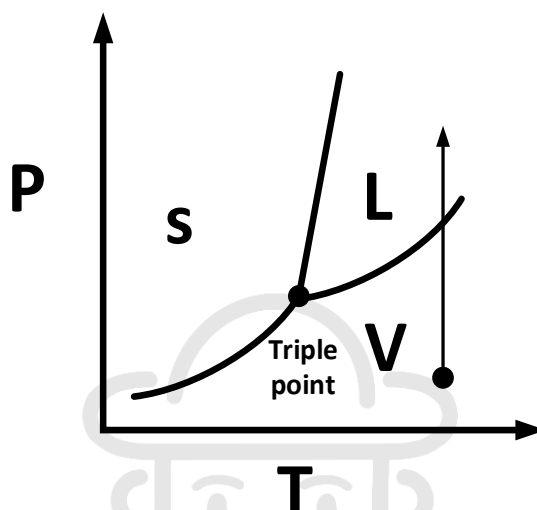
Problem 7

【Solution】

For this shape-stabilized compound, the triple point is,

$$P^{sat} = 10^{3.2 - \frac{1500}{T}} = P^{sub} = \frac{10^{-8}}{T}, \quad T = 113.2(K) = -159.9(^{\circ}C)$$

因此，此物質於 $30^{\circ}C$ 下，應該在該物質三相點的右邊



因此，假設該物質在 $30^{\circ}C$ 與 20 bar 的條件下為液態，相對於理想氣體，其 fugacity 可被計算為：

$$P^{sat} = 10^{3.2 - \frac{1500}{273.15+30}} = 0.0178 \text{ (bar)}$$

因此：

$$f^L = P^{sat} \underbrace{\left(\frac{f}{P}\right)_{sat,T}}_{P^{sat} \text{ very low} \approx 1} \exp\left[\frac{V(P - P^{sat})}{RT}\right] \approx P^{sat} \exp\left[\frac{V(P - P^{sat})}{RT}\right]$$

$$f^L = P^{sat} \exp\left[\frac{V(P - P^{sat})}{RT}\right] = 0.0178 \times \exp\left[\frac{\frac{300}{1.5} \times 10^{-6} (20 - 0.0178) \times 10^5}{8.314 \times (273.15 + 30)}\right] = \underline{\underline{0.0209 \text{ (bar)}}}$$

(本題與 110 年中興化熱化反，化熱部分-Problem 3 雷同，因此關於此題的細節討論請參考該

題。本題可參考 Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

p.320~322, Illustration 7.4-8 與 7.4-9；為利用 sublimation 做固體計算的題目。)

Problem 8

【Solution】

For property θ ,

$$d(n\theta) = \left[\frac{\partial(n\theta)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(n\theta)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial(n\theta)}{\partial n_i}\right]_{P,T,n_j} dn_i$$

$$d(n\theta) = n\left(\frac{\partial\theta}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial\theta}{\partial T}\right)_{P,x} dT + \sum_i \bar{\theta}_i dn_i$$

$$\because dn_i = d(nx_i) = x_i dn + n dx_i, \quad d(nM) = n dM\theta + \theta dn$$

$$nd\theta + \theta dn = n\left(\frac{\partial\theta}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial\theta}{\partial T}\right)_{P,x} dT + \sum_i \bar{\theta}_i (x_i dn + n dx_i)$$

$$n \underbrace{\left[d\theta - \left(\frac{\partial\theta}{\partial P}\right)_{T,x} dP - \left(\frac{\partial\theta}{\partial T}\right)_{P,x} dT - \sum_i \bar{\theta}_i dx_i\right]}_0 + \underbrace{[\theta dn - \sum_i x_i \bar{\theta}_i] dn}_0 = 0$$

$$d\theta - \left(\frac{\partial\theta}{\partial P}\right)_{T,x} dP - \left(\frac{\partial\theta}{\partial T}\right)_{P,x} dT - \sum_i \bar{\theta}_i dx_i = 0$$

$$\because \theta = \sum_i x_i \bar{\theta}_i, \quad d\theta = \sum_i x_i d\bar{\theta}_i + \sum_i \bar{\theta}_i dx_i$$

