106 年台科大化熱化反

Part I. 化工動力學

<u>Problem 1</u>
【Solution】

(1)

觀察速率常數

$$k_A[=]M^{-1}\min^{-1}，total\ order = 2$$

∵ A 與 B 同 order

$$\underline{\underline{rate\ law = -k_A C_A C_B}}$$

(2)

By Arrhenius equation,

$$k(50°C) = k(20°C)\exp[\frac{-Ea}{R}(\frac{1}{50+273} - \frac{1}{20+273})]$$

$$= 0.5\exp[\frac{-8000}{1.987}(\frac{1}{323} - \frac{1}{293})] = \underline{\underline{1.792}}\ (L/mol \cdot \min)$$

(3)

$$C_C = C_{A0}x_A = \frac{20}{100}x_A = 0.1，x_A = 0.5$$

$$F_{A,rec} = V_R C_A = 50 \times \frac{20}{100}(1-0.5) = 5\ (mol/\min)$$

For F_B,

$$F_{B,rec} = V_R C_B = 50 \times \frac{20}{100}(\frac{30}{20} - 2 \times 0.5) = 5\ (mol/\min)$$

$$\begin{cases} F_{A,in} = 20+5 = 25\ (mol/\min) \\ F_{B,in} = 30+5 = 35\ (mol/\min) \end{cases}$$

(4)

For recycle CSTR,

$$\frac{V}{F_{A0}} = (R+1) \cdot \frac{x_{Af} - (\frac{R}{R+1})x_{Af}}{k_A C_A C_B}$$

$$R = \frac{V_R}{V_0} = \frac{50}{100} = 0.5$$

$$V = (R+1) \cdot \frac{x_{Af} - (\frac{R}{R+1})x_{Af}}{k_A C_{A0}^2 (1 - x_A)(\theta_B - 2x_A)}$$

$$= 20(0.5+1) \times \frac{0.5 - (\frac{0.5}{0.5+1}) \times 0.5}{1.792 \times (\frac{20}{100})^2 \times (1-0.5)(\frac{3}{2} - 2 \times 0.5)} = \underline{\underline{558.036 \ (L)}}$$

(5)

$$V = \frac{F_{A0} x_A}{-r_A} = \frac{F_{A0} x_A}{k_A C_A C_B} = \frac{20 \times 0.5}{1.792 \times (\frac{20}{100})^2 \times (1-0.5)(\frac{3}{2} - 2 \times 0.5)} = \underline{\underline{558.036 \ (L)}}$$

Problem 2

【Solution】

(1)

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

$$C_B = \frac{2C_{A0} x_A}{(1+x_A)}$$

(2)

$$-r_A = k_A (C_A - \frac{C_B^2}{K_C})$$

(3)

$$F_{A0} = C_{A0} v_0 = \frac{P_{A0}}{RT} v_0 = \frac{3}{0.082 \times 400} \times 4000 = \underline{\underline{365.85}} \ (mol/s)$$

(4)

At equilibrium, the reactor volume is 1.5 times the initial one,

$$\frac{V}{V_0} = (1+\varepsilon x_{Ae}) = (1+x_{Ae}) = 1.5$$

$$x_{Ae} = 0.5$$

$$K_C = \frac{C_{Be}^2}{C_{Ae}} = \frac{4C_{A0}^{\cancel{2}} x_{Ae}^2}{(1+x_{Ae})^{\cancel{2}}} \frac{(1+\cancel{x_{Ae}})}{\cancel{C_{A0}}(1-x_{Ae})} = \frac{4 \times 0.5^2 \times \dfrac{3}{0.082 \times 400}}{(1+0.5)(1-0.5)} = 0.1219$$

(5)

By design equation,

$$V = \int_0^{x_A} \frac{F_{A0}}{-r_A} dx_A = \int_0^{0.4} \frac{F_{A0}}{k_A(C_A - \frac{C_B^2}{K_C})} dx_A$$

$$= \int_0^{0.4} \frac{F_{A0}}{k_A[C_{A0}\frac{1-x_A}{1+x_A} - C_{A0}^2 \frac{4x_A^2}{K_C(1+x_A)^2}]} dx_A$$

$$= \int_0^{0.4} \frac{365.85}{0.5[\frac{3}{0.082 \times 400}\frac{1-x_A}{1+x_A} - (\frac{3}{0.082 \times 400})^2 \frac{4x_A^2}{0.1219(1+x_A)^2}]} dx_A$$

$$= \int_0^{0.4} \frac{365.85}{A} dx_A$$

[計算機數值解]

$$\underline{\underline{V = 6736.36 \ (L)}}$$

[Simpson's rule]

x_A	0	0.2	0.4
A	0.045732	0.026677	0.0084
1/A	21.86667	37.48571	119.0519

$$V = \frac{h}{3}[f(0) + 4f(0.2) + f(0.4)] \times 365.85$$

$$= \frac{0.2}{3}[21.867 + 4 \times 37.486 + 119.052] \times 365.85$$

$$= \underline{\underline{7094.18 \ (L)}}$$

(6)

$$x = 0.9 > x_{Ae}, \text{ which is impossible}$$

Problem 3

【Solution】

(1)

$$r_{\cdot C} = k_1 C_A C_B - k_2 C_{\cdot C} - k_3 C_{\cdot C}^2$$

(2)

By PSSH, $r_{\cdot C} = 0$

$$r_{\cdot C} = k_1 C_A C_B - k_2 C_{\cdot C} - k_3 C_{\cdot C}^2 = 0$$

$$\because F_D = F_{A0} \times 0.5 x_A = 2.5$$

$$10 \times 0.5 x_A = 2.5 \text{，} \quad x_A = 0.5$$

$$\begin{cases} C_A = C_{A0}(1 - x_A) = \dfrac{10}{10}(1 - 0.5) = 0.5 \\ C_B = C_{A0}(1 - x_A) = \dfrac{10}{10}(1 - 0.5) = 0.5 \end{cases}$$

代回：

$$0.1 \times 0.5^2 - C_{\cdot C} - 1.5 C_{\cdot C}^2 = 0$$

$$\underline{\underline{C_{\cdot C} = 0.024 \ (M)}}$$

(3)

$$V = \frac{F_{A0} x_A}{-r_A} = \frac{F_{A0} x_A}{k_1 C_A C_B - k_2 C_{\cdot C}} = \frac{10 \times 0.5}{0.1 \times 0.5^2 - 1 \times 0.024} = \underline{\underline{5726.35 \ (L)}}$$

Problem 4

【Solution】

(1) 喝水可稀釋體內病毒，使病毒作用速率降低

(2) 大顆粒：表面積降低，反應速率變慢

　　小顆粒：porosity 降低，$\Delta P\uparrow$

(3)

$$rate = -r_A = k(T)C_A$$

$$= k(T)C_{A0}(1-x_A)$$

∵速率由溫度、轉化率控制，有可能反應後 $x_A\uparrow$，但 T$\uparrow$使速率$\uparrow$更多

(4)

Define selectivity, $S_{D/U}$

$$S_{D/U} = \frac{-r_{1A}}{-r_{2A}} = \frac{10\exp[\frac{-1000}{T}]C_A^2 C_B^{0.5}}{10^9 \exp[\frac{-10000}{T}]C_A C_B}$$

For temperature,

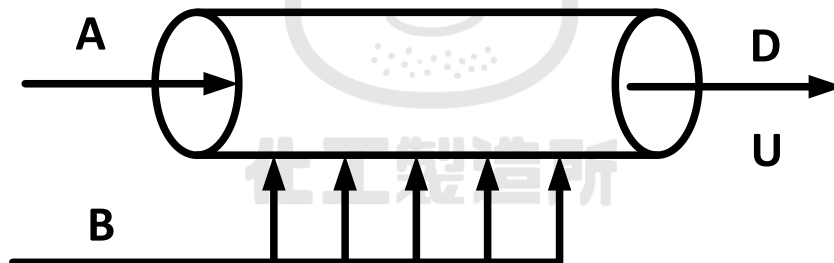$$E_{a1} < E_{a2} \text{ , } T\downarrow, S_{D/U}\uparrow$$

For C_A,

$$S_{D/U} \propto C_A \rightarrow C_A\uparrow S_{D/U}\uparrow$$

For C_B,

$$S_{D/U} \propto C_B^{-0.5} \rightarrow C_B\downarrow S_{D/U}\uparrow$$

We may need a ***PFR with pure A inlet and a side stream B at a low temperature***

Part II. 化工熱力學

Problem 5

【Solution】

(a)

$$\Delta_{mix}G = \Delta_{mix}G^{IM} + G^E$$

For G^E,

$$G^E = H^E - \cancel{TS^E}_{\text{regular solution}} = nRT\xi x_A x_B$$

$$\underline{\underline{\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B + nRT\xi x_A x_B)}}$$

(b)

$$x = \frac{2}{2+8} = 0.2$$

$G = nRT\{x \ln x + (1-x)\ln(1-x)[0.876 - 0.21(5x-3) + 0.038(5x-3)^2]\}$

$= (2+8) \times 8.314 \times 303.15\{0.2 \ln 0.2 + 0.8 \ln 0.8 + 0.2 \times 0.8[0.876 - 0.21(5 \times 0.2 - 3) + 0.038(5 \times 0.2 - 3)^2\}$

$= -6772.82 \ (J)$

(本題改編自：Atkins, P.; De Paula, J.; Keeler, J. Atkins' Physical Chemistry, 9th ed.; p 205,

Problem 5.15.)

Problem 6
【Solution】

By Raoult's law basis,

$$r_C(RL) = \frac{P_C}{x_C P_C^{sat}}$$

Henry's law basis,

$$r_C(HL) = \frac{P_C}{x_C k_C}$$

$$a_C = r_C x_C \quad , \quad P_C^{sat} = 31.2$$

x_C	0.2	0.4	0.6
$r_C(R)$	1.586538	1.201923	1.148504
$r_C(HL)$	2.25	1.704545	1.628788
$a_C(R)$	0.317308	0.480769	0.689103
$a_C(HL)$	0.45	0.681818	0.977273

Problem 7

【Solution】

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

By Maxwell relation,

$$(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$$

For $(\frac{\partial S}{\partial T})_P$

$\because dH = TdS + VdP$

$$(\frac{\partial S}{\partial T})_P = \frac{1}{T}(\frac{\partial H}{\partial T})_P - V(\frac{\cancel{\partial P}}{\cancel{\partial T}})_P = \frac{C_P}{T}$$

代回：

$$(\frac{\partial V}{\partial S})_P = \frac{(\frac{\partial V}{\partial T})_P}{\frac{C_P}{T}} = \frac{VT\alpha}{C_P}$$

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Problem 1
【**Solution**】

For Carnot cycle,

$$\eta = 1 - \frac{T_{low}}{T_{high}}$$

$$0.44 = 1 - \frac{T_{low}}{150 + 273.15} \quad , \quad \underline{\underline{T_{low} = 236.964 \ (K)}}$$

Problem 2
【**Solution**】

(a)

$$dU = TdS - PdV$$

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

$$\underline{\underline{(\frac{\partial S}{\partial T})_V = \frac{C_V}{T}}}$$

(b)

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

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

$$(\frac{\partial S}{\partial T})_P = \frac{T(\frac{\partial S}{\partial T})_V + T(\frac{\partial P}{\partial T})_V(\frac{\partial V}{\partial T})_P}{T} = \frac{C_V + C_P - C_V}{T} = \underline{\underline{\frac{C_P}{T}}}$$

Problem 3

【Solution】

(a)

$$\Delta \underline{S} = \int_{T_i}^{T_f} \frac{C_P}{T} \, dT - R \ln \frac{P_f}{P_i}$$

$$= C_P^* \ln \frac{T_f}{T_i} - R \ln \frac{P_f}{P_i} = 29.3 \ln \frac{575}{290} - 8.314 \ln \frac{10}{1}$$

$$= \underline{\underline{0.911}} \; (J / mol \cdot K)$$

(b)

By energy balance (steady state, open system),

$$\Delta H + \cancel{\Delta(\frac{v^2}{2g_c})} + \cancel{\frac{g}{g_c} \Delta z} = \cancel{Q}_{adiabatic} + W$$

$$W = \Delta H = C_P^*(T_f - T_i) = 29.3(575 - 290) = \underline{\underline{8350.5}} \; (J / mol)$$

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

5th ed.; p 128, Illustration 4.5-1.)

Problem 4

【Solution】

(a)

By mole balance of benzene,

$$0.4 \times 1 \times 10^4 = 0.96D + x_B B$$

By mole balance of TMP,

$$0.6 \times 1 \times 10^4 \times 0.93 = 0.96D$$

$$D = 3875 \ (mol/hr)$$

$$\begin{cases} B = 10^4 - 3875 = 6125 \ (mol/hr) \\ x_B = 0.0457 \\ x_{TMP} = 1 - x_B = 0.9543 \end{cases}$$

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

5th ed.; p 537, Problem 10.1-13.)

(b)

Assume Raoult's law is applicable,

$$\begin{cases} x_5 P_{C_5}^{vap} = y_5 P \\ x_6 P_{C_6}^{vap} = y_6 P \\ x_7 P_{C_7}^{vap} = y_7 P \end{cases}, \begin{cases} 0.55 \times 2.755 = y_5 P \\ 0.25 \times 1.021 = y_6 P \\ 0.20 \times 0.390 = y_7 P \end{cases}$$

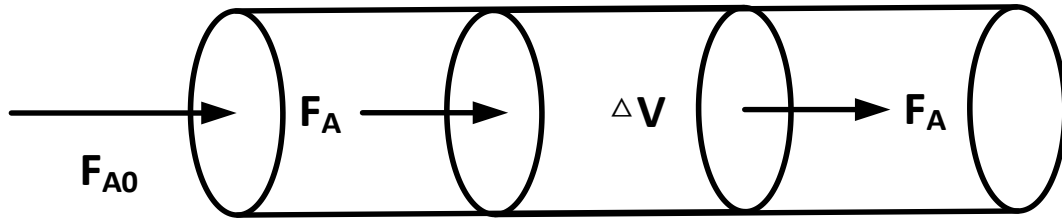三式相加

$$\underline{\underline{P = 1.8485 \ (bar)}}$$

代回得

$$\begin{cases} y_5 = 0.820 \\ y_6 = 0.138 \\ y_7 = 0.042 \end{cases}$$

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

5th ed.; p 518, Problem 10.1-8.)

