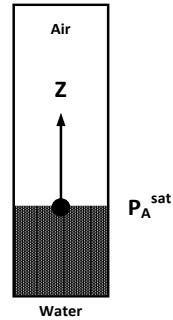


104 年中央單操輸送

Problem 1

【Solution】



(a) Assume : The change of the volumes of the air and water are not too much

By pseudo-steady-state mole balance of water in the air,

$$k_p A_c (C_A^{sat} - C_A) = \frac{\partial \left(\frac{P_A V_{air}}{RT} \right)}{\partial t} = V_{air} \frac{\partial C_A}{\partial t}$$

$$k_p \int_0^t dt = \frac{V_{air}}{A_c} \int_0^{C_A} \frac{dC_A}{(C_A^{sat} - C_A)}$$

$$k_p = \frac{V_{air}}{t A_c} \ln \frac{C_A^{sat}}{C_A^{sat} - C} = \frac{V_{air}}{t A_c} \ln \frac{P_A^{sat}}{P_A^{sat} - P}$$

$$\begin{cases} V_{air} = (19.2 - 0.8) = 18.4 (L) = 18.4 \times 10^{-3} (m^3) \\ A_c = 150 cm^2 = 150 \times 10^{-4} (m^2) \end{cases}$$

$$k_p = \frac{18.4 \times 10^{-3}}{3 \times 60 \times 150 \times 10^{-4}} \ln \frac{23.8}{23.8(1 - \frac{0.05}{100})}$$

$$\underline{\underline{k_p = 3.408 \times 10^{-6} (m / s)}}$$

(b)

$C_A = C_A^{sat} \times 0.9$ 代入

$$t = \frac{V_{air}}{k_p A_c} \ln \frac{P_A^{sat}}{P_A^{sat} - P}$$
$$t = \frac{18.4 \times 10^{-3}}{3.408 \times 10^{-6} \times 150 \times 10^{-4}} \ln \frac{23.8}{23.8(1-0.9)}$$
$$= \underline{\underline{828723 \text{ (s)}}}$$

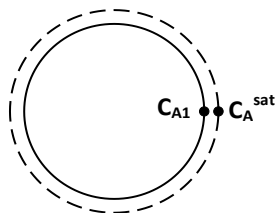
(※本題改編自：Cussler, E. L. *Diffusion: Mass Transfer in Fluid Systems*, 3rd ed.; p 238~239,

Example 8.1-1。原題之第一小題為 5%，與本題不同。)



Problem 2

【Solution】



By pseudo-steady-state mole balance on the bubble, and assume the water is in excess, then the concentration of oxygen in the bulk is zero, then

$$-k_c(4\pi r^2)(C_A^{sat} - 0) = \frac{\partial(\frac{4}{3}\pi r^3 C_{A1})}{dt} = 4\pi r^2 C_{A1} \cdot \frac{dr}{dt}$$

$$k_c = -\frac{C_{A1}}{C_A^{sat}} \cdot \frac{dr}{dt}$$

$$\text{積分得 } k_c = -\frac{C_{A1}}{C_A^{sat}} \cdot \frac{r_2 - r_1}{t}$$

where C_{A1} is the concentration in the bubble, and C_A^{sat} refers to the oxygen at saturation concentration in water.

$$\text{For } C_{A1} = \frac{P_{A1}}{RT} = \frac{1 \text{ (atm)}}{0.082 \times 298.15} = 0.041 \text{ (mol / L)} \text{ (Standard condition)}$$

$$k_c = -\frac{0.041}{1.5 \times 10^{-3}} \times \frac{0.054 - 0.1}{2 \times 7 \times 60} = \underline{\underline{1.493 \times 10^{-3} \text{ (cm / s)}}}$$

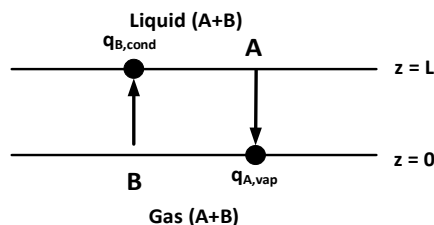
(本題改編自：Cussler, E. L. *Diffusion: Mass Transfer in Fluid Systems*, 3rd ed.; p 242,

Example 8.1-4)

Problem 3

【Solution】

Let $\begin{cases} \text{acetone} = A \\ \text{methanol} = B \end{cases}$



By energy balance, the condensation of methanol vapor provides the energy for vaporization of acetone, then,

$$q_{B,cond} = q_{A,vap} \quad , \quad H_{B,cond} \dot{m}_B = H_{A,vap} \dot{m}_A$$

$$H_A^{vap} M_A N_A dA = H_B^{cond} M_B N_B dA \quad , \quad (M = \text{分子量})$$

$$538.9 \times 58 N_A = 1104 \times 32 N_B$$

$$N_A = 1.13 N_B \quad (\text{方向相反})$$

By Fick's law of B,

$$N_B = -\mathcal{D}_{AB} \frac{\partial C_B}{\partial z} + y_B (N_A + N_B) = -\mathcal{D}_{AB} \frac{\partial C_B}{\partial z} + y_B (-1.13 N_B + N_B)$$

$$N_B = -\mathcal{D}_{AB} \frac{\partial C_B}{\partial z} - 0.13 y_B N_B$$

$$N_B = -\mathcal{D}_{AB} \frac{P}{RT} \frac{dy_B}{dz} - 0.13 y_B N_B$$

$$N_B = \frac{-P \mathcal{D}_{AB}}{RT} \cdot \frac{1}{(1 + 0.13 y_B)} \cdot \frac{dy_B}{dz}$$

積分：

$$N_B \int_0^L dz = \frac{-P \mathcal{D}_{AB}}{RT} \int_{y_{B,gas}}^{y_{B,liquid}} \frac{1}{(1 + 0.13 y_B)} \cdot dy_B \quad , \quad N_B = \frac{-P \mathcal{D}_{AB}}{0.13 R T L} \ln \left(\frac{1 + 0.13 y_{B,liquid}}{1 + 0.13 y_{B,gas}} \right)$$

將 $P = 1.013 \times 10^5 \text{ Pa}$ 、 $T = 330 \text{ K}$ 、 $L = 0.1 \times 10^{-3} \text{ m}$ 代入：

$$N_B = \frac{-1.013 \times 10^5 \mathcal{D}_{AB}}{0.13 \times 8.314 \times 330 \times 0.1 \times 10^{-3}} \ln \left(\frac{1 + 0.13 y_{B,liquid}}{1 + 0.13 y_{B,gas}} \right) = -2.84 \times 10^{-6} \mathcal{D}_{AB} \ln \left(\frac{1 + 0.13 y_{B,liquid}}{1 + 0.13 y_{B,gas}} \right) \quad (\text{mol} / \text{m}^2 \cdot \text{s})$$

Problem 4

【Solution】

∵ the thermal conductivity varies with temperature,

$$\frac{T-T_0}{T_1-T_0} = \frac{k-k_0}{k_1-k_0} \equiv \theta$$

By energy balance of the shell,

$$(4\pi r^2)q_r''|_r - (4\pi r^2)q_r''|_{r+dr} = 0 \quad (\text{steady state})$$

同除 $4\pi r^2 \rightarrow 0$,

$$\frac{d(r^2 q_r'')}{dr} = 0$$

By Fourier's law,

$$q_r'' = -k \frac{dT}{dr} = -k(T_1 - T_0) \frac{d\theta}{dr} \quad \text{代入}$$

$$\frac{d}{dr} (r^2 k \frac{d\theta}{dr}) = 0$$

$$k \frac{d\theta}{dr} = \frac{c_1}{r^2}, \quad [(k_1 - k_0)\theta + k_0] \frac{d\theta}{dr} = \frac{c_1}{r^2}$$

$$\frac{1}{2}(k_1 - k_0)\theta^2 + k_0\theta = \frac{-c_1}{r} + c_2 \quad \begin{cases} r=r_0, T=T_0 \rightarrow \theta=0 \\ r=r_1, T=T_1 \rightarrow \theta=1 \end{cases}$$

$$\begin{cases} c_1 = \frac{(k_1 + k_0)}{2(\frac{1}{r_1} - \frac{1}{r_0})} \\ c_2 = \frac{(k_1 + k_0)}{2(\frac{r_0}{r_1} - 1)} \end{cases} \quad \text{代入}$$

$$\begin{aligned} q &= 4\pi r_0^2 q_r''|_{r_0} = 4\pi r_0^2 \left[-k(T_1 - T_0) \frac{d\theta}{dr} \right] \Big|_{r_0} \\ &= 4\pi r_0^2 (T_0 - T_1) \frac{c_1}{r_0^2} = \frac{2\pi(k_1 + k_0)r_0 r_1}{r_0 - r_1} (T_0 - T_1) \end{aligned}$$

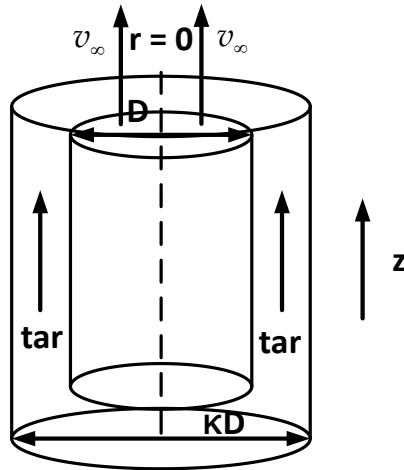
(本題改編自：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.;

p 326, Example 10B.14.)

Problem 5

【Solution】

Let the diameter of the pit is κD



(a)

By Navier-Stokes equation, assume :

$$(1) \quad v_r = v_\theta = 0$$

$$(2) \quad \text{Axial-symmetric, } v_z = f(r, \theta, z, t)$$

(3) The fluid moves through the annular region solely by the motion of the cylinder,

the pressure term or modified pressure term would be constant.

代入 z 方向 Navier-Stokes equation,

$$\rho \frac{\partial v_z}{\partial t} = \mu \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) \right] - \frac{dp}{dz} + \rho g_z = \mu \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) \right] - \frac{dP}{dz}$$

$$\rho \frac{\partial v_z}{\partial t} = \mu \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) \right]$$

令：

$$\begin{cases} v_z^* = \frac{v_z}{v_\infty} \\ t^* = \frac{t}{D / v_\infty} \\ r^* = \frac{r}{D} \end{cases}$$

代入

$$\rho \frac{v_{\infty}}{D/v_{\infty}} \frac{\partial v_z^*}{\partial t^*} = \frac{\mu v_{\infty}}{D^2} \left[\frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* \frac{\partial v_z^*}{\partial r^*}) \right]$$

同除 $\frac{\rho v_{\infty}^2}{D}$

$$\frac{\partial v_z^*}{\partial t^*} = \frac{\mu}{\rho v_{\infty} D} \left[\frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* \frac{\partial v_z^*}{\partial r^*}) \right] = \frac{1}{\text{Re}_D} \left[\frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* \frac{\partial v_z^*}{\partial r^*}) \right]$$

$$\text{Where } \text{Re}_D = \frac{\rho v_{\infty} D}{\mu}$$

For dimensionless boundary conditions,

$$\begin{cases} r = \frac{D}{2}, r^* = \frac{1}{2} \rightarrow v_z^* = 1 \\ r = \frac{\kappa D}{2}, r^* = \frac{\kappa}{2} \rightarrow v_z^* = 0 \end{cases}$$

For dimensionless initial condition,

$$t^* = 0, v_z^* = 0$$

To mock the real system,

$$\text{Re}_{D,real} = \text{Re}_{D,mock}$$

$$\frac{v_{\infty} \times 15 \times 10^{-2}}{6 \times 10^{-4}} = \frac{v_{\infty} \times D \times 1261}{1.41}$$

$$\underline{\underline{D = 0.279 \text{ (m)} = 27.9 \text{ (cm)}}}$$

(b)

Steady state,

$$\frac{1}{\text{Re}} \left[\frac{1}{r^*} \frac{\partial}{\partial r^*} (r^* \frac{\partial v_z^*}{\partial r^*}) \right] = 0$$

$$\frac{\partial v_z^*}{\partial r^*} = \frac{c_1}{r^*}$$

$$v_z^* = c_1 \ln r^* + c_2$$

代入 B.C. :

$$\begin{cases} c_1 = \frac{-1}{\ln \kappa} \\ c_2 = -c_1 \ln \frac{\kappa}{2} = \frac{\ln \frac{\kappa}{2}}{\ln \kappa} \end{cases}, \quad \boxed{v_z^* = \frac{\ln \frac{\kappa}{2r^*}}{\ln \kappa}}$$

(c)

$$\begin{aligned} |\tau_{rz}| &= \left| -\mu \frac{\partial v_z}{\partial r} \right| = \left| \frac{-\mu v_\infty}{D} \frac{\partial v_z^*}{\partial r^*} \right| \\ \left| \tau_{rz} \right|_{r^*=\frac{1}{2}} &= \frac{2v_\infty \mu}{D} \ln \kappa \\ C_D &= \frac{\left| \tau_{rz} \right|_{r^*=\frac{1}{2}}}{\frac{1}{2} \rho v_\infty^2} = \frac{\frac{2v_\infty \mu}{D} \ln \kappa}{\frac{1}{2} \rho v_\infty^2} = \frac{4\mu}{\rho D v_\infty} \ln \kappa = \frac{4 \ln \kappa}{\text{Re}} \end{aligned}$$

For drag force,

$$\begin{aligned} F_D &= \pi D L \left(\frac{1}{2} \rho v_\infty^2 \right) C_D = \pi D L \left(\frac{1}{2} \rho v_\infty^2 \right) \frac{4 \ln \kappa}{\text{Re}} \\ &= 2\pi L \mu v_\infty \ln \kappa = 2\pi \times 1.5 \times \mu \times 2 \times 10^{-3} \ln \kappa = \underline{\underline{0.0188 \mu \ln(\kappa) (N)}} \end{aligned}$$

除了須已知 bone 與 pit 的大小關係外(κ)，尚須 tar 本身的黏度才可得到精確的數值。

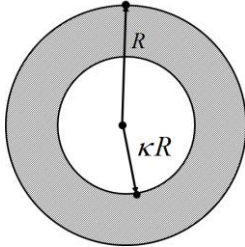
(本題假設與計算可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 65,

Problem 2B-7.)

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Problem 1

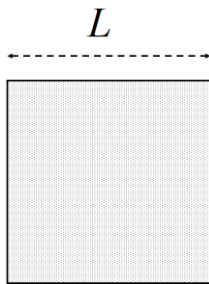
【Solution】



Equivalent diameter,

$$D_{eq} = 4 \frac{\text{cross-sectional area}}{\text{wetted perimeter}}$$

$$= 4 \frac{\pi R^2 - \pi(\kappa R)^2}{2\pi R + 2\pi(\kappa R)} = \frac{4\pi R^2(1 - \kappa^2)}{2\pi R(1 + \kappa)} = \underline{\underline{2(1 - \kappa)R}}$$



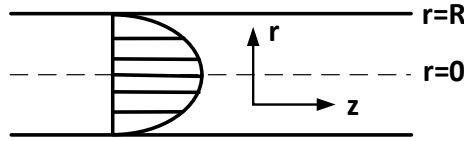
$$D_e = \underline{\underline{4 \frac{L^2}{4L} = L}}$$

(本題可參考：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass*

Transfer, 5th ed.; p 176.)

Problem 2

【Solution】



By the equation of motion,

$$\rho \frac{D\vec{v}}{Dt} = -\nabla P - [\nabla \cdot \vec{\tau}] + \rho \vec{g}$$

For flow in z-direction,

$$\nabla \cdot \vec{\tau} + \nabla P = \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) + \frac{\partial P}{\partial z} = 0$$

$$\tau_{rz} = \frac{r}{2} \left(\frac{-\partial P}{\partial z} \right) + \frac{c_1}{r} = m \left(\frac{-dv_z}{dr} \right)^n$$

$$\left(\frac{-dv_z}{dr} \right)^n = \frac{r}{2m} \left(\frac{-\partial P}{\partial z} \right) + \frac{\alpha_1}{r}$$

$$\frac{-dv_z}{dr} = \left[\frac{r}{2m} \left(\frac{-\partial P}{\partial z} \right) \right]^{\frac{1}{n}} + \beta_1 r^{\frac{-1}{n}}$$

$$v_z = \frac{-n}{n+1} r \left[\frac{r}{2m} \left(\frac{-\partial P}{\partial z} \right) \right]^{\frac{1}{n}} - \frac{n}{n-1} \beta_1 r^{1-\frac{1}{n}} + \beta_2 \quad \begin{cases} r=0, \frac{dv_z}{dr} = 0 \\ x=R, v_z = 0 \end{cases}$$

$$\begin{cases} \beta_1 = 0 \\ \beta_2 = \frac{n}{n+1} R \left[\frac{R}{2m} \left(\frac{-\partial P}{\partial z} \right) \right]^{\frac{1}{n}} \end{cases}$$

$$v_z = \frac{n}{n+1} \left[\frac{1}{2m} \left(\frac{-\partial P}{\partial z} \right) \right]^{\frac{1}{n}} R^{\frac{n+1}{n}} \left[1 - \left(\frac{r}{R} \right)^{\frac{n+1}{n}} \right]$$

For Q,

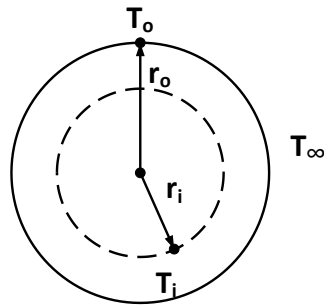
$$\begin{aligned} Q &= \int_0^{2\pi} \int_0^R v_z r dr d\theta = 2\pi \int_0^R \frac{n}{n+1} \left[\frac{1}{2m} \left(\frac{-\partial P}{\partial z} \right) \right]^{\frac{1}{n}} R^{\frac{n+1}{n}} r \left[1 - \left(\frac{r}{R} \right)^{\frac{n+1}{n}} \right] dr \\ &= 2\pi \frac{n}{n+1} \left[\frac{1}{2m} \left(\frac{-\partial P}{\partial z} \right) \right]^{\frac{1}{n}} R^{\frac{n+1}{n}} \cdot \frac{n+1}{3n+1} R^2 = \frac{\pi n}{(3n+1)} \left[\frac{1}{2m} \left(\frac{-\partial P}{\partial z} \right) \right]^{\frac{1}{n}} R^{\frac{3n+1}{n}} \end{aligned}$$

$$\text{where, } \left(\frac{-\partial P}{\partial z} \right) = \frac{P_0 - P_L}{L}$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 245.)

Problem 3

【Solution】



(a)

By steady state energy balance,

$$q_k(\text{conduction}) = q_c(\text{convection})$$

$$\frac{(T_i - T_o)}{\frac{\ln(\frac{r_o}{r_i})}{2\pi kL}} = \frac{T_o - T_\infty}{\frac{1}{h(2\pi r_o L)}}$$

$$Q_r = \frac{T_i - T_o + T_o - T_\infty}{\frac{\ln(\frac{r_o}{r_i})}{2\pi kL} + \frac{1}{h(2\pi r_o L)}} = \frac{2\pi L(T_i - T_\infty)}{\frac{\ln \frac{r_o}{r_i}}{k} + \frac{1}{hr_o}}$$

(b)

Let $\frac{dQ_r}{dr_o} = 0$,

$$\underbrace{2\pi L(T_i - T_\infty)}_{\neq 0} \cdot \frac{\left[\frac{1}{kr_o} - \frac{1}{r_o^2 h}\right]}{\underbrace{\left[\frac{\ln \frac{r_o}{r_i}}{k} + \frac{1}{hr_o}\right]^2}_{\text{分母} \neq 0}} = 0$$

$$\frac{1}{kr_o} - \frac{1}{r_o^2 h} = 0, \quad r_o = r_o^{\text{critical}} = \underline{\underline{\frac{k}{h}}}$$

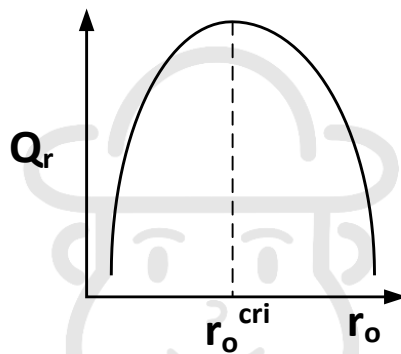
(c)

隨著 r_o 變大會有兩種效應產生：

$$\begin{cases} \text{heat conduction rate} \downarrow \\ \text{heat convection rate} \uparrow \end{cases}$$

因此 Q_r 是兩種熱傳方式綜合起來的結果，若是：

$$\begin{cases} r_o < \frac{k}{h} \rightarrow \begin{cases} r_o \uparrow, Q_r \uparrow \\ r_o \downarrow, Q_r \downarrow \end{cases} \\ r_o > \frac{k}{h} \rightarrow \begin{cases} r_o \uparrow, Q_r \downarrow \\ r_o \downarrow, Q_r \uparrow \end{cases} \end{cases}$$

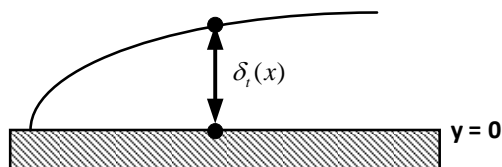


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Problem 4

【Solution】

(a)



By equation of change of energy,

$$\rho \hat{C}_p (v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y}) = k \frac{\partial^2 T}{\partial y^2} \quad \left\{ \begin{array}{l} y = \delta_t \rightarrow T = T_\infty \\ y = \delta_t \rightarrow \frac{\partial T}{\partial y} = 0 \\ y = 0 \rightarrow T = T_s \\ y = 0 \rightarrow v_x = v_y = 0 \end{array} \right.$$

$$\int_0^{\delta_t} v_x \frac{\partial T}{\partial x} dy + \int_0^{\delta_t} v_y \frac{\partial T}{\partial y} dy = \alpha \int_0^{\delta_t} \frac{\partial^2 T}{\partial y^2} dy$$

