106 年台大化熱化反

Problem 1
【Solution】

By total energy balance on CSTR：$in - out + gen = \cancel{accu}$

$$\sum_i F_{A0}\theta_{i0}H_{io} - \sum_i F_{A0}(\theta_{i0} + v_i X_A)H_i + Q - \dot{W}_s = 0,$$

where v_i is the stoichiometric number.

$\because \dot{W}_s = 0$ and adiabatic(Q=0)，且合併整理

$$\sum_i F_{A0}\theta_{i0}(H_{io} - H_i) - \sum_i F_{A0}v_i X_A H_i = 0$$

$\because H_{io} - H_i = \int_{T_i}^{T_{io}} C_{pi}dT$，$\sum_i v_i H_i = \Delta H_{rxn}$ 代入，

$$\sum_i F_{A0}\int_{T_i}^{T_{io}} C_{pi}\theta_{i0}dT - F_{A0}X_A\Delta H_{rxn} = 0$$

移項並整理：

$$X_A = \frac{\sum_i F_{A0}\int_{T_i}^{T_{io}} C_{pi}\theta_{i0}dT}{F_{A0}\Delta H_{rxn}} = \frac{\sum_i \int_{T_{i0}}^{T_i} C_{pi}\theta_{i0}dT}{-\Delta H_{rxn}} = \frac{\int_{T_0}^{T} C_{pA}dT}{-[H_B^\circ - H_A^\circ + \int_{298}^{T}(C_{PB} - C_{pA})dT]} -----(1)$$

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：

$$V = \frac{F_{A0}X_A}{-r_A} = \frac{F_{A0}X_A}{k(T)C_{A0}(1 - X_A)}$$
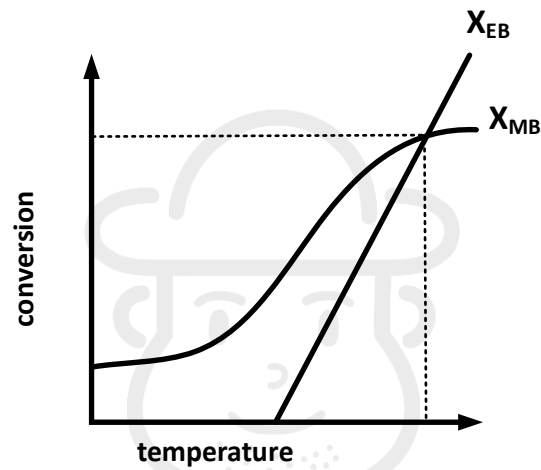
$$X_A = \frac{VkC_{A0}}{F_{A0} + VkC_{A0}}$$

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：

$$X_A = \frac{V k_0 e^{\frac{-E}{RT}} C_{A0}}{F_{A0} + V k_0 e^{\frac{-E}{RT}} C_{A0}} - - - - - (2)$$

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,

$$V = \frac{F_{A0} X_A}{kC_{A0}(1 - X_A)} = \frac{10 \times 0.8}{k_0 \, e^{\frac{-20 \times 10^3}{1.987 \times 350}} \times 1 \times (1 - 0.8)}$$

$$k_0 V = 1.23 \times 10^{14}$$

For PFR, design equation,

$$V = \int_0^{X_A} \frac{F_{A0} dX_A}{-r_A} = \int_0^{X_A} \frac{F_{A0} dX_A}{kC_{A0}(1 - X_A)} = \int_0^{X_A} \frac{10 dX_A}{k_0 e^{\frac{-20 \times 10^3}{1.987 \times 315}} \times 1 \times (1 - X_A)}$$

$$V k_0 = 1.23 \times 10^{14} = \int_0^{X_A} \frac{10 dX_A}{1.326 \times 10^{-14} \times 1 \times (1 - X_A)}$$

$$\underline{\underline{X_A \approx 0.15}}$$

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,

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

where $\quad \varepsilon = \delta y_{A0} = -\frac{1}{2} \times \frac{1}{2} = -0.25$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{10 \times 0.5}{0.082 \times 373} = 0.163 \ (mol/L)$$

combine,

$$V = \int_0^{X_A} \frac{F_{A0}dX_A}{-r_A} = \int_0^{X_A} \frac{F_{A0}dX_A}{\dfrac{kC_{A0}(1-X_A)}{(1+\varepsilon X_A)}} \quad \text{，代入數字}$$

$$V = \int_0^{0.842} \frac{dX_A}{\dfrac{0.1 \times 0.163(1-X_A)}{(1-0.25X_A)}} = \underline{\underline{97.563(L)}}$$

