

# 106 年中央化熱化反

## Problem 1

### 【Solution】

$$\begin{aligned}\Delta G^\circ &= \sum_P \nu_i G_i^\circ - \sum_R \nu_i G_i^\circ \\ &= (G_{2H_2O(g)}^\circ + G_{CO_2(g)}^\circ) - (G_{CH_4(g)}^\circ + G_{2O_2(g)}^\circ) \\ &= (-288.59) - 394.359 - (-50.8) = \underline{\underline{-632.149 \text{ (kJ)}}}\end{aligned}$$

$$\Delta H^\circ = (-241.83) - 393.509 - (-74.87) = \underline{\underline{-560.469 \text{ (kJ)}}}$$

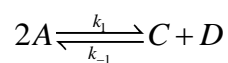
For  $\Delta G @ 477^\circ \text{C}$ , assume  $\Delta C_p \approx 0$

$$\begin{aligned}\frac{d(\Delta G / RT)}{dT} &= \frac{-\Delta H^\circ}{RT^2} \\ \left(\frac{\Delta G}{RT}\right)_{477^\circ \text{C}} - \left(\frac{\Delta G}{RT}\right)_{25^\circ \text{C}} &= \frac{-560.469 \times 10^3}{8.314} \left(\frac{1}{750.15} - \frac{1}{298.15}\right) \\ \frac{\Delta G}{8.314 \times 750.15} &= \frac{-560.469 \times 10^3}{8.314} \left(\frac{1}{750.15} - \frac{1}{298.15}\right) - \frac{632.149 \times 10^3}{8.314 \times 298.15} \\ \frac{\Delta G}{8.314 \times 750.15} &= \frac{-560.469 \times 10^3}{8.314} \left(\frac{1}{750.15} - \frac{1}{298.15}\right) - \frac{632.149 \times 10^3}{8.314 \times 298.15} \\ \Delta G_{(477^\circ \text{C})} &= \underline{\underline{-740.816 \text{ (kJ)}}}\end{aligned}$$

## **Problem 2**

### **【Solution】**

Reaction,



For equilibrium conversion,

$$K = \frac{C_C C_D}{C_A^2} = \left[ \frac{C_{A0} \left( \frac{1}{2} x_{Ae} \right)}{C_{A0} (1 - x_{Ae})} \right]^2 = 16, \quad x_{Ae} = 0.889$$

For the size of CSTR, design equation,

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

Rate equation,

$$\begin{aligned} -r_A &= k_1 C_A^2 - k_{-1} C_C C_D \\ &= k_1 C_{A0}^2 \left[ (1 - x_A)^2 - \frac{1}{4K} x_A^2 \right] \end{aligned}$$

Combine,

$$\begin{aligned} V &= \frac{F_{A0} x_A}{k_1 C_{A0}^2 \left[ (1 - x_A)^2 - \frac{1}{K} x_A^2 \right]} = \frac{100 \times 1.5 \times 0.8 \times 0.89}{10 \times 1.5^2 \left[ (1 - 0.8 \times 0.89)^2 - \frac{1}{16 \times 4} (0.8 \times 0.89)^2 \right]} \\ &= \underline{\underline{63.27 \text{ (L)}}} \end{aligned}$$

### **Problem 3**

#### **【Solution】**

(a)

Rate equation,

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

For CSTR,

$$V = \frac{F_{A0} x_{AC}}{-r_A}$$

Combine,

$$V = \frac{F_{A0} x_{AC}}{kC_{A0}^2 (1 - x_{AC})^2} = 200$$
$$V = \frac{(5+5)x_{AC}}{0.07 \times \left(\frac{2}{2}\right)^2 (1 - x_{AC})^2} = 200, \quad x_{AC} = 0.439$$

For PFR,

$$V = \int_{x_{AC}}^{x_{AP}} \frac{F_{A0} dx_A}{kC_{A0}^2 (1 - x_A)^2} = 800$$
$$\int_{0.439}^{x_{AP}} \frac{(5+5)dx_A}{0.07 \times \left(\frac{2}{2}\right)^2 (1 - x_A)^2} = 800, \quad \underline{\underline{x_{AP} = 0.864}}$$

(b)

For PFR operated at 300K,

$$\int_0^{x_{AP}} \frac{(5+5)dx_A}{0.07 \times \left(\frac{2}{2}\right)^2 (1 - x_A)^2} = 800$$
$$x_{AP} = 0.848$$

For CSTR operated at 350K,

By Arrhenius law,

$$k(350) = k(300) \exp\left[\frac{-20 \times 10^3}{1.987} \left(\frac{1}{350} - \frac{1}{300}\right)\right] = 8.447$$

代入 CSTR,

$$V = \frac{(5+5) \times 0.848}{8.447 \times \left(\frac{2}{2}\right)^2 (1-0.848)^2} = \underline{\underline{43.45 \text{ (dm}^3\text{)}}}$$

(c)

By design equation of batch reactor,

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = -\frac{dC_A}{dt} = C_{A0} \frac{dx_A}{dt}$$

Combine with the rate equation,

$$-r_A = kC_{A0}^2 (1-x_A)^2 = C_{A0} \frac{dx_A}{dt}$$

$$kC_{A0} \int_0^t dt = \int_0^{x_A} \frac{dx_A}{(1-x_A)^2}$$

$$8.447 \times 1 \times t = \int_0^{0.9} \frac{dx_A}{(1-x_A)^2}$$

$$\underline{\underline{t = 1.065 \text{ (min)}}}$$

### **Problem 4**

#### **【Solution】**

For A, by design equation,

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

Rate equation,

$$-r_A = k_1 C_A$$

Combine,

$$V = \frac{F_{A0}x_A}{k_1 C_A}, \quad \tau = \frac{C_{A0}x_A}{k_1 C_A} = \frac{C_{A0} - C_A}{k_1 C_A} = 1000$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{117 \times 10^3}{8.314 \times 700} = 20.10 \text{ (mole / m}^3\text{)} = 0.02010 \text{ (mole / dm}^3\text{)}$$

$$\frac{0.02010 - C_A}{1.0 \times 10^{-3} C_A} = 1000, \quad \underline{\underline{C_A = 0.010 \text{ (M)}}}$$

For R,

$$\tau = \frac{C_R}{k_1 C_A - k_2 C_R - k_3 C_R C_S} \text{ ---(1)}$$

For S,

$$\tau = \frac{C_S}{k_2 C_R - k_3 C_R C_S} \text{ ---(2)}$$

For RS,

$$\tau = \frac{C_{RS}}{k_3 C_R C_S}$$

也可由 Mass balance 求出

$$C_{A0} = C_A + C_R + C_S + C_{RS}$$

By (2) :

$$C_S = \frac{\tau k_2 C_R}{k_3 C_R \tau + 1} \text{ 代回(1)}$$

$$\tau = \frac{C_R}{k_1 C_A - k_2 C_R - \frac{\tau k_3 k_2 C_R^2}{k_3 C_R \tau + 1}}, \begin{cases} C_R = 0.00452 \text{ (M)} \\ C_S = 0.00539 \text{ (M)} \end{cases}$$

$$C_{RS} = C_{A0} - C_A - C_R - C_S$$

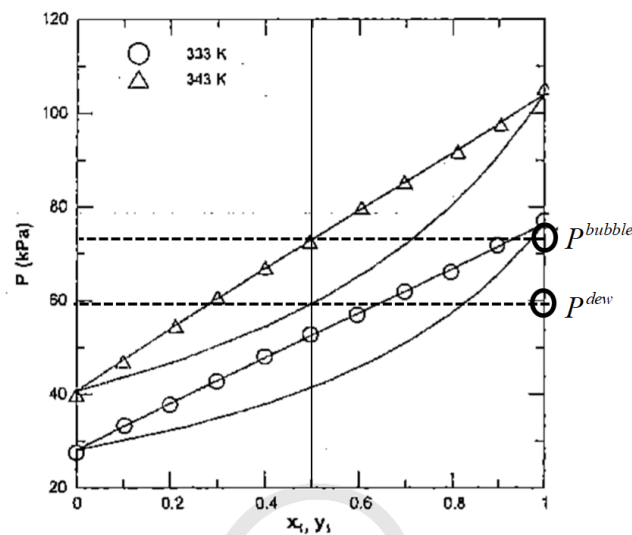
$$= 0.020 - 0.010 - 0.00452 - 0.00539 = 7.815 \times 10^{-5} \text{ (M)}$$

$$\begin{cases} C_A = 0.010 \text{ (M)} \\ C_R = 0.00452 \text{ (M)} \\ C_S = 0.00539 \text{ (M)} \\ C_{RS} = 7.815 \times 10^{-5} \text{ (M)} \end{cases}$$

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**Problem 5**  
**【Solution】**

(a)



如圖：equimolar condition 為  $x_1 = y_1 = 0.5$  處

$$\begin{cases} P^{bubble} = 72 \text{ kPa} \\ P^{dew} = 60 \text{ kPa} \end{cases}$$

(b)

Assume,  $\begin{cases} \text{vapor phase} \rightarrow \text{ideal gas} \\ \text{liquid phase} \rightarrow \text{ideal solution} \end{cases}$ , Raoult's law applicable

@bubble point,

$$x_{C_6} = 0.50, \quad x_{C_7} = 0.25, \quad x_{C_8} = 0.25$$

By Raoult's law,

$$y_{C_6} = \frac{P_{C_6}^{vap} x_{C_6}}{P} = \frac{1.049 \times 0.50}{P}$$

$$y_{C_7} = \frac{P_{C_7}^{vap} x_{C_7}}{P} = \frac{0.402 \times 0.25}{P}$$

$$y_{C_8} = \frac{P_{C_8}^{vap} x_{C_8}}{P} = \frac{0.157 \times 0.25}{P}$$

By  $y_{C_6} + y_{C_7} + y_{C_8} = 1$  ,

$$P = 0.664(\text{bar}) \begin{cases} y_{C_6} = 0.789 \\ y_{C_7} = 0.151 \\ y_{C_8} = 0.059 \end{cases}$$

(c)

Assume,  $\begin{cases} \text{vapor phase} \rightarrow \text{ideal gas} \\ \text{liquid phase} \rightarrow \text{ideal solution} \end{cases}$  , Raoult's law applicable

@dew point,

$$y_{C_6} = 0.50 \text{ , } y_{C_7} = 0.25 \text{ , } y_{C_8} = 0.25$$

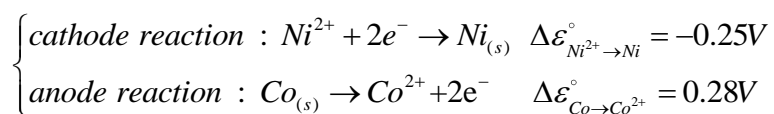
By Raoult's law,

$$\begin{aligned} x_{C_6} &= \frac{y_{C_6} P}{P_{C_6}^{\text{vap}}} = \frac{0.50 P}{1.049} \\ x_{C_7} &= \frac{y_{C_7} P}{P_{C_7}^{\text{vap}}} = \frac{0.25 P}{0.402} \\ x_{C_8} &= \frac{y_{C_8} P}{P_{C_8}^{\text{vap}}} = \frac{0.25 P}{0.157} \end{aligned}$$

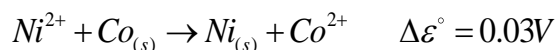
By  $x_{C_6} + x_{C_7} + x_{C_8} = 1$  ,

$$P = 0.371(\text{bar}) \begin{cases} x_{C_6} = 0.177 \\ x_{C_7} = 0.231 \\ x_{C_8} = 0.592 \end{cases}$$



**Problem 6****【Solution】****(a)**

Net cell reaction,

**(b)**

$$\underline{\underline{\Delta\epsilon^{\circ} = 0.03V}}$$

$$\Delta G^{\circ} = -nF\Delta\epsilon^{\circ} = -2 \times 96485 \times 0.03 = \underline{\underline{-5789.1 \text{ (J)}}}$$

$$\Delta G^{\circ} = -RT \ln K = -8.314 \times 298.15 \ln K = -5789.1$$

$$\underline{\underline{K_{eq} = 10.33}}$$

**(c)**

$$Q = \frac{[Co^{2+}]}{[Ni^{2+}]} = \frac{c_1}{c_2} = \frac{1}{0.0010} = \underline{\underline{1000}}$$

$$\begin{aligned} \Delta\epsilon &= \Delta\epsilon^{\circ} - \frac{RT}{nF} \ln Q = 0.03 - \frac{8.314 \times 298.15}{2 \times 96485} \ln 1000 \\ &= \underline{\underline{-0.0587 \text{ (V)}}} \end{aligned}$$

$$\Delta G = RT \ln \frac{Q}{K} = 8.314 \times 298.15 \ln \frac{1000}{10.33} = \underline{\underline{11334.90 \text{ (J)}}}$$

**(d)**

$$\Delta\epsilon^{\circ} > 0 \rightarrow \text{spontaneous}$$

**(e)**

$$\Delta\epsilon < 0 \rightarrow \text{non-spontaneous}$$

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## Problem A1

### 1. Ans : (D)

#### 【Solution】

$$r_{avg} = \frac{0.057 - 0.046}{800.0 - 400.0} = 2.75 \times 10^{-5} \approx \underline{\underline{2.8 \times 10^{-5} (M / s)}}$$

### 2. Ans : (D)

#### 【Solution】

For second-order reaction,

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \begin{cases} [A]_0 = 0.71 (M) \\ t = 18s \\ [A] = \frac{[A]_0}{2} = 0.355 (M) \end{cases}$$
$$\frac{1}{0.355} - \frac{1}{0.71} = 18k, \quad \underline{\underline{k = 0.078 (M^{-1}s^{-1})}}$$

### 3. Ans : (B)

For first-order reaction,

$$\ln \frac{[A]_0}{[A]} = kt, \quad \ln \frac{100}{100-13} = 60k$$
$$\underline{\underline{k = 2.32 \times 10^{-3} (s^{-1})}}$$

For half-life,

$$\frac{[A]_0}{[A]} = \frac{2}{1} = 2 \text{ 代入}$$

$$\ln 2 = 2.32 \times 10^{-3} t_{\frac{1}{2}}, \quad t_{\frac{1}{2}} = 298.63 \approx 299 (\text{min})$$

### 4. Ans : (C)

For zero-order reaction,

$$[A]_0 - [A] = kt$$

$$0.537 - 0.100 = 0.075t, \quad \underline{\underline{t = 5.83 (s)}}$$

5. Ans : (C)

For second-order reaction,

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[A]} - \frac{1}{0.0440} = 0.80 \times 6.0, \quad \underline{\underline{[A] = 0.0363 \text{ (M)}}}$$



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**Problem B1****【Solution】**

$$\Phi = \sqrt{\frac{ka^2}{D_A}} \quad , \quad k = \frac{\Phi^2 D_A}{a^2}$$

where  $a$  is characteristic length,

$$a = \frac{V}{A} = \frac{R}{3} \quad (\text{for sphere})$$

$$R_{Ap} = \frac{1}{\Phi} \left[ \frac{1}{3\Phi} - \frac{1}{\tanh 3\Phi} \right] \cdot \frac{\Phi^2 D_A}{a^2} C_{As}$$

$$\Phi \left[ \frac{1}{3\Phi} - \frac{1}{\tanh 3\Phi} \right] = \frac{R_{Ap} a^2}{D_A C_{As}}$$

$$R_{Ap} = -2.5 \times 10^{-5} \times 0.85 = -2.125 \times 10^{-5} \quad (\text{mole} / \text{cm}^3 \cdot \text{s})$$

$$C_{As} = \frac{P_{As}}{RT} = \frac{0.7}{0.082 \times 450} \times \frac{1L}{1000 \text{cm}^3} = 1.897 \times 10^{-5} \quad (\text{mole} / \text{cm}^3)$$