For $\int_0^{\delta_t} v_y \frac{\partial T}{\partial y} dy$, by IBP (integration by parts),

$$\begin{aligned} \int_0^{\delta_t} v_y \frac{\partial T}{\partial y} dy &= v_y T \Big|_0^{\delta_t} - \int_0^{\delta_t} T \frac{\partial v_y}{\partial y} dy = v_y T \Big|_{\delta_t} - \cancel{v_y T \Big|_0} - \int_0^{\delta_t} T \frac{\partial v_y}{\partial y} dy \\ &= v_y \Big|_{\delta_t} T_\infty - \int_0^{\delta_t} T \frac{\partial v_y}{\partial y} dy \end{aligned}$$

代回：

$$\int_0^{\delta_t} v_x \frac{\partial T}{\partial x} dy + \underbrace{v_y \Big|_{\delta_t} T_\infty - \int_0^{\delta_t} T \frac{\partial v_y}{\partial y} dy}_{(2)} = \alpha \left(\cancel{\frac{\partial T}{\partial y} \Big|_{\delta_t}} - \frac{\partial T}{\partial y} \Big|_0 \right)$$

(1)

By continuity equation,

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0$$

$$\underbrace{\frac{\partial v_y}{\partial y} = -\frac{\partial v_x}{\partial x}}_{(2)}, \quad \underbrace{v_y|_{\delta_t} = -\int_0^{\delta_t} \frac{\partial v_x}{\partial x} dy}_{(1)} \text{ 代回}$$

$$\int_0^{\delta_t} (v_x \frac{\partial T}{\partial x} dy + T \frac{\partial v_x}{\partial x} - T_\infty \frac{\partial v_x}{\partial x}) dy = -\alpha \frac{\partial T}{\partial y} \Big|_0$$

$$\int_0^{\delta_t} \frac{\partial [v_x(T_\infty - T)]}{\partial x} dy = \alpha \frac{\partial T}{\partial y} \Big|_0$$

By Leibniz integral rule,

$$\int_0^{\delta_t} \frac{\partial}{\partial x} [v_x(T_\infty - T)] dy = \frac{d}{dx} \int_0^{\delta_t} [v_x(T_\infty - T)] dy - \frac{d\delta_t}{dx} [v_x \underbrace{(T_\infty - T)}_{T(\delta_t)=T_\infty}] \Big|_{y=\delta_t}$$

代回：

$$\boxed{\frac{d}{dx} \int_0^{\delta_t} [v_x(T_\infty - T)] dy = \alpha \frac{\partial T}{\partial y} \Big|_{y=0}}$$

(b)

$$\because \text{Pr} \approx 1, \quad \delta_t \approx \delta_v = \delta$$

$$\text{For velocity profile, } v = a + by \begin{cases} y = 0, v = 0 \\ y = \delta, v = v_\infty \end{cases}$$

$$\text{For temperature profile, } T = \alpha + \beta y \begin{cases} y = 0, T = T_s \\ y = \delta, T = T_\infty \end{cases}$$

$$\begin{cases} a = 0 \\ b = \frac{v_\infty}{\delta} \end{cases}, \quad \begin{cases} \alpha = T_s \\ \beta = \frac{T_\infty - T_s}{\delta} \end{cases} \Rightarrow \begin{cases} \frac{v}{v_\infty} = \frac{y}{\delta} \\ \frac{T - T_s}{T_\infty - T_s} = \frac{y}{\delta} \end{cases}$$

$$\begin{cases} v_x = v_\infty \frac{y}{\delta} = v_\infty \eta \\ T_\infty - T = (T_\infty - T_s) \frac{T_\infty - T}{T_\infty - T_s} = (T_\infty - T_s) \left(1 - \frac{T - T_s}{T_\infty - T_s}\right) = (T_\infty - T_s) \left(1 - \frac{y}{\delta}\right) = (T_\infty - T_s)(1 - \eta) \end{cases}$$

代回：

$$\begin{aligned}\int_0^{\delta_t} [v_x(T_\infty - T)] dy &= \int_0^{\delta_t} [v_\infty \eta (T_\infty - T_s)(1 - \eta)] dy \\ &= \delta v_\infty (T_\infty - T_s) \int_0^1 \eta(1 - \eta) d\eta = \frac{1}{6} \delta v_\infty (T_\infty - T_s)\end{aligned}$$

代回：

$$\begin{aligned}\frac{d}{dx} \left[\frac{1}{6} \delta v_\infty (T_\infty - T_s) \right] &= \alpha \frac{\partial T}{\partial y} \Big|_{y=0} = \alpha \frac{(T_\infty - T_s)}{\delta} \\ \frac{1}{6} v_\infty \frac{d\delta}{dx} &= \frac{\alpha}{\delta}, \quad \boxed{\delta = \sqrt{\frac{12x}{v_\infty}} \alpha}\end{aligned}$$

$$@ y=0, \quad -k \frac{\partial T}{\partial y} \Big|_{y=0} = h(T_s - T_\infty)$$

$$\begin{aligned}Nu_x = \frac{hx}{k} &= \frac{\frac{\partial T}{\partial y} \Big|_{y=0} x}{(T_\infty - T_s)} = \frac{\frac{1}{\alpha} \frac{d}{dx} \left[\frac{1}{6} \delta v_\infty (T_\infty - T_s) \right] x}{T_\infty - T_s} \\ &= \frac{1}{\alpha} \frac{1}{6} v_\infty x \frac{d\delta}{dx} = \frac{1}{\sqrt{12}} \sqrt{\frac{v_\infty x}{\alpha}} = \frac{1}{\sqrt{12}} \sqrt{\frac{v_\infty x}{v}} \sqrt{\frac{v}{\alpha}} = \underline{\underline{0.288 Re_x^{\frac{1}{2}} Pr^{\frac{1}{2}}}} \approx \underline{\underline{0.288 Re_x^{\frac{1}{2}}}}\end{aligned}$$

※(a)小題為著名的 *von Kármán energy balance*

(b)小題假設為 thermal boundary layer 與 velocity boundary layer 差不多 ($Pr \approx 1$)，因此在積分

時兩者皆以 δ 來做計算，若是假設兩者不同，即

$$\begin{cases} \text{velocity boundary layer} = \delta \\ \text{thermal boundary layer} = \delta_t \end{cases}, \quad \delta \neq \delta_t$$

則另需要給定 *von Kármán momentum balance* 才可以推出 δ 值進而推出 δ_t

其形式如下：

$$\mu \frac{\partial v_x}{\partial y} \Big|_{y=0} = \frac{d}{dx} \int_0^\infty \rho v_x (v_\infty - v_x) dy + \frac{dv_e}{dx} \int_0^\infty \rho (v_\infty - v_x) dy + \underbrace{\int_0^\infty \rho g_x \beta (T - T_\infty) dy}_{\text{通常可假設}=0}$$

(詳細可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 388~389,

Example 12.4-1.)

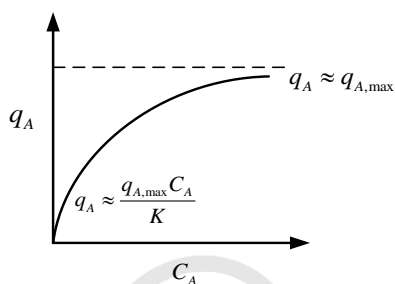
Problem 5

【Solution】

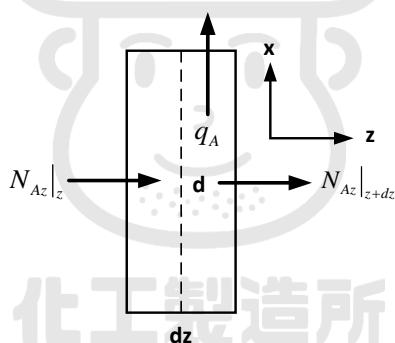
(a)

$$q_A \approx \begin{cases} q_{A,\max} & \text{when } C_A \text{ is high} \\ \frac{q_{A,\max} C_A}{K} & \text{when } C_A \text{ is low} \end{cases}$$

(b)



(c)



By mass balance of the solute A,

$$N_{Az} \left(\frac{\pi}{4} d^2 \right) \Big|_z - N_{Az} \left(\frac{\pi}{4} d^2 \right) \Big|_{z+dz} - q_A (\pi d) dz = \frac{\partial \left(C_A \frac{\pi}{4} d^2 dz \right)}{\partial t}$$

同除 $\frac{\pi}{4} d^2 dz \rightarrow 0$

$$\frac{-\partial N_{Az}}{\partial z} - \frac{4}{d} q_A = \frac{\partial C_A}{\partial t}$$

For N_{Az} , by Fick's law,

$$N_{Az} = -\mathcal{D}_{AB} \frac{\partial C_A}{\partial z} + \underbrace{y_A}_{\text{dilute}} (N_{Az} + N_{Bz}) = -\mathcal{D}_{AB} \frac{\partial C_A}{\partial z}$$

代回

Governing equation,

$$\mathcal{D}_{AB} \frac{\partial^2 C_A}{\partial z^2} - \frac{4}{d} q_A = \frac{\partial C_A}{\partial t}$$

Boundary conditions,

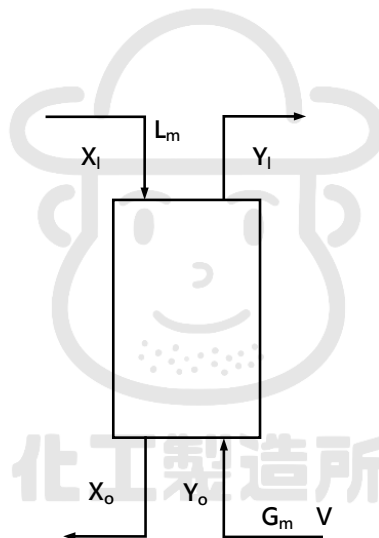
$$\begin{cases} z=0 \rightarrow C_A = C_{As} \\ z=L \rightarrow \frac{dC_A}{dz} = 0 \text{ (impermeable)} \end{cases}$$

Initial condition,

$$t=0 \rightarrow C_A = C_{As}$$

Problem 6

【Solution】



$\because y_o = 0.0136, y_i = 0.0008, x_l = 0$, the system is very dilute in the concentration of CO_2 . Therefore,

$$X_i = \frac{x_i}{1-x_i} \approx x_i, Y_i = \frac{y_i}{1-y_i} \approx y_i, G_m \approx G, L_m \approx L$$

For x_o , by mole balance,

$$G(y_o - y_l) = L(x_o - x_l), 2 \times (0.0136 - 0.0008) = 3.9 \times (x_o - 0)$$

$$x_o = 0.00656$$

Then the height of the tower is,

$$l = \frac{G}{K_y a} \left[\left(\frac{1}{1 - \frac{mG}{L}} \right) \ln \left(\frac{y_0 - mx_o}{y_l - mx_l} \right) \right]$$

For m , because if the amine is in equilibrium with the entering gas, it would contain 0.75 mol% CO_2 , then

$$y_o = 0.0136 = 0.0075m, \quad m = 1.813 \text{ 代入:}$$

$$l = \frac{2.0}{\frac{\pi}{4} \times 30^2 \times 4 \times 10^{-5}} \left[\left(\frac{1}{1 - \frac{1.813 \times 2.0}{3.9}} \right) \ln \left(\frac{0.0136 - 1.813 \times 0.00656}{0.0008 - 1.813 \times 0} \right) \right] = \underline{\underline{759.03 \text{ (cm)}}}$$

※注意，此題 G 與 L 代表的是 flux，因此題目雖然給了莫耳流率，必須除以塔截面積才是正確的

計算方式。本題改編自：Cussler, E. L. *Diffusion: Mass Transfer in Fluid Systems*, 3rd ed.;

p 318~319, Example 10.3-1.



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Problem 1

【Solution】

For steel pipe and other rough pipes,

$$f = \begin{cases} f(\text{Re}) \text{ for } \text{la min ar flow} \\ f(\frac{\varepsilon}{D}) \text{ for } \text{turbulent flow } (\text{Re} > 10^6) \end{cases}$$

where ε is the relative roughness factor

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*,

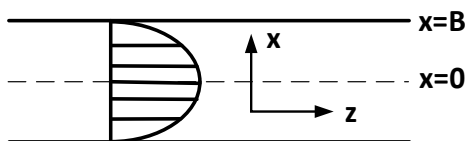
7th ed.; p 107/113~116.)



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Problem 2

【Solution】



By the equation of motion,

$$\rho \frac{D\vec{v}}{Dt} = -\nabla P - [\nabla \cdot \vec{\tau}] + \rho \vec{g}$$

For flow in z-direction,

$$\nabla \cdot \vec{\tau} + \nabla P = \frac{\partial \tau_{xz}}{\partial x} + \frac{\partial P}{\partial z} = 0$$

$$\tau_{xz} = \left(\frac{-\partial P}{\partial z} \right) x + c_1$$

For $0 \leq x \leq B$,

$$\begin{aligned} \tau_{xz} &= m \left(\frac{-dv_z}{dx} \right)^n \quad \text{代入} \\ m \left(\frac{-dv_z}{dx} \right)^n &= \left(\frac{-\partial P}{\partial z} \right) x + c_1, \quad \left(\frac{-dv_z}{dx} \right)^n = \frac{1}{m} \left(\frac{-\partial P}{\partial z} \right) x + \alpha_1 \\ v_z &= \frac{-n}{n+1} \left[\frac{1}{m} \left(\frac{-\partial P}{\partial z} \right) x \right]^{\frac{n+1}{n}} + \beta_1 x + \beta_2 \quad \begin{cases} x=0, \quad \frac{dv_z}{dx} = 0 \\ x=B, \quad v_z = 0 \end{cases} \\ \begin{cases} \beta_1 = 0 \\ \beta_2 = \frac{n}{n+1} \left[\frac{1}{m} \left(\frac{-\partial P}{\partial z} \right) \right]^{\frac{1}{n}} B^{\frac{n+1}{n}} \end{cases} \\ \underline{\underline{v_z = \frac{n}{n+1} \left[\frac{1}{m} \left(\frac{-\partial P}{\partial z} \right) \right]^{\frac{1}{n}} B^{\frac{n+1}{n}} \left[1 - \left(\frac{x}{B} \right)^{\frac{n+1}{n}} \right]}} \end{aligned}$$

For $Q(-B \leq x \leq B) = 2Q(0 \leq x \leq B)$

$$Q = 2 \int_0^W \int_0^B v_z dx dy = \frac{2WB^2n}{2n+1} \left[\left(\frac{-\partial P}{\partial z} \right) B \right]^{\frac{1}{n}}$$

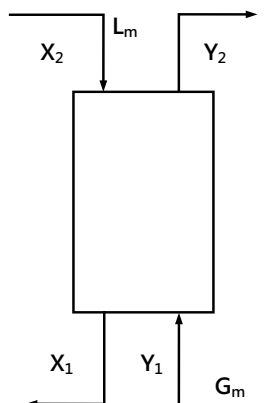
$$\text{where, } \left(\frac{-\partial P}{\partial z} \right) = \frac{P_0 - P_L}{L}$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 243,

Example 8.3-2.)

Problem 3

【Solution】



$$X_2 = 0, Y_1 = 0.04, X_1 = 0.015$$

For Y_2 , which is 3% of Y_1 , we have $Y_2 = 0.04 \times 0.03 = 0.0012$

(a) To calculate the height of the absorber,

$$Z = \frac{G'_m}{K_G a} \frac{Y_1 - Y_2}{(Y - Y_e)_{lm}}$$

H_{OG} N_{OG}

For $(Y - Y_e)_{lm}$, we have,

$$(Y - Y_e)_{lm} = \frac{(Y_1 - Y_{1e}) - (Y_2 - Y_{2e})}{\ln\left(\frac{Y_1 - Y_{1e}}{Y_2 - Y_{2e}}\right)} = \frac{(0.04 - 2.5 \times 0.015) - (0.0012 - 0)}{\ln\left(\frac{0.04 - 2.5 \times 0.015}{0.0012 - 0}\right)} = 1.77 \times 10^{-3}$$

代入：

$$Z = \frac{0.017}{0.03} \cdot \frac{(0.04 - 0.0012)}{1.77 \times 10^{-3}} = 12.41 \text{ (m)}$$

(b)

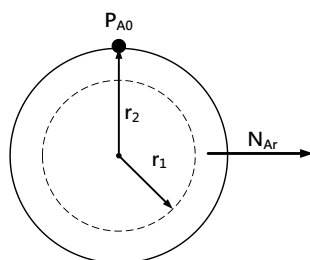
The number of transfer units is the log-mean term for the calculation of height, which is,

$$N_{OG} = \frac{Y_1 - Y_2}{(Y - Y_e)_{lm}} = \frac{(0.04 - 0.0012)}{1.77 \times 10^{-3}} = \underline{\underline{21.91}}$$

(本題改編自：Coulson, J.; Richardson, J.; Backhurst, J.; Harker, J. *Chemical Engineering*, 5th ed.; Volume 2, p 1170, Problem 12.4.)

Problem 4

【Solution】



Assume,

$$\begin{cases} \text{naphthalene} = A \\ \text{air} = B \end{cases}$$

By pseudo-steady-state assumption on the naphthalene particle,

$$-(4\pi r^2)N_{Ar}|_r = \frac{d(\frac{4}{3}\pi r^3 \rho)}{Mdt} = \frac{4\pi r^2 \rho}{M} \frac{dr}{dt}$$

$$N_{Ar}|_r = \frac{-\rho}{M} \frac{dr}{dt}$$

For N_{Ar} , by Fick's law,

$$N_{Ar} = -\mathcal{D}_{AB} \frac{dC_{Ar}}{dr} + \underbrace{y_A}_{\text{very dilute}} (N_{Ar} + N_{Br}) = \frac{-\mathcal{D}_{AB} P}{RT} \frac{dy_{Ar}}{dr}$$

$$N_{Ar} = \frac{w_{Ar}}{4\pi r^2} = \frac{-\mathcal{D}_{AB} P}{RT} \frac{dy_{Ar}}{dr}, \quad \frac{w_{Ar}}{4\pi} \int_r^\infty \frac{dr}{r^2} = \frac{-\mathcal{D}_{AB} P}{RT} \int_{y_{A0}}^0 dy_{Ar}$$

$$w_{Ar} = 4\pi r \frac{\mathcal{D}_{AB} P}{RT} (y_{A0} - 0)$$

$$N_{Ar} = \frac{w_{Ar}}{4\pi r^2} = \frac{\mathcal{D}_{AB} P_{A0}}{RT r} \quad \text{代入}$$

$$\frac{\mathcal{D}_{AB} P_{A0}}{RT r} = \frac{-\rho}{M} \frac{dr}{dt}, \quad dt = \frac{-\rho RT}{\mathcal{D}_{AB} P_{A0} M} r dr, \quad \int_0^t dt = \frac{-\rho RT}{\mathcal{D}_{AB} P_{A0} M} \int_{r_0}^{r_1} r dr$$

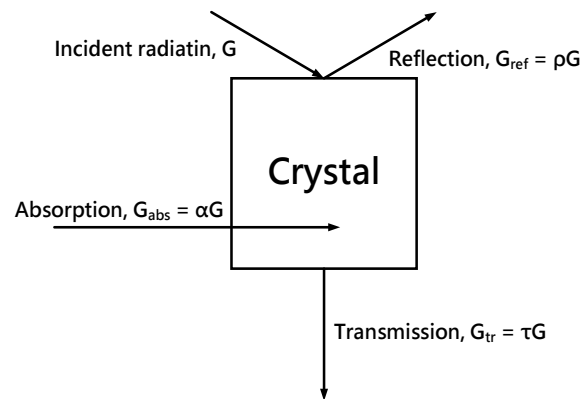
$$t = \frac{\rho RT}{2\mathcal{D}_{AB} P_{A0} M} (r_0^2 - r_1^2)$$

$$= \frac{1.145 \times 10^3 \times 8.314 \times (273 + 60)}{2 \times 8.19 \times 10^{-6} \times 245 \times 128 \times 10^{-3}} \left[\left(\frac{3}{2} \times 10^{-2} \right)^2 - \left(\frac{1.5}{2} \times 10^{-2} \right)^2 \right]$$

$$= \underline{\underline{1041390.4 \text{ (s)}}}$$

Problem 5

【Solution】



(a)

By energy balance on the crystal,

$$\underbrace{\alpha G}_{\text{energy absorbed}} - \underbrace{E(\text{emissive power})}_{\text{energy release}} = 0$$

Assume the crystal is opaque,

$$E - \alpha G = \varepsilon \sigma (T_c^4 - T_\infty^4) - \alpha G = 0$$

$$0.8 \times 5.67 \times 10^{-8} (T_c^4 - 300^4) - 0.08 \times 1 \times 10^{13} \times 10^6 \times 10 \times 1.6 \times 10^{-16} = 0$$

$$\underline{\underline{T_c = 436.4 \text{ (K)}}}$$

(b)

By energy balance of the crystal,

$$(G - G_{ref} - E)A = \frac{\partial(\rho V C_p T_c)}{\partial t}$$

$$[\alpha G - \varepsilon \sigma (T_c^4 - 300^4)] = \rho \frac{V}{A} C_p \frac{\partial T_c}{\partial t}$$

$$\int_0^t dt = \int_{T_0}^{T_1} \frac{\rho L C_p}{[\alpha G - \varepsilon \sigma (T_c^4 - 300^4)]} dT_c$$

$$t = \int_{300}^{273+40} \frac{1.2 \times 10^{-3} \times 0.2 \times 6}{0.08 \times 1 \times 10^{13} \times 10 \times 1.6 \times 10^{-16} - 0.8 \times 5.67 \times 10^{-8} \times 10^{-6} (T_c^4 - 300^4)} dT_c = \underline{\underline{15.02 \text{ (s)}}}$$

(c)

Assume this case is similar with the case of fluid flowing above a plate,

$$\delta(x) = \frac{5x}{\sqrt{\text{Re}_x}} = \frac{5x}{\sqrt{\frac{v_\infty x}{\nu}}} = \frac{5x}{\sqrt{\frac{1.5x}{1.9 \times 10^{-6}}}} = 5.627 \times 10^{-3} \sqrt{x}$$

$$\therefore \left(\frac{\delta}{\delta_T}\right)^3 = \text{Pr},$$

$$\left[\frac{5.627 \times 10^{-3} \sqrt{x}}{\delta_T(x)}\right] = 0.69^{\frac{1}{3}}$$

$$\underline{\underline{\delta_T(x) = 6.368 \times 10^{-3} \sqrt{x}}}$$

$\text{Pr} = \frac{\text{momentum boundary layer thickness}}{\text{thermal boundary layer thickness}}$
--

(d)

For Biot number,

$$Bi = \frac{hL_e}{k_s},$$

Where $\begin{cases} L_e = \text{characteristic length} \\ k_s = \text{the conductivity of the crystal} \end{cases}$

但此題並未給定 crystal 的 conductivity 值，應該沒辦法往下算

若題目給定 crystal 之 thermal conductivity，且檢查結果 $Bi < 0.1$ ，則 crystal 經由

液態氮向外之熱傳可用 lumped-capacity analysis 做計算，即

$$\underbrace{(G - G_{ref} - E)A}_{\text{radiation}} - \underbrace{hA(T - T_{100K})}_{\text{convection}} = \frac{\partial(\rho V C_p T_c)}{\partial t}$$

For h , we use average heat transfer coefficient over the length of the crystal, which is

$$\begin{aligned} \bar{h}_L &= \frac{\int_0^L \bar{h}_x dx}{L} = \frac{\int_0^L \frac{k}{\delta_t} dx}{L} = \frac{9.8 \times 10^{-3}}{0.2 \times 10^{-3}} \times \int_0^L \frac{1}{6.368 \times 10^{-3} \sqrt{x}} \\ &= \frac{9.8 \times 10^{-3}}{0.2 \times 10^{-3}} \times \frac{2}{6.638 \times 10^{-3}} \cdot \sqrt{0.2 \times 10^{-3}} = 208.78 \text{ (W / m}^2 \cdot \text{K)} \end{aligned}$$

代回：

$$[\alpha G - \varepsilon \sigma (T_c^4 - 100^4)] - h(T - T_{100K}) = \rho \frac{V}{A} C_P \frac{\partial T_c}{\partial t}$$

$$\int_0^t dt = \int_{100}^{T_1} \frac{\rho L C_P}{[\alpha G - \varepsilon \sigma (T_c^4 - 100^4)] - h(T - T_{100K})} dT_c$$

$$t = \int_{100}^{273.15+30} \frac{1.2 \times 10^{-3} \times 0.2 \times 6}{0.08 \times 1 \times 10^{13} \times 10 \times 1.6 \times 10^{-16} - 0.8 \times 5.67 \times 10^{-8} \times 10^{-6} (T_c^4 - 100^4) - 208.78 \times 10^{-6} (T_c - 100)} dT_c$$

< 0

The sample will never reach 30 °C during the test.