$$\sum_i x_i d\bar{\theta}_i + \cancel{\sum_i \bar{\theta}_i dx_i} - \left(\frac{\partial\theta}{\partial P}\right)_{T,x} dP - \left(\frac{\partial\theta}{\partial T}\right)_{P,x} dT - \cancel{\sum_i \bar{\theta}_i dx_i} = 0$$

$$\left(\frac{\partial\theta}{\partial P}\right)_{T,x} dP + \left(\frac{\partial\theta}{\partial T}\right)_{P,x} dT - \sum_i x_i d\bar{\theta}_i = 0$$

At constant T, P,

$$\boxed{\sum_i x_i d\bar{\theta}_i = 0}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 383~385.)

(本題與 110 年中興化熱化反，化熱部分-Problem 4-(a)雷同)

112 年中興化熱化反

Problem 1

【Solution】

(A)

$$r_p = k_3[E][S] - k_4[P][E]$$

By pseudo-steady-state assumption,

$$r_{E \cdot S} = k_1[E][S] - k_2[E \cdot S] - k_3[E \cdot S] + k_4[P][E] = 0$$

$$[E \cdot S] = \frac{(k_1[S] + k_4[P])[E]}{k_2 + k_3}$$

By enzyme mass balance,

$$[E]_0 = [E] + [E \cdot S] = [E] + \frac{(k_1[S] + k_4[P])[E]}{k_2 + k_3} = [E] \left[1 + \frac{(k_1[S] + k_4[P])}{k_2 + k_3} \right] = [E] \left[\frac{k_2 + k_3 + (k_1[S] + k_4[P])}{k_2 + k_3} \right]$$

$$[E] = \frac{(k_2 + k_3)[E]_0}{k_2 + k_3 + k_1[S] + k_4[P]}$$

代回：

$$r_p = k_3[E][S] - k_4[P][E] = [E](k_3[S] - k_4[P]) = \frac{(k_2 + k_3)(k_3[S] - k_4[P])[E]_0}{k_2 + k_3 + k_1[S] + k_4[P]}$$

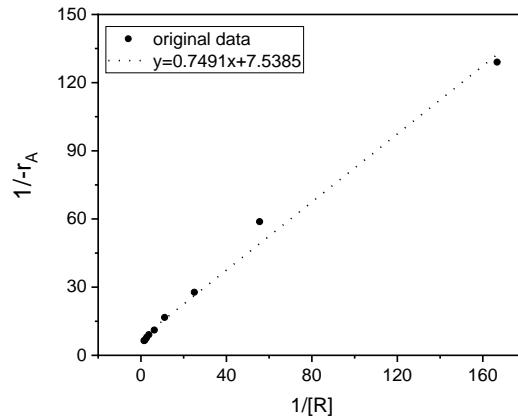
(B)

速率表示式取導數：

$$\frac{1}{-r_A} = \frac{C_A + C_M}{k_3 C_A C_{E0}} = \frac{1}{k_3 C_{E0}} + \frac{C_M}{k_3 C_A C_{E0}}$$

若表示式符合，將數據整理為 $\frac{1}{-r_A} - \frac{1}{C_A}$ ，應為線性關係：

C_A	0.68	0.53	0.38	0.27	0.16	0.09	0.04	0.018	0.006
$1/C_A$	1.47	1.89	2.63	3.70	6.25	11.11	25.00	55.56	166.67
$-r_A$	0.155	0.15	0.13	0.11	0.09	0.06	0.036	0.017	0.00775
$1/(-r_A)$	6.4516	6.6666	7.6923	9.0909	11.1111	16.6666	27.7777	58.8235	129.032



The data give can be reasonably fitted by the kinetic equation offered as the Michaelis-Menten type. (算出來 R^2 為 0.9906)

