104 年中興單操輸送

Problem 1
【Solution】

(1)

Assume：

(1) $v_y = v_z = 0$

(2) $v_x = v_x(\cancel{t}, x, y, \cancel{z})$

$$\rho v_x dydz\big|_x - \rho v_x dydz\big|_{x+dx} = 0$$

同除 $dxdydz \to 0$，

$$\frac{d(\rho v_x)}{dx} = 0 \xrightarrow{constant\ \rho} \underline{\underline{\frac{dv_x}{dx} = 0}}$$

(2)

$\because \dfrac{dv_x}{dx} = 0$ ， $v_x = v_x(y)$

By momemtum balance,

$$\rho v_x v_x dydz\big|_x - \rho v_x v_x dydz\big|_{x+dx} + \tau_{yx} dxdz\big|_y - \tau_{yx} dxdz\big|_{y+dy} + pdydz\big|_x - pdydz\big|_{x+dx} - \rho g sin\theta dxdydz = 0$$

同除 $dxdydz \to 0$

$$-\underbrace{\frac{\partial(\rho v_x v_x)}{\partial x}}_{v_x \neq v_x(x)} - \frac{\partial \tau_{yx}}{\partial y} - \frac{\partial p}{\partial x} - \rho g sin\theta = 0$$

$\because v_z = v_z(x)$ ，且上方接觸空氣，無壓降

$$\underline{\underline{-\frac{\partial \tau_{yx}}{\partial y} - \rho g sin\theta = 0}}$$

(3)

$$\frac{\partial \tau_{yx}}{\partial y} = -\rho g sin\theta \text{ , } \tau_{yx} = -(\rho g \sin\theta)y + c_1$$

$\because y = \delta, \ \tau_{yx} = 0$ (free surface)

$$c_1 = (\rho g \sin\theta)\delta$$

$$\tau_{yx} = -\mu \frac{dv_x}{dy} = -(\rho g \sin\theta)\delta \cdot (\frac{y}{\delta} - 1)$$

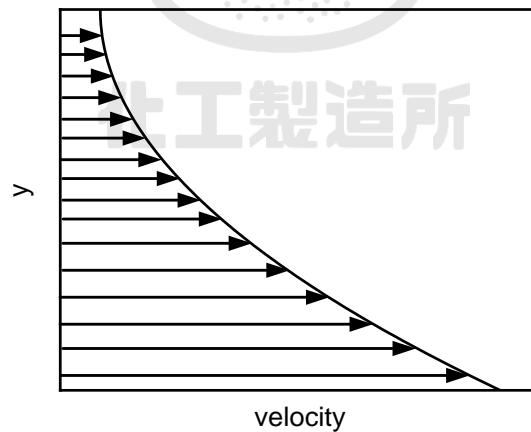$$\frac{dv_x}{dy} = \frac{(\rho g \sin\theta)\delta}{\mu} \cdot (\frac{y}{\delta} - 1) \text{ , } v_x = \frac{(\rho g \sin\theta)\delta^2}{\mu} \cdot (\frac{y^2}{2\delta^2} - \frac{y}{\delta}) + c_2$$

$\because y = 0, \ v_x = U$

$$c_2 = U$$

$$v_x = \frac{(\rho g \sin\theta)\delta^2}{\mu} \cdot (\frac{y^2}{2\delta^2} - \frac{y}{\delta}) + U$$

【Velocity Profile】

velocity

Problem 2

【Solution】

(1)

The number of heat transfer unit of a heat-exchanger is defined as,

$$NTU = \frac{UA}{C_{min}}$$

C_{min} is the smaller heat capacity coefficient

$$\begin{cases} C_A = 1 \times 1.5 = 1.5 \ (kJ / K \cdot s) \\ C_B = 0.2 \times 5 = 1 \ (kJ / K \cdot s) \end{cases} , \begin{cases} C_{min} = 1 \ (kJ / K \cdot s) \\ C_{max} = 1.5 \ (kJ / K \cdot s) \end{cases}$$

$$NTU = \frac{300 \times 10}{1 \times 10^3} = \underline{\underline{3}}$$

(2)

For the effectiveness of a co-current heat exchanger,

$$\varepsilon = \frac{1 - \exp[-NTU(1 + \frac{C_{min}}{C_{max}})]}{1 + \frac{C_{min}}{C_{max}}} = \frac{1 - \exp[-3 \times (1 + \frac{1}{1.5})]}{1 + \frac{1}{1.5}} = \underline{\underline{0.596}}$$

(3)

$$q = \varepsilon C_{min}(T_{H,in} - T_{c,in}) = 0.596 \times 1 \times 10^3 (400 - 300) = \underline{\underline{5.96 \times 10^4 \ (W)}}$$

(本題可參考：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass Transfer*, 5th ed.; p 340/347~349.)

Problem 3
【Solution】

By mole balance in each region,

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

同除 $4\pi dr \to 0$

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

For region I,

$$r_A = -k_A C_A \quad , \quad N_A = -D_{AB}\frac{dC_A}{dr} + y_A \underbrace{(N_A + N_B)}_{N_A = -N_B}$$

$$\frac{d}{dr}(r^2 D_{AB}\frac{dC_A}{dr}) - k_A C_A r^2 = 0 \quad , \quad \frac{d}{dr}(r^2\frac{dC_A}{dr}) - \frac{k_A}{D_{AB}}C_A r^2 = 0$$

Let $f = rC_A$ 代入：

$$\frac{d^2 f}{dr^2} - \frac{k_A}{D_{AB}}f = 0$$

$$f = c_1 \sinh(\sqrt{\frac{k_A}{D_{AB}}}r) + c_2 \cosh(\sqrt{\frac{k_A}{D_{AB}}}r)$$

$$C_A = \frac{c_1}{r}\sinh(\sqrt{\frac{k_A}{D_{AB}}}r) + \frac{c_2}{r}\cosh(\sqrt{\frac{k_A}{D_{AB}}}r)$$

For region II,

$$r_A = 0 \text{ 代入：} \quad \frac{-d(r^2 N_A)}{dr} = 0$$

Assume after the reaction, A is very dilute,

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

$$\frac{d}{dr}(r^2 D_{AB}\frac{dC_A}{dr}) = 0 \quad , \quad C_A = \frac{c_3}{r} + c_4$$

For boundary conditions,

$$\begin{cases} r = R, C_{A,I} = C_{AR} \\ r = 0.5R, C_{A,I} = C_{A,II} \\ r = 0.5R, \dfrac{dC_{A,I}}{dr} = \dfrac{dC_{A,II}}{dr} \\ r = 0, C_{A,II} \text{ is finite} \end{cases}$$

For the 4th boundary condition, we have $c_3 = 0$

For other boundary conditions, we have

B.C.1：

$$C_{AR} = \frac{c_1}{R} \sinh(\sqrt{\frac{k_A}{D_{AB}}}R) + \frac{c_2}{R} \cosh(\sqrt{\frac{k_A}{D_{AB}}}R)$$

B.C.2：

$$\frac{c_1}{0.5R} \sinh(\frac{R}{2}\sqrt{\frac{k_A}{D_{AB}}}) + \frac{c_2}{0.5R} \cosh(\frac{R}{2}\sqrt{\frac{k_A}{D_{AB}}}) = c_4$$

B.C.3：

$$\frac{-c_1}{(0.5R)^2} \sinh(\frac{R}{2}\sqrt{\frac{k_A}{D_{AB}}}) + \frac{c_1}{0.5R}\sqrt{\frac{k_A}{D_{AB}}} \cosh(\frac{R}{2}\sqrt{\frac{k_A}{D_{AB}}})$$

$$-\frac{c_2}{(0.5R)^2} \cosh(\frac{R}{2}\sqrt{\frac{k_A}{D_{AB}}}) + \frac{c_1}{0.5R}\sqrt{\frac{k_A}{D_{AB}}} \sinh(\frac{R}{2}\sqrt{\frac{k_A}{D_{AB}}}) = 0$$

After solving c_1, c_2, and c_4, we can obtain the concentration profile in both

regions.

Problem 4

【Solution】

(1)

$$Fr = \frac{v_\infty^2}{gL} = \frac{inertial\ force}{gravitational\ force}$$

(2)

$$Pe_h = \frac{v_\infty L}{\alpha} = \frac{convective\ heat\ transfer\ rate}{diffusive\ heat\ tranfer\ rate}$$

$$Pe_m = \frac{v_\infty L}{D_{AB}} = \frac{convective\ mass\ transfer\ rate}{diffusive\ mass\ tranfer\ rate}$$
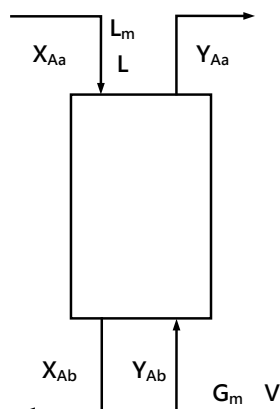
(3)

$$Sc = \frac{\upsilon}{D_{AB}} = \frac{momentum\ diffusivity}{mass\ diffusivity}$$

(本題可參考：**Welty, J.; Rorrer, G.; Foster, D.** *Fundamentals of Momentum, Heat, and Mass Transfer*, **5th ed.; p 127/570/519.**)

Problem 5
【Solution】

G_m = gas molar flow rate on a solute-free basis.

L_m = liquid flow rate on a solute-free basis.

$$X_{Aa} = 0 \text{ , } Y_{Ab} = 0.02 \text{ , } Y_{Aa} = 0.002$$

$$G_m = 30 \times \frac{100}{100+2} = 29.41 \ (kmol \ / \ hr)$$

(1)

For minimum rate of water, the equilibrium line intersects with operation line

$$X_{Ab} = 0.02$$

By mole balance of ethanol,

$$G_m(Y_{Aa} - Y_{Ab}) = L_m(X_{Aa} - X_{Ab})$$

$$29.41(0.002 - 0.02) = L_m(0 - 0.02) \text{ , } \underline{\underline{L_m = 26.47 \ (kmol \ / \ hr)}}$$

(2)

If the liquid/gas ratio is 1, by mole balance of ethanol,

$$(Y_{Aa} - Y_{Ab}) = (X_{Aa} - X_{Ab})$$

$$0.002 - 0.02 = 0 - X_{Ab} \text{ , } X_{Ab} = 0.018$$

For the calculation of number of mass transfer unit,

$$Y_{Aa}^* = X_{Aa} = 0 \text{ , } Y_{Ab}^* = X_{Ab} = 0.018$$

∵ The slope of operating line = equilibrium line,

$$N_{Oy} = \frac{Y_{Ab} - Y_{Aa}}{Y_{Ab} - Y_{Ab}^*} = \frac{0.02 - 0.002}{0.02 - 0.018} = \underline{\underline{9}}$$

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering***,**
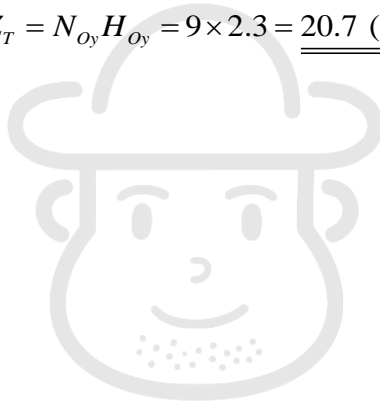
7th ed.; p 581~582.)

(3)

If the liquid/gas ratio is 1, by mole balance of ethanol,

$$H_{Oy} = \frac{G_m}{K_y aS} = \frac{G_m^{0.5}}{5S} = \frac{(\frac{29.41}{3600})^{0.5}}{5 \times [\frac{\pi}{4}(0.1)^2]} = 2.3 \ (m)$$

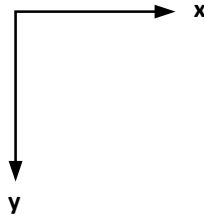$$Z_T = N_{Oy} H_{Oy} = 9 \times 2.3 = \underline{\underline{20.7 \ (m)}}$$

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Problem 1
【Solution】

Assume the coordinate of the system is,

By the equation of continuity,

$$\frac{\partial \rho}{\partial t} + \nabla \bullet (\rho \vec{v}) = 0$$

$\because$ incompressible, ρ is constant

$$\nabla \bullet (\vec{v}) = \underbrace{\frac{\partial v_x}{\partial x}}_{v_x=0} + \frac{\partial v_y}{\partial y} + \underbrace{\frac{\partial v_z}{\partial z}}_{v_z=0} = 0$$

$$v_y = f(\cancel{t}, x, \cancel{y}, \cancel{z}) \text{ only}$$

By shell balance of momentum,

$$\rho v_y v_y dxdz\big|_y - \rho v_y v_y dxdz\big|_{y+dy} + \tau_{xy} dydz\big|_x - \tau_{xy} dydz\big|_{x+dx} + pdxdz\big|_y - pdxdz\big|_{y+dy} + \rho g dxdydz = 0$$

同除 $dxdydz \to 0$

$$\underbrace{\frac{-\partial(\rho v_y v_y)}{\partial y}}_{v_y = f(y)} - \frac{\partial \tau_{xy}}{\partial x} - \frac{dp}{dy} + \rho g = -\frac{\partial \tau_{xy}}{\partial x} - \frac{dP}{dy} = 0$$

$$\tau_{xy} = -\mu \frac{dv_y}{dx} = \frac{-dP}{dy}x + c_1 \quad , \quad v_y = \frac{1}{2\mu}(\frac{dP}{dy})x^2 + C_1 x + C_2$$

For fluid I,

$$v_{y1} = \frac{1}{2\mu_1}(\frac{dP}{dy})x^2 + C_{11}x + C_{12}$$

For fluid 2,

$$v_{y2} = \frac{1}{2\mu_2}(\frac{dP}{dy})x^2 + C_{21}x + C_{22}$$

Boundary conditions,

$$\begin{cases} x = 0, v_y = v_A \\ x = L_1, v_{y1} = v_{y2} \\ x = L_1, \tau_1 = \tau_2 \\ x = L_1 + L_2, v_{y2} = -v_B \end{cases}$$

For B.C.1,

$$C_{12} = v_A$$

For B.C.2,

$$\frac{1}{2\mu_1}(\frac{dP}{dy})L_1^2 + C_{11}L_1 + v_A = \frac{1}{2\mu_2}(\frac{dP}{dy})L_1^2 + C_{21}L_1 + C_{22}$$

For B.C.3,

$$\mu_1 C_{11} = \mu_2 C_{21}$$

For B.C.4,

$$\frac{1}{2\mu_2}(\frac{dP}{dy})(L_1 + L_2)^2 + C_{21}(L_1 + L_2) + C_{22} = -v_B$$

$$C_{21} = \frac{\frac{-1}{2\mu_2}(\frac{dP}{dy})(2L_1L_2 + L_2^2) - \frac{L_1^2}{2\mu_1}(\frac{dP}{dy})}{(L_2 + L_1\frac{\mu_2}{\mu_1})} - v_B - v_A$$

$$C_{11} = \frac{\mu_1}{\mu_2}C_{21} = \frac{\mu_1}{\mu_2}[\frac{\frac{-1}{2\mu_2}(\frac{dP}{dy})(2L_1L_2 + L_2^2) - \frac{L_1^2}{2\mu_1}(\frac{dP}{dy})}{(L_2 + L_1\frac{\mu_2}{\mu_1})} - v_B - v_A]$$

$$C_{22} = -v_B - \frac{1}{2\mu}(\frac{dP}{dy})(L_1 + L_2)^2 - C_{21}(L_1 + L_2)$$

$$= -v_B - \frac{1}{2\mu}(\frac{dP}{dy})(L_1 + L_2)^2 - (L_1 + L_2)[\frac{\frac{-1}{2\mu_2}(\frac{dP}{dy})(2L_1L_2 + L_2^2) - \frac{L_1^2}{2\mu_1}(\frac{dP}{dy})}{(L_2 + L_1\frac{\mu_2}{\mu_1})} - v_B - v_A]$$

$$\boxed{v_{y1} = \frac{1}{2\mu_1}(\frac{dP}{dy})x^2 + \frac{\mu_1}{\mu_2}[\frac{\frac{-1}{2\mu_2}(\frac{dP}{dy})(2L_1L_2 + L_2^2) - \frac{L_1^2}{2\mu_1}(\frac{dP}{dy})}{(L_2 + L_1\frac{\mu_2}{\mu_1})} - v_B - v_A]x + v_A}$$

$$v_{y2} = \frac{1}{2\mu_2}(\frac{dP}{dy})x^2 + C_{21}x - v_B - \frac{1}{2\mu}(\frac{dP}{dy})(L_1 + L_2)^2 - C_{21}(L_1 + L_2)$$

$$= \frac{1}{2\mu_2}(\frac{dP}{dy})x^2 + C_{21}[x - (L_1 + L_2)] - v_B - \frac{1}{2\mu}(\frac{dP}{dy})(L_1 + L_2)^2$$

$$= \frac{1}{2\mu_2}(\frac{dP}{dy})x^2 + [\frac{\frac{-1}{2\mu_2}(\frac{dP}{dy})(2L_1L_2 + L_2^2) - \frac{L_1^2}{2\mu_1}(\frac{dP}{dy})}{(L_2 + L_1\frac{\mu_2}{\mu_1})} - v_B - v_A][x - (L_1 + L_2)] - v_B - \frac{1}{2\mu}(\frac{dP}{dy})(L_1 + L_2)^2$$

(本題改編自：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass Transfer*, "6"th ed.; p 123, Problem 9.22.)

Problem 2

【Solution】

(a)

For N_A, by Fick's law,

$$N_A = -D_{AB} \frac{dC_A}{dz} + \underset{\text{very dilute}}{\cancel{y_A}} (N_A + N_B + N_C...) = -D_{AB} \frac{dC_A}{dz}$$

$$\int_0^\delta N_A dz = -D_{AB} \int_0^{C_{A0}} dC_A \quad , \quad N_A = \frac{-D_{AB} C_{A0}}{\delta}$$

代回：

$$\frac{D_{AB} C_{A0}}{\delta} = \frac{\rho}{M} \frac{d\delta}{dt} \quad , \quad \frac{M D_{AB} C_{A0}}{\rho} dt = \delta d\delta$$

$$\frac{\delta^2}{2} = \frac{M D_{AB} C_{A0}}{\rho} t \quad , \quad \delta = \sqrt{\frac{2 M D_{AB} C_{A0}}{\rho} t}$$

(b)

$$t = \frac{\rho \delta^2}{2 M D_{AB} C_{A0}}$$

For Knudsen diffusivity,

$$D_{KA} = 4850 \cdot 0.5 \times 10^{-4} \sqrt{\frac{700}{184 + 19 \times 6}} = 0.37 \ (cm^2 / s)$$

$$C_{A0} = y_{A0} C = 0.00001 \times \frac{75}{8.314 \times 700} = 1.289 \times 10^{-7} \ (mol / m^3) = 1.289 \times 10^{-13} \ (mol / cm^3)$$

$$t = \frac{19.4 \times (2 \times 10^{-4})^2}{2 \times 184 \times 0.37 \times 1.289 \times 10^{-13}} = 44213 \ (s) = \underline{\underline{12.28 \ (hr)}}$$

(本題改編自：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass*

***Transfer*, 5th ed.; p 492, Problem 26.17.)**

Problem 3

【Solution】

(a)

$\iint_{c.s.} \rho(v \cdot n)dA$ is the net outward flow of mass across the control surface, or the net mass efflux from the control volume.

(本題改編自：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass Transfer*, 5th ed.; p 35.)