Problem 5

【Solution】

Consider the following configuration,

By mole balance in the control volume,

$$F_A\big|_V - F_A\big|_{V+\Delta V} + r\Delta V = 0$$

同除 $\Delta V \to 0$

$$\frac{-dF_A}{dV} + r = 0$$

∵ rate equation,

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

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

代回

$$\frac{-d[F_{A0}(1-x_A)]}{dV} = -r$$

$$F_{A0}\frac{dx_A}{dV} = -r$$

$$dV = \frac{F_{A0}}{-r}dx_A = \frac{F_{A0}dx_A}{-r_A} = \frac{F_{A0}dx_A}{kC_{A0}(1-x_A)}$$

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

Problem 6

【Solution】

(a)

$$r_D = k_4[I]$$

By PSSH on $[I]$

$$r_I = k_1[H] - k_2[I][H] + 2k_2[I][H] - k_3[I] - k_4[I] = 0$$

$$[I] = \frac{k_1[H]}{k_3 + k_4 - k_2[H]}$$

$$\underline{\underline{r_D = \frac{k_1 k_4[H]}{k_3 + k_4 - k_2[H]}}}$$

(b)

$[H]$ *is very small,*

$$\underline{\underline{r_D \approx \frac{k_1 k_4[H]}{k_3 + k_4}}}$$

Problem 7

【Solution】

(a)

B 並未在 rate law 之分母出現 => 應該不吸附在觸媒上

(b)

For an isothermal CSTR with catalyst,

$$W = \frac{F_{A0} \cdot x_A}{-r_A} = \frac{F_{A0} x_A}{\dfrac{kC_A}{1+KC_A}} = \frac{F_{A0} x_A}{\dfrac{kC_{A0}(1-x_A)}{1+KC_{A0}(1-x_A)}}$$

$$W = \cfrac{1 \times 0.8}{\left[\cfrac{0.01 \times \cfrac{3.17}{0.082(500+273)}(1-0.8)}{1+125 \times \cfrac{3.17}{0.082(500+273)}(1-0.8)}\right]} = 17999.78 \ (g)$$

$$V = \frac{W}{\rho_b} = \frac{17999.78}{0.1} = 179997.8 \ (cm^3) = \underline{\underline{179.9 \ (L)}}$$

Problem 8

【Solution】

(a)

For PFR,

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

Rate equation,

$$-r_A = k_r C_A - k_b C_B^2$$

$$= \frac{k_r C_{A0}(1-x_A)}{(1+x_A)} - \frac{4k_b C_{A0}^2 x_A^2}{(1+x_A)^2}$$

Combine,

$$V = \int_0^{x_{A0}} \frac{F_{A0}}{\dfrac{k_r C_{A0}(1-x_A)}{(1+x_A)} - \dfrac{4k_b C_{A0}^2 x_A^2}{(1+x_A)^2}} dx_A$$

For C_{A0}

$$C_{A0} = \frac{1}{0.082(946+273.15)} = 0.01 \ (mol/L)$$

代入

[計算機數值解]

$$V = \int_0^{0.4} \frac{1\times10^3}{\dfrac{2\times10^2\times0.01(1-x_A)}{(1+x_A)} - \dfrac{4\times2\times10^4\times0.01^2 x_A^2}{(1+x_A)^2}} dx_A = \underline{\underline{508.308 \ (L)}}$$

[Simpson's rule]

令

$$V = \int_0^{0.4} \frac{F_{A0}}{A} dx_A$$

x_A	0	0.2	0.4
A	2.000594	1.111375	0.203948
1/A	0.499852	0.899786	4.903206

$$V = 1000 \times \frac{0.2}{3}[0.499 + 4\times0.899 + 4.903] = \underline{\underline{600.417 \ (L)}}$$

(b)

At equilibrium,

$$K_C = \frac{k_f}{k_b} = \frac{C_B^2}{C_A} = \frac{4C_{A0}^2(\frac{x_A}{1+x_A})^2}{C_{A0}(\frac{1-x_A}{1+x_A})}$$

$$\frac{2\times10^2}{2\times10^4} = \frac{4\times0.01x_A^2}{(1-x_A)(1+x_A)}$$

$$\underline{\underline{x_A = 0.447}}$$

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Problem 1
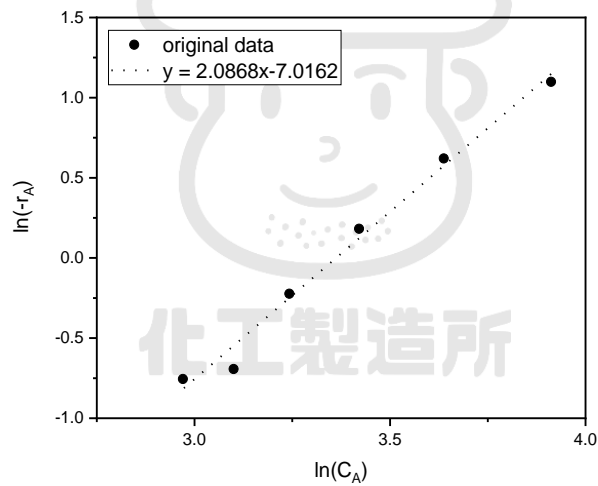【Solution】

$\because C_{B0} >> C_{A0}$

假設 rate law,

$$-r_A = k' C_A^n C_B \approx k C_A^n$$

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

$$\ln(-r_A) = n \ln C_A + \ln k$$

Plot $\ln(-r_A) - \ln C_A$ diagram

$$slope = n = 2$$

將 $C_{A0} = 50$, $-r_A = 3.0$, $k = 0.5 \times 10^3$ 代回
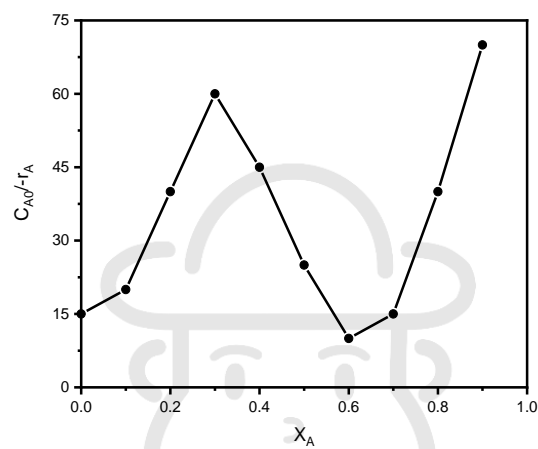
$$\ln 3.0 = 2 \ln 50 + \ln(k' \times 0.5 \times 10^{-3})$$

$$\underline{\underline{k' = 2.4 \times 10^{-6}}}$$

$$\underline{\underline{-r_A = 2.4 \times 10^{-6} C_A^2 C_B}}$$

Problem 2

【Solution】

將 $\dfrac{C_{A0}}{-r_A} - x_A$ 關係繪出

1. $0 \leq x_A \leq 0.6$ 為 CSTR

$$V = v_0 \left.\frac{C_{A0}}{-r_A}\right|_{x_A=0.6} (0.6-0) = 30 \times 10 \times 0.6 = 180 \ (L)$$

2. $0.6 \leq x_A \leq 0.9$ 為 PFR

$$V = \int_{0.6}^{0.9} \frac{F_{A0}}{-r_A} dx_A = v_0 \int_{0.6}^{0.9} \frac{C_{A0}}{-r_A} dx_A$$

x_A	0.6	0.75	0.9
$\dfrac{C_{A0}}{-r_A}$	10	27.5	70

$$V_{PFR,2} = 30 \times \frac{0.15}{3}[10 + 4 \times 27.5 + 70] = 285 \ (L)$$

$$V_{total} = 180 + 285 = \underline{\underline{465.5}} \ (L)$$

Problem 3

【**Solution**】

(a)

By Arrhenius equation,

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

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

If we have two k with two temperature,

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

$$\ln \frac{k_1}{k_2} = \frac{-E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

$$E_a = \frac{R\ln\frac{k_1}{k_2}}{(\frac{1}{T_2} - \frac{1}{T_1})}$$

(b)

將 k、T 代入

$$E_a = \frac{8.314\ln\frac{0.001}{0.005}}{(\frac{1}{273.15+100} - \frac{1}{273.15+0})} = \underline{\underline{13638.57 \ (J/mol)}}$$

$$A = ke^{\frac{E_a}{RT}} = 0.001 \times e^{\frac{13868.57}{8.314 \times (273.15+0)}} = \underline{\underline{0.406}}$$

Problem 4

【Solution】

(1) Negligible kinetic and potential energy changes

(2) Closed system

Problem 5

【Solution】

$$P_1 = 20\,psia \xrightarrow{Step1} \begin{matrix} P_2 = 1000\,psia \\ T_2 = ? \end{matrix} \xrightarrow[cooler]{Step2} \begin{matrix} P_3 = 1000\,psia \\ T_3 = 60\,°F \end{matrix} \xrightarrow[compressor]{Step3} \begin{matrix} P_4 = ? \\ T_4 = ? \end{matrix} \xrightarrow[cooler\,/\,heater]{Step4} \begin{matrix} P_5 = ? \\ T_5 = 60\,°F \\ x_5^L = 0.75 \\ x_5^V = 0.25 \end{matrix}$$

with $T_1 = 60\,°F$

For Step 1 (adiabatic compression)

By energy balance (open system, steady state),

$$\Delta H + \Delta(\frac{v^2}{2g_c}) + \frac{g}{g_c}\Delta z = \cancel{Q} + W$$

$$\Delta H = W$$

By entropy balance,

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

$$\hat{S}_1 = \hat{S}_2$$

By the phase diagram

$$\hat{S}_1 = 0.49(Btu\,/\,lb_m \cdot R) \longrightarrow \begin{matrix} \hat{S}_2 = 0.49(Btu\,/\,lb_m \cdot R) \\ \hat{H}_2 = 205(Btu\,/\,lb_m) \\ T_2 = 250\,°F \end{matrix}$$

with $\hat{H}_1 = 165(Btu\,/\,lb_m)$

$$W = \Delta H = \hat{H}_2 - \hat{H}_1 = 205 - 165 = 40\ (Btu\,/\,lb_m)$$

For Step 2

By energy balance,

$$\Delta H + \cancel{\Delta(\frac{v^2}{2g_c})} + \cancel{\frac{g}{g_c}\Delta z} = Q + \cancel{W}$$

$$
\begin{array}{l}
P_2 = 100(psia) \\
\hat{H}_2 = 200(Btu/lb_m)
\end{array}
\longrightarrow
\begin{array}{l}
P_3 = 100(psia) \\
T_3 = 60°\mathrm{F} \\
\hat{H}_3 = 162(Btu/lb_m)
\end{array}
$$

$$Q = \Delta H = \hat{H}_3 - \hat{H}_2 = 162 - 200 = -38 \ (Btu/lb_m)$$

For Step 3

By energy balance,

$$\Delta H + \cancel{\Delta(\frac{v^2}{2g_c})} + \cancel{\frac{g}{g_c}\Delta z} = \cancel{Q} + W$$

By entropy balance,

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

$$\hat{S}_3 = \hat{S}_4$$

By the phase diagram

$$
\begin{array}{l}
\hat{S}_3 = 0.40(Btu/lb_m \cdot R) \\
\hat{H}_3 = 162(Btu/lb_m)
\end{array}
\longrightarrow
\begin{array}{l}
\hat{S}_4 = 0.40(Btu/lb_m \cdot R) \\
P_4 = P_5 = 750(psia) \\
\hat{H}_4 = 205(Btu/lb_m)
\end{array}
$$

$$W = \Delta H = \hat{H}_4 - \hat{H}_3 = 220 - 162 = 58 \ (Btu/lb_m)$$

For Step 4

By energy balance,

$$\Delta H + \cancel{\Delta(\frac{v^2}{2g_c})} + \cancel{\frac{g}{g_c}\Delta z} = Q + \cancel{W}$$

$$\hat{H}_4 = 220(Btu/lb_m) \longrightarrow \hat{H}_5(x_5^L = 0.75, x_5^V = 0.25) = 162(Btu/lb_m)$$

$$Q = \Delta H = \hat{H}_5 - \hat{H}_4 = 75 - 220 = -145 \ (Btu/lb_m)$$

$$\begin{cases} W = 40 + 58 = 98 \ (Btu/lb_m) \\ Q = -38 - 145 = -183(Btu/lb_m) \end{cases}$$

For ideal gas,

$$\begin{aligned} W &= (H_2 - H_1) + (H_4 - H_3) = C_p(T_2 - T_1 + T_4 - T_3) \\ &= 0.2(250 - 60 + 300 - 60) \\ &= \underline{\underline{86 \ (Btu/lb_m)}} \end{aligned}$$

$$\begin{aligned} Q &= (H_3 - H_2) + (H_5 - H_4) = C_p(T_3 - T_2 + T_5 - T_4) \\ &= 0.2(60 - 250 + 60 - 300) \\ &= \underline{\underline{-86 \ (Btu/lb_m)}} \end{aligned}$$

(※題目未給 C_p 數據，經查表，在 60~300°F範圍內 $C_p \approx 0.2 \ (Btu/lb \cdot °F)$)

(2)

∵By energy balance of the discharge process,

$$\Delta H + \cancel{\Delta(\frac{v^2}{2g_c})} + \cancel{\frac{g}{g_c}\Delta z} = \cancel{Q} + \cancel{W} = 0$$

$$\hat{H}_i = 75 \longrightarrow \begin{array}{l} \hat{H}_f = 75 \\ P_f = 14.7 \ (psia) \end{array}$$

對應至 phase diagram，應為 ***solid-vapor mixture***

Problem 6

【**Solution**】

(1)

By phase equilibrium relationship,

$$dG^{\alpha} = dG^{\beta}$$

$$-S^{\alpha}dT + V^{\alpha}dP = -S^{\beta}dT + V^{\beta}dP$$

$$\frac{dP}{dT} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} = \frac{\Delta S}{\Delta V} = \underline{\frac{\Delta H}{T\Delta V}}$$

(2)

For solid-gas equilibrium,

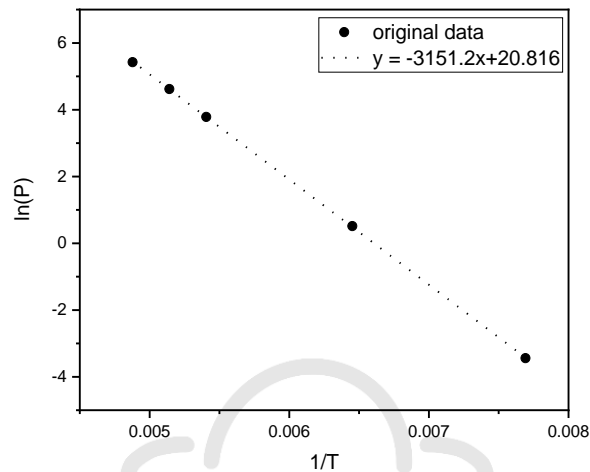$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \approx \frac{\Delta H}{\frac{RT^2}{P}}$$

$$\frac{dP}{P} = \frac{\Delta H}{RT^2}dT$$

$$\frac{d\ln P}{d(\frac{1}{T})} = \frac{-\Delta H}{R}$$

Plot $\ln P - \dfrac{1}{T}$ diagram,

lnP	-3.44202	0.515216	3.784644	4.618086	5.42495
1/T	0.007692	0.006452	0.005405	0.005141	0.004878

$$slope = \dfrac{-\Delta H}{8.314} = -3151.2 \text{ , } \underline{\underline{\Delta H_{sub} = 26199.07 \ (J/mol)}}$$