代入：

$$\Phi \left[ \frac{1}{3\Phi} - \frac{1}{\tanh 3\Phi} \right] = \frac{-2.125 \times 10^{-5} \times \left(\frac{0.3}{3}\right)^2}{0.007 \times 1.897 \times 10^{-5}} = -1.60$$

$$\Phi = 1.933 \quad , \quad k = \frac{\Phi^2 D_A}{a^2} = \frac{1.933^2 \times 0.007}{\left(\frac{0.3}{3}\right)^2} = 2.617$$

$$\text{For } R = 0.15 = \frac{0.3}{2}$$

$$\Phi \propto \sqrt{a^2} \propto \sqrt{\left(\frac{R}{3}\right)^2} \propto R = \frac{1.933}{2} = 0.967$$

$$\begin{aligned} R_{Ap} &= -\eta k C_{As} = \frac{1}{0.967} \left[ \frac{1}{\tanh(3 \times 0.967)} - \frac{1}{3 \times 0.967} \right] \times 2.617 \times 1.897 \times 10^{-5} \\ &= \underline{\underline{-3.396 \times 10^{-5} \quad (\text{mole} / \text{cm}^3 \cdot \text{s})}} \end{aligned}$$

**Problem B2****【Solution】**

- (a) : liquid phase  
 (b) : liquid-liquid equilibrium  
 (c) : liquid phase  
 (d) : vapor-liquid equilibrium  
 (e) : vapor phase

**Problem B3****【Solution】**

Let

$$\frac{G^E}{RT} = \frac{1}{RT} (A_{12}x_1x_2 + A_{13}x_1x_3 + A_{14}x_1x_4 + A_{23}x_2x_3 + A_{24}x_2x_4 + A_{34}x_3x_4)$$

$$\frac{nG^E}{RT} = \frac{1}{nRT} (A_{12}n_1n_2 + A_{13}n_1n_3 + A_{14}n_1n_4 + A_{23}n_2n_3 + A_{24}n_2n_4 + A_{34}n_3n_4)$$

For  $r_1$  :

$$\begin{aligned} \ln r_1 &= \frac{\partial}{\partial n_1} \left[ \frac{nG^E}{RT} \right]_{T,P,n_{j \neq 1}} \\ &= \frac{1}{RT} \left[ A_{12}n_2 \left( \frac{1}{n} - \frac{n_1}{n^2} \frac{\partial n}{\partial n_1} \right) + A_{13}n_3 \left( \frac{1}{n} - \frac{n_1}{n^2} \frac{\partial n}{\partial n_1} \right) + A_{14}n_4 \left( \frac{1}{n} - \frac{n_1}{n^2} \frac{\partial n}{\partial n_1} \right) - \frac{A_{23}n_2n_3 + A_{24}n_2n_4 + A_{34}n_3n_4}{n^2} \right] \\ &= \frac{1}{RT} [A_{12}x_2(1-x_1) + A_{13}x_3(1-x_1) + A_{14}x_4(1-x_1) - A_{23}x_2x_3 - A_{24}x_2x_4 - A_{34}x_3x_4] \end{aligned}$$

### Problem B4

#### 【Solution】

將  $\frac{\Delta G^{EX}}{RT}$  展開：

$$\begin{aligned}\frac{\Delta G^{EX}}{RT} &= x_B(1-x_B)[2+0.2(2x_B-1)-0.8(4x_B^2-4x_B+1)] \\ &= (x_B-x_B^2)(1+3.6x_B-3.2x_B^2) \\ &= x_B+2.6x_B^2-6.8x_B^3+3.2x_B^4\end{aligned}$$

$$\frac{d^2(\Delta G^{EX}/RT)}{dx_B^2} = 5.2 - 40.8x_B + 38.4x_B^2$$

For the phase separation to occur,

$$\frac{d^2(\Delta G^{EX}/RT)}{dx_B^2} < \frac{-1}{x_B x_C} = \frac{1}{x_B(x_B-1)}$$

$$5.2 - 40.8x_B + 38.4x_B^2 < \frac{1}{x_B(x_B-1)}$$

$$38.4x_B^4 - 79.2x_B^3 + 46x_B^2 - 5.2x_B - 1 < 0$$

$$x_B = -0.09621, 0.35099, 0.68974, 1.11797 \text{ (若 } = 0 \text{)}$$

$$\boxed{0 < x_B < 0.35099} \text{ 、 } \boxed{0.68974 < x_B < 1} \text{ (region of immiscibility)}$$

**Problem B5****【Solution】**

(1)

Let

$$nM = M(T, P, n_1, n_2, \dots, n_i, \dots)$$

By the total differential of  $nM$ 

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

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

Where,

$$\begin{cases} dn_i = d(nx_i) = ndx_i + x_i dn \\ d(nM) = ndM + Mdn \end{cases} \text{代入}$$

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

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

Where,

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

$$\boxed{\left( \frac{\partial M}{\partial P} \right)_{T,x} dP + \left( \frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i x_i \bar{M}_i = 0} \quad \text{--- Gibbs-Duhem equation}$$

The Gibbs-Duhem equation shows that *the partial properties of species making up a solution are not independent of one another.*

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

(2)

① By Gibbs-Duhem equation of  $\mu_i$

$$\mu_i = RT d \ln \hat{f}_i \text{ 代入}$$

$$x_A d \ln \hat{f}_A + x_B d \ln \hat{f}_B = 0 \quad (@ \text{ constant T, P})$$

$$x_A \frac{d \ln \hat{f}_A}{dx_A} + x_B \frac{d \ln \hat{f}_B}{dx_A} = 0, \quad x_A \frac{d \ln \hat{f}_A}{dx_A} = x_B \frac{d \ln \hat{f}_B}{dx_B}$$

$$\frac{\frac{d \hat{f}_A / x_A}{\hat{f}_A / x_A}}{\hat{f}_A / x_A} = \frac{\frac{d \hat{f}_B / x_B}{\hat{f}_B / x_B}}{\hat{f}_B / x_B}$$

In the limit of  $\begin{cases} x_A \rightarrow 1 \\ x_B \rightarrow 0 \end{cases}$  (ideal solution based on Henry's law)

$$\lim_{x_A \rightarrow 1} \frac{\frac{d \hat{f}_A / dx_A}{\hat{f}_A / x_A}}{\hat{f}_A / x_A} = \lim_{x_B \rightarrow 0} \frac{\frac{d \hat{f}_B / dx_B}{\hat{f}_B / x_B}}{\hat{f}_B / x_B} = 1$$

$$\frac{1}{\hat{f}_A} \left( \frac{d \hat{f}_A}{dx_A} \right)_{x_A \rightarrow 1} = 1, \quad \left( \frac{d \hat{f}_A}{dx_A} \right)_{x_A \rightarrow 1} = \hat{f}_A$$

which obeys Lewis/Randall rule.

② By Gibbs-Duhem equation of  $\mu_i$

$$x_A \frac{d \ln \hat{f}_A}{dx_A} = x_B \frac{d \ln \hat{f}_B}{dx_B}$$

If  $\hat{f}_A = x_A P_A^{sat}$  (Raoult's law)

$$x_A \frac{d \ln \hat{f}_A}{dx_A} = x_A \frac{d \ln(x_A P_A^{sat})}{dx_A} = 1$$

$$x_B \frac{d \ln \hat{f}_B}{dx_B} = 1, \quad \ln \hat{f}_B = \ln x_B + C$$

$$\text{令 } e^C = H_B \text{ (Henry's law constant)}, \quad \underline{\underline{\hat{f}_B = H_B x_B}}$$



(3)

By Gibbs-Duhem equation of  $\overline{G}_i$

$$\overline{G}_i = \overline{G}_i^\circ + \ln a_i \text{ 代入}$$

$$x_A d \ln a_A + x_B d \ln a_B = 0$$

$$x_A d\left[\frac{-x_B}{x_A} \phi\right] + x_B d \ln a_B = 0$$

$$d \ln a_B = \frac{x_A}{x_B} d\left[\frac{x_B}{x_A} \phi\right] = \frac{1}{r} d(r\phi)$$

$$d \ln a_B = d\phi + \frac{\phi}{r} dr = d\phi + \frac{\phi-1}{r} dr + \frac{1}{r} dr$$

$$d \ln \frac{a_B}{r} = d\phi + \frac{\phi-1}{r} dr$$

$$\underline{\underline{\ln \frac{a_B}{r} = \phi - \phi(r=0) + \int_0^r \frac{\phi-1}{r} dr \text{ 得證}}}$$

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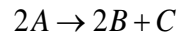
# 108 年中央化熱化反

## Problem 1

### **【Solution】**

令  $NOBr = A$  ,  $NO = B$  ,  $Br_2 = C$

Reaction :



For rate equation,

$$-r_A = \frac{-dC_A}{dt} = kC_A^2$$

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

將  $C_{A0} = 0.044$  ,  $t = 6.0$  ,  $k = 0.80$  代入 :

$$\frac{1}{C_A} - \frac{1}{0.044} = 0.80 \times 6, \quad \underline{\underline{C_A = 0.0363 (M)}}$$

(本題與 107 中央化熱化反選擇第 5 題相同)

## Problem 2

### **【Solution】**

For the size of the reactor,

$$\begin{aligned} V &= \frac{F_{A0}x_A}{-r_A} = \frac{F_{A0}x_A}{50C_A + 100C_B} = \frac{F_{A0}x_A}{150C_{A0}(1-x_A)} \\ &= \frac{300 \times 0.90}{150 \times \frac{60}{2}(1-0.90)} = \underline{\underline{0.6 (m^3)}} \end{aligned}$$

For the R/S ratio,

$$\phi\left(\frac{R}{S}\right) = \frac{50C_A}{100C_B} = \frac{50C_{A0}(1-x_A)}{100C_{A0}(1-x_A)} = \underline{\underline{\frac{1}{2}}}$$

(本題改編自 : Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 168, Problem 7.23.)

### **Problem 3**

#### **【Solution】**

For the reaction rate, by rate equation,

$$-r_A = kC_A^n$$

For the 1<sup>st</sup> CSTR,

$$\tau_1 = \frac{C_{A0} - C_{A1}}{kC_{A1}^n}$$

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

$$\tau_2 = \frac{C_{A1} - C_{A2}}{kC_{A2}^n}$$

相除：

$$\frac{\tau_1}{\tau_2} = \frac{C_{A0} - C_{A1}}{C_{A1} - C_{A2}} \times \left(\frac{C_{A2}}{C_{A1}}\right)^n = \frac{1}{4}$$
$$\frac{1 - 0.5}{0.5 - 0.125} \times \left(\frac{0.125}{0.5}\right)^n = \frac{1}{4}, \quad n = 1.20$$

For k, 數據代入 1<sup>st</sup> CSTR,

$$\tau_1 = 100 = \frac{1 - 0.5}{k \times 0.5^{1.20}}, \quad k = 0.01148$$

rate equation :  $\boxed{-r_A = 0.01148 C_A^{1.20}}$

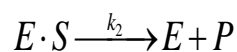
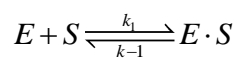
(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 149, Problem 6.15.)

### **Problem 4**

#### **【Solution】**

(1)

令



$$r_p = k_2[E \cdot S]$$

By PSSH,

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

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

By mass balance of enzyme,

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

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

$$r_p = \frac{k_1 k_2 [S][E_t]}{k_{-1} + k_2 + k_1 [S]} = \frac{v_{\max} [S]}{\underline{\underline{K_M + [S]}}} \left\{ \begin{array}{l} v_{\max} = k_2 [E_t] \\ K_M = \frac{k_{-1} + k_2}{k_1} \end{array} \right.$$

(2)

$$\left\{ \begin{array}{l} @ low [S] : r_p \approx \frac{v_{\max} [S]}{K_M} \rightarrow \underline{\underline{first order}} \\ @ high [S] : r_p \approx \frac{v_{\max} [S]}{[S]} = v_{\max} \rightarrow \underline{\underline{zeroth order}} \end{array} \right.$$

(3)

By the design equation of batch reactor,

$$\frac{-dN_s}{dt} = -r_s V = r_p V, \quad \frac{-d[S]}{dt} = -r_s$$

By the rate equation,

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

Combine,

$$\frac{-d[S]}{dt} = \frac{v_{\max} [S]}{K_M + [S]}$$

$$\int_{[S]}^{[S]_0} \frac{K_M + [S]}{v_{\max} [S]} d[S] = \int_0^t dt$$

$$t = \frac{K_M}{v_{\max}} \ln \frac{[S]_0}{[S]} + \frac{[S]_0 - [S]}{v_{\max}}$$

$$t = \frac{K_M}{v_{\max}} \ln \frac{1}{1-X} + \frac{[S]_0 X}{v_{\max}}$$

(本小題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 404~405,

Section 7.2.4.)

### **Problem 5**

#### **【Solution】**

By 1<sup>st</sup> law of thermodynamics (open system, steady state)

$$\Delta H + \frac{\Delta u^2}{2g_c} + \frac{\cancel{g}}{\cancel{g_c}} \cancel{z} = \cancel{\phi} + \cancel{W}$$

horizontal      insulated      no shaft work

$$\Delta H + \frac{1}{2}(u_2^2 - u_1^2) = 0$$

By mass balance of the nitrogen,

$$\dot{m}_1 = \dot{m}_2, \quad \rho_1 u_1 A = \rho_2 u_2 A$$

$$\therefore \rho = \frac{PM}{RT} \propto \frac{P}{T} \quad (M, R \text{ is constant})$$

$$\frac{P_1}{T_1} u_1 = \frac{P_2}{T_2} u_2, \quad u_2 = \frac{P_1 T_2}{P_2 T_1} u_1 \quad \text{代入}$$

$$\underbrace{C_p(T_2 - T_1)}_{\Delta H} + \frac{1}{2} u_1^2 \left[ \left( \frac{P_1 T_2}{P_2 T_1} \right)^2 - 1 \right] = 0$$

$$3.5 \times 8.314(T_2 - 323.15) + \frac{1}{2} \times 6^2 \left[ \left( \frac{700 T_2}{140 \times 323.15} \right)^2 - 1 \right] = 0, \quad \underline{\underline{T_2 = 309.57 \text{ (K)}}}$$

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### **Problem 6**

#### **【Solution】**

(1)

There are two statements on the second law,

(1) Clausius statement :

*It is not possible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a colder body to a hotter body.*

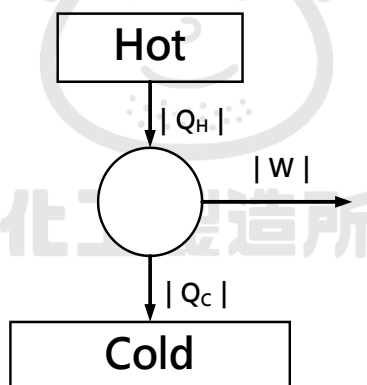
(2) Kelvin-Planck statement :

*It is not possible to construct a device operating in a cycle that results in no effect other than the production of work by transferring heat from a single body.*

The two statements can be summed up by :

$$\dot{S}_{gen} \geq 0$$

To prove the maximum efficiency, consider



By energy balance on the engine,

$$W = |Q_H| - |Q_C|$$

By entropy balance on the engine,

$$0 = \frac{|Q_H|}{T_H} - \frac{|Q_C|}{T_C} + \dot{S}_{gen}$$

$$|Q_C| = \frac{T_C}{T_H} |Q_H| + T_C \dot{S}_{gen}$$

Define efficiency,

$$\eta = \frac{W}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|} = 1 - \frac{T_C}{T_H} - \frac{T_C}{|Q_H|} \dot{S}_{gen}$$

To obtain maximum efficiency, let

$$\dot{S}_{gen} = 0 \text{ (reversible)}$$

$$\eta = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} = \frac{T_1 - T_2}{T_1}$$

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 106, Illustration 4.1.1/Illustration 4.1.2.)

