

104 年台大單操輸送

Problem 1

【Solution】

(a)

By the equation of continuity,

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

$\because \rho$ is constant

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

$v_x=0 \quad v_y=0$

$$v_z = f(x) \text{ only}$$

By shell balance of momentum,

$$\rho v_z v_z dx dy \Big|_z - \rho v_z v_z dx dy \Big|_{z+dz} + \tau_{xz} dy dz \Big|_x - \tau_{xz} dy dz \Big|_{x+dx} + p dx dy \Big|_z - p dx dy \Big|_{z+dz} + \rho g \sin \theta dx dy dz = 0$$

同除 $dx dy dz \rightarrow 0$

$$-\frac{\partial(\rho v_z v_z)}{\partial z} - \frac{\partial \tau_{xz}}{\partial x} - \frac{\partial p}{\partial z} + \rho g \sin \theta = 0$$

$\because v_z = v_z(x)$, 且上方接觸空氣，無壓降

$$\underline{\underline{-\frac{\partial \tau_{xz}}{\partial x} + \rho g \sin \theta = 0 \begin{cases} x=0, \tau_{xz}=0 \\ x=\delta, v_z=0 \end{cases}}}$$

(b)

(1) @ $x = x_0$, $\tau_{xz} = \tau$ (yield stress)

$$\tau = \rho g \sin \theta x_0 \quad , \quad x_0 = \frac{\tau}{\rho g \sin \theta}$$

(2) $x > x_0$, $\tau_{xz} > \tau$, $\tau_{xz} = \tau - \mu \frac{dv_z}{dx}$

$$\tau_{xz} = \tau_0 - \mu \frac{dv_z}{dx} = \rho g \sin \theta x$$

$$v_z = \frac{-1}{2\mu} \rho g \sin \theta \cdot x^2 + \frac{\tau}{\mu} x + c_2$$

$x = \delta, v_z = 0$ 代入

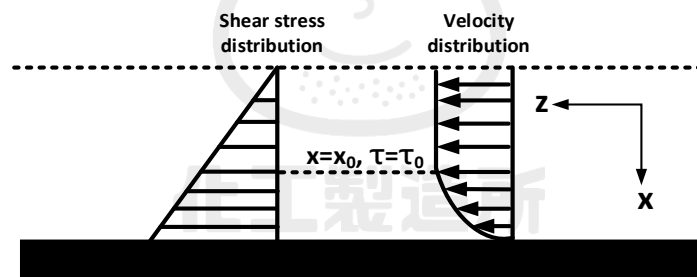
$$c_2 = \frac{\rho g \sin \theta}{2\mu} \delta^2 - \frac{\tau_0}{\mu} \delta$$

$$v_z = \frac{\rho g \delta^2 \sin \theta}{2\mu} \left[1 - \left(\frac{x}{\delta}\right)^2\right] - \frac{\tau \delta}{\mu} \left[1 - \frac{x}{\delta}\right]$$

(3) $x < x_0$, $\tau_{xz} < \tau$, $\frac{dv_z}{dx} = 0$, $v_z = v_z(x_0)$

$$\begin{aligned} v_z = v_z \Big|_{x_0} &= \frac{\rho g \delta^2 \sin \theta}{2\mu} \left[1 - \left(\frac{x_0}{\delta}\right)^2\right] - \frac{\tau \delta}{\mu} \left[1 - \frac{x_0}{\delta}\right] \\ &= \frac{\rho g \delta^2 \sin \theta}{2\mu} \left[1 - \left(\frac{\tau}{\delta \rho g \sin \theta}\right)^2\right] - \frac{\tau \delta}{\mu} \left[1 - \frac{\tau}{\delta \rho g \sin \theta}\right] \end{aligned}$$

依黏滯力與速度分布推導結果，可繪製如下：



(※有關賓漢流體黏滯力與速度分布，可參考社團補充檔案)

(c)

$$\begin{aligned} Q &= \int_0^\delta v_z dx = \int_0^{x_0} v_z dx + \int_{x_0}^\delta v_z dx \\ &= \left\{ \frac{\rho g \delta^2 \sin \theta}{2\mu} \left[1 - \left(\frac{x_0}{\delta} \right)^2 \right] - \frac{\tau \delta}{\mu} \left[1 - \frac{x_0}{\delta} \right] \right\} \cdot x_0 \\ &\quad + \frac{\rho g \delta^2 \sin \theta}{2\mu} \left[\frac{2}{3} \delta - x_0 + \frac{1}{3} \frac{x_0^3}{\delta^2} \right] - \frac{\tau \delta}{\mu} \left[\frac{\delta}{2} - x_0 + \frac{x_0^2}{\delta} \right] \\ &= \frac{\rho g \delta^2 \sin \theta}{2\mu} \left[\frac{2}{3} \delta - \frac{2x_0^3}{3\delta^2} \right] + \frac{\tau \delta}{2\mu} \left(\frac{x_0^2}{\delta} - \delta \right) \end{aligned}$$

$$\text{where, } x_0 = \frac{\tau}{\rho g \sin \theta}$$

(d)

$$F_z = \int_0^W \int_0^L \tau_{xz} \Big|_\delta dz dy = \underline{\underline{WL\delta\rho g \sin \theta}}$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 42-46.

以及：Geankoplis, C. *Transport Processes and Separation Process Principles*, 4th ed.; p 178.)

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Problem 2

【Solution】

By Hagen-Poiseuille equation,

$$Q = \frac{\pi R^4 \Delta P}{8\mu L} = \frac{\Delta P}{\frac{8\mu L}{\pi R^4}}$$

但其是在有條件下推導得到：

- (1) laminar flow
- (2) incompressible fluid
- (3) steady state
- (4) Newtonian flow
- (5) Neglecting end effect
- (6) No-slip condition
- (7) Tubular pipe with constant cross-sectional area
- (8) The fluid must behave as a continuum

因此此描述部分正確。

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

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Problem 3

【Solution】

- (1) Distillation : Separation based on different volatility, (d)
- (2) Extraction : Separation based on different solubility in two solvents, (b)
- (3) Chromatography : Separation based on different affinity with stationary and mobile phases, (e)
- (4) Crystallization : Based on the change of solubility in solvent with the change of equilibrium condition such as temperature or pressure, (c)
- (5) Absorption : Transferring substances by the concentration gradient from one phase to another, (a)



Problem 4

【Solution】

(a) By lumped capacity method,

$$0 - 0 + \dot{q}_i''(4\pi r_i^2) - h(4\pi r_o^2)(T - T_\infty) = \rho C_p \times \frac{4}{3}\pi(r_o^3 - r_i^3) \frac{\partial T}{\partial t}$$

將各數據代入整理：

$$\underline{\underline{1.57 \times 10^5 - 2.26 \times 10^3(T - 300) = 1.64 \times 10^6 \frac{dT}{dt}}}$$

(b) At steady state,

$$1.57 \times 10^5 - 2.26 \times 10^3(T - 300) = 0$$

$$\underline{\underline{T = 369.47 \text{ (K)}}}$$

(本題可參考：Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. *Fundamentals of Heat and Mass Transfer*, 6th ed.; p 48, Problem 1.48.)

Problem 5

【Solution】

根據題意，令 $h_x = ax^{\frac{1}{2}}$ ，則 average heat transfer coefficient, $\overline{h_L}$

$$\overline{h_L} = \frac{\int_0^L h_x dx}{L} = 2aL^{\frac{1}{2}}$$

則

$$\frac{Nu_L}{Nu_L} = \frac{(\frac{\overline{h_L} L}{k})}{(\frac{h_L L}{k})} = \frac{2aL^{\frac{1}{2}}}{aL^{\frac{1}{2}}} = 2$$

(本題可參考：Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. *Fundamentals of Heat and Mass Transfer*, 6th ed.; p 390, Problem 6.23.)

Problem 6

【Solution】

(a)

$$Gr \equiv \frac{\text{buoyant force}}{\text{viscous force}}$$

(b)

(1) $\frac{Gr_L}{Re_\infty^2}$ very large, free convection dominates

(2) $\frac{Gr_L}{Re_\infty^2}$ very small, forced convection dominates

(3) $\frac{Gr_L}{Re_\infty^2} \approx 1$, both should be considered

(c)

(1) $\frac{Gr_L}{Re_\infty^2}$ very large, $Nu = f(Pr, Gr)$

(2) $\frac{Gr_L}{Re_\infty^2}$ very small, $Nu = f(Pr, Re)$

(3) $\frac{Gr_L}{Re_\infty^2} \approx 1$, $Nu = f(Gr_L, Pr, Re)$

(d)

當 free convection 與 forced convection 方向一致，則兩者相加

當 free convection 與 forced convection 方向相反，則兩者相減

(本題可參考：Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. *Fundamentals of Heat and Mass Transfer*, 6th ed.; p 565/593.)

Problem 7**【Solution】**

$$\frac{C_{fx}}{2} = \frac{0.0288}{Re_x^{0.2}} = St \cdot Pr^{\frac{2}{3}} = \frac{Nu_x}{Re_x Pr} Pr^{\frac{2}{3}} = Nu_x Re_x^{-1} Pr^{-\frac{1}{3}}$$

$$\underline{\underline{Nu_x = 0.0288 Pr^{\frac{1}{3}} Re_x^{0.8}}}$$

For Nu_L

$$Nu_x = 0.0288 Pr^{\frac{1}{3}} Re_x^{0.8} = \frac{h_x x}{k}$$

$$h_x = \frac{0.0288 k Pr^{\frac{1}{3}} Re_x^{0.8}}{x} = 0.0288 k Pr^{\frac{1}{3}} \left(\frac{\rho < v >}{\mu} \right)^{0.8} x^{-0.2}$$

$$\overline{h_L} = \frac{\int_0^L h_x dx}{\int_0^L dx} = \frac{\int_0^L 0.0288 k Pr^{\frac{1}{3}} \left(\frac{\rho < v >}{\mu} \right)^{0.8} x^{-0.2} dx}{\int_0^L dx} = \frac{0.036 k Pr^{\frac{1}{3}} \left(\frac{\rho < v > L}{\mu} \right)^{0.8}}{L}$$

$$\underline{\underline{\frac{\overline{h_L} L}{k} = Nu_L = 0.036 Pr^{\frac{1}{3}} Re_L^{0.8}}}$$

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105 年台大單操輸送

Problem 1

【Solution】

(a) Newton's second law (conservation of momentum)

(b) Mole/mass balance

(c) 只有 pump 串聯會增加揚程(Δh)

$$\therefore \Delta h_{total} = a + bQ^2 + a + b\left(\frac{Q}{2}\right)^2 = 2a + \frac{5b}{4}Q^2$$

(d) $\varepsilon = \frac{\text{實際熱傳速率}}{\text{具有無限大熱傳面積時熱傳速率}}$

(e) $Bi = \frac{hL}{k_s} = \frac{\text{internal resistance}}{\text{external resistance}}$

$$Nu = \frac{hL}{k_f} = \frac{\text{heat convection rate}}{\text{heat conduction rate}} \text{ in radial direction}$$

兩者差異在於 Bi 之 *conductivity* 為固體，即考慮物體內部熱傳與外部流體對流之關係； Nu 之 *conductivity* 為流體，即考慮流體徑向熱傳導與對流之關係。

(f) *Free convection*：流體依靠密度差自然產生的對流機制

Forced convection：在外力(pump、風扇)作用下產生之對流機制

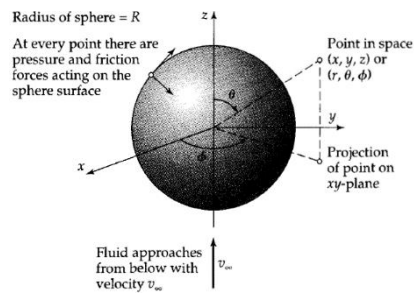
(本題可參考：

(a)(b)：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 80/744.

(d)(e)(f)：Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. *Fundamentals of Heat and Mass Transfer*, 6th ed.; p 686/376-377/560.)

Problem 2

【Solution】



(a)

To derive the equation of drag force on the bubble, we may use

$$\begin{cases} \tau_{rr} (\text{作用在} r \text{平面上} r \text{方向的力}) \\ \tau_{r\theta} (\text{作用在} r \text{平面上} \theta \text{方向的力}) \\ p (\text{壓力為正向力}) \end{cases}$$

(1) 流體為 z 方向流動，作用力作用於 r 平面上

(2) 對稱於 z 軸，不須考慮 ϕ 方向作用力

綜合以上，只需考慮 τ_{rr} 與 $\tau_{r\theta}$ 兩力

將 v_r, v_θ, v_ϕ 分別代入上述 stress

$$\tau_{rr} = -\mu \left[2 \frac{\partial v_r}{\partial r} \right], \quad v_r = v_\infty \left[1 - \left(\frac{R}{r} \right) \right] \cos \theta \text{ 代入}$$

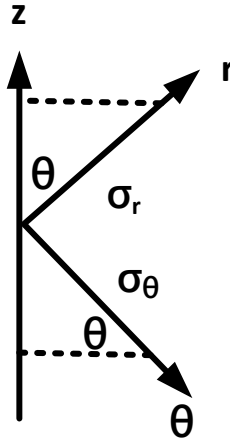
$$\tau_{rr} \Big|_{r=R} = \frac{-2\mu v_\infty R \cos \theta}{r^2} \Big|_{r=R} = \frac{-2\mu v_\infty \cos \theta}{R}$$

$$\tau_{r\theta} = -\mu \left[r \frac{\partial}{\partial r} \left(\frac{v_\theta}{r} \right) + \frac{1}{r} \frac{\partial v_r}{\partial \theta} \right]$$

$$\underline{\underline{\tau_{r\theta} = 0}}$$

(b)

定義座標



Stress in the flow direction,

$$\begin{aligned}
 F_t &= \iint \left(\underbrace{\sigma_r \cos \theta}_{\text{normal force}} - \underbrace{\sigma_\theta \sin \theta}_{\text{tangential force}} \right) dA \\
 &= \int_0^{2\pi} \int_0^\pi [-(\tau_{rr} + p)|_{r=R} \cos \theta - (-\tau_{r\theta})|_{r=R} \sin \theta] R^2 \sin \theta d\theta d\phi \\
 &= \int_0^{2\pi} \int_0^\pi [-(\tau_{rr} + p)|_{r=R} \cos \theta - (-\tau_{r\theta})|_{r=R} \sin \theta] R^2 \sin \theta d\theta d\phi \\
 &= \int_0^{2\pi} \int_0^\pi \left(\frac{3\mu v_\infty \cos \theta}{R} - p_0 + \rho g R \cos \theta \right) \cos \theta R^2 \sin \theta d\theta d\phi \\
 &= \underbrace{4\pi\mu R v_\infty}_{\text{form drag}} + \underbrace{\frac{4}{3}\pi\rho g R^3}_{\text{buoyant force}}
 \end{aligned}$$

Stress vertical to the flow direction, (即計算 friction drag)

$$\begin{aligned}
 F_n &= \iint (\sigma_r \sin \theta + \sigma_\theta \cos \theta) dA \\
 &= \int_0^{2\pi} \int_0^\pi [-(\tau_{rr})|_{r=R} \sin \theta + (-\tau_{r\theta})|_{r=R} \cos \theta] R^2 \sin \theta d\theta d\phi \\
 &= \int_0^{2\pi} \int_0^\pi [-(\tau_{rr})|_{r=R} \sin \theta - (-\tau_{r\theta})|_{r=R} \cos \theta] R^2 \sin \theta d\theta d\phi \\
 &= \int_0^{2\pi} \int_0^\pi \left(\frac{3\mu v_\infty \cos \theta}{R} + \rho g R \cos \theta \right) \sin \theta R^2 \sin \theta d\theta d\phi \\
 &= 0
 \end{aligned}$$

$$\text{Total drag} = \boxed{4\pi\mu R v_\infty}$$

(c)

$$C_D = \frac{F_{drag} / A_c}{\frac{1}{2} \rho v_\infty^2} = \frac{4\pi R \mu v_\infty}{\pi R^2} \times \frac{2}{\rho v_\infty^2} = \frac{8\mu}{\rho v_\infty R}$$
$$= \frac{16\mu}{\rho v_\infty D} = \frac{16}{Re}$$

(d)

因為流體流經空氣，產生之黏滯力低，也就沒有 Friction drag，因此造成與 Stokes' Law 的不同之處。

※本題改編自原文書習題，為 Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 143, Problem 4B.3.所改編，原本的題幹敘述就是(d)小題的答案，詳細內容為：

When a liquid flows around a gas bubble, circulation takes place within the bubble. This circulation lowers the interfacial shear stress, and, to a first approximation, we may assume that it is entirely eliminated.

其假設所造成之影響不只在於最終算 drag 的表示式上，也影響了(1) boundary condition，以及(2)速度分布表達式。在一般推導 Stokes' law 的過程中，最原始所用之 boundary condition 如下：

$$\left\{ \begin{array}{l} (1) r = R, v_r = \frac{-1}{r^2 \sin \theta} \frac{\partial \Psi}{\partial \theta} = 0 \\ (2) r = R, v_\theta = \frac{1}{r \sin \theta} \frac{\partial \Psi}{\partial r} = 0 \\ (3) r \rightarrow \infty, \Psi \rightarrow -\frac{1}{2} v_\infty r^2 \sin^2 \theta \end{array} \right.$$

(1)(2)皆為物體表面之 non-slip condition，(3)則大略可視為距離遙遠處，流體速度為 v_∞ 的變形

表達式(注意此處 ∞ 並不是真的代表無限大，只是用來強調距離非常遠)

而在本題的推導中，原文書特別指示我們須將第(2)個 boundary condition 換成另一種，即：

$$r = R, \quad \frac{d}{dr} \left(\frac{1}{r^2} \frac{df}{dr} \right) + 2 \frac{f}{r^4} = 0$$

(f 為假設函數，為 stream function 的一部分)

其原因就是來自於題目的假設，即流體經過空氣泡時，產生的黏滯力低，可假設為 0，因此最終我們可以從(a)小題的結果發現，此種假設最初應是由 $\tau_{r\theta} = 0$ 開始，才推到上面那個較為複雜的邊界條件。想當然，邊界條件不同，推得之速度分布也不同了。

最後，在 Stokes' law 的最後算出 drag 方面，friction drag 主要就是來自於 $\tau_{r\theta}$ 的貢獻，因此本題為 0，就是主要的差異來源，詳情可參考 Bird, R.; Stewart, W.; Lightfoot, E. *Transport*

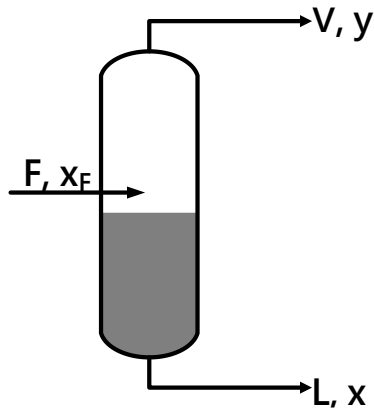
Phenomena, 2nd ed.; p 58-60.



Problem 3

【Solution】

(a) Flash Distillation



By overall mole balance,

$$F = L + V$$

By mole balance of key component,

$$Fx_F = Lx + Vy$$

$$0.5F = 0.75V + xL = 0.75V + x(F - V)$$

$$0.5 = 0.75 \frac{V}{F} + x(1 - \frac{V}{F}) = 0.75f + (1 - f)x$$

By equilibrium,

$$y = 1.2x + 0.2$$

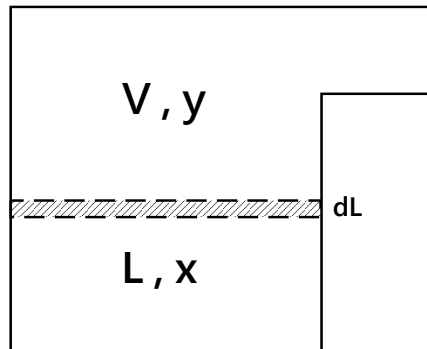
$$0.75 = 1.2x + 0.2$$

$$x = 0.458 \text{ 代回}$$

$$0.5 = 0.75f + (1 - f) \times 0.458$$

$$\underline{\underline{f = 0.143}} \text{ (vaporized fraction)}$$

(b) Differential Distillation



By overall mole balance,

$$V = dL$$

By mole balance of key component,

$$d(xL) = yV, \quad x dL + L dx = y dL$$

$$L dx = (y - x) dL$$

$$\frac{dx}{y - x} = \frac{dL}{L}$$

將 $y = 1.2x + 0.2$ 代入並積分：

$$\int_{0.5}^{0.458} \frac{dx}{1.2x + 0.2 - x} = \int_L^{L'} \frac{dL}{L}$$
$$\ln \frac{L'}{L} = -0.142, \quad L' = 0.869L$$

$$\text{vaporized fraction} = \frac{L - 0.869L}{L} = \underline{\underline{0.131}}$$

Problem 4

【Solution】

(a)

∴ heterogeneous reaction，假設 n 級反應

$$N_A = k_n'' C_A^n, \quad k_n'' [=] \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \left(\frac{\text{mol}}{\text{m}^3} \right)^{-n} [=] \frac{\text{m}^{3n-2}}{\text{mol}^{n-1} \cdot \text{s}}$$

若為 1 級反應則為

$$k_n'' [=] \frac{\text{m}}{\text{s}}$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 544.)

(b)

$$N_A [=] \frac{\text{mole}}{\text{m}^2 \cdot \text{s}}$$

(c)

By mole balance of A,

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

同除 $2\pi r L dr \rightarrow 0$

$$\underline{\underline{\frac{-d(rN_A)}{dr} = 0}}$$

By mole balance of B,

$$N_B (2\pi r L) \Big|_r - N_B (2\pi r L) \Big|_{r+dr} + 0 = 0$$

同除 $2\pi r L dr \rightarrow 0$

$$\underline{\underline{\frac{-d(rN_B)}{dr} = 0}}$$

(d)

∴ reaction :



$$\underline{\underline{\square = -2}}$$

根據(c)小題結果：

$$\frac{-d(rN_A)}{dr} = 0, \quad rN_A \neq f(r)$$

$$\frac{-d(rN_B)}{dr} = 0, \quad rN_B \neq f(r)$$

$$\text{兩式相除得：} \frac{rN_A}{rN_B} = \frac{N_A}{N_B} \neq f(r)$$

$$\text{即 } \frac{N_A}{N_B} \text{ 與 } r \text{ 無關}$$

(e)

By Fick's law,

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

$$= -D_{AB}C \frac{dy_A}{dr} + \frac{1}{2} y_A N_A$$

$$N_A = \frac{D_{AB}r}{1 - \frac{1}{2}y_A} C \frac{dy_A}{dr} \text{ 代回(c)小題結果}$$

$$-\frac{d}{dr} \left[\frac{D_{AB}r}{1 - \frac{1}{2}y_A} C \frac{dy_A}{dr} \right] = 0, \quad \text{積分兩次}$$

$$-2 \ln \left(1 - \frac{1}{2} y_A \right) = c_1 \ln r + c_2 \begin{cases} r = R, y_A = 0 \\ r = \delta R, y_A = y_{A\delta} \end{cases}$$

$$\begin{cases} c_1 = \frac{2 \ln \left(1 - \frac{1}{2} y_{A\delta} \right)}{\ln \frac{1}{\delta}} \\ c_2 = 2 \ln \left(1 - \frac{1}{2} y_{A\delta} \right) \frac{\ln R}{\ln \delta} \end{cases}$$

則

$$N_A = \frac{-D_{AB}C}{1 - \frac{1}{2}y_A} \frac{dy_A}{dr} = -D_{AB}Cc_1 = \frac{2D_{AB}C \ln(1 - \frac{1}{2}y_{A\delta})}{\underline{\underline{r \ln \delta}}}$$



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Problem 5**【Solution】****(a)**

By shell balance of energy,

$$q_x|_x - q_x|_{x+dx} = 0$$

同除 $dx \rightarrow 0$

$$\frac{dq_x}{dx} = 0, \quad \underline{\underline{q_x \neq f(x)}}$$

(b)

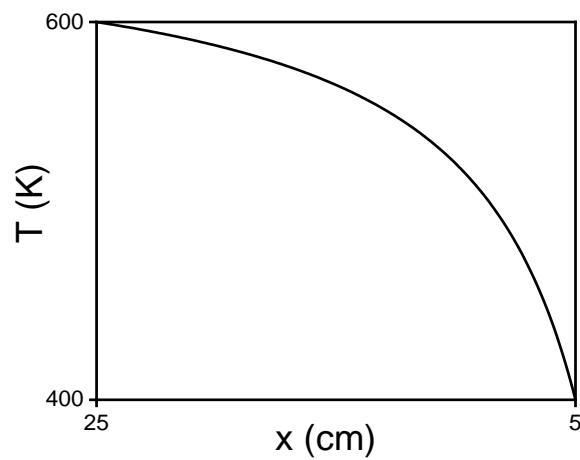
$$-k\left(\frac{\pi}{4}a^2x^2\frac{dT}{dx}\right)\bigg|_x + k\left(\frac{\pi}{4}a^2x^2\frac{dT}{dx}\right)\bigg|_{x+dx} = 0$$

同除 $dx \rightarrow 0$

$$\frac{d(a^2x^2\frac{dT}{dx})}{dx} = 0, \quad \text{積分兩次}$$

$$T = \frac{c_1}{a^2} \frac{1}{x} + c_2 \begin{cases} x = x_1, & T = T_1 \\ x = x_2, & T = T_2 \end{cases}$$

$$\underline{\underline{T = \frac{(T_1 - T_2)}{(\frac{1}{x_1} - \frac{1}{x_2})} \frac{1}{x} + T_1 - \frac{(T_1 - T_2)}{(\frac{1}{x_1} - \frac{1}{x_2})} \frac{1}{x_1}}}$$

**(c)**

$$q_x = -\left(-k \frac{\pi}{4} a^2 x^2\right) \frac{dT}{dx} = k \frac{\pi}{4} \frac{a^2 (T_1 - T_2)}{\left(\frac{1}{x_1} - \frac{1}{x_2}\right)}, \text{ 代入數據(SI 制)}$$

$$q_x = \underline{\underline{-0.613k \text{ (J / s)}}}$$

(此負號代表熱傳方向與 x 軸定義方向相反)

(本題可參考：Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. *Fundamentals of Heat and Mass Transfer*, 6th ed.; p 113, Example 3.4.)



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Problem 1

【Solution】

(a)

$$(1) \nu [=] m^2 / s$$

$$(2) Sh [=] 1$$

$$(3) \varepsilon [=] m$$

$$(4) D_{AB} [=] m^2 / s$$

$$(5) \tau_{yx} [=] kg / m \cdot s^2$$

(b) 黏滯力最主要的來源為分子間引力，若溫度升高，因為分子間距離將增加，因此造成分子間引力下降，使黏度下降。

$$(c) \quad \underbrace{\rho \frac{\partial \bar{v}}{\partial t}}_{\text{rate of increase of momentum per unit volume}} + \underbrace{\rho \bar{v} \cdot \nabla \bar{v}}_{\text{rate of momentum addition by convection per unit volume}} = \underbrace{-\nabla P + \mu \nabla^2 \bar{v}}_{\text{rate of momentum addition by molecule transport per unit volume}} + \underbrace{\rho \bar{g}}_{\text{rate of momentum addition by external force}}$$

(d) By shell balance of energy,

$$q'' A|_x - q'' A|_{x+dx} + \dot{q} A dx = 0$$

同除 $A dx \rightarrow 0$,

$$\frac{dq''}{dx} = -k \frac{d^2 T}{dx^2} = \dot{q}$$

由圖之二階導數判斷： $\underbrace{\dot{q}_A = \dot{q}_B}_{=0, \text{ conduction rate=constant}} < \dot{q}_C$

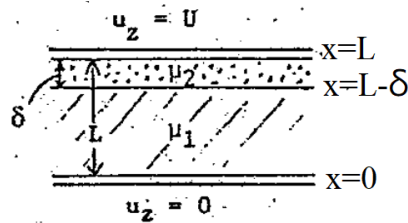
$$\text{則 } |q''_2| = |q''_3| > |q''_4|$$

((d)小題可參考：Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. *Fundamentals of Heat and*

Mass Transfer, 6th ed.; p 182, Problem 3.71.)

Problem 2

【Solution】



- Assume :
- (1) laminar flow
 - (2) Incompressible Newtonian fluid
 - (3) no pressure gradient
 - (4) no gravitation force in the z direction

For **Case B**, by the equation of continuity,

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

\therefore incompressible, ρ is constant

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

$v_x=0$ $v_y=0$

$$v_z = f(x) \text{ only}$$

By shell balance of momentum,

$$\rho v_z v_z dx dy \Big|_z - \rho v_z v_z dx dy \Big|_{z+dz} + \tau_{xz} dy dz \Big|_x - \tau_{xz} dy dz \Big|_{x+dx} = 0$$

同除 $dx dy dz \rightarrow 0$

$$\underbrace{\frac{-\partial(\rho v_z v_z)}{\partial z}}_{v_z=f(z)} - \frac{\partial \tau_{xz}}{\partial x} = 0, \quad \tau_{xz} = -\mu \frac{dv_z}{dx} = c_1$$

$$\begin{cases} v_{z1} = \frac{-c_{11}}{\mu_1} x + c_{21} \\ v_{z2} = \frac{-c_{12}}{\mu_2} x + c_{22} \end{cases}, \text{ B.C. : } \begin{cases} x=0 \quad v_{z1} = 0 \\ x=(L-\delta) \quad v_{z1} = v_{z2} \\ x=(L-\delta) \quad \tau_{xz1} = \tau_{xz2} \\ x=L \quad v_{z2} = U \end{cases}$$

$$\begin{cases} c_{21} = 0 \\ c_{11} = c_{12} = \frac{-U}{\left(\frac{L-\delta}{\mu_1} + \frac{\delta}{\mu_2}\right)} \\ c_{22} = U + \frac{c_{11}}{\mu_2} L \end{cases}$$

$$F_B = \tau_{xz} \Big|_L = -\mu_2 \frac{dv_{z2}}{dx} \Big|_L = c_{12} = \frac{-U}{\left(\frac{L-\delta}{\mu_1} + \frac{\delta}{\mu_2}\right)}$$

For **Case A**, $\mu_1 = \mu_2$

$$F_A = \tau_{xz} \Big|_L = \frac{-U}{\left(\frac{L-\delta}{\mu_1} + \frac{\delta}{\mu_2}\right)} = \frac{-U}{\left(\frac{L-\delta}{\mu_1} + \frac{\delta}{\mu_1}\right)} = \frac{-\mu_1 U}{L}$$

$$\frac{F_A}{F_B} = \frac{(L-\delta + \frac{\delta\mu_1}{\mu_2})}{L}$$

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 56.)

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Problem 3

【Solution】

假設反應： $C + O_2 \rightarrow CO_2$ ， $\delta = 1 - 1 = 0$ ，反應前後氣體總莫耳數不變

(a) $W_{O_2} = 1 \text{ (mol/h)}$, let the mass rate taken by the plant is x

$$\frac{1 \times 0.21 - x}{1} = 0.16, \quad x = 0.05 \text{ (mole/h)}$$

$$N_{O_2, taken} = \frac{x}{400} = 1.25 \times 10^{-4} \text{ (mole/h} \cdot \text{cm}^2\text{)}$$

(b) Same as above,

$$\frac{3 \times 0.21 - x}{3} = 0.19, \quad x = 0.06 \text{ (mole/h)}$$

$$N_{O_2, taken} = \frac{x}{400} = 1.5 \times 10^{-4} \text{ (mole/h} \cdot \text{cm}^2\text{)}$$

(c) 不同意，在此兩個氧氣提供速率下，氧氣提供速率也許皆小於代謝速率，但光從此兩個實驗無法證明這點。

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Problem 4

【Solution】

(a)

$$\begin{aligned} Pr &= \frac{\nu}{\alpha} = \frac{\text{momentum diffusivity}}{\text{thermal diffusivity}} \\ &= \left(\frac{\delta}{\delta_t} \right)^3 = \frac{\text{momentum boundary layer thickness}}{\text{thermal boundary layer thickness}} \end{aligned}$$

$$Re_x = \frac{\rho \langle v \rangle x}{\mu} = \frac{\text{inertial force}}{\text{viscous force}}$$

$$Nu_x = \frac{h_x x}{k} = \frac{\text{convective heat transfer}}{\text{conductive heat transfer}} \text{ rate in radial direction}$$

∴ the temperature profile is assumed to be linear function of $\frac{y}{\delta_t}$

the temperature profile,

$$T = (T_\infty - T_s) \frac{y}{\delta_t} + T_s$$

$$\frac{d}{dx} \left[\int_0^{\delta_t} (T_\infty - T_s + \frac{(T_s - T_\infty)y}{\delta_t}) (\frac{v_\infty y}{\delta}) dy \right] = \alpha (\frac{T_\infty - T_s}{\delta_t})$$

$$\frac{d}{dx} \left[\frac{v_\infty (T_\infty - T_s)}{2\delta} \delta_t^2 + \frac{(T_s - T_\infty) \delta_t^2 v_\infty}{3\delta} \right] = \alpha (\frac{T_\infty - T_s}{\delta_t})$$

$$\frac{d}{dx} [v_\infty (\frac{\delta_t}{6\delta}) \delta_t] = \frac{\alpha}{\delta_t} \quad , \quad \text{令 } \frac{\delta_t}{\delta} = \Delta \neq f(x) \text{ 代入}$$

$$v_\infty \frac{\Delta}{6} \frac{d\delta_t}{dx} = \frac{\alpha}{\delta_t} \quad , \quad \delta_t = \sqrt{\frac{\alpha}{v_\infty} \left(\frac{12}{\Delta} \right) x}$$

$$\therefore \delta = \sqrt{\frac{12\nu x}{v_\infty}} \quad , \quad \frac{\delta_t}{\delta} = \sqrt{\frac{\alpha}{\nu} \left(\frac{1}{\Delta} \right)} = \Delta$$

$$\Delta^3 = \frac{\alpha}{\nu} = Pr^{-1} \quad , \quad \Delta = \frac{\delta_t}{\delta} = Pr^{\frac{1}{3}}$$

$$\delta_t = \delta \text{Pr}^{-\frac{1}{3}} = \underline{\underline{\sqrt{\frac{12\nu x}{v_\infty}} \text{Pr}^{-\frac{1}{3}}}}$$

(c)

@y=0, conduction rate=convection rate

$$-k \left. \frac{dT}{dy} \right|_{y=0} = h_x (T_s - T_\infty)$$

$$-k(T_\infty - T_s) = h_x \delta_t (T_s - T_\infty)$$

$$\frac{h_x}{k} = \frac{1}{\delta_t} = \sqrt{\frac{v_\infty}{12\nu x}} \text{Pr}^{\frac{1}{3}}$$

$$\frac{h_x x}{k} = Nu_x = \underline{\underline{\sqrt{\frac{1}{12}} \text{Re}_x^{\frac{1}{2}} \text{Pr}^{\frac{1}{3}}}}}$$



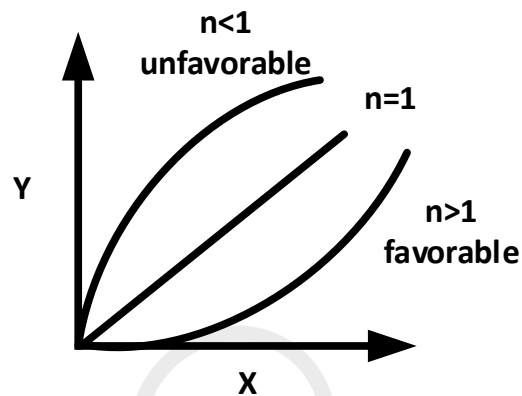
Problem 5

【Solution】

(a)

Freundlich isotherm,

$$Y = cX^n$$



$$\begin{cases} n < 1, \text{unfavorable} \rightarrow \text{需要高濃度}(X)\text{才有顯著的吸附效果}(Y) \\ n = 1, \text{linear} \\ n > 1, \text{favorable} \rightarrow \text{只需要低濃度}(X)\text{就有顯著的吸附效果}(Y) \end{cases}$$

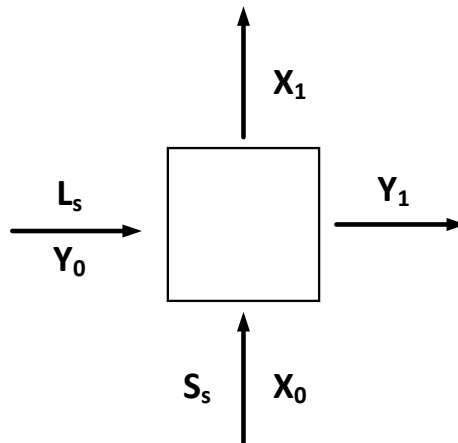
根據對照，題目之 n 值為 $1.5 > 1$ ，**favorable**

※本題可在 McCabe 原文書第 7 版 p 840~841 找到類似的觀念討論，只是要注意 McCabe 所定

義之 XY 定義與題目相反，因此 n 與吸附性的關係與題目相反

(本題可參考：Gavhane, K. A. *Mass Transfer - II*, 1st ed; p 3.6.)

