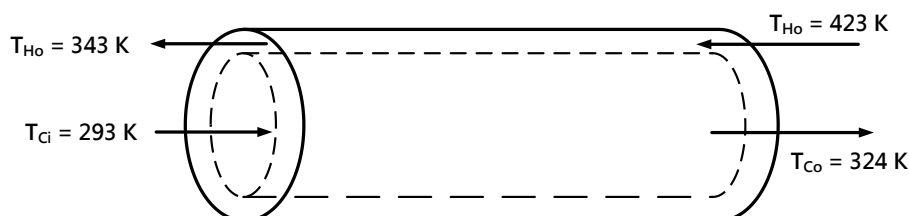


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Problem 5

【Solution】

(1) Counter-current



$$LMTD = \frac{(T_{Hi} - T_{Co}) - (T_{Ho} - T_{Ci})}{\ln\left(\frac{T_{Hi} - T_{Co}}{T_{Ho} - T_{Ci}}\right)}$$

$$= \frac{(423 - 324) - (343 - 293)}{\ln\left(\frac{423 - 324}{343 - 293}\right)} = \underline{\underline{71.73 \text{ (K)}}}$$

By energy balance,

$$\dot{m}_H C_{PH} (T_{Hi} - T_{Ho}) = U_i A (LMTD)$$

$$\frac{3220}{3600} \times 2.3 \times 10^3 (423 - 343) = 366 A \times 71.73$$

$$\underline{\underline{A = 6.27 \text{ (m}^2\text{)}}}$$

(2) Co-current

$$LMTD = \frac{(T_{Hi} - T_{Ci}) - (T_{Ho} - T_{Co})}{\ln\left(\frac{T_{Hi} - T_{Ci}}{T_{Ho} - T_{Co}}\right)}$$

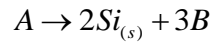
$$= \frac{(423 - 293) - (343 - 324)}{\ln\left(\frac{423 - 293}{343 - 324}\right)} = \underline{\underline{57.72 \text{ (K)}}}$$

$$\Rightarrow \frac{3220}{3600} \times 2.3 \times 10^3 (423 - 343) = 366 A \times 71.73$$

$$\underline{\underline{A = 12.66 \text{ (m}^2\text{)}}}$$

Problem 6**【Solution】**

Let the reaction,



$N_B = -3N_A$ 代入題目方程式

$$N_A = -cD_{AB} \frac{dx_A}{dz} + x_A(N_A - 3N_A)$$

$$= -cD_{AB} \frac{dx_A}{dz} - 2x_A N_A$$

$$(1 + 2x_A)N_A = -cD_{AB} \frac{dx_A}{dz}$$

$$\int_0^\delta N_A dz = -cD_{AB} \int_{x_{A1}}^{x_{A2}} \frac{dx_A}{(1 + 2x_A)}$$

$$N_A \delta = \frac{-cD_{AB}}{2} \ln\left(\frac{1 + 2x_{A2}}{1 + 2x_{A1}}\right)$$

$$N_A = \frac{-cD_{AB}}{2\delta} \ln\left(\frac{1 + 2x_{A2}}{1 + 2x_{A1}}\right)$$

Problem 7**【Solution】**

(1)

$$\frac{u_1^2}{2} - \frac{u_2^2}{2} + \frac{P_1 - P_2}{\rho} = 0$$

$$u_1 = \sqrt{\frac{2(P_1 - P_2)}{\rho}}$$

(2)

$$u_1 = \sqrt{\frac{2 \times 2.2}{0.98 \times 10^{-3}}} = 0.067 \text{ (m / s)}$$

因為 u_1 是在管中央位置， $u_1 = v_{\max}$

$$\begin{aligned} Q &= \langle v \rangle \frac{\pi}{4} D^2 = \frac{v_{\max}}{2} \times \frac{\pi}{4} D^2 \\ &= \frac{1}{2} \times 0.067 \times \frac{\pi}{4} \times (2.66 \times 10^{-2})^2 \\ &= \underline{\underline{1.862 \times 10^{-5} \text{ (m}^3 \text{ / s)}}} \end{aligned}$$

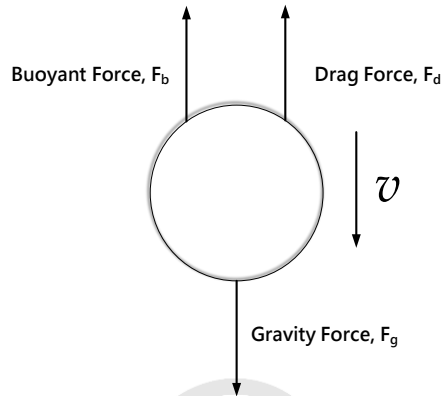


105 年台科大單操輸送

Problem 1

【Solution】

(a)



By force balance,

$$F = ma = m \frac{dv}{dt} = F_g - F_b - F_d$$

As the particle reaches terminal velocity,

$$0 = \frac{\pi}{6} D_p^3 \rho_p g - \frac{\pi}{6} D_p^3 \rho_f g - 3\pi\mu D_p v_t$$

$$\underline{\underline{v_t = \frac{D_p^2 (\rho_p - \rho_f) g}{18\mu}}}$$

(b)

$$v_t = \frac{D_p^2 (\rho_p - \rho_f) g}{18\mu} = \frac{(0.8 \times 10^{-6})^2 \times (1.0 \times 10^3 - 1.2) \times 9.8}{18 \times 18.2 \times 10^{-6}} = 1.91 \times 10^{-5} \text{ (m)}$$

$$t = \frac{20}{v_t} = \frac{20}{1.91 \times 10^{-5}} = 1.06 \times 10^6 \text{ (s)}$$

$$\underline{\underline{L = 5 \times 1.04 \times 10^6 = 5.23 \times 10^6 \text{ (m)}}}$$

(c)

$$C_c = 1 + \frac{2.52 \times 6.6 \times 10^{-8}}{2.8 \times 10^{-6}} = 1.21$$

By force balance,

$$0 = \frac{\pi}{6} D_p^3 \rho_p g - \frac{\pi}{6} D_p^3 \rho_f g - \frac{3\pi\mu D_p v_t}{C_c}$$

$$v_t = \frac{D_p^2 (\rho_p - \rho_f) g}{18\mu} C_c = 1.91 \times 10^{-5} \times 1.21 = 2.31 \times 10^{-5} \text{ (m/s)}$$

$$L = 5 \times \frac{20}{2.31 \times 10^{-5}} = \underline{\underline{4.33 \times 10^6 \text{ (m)}}}$$



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Problem 2

【Solution】

Because the velocity and temperature profile can be approximated by a cubic equation, let

$$\begin{cases} \eta = \frac{y}{\delta} \\ \eta_T = \frac{y}{\delta_T} \end{cases}, \begin{cases} \frac{v_x}{v_\infty} = a + b\eta + c\eta^2 + d\eta^3, 0 \leq y \leq \delta \\ \frac{T - T_s}{T_\infty - T_s} = A + B\eta_T + C\eta_T^2 + D\eta_T^3, 0 \leq y \leq \delta_T \end{cases}$$

Boundary conditions,

$$\begin{cases} y=0, \frac{v_x}{v_\infty} = 0 \\ y=\delta, \frac{v_x}{v_\infty} = 1 \\ y=\delta, \frac{dv_x}{dy} = 0 \\ y=0, \frac{d^2v_x}{dy^2} = 0 \end{cases}, \begin{cases} y=0, \frac{T - T_s}{T_\infty - T_s} = 0 \\ y=\delta_T, \frac{T - T_s}{T_\infty - T_s} = 1 \\ y=\delta_T, \frac{dT}{dy} = 0 \\ y=0, \frac{d^2T}{dy^2} = 0 \end{cases}$$

可解出

$$\begin{cases} a = A = 0 \\ b = B = \frac{3}{2} \\ c = C = 0 \\ d = D = \frac{-1}{2} \end{cases}$$

For momentum equation,

Because the flow is past over a “flat” plate, $v_\infty \neq f(x)$

$$\begin{aligned} & \int_0^\infty \rho v_x (v_\infty - v_x) dy \\ &= \rho v_\infty^2 \delta \int_0^1 \frac{v_x}{v_\infty} \left(1 - \frac{v_x}{v_\infty}\right) d\eta \\ &= \rho v_\infty^2 \delta \int_0^1 \left(\frac{3}{2}\eta - \frac{1}{2}\eta^3\right) \left(1 - \frac{3}{2}\eta + \frac{1}{2}\eta^3\right) d\eta \\ &= \frac{39}{280} \rho v_\infty^2 \delta \end{aligned}$$

代回

$$\mu \frac{\partial v_x}{\partial y} \bigg|_{y=0} = \frac{\mu v_\infty}{\delta} \frac{\partial(\frac{v_x}{v_\infty})}{\partial \eta} \bigg|_{\eta=0} = \frac{3\mu v_\infty}{2\delta} = \frac{39}{280} \rho v_\infty^2 \frac{d\delta}{dx} , \quad \delta = \sqrt{\frac{280}{13} \frac{\nu x}{v_\infty}}$$

$\because @ y = 0,$

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

$$\frac{k(T_\infty - T_s)}{\delta_T} \frac{\partial(\frac{T - T_s}{T_\infty - T_s})}{\partial \eta_T} \bigg|_{\eta_T=0} = h(T_\infty - T_s)$$

$$\frac{h}{k} = \frac{\partial(\frac{T - T_s}{T_\infty - T_s})}{\partial \eta_T} \bigg|_{\eta_T=0} \cdot \frac{\delta}{\delta_T} \cdot \frac{1}{\delta} = \frac{3}{2} \text{Pr}^{\frac{1}{3}} \sqrt{\frac{13}{280} \frac{\nu x}{v_\infty}}$$

$$Nu_x = \frac{hx}{k} = \frac{3}{2} \sqrt{\frac{13}{280}} \text{Pr}^{\frac{1}{3}} \text{Re}^{\frac{1}{2}} = \underline{\underline{0.323 \text{Pr}^{\frac{1}{3}} \text{Re}^{\frac{1}{2}}}}$$

【補充】 $y = 0, \frac{\partial^2 v_x}{\partial y^2} = 0$

By momentum balance,

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = v_\infty \frac{\partial v_\infty}{\partial x} + \mu \frac{\partial^2 v_x}{\partial y^2}$$

@ $y = 0, v_x = v_y = 0$, 且 $v_\infty \neq f(x)$ 代入

$$\mu \frac{\partial^2 v_x}{\partial y^2} = 0 , \quad \frac{\partial^2 v_x}{\partial y^2} = 0 \text{ 得證}$$

【補充】 $y=0, \frac{\partial^2 T}{\partial y^2} = 0$

By energy balance,

$$\rho C_p (v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y}) = k \frac{\partial^2 T}{\partial y^2} + \mu (\frac{\partial v_x}{\partial y})^2$$

@ $y=0, v_x = v_y = \frac{\partial v_x}{\partial y} = 0$

$$k \frac{\partial^2 T}{\partial y^2} = 0, \quad \frac{\partial^2 T}{\partial y^2} = 0 \text{ 得證}$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 387~390.)



Problem 3

【Solution】

(a)

By shell balance of A,

$$N_{Az} \cdot A|_z - N_{Az} \cdot A|_{z+dz} = 0$$

同除 $dz \rightarrow 0$

$$\frac{-dN_{Az}}{dz} = 0, \quad N_{Az} \neq f(z)$$

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

$$N_{Az} = -cD_{AB} \frac{dx_A}{dz} + x_A(N_{Az} + \cancel{N_{Bz}})$$

$$N_{Az} = -\frac{cD_{AB}}{1-x_A} \frac{dx_A}{dz} \quad \text{代回}$$

$$\frac{d}{dz} \left(\frac{1}{1-x_A} \frac{dx_A}{dz} \right) = 0$$

積分兩次

$$-\ln(1-x_A) = c_1 z + c_2 \quad \begin{cases} z=Z, x_A=x_{A1} \\ z=0, x_A=x_{A2} \end{cases}$$

$$\text{可解出} \quad \begin{cases} c_1 = \frac{\ln(\frac{1-x_{A2}}{1-x_{A1}})}{Z} \\ c_2 = -\ln(1-x_{A2}) \end{cases}$$

原式整理可得

$$\left(\frac{1-x_A}{1-x_{A2}} \right) = \left(\frac{1-x_{A1}}{1-x_{A2}} \right)^{\frac{z}{Z}}, \quad \frac{x_B}{x_{B2}} = \left(\frac{x_{B1}}{x_{B2}} \right)^{\xi}$$

則

$$N_{Az} = N_{Az}|_{z=0} = \frac{-cD_{AB}}{(1-x_A)} \frac{dx_A}{dz} \bigg|_{z=0} = \frac{cD_{AB}}{x_{B2}} \frac{dx_B}{dz} \bigg|_{z=0}$$

$$= \frac{cD_{AB}}{Z} \ln \frac{x_{B1}}{x_{B2}} = \frac{D_{AB}P}{RTZ} \frac{(p_{A1}-p_{A2})}{(p_{A1}-p_{A2})} = -\frac{D_{AB}P}{RTZ} \frac{(p_{A1}-p_{A2})}{(p_{B2}-p_{B1})} = \frac{-D_{AB}P}{RTZ} \frac{(p_{A1}-p_{A2})}{p_{B,lm}}$$

$$\ln \frac{x_{B1}}{x_{B2}} \quad \ln \frac{x_{B1}}{x_{B2}}$$

(※最後結果會有個負號，因為座標方向與真正的質傳方向相反，題目有誤)

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 546~548.)

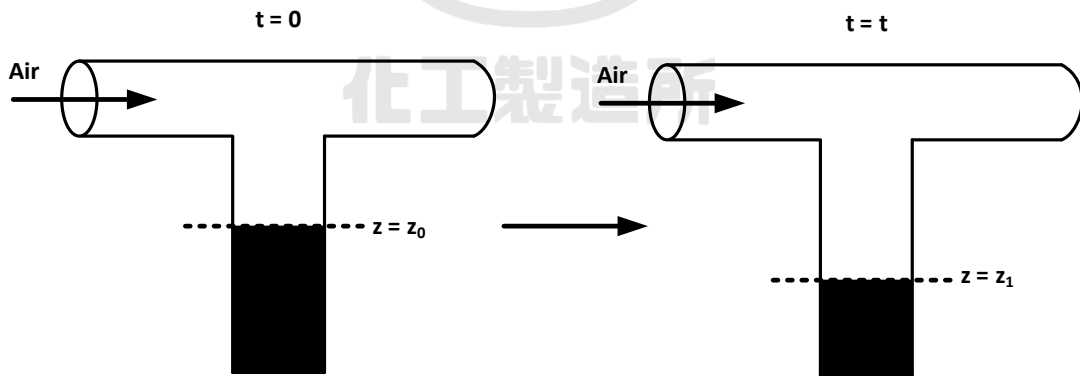
(b)

By quasi-steady state method,

$$\frac{-D_{AB}P}{RTZ} \frac{(p_{A1}-p_{A2})}{p_{B,lm}} \cdot A = \frac{\rho A}{M} \frac{dZ}{dt}$$

$$\int_{z_0}^{z_1} Z dZ = \frac{-D_{AB}P}{RT} \frac{(p_{A1}-p_{A2})}{p_{B,lm}} \frac{\rho}{M} \int_0^t dt$$

$$\boxed{\frac{1}{2}(z_1^2 - z_0^2) = \frac{-D_{AB}P}{RT} \frac{(p_{A1}-p_{A2})}{p_{B,lm}} \frac{\rho}{M} t}$$



可以利用前後的液體高度差 ($z=0$ 為 T 型管頂端)

與時間的關係來測量擴散係數

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

2nd ed.; p 549, Example 18.2-1.)