(2)

If  $\alpha$  and  $\beta$  phases are in equilibrium,

$$d\underline{G}^\alpha = d\underline{G}^\beta$$

(題目應改為  $d\underline{G} = \underline{V}dP - \underline{S}dT$ )

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

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

$$\because \underline{\Delta S} = \frac{\underline{\Delta H}}{T}$$

$$\boxed{\frac{dP^{sat}}{dT} = \frac{\underline{\Delta H}}{T\underline{\Delta V}}}$$

For melting of ice,

$$\begin{cases} \underline{\Delta H} > 0 \\ \underline{\Delta V} < 0 \end{cases}$$

***The change of melting temperature is in inverse relationship with pressure, so the melting temperature of ice decreases with increasing pressure***

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 221.)



(3)

For process in a closed system with constant T and P,

by 1<sup>st</sup> law,

$$\frac{dU}{dt} = \dot{Q} - P \frac{dV}{dt} = \dot{Q} - \frac{d}{dt}(PV)$$

by entropy balance,

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

Combine,

$$\frac{dU}{dt} + \frac{d}{dt}(PV) - \frac{d}{dt}(TS) = -T \dot{S}_{gen}$$

$$\frac{dH}{dt} - \frac{d(TS)}{dt} = -T \dot{S}_{gen}$$

$$\left( \frac{dG}{dt} \right)_{T,P} = -T \dot{S}_{gen} \leq 0$$

*For self-assembling process, the configurational entropy should decrease. However, the process also releases heat to form bonds between monomers to compensate the loss of the entropy, that is,*

$$\Delta G = \Delta H - T \Delta S < 0$$

<0                      <0

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

P 289)

**Problem 7****【Solution】****(a)**

$$\ln(x_i r_i) = \frac{-18.804 \times 10^3}{8.314 \times 300} \times \left(1 - \frac{300}{273.15 + 80.2}\right)$$

$$x_i r_i = 0.320$$

For ideal solubility, let  $r_i = 1$

$$x_{i,ideal} = 0.320$$

**(b)**

By Clausius-Clapeyron equation,

$$\frac{d \ln P^{sub}}{dT} = \frac{\Delta H^{sub}}{RT^2}, \quad 2.303 \frac{d \log_{10} P^{sub}}{dT} = \frac{\Delta H^{sub}}{RT^2}$$

$$\frac{\Delta H^{sub}}{RT^2} = 2.303 \times \frac{3783}{T^2}$$

$$\Delta H^{sub} = 8.314 \times 2.303 \times 3783 = 72420.6 \text{ (J / mol)}$$

$$\Delta H^{vap} = \Delta H^{sub} - \Delta H^{fus} = 72420.6 - 18804 = 53616.6 \text{ (J / mol)}$$

$$\delta = \sqrt{\frac{\Delta H^{vap} - RT}{v_i}} = \sqrt{\frac{53616.6 - 8.314 \times 300}{124}} = \underline{\underline{20.3 \text{ (J / cm}^3\text{)}^{\frac{1}{2}}}}$$

(c)

令

$$\begin{cases} \text{naphthalene} = 1 \\ \text{neopentane} = 2 \end{cases}, \begin{cases} v_1 = 124 \\ v_2 = 124 \\ \delta_1 = 20.3 \\ \delta_2 = 12.7 \end{cases} @T=300K$$

By the result of (a)

$$r_i x_i = 0.320, \quad r_i = \frac{0.320}{x_i}$$

$$RT \ln \frac{0.320}{x_i} = v_1 \left( \frac{x_2 v_2}{x_1 v_1 + x_2 v_2} \right)^2 (\delta_1 - \delta_2)^2$$

$$8.314 \times 300 \ln \frac{0.320}{x_1} = 124 \left[ \frac{124(1-x_1)}{124x_1 + 124(1-x_1)} \right]^2 (20.3 - 12.7)^2, \quad \underline{\underline{x_1 = 0.0203}}$$

(本题可参考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*,

5th ed.; p 691~693, Illustration 12.1-1.)

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# 109 年中央化熱化反

## Problem 1

(a) Ans : (F)

**【Solution】**

Compressibility factor,

$$z = \frac{V_m}{V_m^\circ} \begin{cases} V_m = \text{measure molar volume} \\ V_m^\circ = \text{molar volume of ideal gas} \end{cases}$$

$$z \begin{cases} > 1, \text{repulsive force dominant, usually at high } P \text{ and } T \\ = 1, \text{ideal gas} \\ < 1, \text{attractive force dominant, usually at low } P \text{ and } T \end{cases}$$

(本題可參考：Atkins, P.; De Paula, J.; Keeler, J. *Atkins' Physical Chemistry*, 9th ed.; p 30.)

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 257, Figure 6.6-3.)

(b) Ans : (F)

**【Solution】**

$$\text{Residual volume, } V^R \equiv V - V^{ig} = V - \frac{RT}{P}$$

$$\begin{aligned} \lim_{P \rightarrow 0} V^R &= \lim_{P \rightarrow 0} \left( V - \frac{RT}{P} \right) = \lim_{P \rightarrow 0} RT \left( \frac{Z-1}{P} \right) \\ &= RT \lim_{P \rightarrow 0} \left( \frac{\partial Z}{\partial P} \right)_T \end{aligned}$$

$\frac{V^R}{RT}$  in the limits as  $P \rightarrow 0$  at given T equals to the *slope of Z vs. P isotherm* at

$P = 0$ , which is not in general zero

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 210.)

(c) Ans : (F)

【Solution】

Closed system is a system where there are no mass flows in or out

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 4th ed.; p 3.)

(d) Ans : (T)

【Solution】

Redlich / Kwong equation 提出的理論是根據 van der Waals 方程式增改而來

因此應比 van der Waals 方程式完備

(e) Ans : (F)

【Solution】

$$\underline{\theta}^{ex} = \sum_i x_i (\bar{\theta}_i - \theta_i^{IM}) , \text{ 故應為}$$

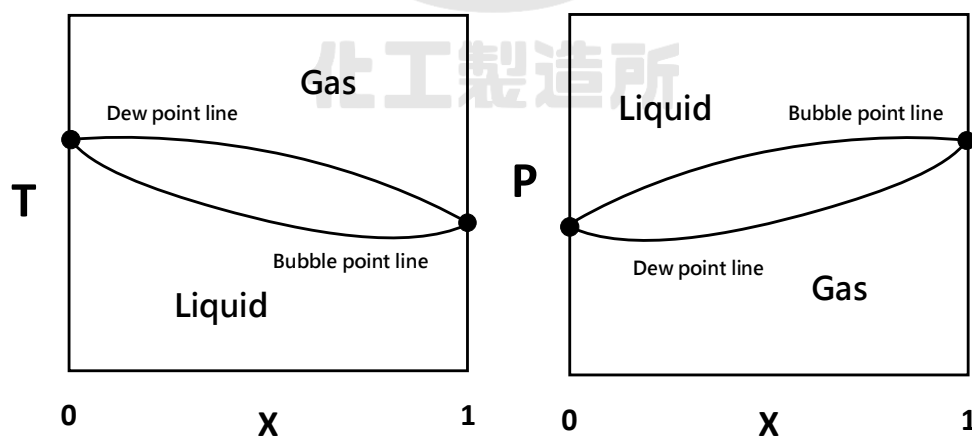
All *excess properties* are zero for an ideal solution.

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 4th ed.; p

411.)

(f) Ans : (F)

【Solution】



(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 4th ed.;

p 496~497.)

(g) **Ans : (F)**

**【Solution】**

$$\overline{G_i^E} = RT \ln r_i$$

For ideal solution,  $\overline{G_i^E} = 0$

$$r_i = 1$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 417.)

(h) **Ans : (F)**

**【Solution】**

**Lost work** is derived to solve to problem of irreversible process that it must be accompanied by some kind of work lost.

Every process must obey the 1<sup>st</sup> law of thermodynamics.

(i) **Ans : (F)**

**【Solution】**

The frictional effect can be described by the lost work,

$$\begin{cases} \dot{W}_s = \Delta\left[\left(H + \frac{g}{g_c} v^2 + \frac{g}{g_c} z\right)\right] - \dot{Q} \\ \dot{W}_{ideal} = \Delta\left[\left(H + \frac{g}{g_c} v^2 + \frac{g}{g_c} z\right)\right] - T \Delta(S \dot{m})_{fs} \end{cases}$$

$$\dot{W}_{lost} = T \Delta(S \dot{m})_{fs} - \dot{Q} = T \dot{S}_{gen} \geq 0$$

We can describe the effect of friction without violating the 2<sup>nd</sup> law.

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 185.)

(j) **Ans : (F)**

**【Solution】**

By Gibbs-Duhem equation for  $\mu_i$  at constant T, P

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

$$x_1 \frac{d \ln \hat{f}_1}{dx_1} + x_2 \frac{d \ln \hat{f}_2}{dx_1} = 0, \quad \frac{d \ln \hat{f}_1 / dx_1}{\hat{f}_1 / x_1} = \frac{d \ln \hat{f}_2 / dx_2}{\hat{f}_2 / x_2}$$

$$\lim_{x_1 \rightarrow 1} \frac{d \ln \hat{f}_1 / dx_1}{\hat{f}_1 / x_1} = \lim_{x_2 \rightarrow 0} \frac{d \ln \hat{f}_2 / dx_2}{\hat{f}_2 / x_2} = 1 \quad (\text{Henry's law})$$

$$\lim_{x_1 \rightarrow 1} \frac{d \ln \hat{f}_1}{dx_1} = \hat{f}_1 \quad (\text{Lewis-Randall rule})$$

當一成分滿足一個條件，另一成分就滿足另一個

因此可行性應該是相同的

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 433~434.)

(k) **Ans : (F)**

**【Solution】**

Fugacity coefficient,  $\phi_i$ , is the dimensionless ratio of pressure and fugacity. Thus fugacity coefficient is dimensionless.

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 395~396.)

(l) **Ans : (F)**

**【Solution】**

$$\lim_{P \rightarrow 0} \frac{f_i}{P} = 1, \text{ not infinity}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 395~396.)

(m) **Ans : (F)**

**【Solution】**

$$\begin{cases} M = \sum_i x_i \overline{M}_i \\ nM = \sum_i n_i \overline{M}_i \end{cases}$$

The term  $\overline{M}_i$  should be partial molar property of species i **in solution**.

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 383~384.)

(n) **Ans : (F)**

**【Solution】**

Steady-Flow(Steady-State) indicates that the accumulation term,  $\frac{d(mU)}{dt}$  is zero.

$$\Rightarrow \Delta \left[ \left( H + \frac{g}{g_c} v^2 + \frac{g}{g_c} z \right) \dot{m} \right]_{fs} = \dot{Q} + \dot{W}_s$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 51.)

(o) **Ans : (T)**

**【Solution】**

Simple Fluid(簡單流體)是指除了固體以外的物質(氣體與液體)的總稱，任何物質在  $P \rightarrow 0$  的狀況下應該接近液體/氣體的行為。



(p) Ans : (F)

**【Solution】**

Different types of ideal gas have different values of  $C_p$

$$\begin{cases} \text{monatomic} : C_p = 2.5R \\ \text{diatomic} : C_p = 3.5R \end{cases}$$

(q) Ans : (F)

**【Solution】**

Work is a path function, dependent on the path of the process.

(r) Ans : (F)

**【Solution】**

Work, by definition is

$$dW = Fd\ell$$

If the work is accomplished by change of volume of a fluid,

$$dW = -PAd\frac{V}{A} = -PdV \text{ (才是题目的形式)}$$

(本题可参考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 8~9.)

(s) Ans : (F)

**【Solution】**

For an isolated system, by entropy balance,

$$\frac{dS}{dt} = \sum_k \cancel{\dot{M}_k S_k} + \sum_{\text{adiabatic}} \cancel{\frac{\dot{Q}}{T}} + \dot{S}_{gen}, \quad \frac{dS}{dt} = \dot{S}_{gen} \geq 0$$

Therefore, for an isolated system, the entropy of the system is not always constant; otherwise, it may increase as the time passes by.

(t) **Ans : (F)**

**【Solution】**

For heat to be represented as  $TdS$ , the process must be reversible, that is,

$$dQ_{rev} = TdS^t$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 168.)

(u) **Ans : (F)**

**【Solution】**

First, by the 1<sup>st</sup> law of thermodynamics for reversible process

$$dU = dQ_{rev} + dW_{rev} = dQ_{rev} - PdV$$

$$dH = dU + d(PV) = dQ_{rev} + VdP$$

By the 2<sup>nd</sup> law of thermodynamics,

$$dQ_{rev} = TdS \text{ 代入}$$

$$dH = TdS + VdP$$

Despite the fact that the equation is derived for the special case of a reversible process. However, it contains only properties of the system. Properties depend on state alone, not on the kind of process that leads to the state. Therefore, ***the equation is not restricted in application to the reversible process.***

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 199~200.)

(v) **Ans : (F)**

**【Solution】**

The second law of thermodynamics states that "no apparatus can operate in a **cyclic process** to convert heat **completely** into work without producing other effects."

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 160.)

(w) Ans : (F)

**【Solution】**

The entropy change should be equal to or larger than zero, not necessarily zero.

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;  
p 102~103.)

(x) Ans : (F)

**【Solution】**

The relation is applicable when

- (1) *The working fluid is ideal gas*
- (2) *Heat capacities are constant*
- (3) *Adiabatic and reversible process*

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical  
Engineering Thermodynamics*, 7th ed.; p 77.)

(y) Ans : (F)

**【Solution】**

For negative deviation

$$r_i = \frac{y_i P}{x_i P_i^{sat}} < 1$$

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## Problem 2

### 【Solution】

(a)

$$\begin{cases} \text{liquid phase: Flory-Huggins model applicable} \\ \text{gas phase: ideal solution} \end{cases}$$

For vapor-liquid equilibrium,

$$\begin{cases} y_1 P = x_1 r_1 P_1^{sat} \\ y_2 P = x_2 r_2 P_2^{sat} \end{cases}$$

where  $r_1, r_2$  are activity coefficients based on Flory-Huggins model

$$\begin{cases} \ln r_1 = \ln \frac{\phi_1}{x_1} + (1 - \frac{1}{m})\phi_2 + \chi\phi_2^2 \\ \ln r_2 = \ln \frac{\phi_2}{x_2} + (m-1)\phi_1 + m\chi\phi_1^2 \end{cases}, \begin{cases} 1 = \text{polymer} \\ 2 = \text{solvent} \end{cases}$$
$$\begin{cases} \chi = \text{Flory parameter} \\ m = \frac{v_1}{v_2} \\ v_1, v_2 = \text{some measure of the volume of species 1 or 2} \\ \phi_1 = \frac{x_1 v_1}{x_1 v_1 + x_2 v_2} = \frac{x_1}{x_1 + m x_2} = \text{volume fraction of 1} \\ \phi_2 = \frac{x_2 v_2}{x_1 v_1 + x_2 v_2} = \frac{m x_2}{x_1 + m x_2} = \text{volume fraction of 2} \end{cases}$$

In polymer-solution system,  $v_2 = 1$  because there is one segment for one solvent molecule.

By Antoine equation,  $P_1^{sat} = \exp[A + \frac{B}{C+T}]$

For bubble-point,  $x_1 = y_1$

$$P = r_1 P_1^{sat} = \exp\left[\frac{\phi_1}{x_1} + (1 - \frac{1}{m})\phi_2 + \chi\phi_2^2 + A + \frac{B}{C+T}\right]$$

(本题可参考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

p 454.)