By integration method, we have,

$$-r_A = \frac{-dC_A}{dt} = \frac{k_3 C_A C_{E0}}{C_A + C_M}$$

$$-\left(\frac{C_A + C_M}{k_3 C_A C_{E0}}\right) dC_A = dt, \quad -\int_{C_{A0}}^{C_A} \left(1 + \frac{C_M}{C_A}\right) dC_A = \int_0^t k_3 C_{E0} dt$$

$$(C_{A0} - C_A) + C_M \ln\left(\frac{C_{A0}}{C_A}\right) = k_3 C_{E0} t$$

將任意 2 點代入(這裡代入 $t=4, t=8$ 做示範)：

$$(1.2 - 0.38) + C_M \ln\left(\frac{1.2}{0.38}\right) = 0.02 \times 4 k_3 \quad \text{---(1)}$$

$$(1.2 - 0.04) + C_M \ln\left(\frac{1.2}{0.04}\right) = 0.02 \times 8 k_3 \quad \text{---(2)}$$

解出此一元二次方程式：

$$\begin{cases} k_3 = 16.5 \text{ (hr}^{-1}\text{)} \\ C_M = 0.435 \text{ (mmol / L)} \end{cases}$$

若使用微分法的數據做計算，可得：

$$\frac{1}{-r_A} = \frac{1}{k_3 C_{E0}} + \frac{C_M}{k_3 C_A C_{E0}} = \frac{0.7491}{C_A} + 7.5385$$

$$\begin{cases} k_3 = 6.632 \text{ (hr}^{-1}\text{)} \\ C_M = 0.099 \text{ (mmol / L)} \end{cases}$$

此二者差異來源為儘管看似符合 model，然而還是有誤差，因此不管是在微分抑或積分都會受到取的點的不同而有不同的誤差大小(比方取的兩個點剛好 model 算出來的結果都比實際大，就會有偏大的誤差。

Problem 2

【Solution】

(A)

By the design equation of PFR,

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

By the rate expression,

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

$$(\varepsilon = 0)$$

Combine,

$$V = \int_0^x \frac{F_{A0}}{kC_{A0}^2(1-x_A)^2} dx_A = \frac{F_{A0}}{kC_{A0}^2} \left(\frac{1}{1-x_A} \right) \Big|_0^x = \frac{F_{A0}}{kC_{A0}^2} \left(\frac{1}{1-X} - 1 \right)$$

(B)

By the design equation of PFR,

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

By the rate expression,

$$-r_A = kC_A^2 = kC_{A0}^2 \frac{(1-x_A)^2}{(1+\varepsilon x_A)^2}$$

$$(\varepsilon = \delta y_{A0} = 0.55 \times \frac{6+1-4}{4} = 0.4125, \text{ 不可直接將上一題結論拿來用})$$

Combine,

$$V = \int_0^{x_A} \frac{F_{A0}}{kC_{A0}^2 \frac{(1-x_A)^2}{(1+0.4125x_A)^2}} dx_A$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{11.4 \times 0.55}{0.082 \times (649 + 273.15)} = 0.083 \text{ (mol / L)}$$

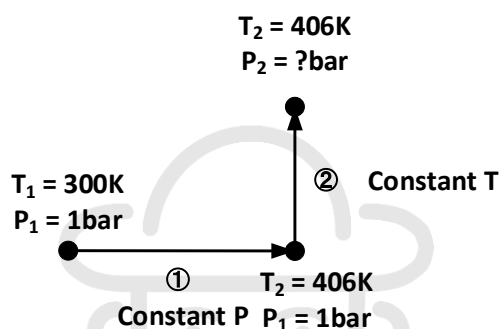
$$V = \int_0^{0.88} \frac{10}{10 \times 0.083^2 \frac{(1-x_A)^2}{(1+0.4125x_A)^2}} dx_A = \underline{\underline{1790.4 \text{ (L)}}}$$

Problem 3**【Solution】**

$$W = -\int_{V_1}^{V_2} P dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_1}{V_2}$$

$$W = 5 \times 8.314 \times (273.15 + 25) \ln \frac{10}{30} = \underline{\underline{-13616.3 \text{ (J)}}}$$

(負號代表對外做功)