(3)

For pure solid state, fugacity,

$$f = P^{sat}(T)\exp[\dfrac{V^S(P - P^{sat})}{RT}]$$

For saturated vapor data,

$$\ln \dfrac{P_2}{P_1} = \dfrac{-\Delta H}{R}(\dfrac{1}{T_2} - \dfrac{1}{T_1})$$

For 190K,

$$\ln \dfrac{P_{190K}}{101.3} = \dfrac{-26199.07}{8.314}(\dfrac{1}{190} - \dfrac{1}{194.5})$$

$$P_{190K} = 69.02kPa$$

代回

$$f = 69.02e^{\frac{2.8 \times 10^{-5}(200 \times 10^5 - 69.02 \times 10^3)}{8.3145 \times 190}} = \underline{\underline{98.26}} \ (kPa)$$

Problem 7

【Solution】

(a)

For 50% mass ethanol mixture

$$x_E = \frac{\dfrac{0.5}{46}}{\dfrac{0.5}{46} + \dfrac{0.5}{18}} = 0.281$$

$$x_W = 1 - x_E = 0.719$$

對圖可得

$$\begin{cases} \overline{V}_E = 56 \ (cm^3 / mol) \\ \overline{V}_W = 17.6 \ (cm^3 / mol) \end{cases}$$

$$100 = n_T (0.281 \times 56 + 0.719 \times 17.6)$$

$$n_T = 3.522$$

$$\begin{cases} V_E = n_T x_E \underline{V}_E = 3.522 \times 0.281 \times 58 = 57.4 \ (cm^3) \\ V_W = n_T x_W \underline{V}_W = 3.522 \times 0.719 \times 18 = 45.58 \ (cm^3) \end{cases}$$

(b)

$$n_E = \frac{57.4 + 1}{58} = 1.01 \ (mol)$$

$$n_W = \frac{45.58}{18} = 2.53 \ (mol)$$

$$\begin{cases} x_E = 0.285 \\ x_W = 0.715 \end{cases}$$

$$\begin{cases} \overline{V}_E = 56.1 \ (cm^3 / mol) \\ \overline{V}_W = 17.5 \ (cm^3 / mol) \end{cases}$$

$$\Delta V = 1.01 \times 56.1 + 2.53 \times 17.5 - 100 = \underline{\underline{0.94 \ (cm^3)}}$$

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Problem 1

【Solution】

(a)

$$dU = dQ + dW$$

$$\begin{cases} dQ_{rev} = TdS \\ dW_{rev} = -PdV \end{cases}$$

(b)

For closed, ideal gas system,

$$dU = dQ + dW$$

$$C_V dT = TdS - PdV$$

$$dS = \frac{C_V}{T}dT + \frac{P}{T}dV = \frac{C_V}{T}dT + \frac{R}{V}dV$$

$$\int_{S_0}^{S} dS = \int_{T_0}^{T} \frac{C_V}{T}dT + \int_{V_0}^{V} \frac{R}{V}dV$$

$$S = C_V \ln\frac{T}{T_0} + R\ln\frac{V}{V_0} + S_0$$
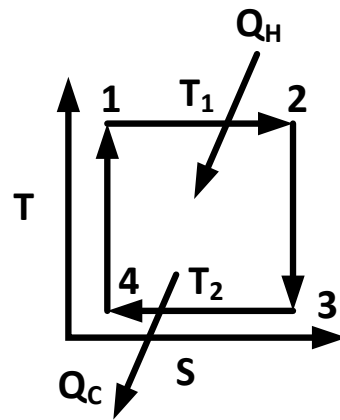
(c)

For isentropic process,

$$0 = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$$

$$\frac{T_2}{T_1} = (\frac{V_2}{V_1})^{\frac{-R}{C_V}} = (\frac{V_2}{V_1})^{\frac{C_V - C_p}{C_V}}$$

$$\frac{T_2}{T_1} = (\frac{V_2}{V_1})^{1-\gamma}$$

(d)

(1)

(2)

$$|W| = enclosed\ area = (T_1 - T_2)(S_2 - S_1)$$

(3)

For a cyclic process, the state function change = 0

$$\Delta S = 0$$

(4)

1. Friction

2. non-uniform T, P distribution

Problem 2

【Solution】

(a)

$$\Delta G_{fr}^{\circ} = -237.2 \ (kJ/mol)$$

$$\Delta H_{fr}^{\circ} = -285.8 \ (kJ/mol)$$

$$\Delta S_{fr}^{\circ} = 69 - (\frac{1}{2} \times 205 + 130.5) = -163.1 \ (J/mol \cdot K)$$

=>

$$\Delta H_{fr}^{\circ} - T\Delta S_{fr}^{\circ} = [-285.8 - (25 + 273.15) \times (-163.1)] \times 10^{-3}$$

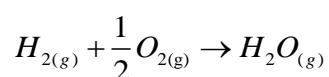$$= -237.17 \ (kJ/mol) \approx \Delta G_{fr}^{\circ}$$

(b)

(1) Standard state：25°C $\begin{cases} 1 \ atm \ for \ gaseous \ species \\ 1 \ M \ for \ aqueous \ solutions \end{cases}$

Under the above condition, we can calculate the Gibbs free energy change of reaction

and to obtain the equilibrium constant at standard state.

(2)

Consider the reaction,

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$$

$$\Delta G_{rxn} = -RT \ln K = -nF\varepsilon^{\circ}$$

$$-237.2 = -2 \times 96500 \varepsilon^{\circ} \times 10^{-3}$$

$$\underline{\varepsilon^{\circ} = 1.23V}$$

(3)

The amount of heat per mole of hydrogen is,

$$\left| \Delta H_{fr}^{\circ} \right| = 285.8 \ (kJ/mol)$$

(c)

By the energy balance equation,

$$dU = dQ + dW = -PdV$$

$$C_V dT = -PdV = \frac{-RT}{V}dV$$

$$\int_{T_1}^{T_2} \frac{C_V}{T} dT = \int_{V_1}^{V_2} \frac{-R}{V} dV$$

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = -R \ln \frac{T_2}{T_1} - R \ln \frac{P_1}{P_2}$$

$$\underline{\underline{\frac{T_2}{T_1} = (\frac{P_2}{P_1})^{\frac{R}{C_p}} = (\frac{P_2}{P_1})^{\frac{C_p - C_V}{C_V}} = (\frac{P_2}{P_1})^{\frac{\gamma-1}{\gamma}}}}$$

$$\begin{cases} T_1 = 298K \\ P_1 = 10MPa \text{ 代入} \\ P_2 = 70MPa \end{cases}$$

$$T_2 = 29(\frac{70}{10})^{\frac{1.41-1}{1.41}} = 524.75\ (K)$$
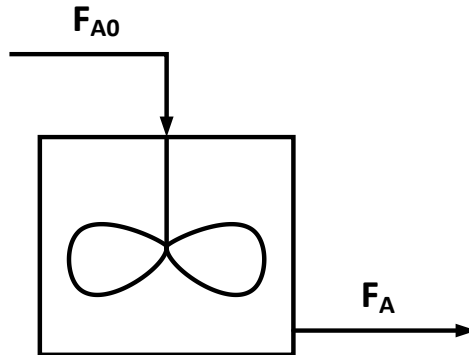
$$\underline{\underline{\Delta T = 524.75 - 298 = 226.75\ (K)}}$$

<u>To deal with the large temperature difference, we may need a cooling system after the compression.</u>

Problem 3
【Solution】

For CSTR, by balance,

$$F_{A0} - F_A + r_A V = 0$$

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

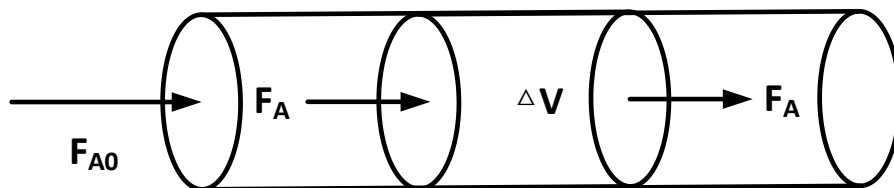$\because$ *rate equation*

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

$$V = \frac{F_{A0} x_A}{kC_{A0}(1 - x_A)}$$

For PFR,

Consider the following configuration,

By mole balance in the control volume,

$$F_A\big|_V - F_A\big|_{V+\Delta V} + r_A \Delta V = 0$$

同除 $\Delta V \to 0$

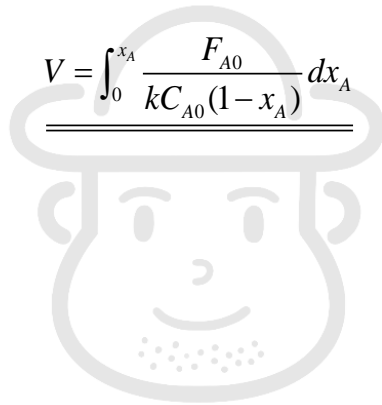$$\frac{-dF_A}{dV} + r_A = 0$$

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

代回

$$\frac{-d[F_{A0}(1 - x_A)]}{dV} = -r_A$$

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

$$dV = \frac{F_{A0}dx_A}{-r_A} = \frac{F_{A0}dx_A}{kC_{A0}(1 - x_A)}$$

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

Problem 4

【Solution】

For CSTR, by design equation,

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

By rate equation,

$$-r_A = kC_AC_B = kC_{A0}^2(1-x_A)(\frac{1}{0.01} - x_A)$$

Combine,

$$V = \frac{F_{A0}x_A}{kC_{A0}^2(1-x_A)(100-x_A)}$$

For x_A, $\because F_{A1} = 0.005$

$$x_A = \frac{F_{A0}-F_{A1}}{F_{A0}} = \frac{0.01\times1 - 0.005}{0.01\times1} = 0.5 代入$$

$$V = \frac{0.01\times0.1\times0.5}{0.01\times0.01^2(1-0.5)(100-0.5)} = \underline{\underline{100.5\ (L)}}$$

For PFR, design equation,

$$V = \int_{x_{A1}}^{x_{A2}} \frac{F_{A0}}{-r_A} dx_A = \int_{0.5}^{0.8} \frac{F_{A0}}{kC_{A0}^2(1-x_A)(100-x_A)} dx_A$$

$$V = \int_{0.5}^{0.8} \frac{1\times0.01}{0.01\times0.01^2(1-x_A)(100-x_A)} dx_A = \underline{\underline{92.25\ (L)}}$$

$$\underline{\underline{V_{total} = 100.5 + 92.25 = 192.75\ (L)}}$$

Problem 5
【Solution】

$$K = \frac{C_B C_C}{C_A} = \frac{C_{A0}^2 (\theta_B + x_{Ae})(\theta_C + x_{Ae})}{C_{A0}(1 - x_{Ae})}$$

$$K(1 - x_{Ae}) = C_{A0}(\theta_B + x_{Ae})(\theta_C + x_{Ae})$$

$$K - K x_{Ae} = C_{A0}\theta_B \theta_C + C_{A0}(\theta_B + \theta_C)x_{Ae} + x_{Ae}^2$$

$$x_{Ae}^2 + (K + C_{A0}\theta_B + C_{A0}\theta_C)x_{Ae} + (C_{A0}\theta_B \theta_C - K) = 0$$

$$x_{Ae} = \frac{-(K + C_{A0}\theta_B + C_{A0}\theta_C) \pm \sqrt{(K + C_{A0}\theta_B + C_{A0}\theta_C)^2 - 4(C_{A0}\theta_B \theta_C - K)}}{2}$$

取 > 0

$$\boxed{x_{Ae} = \frac{-(K + C_{A0}\theta_B + C_{A0}\theta_C) + \sqrt{(K + C_{A0}\theta_B + C_{A0}\theta_C)^2 - 4(C_{A0}\theta_B \theta_C - K)}}{2}}$$

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Problem 1

【Solution】

For $\Delta \hat{S}$,

$$\Delta \hat{S} = \int_{P_1}^{P_2} (\frac{\partial \hat{S}}{\partial P})_T \, dP = -\int_{P_1}^{P_2} (\frac{\partial \hat{V}}{\partial T})_P \, dP$$

$$= \hat{V} \int_{P_2}^{P_1} \frac{1}{\hat{V}} (\frac{\partial \hat{V}}{\partial T})_P \, dP = \hat{V} \beta (P_1 - P_2)$$

$$= 1.551 \times 10^{-3} \times 2.095 \times 10^{-3} (270 - 1000)$$

$$= \underline{\underline{-2.372 \times 10^{-3} \, (kJ / kg \cdot K)}}$$

For $\Delta \hat{H}$

$$d\hat{H} = \cancel{\hat{C}_p \, dT} + [\hat{V} - T(\frac{\partial \hat{V}}{\partial T})_P] \, dP$$

$$\Delta \hat{H} = \int_{P_1}^{P_2} [\hat{V} - T(\frac{\partial \hat{V}}{\partial T})_P] \, dP = \hat{V} \int_{P_1}^{P_2} [1 - \frac{T}{\hat{V}} (\frac{\partial \hat{V}}{\partial T})_P] \, dP$$

$$= \hat{V} \int_{P_1}^{P_2} [1 - T\beta] \, dP = \hat{V}(1 - T\beta)(P_2 - P_1)$$

$$= 1.551 \times 10^{-3} (1 - 350 \times 2.095 \times 10^{-3})(1000 - 290)$$

$$= \underline{\underline{0.302 \, (kJ / kg)}}$$

Problem 2
【Solution】

By energy balance equation (open system, steady state).

$$\Delta H + \Delta(\frac{v^2}{2g_c}) + \frac{g}{g_c}\Delta z = Q + W$$

For $\Delta(\frac{v^2}{2g_c})$, by mass balance,

$$\dot{m}_{in} = \dot{m}_{out}$$

$$\rho_{in}(\pi R_{in}^2)v_{in} = \rho_{out}(\pi R_{out}^2)v_{out}$$

$$\frac{1}{31.40} \times \pi \times 5^2 \times 10 = \frac{1}{0.5438} \times \pi \times 1.5^2 v_{out}$$

$$v_{out} = 1.92 \ (m/s)$$

代回

$$(33.97 - 30.68) \times 10^3 + (\frac{1.92^2 - 10^2}{2}) = Q + 25.0 \times 10^3$$

$$Q = -21758.16 \ (J/mol)$$

$$\dot{Q} = Q\dot{n} = \frac{-21758.16}{31.40} \times 10^3 \times \pi \times (5 \times 10^{-2})^2 \times 10 \times 10^{-3} = \underline{\underline{-52.42 \ (kJ/s)}}$$

Problem 3
【Solution】

$$P = \frac{RT}{V} - \frac{a - bRT^{1.5}}{\sqrt{T}V^2} = \frac{RT}{V} - \frac{a}{\sqrt{T}V^2} + \frac{bRT}{V^2}$$
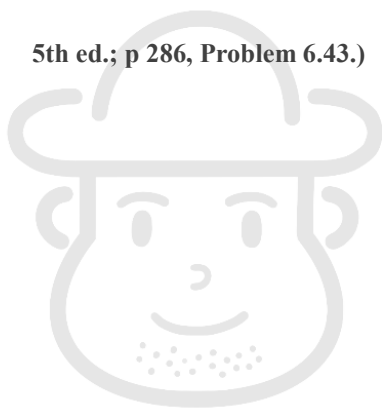
$$\frac{PV}{RT} = Z = 1 - \frac{a}{RT\sqrt{T}}\frac{1}{V} + \frac{b}{V} = 1 + \underbrace{(b - \frac{a}{RT^{1.5}})}_{令為B}\frac{1}{V}$$

@Boyle temperature, B = 0

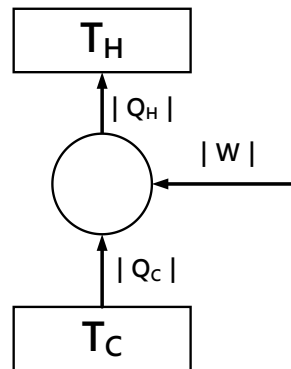$$b - \frac{a}{RT_B^{1.5}} = 0 \quad , \quad \underline{\underline{T_B = (\frac{a}{bR})^{\frac{2}{3}}}}$$

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

5th ed.; p 286, Problem 6.43.)