(b)



$$\begin{cases} X_0 = 0 \\ L_s = 1000(kg) \\ Y_0 = 9.6(kg / kg) \\ Y_1 = 0.96(kg / kg) \end{cases}$$

By mass balance,

$$S_s(X_1 - X_0) = L_s(Y_0 - Y_1)$$

$$X_1 = \left(\frac{Y_1}{1.0 \times 10^{-4}} \right)^{\frac{1}{1.5}} = \left(\frac{0.96}{1.0 \times 10^{-4}} \right)^{\frac{1}{1.5}} = 451.70(kg / kg) \text{ 代回}$$

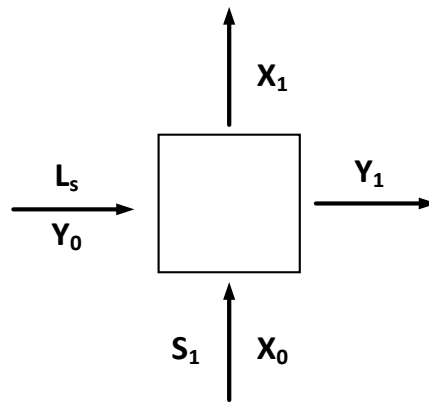
$$S_s(451.70 - 0) = 1000(9.6 - 0.96)$$

$$\underline{\underline{S_s = 19.12(kg)}}$$

(本題改編自：Gavhane, K. A. *Mass Transfer - II*, 1st ed; p 3.39~3.42, Example 3.4.)

(c)

First stage,



$$\begin{cases} X_0 = 0 \\ L_s = 1000(kg) \\ Y_0 = 9.6(kg / kg) \end{cases}$$

By mass balance,

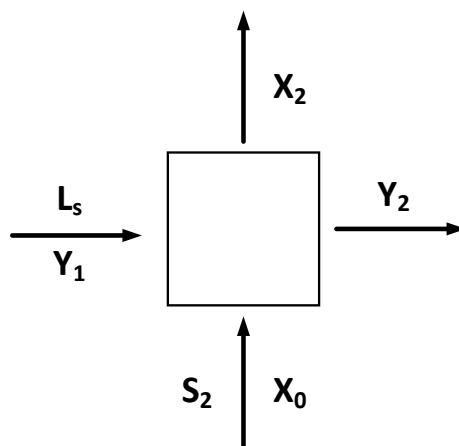
$$S_1(X_1 - X_0) = L_s(Y_0 - Y_1)$$

$$Y_1 = 1.0 \times 10^{-4} X_1^{1.5} \text{ 代入}$$

$$S_1(X_1 - 0) = 1000(9.6 - 1.0 \times 10^{-4} X_1^{1.5})$$

$$S_1 = \frac{9600}{X_1} - 0.1 X_1^{0.5}$$

Second stage,



$$\begin{cases} X_0 = 0 \\ L_s = 1000(kg) \\ Y_2 = 0.96 \end{cases}$$

By mass balance,

$$S_2(X_2 - X_0) = L_s(Y_1 - Y_2)$$

$$Y_2 = 1.0 \times 10^{-4} X_2^{1.5} \text{ 代入}$$

$$S_2(X_2 - 0) = 1000(1.0 \times 10^{-4} X_1^{1.5} - 1.0 \times 10^{-4} X_2^{1.5})$$

$$S_2 = \frac{0.1}{X_2} (X_1^{1.5} - X_2^{1.5})$$

The total amount of carbon is,

$$S_1 + S_2 = \frac{9600}{X_1} - 0.1 X_1^{0.5} + \frac{0.1}{X_2} (X_1^{1.5} - X_2^{1.5})$$

For minimum amount of carbon, let

$$\frac{d(S_1 + S_2)}{dX_1} = 0$$

$$\frac{-9600 X_2 X_1^{-0.5} - 0.05 X_1^{0.5} X_2 + 0.15 X_1^3}{X_1^{2.5} X_2} = 0, \quad X_2 = \frac{0.15 X_1^3}{9600 X_1^{0.5} + 0.05 X_1^2}$$

又

$$X_2 = \left(\frac{Y_2}{1.0 \times 10^{-4}} \right)^{\frac{1}{1.5}} = \left(\frac{0.96}{1.0 \times 10^{-4}} \right)^{\frac{1}{1.5}} = 451.70(kg / kg)$$

可解出

$$X_1 = 1027.84(kg / kg)$$

代回：

$$(S_1 + S_2)_{\min} = \frac{9600}{1027.84} - 0.1 \times (1027.84)^{0.5} + \frac{0.1}{451.70} (1027.84^{1.5} - 451.70^{1.5}) = \underline{\underline{11.30(kg)}}$$

(本題可參考：Gavhane, K. A. *Mass Transfer - II*, 1st ed; p 3.38~3.39.)

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Problem 1

【Solution】

- (1) a type of equipment measuring pressure.
- (2) terminal
- (3) steady
- (4) fluid
- (5) the velocity distribution is independent of the direction of the flow
- (6) the transition time from unsteady-state to steady-state
- (7) the type of the flow where the effect of viscous force can be neglected
- (8) Bernoulli
- (9) mechanics
- (10) parabolic
- (11) Ergun
- (一) potential
- (二) immiscible
- (三) porosity
- (四) reciprocating
- (五) laminar
- (六) creeping
- (七) dilatant
- (八) Reynolds
- (九) Compressible
- (十) hydraulic



Problem 2

【Solution】

A. True

B. False

For pool boiling, it is an example of natural convection

C. False

By Stefan-Boltzmann law, the radiation rate $\propto T^4$

D. True

E. True

F. False

Nusselt's film condensation theory describes the heat transfer in the case of
laminar film condensation on vertical surface

G. True

H. False

$$Sh \equiv \frac{\text{mass convection rate}}{\text{mass diffusion rate}} \text{ in radial direction} = \frac{k_c L}{D_{AB}}$$

I. False

Both analogies are applicable in heat and mass transfer

J. True

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

A : p 282/C : 491/J : 148.

Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. *Fundamentals of Heat and Mass Transfer*,

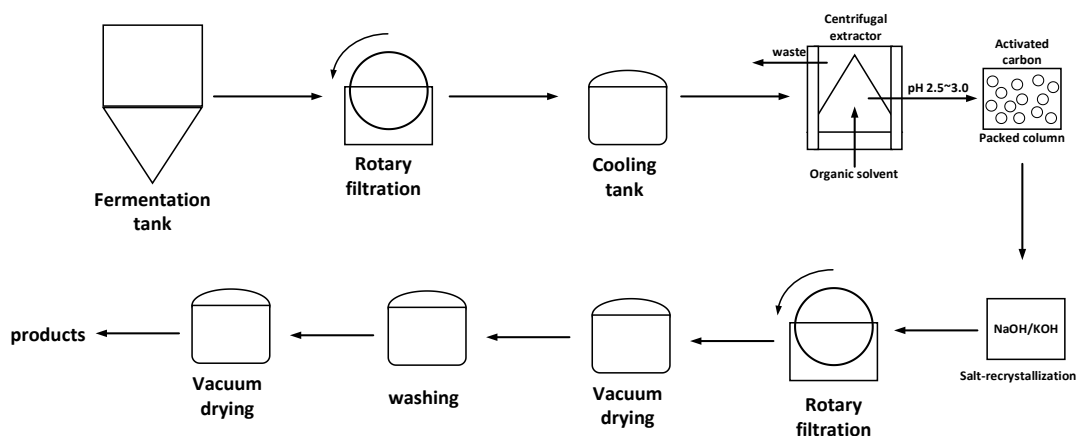
6th ed.; D : p 690/643.

Welty, J.; Rorrer, G.; Foster, D. *Fundamentals of Momentum, Heat, and Mass Transfer*, 5th ed.;

B : p 323/F : p 328/H : p 520/I : p.534 ~ 539.)

Problem 3

【Solution】



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

p 70, Problem 2C.4.)

Problem 4

【Solution】

Forced convection relation,

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

而

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

$$Re = \frac{\rho \langle v \rangle L}{\mu}$$

$$Pr = \frac{\nu}{\alpha} = \frac{\mu C_p}{k}$$

Total variables : $h, L, k, \rho, \langle v \rangle, \mu, C_p$

Fundamental units : M, L, T, θ

共可決定 $7-4=3$ 個無因次群，定義為 π_1, π_2, π_3

令 repeating variables : L, μ, k, ρ

For π_1

$$\pi_1 = h \times L^a \times \mu^b \times k^c \times \rho^d$$

$$\pi_1 = (M^1 T^{-3} \theta^{-1}) \times (L)^a \times (ML^{-1} T^{-1})^b \times (MT^{-3} \theta^{-1} L)^c \times (ML^{-3})^d = 1$$

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

$$\pi_1 = \frac{hL}{k} = Nu$$

For π_2

$$\pi_2 = \langle v \rangle \times L^e \times \mu^f \times k^g \times \rho^h$$

$$\pi_2 = (LT^{-1}) \times (L)^e \times (ML^{-1} T^{-1})^f \times (MT^{-3} \theta^{-1} L)^g \times (ML^{-3})^h = 1$$

$$\begin{cases} M : f + g + h = 0 \\ L : 1 + e - f + g - 3h = 0 \\ T : -1 - f - 3g = 0 \\ \theta : -g = 0 \end{cases} \Rightarrow \begin{cases} e = 1 \\ f = -1 \\ g = 0 \\ h = 1 \end{cases}$$

$$\pi_2 = \frac{\langle v \rangle L \rho}{\mu} = Re$$

For π_3

$$\pi_3 = C_p \times L^i \times \mu^j \times k^k \times \rho^l$$

$$\pi_3 = (L^2 T^{-2} \theta^{-1}) \times (L)^i \times (ML^{-1} T^{-1})^j \times (MT^{-3} \theta^{-1} L)^k \times (ML^{-3})^l = 1$$

$$\begin{cases} M : j + k + l = 0 \\ L : 2 + i - j + k - 3l = 0 \\ T : -2 - j - 3k = 0 \\ \theta : -1 - k = 0 \end{cases} \Rightarrow \begin{cases} i = 0 \\ j = 1 \\ k = -1 \\ l = 0 \end{cases}$$

$$\pi_3 = \frac{C_p \mu}{k} = Pr$$

則 3 個無因次群： Nu, Re, Pr

Problem 5

【Solution】

※注意題目給的圖有錯，內部圓柱的速度(U)應為 2m/s，非圖上所示之 0.1m/s

(a)(c)

Assume : (1) laminar flow

(2) $P=P(z)$

By the equation of continuity

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

∵ incompressible fluid, ρ is constant

$$\nabla \cdot (\vec{v}) = \frac{1}{r} \frac{\partial}{\partial r} (r v_r) + \frac{1}{r} \frac{\partial}{\partial \theta} v_\theta + \frac{\partial}{\partial z} v_z = 0$$

$\bar{v}_z = f(r)$ only

By Navier-Stokes equation,

$$\rho \left(\frac{\partial \bar{v}_z}{\partial t} + \bar{v}_r \frac{\partial \bar{v}_z}{\partial r} + \frac{\bar{v}_\theta}{r} \frac{\partial \bar{v}_z}{\partial \theta} + \bar{v}_z \frac{\partial \bar{v}_z}{\partial z} \right) = \mu \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \bar{v}_z}{\partial r} \right) + \frac{\partial^2 \bar{v}_z}{\partial \theta^2} + \frac{\partial^2 \bar{v}_z}{\partial z^2} \right] - \frac{\partial p}{\partial z} + \rho g_z$$

$$\mu \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \bar{v}_z}{\partial r} \right) - \frac{\partial p}{\partial z} + \rho g_z = 0$$

$$\mu \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \bar{v}_z}{\partial r} \right) = \frac{\partial P}{\partial z} \begin{cases} r = r_i & v_z = U \\ r = r_o & v_z = 0 \end{cases}, \text{積分兩次}$$

$$v_z = \frac{r^2}{4\mu} \frac{\partial P}{\partial z} + c_1 \ln r + c_2$$

$$\text{代入 B.C.} \begin{cases} c_1 = \frac{1}{\ln(\frac{r_i}{r_o})} \left[U - \frac{1}{4\mu} \frac{\partial P}{\partial z} (r_i^2 - r_o^2) \right] = -4.9326 - 3.0829 \frac{\partial P}{\partial z} \\ c_2 = 5.419 + 1.1368 \frac{\partial P}{\partial z} \end{cases}$$

$$v_z = \frac{r^2}{4} \frac{\partial P}{\partial z} + (-4.9326 - 3.0829 \frac{\partial P}{\partial z}) \ln r + 5.419 + 1.1368 \frac{\partial P}{\partial z}$$

For $\frac{\partial P}{\partial z}$, \because bottom is closed, then no fluid can exit the cylinder, $Q=0$

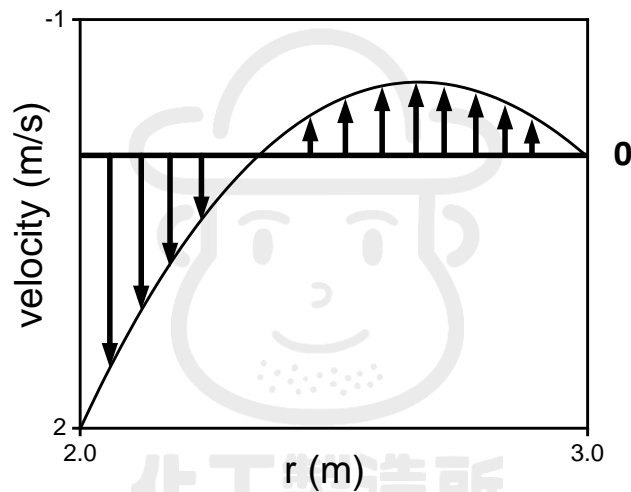
$$2\pi \int_{r_0}^{r_i} v_z r dr = 2\pi \int_{r_0}^{r_i} \left[\frac{r^2}{4} \frac{\partial P}{\partial z} + (-4.9326 - 3.0829 \frac{\partial P}{\partial z}) \ln r + 5.419 + 1.1368 \frac{\partial P}{\partial z} \right] r dr = 0$$

$$(-0.2092 \frac{\partial P}{\partial z} + 2.1657) = 0$$

$$\frac{\partial P}{\partial z} = 10.352, \text{ 代回}$$

$$v_z = \underline{\underline{2.588r^2 - 36.8377 \ln r + 17.1875}}$$

(b)



(※本題較簡易的想法為，因上下蓋關閉，因此在速度往下的同時，勢必會有一區往上流已平衡，直到處碰管壁($r=3$)時回到 0。形狀部分則因有壓力影響呈現拋物線分布)

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

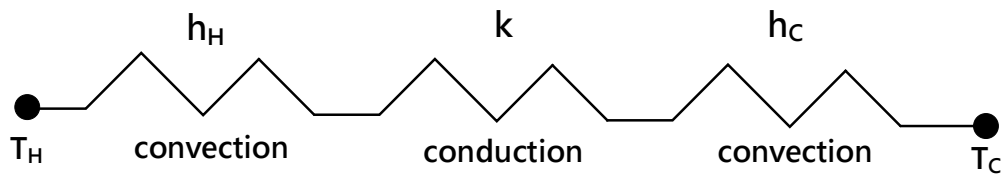
p 70, Problem 2C.4.)

Problem 6**【Solution】**

$$\because q = \frac{\Delta T}{\sum R}$$

$$\Delta T = T_H - T_C$$

For $\sum R$, by 串聯



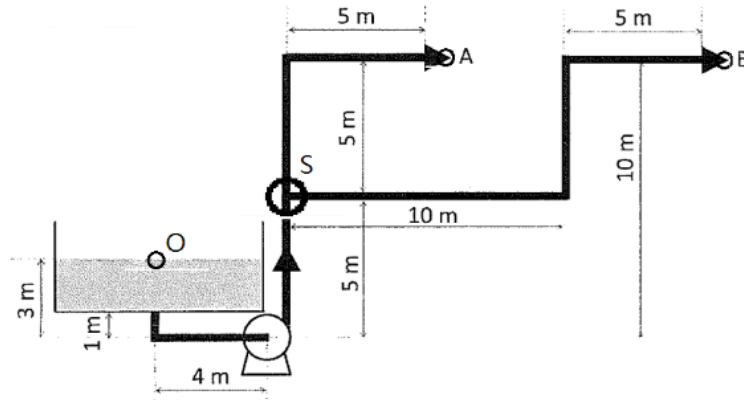
$$\sum R = \frac{1}{2\pi R_i L h_H} + \frac{\ln \frac{R_o}{R_i}}{2\pi k L} + \frac{1}{2\pi R_o L h_C}$$

$$q = \frac{\Delta T}{\sum R} = \frac{T_H - T_C}{\frac{1}{2\pi R_i L h_H} + \frac{\ln \frac{R_o}{R_i}}{2\pi k L} + \frac{1}{2\pi R_o L h_C}}$$

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Problem 7

【Solution】



(a)

$$\because Q, A \text{ 相同}, v_{\text{suction}} = v_S = 6 \text{ (m/s)}$$

By mass balance,

$$\dot{m}_S = \dot{m}_A + \dot{m}_B$$

$$\frac{\pi}{4} \times D^2 \times 6 = \frac{\pi}{4} \times D^2 \times v_A + \frac{\pi}{4} \times D^2 \times v_B$$

Assume Hagen Poiseuille equation is applicable,

$$Q_A : Q_B = \frac{\Delta P_{SA}}{L_{SA}} : \frac{\Delta P_{SB}}{L_{SB}} = \frac{1 \text{ atm} - P_S}{L_{SA}} : \frac{1 \text{ atm} - P_S}{L_{SB}} = \frac{1}{L_{SA}} : \frac{1}{L_{SB}} = \frac{1}{10} : \frac{1}{20} = 2 : 1 = v_A : v_B$$

$$\frac{\pi}{4} \times D^2 \times 6 = \frac{\pi}{4} \times D^2 \times v_A + \frac{\pi}{4} \times D^2 \times \frac{1}{2} v_A$$

$$\begin{cases} v_A = 4 \text{ (m/s)} \\ v_B = \frac{1}{2} v_A = 2 \text{ (m/s)} \end{cases}$$

<check> The validity of Hagen-Poiseuille equation (laminar flow)

$$\text{Re}_S = \frac{\rho v_S D}{\mu} = \frac{1000 \times 6 \times 0.1}{0.001} = 6 \times 10^5 \text{ (Turbulent)}$$

$$\text{Re}_A = \frac{\rho v_A D}{\mu} = \frac{1000 \times 4 \times 0.1}{0.001} = 4 \times 10^5 \text{ (Turbulent)}$$

$$\text{Re}_B = \frac{\rho v_B D}{\mu} = \frac{1000 \times 2 \times 0.1}{0.001} = 2 \times 10^5 \quad (\text{Turbulent})$$

由此可知此題假設從頭到尾皆為 turbulent flow 較為合理，且

$$\frac{k}{D} = \frac{0.002}{0.1} = 0.02, \quad \text{turbulent 範圍內 } f = 0.0125$$

By mass balance,

$$v_A = 6 - v_B$$

By mechanical energy balance of A, from S to A

$$\dot{m}_A \left[\frac{g}{g_c} (h_S - h_A) + \frac{P_S - P_A}{\rho} + \frac{1}{2g_c} (v_S^2 - v_A^2) - h_f^{SA} \right] = 0$$

$$g(h_S - h_A) + \frac{P_S - P_A}{\rho} + \frac{1}{2} (v_S^2 - v_A^2) - h_f^{SA} = 0 \text{-----(1)}$$

同理，By mechanical energy balance of B, from S to B

$$g(h_S - h_B) + \frac{P_S - P_B}{\rho} + \frac{1}{2} (v_S^2 - v_B^2) - h_f^{SB} = 0 \text{-----(2)}$$

$$\because P_A = P_B = P_{atm}, \quad h_B = h_A, \quad (1)-(2)$$

$$\frac{1}{2} (v_B^2 - v_A^2) + (h_f^{SB} - h_f^{SA}) = 0$$

For $h_f^{SB} - h_f^{SA}$,

$$h_f^{SB} - h_f^{SA} = \frac{4f}{2D} [L_{SB} v_B^2 - L_{SA} v_A^2] = \frac{4 \times 0.0125}{2 \times 0.1} [20v_B^2 - 10v_A^2]$$

代回，並代入 mass balance,

$$\frac{1}{2} [v_B^2 - (6 - v_B)^2] + \frac{4 \times 0.0125}{2 \times 0.1} [20v_B^2 - 10(6 - v_B)^2] = 0$$

$$\boxed{\begin{cases} v_A = 3.45 \text{ (m/s)} \\ v_B = 2.55 \text{ (m/s)} \end{cases}}$$

(b)

By mechanical energy balance equation,

$$\begin{aligned}
 & \dot{m}_o \left(\frac{g}{g_c} h_o + \cancel{\frac{P}{\rho}} + \cancel{\frac{1}{2g_c} v_o^2} + \dot{W}_s - h_f^{OS} \right) - \dot{m}_A h_f^{SA} - \dot{m}_B h_f^{SB} \\
 & \quad P_0 = P_A = P_B = P_{atm} \quad \text{storage is large enough} \\
 & = \dot{m}_A \left(\frac{g}{g_c} h_A + \cancel{\frac{P}{\rho}} + \frac{1}{2g_c} v_A^2 \right) + \dot{m}_B \left(\frac{g}{g_c} h_B + \cancel{\frac{P}{\rho}} + \frac{1}{2g_c} v_B^2 \right) \\
 & 6 \times (gh_o + \dot{W}_s - h_f^{OS}) - 3.45 h_f^{SA} - 2.55 h_f^{SB} = 3.45 (gh_A + \frac{1}{2} v_A^2) + 2.55 (gh_B + \frac{1}{2} v_B^2) \\
 & \begin{cases} h_f^{OS} = 4 \times 0.0125 \times \frac{10}{0.1} \times \frac{6^2}{2} = 90 \\ h_f^{SA} = 4 \times 0.0125 \times \frac{10}{0.1} \times \frac{3.45^2}{2} = 29.776 \text{ 代回} \\ h_f^{SB} = 4 \times 0.0125 \times \frac{20}{0.1} \times \frac{2.55^2}{2} = 32.483 \end{cases} \\
 & 6 \times (9.8 \times 3 + \dot{W}_s - 90) - 3.45 \times 29.776 - 2.55 \times 32.483 \\
 & = 3.45 (9.8 \times 10 + \frac{1}{2} \times 3.45^2) + 2.55 (9.8 \times 10 + \frac{1}{2} \times 2.55^2) \\
 & \dot{W}_s = 194.33 \text{ (m}^2 / \text{s}^2) \quad , \quad P_p = \frac{194.33}{0.7} \times \frac{\pi}{4} \times 0.1^2 \times 6 \times 1000 = \underline{\underline{13082.36 \text{ (J / s)}}}
 \end{aligned}$$

(c)

$$\begin{aligned}
 NPSH &= \frac{g_c}{g} \left(\frac{P_0 - P_v}{\rho} - h_L \right) + h_0 \\
 &= \frac{(1-0.02) \times 1.013 \times 10^5}{1000} - 4 \times 0.0125 \times \frac{4+1}{0.1} \times \frac{6^2}{2} + 3 = 8.53 > 6 \text{ (m)} \\
 & \quad 9.8
 \end{aligned}$$

This pump is able to work without cavitation.

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Problem 1

【Solution】

(a) By mass balance of the urea in the blood,

$$\text{removing rate} = 200 \times 1.90 - 195 \times 1.75 = \underline{\underline{38.75 \text{ (mg / min)}}}$$

(b) The removed urea from the blood will enter into the dialyzing fluid, so the

concentration of urea in the dialysate will be,

$$\frac{38.75}{1250} = \underline{\underline{0.031 \text{ (mg / ml)}}}$$

(c) urea concentration = $\frac{\text{原有 urea} - \text{去除 urea}}{\text{溶液體積}}$

$$\frac{5 \times 10^3 \text{ (ml)} \times 2.9 \text{ (mg / ml)} - 38.75 \text{ (mg / min)} \times 60 \text{ (min / hr)} \times 3.5 \text{ hr}}{5 \times 10^3 \text{ (ml)}} = \underline{\underline{1.2725 \text{ (mg / ml)}}}$$

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Problem 2

【Solution】

Assume : (1) laminar, incompressible flow

(2) $p = p(z)$ only

By continuity equation

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

\therefore incompressible, $\nabla \cdot \vec{v} = 0$

$$\nabla \cdot (\vec{v}) = \underbrace{\frac{1}{r} \frac{\partial}{\partial r} (r v_r)}_{v_r=0} + \underbrace{\frac{1}{r} \frac{\partial}{\partial \theta} v_\theta}_{v_\theta=0} + \frac{\partial}{\partial z} v_z = 0$$

$v_z = f(r)$ only

By shell balance of momentum in the z-direction,

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

同除 $dr d\theta dz \rightarrow 0$,

$$\begin{aligned} & \underbrace{\frac{-\partial(r \rho v_z v_z)}{\partial z}}_{v_z \neq f(z)} - \frac{\partial(r \tau_{rz})}{\partial r} - \frac{\partial(rp)}{\partial z} + \rho g r = 0 \\ & \frac{\partial(r \tau_{rz})}{\partial r} = -\frac{\partial(rp)}{\partial z} + \rho g r = \frac{-\partial P}{\partial z} r \\ & \tau_{rz} = \frac{r}{2} \left(\frac{-\partial P}{\partial z} \right) + \frac{c_1}{r} \end{aligned}$$

$\therefore r = \lambda R$, v_z reaches maximum, $\tau_{rz} = 0$ (free surface)

$$c_1 = \frac{-\lambda^2 R^2}{2} \left(\frac{-\partial P}{\partial z} \right) \text{ 代回}$$

$$\tau_{rz} = \frac{r}{2} \left(\frac{-\partial P}{\partial z} \right) - \frac{\lambda^2 R^2}{2r} \left(\frac{-\partial P}{\partial z} \right)$$

At $r = R$,

$$\tau_{rz} \Big|_{r=R} = \frac{R}{2} \left(\frac{-\partial P}{\partial z} \right) - \frac{\lambda^2 R}{2} \left(\frac{-\partial P}{\partial z} \right)$$

※(1)此題不可使用下面附的 Navier-Stokes equation，因其是在 Newtonian fluid 條件下所推得

(2)本題只討論 shear stress 分布，不一定需要討論 $\frac{dv_z}{dr}$ 與距離之關係，若題目進一步要求速度

分布，則一定要討論

(本題可參考：Chen, Y.; Chen, L.; Tung, K *Semianalytical Solution for Power-Law Polymer*

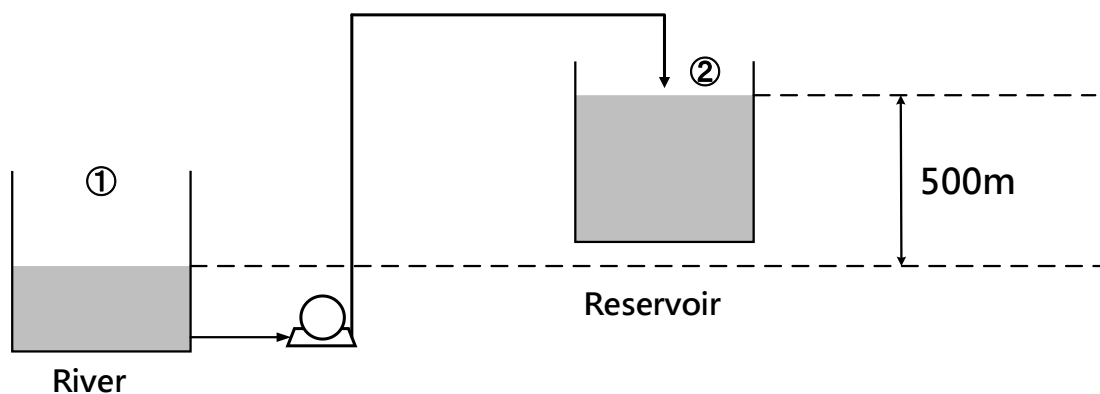
Solution Flow in a Converging Annular Spinneret; 2015.)



Problem 3

【Solution】

設①為 river，設②為 resirvoir



For each pipe,

$$Q = 20000 \text{ (gal / min)} \times \frac{1 \text{ (ft}^3\text{)}}{7.48 \text{ (gal)}} \times \frac{1 \text{ (min)}}{60 \text{ (sec)}} = 44.56 \text{ (ft}^3\text{ / s)}$$

(a) By mechanical energy balance equation,

$$\dot{W}_s = \frac{1}{2g_c} (v_1^2 - v_2^2) + \frac{g}{g_c} (z_1 - z_2) + \frac{1}{\rho} (P_1 - P_2) - h_f$$

For v_2 ,

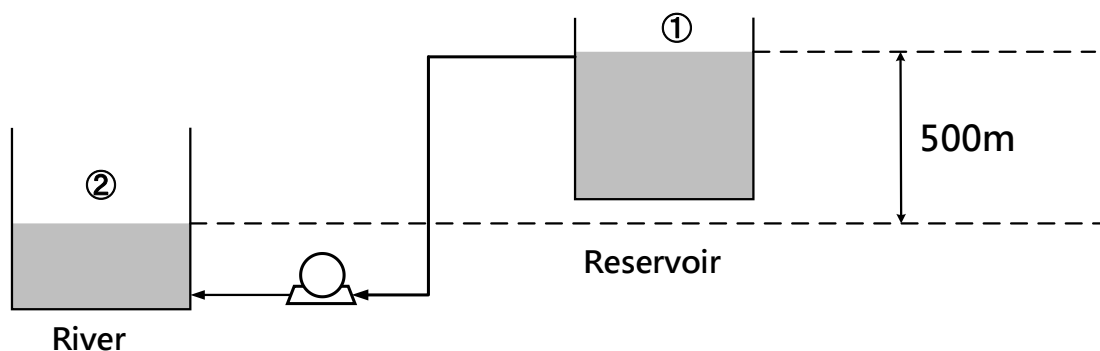
$$Q = 44.56 = \frac{\pi}{4} \left(\frac{30 \text{ in}}{12 \text{ in / ft}} \right)^2 v_2, \quad v_2 = 9.078 \text{ (ft / s)} \text{ 代回}$$

$$\dot{W}_s = \frac{1}{2 \times 32.174} (0^2 - 9.078^2) + 32.174(0 - 500) - 32.174(15)$$

$$\dot{W}_s = -16570.89 \text{ (ft}^3\text{ / s}^2\text{)}$$

$$\dot{P}_p = \left| \frac{\dot{W}_s \dot{m}}{\eta} \times 2 \right| = \left| \frac{\dot{W}_s \rho Q}{\eta} \times 2 \right| = \left| \frac{-16570.89 \times 62.4 \times 44.56}{0.85} \times 2 \right| = \underline{\underline{1.084 \times 10^8 \text{ (lb - ft}^2\text{ / s)}}}$$

設①為 resirvoir，設②為 river



(b) By mechanical energy balance equation,

$$\dot{W}_s = \frac{1}{2g_c}(v_1^2 - v_2^2) + \frac{g}{g_c}(z_1 - z_2) + \frac{1}{\rho}(P_1 - P_2) - h_f$$

$$\dot{W}_s = \frac{1}{2 \times 32.174}(0^2 - 9.078^2) + 32.174(500 - 0) - 32.174(15)$$

$$\dot{W}_s = 15605.67 \text{ (ft}^3 / \text{s}^2)$$

設 pump 效率同樣為 0.85

$$\dot{P}_t = \left| \dot{W}_s \dot{m} \times 2 \right| = \left| \dot{W}_s \rho Q \times 2 \right| = \left| 15605.67 \times 0.85 \times 62.4 \times 44.56 \times 2 \right| = \underline{\underline{7.376 \times 10^7 \text{ (lb} - \text{ft}^2 / \text{s)}}}$$

(c)

$$\text{Overall efficiency, } \eta_o \equiv \frac{\text{water power (output)}}{\text{shaft power (input)}} = \frac{P_t}{P_p} = \frac{7.376 \times 10^7}{1.084 \times 10^8} = \underline{\underline{0.68}}$$

※意即測量”水由水庫流進河中所可產生之功”與”把水重新打回水庫中”所需功的”比值”

Problem 4**【Solution】**

(a) thermally fully-developed condition

$$\frac{\partial}{\partial x} \left[\frac{T_s(x) - T(x, r)}{T_s(x) - T_m(x)} \right] = 0 \quad \begin{cases} T_s(x) = \text{surface temperature} \\ T(x, r) = \text{temperature} \\ T_m(x) = \text{mean temperature} \end{cases}$$

(b) Reynolds number for the internal flows

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

(c) Reynolds analogy

$$\frac{C_f}{2} = \text{St} \quad \begin{cases} C_f = \text{friction factor} \\ \text{St} = \text{Stanton number} \end{cases}$$

(d) Grashof number

$$\text{Gr} \equiv \frac{\text{buoyant force}}{\text{viscous force}} = \frac{\rho^2 g \beta L^3 \Delta T}{\mu^2}$$

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Problem 5

【Solution】

(a) By mole balance of O_2

$$N_{O_2}''(4\pi r^2)\Big|_r - N_{O_2}''(4\pi r^2)\Big|_{r+dr} = 0$$

同除 $4\pi dr \rightarrow 0$

$$\frac{-d(r^2 N_{O_2}'')}{dr} = 0$$

(b) By Fick's law,

$$N_{O_2}'' = -D_{AB} \frac{dC_{O_2}}{dr} + y_A(N_{O_2}'' + N_{CO_2}'')$$

\therefore reaction, $C(s) + O_2(g) \rightarrow CO_2(g)$, $N_{O_2}'' = -N_{CO_2}''$

$$\text{則 } N_{O_2}'' = -D_{AB} \frac{dC_{O_2}}{dr}$$

(c) 將(b)結果代入(a)小題結果：

$$\frac{d}{dr} \left(r^2 \frac{dC_{O_2}}{dr} \right) = 0$$
$$C_{O_2} = \frac{-c_1}{r} + c_2, \quad \text{B.C.} \begin{cases} r = r_0 & -D_{AB} \frac{dC_{O_2}}{dr} \Big|_{r=r_0} = -k_1'' C_{O_2}(r_0) \\ r \rightarrow \infty & C_{O_2} = C_{O_2}^\infty \end{cases}$$

B.C.1 代入：

$$-D_{AB} \frac{c_1}{r_0^2} = -k_1'' C_{O_2}(r_0)$$

$$c_1 = \frac{k_1''}{D_{AB}} r_0^2 C_{O_2}(r_0)$$

B.C.2 代入：

$$c_2 = C_{O_2}^\infty$$

則

$$C_{O_2} = \frac{-\frac{k_1''}{D_{AB}} r_0^2 C_{O_2}(r_0)}{r} + C_{O_2}^\infty$$

$$C_{O_2}^\infty = \frac{P_{O_2}}{RT} = \frac{1 \text{ (atm)}}{8.205 \times 10^{-2} \times 1450} = 8.405 \times 10^{-3} \text{ (kmol / m}^3\text{)}$$

At $r = r_0$,

$$C_{O_2}(r_0) = \frac{-\frac{k_1''}{D_{AB}} r_0^2 C_{O_2}(r_0)}{r_0} + C_{O_2}^\infty$$

$$C_{O_2}(r_0) = \frac{-0.1}{1.71 \times 10^{-4}} \times (1 \times 10^{-3})^2 C_{O_2}(r_0) \times \frac{1}{1 \times 10^{-3}} + 8.405 \times 10^{-3}$$

$$C_{O_2}(r_0) = 5.3 \times 10^{-3} \text{ (kmol / m}^3\text{)}$$

則

$$W_A = -k_1''(4\pi r_0^2)C_{O_2}(r_0) = \underline{\underline{-6.66 \times 10^{-9} \text{ (kmol / s)}}}$$

(本題可參考：Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. *Fundamentals of Heat and Mass Transfer*, 6th ed.; p 920, Problem 14.29.)

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Problem 6**【Solution】**

(a) By lumped analysis on the insulated vessel,

$$UA(T_h - T) = \frac{\partial}{\partial t}(\rho V_c CT) = \rho V_c C \frac{\partial T}{\partial t} ,$$

Where U is the overall heat transfer coefficient

$$\frac{UA}{\rho V_c C} \int_0^t dt = \int_{T_i}^T \frac{dT}{T_h - T}$$

$$A = \frac{\rho V_c C}{Ut} \ln \frac{T_h - T_i}{T_h - T}$$

For $U = \frac{1}{\frac{1}{h_i} + \frac{1}{h_0}}$

(b)

$$A = \frac{1200 \times 2.25 \times 2200}{\frac{1}{\frac{1}{10000} + \frac{1}{2000}} \times 60 \times 60} \ln \frac{500 - 300}{500 - 450} = 1.372 \text{ (m}^2\text{)}$$

$$A = 1.372 = \pi(20 \times 10^{-3})L$$

$$\underline{\underline{L = 21.84 \text{ (m)}}}$$

(本題可參考：Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. *Fundamentals of Heat and Mass*

Transfer, 6th ed.; p 321, Problem 5.15.)

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Problem 1

【Solution】

(1)

(a) Rate of strain $= \frac{dv_x}{dy} [=] \frac{1}{s}$

(b) Thermal diffusivity $[=] m^2 / s$

(c) NPSH $[=] m$

(d) Fanning friction factor $[=] 1$ (dimensionless)

(e) Reynolds stress $[=] kg / s^2 \cdot m$

(2)

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho \vec{v} \cdot \nabla \vec{v} = \mu \nabla^2 \vec{v} - \nabla p + \rho \vec{g}$$

無因次化每一個方程式的項可得：

$$\frac{\rho U}{t_0} \frac{D \vec{v}^*}{Dt^*} = \frac{\mu U}{L^2} \nabla^{*2} \vec{v}^* - \frac{p_0}{L} \nabla^* p^* + \rho \vec{g}$$

同除 $\frac{\mu U}{L^2}$

$$\frac{\rho L^2}{t_0 \mu} \frac{D \vec{v}^*}{Dt^*} = \nabla^{*2} \vec{v}^* - \frac{p_0 L}{\mu U} \nabla^* p^* + \frac{\rho L^2}{\mu U} \vec{g}$$

令 $\begin{cases} t_0 = \frac{L}{U} \\ p_0 = \frac{\mu U}{L} \end{cases} \Rightarrow$

$$\text{Re} \frac{D \vec{v}^*}{Dt^*} = \nabla^{*2} \vec{v}^* - \nabla^* p^* + \frac{\rho L^2}{\mu U} \vec{g}$$

(a) For steady velocity field, the velocity profile is independent of time

Therefore,

$$\rho \frac{\partial \bar{v}}{\partial t} \text{ can be neglected}$$

(b)

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

If Re is very small, *inertial force* \ll *viscous force*

$$\frac{D\bar{v}^*}{Dt^*} \text{ can be neglected}$$

(c) For ideal flow, *inertial force* \gg *viscous force*

$$\mu \nabla^2 \bar{v} \text{ can be neglected}$$

※(a)(b)(c)三題可不須無因次化就可作答，只不過可用於強調(b)小題同時須消除兩項。

(d) Yes, the constraints of Navier-Stokes equation is constant ρ and μ , which can be satisfied by a compressible Newtonian fluid flowing incompressibly.