Problem 4
【Solution】

根據題目所給之速率定律式：
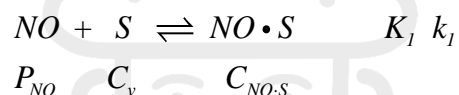
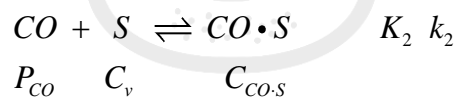$$-r_{NO} = \frac{kP_{NO}P_{CO}}{(1+K_1P_{NO}+K_2P_{CO})^2}$$

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

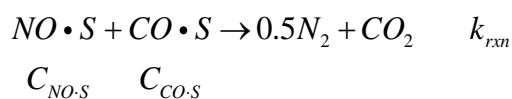NO adsorption：

$$NO + S \rightleftharpoons NO \cdot S \qquad K_1 \ k_1$$
$$P_{NO} \quad\ C_v \qquad\ C_{NO \cdot S}$$

CO adsorption：

$$CO + S \rightleftharpoons CO \cdot S \qquad K_2 \ k_2$$
$$P_{CO} \quad\ C_v \qquad\ C_{CO \cdot S}$$

Surface reaction：

$$NO \cdot S + CO \cdot S \rightarrow 0.5N_2 + CO_2 \qquad k_{rxn}$$
$$C_{NO \cdot S} \quad\ C_{CO \cdot S}$$

假設 surface reaction is rate-determining,

$$\text{reaction rate,} \quad r = k_{rxn}C_{NO \cdot S}C_{CO \cdot S}$$

For $C_{NO \cdot S}$, $\because \dfrac{-r_{NO}}{k_1} \simeq 0$

$$C_{NO \cdot S} = K_1 C_v P_{NO}$$

For $C_{CO \cdot S}$, $\because \dfrac{-r_{CO}}{k_2} \simeq 0$

$$C_{CO \cdot S} = K_2 C_v P_{CO}$$

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, $\quad -r_A = k_{rxn} C_{NO \cdot S} C_{CO \cdot S} = \dfrac{k_{rxn} C_t^2 P_{NO} P_{CO}}{(1 + K_1 P_{NO} + K_2 P_{CO})^2} = \dfrac{k P_{NO} P_{CO}}{(1 + K_1 P_{NO} + K_2 P_{CO})^2}$

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, P10-8ʙ.)**

Problem 5

【Solution】

$\because$ at vapor-liquid equilibrium $\overset{\wedge V}{f_A} = \overset{\wedge L}{f_A}$

且 the mole fraction of component B in the vapor phase is negligible,

$$\overset{\wedge V}{f_A} \approx f_A^V(pure)$$

由 fugacity coefficient 可反推 fugacity：

$$d\ln\phi = \frac{Z-1}{P}dP$$

積分: $\int_0^{\ln\phi} d\ln\phi = \int_0^P \frac{(1-aP+bP^2)-1}{P}dP$

$$\ln\phi = \ln\frac{f}{P} = -aP + \frac{b}{2}P^2$$

$$\ln\frac{f}{15.0} = -2\times10^{-3}\times15.0 + \frac{3.5\times10^{-6}}{2}\times15.0^2$$