Problem 4

【Solution】

By energy balance,

$$|Q_H| = |W| + |Q_C|$$

By entropy balance (maximum efficiency),

$$\frac{dS}{dt} = \sum_k \dot{M}_k S_k + \frac{|Q_C|}{T_C} - \frac{|Q_H|}{T_H} + \dot{S}_{gen}$$

$$\frac{-C_p dT_C}{T_C} - \frac{dQ_H}{T_H} = 0$$

$$\int_0^{Q_H} dQ_H = C_p T_H \int_{T_f}^{T_i} \frac{dT_C}{T_C}$$

$$Q_H = C_p T_H \ln \frac{T_i}{T_f} = 7.6 \times (273 + 45) \ln \frac{273.15 + 25}{273.15 - 15} = 348.15 \ (kJ / kg)$$

$$|Q_C| = C_p (T_i - T_f) = 7.6 \times (25 + 15) = 304 \ (kJ / kg)$$

$$|W| = |Q_H| - |Q_C| = 348.15 - 304 = 44.15 \ (kJ / kg)$$

For 31% efficiency,

$$\dot{W} = \frac{|W|}{0.31} \times \dot{M} = \frac{44.15}{0.31} \times 15 = \underline{\underline{2136.5 \ (kJ / s)}}$$

Problem 5

【Solution】

By design equation,

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

For $x_{A,run1}$

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

For $x_{A,run2}$

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

代入

$$V_1 = V_2$$

$$\frac{2 \times 0.9}{k C_{A0}^{n-1}(1-0.9)^n} = \frac{15 \times 0.75}{k C_{A0}^{n-1}(1-0.75)^n} \quad , \quad \boxed{n = 2}$$

For activation energy,

by run 2,3 ,

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

$$V_2 = V_3$$

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

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

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

Problem 6

【Solution】

(a)

Check,

$$
\frac{observed\ rate}{rate\ if\ film\ resistance\ controls} = \frac{k_{obs}'' V_P}{k_g S_{ex}} = \frac{\dfrac{-r_{A,obs}''}{C_{Ag}} \times \dfrac{\pi}{6} d_p^3}{k_g (\pi d_p^2)} = \frac{-r_{A,obs}'' d_P}{6 k_g C_{Ag}}
$$

$$
= \frac{1 \times 10^5 \times 2.4 \times 10^{-3}}{6 \times 20 \times 300} = \frac{1}{150} \ll 1
$$

The film resistance should not influence the rate of reaction

(b)

Define Weisz modulus,

$$
M_W = \frac{(-r_A'')_{obs} L^2}{D_e C_{Ag}}
$$

$$
L = characteristic\ size \equiv
$$

$$
\frac{volume\ of\ particle}{exterior\ surface\ available\ for\ reactant\ penetration}
\begin{cases}
\dfrac{thickness}{2} & for\ flat\ plates \\[2mm]
\dfrac{R}{2} & for\ cylinders \\[2mm]
\dfrac{R}{3} & for\ spheres
\end{cases}
$$

將數據代入

$$
M_W = \frac{1 \times 10^5 \times [(\dfrac{2.4}{2 \times 3}) \times 10^{-3}]^2}{5 \times 10^{-5} \times 20} = 16 > 4
$$

Yes, the run have been made in the regime of strong pore diffusion

※此處也可定義 Thiele Modulus 來判斷 pore diffusion 影響的程度

$$M_T = L\sqrt{\frac{k''}{D_e}}$$

而其與 Weisz modulus 的關係為：$M_W = M_T^2 \varepsilon$

$$\varepsilon = effectiveness\ factor = \frac{\tanh M_T}{M_T}$$

而標準為：

$$\begin{cases} diffussion\ free \begin{cases} M_T < 0.4 \\ M_W < 0.15 \end{cases} \\ strong\ diffusion \begin{cases} M_T > 4 \\ M_W > 4 \end{cases} \end{cases}$$

(c)

$$\Delta T_{max,pellet} = \frac{D_e(C_{Ag} - 0)(-\Delta H_r)}{k_{eff}} = \frac{5 \times 10^{-5} \times 20 \times 160}{1.6} = 0.1°C$$

$$\Delta T_{max,film} = \frac{L(-r''_{A,obs})(-\Delta H_r)}{h} = \frac{4 \times 10^{-4} \times 10^5 \times 160}{160} = 40°C$$

**The pellet can be considered to be uniform in temperature, but hotter than the external fluid because most of the temperature difference occurs across the film**

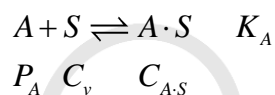(本題改編自：Levenspiel, O. _Chemical Reaction Engineering_, 3rd ed.; p 407~408, Example 18.1.)
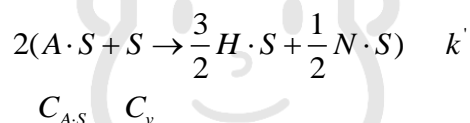
Problem 7

【Solution】

觀察 Rate law,

(1) 分子有 A，速率決定步驟有 A 的參與

(2) 分母只有 H 存在，相對於 A 與 N(氮氣)，H(氫氣)應該吸附力較強

(3) 假設主要被吸附之物質為 H 與 N，其餘中間產物微量

Mechanism：

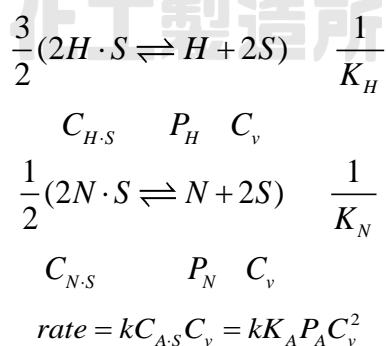Adsorption of NH_3

$$A + S \rightleftharpoons A \cdot S \quad K_A$$
$$P_A \quad C_v \qquad C_{A \cdot S}$$

Dissociation reaction of NH_3 (假設為速率決定步驟)

$$2(A \cdot S + S \rightarrow \frac{3}{2} H \cdot S + \frac{1}{2} N \cdot S) \quad k^{'}$$
$$C_{A \cdot S} \quad C_v$$

Desorption of N_2 and H_2,

$$\frac{3}{2}(2H \cdot S \rightleftharpoons H + 2S) \quad \frac{1}{K_H}$$
$$C_{H \cdot S} \quad P_H \quad C_v$$
$$\frac{1}{2}(2N \cdot S \rightleftharpoons N + 2S) \quad \frac{1}{K_N}$$
$$C_{N \cdot S} \qquad P_N \quad C_v$$
$$rate = kC_{A \cdot S}C_v = kK_A P_A C_v^2$$

For C_v, by site balance,

$$C_t = C_v + C_{A \cdot S} + C_{H \cdot S} + C_{N \cdot S} = C_v(1 + K_A P_A + \underbrace{\sqrt{K_H P_H}}_{\gg 1} + \sqrt{K_N P_N}) \approx C_v\sqrt{K_H P_H}$$

$$C_v = \frac{C_t}{\sqrt{K_H P_H}} \quad 代回 \boxed{rate = \frac{C_t k^{'} K_A P_A}{K_H P_H} = \frac{k K_A P_A}{K_H P_H}}$$

Problem 8

【Solution】Ans：(C)

(a)(b)

We can't tell whether the reaction is exothermic or endothermic merely by the rate of the reaction.

(c)(d)

At T = 600 (higher T), the rate is nearly independent of P_C

$$\Rightarrow \quad \text{C is not adsorbed}$$

At T = 500 (lower T), the rate is slower with increasing P_C

$$\Rightarrow \quad \text{C is adsorbed}$$

Therefore, the adsorption of C is favorable at lower T

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Problem 1

【Solution】

(a)

Species	Initially (mol/s)	Change (mol/s)	Remaining (mol/s)
A	F_{A0}	$-F_{A0}x_A$	$F_{A0}(1-x_A)$
B	0	$+\dfrac{1}{2}F_{A0}x_A$	$\dfrac{1}{2}F_{A0}x_A$
C	0	$+F_{A0}x_A$	$+F_{A0}x_A$

(b)

For PFR, design equation,

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

For rate law,

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

$$\varepsilon = \delta y_{A0} = \frac{1}{2}\times 1 = 0.5$$

Combine,

$$V = \int_0^{0.8} \frac{F_{A0}}{kC_{A0}(\frac{1-x_A}{1+0.5x_A})}\,dx_A = \int_0^{0.8} \frac{10}{20\times0.1\times(\frac{1-x_A}{1+0.5x_A})}\,dx_A = \underline{\underline{10.07\ (L)}}$$

Problem 2

【Solution】

(a)

Species	Initially (mol/s)	Change (mol/s)	Remaining (mol/s)
A	F_{A0}	$-F_{A0}x_A$	$F_{A0}(1-x_A)$
C	0	$+F_{A0}x_A$	$F_{A0}x_A$
D	0	$+2F_{A0}x_A$	$+2F_{A0}x_A$

(b)

At the maximum conversion, let $x_A = x_{Ae}$ (equilibrium conversion)

For PFR, design equation,

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

For rate law,

$$-r_A = k_f C_A - k_b C_C C_D^2 = k_f C_{A0}\frac{(1-x_A)}{(1+\varepsilon x_A)} - k_b C_{A0}^3 \frac{4x_A^3}{(1+\varepsilon x_A)^3}$$

$$\varepsilon = \delta y_{A0} = 2 \times 1 = 2$$

Combine,

$$V = \int_0^{x_{Ae}} \frac{F_{A0}}{k_f C_{A0}\frac{(1-x_A)}{(1+\varepsilon x_A)} - k_b C_{A0}^3 \frac{4x_A^3}{(1+\varepsilon x_A)^3}} dx_A$$

Problem 3

【Solution】

(a)

For the death rate,

$$r_D = k_4[I]$$

By pseudo-steady state assumption,

$$r_I = k_1[H] - k_2[I][H] + 2k_2[I][H] - k_3[I] - k_4[I] = 0$$

$$[I] = \frac{k_1[H]}{-k_2[H] + k_3 + k_4}$$

代回：

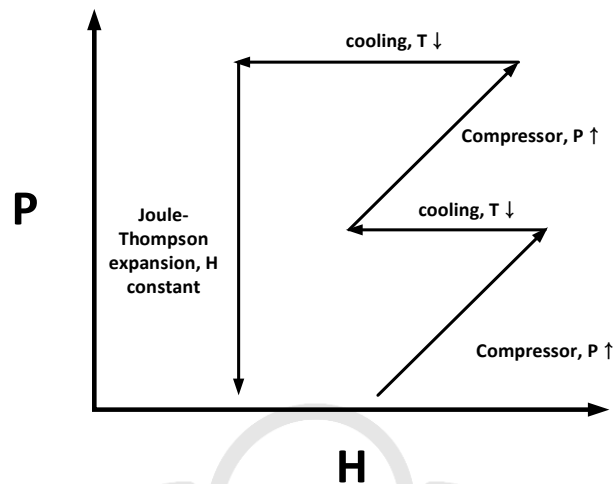$$r_D = \frac{k_1 k_4[H]}{-k_2[H] + k_3 + k_4}$$

(b)

If $[H]$ is very small,

$$r_D = \frac{k_1 k_4[H]}{-k_2[H] + k_3 + k_4} = \frac{k_1 k_4[H]}{k_3 + k_4}$$

Problem 4

【Solution】

(a)

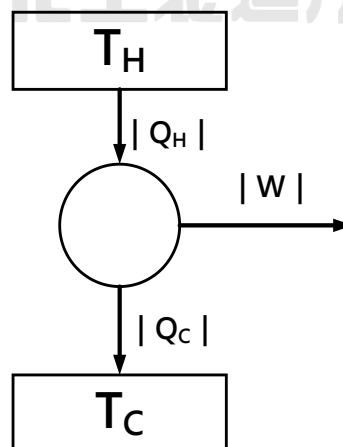The liquefaction process can be illustrated as,

Where, the gas will tend to liquify under high pressure and low temperature, and after the Joule-Thomson expansion, the feed will leave as gas and liquid states.

The ideal gas has no intermolecular forces, and can't be liquified.

(b)

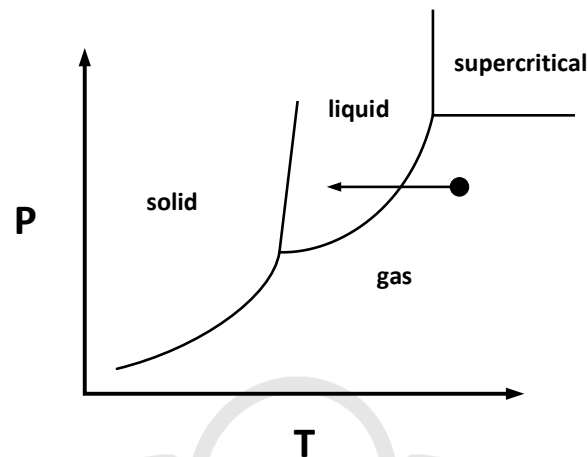Consider the engine operates between a hot reservoir and a cold reservoir,

The reversible efficiency is,

$$\eta = \frac{|W|}{|Q_H|} = 1 - \frac{T_c}{T_H}$$

The working fluid will not affect the efficiency of the reversible engine, which will be dominated by whether it's reversible or not.

(c)

By a typical phase diagram, we can read that,

If we cool a gas below its critical temperature, the gas will slowly be liquified. When the gas is at the boundary of liquid and gas, the gas will coexist as both liquid and gas. For ideal gas, again, it will not liquified at all, so we can observe such behavior.