(b)

令兩 liquid 相分別為 I 與 II，兩成分為 1 與 2

For liquid-liquid equilibrium,

$$x_1^I r_1^I = x_1^{II} r_1^{II} \quad , \quad x_2^I r_2^I = x_2^{II} r_2^{II}$$

$$\ln r_1 = \ln \frac{\phi_1}{x_1} + \left(1 - \frac{1}{m}\right) \phi_2 + \chi \phi_2^2$$

$$\ln r_2 = \ln \frac{\phi_2}{x_2} - (m-1) \phi_1 + m \chi \phi_1^2$$

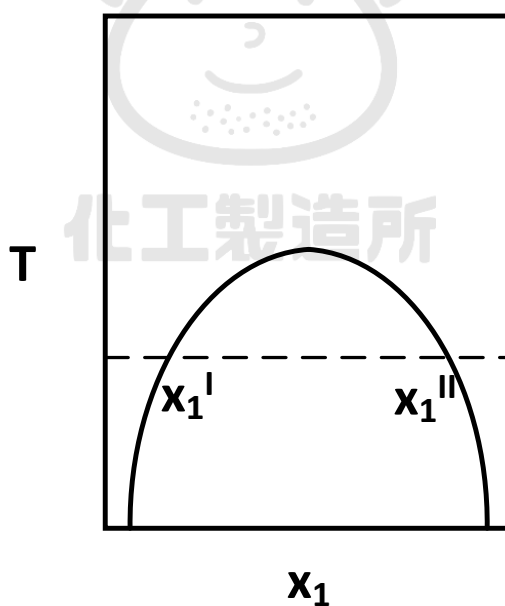
$$\chi = \chi(T)$$

Therefore,

$$\ln\left(\frac{\phi_1^I x_1^I}{\phi_1^{II} x_1^{II}}\right) + \left(1 - \frac{1}{m}\right)(\phi_2^I x_2^I - \phi_2^{II} x_2^{II}) + \chi[(\phi_2^I x_2^I)^2 - (\phi_2^{II} x_2^{II})^2] = 0$$

$$\ln\left(\frac{\phi_2^I x_2^I}{\phi_2^{II} x_2^{II}}\right) - (m-1)(\phi_1^I x_1^I - \phi_1^{II} x_1^{II}) + \chi[(\phi_1^I x_1^I)^2 - (\phi_1^{II} x_1^{II})^2] = 0$$

可解出  $T - x_1^I - x_1^{II}$  關係，決定 immiscibility gap

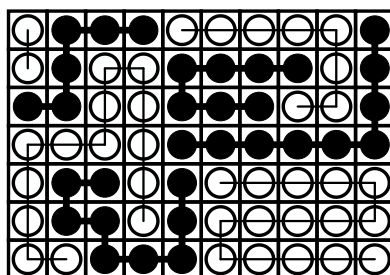


(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

p 632~633, Illustration 11.2-6.)

※Flory Huggins theory 主要可用於高分子-高分子溶液系統、高分子-溶劑系統等等，是最簡單能描述高分子系統熱力學行為之方程式，其理論大致如下：

假設高分子 1 單條分子鏈有  $v_1$  個單體單元(即聚合度，degree of polymerization，在 Sandler 原文書內並沒有特別定義，不過有些高分子原文書是利用此參數做推導)，且高分子 2 單條分子鏈有  $v_2$  個單體單元，若假設兩條高分子鏈的單體單元佔的單位體積相同(即同樣都佔一格)，則：



(實心球為高分子 1 單體單元、空心為 2 單體單元)

由上圖可知，我們知道一條高分子鏈的長度，就是有幾顆球串在一起的長度(通常會假設同種高分子長度相同以簡化，只是這裡畫得比較不規律，較符合真實情況)而以同種高分子而言，其所有高分子鏈所佔的體積，正好就是該高分子條數乘以一條高分子有多少單體單元，也就是為什麼在體積分率  $\phi$  計算上，會有  $x_1 v_1$  或  $x_2 v_2$  的出現。且理所當然，若是高分子-溶劑系統，代表溶劑的  $v$  數值應為 1，因為溶劑是以單一個分子存在，不會有兩三個串在一起的情況。

利用此種模型，我們可以根據統計熱力學觀點，即  $S = k_B \ln N$  的想法，再進行一系列的假設與推導後，就能夠推導出在一高分子系統中，其混合溶液之自由能等熱力學參數，以 Sandler 所介紹的版本為例，溶液系統之 Excess Gibbs energy 為：

$$\frac{G^{ex}}{RT} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \chi(x_1 + m x_2) \phi_1 \phi_2$$

而值得注意的是，此表示式有  $\chi$  (音同“開”)的參數，主要用於代表溫度對系統的相容性的影響。

一般來說， $\chi$  越小，代表系統越易互溶； $\chi$  越大，代表系統越易相分離，此參數可以用實驗得到。礙於篇幅，在這裡無法介紹太多，若有興趣可以自行查閱高分子相關書籍。

**Problem 3****【Solution】**

(a)

$$\Delta G = \Delta H - T\Delta S$$

$$-30.8 = -13.1 - (273.15 + 25)\Delta S$$

$$\underline{\underline{\Delta S = 0.059 \text{ (kJ / mol} \cdot \text{K)}}}$$

(b)

$$\therefore \ln K = \frac{-\Delta G}{RT}$$

$$\Delta H = -RT^2 \frac{d(\frac{\Delta G}{RT})}{dT} = RT^2 \frac{d \ln K}{dT}$$

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} = \frac{(\Delta H + \int_{T_0}^T \Delta C_p dT)}{RT^2}$$

$$\ln \frac{K_{(298.15)}}{K_{(T)}} = \frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right)$$

For T=298.15(K)

$$K_{(298.15)} = e^{\frac{-\Delta G}{RT}} = e^{\frac{30.8 \times 10^3}{8.314 \times 298.15}} = 2.49 \times 10^5$$

$$\begin{cases} K_{(30^\circ\text{C})} = 2.28 \times 10^5 \\ K_{(40^\circ\text{C})} = 1.93 \times 10^5 \end{cases}$$

$$K = \frac{M_{WA}}{M_W M_A} = \frac{M_A x_A}{M_A^2 (1-x_A)^2} \begin{cases} @ 30^\circ\text{C} \Rightarrow x_A = 0.81, (1-x_A) = 0.19 \\ @ 40^\circ\text{C} \Rightarrow x_A = 0.79, (1-x_A) = 0.21 \end{cases}$$

(※本題題目有誤，應為  $\Delta_{\text{bnd}} G = -RT \ln K$ ，若照題目所給的列式應該會算不出正常的數字)

### **Problem 4**

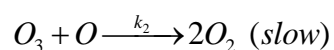
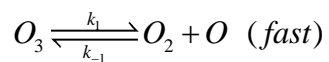
#### **【Solution】**

(a)

Overall order of reaction=2-1=1

(b)

Mechanism :



By rate-determining-step method,

$$-r_{O_3} = k_2 [O_2][O]$$

$$\therefore \frac{[O_2][O]}{[O_3]} = \frac{k_1}{k_{-1}}$$

$$[O] = \frac{k_1}{k_{-1}} \frac{[O_3]}{[O_2]} = K \frac{[O_3]}{[O_2]} \quad \text{代回}$$

$$-r_{O_3} = k_2 K [O_3]^2 [O_2]^{-1} = k [O_3]^2 [O_2]^{-1}$$

Test of the mechanism,

$$\begin{cases} \text{with } [O_3] \gg [O_2], \text{ check } -r_{O_3} \text{ vs. } [O_2] \\ \text{with } [O_3] \ll [O_2], \text{ check } -r_{O_3} \text{ vs. } [O_3] \end{cases}$$



### **Problem 5**

#### **【Solution】**

For mixed flow reactor, design equation,

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

By rate equation,

$$-r_A = \frac{0.1C_A}{1+0.5C_A} = \frac{0.1C_{A0}(1-x_A)}{1+0.5C_{A0}(1-x_A)}$$

Combine,

$$V = \frac{\frac{F_{A0}x_A}{0.1C_{A0}(1-x_A)}}{\frac{1+0.5C_{A0}(1-x_A)}{1+0.5 \times 2(1-0.95)}} = \frac{25 \times 2 \times 0.95}{0.1 \times 2 \times (1-0.95)} = \underline{\underline{4987.5 \text{ (L)}}}$$

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 114, Problem 5.9.)

### **Problem 6**

#### **【Solution】**

For the reaction rate, by the rate equation,

$$-r_A = kC_A^n$$

For the 1<sup>st</sup> CSTR,

$$\tau_1 = \frac{C_{A0} - C_{A1}}{kC_{A1}^n}$$

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

$$\tau_2 = \frac{C_{A1} - C_{A2}}{kC_{A2}^n}$$

相除：

$$\frac{\tau_1}{\tau_2} = \frac{C_{A0} - C_{A1}}{C_{A1} - C_{A2}} \times \frac{C_{A2}^n}{C_{A1}^n} = \frac{1}{2}$$
$$\frac{1-0.5}{0.5-0.25} \times \left(\frac{0.25}{0.5}\right)^n = \frac{1}{2}, \quad n = 2$$

$$\text{Rate equation: } \underline{\underline{-r_A = kC_A^2}}$$

For k, 數據代入 1<sup>st</sup> CSTR,

$$\tau_1 = 96 = \frac{1-0.5}{k \times 0.5^2}, \quad k = 0.0208$$

$$\text{rate equation : } \boxed{-r_A = 0.0208 C_A^2}$$

(本題與中央 108 年化熱化反第 3 題雷同.)

### **Problem 7**

#### **【Solution】**

(a)

Possible mechanism : (Dual-Site Mechanism)

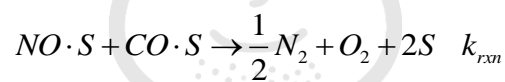
Adsorption of NO :



Adsorption of CO :



Surface reaction :

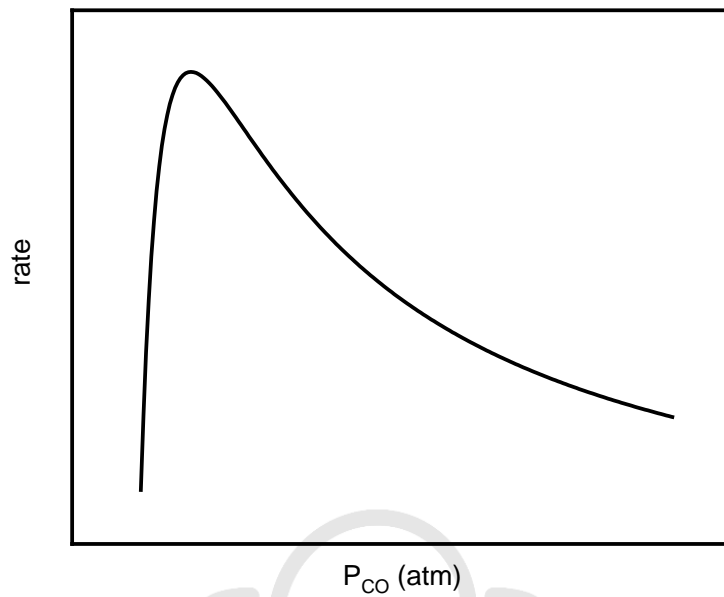


(b)

分子出現 NO 與 CO , surface reaction is rate-determining

(c)

將  $-r'_N$  與  $P_{CO}$  趨勢畫出(假定  $k, K_1, K_2, P_{NO} = 1$ )



則的確在一定的限度內( $P_{CO}^{cri}$ )，增加 CO 之分壓可以增加反應速率，並在  $P_{CO}^{cri}$  達成最大值，但超過此值以後反應速率即下降，無法達成效果。

# 110 年中央化熱化反

## 一、單選題

(1) Ans : (D)

(2) Ans : (C)

**【Solution】**

For first order reaction,

$$\ln \frac{C_A}{C_{A0}} = -kt$$

$$\ln \frac{1}{2} = -kt_{\frac{1}{2}}, \quad t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

(3) Ans : (B)

(4) Ans : (B)

(5) Ans : (D)

(6) Ans : (D)

(7) Ans : (C)

$$\begin{cases} M_T < 0.4, \text{ diffusion free} \\ M_T > 0.4, \text{ strong pore diffusion} \end{cases}$$

(本題可參考：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 388.)

(8) Ans : (B)

$$Q = \frac{P_{NO_2}^2 \downarrow \downarrow}{P_{N_2O_2} \downarrow}, \quad Q < K, \quad \text{反應傾向右邊}$$

(9) Ans : (B)

(10) Ans : (B)

(11) Ans : (C)

(12) Ans : (B)

$$100\% \xrightarrow{t_{1/2}} 50\% (x_A = 0.5) \xrightarrow{t_{1/2}} 25\% (x_A = 0.75)$$

$$t = 2t_{1/2} = 2 \times 12 = 24 \text{ (mins)}$$

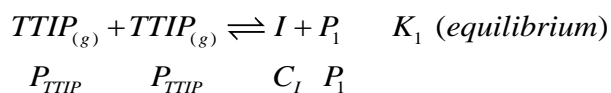
## 二、計算題

### Problem 1

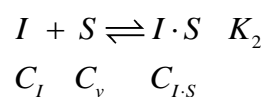
#### 【Solution】

(a)

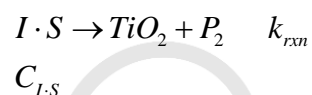
First-step reaction :



Adsorption of I :



Surface reaction :



∵ Surface reaction is rate-determining,

$$r = k_{rxn} C_{I \cdot S}$$

For  $C_{I \cdot S}$ , by site balance,

$$C_t = C_{I \cdot S} + C_v = C_v (1 + K_2 C_I)$$

$$C_v = \frac{C_t}{(1 + K_2 C_I)}, \quad C_{I \cdot S} = \frac{K_2 C_t C_I}{(1 + K_2 C_I)}$$

For  $C_I$ , by the first-step reaction,

$$K_1 = \frac{P_1 C_I}{P_{TTIP}^2}, \quad C_I = \frac{P_{TTIP}^2 K_1}{P_1}$$

代入

$$r = \frac{KK_1 P_{TTIP}^2}{P_1 + K_1 K_2 P_{TTIP}^2}$$

(b)

At 200°C (lower temperature)

(1) With low  $P_{TTIP}$ ,

$$P_1 \gg K_1 K_2 P_{TTIP}^2$$
$$r \propto \frac{K K_1 P_{TTIP}^2}{P_1} \propto P_{TTIP}^2$$

(2) With high  $P_{TTIP}$ ,

$$P_1 \ll K_1 K_2 P_{TTIP}^2$$
$$r \propto \frac{K K_1 P_{TTIP}^2}{K_1 K_2 P_{TTIP}^2} \propto P_{TTIP}^0$$

(3) @300°C

If  $K_2$  is very small, (adsorption is weak at higher temperature)

$$P_1 \gg K_1 K_2 P_{TTIP}^2$$
$$r \propto \frac{K K_1 P_{TTIP}^2}{P_1} \propto P_{TTIP}^2$$

(Second-order over the entire pressure range)

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

5th ed.; p 488, Problem 10-15A.)

(本題與 104 年台科化熱化反-化工動力學部分 Problem 2 雷同)

## **Problem 2**

### **【Solution】**

Consider there are  $C$  components distributed among  $\pi$  phases, there are

$$(C+1)\pi \text{ variables}$$

Reaching equilibrium, each of the phases may have the same T, P

$$T^I = T^{II} = T^{III} \dots = T^{\pi}$$

$$P^I = P^{II} = P^{III} \dots = P^{\pi}$$

Each of T and P provides  $(\pi - 1)$  restrictions

For each species, the partial Gibbs free energy will be equal among all the phases,

$$\bar{G}_1^I = \bar{G}_1^{II} = \bar{G}_1^{III} \dots = \bar{G}_1^{\pi}$$

...

$$\bar{G}_C^I = \bar{G}_C^{II} = \bar{G}_C^{III} \dots = \bar{G}_C^{\pi}$$

Providing  $C(\pi - 1)$  restrictions

$$F(\text{degree of freedom}) = (\pi + 1)P - 2(\pi - 1) - C(\pi - 1) = C - \pi + 2$$

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*,

5th ed.; p 404-405.)