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Problem 1

【Solution】

(a)

$$\text{Pr} \equiv \frac{\text{momentum diffusivity}}{\text{thermal diffusivity}} = \frac{\nu}{\alpha} = \frac{\mu C_p}{k}$$

(b)

$$\text{Nu} \equiv \frac{\text{conductive thermal resistance}}{\text{convective thermal resistance}} = \frac{hL}{k}$$

(c)

$$\text{St} = \frac{h}{\rho v_{\infty} C_p}$$

(d)

$$\text{Re} \equiv \frac{\text{inertial force}}{\text{viscous force}} = \frac{\rho v_{\infty} L}{\mu}$$

(e)

$$\underline{\underline{\text{St} = \frac{\text{Nu}}{\text{Re Pr}}}}$$

Problem 2

【Solution】

By shell balance of energy outside the sphere, assuming k is constant,

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

同除 $4\pi dr \rightarrow 0$

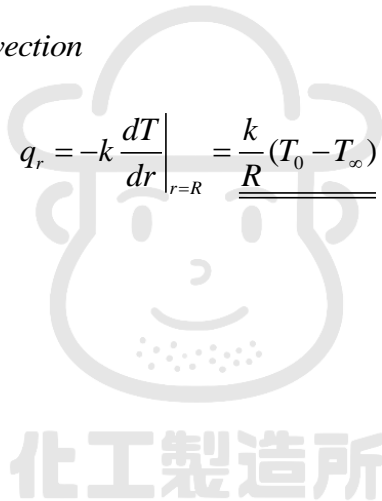
$$\frac{d(r^2 q_r)}{dr} = 0, \quad \frac{d}{dr}(r^2 k \frac{dT}{dr}) = 0 \begin{cases} r = R, T = T_0 \\ r \rightarrow \infty, T = T_\infty \end{cases}$$

$$T = \frac{-c_1}{r} + c_2 \begin{cases} c_1 = (T_\infty - T_0)R \\ c_2 = T_\infty \end{cases}$$

$$T = (T_0 - T_\infty) \frac{R}{r} + T_\infty$$

@ $r = R$, *conduction = convection*

$$q_r = -k \frac{dT}{dr} \Big|_{r=R} = \underline{\underline{\frac{k}{R}(T_0 - T_\infty)}}$$



Problem 3

【Solution】

For constant rate drying,

$$t = \frac{(X_1 - X_2)}{AR}$$

$$X_1 = \frac{100 \times 30}{100(1-0.3)} = 0.428 \left(\frac{\text{kg water}}{\text{kg dry solid}} \right)$$

For w_2

$$\frac{m_w}{(100)(1-0.3) + m_w} = 0.20, \quad m_w = 17.5$$

$$X_2 = \frac{m_w}{100(1-0.3)} = 0.25$$

$$t_c = \frac{(0.428 - 0.25) \times 70}{0.03 \times 70 \times 0.001} = \underline{\underline{5952.38 \text{ (s)}}}$$

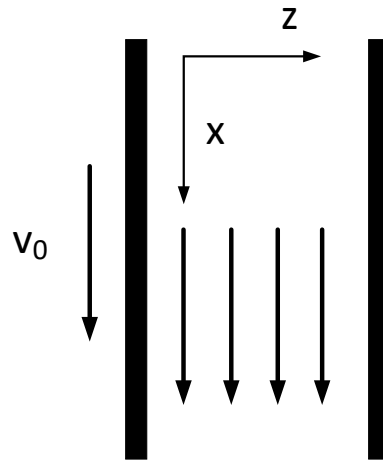
(本題可參考：Coulson, J.; Richardson, J.; Backhurst, J.; Harker, J. *Chemical Engineering*,

5th ed.; Volume 2, p 922, Example 16.4.)

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Problem 4

【Solution】



(a)

Assumptions :

- (1) incompressible/Newtonian
- (2) steady state
- (3) fully developed in x-direction
- (4) $v_x \neq f(y)$

By equation of continuity,

$$\cancel{\frac{\partial \rho}{\partial t}} + \frac{\partial(\rho v_x)}{\partial x} + \underbrace{\frac{\partial(\rho v_y)}{\partial y}}_{v_y=0} + \underbrace{\frac{\partial(\rho v_z)}{\partial z}}_{v_z=0} = 0$$

$$\frac{\partial(\rho v_x)}{\partial x} = 0, \quad v_x \neq f(x)$$

By the momentum balance in the control volume,

$$(\rho v_x v_x) dydz \Big|_x - (\rho v_x v_x) dydz \Big|_{x+dx} + \tau_{zx} dx dy \Big|_z - \tau_{zx} dx dy \Big|_{z+dz} + p dydz \Big|_x - p dydz \Big|_{x+dx} + \rho g dx dy dz = 0$$

同除 $dx dy dz \rightarrow 0$

$$\underbrace{\frac{-\partial(\rho v_x v_x)}{\partial x}}_{v_x \neq f(x)} - \frac{\partial \tau_{zx}}{\partial z} - \frac{\partial p}{\partial x} + \rho g = 0$$

$$\therefore \text{Newtonian, } \tau_{zx} = -\mu \frac{dv_x}{dz}$$

$$\mu \frac{d^2 v_x}{dz^2} - \frac{\partial p}{\partial x} + \rho g = 0$$

$$\therefore \frac{\partial p}{\partial x} \propto v_x \text{ with proportionality} = -1$$

$$\underline{\underline{\mu \frac{d^2 v_x}{dz^2} + v_x + \rho g = 0}}$$

(b)

$$\begin{cases} z=0, v_x = v_0 \\ z=B, v_x = 0 \end{cases}$$

(c)

$$\text{令 } v_x + \rho g = f$$

$$\mu \frac{d^2 f}{dz^2} + f = 0$$

$$f = c_1 \cos \frac{z}{\sqrt{\mu}} + c_2 \sin \frac{z}{\sqrt{\mu}} \begin{cases} z=0, f = v_0 + \rho g \\ z=B, f = \rho g \end{cases}$$

$$\begin{cases} c_1 = v_0 + \rho g \\ c_2 = \frac{\rho g - (v_0 + \rho g) \cos \frac{B}{\sqrt{\mu}}}{\sin \frac{B}{\sqrt{\mu}}} \end{cases}$$

$$\underline{\underline{v_x = f - \rho g = c_1 \cos \frac{z}{\sqrt{\mu}} + c_2 \sin \frac{z}{\sqrt{\mu}} - \rho g}}$$

(d)

$$\begin{aligned} \langle v_x \rangle &= \frac{\int_0^B \int_0^W v_x dy dz}{\int_0^B \int_0^W dy dz} = \frac{W[\sqrt{\mu}(c_1 \sin \frac{B}{\sqrt{\mu}} - c_2 \cos \frac{B}{\sqrt{\mu}}) - \rho g]}{BW} \\ &= \frac{\sqrt{\mu}}{B} (v_0 + \rho g) \sin \frac{B}{\sqrt{\mu}} - \frac{\sqrt{\mu}}{B} \left[\frac{\rho g - (v_0 + \rho g) \cos \frac{B}{\sqrt{\mu}}}{\sin \frac{B}{\sqrt{\mu}}} \right] \cos \frac{B}{\sqrt{\mu}} - \frac{\rho g}{B} \end{aligned}$$

(e)

@ $z = 0$

$$\tau_{zx} = -\mu \left. \frac{dv_x}{dz} \right|_{z=0} = \frac{c_1}{\sqrt{\mu}} = \frac{\rho g - (v_0 + \rho g) \cos \frac{B}{\sqrt{\mu}}}{\sqrt{\mu} \sin \frac{B}{\sqrt{\mu}}}$$

@ $z = B$

$$\tau_{zx} = -\mu \left. \frac{dv_x}{dz} \right|_{z=B} = \frac{-c_1}{\sqrt{\mu}} \sin \frac{B}{\sqrt{\mu}} + \frac{c_2}{\sqrt{\mu}} \cos \frac{B}{\sqrt{\mu}} = \frac{-(v_0 + \rho g)}{\sqrt{\mu}} \sin \frac{B}{\sqrt{\mu}} + \left[\frac{\rho g - (v_0 + \rho g) \cos \frac{B}{\sqrt{\mu}}}{\sqrt{\mu} \sin \frac{B}{\sqrt{\mu}}} \right] \cos \frac{B}{\sqrt{\mu}}$$

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Problem 5

【Solution】

$$\begin{array}{lll} D [=] L & d [=] L & \sigma [=] \frac{N}{m^2} [=] \frac{M}{T^2} \\ \rho [=] \frac{kg}{m^3} [=] \frac{M}{L^3} & \mu [=] \frac{kg}{m \cdot s} [=] \frac{M}{LT} & g [=] \frac{m}{s^2} [=] \frac{L}{T^2} \end{array}$$

Fundamental units : M, L, T

Total variable : $D, d, \rho, \sigma, \mu, g$

共可決定 $6-3=3$ 個無因次群，定義為 π_1, π_2, π_3

令 repeating unit 為 d, ρ, g

For π_1

$$\begin{aligned} \pi_1 &= D d^a \rho^b g^c \\ L \cdot L^a \cdot (ML^{-3})^b \cdot (LT^{-2})^c &= 1 \\ \begin{cases} L: 1+a-3b+c=0 \\ T: -2c=0 \\ M: b=0 \end{cases} &\Rightarrow \begin{cases} a=-1 \\ b=0 \\ c=0 \end{cases} \\ \pi_1 &= \frac{D}{d} \end{aligned}$$

For π_2

$$\begin{aligned} \pi_2 &= \sigma d^d \rho^e g^f \\ (MT^{-2}) \cdot L^d \cdot (ML^{-3})^e \cdot (LT^{-2})^f &= 1 \\ \begin{cases} L: d-3e+f=0 \\ T: -2-2f=0 \\ M: 1+e=0 \end{cases} &\Rightarrow \begin{cases} d=-2 \\ e=-1 \\ f=-1 \end{cases} \\ \pi_2 &= \frac{\sigma}{d^2 \rho g} \end{aligned}$$

For π_3

$$\pi_3 = m d^g \rho^h g^i$$

$$(ML^{-1}T^{-1}) \cdot L^g \cdot (ML^{-3})^h \cdot (LT^{-2})^i = 1$$

$$\begin{cases} L: -1 + g - 3h + i = 0 \\ T: -1 - 2i = 0 \\ M: 1 + h = 0 \end{cases} \Rightarrow \begin{cases} g = \frac{-3}{2} \\ h = -1 \\ i = -\frac{1}{2} \end{cases}$$

$$\pi_3 = \frac{\mu}{\underline{\underline{d^{\frac{3}{2}} \rho g^{\frac{1}{2}}}}}$$



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Problem 5

【Solution】

$$\tau = -\mu \frac{dv_x}{dr} = -\mu \left(\frac{-2v_{\max} r}{R^2} \right)$$

For the shear stress on the wall,

$$\tau \Big|_{r=R} = -\mu \left(\frac{-2v_{\max} r}{R^2} \right) \Big|_{r=R} = 0.01 \times \left(\frac{2 \times 1.2}{\frac{0.25}{2}} \right) = \underline{\underline{0.192 \text{ (g / cm} \cdot \text{s}^2)}}}$$

Problem 6

【Solution】

$$\frac{D_{KA-235}}{D_{KA-238}} = \frac{97.0r \sqrt{\frac{T}{M_{235}}}}{97.0r \sqrt{\frac{T}{M_{238}}}} = \sqrt{\frac{M_{238}}{M_{235}}} = \sqrt{\frac{352.038}{349.028}} = \underline{\underline{1.0043}}$$

Problem 7

【Solution】

(1)

By the definition of Reynolds number,

$$\text{Re} = \frac{\rho v D}{\mu} \propto D \quad (\text{管子前後總截面積不變, } v \text{ 不變})$$

$\therefore D \downarrow$

$\text{Re} \downarrow$, turbulent \rightarrow laminar

(2)

$$f \propto \frac{1}{\text{Re}}, \text{Re} \downarrow, f \uparrow$$

$$\Delta P \uparrow$$

Problem 8**【Solution】**

(A)

$$\Delta T_{lm} = \frac{(98.5 - 46.5) - (49.0 - 15.5)}{\ln\left(\frac{98.5 - 46.5}{49.0 - 15.5}\right)} = \underline{\underline{42.07^\circ\text{C}}}$$

For ΔT_m ,

$$\begin{cases} Y = \frac{46.5 - 15.5}{98.5 - 15.5} = 0.373 \\ Z = \frac{98.5 - 49.0}{46.5 - 15.5} = 1.60 \end{cases}, F_T = 0.82$$

$$\Delta T_m = 42.07 \times 0.82 = \underline{\underline{34.5^\circ\text{C}}}$$

(B)

By energy balance,

$$\dot{m}_c C_{pc} \Delta T_c = UA \Delta T_m$$

$$12.6 \times (46.5 - 15.5) \times 4180 = 3500A \times 34.5$$

$$\underline{\underline{A = 13.52 \text{ (m}^2\text{)}}}$$

Problem 9

【Solution】

By overall mole balance,

$$F = L + V$$

$$100 = 58 + L, \quad L = 42$$

By mole balance of A,

$$Fx_F = Vy_A + Lx_A$$

$$100 \times 0.55 = 58y_A + 42x_A$$

$$y_A = -0.724x_A + 0.948$$

$$\therefore \alpha_{AB} = \frac{\frac{y_A}{x_A}}{\left(\frac{1-y_A}{1-x_A}\right)} = 2.86$$

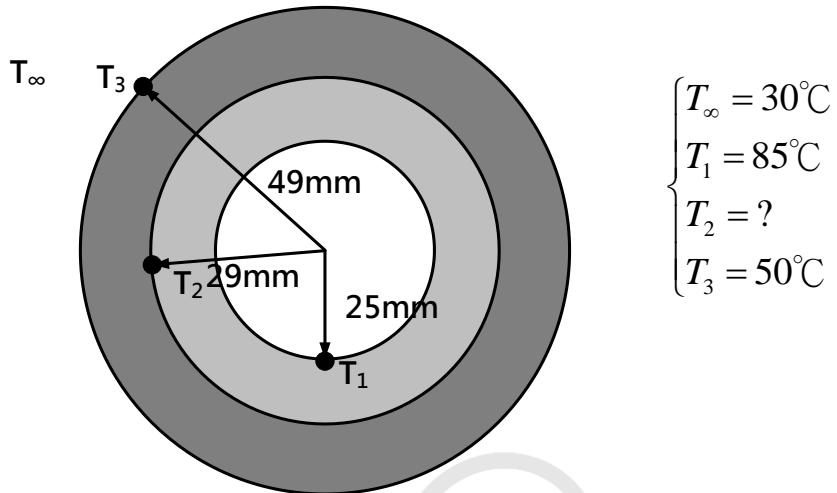
$$\frac{y_A}{x_A} = \frac{1-y_A}{1-x_A} \times 2.86, \text{ 代入}$$

$$\frac{-0.724x_A + 0.948}{x_A} = \frac{1 - (-0.724x_A + 0.948)}{(1-x_A)} \times 2.86 \rightarrow \begin{cases} x_A = 0.401 \\ y_A = 0.657 \end{cases}$$

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Problem 6

【Solution】



(a)

By Fourier's law,

$$q_k = -k(2\pi rL) \frac{dT}{dr} \neq f(r)$$

$$\int_{r_1}^{r_2} \frac{q_k}{r} dr = -2\pi kL \int_{T_1}^{T_2} dT$$

$$q_k = \frac{2\pi kL(T_1 - T_2)}{\ln \frac{r_2}{r_1}} = \frac{\Delta T}{R}$$

$$R = \frac{\ln(\frac{r_1}{r_2})}{2\pi kL} = \frac{\Delta r}{k(2\pi \Delta r L)} = \frac{\Delta r}{kA_{lm}}$$

$$\ln \frac{r_2}{r_1}$$

(b)

By Ohm's law,

$$q = \frac{T_1 - T_3}{\sum R} = \frac{T_1 - T_3}{\frac{1}{h_1(2\pi r_1 L)} + \frac{\ln \frac{r_2}{r_1}}{2\pi k_s L} + \frac{\ln \frac{r_3}{r_2}}{2\pi k_i L}}$$

For h_i

$$\because @ 85^\circ\text{C}, \nu = 0.344 \times 10^{-6} (\text{m}^2 / \text{s}), \text{Pr} = 2.08, k = 0.673$$

$$\text{Re} = \frac{vD}{\nu} = \frac{5 \times 50 \times 10^{-3}}{0.344 \times 10^{-6}} = 7.267 \times 10^5$$

$$\text{Nu} = \frac{hD}{k} = 0.027 \text{Re}^{0.8} \text{Pr}^{\frac{1}{3}} \left(\frac{\mu_b}{\mu_w} \right)^{\frac{1}{4}}$$

(The viscosity of hot water is not varied with temperature)

$$\frac{h \times 50 \times 10^{-3}}{0.673} = 0.027 \times (7.267 \times 10^5)^{0.8} \times 2.03^{\frac{1}{3}}$$

$$h = 22419.2 (\text{W} / \text{m}^2 \cdot \text{K})$$

代回

$$q = \frac{85 - 50}{\frac{1}{22419.2 \times (2\pi \times 25 \times 10^{-3})} + \frac{\ln \frac{25+4}{25}}{2\pi \times 45 \times 10} + \frac{\ln \frac{25+4+20}{25+4}}{2\pi \times 0.18 \times 10}} = \underline{\underline{753.35 \text{ (W)}}}$$

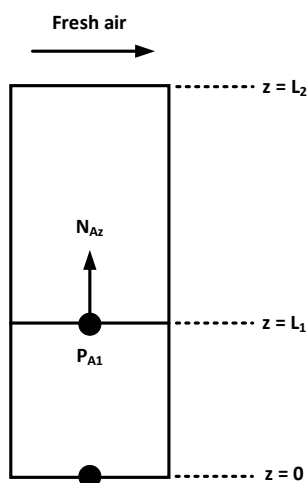
(c)

$$q = \frac{T_2 - T_3}{\frac{\ln \frac{49}{29}}{2\pi \times 0.18 \times 10}} = 753.35 = \frac{T_2 - 50}{\frac{\ln \frac{49}{29}}{2\pi \times 0.18 \times 10}}$$

$$\underline{\underline{T_2 = 84.94 (^\circ\text{C})}}$$

Problem 7

【Solution】



- Assume :
- (1) one-directional diffusion
 - (2) steady state
 - (3) $\begin{cases} A = H_2O \\ B = air \end{cases}$ and B is stagnant

By Fick's law,

$$N_{Az} = -cD_{AB} \frac{dy_A}{dz} + y_A (N_{Az} + \cancel{N_{Bz}}_{stagnant})$$

$$\int_{L_1}^{L_2} N_{Az} dz = -D_{AB} c \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1 - y_A}$$

$$N_{Az} = \frac{D_{AB} c}{L_2 - L_1} \ln \frac{1 - y_{A2}}{1 - y_{A1}} = \frac{D_{AB} P}{RT(L_2 - L_1)} \ln \frac{P - P_{A2}}{P - P_{A1}}$$

For P_{A2} ,

@ 20°C and dew point, by the humidity chart,

$$H = 0.015 \frac{kg H_2O}{kg air}$$

$$P_{A2} = \frac{\frac{0.015}{18}}{\frac{1}{28.8} + \frac{0.015}{18}} \times 1.013 \times 10^5 = 2374.22 (Pa)$$

將數據代回：

$$N_{Az} = \frac{2.5 \times 10^{-6} \times 1.013 \times 10^5}{8.314 \times 303.15 \times (3.0 - 1.5)} \ln \frac{1.013 \times 10^5 - 2374.22}{1.013 \times 10^5 - 4245} = 7.67 \times 10^{-7} \text{ (mol / m}^2 \cdot \text{s)}$$

$$w_{Az} = N_{Az} A = 7.67 \times 10^{-7} \times \frac{\pi}{4} \times 1^2 = \underline{\underline{6.027 \times 10^{-7} \text{ (mol / s)}}}$$

After 20 days,

by quasi-steady-state mole balance,

$$-N_{Az} A_z = \frac{d}{dt} \left(\frac{\rho A L_1}{M} \right) = \frac{\rho A}{M} \frac{d}{dt} (L_1 - L_2)$$

$$\frac{-D_{AB} P}{RT(L_2 - L_1)} \ln \frac{P - P_{A2}}{P - P_{A1}} = \frac{\rho A}{M} \frac{d}{dt} (L_1 - L_2)$$

$$\frac{D_{AB} P}{RT} \ln \frac{P - P_{A2}}{P - P_{A1}} \int_0^t dt = \frac{\rho A}{M} \int_{\Delta z_1}^{\Delta z_2} (L_2 - L_1) d(L_2 - L_1)$$

$$\frac{D_{AB} P}{RT} \ln \frac{P - P_{A2}}{P - P_{A1}} t = \frac{\rho A}{2M} (\Delta z_2^2 - \Delta z_1^2)$$

$$\frac{2.5 \times 10^{-6} \times 1.013 \times 10^5}{8.314 \times 303.15} \ln \frac{1.013 \times 10^5 - 2374.22}{1.013 \times 10^5 - 4245} \times 20 \times 86400 = \frac{1.0 \times 10^3 \times \frac{\pi}{4} \times 1^2}{2 \times 18 \times 10^{-3}} (\Delta z_2^2 - 2.5^2)$$

$$\Delta z_2^2 = 2.50003 \text{ (m)}$$

$$\text{Liquid level : } 3 - 2.50003 = \underline{\underline{0.49997 \text{ (m)}}}$$

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

Transfer, 5th ed.; p 448, Problem 26.3.)