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Problem 1

【Solution】

(a)

The continuum assumption is valid when the molecule mean free path is much less than the length scale of the tube.

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 52.)

(b)

$$\text{Scaling factors : } \begin{cases} v = \text{velocity of the fluid} \\ \rho = \text{density of the fluid} \\ \mu = \text{viscosity of the fluid} \\ D = \text{diameter of the tube} \end{cases}$$

$$Re = \frac{\rho v D}{\mu} = \frac{\text{inertial force}}{\text{viscous force}}$$

(c)

$$\begin{cases} I.C. : t = 0, v = 0 \\ B.C. : r = \frac{D}{2}, v = 0 \\ B.C. : r \rightarrow \infty, v = v_{\infty} \end{cases}, \text{ 令 } \begin{cases} t^* = \frac{t}{t_0} \\ v^* = \frac{v}{v_{\infty}} \\ r^* = \frac{r}{D} \end{cases}$$

$$\begin{cases} t^* = 0, v^* = 0 \\ r = \frac{1}{2}, v^* = 0 \\ r \rightarrow \infty, v^* = 1 \end{cases}$$

(d)

By the equation of change of momentum,

$$\rho \frac{Dv}{Dt} = \mu \nabla^2 v - \nabla P + \cancel{\rho g} \quad , \quad \text{令} \quad \left\{ \begin{array}{l} P^* = \frac{P}{P_B} \\ \frac{D}{Dt} = \frac{D}{Dt^*} \cdot \frac{1}{t_0} \\ \nabla = \frac{1}{D} \nabla^* \\ \nabla^2 = \frac{1}{D^2} \nabla^{*2} \end{array} \right.$$

$$\rho \frac{v_\infty}{t_0} \frac{Dv^*}{Dt^*} = \frac{v_\infty \mu}{D^2} \nabla^{*2} v^* - \frac{P_B}{D} \nabla^* P^* \quad , \quad \frac{Dv^*}{Dt^*} = \frac{t_0 \mu}{\rho D^2} \nabla^{*2} v^* - \frac{P_B t_0}{\rho v_\infty D} \nabla^* P^*$$

$$\text{令 } t_0 = \frac{D}{v_\infty}$$

$$\frac{Dv^*}{Dt^*} = \frac{\mu}{\rho v_\infty D} \nabla^{*2} v^* - \frac{P_B}{\rho v_\infty^2} \nabla^* P^* = \frac{1}{Re} \nabla^{*2} v^* - \frac{P_B}{\rho v_\infty^2} \nabla^* P^*$$

(e)

$$\left\{ \begin{array}{l} \text{velocity : } Re = \frac{\rho v_\infty D}{\mu} \rightarrow v_\infty \propto \frac{1}{D} \text{ in the same } Re \text{ value} \\ \text{pressure : } \frac{P_B}{\rho v_\infty^2} \end{array} \right.$$

(f)

For real system,

$$Re_{real} = \frac{v_\infty D}{\nu} = \frac{40 \times 10^{-2} \times 1 \times 10^{-3}}{3 \times 10^{-6}} = 133.33$$

For mock system,

$$Re_{mock} = \frac{v_\infty D}{\nu} = \frac{v_\infty \times 10 \times 10^{-2}}{1 \times 10^{-6}} = 133.33$$

$$\underline{\underline{v_{\infty, mock} = 1.33 \times 10^{-3} \text{ (m / s)}}}$$

Problem 2

【Solution】

(a)

Wiedemann-Franz-Lorenz equation,

$$\frac{k}{k_e T} = L = \text{constant} \begin{cases} k = \text{thermal conductivity} \\ k_e = \text{electrical conductivity} \\ L = \text{Lorenz number} \approx 22 \sim 29 \times 10^{-9} (\text{volt}^2 / \text{K}^2) \end{cases}$$

for pure metal at 0°C and little changes with temperature above 0°C.

$$\begin{cases} \text{non-metal : water} > \text{engine oil} \\ \text{metal : } k \propto k_e, k_{e,\text{copper}} > k_{e,\text{iron}} \rightarrow k_{\text{copper}} > k_{\text{iron}} \end{cases}$$

Thermal conductivity,

$$\boxed{\text{copper} > \text{iron} > \text{water} > \text{engine oil}}$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 280~281.)

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(b)

(i)

Correct, $k = 1.9891 \times 10^{-4} \frac{\sqrt{\frac{T}{M}}}{\sigma^2 \Omega_k}$, independent of pressure.

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 275.)

(ii)

Correct, $k = 1.9891 \times 10^{-4} \frac{\sqrt{\frac{T}{M}}}{\sigma^2 \Omega_k} \propto \sqrt{T}$

(c)

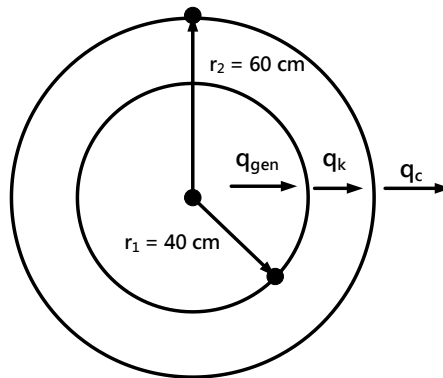
$$Pr = \frac{\nu}{\alpha} = \frac{\text{momentum diffusivity}}{\text{thermal diffusivity}} = \text{Prandtl number}$$

(d)

$$Bi = \frac{h(\frac{V}{A})}{k} = \frac{\text{internal thermal resistance}}{\text{external thermal resistance}}$$
$$Fo = \frac{\alpha t}{(\frac{V}{A})^2} = \frac{\text{heat diffusion rate}}{\text{heat storage rate}}$$

Problem 3

【Solution】



(a)

At the tube surface along y-direction, T is constant = 25°C

$$\boxed{\frac{dT}{dy} = 0}$$

(b)

By the equation of continuity of energy in r-direction,

$$\rho C_p \left(\frac{\partial T}{\partial t} + \vec{v} \cdot \nabla T \right) = k \nabla^2 T + \cancel{\mu \Phi_v}$$

$$k \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \right] = 0 \quad (\text{only r-direction conduction})$$

積分兩次

$$T = c_1 \ln r + c_2 \quad \begin{cases} r = r_1, T = T_2 \\ r = r_2, h(T_1 - T_{air}) = -k \frac{dT}{dr} \Big|_{r=r_2} \end{cases}$$

$$\begin{cases} T_2 = c_1 \ln r_1 + c_2 \\ h(T_1 - T_{air}) = -k \frac{c_1}{r_2} \end{cases} \rightarrow \begin{cases} c_1 = \frac{h(T_{air} - T_1)r_2}{k} \\ c_2 = T_2 + \frac{h(T_1 - T_{air})r_2}{k} \ln r_1 \end{cases}$$

$$T = \frac{h(T_{air} - T_1)r_2}{k} \ln \frac{r}{r_1} + T_2$$

$r = r_2$ 代入：

$$T = \frac{h(T_{air} - T_1)r_2}{k} \ln \frac{r_2}{r_1} + T_2 = T_1$$

$$\frac{100(298 - T_1) \times 60 \times 10^{-2}}{50} \ln \frac{60}{40} + (200 + 273) = T_1$$

$$\underline{\underline{T_1 = 415.72 \text{ (K)} = 142.72 \text{ (}^\circ\text{C)}}}$$

(c)

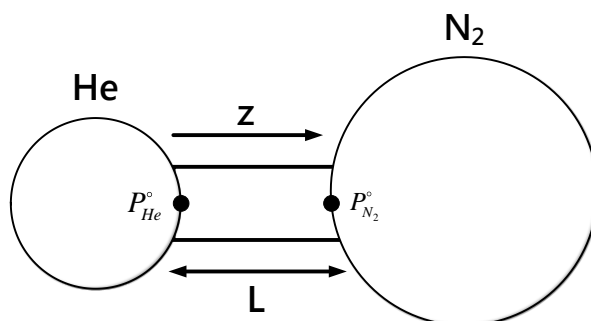
$$\underline{\underline{q'' = q_c'' = h(T_1 - T_{air}) = 100(142.72 - 25) = 11772.16 \text{ (W / m}^2\text{)}}}$$



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Problem 4

【Solution】



(a)

By Fick's law,

$$N_{He} = -\mathcal{D}_{He-N_2} \frac{dC_{He}}{dz} + \cancel{y_{He}}_{\text{very dilute}} (N_{He} + N_{N_2})$$

$$N_{He} = -\mathcal{D}_{He-N_2} \frac{dC_{He}}{dz} = \frac{-\mathcal{D}_{He-N_2}}{RT} \frac{dP_{He}}{dz}$$

$$\int_0^L N_{He} dz = \int_{P_{He}^o}^{P_{He,L}} \frac{-\mathcal{D}_{He-N_2}}{RT} dP_{He}$$

$$N_{He} = \frac{-\mathcal{D}_{He-N_2}}{RTL} (P_{He,L} - P_{He}^o) = \frac{-0.894 \times 10^{-4}}{8.314 \times 340 \times 8 \times 10^{-2}} (0.012 - 0.055) \times 1.013 \times 10^5$$

$$= 1.72 \times 10^{-3} \text{ (mole / m}^2 \cdot \text{s)} = \underline{\underline{1.72 \times 10^{-6} \text{ (kgmole / m}^2 \cdot \text{s)}}}$$

(本題也可以直接假設 equimolar-counter-diffusion 來解題)

(b)

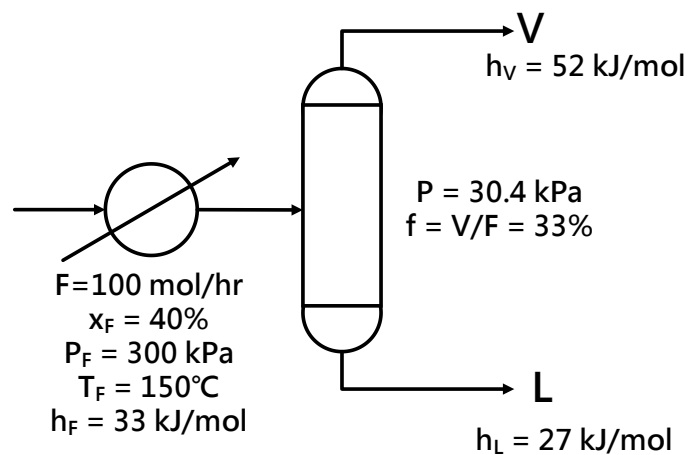
∵ The pressure of the system is constant and there are only two components,

the system can be considered as an equimolar-counter-diffusion system.

$$\underline{\underline{N_{N_2} = -N_{He} = -1.72 \times 10^{-6} \text{ (kgmole / m}^2 \cdot \text{s)}}}$$

Problem 5

【Solution】

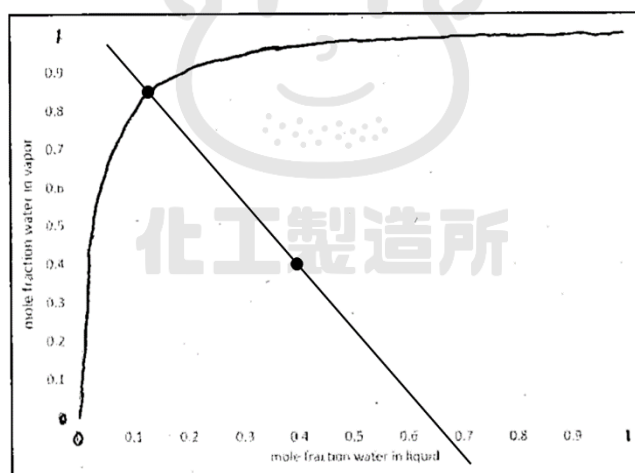


(a)

For operating line,

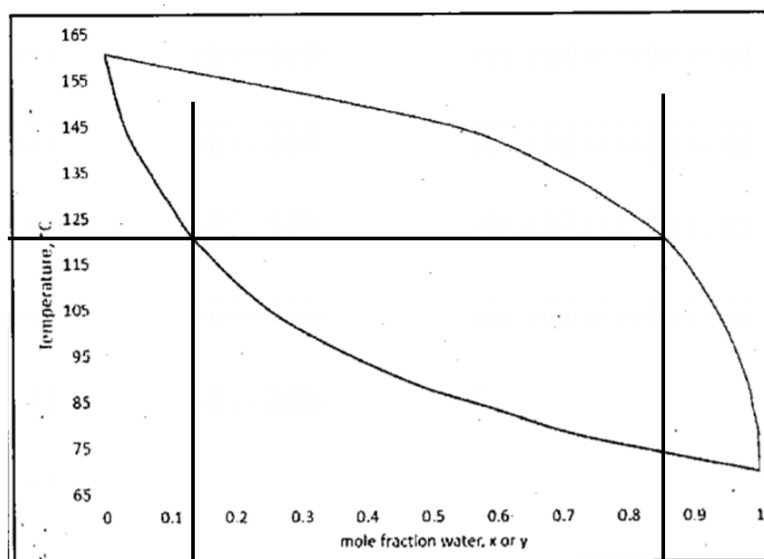
$$y_A = \frac{f-1}{f} x_A + \frac{x_F}{f} = \frac{0.33-1}{0.33} x_A + \frac{0.4}{0.33} = -2x_A + 1.21$$

在 $y_A - x_A$ 圖上畫過 $(x_F, x_F) = (0.4, 0.4)$ 、斜率為 2 之直線



可知 operating line 與 equilibrium line 交於 $(x_A, y_A) = (0.12, 0.85)$

再對至 $x_A - y_A - T$ 圖可得溫度為 123°C



(b)

By energy balance,

$$Fh_F + Q = Lh_L + Vh_v$$

By mole balance,

$$\begin{cases} F = L + V \\ Fx_F = Lx_A + Vy_A \end{cases}, \begin{cases} L = 61.64 \\ V = 38.36 \end{cases}$$

代回 Energy balance,

$$100 \times 33 \times 10^3 + Q = 61.64 \times 27 \times 10^3 + 38.36 \times 52 \times 10^3$$

$$\underline{\underline{Q = 359000 \text{ (kJ)}}}$$

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Problem 1

【Solution】

(a)

$$Re = \frac{\text{inertial force}}{\text{viscous force}}$$

(b)

$$f = \frac{\text{drag force}}{\text{inertial force}}$$

(c)

$$Re_h = \frac{4R_h \langle v \rangle \rho}{\mu}, \text{ where } R_h = \frac{\text{cross-sectional area}}{\text{wetted area}}$$

$$f = \left(\frac{R_h}{L}\right) \left(\frac{P_0 - P_L}{\frac{1}{2} \rho \langle v \rangle^2}\right)$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 183.)

(d)

當 Reynolds number 變大，inertial force \gg viscous force

則 $f \propto \frac{1}{\text{inertial force}}$ 就變小，但不代表 shear stress 變小，只是相對於 inertial

force 來說影響程度變小

(e)

By Hagen-Poiseuille equation, (假設在圓管內流動)

$$Q = \frac{\pi(P_0 - P_L)R^4 \rho}{8\mu L} = \rho \pi R^2 \langle v \rangle$$

$$(P_0 - P_L) = \frac{8\mu L \rho \pi R^2 \langle v \rangle}{\pi R^4 \rho} = \frac{8\mu L \langle v \rangle}{R^2}$$

$$f = \frac{D}{4L} \times \frac{8\mu L \langle v \rangle}{\left(\frac{D}{2}\right)^2} \times \frac{2}{\rho \langle v \rangle^2} = \frac{16\mu}{\rho \langle v \rangle D} = \frac{16}{\text{Re}}$$

(f)

The thickness of the viscous sublayer will become less with increasing Reynolds number, or even less than the roughness of the pipe. Therefore the effect of roughness is dominate.

(g)

The dependence of f on L/D arises from the development of the time-averaged velocity distribution from its flat entry shape toward more rounded profiles.

For laminar flow with small enough Re , the shape of the velocity distribution is “fully-developed”. In the transportation of fluids, the entrance length is usually a small fraction of the total.

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 181.)

(h)

The same reason as **(f)**, if the roughness of the wall increases, it will hinder the transportation of the flow.

(i)

The value of D will contribute the resistance of the transportation of the flow.

(j)

If a rough pipe is smoothed, the friction factor is reduced. When further smoothing brings about no further reduction in the friction factor for a given Reynolds number, the tube is said to be “hydraulically smooth”.

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 114.)

Problem 2**【Solution】****(a) Incorrect**

Stream function 不可用於 compressible flow，這樣才有 exact equation

$$\nabla \cdot \vec{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \text{ 可以使用}$$

(b) Incorrect

Velocity potential 可用於 3D 流場

(c) Incorrect

$$\begin{cases} v_x = \frac{\partial \phi}{\partial x} = 5x^2 - 5y^2 = \frac{\partial \psi}{\partial y} \\ v_y = \frac{\partial \phi}{\partial y} = -10xy = -\frac{\partial \psi}{\partial x} \end{cases}, \psi = 5x^2y - \frac{5}{3}y^3$$

(d) Correct

$$\vec{v} = \nabla \phi = u_\infty L \left(\frac{2x - 3y^2}{L^3} \vec{e}_x - \frac{6xy}{L^3} \vec{e}_y \right)$$

For irrotational flow, $\nabla \times \vec{v} = 0$

<check>:

$$\nabla \times \vec{v} = 0\vec{e}_x + 0\vec{e}_y + (-6y + 6y)\vec{e}_z = 0$$

(e) Correct

Problem 3**【Solution】****(a)**

$$Bi = \frac{h(\frac{V}{A})}{k} = \frac{\text{internal resistance}}{\text{external resistance}} \text{ to heat transfer}$$

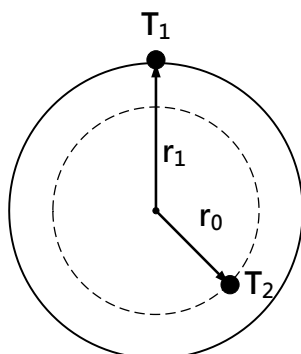
$$Nu = \frac{hL}{k_f} = \frac{\text{conductive resistance}}{\text{convective resistance}} \text{ of the fluid}$$

Biot number has the conductivity of the main object while Nu uses that of the external fluid.