※此題問的是 N-S equation 能否用於描述”不可壓縮流體”，參考 Bird 第 2 版第 84 頁的敘述，只需要此系統密度 ρ 與 μ 維持恆定即可，而 compressible fluid 雖然物理本質會使得其密度隨著時間與受力狀況等條件改變，但在特定情況下一樣有可能使其維持恆定(稱為 incompressible flow)，類似於物體受力”不一定”產生”速度變化”，因為”合力可以是 0”。

(e) Yes, the origin of the Navier-Stokes equation is merely the conservation of momentum of the fluid with constant ρ and μ , and both laminar and turbulent flow is applicable.

※在 BSL 第二版 CH5 的章節介紹中(p.152)，有關於 equation of change 適用於 turbulent flow 的敘述如下：*Since the sizes of the turbulent eddies are several orders of magnitude larger than the mean free path of the molecules of the fluid, the equations of change are applicable.*

因素流並不像層流一般均勻，能大範圍分析整塊流體；而是只能分割成較小塊的渦流區作分析，

然而，因其尺度依舊遠大於分子尺度，還是可視為一塊一塊連續體，還是能用 equation of change 進行分析；若此時 ρ 與 μ 皆恆定，則 N-S equation 依舊可用。

(3)

The rate of change of fish concentration observed by a person fixed on a boat traveling on the lake is the “substantial derivative”, which is,

$$\frac{DC}{Dt} = \frac{\partial C}{\partial t} + \vec{v} \cdot \nabla C$$

將 $C = 5t + 3x + 2y + z$ 代入

$$\begin{aligned} \frac{DC}{Dt} &= \frac{\partial C}{\partial t} + \vec{v} \cdot \nabla C \\ &= 5 + (5i + 2j + 0k) \cdot (3i + 2j + k) = \underline{\underline{24 \text{ (\# of fish / m}^3 \cdot \text{min)}}} \end{aligned}$$

※此題出自於 BSL 第二版 p.83 對於偏微分、全微分、以及質點微分的觀念，介紹如下：

(1) Observer is on a bridge recording the rate of change of the fish concentration at a fixed location, the result is partial derivative.

(2) Observer is on a motor boat and speed around the river, sometimes going upstream, sometimes downstream, and sometimes across the current. At any instant, the time rate of change of the observed fish concentration is total time derivative.

(3) Observer is on a canoe(獨木舟), just floating along with the current, observing the fish concentration. In this case the velocity of the observer is the same as the stream. At any moment, the time rate of change is reported as substantial derivative (meaning the time rate of change is reported as one moves with the “substance”).

由此可知，若觀察者固定不動，只觀察同一片區域魚群的變化，就是偏微分；若是觀察者本身具有速度，就算固定觀看相對於觀察者同樣的相對位置的區域(比如說固定看離觀察者 10 公尺處的魚群)，此時觀察者在具有速度的情況下，實際上觀察的位置也有改變，因此在記錄數據時，也需要一併將自身速度的影響考慮進來；若速度是自由的(比方馬達船)，則用全微分；若速度與河流速度相同(比方自由漂流)，則用質點微分。再回來看此題題目，雖然題目使用了偏微分的符號，然而其題意應解讀為“在船上的人所觀察到之濃度隨時間之變化”，即“time rate of change”，因

此應自動理解為全微分或質點微分。而此題解法是將題目所給之速度條件視為與河流相同，因此採用質點微分解題。

(4)

(a)

Distribution coefficient : The ratio of mole fractions of a species in one liquid phase to another.

$$K_D = \frac{x_i^{(1)}}{x_i^{(2)}}$$

Selectivity : The ratio of the distribution coefficient of one solute to another.

$$\beta_{ij} = \frac{K_{Di}}{K_{Dj}}$$

(本題可參考：Seader, J.; Henley, E.; Roper, D. Separation Process Principles, 3rd ed; p 39.)

(b)

The **volatility** in the distillation is the equivalent of distribution coefficient in the extraction. It is defined as

$$\text{volatility} = \frac{\text{mole fraction of key component in gas phase}}{\text{mole fraction of key component in liquid phase}} = \frac{y_A}{x_A}$$

On the other hand, the **relative volatility** is the equivalent of selectivity, which is defined as

$$\alpha_{AB} = \frac{\text{volatility of A}}{\text{volatility of B}} = \frac{y_A / x_A}{y_B / x_B}$$

(本題可參考：Seader, J.; Henley, E.; Roper, D. Separation Process Principles, 3rd ed; p 39.)

(5)

Point X is the **loading point**, where gas begins to hinder the downward flow of liquid, and liquid begins to load the bed, replacing gas and causing a sharp pressure drop increase.

Point Y is the **flooding point**, where the gas drag force is sufficient to entrain the

entire liquid.

(本題可參考：Seader, J.; Henley, E.; Roper, D. Separation Process Principles, 3rd ed; p 237.)

Problem 2

【Solution】

(1)

For a binary system with a constant average velocity in the z direction, the molar flux in the z direction relative to the molar-average velocity may also be expressed by

$$J_{A,z} = c_A(v_{A,z} - V_z) = -D_{AB} \frac{dc_A}{dz}$$

$$c_A(v_A - \bar{v}) = -D_{AB} \frac{dc_A}{dz}$$

$$c_A v_A = -D_{AB} \frac{dc_A}{dz} + c_A \bar{v}$$

∴

$$\bar{v} = \frac{1}{c} (c_A v_A + c_B v_B)$$

$$c_A \bar{v} = y_A (c_A v_A + c_B v_B) = y_A (N_A + N_B) \text{ 代回}$$

$$c_A v_A = N_A = -D_{AB} \frac{dc_A}{dz} + y_A (N_A + N_B)$$

(2)

Assumption : Isothermal + Isobaric $\begin{cases} \text{total concentration } C \text{ is constant} \text{-----(1)} \\ \text{the molar flux of } A = \text{the molar flux of } B \text{-----(2)} \end{cases}$

For (1)

$$C_A + C_B = C$$

微分

$$\frac{dC_A}{dx} + \frac{dC_B}{dx} = 0$$

$$\frac{dC_A}{dx} = -\frac{dC_B}{dx} \text{-----(3)}$$

For (2)

$$N_A = -N_B$$

$$-D_{AB} \frac{dC_A}{dx} = -(-D_{BA} \frac{dC_B}{dx}) \text{----- (4)}$$

將(3)代入(4)

$$\begin{aligned} -D_{AB} \frac{dC_A}{dx} &= -(D_{BA} \frac{dC_A}{dx}) \\ \therefore \frac{dC_A}{dx} &\neq 0, D_{AB} = D_{BA} \text{ 得證} \end{aligned}$$

(3)

假設，A 沿著 z 軸方向擴散，根據 Fick's law

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

$$N_A = \frac{-D_{AB}C}{1-y_A} \frac{dy_A}{dz} > 0$$

$$\therefore \frac{-D_{AB}C}{1-y_A} < 0, \frac{dy_A}{dz} < 0$$

即表示 y_A 隨傳遞方向(z 方向)遞減

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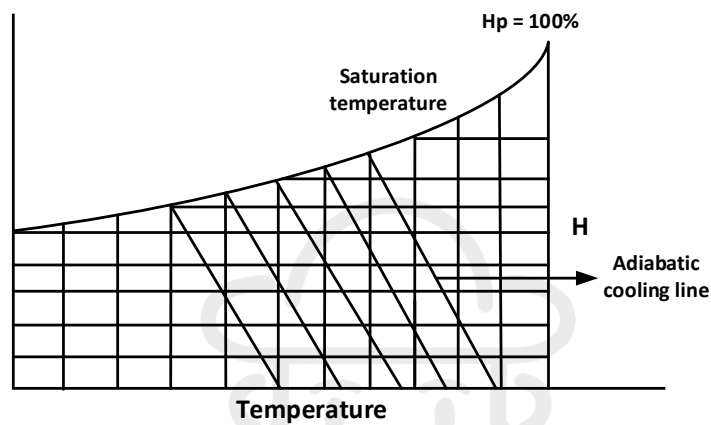
Problem 3

【Solution】

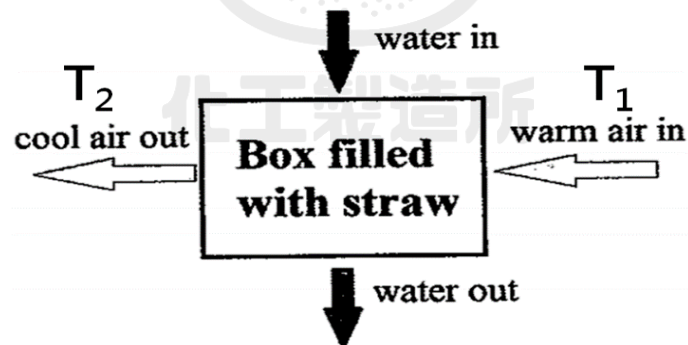
(1)

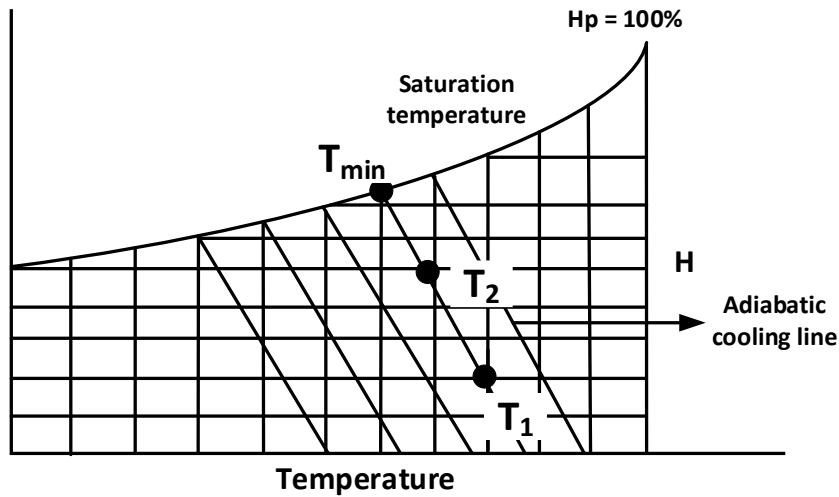
此裝置原理在於將溫暖空氣(warm air)與通入裝置並被水氣加濕後釋放到大氣中。而空氣裡的水氣會吸收人體釋放的熱而氣化使體感溫度降低，並因此達到冷氣調節的功能。

(2)



操作方法





假設進口空氣溫度、濕度狀況為 T_1 ；出口空氣溫度、濕度為 T_2

若此程序為絕熱加濕程序，則出口溫度 T_2 將在絕熱飽和線軌跡上

而若濕度達成 100%，則到達 T_{min} ，則有最大的降溫溫差(mix temperature drop)

(3)

與印度相比之下，因台灣平均濕度較高，即 T_1 位置較靠近 T_2 ，所以效果將會比較差，較不適合使用。

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Problem 4

【Solution】

(1)

By overall heat balance, $\dot{m}h - \dot{m}h + \dot{Q}_{gen} = \dot{Q}_{out}$ (steady-state)

$$-h(T_1 - T_a) \cdot 4\pi R_C^2 + S_n \cdot \frac{4}{3}\pi R_F^3 = 0$$

$$T_1 = T_a + \frac{S_n R_F^3}{3R_C^2 h}$$

(2)

By heat balance in the aluminum cladding region, $\dot{Q}_{in} - \dot{Q}_{out} + \dot{Q}_{gen} = \dot{Q}_{out}$

$$-k(4\pi r^2) \frac{dT_C}{dr} \Big|_r - \left[-k(4\pi r^2) \frac{dT_C}{dr} \right] \Big|_{r+dr} = 0$$

同除 $4\pi k dr \rightarrow 0$

$$\frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) = 0, \quad \begin{cases} r = R_F & -k_F \frac{dT_F}{dr} = -k_C \frac{dT_C}{dr} \\ r = R_F & S_n \left(\frac{4}{3}\pi R_F^3 \right) = -k_C (4\pi R_F^2) \frac{dT_C}{dr} \\ r = R_C & T_C = T_1 \\ r = R_C & -k_C (4\pi R_C^2) \frac{dT_C}{dr} = h(4\pi R_C^2) [T_C(R_C) - T_a] \\ r = R_F & T_C = T_0 \end{cases}$$

將微分式積分兩次

$$\frac{dT_C}{dr} = \frac{c_1}{r^2} \text{-----(1)}$$

$$T_C = -\frac{c_1}{r} + c_2 \text{-----(2)}$$

取 B.C.2、B.C.4 以解出 $T_0 - T_1$

將(1)代入 B.C.2

$$c_1 = \frac{-S_n R_F^3}{3k_C}$$

將(1)、(2)代入 B.C.4

$$c_2 = T_a + c_1 \left(\frac{1}{R_C} - \frac{k_C}{hR_C^2} \right) = T_a - \frac{S_n R_F^3}{3k_C} \left(\frac{1}{R_C} - \frac{k_C}{hR_C^2} \right)$$

$$T_C = \frac{S_n R_F^3}{3k_C} \left[\frac{1}{r} - \frac{1}{R_C} + \frac{k_C}{hR_C^2} \right] - T_a$$

$$T_0 - T_1 = T_C(R_F) - T_C(R_C) = \frac{S_n R_F^3}{3k_C} \left[\frac{1}{R_F} - \frac{1}{R_C} \right]$$

※此小題因為必須先寫出可用於解出 T_c 之邊界條件，因此最後計算 $T_0 - T_1$ 時順便使用所列之邊界條件做後續的計算。然而，也有較快速的解法：

By energy balance on the cladding,

heat generated by the fissionable material into the cladding = heat conducted out by the cladding

$$\frac{4\pi}{3} R_F^3 \cdot S_n = \frac{4\pi k_C \cdot (T_0 - T_1)}{\left(\frac{1}{R_F} - \frac{1}{R_C} \right)}$$

(即 B.C.2 變化形態)

整理並消去重複的項：

$$T_0 - T_1 = \frac{S_n R_F^3}{3k_C} \left[\frac{1}{R_F} - \frac{1}{R_C} \right]$$

(3)

By heat balance in the fissionable material region, $in - out + gen = \cancel{acc}$

$$-k_F(4\pi r^2) \frac{dT_F}{dr} \Big|_r - [-k_F(4\pi r^2) \frac{dT_F}{dr} \Big|_{r+dr}] + S_n(4\pi r^2 dr) = 0$$

同除 $4\pi k dr \rightarrow 0$

$$\frac{dT}{dr} = \frac{-S_n r}{3k_F} + \frac{c_3}{r^2}$$

$$T = \frac{-S_n r^2}{6k_F} - \frac{c_3}{r} + c_4 \quad \begin{cases} r=0 & \frac{dT}{dr} = 0 \\ r=R_F & T=T_0 \end{cases}$$

$$\begin{cases} c_3 = 0 \\ c_4 = T_0 + \frac{S_n R_F^2}{6k_F} \end{cases}$$

$$T = \frac{S_n R_F^2}{6k_F} \left(1 - \frac{r^2}{R_F^2}\right) + T_0$$

$$T_{\max} = T \quad (r=0)$$

$$T(r=0) = T_0 + \frac{S_n R_F^2}{6k_F}$$

(本题可参考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 296-298.)

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Problem 1

【Solution】

1. False

For a steady, fully developed, laminar flow in a circular tube,

$$\frac{\bar{v}_z}{v_{z,max}} \approx 1 - \left(\frac{r}{R}\right)^2, \quad \frac{\langle \bar{v}_z \rangle}{v_{z,max}} \approx \frac{1}{2}$$

$$P_o - P_L = \left(\frac{8\mu L}{\pi \rho R^4}\right) w \propto w \quad (\text{Re} < 2100)$$

For turbulent flow,

$$\frac{\bar{v}_z}{v_{z,max}} \approx \left(1 - \frac{r}{R}\right)^{\frac{1}{7}}, \quad \frac{\langle \bar{v}_z \rangle}{v_{z,max}} \approx \frac{4}{5}$$

$$P_o - P_L \approx 0.0198 \left(\frac{2}{\pi}\right)^{\frac{7}{4}} \left(\frac{\mu^{\frac{1}{4}} L}{\rho R^4}\right) w^{\frac{7}{4}} \propto w^{\frac{7}{4}} \quad (10^4 < \text{Re} < 10^5)$$

The pressure drop is not directly proportional to the mass flow rate.

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 154~155.)

<補充>

在 McCabe 原文書內也有提到壓降與平均速度的關係：

$$\begin{cases} \text{laminar flow (Re} < 2100\text{): } \frac{\Delta P}{L} \propto \bar{v} \\ \text{turbulent flow (2500} < \text{Re} < 10^6\text{): } \frac{\Delta P}{L} \propto (\bar{v})^{1.8} \\ \text{very turbulent flow (Re} > 10^6\text{): } \frac{\Delta P}{L} \propto (\bar{v})^2 \end{cases}$$

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

7th ed.; p 116.

2. True

The power number N_p , which is defined as,

$$N_p \equiv \frac{P}{n^3 D_a^5 \rho} \left\{ \begin{array}{l} P = \text{the power requirement (resistance to drag)} \\ D_a = \text{impeller diameter} \\ n = \text{angular velocity} \\ \rho = \text{density of the fluid} \end{array} \right.$$

is analogous to a friction factor or a drag coefficient. It is proportional to the ratio of the drag force acting on a unit area of the impeller and the inertial stress.

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 259.)

Power number 之推導可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 257.)

3. False

With shear-thinning or pseudoplastic liquids, a turbine may give a local region or high shear rate around the impeller, but near the wall the shear rate is much lower and the apparent viscosity may be much higher. Therefore, the velocity will be much less than that with a Newtonian fluid.

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 257.)

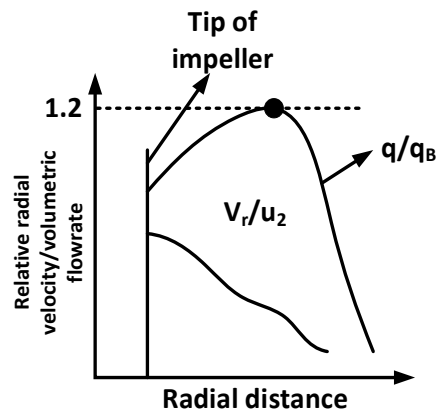
4. True

If the particles are very small, brownian movement appears. This is a random motion imparted to the particle by collisions between the particle and the molecules of the surrounding fluid. The random movement of the particle tends to suppress the effect of the force of gravity, so settling does not occur. Application of centrifugal force reduces the relative effect of brownian movement.

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 171.)

5. True

參考下圖：



可以發現隨著距離 tip 越遠，r 方向的流體速度應該會逐漸下降，符合第一段敘述。

而液體的實際流量則會達到一峰值(1.2 倍 q_B)以後開始下降，也符合第二段敘述

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 255, FIGURE 9.11.)

6. True

In agitation process, Froude number can be defined as,

$$Fr \equiv \frac{n^2 D_a}{g} = \frac{\text{inertial stress}}{\text{gravitational force}} \text{ per unit area acting on the fluid}$$

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 259.)

7. True

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 268.)

8. False

在非球體的沉降過程中，因其幾何形狀對流體的方向關係會一直變動而損耗能量，有效的拖曳力(drag)會比流體流經固定方位還來的高

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 170.)

9. True

The stagnation temperature of a high-speed fluid is defined as the temperature the fluid would attain were it brought to rest adiabatically without the development of shaft work.

By total energy balance,

$$m[\Delta H + \Delta(\frac{u^2}{2}) + \cancel{\Delta z}] = \cancel{\dot{Q}}_{\text{adiabatic}} - \cancel{\dot{W}}_{\text{no shaft work}}$$

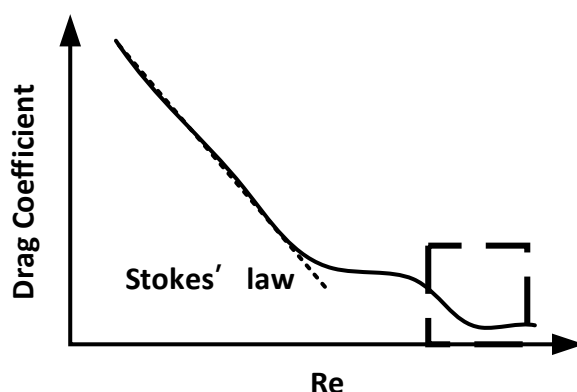
$$H_2 - H_1 + \underbrace{\frac{u_2^2}{2} - \frac{u_1^2}{2}}_{\text{stagnation}} = 0$$

$H_2 = H_1$ ，即進與出口之間，stagnation enthalpy 為定值

代表進與出口之間 stagnation temperature 維持定值

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 137.)

10. True



如圖，可以觀察到 drag coefficient，在 Re 極大處 ($\approx 2 \times 10^5$) 有一個小急降

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 187.

原文書將 friction coefficient 與 drag coefficient 一起討論，不過該頁指的是 drag coefficient)

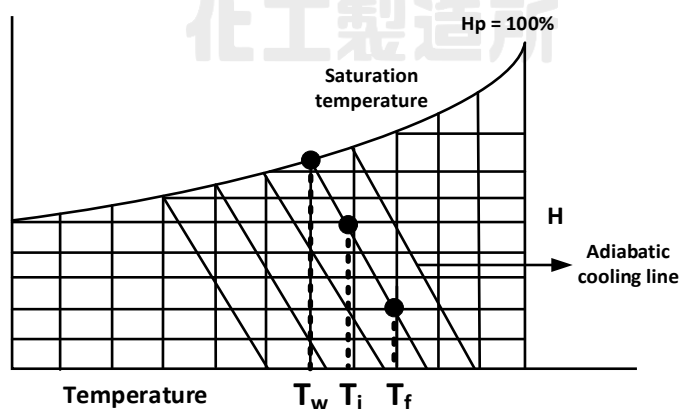
Problem 2

【Solution】

1. Ans : (D)

假設此過程未吸/放熱(單純利用化學物質吸收水分，且未起反應)

此過程會在絕熱飽和曲線上移動，如圖：



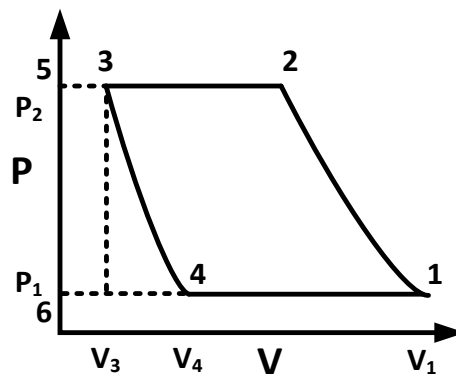
(A) wet bulb temperature (T_w) 不變

(B)(D) Dry bulb temperature 增加

(C) dew point temperature 應不變，且相對於原始溫度也是降低

2. Ans : (B)

一個典型的 compressor 其工作路徑如下：



$$\begin{cases} 1 \rightarrow 2 : \text{compression of the gas} \\ 2 \rightarrow 3 : \text{constant - pressure expansion} \\ 3 \rightarrow 4 : \text{expansion of the residual gas} \\ 4 \rightarrow 1 : \text{constant - pressure introduction of fresh gas} \end{cases}$$

The work done on the gas can be calculated as,

$$W = W_{1256} - W_{4356}$$

Assume the compression and the expansion processes are isentropic,

$$\begin{aligned} W_{1256} &= -\int_{V_1}^{V_2} P dV + P_2 V_2 - P_1 V_1 = -\int_{V_1}^{V_2} P dV + \int_{P_1 V_1}^{P_2 V_2} d(PV) = \int_{P_1}^{P_2} V dP = \int_{P_1}^{P_2} \left(\frac{\alpha}{P}\right)^\gamma dP \\ &= \frac{\alpha^{\frac{1}{\gamma}}}{-\frac{1}{\gamma} + 1} \left[(P_2)^{\frac{-1}{\gamma} + 1} - (P_1)^{\frac{-1}{\gamma} + 1} \right] = \left(\frac{\alpha}{P_1}\right)^{\frac{1}{\gamma}} P_1 \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] = P_1 V_1 \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] \end{aligned}$$

同理

$$W_{4356} = P_4 V_4 \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_3}{P_4}\right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] = P_1 V_4 \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}} - 1 \right]$$

The work done per cycle is then,

$$W = P_1 V_1 \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] - P_1 V_4 \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}} - 1 \right]$$

For isentropic conditions,

$$V_4 = V_3 \left(\frac{P_2}{P_1} \right)^{\frac{1}{\gamma}}$$

$$V_1 - V_4 = (V_1 - V_3) + V_3 - V_3 \left(\frac{P_2}{P_1} \right)^{\frac{1}{\gamma}} = \underbrace{(V_1 - V_3)}_{V_s} \left[1 + \underbrace{\frac{V_3}{V_1 - V_3}}_c - \frac{V_3}{V_1 - V_3} \left(\frac{P_2}{P_1} \right)^{\frac{1}{\gamma}} \right]$$

$$V_1 - V_4 = V_s \left[1 + c - c \left(\frac{P_2}{P_1} \right)^{\frac{1}{\gamma}} \right] \left\{ \begin{array}{l} V_s = \text{swept volume} \\ c = \text{clearance} \\ \frac{P_2}{P_1} = \frac{\text{outlet pressure}}{\text{inlet pressure}} = \text{compression ratio} \end{array} \right.$$

Define, theoretical volumetric efficiency,

$$\text{volumetric efficiency} \equiv \frac{\text{volume of fluid discharged}}{\text{volume swept by the piston or plunger}} = \frac{[1 + c - c \left(\frac{P_2}{P_1} \right)^{\frac{1}{\gamma}}]}{1}$$

由上式可知，當 compression ratio 變高，volumetric efficiency 變低

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

Chemical Engineering, 6th ed.; Volume 1, p 351~353.)

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3. Ans : (D)

The assumptions of McCabe-Thiele method include,

- (1) constant molar heat of vaporization
- (2) no heat losses (adiabatic)
- (3) no heat of mixing
- (4) constant molar vapor flow and constant molar reflux flow in any section of the column

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

4. Ans : (A)

Consider unit mass of particles containing n_i particles of characteristic dimension d_i , constituting a mass fraction of x_i , then:

$$x_i = n_i k \rho_s d_i^3 \quad (k \text{ is a constant})$$

$$\sum x_i = 1 = \rho_s k \sum (n_i d_i^3)$$

$$n_i = \frac{1}{\rho_s k} \frac{x_i}{d_i^3}$$

The volume-surface mean diameter (surface mean temperature) can be calculated as,

$$d_s = \frac{\sum (n_i d_i) S_i}{\sum (n_i S_i)} = \frac{\sum (n_i d_i^3)}{\sum (n_i d_i^2)}$$

Replace n_i with $\frac{1}{\rho_s k} \frac{x_i}{d_i^3}$,

$$d_s = \frac{\sum x_i}{\sum \frac{x_i}{d_i}} = \frac{1}{\sum \frac{x_i}{d_i}}$$

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

Chemical Engineering, 5th ed.; Volume 2, p 11~13.)

5. Ans : (B)

If the only purpose of the stirrer is to suspend solids, a propeller or other axial-flow impeller such as pitched-blade turbine would be chosen.

Helical-ribbon and anchor impellers are used for highly viscous liquids.

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 273/249.)

6. Ans : (B)

As the fluid viscosity is reduced, the friction on the flow decreases. Therefore, the pressure drop of the flow decreases.

7. Ans : (C)

The fluid pressure on a plate is independent of the geometry of the container.

So the force F from the fluid pressure on the plate X can be simply calculated as,

$$F = PA = (\rho_L g H) A = \underline{\underline{\rho_L A H g}}$$

8. Ans : (C)

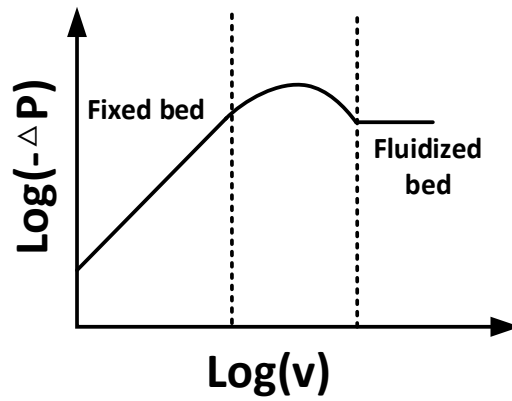
The root-mean-square components are equal for all directions at a given point. In this situation the turbulence is said to be isotropic.

$$\overline{(u')^2} = \overline{(v')^2} = \overline{(w')^2}$$

Nearly isotropic turbulence exists when there is no velocity gradient, as at the centerline of a pipe or beyond the outer edge of a boundary layer and downstream of a grid placed in the flow.

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 58-59.)

9. Ans : (B)



如上圖，可以發現隨著流體速度上升，壓降越來越大，直到固定床流體化後壓力呈現定值，而圖中轉折是固定床流體化過程中不穩定導致。

因此流體化床之壓降(水平線)運作之壓降相比固定床(上升階段)來說還要來的大

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

Chemical Engineering, 5th ed.; Volume 2, p 294.)

10. Ans : (D)

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Problem 3

【Solution】

If the suction pressure is only slightly greater than the vapore pressure of the working fluid, some liquid may flash to vapor inside the pump, which is called cavitation.

The cavitation effect will reduce the pump capacity and causes severe corrosion.

The reason why cavitation occurs tipycally only in the centrifugal pumps not displacement pumps is mainly because of the ways they operate. For centrifugal pumps, the bubbles would be unstable and broken under the impact of impeller, and thus causing the bubbles to collapse, and do damaging on the pump.

The positive displacement pump operates with a moving piston or plunger with fixed chamber (reciprocating pumps) or a rotary chamber (rotary pumps). Both types of pumps offer a stable environment for bubbles, so the bubbles will be stabilized. The main influence of the bubbles on the displacement pump is the reduction of the flow rate which can be transferred by the pump in one cycle.

事實上任何 pump 都會有 cavitation 的風險，只要吸進來的液體壓力變夠小就有機會形成泡泡或汽化造成空蝕現象，在正位移式 pump 的運作中，是利用活塞形成負壓吸收液體後往前加壓將液體推出(可參考網路上影片)，因此在形成負壓的過程中依舊有可能產生空蝕現象，然而其形成負壓時間與程度相較只往同一方向高速運轉並形成負壓吸水再離心推出之離心泵短且穩定(畢竟接下來還要往回推)，所以一般較離心泵為穩定，cavitation 的影響較不顯著。

(本題可參考：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*, 7th ed.; p 204/206~209.)

Problem 4**【Solution】**

By the equation of continuity,

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad (\text{incompressible})$$

$$v_x = \frac{2}{x} \text{ 代入}$$

$$\begin{aligned} \frac{\partial v_y}{\partial y} &= -\frac{\partial v_x}{\partial x} = -\frac{d(\frac{A}{x})}{dx} = \frac{2}{x^2} \\ v_y &= \int \frac{2}{x^2} dy = \frac{2y}{x^2} \end{aligned}$$

(本題可參考：Pritchard, P. J.; Mitchell, J. W. *Fox and McDonald's Introduction to Fluid Mechanics*; 8th ed; p 256, Problem 5.6.)



Problem 5**【Solution】****(a)**

For the bed density,

$$\rho_{bed} = \frac{W_{bed}}{V_{bed}} = \frac{250000 \times 7800 \times \frac{\pi}{6} (1 \times 10^{-2})^3}{\frac{\pi}{4} \times 0.3^2 \times 3} = 4814.8 (kg / m^3)$$

$$\varepsilon = 1 - \frac{\rho_{bed}}{\rho_p} = 1 - \frac{4814.8}{7800} = \underline{\underline{0.3827}}$$

(b)

By Ergun equation,

$$\frac{\Delta p}{L} = \frac{150 \bar{v} \mu (1 - \varepsilon)^2}{\Phi_s^2 D_p^2 \varepsilon^3} + \frac{1.75 \rho \bar{v}^2 (1 - \varepsilon)}{\Phi_s D_p \varepsilon^3}$$

∵ The quartz particles are spherical,

$$\Phi_s = 1$$

將各項數據代入：

$$\frac{\Delta p}{3} = \frac{150 \times 0.1 \times 1.2 \times 10^{-3}}{(1 \times 10^{-2})^2} \frac{(1 - 0.3827)^2}{0.3827^3} + \frac{1.75 \times 1.193 \times 10^3 \times (0.1)^2}{1 \times 10^{-2}} \left(\frac{1 - 0.3827}{0.3827^3} \right)$$

$$\underline{\underline{\Delta p = 72639.69 (N / m^2)}}$$

(c)

在 U 型管流動的酒經過流體化床時，會產生壓降，其壓降可由 U 型管右側高出 H 的酒來做補充：

$$\Delta p = \rho g H$$

$$72639.69 = 1.193 \times 10^3 \times 9.8 H$$

$$\underline{\underline{H = 6.213 (m)}}$$

Problem 6

【Solution】

(1)

Assumptions, (1) Incompressible and Newtonian fluid

(2) Steady state

(3) Fully-developed in z direction, $v_r = v_\theta = 0$

(4) θ -symmetric

By the equation of continuity,

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

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

By the equation of change,

r -direction:

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta^2}{r} + v_z \frac{\partial v_r}{\partial z} \right) = -\frac{\partial p}{\partial r} + \left[\frac{1}{r} \frac{\partial(r \tau_{rr})}{\partial r} + \frac{1}{r} \frac{\partial \tau_{\theta r}}{\partial \theta} - \frac{\tau_{\theta\theta}}{r} + \frac{\partial \tau_{rz}}{\partial z} \right] + \rho g_r$$

$$\boxed{-\frac{\partial p}{\partial r} = 0}$$

θ -direction:

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

$$\boxed{-\frac{1}{r} \frac{\partial p}{\partial \theta} = 0}$$

z -direction:

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

$$\boxed{-\frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial(r \tau_{rz})}{\partial r} = 0}$$

(2)

The boundary conditions should be,

$$\left\{ \begin{array}{l} r = R - \delta, \tau_{rz}^c = \tau_{rz}^p \rightarrow -\mu_c \frac{dv_z}{dr} = -\mu_p \frac{dv_z}{dr} \\ r = R - \delta, v_z^c = v_z^p \\ r = R, v_z^p = 0 \\ r = 0, \frac{dv_z^c}{dr} = 0 \end{array} \right.$$

(按照題意，在 vessel 內中心區域紅血球較多，且 vessel 內有一層厚度為 δ 的 plasma layer，因此 vessel 半徑為 R ，中心區域為 $R - \delta$)



Problem 7

【Solution】

(a)

Assumptions: (1) conduction only occurs on the r-direction

(2) no generation

(3) steady-state

(4) constant properties

By shell balance of energy in the control volume, ($\cancel{in} - \cancel{out} + \cancel{gen} = \cancel{acc}$)

$$q_r'' \left(\frac{4\pi r^2}{2} \right) \bigg|_r - q_r'' \left(\frac{4\pi r^2}{2} \right) \bigg|_{r+dr} = 0$$

hemisphere

同除 $2\pi dr \rightarrow 0$

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

By Fourier's law,

$$q_r'' = -k \frac{dT}{dr} \text{ 代入, } \boxed{k \frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) = 0}$$

(本題因 substrate 幾何形狀未知，且 transistor 之傳導為球座標 r 方向，因此利用 transistro 當作 control volume 來求 substrate 溫度分布)

(b)

The boundary conditions are,

$$\begin{cases} r = r_0 \rightarrow T = T_0 \\ r = \infty \rightarrow T = T_\infty \end{cases}$$

(c)

將(a)小題之結果積分

$$\frac{dT}{dr} = \frac{c_1}{r^2}, \quad T = \frac{-c_1}{r} + c_2$$

代入 boundary conditions,

$$\begin{cases} c_1 = r_0(T_\infty - T_0) \\ c_2 = T_\infty \end{cases}$$

$$T = \underline{\underline{\frac{(T_0 - T_\infty)r_0}{r} + T_\infty}}$$

(d)

For the heat rate,

$$q_r = q_r'' = -k(2\pi r^2) \frac{dT}{dr} = -k(2\pi r^2) \frac{c_1}{r^2} = \underline{\underline{2k\pi r_0(T_0 - T_\infty)}}$$

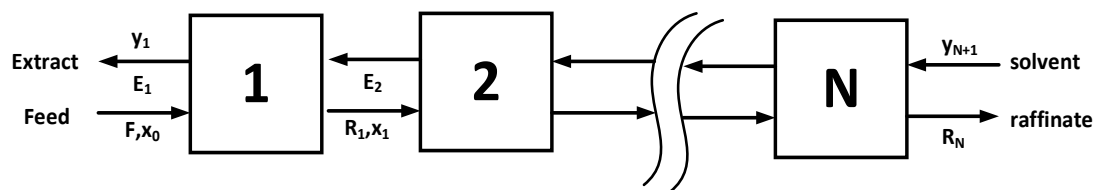
(本題改編自：Incropera, F.; Lavine, A.; Bergman, T. *Fundamentals of Heat and Mass Transfer*,

6th ed. ; p 181, Problem 3.18.)