Problem 8

【Solution】

By continuity equation,

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

$$\frac{\partial v_\theta}{\partial \theta} = 0 \rightarrow v_\theta = f(\cancel{t}, r, \cancel{\theta}, \cancel{z})$$

By N-S equation in cylinder coordinate,

r-direction,

$$-\rho \frac{v_\theta^2}{r} = \frac{-\partial p}{\partial r}, \quad p = p(r)$$

z-direction,

$$\frac{-\partial p}{\partial z} = 0, \quad p \neq p(z)$$

θ -direction,

$$\begin{aligned} \rho \left(\cancel{\frac{\partial v_\theta}{\partial t}} + \cancel{v_r \frac{\partial v_\theta}{\partial r}} + \cancel{\frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta}} + \cancel{\frac{v_r v_\theta}{r}} + \cancel{v_z \frac{\partial v_\theta}{\partial z}} \right) = \\ \cancel{\frac{-1}{r} \frac{\partial p}{\partial \theta}} + \mu \left[\cancel{\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r v_\theta) \right)} + \cancel{\frac{1}{r^2} \frac{\partial^2 v_\theta}{\partial r^2}} + \cancel{\frac{2}{r^2} \frac{\partial v_\theta}{\partial \theta}} + \cancel{\frac{\partial^2 v_\theta}{\partial z^2}} \right] + \cancel{\rho g_\theta} \\ \mu \left[\frac{\partial}{\partial r} \frac{1}{r} \frac{\partial}{\partial r} (r v_\theta) \right] = \frac{1}{r} \frac{\partial p}{\partial \theta} = f(r) \end{aligned}$$

$$p = r f(r) \theta + c$$

$$\because p(\theta) = p(\theta + 2\pi)$$

$$r f(r) \theta + c = r f(r) (\theta + 2\pi) + c$$

$$f(r) = 0$$

$$\boxed{\mu \left[\frac{\partial}{\partial r} \frac{1}{r} \frac{\partial}{\partial r} (r v_\theta) \right] = 0 \begin{cases} r = R_i, v_\theta = R_i \Omega \\ r = R_o, v_\theta = 0 \end{cases}}$$

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Problem 5

【Solution】

(a) temperature gradient

(b) conduction/convection/radiation

$$(c) Nu \equiv \frac{hL}{k} = \frac{\text{conductive thermal resistance}}{\text{convective thermal resistance}}$$

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

Problem 6

【Solution】

$$\therefore t^* = \frac{L\rho_b(W_{sat} - W_0)}{u_0 c_0} = \frac{L\rho_b W_{sat}}{u_0 c_0}$$

$$\begin{aligned} t_b &= t^* \left(1 - \frac{LUB}{L}\right) \\ &= \frac{L\rho_b W_{sat}}{u_0 c_0} \left(1 - \frac{LUB}{L}\right) \propto L \left(1 - \frac{LUB}{L}\right) \propto (L - LUB) \end{aligned}$$

$$\frac{t_{b1}}{t_{b2}} = \frac{3.8}{10} = \frac{14-4}{L_2-4}, \quad \underline{\underline{L_2 = 30.31 (m)}}$$

Problem 7

【Solution】

(a) (1) uniform surface

(2) monolayered-adsorption

(3) no interaction between adsorbed sites

(b)

$$q \equiv \frac{\text{heat needed to vaporize 1 mole of feed}}{\text{molar latent heat of the feed}}$$

(c)

$\therefore NH_3$ 在水中溶解度極大，因此液相所受之阻力較小，質傳由氣相控制

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Problem 6

【Solution】

(a)

$$\text{Assume only } \begin{cases} v = v_x(t, y) \\ T = T(t, y) \\ w = w_A(t, y), \text{ no reaction} \end{cases}$$

Momentum,

$$\frac{\partial v_x}{\partial t} = \frac{-1}{\rho} \frac{\partial p}{\partial x} + \nu \left[\frac{\partial^2 v_x}{\partial y^2} \right] + g_x$$

Heat,

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial y^2} + \frac{\mu}{\rho C_p} \left(\frac{\partial v_x}{\partial y} \right)^2$$

Mass,

$$\frac{\partial w_A}{\partial t} = D_{AB} \frac{\partial^2 w_A}{\partial y^2}$$

$\nu \text{ [=]} \alpha \text{ [=]} D_{AB} \text{ [=]} m^2 / s$

(b)

題目似乎有誤，應改為：

$$\nabla = \frac{\partial}{\partial r} \bar{\delta}_r + \frac{1}{r} \frac{\partial}{\partial \theta} \bar{\delta}_\theta + \frac{\partial}{\partial z} \bar{\delta}_z$$

$$\text{令 } \bar{v} = v_r(r, \theta) \bar{\delta}_r + v_\theta(r, \theta) \bar{\delta}_\theta$$

$$\because \text{incompressible flow}, \nabla \cdot \bar{v} = 0$$

$$\begin{aligned} \nabla \cdot \bar{v} &= \left(\frac{\partial}{\partial r} \bar{\delta}_r + \frac{1}{r} \frac{\partial}{\partial \theta} \bar{\delta}_\theta \right) \cdot (v_r \bar{\delta}_r + v_\theta \bar{\delta}_\theta) \\ &= \frac{\partial v_r}{\partial r} (\bar{\delta}_r \cdot \bar{\delta}_r) + \frac{v_r}{r} \frac{\partial \bar{\delta}_r}{\partial \theta} \cdot \bar{\delta}_\theta + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} (\bar{\delta}_\theta \cdot \bar{\delta}_\theta) + \frac{v_\theta}{r} \frac{\partial \bar{\delta}_\theta}{\partial \theta} \cdot \bar{\delta}_r \\ &= \frac{\partial v_r}{\partial r} + \frac{v_r}{r} + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} = 0 \end{aligned}$$

整理：

$$\frac{1}{r} \frac{\partial(rv_r)}{\partial r} + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} = 0, \quad \frac{\partial(rv_r)}{\partial r} + \frac{\partial v_\theta}{\partial \theta} = 0$$

令 $\psi = \psi(r, \theta)$ ，可知若

$$\begin{cases} v_r = \frac{-1}{r} \frac{\partial \psi}{\partial \theta} \\ v_\theta = \frac{\partial \psi}{\partial r} \end{cases}, \text{可使以上 continuity equation 滿足}$$

ψ 即為 stream function

Problem 7**【Solution】**

(a)

$$H \equiv \frac{\text{water vapor (kg)}}{\text{dry air (kg)}}$$

$$H_p = \frac{\text{actual humidity}}{\text{saturation humidity}} \times 100$$

$$H_R \equiv \frac{\text{actual partial pressure of water}}{\text{saturation pressure of water vapor}} \times 100$$

(b)

$$t = \frac{L_s}{AR_C} \Delta X = \frac{L_s (X_1 - X_2)}{AR_C}$$

For R_C ,

$$R_C = \frac{h}{\lambda_w} (T - T_w) \times 3600$$

For h ,

$$h = 0.0204 \times G^{0.8}$$

$$G = v_{air} \rho_{air} = \frac{v_{air}}{V_{air}}$$

$$\therefore \bar{V}_{air} (\text{specific volume}) @ 60^\circ\text{C} = 7.671 \text{ (m}^3 / \text{kg)}$$

$$G = \frac{3.05 \times 3600}{7.671} = 1431.36 \text{ (kg / m}^2 \cdot \text{h)}$$

$$h = 0.0204 \times (1431.36)^{0.8} = 6.827 \text{ (W / m}^2 \cdot \text{K)}$$

For $\lambda_w = \lambda_w (29.4^\circ\text{C})$

$$\lambda_w (27^\circ\text{C}) = 2550.18 - 113.25 = 2437.55 \text{ (kJ / kg)}$$

$$\lambda_w (30^\circ\text{C}) = 2556.3 - 123.79 = 2430.51 \text{ (kJ / kg)}$$

By 內插法

$$\frac{29.4-30}{27-30} = \frac{\lambda_w - 2430.51}{2437.55 - 2430.51} \quad , \quad \lambda_w = 2431.918 \text{ (kJ / kg)}$$

代回：

$$R_c = \frac{6.827}{2431.918 \times 10^3} (60 - 29.4) \times 3600 = 0.3092 \left(\frac{\text{kg} \cdot H_2O}{h \cdot m^2} \right)$$

再代回：

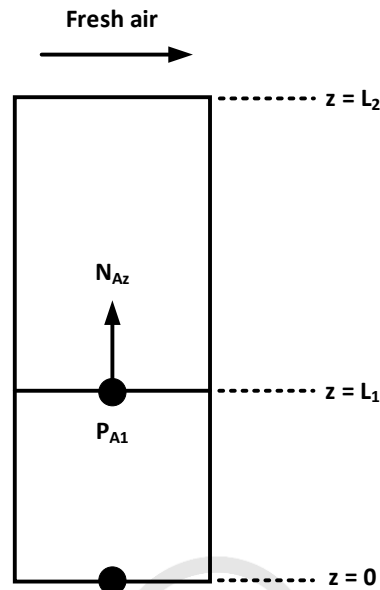
$$t = \frac{11.34 \times (0.35 - 0.22)}{0.61^2 \times 0.3092} = \underline{\underline{12.81 \text{ (hr)}}}$$



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Problem 7

【Solution】



- Assume :
- (1) one-directional diffusion
 - (2) steady state
 - (3) $\begin{cases} A = A \\ B = \text{air} \end{cases}$ and B is stagnant

By Fick's law,

$$N_{Az} = -cD_{AB} \frac{dy_A}{dz} + y_A(N_{Az} + \cancel{N_{Bz}}_{\text{stagnant}})$$

$$\int_{L_1}^{L_2} N_{Az} dz = -D_{AB} c \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1 - y_A}$$

$$N_{Az} = \frac{D_{AB} c}{L_2 - L_1} \ln \frac{1 - y_{A2}}{1 - y_{A1}} = \frac{D_{AB} P}{RT(L_2 - L_1)} \ln \frac{P - P_{A2}}{P - P_{A1}}$$

For P_{A2} ,

@ 0°C and dew point, by humidity the chart,

$$H = 0.005 \frac{\text{kg } H_2O}{\text{kg air}}$$

$$P_{A2} = \frac{\frac{0.005}{1} \times 18}{\frac{0.005}{28.8} + \frac{1}{18}} \times 755 = 5.992 \text{ (mmHg)}$$

by quasi-steady-state mole balance,

$$-N_{Az} A_z = \frac{d}{dt} \left(\frac{\rho A L_1}{M} \right) = \frac{\rho A}{M} \frac{d}{dt} (L_1 - L_2)$$

$$\frac{-D_{AB} P}{RT(L_2 - L_1)} \ln \frac{P - P_{A2}}{P - P_{A1}} = \frac{\rho A}{M} \frac{d}{dt} (L_1 - L_2)$$

$$\frac{D_{AB} P}{RT} \ln \frac{P - P_{A2}}{P - P_{A1}} \int_0^t dt = \frac{\rho A}{M} \int_{\Delta z_1}^{\Delta z_2} (L_2 - L_1) d(L_2 - L_1)$$

$$\frac{D_{AB} P}{RT} \ln \frac{P - P_{A2}}{P - P_{A1}} t = \frac{\rho A}{2M} (\Delta z_2^2 - \Delta z_1^2)$$

For Δz_2

$$\Delta z_2 = \Delta z_1 + \frac{\Delta V}{\Delta A} = 17.1 + \frac{0.0208}{0.82} = 17.134 \text{ (cm)}$$

$$\frac{D_{AB} \times \frac{755}{760} \times 1}{82.05 \times 273.15} \ln \frac{755 - 5.99}{755 - 33} \times 10 = \frac{1.59 \times 0.82}{2 \times 154} (17.134^2 - 17.1^2)$$

$$\underline{\underline{D_{AB} = 303.987 \text{ (cm}^2 \text{ / h)}}}$$

(本題與 108 年台科大單操輸送 Problem 7 相似)

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

Transfer, 5th ed.; p 448, Problem 26.3.)

111 年台科大單操輸送

Problem 6

【Solution】

(a)

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,

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

同除 $dr d\theta dz \rightarrow 0$,

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

$$\frac{\partial(r \tau_{rz})}{\partial r} = r \underbrace{\frac{d(p)}{dz}}_{\text{constant } A} = rA$$

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

$$\underline{\underline{-\mu \frac{d}{dr} \left[r \left(\frac{dv_z}{dr} \right) \right] = rA}}$$

(b)

由(a)小題推導之 governing equation 積分可得：

$$v_z = \frac{-r^2}{4\mu} A + C_1 \ln r + C_2 \begin{cases} r = \kappa R, v_z = 0 \\ r = R, v_z = 0 \end{cases} \begin{cases} C_1 = \frac{R^2(\kappa^2 - 1)A}{4\mu \ln \kappa} \\ C_2 = \frac{-R^2(\kappa^2 - 1)A}{4\mu \ln \kappa} \ln R + \frac{R^2 A}{4\mu} \end{cases}$$

$$\underline{\underline{\text{得： } v_z = \frac{R^2 A}{4\mu} \left(1 - \frac{r^2}{R^2} \right) + \frac{R^2(\kappa^2 - 1)A}{4\mu \ln \kappa} \ln \frac{r}{R}}}$$

Problem 7

【Solution】

(a) By mole balance of fragrance (A),

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

同除 $4\pi dr \rightarrow 0$

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

$$N_A'' = -D_{AB} \frac{P}{RT} \frac{dy_A}{dr} + y_A (N_A'' + \cancel{N_B''})$$

stagnant

$$\text{則 } N_A'' = -\frac{D_{AB}P}{RT} \cdot \frac{1}{1-y_A} \cdot \frac{dy_A}{dr}$$

代入：

$$\frac{d}{dr} \left[r^2 \frac{dy_A}{(1-y_A)dr} \right] = 0, \quad \frac{1}{1-y_A} \cdot \frac{dy_A}{dr} = \frac{C_1}{r^2}$$

$$\ln(1-y_A) = \frac{C_1}{r} + c_2 \begin{cases} r = r_1, y_A = y_{A0} \\ r \rightarrow \infty, y_A = 0 \end{cases}$$

則 $C_1 = r_1 \ln(1-y_{A0})$ 代回：

$$W_A \Big|_{r=r_1} = (4\pi r_1^2) \cdot N_A'' \Big|_{r=r_1} = (4\pi r_1^2) \cdot \left(-\frac{D_{AB}P}{RT} \cdot \frac{C_1}{r_1^2} \right) = -\frac{4\pi D_{AB}P r_1}{RT} \ln(1-y_{A0}) = -\frac{4\pi D_{AB}P r_1}{RT} \ln\left(\frac{P-P_{A0}}{P}\right)$$

$$W_A \Big|_{r=r_1} = -\frac{4\pi \times 6.92 \times 10^{-6} \times 1.013 \times 10^5 \times 1.0 \times 10^{-3}}{8.314 \times 318} \ln\left(\frac{1 - \frac{0.555}{760}}{1}\right) = \underline{\underline{2.43 \times 10^{-9} \text{ (mole / s)}}}$$