(b)

$\dfrac{\partial c}{\partial t}$ represents a fixed point of observation.

$\dfrac{dc}{dt}$ represents the observation from the observer with arbitrarily chosen velocities.

$\dfrac{Dc}{Dt}$ represents the observation from the observer if the observer moving with the river current.

(本題可參考：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass Transfer*, 5th ed.; p 101.)

Problem 4

【Solution】

(a)

$$Bi = \frac{h(\frac{V}{A})}{k_s} = \frac{internal\ thermal\ resistance}{external\ thermal\ resistance}$$

$$Pe_h = \frac{v_\infty L}{\alpha} = \frac{convective\ heat\ transfer\ rate}{diffusive\ heat\ tranfer\ rate}$$

$$\Pr = \frac{\upsilon}{\alpha} = \frac{momentum\ diffusivity}{thermal\ diffusivity}$$

$$Nu = \frac{hL}{k} = \frac{conductive\ thermal\ resistance}{convective\ thermal\ resistance} of\ the\ fluid$$

(本題可參考：**Welty, J.; Rorrer, G.; Foster, D.** *Fundamentals of Momentum, Heat, and Mass Transfer*, **5th ed.; p 254/570/275/276.**)

(b)

If a small metal ball (with very small radius and large conductivity) is heated in a hot water, the process may be able to be analyzed with lumped-parameter analysis.
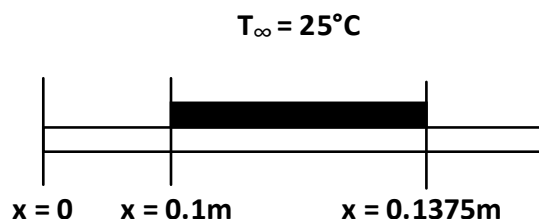
(c)

Water may have a larger Prandtl number because it has a apparently larger viscosity compared to air.

(本題可參考：**Bird, R.; Stewart, W.; Lightfoot, E.** *Transport Phenomena*, **2nd ed.; p 268~270.**)

Problem 5

【Solution】

(a)

$$T_\infty = 25°C$$

x = 0   x = 0.1m   x = 0.1375m

For the heat transfer coefficient, by the local Nusselt number,

$$Nu_x = \frac{h_x x}{k} = 0.332 \operatorname{Re}_x^{1/2} \operatorname{Pr}^{1/3} = 0.332(\frac{\rho \upsilon x}{\mu})^{0.5} \operatorname{Pr}^{1/3}$$

$$h_x = 0.332 k (\frac{\rho \upsilon}{\mu})^{0.5} \operatorname{Pr}^{1/3} x^{-0.5}$$

$$\bar{h} = \frac{\int_{L_1}^{L_2} 0.332 k (\frac{\rho \upsilon}{\mu})^{0.5} \operatorname{Pr}^{1/3} x^{-0.5} dx}{L_2 - L_1} = \frac{0.664 k (\frac{\upsilon}{\upsilon})^{0.5} \operatorname{Pr}^{1/3} (L_2^{0.5} - L_1^{0.5})}{L_2 - L_1}$$

$$= \frac{0.664 \times 3 \times 10^{-2} (\frac{20}{2 \times 10^{-5}})^{0.5} (\frac{2 \times 10^{-5}}{3 \times 10^{-5}})^{1/3} \times (0.1375^{0.5} - 0.1^{0.5})}{0.1375 - 0.1} = 25.33 \ (W/m^2 K)$$

To determine the steady state temperature,

$$\bar{h} \times (37.5 \times 10^{-3})^2 (T - 25) = 95 \text{，} \underline{T = 2692°C}$$

(※若將題目改為 0.95W，則溫度為 51.67°C，較符合常理)

(b)

From the expression of Nusselt number, we know,

$$Nu_x = \frac{h_x x}{k} = 0.332 \operatorname{Re}_x^{1/2} \operatorname{Pr}^{1/3} \propto \operatorname{Re}^{1/2}$$

If we increase the flow rate of the air, the Reynolds number of the system is increased, and so is the heat transfer coefficient.

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Problem 1

【Solution】

(1)

For incompressible fluid,

$$\frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + v \cdot \nabla \rho = 0$$

By the equation of continuity,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) = \underbrace{\frac{\partial \rho}{\partial t} + v \cdot \nabla \rho}_{=0} + \rho \nabla \cdot v = 0 \quad , \quad \nabla \cdot v = 0$$

(2)

$$\nabla \cdot v = \frac{\partial}{\partial x}(\frac{y}{x^2 - y^2}) + \frac{\partial}{\partial y}(\frac{x}{x^2 - y^2}) = \frac{-2xy}{(x^2 - y^2)^2} + \frac{2xy}{(x^2 - y^2)^2} = 0$$

<u>The flow is incompressible.</u>

(3)

$$\nabla \times v = \frac{\partial}{\partial x}(\frac{x}{x^2 - y^2}) - \frac{\partial}{\partial y}(\frac{y}{x^2 - y^2}) = \frac{(x^2 - y^2) - 2x^2}{(x^2 - y^2)^2} + \frac{(x^2 - y^2) + 2y^2}{(x^2 - y^2)^2} \neq 0$$

<u>The flow is irrotational</u>

Problem 5

【Solution】

By shell balance of energy in the region of $r_1 \leq r \leq r_2$

$$q^{"}(2\pi rL)dr\Big|_{r} - q^{"}(2\pi rL)dr\Big|_{r+dr} + q_0(2\pi rL)dr = 0$$

同除 $2\pi Ldr \to 0$

$$\frac{d(rq^{"})}{dr} + q_0 r = 0$$

$$q^{"} = -k\frac{dT}{dr} = -\frac{q_0 r}{2} + \frac{c_1}{r}$$

$$T = \frac{q_0 r^2}{4k} + C_1 \ln r + C_2 \begin{cases} r = r_1, T = T_1 \\ r = r_2, T = T_2 \end{cases}$$

$$T_1 = \frac{q_0 r_1^2}{4k} + C_1 \ln r_1 + C_2$$

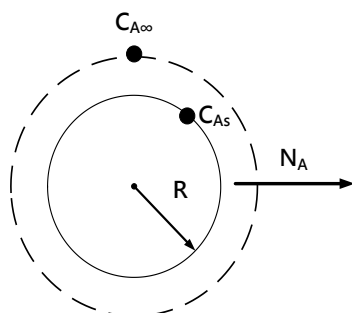$$T_2 = \frac{q_0 r_2^2}{4k} + C_1 \ln r_2 + C_2$$

$$C_1 = \frac{T_2 - T_1 - \frac{q_0}{4k}(r_2^2 - r_1^2)}{\ln\frac{r_2}{r_1}} \quad , \quad C_2 = T_1 - \frac{q_0 r_1^2}{4k} - C_1 \ln r_1$$

$$T = \frac{q_0 r^2}{4k} + C_1 \ln r + C_2 = \frac{q_0 r^2}{4k} + C_1 \ln r + T_1 - \frac{q_0 r_1^2}{4k} - C_1 \ln r_1$$

$$= \frac{q_0 r_1^2}{4k}[(\frac{r}{r_1})^2 - 1] + C_1 \ln\frac{r}{r_1} + T_1 = T_1 + \frac{q_0 r_1^2}{4k}[(\frac{r}{r_1})^2 - 1] + \frac{T_2 - T_1 - \frac{q_0}{4k}(r_2^2 - r_1^2)}{\ln\frac{r_2}{r_1}} \ln\frac{r}{r_1}$$

Problem 6
【Solution】

By shell balance of mass in spherical cooridinate,

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

同除 $4\pi dr \to 0$

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

By Fick's law,

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

代回：

$$\frac{d}{dr}(r^2\frac{dC_A}{dr}) = 0 \ , \ C_A = \frac{-c_1}{r} + c_2 \begin{cases} r = R, C_A = C_{As} \\ r = \infty, C_A = C_{A\infty} \end{cases}$$

$$\begin{cases} c_1 = R(C_{A\infty} - C_{As}) \\ c_2 = C_{A\infty} \end{cases}$$

$$C_A = \frac{R}{r}(C_{As} - C_{A\infty}) + C_{A\infty}$$
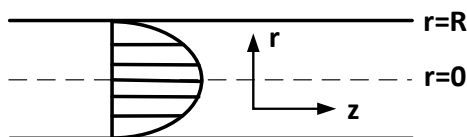
@ $r = R$, $N_{A,diffusion} = N_{A,convection}$

$$-D_{AB}\frac{dC_A}{dr}\bigg|_{r=R} = k(C_{As} - C_{A\infty})$$

$$\frac{R}{R^2}D_{AB}(C_{As} - C_{A\infty}) = k(C_{As} - C_{A\infty}) \ , \ \frac{kR}{D_{AB}} = 1$$

$$\underline{\underline{Sh = \frac{kD}{D_{AB}} = \frac{2kR}{D_{AB}} = 2}}$$

Problem 7
【Solution】

By the equation of motion,

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

For flow in z-direction,

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

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

$$(m = \frac{K}{g_c})$$

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

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

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

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

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

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

Problem 8

【Solution】

D'Alembert paradox describes that for an uniform incompressible, inviscid potential flow, the mathematical results show that there is no drag if the flow is approaching an object. However, in real cases, the drag is really larger even when the Reynolds number of a system is very large.

對於一個均勻不可壓縮、非黏性勢流系統中,當一物體於此系統中穩定相對運動時,其於數學上將不受任何拖曳力。然而,我們知道於高雷諾數時,於流場中的物體依舊會受到可觀的拖曳力(可參考 drag coefficient-Reynolds number 關係圖)。

To solve this problem, Prandtl stated that there is a thin boundary layer even for flow with high velocity, where the viscous force can't be negligible, thus satisfying the non-slip boundary condition and the existence of viscous force.

此種問題直至 Prandtl 提出邊界層理論才有完整的模型描述,亦即即便在雷諾數很大的流場中,依舊會有一區域,其黏滯力效應不可忽略。

(本題可參考:**Bird, R.; Stewart, W.;** *Lightfoot, E. Transport Phenomena*, **2nd ed.; p 128~130.**
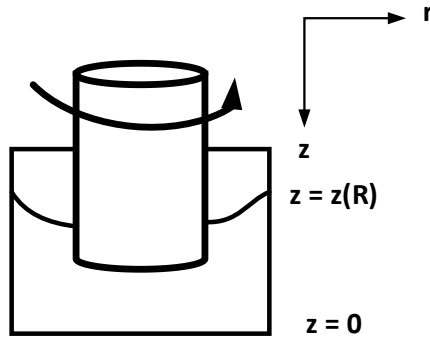
Munson, B. *Fundamentals of Fluid Mechanics*, **6th ed.; p 300~302/489~492**

Philip J. Pritchard. *Fox and McDonald's Intoduction to Fluid Mechanics*, **8th ed.; p 38~41.)**

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Problem 3

【Solution】

To determine the shape of the liquid phase, we first derive the velocity profile.

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,

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

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

By the Navier Stokes equation in θ direction,

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

$$= \cancel{\frac{-1}{r}\frac{\partial p}{\partial \theta}} + \mu[\frac{\partial}{\partial r}(\frac{1}{r}\frac{\partial}{\partial r}(r v_\theta)) + \cancel{\frac{1}{r^2}\frac{\partial^2 v_\theta}{\partial \theta^2}} + \cancel{\frac{\partial^2 v_\theta}{\partial z^2}} + \cancel{\frac{2}{r^2}\frac{\partial v_r}{\partial \theta}}] + \cancel{\rho g_\theta}$$

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

$$c_1 = \frac{-2\kappa}{1-\kappa^2}\Omega_i \quad , \quad c_2 = \frac{\kappa^2}{1-\kappa^2}\Omega_i R^2$$

$$v_\theta = (\frac{-2\kappa^2}{1-\kappa^2}\Omega_i)\frac{r}{2} + (\frac{\kappa^2}{1-\kappa^2}\Omega_i R^2)\frac{1}{r} = \frac{\kappa^2}{1-\kappa^2}(\frac{R^2-r^2}{r})\Omega_i$$

To determine the shape of the free liquid surface, by Navier-Stokes equation with r and z components,

$$\frac{-\partial p}{\partial r} = \frac{-\rho v_\theta^2}{r}$$

$$\frac{-\partial p}{\partial z} = -\rho g_z$$

Integrate the z-direction,

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

代回 r 方向,

$$\frac{\partial p}{\partial r} = f'(r) = \frac{\rho v_\theta^2}{r} = \frac{\rho[\frac{\kappa^2}{1-\kappa^2}(\frac{R^2-r^2}{r})\Omega_i]^2}{r} = \rho(\frac{\kappa^2\Omega_i}{1-\kappa^2})^2(\frac{R^4}{r^3} - \frac{2R^2}{r} + r)$$

Integrate with r,

$$f = \rho(\frac{\kappa^2\Omega_i}{1-\kappa^2})^2(-\frac{R^4}{2r^2} - 2R^2\ln r + \frac{r^2}{2}) + C$$

And the pressure distribution becomes,

$$p(r,z) = \rho g_z z + \rho(\frac{\kappa^2\Omega_i}{1-\kappa^2})^2(-\frac{R^4}{2r^2} - 2R^2\ln r + \frac{r^2}{2}) + C$$

Because the liquid is open to the atmosphere at the top, and z is used to describe the

height of the liquid-gas interface,

$$p(r,z) = p(R,z_R) = p_{atm} \quad , \quad p(r,z) = p(R,z_R)$$

$$\rho g_z z + \rho(\frac{\kappa^2\Omega_i}{1-\kappa^2})^2(-\frac{R^4}{2r^2}-2R^2\ln r+\frac{r^2}{2})+C = \rho g_z z_R + \rho(\frac{\kappa^2\Omega_i}{1-\kappa^2})^2(-\frac{\cancel{R^2}}{2}-2R^2\ln R+\frac{\cancel{R^2}}{2})+C$$

$$\rho g_z(z-z_R) = \frac{\rho}{2}(\frac{\kappa^2\Omega_i R}{1-\kappa^2})^2[\frac{R^2}{r^2}-4\ln\frac{R}{r}-\frac{r^2}{R^2}]$$

$$(z-z_R) = \frac{\rho}{2g_z}(\frac{\kappa^2\Omega_i R}{1-\kappa^2})^2[\frac{R^2}{r^2}-4\ln\frac{R}{r}-\frac{r^2}{R^2}]$$

將 $r/R=\xi$ 代入：

$$(z-z_R) = \frac{\rho}{2g_z}(\frac{\kappa^2\Omega_i R}{1-\kappa^2})^2[\xi^{-2}+4\ln\xi-\xi^2]$$

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

Problem 3B.15.)

Problem 4

【Solution】

Assume $T = T(r)$ only,

by equation of energy,

$$\rho c_p (\frac{\partial T}{\partial t} + \overline{v} \cdot \nabla T) = k \nabla^2 T + \not{q}$$

$$\rho c_p (\frac{\partial T}{\partial t}) = k [\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial T}{\partial r})] \begin{cases} I.C.: t = 0, T = T_0 \\ B.C.: r = 0, T = finite \\ B.C.: r = R, -k \frac{\partial T}{\partial r} = h(T - T_b) \end{cases}$$

Problem 5
【Solution】

By mechanical energy balance of the liquid, from 1 to 2

$$g(\cancel{h_1 - h_2}) + \frac{P_1 - P_2}{\rho} + \frac{1}{2}(v_1^2 - v_2^2) - h_f = 0$$
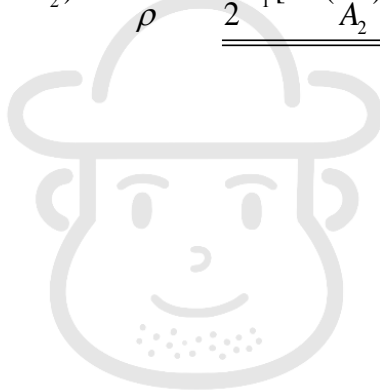
where the loss term, h_f, denotes the energy change

By mass balance between 1 and 2,

$$A_1 v_1 = A_2 v_2 \;,\; v_2 = \frac{A_1}{A_2} v_1$$

代回：

$$h_f = \frac{1}{2}(v_1^2 - v_2^2) + \frac{P_1 - P_2}{\rho} = \frac{1}{2} v_1^2 [1 - (\frac{A_1}{A_2})^2] + \frac{P_1 - P_2}{\rho}$$

Problem 6

【Solution】 Ans: (A)

Assume, (1) The flow is fully-developed in z-direction

(2) $v_r = v_\theta = 0$, $v_z = f(\cancel{t}, r, \cancel{\theta}, z)$

(3) Incompressible Newtonian fluid

(4) The gravity effect can be neglected

By the equation of continuity,

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

By Navier-Stokes equation in z-direction,

$$\mu[(\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial v_z}{\partial r}))] - \frac{\partial p}{\partial z} = 0$$

$$\mu[(\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial v_z}{\partial r}))] = \frac{\partial p}{\partial z}$$

$$\frac{\partial v_z}{\partial r} = \frac{\partial v_z}{\partial r} = \frac{1}{2\mu}(\frac{\partial p}{\partial z})r + \frac{c_1}{r}$$

$$v_z = \frac{1}{4\mu}(\frac{\partial p}{\partial z})r^2 + c_1 \ln r + c_2 \quad \begin{cases} r = \dfrac{d}{2}, v_z = 0 \\ r = \dfrac{D}{2}, v_z = 0 \end{cases}$$

$$c_1 = \frac{\dfrac{-1}{4\mu}(\dfrac{\partial p}{\partial z})(\dfrac{D^2}{4} - \dfrac{d^2}{4})}{\ln\dfrac{D}{d}}$$

For maximum velocity, let $\dfrac{\partial v_z}{\partial r} = 0$

$$r = \sqrt{\frac{-2\mu c_1}{(\dfrac{\partial p}{\partial z})}} = \sqrt{\frac{\dfrac{2\mu \times \dfrac{1}{4\mu}(\dfrac{\partial p}{\partial z})(\dfrac{D^2}{4} - \dfrac{d^2}{4})}{\ln(\dfrac{D}{d})}}{(\dfrac{\partial p}{\partial z})}} = \sqrt{\frac{(D^2 - d^2)}{8\ln(\dfrac{D}{d})}}$$

Problem 7

【Solution】

Firstly, check the Biot number of the system,

$$Bi = \frac{h(\frac{V}{A})}{k} = \frac{h(\frac{\pi}{4}D^2 L)}{k(\pi DL + \frac{\pi}{4}D^2 \times 2)} = \frac{8500 \times (\frac{\pi}{4} \times 0.1^2 \times 0.1)}{1.21(\pi \times 0.1 \times 0.1 + \frac{\pi}{2} \times 0.1^2)} = 117 > 0.1$$

We can't use lumped-capacity analysis here.