化工製造所

### **Problem 3**

#### **【Solution】**

(a)

At steady state, by mass balance,

$$\rho_1 A_1 u_1 = \rho_2 A_2 u_2 \quad , \quad A_1 = A_2$$

$\therefore$  *incompressible*

$$\rho_1 = \rho_2$$

$$\underline{\underline{u_1 = u_2}}$$

(b)

$$\therefore dS = C_p \frac{dT}{T} - \cancel{\beta} V dP = C_p \frac{dT}{T}$$

*incompressible*

By entropy balance,

$$dS = \frac{C_p}{T} dT = \dot{S}_{gen} > 0 \text{ (irreversible)}$$

$$dT > 0 \quad , \quad \boxed{T_1 < T_2}$$

(c)

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

$$\Delta H + \frac{\Delta u^2}{2g_c} + \cancel{\frac{g}{g_c} \Delta z} = \cancel{\dot{Q}}_{adiabatic} + \dot{W}$$

$u_1 = u_2$

$$dH = C_p dT + (1 - \cancel{\beta} T) V dP = C_p dT + V dP = 0$$

*incompressible*

$$\therefore dT > 0 \quad , \quad dP < 0 \quad , \quad \boxed{P_1 > P_2}$$

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 259, Example 7.1.)



**Problem 4****【Solution】**

(a)

Assume,

$$\begin{cases} \text{gas phase: ideal gas} \\ \text{liquid phase: ideal solution} \end{cases}, \text{ Raoult's law is applicable}$$

For perfluoro-n-heptane,

$$y_1 P = x_1 P_1^{sat}$$

For n-heptane,

$$y_2 P = x_2 P_2^{sat}$$

$$y_1 \times 0.6 = 0.6 \times 0.1101 \Rightarrow y_1 = 0.11$$

$$y_2 \times 0.6 = 0.4 \times 0.0601 \Rightarrow y_2 = 0.04$$

 $y_1 + y_2 \neq 1$  , ideal solution model is not applicable

(b)

$$\because \underline{G}^{ex} = (x_1 \underline{V}_1 + x_2 \underline{V}_2) \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 \begin{cases} \Phi_1 = \frac{x_1 \underline{V}_1}{x_1 \underline{V}_1 + x_2 \underline{V}_2} \\ \Phi_2 = \frac{x_2 \underline{V}_2}{x_1 \underline{V}_1 + x_2 \underline{V}_2} \end{cases}$$

$$\begin{aligned} RT \ln r_1 &= \frac{\partial}{\partial n_1} (n \underline{G}^{ex})_{T,P,n_2} = \frac{\partial}{\partial n_1} \left[ \frac{(n_1 \underline{V}_1 + n_2 \underline{V}_2) n_1 \underline{V}_1 n_2 \underline{V}_2}{(n_1 \underline{V}_1 + n_2 \underline{V}_2)^2} (\delta_1 - \delta_2)^2 \right]_{T,P,n_2} \\ &= \frac{\partial}{\partial n_1} \left[ \frac{n_1 \underline{V}_1 n_2 \underline{V}_2}{(n_1 \underline{V}_1 + n_2 \underline{V}_2)} (\delta_1 - \delta_2)^2 \right]_{T,P,n_2} = \frac{n_2 \underline{V}_1 \underline{V}_2 (n_1 \underline{V}_1 + n_2 \underline{V}_2) - \underline{V}_1 n_1 \underline{V}_1 n_2 \underline{V}_2}{(n_1 \underline{V}_1 + n_2 \underline{V}_2)^2} (\delta_1 - \delta_2)^2 \\ &= \frac{\cancel{n_1 \underline{V}_1^2 n_2 \underline{V}_2} + n_2^2 \underline{V}_2^2 \underline{V}_1 - \cancel{n_1 \underline{V}_1^2 n_2 \underline{V}_2}}{(n_1 \underline{V}_1 + n_2 \underline{V}_2)^2} (\delta_1 - \delta_2)^2 = \underline{V}_1 \left[ \frac{n_2 \underline{V}_2}{n_1 \underline{V}_1 + n_2 \underline{V}_2} \right]^2 (\delta_1 - \delta_2)^2 \\ &= \underline{V}_1 \left[ \frac{x_2 \underline{V}_2}{x_1 \underline{V}_1 + x_2 \underline{V}_2} \right]^2 (\delta_1 - \delta_2)^2 = \underline{V}_1 \Phi_2^2 (\delta_1 - \delta_2)^2 \end{aligned}$$

$$\boxed{RT \ln r_1 = \underline{V}_1 \Phi_2^2 (\delta_1 - \delta_2)^2}$$

同理

$$\begin{aligned}
 RT \ln r_2 &= \frac{\partial}{\partial n_2} (nG^{ex})_{T,P,n_1} = \frac{\partial}{\partial n_2} \left[ \frac{(n_1 \underline{V}_1 + n_2 \underline{V}_2) n_1 \underline{V}_1 n_2 \underline{V}_2}{(n_1 \underline{V}_1 + n_2 \underline{V}_2)^2} (\delta_1 - \delta_2)^2 \right]_{T,P,n_1} \\
 &= \frac{\partial}{\partial n_2} \left[ \frac{n_1 \underline{V}_1 n_2 \underline{V}_2}{(n_1 \underline{V}_1 + n_2 \underline{V}_2)} (\delta_1 - \delta_2)^2 \right]_{T,P,n_1} = \frac{n_1 \underline{V}_1 \underline{V}_2 (n_1 \underline{V}_1 + n_2 \underline{V}_2) - \underline{V}_2 n_1 \underline{V}_1 n_2 \underline{V}_2}{(n_1 \underline{V}_1 + n_2 \underline{V}_2)^2} (\delta_1 - \delta_2)^2 \\
 &= \frac{n_1^2 \underline{V}_1^2 \underline{V}_2 + n_1 \underline{V}_1 n_2 \underline{V}_2^2 - n_1 \underline{V}_1 n_2 \underline{V}_2^2}{(n_1 \underline{V}_1 + n_2 \underline{V}_2)^2} (\delta_1 - \delta_2)^2 = \underline{V}_2 \left[ \frac{n_1 \underline{V}_1}{n_1 \underline{V}_1 + n_2 \underline{V}_2} \right]^2 (\delta_1 - \delta_2)^2 \\
 &= \underline{V}_2 \left[ \frac{x_1 \underline{V}_1}{x_1 \underline{V}_1 + x_2 \underline{V}_2} \right]^2 (\delta_1 - \delta_2)^2 = \underline{V}_2 \Phi_1^2 (\delta_1 - \delta_2)^2
 \end{aligned}$$

$$RT \ln r_2 = \underline{V}_2 \Phi_1^2 (\delta_1 - \delta_2)^2$$

(c)

$$\begin{aligned}
 r_1 &= \exp \left[ \frac{\underline{V}_1}{RT} \Phi_2^2 (\delta_1 - \delta_2)^2 \right] = \exp \left[ \frac{226}{1.987 \times 298} \left( \frac{148 \times 0.4}{226 \times 0.6 + 148 \times 0.4} \right)^2 (12.3 - 7.4)^2 \right] = 2.331 \\
 r_2 &= \exp \left[ \frac{\underline{V}_2}{RT} \Phi_1^2 (\delta_1 - \delta_2)^2 \right] = \exp \left[ \frac{148}{1.987 \times 298} \left( \frac{226 \times 0.6}{226 \times 0.6 + 148 \times 0.4} \right)^2 (12.3 - 7.4)^2 \right] = 18.318
 \end{aligned}$$

代回

$$\begin{cases} y_1 P = x_1 r_1 P_1^{sat} \\ y_2 P = x_2 r_2 P_2^{sat} \end{cases}, \begin{cases} y_1 \times 0.6 = 2.331 \times 0.6 \times 0.1101 \rightarrow y_1 = 0.257 \\ y_2 \times 0.6 = 18.318 \times 0.4 \times 0.0601 \rightarrow y_2 = 0.734 \end{cases}$$

$$y_1 + y_2 = 0.9906 \approx 1$$

(d)

根據 A 與 C 小題結果，因 regular solution model (c 小題結果) 之  $y_1 + y_2$  較接近

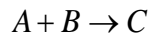
1，所以 regular solution model 較為合適

# 111 年中央化熱化反

## Problem 1

### **【Solution】**

By the unit of the reaction rate constant, we can obtain the reaction order of the reaction is 1, and assume the rate law is,



$$-r_A = kC_A$$

To produce  $200 \times 10^6$  pounds of EG (C) per year, we may need the reactant A flow rate,

$$F_{A0} = \frac{F_C}{x_A} = \frac{200 \times 10^6}{\frac{365 \times 24 \times 60 \times 62}{0.8}} = 7.67 \text{ (lbmol / min)}$$

(a) For CSTR, by design equation,

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

$\therefore$  The volumetric flow rate of water is the same as the reactant solution,

$$C_{A0} = \frac{C_{A0,i}}{2} = \frac{1}{2} = 0.5 \text{ (lbmol / ft}^3\text{)}$$

$$V = \frac{7.67 \times 0.8}{0.311 \times 0.5(1-0.8)} = 197.3 \text{ (ft}^3\text{)}$$

(b)

If the feed stream is divided equally, entering each of the CSTR

$$F_{A0,1} = \frac{F_{A0}}{2}$$

For CSTR, by design equation,

$$V = \frac{F_{A0,1}x_A}{-r_A} = \frac{F_{A0,1}x_A}{kC_{A0}(1-x_A)} = \frac{\frac{7.67}{2}x_A}{0.311 \times 0.5(1-x_A)} = 800 \times 0.133$$

$$\underline{\underline{x_A = 0.812}}$$

(c)

For the first CSTR,

$$V = \frac{F_{A0}x_{A,1}}{kC_{A0}(1-x_{A,1})}$$
$$800 \times 0.133 = \frac{7.67x_{A,1}}{0.311 \times 0.5(1-x_{A,1})}, \quad x_{A,1} = 0.683$$

For the second CSTR,

$$V = \frac{F_{A0}(x_{A,2} - x_{A,1})}{kC_{A0}(1-x_{A,2})}$$
$$800 \times 0.133 = \frac{7.67(x_{A,2} - 0.683)}{0.311 \times 0.5(1-x_{A,2})}, \quad \underline{\underline{x_{A,2} = 0.899}}$$

(本小題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 163~167, Example 4-2.)

## **Problem 2**

### **【Solution】**

(a) The reaction is elementary, so the rate law is,

$$-r_A = kC_A, \quad \underline{\underline{\text{1st-order reaction}}}$$

For the reaction constant, k,

$$k_{27} = \frac{-r_A}{C_A} = \frac{2.5 \times 10^{-6}}{0.025} = \underline{\underline{1 \times 10^{-4} \text{ (min}^{-1}\text{)}}}$$
$$k_{87} = \frac{-r_A}{C_A} = \frac{0.0015}{0.05} = \underline{\underline{0.03 \text{ (min}^{-1}\text{)}}}$$

For the activation energy, consider run 2 and run 3,

$$\frac{-r_{A,2}}{-r_{A,3}} = \frac{k_{27}C_A}{k_{87}C_A} = \frac{k_{27}}{k_{87}} = e^{\frac{-E_a}{R}(\frac{1}{T_2} - \frac{1}{T_3})}$$
$$\frac{5.0 \times 10^{-6}}{0.0015} = e^{\frac{-E_a}{8.314}(\frac{1}{273.15+27} - \frac{1}{273.15+87})}, \quad \underline{\underline{E_a = 85436.5 \text{ (J / mol)}}}$$

(b)

By the design equation of PFR,

$$V = \int_0^{x_A} \frac{F_{A0} dx_A}{k_{127} \frac{C_{A0}(1-x_A)}{(1+\varepsilon x_A)}}$$

$$\varepsilon = \delta y_{A0} = (1+2-1) \times 1 = 2$$

For  $k_{127}$ ,

$$\frac{k_{127}}{k_{27}} = e^{\frac{-85436.5}{8.314} \left( \frac{1}{273.15+127} - \frac{1}{273.15+27} \right)}, \quad k_{127} = 0.520 \text{ (min}^{-1}\text{)}$$

代入：

$$\begin{aligned} V &= \int_0^{x_A} \frac{F_{A0} dx_A}{k_{127} C_{A0} \frac{(1-x_A)}{(1+2x_A)}} = \int_0^{x_A} \frac{F_{A0} dx_A}{k_{127} \frac{P_{A0}}{RT} \frac{(1-x_A)}{(1+2x_A)}} \\ &= \int_0^{0.9} \frac{2 dx_A}{0.520 \times \frac{5}{0.082 \times (273.15+127)} \times \frac{(1-x_A)}{(1+2x_A)}} = \underline{\underline{128.9 \text{ (L)}}} \end{aligned}$$

### Problem 3

#### 【Solution】

(a)

Assume 1 = anthracene, 2 = ethylene

By the question statement,

$$f_1^S(T, P) = \overline{f_1^F}(T, P, \underline{y})$$

$$P_{sub,1} \exp\left[\frac{V_1^S(P - P_{sub,1})}{RT}\right] = y_1 P \overline{\Phi_1}$$

Assume the fluid phase can be described by ideal-gas law,  $\overline{\Phi_1} = 1$

$$1.78 \times 10^{-3} \exp\left[\frac{\frac{1}{1.28} \times 178 \times 10^{-6} (10 \times 10^5 - 1.78 \times 10^{-3})}{8.134 \times (273.15 + 25)}\right] = y_1 \times 10 \times 10^5$$

$$\underline{\underline{y_1 = 1.88 \times 10^{-9}}}$$

(178 為 anthracene 之分子量)

(b)

By the question statement,

For the  $(2\sum_{j=1}^n y_j B_{ij} - B_{mixt})$  term,

$$\begin{aligned}(2\sum_{j=1}^n y_j B_{ij} - B_{mixt}) &= (2\sum_{j=1}^2 y_j B_{ij} - B_{mixt}) \\ &= 2y_1 B_{i1} + 2y_2 B_{i2} - B_{mixt} = 2B_{i2} - B_{ETH}\end{aligned}$$

For  $B_{i2}$ ,

$$\begin{aligned}B_{i2} &= b_{i2} - \frac{a_{i2}}{RT} = 0.5(b_1 + b_2) - \frac{\sqrt{a_1 a_2}}{RT} \\ &= 0.5\left(\frac{8.314 \times 877.75}{8 \times 3.39 \times 10^6} + \frac{8.314 \times 282.35}{8 \times 5.04 \times 10^6}\right) - \frac{\sqrt{\frac{27^2}{64^2} \times 8.314^4 \left(\frac{877.75^2 \times 282.35^2}{3.39 \times 5.04 \times 10^{12}}\right)}}{8.314 \times 298.15} = -5.416 \times 10^{-4}\end{aligned}$$

For  $B_{ETH}$

$$\begin{aligned}B_{ETH} &= b_{22} - \frac{a_{22}}{RT} = b_2 - \frac{a_2}{RT} \\ &= \frac{8.314 \times 282.35}{8 \times 5.04 \times 10^6} - \frac{27}{64} \times \frac{8.314^2 \left(\frac{282.35^2}{5.04 \times 10^6}\right)}{8.314 \times 298.15} = -1.278 \times 10^{-4} \\ 2B_{i2} - B_{ETH} &= 2 \times (-5.416 \times 10^{-4}) + 1.278 \times 10^{-4} = -9.555 \times 10^{-4} \\ \Phi_1 &= \exp[-9.555 \times 10^{-4} \times \frac{10 \times 10^5}{8.314 \times 298.15}] = 0.680\end{aligned}$$

代回：

$$\begin{aligned}1.78 \times 10^{-3} \exp\left[\frac{\frac{1}{1.28} \times 178 \times 10^{-6} (10 \times 10^5 - 1.78 \times 10^{-3})}{8.134 \times (273.15 + 25)}\right] &= y_i \times 10 \times 10^5 \times 0.68 \\ \underline{\underline{y_1}} &= \underline{\underline{2.768 \times 10^{-9}}}\end{aligned}$$

#### **Problem 4**

##### **【Solution】**

(a)

For two phases are able to coexist,

$$\underline{\underline{\left(\frac{\partial^2 G}{\partial x_i^2}\right) > 0}}$$

where i denotes the fraction of either  $L_o$  or  $L_d$

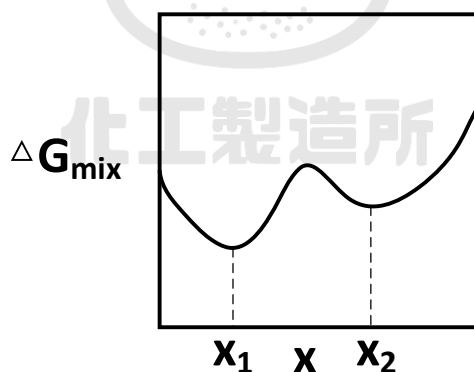
(b)

The thermodynamic properties of  $L_o$  and  $L_d$  will approach each other when the composition approaches the miscibility gap because the two phases become one phase when it reaches the miscibility gap.