Problem 8

【Solution】

(a)

Assume the temperature distribution is linear in y direction, which is,

$$T(y) = (T_v - T_w) \frac{y}{\delta} + T_w$$

By energy balance on the film, (per unit length)

$$q_{conduction} = q_{condensation}$$

$$-k_f \cdot dx \cdot \frac{dT}{dy} \Big|_{y=0} = -h_v dm$$

For dm , by momentum balance in the film, (per unit length)

$$\tau_{yx} dx \Big|_{dy} - \tau_{yx} dx \Big|_{y+dy} + \rho_v g dx dy = 0$$

同除 $dx dy \rightarrow 0$

$$\frac{-d\tau_{yx}}{dy} + \rho_v g = 0$$

$\tau_{yx} = -\mu \frac{dv_x}{dy}$ 代入：

$$v_x = \frac{-\rho_v g}{2\mu} y^2 + C_1 y + C_2 \begin{cases} y=0, v_x=0 \\ y=\delta, \frac{dv_x}{dy}=0 \end{cases}$$
$$\begin{cases} C_1 = \frac{\rho_v g}{\mu} \delta, & v_x = \frac{\rho_v g}{\mu} (\delta y - \frac{y^2}{2}) \\ C_2 = 0 \end{cases}$$

$$m = \int_0^\delta \rho_v v_x dy = \frac{\rho_v^2 g \delta^3}{3\mu_v} \quad (\text{per unit length})$$

代回 energy balance 結果：

$$-k_f \cdot dx \cdot \left(\frac{T_v - T_w}{\delta} \right) = -h_v d \left(\frac{\rho_v^2 g \delta^3}{3\mu_v} \right) = \frac{h_v \rho_v^2 g \delta^2}{\mu_v} d\delta$$

$$k_f (T_v - T_w) \int_0^\delta dx = \frac{h_v \rho_v^2 g}{\mu_v} \int_0^\delta \delta^3 d\delta, \quad \delta = \underline{\underline{\left[\frac{4\mu_v k_f (T_v - T_w)}{h_v \rho_v^2 g} \right]^{1/4}}}$$

(b)

At $P = 68.9 \text{ kPa}$, the saturated temperature is,

$$\frac{T_v - 85}{90 - 85} = \frac{68.9 - 57.83}{70.14 - 57.83}, \quad T_v = 89.5^\circ\text{C} = 362.64 \text{ (K)}$$

For the viscosity, we use the average value between T_v and T_w

$$T = T_w, \quad \mu_w = 0.3310$$

$$T = T_v, \quad \mu_v = 0.3183$$

$$\mu_{avg} = \frac{0.3310 + 0.3183}{2} = 0.3247 \text{ (cp)}$$

For the specific gravity, we use the average value between T_v and T_w

$$T = T_w, \quad \rho_w = 967.8 \text{ (kg / m}^3\text{)}$$

$$T = T_v, \quad \rho_v = 985.6 \text{ (kg / m}^3\text{)}$$

(Specific volume 倒數)

$$\rho_{avg} = 976.7 \text{ (kg / m}^3\text{)}$$

For the thermal conductivity, we use the average value between T_v and T_w

$$T = T_w, \quad k_w = 0.673 \text{ (W / m} \cdot \text{K)}$$

$$T = T_v, \quad k_v = 0.676 \text{ (W / m} \cdot \text{K)}$$

$$k_{avg} = 0.674 \text{ (W / m} \cdot \text{K)}$$

For the latent heat, 由 $T = 89.5^\circ\text{C}$ 查表內插可知

$$h_v = 2651.1 - 353.8 = 2297.3 \text{ (kJ / kg)}$$

代回：

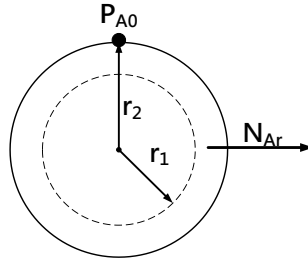
$$\delta = \left[\frac{4\mu_v k_f (T_v - T_w)}{h_v \rho_v^2 g} \right]^{1/4} = \left[\frac{4 \times 0.3247 \times 10^{-3} \times 0.674 \times (89.5 - 86.11)}{2297.3 \times 10^3 \times 976.7^2 \times 9.8} \right]^{1/4} = \underline{\underline{1.08 \times 10^{-4} \text{ (m)}}}$$

112 年台科大單操輸送

Problem 1

【Solution】

(a)



Assume,

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

- (1) The system is in pseudo-steady state.
- (2) Constant temperature and pressure.
- (3) $P_{A1} \ll 1 \text{ atm}$, the naphthalene is very dilute.
- (4) The partial pressure of naphthalene is negligible in the bulk.

By mole balance on the naphthalene sphere

$$r_{\text{evaporate}} = (4\pi r^2) N_{Ar} \Big|_{r=R(t)}$$

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

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

$$N_{Ar} = \frac{w_{Ar}}{4\pi r^2} = \frac{-\mathcal{D}_{AB} P}{RT} \frac{dy_{Ar}}{dr}, \quad \frac{w_{Ar}}{4\pi} \int_r^\infty \frac{dr}{r^2} = \frac{-\mathcal{D}_{AB} P}{RT} \int_{y_{A1}}^0 dy_{Ar}$$

$$w_{Ar} = N_{Ar} (4\pi r^2) = 4\pi r \frac{\mathcal{D}_{AB} P}{RT} (y_{A1} - 0) = 4\pi r \frac{\mathcal{D}_{AB} P_{A1}}{RT} \text{ 代回 :}$$

$$r_{\text{evaporate}} = 4\pi [R(t)] \frac{\mathcal{D}_{AB} P_{A1}}{RT} \text{ (kmol / s)} = \underline{\underline{4\pi [R(t)] \frac{\mathcal{D}_{AB} M P_{A1}}{RT} \text{ (kg / s)}}}$$

(b)

By the general equation of continuity,

$$\frac{\partial C_A}{\partial t} + \nabla \cdot (N_A) = \cancel{R_A}$$

$$\nabla \cdot (N_A) = 0$$

$$N_{Ar} = \frac{-\mathcal{D}_{AB} P}{RT} \frac{dy_{Ar}}{dr} \text{ 代入 :}$$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{-\mathcal{D}_{AB} P}{RT} \frac{dy_{Ar}}{dr} \right) = 0, \quad \frac{\partial}{\partial r} \left(r^2 \frac{dP_{Ar}}{dr} \right) = 0$$

$$P_{Ar} = \frac{c_1}{r} + c_2 \begin{cases} r = R(t), P_{Ar} = P_{A1} \\ r = \infty, P_{Ar} = 0 \end{cases}, \quad \underline{\underline{P_{Ar} = \frac{R(t)}{r} P_{A1}}}$$

(c)

By pseudo-steady state assumption on the naphthalene sphere,

$$-(4\pi r^2) N_{Ar} \Big|_{r=R(t)} = \frac{d\left(\frac{4}{3}\pi [R(t)]^3 \rho\right)}{dt} = 4\pi [R(t)]^2 \rho \frac{dR(t)}{dt}$$

$$4\pi [R(t)] \frac{\mathcal{D}_{AB} M P_{A1}}{RT} = -4\pi [R(t)]^2 \rho \frac{dR(t)}{dt}$$

$$\int_0^r dt = \frac{-RT \rho}{\mathcal{D}_{AB} M P_{A1}} \int_{r_1}^0 [R(t)] dR(t)$$

$$t = \frac{RT \rho}{2 \mathcal{D}_{AB} M P_{A1}} r_1^2 = \frac{8.314 \times (273.15 + 27) \times 1.14 \times 10^3}{2 \times 7 \times 10^{-6} \times 128 \times \frac{0.6}{760} \times 10^5} \times (2 \times 10^{-3})^2 = \underline{\underline{80.43 \text{ (s)}}}$$

Problem 2

【Solution】

(a) Correct

Backward-feed evaporator 是新鮮進料與加熱用蒸氣進料方向相反的一種蒸發設計，在蒸氣剛進入系統時，溫度較高，此時若濃產物黏度較高，就能夠有效降低其黏度，並且增加熱交換效率。

(本題可參考：Geankoplis, C. *Transport Processes and Separation Process Principles*, 4th ed.; p 533.)

(b) Correct

(本題可參考：Geankoplis, C. *Transport Processes and Separation Process Principles*, 4th ed.; p 565~566.)

(c) Correct

The bound moisture in the solid exerts a vapor pressure less than that of liquid water at the same temperature.

(本題可參考：Geankoplis, C. *Transport Processes and Separation Process Principles*, 4th ed.; p 575.)

(d) Incorrect

$$q = \frac{\text{heat needed to vaporize 1 mol of feed at entering conditions}}{\text{molar latent heat of vaporization of feed}}$$

(本題可參考：Geankoplis, C. *Transport Processes and Separation Process Principles*, 4th ed.; p 710.)

(e) Incorrect

Reflux can increase the purity of the overhead product, but may increase the cost of cooling water.

(f) Correct

(本題可參考：Geankoplis, C. *Transport Processes and Separation Process Principles*, 4th ed.; p 765.)

Problem 3

【Solution】

(a)

$$\underline{\underline{\tau_{rz} = -\mu \frac{dv_r}{dz}}}$$

(b)

Momentum Flux

(c)

In the same way,

$$v_r = \frac{1}{r} \frac{\partial \Psi}{\partial \theta} \quad , \quad v_\theta = -\frac{\partial \Psi}{\partial r}$$

(d)

To determine the height of the interface,

Assume :

(1) The flow is steady and fully developed in θ -direction

(2) $v_r = v_z = 0$.

(3) Incompressible Newtonian fluid.

By the equation of continuity,

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

$$\frac{\partial v_\theta}{\partial \theta} = 0 \quad , \quad v_\theta = f(\cancel{t}, r, \cancel{\theta}, \cancel{z}) = f(r) \text{ only}$$

By the Navier Stokes equation in θ direction,

$$\begin{aligned} & \rho \left(\cancel{\frac{\partial v_\theta}{\partial t}} + \cancel{v_r \frac{\partial v_\theta}{\partial r}} + \cancel{\frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta}} + \cancel{v_z \frac{\partial v_\theta}{\partial z}} + \cancel{\frac{v_\theta v_r}{r}} \right) \\ &= \cancel{\frac{-1}{r} \frac{\partial p}{\partial \theta}} + \mu \left[\cancel{\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r v_\theta) \right)} + \cancel{\frac{1}{r^2} \frac{\partial^2 v_\theta}{\partial \theta^2}} + \cancel{\frac{\partial^2 v_\theta}{\partial z^2}} + \cancel{\frac{2}{r^2} \frac{\partial v_r}{\partial \theta}} \right] + \cancel{\rho g_\theta} \end{aligned}$$

$$\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (rv_\theta) \right) = 0, \quad v_\theta = \frac{c_1}{2} r + \frac{c_2}{r} \begin{cases} r=0, v_\theta=0 \\ r=R, v_\theta=\omega R \end{cases}$$

$$c_1 = 2\omega, \quad c_2 = 0$$

$$v_\theta = \omega r$$

To determine the height of the interface, by Navier-Stokes equation with r and z components,

$$\begin{aligned} \frac{-\partial p}{\partial r} &= \frac{-\rho v_\theta^2}{r} \\ \frac{-\partial p}{\partial z} &= -\rho(-g_z) \end{aligned}$$

Integrate the z-direction,

$$p = -\rho g_z z + f(r)$$

代回 r 方向，

$$\frac{\partial p}{\partial r} = f'(r) = \frac{\rho v_\theta^2}{r} = \frac{\rho [\omega r]^2}{r} = \rho \omega^2 r$$

Integrate with r,

$$f = \frac{\rho \omega^2 r^2}{2} + C$$

And the pressure distribution becomes,

$$p(r, z) = -\rho g_z z + \frac{\rho \omega^2 r^2}{2} + C$$

Because the liquid is open to the atmosphere at the top,

$$p(r, h(r)) = p(R, h(R)) = P_0, \quad p(r, h(r)) = p(R, h(R))$$

$$-\rho g_z h(r) + \frac{\rho \omega^2 r^2}{2} + C = -\rho g_z h(R) + \frac{\rho \omega^2 R^2}{2} + C$$

$$-\rho g_z (h - h(R)) = \frac{\rho \omega^2 R^2}{2} \left[1 - \left(\frac{r}{R} \right)^2 \right]$$

$$h(r) = \frac{\omega^2 R^2}{2g_z} \left[\left(\frac{r}{R} \right)^2 - 1 \right] + h(R)$$

∴ The total volume is V_0

$$V_0 = \int_0^R 2\pi r[h(r)]dr = \frac{\pi\omega^2 R^2}{g_z} \int_0^R r\left[\left(\frac{r}{R}\right)^2 - 1\right] + h(R)dr$$

$$V_0 = \frac{\pi\omega^2 R^2}{g_z} \left(-\frac{1}{4R^2}\right) + R \cdot h(R)$$

$$h(R) = \frac{V_0 + \frac{\pi\omega^2}{4g_z}}{R}$$

代入：

$$\underline{\underline{h(r) = \frac{\omega^2 R^2}{2g_z} \left[\left(\frac{r}{R}\right)^2 - 1\right] + \frac{V_0 + \frac{\pi\omega^2}{4g_z}}{R}}}$$

(本題改編自：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 110, Problem 3B.15.)

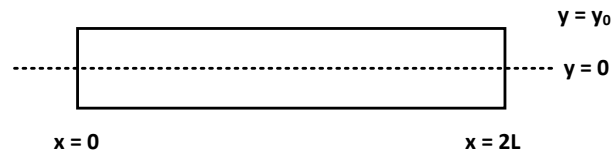
Problem 4

【Solution】

(a)

The positive sign is used to ensure the heat flux is in the same direction with the temperature gradient.

(b)



By the general energy equation, assume steady state

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0$$

$$\begin{cases} x=0, T=T_b \\ x=2L, T=T_a \\ y=0, \frac{\partial T}{\partial y} = 0 \text{ (symmetry)} \\ y=y_0, -k \frac{\partial T}{\partial y} = h(T-T_\infty) \end{cases}$$

Let,

$$\theta = \frac{T - T_b}{T_\infty - T_b}$$

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} = 0 \quad \begin{cases} x=0, \theta=0 \\ x=2L, \theta=\theta_a \\ y=0, \frac{\partial \theta}{\partial y} = 0 \\ y=y_0, -k \frac{\partial \theta}{\partial y} = h\theta \end{cases}$$

By separation of variable, let

$$\theta(x, y) = X(x)Y(y)$$

$$\frac{1}{X} \frac{d^2 X}{dx^2} = \frac{-1}{Y} \frac{d^2 Y}{dy^2} = \lambda^2$$

For $Y(y)$,

$$Y(y) = A \cos(\lambda y) + B \sin(\lambda y) \begin{cases} y = 0, \frac{dY}{dy} = 0 & \text{--- (1)} \\ y = y_0, \frac{dY}{dy} = \frac{hY}{-k} & \text{--- (2)} \end{cases}$$

By B.C. (1)

$$-A\lambda \sin(0) + B\lambda \cos(0) = 0, \quad \boxed{B = 0}$$

By B.C. (2)

$$\begin{aligned} -A\lambda \sin(\lambda y_0) &= \frac{-h}{k} [A \cos(\lambda y_0)] \\ \lambda &= \frac{h \cos(\lambda y_0)}{k \sin(\lambda y_0)} \end{aligned}$$

Let $\lambda = \beta_n$

$$\beta_n = \frac{h \cos(\beta_n y_0)}{k \sin(\beta_n y_0)}$$

$$Y(y) = A \cos(\beta_n y)$$

For $X(x)$,

$$X(x) = C \sinh(\beta_n x) + D \cosh(\beta_n x) \begin{cases} x = 0, X = 0 & \text{--- (3)} \\ y = 2L, X = \theta_a & \text{--- (4)} \end{cases}$$

By B.C. (3)

$$C \sinh(0) + D \cosh(0) = 0, \quad \boxed{D = 0}$$

$$\theta(x, y) = C \sinh(\beta_n x) \cdot A \cos(\beta_n y) = \alpha_n \sinh(\beta_n x) \cos(\beta_n y)$$

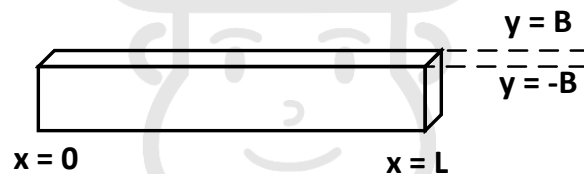
By B.C. (4)

$$\theta_a = \alpha_n \sinh(2L\beta_n) \cos(\beta_n y)$$

$$\alpha_n = \frac{\int_0^{y_0} \theta_a \cos(\beta_n y) dy}{\int_0^{y_0} \cos^2(\beta_n y) dy}$$

$$\theta(x, y) = \sum_{n=1}^{\infty} \alpha_n \sinh(\beta_n x) \cos(\beta_n y), \quad \alpha_n = \frac{\int_0^{y_0} \theta_a \cos(\beta_n y) dy}{\int_0^{y_0} \cos^2(\beta_n y) dy}$$