To use the chart attached, we need to calculate the following parameter,

$$\frac{T - T_s}{T_0 - T_s} = \frac{310 - 373}{292 - 373} = 0.778$$

對照代表圓柱的線，可得橫軸 $\frac{\alpha t}{x_1^2} \approx 0.1$

$$\frac{\alpha t}{x_1^2} = \frac{kt}{\rho c_p x_1^2} = \frac{1.21t}{2310 \times 0.21 \times 4184 \times (\frac{0.1}{2})^2} = 0.1$$

$$\underline{\underline{t = 419.35 \ (s)}}$$

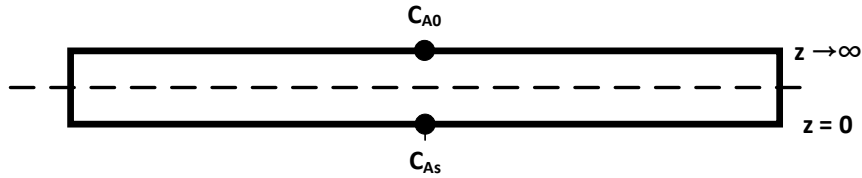(本題改編自：**Welty, J.; Rorrer, G.; Foster, D.** *Fundamentals of Momentum, Heat, and Mass Transfer*, **5th ed.; p 257, Example 2.**)

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Problem 6
【Solution】

By Fick's second law of diffusion (no homogeneous reaction),

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial z^2}$$

By combination of variables, let $\eta = \dfrac{z}{\sqrt{4D_{AB}t}}$

$$\frac{\partial C_A}{\partial t} = \frac{\partial C_A}{\partial \eta}\frac{\partial \eta}{\partial t} = \frac{-\eta}{2t}\frac{\partial C_A}{\partial \eta}$$

$$\frac{\partial^2 C_A}{\partial z^2} = \frac{\partial}{\partial z}[\frac{\partial C_A}{\partial \eta}\frac{\partial \eta}{\partial z}] = \frac{\partial}{\partial z}[\frac{1}{\sqrt{4D_{AB}t}}\frac{\partial C_A}{\partial \eta}] = \frac{\partial}{\partial \eta}[\frac{1}{\sqrt{4D_{AB}t}}\frac{\partial C_A}{\partial \eta}]\frac{\partial \eta}{\partial z} = \frac{1}{4D_{AB}t}\frac{\partial^2 C_A}{\partial \eta^2}$$

$$\frac{-\eta}{2t}\frac{\partial C_A}{\partial \eta} = D_{AB}\cdot\frac{1}{4D_{AB}t}\frac{\partial^2 C_A}{\partial \eta^2} \ , \ \frac{\partial^2 C_A}{\partial \eta^2} + 2\eta\frac{\partial C_A}{\partial \eta} = 0$$

The solution is,

$$C_A = c_1\int_0^\eta e^{-\eta^2}d\eta + c_2 \begin{cases} z = 0 \rightarrow \eta = 0, C_A = C_{As} \\ z \rightarrow \infty, \eta \rightarrow \infty, C_A = C_{A0} \\ t = 0, \eta \rightarrow \infty, C_A = C_{A0} \end{cases}$$

B.C.1 代入：

$$C_A = c_2 = C_{As}$$

B.C.2 代入：

$$C_{A0} = c_1\int_0^\infty e^{-\eta^2}d\eta + C_{As} \ , \ c_1 = \frac{C_{A0} - C_{As}}{\dfrac{\sqrt{\pi}}{2}}$$

$$C_A = \frac{2}{\sqrt{\pi}}(C_{A0} - C_{As})\int_0^\infty e^{-\eta^2}d\eta + C_{As}$$

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To determine the flux of oxygen,

$$N_A = -D_{AB} \frac{dC_A}{dz}\bigg|_{z=0} = -D_{AB} \frac{d}{dz}(\frac{2}{\sqrt{\pi}}(C_{A0}-C_{As})\int_0^\infty e^{-\eta^2}d\eta + C_{As})$$

$$= -D_{AB}(C_{A0}-C_{As})\cdot\frac{2}{\sqrt{\pi}}\cdot\frac{1}{\sqrt{4D_{AB}t}}$$

$$= -1\times10^{-11}(0.5-5)\cdot\frac{2}{\sqrt{\pi}}\cdot\frac{1}{\sqrt{4\times1\times10^{-11}\times10}} = 2.54\times10^{-6}\ (mol/s/m^2)$$

Problem 7
【Solution】

The viscosity is the resistance of a fluid to defromation rate,

$$\mu = \frac{\tau}{-\frac{dv}{dx}}[=]kg/(m\cdot s)$$

Problem 8
【Solution】

$$\tau = -\mu(\nabla v + (\nabla v)^\dagger) + (\frac{2}{3}\mu - \kappa)(\nabla \cdot v)]$$

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

p 843.)

Problem 9

【**Solution**】

(a)

For turbulent flow on a plate, the boundary layer thickness can be described by,

$$\frac{\delta}{x} = \frac{0.376}{\mathrm{Re}_x^{1/5}} \;,\; \frac{\delta}{5} = \frac{0.376}{(2.5 \times 10^8)^{1/5}}$$

$$\underline{\underline{\delta = 0.039 \; (m)}}$$

(本題可參考：**Welty, J.; Rorrer, G.; Foster, D.** *Fundamentals of Momentum, Heat, and Mass Transfer*, **5th ed.; p 163~164.**)

※若為 **Laminar flow**，則其邊界層厚度可近似為：

$$\frac{\delta}{x} = \frac{4.64}{\sqrt{\mathrm{Re}_x}} \quad \textbf{(von Karman momentum integral)}$$

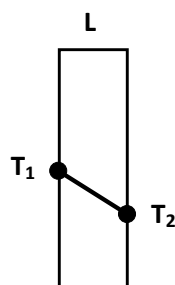**(b)** As the result of (a), the flow system is **<u>turbulent flow</u>**

(c)

For turbulent flow past a plate, the friction coefficient is,

$$C_{fx} = \frac{0.0576}{\mathrm{Re}_x^{1/5}} = \frac{0.0576}{(\frac{\rho v}{\mu})^{1/5}} x^{-1/5}$$

$$F = 2 \times \frac{0.0576}{(\frac{\rho v}{\mu})^{1/5}} \int_0^W \int_0^L x^{-1/5} dx \times \frac{1}{2} \rho v_\infty^2 = \frac{0.0576 \times \frac{5}{4} W}{(\frac{\rho v_\infty}{\mu})^{1/5}} L^{4/5} \times \rho v_\infty^2 = \frac{0.0576 \times \frac{5}{4} WL}{(\frac{\rho v_\infty L}{\mu})^{1/5}} \times \rho v_\infty^2$$

$$= \frac{0.0576 \times \frac{5}{4} \times 500}{(\frac{998 \times 50 \times 5}{9.93 \times 10^{-4}})^{1/5}} \times 998 \times 50^2 = \underline{\underline{2.97 \times 10^6 \; (N)}}$$

【Solution】

For a plane wall in steady state without heat generation, the temperature prfile is linear.

For the steady state heat transfer rate, by Ohm's law,

$$q = \frac{(T_1 - T_2)}{\dfrac{L}{kA}} = \underline{\underline{\frac{kA}{L}(T_1 - T_2)}}$$

Problem 10

【Solution】

(a) By shell balance of energy, assume,

(1) Steady state

(2) Consider only x-direction

$$q_x^{"}(dydz)\Big|_x - q_x^{"}(dydz)\Big|_{x+dx} + q_k\,dxdydz = 0$$

同除 $dxdydz \to 0$

$$\frac{dq_x^{"}}{dx} = q_0(1 - \frac{x}{L}) \quad , \quad q_x^{"} = q_0(x - \frac{x^2}{2L}) + c_1$$

$\because\ x = L$, the wall is insulated,

$$q_x^{"}\Big|_{x=L} = \frac{q_0 L}{2} + c_1 = 0 \quad , \quad c_1 = -\frac{q_0 L}{2}$$

$$q_x^{"} = -k\frac{dT}{dx} = q_0(x - \frac{x^2}{2L}) - \frac{q_0 L}{2}$$

$$T = \frac{q_0}{k}(\frac{x^3}{6L} - \frac{x^2}{2}) + \frac{q_0 L}{2k}x + c_2$$

$\because x = 0, T = T_0$

$$c_2 = T_0$$

$$\underline{\underline{T = \frac{q_0}{k}(\frac{x^3}{6L} - \frac{x^2}{2}) + \frac{q_0 L}{2k}x + T_0}}$$

(b) By the discussion of (a), we know that when $x = L$, $\dfrac{dT}{dx} = 0$, which indicated the maximum temperature occurs at $x = L$.

(c)

At $x = L$,

$$T = \frac{q_0}{k}(\frac{L^2}{6} - \frac{\cancel{L^2}}{\cancel{2}}) + \frac{q_0 \cancel{L^2}}{\cancel{2k}} + T_0 = \frac{q_0 L^2}{6k} + T_0 = \frac{180 \times 10^3 \times L^2}{6 \times 0.6} + 320 = \underline{\underline{320 + 50000L^2}}$$

(本題改編自：**Welty, J.; Rorrer, G.; Foster, D.** *Fundamentals of Momentum, Heat, and Mass Transfer*, **5th ed.; p 248, Problem 17.24.**，原題有給定厚度 L 為 0.06 m，代入可得系統最高溫為 500K。)

※**Temperature profile**：
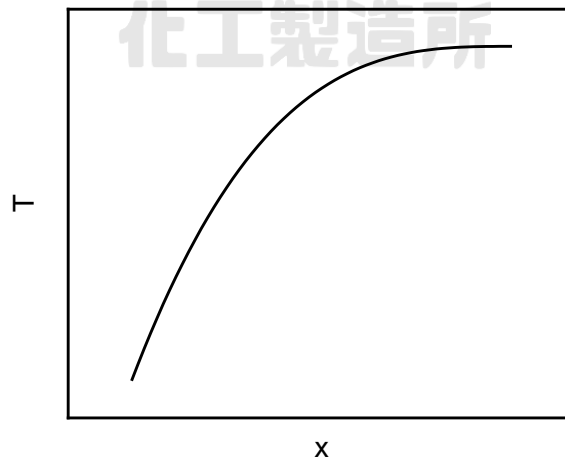
Problem 11

【Solution】

$$D_{AB} [=] m^2/s$$

$$k_c [=] m/s^2$$

Problem 12

【Solution】

If we consider that Knudsen diffusion and molecular diffusion compete with each other by a "resistance in series" approach, the effective diffusivity is,

$$\frac{1}{D_{Ae}} = \frac{1-\alpha y_A}{D_{AB}} + \frac{1}{D_{KA}}$$

where,

$$D_{KA} = \frac{d_{pore}}{3} \sqrt{\frac{8\kappa NT}{\pi M_A}}$$

$$\alpha = 1 + \frac{N_B}{N_A}$$

The diffusion process is a combination of Kndusen diffusion in pore and normal molecular diffusion.

For special case with $\alpha = 0$ or $N_A = -N_B$

$$\frac{1}{D_{Ae}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}}$$

(本題可參考：**Welty, J.; Rorrer, G.; Foster, D.** *Fundamentals of Momentum, Heat, and Mass Transfer*, **5th ed.; p420~421.**。)

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<u>**Problem 4**</u>
【**Solution**】

(1)

If the flow is incompressible,

$$\nabla \cdot v = 0 ,$$

and we can find a stream function, Ψ, satisfying,

$$\begin{cases} v_x = \dfrac{\partial \Psi}{\partial y} = \dfrac{-2y}{x^2 - y^2} \\[3mm] v_y = -\dfrac{\partial \Psi}{\partial x} = \dfrac{-2x}{x^2 - y^2} \end{cases}$$

Back into the continuity equation, we have

$$\nabla \cdot v = \frac{\partial}{\partial x}(\frac{-2y}{x^2 - y^2}) + \frac{\partial}{\partial y}(\frac{-2x}{x^2 - y^2}) = \frac{4xy}{(x^2 - y^2)^2} - \frac{4xy}{(x^2 - y^2)^2} = 0$$

<u>**The flow is incompressible**</u>

(2)

If $\nabla \times v = 0$, we can find a function ϕ such that the relation is satisfied,

$$\frac{\partial v_x}{\partial y} = \frac{\partial^2 \phi}{\partial x \partial y} = \frac{\partial v_y}{\partial x}$$

For $\dfrac{\partial v_x}{\partial y}$,

$$\frac{\partial v_x}{\partial y} = \frac{\partial}{\partial y}(\frac{-2y}{x^2 - y^2}) = \frac{-2(x^2 - y^2) - (-2y)(-2y)}{(x^2 - y^2)^2} = \frac{-2x^2 - 2y^2}{(x^2 - y^2)^2}$$

For $\dfrac{\partial v_y}{\partial x}$,

$$\frac{\partial v_y}{\partial x} = \frac{\partial}{\partial x}(\frac{-2x}{x^2 - y^2}) = \frac{-2(x^2 - y^2) - (2x)(-2x)}{(x^2 - y^2)^2} = \frac{2x^2 + 2y^2}{(x^2 - y^2)^2}$$

<u>**The flow doesn't have a velocity potential**</u>
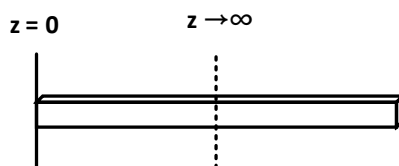
(本題可參考：**Welty, J.; Rorrer, G.; Foster, D.** *Fundamentals of Momentum, Heat, and Mass Transfer*, **5th ed.; p 114~118.**)

Problem 5

【Solution】

(1)

Consider only the z-direction diffusion, by Fick's law,

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial x^2}$$

By combination of variables, let $\eta = \dfrac{z}{\sqrt{4D_{AB}t}}$

$$\frac{\partial C_A}{\partial t} = \frac{\partial C_A}{\partial \eta}\frac{\partial \eta}{\partial t} = \frac{-\eta}{2t}\frac{\partial C_A}{\partial \eta}$$

$$\frac{\partial^2 C_A}{\partial z^2} = \frac{\partial}{\partial z}[\frac{\partial C_A}{\partial \eta}\frac{\partial \eta}{\partial z}] = \frac{\partial}{\partial z}[\frac{1}{\sqrt{4D_{AB}t}}\frac{\partial C_A}{\partial \eta}] = \frac{\partial}{\partial \eta}[\frac{1}{\sqrt{4D_{AB}t}}\frac{\partial C_A}{\partial \eta}]\frac{\partial \eta}{\partial z} = \frac{1}{4D_{AB}t}\frac{\partial^2 C_A}{\partial \eta^2}$$

$$\frac{-\eta}{2t}\frac{\partial C_A}{\partial \eta} = D_{AB}\cdot\frac{1}{4D_{AB}t}\frac{\partial^2 C_A}{\partial \eta^2} \ , \ \frac{\partial^2 C_A}{\partial \eta^2}+2\eta\frac{\partial C_A}{\partial \eta}=0$$

The solution is,

$$C_A = c_1\int_0^\eta e^{-\eta^2}d\eta + c_2 \begin{cases} z=0 \rightarrow \eta=0, C_A=C_{As} \\ z\rightarrow\infty, \eta\rightarrow\infty, C_A=0 \\ t=0, \eta\rightarrow\infty, C_A=0 \end{cases}$$

B.C.1 代入：

$$C_A = c_2 = C_{As}$$

B.C.2 代入：

$$0 = c_1\int_0^\infty e^{-\eta^2}d\eta + C_{As} \ , \ c_1 = \frac{-C_{As}}{\frac{\sqrt{\pi}}{2}}$$

$$C_A = C_{As}[1-\frac{2}{\sqrt{\pi}}\int_0^\infty e^{-\eta^2}d\eta] = C_{As}[1-erf(\eta)]$$

(2)

For η,

$$\eta = \frac{z}{\sqrt{4D_{AB}t}} = \frac{2 \times 10^{-3}}{\sqrt{4 \times 2.5 \times 10^{-11} \times 10 \times 3600}} = 1.054$$

For $erf(1.054)$,

$$erf(1.054) \approx \frac{erf(1) + erf(1.1)}{2} = 0.86145$$

$$C_A = 0.001[1 - 0.86145] = 1.3855 \times 10^{-4} = \underline{\underline{0.01385\%}}$$

Problem 6

【Solution】

By shell balance of energy, assume,

(1) Steady state   (2) Consider only r-direction

$$q_r^{"}(2\pi rL)\big|_r - q_r^{"}(2\pi rL)\big|_{r+dr} + q_k(2\pi rLdr) = 0$$

同除 $2\pi Ldr \rightarrow 0$

$$\frac{d(rq_r^{"})}{dr} + q_k r = 0 \quad , \quad \frac{d(rq_r^{"})}{dr} + \frac{I^2}{k_e}r = 0$$

$$(k_e = electrical\ conductivity \propto \frac{1}{resistance})$$

By definition, the current density, $I[=]amp/m^2$ is,

$$I = \frac{k_e(\Delta V)}{L} \quad , \quad \frac{d(rq_r^{"})}{dr} + \frac{k_e(\Delta V)^2}{L^2}r = 0$$

$$q_r^{"} = -k\frac{dT}{dr} = \frac{-k_e(\Delta V)^2}{2L^2}r + \frac{c_1}{r}$$

$\because r = 0, \ T = finite$,

$$c_1 = 0 \quad , \quad \frac{dT}{dr} = \frac{k_e(\Delta V)^2}{2kL^2}r$$

$$T = \frac{k_e(\Delta V)^2}{4kL^2}r^2 + c_2$$

$r = R, T = T_R$,

$$c_2 = T_R - \frac{k_e(\Delta V)^2 R^2}{4kL^2}$$

$$T = \frac{k_e(\Delta V)^2}{4kL^2}r^2 + T_R - \frac{k_e(\Delta V)^2 R^2}{4kL^2}$$

At the wire axis, $R = 0$, $T = T_0$

$$T_R - T_0 = \frac{k_e(\Delta V)^2 R^2}{4kL^2}$$

$$20 - 10 = \frac{59.6 \times 10^6 (\Delta V)^2 \times (2 \times 10^{-3})^2}{4 \times 390 \times (5^2)} \quad , \quad \underline{\underline{\Delta V = 40.4\ (V)}}$$

(本題改編自：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, **2nd ed.; p 295,**

Example 10.2-1.)

Problem 7

【Solution】

(1) For a given complex velocity potential, we have, by definition,

$$w(z) = \phi(x, y) + i\Psi(x, y)$$

$$\frac{dw}{dz} = -v_x + iv_y$$

∵ $w(z) = v_\infty(z + \frac{R^2}{z})$,

$$\frac{dw}{dz} = v_\infty(1 - \frac{R^2}{z^2})$$

∵ $z = x + iy = r\sin\theta + ir\cos\theta = re^{i\theta}$

$$\frac{dw}{dz} = v_\infty(1 - \frac{R^2}{z^2}) = v_\infty(1 - \frac{R^2}{r^2}e^{-2i\theta}) = v_\infty(1 - \frac{R^2}{r^2}\cos 2\theta) + iv_\infty(\frac{R^2}{r^2}\sin 2\theta)$$

$$\underline{\underline{v_x = -v_\infty(1 - \frac{R^2}{r^2}\cos 2\theta)}} \quad \text{、} \quad \underline{\underline{v_y = v_\infty(\frac{R^2}{r^2}\sin 2\theta)}}$$

(b)

By Bernoulli equation for incompressible, potential flow,

$$(\frac{1}{2}\rho v^2 + p)_{r=R} = \frac{1}{2}\rho v_\infty^2 + p_\infty$$

For $(v^2)_{r=R}$

$$(v^2)_{r=R} = (v_x^2 + v_y^2)_{r=R} = v_\infty^2[(1 - \cos 2\theta)^2 + (\sin 2\theta)^2]$$

$$= v_\infty^2[1 - 2\cos 2\theta + \cos^2 2\theta + (\sin 2\theta)^2]$$

$$= v_\infty^2[2 - 2\cos 2\theta] = v_\infty^2[2 - 2(1 - 2\sin^2\theta)]$$

$$= 4v_\infty^2\sin^2\theta$$

代回：

$$\frac{1}{2}\rho \times (4v_\infty^2\sin^2\theta) + p = \frac{1}{2}\rho v_\infty^2 + p_\infty$$

$$\underline{\underline{p = \frac{1}{2}\rho v_\infty^2(1 - 4\sin^2\theta) + p_\infty}}$$

(本題改編自：**Bird, R.; Stewart, W.; Lightfoot, E.** *Transport Phenomena*, **2nd ed.; p 128~129, Example 4.3-1.**)

在 106 年中興單操輸送 Problem 8 所提及之 D'Alembert paradox，可以用此範例做說明：

若考慮 tengential force

$$p = \int_0^{2\pi} [\frac{1}{2}\rho v_\infty^2 (1 - 4\sin^2\theta) + p_\infty]R\sin\theta d\theta = 0$$

若考慮 normal force

$$p = \int_0^{2\pi} [\frac{1}{2}\rho v_\infty^2 (1 - 4\sin^2\theta) + p_\infty]R\cos\theta d\theta = 0$$

也就代表在此狀態下，數學證明出物體所受到的 drag force 為 0，然而卻與實際情況矛盾，就算在高雷諾數下，物體所受到之拖曳力依舊可觀。直至 Prandtl 提出邊界層理論，並且可用於說明 Stagnation point 的產生以及分離點後渦流的生成後，才得以解釋與解決。

(關於 D'Alembert apradox 之描述可參考：Bird, R.; Stewart, W.; *Lightfoot, E. Transport Phenomena*, 2nd ed.; p 128~130.