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Problem 8

【Solution】



∵ The pure solvent is equal in mass to the feed, let $F = S = 1$

(1) 找出 M 點

$$\begin{cases} x_{w,M} = \frac{Fx_{w,0} + Sy_{w,N+1}}{F + S} = \frac{1 \times 0.6 + 1 \times 0}{1 + 1} = 0.3 \\ x_{a,M} = \frac{Fx_{a,0} + Sy_{a,N+1}}{F + S} = \frac{1 \times 0.4 + 1 \times 0}{1 + 1} = 0.2 \\ x_{M,M} = \frac{Fx_{M,0} + Sy_{M,N+1}}{F + S} = \frac{1 \times 0 + 1 \times 1}{1 + 1} = 0.5 \end{cases}$$

$$M = (x_w, x_a, x_M) = (0.3, 0.2, 0.5)$$

(2) 找出 R_N , E_1

在 E_1 內，acetone 與 MIK 之組成比例為

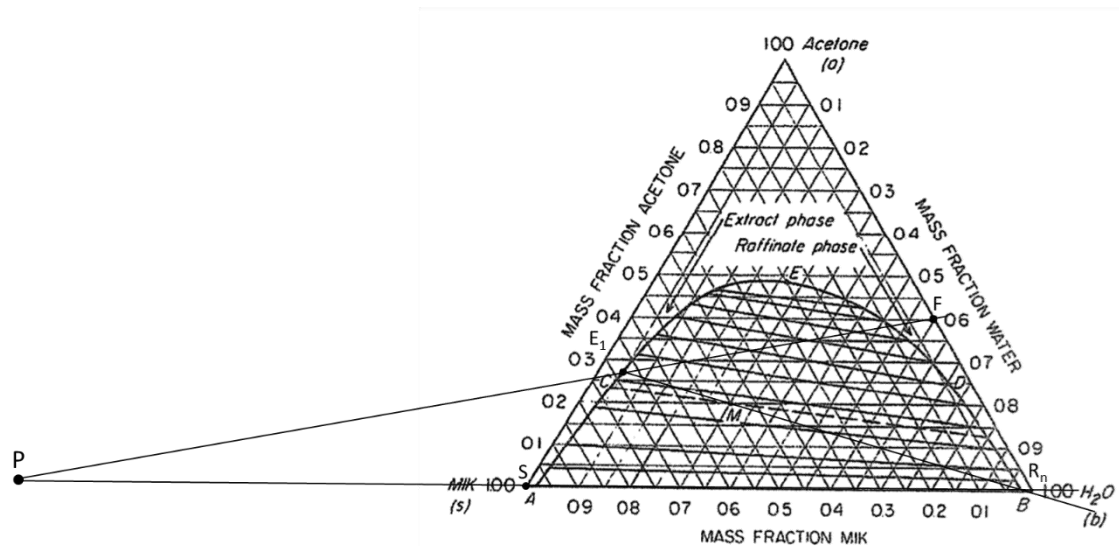
$$\frac{x_a}{x_M} = \frac{1 \times 0.4 \times 0.99}{1} = 0.396$$

利用 trial and error, 在 extract line 上點出 E_1 ($x_a : x_M = 0.27 : 0.68$)

連接 $\overline{E_1M}$ 與 raffinate line 交於 R_N

(3) 找出 P 點

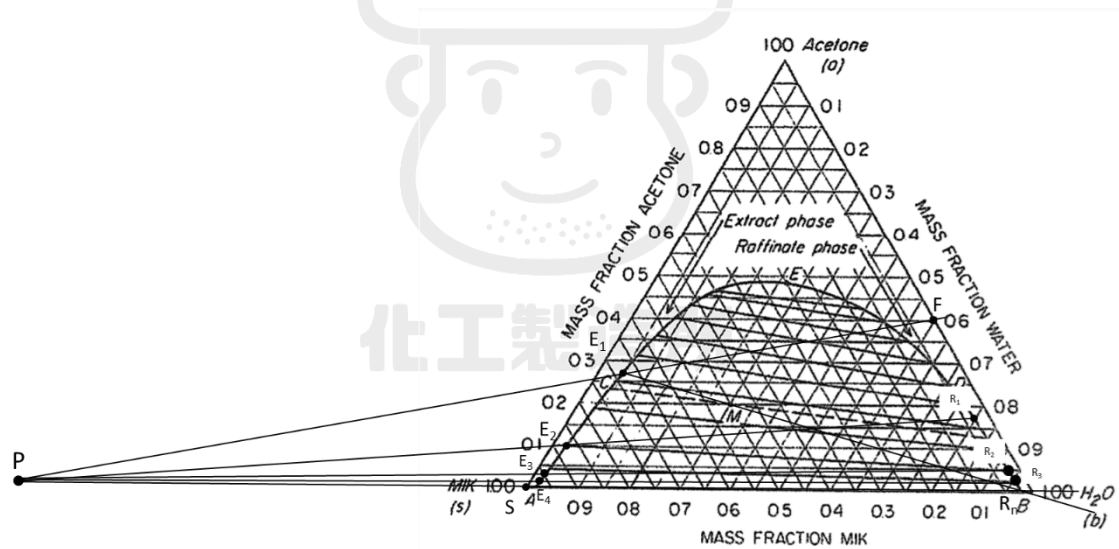
連接 $\overline{FE_1}$ 與 $\overline{SR_N}$, 交於 P 點, 做圖如下:



(4) 做理論版數：

做過 E_1 之 tie line，交 raffinate line 於 R_1

再連接 $\overline{R_1P}$ ，交 extract line 於 E_2 ，以此類推



做圖結果如下，大概需要 (a) 4 個 ideal stages

而除去 MIK 後，extract 之組成為：

(b)

$$\begin{cases} \text{water} = 0.05 \\ \text{acetone} = 0.95 \end{cases}$$

(此題因電腦作圖緣故有些許誤差產生，若最終答案有誤差請參考作法即可)

(本題改編自：McCabe, W.; Smith, J.; Harriott, P. *Unit Operations of Chemical Engineering*,

7th ed.; p 784~786, Example 23.3.

原文書之作法為利用 Ternary phase diagram 轉為 McCabe-Thiele diagram 作圖的方式

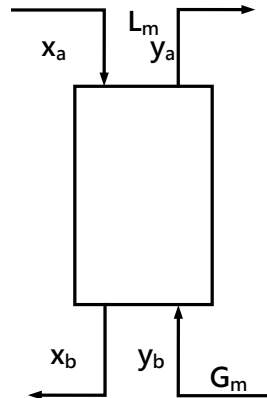
Number of ideal stages 為 3.4

唯其討論也很繁瑣，因此有興趣的同學可以自行翻閱，在此不另詳述)



Problem 9

【Solution】



$$\begin{cases} x_a = X_a = 0 \\ y_b \approx Y_b = 315 \times 10^{-6} \\ y_a \approx Y_a = 31 \times 10^{-6} \end{cases}$$

假設液相 Caustic soda (即 $NaOH$) 的濃度很高，因此在 CO_2 被大量吸收的情況

下，液相 CO_2 蒸氣壓很小，即 $y_a^* \approx y_b^* = 0$

$$G_m = \frac{0.34}{29(\text{air most})} = 0.0117 (\text{kmol} / \text{m}^2 \text{s})$$

The mean molecular weight of the liquid phase is,

$$\frac{100 + 900}{\frac{100}{40} + \frac{900}{18}} = 19.05$$

$$L'_m = \frac{3.94}{19.05} = 0.207 (\text{kmol} / \text{m}^2 \text{s})$$

The total height of a column can be calculated as,

$$Z = H_{OG} N_{OG}$$

$$N_{OG} = \frac{(y_b - y_a)}{\ln \frac{y_b - y_b^*}{y_a - y_a^*}} = \frac{(315 - 31) \times 10^{-6}}{\ln \frac{315 \times 10^{-6} - 0}{31 \times 10^{-6}}} = 2.318$$

$$H_{OG} = \frac{G'_m}{K_G a P} = \frac{0.0117}{K_G a \times \underbrace{1.013 \times 10^5}_{\text{atmospheric pressure}}}$$

$$3 = \frac{0.0117}{K_G a \times \underbrace{1.013 \times 10^5}_{\text{atmospheric pressure}}} \times 2.318$$

$$\underline{\underline{K_G a = 8.945 \times 10^{-8} [\text{kmol} / \text{m}^3 \text{s} (\text{N} / \text{m}^2)]}}$$

(本題改編自：Coulson, J.; Richardson, J.; Backhurst, J.; Harker, J. *Chemical Engineering*, 5th ed.; Volume 2, p 1169, Problem 12.1.)

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Problem 10

【Solution】

(1) air at 294K and 40 % relative humidity

→ air at $294 \times \frac{9}{5} - 460 = 69.2(^{\circ}\text{F})$, 40 % relative humidity (A 點)

其 humidity (A 點水平向左對) 為 0.006 (lb/lb)

(2) The air is heated to 366K in a reheater before entering the dryer

→ air at $366 \times \frac{9}{5} - 460 = 198.8(^{\circ}\text{F})$, 為 A 點水平對至溫度為 198.8($^{\circ}\text{F}$) 的地方(B)

(3) The air is dried to 60% relative humidity adiabatically

→ B 點沿絕熱飽和曲線往左上方移動至 60% relative humidity 處，為 C 點

C 點 humidity 為 0.028(lb/lb)

Dry bulb temperature 為 104($^{\circ}\text{F}$)

整個過程，單位質量空氣可帶走之水量為

$$0.028 - 0.006 = 0.022(\text{lb water} / \text{lb dry air})$$

(4) 計算總共需蒸發之水量：

濕進料：

$$42\% \text{ water} = \frac{42}{100 - 42} = 0.724(\text{lb water} / \text{lb dry solids})$$

出料：

$$4\% \text{ water} = \frac{4}{100 - 4} = 0.0417(\text{lb water} / \text{lb dry solids})$$

進出料所需蒸發之水分為：(0.724 - 0.0417) = 0.682(lb water / lb dry solids)

而出料含有的 dry solids 量為：

$$0.126\left(\frac{\text{kg}}{\text{s}}\right) \times 2.20\left(\frac{\text{lb}}{\text{kg}}\right) \times \frac{100 - 4}{100} = 0.2667(\text{lb} / \text{s})$$

總共所需的空氣質量流率：

$$\frac{0.2667 \times 0.682}{0.022} = 8.272 (\text{lb} / \text{s})$$

而 $69.2(^{\circ}\text{F})$ 時，specific volume 為 $12.9(\text{ft}^3 / \text{lb})$

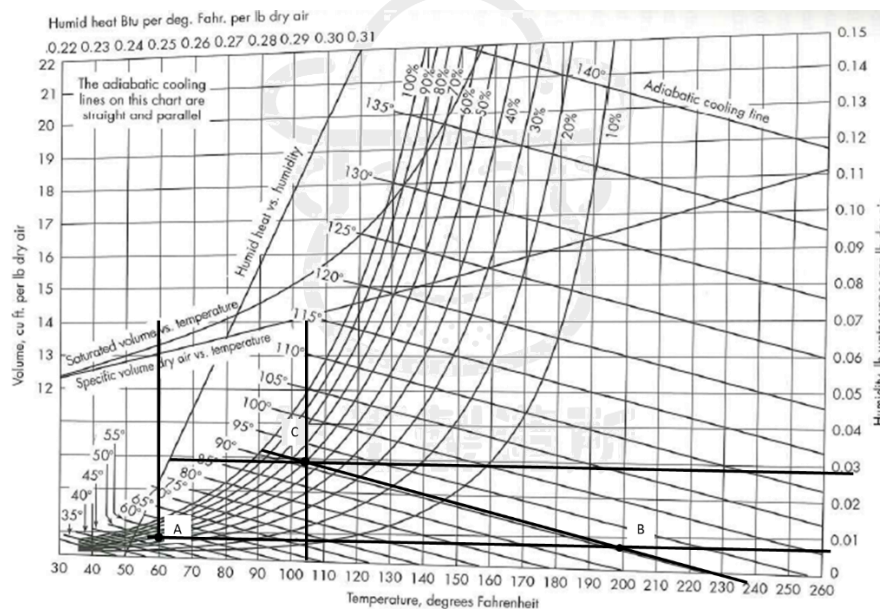
總計空氣體積流率為： $\underline{\underline{8.272 \times 12.9 = 106.71(\text{ft}^3 / \text{s})}}$

乾燥空氣之 humid heat 為： $0.242(\text{Btu} / ^{\circ}\text{F} \cdot \text{lb})$

Preheater 所需之加熱功率為：

$$0.242(198.8 - 69.2) \times 8.272 = \underline{\underline{259.45(\text{Btu} / \text{s})}}$$

作圖軌跡如下：



Second case,

(1) The water enters and leaves at 340K, which is

$$340 \times \frac{9}{5} - 460 = 152(^{\circ}\text{F})$$

The inlet humidity is, 0.006 (lb/lb)

The outlet humidity (60% relative humidity) is, 0.131 (lb/lb)

整個過程，單位質量空氣可以帶走之水量為：

$$0.131 - 0.006 = 0.125(\text{lb} / \text{lb})$$

總共所需的空氣質量流率：

$$\frac{0.2667 \times 0.682}{0.125} = 1.456(\text{lb} / \text{s})$$

總計空氣體積流率為： $1.456 \times 12.9 = \underline{\underline{18.78(\text{ft}^3 / \text{s})}}$

Preheater 所需之加熱功率為：

$$0.242(152 - 69.2) \times 1.456 = \underline{\underline{29.17(\text{Btu} / \text{s})}}$$

$$\left\{ \begin{array}{l} (a) \ 106.71 \ (\text{ft}^3 / \text{s}) \\ (b) \ 259.45 \ (\text{Btu} / \text{s}) \\ (c) \ 18.78 \ (\text{ft}^3 / \text{s}) \\ (d) \ 29.17 \ (\text{Btu} / \text{s}) \end{array} \right.$$

(本題改編自：Coulson, J.; Richardson, J.; Backhurst, J.; Harker, J. *Chemical Engineering*,
5th ed.; Volume 2, p 1181, Problem 16.7.)

Problem 11

【Solution】

先將題目所給之 x_A , y_A 數據轉為 $y_A - x_A$ 圖 $\begin{cases} A = \text{benzene, 分子量} = 12 \times 6 + 6 = 78 \\ B = \text{toluene, 分子量} = 12 \times 7 + 8 = 92 \end{cases}$

計算進料、出料組成：

$$\begin{cases} x_F = \frac{\frac{40}{78}}{\frac{40}{78} + \frac{60}{92}} = 0.44 \\ x_D = \frac{\frac{0.97}{78}}{\frac{0.97}{78} + \frac{0.03}{92}} = 0.974 \\ x_W = \frac{\frac{0.02}{78}}{\frac{0.02}{78} + \frac{0.98}{92}} = 0.023 \end{cases}$$

將 x_F 、 x_D 、 x_W 標注於對角線上

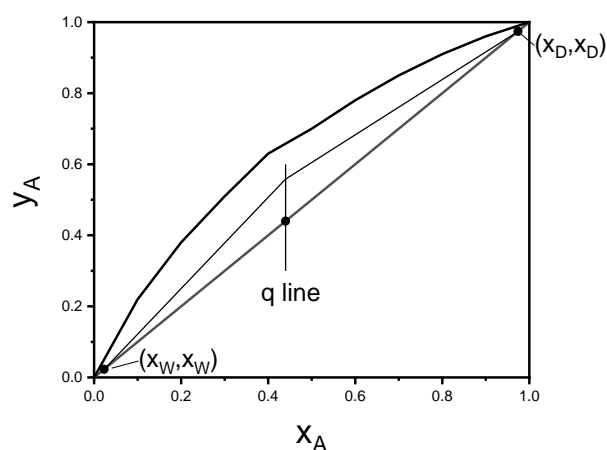
\because The feed is liquid at boiling-point, $q=1$, q-line 為通過 x_F 之垂直線

而上段操作線：

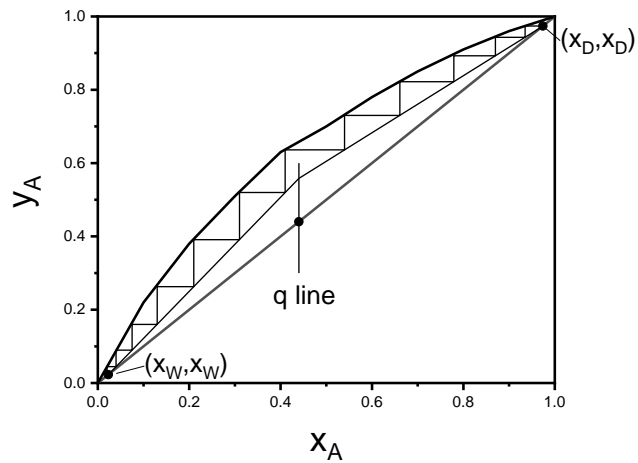
$$\text{斜率} = \frac{R}{R+1} = \frac{3.5}{3.5+1} = 0.778$$

$$y = 0.778x + 0.216$$

下段操作線：為通過(q-line 與上段操作線交點)與 x_W 的直線，可作圖如下：



而其作圖計算板數的結果如下：



如圖，大概需要 12 個理論板

若是效率為 0.6，則需要

$$\frac{10}{0.6} = 20 \text{ 個理論板}$$

計算塔頂與塔頂流量：

By mass balance,

$$F = D + W$$

$$4 = D + W$$

By mass balance of the key component,

$$F x_F = D x_D + W x_W$$

$$4 \times 0.4 = 0.97 D + 0.02 W$$

$$\begin{cases} D = 1.6 (\text{kg} / \text{s}) \\ W = 2.4 (\text{kg} / \text{s}) \end{cases}$$

$$\begin{cases} (a) D = 1.6 (\text{kg} / \text{s}) \\ (b) W = 2.4 (\text{kg} / \text{s}) \\ (c) 10 \text{ plates} \\ (d) 16.67 \text{ plates} \end{cases}$$

(本題改編自：Coulson, J.; Richardson, J.; Backhurst, J.; Harker, J. *Chemical Engineering*,

5th ed.; Volume 2, p 1165, Problem 11.10.)

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Problem 1

【Solution】

(a) Biot number, $Bi \equiv \frac{hL}{k_s}$

(b) Reynolds number, $Re \equiv \frac{\rho VL}{\mu}$

(c) Fourier number, $Fo \equiv \frac{\alpha t}{L^2}$

(d) Schmidt number, $Sc \equiv \frac{\nu}{D_{AB}}$

(e) Prandtl number, $Pr \equiv \frac{\nu}{\alpha}$

(本題可參考：Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. Fundamentals of Heat and Mass Transfer, 6th ed.; p 376~377, Table 6.2.)

Problem 2

【Solution】

∵ The system is at steady state,

$$q_{conduction} = q_{radiation}$$

And the system is in series, thus

$$q_{A \rightarrow B} = \frac{T_A - T_{middle}}{R_A} = \frac{T_{middle} - T_B}{R_B} = \frac{T_A - T_B}{R_A + R_B}$$

For radiation process at A region, the total thermal resistance is,

$$R_{A,rad} + R_{B,k} = \frac{1}{\varepsilon \sigma A (1200 + T_{middle})(1200^2 + T_{middle}^2)} + \frac{L}{kA}$$

For radiation process at B region, the total thermal resistance is,

$$R_{A,k} + R_{B,rad} = \frac{L}{kA} + \frac{1}{\varepsilon\sigma A(T_{middle} + 300)(T_{middle}^2 + 300^2)}$$

$$\because (1200 + T_{middle})(1200^2 + T_{middle}^2) > (T_{middle} + 300)(T_{middle}^2 + 300^2) \quad , \quad R_{A,rad} < R_{B,rad}$$

Therefore, the region A should be the radiation process.

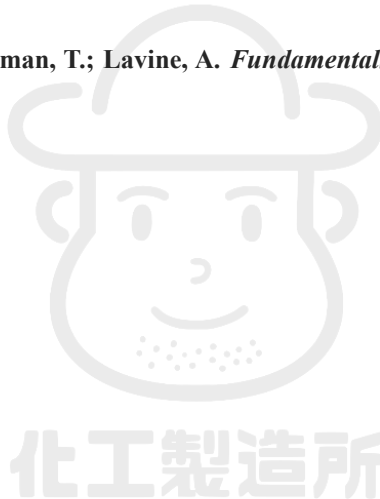
Problem 3

【Solution】

In alloys, there are more purities in the lattices, thus creating more obstacles for energy to be transferred by electrons, lowering the mean free path of the of the electron carrying thermal energy, which will decrease the thermal conductivities of alloys.

(※關於微觀的熱傳導機制，例如電子傳遞、聲子傳遞，與不同金屬、陶瓷結構的關係，可參考

Incropera, F.; Dewitt, D.; Bergman, T.; Lavine, A. *Fundamentals of Heat and Mass Transfer*, 6th ed.; p 61~64.)



Problem 4

【Solution】

We can make the following assumptions :

- (1) The mass transfer rate is equally in every direction, so we can consider only the z-direction mass transfer.
- (2) The volume of cup is infinite to the volume of dye.

Under these circumstances, we can relate the unsteady state concentration profile to,

$$\frac{C_A}{C_{A0}} = f\left(\operatorname{erf} \frac{z}{\sqrt{4D_{AB}t}}\right)$$

If we have identical $\frac{C_A}{C_{A0}}$ value, we may have the same z and t value.

∵ the volumes of the dye and the cup are fixed, after the concentration reaches uniformity,

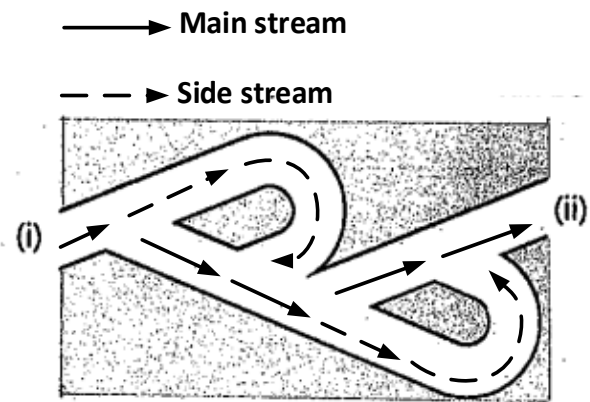
$$\frac{C_{A,\text{uniform}}}{C_{A0}} = \text{constant}$$

Therefore, it takes same time to make the two systems reaches uniformity.

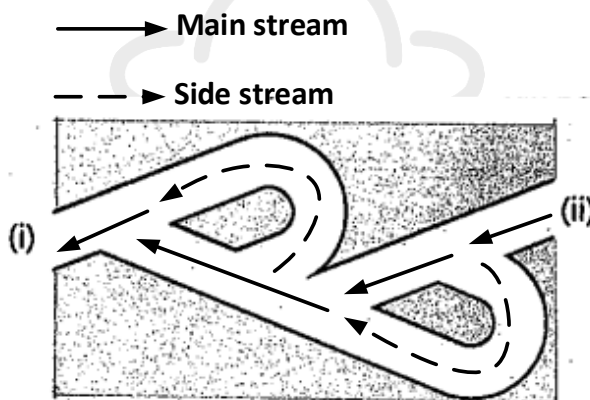
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Problem 5
【Solution】

(a)



(b)



(c)

Check valve (逆止閥)是一個在管路中能夠防止液體逆流的閥件，而由(a)小題所繪製之流通情況，我們可以預期在支流流經轉彎處時，會造成一定的動量損耗以及方向改變為原本流向相反的情形，因此能夠有效的阻止流體由(i)流相(ii)；

而(b)小題則不論是主流或者支流，皆具有同一個流動方向，並不會受到太大的阻礙，因此 Tesla valve 可視為能控制水流只由(ii)流向(i)的逆止閥。

Problem 6

【Solution】

Assume the heat conductivity, convection coefficient, and emissivity related to this problem are the same in both cases, then,

(1) The total heat transfer rate on the left at every moment is,

$$q_{\text{left}} = kA_k(T_{\text{room}} - T_{\text{water}}) + hA_c(T_{\text{room}} - T_{\text{water}}) + \sigma\epsilon A(T_{\text{room}}^4 - T_{\text{water}}^4)$$

(2) The total heat transfer rate on the right at every moment is,

$$q_{\text{right}} = kA_k(T_{\text{water}} - T_{\text{room}}) + hA_c(T_{\text{water}} - T_{\text{room}}) + \sigma\epsilon A(T_{\text{water}}^4 - T_{\text{room}}^4)$$

If $|T_{\text{water}} - T_{\text{room}}|$ is the same, the heat transfer rate by conduction and convection will be the same.

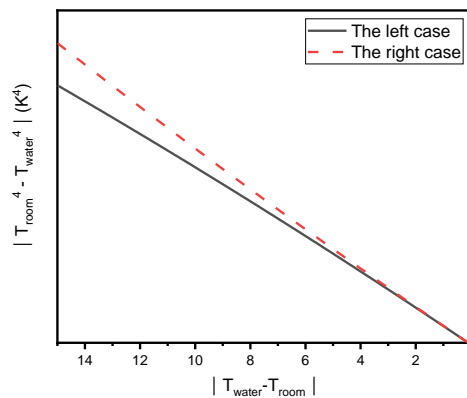
However, if we consider the contribution of radiation, we may find a different result.

If we plot $|T_{\text{room}}^4 - T_{\text{water}}^4|$ against $|T_{\text{water}} - T_{\text{room}}|$ for both cases and under the strictions,

$$\begin{cases} 273.15 + 10 \leq T_{\text{water}} \leq 273.15 + 25 & \text{for the left case} \\ 273.15 + 25 \leq T_{\text{water}} \leq 273.15 + 40 & \text{for the right case} \end{cases}$$

we can find when the value of $|T_{\text{water}} - T_{\text{room}}|$ is the same, the value of $|T_{\text{room}}^4 - T_{\text{water}}^4|$ is

larger on the right case. Therefore, we can draw a conclusion that, **at every moment, the value of the heat transfer by radiation is greater on the right case than that on the left case, so the right case will reach room temperature earlier.**



Problem 7

【Solution】

Check the value of Biot number of the system,

$$Bi = \frac{h \frac{V}{A_s}}{k} = \frac{200 \times \frac{\frac{4}{3} \pi \times (1 \times 10^{-3})^3}{4 \pi \times (1 \times 10^{-3})^2}}{15} = 4.4 \times 10^{-3} \ll 0.1$$

The lumped-capacitance method is valid.

By energy balance,

$$-hA_s(T - T_\infty) = \rho VC \frac{dT}{dt}$$

Let $\theta = T - T_\infty$, we obtain,

$$-hA_s\theta = \rho VC \frac{d\theta}{dt}$$

$$\frac{\rho VC}{hA_s} \int_{\theta_i}^{\theta} \frac{d\theta}{\theta} = - \int_0^t dt, \quad \frac{\rho VC}{hA_s} \ln \frac{\theta_i}{\theta} = t$$

$$\frac{\theta_i}{\theta} = \frac{T_i - T_\infty}{T - T_\infty} = \exp\left[\frac{hA_s}{\rho VC} t\right]$$

$$\frac{95 - 30}{T - 30} = \exp\left[\frac{200 \times 4\pi \times (1 \times 10^{-3})^2}{7500 \times \frac{4}{3} \pi \times (1 \times 10^{-3})^3 \times 500} \times 1\right]$$

$$\underline{\underline{T \approx 85^\circ\text{C}}}$$

Problem 8

【Solution】

(a)

By mass balance on the oxygen bubble,

$$\underline{\underline{-N_{O_2} \cdot A = C_{O_2} \cdot \frac{d}{dt} \left(\frac{4}{3} \pi r^3 \right)}}$$

(b)

∵ The amount of water is in excess, we can assume the concentration of oxygen is zero in the bulk solution, so

$$N_{O_2} = k_m (C_{O_2, sat} - 0)$$

代入 mass balance,

$$\begin{aligned} -k_m (C_{O_2, sat} - 0) \cdot 4\pi r^2 &= C_{O_2} \cdot \frac{d}{dt} \left(\frac{4}{3} \pi r^3 \right) = 4\pi r^2 \cdot C_{O_2} \cdot \frac{dr}{dt} \\ -k_m \frac{C_{O_2, sat}}{C_{O_2}} &= \frac{dr}{dt}, \quad \int_0^t -k_m \frac{C_{O_2, sat}}{C_{O_2}} dt = \int_{r_1}^{r_2} dr \\ -k_m \frac{C_{O_2, sat}}{C_{O_2}} t &= (r_2 - r_1) \end{aligned}$$

∵

$$C_{O_2, sat} = 40 \left(\frac{mg}{L} \right) = \frac{40}{32} \times 10^{-3} = 1.25 \times 10^{-3} \text{ (mol / L)}$$

$$C_{O_2} = \frac{P}{RT} = \frac{1}{0.082 \times (27 + 273.15)} = 0.040 \text{ (mol / L)}$$

代入：

$$-k_m \frac{1.25 \times 10^{-3}}{0.040} \times 10 \times 60 = (0.5 - 1) \times 10^{-3}$$

$$\underline{\underline{k_m = 2.98 \times 10^{-5} \text{ (m / s)}}}$$

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

Example 8.1-4)

Problem 9

【Solution】

(a) Firstly, by the question statement, we obtain,

$$x_F = 0.3, \quad x_D = 0.95, \quad \text{and} \quad x_W = 0.05$$

Under minimum reflux ratio, the q-line, equilibrium line, enriching line, and stripping line are all intersecting on the same point, so

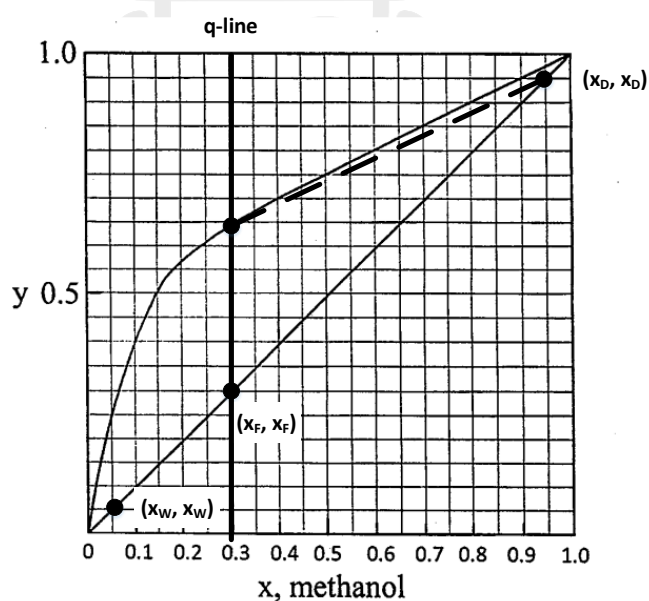
(1) q-line :

\because the feed is a saturated liquid, q line is a vertical line passing through

$$(x_F, x_F).$$

(2) Enriching line :

The enriching line will pass through the intersection of the q-line and equilibrium line, and so as the point (x_D, x_D)



By the above figure, the enriching line (dashed) passes through (0.95, 0.95) and (0.3, 0.64). Therefore, the minimum reflux ratio can be calculated as,

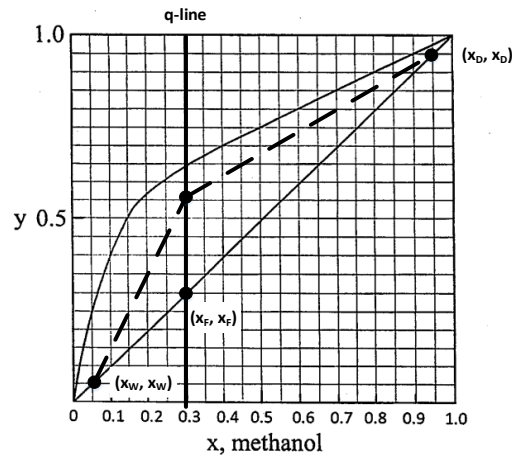
$$slope = \frac{R_m}{R_m + 1} = \frac{0.95 - 0.64}{0.95 - 0.3}$$

$$\underline{\underline{R_m = 0.91}}$$

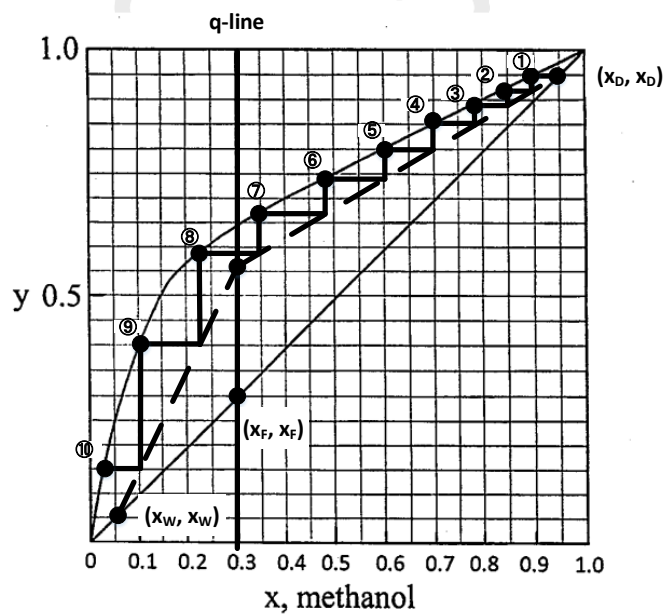
(b) If the reflux ratio is 2, then for the enriching line,

$$\text{slope} = \frac{R}{R+1} = \frac{2}{2+1} = \frac{2}{3}$$

which passes through (0.95, 0.95), so we can draw the figure as,



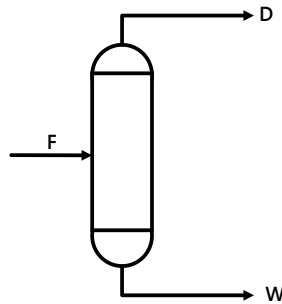
Therefore, by McCabe-Thiele graphical method,



- (1) The optimum feed plate is at th 8th plate
- (2) The number of theoretical stages is 10
- (3) The composition at the 5th plate is (0.6, 0.8)

(c)

By overall mass balance,



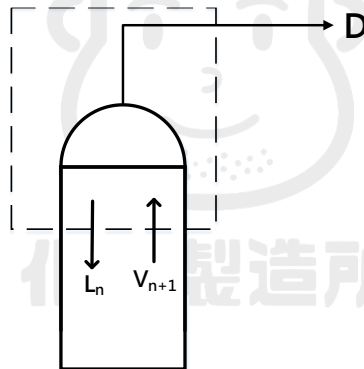
$$F = D + W \quad , \quad 1000 = D + W$$

By methanol mass balance,

$$Fx_F = Dx_D + Wx_W \quad , \quad 1000 \times 0.3 = 0.95D + 0.05W$$

$$\begin{cases} D = 277.8 \text{ (mol / hr)} \\ W = 722.2 \text{ (mol / hr)} \end{cases}$$

At enriching section,



By overall mass balance,

$$\underbrace{V_{n+1} = V_n}_{\text{恆莫耳溢流}} = L_n + D = 2D + D = 3D = 3 \times 277.8 = 833.4 \text{ (mol / hr)}$$

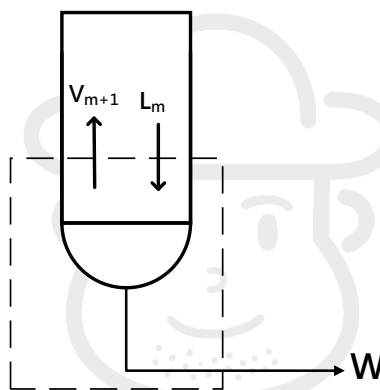
$$L_n = 2D = 555.6 \text{ (mol / hr)}$$

At feed plate, by the definition of q-line,

$$\begin{cases} L_m = L_n + qF = L_n + F = 555.6 + 1000 = \underline{\underline{1555.6 \text{ (mol / hr)}}} \\ V_m = V_n - (1-q)F = V_n = \underline{\underline{833.4 \text{ (mol / hr)}}} \end{cases}$$

which L_m and V_m are the liquid molar flux and the vapor molar flux in the stripping section.

※在恆莫耳溢流(McCabe Thiele method 的假設之一)的情況下，整個 enriching section 的氣體與液體莫耳流量相同；整個 stripping section 也是相同情形，因此一旦確定 feed plate 區域流往或流自 stripping section 的流量，即可視為 stripping section 的流量，而若是考慮 stripping section 的質量平衡：



$$V_{m+1} = V_m = L_m - W$$

$$W = L_m - V_m = 1555.6 - 833.4 = \underline{\underline{722.2 \text{ (mol / hr)}}}$$

與上方整個塔的莫爾平衡結果相同。

(本題可參考：Coulson, J.; Richardson, J.; Backhurst, J.; Harker, J. *Chemical Engineering*, 5th ed., Volume 2; p 564~566, Example 11.7.)