※本題不需也不能將對流項如同一般 fin 題型一樣，納入微分方程式裡。因在所有熱傳問題中，對流項都應該擺在邊界條件，除非取的 control volume 能夠納入對流的影響，如大部分的 fin 解溫度分布問題。然而，在一般 fin 問題的簡化上，是假設 fin 溫度分布只與 x 方向有關(可參考 BSL 第二版 p.308 上方表格，有所有 fin 問題簡化的條件)，因此假設同樣以二維方程式，且對流項置於邊界條件時：



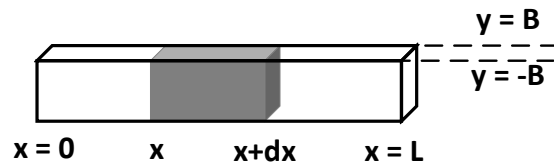
$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0 \quad \left\{ \begin{array}{l} y = -B, \quad \underbrace{-k \frac{\partial T}{\partial y} = -h(T - T_{\infty})}_{\text{fin 溫度高，向 -y 方向傳熱，因此 } h \text{ 前面有負號}} \\ y = B, \quad -k \frac{\partial T}{\partial y} = h(T - T_{\infty}) \end{array} \right.$$

$$\frac{\partial^2}{\partial x^2} \underbrace{\left[\int_{-B}^B T dy \right]}_{T \neq T(y)} + \int_{-B}^B \frac{\partial^2 T}{\partial y^2} dy = 0, \quad \frac{\partial^2}{\partial x^2} (2BT) + \frac{\partial T}{\partial y} \bigg|_{-B}^B = 0$$

$$(2B) \frac{\partial^2 T}{\partial x^2} - \frac{2h(T - T_{\infty})}{k} = 0$$

$$\boxed{\frac{\partial^2 T}{\partial x^2} - \frac{h(T - T_{\infty})}{kB} = 0}$$

此形式剛好與直接使用 control volume 做熱量平衡結果相同，如：



By energy balance,

$$(2WB)q_x|_x - (2WB)q_x|_{x+dx} - 2h(Wdx)(T - T_\infty) = 0$$

同除 $2BWdx \rightarrow 0$

$$\frac{-dq_x}{dx} - \frac{h}{B}(T - T_\infty) = 0$$

$$\because q_x = -k \frac{\partial T}{\partial x}$$

$$k \frac{d^2 T}{dx^2} - \frac{h}{B}(T - T_\infty) = 0$$

$$\boxed{\frac{d^2 T}{dx^2} - \frac{h}{kB}(T - T_\infty) = 0}$$

然而，此方法必須建立在 $T = T(x)$ ，與 y 方向無關的前提下，才可做使用。

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104 年台科大化熱化反

Part I. 化工熱力學

Problem 1

【Solution】

(a)

(1) **Shaft work** : the mechanical energy flow that occurs without a deformation of the system boundaries. For example, the work done by turbine or engine.

(2) **Boundary work** : the work resulting from the movement of the system boundaries.

(3) **Pressure work** : work arising from the fact that as an element moves, it does work on the fluid ahead of it and the fluid behind it.

(b)

Because when the two fluids are mixed, there may be additional interactions on the solvent-solute system which cause the system to behave non-ideally.

(c)

A molecule can be considered to be a collection of functional groups, and the volume R_i and surface area Q_i of functional group i will be approximately the same in any molecule in which that group occurs.

一個化合物可以視為其擁有的官能基加總而成的物質，而 activity 也可以此算出

The advantage is that from a relatively small number of functional groups, the properties of the millions upon millions of different molecules can be determined.

好處是只要知道官能基與 activity 的關係，就可以利用少量的資料去推估好幾千萬種分子的性質

However, each group may be affected by its neighboring groups, but the model doesn't account for it.

然而不同分子雖然可能有相同的官能基團，但分子分子間具有的作用力大小與類別可能有所不同，這是此模型會有的限制以及誤差來源



Problem 2

【Solution】

$$M_{\text{loading},1} = M_i - M_f = \rho_i V_i - \rho_f V_f = 0.81721 \times 100 - 0.87619 \times 92.25 = 0.8924 \text{ (g)}$$

$$M_{\text{loading},2} = M_i - M_f = \rho_i V_i - \rho_f V_f = 0.87619 \times 92.25 - 0.81721 \times 83.79 = 12.35 \text{ (g)}$$

$$M_{\text{loading},3} = M_i - M_f = \rho_i V_i - \rho_f V_f = 0.81721 \times 83.79 - 0.94278 \times 72.40 = 0.2167 \text{ (g)}$$

$$M_{\text{loading},4} = M_i - M_f = \rho_i V_i - \rho_f V_f = 0.94278 \times 72.40 - 0.81721 \times 65.50 = 14.73 \text{ (g)}$$

The total mass loaded will be,

$$M_{\text{total}} = 0.8924 + 12.35 + 0.2167 + 14.73 = \underline{\underline{28.194 \text{ (g)}}}$$

Problem 3

【Solution】

(a)

\therefore isentropic,

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

$$(0.5 \text{ MPa, saturated}) = 6.8213 \text{ (kJ / kg} \cdot \text{K)}$$

$$\hat{S}_{out}^V(2.0 \text{ MPa}) = 6.8213 \text{ (kJ / kg} \cdot \text{K)}$$

查 superheated vapor table, 內插

$$\frac{T - 300}{350 - 300} = \frac{6.8213 - 6.7664}{6.9563 - 6.7664}, \quad T = \underline{\underline{341.45 \text{ (}^\circ\text{C)}}}$$

(b)

For ideal case,

By energy balance (open system, steady state),

$$\Delta \hat{H} + \underbrace{\Delta \left(\frac{v^2}{2g_c} + \frac{g}{g_c} \Delta z \right)}_{\text{negligible}} = \underbrace{\cancel{\dot{Q}}}_{\text{insulated}} + W$$

$$W = \hat{H}_{out} - \hat{H}_{in}$$

$$\hat{H}_{out}^V (0.5 \text{ MPa, saturated}) = 2748.7 \text{ (kJ / kg)}$$

For $\hat{H}_{out}^V (2.0 \text{ MPa, } T = 341.45^\circ\text{C})$:

查 superheated vapor table 並查表可得

$$\frac{314.45 - 300}{350 - 300} = \frac{\hat{H}_{in}^V - 3023.5}{3137 - 3023.5}$$

$$\hat{H}_{in}^V = 3056.3 \text{ (kJ / kg)} \text{ 代回}$$

$$\begin{aligned} \dot{W}_{actual} &= 0.6 \dot{W}_{ideal} = 0.6 \dot{W}_{ideal} \dot{M} \\ &= 0.6 \times \frac{5000}{3600} \times (2748.7 - 3056.3) \\ &= -256.34 \text{ (kJ / s)} = \underline{\underline{-256.34 \text{ (kW)}}} \end{aligned}$$

(c)

By entropy balance,

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

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

$$\hat{S}_{in}^V = 6.8213 \text{ (kJ / kg} \cdot \text{K)}$$

For \hat{S}_{out}^V , by energy balance,

$$W = \hat{H}_{out} - \hat{H}_{in}$$

$$\frac{-256.34}{\frac{5000}{3600}} = \hat{H}_{out} - 3056.3, \quad \hat{H}_{out} = 2871.71 \text{ (kJ / kg)}$$

查 superheated vapor table 並內插可得

$$\frac{2871.74 - 2855.4}{2960.7 - 2855.4} = \frac{\hat{S}_{out}^V - 7.0592}{7.2709 - 7.0592}$$

$$\hat{S}_{out}^V = 7.092 \text{ (kJ / kg} \cdot \text{K)}$$

$$\dot{S}_{gen} = \dot{M}(\hat{S}_{out} - \hat{S}_{in}) = 5000(7.092 - 6.8213) = \underline{\underline{1353 \text{ (kJ / K} \cdot \text{h)}}}$$

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

p 150, Problem 4.40.)

化工製造所

Part II. 化工動力學

Problem 1

【Solution】

(a) For CSTR, design equation,

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

Rate equation,

$$-r_A = kC_A = kC_{A0} \frac{(1-x_A)}{(1+\varepsilon x_A)} \quad \left(\frac{P}{P_0}\right) \quad \left(\frac{T_0}{T}\right)$$

no pressure drop $P=P_0$ isothermal

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

Combine,

$$V = \frac{F_{A0}x_A}{kC_{A0} \frac{(1-x_A)}{(1+x_A)}} = \frac{2.5 \times 0.9}{0.044 \times \frac{10}{0.082 \times 400} \times \frac{1-0.9}{1+0.9}} = \underline{\underline{3186.82 \text{ (L)}}}$$

(b) For PFR,

$$V = \int_0^{x_A} \frac{F_{A0}}{-r_A} dx_A = \int_0^{0.9} \frac{2.5}{0.044 \times \frac{10}{0.082 \times 400} \frac{(1-x_A)}{(1+x_A)}} dx_A = \underline{\underline{690.51 \text{ (L)}}}$$

(c)

$$K_e = \frac{C_{Be} C_{Ce}}{C_{Ae}} = \frac{(C_{A0} \frac{x_{Ae}}{1+x_{Ae}})^2}{C_{A0} \frac{1-x_{Ae}}{1+x_{Ae}}} = \frac{C_{A0}}{(1+x_{Ae})} \frac{x_{Ae}^2}{(1-x_{Ae})}$$

$$0.11 = \frac{10}{0.082 \times 400} \frac{x_{Ae}^2}{(1+x_{Ae})(1-x_{Ae})}$$

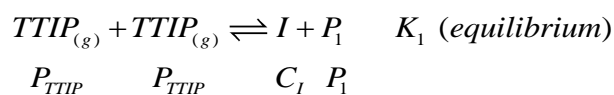
$$\underline{\underline{x_{Ae} = 0.515}}$$

Problem 2

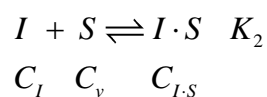
【Solution】

(a)

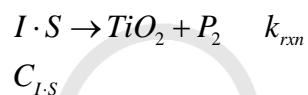
First-step reaction :



Adsorption of I :



Surface reaction :



\therefore 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,

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

代回

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

(b)

(1) With low P_{TTIP} ,

$$P_1 \gg K_1 K_2 P_{TTIP}^2$$

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

(2) With high P_{TTIP} ,

$$P_1 \ll K_1 K_2 P_{TTIP}^2$$

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

(3) @300°C

If K_2 is very small,

$$P_1 \gg K_1 K_2 P_{TTIP}^2$$

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

(Second-order over the entire pressure range)

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

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

Problem 3

【Solution】

(a)

By the combination of design equation and rate equation,

$$V = \frac{F_{A0}x_A}{-r_A} = \frac{F_B}{r_B} = \frac{F_C}{r_C}$$
$$= \frac{F_{A0}x_A}{k_1 C_A \left(\frac{T_0}{T}\right)} = \frac{F_B}{[k_1 C_A - k_2 C_B] \left(\frac{T_0}{T}\right)} = \frac{F_C}{k_2 C_B \left(\frac{T_0}{T}\right)}$$

∵ All the reactions take place in the same reactor,

$$\frac{F_{A0}x_A}{k_1 C_A} = \frac{F_C}{k_2 C_B}, \quad \frac{\cancel{F_{A0}} x_A}{\cancel{k_1} \cancel{F_{A0}} (1-x_A)} = \frac{\frac{1}{10} \cancel{F_{A0}} x_A}{\frac{10}{10+1} \cancel{k_2} \cancel{F_{A0}} x_A}$$
$$\frac{0.5}{2 \times 10^9 \exp\left[\frac{-31000}{1.986} \cdot \frac{1}{T}\right] \times (1-0.5)} = \frac{\frac{1}{11} \times 0.5}{1 \times 10^{11} \exp\left[\frac{-40000}{1.986} \cdot \frac{1}{T}\right] \times \frac{10}{11} \times (1-0.5)}$$
$$\underline{\underline{T = 729.2 \text{ (R)} = 262.9 \text{ (}^\circ\text{F)}}}$$

(b)

結果代回：

$$V = \frac{F_{A0}x_A}{k_1 C_{A0}(1-x_A)} = \frac{7.85 \times 0.5}{2 \times 10^9 \exp\left[\frac{-31000}{1.986} \times \frac{1}{729.2}\right] (1-0.5) \left(\frac{400+460}{729.2}\right)} = \underline{\underline{6.586 \text{ (ft}^2\text{)}}}$$

(c)

By energy balance,

$$\dot{Q} - \dot{W}_s - \sum_i F_{A0} \theta_i C_{pi} (T - T_{i0}) - \Delta H_{Rx1}(T) F_{A0} x_A - \Delta H_{Rx2} F_C = 0$$

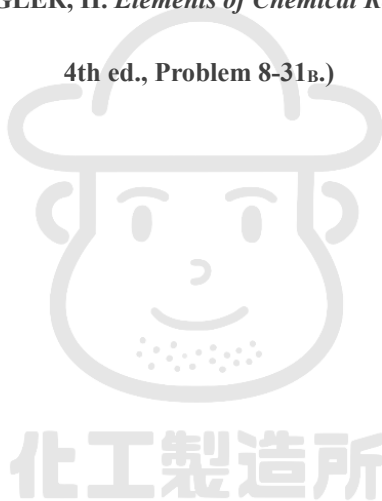
$$UA(T_a - T) - F_{A0} C_{pA} (T - T_{i0}) - \underbrace{\Delta H_{Rx1}^\circ F_{A0} x_A}_{\Delta C_p = 0} - \underbrace{\Delta H_{Rx2}^\circ F_C}_{\Delta C_p = 0} = 0$$

$$\frac{400}{3600} A (350 - 269.2) - 0.05 \times 25 (269.2 - 400) - 15000 \times 0.05 \times 0.5 - 20000 \times 0.05 \times 0.5 \times \frac{1}{11} = 0$$

$$\underline{\underline{A = 28.623 \text{ (ft}^2\text{)}}}$$

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

4th ed., Problem 8-31B.)



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Part I. 化工熱力學

Problem 1

【Solution】

(a)

The first law of thermodynamics is equivalent to “energy balance”.

For a closed system,

$$\Delta U = Q + W$$

The second law of thermodynamics has one axiom, which is that the entropy generation of a system must be positive, that is,

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

There are two statements about the second law,

Clausius Statement of the Second Law:

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.

Kelvin-Planck Statement of the Second Law:

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.

(本題可參考：Sandler, S. Chemical, Biochemical and Engineering Thermodynamics, 5th ed.; p 105~107.)

(b)

The term TS_{gen} represents the additional work needed or the less work able to deliver compared to the reversible process when the process is irreversible.

(c)

The term C.O.P. is defined as,

$$C.O.P. \equiv \frac{\text{heat removed from low-temperature region}}{\text{net work required for heat removal}}$$

(d)

$$f = P \exp\left[\frac{G(T, P) - G^{IG}(T, P)}{RT}\right] = \underline{\underline{P \exp\left[-\frac{1}{RT} \int_0^P \left(\underline{V} - \frac{RT}{P}\right) dP\right]}}$$

(e)

Two fluids that have the same values of reduced temperature and pressure and therefore the same reduced volume will have the same compressibility factor, so they will deviate from ideal gas behavior about the same degree.

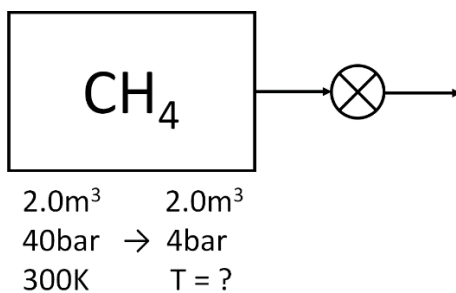
(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*,

5th ed.; p 253.)



Problem 2

【Solution】



(a)

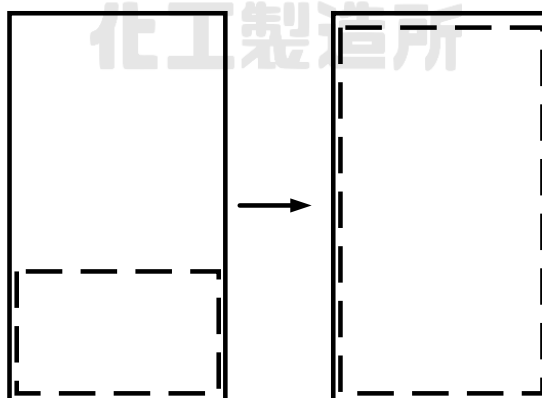
In order to assume the exhaustion process as a reversible one, we have the assumptions that,

- (1) The exhaustion process is taken slowly
- (2) There is no friction during the process

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 141, Problem 4.12.)