得 $f = f_V^A(pure) = \underline{\underline{14.56\,bar}}$

Problem 6

【Solution】

By Henry's law,

$$f_V^A = H_A x_A , \ x_A = 0.06 \text{ 代入}$$

$$H_A = \frac{14.56}{0.06} = \underline{\underline{242.7\,bar}}$$

Problem 7

【Solution】

@VLE, $\hat{f}_A^V = \hat{f}_A^L$

$$y_A r_A^V f_V^A = x_A r_A^L H_A$$

∵ obey Henry's law, $r_A^L \approx 1$

$$0.5 \times 1.12 \times 14.56 = x_A \times 1 \times 242.7$$

$$x_A \approx \underline{0.0336}$$

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, $\mu \equiv (\frac{\partial T}{\partial P})_H$

if $(\frac{\partial T}{\partial P})_H > 0$, both the pressure and the temperature will drop.

if $\mu \equiv (\frac{\partial T}{\partial P})_H < 0$, the pressure will drop followed by an 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.

<div align="center">※此題證明可參考 104 台大物化選擇第 10 題</div>

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**

<u>Problem 15</u>
【**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, $\mathbf{S^V + S^L}$ will be maximum at equilibrium.

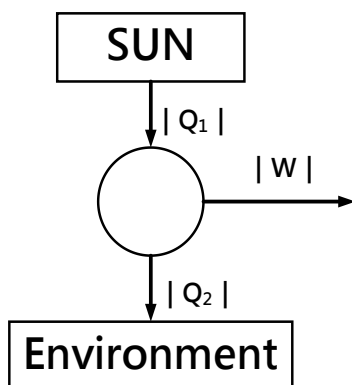(8~15 題可參考：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 61/61/211/110/287/836, Problem 13.17/289/288.)

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【**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,

$$\Delta S = \underbrace{\sum_{closed\ system} M_k S_k}_{} + \underbrace{\frac{4}{3}\frac{|Q_1|}{T_R}}_{radiation} - \underbrace{\frac{|Q_2|}{T}}_{conduction} + \underbrace{S_{gen}}_{maximum} = 0$$

$$\Delta S = \frac{4}{3}\frac{|Q_1|}{T_R} - \frac{|Q_2|}{T} = \frac{4}{3}\times\frac{|Q_1|}{6500} - \frac{|Q_2|}{300} = 0$$

$$\frac{|Q_2|}{|Q_1|} = 0.0615 \text{ , } \eta=1-\frac{|Q_2|}{|Q_1|}=0.9384 \text{ , } \underline{\textbf{選(b)}}$$

(**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,

$$\dot{m}_1 + \dot{m}_2 = \dot{m}_3 = 10 \ kg \ / \ \min$$

By energy balance,

$$\Delta H + \underbrace{\frac{\Delta v^2}{2g_c} + \frac{g}{g_c}\Delta z}_{negligible} = \cancel{Q} + \cancel{W}$$

$$\Delta H = \Delta H_3 - (\Delta H_1 + \Delta H_2) = 0$$

$$\dot{m}_3 C_P T_3 - (\dot{m}_2 C_P T_2 + \dot{m}_1 C_P T_1) = 0$$

$$10 C_P T_3 - (5 C_P \times 50 + 5 C_P \times 80) = 0$$

$$\underline{\underline{T_3 = 65 \degree C}} \text{，} \underline{\textbf{選(d)}}$$

(本題可參考：**Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 94,**

Problem 3.13.)

3.<u>Ans：(d)</u>

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

5th ed.; p 19.)

Problem 4

【**Solution**】

$$\Delta S = \underbrace{nC_y \ln(\frac{T_f}{T_i})}_{isothermal} + nR \ln(\frac{V_f}{V_i})$$

$$\Delta S = nR \ln(\frac{V_f}{V_i}) = 1 \times 8.314 \times \ln(\frac{10}{1}) = \underline{\underline{19.14}} \ (J / K) \ , \ \underline{\textbf{選(a)}}$$

(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=**2**，**選(b)**

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

5th ed.; p 405.)