Munson, B. *Fundamentals of Fluid Mechanics*, 6th ed.; p 300~302(有壓力造成之拖曳力計算方式)

Philip J. Pritchard. *Fox and McDonald's Intoduction to Fluid Mechanics*, 8th ed.; p 38~41.)

110 年中興單操輸送

Problem 1

【Solution】

(a)

$\because v_x = v_y = 0$, $v_z = v_z(x, y)$, and the gravity effect can be ignored, by Navier Stoke equation,

$$\rho(\cancel{\frac{\partial v_z}{\partial t}} + v_x\cancel{\frac{\partial v_z}{\partial x}} + v_y\cancel{\frac{\partial v_z}{\partial y}} + v_z\cancel{\frac{\partial v_z}{\partial z}}) = -\frac{\partial P}{\partial z} + \mu(\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} + \cancel{\frac{\partial^2 v_z}{\partial z^2}}) + \cancel{\rho g_z}$$

$$\underline{\underline{\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} = \frac{1}{\mu}(\frac{\partial P}{\partial z}) = K}}$$

(b)

Let $v_z = W(1 - \frac{x^2}{a^2} - \frac{y^2}{b^2})$

$$-W(\frac{2}{a^2} + \frac{2}{b^2}) = K$$

$$W = \frac{-K}{(\frac{2}{a^2} + \frac{2}{b^2})} = \frac{-K}{(\frac{2a^2 + 2b^2}{a^2 b^2})} = -\frac{a^2 b^2 K}{2a^2 + 2b^2}$$

$$\underline{\underline{v_z = W(1 - \frac{x^2}{a^2} - \frac{y^2}{b^2}) = -\frac{a^2 b^2 K}{2a^2 + 2b^2}(1 - \frac{x^2}{a^2} - \frac{y^2}{b^2})}}$$

(c)

For the maximum velocity, $(x, y) = (0, 0)$ 代入：

$$\underline{\underline{v_{z,\max} = -\frac{a^2 b^2 K}{2a^2 + 2b^2}}}$$

For the average velocity, calculate the volumatric flow rate first, which is,

$$Q = \iint v_z dA = \iint -\frac{a^2 b^2 K}{2a^2 + 2b^2}(1 - \frac{x^2}{a^2} - \frac{y^2}{b^2})dxdy$$

Let $x = au$, $y = bv$

$$J(u,v) = \begin{vmatrix} \dfrac{\partial x}{\partial u} & \dfrac{\partial x}{\partial v} \\ \dfrac{\partial y}{\partial u} & \dfrac{\partial y}{\partial v} \end{vmatrix} = \begin{vmatrix} a & 0 \\ 0 & b \end{vmatrix} = ab$$

原式：

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 \rightarrow u^2 + v^2 = 1$$

$$Q = \iint -\frac{a^2 b^2 K}{2a^2 + 2b^2}(1 - \frac{x^2}{a^2} - \frac{y^2}{b^2})dxdy = -\frac{a^3 b^3 K}{2a^2 + 2b^2}\iint(1 - u^2 - v^2)dudv$$

$$= -\frac{a^3 b^3 K}{2a^2 + 2b^2}\int_0^{2\pi}\int_0^1 (1 - r^2)rdrd\theta = -\frac{a^3 b^3 \pi K}{4a^2 + 4b^2}$$

The average velocity can be calculated as,

$$v_z = \frac{Q}{\pi ab} = -\frac{a^2 b^2 K}{4a^2 + 4b^2}$$

Problem 2

【Solution】

(a)

$$\delta[=]L \qquad\qquad x[=]L \qquad\qquad U[=]\frac{m}{s}[=]\frac{L}{T}$$

$$\mu[=]\frac{kg}{m\cdot s}[=]\frac{M}{LT} \qquad \rho[=]\frac{kg}{m^3}[=]\frac{M}{L^3} \qquad a[=]\frac{m}{s}[=]\frac{L}{T}$$

Fundamental units：M, L, T

Total variable：$\delta, x, U, \mu, \rho, a$

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 ρ, U, x

For π_1

$$\pi_1 = \delta\rho^a U^b x^c$$

$$L\cdot(ML^{-3})^a \cdot(LT^{-1})^b \cdot(L)^c = 1$$

$$\begin{cases} L:1-3a+b+c=0 \\ T:-b=0 \\ M:a=0 \end{cases} => \begin{cases} a=0 \\ b=0 \\ c=-1 \end{cases}$$

$$\pi_1 = \frac{\delta}{x}$$

For π_2

$$\pi_2 = \mu\rho^d U^e x^f$$

$$(ML^{-1}T^{-1})\cdot(ML^{-3})^d \cdot(LT^{-1})^e \cdot(L)^f = 1$$

$$\begin{cases} L:-1-3d+e+f=0 \\ T:-1-e=0 \\ M:1+d=0 \end{cases} => \begin{cases} d=-1 \\ e=-1 \\ f=-1 \end{cases}$$

$$\pi_2 = \frac{\mu}{\rho U x}$$

For π_3

$$\pi_3 = a\rho^g U^h x^i$$

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

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

$$\underline{\underline{\pi_3 = \frac{a}{U}}}$$

(b)

$$\pi_1 = \frac{\delta}{x} = dimensionless\ boundary\ layer\ thickness$$

$$\pi_2 = \frac{\mu}{\rho U x} = \frac{1}{Reynolds\ number} = \frac{viscous\ force}{inertial\ force}$$

$$\pi_3 = \frac{a}{U} = \frac{1}{Mach\ number} = \frac{speed\ of\ sound}{speed\ of\ fluid}$$

(Mach number 定義可參考：Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass Transfer*, 5th ed.; p 9~10，為流體速度與音速之比值。)

(c)

For Reynolds number,

$$Re = \frac{\rho U x}{\mu} = \frac{1.165 \times 30 \times 1}{1.86 \times 10^{-5}} = 1.88 \times 10^6$$
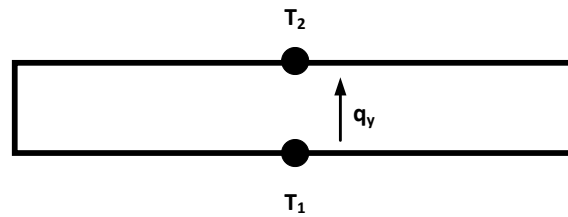
For Mach number,

$$M = \frac{U}{a} = \frac{30}{349} = 0.086$$

Reynolds number is the dominating parameter to determine the boundary layer thickness.

Problem 4

【Solution】

(a)

Fourier's law of conduction is,

$$q = -k\nabla T$$

(b)

Assume only y-direction conduction,

$$q_y = -k\frac{dT}{dy}$$

For constant cross-sectional area and steady state,

$$q_k \int_0^L dy = -k\int_{T_1}^{T_2} dT$$

$$q_k = \frac{k(T_1 - T_2)}{L} = \frac{Q}{A}$$

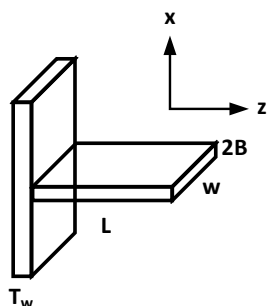$$\frac{3}{930} = \frac{k(26-24)}{0.64} \text{ , } k = 1.032\times10^{-3} \ (W/cm\cdot K)$$

(本題改編自：Bird, R.; Stewart, W.; Lightfoot, E. _Transport Phenomena_, 2nd ed.; p 270,

Example 9.1-1.)

Problem 5

【Solution】

(a)

By energy balance of the fin area,

$$2BWq_z|_z - 2BWq_z|_{z+dz} - h(2Wdz)(T-T_a) = 0$$

同除 $2BWdz \to 0$

$$\frac{-dq_z}{dz} - \frac{h}{B}(T-T_a) = 0$$

$\because q_z = -k\dfrac{dT}{dz}$

$$\frac{d^2T}{dz^2} - \frac{h}{kB}(T-T_a) = 0$$

Let $\theta = \dfrac{T-T_a}{T_w-T_a}$, $\zeta = \dfrac{z}{L}$, $N^2 = \dfrac{hL^2}{kB}$

$$\frac{d^2\theta}{d\zeta^2} - N^2\theta = 0 \begin{cases} z=0, T=T_w \to \zeta=0, \theta=1 \\ z=L, \dfrac{dT}{dz}=0 \to \zeta=1, \dfrac{d\theta}{d\zeta} \end{cases}$$

$$\theta = c_1\sinh(N\zeta) + c_2\cosh(N\zeta) \begin{cases} c_2 = 1 \\ c_1 = -\tanh(N) \end{cases}$$

$$\theta = -\tanh(N)\sinh(N\zeta) + \cosh(N\zeta) = \cosh(N\zeta) - \frac{\sinh(N)}{\cosh(N)}\sinh(N\zeta)$$

$$= \frac{\cosh(N\zeta)\cosh(N) - \sinh(N\zeta)\sinh(N)}{\cosh(N)} = \frac{\cosh(N-N\zeta)}{\cosh(N)} = \frac{\cosh[N(1-\zeta)]}{\cosh(N)}$$

(Note, $\cosh(a)\cosh(b) - \sinh(a)\sinh(b) = \cosh(a-b) = \cosh(b-a)$)

$$\theta = \frac{\cosh[N(1-\zeta)]}{\cosh(N)} \quad , \quad \frac{T-T_a}{T_w-T_a} = \frac{\cosh[\sqrt{\frac{hL^2}{kB}}(1-\frac{z}{L})]}{\cosh\sqrt{\frac{hL^2}{kB}}}$$

(b)

For the effectiveness of the fin, by definition,

$$\eta = \frac{actual\ rate\ of\ heat\ loss\ from\ the\ fin}{rate\ of\ heat\ loss\ from\ an\ isothermal\ fin\ at\ T_w}$$

$$\eta = \frac{2\times\int_0^W\int_0^L h(T-T_a)dzdy}{2\times\int_0^W\int_0^L h(T_w-T_a)dzdy} = \frac{\int_0^W\int_0^1 \theta d\zeta dy}{\int_0^W\int_0^1 d\zeta dy} = \frac{\int_0^1 \frac{\cosh[N(1-\zeta)]}{\cosh(N)}d\zeta}{\int_0^1 d\zeta}$$

$$= \frac{1}{\cosh(N)}\{\frac{-1}{N}\sinh[N(1-\zeta)\}\Big|_0^1 = \frac{\tanh(N)}{N}$$

(※此題題目所需求出之 **effectiveness** 是根據 **Bird** 原文書中之定義給出，與 **3W** 之 **efficiency** 定義相同，皆是以實際/最大熱傳速率作為定義，並沒有寫錯。)

(c)
By the result of (a),

$$\frac{T-T_a}{T_w-T_a} = \frac{\cosh[\sqrt{\frac{hL^2}{kB}}(1-\frac{z}{L})]}{\cosh\sqrt{\frac{hL^2}{kB}}}$$

$$\frac{T_1-T_a}{T_w-T_a} = \frac{\cosh[\sqrt{\frac{hL^2}{kB}}(1-\frac{L}{L})]}{\cosh\sqrt{\frac{hL^2}{kB}}} = \frac{\cosh(0)}{\cosh\sqrt{\frac{hL^2}{kB}}}$$

$$\frac{500-T_a}{350-T_a} = \frac{\cosh(0)}{\cosh\sqrt{\frac{120\times 0.2^2}{60\times\frac{0.08}{12}}}} \quad , \quad T_a = 510\ (^\circ\text{F})$$

(本題組改編自：**Bird, R.; Stewart, W.; Lightfoot, E.** *Transport Phenomena*, **2nd ed.; p 307~309** 之示範與 **p 309~310, Example 10.7-1.**

3W 中 **efficiency** 之定義可參考：**Welty, J.; Rorrer, G.; Foster, D.** *Fundamentals of Momentum, Heat, and Mass Transfer*, **5th ed.; p 237.**)

111 年中興單操輸送

Problem 1

【Solution】

$\because D_{tank} \gg D_{jet}$, by pseudo-steady state mass balance,

$$-\rho A_{jet} V = \frac{d(\rho A_{tank} h)}{dt}$$

$$-\rlap{/}{\rho}(\frac{\pi}{4} D_{jet}^2)V = \rlap{/}{\rho}(\frac{\pi}{4} D_{tank}^2)\frac{dh}{dt}$$

$$\int_{h_0}^{h} \frac{1}{\sqrt{h}} dh = -\int_0^t \frac{\sqrt{2g}D_{jet}^2}{D_{tank}^2}$$

$$2(\sqrt{h_0} - \sqrt{h}) = \frac{\sqrt{2g}D_{jet}^2}{D_{tank}^2}t$$

$$\sqrt{h} = \sqrt{h_0} - \frac{\sqrt{2g}D_{jet}^2}{2D_{tank}^2}t = \sqrt{1.2} - \frac{\sqrt{2\times9.8}\times(1.3\times10^{-2})^2}{2\times0.9^2}t = \underline{\underline{1.09 - 4.62\times10^{-4}t}}$$

(本題改編自：**Nakayama Y.** *Introduction to Fluid Mechanics*, **2nd ed; p 66~68.**)

Problem 2

【Solution】

(a)

Assume：

(1) Fully-developed in r-direction

(2) $v_r = v_\theta = 0$

(3) Gravity effect is negligible

(4) Constant ρ and μ

(5) Steady state

By the equation of continuity,

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

$$\frac{\partial v_z}{\partial z} = 0 \text{，} v_z = f(t, r, \theta, z)$$

By shell balance of momentum,

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

同除 $drd\theta dz \to 0$

$$-\frac{\partial(r\rho v_z v_z)}{\partial z} - \frac{\partial(r\tau_{rz})}{\partial r} - \frac{\partial(rp)}{\partial z} = 0$$

$$-\frac{\partial(r\tau_{rz})}{\partial r} = \frac{\partial p}{\partial z}r \text{，} \tau_{rz} = -\frac{r}{2}(\frac{\partial p}{\partial z}) + \frac{c_1}{r}$$

$\because r = 0, \dfrac{dv_z}{dr} = 0$

$$c_1 = 0$$

$$\tau_{rz} = -\mu\frac{dv_z}{dr} = -\frac{r}{2}(\frac{\partial p}{\partial z}) \text{，} v_z = \frac{r^2}{4\mu}(\frac{\partial p}{\partial z}) + c_2$$

$\because r = R, v_z = 0$

$$c_2 = -\frac{R^2}{4\mu}(\frac{\partial p}{\partial z})$$

$$v_z = \frac{R^2}{4\mu}(\frac{\partial p}{\partial z})[(\frac{r}{R})^2 - 1]$$

For the average velocity,

$$V = \frac{\int_0^{2\pi}\int_0^R v_z r\,dr\,d\theta}{\int_0^{2\pi}\int_0^R r\,dr\,d\theta} = \frac{R^2}{8\mu}(\frac{-\partial p}{\partial z})$$

(b)

$$\tau_w[=]N/m^2 = \frac{kg\cdot m}{s^2 m^2} = MT^{-2}L^{-1}$$

$$V[=]\frac{m}{s}[=]\frac{L}{T} \quad \mu[=]\frac{kg}{m\cdot s}[=]\frac{M}{LT} \quad \rho[=]\frac{kg}{m^3}[=]\frac{M}{L^3}$$

$$\varepsilon[=]L \qquad D[=]L$$

Fundamental units：M,L,T

Total variable：$\tau_w,V,\mu,\rho,\varepsilon,D$

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 ρ,D,V

For π_1

$$\pi_1 = \varepsilon\rho^a D^b V^c$$

$$L\cdot(ML^{-3})^a\cdot(L)^b\cdot(LT^{-1})^c = 1$$

$$\begin{cases}L:1-3a+b+c=0\\T:-c=0\\M:a=0\end{cases} => \begin{cases}a=0\\b=-1\\c=0\end{cases}$$

$$\pi_1 = \frac{\varepsilon}{D}$$

For π_2

$$\pi_2 = \mu\rho^d D^e V^f$$

$$(ML^{-1}T^{-1}) \cdot (ML^{-3})^d \cdot (L)^e \cdot (LT^{-1})^f = 1$$

$$\begin{cases} L: -1-3d+e+f=0 \\ T: -1-f=0 \\ M: 1+d=0 \end{cases} => \begin{cases} d=-1 \\ e=-1 \\ f=-1 \end{cases}$$

$$\underline{\underline{\pi_2 = \frac{\mu}{\rho VD}}}$$

For π_3

$$\pi_3 = \tau_w\rho^g D^h V^i$$

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

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

$$\underline{\underline{\pi_3 = \frac{\tau_w}{\rho V^2}}}$$

(c)

$$\pi_1 = \frac{\varepsilon}{D} = relative\ roughness$$

$$\pi_2 = \frac{\mu}{\rho VD} = \frac{1}{Reynolds\ number} = \frac{viscous\ force}{inertial\ force}$$

$$\pi_3 = \frac{\tau_w}{\rho V^2} = C_D = drag\ coefficient = \frac{drag\ force}{inertial\ force}$$

$$(正確之 C_D = \frac{\tau_w}{\frac{1}{2}\rho V^2}，差一個常數，但物理意義相同)$$

Problem 4
【Solution】

$$\text{Fourier's law of conduction：} \underline{\underline{q = -k\nabla T}}$$

$$\text{Thermal diffusivity：} \alpha = \frac{k}{\rho C_p} = \frac{heat\ transfer\ rate}{heat\ storage\ rate}$$

Problem 5
【Solution】

By dimensional analysis,

$$\Gamma[=](\frac{\delta^3 \rho^2 g}{\mu}) = m^3 \times \frac{kg^2}{m^6} \times \frac{m}{s^2} \times \frac{m \cdot s}{kg}[=]\frac{kg}{m \cdot s}$$
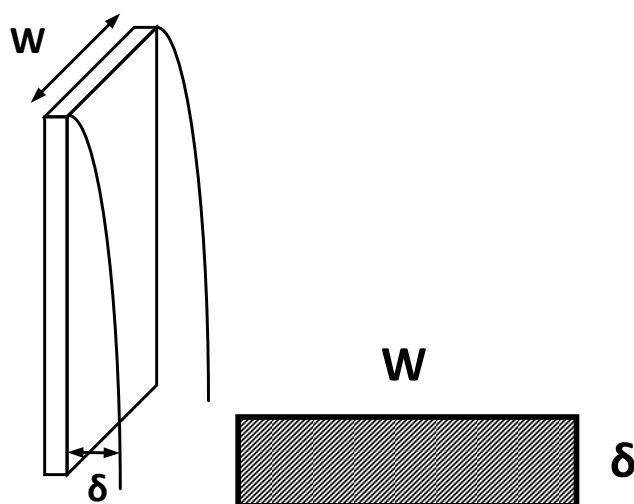
將數據代入：

$$\Gamma = (\frac{\delta^3 \rho^2 g}{3\mu}) = (\frac{\delta^3 \rho g}{3\upsilon}) = [\frac{(2\times10^{-3})^3 \times (1\times10^3) \times 9.8}{3\times 2\times10^{-4}}] = \underline{\underline{0.131\ (kg\ /\ m\cdot s)}}$$

To check whether the falling oil is laminar or not,

$$\text{Re} = \frac{<v>(\frac{4A}{P})}{\upsilon} = \frac{<v>(\frac{4\delta W}{W})}{\upsilon} = \frac{4<v>\delta}{\upsilon}$$

※Falling film 非傳統圓管，其直徑項需用等效水力直徑(hydraulic diameter)做計

算：

For $<v>$,

$$\rho <v> A = Q \text{ , } \rho <v> = \frac{Q}{A} = \frac{\Gamma}{\delta}$$

$$<v> = \frac{\Gamma}{\delta\rho} = \frac{0.131}{2\times10^{-3}\times1\times10^{3}} = 0.065 \ (m/s)$$

$$\text{Re} = \frac{4<v>\delta}{\upsilon} = \frac{4\times0.065\times2\times10^{-3}}{2\times10^{-4}} = 2.6$$

The falling oil is a laminar flow.