(b)

$$Nu = f(Re, Gr, Pr) \left\{ \begin{array}{l} Re = \frac{\text{inertial force}}{\text{viscous force}} \\ Gr = \frac{\text{buoyant force}}{\text{viscous force}} \\ Pr = \frac{\text{momentum diffusivity}}{\text{thermal diffusivity}} \end{array} \right.$$

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Problem 4**【Solution】**

$$\text{Let } k = a + bT \begin{cases} a = \frac{k_1 - k_0}{T_1 - T_0} \\ b = k_0 - aT_0 = \frac{k_0T_1 - k_1T_0}{T_1 - T_0} \end{cases}$$

Assume : (1) Steady-State

(2) only r-direction heat conduction

By Fourier's law,

$$q_r = -k(2\pi rL) \frac{dT}{dr} = -(a + bT)(2\pi rL) \frac{dT}{dr}$$

$$\int_{r_0}^{r_1} \frac{q_r}{r} dr = -2\pi L \int_{T_0}^{T_1} (a + bT) dT$$

$$q_r \ln \frac{r_1}{r_0} = 2\pi L \left[a(T_0 - T_1) + \frac{b}{2}(T_0^2 - T_1^2) \right]$$

$$\begin{aligned} q_r &= \frac{2\pi L}{\ln \frac{r_1}{r_0}} \left[a(T_0 - T_1) + \frac{b}{2}(T_0^2 - T_1^2) \right] \\ &= \frac{2\pi L}{\ln \frac{r_1}{r_0}} \left[(k_0 - k_1) + \frac{(T_0 + T_1)}{2}(k_1T_0 - k_0T_1) \right] \end{aligned}$$

(※本題解法可與 104 年中央化材所 Problem 4 互相對照)

Problem 5**【Solution】****(a)**

By Fick's first law,

$$N_{Ar} = \frac{w_A}{4\pi r^2} = -\mathcal{D}_{AB}c \frac{dy_A}{dr} + \cancel{\gamma_A} \text{ (} N_A + N_B \text{)}_{\text{very dilute}}$$

$$\int_a^\infty \frac{w_A}{4\pi r^2} dr = -\mathcal{D}_{AB}c \int_{X_{A1}}^0 dy_A$$

$$\frac{w_A}{4\pi} \left(\frac{1}{a}\right) = \mathcal{D}_{AB}cX_{A1} \quad , \quad w_A = 4\pi\mathcal{D}_{AB}cX_{A1}a$$

$$\underline{\underline{N_{Ar} = \frac{w_A}{4\pi r^2} = \frac{\mathcal{D}_{AB}cX_{A1}a}{r^2}}}$$

(b)

$$\underline{\underline{w_A = 4\pi\mathcal{D}_{AB}cX_{A1}a}}$$

(c)For $a(t)$, by pseudo-steady-state assumption

$$w_A = \frac{-d}{dt} \left(\frac{4}{3} \frac{\rho}{M_A} \pi a^3 \right) = -4\pi a^2 \frac{\rho}{M_A} \frac{da}{dt}$$

$$\mathcal{D}_{AB}cX_{A1} = -a \frac{\rho}{M_A} \frac{da}{dt} \quad , \quad \int_0^t \mathcal{D}_{AB}cX_{A1} dt = -\int_{a_0}^a \frac{\rho}{M_A} a da = \frac{1}{2} \frac{\rho}{M_A} (a_0^2 - a^2)$$

$$\underline{\underline{a(t) = \sqrt{a_0^2 - \frac{2M_A\mathcal{D}_{AB}cX_{A1}t}{\rho}}}}$$

$$w_A \propto a$$

If a of the particles is small, the diffusion rate will be small and it will stabilize the particles.

(d)

$$N_{Ar}(a_0) = \frac{\mathcal{D}_{AB}cX_{A1}a_0}{a_0^2} = \underline{\underline{\frac{\mathcal{D}_{AB}cX_{A1}}{a_0}}}$$

(e)

$$\frac{1}{2}(a_0^2 - a^2) = \frac{\mathcal{D}_{AB} c X_{A1} M_A}{\rho_A} t, \quad t = \frac{\rho_A (a_0^2 - a^2)}{\underline{\underline{2 \mathcal{D}_{AB} c X_{A1} M_A}}}$$

(f)

$$t_0 = \frac{\rho a_0^2}{\underline{\underline{2 \mathcal{D}_{AB} c X_{A1} M_A}}}$$

(g)

$$\frac{t}{t_0} = 1 - \frac{a^2}{a_0^2} = 1 - \left(\frac{a}{a_0}\right)^2$$

(h)

$$\frac{t}{t_0} \rightarrow 0$$

(time for change in size is large)

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Problem 1

【Solution】

(a)

$$\begin{aligned}\tau &= \tau_{yx} = \mu \frac{\partial u_x}{\partial y} = \mu(3 - 3y^2) \\ &= \rho \nu (3 - 3y^2) = (10^{-3} \times 10^{-6}) \times (7 \times 10^{-7} \times 10^4)(3 - 3y^2) \\ &= \underline{\underline{7 \times 10^{-6}(3 - 3y^2) \text{ (kg / cm} \cdot \text{s}^2)}}\end{aligned}$$

(b)

$y = 0.8\text{mm}$ 代入 τ_{yx}

$$\tau_{yx}|_{y=0.8} = 7 \times 10^{-6}(3 - 3 \times 0.8^2) = \underline{\underline{7.56 \times 10^{-6} \text{ (kg / cm} \cdot \text{s}^2)}}\quad \text{化工製造所}$$

(c)

$$\tau_{xx} = -\mu \left[2 \frac{\partial u_x}{\partial x} \right] = 0$$

There is no momentum flux in the x-direction.

Problem 2**【Solution】****(a)**

For Stokes' law to be applicable,

$$f = \frac{24}{Re} = \frac{24\mu}{\rho v_{\infty} D_p} = \frac{24\mu}{\rho \sqrt{\frac{4(\rho_p - \rho)gD_p}{3\rho f}} D_p} \quad (Re < 1)$$

$$f^{\frac{1}{2}} = \frac{24\mu}{\rho \sqrt{\frac{4(\rho_p - \rho)gD_p}{3\rho}} D_p} > 24^{\frac{1}{2}}$$

$$\begin{cases} \mu = 1.8 \times 10^{-5} \text{ (kg / m} \cdot \text{s)} \\ \rho = 1.18 \text{ (kg / m}^3\text{)} \\ \rho_p = 4000 \text{ (kg / m}^3\text{)} \end{cases} \quad \text{代入}$$

$$\frac{24 \times 1.8 \times 10^{-5}}{1.18 \sqrt{\frac{4(4000 - 1.18) \times 9.8 D_p}{3 \times 1.18}}} > 24^{0.5}$$

$$\underline{\underline{D_p < 5.0 \times 10^{-5} \text{ (m)} = 50 \mu\text{m} \text{ 得證}}}$$

(b)For $D_p = 10 \mu\text{m}$, Stokes' law is applicable,

$$v_t = \sqrt{\frac{4(\rho_p - \rho)gD_p}{3f\rho}}, \quad f = \frac{24}{Re} = \frac{24\mu}{\rho v_t D_p}$$

$$v_t = \frac{gD_p^2(\rho_p - \rho)}{18\mu} = \frac{9.8 \times (10 \times 10^{-6})^2 (4000 - 1.18)}{18 \times 1.8 \times 10^{-5}} = \underline{\underline{0.012 \text{ (m / s)}}}$$

For $D_p = 140.250 \text{ (}\mu\text{m)}$, Stokes' law isn't applicable,

$$v_t = \sqrt{\frac{4(\rho_p - \rho)gD_p}{3f\rho}}, \quad Re = \frac{\rho v_t D_p}{\mu}$$

$$Re = \frac{\rho D_p}{\mu} \sqrt{\frac{4(\rho_p - \rho)gD_p}{3f\rho}}$$

$D_p = 140 \times 10^{-6} \text{ (m)}$ 代入

$$\text{Re} = \frac{1.18 \times 140 \times 10^{-6}}{1.80 \times 10^{-5}} \sqrt{\frac{4(4000 - 1.18) \times 9.8 \times 140 \times 10^{-6}}{3 \times 1.18 f}} = \frac{22.85}{\sqrt{f}}$$

令：

$$\begin{cases} f = 1 \rightarrow \text{Re} = 22.85 \\ f = 100 \rightarrow \text{Re} = 2.285 \end{cases} \text{兩點畫一直線}$$
$$\begin{cases} f = 5.22 \\ \text{Re} = 10 \end{cases} \text{時會與題目圖形曲線得到交點}$$

$$10 = \frac{1.18 v_t \times 140 \times 10^{-6}}{1.8 \times 10^{-5}}, \quad \underline{\underline{v_t = 1.089 \text{ (m/s)}}}$$

$D_p = 250 \times 10^{-6} \text{ (m)}$ 代入

$$\text{Re} = \frac{1.18 \times 250 \times 10^{-6}}{1.80 \times 10^{-5}} \sqrt{\frac{4(4000 - 1.18) \times 9.8 \times 250 \times 10^{-6}}{3 \times 1.18 f}} = \frac{54.528}{\sqrt{f}}$$

令：

$$\begin{cases} f = 1 \rightarrow \text{Re} = 54.528 \\ f = 100 \rightarrow \text{Re} = 5.428 \end{cases} \text{兩點畫一直線}$$
$$\begin{cases} f = 1.858 \\ \text{Re} = 40 \end{cases} \text{時會與題目圖形曲線得到交點}$$

$$40 = \frac{1.18 v_t \times 250 \times 10^{-6}}{1.8 \times 10^{-5}}, \quad \underline{\underline{v_t = 2.44 \text{ (m/s)}}}$$

之所以可以利用 Re 與 f 做圖畫出直線即是因為：

$$\text{Re} = \frac{D v_t \rho}{\mu}, \quad f = \frac{4}{3} \frac{a D}{v_t^2} \left(\frac{\rho_p - \rho}{\rho} \right)$$

$$\frac{\text{Re}}{f} = \frac{3}{4} \frac{v_t^3 \rho^2}{\mu a (\rho_p - \rho)}, \quad \text{Re} = \frac{v_t^3 \rho^2}{\mu a (\rho_p - \rho)} f = C f$$

只不過這題我們並不知道 C，因為不知道速度 v_s

因此才改用 $\text{Re} \sqrt{f} = \text{定值}$ 的方式求出符合 Re 與 f 關係式的兩點

再畫出直線就可反推 C 得到斜率，也就是 v_s

而這題也可以順利求得正確的 Reynolds number

本題另種題型可以參考： Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.;

p 188, Example 6.3.1.

Problem 3

【Solution】

(a)

$$q_{c,x_0} = q_{k,x_0 \rightarrow x_1} = q_{k,x_1 \rightarrow x_2} = q_{k,x_2 \rightarrow x_3} = q_{c,x_3}$$

$$\frac{T_a - T_0}{\frac{1}{h_0}} = \frac{T_0 - T_1}{\frac{x_1 - x_0}{k^{01}}} = \frac{T_1 - T_2}{\frac{x_2 - x_1}{k^{12}}} = \frac{T_2 - T_3}{\frac{x_3 - x_2}{k^{23}}} = \frac{T_3 - T_h}{\frac{1}{h_3}}$$

$$\frac{T_a - T_h}{\frac{1}{h_0} + \frac{x_1 - x_0}{k^{01}} + \frac{x_2 - x_1}{k^{12}} + \frac{x_3 - x_2}{k^{23}} + \frac{1}{h_3}} = U(T_a - T_h)$$

$$U = \left(\frac{1}{h_0} + \frac{x_1 - x_0}{k^{01}} + \frac{x_2 - x_1}{k^{12}} + \frac{x_3 - x_2}{k^{23}} + \frac{1}{h_3} \right)^{-1}$$

(b)

At steady state,

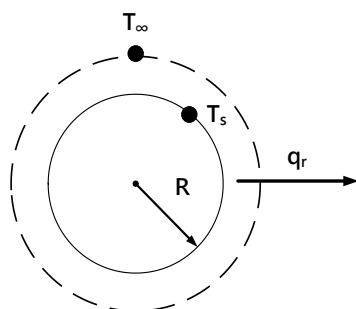
$$q_{01} = q_{12} = q_{23}$$

$$-k^{01} \left. \frac{dT}{dx} \right|_{01} = -k^{12} \left. \frac{dT}{dx} \right|_{12} = -k^{23} \left. \frac{dT}{dx} \right|_{23}$$

$$\therefore \left. \frac{dT}{dx} \right|_{01} < \left. \frac{dT}{dx} \right|_{23} < \left. \frac{dT}{dx} \right|_{12}, \quad \underline{\underline{k_{01} > k_{23} > k_{12}}}$$

Problem 4

【Solution】



(a)

$$\text{Assume : } \begin{cases} \text{steady - state} \\ \text{no heat generation} \\ \text{only } r - \text{direction conduction} \end{cases}$$

By equation of change of energy in spherical coordinate,

$$\rho \hat{C}_p \left(\frac{\partial T}{\partial t} + \vec{v} \cdot \nabla T \right) = k \nabla^2 T + \mu \phi_v$$

$$k \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 T}{\partial \phi^2} \right] = 0$$

積分 2 次：

$$T = \frac{-c_1}{r} + c_2, \quad \begin{cases} r = R, T = T_s \\ r = \infty, T = T_\infty \end{cases}, \quad \begin{cases} c_1 = R(T_\infty - T_s) \\ c_2 = T_\infty \end{cases}$$

$$\underline{\underline{T = \frac{R}{r} (T_s - T_\infty) + T_\infty}}$$

(b)

$$@ r = R, \quad q_k = q_c$$

$$-k \left. \frac{dT}{dr} \right|_{r=R} = h(T_s - T_\infty)$$

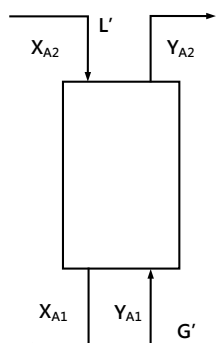
$$\frac{R}{R^2} k(T_s - T_\infty) = h, \quad \frac{hR}{k} = 1$$

$$\underline{\underline{Nu = \frac{hD}{k} = \frac{2hR}{k} = 2}}$$

Problem 5

【Solution】

(a)



(b)

假設空氣量 \gg acetone，因此分子量 $G' \approx \text{分子量}_{air} = 28.8$

$$\begin{cases} G' = \frac{1 \times 10^3}{28.8} = 34.72 \text{ (mole / m}^2 \cdot \text{s)} \\ L' = \frac{1.6 \times 10^3}{18} = 88.89 \text{ (mole / m}^2 \cdot \text{s)} \end{cases}, \begin{cases} y_{A1} = 0.015 \\ y_{A2} = 0.00015 \\ x_{A2} = 0 \end{cases}$$

By mole balance of acetone,

$$34.72(0.015 - 0.00015) = 88.89(x_{A1} - 0)$$

$$x_{A1} = 5.8 \times 10^{-3}$$

$$\begin{cases} x_{A1}^* = \frac{y_{A1}}{1.75} = \frac{0.015}{1.75} = 8.57 \times 10^{-3} \\ x_{A2}^* = \frac{y_{A2}}{1.75} = \frac{0.00015}{1.75} = 8.57 \times 10^{-5} \end{cases}$$

$$N_{OL} = \frac{(x_{A1} - x_{A2})}{\left[\frac{(x_{A1}^* - x_{A1}) - (x_{A2}^* - x_{A2})}{\ln \frac{x_{A1}^* - x_{A1}}{x_{A2}^* - x_{A2}}} \right]} = \frac{5.8 \times 10^{-3} - 0}{\left[\frac{(8.57 \times 10^{-3} - 5.8 \times 10^{-3}) - (8.57 \times 10^{-5} - 0)}{\ln \frac{8.57 \times 10^{-3} - 5.8 \times 10^{-3}}{8.57 \times 10^{-5} - 0}} \right]} = \underline{\underline{7.509}}$$

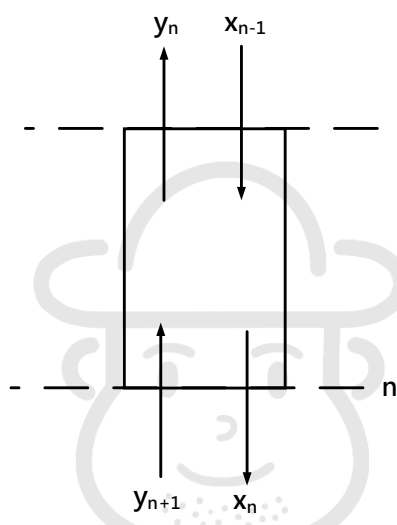
(c)

$$\begin{cases} y_{A1}^* = 1.75x_1 = 0.010 \\ y_{A2}^* = 1.75x_2 = 0 \end{cases}$$

$$N_{OG} = \frac{y_{A1} - y_{A2}}{\left[\frac{(y_{A1} - y_{A1}^*) - (y_{A2} - y_{A2}^*)}{\ln \frac{y_{A1} - y_{A1}^*}{y_{A2} - y_{A2}^*}} \right]} = \frac{0.015 - 0.00015}{\left[\frac{(0.015 - 0.010) - (0.00015 - 0)}{\ln \frac{0.015 - 0.010}{0.00015 - 0}} \right]} = \underline{\underline{10.64}}$$

Problem 6

【Solution】



For total reflux, $y_{n+1} = x_n$

$$\frac{y_A}{y_B} = \alpha_{AB} \frac{x_A}{x_B}$$

$$\frac{y_n}{1 - y_n} = \alpha_{AB} \frac{x_{n+1}}{1 - x_{n+1}}, \quad \frac{x_n}{1 - x_n} = \alpha_{AB} \frac{x_{n+1}}{1 - x_{n+1}}$$

$$\frac{x_D}{1 - x_D} = \alpha_{AB} \frac{x_1}{1 - x_1} = (\alpha_{AB})^2 \left(\frac{x_2}{1 - x_2} \right) = (\alpha_{AB})^3 \left(\frac{x_3}{1 - x_3} \right) = (\alpha_{AB})^n \left(\frac{x_n}{1 - x_n} \right) = (\alpha_{AB})^{n+1} \left(\frac{x_w}{1 - x_w} \right)$$

$$n = \frac{\ln \left[\frac{x_D}{1 - x_D} \cdot \frac{1 - x_w}{x_w} \right]}{\ln \alpha_{AB}} - 1 = \frac{\ln \left[\frac{0.9}{1 - 0.9} \cdot \frac{1 - 0.1}{0.1} \right]}{\ln 2.4} - 1 = \underline{\underline{4.02 \text{ (plates)}}}$$

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Problem 1

【Solution】

(a)

$$\text{Reynolds number, } Re \equiv \frac{\text{inertial force}}{\text{viscous force}}$$

(b)

Molecular momentum flux,

$$\tau = - \sum_{n=1}^Z m_n (v_x|_{y-} - v_x|_{y+}) \left\{ \begin{array}{l} v_x = x\text{-directional average velocity} \\ m_n = \text{the mass of the molecule} \end{array} \right.$$

(本題可參考：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass Transfer*, 5th ed.; p 84.)

(c)

The Prandtl mixing length plays roughly the same role in turbulent flow as the mean free path in kinetic theory,

$$\tau_{yx}^{(t)} = -\rho l^2 \left| \frac{d\bar{v}_x}{dy} \right| \frac{d\bar{v}_x}{dy} \left\{ \begin{array}{l} \text{wall turbulence} \rightarrow l = \kappa_1 y \\ \text{free turbulence} \rightarrow l = \kappa_2 b \end{array} \right.$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 163.)

(本題可參考：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass*

Transfer, 5th ed.; p158~159.)

(d)

For a two dimensional, incompressible and irrotational flow, we can introduce a function so that,

$$\bar{v} = -\nabla \phi$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 126~127.)

(e)

For a turbulent flow, the turbulent momentum flux tensor,

$$\overline{\tau^{(t)}} = \rho \overline{v'v'}$$

which is also called **Reynolds stress**

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 158.)

(f)

The term form drag can be interpreted as the force exerted by the fluid on the solid, acting normal to the surface.

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 60.)

(g)

The fanning friction factor,

$$f = \frac{1}{4} \left(\frac{D}{L} \right) \left(\frac{P_0 - P_L}{\frac{1}{2} \rho \langle v \rangle^2} \right)$$

can be calculated from the experimental data and used as a prediction of friction drag

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 178~179.)

(h)

By introducing the eddy diffusivity, ε_M

we can calculate the Reynolds stress as in the case of laminar flow,

$$(\tau_{yx})_{turb} = \rho \varepsilon_M \frac{d\bar{v}_x}{dy}$$

Eddy diffusivity is the analogy of the kinetic viscosity in laminar flow, which is a property of the flow and not of the fluid.

(本題可參考：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass Transfer*, 5th ed.; p158.)

(i)

The divergence of velocity is,

$$\nabla \cdot \vec{v}$$

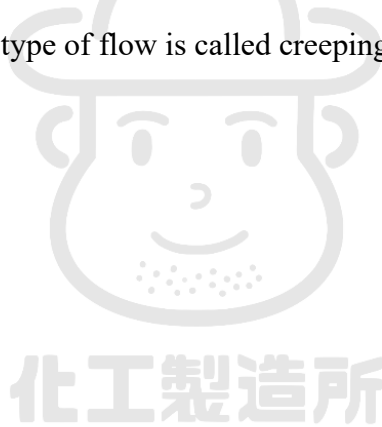
Which will be zero for an incompressible fluid when considering its continuity equation.

(j)

For a flow with very low speeds or large viscosity, its Reynolds number

$$Re = \frac{\text{inertial force}}{\text{viscous force}} \ll 1$$

This type of flow is called creeping flow.