Problem 6

【Solution】

By $dG = RT \ln f$, $G - G^* = RT \ln \dfrac{f}{f^*}$,

where * denotes the properties of reference state

for *G*,

$G = H - TS$

$= [2924.5 - 6.21 \times (300 + 273)](kJ/kg) \times 18(kg/kmol) = -11408.94(kJ/kmole)$

for *G**,

$G^* = H^* - T^* S^*$

$= [3076.5 - 9.28 \times (300 + 273)](kJ/kg) \times 18(kg/kmol) = -40336.92(kJ/kmole)$

For f^*, at low pressure, $f^* \approx P^* = 0.01 MPa$

代入：

$$-11408.94 - (-40336.92) = 8.314 \times (300 + 273) \ln(\frac{f}{0.01})$$

$\underline{f = 4.336 MPa}$，**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**】

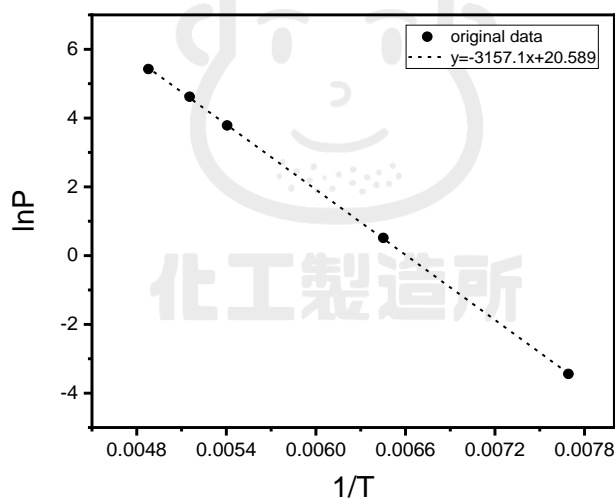By Clapeyron Clausius equation,

$$\frac{d \ln P}{dT} = \frac{\Delta H_{sub}}{RT^2} \text{，積分}$$

$$\ln P = \frac{-\Delta H}{RT}$$

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}

則斜率$=-3157.1=\dfrac{-\Delta H_{sub}}{R} = \dfrac{-\Delta H_{sub}}{8.314}$

$$\Delta H_{sub} = 26248 \ (J/mol) \text{，} \underline{\textbf{選(c)}}$$

(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,

$$\frac{d\cancel{S}}{\cancel{dt}}\bigg|_{s.s} = \sum_i \dot{M}_k \hat{S}_k + \sum \cancel{\frac{\dot{Q}}{T}}_{adiabatic} + \dot{S}_{gen}$$

$$\dot{S}_{gen} = -\sum_i \dot{M}_k \hat{S}_k = N_2 \Delta \underline{S}_2 + N_3 \Delta \underline{S}_3$$

$$N_2 \Delta \underline{S}_2 + N_3 \Delta \underline{S}_3 = [N_2 C_P \ln(\frac{T_f}{T_i}) - N_2 R \ln(\frac{P_f}{P_i})] + [N_3 C_P \ln(\frac{T_f}{T_i}) - N_3 R \ln(\frac{P_f}{P_i})]$$

$$= \frac{N_1}{2}[29.3\ln\left(\frac{273-20}{273+20}\right) - 8.314\ln(\frac{1}{4}) + 29.3\ln\left(\frac{273+60}{273+20}\right) - 8.314\ln(\frac{1}{4})]$$

$$= \underline{\underline{11.25 N_1 (J/K)}} \quad , \underline{\textbf{選(d)}}$$

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

p 135-136, Illustration 4.5-6.)

Problem 9

【Solution】

By overall mass balance,

$$m_{90\%} + m_{water} = m_{20\%}$$

By mass balance of sulfuric acid,

$$m_{90\%}x_{90\%} + m_{water}x_{water} = m_{20\%}x_{20\%}$$

$$m_{90\%} \times 0.9 + m_{water} \times 0 = m_{20\%} \times 0.2$$

$$\begin{cases} m_{90\%} = \dfrac{2}{9}m_{20\%} \\ m_{water} = \dfrac{7}{9}m_{20\%} \end{cases}$$