Problem 4**【Solution】****【Process ①】**

$$\Delta U_1 = nC_V \Delta T = 1 \times (30 - 8.314) \times (406 - 300) = 2298.7 \text{ (kJ)}$$

$$\Delta H_1 = nC_p \Delta T = 1 \times 30 \times (406 - 300) = 3180 \text{ (kJ)}$$

$$Q_1 = nC_p \Delta T = 1 \times 30 \times (406 - 300) = 3180 \text{ (kJ)}$$

(For constant pressure, $Q = \Delta H$)

$$W_1 = \Delta U_1 - Q_1 = 2298.7 - 3180 = -881.3 \text{ (kJ)}$$

【Process ②】

$$\Delta U_2 = nC_V \Delta T = 1 \times (30 - 8.314) \times 0 = 0 \text{ (kJ)}$$

$$\Delta H_2 = nC_p \Delta T = 1 \times 30 \times 0 = 0 \text{ (kJ)}$$

$$W_2 = -\int_{V_{i2}}^{V_{f2}} P dV = -\int_{V_{i2}}^{V_{f2}} \frac{nRT}{V} dV = nRT \ln \frac{V_{i2}}{V_{f2}} = nRT \ln \frac{P_{f2}}{P_{i2}}$$

Because the final volume is the same as the initial volume,

$$V_{i1} = V_{f2}$$

$$\frac{T_{i1}}{T_{f2}} = \frac{P_{i1}}{P_{f2}} = \frac{P_{f1}}{P_{f2}} = \frac{P_{i2}}{P_{f2}} = \frac{300}{406}$$

$$W_2 = nRT \ln \frac{406}{300} = 1 \times 8.314 \times 406 \ln \frac{406}{300} = 1021.3 \text{ (kJ)}$$

$$Q_2 = \Delta U_2 - W_2 = 0 - 1021.3 = -1021.3 \text{ (kJ)}$$

$$\Delta U = \Delta U_1 + \Delta U_2 = 2298.7 \text{ (kJ)}$$

$$\Delta H = \Delta H_1 + \Delta H_2 = 3180 \text{ (kJ)}$$

$$Q = Q_1 + Q_2 = 3180 - 1021.3 = 2157.7 \text{ (kJ)}$$

$$W = W_1 + W_2 = -881.3 + 1021.3 = 140.0 \text{ (kJ)}$$

Problem 5

【Solution】

(a)

After the quenching process, the temperatures are determined by,

$$m_c C_{p,c} \Delta T_c = m_o C_{p,o} \Delta T_o$$

$$40 \times 0.5(450 - T_f) = 160 \times 2.5(T_f - 25)$$

$$T_f = 45.24^\circ\text{C} = 318.39 \text{ (K)}$$

$$\Delta S_c = m_c \int \frac{dQ}{T} = m_c \int_{T_1}^{T_2} \frac{C_{p,c} dT}{T} = m_c C_{p,c} \ln \frac{T_2}{T_1} = 40 \times 0.5 \ln \frac{318.39}{450 + 273.15} = \underline{\underline{-16.4 \text{ (kJ / K)}}}$$

(b)

$$\Delta S_o = m_o C_{p,o} \ln \frac{T_2}{T_1} = 160 \times 2.5 \ln \frac{318.39}{25 + 273.15} = \underline{\underline{26.27 \text{ (kJ / K)}}}$$

$$(c) \Delta S_{c+o} = -16.4 + 26.27 = \underline{\underline{9.86 \text{ (kJ / K)}}}$$

113 年中興化熱化反

Problem 1

【Solution】

(a)

By the reaction mechanism,

$$-r_s = k_1[E][S] - k_{-1}[ES]$$

Assume the pseudo-steady state assumption is applicable for the enzyme-substrate complex,

$$r_{ES} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0$$

$$[ES] = \frac{k_1}{k_{-1} + k_2} [E][S]$$

Define the total enzyme concentration, $[E_t]$, by mass balance of enzyme,

$$[E_t] = [E] + [ES] = [E] \left(1 + \frac{k_1}{k_{-1} + k_2} [S] \right)$$

代回：

$$\begin{aligned} -r_s &= k_1[E][S] - k_{-1}[ES] = k_1[E][S] - \frac{k_{-1}k_1}{k_{-1} + k_2} [E][S] = \frac{k_1k_2[E][S]}{k_{-1} + k_2} \\ -r_s &= \frac{k_1k_2[E_t][S]}{k_{-1} + k_2 \left(1 + \frac{k_1}{k_{-1} + k_2} [S] \right)} = \frac{k_1k_2[E_t][S]}{(k_{-1} + k_2 + k_1[S])} = \frac{k_2[E_t][S]}{\left(\frac{k_{-1} + k_2}{k_1} + [S] \right)} \end{aligned}$$