Problem 10

【Solution】

(a)

By simplifying the ϕ -component of the equation of continuity, we get,

$$\rho \left(\underbrace{\frac{\partial v_\phi}{\partial t}}_{v_\phi \neq v_\phi(t)} + \underbrace{v_r \frac{\partial v_\phi}{\partial r}}_{v_r=0} + \underbrace{\frac{v_\theta}{r} \frac{\partial v_\phi}{\partial \theta}}_{v_\theta=0} + \underbrace{\frac{v_\phi}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi}}_{v_\phi \neq v_\phi(\phi)} + \underbrace{\frac{v_\phi v_r + v_\theta v_\phi \cot \theta}{r}}_{v_\theta=v_r=0} \right) = - \underbrace{\frac{1}{r \sin \theta} \frac{\partial p}{\partial \phi}}_{p \neq p(\phi)}$$

$$+ \mu \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial v_\phi}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (v_\phi \sin \theta) \right) + \underbrace{\frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 v_\phi}{\partial \phi^2}}_{v_\phi \neq v_\phi(\phi)} + \underbrace{\frac{2}{r^2 \sin \theta} \frac{\partial v_r}{\partial \phi}}_{v_r=0} + \underbrace{\frac{2 \cot \theta}{r^2 \sin \theta} \frac{\partial v_\theta}{\partial \phi}}_{v_\theta=0} \right] + \underbrace{\rho g_\phi}_{g_\phi=0}$$

整理可得：

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

(b)

$$\begin{cases} r = \kappa R, v_\phi = \Omega \kappa R \sin \theta \\ r = R, v_\phi = 0 \\ \theta = 0, v_\phi = 0 \end{cases}$$

(c)

No, if we let $r = R$, we may not get $v_\phi = 0$. The alternative solution form guessed

is,

$$v_\phi = f(r) \sin \theta$$

(d)

To obtain the the troque needed to hold the outer shell stationary, we may need $\tau_{r\phi}$,

which is,

$$\tau_{r\phi} = -\mu \left[\frac{1}{r \sin \theta} \frac{\partial v_r}{\partial \phi} + r \frac{\partial}{\partial r} \left(\frac{v_\phi}{r} \right) \right] = -\mu r \frac{\partial}{\partial r} \left(\frac{v_\phi}{r} \right)$$

The torque needed is,

$$\Gamma = \int_0^{2\pi} \int_0^\pi (\tau_{r\phi})_{r=R} R \sin \theta R^2 \sin \theta d\theta d\phi$$

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

p 95, Example 3.6-5)

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Problem 1

【Solution】

True : (a)(d)(e)/ False : (b)(c)

Hagen Poiseuille equation is obtained under the following assumptions,

- (1) Laminar flow
- (2) Steady flow
- (3) Incompressible flow
- (4) Newtonian fluid
- (5) Neglected entrance effect
- (6) No-slip at the wall
- (7) The fluid behaves as a continuum

※事實上可以利用(b)與(c)推導出圓管的速度分布與其相關性質，然而 Hagen-Poiseuille equation 特指：

$$Q = \frac{\pi R^4 \Delta P}{8\mu L}$$

條件較為嚴格

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

Problem 2

【Solution】

True : (a)(b)(c)(e)/ False : (d)

- (a) The equation of continuity is merely obtained from mass balance, so applicable.
- (b) The equation of motion is merely the result of momentum balance, so applicable.
- (c) Navier-Stokes is derived based on the equation of motion and the assumptions of
(1) constant ρ and (2) constant μ
- (d) (e) By Navier-Stokes equation,

$$\rho \frac{Dv}{Dt} = -\nabla P + \rho g + \mu \nabla^2 v$$

If Reynolds number $\ll 1$, viscous term \gg inertial term

$$\cancel{\rho \frac{Dv}{Dt}} = -\nabla P + \rho g + \mu \nabla^2 v$$

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

(Stokes flow equation)

If Reynolds number $\gg 1$, viscous term \ll inertial term

$$\rho \frac{Dv}{Dt} = -\nabla P + \rho g + \cancel{\mu \nabla^2 v}$$

$$\rho \frac{Dv}{Dt} + \nabla P - \rho g = 0$$

(Euler equation)

(本題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 77~85.)

Problem 3

【Solution】

True : (a)(b)(c)(e)/ False : (d)

(a) True

(b) Stripping：溶質由液體傳遞至氣體 ↔ Absorption：溶質由氣體傳遞至液體。

(c) True. 比如活性碳可除濕乾燥。

(d) False. Counterflow 可以提供較大的質傳驅動力，有較高的質傳速率與效率。

(e) True.

Problem 4

【Solution】

True : (a)(b)(c)(e)/ False : (d)

(a) True.

$$Sc = \frac{\text{momentum diffusivity}}{\text{mass diffusivity}}, \quad Pr = \frac{\text{momentum diffusivity}}{\text{thermal diffusivity}}$$

They are analogous to each other

※而熱傳中的 Nusselt number 則與質傳之 Sherwood number 相似：

$$Nu = \frac{\text{convective heat transfer}}{\text{thermal diffusion}}, \quad Sh = \frac{\text{convective mass transfer}}{\text{mass diffusion}}$$

(b) True. They all have the dimension as, L^2/T

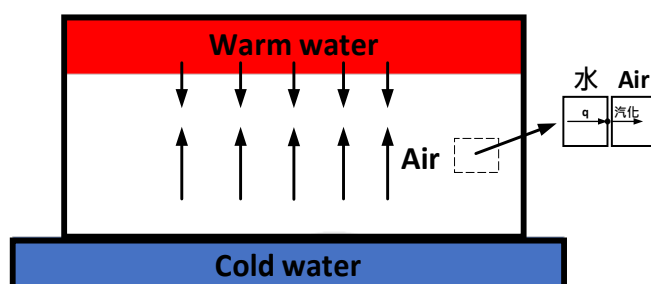
(c) True. For gaseous substances below 10 atm, their dependence of the related parameters on pressure is negligible by the prediction of collision theory.

(本小題可參考：Bird, R.; Stewart, W.; Lightfoot, E. *Transport Phenomena*, 2nd ed.; p 25/275.

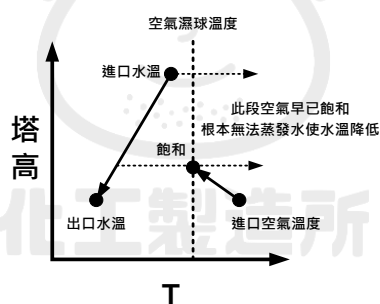
推導比較偏向物化，可參考 Atkins, P.; De Paula, J.; Keeler, J. *Atkins' Physical Chemistry*, 9th ed.; p 757~758.)

(d) False. The wet-bulb temperature of the air should be below the temperature of water it makes contact; otherwise, the cooling efficiency of the tower may be lowered。

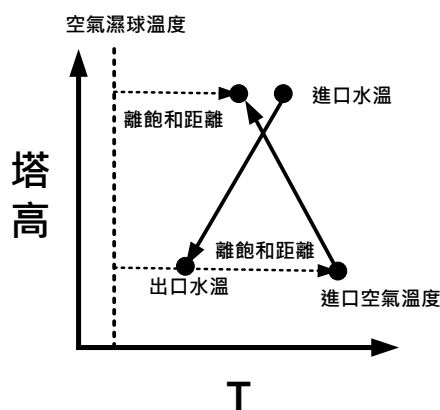
※Cooling tower 是利用乾燥空氣與水做接觸(通常為 countercurrent)，使水因水蒸氣壓梯度(水為飽和，空氣小於飽和)產生質傳至空氣中，而表面水吸收其餘水分子熱量產生汽化，使得液態水溫度降低的裝置，主要由質傳引起的蒸發降低溫度，而非靠空氣冷產生溫度梯度做冷卻。



若氣體 wet-bulb temperature 大於與其接觸之水的溫度，則空氣越容易達到飽和，無法使水有效的蒸發帶走熱量(可參考以下示意圖)：



而若是空氣濕球溫度小於水溫，則可以確保一定能夠蒸發水使水降溫：



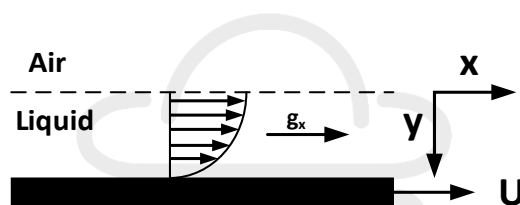
- (e) True. In the nucleate boiling region, the heat transfer is facilitated by the bubbles formed on the heating surface. So it has a large heat transfer coefficient than other boiling regions. While in film boiling region, the heating surface is covered with a vapor blanket, so the interface of heating surface and the liquid is interfered, thus lowering the effective heat transfer coefficient.

(本小題可參考：Incropera, F.; Lavine, A.; Bergman, T. *Fundamentals of Heat and Mass Transfer*, 6th ed, p 624~626.)

Problem 5

【Solution】 Yes : (a)(b)(d)(e)/No : (c)

Consider the flow system,



By the equation of motion, we have (no pressure drop)

$$-\frac{\partial \tau_{yx}}{\partial y} + \rho g_x = 0, \quad \tau_{yx} = \rho g_x y + c_1$$

$$\because y=0, \tau_{yx}=0, \quad c_1=0$$

$$\tau_{yx} = -\mu \frac{\partial v_x}{\partial y} = \rho g_x y, \quad v_x = \frac{-\rho g_x}{2\mu} y^2 + c_2$$

$$\because y=B, v_x=U, \quad c_2 = U + \frac{\rho g_x}{2\mu} B^2$$

$$v_x = \underbrace{\frac{-\rho g_x}{2\mu} y^2}_{\text{parabolic}} + \underbrace{U}_{\text{linear, depends on } y=B} + \frac{\rho g_x}{2\mu} B^2$$

$$(a) \quad g_x > 0, U = 0 \quad (b) \quad g_x > 0, U > 0$$

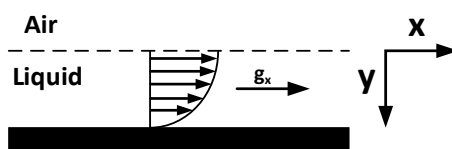
$$(c) \quad g_x = 0, U = 0, \text{ 但此時應無速度, 錯}$$

$$(d) \quad g_x < 0, U > 0 \quad (e) \quad g_x = 0, U > 0$$

※本題也可以利用 superposition 的觀念做答，將此系統拆分成兩大系統：

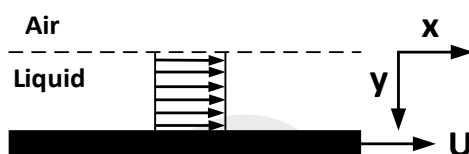
(1) 有重力影響但外板不移動

(注意上方接觸空氣，因此非對稱，只有半個拋物線)



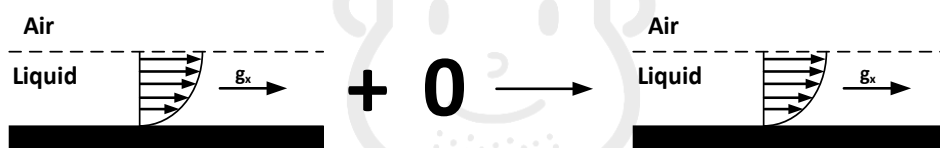
(2) 無重力影響，但外板移動

(注意上方接觸空氣，且無其他影響，導致整體系統呈現 plug flow)



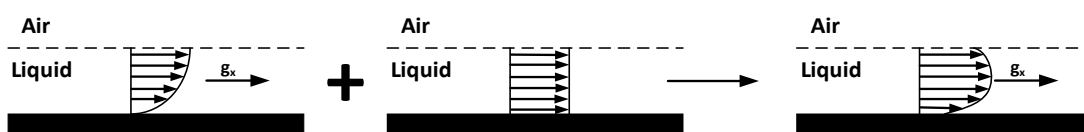
並且最終將兩種系統加起來即可：

(a)



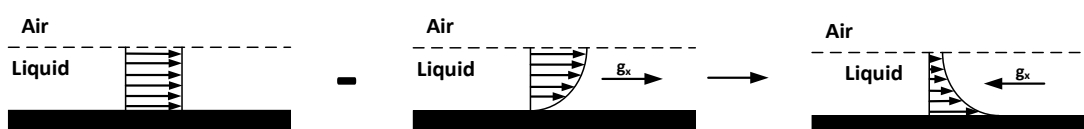
(0 代表下板不移動)

(b)



(c) 下板速度為 0，且為線性，無重力影響，因此流體應不會動

(d)



(“-“代表方向相反)

(e) plug flow 代表只有下板動，無重力影響。

Problem 6**【Solution】****(a)**

Let the dimensionless velocity, time, and length is,

$$v_{\theta} = \frac{v_{\theta}}{v_0} \quad , \quad \tilde{t} = \frac{t}{v_0 / l_0} \quad , \quad \tilde{r} = \frac{r}{l_0}$$

The PDE becomes,

$$\frac{\rho v_0^2}{l_0} \frac{\partial v_{\theta}}{\partial \tilde{t}} = \frac{\mu v_0}{l_0^2} \frac{\partial}{\partial \tilde{r}} \left[\frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} (\tilde{r} v_{\theta}) \right]$$

(b)

左右同除 $\frac{\mu v_0}{l_0^2}$:

$$\frac{\rho v_0 l_0}{\mu} \frac{\partial v_{\theta}}{\partial \tilde{t}} = \frac{\partial}{\partial \tilde{r}} \left[\frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} (\tilde{r} v_{\theta}) \right]$$

Define,

$$\text{Re} = \frac{\rho v_0 l_0}{\mu} = \frac{\text{inertial force}}{\text{viscous force}}$$

(c)

For the similarity analysis, the Reynolds number of both systems should be the same,

$$\text{Re}_A = \text{Re}_B$$

$$\because v_0 = \Omega r \quad , \quad l_0 = r$$

$$\frac{\rho(\Omega R)R}{\mu} = \frac{\rho(3\Omega_B R)(3R)}{\mu} \quad , \quad \underline{\underline{\Omega_B = \frac{1}{9}\Omega}}$$

Problem 7

【Solution】

Assume,

(1) Fully developed flow, $v_x = v_y = 0$

(2) $v_z \neq v_z(y)$

(3) Steady flow

(4) Constant ρ and μ

By the equation of continuity,

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

$$\frac{\partial v_z}{\partial z} = 0, \quad v_z = v_z(x) \quad \text{only}$$

By the equation of motion,

$$\rho \left(\frac{\partial v_z}{\partial t} + v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \right) = - \frac{\partial p}{\partial z} - \left[\frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{yz}}{\partial y} + \frac{\partial \tau_{zz}}{\partial z} \right] + \rho g \sin \beta$$

$$\frac{\partial \tau_{xz}}{\partial x} = \rho g \sin \beta, \quad \tau_{xz} = (\rho g \sin \beta)x + c_1$$

$\because x = 0, \tau_{xz} = 0$ (free surface),

$$\tau_{xz} = (\rho g \sin \beta)x$$

To make the Bingham fluid to flow, the shear stress should be $\geq \tau_0$

$$\tau_{xz} = (\rho g \sin \beta)x \geq \tau_0$$

$x = H$ 代入：

$$(\rho g \sin \beta)H \geq \tau_0$$

$$\sin \beta \geq \frac{\tau_0}{H \rho g}, \quad \beta \geq \sin^{-1} \left(\frac{\tau_0}{H \rho g} \right)$$

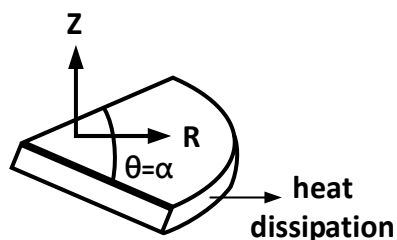
※本題需求黏滯力分布與角度之關係，因此只需要用到 equation of motion in terms of shear stress，

不需要使用 Navier-Stokes equation；且本題為非牛頓流體，本來就不能用。

Problem 8

【Solution】

(a)



(這裡的 wedge 指長的像 pizza 一樣的形狀，為具有厚度的扇形，若是完整的圓則變成圓柱)

The Biot number is defined as,

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

The temperature distribution of the wedge may depend on both the z and r direction, to simply the problem into the one associated only with the r direction, we should check if it's independent of z direction,

$$V = \text{solid's volume} = \pi R^2 \times \frac{\alpha}{2\pi} \times H = \frac{\alpha H R^2}{2}$$

$$A_s = \pi R^2 \times \frac{\alpha}{2\pi} = \frac{\alpha R^2}{2}$$

$$Bi = \frac{\frac{\alpha H R^2}{2} h(\frac{2}{\alpha H^2})}{k} = \frac{hH}{k}$$

Because the thickness of the wedge is thin (thin cylindrical wedge from the question statement),

$$Bi = \frac{hH}{k} \text{ may be very small,}$$

we can simplify the system into an one-dimensional one (r direction)

(b)

Assume $T \neq T(\theta)$ due to symmetry and insulation, by the overall equation of energy in cylindrical coordinate (including convection in z direction in equation),

$$-k(\alpha r H) \frac{dT}{dr} \Big|_r - [-k(\alpha r H) \frac{dT}{dr} \Big|_{r+dr}] - 2\alpha r dr h(T - T_a) = 0$$

同除 $(k\alpha H)dr \rightarrow 0$,

$$\frac{d}{dr} \left(r \frac{dT}{dr} \right) - \frac{2hr}{kH} (T - T_a) = 0$$

展開並整理：

$$\frac{dT}{dr} + r \frac{d^2 T}{dr^2} - \left(\frac{2h}{kH} \right) r (T - T_a) = 0$$

同乘 r

$$r^2 \frac{d^2 T}{dr^2} + r \frac{dT}{dr} - \left(\frac{2h}{kH} \right) r^2 (T - T_a) = 0$$

令 $T - T_a = \theta$ ，對照題目所給方程式，可得：

$$r^2 \frac{d^2 \theta}{dr^2} + r \frac{d\theta}{dr} - \left(\frac{2h}{kH} \right) r^2 \theta = 0, \quad \lambda^2 = \frac{2h}{kH}$$

$$\theta = c_1 I_0(\lambda r) + c_2 K_0(\lambda r)$$

$\because r=0, \theta = \text{finite},$

$$\theta(r=0) = c_1 I_0(0) + c_2 K_0(0)$$

$K_0(0) = \infty, c_2 = 0$

$\because r=R, T=T_h, \theta=T_h-T_a$

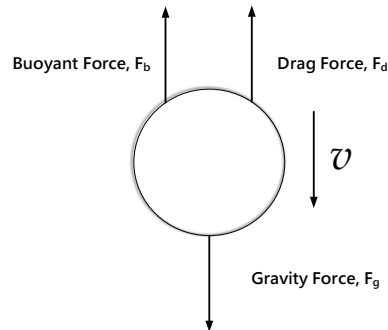
$$T_h - T_a = c_1 I_0(\lambda R), \quad c_1 = \frac{T_h - T_a}{I_0(\lambda R)}$$

$$T(r) = (T_h - T_a) \frac{I_0(\lambda r)}{I_0(\lambda R)} = (T_h - T_a) \frac{I_0\left(\sqrt{\frac{2h}{kH}} r\right)}{I_0\left(\sqrt{\frac{2h}{kH}} R\right)}$$

Problem 9

【Solution】

(a)



By force balance on the particle,

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

As the particle reaches terminal velocity,

$$m \frac{dv}{dt} = \frac{1}{6} \pi D^3 \rho_d g - \frac{1}{6} \pi D^3 \rho g - F_d = 0$$

For F_d , by the definition of friction factor,

$$F_d = (\pi R^2) \left(\frac{1}{2} \rho v^2 \right) f$$

projecting area

$$\frac{(\rho_d - \rho) \pi D^3 g}{6} - \frac{\pi \rho_d v^2 D^2}{8} f = 0, \quad \frac{(\rho_d - \rho) D g}{6} - \frac{\rho v^2}{8} f = 0$$

For ρ_d

$$\rho_d = \frac{2}{\frac{\pi}{6} \times 4^3} \times 1000 = 59.68 \text{ (kg / m}^3\text{)}$$

For the friction factor, try $f = 0.44$, (the diameter and density of the ball may be large enough)

$$\frac{(\rho_d - \rho) D g}{6} - \frac{\rho v^2}{8} \times 0.44 = 0$$

$$\frac{(59.68-1.2) \times 4 \times 10^{-2} \times 9.8}{6} - \frac{1.2v^2}{8} \times 0.44 = 0$$

$$v = 7.61 \text{ (m/s)}$$

【Check for Reynolds number】

$$\text{Re} = \frac{\rho v D}{\mu} = \frac{1.2 \times 7.61 \times 4 \times 10^{-2}}{2 \times 10^{-5}} = 18620$$

The value of 0.44 can be used as the friction factor in this case

(a)

In this case, the force balance equation is still applicable,

$$\frac{(\rho_d - \rho) D g}{6} - \frac{\rho v^2}{8} f = 0$$

For the friction factor, try $f = (\sqrt{24/\text{Re}} + 0.54)^2$,

(the diameter and density of the ball may be small enough)

$$\frac{(\rho_d - \rho) D g}{6} - \frac{\rho v^2}{8} \times \left(\sqrt{\frac{24\mu}{\rho v D}} + 0.54 \right)^2 = 0$$

$$\frac{(1100-1000) \times 0.07 \times 10^{-3} \times 9.8}{6} - \frac{1000v^2}{8} \times \left(\sqrt{\frac{24 \times 0.002}{1000v \times 0.07 \times 10^{-3}}} + 0.54 \right)^2 = 0$$

$$v = 1.31 \times 10^{-4} \text{ (m/s)}$$

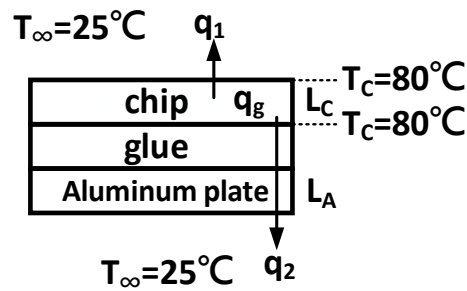
【Check for Reynolds number】

$$\text{Re} = \frac{\rho v D}{\mu} = \frac{1000 \times 1.31 \times 10^{-4} \times 0.07 \times 10^{-3}}{0.002} = 4.59 \times 10^{-3}$$

Which is applicable for this case.

Problem 10

【Solution】



By energy balance on the chip,

$$q_g - q_1 - q_2 = 0$$

For $q_g = q_e A$ (q_e 單位為 W/m^2)

For q_1 , because the system is in steady state,

$$q_1 = q_{con}$$

$$q_1 = hA(T_{chip} - T_{\infty})$$

For q_2 , because the system is in steady state,

$$q_2 = q_{glue} = q_{plate} = q_{con}$$

$$q_2 = \frac{(T_{chip} - T_{\infty})}{R_{glue} + \frac{L_{plate}}{k_{plate}A} + \frac{1}{hA}}$$

代入 energy balance, 且同除 A

$$\begin{aligned} q_e \cancel{A} - h \cancel{A} (T_{chip} - T_{\infty}) - \frac{(T_{chip} - T_{\infty})}{R_{glue} \cancel{A} + \frac{L_{plate}}{k_{plate} \cancel{A}} + \frac{1}{h \cancel{A}}} &= 0 \\ 1 \times 10^4 - 100(80 - 25) - \frac{(80 - 25)}{R \times (2 \times 10^{-2})^2 + \frac{2 \times 10^{-3}}{240} + \frac{1}{100}} &= 0 \\ \underline{\underline{R = 5.53 \text{ (K/W)}}} \end{aligned}$$

(b)

Because the thickness of the aluminum plate contributes the thermal resistance of the system, which is,

$$R_{plate} = \frac{L_{plate}}{k_{plate}A}$$

where L_{plate} is the thickness of the aluminum plate.

the statement would be true.

Problem 11

【Solution】

(a)

By overall mole balance,

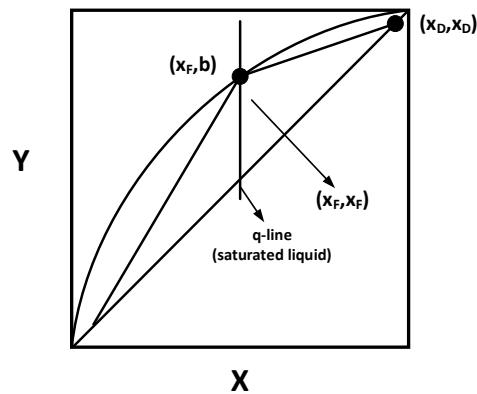
$$F = D + B, \quad D + B = 100$$

By the mole balance of benzene,

$$Fx_F = Bx_B + Dx_D, \quad 100 \times 0.50 = 0.90D + 0.1B$$

$$\begin{cases} D = 50 \text{ (kmol / h)} \\ B = 50 \text{ (kmol / h)} \end{cases}$$

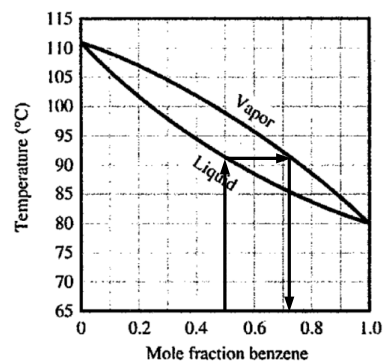
(b)



Under the minimum reflux ratio, the q-line, operation line and equilibrium line would all intersect, and the slope of operation line would be,

$$\frac{x_D - b}{x_D - x_F} = \frac{R_m}{R_m + 1}$$

By the phase diagram attached, we can read the point (x_F, b) ,



For b, the vapor concentration of benzene, can be obtained as 0.71

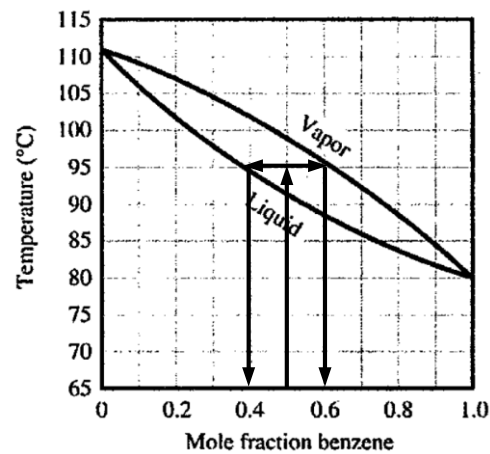
$$\frac{0.90 - 0.71}{0.90 - 0.50} = \frac{R_m}{R_m + 1} \quad , \quad \underline{\underline{R_m = 0.90}}$$

(c)

If the feed is 50% saturated liquid, the composition of liquid and vapor can be calculated by the lever-arm rule,

$$\frac{L}{V} = \frac{|z - y|}{|z - x|} = \frac{0.5}{0.5} = 1$$

By the phase diagram attached,



The compositions of liquid and vapor are,

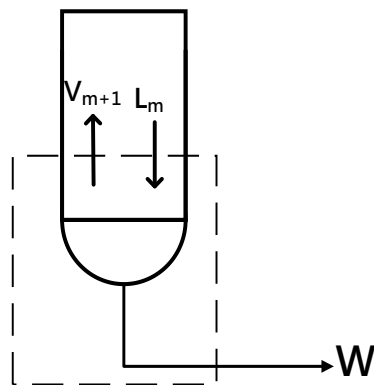
$$\left\{ \begin{array}{l} \text{vapor} \\ \text{liquid} \end{array} \right\} \left\{ \begin{array}{l} \text{Toluene} = 0.4 \\ \text{Benzene} = 0.6 \\ \text{Toluene} = 0.6 \\ \text{Benzene} = 0.4 \end{array} \right.$$

The relative volatility (Benzene to Toluene) is,

$$\alpha = \frac{0.6 \times 0.6}{0.4 \times 0.4} = \underline{\underline{2.25}}$$

(d)

For stripping section,



By overall balance,

$$L_m = V_{m+1} + W$$

By key component balance,

$$L_m x_m - V_{m+1} y_{m+1} = W x_w$$

$$\text{斜率} : \frac{L_m}{V_{m+1}} = \frac{L_m}{L_m - W} > 1$$

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

7th ed.; p 672.)

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1. Ans : (b)

【Solution】

For ideal gas,

$$Z_{id} = \frac{PV_{id}}{RT} = 1$$

For the real gas,

$$Z = \frac{PV_{real}}{RT} = \frac{P(0.88V_{id})}{RT} = \underline{\underline{0.88}}$$

2. Ans : (e)

【Solution】

$$W = -\int P dV = -nRT \int_{V_i}^{V_f} \frac{1}{V} dV$$

$$W = -5.2 \times 10^{-2} \times 8.314 \times 260 \ln \frac{1}{3} = \underline{\underline{123.49}} \text{ (J)}$$

3. Ans : (a)

【Solution】

$$\Delta_r H^\circ = \Delta_r U^\circ + \Delta(PV) = \Delta_r U^\circ + \Delta n RT$$

$$\Delta_r H^\circ = -1373 \text{ (kJ / mol}^{-1}\text{)} + \frac{(2+3-3) \times 8.314 \times 298}{1000}$$

$$\Delta_r H^\circ = \underline{\underline{-1368 \text{ (kJ / mol)}}}$$

4. Ans : (c)

【Solution】

$$\begin{aligned} dU &= \underbrace{C_V dT}_{\text{isothermal}} + [T(\frac{\partial P}{\partial T})_V - P] dV \\ &= \int_1^{24.8} \frac{a}{V^2} dV = \int_1^{24.8} \frac{1.352}{V^2} dV \\ &= 1.297 \times \frac{8.314}{0.082} = \underline{\underline{131.55 \text{ (J / mol)}}} \end{aligned}$$

5. Ans : (c)

【Solution】

$$\Delta S = nC_{V,m} \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

$$\Delta S = n(C_{P,m} - R) \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

$$\Delta S = 1 \times \frac{3}{2} \times 8.314 \ln \frac{600}{300} + 1 \times 8.314 \ln \frac{50}{30} = \underline{\underline{12.89 (J / K)}}$$

6. Ans : (d)

【Solution】

$$\hat{\mu}_i - \hat{\mu}_i^{ig} = RT \ln \hat{f}_i - RT \ln P_i = RT \ln \frac{\hat{f}_i}{P} = RT \ln \hat{\phi}_i$$

$$RT \ln \hat{\phi}_i = 8.314 \times 200 \ln 0.72 = \underline{\underline{-546.23 (J / mol)}}$$

7. Ans : (b)

【Solution】

By Clapeyron equation,

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

$$\Delta V = (V_L - V_s) = \left(\frac{1}{\rho_L} - \frac{1}{\rho_s} \right) (cm^3 / g) \times 78 (g / mol) \times 10^{-6} (m^3 / cm^3)$$

$$= \left(\frac{1}{0.879} - \frac{1}{0.891} \right) \times \frac{78}{10^6} = 1.195 \times 10^{-6} (m^3 / mole)$$

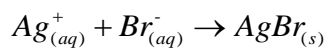
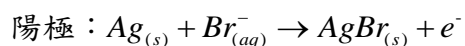
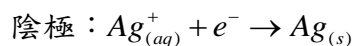
$$\frac{dP}{dT} = \frac{(1000-1) \times 10^5}{dT} = \frac{\Delta H}{T \Delta V} = \frac{10.59 \times 10^3}{T \times (1.195 \times 10^{-6})}$$

$$\frac{(1000-1) \times 10^5 \times (1.195 \times 10^{-6})}{10.59 \times 10^3} = \int_{5.5+273}^T \frac{dT}{T}$$

$$T = \underline{\underline{281.65 (K)}}$$

8. Ans : (e)

【Solution】



By Nernst equation,

$$\Delta E = \Delta E^{\circ} - \frac{RT}{nF} \ln Q, \quad 0 = \Delta E^{\circ} - \frac{RT}{nF} \ln K_{sp} = \Delta E^{\circ} - \frac{RT}{nF} \ln \left(\frac{1}{[Ag^{+}][Br^{-}]} \right), \quad \text{選(e)}$$

9. Ans : (d)

10. Ans : (a)

【Solution】

For spontaneity, we have the following criteria for different conditions,

$$dU_{S,V} \leq 0 \quad dH_{S,P} \leq 0$$

$$dA_{T,V} \leq 0 \quad dG_{T,P} \leq 0$$

$$dS_{U,V} \geq 0 \quad dS_{H,P} \geq 0$$

<證明> $dS_{U,V} \geq 0$ 、 $dU_{S,V} \leq 0$ 、 $dH_{S,P} \leq 0$

For $dS_{U,V}$

By First law,

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

By Second law,

$$dS = \frac{Q}{T} + S_{gen} \quad (\text{假設 closed system})$$

$$Q = TdS - TS_{gen} \quad \text{代回}$$

$$dU = TdS - TS_{gen} - PdV, \quad dS = \frac{dU}{T} + \frac{P}{T}dV + S_{gen}$$

At constant U and V,

$$dS_{U,V} = TS_{gen} \geq 0$$

For $dU_{S,V}$

$$dU = TdS - TS_{gen} - PdV$$

$$dU_{S,V} = 0 - 0 - TS_{gen} \leq 0$$

For $dH_{S,P} \leq 0$

$$dH = dU + PdV + VdP = TdS - TS_{gen} - PdV + PdV + VdP = TdS + VdP - TS_{gen}$$

$$dH_{S,P} = 0 + 0 - TS_{gen} \leq 0$$

11.

【Solution】

Pasteurizing rate, $r \propto \frac{1}{t}$

$$\text{Also, } r = k_0 e^{\frac{-Ea}{RT}}$$

$$\frac{r_{63^\circ\text{C}}}{r_{74^\circ\text{C}}} = \frac{1}{\frac{30 \times 60}{15}} = \frac{e^{\frac{-Ea}{8.314(63+273)}}}{e^{\frac{-Ea}{8.314(74+273)}}}, \quad Ea = \underline{\underline{421.885 \text{ (kJ / mol)}}}$$

12.

【Solution】

$$(a) r_{CS_2} = \frac{n_{CS_2}}{V} \times \frac{1}{t} = \frac{\frac{0.1}{12+64}}{\frac{10}{60} \times 35.2} = \underline{\underline{2.24 \times 10^{-4} (mole / cm^3 \cdot hr)}}$$

(b) For PFR, design equation,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A}$$

For X_A

$$F_{CS_2} = F_{CH_4} X_A = 2.24 \times 10^{-4} \times 35.2 = 7.89 \times 10^{-3} = 0.119 X_A$$

$$X_A = 0.066$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{1 \times \frac{1}{3}}{0.082 \times (600 + 273)} = 4.656 \times 10^{-3} (mole / L)$$

代回 rate equation 與 design equation 合併,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{k C_{A0}^2 (1 - X_A)(2 - 2X_A)}$$

$$\frac{35.2}{1000} = \int_0^{0.066} \frac{0.1190 dX_A}{k \times (4.656 \times 10^{-3})^2 (1 - X_A)(2 - 2X_A)}$$

$$\underline{\underline{k = 5509.92 (M^{-1} hr^{-1})}}$$

13.

【Solution】

$$r_{C_6H_6} = k_3[C_6H_5\cdot][H_2]$$

By PSSH, $r_{H\cdot} = r_{C_6H_5\cdot} = 0$

$$r_{H\cdot} = 2k_1[H_2] - k_2[H\cdot][C_6H_5CH_3] + k_3[C_6H_5\cdot][H_2] - k_4[H\cdot]^2 = 0$$

$$r_{C_6H_5\cdot} = k_2[H\cdot][C_6H_5CH_3] - k_3[C_6H_5\cdot][H_2] = 0$$

兩式相加,

$$2k_1[H_2] - k_4[H\cdot]^2 = 0$$

$$[H\cdot] = \sqrt{\frac{2k_1[H_2]}{k_4}} = k'[H_2]^{\frac{1}{2}}$$

代入 $r_{C_6H_5\cdot}$,

$$[C_6H_5\cdot] = \frac{k_2[H\cdot][C_6H_5CH_3]}{k_3[H_2]} = \frac{k_2k'[H_2]^{\frac{1}{2}}[C_6H_5CH_3]}{k_3[H_2]}$$

$$r_{C_6H_6} = \frac{k_2k'[H_2]^{\frac{1}{2}}[C_6H_5CH_3]}{k_3}, \text{ where}$$

$$k' = \sqrt{\frac{2k_1}{k_4}}$$

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1. Ans : (c)

【Solution】

Define selectivity of D to U, $S_{D/U} \equiv \frac{r_D}{r_U} = \frac{15e^{-(273/T)}C_A^{0.5}C_C}{200e^{-(2000/T)}C_A C_C} = 0.075e^{1727/T}C_A^{-0.5}$

For temperature, $S \propto e^{1/T}$, to maximum S , **low temperature** should be applied.

For concentration (reactor type), $S \propto C_A^{-0.5}$, to maximum S , **low concentration of A**

should be applied => CSTR should be used.

2. Ans : (a)

【Solution】

$$C_A = \frac{(\varepsilon + 1)P_0 - P}{\delta RT} = \frac{[(2+1-1+1) \times 1 \times 7.5 - 15.8]}{760} = 1.77 \times 10^{-4} \text{ (M)}$$

3. Ans : (d)

【Solution】

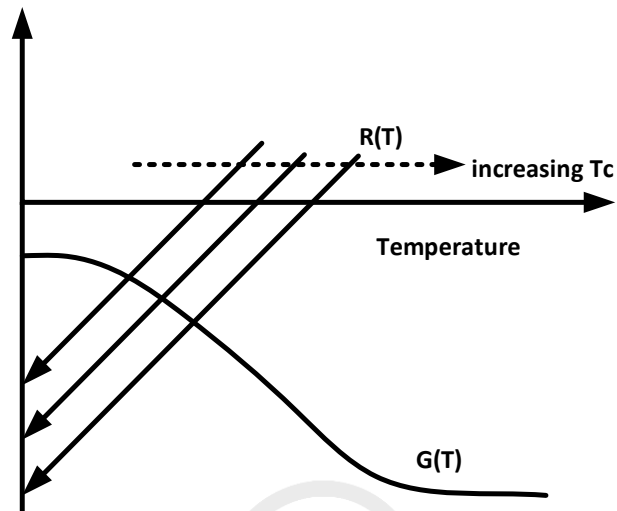
$$-r_A = \frac{-dC_A}{dt} = \frac{1}{\delta RT} \frac{dP}{dt}, \text{ by differential method}$$

$$-r_{A,10\min} = \frac{1}{\delta RT} \frac{P_{15.0\min} - P_{5.0\min}}{15.0 - 5.0} = \frac{1}{2 \times 0.082 \times 303} \frac{(17.9 - 12.5)}{15.0 - 5.0} = 1.43 \times 10^{-5} \text{ (M / min)}$$

4. Ans : (c)

【Solution】

若為 adiabatic reactor with endothermic reaction，則其 $R(T)$ 與 $G(T)$ 圖：



此圖交點即為 steady state point, 只可能有一個 steady state point.