By energy balance,

$$\Delta H + \underbrace{\cancel{\frac{\Delta v^2}{2g_c}} + \cancel{\frac{g}{g_c}}\Delta z}_{negligible} = Q + \cancel{W}$$

$$Q = \Delta H = m_{20\%}H_3 - (m_{90\%}H_1 - m_{water}H_2)$$

$$Q = 87\dot{m}_3 - \frac{2}{9}(-183)\dot{m}_3 - \frac{7}{9}(91)\dot{m}_3 = 56.89\dot{m}_3 \ (kJ/kg\,20\%)$$

$$總需加熱：56.89\dot{m}_3 \times \frac{9}{2\dot{m}_3} = 256 \ (kJ/kg\,90\%)，選(c)$$

(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,

$$\Delta H + \underbrace{\frac{\Delta v^2}{2g_c} + \frac{g}{g_c}\Delta z}_{negligible} = \cancel{Q} + \cancel{W}$$

$$\Delta H = 0 = \dot{m}_3 H_3' - \frac{2}{9}\dot{m}_3(-183) - \frac{7}{9}\dot{m}_3(91) = 0$$

$$H_3' = 30.11 \text{，小於 65.56°C時之 } H_3 \text{，溫度應低於 65.56°C，} \underline{\textbf{選(a)}}$$

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

p 377-378, Illustration 8.4-2.)

Problem 11

【Solution】

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

For $(\frac{\partial U}{\partial T})_P = C_V(\frac{\partial T}{\partial T})_P + [T\left(\frac{\partial P}{\partial T}\right)_V - P](\frac{\partial V}{\partial T})_P$

$$= C_V + [T\left(\frac{\partial P}{\partial T}\right)_V - P](\frac{\partial V}{\partial T})_P$$

For $(\frac{\partial U}{\partial T})_V = C_V(\frac{\partial T}{\partial T})_V + [T\left(\frac{\partial P}{\partial T}\right)_V - P](\frac{\partial V}{\partial T})_V = C_V$

$\because$

$$C_V + [T\left(\frac{\partial P}{\partial T}\right)_V - P](\frac{\partial V}{\partial T})_P \neq C_V$$

$\therefore$

$$(\frac{\partial U}{\partial T})_P \neq (\frac{\partial U}{\partial T})_V \text{ 得證}$$

(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=∞

$$K = \frac{C_B}{C_A} = \frac{10.0 - 2.0}{2.0} = 4$$

So the rate equation,

$$-r_A = k_1 C_A - k_2 C_B = k_1(C_A - \frac{1}{K}C_B)$$
$$= k_1[C_A - \frac{1}{4}(10.0 - C_A)] = k_1(1.25C_A - 2.5)$$

Combine with the design equation, we have

$$-r_A = \frac{-dC_A}{dt} = k_1(1.25C_A - 2.5)$$

Integrate the above equation, with $t = 0, C_{A0} = 10$ and t=0.5, C_A=6.9

$$\int_{10.0}^{6.9} \frac{-dC_A}{1.25C_A - 2.5} = \int_0^{0.5} k_1 dt$$

$$k_1 = 0.784\,(hr^{-1})$$

題目要求 t=1.5 hr 時之 C_A，則

$$\int_{10.0}^{C_A} \frac{-dC_A}{1.25C_A - 2.5} = \int_0^{1.5} 0.784 dt$$

$$\underline{\underline{C_A = 3.838\,(mol\,/\,L)}}$$

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,

$$V = \int_0^{X_A} \frac{F_{A0}dX_A}{-r_A} = \int_0^{X_A} \frac{F_{A0}dX_A}{kC_{A0}^2(1-X_A)^2}$$

$$\tau = \int_0^{X_A} \frac{C_{A0}dX_A}{kC_{A0}^2(1-X_A)^2} = \int_0^{0.3} \frac{3dX_A}{0.0015 \times 3^2(1-X_A)^2}$$

$$\tau = 95.238 \, (\text{min})$$

Problem 15
【Solution】

For 1st CSTR： $\tau = \dfrac{C_{A0}-C_{A1}}{kC_{A1}}$, $C_{A1} = \dfrac{C_{A0}}{1+k\tau}$