(c)

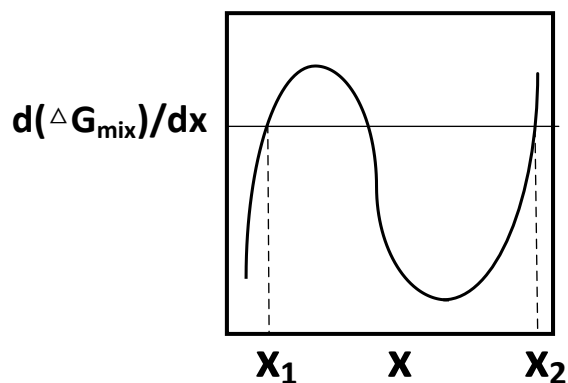
##### **【Path A】**

For an ordinary liquid-liquid phase separation occurs, the  $\Delta G_{mix} - x$  diagram can be shown as,



Where phase separation occurs at  $x = x_1$  and  $x = x_2$

The 1<sup>st</sup> derivative of  $\Delta G_{mix}$  with respect to  $x$  is,

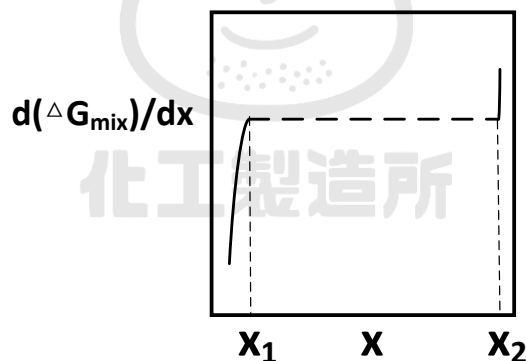


基本上，自由能對組成的一次微分跟 chemical potential 或 activity 有關：

$$(\mu_i = RT \ln a_i)$$

因此在產生相分離時，其兩相相同成分的自由能必須保持相同以維持相平衡條件。

另一方面，我們並不會看到二次微分有  $< 0$  的情況發生(不穩定)，因此在上圖的  $x_1$  與  $x_2$  之間我們並不會真的看到 N 字型的區域，應為(也有可能左右顛倒，端看該曲線代表哪一個成分)：

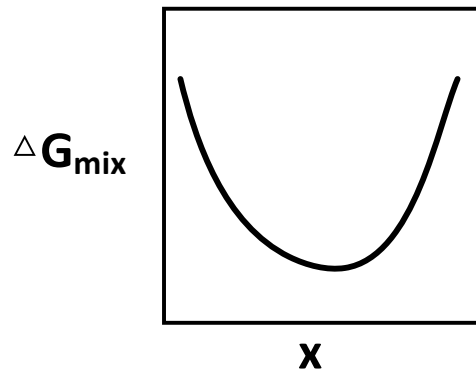


然而，不論是哪張圖，其自由能-組成一次微分曲線皆連續。

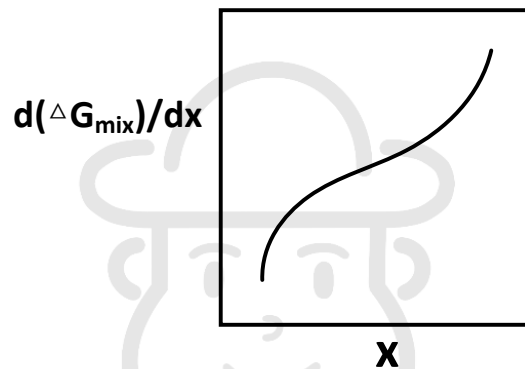


**【Path B】**

對於不會形成相分離的自由能-相圖曲線，其可繪製為：



其自由能一次微分-組成關係大略可繪製為：



形狀可以說與形成相分離組相似，只不過其曲率變化較為緩和，並不會出現斜率為負的區域。然而同樣，其自由能-組成一次微分關係，也不會出現不連續的情形。

(本題可參考：Gaskell, D.; Laughlin, D. *Introduction to Thermodynamics of Materials*, 6th Edition, 6th ed.; p.341~p.346.)

(d)

Given  $d\underline{G} = \underline{V}dP - \underline{S}dT$ , for  $\alpha$  and  $\beta$  phase in equilibrium,

$$d\underline{G}_\alpha = \underline{V}_\alpha dP - \underline{S}_\alpha dT$$

$$d\underline{G}_\beta = \underline{V}_\beta dP - \underline{S}_\beta dT$$

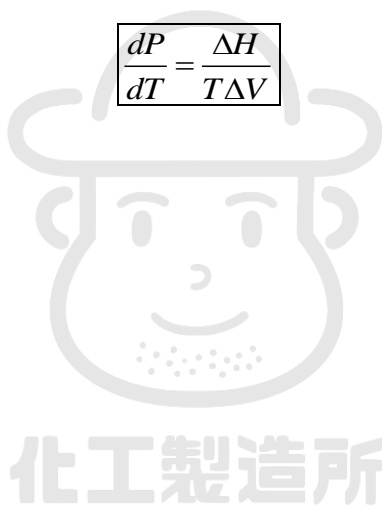
$$\because d\underline{G}_\alpha = d\underline{G}_\beta$$

$$(\underline{V}_\beta - \underline{V}_\alpha)dP - (\underline{S}_\beta - \underline{S}_\alpha)dT = 0$$

$$\frac{dP}{dT} = \frac{(\underline{S}_\beta - \underline{S}_\alpha)}{(\underline{V}_\beta - \underline{V}_\alpha)} = \frac{\Delta S}{\Delta V}$$

$$\because \text{At equilibrium, } \Delta S = \frac{\Delta H}{T}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}}$$



(e)

In the 2D version of Clapeyron equation, we replace the contribution of volume with surface area, and pressure with surface tension

$$d\underline{G} = \underline{A}d\pi - \underline{S}dT$$

where  $\pi$  denotes the surface tension, and  $A$  is the molecular area.

$$d\underline{G}_\alpha = \underline{A}_\alpha d\pi - \underline{S}_\alpha dT$$

$$d\underline{G}_\beta = \underline{A}_\beta d\pi - \underline{S}_\beta dT$$

$$\because d\underline{G}_\alpha = d\underline{G}_\beta$$

$$(\underline{A}_\beta - \underline{A}_\alpha)d\pi - (\underline{S}_\beta - \underline{S}_\alpha)dT = 0$$

$$\frac{d\pi}{dT} = \frac{(\underline{S}_\beta - \underline{S}_\alpha)}{(\underline{A}_\beta - \underline{A}_\alpha)} = \frac{\Delta S}{\Delta A}$$

(f)

For the entropy difference between  $L_o$  and  $L_d$ ,

$$\frac{\pi_1 - \pi_2}{T_{i1} - T_{i2}} = \frac{S_d - S_o}{A_d - A_o}, \quad \frac{(30-25) \times 10^{-3}}{30-25} = \frac{S_d - S_o}{(100-50) \times 10^{-20}}$$
$$\underline{\underline{S_d - S_o = 5 \times 10^{-22} \text{ (J / K)}}}$$

(g)

The two phases become one phase when the composition is at the miscibility critical point, so the entropy difference will decrease.

(h)

By Gibbs phase rule,

$$f = C - P + 2 - 3 = 3 - 2 + 2 - 3 = 0$$

(The composition is fixed at the diamond point)

The degree of freedom is 0, so the experiment may be feasible.

## 112 年中央化熱化反

### Problem 1

#### **【Solution】**

By the given Gibbs-Helmholtz equation,

$$\frac{\partial(\frac{\Delta \underline{G}}{T})}{\partial(\frac{1}{T})}_P = \left[ \frac{\partial(\frac{\underline{G}^{real} - \underline{G}^{ideal}}{T})}{\partial(\frac{1}{T})} \right]_P = \Delta \underline{H}$$

$$\therefore RT \ln\left(\frac{f}{P}\right) = \underline{G}^{real} - \underline{G}^{ideal} = RT\left[\left(0.07 - \frac{28.70}{T}\right)P - \left(0.0011 - \frac{0.420}{T}\right)P^2\right]$$

$$\frac{\underline{G}^{real} - \underline{G}^{ideal}}{T} = R\left[\left(0.07 - \frac{28.70}{T}\right)P - \left(0.0011 - \frac{0.420}{T}\right)P^2\right]$$

$$\left[ \frac{\partial(\frac{\underline{G}^{real} - \underline{G}^{ideal}}{T})}{\partial(\frac{1}{T})} \right]_P = R(-28.70P + 0.420P^2) = \Delta \underline{H}$$

$$\begin{aligned}\Delta \underline{H} &= R(-28.70P + 0.420P^2) = 8.314 \times (-28.70 \times 10 + 0.420 \times 10^2) \\ &= \underline{\underline{-2036.93 \text{ (J / mol)}}}\end{aligned}$$

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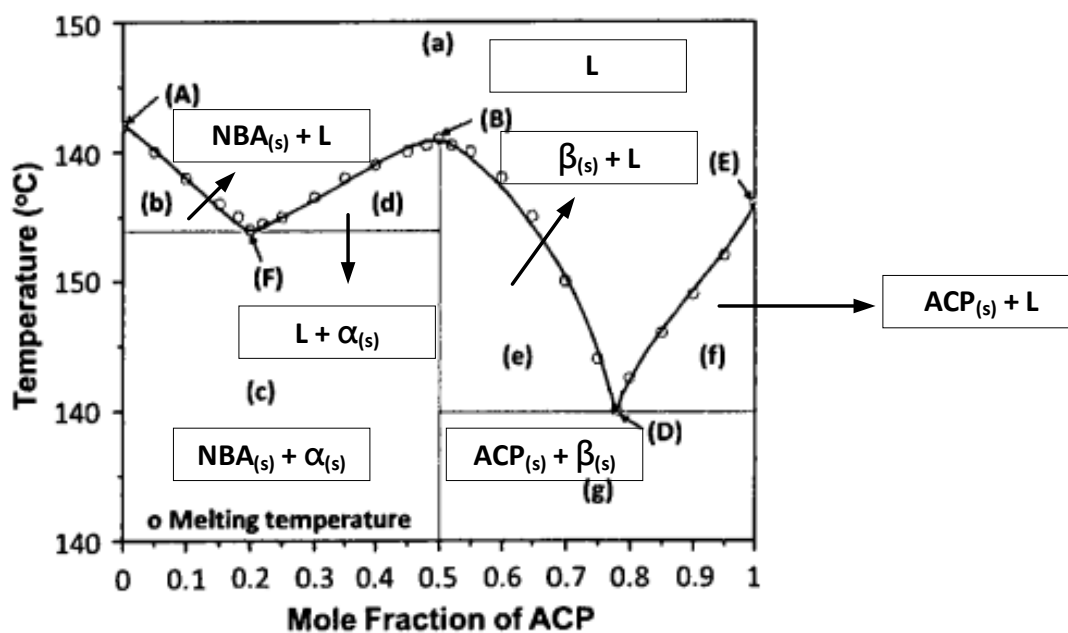
## Problem 2

### 【Solution】

(1) 2 eutectic points, which are (F) and (D).

(2) As the figure shows, (b)(d)(e)(f) are the solid-liquid equilibrium regions, where

$\alpha_{(s)}$  and  $\beta_{(s)}$  are solids that contain both ACP and NBA.



(3) As the figure shows, ACP solids can be observed in region (g) and (f).

(本題出自文獻：Umesh Neupane, R.N. Rai, *Co-crystals formation specified from binary phase diagram studies; Their thermochemical, spectroscopic and optical properties*, The Journal of Chemical Thermodynamics, Volume 161, 2021, 106513, ISSN 0021-9614, <https://doi.org/10.1016/j.jct.2021.106513>.)

**Problem 3****【Solution】**

(1)

By the mathematical definition,

$$\ln(r_1) = \left[ \frac{\partial(\frac{nG^E}{RT})}{\partial n_1} \right]_{n_2} = \left[ \frac{\partial(\frac{\alpha\beta n_1 n_2}{\alpha n_1 + \beta n_2})}{\partial n_1} \right]_{n_2} = \frac{\alpha\beta n_2(\alpha n_1 + \beta n_2) - \alpha(\alpha\beta n_1 n_2)}{(\alpha n_1 + \beta n_2)^2} = \frac{\alpha\beta^2 n_2^2}{(\alpha n_1 + \beta n_2)^2}$$

$$\ln(r_1) = \frac{\alpha\beta^2 n_2^2}{(\alpha n_1 + \beta n_2)^2} = \frac{\alpha\beta^2 x_2^2}{(\alpha x_1 + \beta x_2)^2} = \alpha \left( \frac{\beta x_2}{\alpha x_1 + \beta x_2} \right)^2 = \frac{\alpha}{\left( \frac{\alpha x_1 + \beta x_2}{\beta x_2} \right)^2}$$

$$\ln(r_1) = \left[ \frac{\partial(\frac{nG^E}{RT})}{\partial n_2} \right]_{n_1} = \left[ \frac{\partial(\frac{\alpha\beta n_1 n_2}{\alpha n_1 + \beta n_2})}{\partial n_2} \right]_{n_1} = \frac{\alpha\beta n_1(\alpha n_1 + \beta n_2) - \beta(\alpha\beta n_1 n_2)}{(\alpha n_1 + \beta n_2)^2} = \frac{\alpha^2 \beta n_1^2}{(\alpha n_1 + \beta n_2)^2}$$

$$\ln(r_2) = \frac{\alpha^2 \beta n_1^2}{(\alpha n_1 + \beta n_2)^2} = \frac{\alpha^2 \beta x_1^2}{(\alpha x_1 + \beta x_2)^2} = \beta \left( \frac{\alpha x_1}{\alpha x_1 + \beta x_2} \right)^2 = \frac{\beta}{\left( \frac{\alpha x_1 + \beta x_2}{\alpha x_1} \right)^2}$$

$$\begin{cases} A = \left( \frac{\alpha x_1 + \beta x_2}{\beta x_2} \right)^2 = \left( 1 + \frac{\alpha x_1}{\beta x_2} \right)^2 \\ B = \left( \frac{\alpha x_1 + \beta x_2}{\alpha x_1} \right)^2 = \left( 1 + \frac{\beta x_2}{\alpha x_1} \right)^2 \end{cases}$$

(2)

Assume,

$$\begin{cases} \text{vapor phase} = \text{ideal gas} \\ \text{liquid phase} = \text{real solution with the van Laar model applicable} \end{cases}$$

1 = water, 2 = furfural (呋喃 甲醛)

At equilibrium,

$$\begin{cases} r_1 x_1 P_1^{sat} = y_1 P \\ r_2 x_2 P_2^{sat} = y_2 P \end{cases}, \begin{cases} r_1 = \frac{y_1 P}{x_1 P_1^{sat}} \\ r_2 = \frac{y_2 P}{x_2 P_2^{sat}} \end{cases}$$
$$\begin{cases} r_1 = \frac{y_1 P}{x_1 P_1^{sat}} = \frac{0.81 \times 1.013}{0.10 \times 1.41} = 5.82 \\ r_2 = \frac{y_2 P}{x_2 P_2^{sat}} = \frac{0.19 \times 1.013}{0.90 \times 0.169} = 1.26 \end{cases}$$

代回：

$$\alpha = \left(1 + \frac{x_2 \ln r_2}{x_1 \ln r_1}\right)^2 \ln r_1 = \left[1 + \frac{0.90 \ln(1.26)}{0.10 \ln(5.82)}\right]^2 \ln(5.82) = \underline{\underline{8.547}}$$
$$\beta = \left(1 + \frac{x_1 \ln r_1}{x_2 \ln r_2}\right)^2 \ln r_2 = \left[1 + \frac{0.10 \ln(5.82)}{0.90 \ln(1.26)}\right]^2 \ln(1.26) = \underline{\underline{0.789}}$$

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#### **Problem 4**

#### **【Solution】**

(1)

In a bed reactor packed with catalyst, the effect of the particle size on the conversion is controlled by two effects,

#### **1. The pressure drop parameter,**

$$\alpha = \frac{2\beta_0}{\rho_c(1-\phi)A_c P_0} \propto \beta_0 \propto \frac{1}{D_p}$$

If  $D_p \uparrow$ ,  $\alpha \downarrow$ , the pressure drop is decreased, and  $X_A \uparrow$ .