Problem 2

【Solution】

By Navier-Stokes equation,

$$\rho \frac{Du}{Dt} = \mu \nabla^2 u - \nabla p + \rho g$$

將題目所列之 dimensionless relations 代入

$$\frac{Du}{Dt} = \frac{u_\infty}{L} \frac{Du^*}{Dt^*} = \frac{u_\infty^2}{L} \frac{Du^*}{Dt^*}$$

$$\mu \nabla^2 u = \frac{\mu u_\infty}{L^2} \nabla^{*2} u^*$$

$$\nabla p = \frac{\rho u_\infty^2}{L} \nabla^* p^*$$

=>

$$\rho \frac{u_\infty^2}{L} \frac{Du^*}{Dt^*} = \frac{\mu u_\infty}{L^2} \nabla^{*2} u^* - \frac{\rho u_\infty^2}{L} \nabla^* p^* + \rho g$$

同除 $\frac{\rho u_\infty^2}{L}$

$$\frac{Du^*}{Dt^*} = \frac{\mu}{\rho u_\infty L} \nabla^{*2} u^* - \nabla^* p^* + \frac{gL}{u_\infty^2}$$

$$\boxed{\frac{Du^*}{Dt^*} = \frac{1}{Re} \nabla^{*2} u^* - \nabla^* p^* + \frac{gL}{u_\infty^2}}$$

Problem 3**【Solution】**

(a)

$$\varepsilon = 1 - \frac{\rho_b}{\rho_p} = 1 - \frac{962}{1600} = 0.398$$

(b)

$$D_p = \frac{6}{a_v} = \frac{6}{S_p / V_p}$$

$$S_p = 2\left(\frac{\pi D^2}{4}\right) + \pi Dh = \frac{3}{2}\pi D^2 \text{ (total surface area)}$$

$$V_p = \frac{\pi}{4} D^2 h = \frac{\pi}{4} D^3$$

$$D_p = \frac{6}{\frac{3}{2}\pi D^2 \times \frac{4}{\pi D^3}} = D = \underline{\underline{0.02 \text{ (m)}}}$$

(c)

$$a = a_v(1 - \varepsilon) = \frac{6}{D}(1 - \varepsilon) = \frac{6}{0.02}(1 - 0.398) = \underline{\underline{180.6 \text{ (m}^{-1}\text{)}}}$$

(本題可參考：Geankoplis, C. *Transport Processes and Separation Process Principles*,

4th ed.; p 126, Example 3.1-3.)

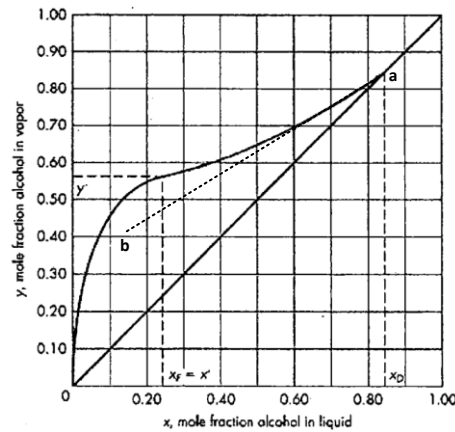
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Problem 4

【Solution】

Minimum reflux ratio

Operation line that is tangent to the equilibrium line corresponds to the line ***ab*** in the following figure,



Minimum operating ratio

Operation line corresponds to the diagonal line shown on the figure.

(※對於 operation line 會超過 equilibrium line 之 minimum reflux ratio line 可參考：

McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.;

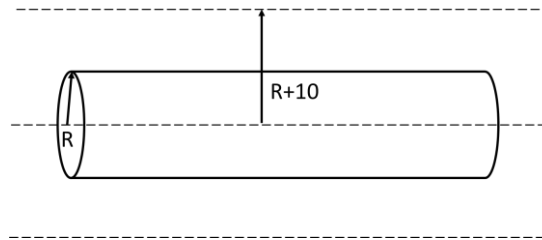
p 688~691.)

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Problem 5

【Solution】

(a)



To describe the system, we introduce cylindrical coordinates.

Assumptions,

- (1) Pipe is long enough so that the diffusion is only in r-direction
- (2) No reaction
- (3) Steady-state

(b)

By the general equation of continuity,

$$\underbrace{\frac{\partial C_A}{\partial t}}_{s.s} + \nabla \cdot N_A = \underbrace{R_A}_{\text{no reaction}}$$
$$\boxed{\frac{d}{dr}(rN_A) = 0}$$

(c)

By Fick's flux equation,

$$N_A = -cD_{AB} \frac{dy_A}{dr} + y_A(N_A + \cancel{N_B})$$

$$\boxed{N_A = \frac{-cD_{AB}}{1-y_A} \frac{dy_A}{dr}}$$

(d)

N_A 代入(b)之 general differential equation,

$$\frac{d}{dr} \left(r \frac{-cD_{AB}}{1-y_A} \frac{dy_A}{dr} \right) = 0$$

$$\boxed{\frac{d}{dr} \left(\frac{r}{1-y_A} \frac{dy_A}{dr} \right) = 0}$$

(本題可參考：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass Transfer*, 5th ed.; p 448, Problem 25.6.)



Problem 6

【Solution】

(a)

By entropy balance of the steam passing through the turbine,

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

$$\hat{S}_{in} = \hat{S}_{out}$$

By energy balance,

$$\dot{M} \Delta H = \dot{W}_s = -F \cdot v$$

(在穩定航行下船所需要的前進功率)

$$20 \times (H_{out} - H_{in}) = -3.86 \times 10^6 \times 37 \times \frac{1000}{3600}$$

$$H_{out} - H_{in} = -1983.61$$

此時若可找出一 T、P 狀態下之 steam 滿足 entropy 以及 energy balance 即可繼續作答，唯獨題目少給了 1 bar、100°C 時 steam 之熱力學參數，無法繼續往下算

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Problem 1

【Solution】

(a) The net positive suction head (NPSH) is by which the value of the pressure in the pump inlet exceeding the vapor pressure.

The pump must work under enough NPSH because some of the liquid in the pump may flash into vapor inside the pump, causing cavitation and damaging the pump.

(b)

(1) Venturi meter : The device measures the pressure drop when the fluid passes through a throat, where the velocity of the fluid increases. By Bernoulli equation, the pressure drop and the velocity difference can be related together.

(2) Orifice meter : The basic principle of the designation of orifice meter is the same as the venturi meter.

(3) Rotameter : The fluid flows with constant pressure drop, but the area where the fluid passes through is varied. Therefore, the float inside the rotameter will be suspended and can indicate the flow rate under that condition.

((b)小題題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 214~225.)

Problem 2

【Solution】

By the equation of continuity,

$$\underbrace{\frac{\partial \rho}{\partial t}}_{\text{incompressible}} + \frac{1}{r} \frac{\partial}{\partial r} (\underbrace{\rho r v_r}_{v_r=0}) + \frac{1}{r} \frac{\partial}{\partial \theta} (\underbrace{\rho r v_\theta}_{v_\theta=0}) + \frac{\partial}{\partial z} (\rho v_z) = 0$$

$$v_z = v_z(r, \theta, z, t)$$

By momentum balance in the falling film region,

$$\rho v_z v_z r dr d\theta \Big|_z - \rho v_z v_z r dr d\theta \Big|_{z+dz} + \tau_{rz} r d\theta dz \Big|_r - \tau_{rz} r d\theta dz \Big|_{r+dr} + \rho g r dr d\theta dz = 0$$

同除 $dr d\theta dz \rightarrow 0$,

$$\underbrace{\frac{-\partial(r \rho v_z v_z)}{\partial z}}_{v_z \neq f(z)} - \frac{\partial(r \tau_{rz})}{\partial r} + \rho g r = 0$$

$$\frac{\partial(r \tau_{rz})}{\partial r} = +\rho g r, \quad \tau_{rz} = \frac{1}{2} \rho g r + \frac{c_1}{r}$$

$$\because \tau_{rz} = -\mu \left(\frac{dv_z}{dr} \right)$$

$$-\mu \left(\frac{dv_z}{dr} \right) = \frac{1}{2} \rho g r + \frac{c_1}{r}$$

$$v_z = -\frac{\rho g}{4\mu} r^2 + C_1 \ln r + C_2 \quad \begin{cases} r=R, v_z=0 \\ r=aR, \frac{dv_z}{dr}=0 \end{cases}$$

$$\begin{cases} C_1 = \frac{\rho g}{2\mu} a^2 R^2 \\ C_2 = \frac{\rho g}{4\mu} R^2 - \frac{\rho g}{2\mu} a^2 R^2 \ln R \end{cases}$$

代回：

$$v_z = -\frac{\rho g}{4\mu} r^2 + C_1 \ln r + C_2 = \frac{\rho g R^2}{4\mu} \left[1 - \left(\frac{r}{R} \right)^2 + 2a^2 \ln \frac{r}{R} \right]$$

For the mass flow rate,

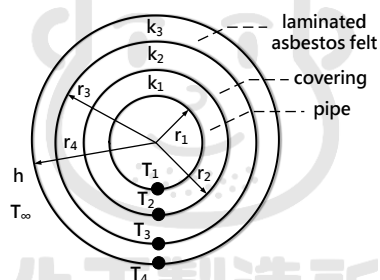
$$\begin{aligned}
 w &= \int_0^{2\pi} \int_R^{aR} \rho v_z r dr d\theta = \frac{\pi \rho^2 g R^2}{2\mu} \int_R^{aR} r - \frac{r^3}{R^2} + 2a^2 r \ln \frac{r}{R} dr \\
 &= \frac{\pi \rho^2 g R^2}{2\mu} \left[\frac{1}{2} (r^2) \Big|_R^{aR} - \frac{1}{4R^2} (r^4) \Big|_R^{aR} + 2a^2 \left(\frac{r^2}{2} \ln \frac{r}{R} - \frac{r^2}{4} \right) \Big|_R^{aR} \right] \\
 &= \frac{\pi \rho^2 g R^2}{2\mu} \left[\frac{1}{2} R^2 (a^2 - 1) - \frac{1}{4} R^2 (a^4 - 1) + 2a^2 R^2 \left(\frac{a^2}{2} \ln a - \frac{a^2}{4} + \frac{1}{4} \right) \right] \\
 &= \frac{\pi \rho^2 g R^4}{8\mu} [2(a^2 - 1) - (a^4 - 1) + 4a^2 \ln a - 2a^4 + 2a^2] \\
 &= \frac{\pi \rho^2 g R^4}{8\mu} (-1 + 4a^2 - 3a^4 + 4a^4 \ln a)
 \end{aligned}$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.;

p 64, Problem 2B.6.)

Problem 3

【Solution】



(a)

Assume the system is in steady state, by Ohm's law

$$\begin{aligned}
 \frac{q}{L} &= \frac{\Delta T}{L \sum R} \left\{ \begin{aligned} \Delta T &= T_1 - T_4 = 900 - 122 = 778 \text{ (}^\circ\text{F)} \\ L \sum R &= \frac{\ln \frac{r_2}{r_1}}{2\pi k_1} + \frac{\ln \frac{r_3}{r_2}}{2\pi k_2} + \frac{\ln \frac{r_4}{r_3}}{2\pi k_3} \end{aligned} \right. \\
 L \sum R &= \frac{\ln \frac{2.37}{2.07}}{2\pi \times 23.5} + \frac{\ln \frac{2.37}{2}}{2\pi \times 0.058} + \frac{\ln \frac{2.37}{2} + 1.25}{2\pi \times 0.042} = 4.654 \\
 \frac{q}{L} &= \frac{\Delta T}{L \sum R} = \frac{778}{4.654} = 167.16 \text{ (Btu / ft} \cdot \text{hr)}
 \end{aligned}$$

(b)

By Ohm's law

$$\frac{q}{L} = \frac{\Delta T}{L \sum R} \begin{cases} \Delta T = T_1 - T_3 = 900 - T_3 \\ L \sum R = \frac{\ln \frac{r_2}{r_1}}{2\pi k_1} + \frac{\ln \frac{r_3}{r_2}}{2\pi k_2} \\ L \sum R = \frac{\ln \frac{2.37}{2.07}}{2\pi \times 23.5} + \frac{\ln(\frac{\frac{2.37}{2} + 1.25}{\frac{2.37}{2}})}{2\pi \times 0.058} = 1.977 \end{cases}$$
$$\frac{q}{L} = \frac{\Delta T}{L \sum R} = \frac{900 - T_3}{1.977} = 167.16, \quad T_3 = \underline{\underline{569.48 (^\circ F)}}$$

(c)

$$\frac{q}{L} = \frac{hA(T_4 - T_\infty)}{L}$$
$$\frac{h \times 2\pi \left(\underbrace{\frac{\frac{2.37}{2} + 1.25 + 2.5}{12}}_{\text{inch to ft}} \right) L \times (122 - 86)}{L} = 167.16, \quad h = \underline{\underline{1.797 (Btu / hr \cdot ft^2 \cdot ^\circ F)}}$$

Problem 4**【Solution】****(b)**

$$\frac{1}{K_G} = \frac{m}{k_L} + \frac{1}{k_G} = \frac{10}{5 \times 10^{-4}} + \frac{1}{0.01} , \underline{\underline{K_G = 4.975 \times 10^{-5} \text{ (kmol / m}^2 \cdot \text{s} \cdot \text{atm)}}}}$$

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{mk_G} = \frac{1}{5 \times 10^{-4}} + \frac{1}{10 \times 0.01} , \underline{\underline{K_L = 4.975 \times 10^{-4} \text{ (kmol / m}^2 \cdot \text{s} \cdot \text{(kmol / m}^3 \text{))}}}}$$

(a)

$$N' = K_L(x_L - x_L^*) = K_L(x_L - \frac{y_G}{m}) = 4.975 \times 10^{-4} (1 \times 10^{-3} \times 10^{-3} - \frac{0}{10}) = \underline{\underline{4.975 \times 10^{-10} \text{ (kmol / m}^2 \cdot \text{s)}}}}$$

(c) The tower is a stripping tower**(d)**By **Two-film theory**

(1) The interface is at equilibrium.

(2) The two phases are in direct contact with each other.

(3) A concentration gradient will exist in each phase.

(本題可參考：Geankoplis, C. *Transport Processes and Separation Process Principles*, 4th ed.;

p 636~637.)

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Problem 1

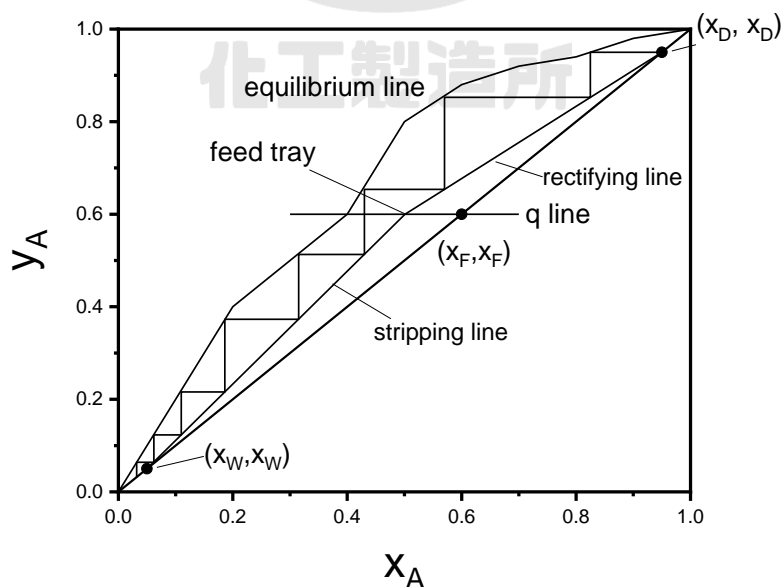
【Solution】

- (a) (1) Constant molar heat of vaporization.
(2) No heat losses.
(3) No heat of mixing.
(4) Constant molar flow rate everywhere.
(5) Negligible pressure drop.
(6) The plates are ideally behaved.

If the top and bottom products are nearly pure in extreme compositions, and, if the two components have similar boiling points, the method could be used.

(本題可參考：Coulson, J.; Richardson, J.; Backhurst, J.; Harker, J. *Chemical Engineering*, 5th ed.; Volume 2, p 566.)

(b)



(此圖是借用其他題目的數據繪製而成，平衡線形狀可以簡單繪製曲線即可，且 q-line 部分不一定為水平線，主要強調通過 feed point，抑或可自行假設進料狀況。)

Problem 2

【Solution】

Assume the system is in steady state, constant P and T,

By shell balance of A,

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

同除 $4\pi dr \rightarrow 0$

$$\frac{d}{dr}(r^2 N_{Ar}) = 0$$

$$r^2 N_{Ar} = \text{constant} = r_1^2 N_{Ar1}$$

By Fick's law,

$$N_{Ar} = -D_{AB}C \frac{dx_A}{dr} + x_A (N_{Ar} + \underbrace{N_{Br}}_{\text{stagnant}})$$

$$N_{Ar} = \frac{-D_{AB}C}{(1-x_A)} \frac{dx_A}{dr} \quad \text{代回}$$

$$r^2 N_{Ar} = r^2 \frac{-D_{AB}C}{(1-x_A)} \frac{dx_A}{dr} = r_1^2 N_{Ar1}$$

$$r_1^2 N_{Ar1} \int_{r_1}^{r_2} \frac{1}{r^2} dr = -D_{AB}C \int_{x_{A1}}^{x_{A2}} \frac{1}{(1-x_A)} dx_A$$

$$r_1^2 N_{Ar1} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) = D_{AB}C \ln \left(\frac{1-x_{A2}}{1-x_{A1}} \right)$$

$$r_1^2 N_{Ar1} \left(\frac{r_2 - r_1}{r_1 r_2} \right) = D_{AB}C \ln \left(\frac{1-x_{A2}}{1-x_{A1}} \right)$$

$$r_1^2 N_{Ar1} = D_{AB}C \left(\frac{r_1 r_2}{r_2 - r_1} \right) \ln \left(\frac{1-x_{A2}}{1-x_{A1}} \right)$$

$$\underline{\underline{N_{Ar1} = \frac{D_{AB}C}{r_2 - r_1} \left(\frac{r_2}{r_1} \right) \ln \left(\frac{1-x_{A2}}{1-x_{A1}} \right)}}$$

(本題改編自：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 572, 18.B.7.)

Problem 3

【Solution】

(a)

(1)

The Navier-Stokes equation is based simplified from the equation of motion based on the assumptions of Newtonian fluid with constant ρ and μ .

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 84.)

(2)

With small Reynolds number, the viscous effect is dominant, the Navier-Stokes equation can be simplified to,

$$-\nabla P + \mu \nabla^2 \underline{v} + \rho \underline{g} = 0$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 85.)

(b)

(1) True

The gravity effect can be included in the modified pressure term.

(2) False

Only applicable to Newtonian fluid. For non-Newtonian fluids, the Hagen Poiseuille equation should be modified to a more general form.

(3) True

The equation can be used when the flow is laminar.

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 52.)

(c)

(1) Yes

The equation of continuity is obtained from merely mass balance, regardless of the fluid type.

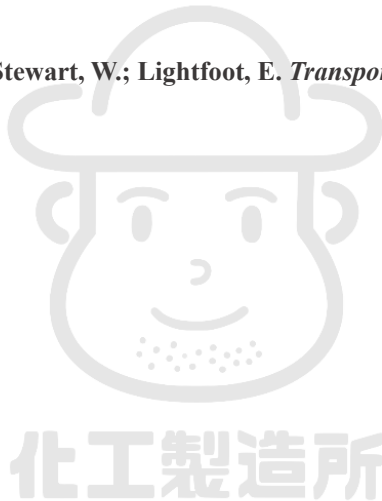
(2) Yes

The equation of motion is based on the momentum balance, regardless of the fluid type.

(3) No

The Stokes equation is based on the Navier-Stokes equation with small Reynolds number, but the flow in this question is compressible, which can not be described by Navier Stokes equation.

(本小題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 85.)



Problem 4**【Solution】****(a)**

By the equation of motion in z-direction, assume steady state,

$$\rho \left(\cancel{\frac{\partial v_z}{\partial t}} + \cancel{v_r} \frac{\partial v_z}{\partial r} + \cancel{\frac{v_\theta}{r}} \frac{\partial v_z}{\partial \theta} + v_z \frac{\partial v_z}{\partial z} \right) = \cancel{\frac{-\partial p}{\partial z}} - \left[\frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) + \cancel{\frac{1}{r}} \frac{\partial \tau_{\theta z}}{\partial \theta} + \cancel{\frac{\partial \tau_{zz}}{\partial z}} \right] + \rho g_z$$

$$-\left[\frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) \right] + \rho g_z = 0$$

$$\left[\frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) \right] = -\rho g \sin(30^\circ) = -\frac{\rho g}{2}$$

(重力與 z 方向相反，有負號)

$$\tau_{rz} = -\frac{\rho g}{4} r + \frac{c_1}{r}$$

$\because r=0$, τ_{rz} is finite, $c_1=0$

$$\tau_{rz} = -\frac{\rho g}{4} r$$

At $r=R$,

$$|\tau_{rz}| = \frac{\rho g R}{4} > \tau_0$$

The fluid is able to flow down.

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(b)

By the equation of motion in z-direction, assume steady state,

$$\rho \left(\frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_z}{\partial \theta} + v_z \frac{\partial v_z}{\partial z} \right) = \frac{-\partial p}{\partial z} - \left[\frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) + \frac{1}{r} \frac{\partial \tau_{\theta z}}{\partial \theta} + \frac{\partial \tau_{zz}}{\partial z} \right] + \rho g_z$$

$$\left[\frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) \right] = \frac{-\partial p}{\partial z} + \rho g_z = \frac{P_0 - P_L}{L} - \frac{\rho g}{2}$$

$$\tau_{rz} = \left(\frac{P_0 - P_L}{2L} - \frac{\rho g}{4} \right) r + \frac{c_2}{r}$$

$\because r=0$, τ_{rz} is finite, $c_2 = 0$

$$\tau_{rz} = \left(\frac{P_0 - P_L}{2L} - \frac{\rho g}{4} \right) r$$

Because the fluid should moves upward,

$$\tau_{rz}|_R = \left(\frac{P_0 - P_L}{2L} - \frac{\rho g}{4} \right) R > \tau_0$$

$$\frac{P_0 - P_L}{2L} R > \frac{\rho g}{8} R + \frac{\rho g}{4} R$$

$$\frac{P_0 - P_L}{2L} > \frac{3\rho g}{8}, \quad P_0 - P_L > \frac{3\rho g L}{4}$$

Problem 5

【Solution】

(1)

In this forced convection process, the two dimensionless numbers should be identical,

$Re = \text{Reynolds number}$

$Pr = \text{Prandtl number}$

(2)

$$Re = \frac{\text{inertial force}}{\text{viscous force}}$$

$$Pr = \frac{\text{momentum diffusivity}}{\text{thermal diffusivity}}$$

(3)

Conceptually, the heat transfer in this case involves conduction from the chip and the convection outward by the fluid flow. With the same heat transfer condition, the flow condition should be the same for both system accounting for the heat convection.