For 2nd CSTR： $\tau = \dfrac{C_{A1}-C_{A2}}{kC_{A2}}$, $C_{A2} = \dfrac{C_{A1}}{1+k\tau} = \dfrac{C_{A0}}{(1+k\tau)^2}$

For nth CSTR： $C_{An} = \dfrac{C_{A0}}{(1+k\tau)^n}$

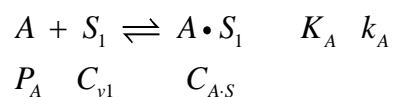$$C_{An} = C_{A0}(1-0.9) = \frac{C_{A0}}{(1+0.025 \times \frac{2}{0.05})^n}$$

n = 3.322，需 4 台 CSTR

Problem 16

【Solution】

Adsorption of A：

$$A + S_1 \rightleftharpoons A \cdot S_1 \qquad K_A \quad k_A$$
$$P_A \quad C_{v1} \qquad C_{A \cdot S}$$

Adsorption of B：

$$B + S_2 \rightleftharpoons B \cdot S_2 \qquad K_B \quad k_B$$
$$P_B \quad C_{v2} \qquad C_{B \cdot S}$$

Surface reaction：

$$A \cdot S_1 + B \cdot S_2 \rightleftharpoons C + S_1 + S_2 \qquad K_{rxn} \quad k_{rxn}$$
$$C_{A \cdot S} \qquad C_{B \cdot S} \qquad P_C \quad C_{v1} \quad C_{v2}$$
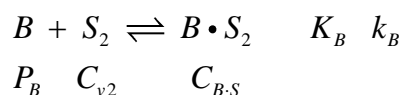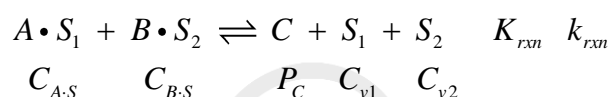
∵ Surface reaction is rate-determining,

$$\text{reaction rate,} \quad r = k_{rxn}[C_{A \cdot S} C_{B \cdot S} - \frac{1}{K_{rxn}} P_C C_{v1} C_{v2}]$$

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

$$C_{A \cdot S} = K_A P_A C_{v1}$$

根據 reactive site 1 balance

$$C_{t1} = C_{v1} + C_{A \cdot S} = C_{v1}(1 + K_A P_A) \quad, \quad C_{A \cdot S} = \frac{K_A P_A}{1 + K_A P_A} C_{v1}$$

For $C_{B \cdot S}$, $\dfrac{-r_B}{k_B} \simeq 0$：

$$C_{B \cdot S} = K_B P_B C_{v2}$$

根據 reactive site 2 balance

$$C_{t2} = C_{v2} + C_{B \cdot S} = C_{v2}(1 + K_B P_B) \quad, \quad C_{B \cdot S} = \frac{K_B P_B}{1 + K_B P_B} C_{t2}$$

代回 reaction rate 表示式，得：

$$r = k_{rxn}[\frac{K_A K_B P_A P_B C_{t1} C_{t2}}{(1+K_A P_A)(1+K_B P_B)} - \frac{P_C C_{t1} C_{t2}}{K_{rxn}(1+K_A P_A)(1+K_B P_B)}]$$

$$= k_{rxn}[\frac{K_A^{'} K_B^{'} P_A P_B}{(1+K_A P_A)(1+K_B P_B)} - \frac{K_{rxn}^{'} P_C}{(1+K_A P_A)(1+K_B P_B)}]$$

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Problem 1

【**Solution**】**(c)**

van der Waals equation of state：

$$(P + \frac{a}{\underline{V}^2})(\underline{V} - b) = RT \tag{1}$$

,where $\underline{V}$ is the molar volume

將(1)式整理成：

$$\frac{P\underline{V}}{RT} = \frac{\underline{V}}{\underline{V} - b} - \frac{a}{RT\underline{V}} = Z \tag{2}$$