Problem 6
【Solution】

For velocity distribution, assume,

(1) $v_r = v_z = 0$

(2) $v_\theta = v_\theta(\not{t}, r, \theta, \not{z})$

By the equation of continuity,

$$\frac{1}{r}(\frac{\partial}{\partial r}\not{rv_r}) + \frac{1}{r}\frac{\partial v_\theta}{\partial \theta} + \frac{\partial \not{v_z}}{\partial z} = 0 \ , \ v_\theta \neq v_\theta(\theta)$$

(也可在假設時就假設與 θ 無關，因為對稱性)

By Navier Stokes equation,

$$\rho(\frac{\partial \not{v_\theta}}{\partial t} + \not{v_r}\frac{\partial \not{v_\theta}}{\partial r} + \frac{\not{v_\theta}}{r}\frac{\partial \not{v_\theta}}{\partial \theta} + \frac{\not{v_r v_\theta}}{r} + \not{v_z}\frac{\partial \not{v_\theta}}{\partial z})$$

$$= -\frac{1}{r}\frac{\not{\partial p}}{\partial \theta} + \mu[\frac{\partial}{\partial r}(\frac{1}{r}\frac{\partial}{\partial r}(rv_\theta)) + \frac{1}{r^2}\frac{\partial^2 \not{v_\theta}}{\partial \theta^2} + \frac{2}{r^2}\frac{\partial \not{v_r}}{\partial \theta} + \frac{\partial^2 \not{v_\theta}}{\partial z^2}] + \rho \not{g_\theta}$$

$$\frac{\partial}{\partial r}(\frac{1}{r}\frac{\partial}{\partial r}(rv_\theta)) = 0$$

$$v_\theta = C_1 r + \frac{C_2}{r}\begin{cases}r = mR, v_\theta = 0 \\ r = R, v_\theta = \Omega_0 R\end{cases}$$

$$C_1 = \frac{-\Omega_0}{m^2 - 1} \ , \ C_2 = \frac{m^2\Omega_0 R^2}{m^2 - 1}$$

$$v_\theta = -\frac{\Omega_0 r}{m^2 - 1} + \frac{m^2\Omega_0 R^2}{(m^2 - 1)}\frac{1}{r}$$

For temperature distribution, consider $T = T(r)$ only.

By the energy equation,

$$\rho C_p(\frac{\not{\partial T}}{\partial t} + \not{v_r}\frac{\partial T}{\partial r} + \frac{\not{v_\theta}}{r}\frac{\partial \not{T}}{\partial \theta} + \not{v_z}\frac{\partial \not{T}}{\partial z}) = k[\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial T}{\partial r}) + \frac{1}{r^2}\frac{\partial^2 \not{T}}{\partial \theta^2} + \frac{\partial^2 \not{T}}{\partial z^2}]$$

$$+2\mu\{(\frac{\partial \not{v_r}}{\partial r})^2 + [\frac{1}{r}(\frac{\partial v_\theta}{\partial \theta} + \not{v_r})]^2 + (\frac{\partial \not{v_z}}{\partial z})^2\} + \mu\{(\frac{\partial \not{v_z}}{\partial z} + \frac{1}{r}\frac{\partial \not{v_z}}{\partial \theta})^2 + (\frac{\partial \not{v_z}}{\partial r} + \frac{\partial \not{v_r}}{\partial z})^2 + [\frac{1}{r}\frac{\partial \not{v_r}}{\partial \theta} + r\frac{\partial}{\partial r}(\frac{v_\theta}{r})]^2\}$$

$$k[\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial T}{\partial r})] + \mu[r\frac{\partial}{\partial r}(\frac{v_\theta}{r})]^2 = 0$$

令 $v_\theta = Ar + \frac{B}{r}$ 代入：

$$\mu[r\frac{\partial}{\partial r}(\frac{v_\theta}{r})]^2 = \mu[-\frac{2B}{r^2}]^2 = \frac{4\mu B^2}{r^4}$$

代回：

$$k[\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial T}{\partial r})] + \frac{4\mu B^2}{r^4} = 0$$

$$T = \frac{-\mu B^2}{kr^2} + \alpha_1 \ln r + \alpha_2 \begin{cases} r = mR, T = T_k \\ r = R, T = T_1 \end{cases}$$

$$\alpha_1 = \frac{\frac{-\mu B^2}{kR^2}[1 - \frac{1}{m^2}] + T_k - T_1}{\ln m} \ , \ \alpha_2 = T_1 + \frac{\mu B^2}{kR^2} - \alpha_1 \ln R$$

$$T = \frac{-\mu B^2}{kr^2} + \alpha_1 \ln r + T_1 + \frac{\mu B^2}{kR^2} - \alpha_1 \ln R$$

$$T = \frac{\mu B^2}{kR^2}[1 - (\frac{R}{r})^2] + \alpha_1 \ln(\frac{r}{R}) + T_1 = \frac{\mu B^2}{kR^2}[1 - (\frac{R}{r})^2] + \{\frac{\frac{-\mu B^2}{kR^2}[1 - \frac{1}{m^2}] + T_k - T_1}{\ln m}\}\ln(\frac{r}{R}) + T_1$$

$$\text{where } B = \frac{m^2 \Omega_0 R^2}{(m^2 - 1)}$$

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Problem 7

【**Solution**】

(a)

In the specification of the pumps, the pressure at the pump inlet must exceed the vapor pressure of the working fluid by a certain value, which is the *net positive suction head, (NPSH):*

$$\text{NPSH} = \frac{1}{g}\left(\frac{P_a - P_v}{\rho} - h_{fs}\right) + Z_a$$

P_a = absolute pressure at surface of the reservoir.

P_v = vapor pressure

h_{fs} = friction in suction line

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

7th ed.; p 204.)

(b)

If the suction pressure is only slightly greater or even lower than the vapor pressure of the working fluid, some liquid may flash to vapor inside the pump, which is called cavitation, and will greatly reduce the pump capacity and cause severe corrosion.

(本題可參考：**McCabe, W.; Smith, J.; Harriott, P.** *Unit Operations of Chemical Engineering,*
7th ed.; p 204.)

(c)-(i)

By the volumetric flow rate, 500 c.c., the velocity in the circulation pipe is,

$$Q = \frac{\pi}{4}D^2 v$$

$$v = \frac{Q}{\frac{\pi}{4}D^2} = \frac{500 \times 10^{-6}}{\frac{\pi}{4} \times (25 \times 10^{-3})^2} = 1.02 \ (m/s)$$

The Reynolds number can thus be calculated as,

$$\mathrm{Re} = \frac{\rho v D}{\mu} = \frac{0.8 \times 1000 \times 1.02 \times 25 \times 10^{-3}}{0.5 \times 10^{-3}} = \underline{\underline{40743}}$$

(c)-(ii)

The Fanning's friction factor is calculated as,

$$f = \frac{0.079}{\mathrm{Re}^{0.25}} = \frac{0.079}{(40743)^{0.25}} = \underline{\underline{5.56 \times 10^{-3}}}$$

(c)-(iii)

If the total length of the pipe considered is L,

$$h_{fs} = \frac{4f}{2D}(Lv^2) = \frac{4 \times 5.56 \times 10^{-3}}{2 \times 25 \times 10^{-3}}(1.02^2 L) = 0.461 \ (m^2/s^2)$$

To convert the unit to m/m, use the specific gravity,

$$h_{fs,(m/m)} = \frac{0.461}{g}L \ (\frac{m^2}{s^2} \times \frac{s^2}{m}) = \frac{0.461}{9.8}L = 0.047L \ (m)$$

$$\underline{\underline{\frac{h_{fs(m/m)}}{L} = 0.047 \ (m/m)}}$$

(The head loss due to the friction in the pipe "per unit length")

(c)-(iv)

Let the total length of the pipe is l_p, by the definition and requirement of the NPSH,

$$NPSH = \frac{1}{g}(\frac{P_a - P_v}{\rho} - h_{fs}) + Z_a$$

$$3 = \frac{P_a - P_v}{\rho g} - h_{fs(m/m)} + Z_a$$

($h_{fs(m/m)}$ 在上一小題已經換過單位了)

$$3 = \frac{1.013 \times 10^5 - 1 \times 10^3}{0.8 \times 10^3 \times 9.8} - 0.047 l_p + \Delta z$$

$$\underline{\underline{\Delta z = 0.0417 l_p - 9.79 \ (m)}}$$

Problem 8

【Solution】

(a)

Consider a control volume in Cartesian coordinate, by mass balance,

$$\rho v_x \Delta y \Delta z|_x - \rho v_x \Delta y \Delta z|_{x+\Delta x} + \rho v_y \Delta x \Delta z|_y - \rho v_y \Delta x \Delta z|_{y+\Delta y} + \rho v_z \Delta x \Delta y|_z - \rho v_z \Delta x \Delta y|_{z+\Delta z} = \frac{\partial \rho (\Delta x \Delta y \Delta z)}{\partial t}$$

同除 $\Delta x \Delta y \Delta z \to 0$,

$$-\frac{\partial(\rho v_x)}{\partial x} - \frac{\partial(\rho v_y)}{\partial y} - \frac{\partial(\rho v_z)}{\partial z} = \frac{\partial \rho}{\partial t}$$

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

(b)

Consider a control volume in cylindrical coordinate, by mass balance,

$$\rho v_r r\Delta\theta\Delta z\big|_r - \rho v_r r\Delta\theta\Delta z\big|_{r+\Delta r} + \rho v_\theta \Delta r\Delta z\big|_\theta - \rho v_\theta \Delta r\Delta z\big|_{\theta+\Delta\theta} + \rho v_z r\Delta\theta\Delta r\big|_z - \rho v_z r\Delta\theta\Delta r\big|_{z+\Delta z}$$

$$= \frac{\partial\rho(r\Delta r\Delta\theta\Delta z)}{\partial t}$$

同除 $\Delta r\Delta\theta\Delta z \to 0$,

$$-\frac{\partial(\rho r v_r)}{\partial r} - \frac{\partial(\rho v_\theta)}{\partial\theta} - \frac{\partial(r\rho v_z)}{\partial z} = \frac{\partial r\rho}{\partial t}$$

同除 r

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

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一、

【Solution】

(a)

$\because G = H - TS$

$$S = -(\frac{\partial G}{\partial T})_P \, 代回$$

$$G = H + T(\frac{\partial G}{\partial T})_P \, , \quad H = G - T(\frac{\partial G}{\partial T})_P$$

$$(\frac{\partial H}{\partial T})_P = (\frac{\partial G}{\partial T})_P - (\frac{\partial T}{\partial T})_P(\frac{\partial G}{\partial T})_P - T(\frac{\partial^2 G}{\partial T^2})_P$$

$$\underline{\underline{C_P = -T(\frac{\partial^2 G}{\partial T^2})_P}}$$

(b)

$$C_P = -T(\frac{\partial^2 G}{\partial T^2})_P = -T(\frac{-27.435}{T} - 0.618 \times 10^{-2}) = 27.435 + 0.618 \times 10^{-2}T$$

$T = 1273 \, (K) \, 代入：$

$$C_P = 27.435 + 0.618 \times 10^{-2} \times 1273 = \underline{\underline{35.30 \, (J/mol-K)}}$$

(c)

By energy balance in open system,

$$\dot{n}(\Delta H + \frac{1}{2g_c}\Delta v^2 + \frac{g}{g_c}\Delta z) = \cancel{Q} + W$$

$$W = \dot{n}\Delta H = \dot{n}\int_{T_i}^{T_f} C_p dT$$

By entropy balance in open system,

$$\frac{d\cancel{S}}{dt}\Big|_{s.s} = \sum \dot{n}_i S_i + \cancel{\sum \frac{\dot{Q}}{T}} + \cancel{\dot{S}_{gen}}\;_{maximum\ work}$$

$$S_{inlet} - S_{outlet} = -\Delta S = 0$$

$$C_P \ln \frac{T_f}{T_i} - R \ln \frac{P_f}{P_i} = C_P \ln \frac{T_f}{T_i} - (C_P - C_V) \ln \frac{P_f}{P_i} = 0 \;,$$

$$\ln \frac{T_f}{T_i} - (1 - \frac{C_V}{C_P}) \ln \frac{P_f}{P_i} = 0$$

$$\ln \frac{T_f}{1473} - (1 - \frac{1}{1.36}) \ln \frac{1}{6} = 0 \;,\; T_f = 916.69\ (K)$$

For $\dot{n}$,

$$\dot{n} = \frac{4.6 \times 10^3}{28} = 164.3\ (mol/s)$$

代回：

$$W_{\max} = \dot{n} \int_{T_i}^{T_f} C_P dT$$

$$= 164.3 \int_{1473}^{916.69} (27.435 + 0.618 \times 10^{-2} T) dT = -3182264\ (J/s)$$

$$= \underline{\underline{-3182.3\ (kW)}}$$

二、

【Solution】

At 25℃ and 1 bar, at equilibrium,

$$f^L_{C_3Hl6} = f^V_{C_3Hl6} \text{ , } k_{C_3H_6}x_{C_3H_6} = y_{C_3H_6}\phi_{C_3H_6}P$$

For $\phi_{C_3H_6}$,

$$\phi_{C_3H_6} = \exp[\frac{1}{RT}\int_0^P (V - \frac{RT}{P})dP]$$

For V,

$$Z = \frac{PV}{RT} = 1 - 7.63\times10^{-3}P - 7.22\times10^{-5}P^2$$

$$V = RT(\frac{1}{P} - 7.63\times10^{-3} - 7.22\times10^{-5}P)$$

代回：

$$\phi_{C_3H_6} = \exp[\int_0^P (\frac{1}{P} - 7.63\times10^{-3} - 7.22\times10^{-5}P - \frac{1}{P})dP]$$

$$\phi_{C_3H_6} = \exp[\int_0^1 (-7.63\times10^{-3} - 7.22\times10^{-5}P)dP] = 0.992$$

$$k_{C_3H_6} = \frac{y_{C_3H_6}\phi_{C_3H_6}P}{x_{C_3H_6}} = \frac{1\times0.992\times1}{0.33\times10^{-4}} = 30071 \ (bar)$$

At 25℃ and 35 bar, at equilibrium,

For $\phi_{C_3H_6}$,

$$\phi_{C_3H_6} = \exp[\int_0^{35} (-7.63\times10^{-3} - 7.22\times10^{-5}P)dP] = 0.732$$

$$x_{C_3H_6} = \frac{y_{C_3H_6}\phi_{C_3H_6}P}{k_{C_3H_6}} = \frac{1\times0.732\times35}{30071} = \underline{\underline{8.53\times10^{-4}}}$$

化工動力學

三、

【Solution】

(a)

For CSTR, the condition at $0^\circ C$ must have lower reaction rate constant, thus will never be favored in view of the conversion, **so we focus on the condition at 77°C**.

For CSTR, the design equation is,

$$V = \frac{v_0 C_{A0} x_A}{-r_A}$$

By the rate equation,

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

Combine,

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

$$v_0 = 5 + 5 = 10 \ (L/\min)$$

$$C_{A0} = \frac{4}{2} = 2 \ (mol/L)$$

At $77^\circ C$,

$$\frac{k_{77}}{k_{27}} = e^{\frac{-E_a}{R}(\frac{1}{77+273.15} - \frac{1}{27+273.15})}$$

$$\frac{k_{77}}{0.07} = e^{\frac{-20\times10^3}{1.987}(\frac{1}{77+273.15} - \frac{1}{27+273.15})}$$

$$k_{77} = 8.41 \ (L/(mol\cdot\min))$$

代回：

$$200 = \frac{10x_A}{8.41\times 2(1-x_A)^2} \quad , \quad x_A = 0.947$$

For PFR, the design equation is,

$$V = \int_0^{x_A} \frac{v_0 C_{A0}}{-r_A} dx_A = \int_0^{x_A} \frac{v_0 C_{A0}}{k_{27} C_{A0}^2 (1-x_A)^2} dx_A = \int_0^{x_A} \frac{v_0}{k_{27} C_{A0} (1-x_A)^2} dx_A$$

$$800 = \int_0^{x_A} \frac{10}{0.07 \times 2 (1-x_A)^2} dx_A \text{ , } x_A = 0.918$$

Thus, CSTR with 77℃ is recommended.

(b)

For batch reactor, the design equation is,

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

$$\int_0^{x_A} \frac{1}{k C_{A0,b} (1-x_A)^2} dx_A = \int_0^t dt = t$$

For PFR,

$$\tau = \int_0^{x_A} \frac{1}{k C_{A0,P} (1-x_A)^2} dx$$

$$\frac{t}{\tau} = \frac{\int_0^{x_A} \dfrac{1}{k C_{A0,b} (1-x_A)^2} dx_A}{\int_0^{x_A} \dfrac{1}{k C_{A0,P} (1-x_A)^2} dx_A} = \frac{C_{A0,P}}{C_{A0,b}} = \frac{2}{1} = 2$$

$$t = 2\tau = 2 \times \frac{V}{v_0} = 2 \times \frac{800}{10} = 160 \text{ (min)}$$

For both cases, the times for the reaction to reach the same conversion as in

PFRs are the same, which are 160 minutes.