Define,

$$\frac{k_{-1} + k_2}{k_1} = K_M, \quad k_2[E_t] = V_{\max}$$

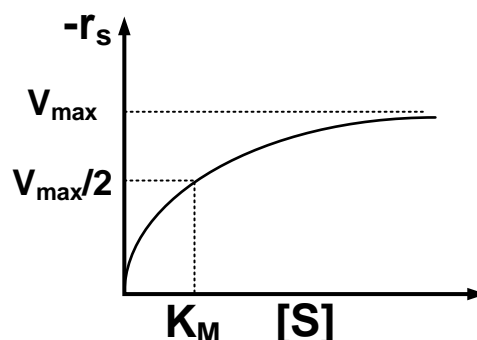
$$-r_s = \frac{V_{\max}[S]}{(K_M + [S])}$$

(Michaelis-Menten equation)

(b)

Pseudo-Steady State assumption

(c)



(d)

We can infer from the Michaelis-Menten curve that the y-axis intercept of the asymptote represents the maximum reaction rate (V_{\max}). By calculating the substrate concentration at half of V_{\max} ($\frac{V_{\max}}{2}$), the Michaelis constant can thereby be obtained. These two parameters provide information on the maximum rate of the enzymatic reaction and the substrate concentration required to reach half of the maximum reaction rate.

(e)

Under the pseudo-steady state assumption, the formation and consumption of the active species occur rapidly, allowing us to neglect any changes in its concentration. In contrast, under the steady-state assumption, the concentration of the intermediate product remains constant over time, independent of the reaction rate.

Problem 2

【Solution】

(a)

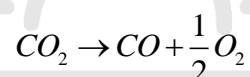
Based on the configuration of the reactor, the reactor can be defined as a **fluidized CSTR**.

Assume:

(1) The reactor is operating under steady-state conditions with pure reactant without inert.

(2) The reactor is well-mixed, ensuring no spatial variations in the concentrations of reactants or catalysts within the reactor.

(3) Assume CO_2 degrades via the reaction,



(4) Assume isothermal but not isobaric.

(5) Neglect the decay of the catalysts.

Mole balance:

$$F_{A0} - F_A = F_A X_A$$

$$F_A = F_{A0}(1 - X_A)$$

Also, in the case of fluidized CSTR,

$$F_{A0} - F_A + (r_A W) = 0$$

$$W = \frac{F_{A0} - F_A}{-r_A} = \frac{F_{A0} X_A}{-r_A}$$

Rate law:

In this sub-question, assume the reaction rate law is (though may not be possible in a catalytic reaction),

$$-r_A = kC_A^n$$

Stoichiometry:

Because the reaction is isothermal but not isobaric, by the stoichiometric relation,

$$-r_A = kC_A^n = k\left[C_{A0}\left(\frac{1-X_A}{1+\frac{1}{2}X_A}\right)\left(\frac{P}{P_0}\right)\right]^n$$

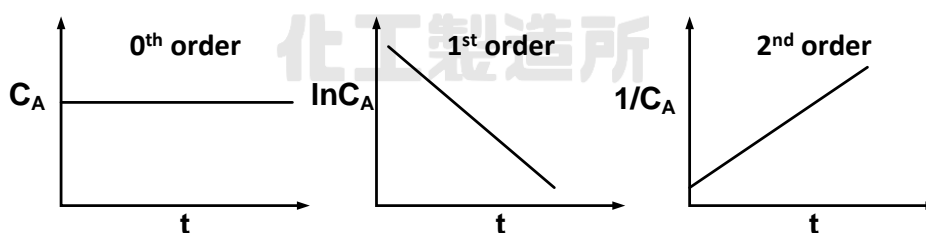
The combination of design equation and reaction rate law:

By combining both the design equation and reaction rate law,

$$W = \frac{F_{A0}X_A}{-r_A} = \frac{F_{A0}X_A}{k\left[C_{A0}\left(\frac{1-X_A}{1+\frac{1}{2}X_A}\right)\left(\frac{P}{P_0}\right)\right]^n}$$

(b)

We can conduct a series of experiments under isothermal and isobaric conditions to determine the concentration of A as a function of time. For the simplest rate laws, corresponding to 0th, 1st, and 2nd reaction orders with respect to the concentration of A, we can generate the following plots by rearranging the concentration-time relationships:



If the reaction obeys typical catalytic reaction mechanism, which has the reaction rate law for example,

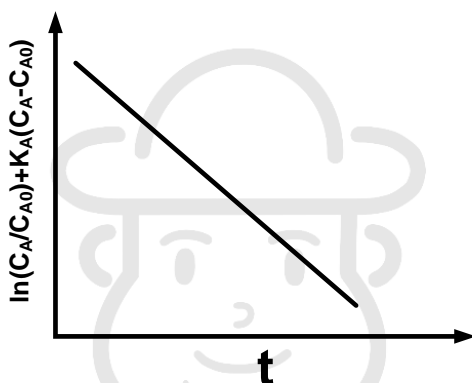
$$-r_A = \frac{kC_A}{1 + K_A C_A}$$

The concentration-time relationships and the related parameters can be determined by,

$$-\frac{dC_A}{dt} = \frac{kC_A}{1 + K_A C_A} \quad , \quad -\left(\frac{1}{kC_A} + \frac{K_A}{k}\right)dC_A = dt$$

$$-\frac{1}{k}\left[\ln \frac{C_A}{C_{A0}} + K_A(C_A - C_{A0})\right] = t$$

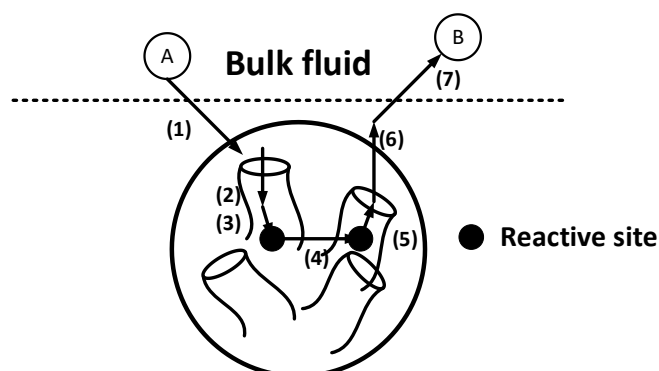
We can plot $\ln \frac{C_A}{C_{A0}} + K_A(C_A - C_{A0})$ against t as follows,



Problem 3

【Solution】

(a)



Take the catalytic reaction $A \rightarrow B$ for example,

- (1) Mass transfer of the reactants from the bulk to the external surface of the catalyst pellet.
- (2) Internal diffusion in the catalyst pore into the vicinity of the active surface site.
- (3) Adsorption of the reactant on the catalytic surface.
- (4) Surface reaction of the reactant into products.
- (5) Desorption of the products from the catalytic surface.
- (6) Internal diffusion from the catalytic surface to the pore entrance.
- (7) Mass transfer of the products from the external surface into the bulk.

(b)

One of the main problems encountered when using immobilized catalysts is the possible leaching of the catalyst from the porous media surface into the surrounding carrier gas or solvents. To address this issue, we can design the porous media with alternative materials or modify the carrier gas/solvent to enhance the interaction between the catalyst and the media, thereby improving attachment. However, these changes may affect the catalytic efficiency and alter the catalyst's lifespan.