將 $\underline{V} = \frac{4.86}{10.0} = 0.486\ (\frac{L}{mol})$

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,

$$\Delta S = nCv\ln(\frac{T_f}{T_i}) + nR\ln(\frac{V_f}{V_i}) = 0$$

將 T_i =273.15 K, V_i =1.0 L , V_f =3.0 L, C_v =1.5R 代入，且將 n 消去，得：

$$\Delta S = 1.5R\ln(\frac{T_f}{273.15}) + R\ln(\frac{3.0}{1.0}) = 0$$

$$\text{得} \underline{\underline{T_f = 131.6K}} \text{，} \underline{\underline{\textbf{選(a)}}}$$
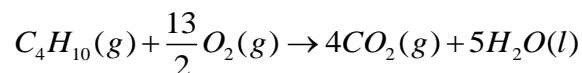
Problem 3

【Solution】(b)

∵反應熱, $\Delta_{rxn}H°=($生成物生成熱-反應物生成熱$)$

$=($反應物燃燒熱-生成物燃燒熱$)$

又 butane 燃燒反應式(25℃下)：

$$C_4H_{10}(g)+\frac{13}{2}O_2(g)\rightarrow 4CO_2(g)+5H_2O(l)$$

則 butane 之莫耳燃燒熱：

$$[4\Delta_f H°(CO_2,g)+5\Delta_f H°(H_2O,l)]-[\Delta_f H°(butane,g)+0]=-2878\ (kJ/mol)$$

將題目所給之數據代入得：

$$[4\times(-393.51)+5\times(-285.83)]-\Delta_f H°(butane,g)=-2878$$

則 $\Delta_f H°(butane,g)=-125.19\ (kJ/mol)$，**選(b)**

Problem 4

【Solution】(d)

∵根據 Joule Thomson coefficient 定義：

$$\mu\equiv(\frac{\partial T}{\partial P})_H=(\frac{\Delta T}{\Delta P})(\text{constant over the range})$$

將題目所給數據代入，即 ΔP=1-32=-31atm，ΔT=-22K

$$\mu=\frac{-22}{-31}=\textbf{0.7097}\text{，}\textbf{選(d)}$$

Problem 5
【Solution】 (d)

$$\Delta S = nC_{v,m} \ln(\frac{T_f}{T_i}) + nR \ln(\frac{V_f}{V_i})$$

$$= 1 \times (2.5-1) \times 8.314 \times \ln(\frac{600}{300}) + 1 \times 8.314 \times \ln(\frac{50}{30}) = \underline{\underline{12.89(J/K)}} \ , \ \underline{\textbf{選(d)}}$$

Problem 6
【Solution】 (e)

$$\Delta S = nC_{p,m} \underbrace{\ln(\frac{T_f}{T_i})}_{isothermal} - nR \ln(\frac{P_f}{P_i}) = -25$$

$$-2 \times 8.314 \times \ln(\frac{P_f}{3.5}) = -25$$

得 $P_f = $ **15.74 atm**，**選(e)**

Problem 7
【Solution】

By modified Raoult's law：

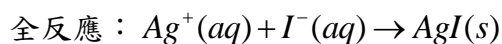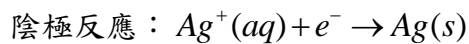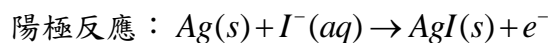$$y_i P = x_i r_i P_i^{sat}$$

將 A (Acetone) 與 B(Ethanol)數據代入，

$$y_A P = x_A r_A P_A^\circ \ \Rightarrow 0.516 \times 1 = 0.4 \times r_A \times \frac{786}{760}$$

$$y_B P = x_B r_B P_B^\circ \Rightarrow (1-0.516) \times 1 = (1-0.4) \times r_B \times \frac{551}{760}$$