四、

【**Solution**】

Defind yield of i,

$$Y_i = \frac{r_i}{-r_A}$$

For B,

$$Y_B = \frac{r_B}{-r_A} = \frac{k_1 C_A - k_3 C_B - k_4 C_B}{k_1 C_A + k_2 C_A} = \frac{k_1 C_A - (k_3 + k_4) C_B}{(k_1 + k_2) C_A} = \underline{\underline{\frac{k_1 C_{A0}(1 - x_A) - (k_3 + k_4) C_B}{(k_1 + k_2) C_{A0}(1 - x_A)}}}$$

For C,

$$Y_C = \frac{r_C}{-r_A} = \frac{k_2 C_A + k_2 C_E + k_3 C_B}{(k_1 + k_2) C_A} = \underline{\underline{\frac{k_2 C_{A0}(1 - x_A) + k_2 C_E + k_3 C_B}{(k_1 + k_2) C_{A0}(1 - x_A)}}}$$
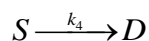
For D,

$$Y_D = \frac{r_D}{-r_A} = \frac{k_4 C_B}{(k_1 + k_2) C_A} = \underline{\underline{\frac{k_4 C_B}{(k_1 + k_2) C_{A0}(1 - x_A)}}}$$

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五、

【**Solution**】

※按照題意，家禽得了疾病(S)才會死亡(D)，因此最後一條反應式應改為：

$$S \xrightarrow{\ k_4\ } D$$

(a)

$$\underline{\underline{r_D = k_4[S]}}$$

(b)

$$r_S = k_1[P][H] - k_2[P][S] + 2k_2[P][S] - k_3[S] + -k_4[S]$$

$$= \underline{\underline{k_1[P][H] + k_2[P][S] - k_3[S] - k_4[S]}}$$

(c)

$$-r_P = k_1[P][H] + k_2[P][S] - k_3[S]$$

By pseudo-steady-state assumptions,

$$r_S = k_1[P][H] + k_2[P][S] - k_3[S] - k_4[S] = 0$$

$$[S] = \frac{k_1[P][H]}{k_3 + k_4 - k_2[P]} \text{ 代回：}$$

$$-r_P = k_1[P][H] + \frac{k_1 k_2[P]^2[H]}{k_3 + k_4 - k_2[P]} - \frac{k_1 k_3[P][H]}{k_3 + k_4 - k_2[P]}$$

$$= \frac{\cancel{k_1 k_3[P][H]} + k_1 k_4[P][H] - \cancel{k_1 k_2[P]^2[H]} + \cancel{k_1 k_2[P]^2[H]} - \cancel{k_1 k_3[P][H]}}{k_3 + k_4 - k_2[P]}$$

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

$$-\frac{d[P]}{dt} = \frac{k_1 k_4 [P][H]}{k_3 + k_4 - k_2[P]}$$

$$t = -\int_{[P_0]}^{\frac{1}{2}[P_0]} (\frac{k_3 + k_4 - k_2[P]}{k_1 k_4 [P][H]}) d[P] = \int_{\frac{1}{2}[P_0]}^{[P_0]} (\frac{k_3 + k_4 - k_2[P]}{k_1 k_4 [P][H]}) d[P]$$

$$t_{1/2} = \frac{(k_3 + k_4)}{k_1 k_4} \ln(2) - \frac{k_2}{k_1 k_4 [H]}([P_0] - \frac{1}{2}[P_0])$$

$$t_{1/2} = \frac{(5\times10^{-6} + 1\times10^{-7})}{1\times10^{-5} \times 1\times10^{-7}} \ln(2) - \frac{1\times10^{-7}}{1\times10^{-5} \times 1\times10^{-7}[H]} \times \frac{1}{2}[P_0]$$

$$t_{1/2} = 3.5\times10^6 - \frac{5\times10^4 [P_0]}{[H]} \ (hr)$$

※因 $\frac{k_3}{k_2} = \frac{k_3}{k_4} = 50$ ，若可視為 $k_3 >> k_2, k_4$ ，且可近似為：

$$-r_P = \frac{k_1 k_4 [P][H]}{k_3 + k_4 - k_2[P]} \approx \frac{k_1 k_4}{k_3}[P][H]$$

最終計算出之半生期為：

$$t_{1/2} = \frac{k_3 \ln(2)}{k_1 k_4 [H]} = \frac{3.46\times10^6}{[H]} \ (hr)$$

然而此種假設建立在：

$$k_3 >> k_2[P] \ , \ [P] << \frac{k_3}{k_2} = 50$$

也就是遠小於 50 隻家禽的數量才可做使用，以大規模來說較不合理。

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Problem 1

【Solution】

For a given point x, the change of the entropy is (isobaric),

$$dS = \frac{C_P}{T} dT$$

$$\Delta S_V = \int_{T_i}^{T_f} \frac{C_P}{T} dT = C_P \ln[\frac{\frac{(T_0 + T_L)}{2}}{T_0 - (\frac{T_0 - T_L}{L})x}]$$

(the subscript V means per unit volume)

From x = 0 to x = L, the total entropy change is,

$$\Delta S_A = \int_0^L \Delta S_V dx = \int_0^L C_P \ln[\frac{\frac{(T_0 + T_L)}{2}}{T_0 - (\frac{T_0 - T_L}{L})x}]dx$$

(the subscript A means per unit area)

$$\Delta S_A = \int_0^L C_P \ln[\frac{\frac{(T_0 + T_L)}{2}}{T_0 - (\frac{T_0 - T_L}{L})x}]dx = \int_0^L C_P\{[\ln(\frac{(T_0 + T_L)}{2}) - \ln[T_0 - (\frac{T_0 - T_L}{L})x]\}dx$$

For $\int_0^L \ln[T_0 - (\frac{T_0 - T_L}{L})x]dx$

$$\int_0^L \ln[T_0 - (\frac{T_0 - T_L}{L})x]dx = x\ln[T_0 - (\frac{T_0 - T_L}{L})x]\Big|_0^L - \int_0^L [\frac{-(\frac{T_0 - T_L}{L})x}{T_0 - (\frac{T_0 - T_L}{L})x}]dx$$

$$\int_0^L \ln[T_0 - (\frac{T_0 - T_L}{L})x]dx = L\ln(T_L) - \int_0^L[1 - \frac{T_0}{T_0 - (\frac{T_0 - T_L}{L})x}dx] = [L - \frac{T_0 L}{(T_0 - T_L)}\ln\frac{T_L}{T_0}]$$

$$\Delta S_A = C_P\{L[\ln(\frac{T_0 + T_L}{2})] - [L - \frac{T_0 L}{(T_0 - T_L)}\ln\frac{T_L}{T_0}]\}$$

(entropy change per unit area)

Problem 2

【**Solution**】

(a)

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

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

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

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

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

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

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

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

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

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

$$\frac{C_P}{T} = \frac{C_V}{T}(\frac{dT}{dT})_P + (\frac{\partial P}{\partial T})_V(\frac{\partial V}{\partial T})_P \; , \; \frac{C_P}{T} - \frac{C_V}{T} = (\frac{\partial P}{\partial T})_V(\frac{\partial V}{\partial T})_P$$

$\because dU = TdS - PdV$

$$(\frac{\partial U}{\partial V})_T = \pi_T = T(\frac{\partial S}{\partial V})_T - P = T(\frac{\partial P}{\partial T})_V - P$$

$$(\frac{\partial P}{\partial T})_V = \frac{\pi_T + P}{T}$$

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

(b)

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

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

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

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

Problem 3

【Solution】

(a)

$$-r_{CH_3OCH_3} = k_1[CH_3OCH_3] + k_2[CH_3^*][CH_3OCH_3]$$

By steady state assumption,

$$r_{CH_3^*} = k_1[CH_3OCH_3] - k_2[CH_3OCH_3][CH_3^*] + k_3[CH_2OCH_3^*] - k_4[CH_3^*][CH_2OCH_3^*] = 0 \quad --(1)$$

$$r_{CH_2OCH_3^*} = k_2[CH_3^*][CH_3OCH_3] - k_3[CH_2OCH_3^*] - k_4[CH_3^*][CH_2OCH_3^*] = 0 \quad --(2)$$

兩式相加：

$$k_1[CH_3OCH_3] - 2k_4[CH_3^*][CH_2OCH_3^*] = 0$$

$$[CH_2OCH_3^*] = \frac{k_1[CH_3OCH_3]}{2k_4[CH_3^*]}$$

代回(2)

$$k_2[CH_3^*][CH_3OCH_3] - \frac{k_1k_3[CH_3OCH_3]}{2k_4[CH_3^*]} - \frac{k_1}{2} = 0$$

$$2k_2k_4[CH_3^*]^2[CH_3OCH_3] - k_1k_4[CH_3^*] - k_1k_3[CH_3OCH_3] = 0$$

$$[CH_3^*] = \frac{k_1k_4 \pm \sqrt{k_1^2k_4^2 + 8k_1k_2k_3k_4[CH_3OCH_3]}}{2k_2k_4[CH_3OCH_3]} = \frac{k_1k_4 + \sqrt{k_1^2k_4^2 + 8k_1k_2k_3k_4[CH_3OCH_3]}}{2k_2k_4[CH_3OCH_3]}$$

$$(k_1k_4 < \sqrt{k_1^2k_4^2 + 8k_1k_2k_3k_4[CH_3OCH_3]} \text{，取正})$$

$$-r_{CH_3OCH_3} = k_1[CH_3OCH_3] + \frac{k_1k_4 + \sqrt{k_1^2k_4^2 + 8k_1k_2k_3k_4[CH_3OCH_3]}}{2k_4}$$

∵ k_1 (initiation) and k_4 (termination) are very small,

$$\underline{\underline{-r_{CH_3OCH_3} \approx \frac{\sqrt{8k_1k_2k_3k_4[CH_3OCH_3]}}{2k_4} = \sqrt{\frac{k_1k_2k_3}{2k_4}}[CH_3OCH_3]^{\frac{1}{2}}}} \quad , \quad \boxed{\begin{cases} n = \dfrac{1}{2} \\ k_0 = \sqrt{\dfrac{k_1k_2k_3}{k_4}} \end{cases}}$$

(b)

$$k_0 = A_0 e^{-\frac{E_0}{RT}} = \sqrt{\frac{k_1 k_2 k_3}{k_4}} = [(A_1 e^{-\frac{E_1}{RT}} A_2 e^{-\frac{E_2}{RT}} A_3 e^{-\frac{E_3}{RT}})(A_4 e^{-\frac{E_4}{RT}})^{-1}]^{\frac{1}{2}} = \frac{A_1 A_2 A_3}{A_4} e^{\frac{-\frac{(E_1+E_2+E_3-E_4)}{2}}{RT}}$$

$$E_0 = \frac{E_1 + E_2 + E_3 - E_4}{2} = \frac{80+15+38-8}{2} = \underline{\underline{62.5}} \ (kcal/mol)$$

Problem 4

【Solution】

For the rate equation,

$$-r_A = k_1 C_A + k_3 C_A = (k_1 + k_3) C_A$$

$$r_R = k_1 C_A - k_2 C_R$$

(a)

By the design equation of mixed flow reactor,

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

Combine,

$$\tau = \frac{C_{A0} - C_A}{(k_1 + k_3) C_A} = \frac{C_R}{k_1 C_A - k_2 C_R}$$

$$C_A = \frac{C_{A0}}{1 + (k_1 + k_3)\tau}$$

$$C_R = k_1 \tau C_A - k_2 \tau C_R \ , \quad C_R = \frac{k_1 \tau C_{A0}}{[1 + (k_1 + k_3)\tau](1 + k_2\tau)}$$

$$\frac{C_R}{C_{A0}} = \frac{k_1 \tau}{[1 + (k_1 + k_3)\tau](1 + k_2\tau)}$$

To determine the maximum concentration of R with τ_{opt},

$$\frac{d(\frac{C_R}{C_{A0}})}{d\tau} = \frac{k_1[1 + (k_1 + k_3)\tau](1 + k_2\tau) - k_1\tau[(k_1 + k_3)(1 + k_2\tau) + k_2(1 + k_1\tau + k_3\tau)]}{\{[1 + (k_1 + k_3)\tau](1 + k_2\tau)\}^2} = 0$$

$$[1 + (k_1 + k_3)\tau](1 + k_2\tau) - \tau[(k_1 + k_3)(1 + k_2\tau) + k_2(1 + k_1\tau + k_3\tau)] = 0$$

展開並整理：

$$k_1 k_2 \tau^2 + k_2 k_3 \tau^2 = 1 \ , \quad \tau = \tau_{opt} = \underline{\underline{\frac{1}{\sqrt{k_2(k_1 + k_3)}}}}$$

代回：

$$\frac{C_{R,\max}}{C_{A0}} = \frac{k_1 \tau_{opt}}{[1 + (k_1 + k_3)\tau_{opt}](1 + k_2\tau_{opt})}$$

$$\frac{C_{R,max}}{C_{A0}} = \frac{\frac{k_1}{\sqrt{k_2(k_1+k_3)}}}{[1+\frac{(k_1+k_3)}{\sqrt{k_2(k_1+k_3)}}](1+\frac{k_2}{\sqrt{k_2(k_1+k_3)}})} = \frac{\frac{k_1}{\sqrt{k_2(k_1+k_3)}}}{(1+\sqrt{\frac{k_1+k_3}{k_2}})(1+\sqrt{\frac{k_2}{k_1+k_3}})}$$

$$\frac{C_{R,max}}{C_{A0}} = \frac{\frac{k_1}{\sqrt{k_2(k_1+k_3)}}}{(1+\sqrt{\frac{k_1+k_3}{k_2}})(1+\sqrt{\frac{k_2}{k_1+k_3}})} = \frac{\frac{k_1}{\sqrt{k_2(k_1+k_3)}}}{(2+\sqrt{\frac{k_1+k_3}{k_2}}+\sqrt{\frac{k_2}{k_1+k_3}})} = \frac{k_1}{(2\sqrt{k_2(k_1+k_3)}+k_1+k_3+k_2)}$$

$$\frac{C_{R,max}}{C_{A0}} = \frac{k_1}{(2\sqrt{k_2(k_1+k_3)}+k_1+k_3+k_2)} = \underline{\underline{\frac{k_1}{(\sqrt{k_1+k_3}+\sqrt{k_2})^2}}}$$

(b)

By the design equation of PFR,

$$\frac{dC_A}{d\tau} = -(k_1+k_3)C_A$$

$$\frac{dC_R}{d\tau} = k_1 C_A - k_2 C_R$$

$$\int_0^\tau d\tau = \int_{C_{A0}}^{C_A} \frac{-1}{(k_1+k_3)C_A} dC_A \text{ , } C_A = C_{A0}e^{-(k_1+k_3)\tau}$$

代回：

$$\frac{dC_R}{d\tau} = k_1 C_{A0} e^{-(k_1+k_3)\tau} - k_2 C_R \text{ , } \frac{dC_R}{d\tau} + k_2 C_R = k_1 C_{A0} e^{-(k_1+k_3)\tau}$$

將 $I = e^{\int k_2 d\tau} = e^{k_2\tau}$ 乘入：

$$\frac{d(C_R e^{k_2\tau})}{d\tau} = k_1 C_{A0} e^{-(k_1+k_3-k_2)\tau}$$

$$C_R = -\frac{k_1}{k_1+k_3-k_2} C_{A0} e^{-(k_1+k_3)\tau} + C e^{-k_2\tau}$$

$\because \tau = 0, \ C_R = 0$

$$\frac{C_R}{C_{A0}} = -\frac{k_1}{k_1+k_3-k_2} e^{-(k_1+k_3)\tau} + \frac{k_1}{k_1+k_3-k_2} e^{-k_2\tau}$$

To determine the maximum concentration of R with τ_{opt},

$$\frac{d(\frac{C_R}{C_{A0}})}{d\tau} = \frac{k_1(k_1+k_3)}{k_1+k_3-k_2}e^{-(k_1+k_3)\tau} - \frac{k_1 k_2}{k_1+k_3-k_2}e^{-k_2\tau} = 0$$

$$e^{-(k_1+k_3-k_2)\tau} = \frac{k_2}{(k_1+k_3)}$$

$$\tau = \tau_{opt} = -\frac{\ln(\frac{k_2}{k_1+k_3})}{k_1-k_2+k_3} = \frac{\ln(\frac{k_1+k_3}{k_2})}{k_1-k_2+k_3}$$

代回：

$$\frac{C_{R,\max}}{C_{A0}} = -\frac{k_1}{k_1+k_3-k_2}e^{-(k_1+k_3)\tau_{opt}} + \frac{k_1}{k_1+k_3-k_2}e^{-k_2\tau_{opt}}$$

$$\frac{C_{R,\max}}{C_{A0}} = -\frac{k_1}{k_1+k_3-k_2}e^{-\frac{(k_1+k_3)}{k_1-k_2+k_3}\ln(\frac{k_1+k_3}{k_2})} + \frac{k_1}{k_1+k_3-k_2}e^{-\frac{k_2}{k_1-k_2+k_3}\ln(\frac{k_1+k_3}{k_2})}$$

$$\frac{C_{R,\max}}{C_{A0}} = \frac{k_1}{k_1+k_3-k_2}\left[\frac{k_1+k_3}{k_2}^{\frac{-k_2}{k_1-k_2+k_3}} - \frac{k_1+k_3}{k_2}^{\frac{-(k_1+k_3)}{k_1-k_2+k_3}}\right] = \frac{k_1}{k_1+k_3-k_2}\frac{k_1+k_3}{k_2}^{\frac{-k_2}{k_1-k_2+k_3}}\left[1 - \frac{k_1+k_3}{k_2}^{\frac{-(k_1-k+k_3)}{k_1-k_2+k_3}}\right]$$

$$\frac{C_{R,\max}}{C_{A0}} = \frac{k_1}{k_1+k_3-k_2}\frac{k_2}{k_1+k_3}^{\frac{k_2}{k_1-k_2+k_3}}\left[1 - \frac{k_2}{k_1+k_3}\right] = \frac{k_1}{k_1+k_3-k_2}\frac{k_2}{k_1+k_3}^{\frac{k_2}{k_1-k_2+k_3}}\left[\frac{k_1+k_3-k_2}{k_1+k_3}\right]$$

$$\frac{C_{R,\max}}{C_{A0}} = \frac{k_1}{k_1+k_3}(\frac{k_2}{k_1+k_3})^{\frac{k_2}{k_1-k_2+k_3}}$$

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Problem 1

【Solution】

(1) If there is one mixed reactor alone

By the design equation of mixed reactor,

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

By the rate equation,

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

Combined with the rate equation,

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

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

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

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

The total cost is,

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

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

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

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

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

【**Check if it's minimum**】

$$\frac{d^2C}{dv_0^2} = 20.02v_0 - 200.2$$

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

The total cost is,

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

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

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

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

此種情況因有 A 回流，造成整體 A 進口流率為：

$$v_0^{'} = v_0 + v_{recycle} > v_0$$

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

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

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

Problem 2

【**Solution**】

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

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

For the shift reaction,

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

(以此結果修正第一條反應式最終平衡結果)

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

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

$$y = 10-3x---(1)$$

By the result of the reforming reaction,

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

By the result of the reforming reaction,

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

將 $y = 10 - 3x$ 代回(2)：

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

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

代回(3)

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

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

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

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

$$\begin{cases} y_{CH_4} = \dfrac{x-y}{20} = \dfrac{2.597-2.207}{20} = 0.0195 \\[2mm] y_{H_2O} = \dfrac{5x-y-z}{20} = \dfrac{5 \times 2.597 - 2.207 - 1.213}{20} = 0.478 \\[2mm] y_{CO} = \dfrac{y-z}{20} = \dfrac{2.207-1.213}{20} = 0.0496 \\[2mm] y_{H_2} = \dfrac{3y+z}{20} = \dfrac{3 \times 2.207 + 1.213}{20} = 0.392 \\[2mm] y_{CO_2} = \dfrac{z}{20} = \dfrac{1.213}{20} = 0.061 \end{cases}$$

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

之結果代入 **shift** 反應做第二步計算，比如：

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

先算出 x, y，再考慮第二步反應算 z，則 $CO = y - z$

這是錯誤的解法，因為同時滿足兩個平衡的 CO 分壓是 $y - z$（兩條反應在同一反應器下進行），而

非滿足 **reforming** 反應的分壓為 y，滿足 **shift** 反應的分壓為 $y - z$；除非兩條反應分別在不同

環境中進行，則可以在第一個反應器先考慮 reforming 的平衡，到第二個反應器 shift 反應才開

始進行，此時再考慮下一步平衡反應。

Problem 3

【Solution】

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

$H_2O = W$

(a)

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

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

對圖，可得：

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

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

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

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

整理：

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

(b)

By the design equation of mixed flow reactor,

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

By the rate equation,

$$r_R = k_1 C_A C_B$$

$$r_S = k_2 C_R C_B$$

$$\frac{C_R}{k_1 C_A C_B} = \frac{C_S}{k_2 C_R C_B}$$

$$\frac{C_R}{C_S} = \frac{k_1 C_A}{k_2 C_R}$$

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

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

$$C_S = 0.7 C_{A0} - C_R \ 代回$$

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

$$C_R^2 + 0.375 C_{A0} C_R - 0.2625 C_{A0}^2 = 0$$

$$C_R = \frac{-0.375 C_{A0} \pm \sqrt{0.140625 C_{A0}^2 + 1.05 C_{A0}^2}}{2} = 0.358 C_{A0}$$

$$C_S = 0.7 C_{A0} - C_R = (0.7 - 0.358) C_{A0} = 0.342 C_{A0}$$

$$\frac{C_R}{C_S} = \frac{0.358}{0.342} = 1.05$$

※本題不可直接用題目所附圖，因題目附圖為 batch or plug flow reactor 專用，mixed flow reactor

適用的圖可參考：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 191, Figure 8.14.，與

題目附圖有些許差異。另外本題單純用算式計算的方式是令 A 的轉化率為 0.7(因無法得知 B 轉

化率為 0.7 時 A 轉化率為多少)，然而若是可用題目附圖近似或題目有給 mixed flow 適用的圖，

就可以將 0.7 視為 B 的轉化率，此時 $-\Delta C_B / C_{A0} = 1.4$ ，可自行嘗試做圖方法求出結果。

本題改編自 Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 202, Problem 8.8.