Problem 5
【**Solution**】

(a)

Before the whole process, the pressure is 250 kPa, by the saturated water table,

$$\underline{\underline{T = 400.59 \ (K)}}$$

For the quality of water, we know liquid water occupies 50% of the volume,

$$0.28 \times 0.5 = V_L W_L = V_G W_G = 0.001067 W_L = 0.7187 W_G \begin{cases} W_L = 131.2 \ (kg) \\ W_G = 0.195 \ (kg) \end{cases}$$

$$quality \ of \ water = \frac{W_G}{W_L + W_G} \times 100\% = \frac{0.195}{131.2 + 0.195} \times 100\% = \underline{\underline{0.148\%}}$$

After the process, the total mass of the piston and the external pressure is the same, so the pressure inside the cylinder is P = 250 kPa,

$$\underline{\underline{T = 400.59 \ (K)}}$$

$$V_f = 0.001067 W_{L,f} + 0.7187 V_{G,f} = 0.28 + 1.05 = 1.33 \ (m^3)$$

And by mass balance on the water + vapor system,

$$W = W_{G,f} + W_{L,f} = W_{G,i} + W_{L,i} = 131.4 \ (kg)$$

$$\begin{cases} W_{L,f} = 129.7 \ (kg) \\ W_{G,f} = 1.66 \ (kg) \end{cases}$$

$$quality \ of \ water = \frac{W_{G,f}}{W_{L,f} + W_{G,f}} \times 100\% = \frac{1.66}{131.4} \times 100\% = \underline{\underline{1.26\%}}$$

(b)

By force balance,

$$(P_{ex} + P_{m+p}) A_c = P_{cylinder} A_c$$

$$(100 \times 10^3 + \frac{M_{m+p} \times 9.8}{0.42}) \times 0.42 = 250 \times 10^3 \times 0.42$$

$$\underline{\underline{M_{m+p} = 6428.5(kg)}}$$

For the work done,

$$W = -(P_{ex} + P_{m+p})\Delta V = -(100 \times 10^3 + \frac{6428.5 \times 9.8}{0.42}) \times 2.5 \times 0.42 = \underline{\underline{-262500 \ (J)}}$$

$$\begin{aligned} Q = \Delta U - W &= U_G(W_{G,f} - W_{G,i}) + U_L(W_{G,f} - W_{G,i}) - W \\ &= [2537.5 \times (1.66 - 0.195) + 535.0 \times (129.7 - 131.2)] \times 10^3 + 262500 \\ &= \underline{\underline{3177437.5 \ (J)}} \end{aligned}$$

The efficiency is,

$$\eta = \left| \frac{W}{Q} \right| = \frac{262500}{3177347.5} \times 100\% = \underline{\underline{8.3\%}}$$

Problem 6

【Solution】

Assume:

(1) All of the related gaseous streams are ideal gas

(2) We can separates the processes into two individual process

① Expansion process:

By energy balance,

$$\cancel{\Delta U} = Q + \cancel{W} \quad , \quad Q = 0$$

By entropy balance,

$$\cancel{\frac{dS}{dt}}_{s.s} = \sum_i \dot{M}_k \hat{S}_k + \cancel{\sum \frac{\dot{Q}}{T}}_{Q=0} + \dot{S}_{gen}$$

$$\dot{S}_{gen} = -\sum_i \dot{M}_k \hat{S}_k = -\dot{M}_k (S_{in} - S_{out})$$

$$= \dot{M}_k (\cancel{C_P \ln \frac{T_{out}}{T_{in}}} - R \ln \frac{P_{out}}{P_{in}}) = -\dot{M}_k R \ln \frac{P_{out}}{P_{in}} = \dot{M}_k R \ln 2 > 0$$

The first process is feasible

② Separating process:

By mass balance of oxygen,

$$\dot{M}_k = \dot{M}_{k,o} + \dot{M}_{k,n}$$

$$0.20 \dot{M}_k = 0.95 \dot{M}_{k,o} + 0.05 \dot{M}_{k,n} \begin{cases} \dot{M}_{k,o} = 0.167 \dot{M}_k \\ \dot{M}_{k,n} = 0.833 \dot{M}_k \end{cases}$$

By energy balance,

$$\cancel{\Delta U} = Q + \cancel{W} \quad , \quad Q = 0$$

By entropy balance,

$$\cancel{\frac{dS}{dt}}_{s.s} = \sum_i \dot{M}_k \hat{S}_k + \cancel{\sum \frac{\dot{Q}}{T}}_{Q=0} + \dot{S}_{gen}$$

$$\dot{S}_{gen} = -\sum_i \dot{M}_k \hat{S}_k = -(\dot{M}_k S_{in} - S_{out,o} \dot{M}_{k,o} - S_{out,n} \dot{M}_{k,n})$$

$$= (S_{out,o} \dot{M}_{k,o} + S_{out,n} \dot{M}_{k,n} - \dot{M}_k S_{in})$$

$$= (0.167 \dot{M}_k R + 0.833 \dot{M}_k R)(0.95 \ln 0.95 + 0.05 \ln 0.05) - \dot{M}_k R(0.2 \ln 0.2 + 0.8 \ln 0.8)$$

$$= 0.3018 \dot{M}_k R > 0$$

<u>The second process is feasible</u>

Therefore, **<u>such a claim can be trusted if the process carried out with the assumption that the working fluid is an ideal gas.</u>**

112 年台科大化熱化反

Problem 1

【Solution】

By the design equation of CSTR,

$$\tau = \frac{C_{A0}x}{-r}$$

By the rate equation,

$$-r = kC_A = kC_{A0}(1-x)$$

Combine,

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

$$x = \frac{kC_{A0}\tau}{C_{A0} + kC_{A0}\tau} = \frac{\tau A e^{\frac{-E_a}{RT}}}{1 + \tau A e^{\frac{-E_a}{RT}}}$$

Problem 2

【Solution】

Assume the metabolism obeys Michaelies-Menten mechanisms,

$$-r_{urea} = \frac{v_{max} C_{urea}}{K_M + C_{urea}}$$

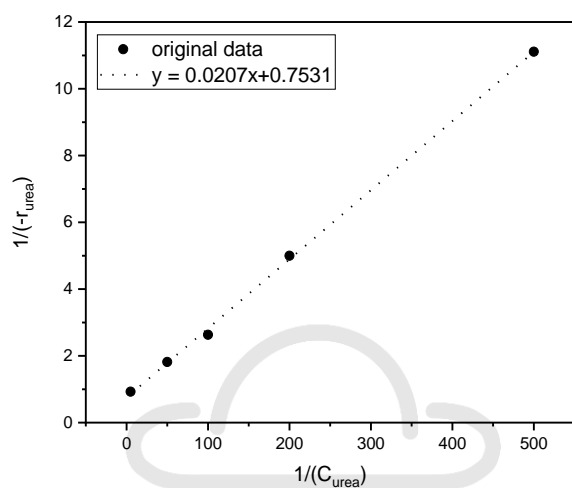$$\frac{1}{-r_{urea}} = \frac{K_M}{v_{max} C_{urea}} + \frac{1}{v_{max}}$$

Plot $\dfrac{-1}{r_{urea}} - \dfrac{1}{C_{urea}}$ relationship,

$\dfrac{1}{-r_{urea}}$	0.926	1.818	2.631	5	11.11

$\dfrac{1}{C_{urea}}$	5	50	100	200	500

(本題於 105 年台科化熱化反 Problem 5 出過，題目設計為(a)小題證明 Michaelies-Menten 關

係，(b)小題再計算反應相關常數。)

$$\begin{cases} \dfrac{1}{v_{max}} = 0.7531 \\ \dfrac{K_M}{v_{max}} = 0.0207 \end{cases} , \quad \begin{cases} v_{max} = 1.328 \\ K_M = 0.0274 \end{cases}$$

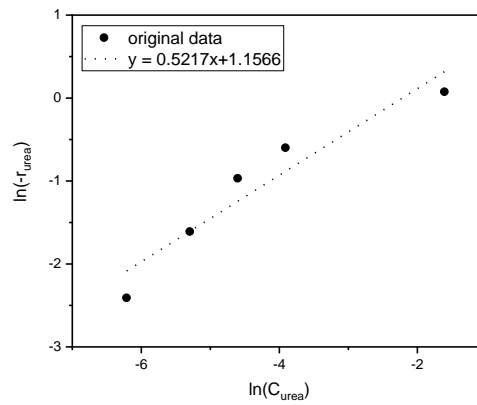$$-r_{urea} = \frac{1.328 C_{urea}}{0.0274 + C_{urea}}$$

※若令反應對 urea 為 n 級反應，

$$-r_{urea} = k C_{urea}^n$$

$$\ln(-r_{urea}) = \ln k + n \ln C_{urea}$$

Plot $\ln(-r_{urea}) - \ln C_{urea}$，
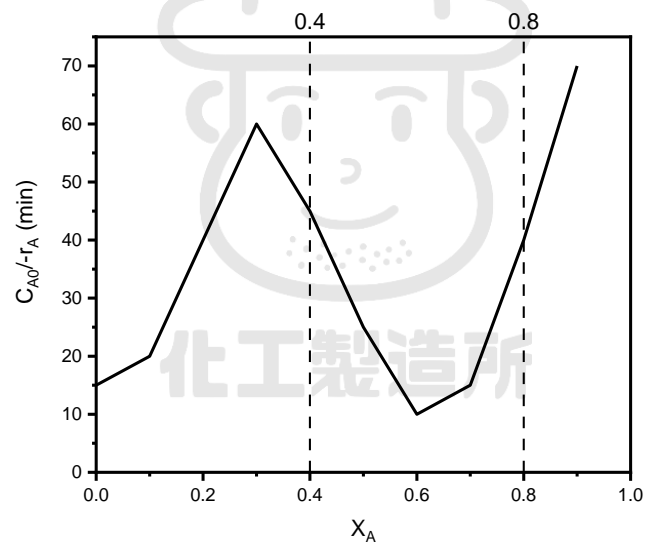
則誤差較大，不適用於此反應

Problem 3

【Solution】

(a)

(1) CSTR first,

$$V_{CSTR} = \frac{v_0 C_{A0} x_A}{-r_A} = 40 \times 45 \times 0.4 = 720 \ (L)$$

$$V_{PFR} = v_0 \int_{0.4}^{0.8} \frac{C_{A0} dx_A}{-r_A} = 40 \times \{\frac{0.8 - 0.4}{3} [f(0.4) + 4f(0.6) + f(0.8)]\}$$

$$V_{PFR} = 40 \times \frac{0.4}{3} (45 + 4 \times 10 + 40) = 666.7 \ (L)$$

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$$V_{Total} = 720 + 666.7 = 1386.7 \ (L)$$

(2) PFR first,

$$V_{PFR} = v_0 \int_0^{0.4} \frac{C_{A0} dx_A}{-r_A} = 40 \times \{\frac{0.4-0}{3}[f(0) + 4f(0.2) + f(0.4)]\}$$

$$V_{PFR} = 40 \times \frac{0.4}{3}(15 + 4 \times 40 + 45) = 1173.3 \ (L)$$

$$V_{CSTR} = \frac{v_0 C_{A0}(x_{Af} - x_{Ai})}{-r_A} = 40 \times 40 \times (0.8 - 0.4) = 640 \ (L)$$

$$V_{Total} = 1173.3 + 640 = 1813.3 \ (L)$$

<u>For this process, the CSTR should be placed firstly to obtain the minimum total reactor volume.</u>

(b)

If the intermediate conversion is still the same as 0.4, the best arrangement is CSTR first and PFR the second.

If the intermediate conversion can be changed, we can use CSTR until the intermediate conversion is 0.6, then using PFR to 0.8.

<u>Problem 4</u>
【**Solution**】

(i)

By Pitzer correlation,

$$Z = Z^0 + \omega Z^1 = 1 + B^0 \frac{P_r}{T_r} + \omega B^1 \frac{P_r}{T_r}$$

$$Z^0 = 1 + B^0 \frac{P_r}{T_r} \ , \ Z^1 = B^1 \frac{P_r}{T_r}$$

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

Engineering Thermodynamics, 7th ed.; p 100~102.)

(ii)

By Pitzer correlation,

$$Z = 1 + \frac{BP}{RT} = 1 + \hat{B}\frac{P_r}{T_r}$$

$$(\hat{B} = \frac{BP_c}{RT_c}, \text{ the reduced form of B})$$

$$\hat{B} = B^0 + \omega B^1$$

$$Z = 1 + \hat{B}\frac{P_r}{T_r} = 1 + (B^0 + \omega B^1)\frac{P_r}{T_r} = 1 + B^0\frac{P_r}{T_r} + \omega B^1\frac{P_r}{T_r}$$

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

Engineering Thermodynamics, **7th ed.; p 100~102.)**

(iii)

將 B^0 與 B^1 代入:

$$Z = 1 + B^0\frac{P_r}{T_r} + \omega B^1\frac{P_r}{T_r} = 1 + (0.083 - \frac{0.422}{T_r^{1.6}})\frac{P_r}{T_r} + 0.0938(0.139 - \frac{0.172}{T_r^{4.2}})\frac{P_r}{T_r}$$

$$Z = \frac{PV}{nRT} = 1 + [0.083 - 0.422(\frac{T_c}{T})^{1.6}]\frac{PT_c}{P_cT} + 0.0938[0.139 - 0.172(\frac{T_c}{T})^{4.2}]\frac{PT_c}{P_cT}$$

將 $P_c = 47.77\ atm$, $T_c = 269.70\ K$, $V = 50\ (L)$

$$n = \frac{15 \times 10^3}{28 + 1 \times 4} = 468.75\ (mol)$$

$$T = 25 + 273.15 = 298.15\ (K)$$

代入:

$$\frac{50P}{468.75 \times 0.082 \times 298.15}$$

$$= 1 + [0.083 - 0.422(\frac{269.70}{298.15})^{1.6}]\frac{269.70P}{47.77 \times 298.15} + 0.0938[0.139 - 0.172(\frac{269.70}{298.15})^{4.2}]\frac{269.70P}{47.77 \times 298.15}$$

$$\underline{\underline{P = 104.7 \ (atm)}}$$

$$\underline{\underline{Z = 0.457}}$$

Problem 5

【Solution】

(i)

$$dH = dU + PdV + VdP = dQ_{rev} - PdV + PdV + VdP$$

$$dH = dQ_{rev} + VdP$$

By the definition of entropy,

$$dS = \frac{dQ_{rev}}{T}$$

$$dH = TdS + VdP \text{ , } dS = \frac{dH}{T} - \frac{V}{T}dP$$

For ideal gas,

$$dH = nC_PdT \text{ , } \frac{V}{T} = \frac{nR}{P}$$

$$dS = \frac{nC_p}{T}dT - \frac{nR}{P}dP$$

$$\Delta S^{ig} = \int_{T_0}^{T} \frac{nC_p}{T}dT - \int_{P_0}^{P} \frac{nR}{P}dP = nC_p \ln\frac{T}{T_0} = nR\ln\frac{P}{P_0}$$

(ii)

By energy balance of the open system,

$$n_1H_1 = n_2H_2 + n_3H_3$$

$$n_1C_PT_1 = n_2C_PT_2 + n_3C_PT_3$$

$$1 \times C_P(273.15 + 20) = 0.5C_P(273.15 - 20) + 0.5C_PT_3$$

$$T_3 = 333.15 \ (K) = 60^\circ\text{C}$$

(iii)

By entropy balance of the open system,

$$\frac{dS}{dt}\Bigg|_{s.s} = \sum_i \dot{n}_k S_k + \sum \frac{\dot{Q}}{T}\Bigg|_{adiabatic} + \dot{S}_{gen}$$

$$\boxed{\dot{S}_{gen} = -\sum_i \dot{n}_k S_k}$$

$$\dot{S}_{gen} = -\dot{n}_1 S_1 + \dot{n}_2 S_2 + \dot{n}_3 S_3 = \frac{1}{2}\dot{n}_1[(S_2 - S_1) + (S_3 - S_1)]$$

$$= \frac{1}{2}\dot{n}_1\left(C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} + C_P \ln \frac{T_3}{T_1} - R \ln \frac{P_3}{P_1}\right)$$

$$= \frac{1}{2}\dot{n}_1\left[C_P \ln\left(\frac{T_2 T_3}{T_1^2}\right) - R \ln\left(\frac{P_2 P_3}{P_1^2}\right)\right]$$

$$\dot{S}_{gen} = \frac{1}{2}\dot{n}_1\left[C_P \ln\left(\frac{T_2 T_3}{T_1^2}\right) - R \ln\left(\frac{P_2 P_3}{P_1^2}\right)\right]$$

$$= \frac{1}{2}\times 1 \times 8.314 \times \left[\frac{7}{2}\ln\left[\frac{(273.15-20)(273.15+60)}{(273.15+20)^2}\right] - \ln\left(\frac{1\times 1}{4^2}\right)\right]$$

$$= 11.25 \ (J/K\cdot s)$$

$$\boxed{\dot{S}_{gen} > 0}$$

The process is thermodynamically feasible.