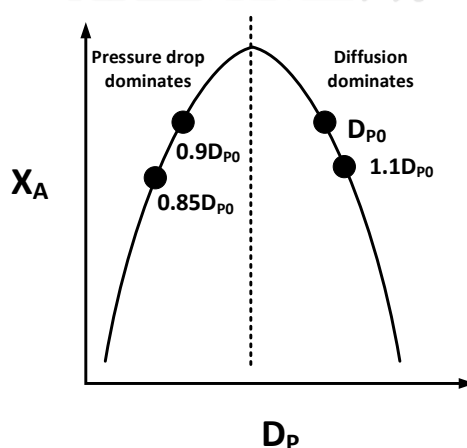
(此段推導可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 177~180.)

#### **2. Reaction rate constant,**

From the point of view of reaction rate in the catalyst particles, the reactant molecules must diffuse into the particle to react. For larger particles, the distance for the reactants must diffuse to react is longer, thus decreasing the reaction rate.

If  $D_p \uparrow$ , *diffusion distance*  $\uparrow$ ,  $X_A \downarrow$ .

Therefore, considering the effects of both (1) and (2) together, we would have the following relationship,



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

Problem 4-8B-(d). 詳細說明可參考同本書：p 187~p 190, Example 4-5.)



(2)

By Set A

$-r_A$  與  $P_C$  無關

By Set B

$$-r_A \propto \frac{1}{1 + K_D P_D + \dots}$$

By Set C

$$-r_A \propto P_B$$

By Set D

$$-r_A \propto \frac{P_A}{1 + K_A P_A + \dots}$$

(濃度低時大約正比，濃度高時趨近定值)

Combine,

$$-r_A = \frac{k P_A P_B}{1 + K_A P_A + K_D P_D}$$

(3)

A 出現於分子與分母，A 有吸附於觸媒上(分母)，且速率決定步驟有 A 參與

B 只出現於分子，速率決定步驟有 B 參與，但無吸附於觸媒上

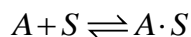
(與 Eley-Rideal mechanism 相同)

C 無出現於分子與分母，代表不吸附在觸媒上，且速率決定步驟不可逆

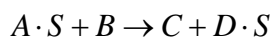
D 出現於分母，代表有吸附於觸媒上，然而其無出現於分子，代表速率決定步驟不可逆

根據以上，合理假設速率決定步驟為表面反應：

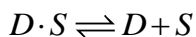
**Adsorption :**



**Surface reaction :**



**Desorption :**



For the determination of the kinetic parameters,

$$\begin{aligned} -r_A &= \frac{kP_A P_B}{1 + K_A P_A + K_D P_D} \\ \frac{1}{-r_A} &= \frac{1 + K_A P_A + K_D P_D}{kP_A P_B} = \frac{1}{kP_A P_B} + \frac{K_A P_A}{kP_A P_B} + \frac{K_D P_D}{kP_A P_B} \\ \frac{P_A P_B}{-r_A} &= \frac{1}{k} + \frac{K_A P_A}{k} + \frac{K_D P_D}{k} \end{aligned}$$

則：

1. 固定  $P_B$ ,  $P_D$

可由  $\frac{P_A P_B}{-r_A} - P_A$  關係求得斜率  $\frac{K_A}{k}$  與截距  $\frac{1}{k}$

2. 固定  $P_A$ ,  $P_B$

可由  $\frac{P_A P_B}{-r_A} - P_C$  求得斜率  $\frac{K_D}{k}$

((2)(3)小題改編自：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 688~693

之章節示範，數據表格之 A 反應速率為 Table 10-6.數據的一半。若考生覺得有需要於第(3)小題提出反應機構後，再推導一次速率定律式雙重驗證，可參考原文書說明，這裡不再重複。)

(4)

By the design equation of PBR,

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

For  $-r_A$ ,

$$-r_A = \frac{kP_A P_B}{1 + K_A P_A + K_D P_D}$$

$$P_A = C_A RT = C_{A0} \left( \frac{1-x_A}{1+\varepsilon x_A} \right) y RT_0 \underset{\varepsilon=0}{=} C_{A0} RT_0 y (1-x_A) = P_{A0} (1-x_A) y$$

where,

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

(Only for  $\varepsilon = 0$ )

$$P_B = P_{A0} (\theta_B - x_A) y$$

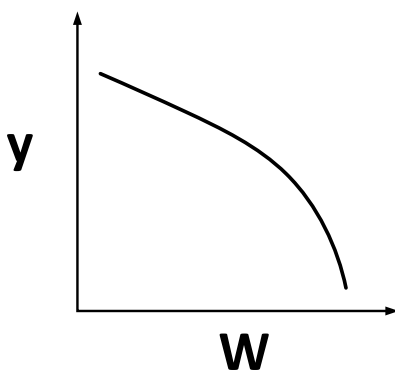
$$P_C = P_{A0} x_A y$$

$$-r_A = \frac{kP_{A0}^2 (1-x_A)(\theta_B - x_A) y^2}{1 + K_A P_{A0} (1-x_A) y + K_C P_{A0} x_A y} = \frac{kP_{A0} (1-x_A)(\theta_B - x_A) y}{1 + K_A (1-x_A) + K_C x_A}$$

Combine,

$$\frac{dx_A}{dW} = \frac{\frac{kP_{A0} (1-x_A)(\theta_B - x_A)}{1 + K_A (1-x_A) + K_C x_A}}{F_{A0}} y = \frac{\frac{kP_{A0} (1-x_A)(\theta_B - x_A)}{1 + K_A (1-x_A) + K_C x_A}}{F_{A0}} (1 - \alpha W)^{\frac{1}{2}}$$

則  $y-W$  圖為：  $y = (1 - \alpha W)^{\frac{1}{2}}$ ，可用  $y = (1 - x)^{\frac{1}{2}}$  去想，或用計算機 table 功能。



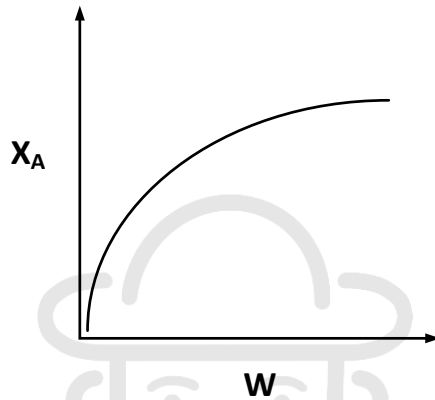
而  $x_A - W$  圖，根據：

$$\frac{dx_A}{dW} = \frac{\frac{kP_{A0}(1-x_A)(\theta_B - x_A)}{1 + K_A(1-x_A) + K_C x_A}}{F_{A0}} (1-\alpha W)^{\frac{1}{2}} \propto (1-\alpha W)^{\frac{1}{2}}$$

其斜率正比於  $(1-\alpha W)^{\frac{1}{2}}$ ，又根據  $(1-\alpha W)^{\frac{1}{2}} - W$  關係(即  $y-W$  關係)，

可知  $W$  較小時， $(1-\alpha W)^{\frac{1}{2}}$  值大， $\frac{dx_A}{dW}$  大； $W$  較大時， $(1-\alpha W)^{\frac{1}{2}}$  值小， $\frac{dx_A}{dW}$

小，則：



( $W$  較小時，斜率大； $W$  較大時，斜率較小)

化工製造所

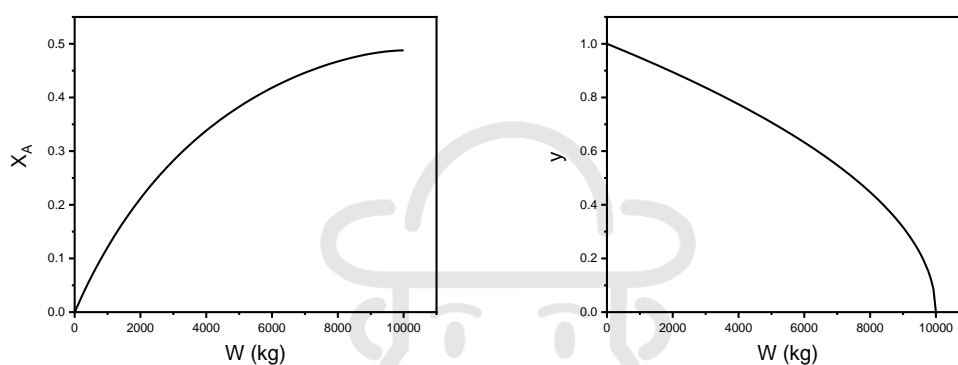
※若根據 polymath 繪圖，可得：

```
#Define the differential equation, which is the design equation of the PBR
d(XA)/d(W) = -rA/FA0

#Define the rate equation
rA = (-k*PA*PB)/(1+KA*PA+KD*PD)

#The parameters or conditions we need or values are,
k = 0.00087
KA = 1.0386
KD = 1.39
FA0 = 40
y = (1-1*10*(-4)*W)^(1/2)
PA = PA0*(1-XA)*y
PB = PA0*(40/25-XA)*y
PD = PA0*XA*y
PA0 = 20*0.25

#The range of weight of catalyst we want to know
W(0) = 0
W(f) = 10000
XA(0) = 0
```



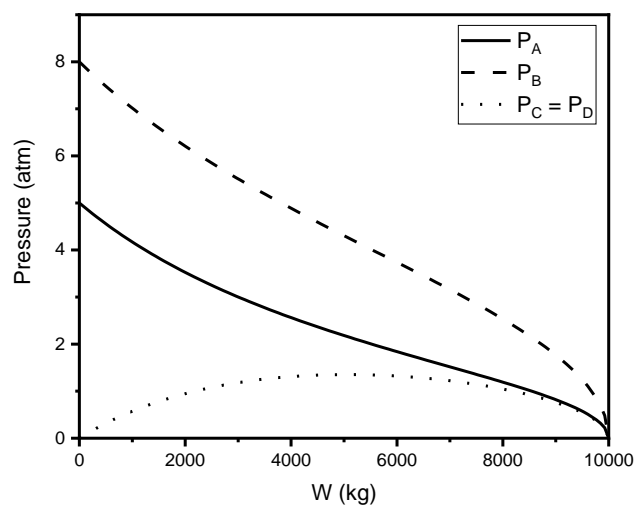
與趨勢推導相同。

此處須注意，計算所需要之  $K_A$  與  $K_D$  由原文書得到，來源為：

FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 694~698,

Example 10-3.

另外，其各成分分壓與觸媒重量關係圖為：



# 113 年中央化熱化反

## Problem 1

### **【Solution】**

(a)

For PFR, the volume is calculated as,

$$V = \int_0^{x_A} \frac{F_{A0}}{-r_A} dx_A = \frac{(100000 + 500000) \times 0.5}{2} = \underline{\underline{150000 \text{ (m}^3\text{)}}}$$

(b)

For CSTR, the volume is calculated as,

$$V = \frac{F_{A0} x_A}{-r_A} = 0.5 \times 100000 = \underline{\underline{50000 \text{ (m}^3\text{)}}}$$

(c)

The volume of the second CSTR is,

$$V = \frac{F_{A0}(x_{A2} - x_{A1})}{-r_A|_{x_{A2}}} = [100000 + (500000 - 100000) \times \frac{0.8 - 0.5}{1 - 0.5}] \times (0.8 - 0.5) = \underline{\underline{102000 \text{ (m}^3\text{)}}}$$

(d)

The volume of the second PFR is,

$$V = \int_{0.5}^{0.8} \frac{F_{A0}}{-r_A} dx_A = \int_{0.5}^{0.8} [100000 + (x_A - 0.5) \times 800000] dx_A = \underline{\underline{66000 \text{ (m}^3\text{)}}}$$

(e)

### **[CSTR]**

If the conversion is  $< 0.5$ , the CSTR volume can be calculated as,

$$6 \times 10^4 = \frac{F_{A0}}{-r_A} x_A = [500000 - 800000 x_A] x_A, \quad x_A = \underline{\underline{0.162, 0.463}}$$

For possible conversion  $> 0.5$ ,

$$6 \times 10^4 = \frac{F_{A0}}{-r_A} x_A = [100000 + 800000(x_A - 0.5)] x_A, \quad x_A = \underline{\underline{0.519}}$$

**[PFR]**

The PFR volume of  $6.4 \times 10^4 \text{ (m}^3\text{)}$  is less than that required to achieve a conversion of 0.5 (question (a)), therefore,

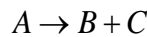
$$60000 = \int_0^{x_A} \frac{F_{A0}}{-r_A} dx_A = \int_0^{x_A} [500000 - 800000x_A] dx_A, \quad \underline{\underline{x_A = 0.134}}$$

(此題改編自：FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 75,

Problem 2-9B.)