Problem 4

【Solution】

(a)

For the stability criterion of a fluid, we have

$$S_{UU} < 0$$

Setting $S = S(U, V)$, we have,

$$NS_{UU} = N \frac{\partial}{\partial U} \bigg|_{N,V} \left(\frac{\partial S}{\partial U} \right)_{N,V} = N \left[\frac{\partial(1/T)}{\partial U} \right]_{N,V} = -\frac{N}{T^2} \left(\frac{\partial T}{\partial U} \right)_{N,V}$$
$$(dU = TdS - PdV, \quad \left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T})$$

\therefore

$$dU = NC_V dT + [T \left(\frac{\partial P}{\partial T} \right)_V - P] dV + GdN$$
$$\left(\frac{\partial U}{\partial T} \right)_{N,V} = NC_V$$
$$NS_{UU} = -\frac{N}{T^2} \left(\frac{\partial T}{\partial U} \right)_{N,V} = -\frac{1}{T^2 C_V} < 0, \quad \boxed{C_V > 0}$$

That is, the constant-volume heat capacity must be positive, so that internal energy increases as the fluid temperature increases.

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

p 293~297. 詳細的 stability criterion 與來源也可在其中研讀，但是是非常冗長的數學推導，若想

放棄的話，推薦至少可以將流體穩定條件的“結論”背起來，即：

$$(1) C_V > 0$$

$$(2) \left(\frac{\partial P}{\partial V} \right) < 0 \text{ 或 } \kappa_T > 0$$

第二點在 113 年台大化熱化反就有使用到

(b)

Starting with $S = S(T, V)$,

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

\therefore

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V = \frac{\left(\frac{\partial U}{\partial T}\right)_V}{\left(\frac{\partial U}{\partial S}\right)_V} = \frac{C_V}{T}$$

Also, by the Maxwell relations,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

\therefore

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_V}{T} \left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = \frac{C_V}{T} + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

By the triple product rule,

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_V}{T} + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = \frac{C_V}{T} - \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 = \frac{C_V}{T} - \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V^2$$

Also, we have,

$$\boxed{C_P = T \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P = C_V - T \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V^2}$$

(c)

For ideal gases,

$$C_P = C_V - T \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V^2 = C_V - T \left(-\frac{RT}{P^2}\right) \left(\frac{R}{V}\right)^2 = C_V + T \left(\frac{V}{P}\right) \left(\frac{R}{V}\right)^2 = \underline{\underline{C_V + R}}$$

Problem 5**【Solution】**

(a)

Taking the two metals as a overall system, by energy balance,

$$\Delta U = \cancel{Q} + \cancel{W}$$

$$\Delta U = \Delta U_1 + \Delta U_2 = 0$$

Assume 1 denotes as the cooler one, and 2 as the hotter one, which both have a constant-volume heat capacity of C_V , therefore,

$$\Delta U = C_V(T - T_{1i}) + C_V(T - T_{2i}) = 0$$

Rearrange,

$$T = \frac{T_{1i} + T_{2i}}{2}$$

(b)

$$T = \frac{T_{1i} + T_{2i}}{2} = \frac{135 + 265}{2} = \underline{\underline{200\ (^{\circ}\text{C})}}$$

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Problem 6

【Solution】

By Gibbs-Duhem equation of μ_i

$$x_1 \frac{d \ln \hat{f}_1}{dx_1} = x_2 \frac{d \ln \hat{f}_2}{dx_2}$$

If $\hat{f}_1 = x_1 H_1$ (Henry's law)

$$x_1 \frac{d \ln \hat{f}_1}{dx_1} = x_1 \frac{d \ln(H_1 x_1)}{dx_1} = 1$$

$$x_2 \frac{d \ln \hat{f}_2}{dx_2} = 1, \quad \ln \hat{f}_2 = \ln x_2 + C$$

When $x_2 \rightarrow 1$, $\hat{f}_2 \rightarrow f_2$,

$$\text{令 } e^C = f_2, \quad \underline{\underline{\hat{f}_2 = x_2 f_2}}$$

That is, when component 1 obeys Henry's law, the Gibbs-Duhem law assures component validity of the Lewis/Randall rule for component 2 as it approaches purity.

Problem 7

【Solution】

The fugacity represents the effective pressure of a non-ideal gas, corresponding to the pressure that an ideal gas would exert under the same temperature conditions.