Problem 6

【Solution】

(i)

The number of arrangement is,

$$W = \frac{N!}{N_A!N_B!} = \frac{N!}{(x_A N)!(x_B N)!} = \underline{\underline{\frac{N!}{(0.8N)!(0.2N)!}}}$$

(ii)

The entropy change can be denoted as the entropy change of mixing,

$$\Delta S_{mix} = \underbrace{k_B \ln(W)}_{solution} - \underbrace{k_B \ln(1)}_{pure\ A} - \underbrace{k_B \ln(1)}_{pure\ B} = k_B \ln(W)$$

$$\ln W = \ln(N!) - \ln[(0.8N)!] - \ln[(0.2N)!]$$

$$= N \ln N - \cancel{N} - 0.8N \ln(0.8N) + \cancel{0.8N} - 0.2N \ln(0.2N) + \cancel{0.2N}$$

$$= N \ln N - 0.8N[\ln(0.8) + \ln(N)] - 0.2N[\ln(0.2) + \ln(N)]$$

$$= \underbrace{N \ln N - 0.8N \ln(N) - 0.2N \ln(N)}_{0} - 0.8N \ln(0.8) - 0.2N \ln(0.2)$$

$$= -N(0.8 \ln 0.8 + 0.2 \ln 0.2)$$

$$\Delta S_{mix} = k_B \ln(W) = -k_B N(0.8 \ln 0.8 + 0.2 \ln 0.2) = -R(0.8 \ln 0.8 + 0.2 \ln 0.2)$$

$$(與 \Delta S_{mix} = -R \sum_{i=A}^{B} x_i \ln x_i \ 結果相同)$$

$$\Delta S_{mix} = -R(0.8 \ln 0.8 + 0.2 \ln 0.2) = -8.314 \times (0.8 \ln 0.8 + 0.2 \ln 0.2) = \underline{\underline{4.16\ (J/mol \cdot K)}}$$

(iii)

$$\Delta S_{mix} = -R\sum_i x_i \ln x_i$$

$$= -R(x_{Co} \ln x_{Co} + x_{Cr} \ln x_{Cr} + x_{Fe} \ln x_{Fe} + x_{Mn} \ln x_{Mn} + x_{Ni} \ln x_{Ni})$$

$$= -5R(0.2\ln 0.2) = -5 \times 8.314(0.2\ln 0.2) = \underline{\underline{13.38}} \ (J/mol \cdot K)$$

相比傳統主要以混合兩種成分的合金來說，高熵合金因含有元素種類較多(至少四~五種以上)，且各元素比例平均，有較高的組合熵(configurational entropy)，因此被稱作為高熵合金(High-Entropy Alloys)。

※假設一合金含有 n 種元素，且每一種元素之分率皆為 $\dfrac{1}{n}$，則以理論來說，其混合熵可被計算為：

$$\Delta S_{mix} = -nR[\frac{1}{n}\ln(\frac{1}{n})] = 8.314\ln(n)$$

由此可知，$n\uparrow, \Delta S_{mix}\uparrow$

# 113 年台科大化熱化反

Part I. 化工動力學

Problem 1
【Solution】

1-1

Advantages: high conversion, low operating cost, continuous operation

Disadvantage: poor temperature control, channeling may occur

(本題可參考網站：https://websites.umich.edu/~elements/5e/asyLearn/bits/pbr/index.htm)

1-2

If we need not consider the death rate of the cells, the relationships of the cell concentration, substrate concentration, and the cell production rate against the dilution rate (proportional to the volumetric flow rate are schemed as:
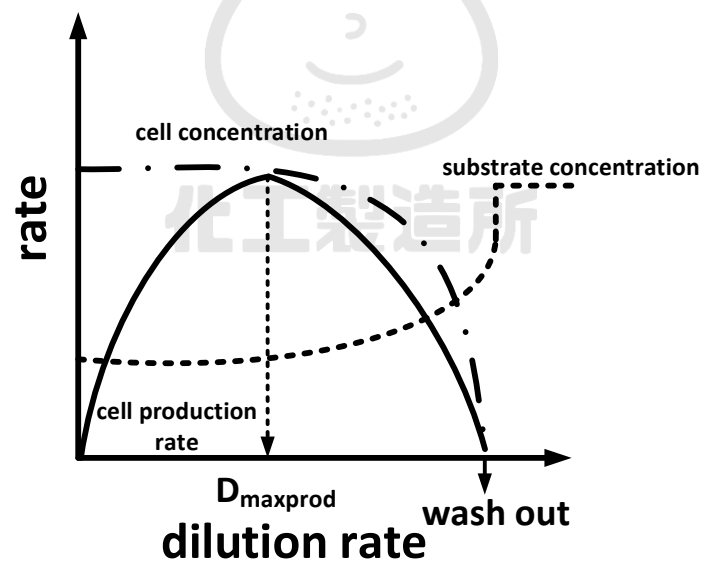
如圖所示：cell concentration 隨著 dilution rate 增加，呈現逐漸遞減的情形，因隨著 dilution rate 變大，cell 更容易被進料沖洗出，導致留存於反應器中的 cell concentration 降低。(本題關於 cell growth reaction 在 CSTR 中的行為可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed., p 435~p438，不在此贅述。)

1-3

(1) Because the reaction rate is dependent on the concentration and temperature of the species,

$$r = f(C_A, C_B, T)$$

Therefore, at the inlet of the reactor, the temperature may not be high enough for the reaction rate to reach its maximum until 1.5 meters downstream from the inlet.

(2) After 5 meters, the reaction may reach its equilibrium conversion, as inferred from the unchanged temperature and conversion rate.

(3) When removing the quartz wool between 6 and 10 meters, the temperature may decrease. As a result, the exothermic reaction (assumably) may continue, increasing the conversion rate

Problem 2
【Solution】

(a)

The unit of k is $\min^{-1}$, so the rate equation should be first order.

By the rate equation,

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

$$\varepsilon = \delta y_{A0} = \left(\frac{5}{2} + \frac{1}{2} - 1\right) \cdot 1 = 2$$

By the design equation,

$$V_{PFR} = F_{A0} \int_0^{X_1} \frac{1}{-r_A} dX$$

$$V_{PFR} = C_{A0} v_0 \int_0^{X_1} \frac{1 + \varepsilon X}{k C_{A0} (1 - X)} dX$$

$$= \frac{v_0}{k} \int_0^{X_1} \frac{1 + \varepsilon X}{(1 - X)} dX = \frac{v_0}{k} \left((1 + \varepsilon) \ln\left(\frac{1}{1 - X_1}\right) - \varepsilon X_1 \right)$$

$$= \frac{10}{0.02} \left(3 \ln\left(\frac{1}{1 - 0.5}\right) - 1 \right) = 540 \text{ L}$$

(b)

By the rate equation,

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

$$\varepsilon = \delta y_{A0} = \left(\frac{5}{2} + \frac{1}{2} - 1\right) \cdot 1 = 2$$

By the design equation,

$$V_{CSTR} = F_{A0} \frac{X_2 - X_1}{-r_{A2}} = C_{A0} v_0 \frac{(X_2 - X_1)(1 + \varepsilon X_2)}{k C_{A0} (1 - X_2)}$$

$$V_{CSTR} = \frac{v_0}{k} \frac{(X_2 - X_1)(1 + \varepsilon X)}{1 - X_2}$$

The temperature is at 1000 K in CSTR.

By Arrhenius equation,

$$k(1000K) = k(800K) \exp\left[\frac{-Ea}{R}\left(\frac{1}{1000} - \frac{1}{800}\right)\right]$$

$$= 0.02 \exp\left[\frac{-9000}{1.987}\left(\frac{1}{1000} - \frac{1}{800}\right)\right] = 0.062 \text{ (min}^{-1})$$

$$1000 = \frac{10}{0.062} \frac{(X_2 - 0.5)(1 + 2X_2)}{1 - X_2}$$

$$X_2 = 0.848 \approx \underline{\underline{0.85}}$$

Problem 3

【Solution】

By the given reaction rate,

$$-r_A = 0.0139C_AC_R = 0.0139C_{A0}^2(1-x_A)(\theta_R - \frac{1}{2}x_A + \frac{3}{2}x_A) = 0.0139C_{A0}^2(1-x_A)(\theta_R + x_A)$$

with

$$\theta_R = \frac{C_{R0}}{C_{A0}} = \frac{1}{5} = 0.2$$

Also,

$$C_{A0} = \frac{F_{A0}}{v_0} = \frac{5}{2.5} = 2 \ (mol/L)$$

For the maximum reaction rate,

$$\frac{d(-r_A)}{dx_A} = 0.0139 \times 2^2 \times [-(\theta_R + x_A) + (1-x_A)] = 0$$

$$[-(0.2 + x_A) + (1-x_A)] = 0.8 - 2x_A = 0$$

At the maximum reaction rate,

$$x_A = 0.4$$

By the design equation of isothermal CSTR,

$$V_{CSTR} = \frac{F_{A0}x_A}{-r_A} = \frac{F_{A0}x_A}{0.0139C_{A0}^2(1-x_A)(0.2+x_A)} = \frac{5 \times 0.4}{0.0139 \times 2^2 \times (1-0.4)(0.2+0.4)} = \underline{\underline{99.92 \ (L)}}$$

Problem 4

【Solution】

By the energy balance equation,

$$X = \dfrac{\sum\limits_{i} \theta_i C_{pi}(T - T_0) - \dfrac{UA(T_a - T)}{F_{A0}}}{-\left[\Delta H_A(T_R) + \Delta C_p(T - T_R)\right]}$$

$$0.7 = \dfrac{400(T - 330) - \dfrac{(50)(2)(350 - T)}{20}}{-\left[10000 - 150(T - 298)\right]}$$

$$T = 318.2 \text{ K}$$

By Arrhenius Law,

$$k(318.2K) = k(300K)\exp\left[\dfrac{-Ea}{R}\left(\dfrac{1}{318.2} - \dfrac{1}{300}\right)\right]$$

$$= 0.08\exp\left[\dfrac{-8300}{8.3}\left(\dfrac{1}{318.2} - \dfrac{1}{300}\right)\right] = 0.097 \ (L^2/mol^2 - s)$$

By the rate equation,

$$-r_A = kC_A{}^2 C_B = kC_{A0}{}^2(1 - X)C_{A0}\left(1 - \dfrac{1}{2}X\right)$$

$$= 0.097(2)^3(1 - 0.7)\left(1 - \dfrac{0.7}{2}\right) = 0.1513 \ (mol/L - s)$$

By the design equation,

$$V = F_{A0}\dfrac{X}{-r_A} = (20)\left(\dfrac{0.7}{0.1513}\right) = \underline{\underline{92.52 \ (L)}}$$

Part II. 化工熱力學

Problem 5

【Solution】

(1)

The total number of molecular arrangement is,

$$\Omega = \frac{N!}{N_A! N_B!} = \frac{(n_1 + n_2)!}{(n_1)!(n_2)!}$$

(2)

The entropy change can be denoted as the entropy change of mixing,

$$\Delta S_{mix} = \underbrace{k \ln(\Omega)}_{solution} - \underbrace{k \ln(1)}_{pure\ 1} - \underbrace{k \ln(1)}_{pure\ 2} = k \ln(\Omega)$$

$$\ln \Omega = \ln(N!) - \ln[(n_1)!] - \ln[(n_2)!]$$

$$= N \ln N - N - x_1 N \ln(x_1 N) + x_1 N - x_2 N \ln(x_2 N) + x_2 N$$

$$= N \ln N - N - x_1 N \ln(N) - x_1 N \ln(x_1) + x_1 N - x_2 N \ln(N) - x_2 N \ln(x_2) + x_2 N$$

$$= \underbrace{N \ln N - x_1 N \ln(N) - x_2 N \ln(N)}_{0} - \underbrace{N - x_1 N - x_2 N}_{0} - x_1 N \ln(x_1) - x_2 N \ln(x_2)$$

$$= -N \left(x_1 \ln(x_1) + x_2 \ln(x_2) \right)$$

$$\Delta S_{mix} = k \ln(\Omega) = -kN \left(x_1 \ln(x_1) + x_2 \ln(x_2) \right) = -R \left(x_1 \ln(x_1) + x_2 \ln(x_2) \right)$$

(本兩小題可參考：112 年台科大化工所考古題化熱化動 Problem 6.)

(3)

$$\Delta H_{mix} = 0 \quad \text{for ideal solution}$$

$$\Delta G_{mix} = RT \sum_i x_i \ln(x_i), \text{ where } x_i \text{ is the mole fraction of ideal solution}$$

Because x_i is always less than one ($\ln(x_i)$ is always negative), ΔG_{mix} is negative.

(本小題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 8th ed.; p 402~403.)