With the same Prandtl number, the situation of thermal boundary layer within which the conduction occurs may be the same.

(4)

$$Nu = f(Re, Pr)$$

When the two dimensionless group are the same, the Nusselt number, which is a function of the two parameters, should give the same functional form between the two systems. By the definition of Nusselt number,

$$Nu = \frac{hL}{k_f}$$

the Nusselt number can give the value of heat transfer coefficient for a given system.

(5)

At the edge of thermal boundary layer, we have,

$$hA(T_s - T_\infty) = \int_0^W \int_0^L -kA \frac{\partial(T - T_s)}{\partial y} \Big|_{y=0} dx dz = \underbrace{\int_0^W \int_0^L \rho C_p v_x (T - T_\infty) dy dz}_{\text{convection}}$$

$$h = \int_0^W \int_0^L \rho C_p v_x [T^* - 1] dy dz$$

$$\therefore T^* = f\left(\frac{y}{\Delta\delta}\right) \quad \left(\Delta = \frac{\delta_T}{\delta}\right)$$

$$h = \int_0^W \int_0^L \rho C_p v_x \left[f\left(\frac{y}{\Delta\delta}\right) - 1\right] dy dz = f(Re, Pr)$$

$$\underline{\underline{\frac{hL}{k} = Nu = f(Re, Pr)}}$$

If the two system have the same Re and Pr, the function from of Nusselt number should be the same because they should give the same value of Nusselt number.

(本小題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 388~390.)

(6)

※題目應改為“in what velocity should you operate the air flow.....”，因模擬系統是在空氣下進行。

Because the Reynolds number should be the same between the model and the real system,

$$\frac{\rho_m v_m L_m}{\mu_m} = \frac{\rho_r v_r L_r}{\mu_r}$$

For model system,

$$\rho_m(300K) = 1.1614 \text{ (kg / m}^3\text{)} , L_m = 10 \text{ cm} , \mu_m = 184.6 \times 10^{-7} \text{ (Pa)}$$

For real system,

$$\rho_r(290K) = \frac{1}{1.001} \times 10^3 \text{ (kg / m}^3\text{)} , L_r = 1 \text{ (mm)} , \mu_r = 1080 \times 10^{-6} \text{ (Pa)}$$

$$\frac{1.1614 \times v_m \times 10 \times 10}{184.6 \times 10^{-7}} = \frac{\frac{1000}{1.001} \times 0.8 \times 1}{1080 \times 10^{-6}}$$
$$\underline{\underline{v_m = 0.117 \text{ (m / s)}}}$$

(7)

For the Prandtl number,

$$\text{Pr}_{\text{water}} = \frac{\left(\frac{\mu}{\rho}\right)}{\left(\frac{k}{\rho c_p}\right)} = \frac{\mu c_p}{k} = \frac{1080 \times 10^{-6} \times 4.184 \times 10^3}{598 \times 10^{-3}} = 7.56$$

$$\text{Pr}_{\text{air}} = \frac{\nu}{\alpha} = \frac{15.89 \times 10^{-6}}{22.5 \times 10^{-6}} = 0.706$$

Because the Prandtl number of the two systems are not the same, the choice may not be right.

(8)

At steady state, assume the air in 27°C is a suitable choice,

$$h(T - T_{\infty}) = q''$$

$$h(55 - 27) = 200 \quad , \quad h = 7.143 \text{ (W / m}^2 \cdot \text{K)}$$

The Nusselt number of the two system should be the same,

$$Nu_m = Nu_r$$

$$\frac{h_m L_m}{k_m} = \frac{h_r L_r}{k_r}$$

$$\frac{7.143 \times 10 \times 10}{26.3 \times 10^{-3}} = \frac{h_r \times 1}{598 \times 10^{-3}}$$

$$\underline{\underline{h_r = 16241.2 \text{ (W / m}^2 \text{K)}}}$$

(9)

As the air flow passes through the surface of the sink, the temperature should be higher because it's heated by the surface of the sink with higher temperature, under the steady state situation,

$$h(T - T_{\infty}) = q''$$

As $T_{\infty} \uparrow$, $T - T_{\infty} \downarrow$

$h \uparrow$ along the path.

(10)

(以下假設 heat sink 為立方體)

【Check the Biot number of the model system】

The Biot number is defined as,

$$Bi = \frac{h(\frac{V}{A_s})}{k} = \frac{\text{resistance to conduction within the solid}}{\text{resistance to convection across the film boundary}}$$

For k , the value of which can be taken as 46 in the temperature range,

$$Bi = \frac{h(\frac{L}{2})}{k_a} = \frac{7.143 \times 10 \times 10^{-2}}{46 \times 2} = 7.76 \times 10^{-3} < 0.1$$

(加熱面積為雙面，所以要除以 2)

(Assume the air in 27°C is a suitable choice)

The lumped-parameter analysis is applicable in this case, by overall energy balance,

$$\begin{aligned}\rho V c_p \frac{\partial T}{\partial t} &= hA(T - T_\infty) \\ \frac{\rho V c_p}{2hA} \int_{T_i}^{T_f} \frac{dT}{(T - T_\infty)} &= \int_0^t dt \\ t &= \frac{\rho L c_p}{2h} \ln\left(\frac{T_i - T_\infty}{T_f - T_\infty}\right) \\ t &= \frac{3970 \times 10 \times 10^{-2} \times 765}{2 \times 5.263} \ln\left(\frac{65 - 27}{40 - 27}\right) = \underline{\underline{22803.6 \text{ (s)}}}\end{aligned}$$

(c_p 在操作溫度範圍內假設與 300K 下數值差不多。)

(11)

$$q = \rho c_p V (T_f - T_i) = 3970 \times 765 \times (10 \times 10^{-2})^3 \times (65 - 40) = \underline{\underline{75926 \text{ (J)}}}$$

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Problem 1

【Solution】

(a)

Enthalpy of pure water at 21.1°C = 95 (kJ/kg)

Enthalpy of pure sulfuric acid at 21.1°C = 10 (kJ/kg)

For 4 mole of water,

$$H_w^\circ = m_w \cdot \underline{H}_w^\circ = \frac{4 \times 18}{1000} \times 95 = 6.84 \text{ (kJ)}$$

For 1 mole of sulfuric acid,

$$H_s^\circ = m_s \underline{H}_s^\circ = \frac{98}{1000} \times 10 = 0.98 \text{ (kJ)}$$

Assume the mixing enthalpy is zero,

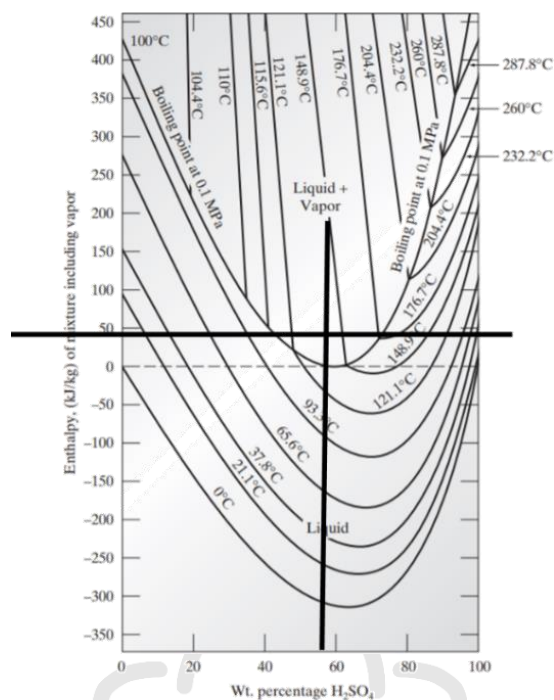
$$H_w^\circ + H_s^\circ = H_{mixture} = m_{mixture} \underline{H}_{mixture}$$

$$\left(\frac{4 \times 18 + 98}{1000} \right) \underline{H}_{mixture} = 6.84 + 0.98, \quad \underline{H}_{mixture} = 46 \text{ (kJ / kg)}$$

For wt% of H_2SO_4 in the solution,

$$wt\% = \frac{98}{4 \times 18 + 98} \times 100 = 57.6\%$$

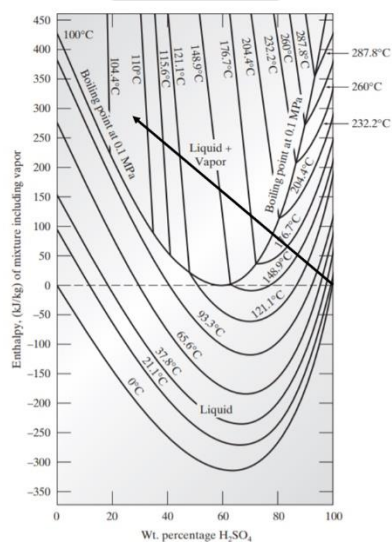
將 $\text{wt}\% = 57.6\%$ 與 $H_{\text{mixture}} = 46 \text{ (kJ/kg)}$ 點描出，



得 $T \approx 140^\circ\text{C}$

(b)

將水加入硫酸的過程轉化為此相圖的途徑應為沿左上角移動：



由圖可知此過程不僅使溫度升高，還可能產生 vapor 因此造成危險。

Problem 2

【Solution】

(a)

By triple-product rule,

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

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

(1)

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p$$

(2)

$$dH = TdS + VdP$$

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

$$\because PV = RT + BP$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \left(\frac{\partial B}{\partial T}\right)_P \text{ 代回}$$

$$\mu = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_p} = \frac{T\left(\frac{\partial B}{\partial T}\right)_P - B}{C_p}$$

(b)

The Joule-Thomson expansion used to liquefy gases can be accomplished by a throttling process, whose initial state should be at low enough temperature and high enough pressure.

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 327~328.)

(c)

不管過程為何，ideal gas 皆不會被液化。

Problem 3

【Solution】

(a)

For $\lim_{x_C \rightarrow 0} r_C = r_C^\infty = 2.7183$ 代入：

$$\ln r_C^\infty = \lim_{x_C \rightarrow 0} \frac{\alpha}{[1 + \frac{\alpha x_C}{\beta x_D}]^2} = \alpha = \ln 2.7183 = 1.00$$

For $\lim_{x_D \rightarrow 0} r_D = r_D^\infty$

$$\ln r_D^\infty = \lim_{x_D \rightarrow 0} \frac{\beta}{[1 + \frac{\beta x_D}{\alpha x_C}]^2} = \beta = \ln 1.6488 = 0.5$$

For VLE,

$$\begin{cases} x_C r_C P_C^{\text{vap}} = y_C P \\ x_D r_D P_D^{\text{vap}} = y_D P \end{cases}, \begin{cases} 0.5 \exp\left[-\frac{1.0}{(1 + \frac{1.0 \times 0.5}{0.5 \times 0.5})^2}\right] \times 1 = y_C P \\ 0.5 \exp\left[-\frac{0.5}{(1 + \frac{0.5 \times 0.5}{1 \times 0.5})^2}\right] \times 0.85 = y_D P \end{cases}$$

$$\because y_C + y_D = 1$$

$$P = 1.089(\text{bar}) \begin{cases} y_C = 0.51284 \\ y_D = 0.48716 \end{cases}$$

(b)

Assume modified Raoult's law is applicable,

$$\begin{cases} x_A P_A^{\text{vap}} r_A = y_A P \\ x_B P_B^{\text{vap}} r_B = y_B P \end{cases}, \begin{cases} \frac{y_A}{x_A} = \frac{P_A^{\text{vap}} r_A}{P} \\ \frac{y_B}{x_B} = \frac{P_B^{\text{vap}} r_B}{P} \end{cases}$$

$$\alpha_{AB} = \frac{P_A^{\text{vap}} r_A}{P_B^{\text{vap}} r_B}$$

For r_A, r_B

$$\ln r_A = \left[\frac{\partial(nG^E / RT)}{\partial n_A} \right]_{T,P,n_B} = Ax_B^2, \quad r_A = \exp[Ax_B^2]$$

$$\ln r_B = \left[\frac{\partial(nG^E / RT)}{\partial n_B} \right]_{T,P,n_A} = Ax_A^2, \quad r_B = \exp[Ax_A^2]$$

$$\text{For } P_A^{\text{vap}} = \exp\left[12.33 - \frac{3850}{273.15 + 35}\right] = 0.849$$

$$P_B^{\text{vap}} = \exp\left[12.58 - \frac{3850}{273.15 + 35}\right] = 1.089$$

$$\alpha_{AB} \Big|_{\substack{x_A \rightarrow 0 \\ x_B \rightarrow 1}} = \frac{0.849e^{0.5}}{1.089e^0} = 1.284$$

$$\alpha_{AB} \Big|_{\substack{x_A \rightarrow 1 \\ x_B \rightarrow 0}} = \frac{0.849e^0}{1.089e^{0.5}} = 0.473$$

$$0.473 \leq \alpha_{AB} \leq 1.284, \quad \text{會形成 azeotrope } (\alpha_{AB} = 1)$$

@Azeotropic point,

$$\alpha_{AB} = \frac{0.849e^{0.5x_B^2}}{1.089e^{0.5(1-x_B)^2}} = 1, \quad \boxed{\begin{cases} x_A = 0.25 \\ x_B = 0.75 \end{cases}}$$

Problem 4**【Solution】**

By design equation,

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

By rate equation,

$$-r_A = kC_A^n$$

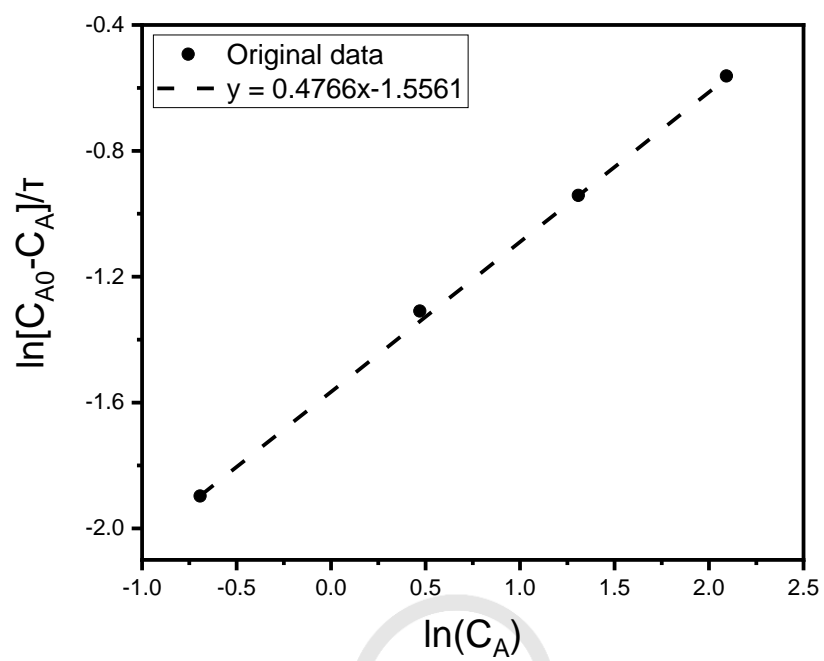
Combine,

$$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{A0} - C_A}{kC_A^n}$$

$$kC_A^n = \frac{C_{A0} - C_A}{\tau}, \quad \ln k + n \ln C_A = \ln \frac{C_{A0} - C_A}{\tau}$$

Plot $\ln \frac{C_{A0} - C_A}{\tau} - \ln C_A$ diagram,

	Run1	Run2	Run3	Run4
C_{A0}	1	2.5	5	10
C_A	0.5	1.6	3.7	8.1
$\ln[(C_{A0} - C_A)/\tau]$	-1.897	-1.309	-0.94161	-0.56212
$\ln C_A$	-0.693	0.470	1.3083	2.0918



$$\begin{cases} \text{slope} = n = 0.477 \\ \text{intercept} = \ln k = -1.5561 \\ \Rightarrow k = e^{-1.5561} = 0.2109 \end{cases}$$

$$-r_A = 0.2109 C_A^{0.477}$$

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Problem 5

【Solution】

For the small CSTR,

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

For the big CSTR,

$$2V = \frac{F_{Ab}x_{Ab}}{kC_{A0}(1-x_{Ab})}$$

上下相除：

$$x_{Ab} = \frac{2x_{As}}{A + 2x_{As} - Ax_{As}} \left(A = \frac{F_{Ab}}{F_{As}} \right)$$

For total conversion,

$$\begin{aligned} x_{At} &= \frac{(F_{As} + F_{Ab}) - F_{As}x_{As} - F_{Ab}x_{Ab}}{F_{As} + F_{Ab}} = \frac{(1+A) - x_{As} - Ax_{Ab}}{(1+A)} \\ &= \frac{(1+A) - x_{As} - \frac{2x_{As}}{A + 2x_{As} - Ax_{As}}}{(1+A)} \end{aligned}$$

For maximum x_{At} , let $\frac{\partial x_{At}}{\partial A} = 0$

$$(x_{As}^3 - 4x_{As}^2 + 3x_{As})A^2 + (4x_{As}^2 - 4x_{As}^3)A + (4x_{As}^3 - 4x_{As}^2) = 0$$

$$A = \frac{(4x_{As}^3 - 4x_{As}^2) \pm \sqrt{48x_{As}^3(x_{As}^2 - 2x_{As} + 1)}}{2(x_{As}^3 - 4x_{As}^2 + 3x_{As})} = \frac{2x_{As} \pm 2\sqrt{3x_{As}}}{x_{As} - 3} = \frac{2x_{As} - 2\sqrt{3x_{As}}}{x_{As} - 3}$$

將：

$$A = \frac{F_{Ab}}{F_{As}} = \frac{2x_{As} - 2\sqrt{3x_{As}}}{x_{As} - 3} \text{ 與}$$

$F_A = F_{Ab} + F_{As}$ 合併即可解出 F_{As} 、 F_{Ab} 值

Problem 6**【Solution】**

(a)

For CSTR operating in isothermal condition,

$$V = \frac{F_{R0}x_R}{-r_R}$$

By rate equation,

$$-r_R = kC_R = kC_{R0}(1-x_R)$$

$$V = \frac{F_{R0}x_R}{kC_{R0}(1-x_R)} \quad , \quad \tau = \frac{x_R}{k(1-x_R)}$$

For k at 450K (k_{450K}),

$$k_{450K} = k_{350K} \cdot e^{\frac{-4 \times 10^3}{1.987} \left(\frac{1}{450} - \frac{1}{350} \right)} = 0.023$$

$$\tau = \frac{x_R}{0.023(1-x_R)} = 100 \quad , \quad \underline{\underline{x_R = 0.703}}$$

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(b)

For adiabatic CSTR, by energy balance,

$$x_{R,EB} = \frac{\sum_i \int_{T_{i0}}^T \theta_{i0} C_{pi} dT}{-[\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT]} = \frac{(20+20)(T-450)}{7.5 \times 10^3}$$

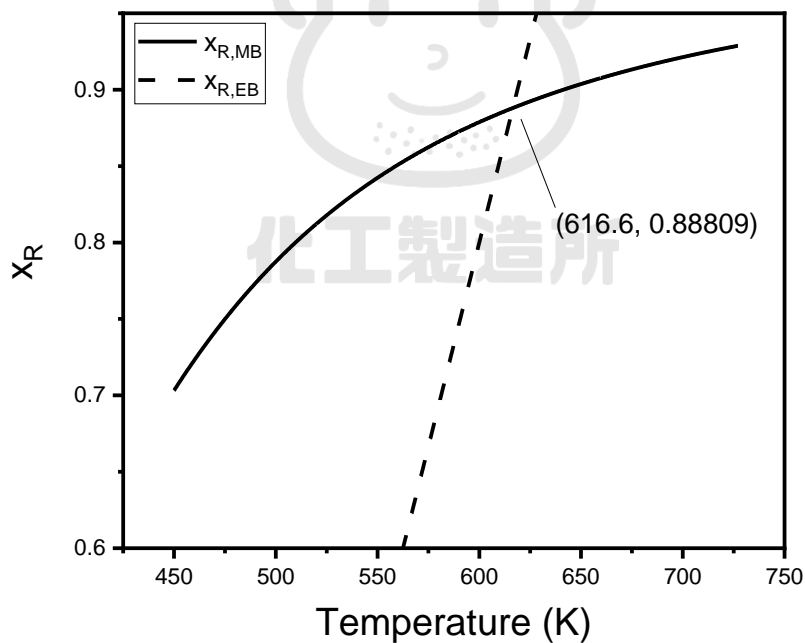
By mass balance,

$$x_{R,MB} = \frac{k\tau}{1+k\tau} = \frac{6.6 \times 10^{-3} e^{\frac{-4 \times 10^3}{1.987} (\frac{1}{T} - \frac{1}{350})} \cdot 100}{1 + 6.6 \times 10^{-3} e^{\frac{-4 \times 10^3}{1.987} (\frac{1}{T} - \frac{1}{350})} \cdot 100}$$

令 $x_{R,MB} = x_{R,EB}$ 可解得

$$T = 616.51 \text{ (K)}, \quad x_R = 0.888$$

而兩平衡式依照 $x_R - T$ 做圖如下：



(c)

By mass balance,

$$x_{R,MB} = \frac{k\tau}{1+k\tau} = \frac{6.6 \times 10^{-3} e^{\frac{-4 \times 10^3}{1.987} (\frac{1}{600} - \frac{1}{350})} \cdot 100}{1 + 6.6 \times 10^{-3} e^{\frac{-4 \times 10^3}{1.987} (\frac{1}{600} - \frac{1}{350})} \cdot 100} = \underline{\underline{0.8788}}$$