(b)

Consider the portion of gas left in the tank after the exhaustion,



By entropy balance,

$$\Delta S = \sum_{\text{closed}} \cancel{M_k S_k} + \cancel{\frac{Q}{T}}_{\text{adiabatic}} + \cancel{S_{\text{gen}}}_{\text{reversible}} = 0$$

For isentropic ($\Delta S = 0$) processes of ideal gas,

$$\left(\frac{T_f}{T_i}\right)^{\frac{C_p^*}{R}} = \left(\frac{P_f}{P_i}\right), \quad \left(\frac{T_f}{300}\right)^{\frac{36}{8.314}} = \frac{4}{40}$$

$$T_f = 176.26(K)$$

$$n_{left} = \left(\frac{PV_i}{RT_i} - \frac{PV_f}{RT_f}\right) = \underline{\underline{2661.55 \text{ (mol)}}}$$

(c)

For isentropic processes of real gas,

$$\hat{S}_i^V = \hat{S}_f^V$$

By the phase diagram,

$$\hat{S}_i^V(4MPa, 300K) = 5.4 \text{ (kJ / kg} \cdot K\text{)}$$

$$\hat{V}_i^V(4MPa, 300K) = 0.04 \text{ (m}^3 \text{ / kg)}$$

$$\hat{S}_f^V(0.4MPa, T) = 5.4 \text{ (kJ / kg} \cdot K\text{)}$$

$$\hat{V}_i^V = 0.22 \text{ (m}^3 \text{ / kg)}$$

$$n_{left} = \left(\frac{2}{\hat{V}_i^V} - \frac{2}{\hat{V}_f^V}\right) \times \frac{1000}{16} = \underline{\underline{2556.82 \text{ (mol)}}}$$

Problem 3

【Solution】

(a)

By energy balance (unsteady, open system),

$$\left(\underline{H} + \frac{v^2}{2g_c} + \frac{g}{g_c}z\right)_{in} \dot{n}_{in} - \left(\underline{H} + \frac{v^2}{2g_c} + \frac{g}{g_c}z\right)_{out} \dot{n}_{out} + d\dot{Q} + d\dot{W} = \frac{d}{dt} \left[n \left(\underline{U} + \frac{v^2}{2g_c} + \frac{g}{g_c}z \right) \right]_{sys}$$

If there is no heating source,

$$-\underline{H}_{out} \dot{n}_{out} + \frac{d}{dt} (n\underline{U})_{sys} = -\dot{n}_{out} \underline{U}_{out}$$
$$\therefore \frac{d}{dt} (n\underline{U})_{sys} < 0$$

For ideal gas,

$$\frac{dT_{sys}}{dt} < 0$$

The room will become cooler

(b)

By the energy balance,

$$-\underline{H}_{out} \dot{n}_{out} + \dot{Q} = \frac{d}{dt} (n\underline{U})_{sys} = -\dot{n}_{out} \underline{U}_{out}$$

$$\dot{n}_{out} (\underline{H}_{out} - \underline{U}_{out}) + \dot{Q} = \dot{n}_{out} [R(T_{out} - 0)]$$

$$\dot{Q} = \dot{n}_{out} [8.314 \times (274 + 273)] = 10 \times 10^3$$

$$\underline{\underline{\dot{n}_{out} = 4.01 \text{ (mol / s)}}}$$

(c)

$$\Delta n = \left(\frac{P_i V_i}{RT_i} \right) - \left(\frac{P_f V_f}{RT_f} \right) = \frac{10}{8.314 \times (27 + 273.15)} (2.5 - 1.0) \times 10^5$$
$$= 601.09 \text{ (mol)}$$

$$t = \frac{\Delta n}{\dot{n}} = \frac{601.09}{4.01} = \underline{\underline{149.92 \text{ (s)}}}$$

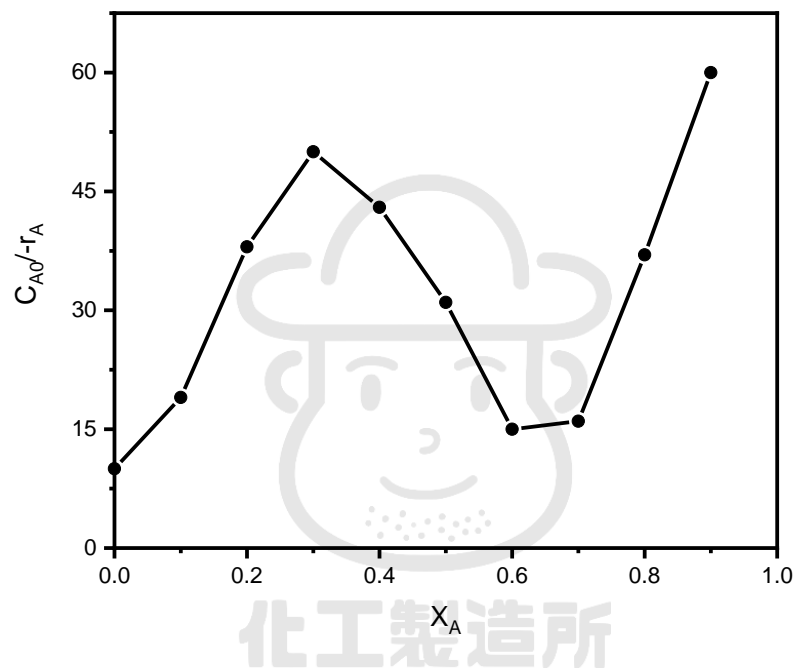
Part II. 化工動力學

Problem 4

【Solution】

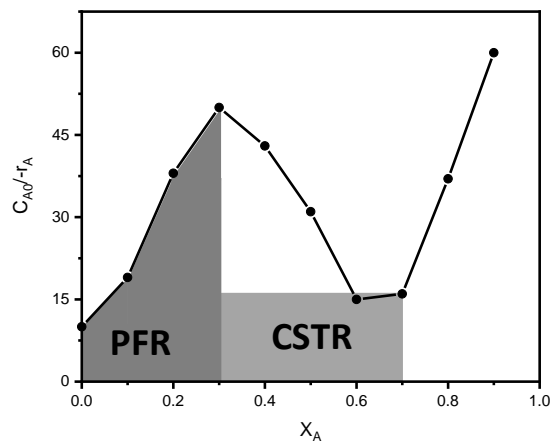
(a)

將 $\frac{C_{A0}}{-r_A} - x_A$ 關係畫圖：



由 $\frac{C_{A0}}{-r_A} - x_A$ 圖呈現先上後下趨勢判斷

應先使用 PFR 後接 CSTR



For total volume,

For PFR,

$$\begin{aligned}
 V_{PFR} &= \int_0^{0.3} \frac{F_{A0}}{-r_A} dx_A = v_0 \int_0^{0.3} \frac{C_{A0}}{-r_A} dx_A \\
 &= 50 \times \frac{0.3 - 0}{3} [f(0) + 4f(0.15) + f(0.3)] \\
 &= 50 \times 0.05 \left[10 + 4 \times \frac{50 + 10}{2} + 50 \right] = 450 (L)
 \end{aligned}$$

For CSTR,

$$\begin{aligned}
 V &= \frac{F_{A0} x_A}{-r_A} = v_0 \frac{C_{A0}}{-r_A} \bigg|_{x_A=0.7} (0.7 - 0.3) \\
 &= 50 \times 16 \times 0.4 = 320 \\
 \underline{\underline{V_{total} = 450 + 320 = 770 (L)}}
 \end{aligned}$$

(c)

應改為兩個 CSTR 做串聯

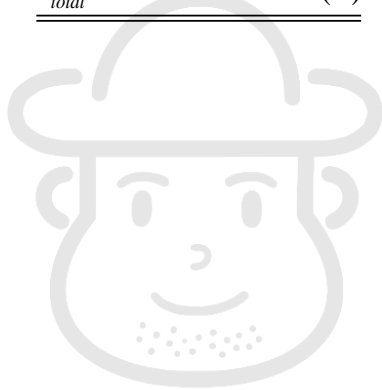
For 1st CSTR,

$$V = \frac{F_{A0}x_A}{-r_A} = v_0 \left. \frac{C_{A0}}{-r_A} \right|_{x_A=0.6} \times 0.6$$
$$= 50 \times 15 \times 0.6 = 450$$

For 2nd CSTR,

$$V = \frac{F_{A0}x_A}{-r_A} = v_0 \left. \frac{C_{A0}}{-r_A} \right|_{x_A=0.7} \times (0.7 - 0.6)$$
$$= 50 \times 16 \times (0.7 - 0.6) = 80$$

$$\underline{\underline{V_{total} = 450 + 80 = 530 \text{ (L)}}}$$

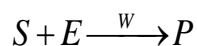


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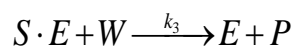
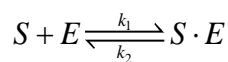
Problem 5

【Solution】

(a)



By Michaelis-Menten mechanism,



$$-r_{urea} = k_1[S][E] - k_2[S \cdot E]$$

By PSSH, $r_E = 0$,

$$r_E = k_2[E \cdot S] - k_1[E][S] + k_3[E \cdot S][W] = 0$$

令 $k_4 = k_3[W]$ 並整理，

$$[E \cdot S] = \frac{k_1[E][S]}{k_2 + k_4} \text{ 代回}$$

$$-r_{urea} = k_1[E][S] \left(1 - \frac{k_2}{k_2 + k_4}\right) = \frac{k_1 k_4 [E][S]}{k_2 + k_4}$$

By enzyme balance,

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

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

$$-r_{urea} = \frac{k_1 k_4 [E]_0 [S]}{k_2 + k_4 + k_1[S]} = \frac{k_4 [E]_0 [S]}{\frac{k_2 + k_4}{k_1} + [S]}$$

令

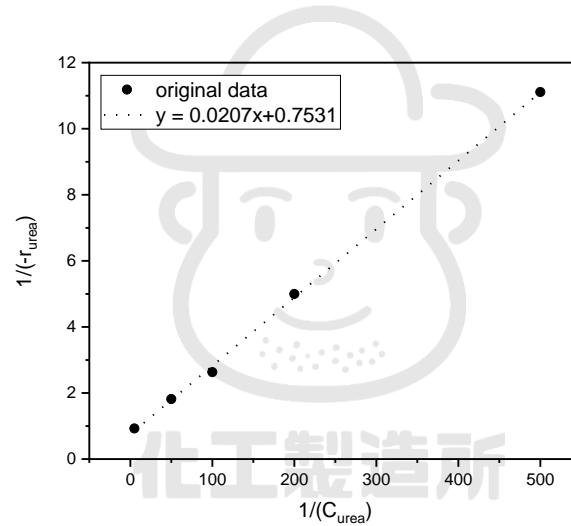
$$\begin{cases} k_4[E]_0 = v_{\max} \\ \frac{k_2 + k_4}{k_1} = K_M \end{cases}, \quad \underline{\underline{-r_{urea} = \frac{v_{\max}[S]}{K_M + [S]}}}$$

(b)

倒數

$$\frac{-1}{r_{urea}} = \frac{K_M + [S]}{v_{\max}[S]} = \frac{K_M}{v_{\max}[S]} + \frac{1}{v_{\max}}$$

Plot $\frac{1}{-r_{urea}} - \frac{1}{[S]}$ diagram,



$$\begin{cases} \text{intercept} = \frac{1}{v_{\max}} = 0.7531 \rightarrow \underline{\underline{v_{\max} = 1.3278 \text{ (M / s)}}} \\ \text{slope} = \frac{K_M}{v_{\max}} = 0.0207 \rightarrow \frac{K_M}{1.3278} = 0.0207 \rightarrow \underline{\underline{K_M = 0.0274 \text{ (M)}}} \end{cases}$$

106 年台科大化熱化反

Part I. 化工動力學

Problem 1

【Solution】

(1)

觀察速率常數

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

∵ A 與 B 同 order

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

(2)

By Arrhenius equation,

$$\begin{aligned} k(50^\circ\text{C}) &= k(20^\circ\text{C}) \exp\left[\frac{-E_a}{R} \left(\frac{1}{50+273} - \frac{1}{20+273}\right)\right] \\ &= 0.5 \exp\left[\frac{-8000}{1.987} \left(\frac{1}{323} - \frac{1}{293}\right)\right] = \underline{\underline{1.792 \text{ (L/mol} \cdot \text{min)}}} \end{aligned}$$

(3)

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

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

For F_B ,

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

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

(4)

For recycle CSTR,

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

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

$$\begin{aligned} V &= (R+1) \cdot \frac{x_{Af} - \left(\frac{R}{R+1}\right)x_{Af}}{k_A C_{A0}^2 (1-x_A)(\theta_B - 2x_A)} \\ &= 20(0.5+1) \times \frac{0.5 - \left(\frac{0.5}{0.5+1}\right) \times 0.5}{1.792 \times \left(\frac{20}{100}\right)^2 \times (1-0.5) \left(\frac{3}{2} - 2 \times 0.5\right)} = \underline{\underline{558.036 \text{ (L)}}} \end{aligned}$$

(5)

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

化工製造所

Problem 2

【Solution】

(1)

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

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

(2)

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

(3)

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

(4)

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

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

$$x_{Ae} = 0.5$$

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

(5)

By design equation,

$$\begin{aligned} V &= \int_0^{x_A} \frac{F_{A0}}{-r_A} dx_A = \int_0^{0.4} \frac{F_{A0}}{k_A (C_A - \frac{C_B^2}{K_C})} dx_A \\ &= \int_0^{0.4} \frac{F_{A0}}{k_A [C_{A0} \frac{1-x_A}{1+x_A} - C_{A0}^2 \frac{4x_A^2}{K_C (1+x_A)^2}]} dx_A \\ &= \int_0^{0.4} \frac{365.85}{0.5 [\frac{3}{0.082 \times 400} \frac{1-x_A}{1+x_A} - (\frac{3}{0.082 \times 400})^2 \frac{4x_A^2}{0.1219(1+x_A)^2}]} dx_A \\ &= \int_0^{0.4} \frac{365.85}{A} dx_A \end{aligned}$$

[計算機數值解]

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

[Simpson's rule]

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

$$\begin{aligned} V &= \frac{h}{3} [f(0) + 4f(0.2) + f(0.4)] \times 365.85 \\ &= \frac{0.2}{3} [21.867 + 4 \times 37.486 + 119.052] \times 365.85 \\ &= \underline{\underline{7094.18 \text{ (L)}}} \end{aligned}$$

(6)

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

Problem 3

【Solution】

(1)

$$r_C = k_1 C_A C_B - k_2 C_C - k_3 C_C^2$$

(2)

By PSSH, $r_C = 0$

$$r_C = k_1 C_A C_B - k_2 C_C - k_3 C_C^2 = 0$$

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

$$10 \times 0.5 x_A = 2.5, \quad x_A = 0.5$$

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

代入：

$$0.1 \times 0.5^2 - C_C - 1.5 C_C^2 = 0$$

$$\underline{\underline{C_C = 0.024 \text{ (M)}}}$$

(3)

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

Problem 4

【Solution】

(1) 喝水可稀釋體內病毒，使病毒作用速率降低

(2) 大顆粒：表面積降低，反應速率變慢

小顆粒：porosity 降低， $\Delta P \uparrow$

(3)

$$\begin{aligned} \text{rate} &= -r_A = k(T)C_A \\ &= k(T)C_{A0}(1-x_A) \end{aligned}$$

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



(4)

Define selectivity, $S_{D/U}$

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

For temperature,

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

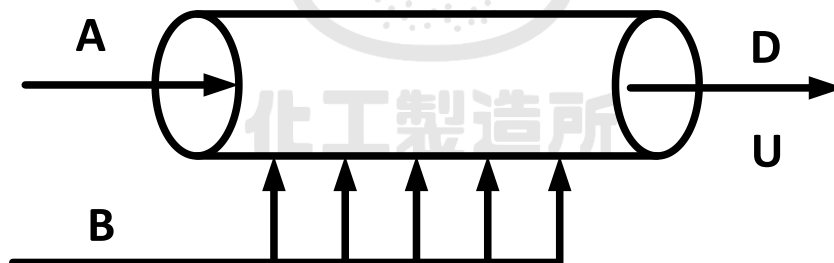
For C_A ,

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

For C_B ,

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

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



Part II. 化工熱力學

Problem 5

【Solution】

(a)

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

For G^E ,

$$G^E = H^E - \cancel{TS^E} = nRT \zeta x_A x_B$$

regular solution

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

(b)

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

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

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

$$= -6772.82 \text{ (J)}$$

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

Problem 5.15.)