(4)

$$\mu_1 = \mu_1{}^\circ + RT\ln\left(\frac{n_1}{n_1 + n_2}\right)$$

$$\mu_1{}' = RT\ln\left(\frac{n_1 + 1}{n_1 + 1 + n_2}\right)$$

$$\Delta\mu = \mu_1{}' - \mu_1 = RT\ln\left(\frac{n_1 + 1}{n_1 + 1 + n_2}\right) - RT\ln\left(\frac{n_1}{n_1 + n_2}\right)$$

$$\Delta\mu = RT\ln\left(\frac{n_1 + 1}{n_1 + 1 + n_2} \cdot \frac{n_1 + n_2}{n_1}\right)$$

$$\Delta\mu = \underline{\underline{RT\ln\left(1 + \frac{n_2}{n_1\left(n_1 + n_2 + 1\right)}\right)}}$$
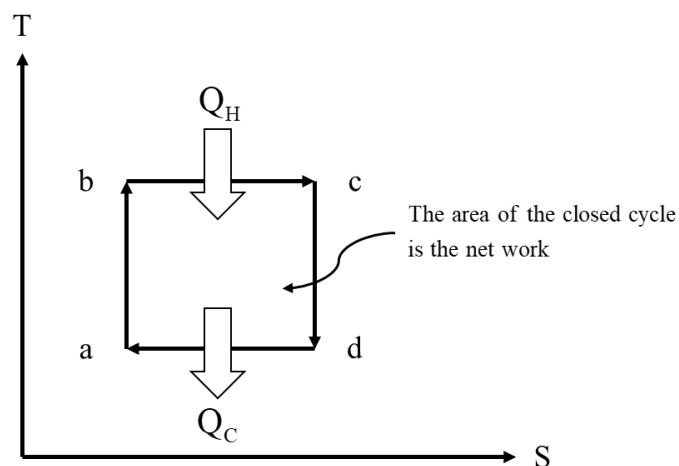
Problem 6
【Solution】

(1)

For Carnot cycle,

$$\eta_{thermal} = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H}$$

$$W = Q_H\left(1 - \frac{T_C}{T_H}\right)$$

For the step $b \to c$,

$$\Delta S_{b \to c} = \frac{Q_H}{T_H}$$

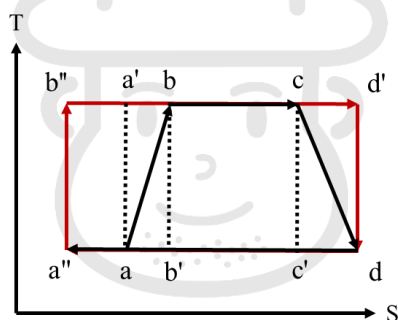$$W = \Delta S_{b \to c} T_H\left(1 - \frac{T_C}{T_H}\right) = \underline{\underline{\Delta S_{b \to c}\left(T_H - T_C\right)}}$$

(※互相參照附圖與公式結果，其所做的可逆功即為 T-S 圖所圍的矩形面積：

長為 $\Delta S_{b \to c}$ 、寬為 $T_H - T_C$。)

(2)

Where a is the beginning of the adiabatic compression up to b, b the beginning of the high temperature isotherm, c the exit of high temperature isotherm and beginning of the adiabatic expansion, and d the end of the adiabatic expansion and beginning of the low temperature isotherm.

The process in red is the corresponding reversible Carnot cycle in T-S diagram, and the one in black emphasizes the effect of each internal irreversibility considered.

Due to the principle of entropy increment, the direction of $a \to b$ is top-right, and the direction of $c \to d$ is bottom-right.

(本小題可參考：**Michel Feidt.; Monica Costea.** *Process in Carnot and Chambadal Modeling of Thermomechanical Engine by Considering Entropy Production and Heat Transfer Entropy*.)

Problem 7

【Solution】

(1)

$$P = I^2 R = (60)^2 (40 \times 10^{-3}) = \underline{\underline{144 \text{ (W)}}}$$

(2)

By entropy balance,

$$\cancel{\frac{dS}{dt}}_{assume\ s.s} = \cancel{\sum \dot{M}_k \hat{S}_k}_{no\ mass\ flow} + \sum \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

$$\boxed{\dot{S}_{gen} = -\sum \frac{\dot{Q}}{T}}$$

$$\dot{S}_{gen,device} = -\frac{144}{348} \approx \underline{\underline{-0.414 \text{ (W/K)}}}$$

$$\dot{S}_{gen,environment} = \frac{144}{298} \approx \underline{\underline{0.483 \text{ (W/K)}}}$$

$$\dot{S}_{gen,total} = 0.483 - 0.414 = \underline{\underline{0.069 \text{ (W/K)}}}$$

114 年台科大化熱化反

Problem 1

【**Solution**】

(a) The ideal solution is defined as a solution that,

$$\overline{H}_i^{id}(T,P,x) = \underline{H}_i(T,P)$$

$$\overline{V}_i^{id}(T,P,x) = \underline{V}_i(T,P)$$

for all temperature and pressures such that,

$$\Delta H_{mix} = 0 \text{ , } \Delta V_{mix} = 0$$

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

5th ed.; p 425~427.)

(b)

$$x_i P_i^{sat} = y_i P$$

When the gas phase behaves as an ideal gas and the liquid phase as an ideal solution.

(c)

When the solution is dilute, the Henry's law states that at constant pressure and temperature, the gas phase fugacity is linearly proportional to its liquid phase mole fraction:

$$\overline{f}_1^V = x_1 H_1$$

where H_1 is the Henry's law constant.

(d)

Chemical potential is equivalent of partial molar Gibbs free energy, which is,

$$\mu_i = (\frac{\partial G}{\partial N_i})_{T,P,N_{j\neq i}} = \overline{G}_i$$

(e)

Fugacity can be treated as a sort of corrected pressure for real fluid, which has the definition of,

$$f = P\exp[\frac{\underline{G}(T,P) - \underline{G}^{IG}(T,P)}{RT}]$$

(f)

For ideal gas,

$$C_p - C_V = R$$

(g)

The simplest form of the Gibbs phase rule for a C-component and P-phases is,

$$F = C - P + 2$$

If we account additional constraint such as chemical reacitons and special constraint, the equation becomes,

$$F = C - P + 2 - R - S$$

(R = number of chemical reactions

S = special constraint)

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

(h)

The Clausius inequility is,

$$dS \geq \frac{dQ}{T}$$

※此不等式可由可逆與不可逆過程做比較推導出：

假設兩程序(一可逆，一不可逆)，由同樣的起點走到同樣的終點，根據第一定律：

$$dU = dQ_{rev} + dW_{rev} = dQ + dW$$

因可逆過程，其對外做功量永遠大於不可逆過程，因此：

$$\left| dW_{rev} \right| \geq \left| dW \right| \ , \ -dW_{rev} \geq -dW \ , \ dW - dW_{rev} \geq 0$$

(注意對外做功 $W < 0$，因此在比較"量值"時前面要有負號

移項：

$$dW - dW_{rev} = dQ_{rev} - dQ \geq 0$$

根據定義，$dQ_{rev} = TdS$

$$dQ - TdS \geq 0 \ , \ TdS - dQ \geq 0$$

$$dS \geq \frac{dQ}{T}$$

假設進一步限定此系統為 idolated system，$dQ = 0$

$$dS \geq 0$$

即為第二定律的一種形式。

(本題改編自：Atkins, P.; De Paula, J.; Keeler, J. Atkins' Physical Chemistry, 9th ed.; p 102~103.)

(i)

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

(j)

$$\eta = 1 - \frac{T_c}{T_h}$$

Problem 2
【Solution】

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

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

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

By mole balance of the each of the cylinder,

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

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

$$T_f = \frac{P_f}{(\frac{P_f - P_i}{T_{in}})(\frac{C_V}{C_P}) + \frac{P_i}{T_i}}$$

For cylinder 1, $P_i = 0$

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

For cylinder 2, $P_i = 1 \ (MPa)$, $T_i = 20 + 273.15 = 293.15 \ (K)$

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

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

p 95, Problem 3.19.)

Problem 3

【**Solution**】

(a) Assume all the four units operate at a steady state while neglecting kinetic and potential energy changes:

【**For 1 to 2 (compressor)**】

By enegy balance in open steady state,

$$\Delta[H + \frac{1}{2g_c}\cancel{v^2} + \frac{g}{g_c}\cancel{z}] = \cancel{Q} + W_s \quad , \quad \Delta H = W_s$$

At state 1,

$$T_1 = 67°C$$

$$P_1 = 1 \ (MPa) = 10 \ bar \ (由 \ satuarated \ line \ 與 \ T = 340K \ 交點往右對出)$$

$$\boxed{H_1 = 326 \ (kJ / kg)} \ (由 \ satuarated \ line \ 與 \ T = 340K \ 交點往下對出)$$

For state 2,

$$P_2 = 80 \ (bar)$$

因為 compressor 按題意為等熵過程：

$$S_1 = S_2 \approx 1.21 \ (kJ / kg \cdot K)$$

(一般要自己內插，不過如果考試沒時間，圖又真的很醜，就大約為 1.2 吧。)

沿等熵線，至 $P_2 = 8MPa$，往下對得：

$$\boxed{H_2 = 340 \ (kJ / kg)}$$

$$W_s = W_{1-2} = \Delta H = H_2 - H_1 = 340 - 326 = \underline{\underline{14}} \ (kJ / kg)$$

【For 2 to 3 (high temperature heat exchanger)】

By enegy balance in open steady state,

$$\Delta[H + \frac{1}{2g_c}\cancel{v^2} + \frac{g}{g_c}\cancel{z}] = Q + \cancel{W_s} \quad , \quad \Delta H = Q$$

At state 2,

$$S_2 \approx 1.21 \ (kJ / kg \cdot K) \ 、 \ H_2 = 240 \ (kJ / kg) \ 、 \ P_2 = 8MPa$$

For state 3,

$$T_3 = 500 \ (K)$$

因為 heat exchanger 為等壓加熱過程，沿著 $P_2 = 8MPa$，往右至 $T_3 = 500 \ (K)$：

$$\boxed{H_3 = 890 \ (kJ / kg)}$$

$$Q = Q_{2-3} = \Delta H = H_3 - H_2 = 890 - 340 = \underline{\underline{550 \ (kJ / kg)}}$$

【For 3 to 4 (turbine)】

By enegy balance in open steady state,

$$\Delta[H + \frac{1}{2g_c}\cancel{v^2} + \frac{g}{g_c}\cancel{z}] = \cancel{Q} + W_s \quad , \quad \Delta H = W_s$$

At state 3,

$$P_3 = 8MPa \ 、 \ T_3 = 500 \ (K) \ 、 \ H_3 = 890 \ (kJ / kg)$$

$$S_3 \approx 2.5 \ (kJ / kg \cdot K)$$

For state 4,

$$P_4 = P_1 = 1 \ (MPa)$$

因為後續的熱交換器為等壓加熱過程，因此 turbine 出口，即熱交換器進口一定是 1.6 (MPa)

因為 turbine 按題意為等熵過程：

$$S_3 = S_4 \approx 2.5 \ (kJ/kg \cdot K)$$

沿等熵線，至 $P_4 = 1MPa$，往下對得：

$$\boxed{H_4 = 780 \ (kJ/kg)}$$

$$W_s = W_{3-4} = \Delta H = H_4 - H_3 = 780 - 890 = \underline{\underline{-110 \ (kJ/kg)}}$$

【For 4 to 1 (low temperature heat exchanger)】

By enegy balance in open steady state,

$$\Delta[H + \frac{1}{2g_c}\cancel{v^2} + \frac{g}{g_c}\cancel{z}] = Q + \cancel{W_s} \ , \ \Delta H = Q$$

At state 4,

$$P_1 = 1 \ (MPa) \ 、 \ H_4 = 780 \ (kJ/kg)$$

For state 1,

$$P_4 = P_1 = 1 \ (MPa) \ , \ H_1 = 326 \ (kJ/kg)$$
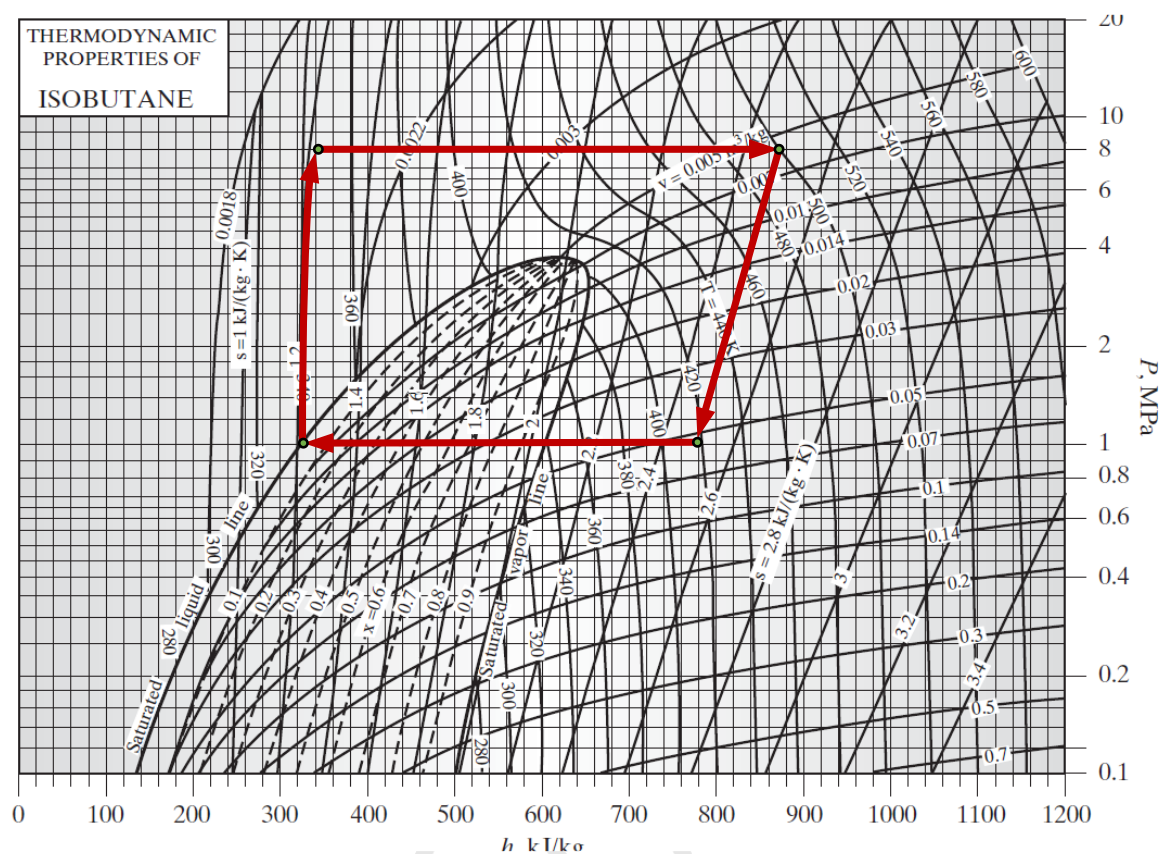
(compressor 時已經對過)

$$Q = Q_{4-1} = \Delta H = H_1 - H_4 = 326 - 780 = \underline{\underline{-454 \ (kJ/kg)}}$$