代回 energy balance,

$$0.8788 = \frac{40(600 - T_{i0})}{7.5 \times 10^3}, \quad T_{i0} = \underline{\underline{435.22 \text{ (K)}}}$$

(d)

By energy balance,

$$x_{R,EB} = \frac{\sum_i \int_{T_{i0}}^T \theta_{i0} C_{pi} dT + \frac{Q}{F_{R0}}}{-[\Delta H_R^\circ(T_R)]} = \frac{40(T - 450) + \frac{800 \times 1 \times \pi \times 3(T - 300)}{80}}{7.5 \times 10^3}$$

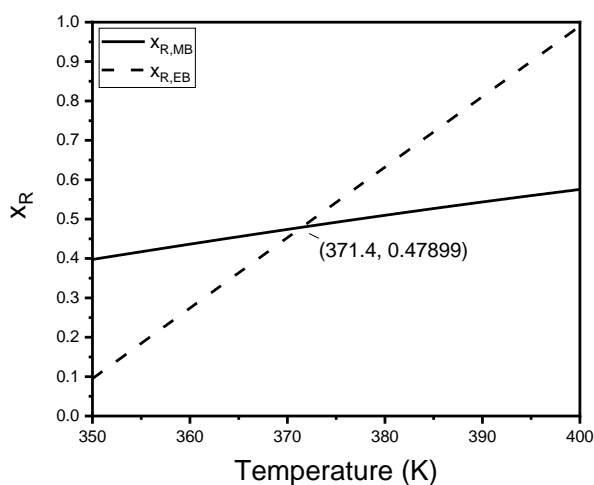
By mass balance,

$$x_{R,MB} = \frac{k\tau}{1+k\tau} = \frac{6.6 \times 10^{-3} e^{\frac{-4 \times 10^3}{1.987} (\frac{1}{T} - \frac{1}{350})} \cdot 100}{1 + 6.6 \times 10^{-3} e^{\frac{-4 \times 10^3}{1.987} (\frac{1}{T} - \frac{1}{350})} \cdot 100}$$

令 $x_{R,MB} = x_{R,EB}$ 可得：

$$T = 371.466 \text{ (K)}, \quad x_R = 0.4776$$

而兩平衡式依照 $x_R - T$ 做圖如下：



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Problem 1

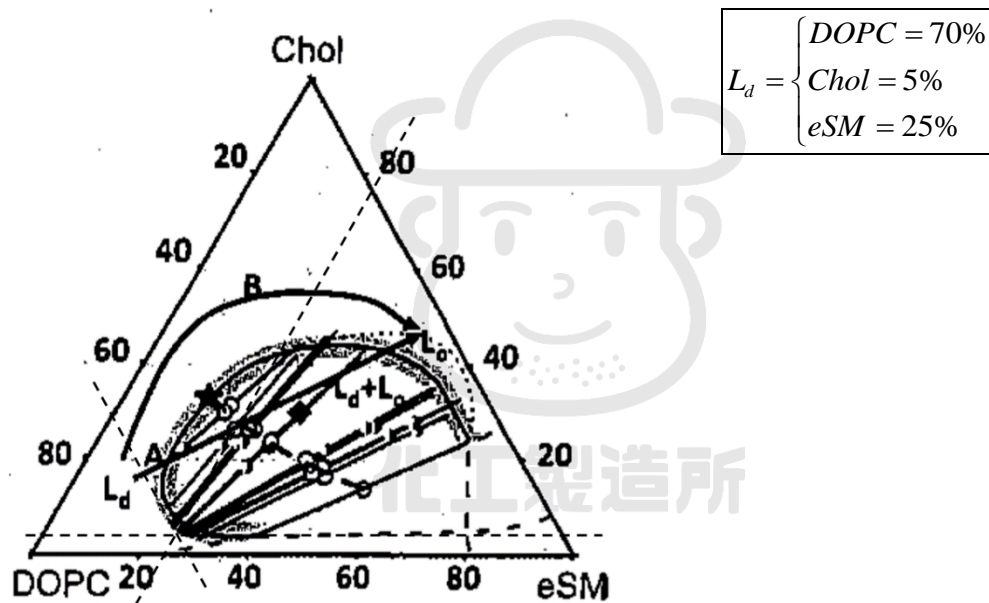
【Solution】

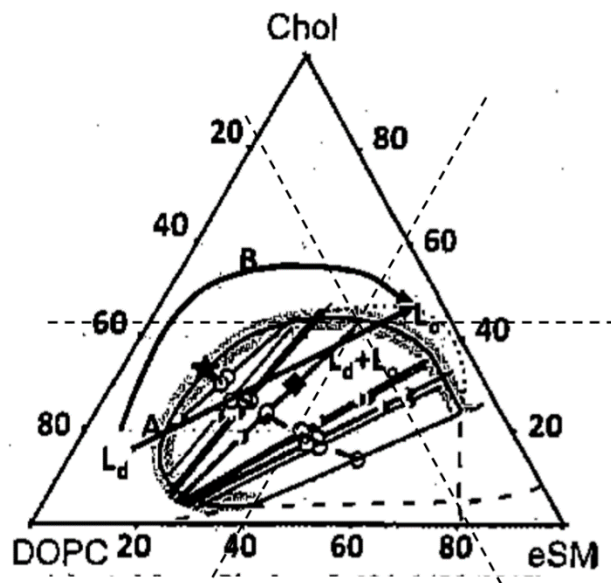
(a)

不一定，相變化與 T、P、組成有關，不同之(T, P)組合有不同的相圖，不能確保在同樣的組成範圍內有同樣兩相平衡的存在。

(b)

如圖，對於 L_d





如圖，對於 L_o

$$L_o = \begin{cases} DOPC = 18\% \\ Chol = 42\% \\ eSM = 40\% \end{cases}$$

(c) Plait point

(d)

$$\begin{cases} \text{path A} = \text{First-order transition} \\ \text{path B} = \text{Second-order transition} \end{cases}$$

(Path A 經過兩相分離，為 first order transition，一次微分不連續，可想成均勻液體相分離為液固兩相。)

(本題可參考：Atkins, P.; De Paula, J.; Keeler, J. *Atkins' Physical Chemistry*, 9th ed.; p 151.)

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(e)

If the process is isothermal and isobaric, by energy balance,

$$W_s = (U_2 + P_2V_2) - (U_1 + P_1V_1) - Q$$

By entropy balance,

$$S_2 = S_1 + \frac{Q}{T} + S_{gen}$$

For ideal behavior,

$$S_{gen} = 0, \quad Q = TS_2 - TS_1 \text{ 代入}$$

$$W_s = (U_2 + P_2V_2 - TS_2) - (U_1 + P_1V_1 - TS_1) = G_2 - G_1$$

If the Gibbs free energy of the well-mixing phase is G_{mix}^{id} ,

the energy needed to separate the phase is

$$\begin{aligned} & (x_{Chol} \underline{G}_{Chol} + x_{DOPC} \underline{G}_{DOPC} + x_{eSM} \underline{G}_{eSM}) - G_{mix}^{id} \\ & = \underline{\underline{-RT(x_{Chol} \ln x_{Chol} + x_{DOPC} \ln x_{DOPC} + x_{eSM} \ln x_{eSM})}}} \end{aligned}$$

At the point indicated by diamond $\begin{cases} x_{Chol} = 0.30 \\ x_{DOPC} = 0.35 \text{ 代入} \\ x_{eSM} = 0.35 \end{cases}$

$$W_s = -8.314 \times (273 + 37) \times (0.30 \ln 0.30 + 0.35 \ln 0.35 + 0.35 \ln 0.35) = \underline{\underline{2824.9 \text{ (J / mole)}}}$$

(本题可参考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 4th ed.;

p 110~111.)

Problem 2

【Solution】

(a)

$$\begin{aligned}\Delta_{fus} \underline{G}(T, P) &= \Delta_{fus} \underline{H} - T \Delta_{fus} \underline{S} \\ &= (\Delta_{fus} \underline{H}_m - T \Delta_{fus} \underline{S}_m) + \int_{T_m}^T \Delta C_p dT - T \int_{T_m}^T \frac{\Delta C_p}{T} dT \\ \because \Delta_{fus} \underline{S}_m &= \frac{\Delta_{fus} \underline{H}_m - \Delta_{fus} \underline{G}(T_m)}{T_m} = \frac{\Delta_{fus} \underline{H}_m}{T_m} \text{ 代入} \\ \Delta_{fus} \underline{G}(T, P) &= \Delta_{fus} \underline{H}_m \left(1 - \frac{T}{T_m}\right) + \int_{T_m}^T \Delta C_p dT - T \int_{T_m}^T \frac{\Delta C_p}{T} dT\end{aligned}$$

假設 $\Delta C_p \sim 0$

$$\Delta_{fus} \underline{G}(T, P) = \Delta_{fus} \underline{H}_m \left(1 - \frac{T}{T_m}\right) = \Delta_{fus} \underline{H}_m \left(\frac{T_m - T}{T_m}\right)$$

When the first liquid crystal of pure solvent forms, the temperature is T_f ,

and equilibrium is reached,

$$\begin{aligned}f_1^s(T_f, P) &= \overline{f_1^L}(T_f, P, x) = x_1 r_1 f_1^L \\ \ln \frac{f_1^L}{f_1^s} &= \ln \frac{1}{r_1 x_1} = \frac{\Delta_{fus} \underline{G}(T_f, P)}{RT_f} \\ \ln r_1 x_1 &= \frac{-\Delta_{fus} \underline{G}(T_f, P)}{RT_f}, \quad \ln r_1 x_1 = \frac{-\Delta_{fus} \underline{H}_m \left(\frac{T_m - T_f}{T_m}\right)}{RT_f}\end{aligned}$$

$$\boxed{\Delta T = T_m - T_f = \frac{-RT_m T_f}{\Delta_{fus} \underline{H}_m} \ln(r_1 x_1)}$$

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

p 704-705.)

(b)

$$\Delta T = T_m - T_f = \frac{RT_m T_f}{\Delta_{fus} \underline{H}_m} \ln(x_1 r_1)$$

For $\begin{cases} \text{ideal gas phase} \\ \text{ideal solution phase} \end{cases}$, Henry's law is applicable

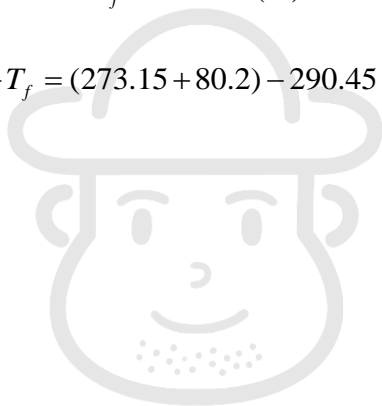
$$P_{CO_2} = H_{CO_2} x_{CO_2} \quad , \quad 12.5 = 50 x_{CO_2}$$

$$x_{CO_2} = x_1 = 0.25 \quad , \quad r_{CO_2} = 1$$

$$\Delta T = \frac{-8.314 \times (273.15 + 80.2) T_f}{18.804 \times 10^3} \ln(0.25 \times 1) = (273.15 + 80.2 - T_f)$$

$$T_f = 290.45 \text{ (K)}$$

$$\Delta T = T_m - T_f = (273.15 + 80.2) - 290.45 = \underline{\underline{62.9 \text{ (K)}}}$$



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Problem 3

【Solution】

For 1st order reaction,

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

For the 1st CSTR,

$$V = \frac{F_{A0}x_{A1}}{-r_A}, \quad \tau = \frac{C_{A0}x_{A1}}{kC_{A0}(1-x_{A1})}$$

$$x_{A1} = 1 - \frac{1}{1 + \tau k}$$

For the 2nd CSTR,

$$\tau = \frac{C_{A0}(x_{A2} - x_{A1})}{kC_{A0}(1-x_{A2})}, \quad \tau = \frac{(x_{A2} - x_{A1})}{k(1-x_{A2})}$$

$$x_{A2} = \frac{k\tau + x_{A1}}{1 + \tau k} = 1 - \frac{1}{(1 + \tau k)^2}$$

For the 3rd CSTR,

$$x_{A3} = 1 - \frac{1}{(1 + \tau k)^3}$$

代入數據：

$$x_{A1} = 0.5 = 1 - \frac{1}{1 + \tau k}, \quad \tau k = 1$$

$$x_{A3} = 1 - \frac{1}{(1+1)^3} = \underline{\underline{0.875}}$$

Problem 4

【Solution】

By energy balance,

$$x_A = \frac{\sum \theta_i \tilde{C}_{pi}(T_0 - T_{i0}) - \frac{\dot{Q} - \dot{W}}{F_{A0}}}{-\Delta H_{Rx}}$$

$$\begin{aligned}\sum \theta_i \tilde{C}_{pi}(T_0 - T_{i0}) &= (1 + 40 + \frac{1}{1.25} \times 40) \times 10^3 (T - 300) \\ &= 72 \times 10^3 (T - 300) (\text{cal} / \text{mol})\end{aligned}$$

$$\dot{Q} = UA(T_a - T) = 75 \times 10^3 (310 - T) (\text{cal} / \text{s})$$

$$\dot{W} = \frac{-20.9 \times 10^3}{4.2} = -4976 (\text{cal} / \text{s})$$

$$\begin{aligned}-\Delta H_{Rx} &= -[\Delta H_{Rx}^\circ + \int_{T_R}^T \Delta C_p dT] = -[(-60 + 25 + 20) + \int_{298}^T (55 - 40 - 40) dT] \times 10^3 \\ &= [15 + 25(T - 298)] \times 10^3\end{aligned}$$

$$x_A = \frac{72 \times 10^3 (T - 300) - [\frac{75 \times 10^3 (310 - T) - 4976}{1}]}{[15 + 25(T - 298)] \times 10^3} = 0.6$$

$$\underline{\underline{T = 306.01 (K)}}$$

For the volume of the reactor, by rate equation,

$$-r_A = k C_A C_B = k C_{A0}^2 (1 - x_A)(0.8 - x_A)$$

by design equation,

$$V = \frac{F_{A0} x_A}{-r_A} = \frac{F_{A0} x_A}{k C_{A0}^2 (1 - x_A)(0.8 - x_A)}$$

For k at 306.01(K), by Arrhenius' law,

$$k(306.01) = k(300) \cdot e^{\frac{-8 \times 10^3}{1.987} (\frac{1}{306.01} - \frac{1}{300})} = 0.01 \times e^{\frac{-8 \times 10^3}{1.987} (\frac{1}{306.01} - \frac{1}{300})} = 0.013$$

$$V = \frac{1.25 \times 0.6}{0.013 \times (\frac{1.25}{5})^2 (1 - 0.6)(0.8 - 0.6)} = \underline{\underline{11522 (L)}}$$

Problem 5

【Solution】

Assume the frequency factor, A, remains the same at both conditions.

For catalyzed reaction at 25°C, by Arrhenius law,

$$k_{cat} = A \cdot e^{\frac{-E_a}{RT}} = A \cdot e^{\frac{-42.0 \times 10^3}{8.314 \times (273.15 + 20)}}$$

For uncatalyzed reaction at T°C,

$$k_{uncat} = A \cdot e^{\frac{-E_a}{RT}} = A \cdot e^{\frac{-10 \times 10^3}{8.314(T + 273.15)}}$$

$$k_{cat} = k_{uncat} \quad , \quad \underline{\underline{T = 215.43 \text{ (}^\circ\text{C)}}}$$



Problem 6**【Solution】**

(a)

By energy balance, (without Q, W)

$$x_{R,EB} = \frac{\sum \theta_i C_{pi} (T - T_{i0})}{-[\Delta H_{Rx}^\circ(T_R) + \Delta C_p (T - T_R)]}$$

$$\sum \theta_i C_{pi} (T - T_{i0}) = (1 \times 100 + 1 \times 150)(T - 350) = 250(T - 350)$$

$$\Delta H_{Rx}^\circ(T_R) = -25 \times 10^3 \text{ (J)}$$

$$\Delta C_p = 100 - 100 = 0$$

$$x_{R,EB} = \frac{250(T - 350)}{-(-25 \times 10^3)} = \frac{250(T - 350)}{(25 \times 10^3)}$$

By thermodynamics,

$$K(T) = \frac{x_{Re}}{1 - x_{Re}}, \quad x_{Re} = \frac{K}{1 + K}$$

For K, by van' Hoff equation,

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}, \quad \ln \frac{K(T)}{K(330K)} = \frac{-\Delta H}{R} \left(\frac{1}{T} - \frac{1}{330} \right)$$

$$\ln \frac{K(T)}{3} = \frac{25 \times 10^3}{8.314} \left(\frac{1}{T} - \frac{1}{330} \right)$$

$$K(T) = 3 \cdot \exp[3006.98 \left(\frac{1}{T} - \frac{1}{330} \right)]$$

$$x_{Re} = \frac{3 \exp[3006.98 \left(\frac{1}{T} - \frac{1}{330} \right)]}{1 + 3 \exp[3006.98 \left(\frac{1}{T} - \frac{1}{330} \right)]}$$

$$\text{令 } x_{Re} = x_{R,EB}$$

$$T = 391.67 \text{ (K)}, \quad x_R = x_{R,\max} = 0.417$$

(b)

For the reactor volume of PFR, by rate equation,

$$-r_R = k(T)C_{R0}[(1-x_R) - \frac{1}{K}x_R]$$

For $k(T)$, by Arrhenius' law,

$$k(T) = 10 \cdot \exp\left[\frac{-100 \times 10^3}{8.314} \left(\frac{1}{T} - \frac{1}{300}\right)\right]$$

$$T = \frac{25 \times 10^3}{250} x_R + 350 = 100x_R + 350$$

(By energy balance)

$$k(T) = 10 \exp\left[\frac{-100 \times 10^3}{8.314} \left(\frac{1}{100x_R + 350} - \frac{1}{300}\right)\right]$$

$$K(T) = 3 \cdot \exp\left[3006.98 \left(\frac{1}{100x_R + 350} - \frac{1}{330}\right)\right]$$

$$\begin{aligned} -r_R &= k(T)C_{R0}[(1-x_R) - \frac{1}{K}x_R] \\ &= C_{R0} \cdot 10 \cdot \exp\left[\frac{-100 \times 10^3}{8.314} \left(\frac{1}{T} - \frac{1}{300}\right)\right] \left[(1-x_R) - \frac{x_R}{3 \cdot \exp\left[3006.98 \left(\frac{1}{100x_R + 350} - \frac{1}{330}\right)\right]}\right] \end{aligned}$$

By design equation,

$$V = \int_0^{x_R} \frac{F_{R0} dx_R}{-r_R} = \int_0^{x_R} \frac{v_{R0} dx_R}{\frac{-r_R}{C_{R0}}}$$

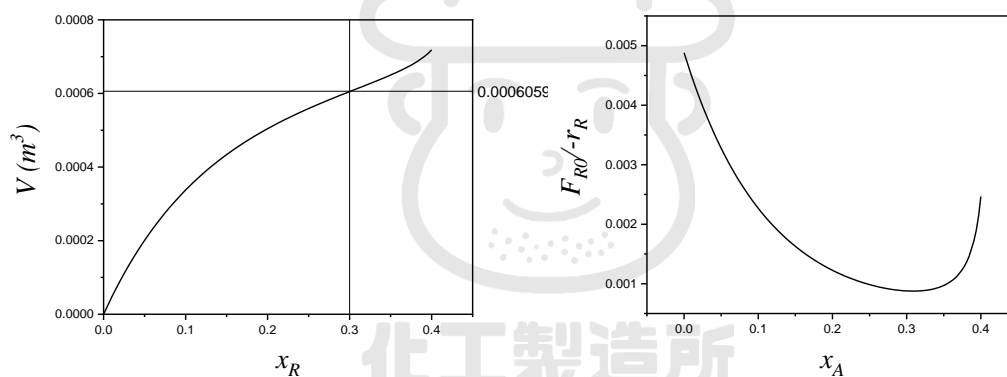
By Simpson's rule,

x_R	$k(T)$	$K(T)$	$-r_R / C_{R0}$	$F_{R0} / -r_R$
0	3072.229	1.782333	3072.2294	0.004882
0.075	6317.71	1.488374	5525.5291	0.002715
0.15	12612.42	1.252139	9209.6508	0.001629
0.225	24487.64	1.060755	13783.773	0.001088
0.300	46314.95	0.904527	17059.414	0.000879

$$V = \frac{0.075}{3} [1 \times 0.004882 + 4 \times 0.002715 + 2 \times 0.001629 + 4 \times 0.001088 + 1 \times 0.000879]$$

$$= \underline{\underline{0.000606 \text{ (m}^3\text{)}}}$$

※若由 polymath 數值解：



```
#To calculate the volume of PFR, we need its design equation, that is,
d(V)/d(xR) = FR0/(-rR)

#The explicit equations or values are,
CR0 = 10*10^3
FR0 = CR0*15
k = 10*exp((-100*10^3)/8.314*(1/T-1/300))
K = 3*exp(25000/8.314*(1/T-1/330))
T = 100*xR+350
rR = -k*CR0*((1-xR) - (1/K)*xR)
a = FR0/(-rR)

#Define the the guess initial value of V to obtain the true value, ranging from xR = 0~0.4
V(0) = 0
xR(0) = 0
xR(f) = 0.4
```

若由電腦數值解，可解得 $\underline{\underline{V = 0.0006059 \text{ (m}^3\text{)}}}$

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Problem 1

【Solution】

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

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

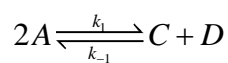
For $\Delta G @ 477^\circ \text{C}$, assume $\Delta C_p \approx 0$

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

Problem 2

【Solution】

Reaction,



For equilibrium conversion,

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

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,

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

For PFR,

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

(b)

For PFR operated at 300K,

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

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) :