Problem 6**【Solution】**

By Raoult's law basis,

$$r_c(RL) = \frac{P_c}{x_c P_c^{sat}}$$

Henry's law basis,

$$r_c(HL) = \frac{P_c}{x_c k_c}$$

$$a_c = r_c x_c, \quad P_c^{sat} = 31.2$$

x_c	0.2	0.4	0.6
$r_c(R)$	1.586538	1.201923	1.148504
$r_c(HL)$	2.25	1.704545	1.628788
$a_c(R)$	0.317308	0.480769	0.689103
$a_c(HL)$	0.45	0.681818	0.977273

Problem 7**【Solution】**

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

By Maxwell relation,

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

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

$$\because dH = TdS + VdP$$

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

代入：

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

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Problem 1

【Solution】

For Carnot cycle,

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

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

Problem 2

【Solution】

(a)

$$dU = TdS - PdV$$

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

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

(b)

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

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

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

Problem 3**【Solution】****(a)**

$$\begin{aligned}\Delta \underline{S} &= \int_{T_i}^{T_f} \frac{C_p}{T} dT - R \ln \frac{P_f}{P_i} \\ &= C_p^* \ln \frac{T_f}{T_i} - R \ln \frac{P_f}{P_i} = 29.3 \ln \frac{575}{290} - 8.314 \ln \frac{10}{1} \\ &= \underline{\underline{0.911 \text{ (J / mol} \cdot \text{K)}}}\end{aligned}$$

(b)

By energy balance (steady state, open system),

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

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

(本题改编自：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*,

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

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Problem 4

【Solution】

(a)

By mole balance of benzene,

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

By mole balance of TMP,

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

$$D = 3875 \text{ (mol / hr)}$$

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

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

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

(b)

Assume Raoult's law is applicable,

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

三式相加

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

代回得

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

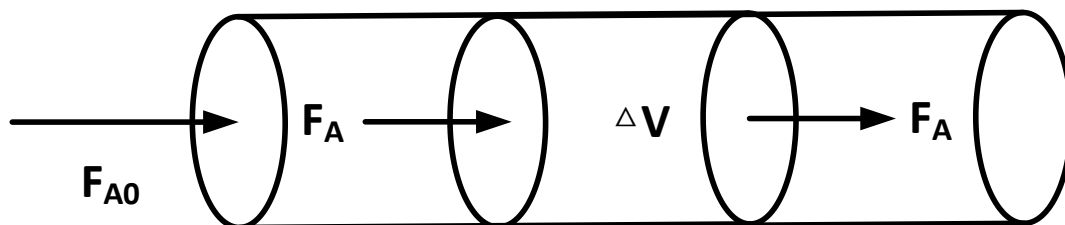
(本題改編自：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*,

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

Problem 5

【Solution】

Consider the following configuration,



By mole balance in the control volume,

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

同除 $\Delta V \rightarrow 0$

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

\therefore rate equation,

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

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

代入

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

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

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

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

Problem 6**【Solution】****(a)**

$$r_D = k_4[I]$$

By PSSH on [I]

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

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

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

(b)*[H] is very small,*

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

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Problem 7**【Solution】**

(a)

B 並未在 rate law 之分母出現 => 應該不吸附在觸媒上

(b)

For an isothermal CSTR with catalyst,

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

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

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

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Problem 8

【Solution】

(a)

For PFR,

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

Rate equation,

$$\begin{aligned} -r_A &= k_r C_A - k_b C_B^2 \\ &= \frac{k_r C_{A0}(1-x_A)}{(1+x_A)} - \frac{4k_b C_{A0}^2 x_A^2}{(1+x_A)^2} \end{aligned}$$

Combine,

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

For C_{A0}

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

代入

[計算機數值解]

$$V = \int_0^{0.4} \frac{1 \times 10^3}{\frac{2 \times 10^2 \times 0.01(1-x_A)}{(1+x_A)} - \frac{4 \times 2 \times 10^4 \times 0.01^2 x_A^2}{(1+x_A)^2}} dx_A = \underline{\underline{508.308 \text{ (L)}}}$$

[Simpson's rule]

令

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

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

$$V = 1000 \times \frac{0.2}{3} [0.499 + 4 \times 0.899 + 4.903] = \underline{\underline{600.417 \text{ (L)}}}$$

(b)

At equilibrium,

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

$$\frac{2 \times 10^2}{2 \times 10^4} = \frac{4 \times 0.01 x_A^2}{(1-x_A)(1+x_A)}$$

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



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Problem 1

【Solution】

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

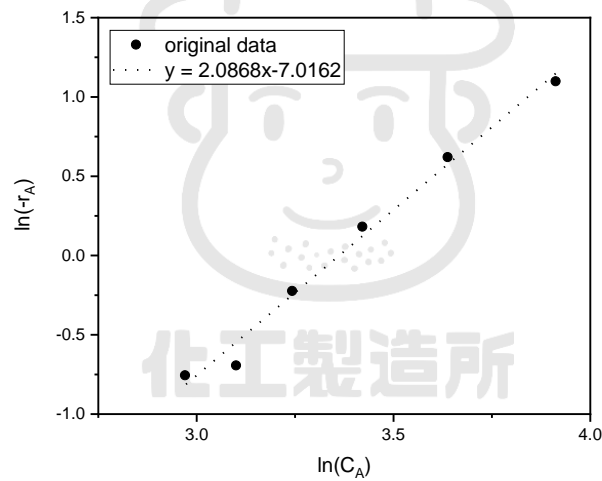
假設 rate law,

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

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

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

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



$$\text{slope} = n = 2$$

將 $C_{A0} = 50$, $-r_A = 3.0$, $k = 0.5 \times 10^{-3}$ 代回

$$\ln 3.0 = 2 \ln 50 + \ln(k' \times 0.5 \times 10^{-3})$$

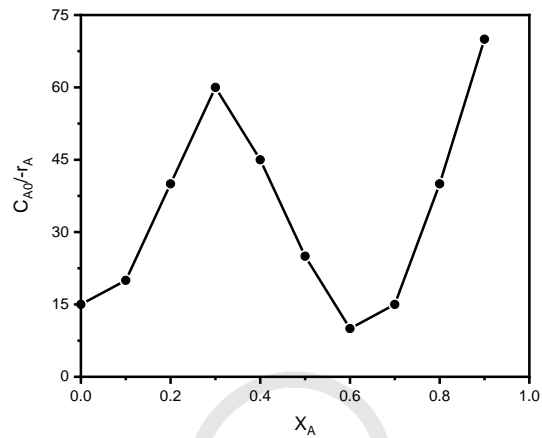
$$\underline{\underline{k' = 2.4 \times 10^{-6}}}$$

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

Problem 2

【Solution】

將 $\frac{C_{A0}}{-r_A} - x_A$ 關係繪出



1. $0 \leq x_A \leq 0.6$ 為 CSTR

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

2. $0.6 \leq x_A \leq 0.9$ 為 PFR

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

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

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

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

Problem 3

【Solution】

(a)

By Arrhenius equation,

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

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

If we have two k with two temperature,

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

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

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

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

(b)

將 k、T 代入

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

$$A = ke^{\frac{E_a}{RT}} = 0.001 \times e^{\frac{13638.57}{8.314 \times (273.15+0)}} = \underline{\underline{0.406}}$$

Problem 4**【Solution】**

(1) Negligible kinetic and potential energy changes

(2) Closed system

Problem 5**【Solution】**

$$\begin{array}{ccccccc}
 P_1 = 20 \text{ psia} & \xrightarrow{\text{Step 1}} & P_2 = 1000 \text{ psia} & \xrightarrow[\text{cooler}]{\text{Step 2}} & P_3 = 1000 \text{ psia} & \xrightarrow[\text{compressor}]{\text{Step 3}} & P_4 = ? \\
 T_1 = 60^\circ\text{F} & & T_2 = ? & & T_3 = 60^\circ\text{F} & & T_4 = ? \\
 & & & & & & \xrightarrow[\text{cooler/heater}]{\text{Step 4}} & P_5 = ? \\
 & & & & & & & T_5 = 60^\circ\text{F} \\
 & & & & & & & x_5^L = 0.75 \\
 & & & & & & & x_5^V = 0.25
 \end{array}$$

For Step 1 (adiabatic compression)

By energy balance (open system, steady state),

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

$$\Delta H = W$$

By entropy balance,

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

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

By the phase diagram

$$\begin{array}{ccc}
 \hat{S}_1 = 0.49(\text{Btu} / \text{lb}_m \cdot R) & \longrightarrow & \hat{S}_2 = 0.49(\text{Btu} / \text{lb}_m \cdot R) \\
 \hat{H}_1 = 165(\text{Btu} / \text{lb}_m) & & \hat{H}_2 = 205(\text{Btu} / \text{lb}_m) \\
 & & T_2 = 250^\circ\text{F}
 \end{array}$$

$$W = \Delta H = \hat{H}_2 - \hat{H}_1 = 205 - 165 = 40 \text{ (Btu} / \text{lb}_m)$$

For Step 2

By energy balance,

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

$$\begin{array}{ll} P_2 = 100(\text{psia}) & P_3 = 100(\text{psia}) \\ \hat{H}_2 = 200(\text{Btu} / \text{lb}_m) & \longrightarrow T_3 = 60^\circ\text{F} \\ & \hat{H}_3 = 162(\text{Btu} / \text{lb}_m) \end{array}$$

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

For Step 3

By energy balance,

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

By entropy balance,

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

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

By the phase diagram

$$\begin{array}{ll} \hat{S}_3 = 0.40(\text{Btu} / \text{lb}_m \cdot R) & \longrightarrow \hat{S}_4 = 0.40(\text{Btu} / \text{lb}_m \cdot R) \\ \hat{H}_3 = 162(\text{Btu} / \text{lb}_m) & P_4 = P_5 = 750(\text{psia}) \\ & \hat{H}_4 = 205(\text{Btu} / \text{lb}_m) \end{array}$$

$$W = \Delta H = \hat{H}_4 - \hat{H}_3 = 205 - 162 = 43 (\text{Btu} / \text{lb}_m)$$

For Step 4

By energy balance,

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

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

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

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

For ideal gas,

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

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

(※題目未給 C_p 數據，經查表，在 $60 \sim 300^\circ\text{F}$ 範圍內 $C_p \approx 0.2 (\text{Btu} / \text{lb} \cdot ^\circ\text{F})$)

(2)

∴ By energy balance of the discharge process,

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

$$\begin{aligned} \hat{H}_i = 75 &\longrightarrow \hat{H}_f = 75 \\ P_f &= 14.7 (\text{psia}) \end{aligned}$$

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

Problem 6**【Solution】**

(1)

By phase equilibrium relationship,

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

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

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

(2)

For solid-gas equilibrium,

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

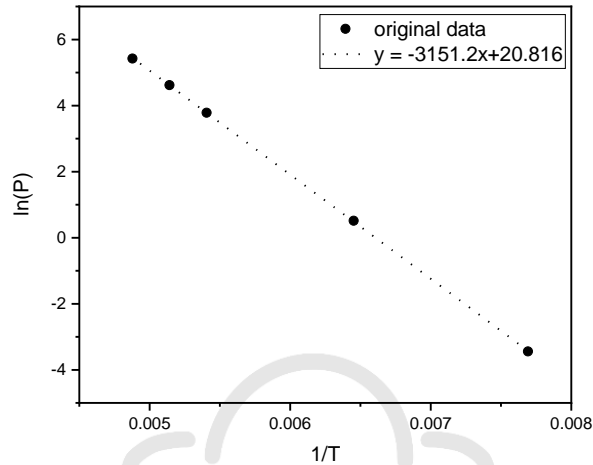
$$\frac{dP}{P} = \frac{\Delta H}{RT^2} dT$$

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

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

$\ln P$	-3.44202	0.515216	3.784644	4.618086	5.42495
$1/T$	0.007692	0.006452	0.005405	0.005141	0.004878



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

(3)

For pure solid state, fugacity,

$$f = P^{\text{sat}}(T) \exp\left[\frac{V^S(P - P^{\text{sat}})}{RT}\right]$$

For saturated vapor data,

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

For 190K,

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

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

代回

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

Problem 7**【Solution】****(a)**

For 50% mass ethanol mixture

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

$$x_W = 1 - x_E = 0.719$$

對圖可得

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

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

$$n_T = 3.522$$

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

(b)

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

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

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

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

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

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Problem 1

【Solution】

(a)

$$dU = dQ + dW$$

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

(b)

For closed, ideal gas system,

$$dU = dQ + dW$$

$$C_V dT = TdS - PdV$$

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

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

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

(c)

For isentropic process,

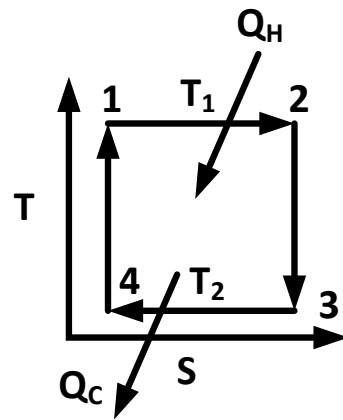
$$0 = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

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

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

(d)

(1)



(2)

$$\underline{|W| = \text{enclosed area} = (T_1 - T_2)(S_2 - S_1)}$$

(3)

For a cyclic process, the state function change = 0

$$\boxed{\Delta S = 0}$$

(4)

1. Friction

2. non-uniform T, P distribution

Problem 2

【Solution】

(a)

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

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

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

=>

$$\begin{aligned}\Delta H_{fr}^{\circ} - T\Delta S_{fr}^{\circ} &= [-285.8 - (25 + 273.15) \times (-163.1)] \times 10^{-3} \\ &= -237.17 \text{ (kJ / mol)} \approx \Delta G_{fr}^{\circ}\end{aligned}$$

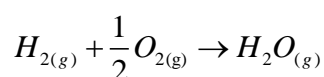
(b)

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

Under the above condition, we can calculate the Gibbs free energy change of reaction and to obtain the equilibrium constant at standard state.

(2)

Consider the reaction,



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

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

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

(3)

The amount of heat per mole of hydrogen is,

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

(c)

By the energy balance equation,

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

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

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

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

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

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

$$T_2 = 29 \left(\frac{70}{10}\right)^{\frac{1.41-1}{1.41}} = 524.75 \text{ (K)}$$

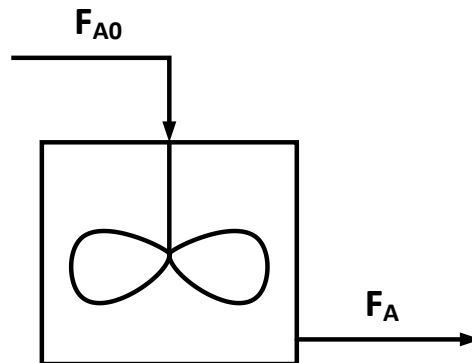
$$\Delta T = 524.75 - 298 = 226.75 \text{ (K)}$$

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

Problem 3

【Solution】

For CSTR, by balance,



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

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

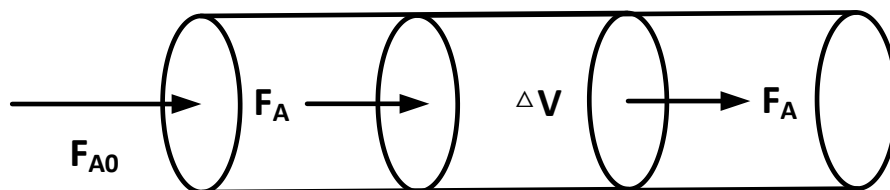
\therefore rate equation

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

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

For PFR,

Consider the following configuration,



By mole balance in the control volume,

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

同除 $\Delta V \rightarrow 0$

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

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

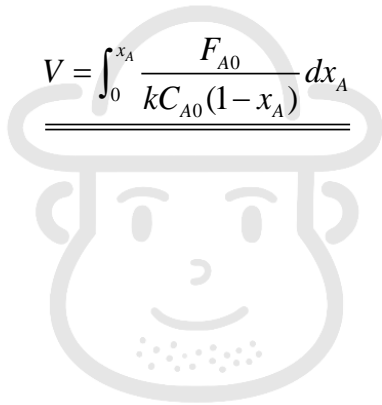
代回

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

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

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

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



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Problem 4

【Solution】

For CSTR, by design equation,

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

By rate equation,

$$-r_A = kC_A C_B = kC_{A0}^2 (1 - x_A) \left(\frac{1}{0.01} - x_A \right)$$

Combine,

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

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

$$x_A = \frac{F_{A0} - F_{A1}}{F_{A0}} = \frac{0.01 \times 1 - 0.005}{0.01 \times 1} = 0.5 \text{ 代入}$$

$$V = \frac{0.01 \times 0.1 \times 0.5}{0.01 \times 0.01^2 (1 - 0.5)(100 - 0.5)} = \underline{\underline{100.5 \text{ (L)}}}$$

For PFR, design equation,

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

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

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

Problem 5**【Solution】**

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

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

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

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

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

取 > 0

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

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Problem 1

【Solution】

For $\Delta \hat{S}$,

$$\begin{aligned}\Delta \hat{S} &= \int_{P_1}^{P_2} \left(\frac{\partial \hat{S}}{\partial P} \right)_T dP = - \int_{P_1}^{P_2} \left(\frac{\partial \hat{V}}{\partial T} \right)_P dP \\ &= \hat{V} \int_{P_2}^{P_1} \frac{1}{\hat{V}} \left(\frac{\partial \hat{V}}{\partial T} \right)_P dP = \hat{V} \beta (P_1 - P_2) \\ &= 1.551 \times 10^{-3} \times 2.095 \times 10^{-3} (270 - 1000) \\ &= \underline{\underline{-2.372 \times 10^{-3} (kJ / kg \cdot K)}}$$

For $\Delta \hat{H}$

$$\begin{aligned}d \hat{H} &= \cancel{\hat{C}_P} dT + [\hat{V} - T \left(\frac{\partial \hat{V}}{\partial T} \right)_P] dP \\ \Delta \hat{H} &= \int_{P_1}^{P_2} [\hat{V} - T \left(\frac{\partial \hat{V}}{\partial T} \right)_P] dP = \hat{V} \int_{P_1}^{P_2} \left[1 - \frac{T}{\hat{V}} \left(\frac{\partial \hat{V}}{\partial T} \right)_P \right] dP \\ &= \hat{V} \int_{P_1}^{P_2} [1 - T \beta] dP = \hat{V} (1 - T \beta) (P_2 - P_1) \\ &= 1.551 \times 10^{-3} (1 - 350 \times 2.095 \times 10^{-3}) (1000 - 290) \\ &= \underline{\underline{0.302 (kJ / kg)}}$$

Problem 2

【Solution】

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

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

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

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

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

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

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

代入

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

$$Q = -21758.16 \text{ (J/mol)}$$

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

Problem 3

【Solution】

$$P = \frac{RT}{V} - \frac{a - bRT^{1.5}}{\sqrt{TV^2}} = \frac{RT}{V} - \frac{a}{\sqrt{TV^2}} + \frac{bRT}{V^2}$$