(本題為原文書之 self test，網址為：

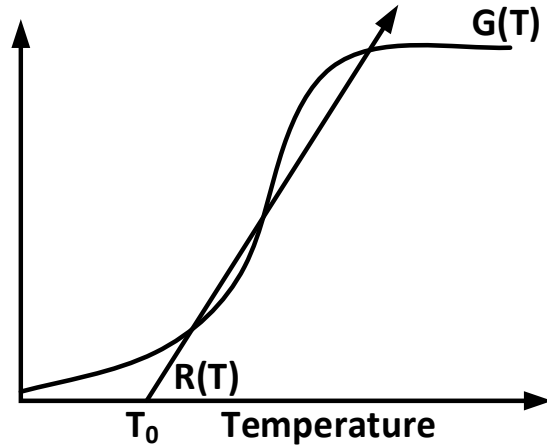
<http://websites.umich.edu/~elements/course/lectures/eight/test9.htm#solution>)

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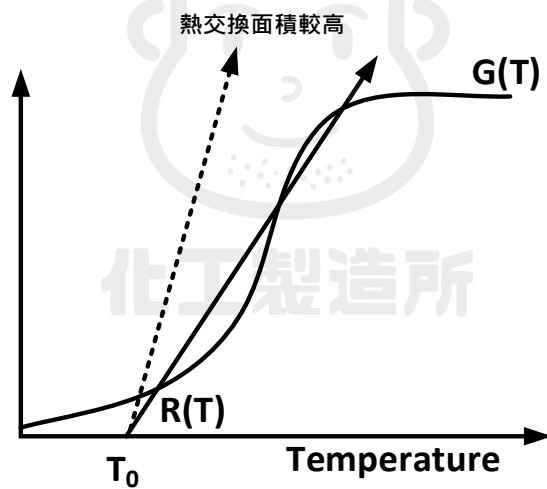
5. Ans : (a)

【Solution】

一般來說，multiple steady state 較常發生於非絕熱之放熱反應，



(B)(C)(D)選項意指維持在低溫與高溫下進行反應，或者在低轉化率中進行反應，然而此三者依舊需要靠外界熱交換來做控制(即 $R(T)$ 項)，因此選(A)較合適



(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 534.)

6. Ans : (c)

【Solution】

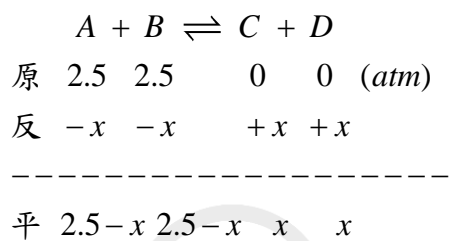
根據 van't Hoff equation,

$$\Delta G = \Delta G^\circ + RT \ln K = 0$$

$$RT \ln K = -\Delta G^\circ = 1.987 \times 500 \ln K = 500$$

$$K = 1.654$$

Reaction : $A + B \rightleftharpoons C + D$



$$K = \frac{x^2}{(2.5-x)^2} = 1.654, \quad x = 1.406$$

$$\text{則轉化率 } X_A = \frac{1.406}{2.5} = \underline{\underline{0.5625}}$$

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7. Ans : (d)

【Solution】

For PFR, design equation,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A}$$

rate equation,

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

combine,

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

$$\tau = \int_0^{X_A} \frac{C_{A0} dX_A}{kC_{A0}(1 - X_A)} = \int_0^{X_A} \frac{dX_A}{k(1 - X_A)}, \text{ 代入數字}$$

$$\tau = \int_0^{0.6} \frac{dX_A}{0.2(1 - X_A)} = \underline{\underline{4.58(\text{min})}}$$

8. Ans : (a)

【Solution】

By energy balance, (closed system)

$$\Delta U = Q + W = 0 \text{ (isothermal)}$$

$$W = -Q$$

By entropy balance,

$$\Delta S = \sum_{\text{closed system}} \cancel{M_k S_k} + \frac{Q}{T} + \cancel{\frac{S_{\text{gen}}}{\text{maximum work}}} = 0$$

$$Q = T \Delta S = T \left[\underbrace{n C_P \ln \frac{T_f}{T_i}}_{\text{isothermal}} - n R \ln \frac{P_f}{P_i} \right]$$

$$-298 \times 1 \times 8.314 \ln \frac{10}{1} = -5704.82 \text{ (J)}, W = -Q = 5704.82 \text{ (J)} = \underline{\underline{5.7 \text{ (kJ)}}}$$

9. Ans : (c)

【Solution】

$$W = -\int P dV = -P_{ex} (V_f - V_i) = -P_{ex} \left(\frac{nRT}{P_f} - \frac{nRT}{P_i} \right)$$

$$W = -P_{ex} nRT \left(\frac{1}{P_f} - \frac{1}{P_i} \right) = -20 \times 1 \times 8.314 \times 298 \left(\frac{1}{10} - \frac{1}{1} \right), \quad \underline{\underline{W = 44569(J)}}$$

10. Ans : (d)

【Solution】

By Clapeyron Clausius equation,

$$\frac{d \ln P}{dT} = \frac{\Delta H_{vap}}{RT^2}$$
$$\ln \frac{P_{(400K)}}{P_{(300K)}} = \ln \frac{10}{5} = \frac{-\Delta H_{vap}}{8.314} \left(\frac{1}{400} - \frac{1}{300} \right)$$
$$\underline{\underline{\Delta H_{vap} = 6915(J/mol)}}$$

11. Ans : (a)

【Solution】

根據上題，將 $P = 7bar$ 代入

$$\ln \frac{7}{5} = \frac{-6915}{8.314} \left(\frac{1}{T_{7bar}} - \frac{1}{300} \right)$$

$$T_{7bar} = 341.4 K$$

因為題目所給之溫度(350 K)大於 7 bar 時之飽和溫度

因此此時相態應為氣態

※此題也可利用飽和溫度反推飽和壓力，再與題目所給之壓力做比較。

12. Ans : (c)

【Solution】



By energy balance,

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

$$-W = Q - \Delta H_{mix}^{id} = Q \quad (\Delta H_{mix}^{id} = 0)$$

By entropy balance,

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

$$\sum_i \dot{M}_k \hat{S}_k + \sum \frac{\dot{Q}}{T} = 0$$

$$\begin{aligned} -\dot{W} = \dot{Q} &= T(\dot{n} \Delta S_{mix}^{id}) = -\dot{n} RT(x_A \ln x_A + x_B \ln x_B) \\ &= -(2+3) \times 8.314 \times 300(0.4 \ln 0.4 + 0.6 \ln 0.6) \\ &= \underline{\underline{8393 \text{ (J / min)}}} \end{aligned}$$

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

5th ed.; p 505, Problem 9.55.)

13. Ans : (a)

【Solution】



By energy balance,

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

$$-W = \Delta H_{mix}^{id} = 0$$

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

p 505, Problem 9.55.)

14. Ans : (e)

【Solution】

By Gibbs phase rule

$$F = c - p + 2$$

c (number of components) : water + CO_2 + sugar + flavor = 4

p (number of phases) : liquid(water + dissolved CO_2 + sugar) + gas(CO_2) = 2

$$F = 4 - 2 + 2 = \underline{4}$$

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

5th ed.; p 405.)

15.

【Solution】

For batch reactor, design equation,

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

rate equation

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

Combine,

$$C_{A0} \frac{dX_A}{dt} = 2kC_{A0}^2 (1 - X_A)^2$$

$$\int_0^{X_A} \frac{dX_A}{2(1 - X_A)^2} = C_{A0} k \int_0^t dt \quad , \text{ 代入數字}$$

$$\int_0^{X_A} \frac{dX_A}{2(1 - X_A)^2} = 2 \times 0.2 \int_0^{1 \times 60} dt$$

$$X_A = 0.98 \quad , \text{ producing } 2 \times 0.98 \times 2 \times 100 = \underline{\underline{392 (mol)}}$$

16.

【Solution】

根據上題，

$$\int_0^{X_A} \frac{dX_A}{2(1 - X_A)^2} = C_{A0} k \int_0^t dt$$

代入 $X_A = 0.8$

$$\int_0^{0.8} \frac{dX_A}{2(1 - X_A)^2} = 2 \times 0.2 \int_0^t dt \quad , \quad \underline{\underline{t = 5 (mins)}}$$

17.

【Solution】

$$C_C = C_{A0} \times 2X_A$$

$$\frac{N_C}{V} = \frac{300}{V} = C_C = C_{A0} \times 2X_A = 2 \times 2 \times 0.8$$

$$V = 93.75 \text{ (L)} = \frac{4}{5} V_{\text{reactor}}$$

$$V_{\text{reactor}} = \underline{\underline{117.2 \text{ (L)}}}$$

18.

【Solution】

For PFR, design equation,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A}$$

rate equation,

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

Combine,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{2kC_{A0}^2 (1 - X_A)^2} = \int_0^{0.8} \frac{\frac{240}{60} \times 2 dX_A}{2 \times 0.2 \times 2^2 (1 - X_A)^2}$$

$$V = \underline{\underline{20 \text{ (L)}}}$$

19.

【Solution】

By energy balance on the CPU, ($\dot{m} - \dot{out} + gen = \dot{acc}$)

$$IV - h(T - T_{am}) = 0$$

$$\underline{\underline{T = \frac{IV}{h} + T_{am}}}$$

20.

【Solution】

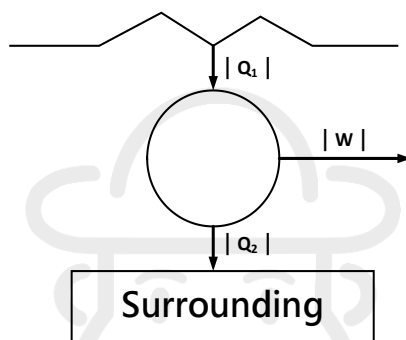
By entropy balance on the CPU,

$$\frac{dS}{dt} = \sum_{\substack{\text{s.s.} \\ \text{closed system}}} \dot{M}_k \hat{S}_k + \sum \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

$$\dot{S}_{gen} = -\frac{\dot{Q}}{T} = \frac{h(T - T_{am})}{T} = h\left(1 - \frac{T_{am}}{T}\right) = h\left(1 - \frac{T_{am}}{\frac{IV}{h} + T_{am}}\right) = \frac{hIV}{IV + hT_{am}}$$

21.

【Solution】



By energy balance on the device,

$$|\dot{Q}_1| - |\dot{Q}_2| - |\dot{W}| = 0$$

$$|\dot{W}| = |\dot{Q}_1| - |\dot{Q}_2|$$

By entropy balance on the device,

$$\frac{dS}{dt} = \sum_{\substack{\text{s.s.} \\ \text{closed system}}} \dot{M}_k \hat{S}_k + \frac{|\dot{Q}_1|}{T} - \frac{|\dot{Q}_2|}{T_{am}} + \dot{S}_{gen} = 0$$

$$|\dot{Q}_2| = \frac{T_{am}}{T} |\dot{Q}_1|$$

By energy balance on the CPU,

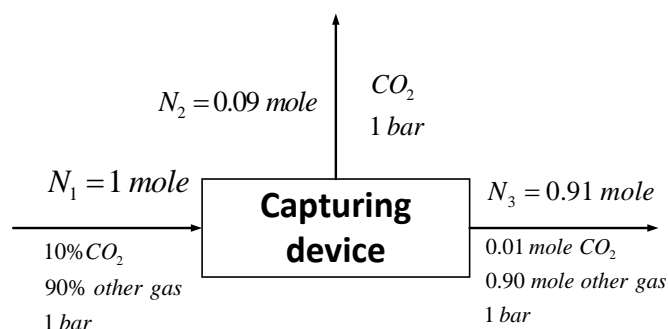
$$IV - |\dot{Q}_1| = 0, \quad |\dot{Q}_1| = IV$$

$$\text{則 } |\dot{W}| = |\dot{Q}_1| - |\dot{Q}_2| = |\dot{Q}_1| \left(1 - \frac{T_{am}}{T}\right) = IV \left(1 - \frac{T_{am}}{T}\right) = IV \left(1 - \frac{T_{am}}{\frac{IV}{h} + T_{am}}\right) = \frac{I^2 V^2}{IV + hT_{am}}$$

22.

【Solution】

根據題意畫出簡圖如下：



假設 other gas 具有不同成分，但有相同之熱力學性質且為理想氣體

By energy balance,

$$\cancel{\Delta H}_{\text{isothermal}} + \cancel{\frac{\Delta v^2}{2g_c}} + \cancel{\frac{g}{g_c} \Delta z}_{\text{negligible}} = Q + W$$

$$W = -Q$$

By entropy balance,

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

$$\dot{Q} = -T \sum_i \dot{M}_k \hat{S}_k = T(\dot{n}_{\text{other}} \Delta \underline{S}_{\text{other}} + \dot{n}_{\text{CO}_2, \text{captured}} \Delta \underline{S}_{\text{CO}_2, \text{captured}} + \dot{n}_{\text{CO}_2, \text{emitted}} \Delta \underline{S}_{\text{CO}_2, \text{emitted}})$$

$$\dot{Q} = T(-\dot{n}_{\text{other}} R \ln \frac{P_{\text{other},f}}{P_{\text{other},i}} - \dot{n}_{\text{CO}_2, \text{captured}} R \ln \frac{P_{\text{CO}_2, \text{capture},f}}{P_{\text{CO}_2, \text{capture},i}} - \dot{n}_{\text{CO}_2, \text{emitted}} R \ln \frac{P_{\text{CO}_2, \text{emitted},f}}{P_{\text{CO}_2, \text{emitted},i}})$$

$$\dot{Q} = -8.314 \times 300 (0.9 \ln \frac{1 \times \frac{0.9}{0.9+0.01}}{1 \times \frac{0.9}{0.9+0.1}} + 0.09 \ln \frac{1}{1 \times \frac{0.1}{0.1+0.9}} + 0.01 \ln \frac{1 \times \frac{0.01}{0.9+0.01}}{1 \times \frac{0.1}{0.9+0.1}})$$

$$W = -\dot{Q} = 673.51 \text{ (J / mole}_{\text{flue gas}}) = 673.51 \times \frac{1 \text{ (mole}_{\text{flue gas}})}{0.09 \text{ (mole}_{\text{CO}_2, \text{captured}})}$$

$$= 7483.42 \text{ (J / mole}_{\text{CO}_2, \text{captured}}) = \underline{\underline{7.483 \text{ (kJ / mole}_{\text{CO}_2, \text{captured}})}})$$

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Problem 1

【Solution】

By total energy balance on CSTR : $in - out + gen = accu$

$$\sum_i F_{A0} \theta_{i0} H_{i0} - \sum_i F_{A0} (\theta_{i0} + v_i X_A) H_i + Q - \dot{W}_s = 0,$$

where v_i is the stoichiometric number.

$\because \dot{W}_s = 0$ and adiabatic ($Q=0$), 且合併整理

$$\sum_i F_{A0} \theta_{i0} (H_{i0} - H_i) - \sum_i F_{A0} v_i X_A H_i = 0$$

$\because H_{i0} - H_i = \int_{T_i}^{T_{i0}} C_{pi} dT$, $\sum_i v_i H_i = \Delta H_{rxn}$ 代入,

$$\sum_i F_{A0} \int_{T_i}^{T_{i0}} C_{pi} \theta_{i0} dT - F_{A0} X_A \Delta H_{rxn} = 0$$

移項並整理：

$$X_A = \frac{\sum_i F_{A0} \int_{T_i}^{T_{i0}} C_{pi} \theta_{i0} dT}{F_{A0} \Delta H_{rxn}} = \frac{\sum_i \int_{T_{i0}}^{T_i} C_{pi} \theta_{i0} dT}{-\Delta H_{rxn}} = \frac{\int_{T_0}^T C_{pA} dT}{-[H_B^* - H_A^* + \int_{298}^T (C_{pB} - C_{pA}) dT]} \quad \text{---(1)}$$

By the design equation of CSTR :

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

By the rate equation :

$$-r_A = k(T) C_A = k(T) C_{A0} (1 - X_A)$$

合併：

$$V = \frac{F_{A0} X_A}{-r_A} = \frac{F_{A0} X_A}{k(T) C_{A0} (1 - X_A)}$$

$$X_A = \frac{V k C_{A0}}{F_{A0} + V k C_{A0}}$$

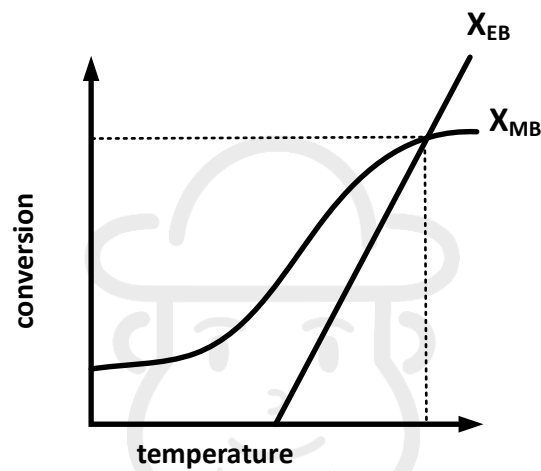
For $k(T)$, by Arrhenius law :

$$k(T) = k_0 e^{\frac{E}{RT}}, \text{ where } k_0 \text{ is the pre-exponential factor}$$

代入：

$$X_A = \frac{V k_0 e^{\frac{-E}{RT}} C_{A0}}{F_{A0} + V k_0 e^{\frac{-E}{RT}} C_{A0}} \text{ ----- (2)}$$

將(1)與(2)式畫成 $X_A - T$ 圖：



根據上圖，則兩條線之交點可決定出口溫度與轉化率

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 531.)

Problem 2

【Solution】

For CSTR, design equation,

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

rate equation,

$$-r_A = kC_{A0}(1 - X_A)$$

Combine,

$$V = \frac{F_{A0} X_A}{kC_{A0}(1 - X_A)} = \frac{10 \times 0.8}{\frac{-20 \times 10^3}{k_0 e^{1.987 \times 350}} \times 1 \times (1 - 0.8)}$$

$$k_0 V = 1.23 \times 10^{14}$$

For PFR, design equation,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A} = \int_0^{X_A} \frac{F_{A0} dX_A}{kC_{A0}(1 - X_A)} = \int_0^{X_A} \frac{10 dX_A}{\frac{-20 \times 10^3}{k_0 e^{1.987 \times 315}} \times 1 \times (1 - X_A)}$$

$$Vk_0 = 1.23 \times 10^{14} = \int_0^{X_A} \frac{10 dX_A}{1.326 \times 10^{-14} \times 1 \times (1 - X_A)}$$

$$\underline{\underline{X_A \approx 0.15}}$$

Problem 3

【Solution】

For outlet stream,

$$y_A = \frac{F_A}{F_A + F_B + F_I} = \frac{F_{A0}(1 - X_A)}{F_{A0}(1 - X_A) + F_{A0}(\theta_B + \frac{1}{2}X_A) + F_{I0}}$$

$$y_A = \frac{0.5F_0(1 - X_A)}{0.5F_0(1 - X_A) + 0.5F_0(0.1 + \frac{1}{2}X_A) + 0.45F_0} = 0.1$$

$$X_A = 0.842$$

For PFR, design equation,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A}$$

rate equation,

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

$$\text{where } \varepsilon = \delta y_{A0} = -\frac{1}{2} \times \frac{1}{2} = -0.25$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{10 \times 0.5}{0.082 \times 373} = 0.163 \text{ (mol / L)}$$

combine,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A} = \int_0^{X_A} \frac{F_{A0} dX_A}{\frac{kC_{A0}(1 - X_A)}{(1 + \varepsilon X_A)}}, \text{ 代入數字}$$

$$V = \int_0^{0.842} \frac{dX_A}{\frac{0.1 \times 0.163(1 - X_A)}{(1 - 0.25X_A)}} = \underline{\underline{97.563(L)}}$$

Problem 4

【Solution】

根據題目所給之速率定律式：

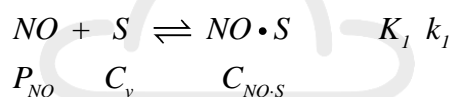
$$-r_{NO} = \frac{kP_{NO}P_{CO}}{(1 + K_1P_{NO} + K_2P_{CO})^2}$$

分析：

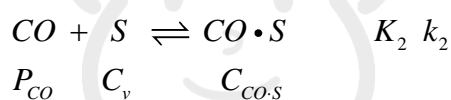
- (1) 分子只有 CO、NO(反應物)，代表此反應不可逆
- (2) 分母有 CO、NO，代表二者皆占用觸媒活性位
- (3) 分母無 N_2 、 CO_2 ，代表生成後即脫附，或者吸附力弱

假設：dual-site mechanism

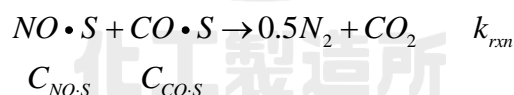
NO adsorption：



CO adsorption：



Surface reaction：



假設 surface reaction is rate-determining,

$$\text{reaction rate, } r = k_{rxn} C_{NO \cdot S} C_{CO \cdot S}$$

$$\text{For } C_{NO \cdot S}, \because \frac{-r_{NO}}{k_1} \approx 0$$

$$C_{NO \cdot S} = K_1 C_v P_{NO}$$

$$\text{For } C_{CO \cdot S}, \because \frac{-r_{CO}}{k_2} \approx 0$$

$$C_{CO \cdot S} = K_2 C_v P_{CO}$$

By balance of enzyme

$$C_t = C_v + C_{NO \cdot S} + C_{CO \cdot S} = C_v(1 + K_1 C_v P_{NO} + K_2 C_v P_{CO})$$

$$C_v = \frac{C_t}{1 + K_1 P_{NO} + K_2 P_{CO}}$$

則 reaction rate, $-r_A = k_{rxn} C_{NO \cdot S} C_{CO \cdot S} = \frac{k_{rxn} C_t^2 P_{NO} P_{CO}}{(1 + K_1 P_{NO} + K_2 P_{CO})^2} = \frac{k P_{NO} P_{CO}}{(1 + K_1 P_{NO} + K_2 P_{CO})^2}$

與題目相符

則此 mechanism 正確。

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 742, P10-8B.)



Problem 5

【Solution】

∵ at vapor-liquid equilibrium $f_A^V = f_A^L$

且 the mole fraction of component B in the vapor phase is negligible,

$$f_A^V \approx f_A^V(\text{pure})$$

由 fugacity coefficient 可反推 fugacity :

$$d \ln \phi = \frac{Z-1}{P} dP$$

$$\text{積分: } \int_0^{\ln \phi} d \ln \phi = \int_0^P \frac{(1 - aP + bP^2) - 1}{P} dP$$

$$\ln \phi = \ln \frac{f}{P} = -aP + \frac{b}{2} P^2$$

$$\ln \frac{f}{15.0} = -2 \times 10^{-3} \times 15.0 + \frac{3.5 \times 10^{-6}}{2} \times 15.0^2$$

$$\text{得 } f = f_V^A(\text{pure}) = \underline{\underline{14.56 \text{ bar}}}$$

Problem 6

【Solution】

By Henry's law,

$$f_V^A = H_A x_A, \quad x_A = 0.06 \text{ 代入}$$

$$H_A = \frac{14.56}{0.06} = \underline{\underline{242.7 \text{ bar}}}$$

Problem 7**【Solution】**

@VLE, $\hat{f}_A^V = \hat{f}_A^L$

$$y_A r_A^V f_V^A = x_A r_A^L H_A$$

\therefore obey Henry's law, $r_A^L \approx 1$

$$0.5 \times 1.12 \times 14.56 = x_A \times 1 \times 242.7$$

$$x_A \approx \underline{\underline{0.0336}}$$

Problem 8**【Solution】 False**

For ideal gas, C_p is only function of T

For real gas, C_p is function of T and P

Problem 9**【Solution】 False**

It depends on the working substances, for ideal gas, the internal energy is only a function of T; whereas for real gas, the internal energy is function of temperature and volume.

Problem 10**【Solution】 False**

It depends on the Joule-Thomson coefficient, $\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H$

if $\left(\frac{\partial T}{\partial P}\right)_H > 0$, both the pressure and the temperature will drop.

if $\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H < 0$, the pressure will drop followed by a increase in the temperature.

Problem 11

【Solution】 False

It depends on whether the work is done on the system or by the system.

If the process does work on the surrounding from the system, then reversible process will exert more work than irreversible.

If the process does work on the system, then it needs less work in reversible process than irreversible.

Problem 12

【Solution】 False

$dS_{U,V} \geq 0$, and the equality comes when the process is reversible.

※此題證明可參考 104 台大物化選擇第 10 題

Problem 13

【Solution】 False

例如，若此增加反應物濃度的過程是在恆壓下，則雖然某反應物的分壓會升高，但也可能因此壓縮到其他反應物的分壓，造成反應可能向反應物方向反應

Problem 14

【Solution】 False

Constant temperature and **volume**, equilibrium corresponds to minimum **Helmholtz free energy**

Constant temperature and **pressure**, equilibrium corresponds to minimum **Gibbs free energy**

Problem 15

【Solution】 False

The **chemical potential, pressure, and temperature** of the liquid phase is equal to the vapor phase.

The **summation of the molar entropy of the liquid and vapor phase, $S^V + S^L$** will be maximum at equilibrium.

(8~15 題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;

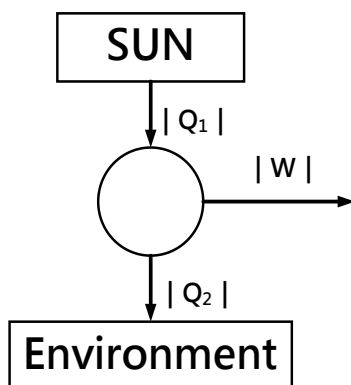
p 61/61/211/110/287/836, Problem 13.17/289/288.)



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Problem 1

【Solution】



By energy balance on the cell,

$$|Q_1| - |Q_2| - |W| = 0$$

$$|W| = |Q_1| - |Q_2|$$

$$\text{Efficiency, } \eta = \frac{|W|}{|Q_1|} = 1 - \frac{|Q_2|}{|Q_1|}$$

By entropy balance on the cell,

$$\Delta S = \sum_{\text{closed system}} \cancel{M_k S_k} + \frac{4}{3} \frac{|Q_1|}{T_R} - \frac{|Q_2|}{T} + \cancel{S_{gen}} = 0$$

radiation conduction maximum

$$\Delta S = \frac{4}{3} \frac{|Q_1|}{T_R} - \frac{|Q_2|}{T} = \frac{4}{3} \times \frac{|Q_1|}{6500} - \frac{|Q_2|}{300} = 0$$

$$\frac{|Q_2|}{|Q_1|} = 0.0615, \quad \eta = 1 - \frac{|Q_2|}{|Q_1|} = 0.9384, \quad \underline{\text{選(b)}}$$

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

p 124-125, Illustration 4.3-2.)

Problem 2

【Solution】



By mass balance,

$$\dot{m}_1 + \dot{m}_2 = \dot{m}_3 = 10 \text{ kg / min}$$

By energy balance,

$$\Delta H + \underbrace{\frac{\Delta v^2}{2g_c} + \frac{g}{g_c} \Delta z}_{\text{negligible}} = \cancel{\dot{Q}} + \cancel{\dot{W}}$$

$$\Delta H = \Delta H_3 - (\Delta H_1 + \Delta H_2) = 0$$

$$\dot{m}_3 C_p T_3 - (\dot{m}_2 C_p T_2 + \dot{m}_1 C_p T_1) = 0$$

$$10 C_p T_3 - (5 C_p \times 50 + 5 C_p \times 80) = 0$$

$$\underline{\underline{T_3 = 65^\circ\text{C}}}, \text{ 選(d)}$$

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 94,

Problem 3.13.)

3. Ans : (d)

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

5th ed.; p 19.)

Problem 4

【Solution】

$$\Delta S = \underbrace{nC_v \ln\left(\frac{T_f}{T_i}\right)}_{\text{isothermal}} + nR \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = 1 \times 8.314 \times \ln\left(\frac{10}{1}\right) = \underline{\underline{19.14}} \text{ (J / K)} , \underline{\underline{\text{選(a)}}}$$

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 405.)

Problem 5

【Solution】

By Gibbs phase rule

$$F = c - p + 2$$

c (number of components) : H_2O + ethanol = 2

p (number of phases) : *solid(ice)* + *liquid(water + ethanol)* = 2

$$F = 2 - 2 + 2 = \underline{\underline{2}} , \underline{\underline{\text{選(b)}}}$$

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*,
5th ed.; p 405.)

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Problem 6

【Solution】

By $dG = RT \ln f$, $G - G^* = RT \ln \frac{f}{f^*}$,

where * denotes the properties of reference state

for G ,

$$G = H - TS$$

$$= [2924.5 - 6.21 \times (300 + 273)] (\text{kJ} / \text{kg}) \times 18 (\text{kg} / \text{kmol}) = -11408.94 (\text{kJ} / \text{kmole})$$

for G^* ,

$$G^* = H^* - T^* S^*$$

$$= [3076.5 - 9.28 \times (300 + 273)] (\text{kJ} / \text{kg}) \times 18 (\text{kg} / \text{kmol}) = -40336.92 (\text{kJ} / \text{kmole})$$

For f^* , at low pressure, $f^* \approx P^* = 0.01 \text{MPa}$

代入：

$$-11408.94 - (-40336.92) = 8.314 \times (300 + 273) \ln \left(\frac{f}{0.01} \right)$$

$$\underline{\underline{f = 4.336 \text{MPa} , \text{選(a)}}}$$

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

p 312-313, Illustration 7.4-2.)

Problem 7

【Solution】

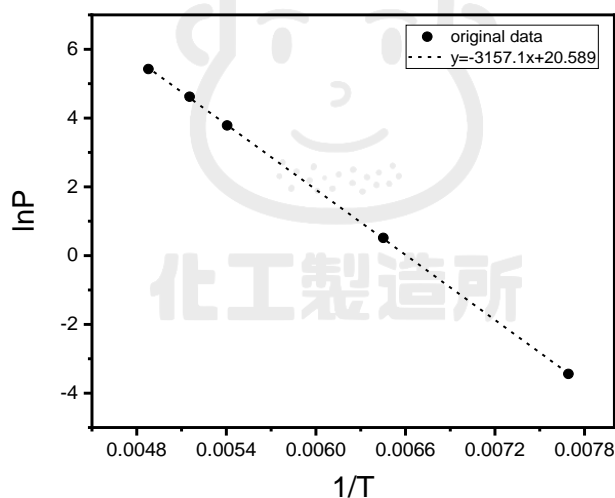
By Clapeyron Clausius equation,

$$\frac{d \ln P}{dT} = \frac{\Delta H_{sub}}{RT^2}, \text{ 積分}$$

$$\ln P = \frac{-\Delta H}{RT}$$

將 $\ln P$ 數據對 $\frac{1}{T}$ 作圖：

P(kPa)	0.032	1.674	44.02	101.3	227
$\ln(P)$	-3.442	0.5152	3.7846	4.618	5.4249
T(K)	130	155	185	194	205
$\frac{1}{T}$	7.6×10^{-3}	6.4×10^{-3}	5.4×10^{-3}	5.1×10^{-3}	4.8×10^{-3}



$$\text{則斜率} = -3157.1 = \frac{-\Delta H_{sub}}{R} = \frac{-\Delta H_{sub}}{8.314}$$

$$\Delta H_{sub} = 26248 \text{ (J/mol)}, \text{ 選(c)}$$

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

p 351, Problem 7.67.)

Problem 8**【Solution】**

By entropy balance on the device,

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

s.s. adiabatic

$$\dot{S}_{gen} = -\sum_i \dot{M}_k \hat{S}_k = N_2 \Delta \underline{S}_2 + N_3 \Delta \underline{S}_3$$

$$\begin{aligned} N_2 \Delta \underline{S}_2 + N_3 \Delta \underline{S}_3 &= [N_2 C_p \ln(\frac{T_f}{T_i}) - N_2 R \ln(\frac{P_f}{P_i})] + [N_3 C_p \ln(\frac{T_f}{T_i}) - N_3 R \ln(\frac{P_f}{P_i})] \\ &= \frac{N_1}{2} [29.3 \ln\left(\frac{273-20}{273+20}\right) - 8.314 \ln\left(\frac{1}{4}\right) + 29.3 \ln\left(\frac{273+60}{273+20}\right) - 8.314 \ln\left(\frac{1}{4}\right)] \\ &= \underline{\underline{11.25 N_1 (J / K)}}, \text{ 選(d)} \end{aligned}$$

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

p 135-136, Illustration 4.5-6.)

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Problem 9

【Solution】

By overall mass balance,

$$m_{90\%} + m_{water} = m_{20\%}$$

By mass balance of sulfuric acid,

$$m_{90\%} x_{90\%} + m_{water} x_{water} = m_{20\%} x_{20\%}$$

$$m_{90\%} \times 0.9 + m_{water} \times 0 = m_{20\%} \times 0.2$$

$$\begin{cases} m_{90\%} = \frac{2}{9} m_{20\%} \\ m_{water} = \frac{7}{9} m_{20\%} \end{cases}$$

By energy balance,

$$\Delta H + \underbrace{\frac{\Delta v^2}{2g_c} + \frac{g}{g_c} \Delta z}_{negligible} = Q + W$$

$$Q = \Delta H = m_{20\%} H_3 - (m_{90\%} H_1 + m_{water} H_2)$$

$$Q = 87 \dot{m}_3 - \frac{2}{9} (-183) \dot{m}_3 - \frac{7}{9} (91) \dot{m}_3 = 56.89 \dot{m}_3 \text{ (kJ / kg 20\%)}$$

$$\text{總需加熱：} 56.89 \dot{m}_3 \times \frac{9}{2 \dot{m}_3} = 256 \text{ (kJ / kg 90\%)} , \text{ 選(c)}$$

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

p 377-378, Illustration 8.4-2.)

Problem 10**【Solution】**

By energy balance,

$$\Delta H + \underbrace{\frac{\Delta v^2}{2g_c} + \frac{g}{g_c} \Delta z}_{\text{negligible}} = \cancel{\dot{Q}} + \cancel{\dot{W}}$$

$$\Delta H = 0 = \dot{m}_3 H'_3 - \frac{2}{9} \dot{m}_3 (-183) - \frac{7}{9} \dot{m}_3 (91) = 0$$

$H'_3 = 30.11$ ，小於 65.56°C 時之 H_3 ，溫度應低於 65.56°C ，選(a)

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

p 377-378, Illustration 8.4-2.)



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Problem 11**【Solution】**

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

$$\text{For } \left(\frac{\partial U}{\partial T} \right)_P = C_v \left(\frac{\partial T}{\partial T} \right)_P + [T \left(\frac{\partial P}{\partial T} \right)_v - P] \left(\frac{\partial V}{\partial T} \right)_P$$

$$= C_v + [T \left(\frac{\partial P}{\partial T} \right)_v - P] \left(\frac{\partial V}{\partial T} \right)_P$$

$$\text{For } \left(\frac{\partial U}{\partial T} \right)_v = C_v \left(\frac{\partial T}{\partial T} \right)_v + [T \left(\frac{\partial P}{\partial T} \right)_v - P] \left(\frac{\partial V}{\partial T} \right)_v = C_v$$

\therefore

$$C_v + [T \left(\frac{\partial P}{\partial T} \right)_v - P] \left(\frac{\partial V}{\partial T} \right)_P \neq C_v$$

\therefore

$$\left(\frac{\partial U}{\partial T} \right)_P \neq \left(\frac{\partial U}{\partial T} \right)_v \text{ 得證}$$

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

5th ed.; p 208-210, Illustration 6.2-1.)

Problem 12

【Solution】

Isothermal/isobaric equilibrium : $dG_{T,P} = 0$

Stable equilibrium system : $d^2G_{T,P} > 0$

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*,
5th ed.; p 290, Table 7.1-1.)



Problem 13

【Solution】

For batch reactor, design equation,

$$-r_A = \frac{-dC_A}{dt}$$

For rate equation,

$$-r_A = k_1 C_A - k_2 C_B$$

To relate k_1, k_2 , we use equilibrium constant K .