Problem 4
【Solution】

(a)
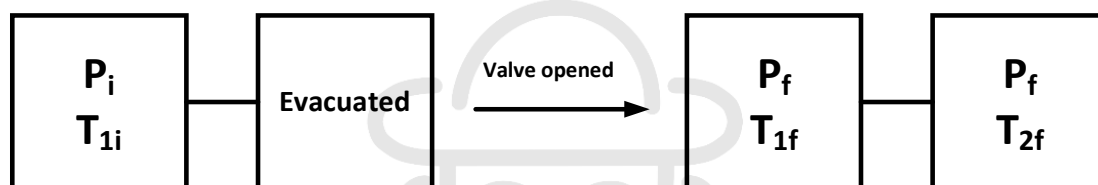
By mole balance of the system,

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

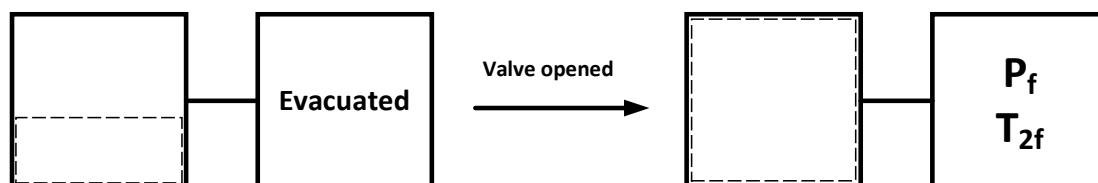$$\frac{40}{200} = P_f(\frac{1}{T_{1f}} + \frac{1}{T_{2f}})$$

By energy balance of the system,

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

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

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

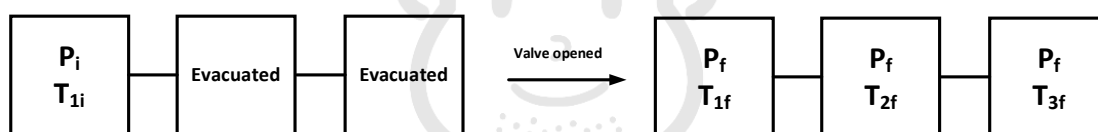the system can be assumed to undergo reversible, adiabatic expansion,

$$(\frac{T_{1f}}{T_{1i}})^{\frac{C_P^*}{R}} = (\frac{P_f}{P_i}) \quad , \quad (\frac{T_{1f}}{200})^{\frac{24.9}{8.3}} = (\frac{20}{40})$$

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

代回 mole balance,

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

(b)

By mole balance of the system,

$$\frac{P_i V_1}{R T_{1i}} + 0 + 0 = \frac{P_f V_1}{R T_{1f}} + \frac{P_f V_2}{R T_{2f}} + \frac{P_f V_3}{R T_{3f}}$$

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

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

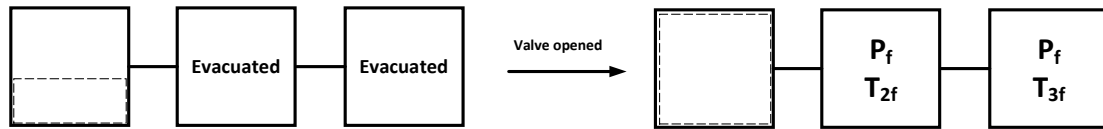$$\frac{40}{200} = P_f (\frac{1}{T_{1f}} + \frac{2}{T_{2f}})$$

By energy balance of the system,

$$\frac{P_i V_f}{R T_{1i}} C_V T_{1i} + 0 = \frac{P_f V_1}{R T_{1f}} C_V T_{1f} + \frac{P_f V_2}{R T_{2f}} C_V T_{2f} + \frac{P_f V_3}{R T_{2f}} C_V T_{2f}$$

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

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

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

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

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

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

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

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

p 76~79, Illustration 3.4-5.)

Problem 5
【Solution】

(a)

By the triple-product rule,

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

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

(b)

$$\frac{\kappa_S}{\kappa_T} = \frac{-\frac{1}{\underline{V}}(\frac{\partial \underline{V}}{\partial P})_{\underline{S}}}{-\frac{1}{\underline{V}}(\frac{\partial \underline{V}}{\partial P})_T}$$

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

$$\frac{\kappa_S}{\kappa_T} = \frac{(\frac{\partial \underline{S}}{\partial P})_{\underline{V}}}{(\frac{\partial \underline{S}}{\partial \underline{V}})_P} \times \frac{(\frac{\partial T}{\partial \underline{V}})_P}{(\frac{\partial T}{\partial P})_{\underline{V}}} = \frac{(\frac{\partial \underline{S}}{\partial P})_{\underline{V}}}{(\frac{\partial \underline{S}}{\partial \underline{V}})_P} \times \frac{(\frac{\partial P}{\partial T})_{\underline{V}}}{(\frac{\partial \underline{V}}{\partial T})_P} = \frac{(\frac{\partial \underline{S}}{\partial T})_{\underline{V}}}{(\frac{\partial \underline{S}}{\partial T})_P} = \underline{\underline{\frac{C_V}{C_P}}}$$

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

P276, Problem 6.8.)

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<u>**Problem 1**</u>
【**Solution**】

(a)

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

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

(b)

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

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

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

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

<u>**Problem 2**</u>
【**Solution**】

(a)

By the definition of equilibrium constant,

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

(b)

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

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

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

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

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

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

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

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

代回：

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

$$\underline{\underline{\ln\left[\frac{X_{Ae}}{X_{Ae}-x_A}\right] = \frac{(M+1)x_A}{M+X_{Ae}}k_1 t}}$$
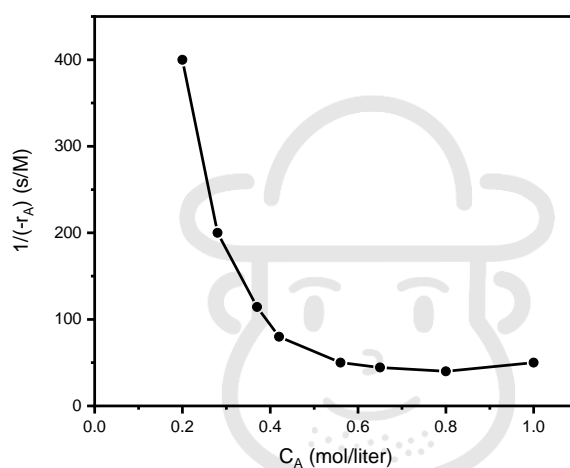
Problem 3

【Solution】

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

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

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

(a)

For PFR, by design equation,

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

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

By Simpson's rule,

$$V = \frac{0.15}{3} \left[\frac{1}{-r_A(0.2)} + \frac{4}{-r_A(0.35)} + \frac{6}{-r_A(0.5)} + \frac{4}{-r_A(0.65)} + \frac{1}{-r_A(0.80)} \right]$$

$$\approx \frac{0.15}{3} [400 + 4 \times 114.28 + 6 \times 50 + 4 \times 44.4 + 40] = \underline{\underline{68.7 \ (L)}}$$

(b)

For CSTR, by design equation,

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

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

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

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

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

Problem 4
【Solution】

(a)

For the reaction heat,

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

For the equilibrium constant,

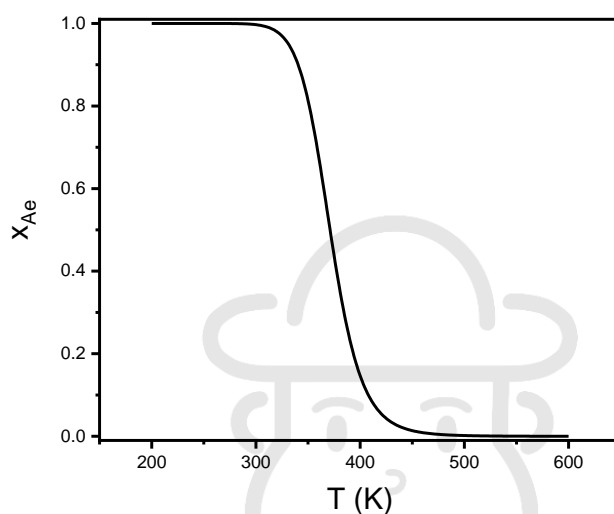$$K_{298} = \exp[-\Delta G_{298}^{\circ} / RT] = \exp[14840 / (8.314 \times 298)] = 399.3$$

By Van't Hoff equation,

$$\frac{\ln K}{\ln K_{298}} = \frac{-\Delta H_r}{R}(\frac{1}{T} - \frac{1}{298})$$

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

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

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

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

(b)

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

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

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

Problem 5

【**Solution**】

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

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

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

By mole balance of the each of the cylinder,

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

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

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

For cylinder 1, $P_i = 0$

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

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

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

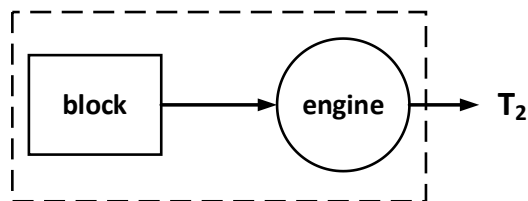**For cylinder 3**, $P_i = 1 \ (MPa)$, $T_i = 20 + 273.15 = 293.15 \ (K)$

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

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

p 95, Problem 3.19.)

Problem 6
【Solution】

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

$$dU = dQ + dW \quad , \quad \underset{solid, C_V \approx C_P}{C_P dT} = dQ + dW$$

By entropy balance on the system,

$$\frac{dS}{dt} = \sum \frac{\dot{Q}}{T_2} + \underset{maximum\ work}{\cancel{\dot{S}_{gen}}} \quad , \quad dQ = T_2 dS = T_2 \frac{C_P}{T} dT$$

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

$$dW = C_P (1 - \frac{T_2}{T}) dT$$

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

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

p 146, Problem 4.7.)

Problem 6

【Solution】

(a)

The Boyle temperature can be calculated as,

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

For inversion temperature, by definition,

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

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

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

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

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

代回：

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

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

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

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

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

The Boyle temperature is about 600 (K)

(b)

From the result of (a), we find,

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

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

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

p 276, Problem 6.15.)

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<u>**Problem 1**</u>

【**Solution**】

By the design equation of MFR,

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

By the rate equation,

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

Combine,

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

At 300 K,

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

$$K_{300K} = 10$$

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

$$\frac{v_{A0}}{T_0} = 0.06$$

At 400 K,

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

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

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

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

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

$$K_{400K} = 2.054$$

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

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

Problem 2
【Solution】

By the design of CSTR,

$$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{A0} - C_A}{k_1 C_A} \quad , \quad C_A = \frac{C_{A0}}{1 + k_1 \tau}$$

$$\tau = \frac{C_B}{k_1 C_A - k_2 C_B}$$

$$C_B = \frac{k_1 C_A}{1 + k_2 \tau} = \frac{k_1 \tau C_{A0}}{(1 + k_1 \tau)(1 + k_2 \tau)}$$

To determine the maximum concentration of B,

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

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

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

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

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

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

Problem 3

【Solution】

(1)

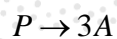|	P	$\leftrightarrow$	$3A$
Initial	100		0
Reaction	$-x$		$+3x$
Final	$100-x$		$3x$

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

The fraction of paradehyde decomposed is $\quad x_P = \dfrac{x}{100} = \dfrac{P_T - 100}{2 \times 100}$

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

(2)

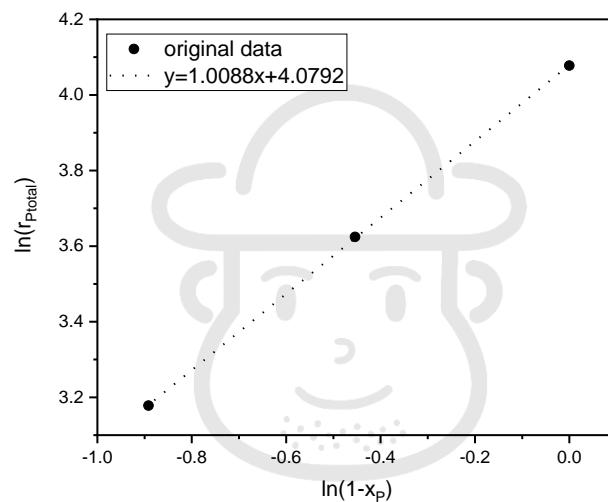$\because t \to \infty$ ， $x_P = 1$, the reaction is irreversible,

$$P \to 3A$$

By the rate expression $\quad -r_P = \dfrac{-dP_P}{dt} = kP_P^n = k[P_{P0}(1-x_P)]^n = \dfrac{1}{2}\dfrac{dP_{total}}{dt} = \dfrac{1}{2}r_{P_{total}}$

$$\frac{1}{2}r_{P_{total}} = k[P_{P0}(1-x_P)]^n$$

$$\ln(r_{P_{total}}) = \ln(k) + n\ln P_{P0} + n\ln(1-x_P) + \ln(2)$$

Plot $\ln(r_{P_{total}}) - \ln(1 + 2x_P)$:

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

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

(3)

For the reaction constant,

$$intercept = \ln(k) + n \ln P_{P0} + \ln(2) = \ln(k) + \ln(100) + \ln(2)$$

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

(4)

By Eyring equation,

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

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

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

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

∵ The reaction is unimolecuar-reaction (反應物係數為 1)

$$E_a = \Delta H^{\neq} + RT = 169445.4 + 8.314 \times (260 + 273.15) = \underline{\underline{173878.0 \ (J/mol)}}$$
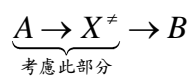
For the specific rate at 280℃, by Arrhenius equation,

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

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

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

$$\underbrace{A \rightarrow X^{\neq}}_{\text{考慮此部分}} \rightarrow B$$

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

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

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

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

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

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

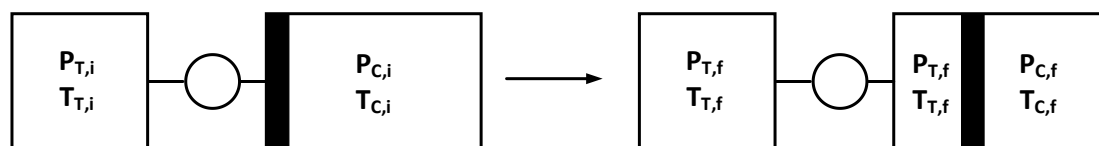$$E_a = \Delta H^{\neq} + 2RT$$

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

Problem 4

【Solution】

(a)

By total energy balance of nitrogen,

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

(tank+cylinder 一起看，系統不對外做功)

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

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

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

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

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

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

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

$$(\frac{T_{C,right,f}}{T_{C,i}}) = (\frac{P_{C,right,f}}{P_{C,i}})^{\frac{R}{C_P^*}}$$

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

By mole balance on the right of the tank,

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

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

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

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

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

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

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

整理：

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

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

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

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

(b)

As the same results of (a),

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

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

(c)

By entropy balance on the whole system,

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

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

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

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

(若考慮過程之後在 cylinder 左端之氮氣，其初始狀態與在 Tank 的氣體相同，而末狀態溫度與

壓力也與留在 Tank 中的氮氣相同，故可合併)

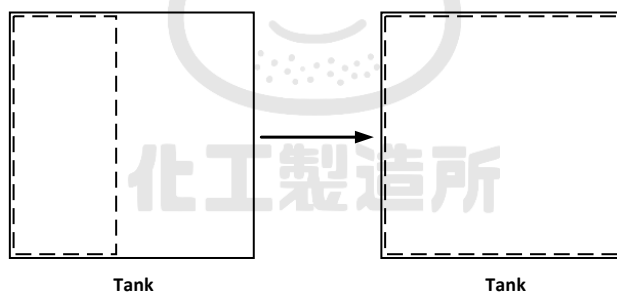$$n_{C,left,f} = \frac{P_{C,left,f}V_{C,left,f}}{RT_{C,left,f}} = \frac{0.2 \times 10^6 \times 0.196}{8.314 \times 421.7} = 11.16 \ (mole)$$

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

$$\dot{S}_{gen} = \Delta S = 25.42(29.3\ln\frac{421.7}{200+273.15} - 8.314\ln\frac{0.2}{0.4}) + 20.87(29.3\ln\frac{350.8}{15+273.15} - 8.314\ln\frac{0.2}{0.1})$$

$$= \underline{\underline{60.80 \ (J/K)}}$$
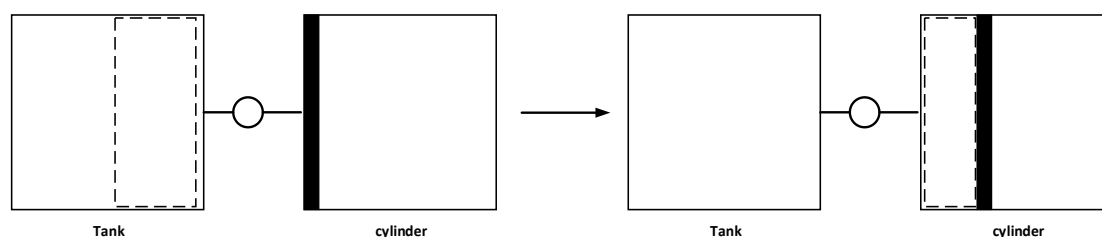
※事實上可不必計算 cylinder 右邊之 entropy generation，因其經歷之過程為"可逆"壓縮，結果

為 0，或若考慮誤差，則應非常接近 0

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

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

Tank   Tank

若系統改為過程後"移動至 cylinder 左半部"之氣體，則其示意圖為：

Tank　　　　cylinder　　　→　　　Tank　　　　cylinder

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

(1) 壓力改變，直至壓力與 cylinder 左半部已有的氣體壓力相同

(2) 溫度改變，直至溫度與 cylinder 左半部已有的氣體溫度相同

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

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

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

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

p 130~131, Illustration 4.5-2.)