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

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

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

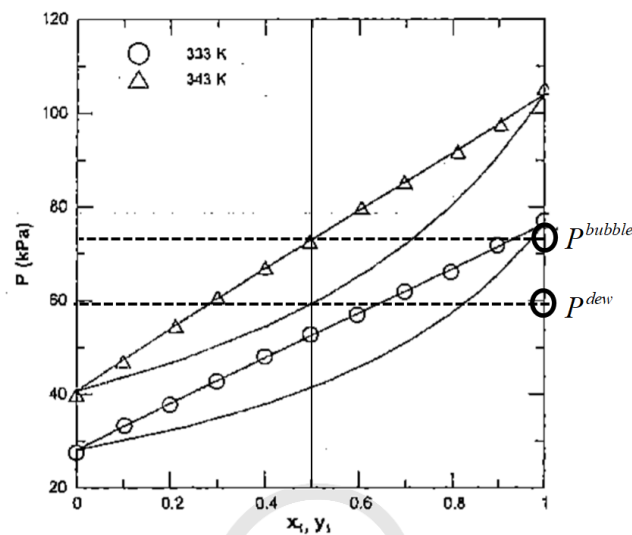
$$= 0.020 - 0.010 - 0.00452 - 0.00539 = 7.815 \times 10^{-5} \text{ (M)}$$

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

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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,

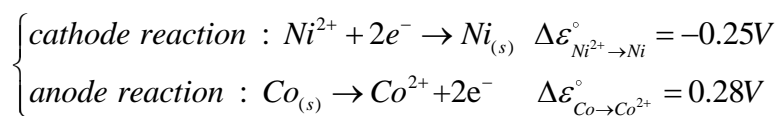
$$x_{C_6} = \frac{y_{C_6} P}{P_{C_6}^{\text{vap}}} = \frac{0.50 P}{1.049}$$

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

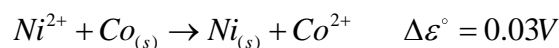
$$x_{C_8} = \frac{y_{C_8} P}{P_{C_8}^{\text{vap}}} = \frac{0.25 P}{0.157}$$

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,

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

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,

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

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



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,

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

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

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

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

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

代入：

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

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

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

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

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

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,

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

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

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

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

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

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,

$$\begin{aligned} & \begin{cases} dn_i = d(nx_i) = n dx_i + x_i dn \\ d(nM) = ndM + Mdn \end{cases} \text{ 代入} \\ ndM + Mdn &= n \left(\frac{\partial M}{\partial P} \right)_{T,x} dP + n \left(\frac{\partial M}{\partial T} \right)_{P,x} dT + \sum_i \bar{M}_i (x_i dn + n dx_i) \\ \underbrace{\left[dM - \left(\frac{\partial M}{\partial P} \right)_{T,x} dP - \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i \bar{M}_i dx_i \right] n}_{=0} &+ \underbrace{\left[M - \sum_i x_i \bar{M}_i \right] dn}_{=0} = 0 \end{aligned}$$

Where,

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

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

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

(本题可参考：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 μ_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 μ_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

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

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

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

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

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

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

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

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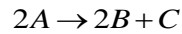
108 年中央化熱化反

Problem 1

【Solution】

令 $NOBr = A$, $NO = B$, $Br_2 = C$

Reaction :



For rate equation,

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

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

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

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

(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,

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

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 1st CSTR,

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

For the 2nd 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 1st CSTR,

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

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

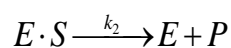
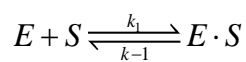
(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 149, Problem 6.15.)

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 1st law of thermodynamics (open system, steady state)

$$\Delta H + \frac{\Delta u^2}{2g_c} + \frac{\cancel{g}}{\cancel{g_c}} \cancel{z} = \cancel{Q}_{\substack{\text{insulated} \\ \text{horizontal}}} + \cancel{W}_{\text{no shaft work}}$$
$$\Delta H + \frac{1}{2}(u_2^2 - u_1^2) = 0$$

By mass balance of the nitrogen,

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

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

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

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

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

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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.

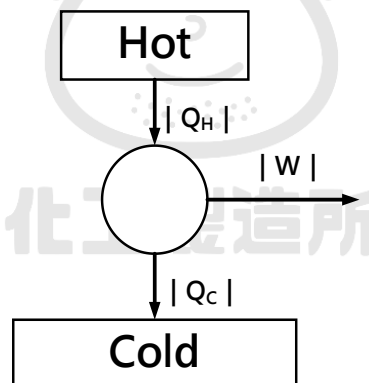
(2) Kelvin-Planck statement :

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 α and β phases are in equilibrium,

$$dG^\alpha = dG^\beta$$

(題目應改為 $dG = VdP - SdT$)

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

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

$$\therefore \Delta S = \frac{\Delta H}{T}$$

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

For melting of ice,

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

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 1st 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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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】

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

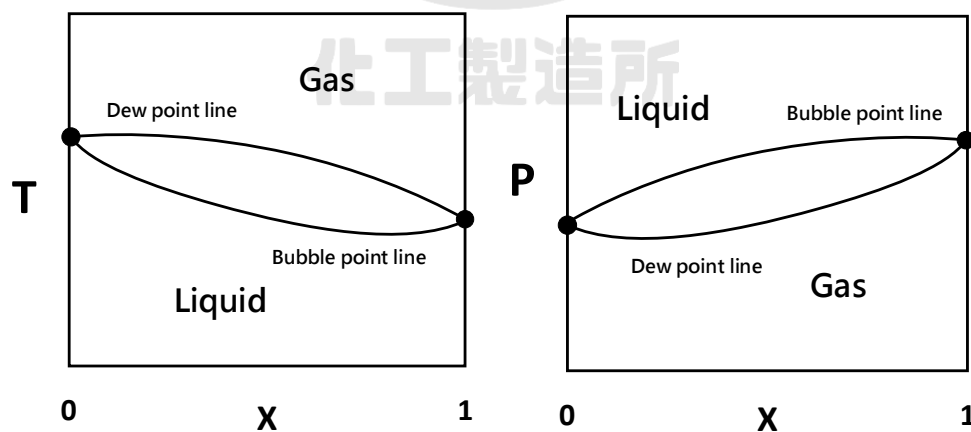
All *excess properties* are zero for an ideal solution.

(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 1st 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 2nd 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 μ_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, $\hat{\phi}_i$, 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,

$$dQ_{rev} = TdS$$

(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 1st law of thermodynamics for reversible process

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

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

By the 2nd 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 only states that “no apparatus can convert heat absorbed completely into work.”.

(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,

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

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

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

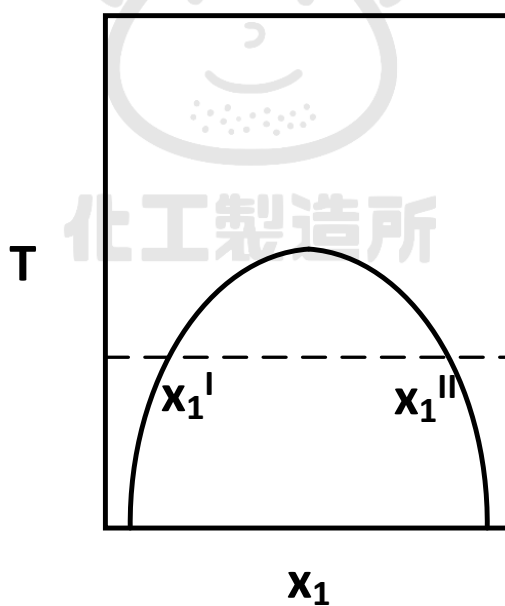
$$\chi = \chi(T)$$

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

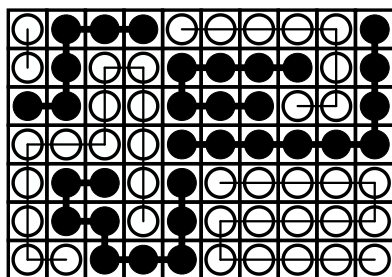


(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

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 ϕ 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 χ (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， χ 越小，代表系統越易互溶； χ 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)

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

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

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} = \frac{(\Delta H + \int_0^T \Delta C_p dT)}{RT^2}$$

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

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

Problem 4

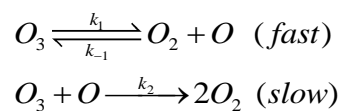
【Solution】

(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,

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

(本题改编自：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 1st CSTR,

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

For the 2nd CSTR,

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

相除：

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

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

For k, 數據代入 1st CSTR,

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

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.)



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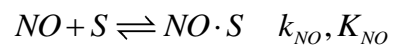
Problem 7

【Solution】

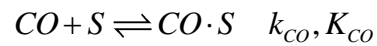
(a)

Possible mechanism : (Dual-Site Mechanism)

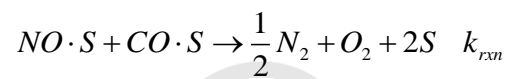
Adsorption of NO :



Adsorption of CO :



Surface reaction :



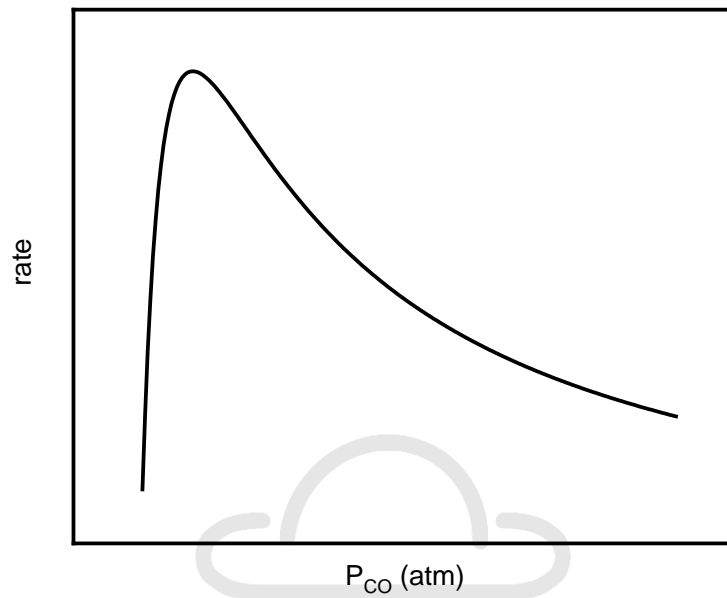
(b)

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

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(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。

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110 年中央化熱化反

一、單選題

(1) Ans : (D)

(2) Ans : (C)

【Solution】

For first order reaction,

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

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

(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)

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

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

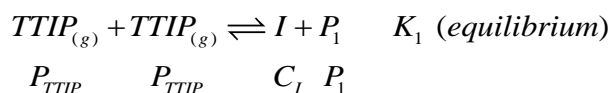
二、計算題

Problem 1

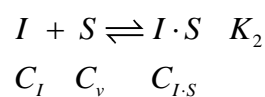
【Solution】

(a)

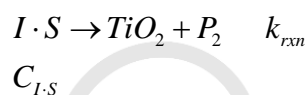
First-step reaction :



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} ,

$$P_1 \gg K_1 K_2 P_{TTIP}^2$$
$$r \propto \frac{KK_1 P_{TTIP}^2}{P_1} \propto P_{TTIP}^2$$

(2) With high P_{TTIP} ,

$$P_1 \ll K_1 K_2 P_{TTIP}^2$$
$$r \propto \frac{KK_1 P_{TTIP}^2}{K_1 K_2 P_{TTIP}^2} \propto P_{TTIP}^0$$

(3) @300°C

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

$$P_1 \gg K_1 K_2 P_{TTIP}^2$$
$$r \propto \frac{KK_1 P_{TTIP}^2}{P_1} \propto P_{TTIP}^2$$

(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 π 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.)

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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),

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

$u_1 = u_2$ *adiabatic*

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

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,

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

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

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

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

(b)

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

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

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

同理

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

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

(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

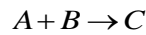
1，所以 **regular solution model 較為合適**

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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 200×10^6 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} ,

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

代回：

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

Problem 3

【Solution】

(a)

Assume 1 = anthracene, 2 = ethylene

By the question statement,

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

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

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)



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(b)

By the question statement,

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

$$\begin{aligned}(2\sum_{j=1}^n y_j B_{ij} - B_{mixt}) &= (2\sum_{j=1}^2 y_j B_{ij} - B_{mixt}) \\ &= 2y_1 B_{11} + 2y_2 B_{12} - B_{mixt} = 2B_{12} - B_{ETH}\end{aligned}$$

For B_{12} ,

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

For B_{ETH}

$$\begin{aligned}B_{ETH} &= b_{22} - \frac{a_{22}}{RT} = b_2 - \frac{a_2}{RT} \\ &= \frac{8.314 \times 282.35}{8 \times 5.04 \times 10^6} - \frac{27}{64} \times \frac{8.314^2 \left(\frac{282.35^2}{5.04 \times 10^6}\right)}{8.314 \times 298.15} = -1.278 \times 10^{-4} \\ 2B_{12} - B_{ETH} &= 2 \times (-5.416 \times 10^{-4}) + 1.278 \times 10^{-4} = -9.555 \times 10^{-4} \\ \Phi_1 &= \exp\left[-9.555 \times 10^{-4} \times \frac{10 \times 10^5}{8.314 \times 298.15}\right] = 0.680\end{aligned}$$

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,

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

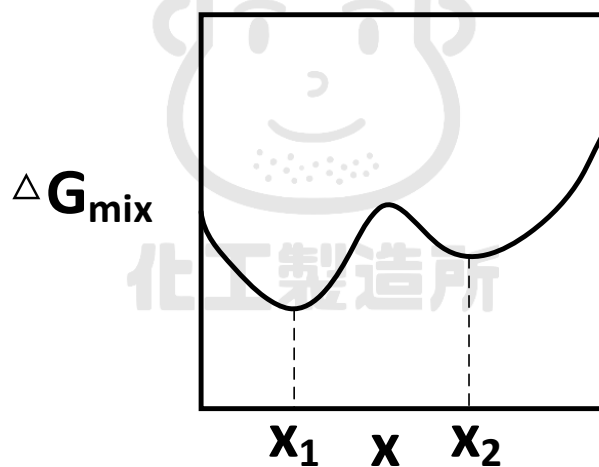
where i denotes the fraction of either L_o or L_d

(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.

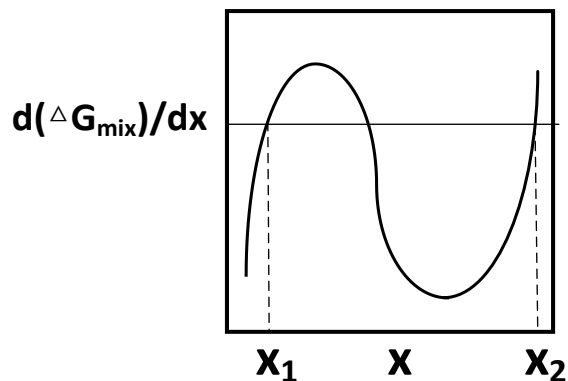
(c)

For an ordinary 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 1st derivative of ΔG_{mix} with respect to x is,



Whether phase separation or not (phase separation occurs along path A, no phase separation occurs along path B), the first derivative of Gibbs energy is continuous.

(d)

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

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

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

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

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

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

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

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

(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 π 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 ,

$$\frac{\pi_1 - \pi_2}{T_{t1} - T_{t2}} = \frac{S_d - S_o}{A_d - A_o}, \quad \frac{(30-25) \times 10^{-3}}{30-25} = \frac{S_d - S_o}{(100-50) \times 10^{-20}}$$

$$\underline{S_d - S_o = 5 \times 10^{-22} \text{ (J / K)}}$$

(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.

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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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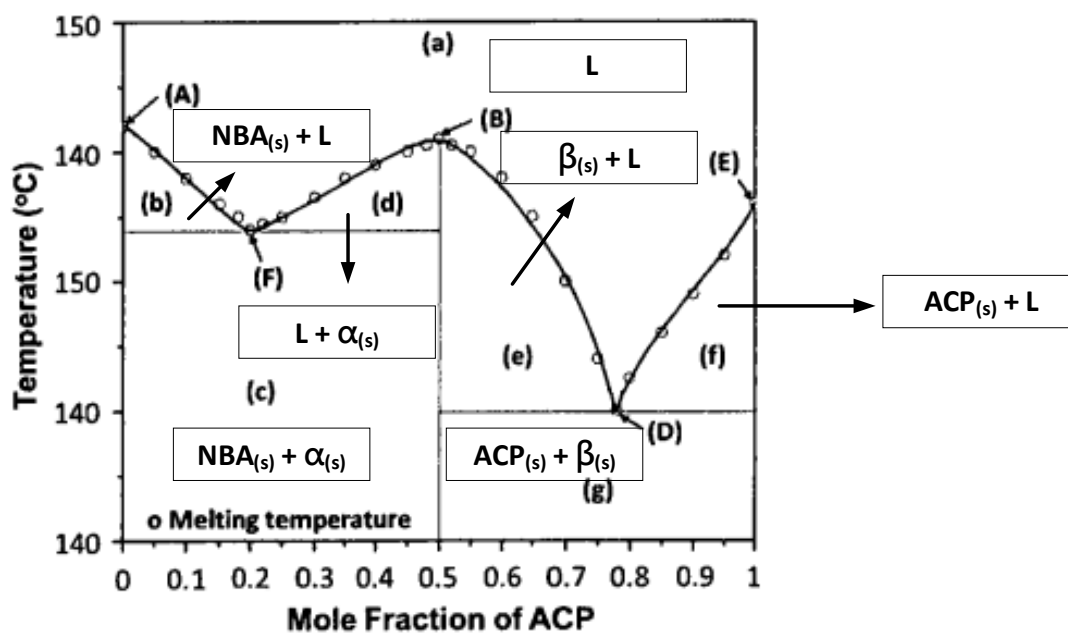
Problem 2

【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,

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

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

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

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

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

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(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 $X_A \uparrow$.

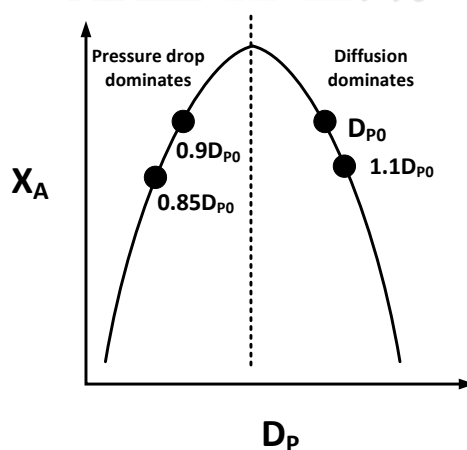
(此段推導可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 177~180.)

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

$$-r_A \propto \frac{1}{1 + K_C P_C + \dots}$$

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,

$$-r_A = \frac{k P_A P_B}{1 + K_A P_A + K_C P_C}$$

(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

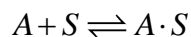
(與 Eley-Rideal mechanism 相同)

C 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

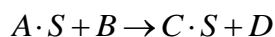
D 無出現於分子與分母，代表不吸附在觸媒上，且速率決定步驟不可逆

根據以上，合理假設速率決定步驟為表面反應：

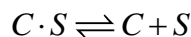
Adsorption :



Surface reaction :



Desorption :



For the determination of the kinetic parameters,

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

則：

1. 固定 P_B , P_C

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 $\frac{K_C}{k}$

((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 $-r_A$,

$$-r_A = \frac{kP_A P_B}{1 + K_A P_A + K_C P_C}$$

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

where,

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

(Only for $\varepsilon = -$)

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

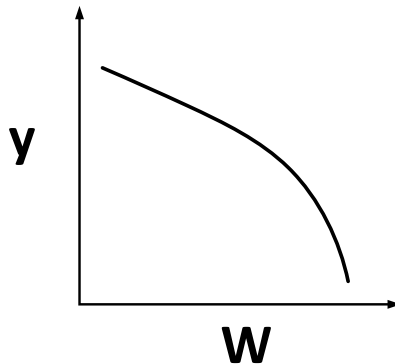
$$P_C = P_{A0} x_A y$$

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

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。



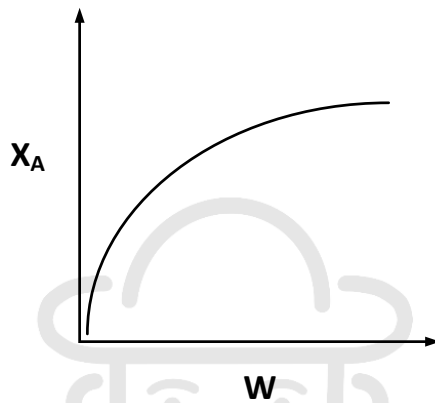
而 $x_A - W$ 圖，根據：

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

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)

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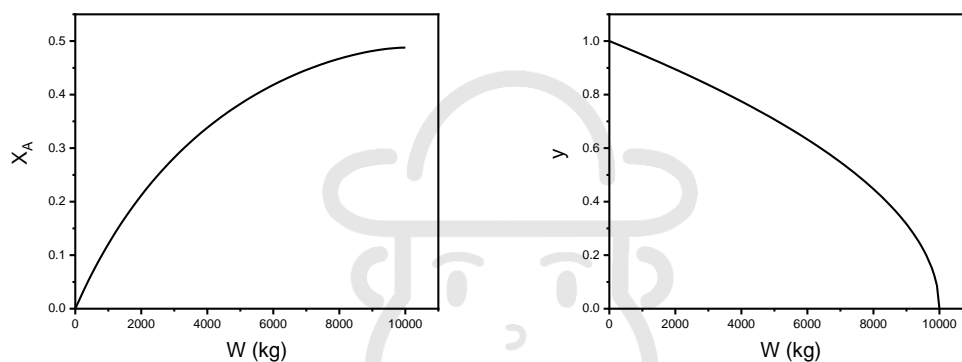
※若根據 polymath 繪圖，可得：

```
#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+KC*PC)

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