By the experiment data, after reaction time $t=\infty$

$$K = \frac{C_B}{C_A} = \frac{10.0 - 2.0}{2.0} = 4$$

So the rate equation,

$$\begin{aligned} -r_A &= k_1 C_A - k_2 C_B = k_1 \left(C_A - \frac{1}{K} C_B \right) \\ &= k_1 \left[C_A - \frac{1}{4} (10.0 - C_A) \right] = k_1 (1.25 C_A - 2.5) \end{aligned}$$

Combine with the design equation, we have

$$-r_A = \frac{-dC_A}{dt} = k_1 (1.25 C_A - 2.5)$$

Integrate the above equation, with $t=0, C_{A0}=10$ and $t=0.5, C_A=6.9$

$$\int_{10.0}^{6.9} \frac{-dC_A}{1.25 C_A - 2.5} = \int_0^{0.5} k_1 dt$$

$$k_1 = 0.784 \text{ (hr}^{-1}\text{)}$$

題目要求 $t=1.5 \text{ hr}$ 時之 C_A ，則

$$\int_{10.0}^{C_A} \frac{-dC_A}{1.25 C_A - 2.5} = \int_0^{1.5} 0.784 dt$$

$$\underline{\underline{C_A = 3.838 \text{ (mol / L)}}}$$

Problem 14**【Solution】**

For PFR, design equation,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A}$$

For rate equation,

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

Combine the above equations,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A} = \int_0^{X_A} \frac{F_{A0} dX_A}{kC_{A0}^2(1 - X_A)^2}$$

$$\tau = \int_0^{X_A} \frac{C_{A0} dX_A}{kC_{A0}^2(1 - X_A)^2} = \int_0^{0.3} \frac{3dX_A}{0.0015 \times 3^2(1 - X_A)^2}$$

$$\tau = \underline{\underline{95.238 \text{ (min)}}}$$

Problem 15**【Solution】**

For 1st CSTR : $\tau = \frac{C_{A0} - C_{A1}}{kC_{A1}}$, $C_{A1} = \frac{C_{A0}}{1 + k\tau}$

For 2nd CSTR : $\tau = \frac{C_{A1} - C_{A2}}{kC_{A2}}$, $C_{A2} = \frac{C_{A1}}{1 + k\tau} = \frac{C_{A0}}{(1 + k\tau)^2}$

For nth CSTR : $C_{An} = \frac{C_{A0}}{(1 + k\tau)^n}$

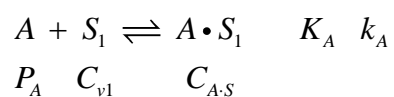
$$C_{An} = C_{A0}(1 - 0.9) = \frac{C_{A0}}{(1 + 0.025 \times \frac{2}{0.05})^n}$$

$$\mathbf{n = 3.322 \text{ , 需 } \underline{\underline{4 \text{ 台 CSTR}}}}$$

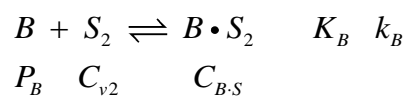
Problem 16

【Solution】

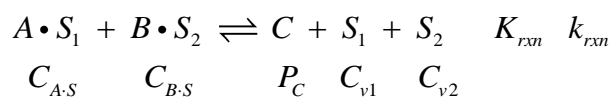
Adsorption of A :



Adsorption of B :



Surface reaction :



∴ Surface reaction is rate-determining,

$$\text{reaction rate, } r = k_{rxn} [C_{A \cdot S} C_{B \cdot S} - \frac{1}{K_{rxn}} P_C C_{v1} C_{v2}]$$

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

$$C_{A \cdot S} = K_A P_A C_{v1}$$

$$C_{t1} = C_{v1} + C_{A \cdot S} = C_{v1} (1 + K_A P_A)$$

$$C_{A \cdot S} = \frac{K_A P_A}{1 + K_A P_A} C_{v1}$$

For θ_B , $\frac{-r_B}{k_B} \approx 0$:

$$C_{B \cdot S} = K_B P_B C_{v2}$$

$$C_{t2} = C_{v2} + C_{B \cdot S} = C_{v2} (1 + K_B P_B)$$

$$C_{B \cdot S} = \frac{K_B P_B}{1 + K_B P_B} C_{t2}$$

代回 reaction rate 表示式，得：

$$r = k_{rxn} \left[\frac{K_A K_B P_A P_B C_{t1} C_{t2}}{(1 + K_A P_A)(1 + K_B P_B)} - \frac{P_C C_{t1} C_{t2}}{K_{rxn} (1 + K_A P_A)(1 + K_B P_B)} \right]$$

$$= k_{rxn} \left[\frac{K'_A K'_B P_A P_B}{(1 + K_A P_A)(1 + K_B P_B)} - \frac{K'_{rxn} P_C}{(1 + K_A P_A)(1 + K_B P_B)} \right]$$



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Problem 1

【Solution】(c)

van der Waals equation of state :

$$(P + \frac{a}{V^2})(V - b) = RT \quad (1)$$

,where \underline{V} is the molar volume

將(1)式整理成：

$$\frac{PV}{RT} = \frac{V}{V - b} - \frac{a}{RTV} = Z \quad (2)$$

將 $\underline{V} = \frac{4.86}{10.0} = 0.486 \left(\frac{L}{mol} \right)$

T=300K、a、b 代入(2)

$$Z = \frac{0.486}{0.486 - 0.0651} - \frac{5.507}{0.082 \times 300 \times 0.486} = \underline{\underline{0.694}}, \text{ 選(c)}$$

Problem 2

【Solution】(a)

∵ reversible + adiabatic,

$$\Delta S = nC_v \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right) = 0$$

將 $T_i = 273.15 \text{ K}$, $V_i = 1.0 \text{ L}$, $V_f = 3.0 \text{ L}$, $C_v = 1.5R$ 代入，且將 n 消去，得：

$$\Delta S = 1.5R \ln\left(\frac{T_f}{273.15}\right) + R \ln\left(\frac{3.0}{1.0}\right) = 0$$

$$\text{得 } \underline{\underline{T_f = 131.6 \text{ K}}}, \text{ 選(a)}$$

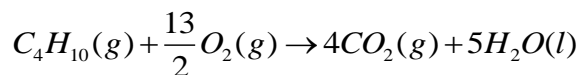
Problem 3

【Solution】(b)

∵ 反應熱, $\Delta_{rxn} H^\circ = (\text{生成物生成熱} - \text{反應物生成熱})$

$$= (\text{反應物燃燒熱} - \text{生成物燃燒熱})$$

又 butane 燃燒反應式(25°C下)：



則 butane 之莫耳燃燒熱：

$$[4\Delta_f H^\circ(CO_2, g) + 5\Delta_f H^\circ(H_2O, l)] - [\Delta_f H^\circ(\text{butane}, g) + 0] = -2878 \text{ (kJ / mol)}$$

將題目所給之數據代入得：

$$[4 \times (-393.51) + 5 \times (-285.83)] - \Delta_f H^\circ(\text{butane}, g) = -2878$$

$$\text{則 } \Delta_f H^\circ(\text{butane}, g) = \underline{\underline{-125.19 \text{ (kJ / mol)}}}, \text{ 選(b)}$$

Problem 4

【Solution】(d)

∵ 根據 Joule Thomson coefficient 定義：

$$\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H = \left(\frac{\Delta T}{\Delta P}\right) (\text{constant over the range})$$

將題目所給數據代入，即 $\Delta P = 1 - 32 = -31 \text{ atm}$ ， $\Delta T = -22 \text{ K}$

$$\mu = \frac{-22}{-31} = \underline{\underline{0.7097}}, \text{ 選(d)}$$

Problem 5

【Solution】(d)

$$\begin{aligned}\Delta S &= nC_{v,m} \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right) \\ &= 1 \times (2.5 - 1) \times 8.314 \times \ln\left(\frac{600}{300}\right) + 1 \times 8.314 \times \ln\left(\frac{50}{30}\right) = \underline{\underline{12.89(J / K)}}, \text{選(d)}\end{aligned}$$

Problem 6

【Solution】(e)

$$\Delta S = \underbrace{nC_{p,m} \ln\left(\frac{T_f}{T_i}\right)}_{\text{isothermal}} - nR \ln\left(\frac{P_f}{P_i}\right) = -25$$

$$-2 \times 8.314 \times \ln\left(\frac{P_f}{3.5}\right) = -25$$

得 $P_f = \underline{\underline{15.74 \text{ atm}}}$ ，選(e)

Problem 7

【Solution】

By modified Raoult's law :

$$y_i P = x_i r_i P_i^{\text{sat}}$$

將 A (Acetone) 與 B (Ethanol) 數據代入，

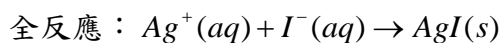
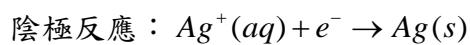
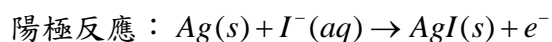
$$y_A P = x_A r_A P_A^\circ \Rightarrow 0.516 \times 1 = 0.4 \times r_A \times \frac{786}{760}$$

$$y_B P = x_B r_B P_B^\circ \Rightarrow (1 - 0.516) \times 1 = (1 - 0.4) \times r_B \times \frac{551}{760}$$

$$\text{得：} \begin{cases} r_A = 1.247 \\ r_B = 1.113 \end{cases}$$

Problem 8

【Solution】



則全反應之反應商數(Q)可表示為：

$$Q = \frac{1}{[\text{Ag}^+][\text{I}^-]}, \text{ 且 } [\text{Ag}^+] = [\text{I}^-]$$

根據能斯特方程式(Nernst Equation)：

$$\Delta E = \Delta E^\circ - \frac{RT}{nF} \ln Q$$

平衡條件下： $0 = \Delta E^\circ - \frac{RT}{nF} \ln K$

移項整理並代入平衡常數表示法：

$$0.95 = \frac{RT}{nF} \ln\left(\frac{1}{[\text{Ag}^+][\text{I}^-]}\right) = \frac{RT}{nF} \ln\left(\frac{1}{[\text{Ag}^+]^2}\right)$$

$$0.95 = \frac{8.314 \times (298K)}{1 \times 96500} \ln\left(\frac{1}{[\text{Ag}^+]^2}\right)$$

則 $[\text{Ag}^+] = \underline{\underline{9.223 \times 10^{-8}}}$ ($\text{mole L}^{-1} \approx \text{mole kg}^{-1}$)

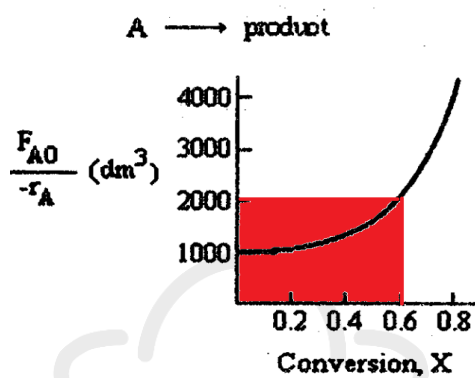
Problem 9

【Solution】

For CSTR :

$$\text{Design equation : } V = \frac{F_{A0}x_A}{-r_A}$$

則 $V=1200 \text{ dm}^3$, 可以利用附圖計算出轉化率, 由上式可知 :

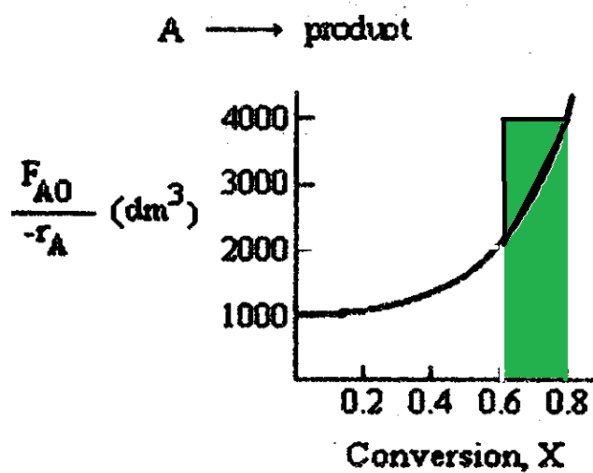


即 CSTR 反應體積為 1200 dm^3 的情形下, 轉化率可達 0.6

For PFR :

$$\text{Design Equation : } V = \int_0^{x_A} \frac{F_{A0} dx_A}{-r_A}$$

則 $V = 600 \text{ dm}^3$, 可以利用附圖計算出轉化率, 由上式可知 :



其面積為

$$(\text{長方形面積}) - (\text{圍起來之三角形面積}) = (0.8 - 0.6) \times 4000 - \frac{(0.8 - 0.6) \times 2000}{2} = 600$$

即代表 PFR 之出口轉化率為 0.8

$$\text{出口轉化率 } X \begin{cases} CSTR = 0.6 \\ PFR = 0.8 \end{cases}$$

Problem 10

【Solution】

(a)

By total energy balance on CSTR : $in - out + gen = \cancel{accu}$

$$\sum_i F_{A0} \theta_{i0} H_{i0} - \sum_i F_{A0} (\theta_{i0} + \nu_i X_A) H_i + Q - \dot{W}_s = 0,$$

where ν_i is the stoichiometric number.

$\therefore \dot{W}_s = 0$ and adiabatic ($Q=0$), 且合併整理

$$\sum_i F_{A0} \theta_{i0} (H_{i0} - H_i) - \sum_i F_{A0} \nu_i X_A H_i = 0$$

$\therefore H_{i0} - H_i = \int_{T_i}^{T_{i0}} C_{pi} dT$, $\sum_i \nu_i H_i = \Delta H_{rxn}$ 代入,

$$\sum_i F_{A0} \int_{T_i}^{T_{i0}} C_{pi} \theta_{i0} dT - F_{A0} X_A \Delta H_{rxn} = 0$$

移項並整理：

$$X_A = \frac{\sum_i F_{A0} \int_{T_i}^{T_{i0}} C_{pi} \theta_{i0} dT}{F_{A0} \Delta H_{rxn}} = \frac{\sum_i \int_{T_{i0}}^{T_i} C_{pi} \theta_{i0} dT}{-\Delta H_{rxn}} = \frac{C_{PA} (T - T_0)}{-\Delta H_{rxn}}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*,

4th ed.; p 482-486.)

(b)

By the design equation of CSTR :

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

By the rate equation :

$$-r_A = k(T)C_A = k(T)C_{A0}(1 - X_A)$$

合併：

$$V = \frac{F_{A0} X_A}{-r_A} = \frac{F_{A0} X_A}{k(T)C_{A0}(1 - X_A)} = \frac{v_0 X_A}{k(T)(1 - X_A)}$$

For $k(T)$, by Arrhenius law :

$$k(T) = A e^{-\frac{E}{RT}}, \text{ where } A \text{ is the pre-exponential factor}$$

代入：

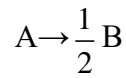
$$V = \frac{F_{A0} X_A}{-r_A} = \frac{F_{A0} X_A}{k(T)C_{A0}(1 - X_A)} = \frac{v_0 X_A}{A e^{-\frac{E}{RT}}(1 - X_A)}$$

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Problem 11

【Solution】

Reaction :



By total energy balance (adiabatic, no shaft work),

$$X_A = \frac{\sum_i \int_{T_{i0}}^{T_i} C_{pi} \theta_{i0} dT}{-\Delta H_{rxn}}$$

For $\sum_i \int_{T_{i0}}^{T_i} C_{pi} \theta_{i0} dT$:

$$\begin{aligned} \sum_i \int_{T_{i0}}^{T_i} C_{pi} \theta_{i0} dT &= C_{PA} \theta_{A0} (T_i - T_{i0}) + C_{PL} \theta_{L0} (T_i - T_{i0}) \\ &= 15(T - 294) + 15(T - 294) \\ &= 30(T - 294) \end{aligned}$$

For $-\Delta H_{rxn}$:

$$\begin{aligned} -\Delta H_{rxn} &= -[\Delta H_{rxn}^\circ(T_R) + \int_{T_R}^T \Delta C_{Pi} dT] \\ &= -\left[(-50 \times \frac{1}{2}) - (-20) + \int_{T_R}^T (30 \times \frac{1}{2} - 15) dT\right] \\ &= 5 \text{ (kcal)} = 5000 \text{ (cal)} \end{aligned}$$

$$\text{Combine : } X_A = \frac{\sum_i \int_{T_{i0}}^{T_i} C_{pi} \theta_{i0} dT}{-\Delta H_{rxn}} = \frac{30(T - 294)}{5000} = 0.8 \text{ , 則 } \underline{\underline{T = 427.33 K}}$$

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Problem 1

【Solution】

假設一系統含有 α 、 β 相，則其達成平衡的條件為：

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

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

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

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

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

5th ed.; p 309-310/p 286-290.)

Problem 2

【Solution】

The thermodynamically reversible process is referred to as a process whose direction can be returned to its original position by inducing infinitesimal changes to some property of the system via its surroundings. Having been reversed, **it leaves no change in either the system or the surroundings.**

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

5th ed.; p 110, Table 4.2-1.)

Problem 3

【Solution】

When the amount of one of the compositions of a mixture reaches its pure state, the partial fugacity of which will be a linear function of its pure state fugacity.

The mathematical representation of the Lewis-Randall Rule is

$$\lim_{x_1 \rightarrow 1} \frac{d \hat{f}_1}{dx_1} = f_1$$

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 436-438.)

Problem 4

【Solution】

Ideal solution is a solution whose enthalpy change of mixing is zero as is the volume change on mixing.

The pressure of the vapor phase obeys either Raoult's law or Henry's law.

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 426-428.)

Problem 5

【Solution】

The statement of the third law of thermodynamics is

“The entropy of all substances in the perfect crystalline state (for solids) or the perfect liquid state is zero at the absolute zero of temperature (0K)”

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 267-268.)

Problem 6

【Solution】

An elementary reaction is a chemical reaction in which one or more chemical species react directly to form products in a single reaction step and with a single transition state. Usually, a reaction is elementary if no reaction intermediates have been detected or need to be postulated to describe the reaction on a molecule scale.

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 84-85.)

Problem 7

【Solution】

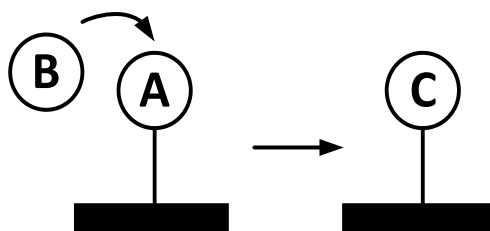
The criterion for a reactor to be differential is that the conversion of the reactants in the bed is extremely small, as is the change in temperature and reactant concentration through the bed. As a result, the reactant concentration through the reactor is essentially constant and approximately equal to the inlet concentration.

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 281-283.)

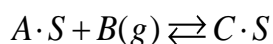
Problem 8

【Solution】

Eley-Rideal mechanism is the reaction between an adsorption molecule on the catalyst surface and a molecule in the gas phase, which can be shown as the following figure.



The generic reaction representation is,



(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 668.)

Problem 9

【Solution】

In the theory of active intermediates, decomposition of the intermediates dose not occur instantaneously after internal activation of the molecule. Because of this reactive property, active intermediates reacts virtually as fast as it is formed, **so the net rate of formation of the an active intermediate is zero.**

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 379-383.)

Problem 10

【Solution】

Damköhler number, Da , is defined as

$$Da \equiv \frac{\text{rate of reaction at entrance}}{\text{Entering flow rate of A}} = \frac{-r_{A0}V}{F_{A0}}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 158.)

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Problem 11**【Solution】****(a)**

Initially, according to ideal gas law,

$$PV = nRT \quad , \quad P \propto n$$

$$n_{\text{左}} : n_{\text{右}} = P_{\text{左}} : P_{\text{右}} = 2 : 1$$

$$n_{\text{左}} = 2n_{\text{右}}$$

For equilibrium temperatures, by energy balance

(All the gas is considered as one system)

$$\Delta U = \underbrace{\emptyset}_{\text{insulated}} + \underbrace{\mathcal{W}}_{\text{no external work}}$$

$$\Delta U = 0 \quad , \quad U_{\text{前}} = U_{\text{後}}$$

$$n_{\text{左}} C_V T_{\text{左}} + n_{\text{右}} C_V T_{\text{右}} = (n_{\text{左}} + n_{\text{右}}) C_V T$$

$$2n_{\text{右}} C_V \times (50 + 273) + n_{\text{右}} C_V \times (50 + 273) = (2n_{\text{右}} + n_{\text{右}}) C_V T$$

$$\underline{\underline{T = 323K}}$$

(b)

The total volume of the compartment is the same between the initial and final state,

$$\frac{n_{\text{左}} RT_{\text{左}}}{P_{\text{左}}} + \frac{n_{\text{右}} RT_{\text{右}}}{P_{\text{右}}} = \frac{(n_{\text{左}} + n_{\text{右}}) RT}{P}$$

$$\frac{2n_{\text{右}} R(50 + 273)}{2} + \frac{n_{\text{右}} R(50 + 273)}{1} = \frac{(2n_{\text{右}} + n_{\text{右}}) R(50 + 273)}{P}$$

$$\underline{\underline{P = 1.5 \text{ (bar)}}}$$

(c)

$$\Delta S = \sum_k \cancel{M_k} \cancel{S_k} + \cancel{\frac{Q}{T}} + S_{gen}$$

closed system adiabatic

$$S_{gen} = \Delta S = n_{\text{右}} \left[\underbrace{C_p \ln\left(\frac{\cancel{T_f}}{T_i}\right)}_{T_f=T_i} - R \ln\left(\frac{P_{f,\text{右}}}{P_{i,\text{右}}}\right) \right] + n_{\text{左}} \left[\underbrace{C_p \ln\left(\frac{\cancel{T_f}}{T_i}\right)}_{T_f=T_i} - R \ln\left(\frac{P_{f,\text{左}}}{P_{i,\text{左}}}\right) \right]$$

$$S_{gen} = n_{\text{右}} \left[-R \ln\left(\frac{P_{f,\text{右}}}{P_{i,\text{右}}}\right) - 2R \ln\left(\frac{P_{f,\text{左}}}{P_{i,\text{左}}}\right) \right]$$

$$= \frac{1 \times 10^5 (N/m^2) \times 1 (m^3)}{8.314 \times (50 + 273) (K)} \times 8.314 \left[-\ln\left(\frac{1.5}{1}\right) - 2 \ln\left(\frac{1.5}{2}\right) \right]$$

$$S_{gen} = \underline{\underline{52.6 \text{ (J/K)}}}$$



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Problem 12**【Solution】**

By modified Raoult's law,

$$y_1 P = r_1 x_1 P_1^{sat}$$

$$y_2 P = r_2 x_2 P_2^{sat}$$

At 1.72 bar,

$$0.88 \times 1.72 = r_1 \times 0.6 \times 2$$

$$0.12 \times 1.72 = r_2 \times 0.4 \times 1$$

$$\begin{cases} r_1 = 1.26 \\ r_2 = 0.516 \end{cases}$$

$$\therefore \Delta \underline{G}_{mix} = \underline{G}^{ex} + \Delta \underline{G}_{mix}^{id}$$

$$\begin{aligned} \Delta \underline{G}_{mix} &= RT[x_1 \ln r_1 + x_2 \ln r_2 + x_1 \ln x_1 + x_2 \ln x_2] \\ &= 8.314 \times 300[0.6 \ln(1.26 \times 0.6) + 0.4(0.516 \times 0.4)] \\ &= \underline{\underline{-1992.87 \text{ (J / mole)}}} \end{aligned}$$

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Problem 13

【Solution】

For PFR, design equation,

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

For rate equation,

$$-r_A = k_{(1000K)} C_A = k_{(1000K)} \frac{C_{A0}(1-x_A)}{(1+\varepsilon x_A)} \quad (\text{isobaric})$$

For ε ,

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

For $k_{(1000K)}$, by Arrhenius law,

$$\frac{k_{(800K)}}{k_{(1000K)}} = \frac{e^{-\frac{E_a}{R \times 800}}}{e^{-\frac{E_a}{R \times 1000}}} = \frac{0.1}{k_{(1000K)}} = \frac{e^{-\frac{40 \times 10^3}{8.314 \times 800}}}{e^{-\frac{40 \times 10^3}{8.314 \times 1000}}}$$
$$k_{(1000K)} = 0.333 \text{ s}^{-1}$$

Design equation and rate equation combine,

$$V = \int_0^{x_A} \frac{F_{A0} dx_A}{k_{(1000K)} C_{A0} \frac{(1-x_A)}{(1+x_A)}} = \int_0^{x_A} \frac{F_{A0} dx_A}{k_{(1000K)} \frac{P_{A0}}{RT} \frac{(1-x_A)}{(1+x_A)}}$$
$$V = \int_0^{0.90} \frac{\frac{60}{60} dx_A}{0.333 \times \frac{10}{0.082 \times 1000} \frac{(1-x_A)}{(1+x_A)}} = \underline{\underline{91.23(L)}}$$

Problem 14**【Solution】**

For series reaction in PBR, we need to obtain the residence time when C_B reaches maximum.

First, for C_A

$$\frac{-dC_A}{dW} = k_1 C_A, \quad C_A = C_{A0} e^{-k_1 W}$$

For $W = 0$, $C_A = C_{A0}$

$$\underline{\underline{C_A = C_{A0} e^{-k_1 W}}}$$

For C_B

$$\frac{dC_B}{dW} = k_1 C_A - k_2 C_B, \quad \text{且 } W = 0, \quad C_B = 0 \text{ 代入}$$

$$\underline{\underline{C_B = k_1 C_{A0} \left(\frac{e^{-k_1 W} - e^{-k_2 W}}{k_2 - k_1} \right)}}$$

For C_B to be maximum, let

$$\frac{dC_B}{dW} = 0$$

$$W_{\max, B} = \frac{\ln \frac{k_1}{k_2}}{k_1 - k_2} = \frac{\ln \frac{0.1}{0.001}}{0.1 - 0.001} = \underline{\underline{46.51 \text{ (s)}}}$$

代入 C_A

$$C_A = C_{A0} e^{-k_1 W} = C_{A0} (1 - x_A), \quad x_A = 0.99$$

代入 PBR 之 design equation,

$$W = \int_0^{x_A} \frac{F_{A0} dx_A}{-r_A} = \int_0^{0.99} \frac{0.005 \times 2 dx_A}{0.1 \times 0.005 \times (1 - x_A)} = \underline{\underline{92.10 \text{ (g)}}}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 321-324,

Example 6-4.)

Problem 15**【Solution】**

$$r_p = k_3[E \cdot S]$$

By PSSH,

$$r_{E \cdot S} = k_1[E][S] - k_{-1}[E \cdot S] - k_2[S][E \cdot S] + k_{-2}[S \cdot E \cdot S] - k_3[E \cdot S] = 0 \text{-----(1)}$$

$$r_{S \cdot E \cdot S} = k_2[S][E \cdot S] - k_{-2}[S \cdot E \cdot S] = 0 \text{-----(2)}$$

$$[S \cdot E \cdot S] = \frac{k_2[S][E \cdot S]}{k_{-2}} \text{ 代回(1)}$$

$$[E \cdot S] = \frac{k_1[E][S]}{k_{-1} + k_3}$$

According to enzyme-balance equation,

$$[E_t] = [E] + [E \cdot S] + [S \cdot E \cdot S]$$

$$[E_t] = [E] + \frac{k_1[E][S]}{k_{-1} + k_3} + \frac{k_1 k_2 [E][S]^2}{(k_{-1} + k_3)k_{-2}}$$

$$[E_t] = [E] \left(1 + \frac{k_1[S]}{k_{-1} + k_3} + \frac{k_1 k_2 [S]^2}{(k_{-1} + k_3)k_{-2}} \right)$$

$$[E] = [E_t] \left(1 + \frac{k_1[S]}{k_{-1} + k_3} + \frac{k_1 k_2 [S]^2}{(k_{-1} + k_3)k_{-2}} \right)^{-1}$$

$$[E \cdot S] = \frac{k_1[E][S]}{(k_{-1} + k_3)} = \frac{k_1[S][E_t]}{(k_{-1} + k_3) \left(1 + \frac{k_1[S]}{k_{-1} + k_3} + \frac{k_1 k_2 [S]^2}{(k_{-1} + k_3)k_{-2}} \right)} = \frac{k_1[S][E_t]}{(k_{-1} + k_3 + k_1[S] + \frac{k_1 k_2 [S]^2}{k_{-2}})}$$

$$r_p = k_3[E \cdot S] = \frac{k_3 k_1 [S][E_t]}{(k_{-1} + k_3 + k_1[S] + \frac{k_1 k_2 [S]^2}{k_{-2}})} = \frac{K_I v_{\max} [S]}{K_M K_I + K_I [S] + [S]^2} \quad \left\{ \begin{array}{l} K_M = \frac{(k_{-1} + k_3)}{k_1} \\ K_I = \frac{k_{-2}}{k_2} \\ v_{\max} = k_3 [E_t] \end{array} \right.$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 414-417.

以及網站：<http://umich.edu/~elements/course/lectures/seven/click25c.htm>)

110 年台大化熱化反

Problem 1

【Solution】

Space time,

τ = the time require to process one reactor volume of the feed
measured at specified conditions

Space velocity,

s = number of reactor volumes of feed
at specified conditions which can be treated in unit time

Note that,

$$\tau = \frac{1}{s}$$

(本題可參考：Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 93.)

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Problem 2

【Solution】

(1) Batch reactor,

A type of reactor which has neither inflow nor outflow of reactants or products.

Usually we can assume that there is no variation in the rate of reaction throughout the reactor volume, which means the system is uniform.

(2) CSTR,

A type of reactor commonly operated at steady state and is assumed to be perfectly mixed; consequently, there is no time dependence or position dependence of the temperature, concentration, or reaction rate inside the CSTR.

(3) PFR

A type of reactor which consists of a cylindrical pipe and is normally operated at steady state. In the tubular reactor, the reactants are continually consumed as they flow down the length of the reactor. Moreover, the flow field model used here is often plug-flow profile.

(本題可參考：FOGLER, H. Elements of Chemical Reaction Engineering,

4th ed.; p 10~17.)

Problem 3

【Solution】

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

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

There are two statements about the second law,

Clausius Statement of the Second Law:

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

Kelvin-Planck Statement of the Second Law:

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

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

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Problem 4**【Solution】**

Because the water phase and the oil phase are immiscible, there may be two phases in the mixture.

$$DOF = c - p + 2 = 2 - 2 + 2 = 2$$

Problem 5 Ans : False**Problem 6 Ans : False**

A Joule-Thomson process should be considered as an isenthalpic-process

Problem 7 Ans : True**【Solution】**

For I in equilibrium with II and II in equilibrium with III,

$$f^I(T, P) = f^{II}(T, P) \text{ 、 } f^{II}(T, P) = f^{III}(T, P)$$

Therefore,

$$f^I(T, P) = f^{III}(T, P)$$

which means phase I is in equilibrium with phase III.

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Problem 8

【Solution】

Rate equation,

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

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

Design equation,

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

Combine,

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

For k , $T = 773K$ 代入，

$$k = 7.80 \times 10^9 \exp\left[\frac{-19200}{773}\right] = 0.127(s^{-1})$$

$$V = \int_0^{0.9} \frac{0.193(1+x_A) dx_A}{0.127(1-x_A)} = 5.616(ft^3)$$

$$V = AL = 5.616 = 0.0388L$$

$$\underline{\underline{L = 144.73(ft)}}$$

(本題可參考：Davis, M. E. E.; Davis, R. J. J. *Fundamentals of Chemical Reaction Engineering*;

p 78~79, Example 3.4-1.

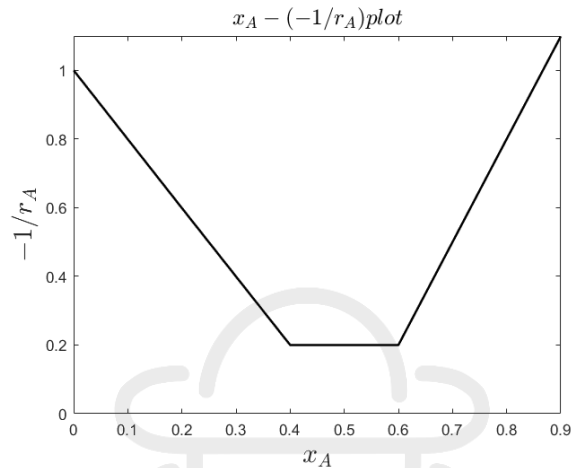
本題也在 98 年成大化動出過，為 Problem 2)

Problem 9

【Solution】

將題目所給定之 $-r_A$ 轉為 $\frac{-1}{r_A}$ ，作出表格如下：

x_A	0	0.2	0.4	0.45	0.5	0.6	0.8	0.9
$-1/r_A$	1	0.6	0.2	0.2	0.2	0.2	0.8	1.1

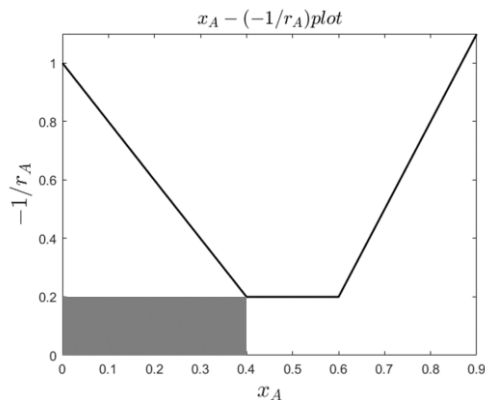


(假設 x_A 在Table未列出的區域呈線性關係)

(a)

For CSTR, the design equation is,

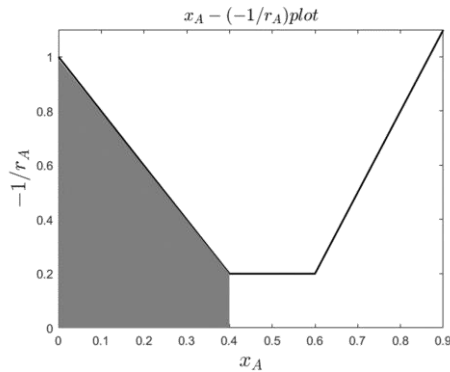
$$V = \frac{F_{A0}x_{Af}}{-r_{Af}}, \text{ 可作圖如下}$$



其體積可計算為： $V_{CSTR} = F_{A0} \times 0.4 \times 0.2 = 300 \times 0.4 \times 0.2 = \underline{\underline{24 \text{ (dm}^3\text{)}}}$

For PFR, the design equation is,

$$V = \int_0^{x_A} \frac{F_{A0}}{-r_{Af}} dx_A, \text{ 可作圖如下}$$



$$\text{其體積可計算為：} V_{PFR} = F_{A0} \times \underbrace{\frac{(0.2+1) \times 0.4}{2}}_{\text{梯形面積}} = 300 \times \frac{(0.2+1) \times 0.4}{2} = \underline{\underline{72 \text{ (dm}^3\text{)}}}$$

(b)

根據 $-1/r_A - x_A$ 關係，其 x_A 應落在 0.6 以後才有機會使得 CSTR 與 PFR 相等

$$V_{CSTR} = F_{A0} \frac{x_A}{-r_A} = F_{A0} x_A (3x_A - 1.6)$$

$$V_{PFR} = F_{A0} \left[\frac{(0.2+1) \times 0.4}{2} + 0.2 \times 0.2 + \frac{(0.2+3x_A-1.6) \times (x_A-0.6)}{2} \right]$$

$$V_{CSTR} = V_{PFR}, \quad \underline{\underline{x_A = 0.683}}$$

※本題出自原文書習題，在原文書給的參考解答中，是以 $x_A = 0.4 \sim 0.6$ 為答案，也就是進料轉化率為 0.4，出料轉化率為 0.6，因在這範圍內不論 PFR 或 CSTR 皆為長方形的面積，兩者相同。

(c)

$$V_{CSTR} = 105 = F_{A0} x_A (3x_A - 1.6)$$

(假定 x_A 直接落在 $x_A = 0.6$ 以右的範圍)

$$105 = 300 x_A (3x_A - 1.6), \quad \underline{\underline{x_A = 0.7}}$$

(d)

72 dm^3 之 PFR 可達到(a)所計算出之轉化率 $x_{A,PFR} = 0.4$

$$V_{CSTR} = 300(x_A - 0.4) \times (3x_A - 1.6) = 24 \quad , \quad \underline{\underline{x_A = 0.643}}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*,

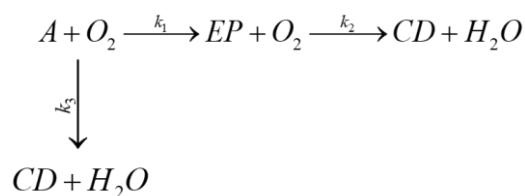
4th ed.; p 74, Problem 2-7B.)



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Problem 10**【Solution】****(a)**

改寫題目所給之方程式：



$$\frac{-dC_A}{dt} = k_3 C_A C_{O_2} + k_1 C_A C_{O_2}$$

$$\frac{dC_{EP}}{dt} = k_1 C_A C_{O_2} - k_2 C_{EP} C_{O_2}$$

$$\frac{dC_{CD}}{dt} = k_2 C_{EP} C_{O_2} + k_3 C_A C_{O_2}$$

The percent selectivity to the epoxide (EP) is,

$$S_{EP} = \frac{r_{EP}}{r_{EP} + r_{CD}} = \frac{k_1 C_A C_{O_2} - k_2 C_{EP} C_{O_2}}{k_1 C_A C_{O_2} - k_2 C_{EP} C_{O_2} + k_2 C_{EP} C_{O_2} + k_3 C_A C_{O_2}} = \frac{k_1 C_A - k_2 C_{EP}}{\underline{\underline{k_1 C_A + k_3 C_A}}}$$

(b)To obtain the maximum selectivity of EP, there must no C_{EP} exists, ($C_{EP} = 0$)

$$S_{EP}^{\max} = \frac{k_1 C_A}{k_1 C_A + k_3 C_A} = \frac{k_1}{\underline{\underline{k_1 + k_3}}}$$

(本題可參考：Davis, M. E. E.; Davis, R. J. J. *Fundamentals of Chemical Reaction Engineering*;

p 43~44, Example 1.5-8~9.)

Problem 11**【Solution】****(a)**

Calculate the vapor pressures of the three gases,

$$P_A^{sat} = 10^{4 - \frac{1170}{49+273-49}} = 0.5179 \text{ (bar)}$$

$$P_B^{sat} = 10^{4 - \frac{1070}{49+273-40}} = 1.6057 \text{ (bar)}$$

$$P_C^{sat} = 10^{5.2 - \frac{1733}{49+273-40}} = 0.1134 \text{ (bar)}$$

Assume Raoult's law is applicable for liquid phase,

$$\begin{cases} P_A^{sat} x_A = P y_A \\ P_B^{sat} x_B = P y_B \\ P_C^{sat} x_C = P y_C \end{cases}$$

Assume the three components are all miscible,

At bubble point, $z_i = x_i$

$$\begin{cases} y_A = \frac{P_A^{sat} x_A}{P} = \frac{0.5179 \times \frac{2}{5}}{1} = 0.207 \\ y_B = \frac{P_B^{sat} x_B}{P} = \frac{1.6057 \times \frac{1}{5}}{1} = 0.321 \\ y_C = \frac{P_C^{sat} x_C}{P} = \frac{0.1134 \times \frac{2}{5}}{1} = 0.045 \end{cases}$$

$y_A + y_B + y_C < 1$, not possible for real case

Assume all the three components are not miscible,

$$\begin{cases} y_A = \frac{P_A^{sat} x_A}{P} = \frac{0.5179 \times 1}{1} = 0.5179 \\ y_B = \frac{P_B^{sat} x_B}{P} = \frac{1.6057 \times 1}{1} = 1.6057 \\ y_C = \frac{P_C^{sat} x_C}{P} = \frac{0.1134 \times 1}{1} = 0.1134 \end{cases}$$

$y_A + y_B + y_C > 1$, not possible for real case

There may be two immiscible solutions

(b)

$\because P_B^{sat} > 1$, so B must be miscible either with A or C.