Problem 5

【Solution】

By Gibbs-Duhem equation,

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

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

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

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

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

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

若繼續整理成較好看的形式：

$x_2 = 1 - x_1$ 代入：

$$\ln r_2 = -2A(1 - x_1 - 1) + \frac{2A - 3B}{2}[(1 - x_1)^2 - 1] + \frac{(3B - 4C)}{3}[(1 - x_1)^3 - 1] + C[(1 - x_1)^4 - 1]$$

$$= 2Ax_1 + \frac{2A - 3B}{2}(-2x_1 + x_1^2) + \frac{(3B - 4C)}{3}(-3x_1 + 3x_1^2 - x_1^3) + C(-4x_1 + 6x_1^2 - 4x_1^3 + x_1^4)$$

$$\underline{\underline{= (A + \frac{3B}{2} - 2C)x_1^2 - (B + \frac{8}{3}C)x_1^3 + Cx_1^4}}$$

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

p 459, Illustration 9.5-3 .)

109 年中興化熱化反

Problem 1

【**Solution**】

Assume the process obeys Arrhenius law,

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

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

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

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

Problem 2

【Solution】

For gaseous system,

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

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

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

For C_B,

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

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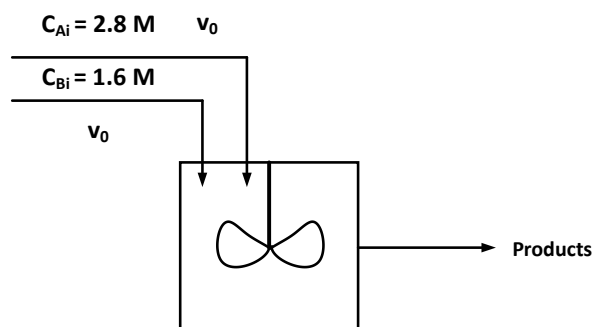
For X_B,

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

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

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

Problem 3
【Solution】

∵ The reaction is $A + 2B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$, and $C_{Bi} < C_{Ai}$, the limiting component is B.

By the design equation of mixed flow-reactor,

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

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

By the rate equation,

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

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

Combine,

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

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

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

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

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

Problem 4

【**Solution**】

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

By the design equation of CSTR,

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

By the rate equation,

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

Combine,

$$V = \frac{F_{A0}x_A}{-r_A} = \frac{F_{A0}x_A}{k_1 C_A^2 + k_2 C_A} = \frac{F_{A0}x_A}{k_1 C_A^2 (1-x_A)^2 + k_2 C_{A0}(1-x_A)}$$

$$V = \frac{10 \times 1 \times 0.6}{2 \times 1^2 (1-0.6)^2 + 1 \times 1 (1-0.6)} = \underline{\underline{8.33}} \ (dm^3)$$

For the overall selectivity of B,

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

※**Selectivity 可分為兩種：**

(1) Instantaneous selectivity

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

(2) Overall selectivity

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

雖然在此題兩者相同，然而實際上有所差別

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

Problem 5

【Solution】

(a)

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

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

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

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

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

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

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

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

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

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

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

$\because \alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_P$, $\kappa_T = \frac{-1}{V}(\frac{\partial V}{\partial P})_T$

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

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

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

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

(b)

For ideal gas, $PV = RT$,

$$\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_P = \frac{R}{PV}$$

$$\kappa_T = -\frac{1}{V}(\frac{\partial V}{\partial P})_T = -\frac{1}{V}(\frac{-RT}{P^2}) = \frac{RT}{P^2V}$$

代回：

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

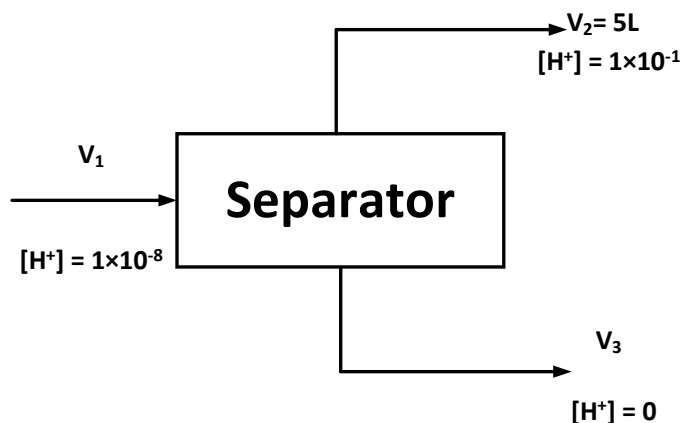**(本題可參考 Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;**

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

Problem 6

【Solution】

(a)

V₁ → Separator

V_1
$[H^+] = 1 \times 10^{-8}$

$V_2 = 5L$
$[H^+] = 1 \times 10^{-1}$

V_3
$[H^+] = 0$

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

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

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

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

For the calculation of minimum work required,

by energy balance,

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

By entropy balance,

$$\Delta S_{sys} = \frac{Q}{T} + \underset{minimum \ work}{\cancel{S_{gen}}} = S_2 - S_1$$

$Q = T(S_2 - S_1)$ 代回(定溫)：

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

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

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

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

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

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

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

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

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

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

代回：

$$W_{\min,2} = -RT[n_2(x_{a2}\ln x_{a2} + x_{w2}\ln x_{w2})]$$

$$= -8.314 \times (273.15 + 37)[277.26(1.8 \times 10^{-3}\ln 1.8 \times 10^{-3} + 0.9982\ln 0.9982)]$$

$$= 9434.04\ (J)$$

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

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

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

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

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

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

$$W_{min,1} = -RT[n_1(x_{a1} \ln x_{a1} + x_{w1} \ln x_{w1})]$$

$$= -8.314 \times (273.15 + 37)[2.76 \times 10^9 (1.8 \times 10^{-10} \ln 1.8 \times 10^{-10} + 0.99999999982 \ln 0.99999999982)]$$

$$= 30218.5 \ (J)$$

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

Problem 7
【**Solution**】

(a)

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

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

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

(b)

The result is the same as (a),

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

※觀察題目：

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

(c)

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

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一、熱力學

Problem 1
【Solution】

(a) False

For general case,

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

(b) False

By entropy balance of surrounding,

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

(c) True

For ideal engines,

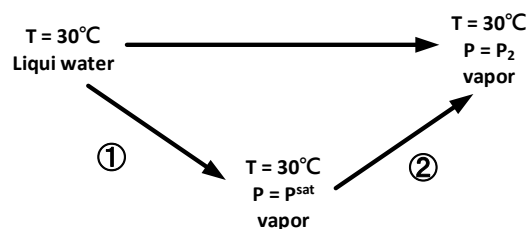$$\eta = 1 - \frac{T_C}{T_H}$$

(d) True

For expansion into a vacuum,

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

(e) False

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

Problem 2

【Solution】

(a)

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

$$\Delta \underline{H}_{vap} = 2431\ (J/g) = 2431 \times 18 = 43758\ (J/mol)$$

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

(b)

$$\Delta S = \Delta S_1 + \Delta S_2 = n(\frac{\Delta \underline{H}_{vap}}{T} - R\ln\frac{P_2}{P^{sat}})$$

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

(c)

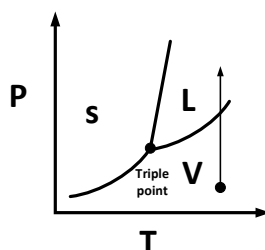$$\Delta G = \Delta H - T\Delta S = 87516 - 465.897(30 + 273.15) = \underline{\underline{-53720.9\ (J)}}$$

Problem 3
【Solution】

For this incompressible compound, the triple point is,

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

If the compound is compressed at 25°C, the path is as,

To determine the state of the compound at 35 bar, we need the fusion line, but lack of data.

Assume the compound is liquid at 25°C and 35 bar,

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

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

$$f^L = P^{sat} \exp[\frac{V(P - P^{sat})}{RT}] = 0.0106 \times \exp[\frac{\frac{205.85}{1.27} \times 10^{-6}(35 - 0.0106) \times 10^5}{8.314 \times (273.15 + 25)}] = \underline{\underline{0.0133 \; (bar)}}$$

Assume the compound is solid at 25°C and 35 bar,

$$P^{sub} = \frac{10^{-9}}{273.15 + 25} = 3.354 \times 10^{-12} \; (bar)$$

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

$$f^L = P^{sub} \exp[\frac{V(P - P^{sub})}{RT}]$$

$$= 3.354 \times 10^{-12} \times \exp[\frac{\frac{205.85}{1.27} \times 10^{-6}(35 - 3.354 \times 10^{-12}) \times 10^5}{8.314 \times (273.15 + 25)}] = \underline{\underline{4.217 \times 10^{-12} \; (bar)}}$$

※根據 Clausius-Clapeyron equation,

$$\frac{d\ln P^{sat}}{dT} = \frac{d(2.303\log_{10}P^{sat})}{dT} = \frac{2.303\times2146}{T^2} = \frac{\Delta H^{vap}}{RT^2}$$

$$\Delta H^{vap} = 2.303\times2146\times8.314 = 41089(J/mol)$$

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

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

<u>Problem 4</u>

【Solution】

(a)

For property M,

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

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

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

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

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

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

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

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

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

At constant T, P,

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

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

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

(b)

By Gibbs-Duhem equation,

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

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

If component 2 follows Henry's law,

$$P_2 = k_2 x_2$$

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

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

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

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

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

二、動力學

Problem 1
【Solution】

(a)

$$-r_A = k_1 C_A C_B$$

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

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

$$r_S = k_2 C_R C_B$$

(b)

For PFR,

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

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

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

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

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

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

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

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

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

For CSTR,

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

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

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

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

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

(c)

For the maximum intermediate product of C_R of PFR,

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

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

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

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

For the maximum intermediate product of C_R of CSTR,

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

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

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

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

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

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

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

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

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

Also,

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

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

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

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

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

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

the exit concentration of A,

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

For CSTR, the maximum concentration of R is independent of the concentration of

A, only depending on the kinetic parameters.

Problem 2

【Solution】

For PBR, the design equation is,

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

By the rate equation,

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

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

Combine,

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

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

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

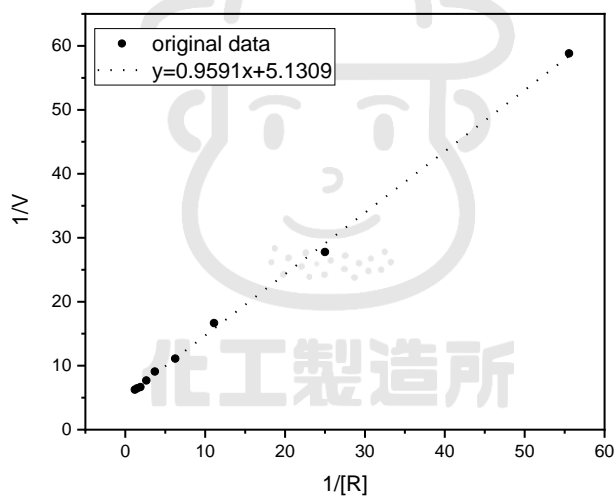中興 － 172

Problem 3

【**Solution**】

Rearrange the rate equation,

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

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

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

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

$$\begin{cases} slope = 0.9591 = \dfrac{K_m}{V_{\max}} \\[2mm] intercept = \dfrac{1}{V_{\max}} = 5.1309 \end{cases}$$

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

111 年中興化熱化反

Problem 1
【Solution】

Assume the process obeys Arrhenius law,

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

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

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

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

與 **109 年中興化熱化反 Problem 1 雷同**)

Problem 2
【Solution】

For gaseous system,

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

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

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

For C_B,

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

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

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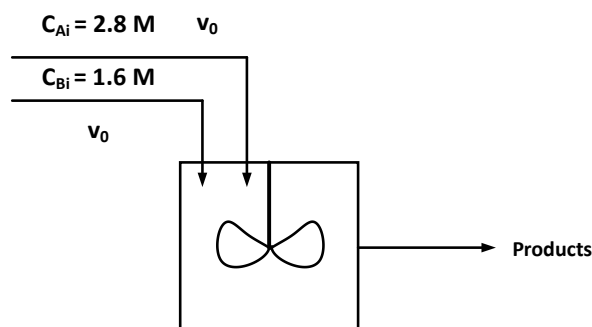
$$120 = 200(1-X_B)(\frac{400 \times 3}{300 \times 4}) \ , \ \underline{\underline{X_B = 0.8}}$$

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

與 **109 年中興化熱化反 Problem 2 雷同。**)

Problem 3
【Solution】

∵ The reaction is $A+2B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$, and $C_{Bi} < C_{Ai}$, the limiting component is B.

By the design equation of mixed flow-reactor,

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

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

By the rate equation,

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

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

Combine,

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

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

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

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

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

與 109 年中興化熱化反 Problem 3 雷同。)

Problem 4

【Solution】

By the design equation of CSTR,

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

By the rate equation,

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

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

Combine,

$$V = \frac{F_{A0}(1+1.2x_A)x_A}{kC_{A0}(1-x_A)}$$

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

Problem 5

【Solution】

By the first law of thermodynamics,

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

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

$$\Delta(v^2) = 2 \times [-1 \times C_p(T_f - T_i) + W] = 2 \times [1.1 \times (25 + 30) - 0.55 \times 10^3] = \underline{\underline{120.9\ (m^2/s^2)}}$$

Which is,

$$v_{inlet}^2 - v_{outlet}^2 = \underline{\underline{120.9\ (m^2/s^2)}}$$

Problem 6

【Solution】

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

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

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

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

將 $F = \alpha(L - L_0)T$ 代入：

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

(以 entropy 的觀點來說，溫度上升，亂度變大；若材料被拉伸，橡膠高分子排列雜亂無章逐漸朝向拉伸方向排列有序，造成亂度下降，以數學模型來則是 $dL > 0$，造成亂度下降。此結果將導致會有一個阻力抵抗拉伸應變，可用於推導楊氏係數、剪切模數等材料特性常數。)
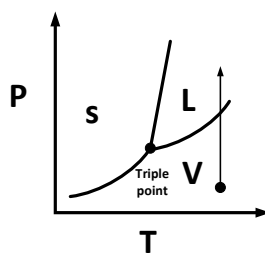
Problem 7
【Solution】

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

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

If the compound is compressed at 30℃, the path is as,

To determine the state of the compound at 20 bar, we need the fusion line, but lack of data.

Assume the compound is liquid at 30℃ and 20 bar,

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

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

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

Assume the compound is solid at 30℃ and 20 bar,

$$P^{sub} = \frac{10^{-8}}{273.15 + 30} = 3.298 \times 10^{-11} \ (bar)$$

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

$$f^L = P^{sub} \exp[\frac{V(P - P^{sub})}{RT}]$$

$$= 3.298 \times 10^{-11} \times \exp[\frac{\frac{300}{1.5} \times 10^{-6}(35 - 3.298 \times 10^{-11}) \times 10^5}{8.314 \times (273.15 + 30)}] = \underline{\underline{4.354 \times 10^{-11}}} \ (bar)$$

(本題與 110 年中興化熱化反，化熱部分-Problem 3 雷同)

Problem 8

【Solution】

For property θ,

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

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

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

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

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

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

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

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

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

At constant T, P,

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

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

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

112 年中興化熱化反

Problem 1

【Solution】

(A)

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

By pseudo-steady-state assumption,

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

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

By enzyme mass balance,

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

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

代回：

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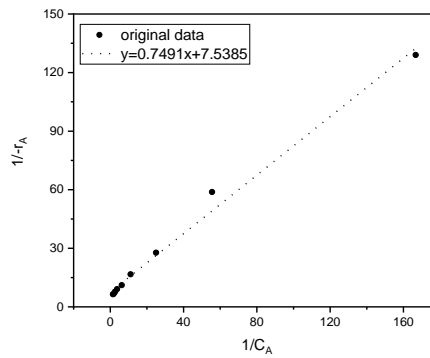
(B)

速率表示式取導數：

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

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

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

The data give can be reasonably fitted by the kinetic equation offered as the

Michaelis-Menten type. (算出來 R^2 為 0.9906)

By integration method, we have,

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

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

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

將任意 2 點代入(這裡代入 t = 4, t = 8 做示範)：

$$(1.2 - 0.38) + C_M \ln(\frac{1.2}{0.38}) = 0.02 \times 4k_3 \; - - - -(1)$$

$$(1.2 - 0.04) + C_M \ln(\frac{1.2}{0.04}) = 0.02 \times 8k_3 \; - - -(2)$$

解出此一元二次方程式：

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

若使用微分法的數據做計算，可得：

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

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

此二者差異來源為儘管看似符合 model，然而還是有誤差，因此不管是在微分抑

或積分都會受到取的點的不同而有不同的誤差大小(比方取的兩個點剛好 model

算出來的結果都比實際大，就會有偏大的誤差。)

Problem 2

【Solution】

(A)

By the design equation of PFR,

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

By the rate expression,

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

$$(\varepsilon = 0)$$

Combine,

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

(B)

By the design equation of PFR,

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

By the rate expression,

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

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

Combine,

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

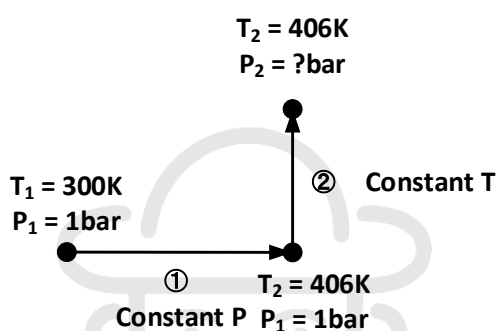$$C_{A0} = \frac{P_{A0}}{RT} = \frac{11.4 \times 0.55}{0.082 \times (649 + 273.15)} = 0.083 \ (mol/L)$$

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

Problem 3
【Solution】

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

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

（負號代表對外做功）

Problem 4
【Solution】

T₂ = 406K
P₂ = ?bar

T₁ = 300K
P₁ = 1bar

② **Constant T**

①

T₂ = 406K
Constant P P₁ = 1bar

【Process ①】

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

$$\Delta H_1 = nC_P \Delta T = 1 \times 30 \times (406 - 300) = 3180 \ (kJ)$$

$$Q_1 = nC_P \Delta T = 1 \times 30 \times (406 - 300) = 3180 \ (kJ)$$

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

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

【Process ②】

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

$$\Delta H_2 = nC_P \Delta T = 1 \times 30 \times 0 = 0 \ (kJ)$$

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

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

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

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

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

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

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

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

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

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

Problem 5
【Solution】

(a)

After the quenching process, the temperatures are determined by,

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

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

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

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

(b)

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

(c)

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