**Problem 2****【Solution】**

The reaction is,



For PFR, the combination of the design equation and rate expression is,

$$V_{PFR} = \int_0^{x_A} \frac{F_{A0}}{-r_A} dx_A = \int_0^{0.80} \frac{v_0}{k_{300} \frac{(1-x_A)}{(1+\varepsilon x_A)}} dx_A = \int_0^{0.80} \frac{v_0}{k_{300} \frac{(1-x_A)}{(1+x_A)}} dx_A$$

For CSTR, the combination of the design equation and rate expression is,

$$V_{CSTR} = \frac{F_{A0} x_A}{-r_A} = \frac{v_0 x_A}{k_{320} \frac{(1-x_A)}{(1+\varepsilon x_A)}} = \frac{v_0 x_A}{k_{320} \frac{(1-x_A)}{(1+0.5x_A)}}$$

相除：

$$\frac{V_{PFR}}{V_{CSTR}} = \frac{\int_0^{0.80} \frac{v_0}{k_{300} \frac{(1-x_A)}{(1+x_A)}} dx_A}{\frac{v_0 x_A}{k_{320} \frac{(1-x_A)}{(1+0.5x_A)}}}, \quad \frac{10}{10} = \frac{\int_0^{0.80} \frac{1}{k_{300} \frac{(1-x_A)}{(1+x_A)}} dx_A}{\frac{0.8}{k_{320} \frac{(1-0.8)}{(1+0.5 \times 0.8)}}}$$

$$\frac{k_{320}}{k_{300}} = 2.315 = \exp\left[-\frac{\Delta H}{R} \left(\frac{1}{320} - \frac{1}{300}\right)\right] = \exp\left[-\frac{\Delta H}{8.314} \left(\frac{1}{320} - \frac{1}{300}\right)\right]$$

$$\underline{\underline{\Delta H = 33500 \text{ (J / mol} \cdot \text{K)}}}$$

(此題改編自：FOGLER, H. Elements of Chemical Reaction Engineering, 5th ed.; p 199,

Problem 5-7B, 亦可參考網址：

<https://public.websites.umich.edu/~elements/5e/studyAid/344W13MidTermExamI+Solution.pdf>)

### Problem 3

#### 【Solution】

(a) By the design equation of CSTR,

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

Combine with the rate expression,

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

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

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

代入：

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

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

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

(b) By the design equation of CSTR,

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



(c)

By energy balance,

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

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

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

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

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

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

代回：

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

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

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

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

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

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

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

其中  $(F_{A0} - F_A)$  就是反應中 A 反應掉的莫爾流量、 $F_C$  就是反應中 C 產生的莫爾流量

根據(a)小題結果，我們知道：

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

代回：

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

因此：

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

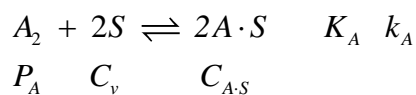
$$\underline{\underline{A = 28.4 \text{ (ft}^2\text{)}}}$$



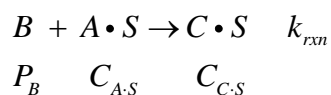
### Problem 4

#### 【Solution】

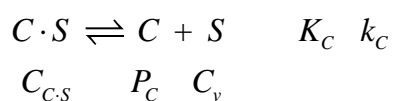
#### Adsorption of A :



#### Surface reaction :



#### Desorption of C :



Assume the surface reaction is rate-determining,

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

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

$$C_{A \cdot S} = \sqrt{K_A P_A} C_v$$

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

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

By site balance,

$$C_t = C_v (1 + \sqrt{K_A P_A} + K_C P_C)$$

代入 reaction rate 表示式，得：

$$r = \frac{k_{rxn} \sqrt{K_A P_A} P_B C_t}{(1 + \sqrt{K_{O_2} P_{O_2}} + K_C P_C)}$$

(此題改編自：FOGLER, H. Elements of Chemical Reaction Engineering, 4th ed.; p 741,

Problem 10-5B(c))

### Problem 5

#### **【Solution】**

(a)

※此題改用以下 equation of state 來做(Berthelot equation of state)：

$$P = \frac{RT}{V-b} - \frac{a}{TV^2}$$

At the critical point, we know that,

$$\left(\frac{\partial P}{\partial V}\right)_T \Big|_{critical} = -\frac{RT_c}{(V_c-b)^2} + \frac{2a}{T_c V_c^3} = 0, \quad \frac{RT_c}{(V_c-b)^2} = \frac{2a}{T_c V_c^3}$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T \Big|_{critical} = \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{T_c V_c^4} = 0, \quad \frac{2RT_c}{(V_c-b)^3} = \frac{6a}{T_c V_c^4}$$

兩式相除：

$$\frac{2}{V_c-b} = \frac{3}{V_c}, \quad V_c = 3b$$

代回：

$$\frac{RT_c}{(3b-b)^2} = \frac{2a}{T_c \times (3b)^3}, \quad a = \frac{27RT_c^2 b}{8}$$

代回 equation of state,

$$P_c = \frac{RT_c}{V_c-b} - \frac{a}{T_c V_c^2}, \quad P_c = \frac{3RT_c}{2V_c} - \frac{9RT_c}{8V_c} = \frac{3RT_c}{8V_c}$$
$$V_c = \frac{3RT_c}{8P_c}$$

代回：

$$V_c = 3b = \frac{3RT_c}{8P_c}, \quad b = \frac{RT_c}{8P_c}$$

$$a = \frac{27RT_c^2 b}{8} = \frac{27R^2 T_c^3}{64P_c}$$

(b)

For the constant-volume heat capacity, we have,

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V = -\frac{2a}{T^2 V^2}, \quad \underline{\underline{C_v = \frac{2a}{T^2 V}}}$$

For the internal energy,

$$dU = C_v dT + [T\left(\frac{\partial P}{\partial T}\right)_V - P]dV$$

$$dU = \frac{2a}{T^2 V} dT + \left[\frac{2a}{TV^2}\right]dV$$

$$\underline{\underline{U = -\frac{2a}{TV} - \frac{2a}{TV} = -\frac{4a}{TV}}}$$

### **Problem 6**

#### **【Solution】**

(a)

Assume the M and E form ideal gas mixture and ideal solution, therefore for ideal solution,

$$P = x_M P_M^{sat} + (1 - x_M) P_E^{sat} = P_E^{sat} + (P_M^{sat} - P_E^{sat}) x_M$$

For ideal gas mixture,

$$y_M = \frac{P_M}{P} = \frac{x_M P_M^{sat}}{P_E^{sat} + (P_M^{sat} - P_E^{sat}) x_M}$$

$$y_M P_E^{sat} + x_M y_M (P_M^{sat} - P_E^{sat}) = x_M P_M^{sat}$$

$$x_M = \frac{y_M P_E^{sat}}{P_M^{sat} - y_M (P_M^{sat} - P_E^{sat})}$$

代入：

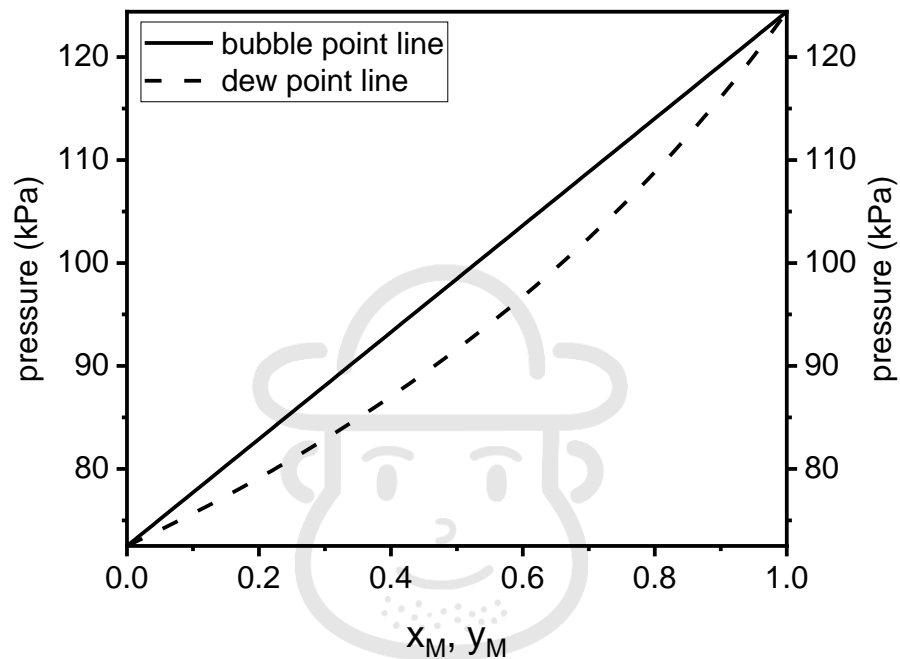
$$P = P_E^{sat} + \frac{(P_M^{sat} - P_E^{sat}) y_M P_E^{sat}}{P_M^{sat} - y_M (P_M^{sat} - P_E^{sat})} = \frac{P_M^{sat} P_E^{sat}}{P_M^{sat} - y_M (P_M^{sat} - P_E^{sat})}$$

For the saturated pressure of M and E,

$$P_M^{sat} = \exp\left[16.5785 - \frac{3638.27}{70 + 239.500}\right] = 124.4 \text{ (kPa)}$$

$$P_E^{sat} = \exp\left[16.8958 - \frac{3795.17}{70 + 230.918}\right] = 72.52 \text{ (kPa)}$$

代入，並繪製出  $P-x-y$ ：



(b)

At the bubble point,  $z_i = x_i$ , by Raoult's law,

$$y_M P = x_M P_M^{sat} \quad , \quad y_M = \frac{x_M P_M^{sat}}{P} = \frac{x_M P_M^{sat}}{x_M P_M^{sat} + x_E P_E^{sat}}$$

$$y_M = \frac{0.75 \times 124.4}{0.75 \times 124.4 + 0.25 \times 72.52} = 0.837$$

$$\begin{cases} \text{liquid phase: } x_M = 0.75, x_E = 0.25 \\ \text{gas phase: } y_M = 0.837, y_E = 0.163 \end{cases}$$

At the dew point,  $z_i = y_i$ , by Raoult's law,

$$y_M P = x_M P_M^{sat}$$

$$x_M = \frac{y_M P}{P_M^{sat}}, \quad x_E = \frac{y_E P}{P_E^{sat}}$$

相除：

$$\frac{x_M}{x_E} = \frac{y_M P_E^{sat}}{y_E P_M^{sat}} = \frac{0.75 \times 72.52}{0.25 \times 124.4} = 1.75$$

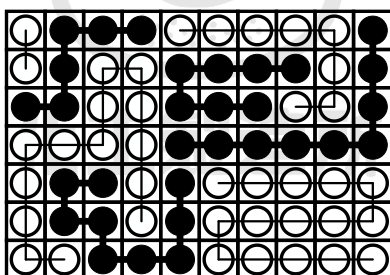
$$\begin{cases} \text{liquid phase: } x_M = \frac{1.75}{1.75+1} = 0.636, \quad x_E = 0.364 \\ \text{gas phase: } y_M = 0.75, \quad y_E = 0.25 \end{cases}$$

### Problem 7

#### **【Solution】**

(a)

假設高分子 1 單條分子鏈有  $x_1$  個單體單元(即聚合度，degree of polymerization)，且高分子 2 單條分子鏈有  $x_2$  個單體單元，若假設兩條高分子鏈的單體單元佔的單位體積相同(即同樣都佔一格)，則：



(實心球為高分子 1 單體單元、空心為高分子 2 單體單元，可以想成一條高分子是一個串珠，其中每一條上有多少串珠，就是聚合度，而每顆串珠的體積都假設為相同，即使 1 與 2 的串珠可能大小不同。)

If we assume the chain is ideal

(如同氣體有理想氣體、溶液有理想溶液，高分子也有其專屬的理想態，也能形成一種高分子的理想溶液狀態)

$$\Delta \underline{S}_{mix} = -k_B [n_1 \ln \phi_1 + n_2 \ln \phi_2] \text{ (與理想溶液類似)}$$

※這段可省略，只是單純探討一些參數：

$$\Delta S_{mix} = -k_B N \left[ \frac{n_1}{N} \ln \phi_1 + \frac{n_2}{N} \ln \phi_2 \right] = -k_B N \left[ \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 \right]$$

$n_i$  = 高分子 i 的鏈數(幾條串珠)， $N$  = lattice site 數(此空間總共有多少顆串珠球)， $\phi_i$  = 高分子 i 的 volume fraction，此轉換的意義是在引出所謂的聚合度的影響：

$$N\phi_i = \text{高分子 i 所占總共體積(幾格 lattice)}$$

$$\frac{N\phi_i}{x_i} = \text{除以聚合度(每條分子佔幾格 lattice)後，就是幾條高分子鏈 } n_i$$

$x_i = 1$  代表此分子為溶劑分子(一個分子只有一個單體單元，一個分子就是一顆珠子)

高分子的  $x_i$  則非 1，通常很大(一條高分子由很多珠子組成)

解答的 entropy 貢獻是利用背的方式寫出來，事實上要從源頭推導要從 Boltzmann's equation

$S = k_B \ln \Omega$  再利用統計連成機率的方式寫出，有點超過化工所的範疇，所以就沒有特別列出。

For enthalpy (energy) contribution,

定義作用力參數  $w_{ij}$  (i 與 j 之間的作用力) 及其個數  $m_{ij}$

$$H = m_{11}w_{11} + m_{22}w_{22} + m_{12}w_{12}$$

其中：

$$m_{11} = \frac{zn_1 - m_{12}}{2}, m_{22} = \frac{zn_2 - m_{12}}{2}$$

$Z$  為 1 與 2 之配位數，也就是旁邊有多少(1+2)，且因為 11 與 22 會重複算兩次，要  $\div 2$ 。

又

$$m_{12} = zn_1\phi_2 = zN\phi_1\phi_2$$

(1 的配位數  $\times$  2 體積分率)

代回：



$$\begin{aligned}
\underline{H} &= \left( \frac{zn_A - m_{AB}}{2} \right) w_{AA} + \left( \frac{zn_B - m_{AB}}{2} \right) w_{BB} + m_{AB} w_{AB} \\
&= \left( \frac{zw_{AA}}{2} \right) n_A + \left( \frac{zw_{BB}}{2} \right) n_B + \left( w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right) m_{AB} \\
&= \left( \frac{zw_{AA}}{2} \right) n_A + \left( \frac{zw_{BB}}{2} \right) n_B + zN \left( w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right) \phi_1 \phi_2 \\
\underline{H} &= \left( \frac{zw_{AA}}{2} \right) n_A + \left( \frac{zw_{BB}}{2} \right) n_B + k_B T \chi_{AB} N \phi_1 \phi_2 \\
\left( \chi_{AB} = \frac{z}{k_B T} \left( w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right) \right), & \text{ 因同''開'', 為 interaction parameter} \\
\Delta \underline{H}_{mix} = \underline{H} - \underline{H}_1 - \underline{H}_2 &= k_B T \chi_{AB} N \phi_1 \phi_2 = k_B T \chi_{AB} n_1 \phi_2 \\
\Delta \underline{G}_{mix} = \Delta \underline{H}_{mix} - T \Delta \underline{S}_{mix} &= k_B T [n_1 \ln \phi_1 + n_2 \ln \phi_2] + k_B T \chi_{AB} n_1 \phi_2 \\
\Delta G_{mix} = \Delta \underline{G}_{mix} N_A &= \underline{\underline{RT [n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{AB}]}}
\end{aligned}$$

(b)

The Gibbs free energy of mixing in polymer solutions represents the favorability of mixing and the stability of the polymer solution. When  $\Delta G_{mix} < 0$ , it indicates good compatibility between the polymer and the solvent molecules. Conversely, when  $\Delta G_{mix} > 0$ , phase separation is anticipated.

### **Problem 8**

#### **【Solution】**

For this fundamental residual-property relation applies to fluids of constant composition, and at constant temperature.

If we begin from,

$$\frac{V^R}{RT} = \left[ -\frac{\partial(\frac{G^R}{RT})}{\partial P} \right]_T$$

(constant temperature)

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT} dP, \quad \frac{G^R}{RT} = \underbrace{\left(\frac{G^R}{RT}\right)_{P=0}}_{\text{constant, set}=0} + \int_0^P \frac{V^R}{RT} dP = \int_0^P \frac{V^R}{RT} dP$$

$$\frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P}$$

For that of enthalpy, we may have,

$$\frac{H^R}{RT} = -T \left[ \frac{\partial(\frac{G^R}{RT})}{\partial T} \right]_P = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

Therefore,

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P}$$

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

p 208-210.)