【Case ①】 A and B are miscible

$$\begin{cases} y_A = \frac{P_A^{sat} x_A}{P} = \frac{0.5179 \times \frac{2}{2+1}}{1} = 0.3453 \\ y_B = \frac{P_B^{sat} x_B}{P} = \frac{1.6057 \times \frac{1}{2+1}}{1} = 0.5352 \\ y_C = \frac{P_C^{sat} x_C}{P} = \frac{0.1134 \times 1}{1} = 0.1134 \end{cases}$$

$y_A + y_B + y_C = 0.9939$, feasible result

$$y_B = \underline{\underline{0.5352}}$$

【Case ②】 B and C are miscible

$$\left\{ \begin{array}{l} y_A = \frac{P_A^{sat} x_A}{P} = \frac{0.5179 \times 1}{1} = 0.5179 \\ y_B = \frac{P_B^{sat} x_B}{P} = \frac{1.6057 \times \frac{1}{2+1}}{1} = 0.5352 \\ y_C = \frac{P_C^{sat} x_C}{P} = \frac{0.1134 \times \frac{2}{2+1}}{1} = 0.0756 \end{array} \right.$$

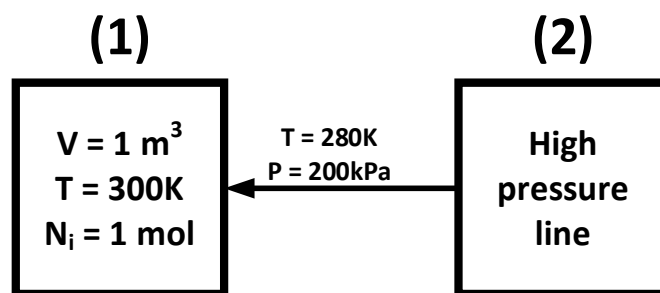
$y_A + y_B + y_C > 1$, not possible for real case



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Problem 12

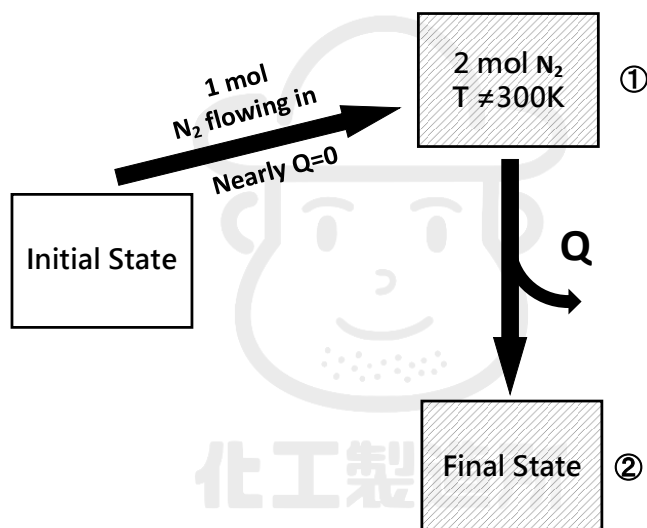
【Solution】



By mass balance of the box (1),

$$n_f = n_i + \Delta n$$

By energy balance of the box, 可先將此過程簡化成兩步驟



From initial state to state ① (nearly adiabatic)

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

$$\int \underline{H}_{in} \dot{n}_{in} dt = \int \frac{d}{dt} (n \underline{U})_{sys} dt, \quad \underline{H}_{in} \Delta n = n_f \underline{U}_f - n_i \underline{U}_i$$

$$\begin{cases} \underline{H}_{in} = C_p \times 280 = 29 \times 280 \\ \underline{U}_i = C_v \times 300 = (29 - 8.314) \times 300 \\ \underline{U}_f = C_v \times 300 = (29 - 8.314) \times T_1 \quad (T_{ref} = 0K) \\ n_i = \Delta n = 1 \\ n_f = 2 \end{cases}$$

$$1 \times 29 \times 280 \times (2 - 1) = 2 \times (29 - 8.314) \times T_1 - 1 \times (29 - 8.314) \times 300$$

$$T_1 = 346.26(K)$$

From state① to state② (higher temperature to T = 300K)

By energy balance, (closed system),

$$\Delta U = Q + \cancel{W}$$

$$Q = n_f C_v \Delta T = 2 \times (29 - 8.314) \times (300 - 346.26) = \underline{\underline{-1914.2(J)}}$$

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*,
5th ed.; p 150, Problem 4.43.)

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Problem 1 : Ans : (d)

【Solution】

$$\begin{aligned}\Delta S &= \sum_{i=A,B} (nC_V \ln \frac{T_{2,i}}{T_{1,i}} + nR \ln \frac{V_{2,i}}{V_{1,i}}) = nR(\ln \frac{V_A + V_B}{V_A} + \ln \frac{V_A + V_B}{V_B}) \\ &= nR(\ln \frac{n_A + n_B}{n_A} + \ln \frac{n_A + n_B}{n_B}) = -nR(\ln x_A + \ln x_B) \\ &= -1 \times 8.3145 \times (\ln 0.5 + \ln 0.5) = 11.526(J / K) \approx \underline{\underline{11.53(J / K)}}\end{aligned}$$

Problem 2 : Ans : (b)

【Solution】

By Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H_{transition}}{T \Delta V_{transition}}$$

For most cases,

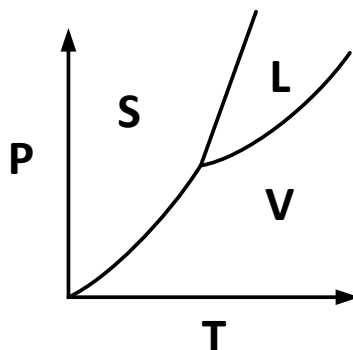
$$\Delta H_{sublimation} > \Delta H_{vaporization} > \Delta H_{fusion} > 0$$

$$\Delta V_{sublimation} \approx \Delta V_{vaporization} > \Delta V_{fusion} > 0$$

$$T \text{ range : } T_{fusion} > T_{vaporization} > T_{sublimation}$$

$$\left(\frac{dP}{dT}\right)_{fusion} > \left(\frac{dP}{dT}\right)_{sublimation} > \left(\frac{dP}{dT}\right)_{vaporization} > 0, \text{ 選(b)}$$

※常見的三相圖：



通常來說， $(\frac{dP}{dT})_{fusion} > 0$ ，除了水與特定物質以外，因 $\Delta V_{fusion} < 0$ ，才會有

$(\frac{dP}{dT})_{fusion} < 0$ 的情形發生。

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

5th ed.; p 335~p 336.)

Problem 3 : Ans : (b)

【Solution】

By Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta S_{transition}}{\Delta V_{transition}}$$

$$\Delta S_{transition} = (\frac{dP}{dT})_{transition} \Delta V_{transition}$$

Near triple point,

$$T_{sub} \approx T_{vap} \approx T_{fus}$$

$$(a) \quad \Delta S_{sublimation} = \Delta S_{fusion} + \Delta S_{vaporization}$$

$$\Delta S_{vaporization} = \Delta S_{sublimation} - \Delta S_{fusion} = (\frac{dP}{dT})_{sublimation} \Delta V_{sublimation} - (\frac{dP}{dT})_{fusion} \Delta V_{fusion} > 0$$

$$\therefore (-\frac{dP}{dT})_{fusion} > (\frac{dP}{dT})_{sublimation} > 0$$

$$\begin{cases} |\Delta V_{sublimation}| > |\Delta V_{fusion}| \\ \Delta V_{fusion} = \frac{\Delta S_{fusion}}{(\frac{dP}{dT})_{fusion}} < 0 \end{cases}, \text{ which are all possible}$$

$$(b) \quad \Delta S_{sublimation} = \Delta S_{fusion} + \Delta S_{vaporization}$$

$$\Delta S_{fusion} = \Delta S_{sublimation} - \Delta S_{vaporization} = (\frac{dP}{dT})_{sublimation} \Delta V_{sublimation} - (\frac{dP}{dT})_{fusion} \Delta V_{fusion}$$

$$\therefore \Delta V_{sublimation} \approx \Delta V_{fusion} = \Delta V$$

$$\Delta S_{fusion} \approx [(\frac{dP}{dT})_{sublimation} - (\frac{dP}{dT})_{fusion}] \Delta V > 0$$

$$(\frac{dP}{dT})_{sublimation} > (\frac{dP}{dT})_{fusion}, \text{ which is contradict to the question statement.}$$

※這是有點顛倒的證明法，事實上根據 Clapeyron equation，

$$\frac{dP}{dT} = \frac{\Delta H_{transition}}{T \Delta V_{transition}}$$

接近 triple point 時， $T_{sublimation} \approx T_{vaporization} = K$

$$\frac{dP}{dT} = \frac{\Delta H_{transition}}{T \Delta V_{transition}} \propto \frac{\Delta H_{transition}}{\Delta V_{transition}}$$

$$\because \Delta H_{sublimation} > \Delta H_{vaporization}, \quad \Delta V_{sublimation} \approx \Delta V_{vaporization}$$

$$\text{Near triple point : } \left(\frac{dP}{dT} \right)_{sublimation} > \left(\frac{dP}{dT} \right)_{vaporization}$$

(c) 同上：

$$\Delta S_{sublimation} = \Delta S_{fusion} + \Delta S_{vaporization} = \left(\frac{dP}{dT} \right)_{fusion} \Delta V_{fusion} + \left(\frac{dP}{dT} \right)_{vaporization} \Delta V_{vaporization} > 0$$

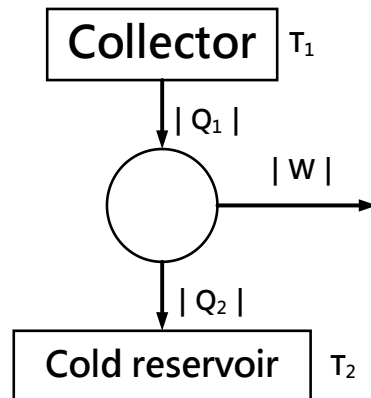
$$\because \left(\frac{-dP}{dT} \right)_{fusion} > \left(\frac{dP}{dT} \right)_{vaporization} > 0$$

$$\begin{cases} |\Delta V_{vaporization}| > |\Delta V_{fusion}| \\ \Delta V_{fusion} = \frac{\Delta S_{fusion}}{\left(\frac{dP}{dT} \right)_{fusion}} < 0 \end{cases}, \text{ which are all possible}$$

(d) 同 Problem (2)的討論

Problem 4 : Ans : (a)

【Solution】



By energy balance on the engine,

$$|Q_1| - |Q_2| - |W| = 0$$

$$|W| = |Q_1| - |Q_2|$$

By entropy balance on the engine,

$$\Delta S = \sum_{\text{closed system}} \cancel{M_k S_k} + \frac{|Q_1|}{T_1} - \frac{|Q_2|}{T_2} + \cancel{S_{\text{gen}}} = 0$$

maximum efficiency

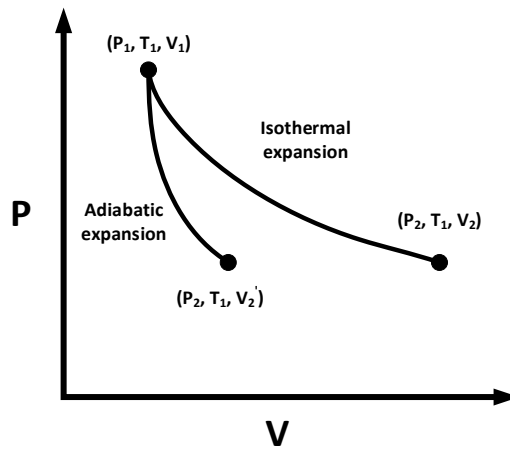
$$\frac{|Q_1|}{|Q_2|} = \frac{T_1}{T_2} \quad \text{代回}$$

$$|W| = |Q_1| \left(1 - \frac{T_2}{T_1}\right) = 2 \times \frac{A \times 100^2}{60} \times \left(1 - \frac{298}{273.15 + 85}\right) = 1000$$

$$\underline{\underline{A = 17.86 \approx 17.9 \text{ m}^2}}$$

Problem 5 : Ans : (c)

【Solution】



For P_1, P_2 , \because expansion, $P_1 > P_2$

For T_1, T_2 , $\because \frac{P_2 V_2}{P_2 V_2'} = \frac{T_1}{T_2}$, $V_2 > V_2'$, $T_1 > T_2$

Problem 6 : Ans : (e)

【Solution】

At equilibrium,

$$n_{NO} = 2 - 2\varepsilon$$

$$y_{NO} = \frac{2 - 2\varepsilon}{3 - \varepsilon}$$

$$n_{O_2} = 1 - \varepsilon$$

$$y_{O_2} = \frac{1 - \varepsilon}{3 - \varepsilon}$$

$$n_{NO_2} = 2\varepsilon$$

$$y_{NO_2} = \frac{2\varepsilon}{3 - \varepsilon}$$

$$n_T = 3 - \varepsilon$$

Problem 7 : Ans : (a)**【Solution】**

$$K_p = \frac{P_{NO_2}^2}{P_{NO}^2 P_{O_2}} = \frac{\left(\frac{2\varepsilon}{3-\varepsilon}\right)^2 P^2}{\left(\frac{2-2\varepsilon}{3-\varepsilon}\right)^2 P^2 \cdot \left(\frac{1-\varepsilon}{3-\varepsilon}\right) P}$$

$$K_p = \frac{(3-\varepsilon) \cdot 4\varepsilon^2}{(2-2\varepsilon)^2 \cdot (1-\varepsilon) P} \Rightarrow K_p P = \frac{(3-\varepsilon) \cdot \varepsilon^2}{(1-\varepsilon)^3}$$

$$(1-\varepsilon)^3 = \frac{(3-\varepsilon) \cdot \varepsilon^2}{K_p P}$$

$\therefore K_p$ is very large, $\varepsilon \rightarrow 1$

$$\varepsilon = 1 - \lim_{\varepsilon \rightarrow 1} \sqrt[3]{\frac{(3-\varepsilon) \cdot \varepsilon^2}{K_p P}} = 1 - \sqrt[3]{\frac{2}{K_p P}}$$

Problem 8**【Solution】**

(a)

$$dA = -PdV - \underbrace{SdT}_{\text{constant } T} = -PdV$$

$$dA = -PdV = VdP - d(PV)$$

$$\therefore P = \frac{nRT}{V-nb} - \frac{an^2}{V^2T}$$

$$PV = \frac{nRT}{1 - \frac{n}{V}b} - \frac{an^2}{VT}$$

$$d(PV) = d\left(\frac{nRT}{1 - \frac{n}{V}b} - \frac{an^2}{VT}\right)$$

$$dP = d\left(\frac{nRT}{V-nb} - \frac{an^2}{V^2T}\right) = \left[\frac{-nRT}{(V-nb)^2} + \frac{2an^2}{V^3T}\right]dV$$

$$dP = V \left[\frac{-nRT}{(V-nb)^2} + \frac{2an^2}{V^3T} \right] dV - d \left(\frac{nRT}{1-\frac{n}{V}b} - \frac{an^2}{VT} \right)$$

$$= \frac{-nRTV}{(V-nb)^2} dV + \frac{2an^2}{V^2T} dV - d \left(\frac{nRT}{1-\frac{n}{V}b} - \frac{an^2}{VT} \right)$$

$$dA = -nRT \left[\frac{nb}{(V-nb)^2} + \frac{1}{V-nb} \right] dV + \frac{2an^2}{V^2T} dV - d \left(\frac{nRT}{1-\frac{n}{V}b} - \frac{an^2}{VT} \right)$$

$$A(T, V) = -nRT \left[\frac{-nb}{V-nb} + \ln(V-nb) \right] - \frac{2an^2}{VT} - \frac{nRT}{1-\frac{n}{V}b} + \frac{an^2}{VT} + C(T)$$

$$= \frac{n^2RTb}{V-nb} - nRT \ln(V-nb) - \frac{an^2}{VT} - \frac{nRT}{1-\frac{n}{V}b}$$

(b)

By Maxwell relations,

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V-nb} + \frac{an^2}{V^2T^2}$$

(c)

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

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P = \frac{nRT}{V-nb} + \frac{an^2}{V^2T} - \frac{nRT}{V-nb} + \frac{an^2}{V^2T} = \frac{2an^2}{V^2T}$$

Problem 9

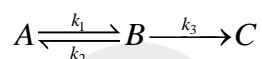
【Solution】

Pseudo Steady State Approximation : The net change of rate of the concentration of an intermediate is negligible compared to its gross rate of formation and consumption; then,

$$\frac{d[I]}{dt} = 0, \text{ where } [I] = \text{the concentration of intermediate}$$

Fast equilibrium approximation : If we are told that one of the reaction is fast in both forward and reverse direction.

For example,



Pseudo Steady State Approximation : $\frac{d[B]}{dt} = k_1[A] - k_2[B] - k_3[B]$
small fast fast fast

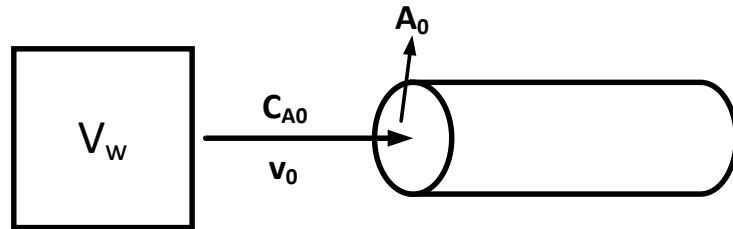
Fast equilibrium Approximation : $\frac{d[B]}{dt} = k_1[A] - k_2[B] - k_3[B]$
small fast fast small

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Problem 10**【Solution】**

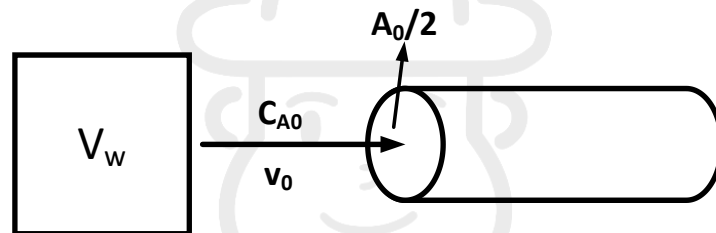
Assume the decomposition reaction is a n-order reaction (usually 1st order reaction)

Initially,



$$\text{Total time} = \frac{V_w}{v_0}$$

Afterward,



$$\text{Total time} = \frac{V_w}{v_0}$$

For PFR, design equation,

$$V = \int_0^{x_A} \frac{C_{A0} v_0 dx_A}{-r_A}$$

Rate expression,

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

Combine,

$$V = \int_0^{x_A} \frac{C_{A0}v_0 dx_A}{kC_{A0}^n(1-x_A)^n} = \frac{C_{A0}v_0}{kC_{A0}^n} \int_0^{x_A} \frac{dx_A}{(1-x_A)^n}$$

If the cross-section area is halved, let the length is the same,

$$\frac{V_2}{V_1} = \frac{\frac{C_{A0}v_0}{k_2C_{A0}^n} \int_0^{x_A} \frac{dx_A}{(1-x_A)^n}}{\frac{C_{A0}v_0}{k_1C_{A0}^n} \int_0^{x_A} \frac{dx_A}{(1-x_A)^n}} = \frac{k_1}{k_2} = \frac{1}{2}$$

$$\frac{k_1}{k_2} = \frac{1}{2} = \frac{k_0 e^{\frac{-E_a}{RT_1}}}{k_0 e^{\frac{-E_a}{RT_2}}} = e^{\frac{-E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})}$$

$$\frac{1}{2} = e^{\frac{-20 \times 10^3}{1.987}(\frac{1}{350} - \frac{1}{T_2})}, \quad \underline{\underline{T_2 = 358.6(K)}}$$

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Problem 11**【Solution】**

$$\frac{d[S_1]}{dt} = k_1[S_2][N_2] - k_{-1}[S_1][N_2] = [N_2](k_1[S_2] - k_{-1}[S_1])$$

By mass balance,

$$[S_1] + [S_2] = [S_1]_0 + [S_2]_0, \quad [S_2] = [S_1]_0 + [S_2]_0 - [S_1]$$

$$\frac{d[S_1]}{dt} = [N_2][k_1([S_1]_0 + [S_2]_0 - [S_1]) - k_{-1}[S_1]]$$

$$\frac{d[S_1]}{dt} = [N_2]k_1([S_1]_0 + [S_2]_0) - [N_2](k_1 - k_{-1})[S_1]$$

$$\frac{d}{dt}(e^{[N_2](k_1 - k_{-1})t}[S_1]) = [N_2]k_1([S_1]_0 + [S_2]_0)e^{[N_2](k_1 - k_{-1})t}$$

$$e^{[N_2](k_1 - k_{-1})t}[S_1] = \frac{[N_2]k_1([S_1]_0 + [S_2]_0)}{[N_2](k_1 - k_{-1})}e^{[N_2](k_1 - k_{-1})t} + C$$

$$[S_1] = \frac{k_1([S_1]_0 + [S_2]_0)}{(k_1 - k_{-1})} + Ce^{-[N_2](k_1 - k_{-1})t}$$

At $t = 0$, $[S_1] = [S_1]_0$

$$C = [S_1]_0 + \frac{k_1([S_1]_0 + [S_2]_0)}{k_1 - k_{-1}} = \frac{(2k_1 - k_{-1})[S_1]_0 + k_1[S_2]_0}{k_1 - k_{-1}}$$

$$[S_1] = -\frac{k_1([S_1]_0 + [S_2]_0)}{k_1 - k_{-1}} + \frac{(2k_1 - k_{-1})[S_1]_0 + k_1[S_2]_0}{k_1 - k_{-1}}e^{-[N_2](k_1 - k_{-1})t}$$

Problem 12**【Solution】**

(a)

$$\frac{-d[O_3]}{dt} = k_1[Cl_2][O_3] + k_2[ClO_2\cdot][O_3] + k_3[ClO_3\cdot][O_3] \quad \text{--- (1)}$$

By pseudo steady state assumptions,

$$\frac{d[ClO\cdot]}{dt} = k_1[Cl_2][O_3] - k_5[ClO\cdot]^2 = 0 \quad \text{--- (2)}$$

$$\frac{d[ClO_2\cdot]}{dt} = k_1[Cl_2][O_3] - k_2[ClO_2\cdot][O_3] + k_3[ClO_3\cdot][O_3] = 0 \quad \text{--- (3)}$$

$$\frac{d[ClO_3\cdot]}{dt} = k_2[ClO_2\cdot][O_3] - k_3[ClO_3\cdot][O_3] - k_4[ClO_3\cdot]^2 = 0 \quad \text{--- (4)}$$

(3) + (4) :

$$k_1[Cl_2][O_3] - k_4[ClO_3\cdot]^2 = 0$$

$$[ClO_3\cdot] = \sqrt{\frac{k_1}{k_4}[Cl_2][O_3]}$$

(1) + (3) :

$$\frac{-d[O_3]}{dt} = 2k_1[Cl_2][O_3] + 2k_3[ClO_3\cdot][O_3] = 2k_1[Cl_2][O_3] + 2k_3\sqrt{\frac{k_1}{k_4}[Cl_2][O_3]^3}$$

(b) At long time scale, $[O_3]$ is very low

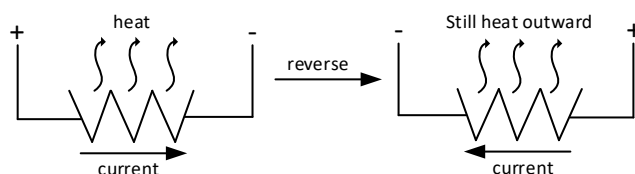
$$\frac{-d[O_3]}{dt} = 2k_1[Cl_2][O_3] + \cancel{2k_3\sqrt{\frac{k_1}{k_4}[Cl_2][O_3]^3}} \approx \underline{\underline{2k_1[Cl_2][O_3]}}$$

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Problem 1

【Solution】

- (a) **True.** The process is irreversible because we can never reverse the electricity current while cooling the heater. Moreover, by the statement of 2nd law of thermodynamics, we can never convert heat 100% back into work.



- (b) **False.** If the concentration, pressure, or temperature, etc., of the species change in a way larger than a differential way from equilibrium, the reversible reaction may occur in an irreversible manner.

(本小題可參考：Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 35~36.)

- (c) **False.** For a closed system, its Gibbs energy will evolve to its lowest value and reach equilibrium under constant temperature and pressure.

$$dG_{T,P} \leq 0$$

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 272~273.)

- (d) **True.** By the second law of thermodynamics, the heat cannot be completely converted into work, but the reverse is possible.

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 106~107, Illustration 4.1-2.)

(e) **False.** The entropy of an isolated system can only increase, which is,

$$\Delta S_{\text{isolated}} = \cancel{\frac{Q}{T}}_{\text{isolated}} + S_{\text{gen}} \geq 0$$

But if we consider a reversible isothermal compression process of ideal gas,

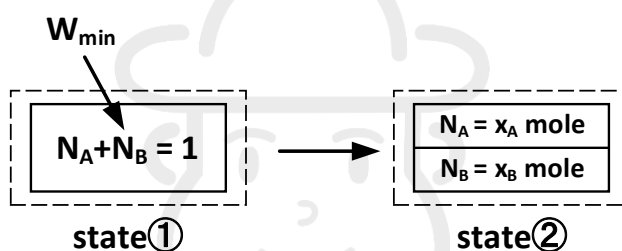
$$\cancel{\Delta U}_{\text{isothermal}} = Q + W, \quad Q = -W < 0$$

$$\Delta S = \frac{Q}{T} + \cancel{S_{\text{gen}}}_{\text{reversible}} < 0$$

Problem 2

【Solution】

If the mixture is a system of ideal solution, consider the process,



System = separator + its content

By energy balance of the closed system,

$$U_2 - U_1 = Q + W_s - (P_2 V_2 - P_1 V_1), \quad P_2 = P_1 (\text{constant } P)$$

By entropy balance,

$$\Delta S_{\text{sys}} = \frac{Q}{T} + \cancel{S_{\text{gen}}}_{\text{minimum work}} = S_2 - S_1$$

$Q = T(S_2 - S_1)$ 代回(定溫) :

$$U_2 - U_1 = TS_2 - TS_1 + W_s - P_2 V_2 - P_1 V_1$$

$$W_s = (U_2 + P_2 V_2 - TS_2) - (U_1 + P_1 V_1 - TS_1) = G_2 - G_1$$

$$W_{\text{min}} = -\Delta G_{\text{mix}}^{\text{id}} = -nRT(x_A \ln x_A + x_B \ln x_B)$$

讀圖

$$= -1 \times 8.314 \times 300(0.8 \ln 0.8 + 0.2 \ln 0.2) = \underline{\underline{1248.1 \text{ (J)}}}$$

Problem 3

【Solution】

(a)

$\therefore dU = TdS - PdV$, for the dS term, we need,

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

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

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

For $\left(\frac{\partial S}{\partial V}\right)_T$, by Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$
$$dU = T\left[\frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV\right] - PdV = C_V dT + \left[-P + T\left(\frac{\partial P}{\partial T}\right)_V\right]dV$$

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 207~208.)

(b)

For ideal gas, $PV = RT$

To prove $C_V = C_V(T)$ for an ideal gas, we start by,

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

在固定 V 下，再對 T 微分：

$$\frac{\partial}{\partial T}\left[\left(\frac{\partial U}{\partial V}\right)_T\right]_V = \frac{\partial}{\partial T}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]_V = \left(\frac{\partial P}{\partial T}\right)_V + T\left(\frac{\partial^2 P}{\partial T^2}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Because U is an exact function,

$$\frac{\partial}{\partial T}\left[\left(\frac{\partial U}{\partial V}\right)_T\right]_V = \frac{\partial}{\partial V}\left[\left(\frac{\partial U}{\partial T}\right)_V\right]_T = \left[\frac{\partial C_V(T, V)}{\partial V}\right]_T$$
$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \cancel{\left(\frac{\partial^2 P}{\partial T^2}\right)_V} = 0, \quad C_V(T, \cancel{V}) = C_V(T)$$

ideal gas=0

which shows heat capacity depends only on temperature.

To prove $U = U(T)$ for an ideal gas, we start by,

Because U is an exact function,

$$\begin{aligned} dU &= C_v(T)dT + [-P + T(\frac{\partial P}{\partial T})_v]dV \\ &= C_v dT + [\cancel{\frac{RT}{V}} - P]dV = \underline{\underline{C_v(T)dT}} \end{aligned}$$

which shows internal energy depends only on temperature.

(本題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;
p 200/212.)

(c)

For general case,

$$\begin{aligned} dU &= C_v dT + [\cancel{P} + T(\frac{\partial P}{\partial T})_v]dV = TdS - PdV \\ C_v dT + [T(\frac{\partial P}{\partial T})_v]dV &= TdS \\ dS &= \frac{C_v}{T} dT + [\frac{1}{T} \cdot (\frac{\partial P}{\partial T})_v]dV = \frac{C_v}{T} dT + \frac{R}{V} dV \\ S(T_2, V_2) - S(T_1, V_1) &= \int_{V_1}^{V_2} \frac{R}{V} dV + \int_{T_1}^{T_2} \frac{C_v}{T} dT = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \end{aligned}$$

(d)

$$W = \int_{V_1}^{V_2} -PdV = -P_{ext}(V_2 - V_1) = \underline{\underline{P_{ext}(V_1 - V_2)}}$$

(e)

By energy balance,

$$\Delta U = \oint_{adiabatic} + W, \quad C_v(T_2 - T_1) = P_{ext}(V_1 - V_2)$$

$$\underline{\underline{T_2 = \frac{P_{ext}(V_1 - V_2)}{C_v} + T_1}}$$

$$(\text{不可直接使用 } \frac{T_1}{T_2} = (\frac{V_2}{V_1})^{\gamma-1}, \text{ 非可逆程序})$$

(f)

By entropy balance,

$$\Delta S = \underbrace{\frac{Q}{T}}_{adiabatic} + S_{gen}$$

$$S_{gen} = \Delta S = C_V \ln \left[\frac{\frac{P_{ext}(V_1 - V_2)}{C_V} + T_1}{T_1} \right] + R \ln \frac{V_2}{V_1} = C_V \ln \left[\frac{P_{ext}(V_1 - V_2)}{C_V T_1} + 1 \right] + R \ln \frac{V_2}{V_1}$$

Problem 4

【Solution】

(a)

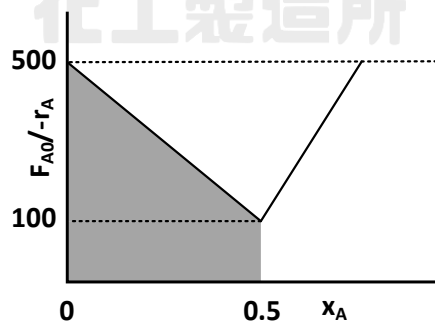
$$\varepsilon = \delta y_{A0} = \left(\frac{2-2-1}{2} \right) \times \frac{1}{2} = \underline{\underline{\frac{-1}{4}}}$$

(b)

By the design equation of PFR,

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

We need to calculate the trapezoidal area from the figure below,



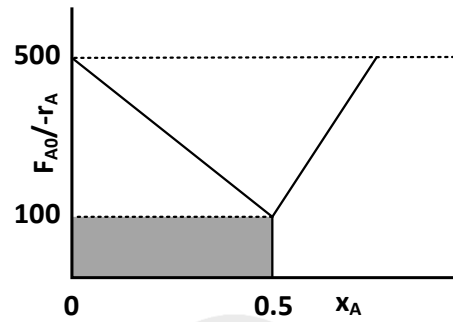
$$V = \frac{(100 + 500) \times 0.5}{2} = \underline{\underline{150 \text{ (dm}^3\text{)}}}$$

(c)

By the design equation of CSTR,

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

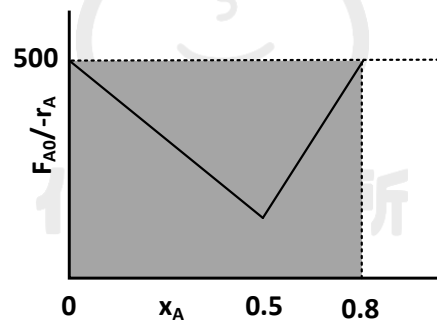
We need to calculate the rectangular area from the figure below,



$$V = 100 \times 0.5 = \underline{\underline{50 \text{ (dm}^3\text{)}}}$$

(d)

Same as problem (c), by the figure below,



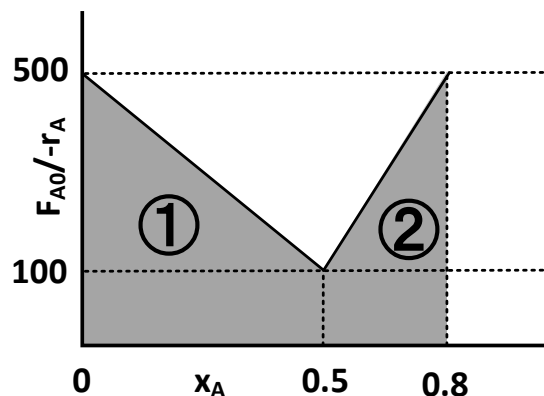
$$V_{CSTR, x_A=0.8} = 500 \times 0.8 = 400 \text{ (dm}^3\text{)}$$

$$\Delta V = 400 - 50 = \underline{\underline{350 \text{ (dm}^3\text{)}}}$$

(e)

※題目也許改為 Part (b)較為合適

Same as problem (b), by the figure below,



$$\Delta V_{PFR} = [(1) + (2)] - (1) = (2)$$

$$\Delta V_{PFR} = \frac{(100 + 500) \times (0.8 - 0.5)}{2} = \underline{\underline{90 \text{ (dm}^3\text{)}}}$$

Problem 5

【Solution】 Ans : (b)

By the design equation of PFR,

$$V = \int_0^{x_X} \frac{F_{X0} dx}{-r_X}$$

For the rate equation,

$$-r_X = kC_X^2 = kC_{X0}^2 \left[\frac{(1-x_X)}{(1+\varepsilon x_X)} \right]^2$$

Combine,

$$V = \int_0^{x_X} \frac{F_{X0} dx}{kC_{X0}^2 \left[\frac{(1-x_X)}{(1+\varepsilon x_X)} \right]^2} = \int_0^{x_X} \frac{F_{X0} (1+\varepsilon x_X)^2}{kC_{X0}^2 (1-x_X)^2} dx$$

$$\because \varepsilon = \frac{(1-2)}{2} \cdot y_{X0} = \frac{-1}{2} y_{X0}$$

If y_{X0} increases, the $(1+\varepsilon x_X)^2$ term would be lowered, so does the volume of PFR

也就是反應物濃度越高，反應速率越快，需要的體積就小

Problem 6

【Solution】

The pressure drop rate can be calculated as,

$$\frac{dy}{dW} = -\frac{\alpha}{2y} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

$$\alpha = \frac{2\beta_0}{A_c \rho_{cat} (1-\phi) P_0}, \quad \beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right]$$

If the cross-sectional area, $A_c \uparrow$, $\alpha \downarrow$

And for the superficial velocity, $G = \frac{\dot{m}}{A_c} \downarrow$, $\alpha \downarrow$

Both result in the decrease of the pressure drop rate

※pressure drop rate 之推導

If we have a gaseous stream flowing down the z-direction of a packed bed, the pressure drop is represented by Ergun equation, which is,

$$\frac{dP}{dz} = \frac{-G(1-\phi)}{\rho g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \left\{ \begin{array}{l} \phi = \text{bed porosity} \\ \rho = \text{gas density} \\ D_p = \text{diameter of particles} \\ G = \text{superficial mass velocity} = \frac{\dot{m}}{A_c} \end{array} \right.$$

$$\because \rho = \frac{\rho_0 v_0}{v} = \rho_0 \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right) \left(\frac{F_{T0}}{F_T} \right) \text{ 代入:}$$

$$\frac{dP}{dz} = - \underbrace{\frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right]}_{\beta_0} \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) \left(\frac{F_T}{F_{T0}} \right) = -\beta_0 \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right) \left(\frac{F_T}{F_{T0}} \right)$$

From $z = 0$ to $z = z$, the total weight of catalyst is,

$$W = (1-\phi) A_c z \rho_{cat}$$

$$dW = (1-\phi)\rho_{cat} A_c dz \text{ 代回 } \frac{dP}{dz}$$

$$\frac{dP}{dW} = -\frac{\beta_0}{(1-\phi)A_c\rho_{cat}} \left(\frac{P_0}{P}\right) \left(\frac{T}{T_0}\right) \left(\frac{F_T}{F_{T0}}\right)$$

令 $y = \frac{P}{P_0}$ 代入：

$$\frac{dy}{dW} = -\frac{\beta_0}{(1-\phi)A_c\rho_{cat}P_0} \left(\frac{1}{y}\right) \left(\frac{T}{T_0}\right) \left(\frac{F_T}{F_{T0}}\right)$$

$$\underline{\underline{\frac{dy}{dW} = -\frac{\alpha}{2y} \left(\frac{T}{T_0}\right) \left(\frac{F_T}{F_{T0}}\right) \text{ , } \alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_{cat}P_0}}}$$

For isothermal operation with $\varepsilon = 0$

$$\frac{dy}{dW} = -\frac{\alpha}{2y} \text{ , } y = (1-\alpha W)^{1/2} = \frac{P}{P_0}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 177~181)

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