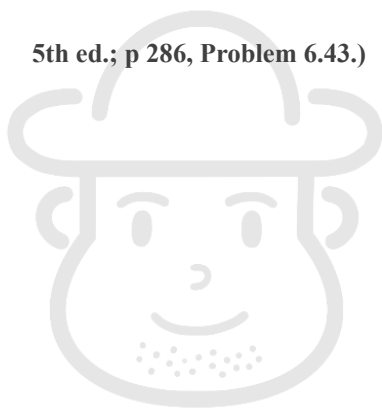
$$\frac{PV}{RT} = Z = 1 - \frac{a}{RT\sqrt{T}} \frac{1}{V} + \frac{b}{V} = 1 + \underbrace{\left(b - \frac{a}{RT^{1.5}}\right)}_{\text{令為} B} \frac{1}{V}$$

@Boyle temperature, $B = 0$

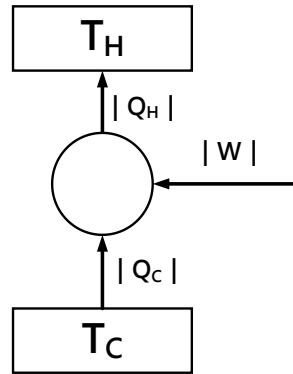
$$b - \frac{a}{RT_B^{1.5}} = 0, \quad T_B = \underline{\underline{\left(\frac{a}{bR}\right)^{\frac{2}{3}}}}$$

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

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



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Problem 4**【Solution】**

By energy balance,

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

By entropy balance (maximum efficiency),

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

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

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

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

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

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

For 31% efficiency,

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

Problem 5

【Solution】

By design equation,

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

For $x_{A,run1}$

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

For $x_{A,run2}$

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

代入

$$V_1 = V_2$$
$$\frac{2 \times 0.9}{kC_{A0}^{n-1}(1-0.9)^n} = \frac{1.5 \times 0.75}{kC_{A0}^{n-1}(1-0.75)^n}, \quad \boxed{n=2}$$

For activation energy,

by run 2,3 ,

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

$$V_2 = V_3$$

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

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

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

Problem 6**【Solution】****(a)**

Check,

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

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

The film resistance should not influence the rate of reaction**(b)**

Define Weisz modulus,

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

 $L = \text{characteristic size} \equiv$

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

將數據代入

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

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

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

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

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

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

而標準為：

$$\left\{ \begin{array}{l} \text{diffusion free} \left\{ \begin{array}{l} M_T < 0.4 \\ M_w < 0.15 \end{array} \right. \\ \text{strong diffusion} \left\{ \begin{array}{l} M_T > 4 \\ M_w > 4 \end{array} \right. \end{array} \right.$$

(c)

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

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

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

(本題改編自：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 407~408, Example 18.1.)

Problem 7

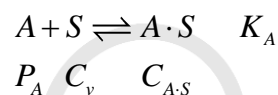
【Solution】

觀察 Rate law,

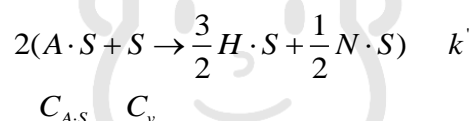
- (1) 分子有 A，速率決定步驟有 A 的參與
- (2) 分母只有 H 存在，相對於 A 與 N(氮氣)，H(氫氣)應該吸附力較強
- (3) 假設主要被吸附之物質為 H 與 N，其餘中間產物微量

Mechanism :

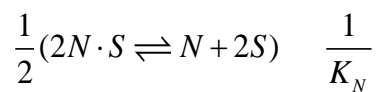
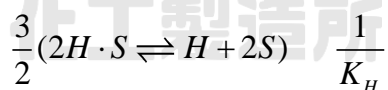
Adsorption of NH_3



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



Desorption of N_2 and H_2 ,



$$rate = kC_{A \cdot S}C_v = kK_A P_A C_v^2$$

For C_v , by site balance,

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

$$C_v = \frac{C_t}{\sqrt{K_H P_H}} \quad \text{代回}$$

$$\text{rate} = \frac{C_t k K_A P_A}{K_H P_H} = \frac{k K_A P_A}{K_H P_H}$$

Problem 8

【Solution】 Ans : (C)

(a)(b)

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

(c)(d)

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

⇒ C is not adsorbed

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

⇒ C is adsorbed

Therefore, the adsorption of C is favorable at lower T

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Problem 1

【Solution】

(a)

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

(b)

For PFR, design equation,

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

For rate law,

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

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

Combine,

$$V = \int_0^{0.8} \frac{F_{A0}}{kC_{A0} \left(\frac{1-x_A}{1+0.5x_A} \right)} dx_A = \int_0^{0.8} \frac{10}{20 \times 0.1 \times \left(\frac{1-x_A}{1+0.5x_A} \right)} dx_A = \underline{\underline{10.07 \text{ (L)}}}$$

Problem 2**【Solution】****(a)**

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

(b)

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

For PFR, design equation,

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

For rate law,

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

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

Combine,

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

Problem 3**【Solution】**

(a)

For the death rate,

$$r_D = k_4[I]$$

By pseudo-steady state assumption,

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

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

代回：

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

(b)

If $[H]$ is very small,

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

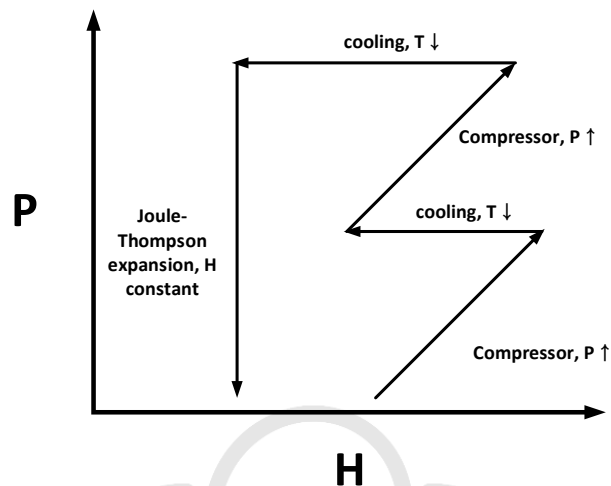
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Problem 4

【Solution】

(a)

The liquefaction process can be illustrated as,

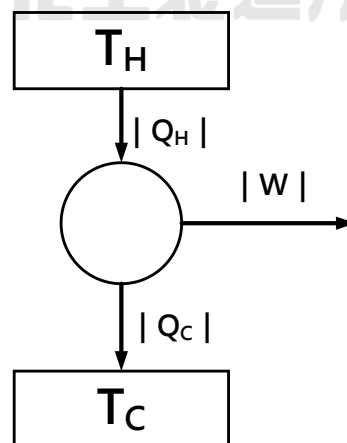


Where, the gas will tend to liquify under high pressure and low temperature, and after the Joule-Thomson expansion, the feed will leave as gas and liquid states.

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

(b)

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



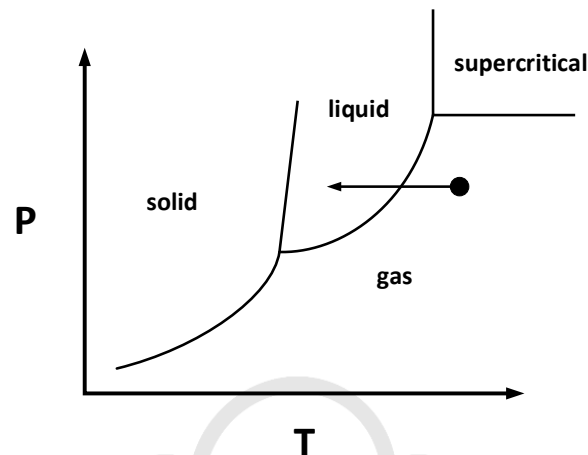
The reversible efficiency is,

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

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

(c)

By a typical phase diagram, we can read that,



If we cool a gas below its critical temperature, the gas will slowly be liquified.

When the gas is at the boundary of liquid and gas, the gas will coexist as both liquid and gas. For ideal gas, again, it will not liquified at all, so we can observe such behavior.

Problem 5

【Solution】

(a)

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

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

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

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

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

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

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

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

And by mass balance on the water + vapor system,

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

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

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

(b)

By force balance,

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

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

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

For the work done,

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

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

The efficiency is,

$$\eta = \left| \frac{W}{Q} \right| = \frac{262500}{3177437.5} \times 100\% = \underline{\underline{8.3\%}}$$

Problem 6

【Solution】

Assume:

- (1) All of the related gaseous streams are ideal gas
- (2) We can separate the processes into two individual processes

① Expansion process:

By energy balance,

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

By entropy balance,

$$\begin{aligned} \frac{d\bar{S}}{dt} &= \sum_i \dot{M}_k \hat{S}_k + \sum_{Q=0} \frac{\dot{Q}}{T} + \dot{S}_{gen} \\ \dot{S}_{gen} &= -\sum_i \dot{M}_k \hat{S}_k = -\dot{M}_k (S_{in} - S_{out}) \\ &= \dot{M}_k (C_p \ln \frac{T_{out}}{T_{in}} - R \ln \frac{P_{out}}{P_{in}}) = -\dot{M}_k R \ln \frac{P_{out}}{P_{in}} = \dot{M}_k R \ln 2 > 0 \end{aligned}$$

The first process is feasible

② Separating process:

By mass balance of oxygen,

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

By energy balance,

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

By entropy balance,

$$\frac{d\bar{S}}{dt} = \sum_i \dot{M}_k \hat{S}_k + \sum_{Q=0} \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

$$\begin{aligned}
\dot{S}_{gen} &= -\sum_i \dot{M}_k \hat{S}_k = -(\dot{M}_k S_{in} - S_{out,o} \dot{M}_{k,o} - S_{out,n} \dot{M}_{k,n}) \\
&= (S_{out,o} \dot{M}_{k,o} + S_{out,n} \dot{M}_{k,n} - \dot{M}_k S_{in}) \\
&= (0.167 \dot{M}_k R + 0.833 \dot{M}_k R)(0.95 \ln 0.95 + 0.05 \ln 0.05) - \dot{M}_k R(0.2 \ln 0.2 + 0.8 \ln 0.8) \\
&= 0.3018 \dot{M}_k R > 0
\end{aligned}$$

The second process is feasible

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



112 年台科大化熱化反

Problem 1

【Solution】

By the design equation of CSTR,

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

By the rate equation,

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

Combine,

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

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

Problem 2

【Solution】

Assume the metabolism obeys Michaelis-Menten mechanisms,

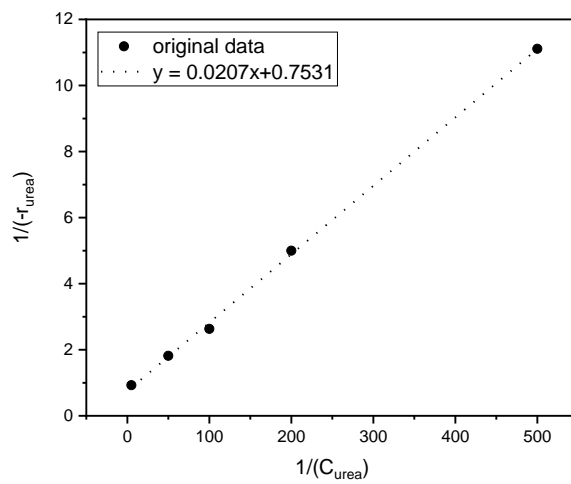
$$-r_{urea} = \frac{v_{max} C_{urea}}{K_M + C_{urea}}$$

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

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

$\frac{1}{-r_{urea}}$	0.926	1.818	2.631	5	11.11
$\frac{1}{C_{urea}}$	5	50	100	200	500

(本題於 105 年台科大化熱化反 Problem 5 出過，題目設計為(a)小題證明 Michaelis-Menten 關係，(b)小題再計算反應相關常數。)



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

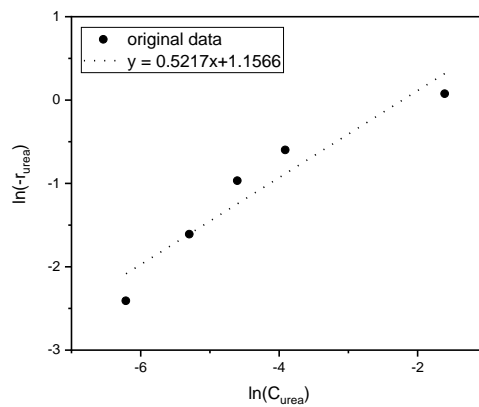
$$\underline{\underline{-r_{urea} = \frac{1.328 C_{urea}}{0.0274 + C_{urea}}}}$$

※若令反應對 urea 為 n 級反應，

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

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

Plot $\ln(-r_{urea}) - \ln C_{urea}$,

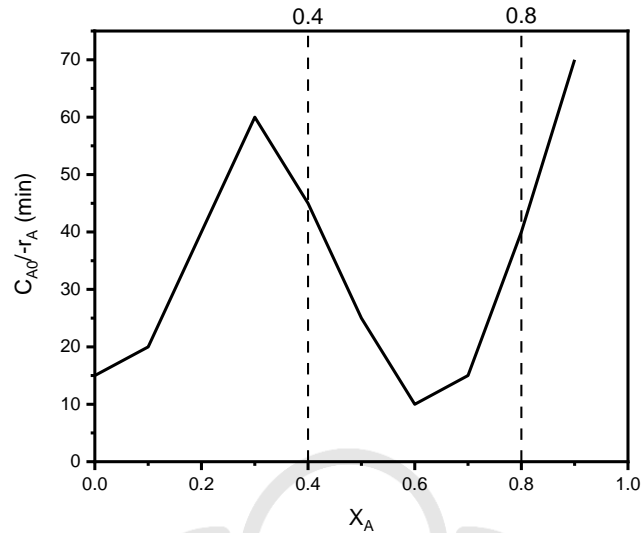


則誤差較大，不適用於此反應

Problem 3

【Solution】

(a)



(1) CSTR first,

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

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

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

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

(2) PFR first,

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

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

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

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

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

(b)

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

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

Problem 4

【Solution】

(i)

By Pitzer correlation,

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

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 100~102.)

(ii)

By Pitzer correlation,

$$Z = 1 + \frac{BP}{RT} = 1 + \hat{B} \frac{P_r}{T_r}$$
$$(\hat{B} = \frac{BP_c}{RT_c}, \text{ the reduced form of } B)$$

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

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

(本題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 100~102.)

(iii)

將 B^0 與 B^1 代入：

$$Z = 1 + B^0 \frac{P_r}{T_r} + \omega B^1 \frac{P_r}{T_r} = 1 + (0.083 - \frac{0.422}{T_r^{1.6}}) \frac{P_r}{T_r} + 0.0938(0.139 - \frac{0.172}{T_r^{4.2}}) \frac{P_r}{T_r}$$
$$Z = \frac{PV}{nRT} = 1 + [0.083 - 0.422(\frac{T_c}{T})^{1.6}] \frac{PT_c}{P_c T} + 0.0938[0.139 - 0.172(\frac{T_c}{T})^{4.2}] \frac{PT_c}{P_c T}$$

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

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

$$T = 25 + 273.15 = 298.15 \text{ (K)}$$

代入：

$$\frac{50P}{468.75 \times 0.082 \times 298.15}$$
$$= 1 + [0.083 - 0.422(\frac{269.70}{298.15})^{1.6}] \frac{269.70P}{47.77 \times 298.15} + 0.0938[0.139 - 0.172(\frac{269.70}{298.15})^{4.2}] \frac{269.70P}{47.77 \times 298.15}$$

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

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

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Problem 5**【Solution】**

(i)

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

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

By the definition of entropy,

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

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

For ideal gas,

$$dH = nC_p dT, \quad \frac{V}{T} = \frac{nR}{P}$$

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

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

(ii)

By energy balance of the open system,

$$n_1 H_1 = n_2 H_2 + n_3 H_3$$

$$n_1 C_p T_1 = n_2 C_p T_2 + n_3 C_p T_3$$

$$1 \times C_p (273.15 + 20) = 0.5 C_p (273.15 - 20) + 0.5 C_p T_3$$

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

(iii)

By entropy balance of the open system,

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

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

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

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

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

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

$$= 11.25 \text{ (J / K} \cdot \text{s)}$$

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

The process is thermodynamically feasible.

Problem 6**【Solution】****(i)**

The number of arrangement is,

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

(ii)

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

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

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

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

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

$$= \underbrace{N \ln N - 0.8N \ln(N) - 0.2N \ln(N)}_0 - 0.8N \ln(0.8) - 0.2N \ln(0.2)$$

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

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

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

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

(iii)

$$\begin{aligned}\Delta S_{mix} &= -R \sum_i x_i \ln x_i \\ &= -R(x_{Co} \ln x_{Co} + x_{Cr} \ln x_{Cr} + x_{Fe} \ln x_{Fe} + x_{Mn} \ln x_{Mn} + x_{Ni} \ln x_{Ni}) \\ &= -5R(0.2 \ln 0.2) = -5 \times 8.314(0.2 \ln 0.2) = \underline{\underline{13.38 \text{ (J / mol} \cdot \text{K)}}}\end{aligned}$$

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

※假設一合金含有 n 種元素，且每一種元素之分率皆為 $\frac{1}{n}$ ，則以理論來說，其

混合熵可被計算為：

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

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

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