統整：

Unit	Point	$Q\,(kJ/kg)$	$W_s\,(kJ/kg)$	$\Delta H\,(kJ/kg)$
Compressor	$1 \rightarrow 2$	0	14	14
HT exhanger	$2 \rightarrow 3$	550	0	550
Turbine	$3 \rightarrow 4$	0	-110	-110
LT exhanger	$4 \rightarrow 1$	-454	0	-454

作圖路徑如下：

(b)

$$\eta = \frac{\left|W_{1-2} + W_{3-4}\right|}{Q_{2-3}} \times 100\% = \frac{\left|14 - 110\right|}{550} \times 100\% = \underline{\underline{17.4}}$$

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

p 196~197, Problem 5.16。此為 Brayton cycle，可參考同本書 p 173~176)

<u>Problem 4</u>

【Solution】

(1)

By the design equation of CSTR, we have

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

The rate laws are expressed as (liquid phase, 1st order):

$$-r_A = (k_1 + k_2)C_A \text{ , } r_R = k_1 C_A \text{ , } r_S = k_2 C_A$$

Combine, we have the relation for the 1st CSTR,

$$\tau_1 = \frac{C_{A0} - C_{A1}}{(k_1 + k_2)C_{A1}} = \frac{C_{R1}}{k_1 C_{A1}} = \frac{C_{S1}}{k_2 C_{A1}} = 2 \text{ (min)}$$

$$\tau_1 = \frac{1 - 0.4}{(k_1 + k_2)0.4} = 2 \text{ , } \boxed{k_1 + k_2 = 0.75 \text{ (min}^{-1})}$$

For the 2nd CSTR,

$$\tau_2 = \frac{C_{A1} - C_{A2}}{(k_1 + k_2)C_{A2}} = \frac{C_{R2}}{k_1 C_{A2}} = \frac{C_{S2}}{k_2 C_{A2}} = 5 \text{ (min)}$$

For A,

$$\frac{0.4 - C_{A2}}{0.75 \times C_{A2}} = 5 \text{ , } C_{A2} = \underline{0.0842} \text{ (\textit{unit of concentration})}$$

$$C_{S2} = 0.4 + (0.4 - 0.0842) \times \underbrace{\frac{0.4}{0.4 + 0.2}}_{\textit{fractional yield of S}} = \underline{\underline{0.61}}$$

$$C_{R2} = C_{A0} - C_{A2} - C_{S2} = 1 - 0.0842 - 0.61 = \underline{0.305}$$

(2)

The selectivity of the desired product is,

$$S = \frac{k_1 C_A^{1.5} C_B^{0.30}}{k_2 C_A^{0.5} C_B^{1.8}} = \frac{k_1}{k_2} C_A^1 C_B^{-1.5}$$

The reaction can be conducted in a PFR or a batch reactor with a controlled **<u>bypass of reactant B into the main A stream</u>**, ensuring higher concentration of A, while suppressing the undesired side reaction, which is more sensitive to the concentration of

B.

Problem 5

【Solution】

(a)

By energy balance of the jacketed CSTR,

$$Q - \not{W} - F_{A0} \sum_i \int_{T_{i0}}^{T} \theta_i C_{pi} dT - \sum_i F_{A0} \Delta H_{rxn,A} x_A = 0$$

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

$$UA(T_a - T) - F_{A0} \int_{T_{i0}}^{T} (C_{PA} + C_{PI}) dT - F_{A0} [(\Delta H_R + \int_{T_R}^{T} \not{\Delta C_P dT}) x_A] = 0$$

$$x_A = x_{A,EB} = \frac{UA(T_a - T) - F_{A0} \int_{T_{i0}}^{T} (C_{PA} + C_{PI}) dT}{F_{A0}(\Delta H_R)}$$

$$\boxed{x_A = x_{A,EB} = \frac{8000(300 - T) - 80 \times 50(T - 450)}{80 \times (-7500)}}$$

For CSTR, the design equation is,

$$\tau = \frac{C_{A0} x_A}{-r_A} = \frac{C_{A0} x_A}{k C_A} = \frac{\not{C_{A0}} x_A}{k \not{C_{A0}} (1 - x_A)} = \frac{x_A}{k(1 - x_A)}$$

$$\boxed{x_A = x_{A,MB} = \frac{\tau k}{1 + \tau k} = \frac{100 \times 6.6 \times 10^{-3} \times \exp[\frac{40000}{1.987}(\frac{1}{350} - \frac{1}{T})]}{1 + 100 \times 6.6 \times 10^{-3} \times \exp[\frac{40000}{1.987}(\frac{1}{350} - \frac{1}{T})]}}$$

令 $x_{A,MB} = x_{A,EB}$
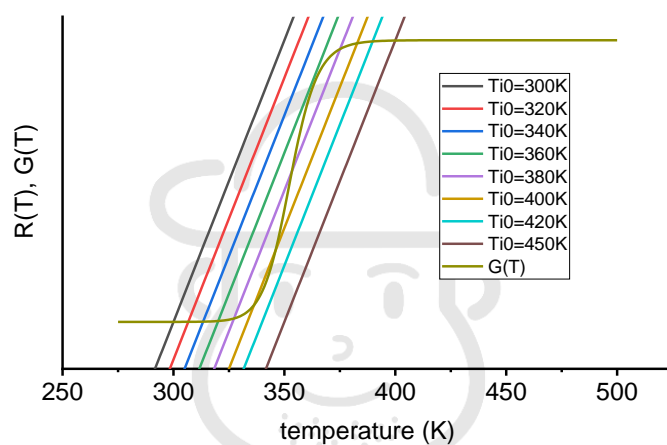
$$\underline{\underline{T \approx 400 \ (K)}}$$

(b)

根據(a)小題推導，我們知道

$$\underbrace{-\left[UA(T_a-T)-F_{A0}\int_{T_{i0}}^{T}(C_{PA}+C_{PI})dT\right]}_{removal,\,R(T)}=\underbrace{-F_{A0}[(\Delta H_R)x_A]}_{generation,\,G(T)}$$

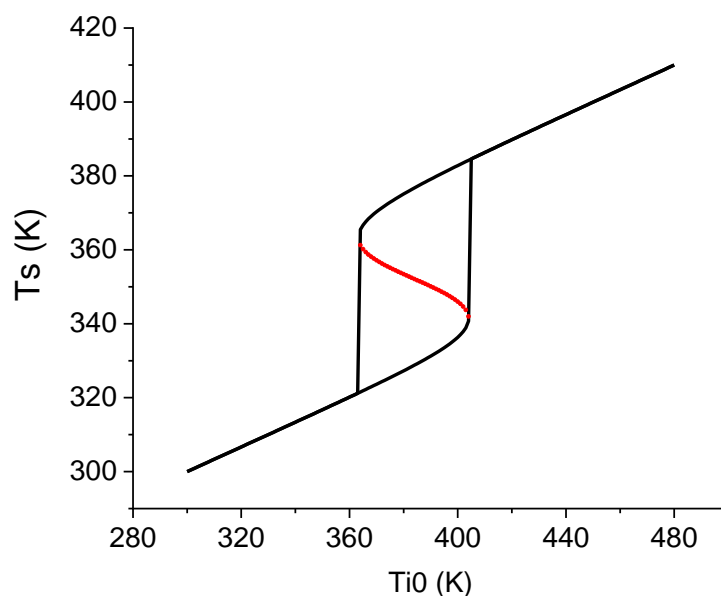$$R(T)=-\left[8000(300-T)-80\times50\times(T-T_{i0})\right]=-4000[(T_{i0}-3T+600)]$$

$$G(T)=-80\times[-7500\times\frac{100\times6.6\times10^{-3}\times\exp[\frac{40000}{1.987}(\frac{1}{350}-\frac{1}{T})]}{1+100\times6.6\times10^{-3}\times\exp[\frac{40000}{1.987}(\frac{1}{350}-\frac{1}{T})]}]$$
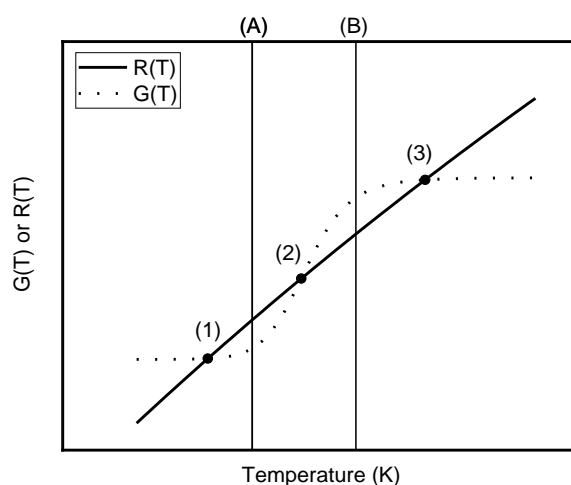

(※圖由電腦精確畫出，同學考試時大概依此趨勢畫出簡圖即可)

此時找出每一個T_{i0}所對應到的$R(T)-G(T)$交點溫度，即是相對應的T_s

※一般來說，**unstable steady state** 的位置在原文書皆以 **G(T)** 與 **R(T)** 對溫度之關係說明，其原理如下(**G(T)**代表熱產生項，**R(T)**代表熱移除項)：

首先，若系統溫度在(A)，則此時 **R(T)>G(T)**，代表熱移除速率快，溫度下移，因此往(1)移動後達到 **steady state**；若系統溫度在(B)，則此時 **G(T)>R(T)**，溫度上移，往(3)移動後達到 **steady state**，都沒有在(2)達到 **steady state** 的可能。而若是直接定溫度在(2)，此時雖然 **R(T)** 與 **G(T)** 產生交點，但微觀來說，任何反應系統並不是固定在同一個狀態就停止，假設此時有一微小的擾動使原先在(2)的系統溫度上移一點，就會因 **G(T)>R(T)** 而直接移動到(3)；反方向亦然。因此我們說(2)並不是穩定的狀態(儘管有交點)，而稱之為 **unstable steady state**。以此，在 $T_s - T_{i0}$ 圖中，同一個 T_{i0} 對應到的 T_s 會有三個，最低溫的為 **lower steady state temperature**;最高溫的為 **upper steady state temperature**;而中間紅色的部分則為 **unstable**，基本上應很難穩定存在。

(c)

※此題原文書只在解答定義 **high conversion** 為 0.98，同樣也並未在題目定義高轉化率門檻，以下按照 0.98 做計算。考試當下也許在 0.95 以上都是可以接受的範圍。

先算該轉化率下穩態溫度：

$$x_A = x_{A,MB} = \frac{\tau k}{1+\tau k} = \frac{100 \times 6.6 \times 10^{-3} \times \exp[\frac{40000}{1.987}(\frac{1}{350} - \frac{1}{T})]}{1 + 100 \times 6.6 \times 10^{-3} \times \exp[\frac{40000}{1.987}(\frac{1}{350} - \frac{1}{T})]} = 0.98$$

$$T = 378.3\ (K)$$

代回能量平衡：

$$x_A = x_{A,EB} = \frac{8000(300-378.3)-80\times50(378.3-T_{i0})}{80\times(-7500)} = 0.98$$

$$\underline{\underline{T_{i0} = 387.9~(K)}}$$

(d)

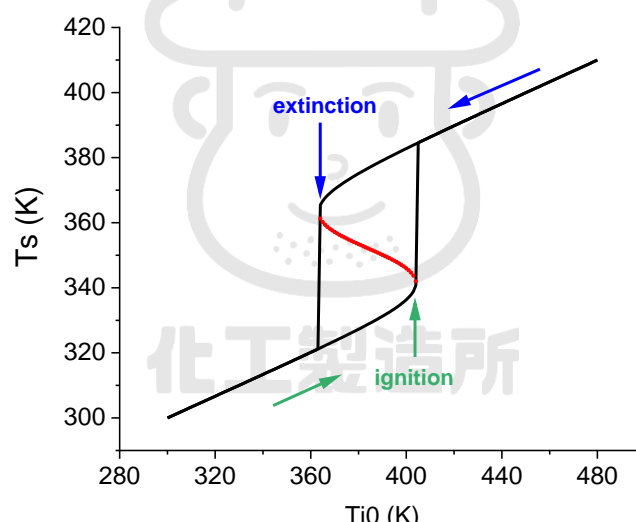根據題意，將 reactor 操作溫度更改為：

$$T = 378.3+5-20 = 363.3~(K)$$

$$x_A = x_{A,MB} = \frac{\tau k}{1+\tau k} = \frac{100\times6.6\times10^{-3}\times\exp[\frac{40000}{1.987}(\frac{1}{350}-\frac{1}{363.3})]}{1+100\times6.6\times10^{-3}\times\exp[\frac{40000}{1.987}(\frac{1}{350}-\frac{1}{363.3})]} = \underline{\underline{0.844}}$$

(e)

如圖，若從高溫進料操作逐漸降低溫度，會到某一個進料溫度後穩態溫度急遽下降，此即為 extinction temperature，大約為 **360(K)**。反之，若是從低溫進料開始慢慢加熱進料溫度，此時過了某一個溫度會發現其相對應的穩態溫度瞬間上升，此即為 ignition temperature，大約為 **404(K)** 附近。

(※本題改編自：**FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed., p 579, Problem P8.16B，相關計算細節可參考同本書 p 522~540。**)

Problem 6

【Solution】

(a)

For the reaction carried out **adiabatically**,

$$x_A = 0 \sim 0.5 \text{ , CSTR}$$

$$x_A = 0.5 \sim 0.8 \text{ , PBR}$$

For the reaction carried out **isothermally**,

(1) If the $F_{A0}/-r_A - x_A$ curve monotonically increases, use only PFR。

(2) If the $F_{A0}/-r_A - x_A$ curve resembles the one under adiabatic conditions:

$$x_A = 0 \sim 0.5 \text{ , CSTR}$$

$$x_A = 0.5 \sim 0.8 \text{ , PFR}$$

(b)※下面小題計算皆基於題目給的絕熱情況 **Levenspiel plot**：

$$W = \frac{F_{A0}x_A}{-r_A} = 30 \times 0.8 = \underline{\underline{24}} \ (kg)$$

(c)

$$W = \frac{F_{A0}x_A}{-r_A} = 20 \times 0.4 = \underline{\underline{8}} \ (kg)$$

(d)

By Simpson's rule,

x_A	$F_{A0}/-r_A$
0	60
0.2	30
0.4	20
0.6	20
0.8	30

$$W = \frac{0.2}{3}[1 \times 60 + 4 \times 30 + 2 \times 20 + 4 \times 20 + 1 \times 30] = \underline{\underline{22}} \ (kg)$$

(e)

By Simpson's rule,

x_A	$F_{A0}/-r_A$
0	60
0.1	40
0.2	30
0.3	25
0.4	20

$$V = \frac{0.1}{3}[1 \times 60 + 4 \times 40 + 2 \times 30 + 4 \times 25 + 1 \times 20] = \underline{\underline{13.3}} \ (kg)$$