得： $\begin{cases} r_A = 1.247 \\ r_B = 1.113 \end{cases}$

Problem 8

【Solution】

陽極反應：$Ag(s)+I^-(aq) \rightarrow AgI(s)+e^-$

陰極反應：$Ag^+(aq)+e^- \rightarrow Ag(s)$

全反應：$Ag^+(aq)+I^-(aq) \rightarrow AgI(s)$

則全反應之反應商數(Q)可表示為：

$$Q = \frac{1}{[Ag^+][I^-]} \text{，且} [Ag^+]=[I^-]$$

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：

$$0.95 = \frac{RT}{nF}\ln(\frac{1}{[Ag^+][I^-]}) = \frac{RT}{nF}\ln(\frac{1}{[Ag^+]^2})$$

$$0.95 = \frac{8.314 \times (298K)}{1 \times 96500}\ln(\frac{1}{[Ag^+]^2})$$

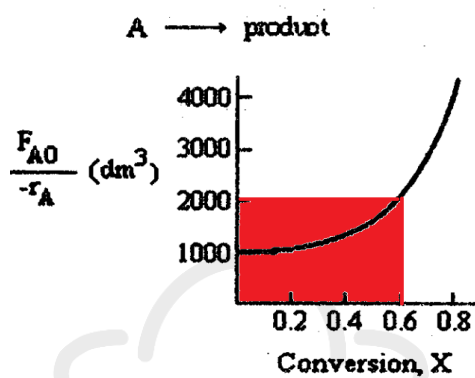則 $[Ag^+] = \underline{9.223 \times 10^{-8}}$ $(moleL^{-1} \approx molekg^{-1})$

Problem 9

【Solution】

For CSTR：

$$\text{Design equation：} V = \frac{F_{A0}x_A}{-r_A}$$

則 V=1200 dm^3，可以利用附圖計算出轉化率，由上式可知：

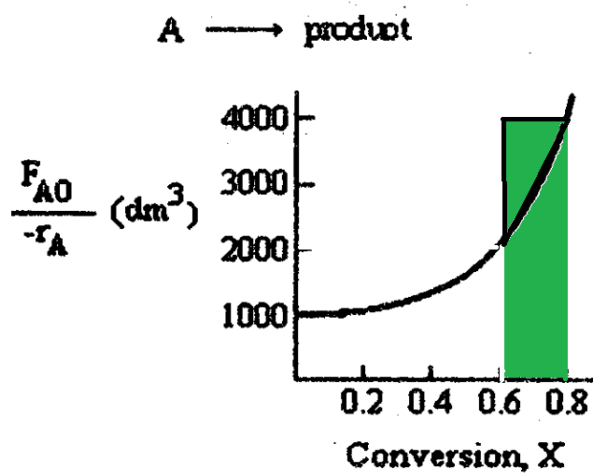即 CSTR 反應體積為 1200 dm^3 的情形下，轉化率可達 0.6

For PFR：

$$\text{Design Equation：} V = \int_0^{x_A} \frac{F_{A0}dx_A}{-r_A}$$

則 V $= 600\,dm^3$，可以利用附圖計算出轉化率，由上式可知：

其面積為

(長方形面積)-(圍起來之三角形面積)$= (0.8 - 0.6) \times 4000 - \dfrac{(0.8 - 0.6) \times 2000}{2} = 600$

即代表 PFR 之出口轉化率為 0.8

$$出口轉化率\ X \begin{cases} CSTR = 0.6 \\ PFR = 0.8 \end{cases}$$

Problem 10
【Solution】

(a)

By total energy balance on CSTR：$in - out + gen = \cancel{accu}$

$$\sum_i F_{A0} \theta_{i0} H_{io} - \sum_i F_{A0}(\theta_{i0} + v_i X_A) H_i + Q - \dot{W}_s = 0,$$

where v_i is the stoichiometric number.

$\because \dot{W}_s = 0$ and adiabatic($Q = 0$)，且合併整理

$$\sum_i F_{A0} \theta_{i0}(H_{io} - H_i) - \sum_i F_{A0} v_i X_A H_i = 0$$

$\because H_{io} - H_i = \displaystyle\int_{T_i}^{T_{io}} C_{pi} dT$，$\displaystyle\sum_i v_i H_i = \Delta H_{rxn}$ 代入，

$$\sum_i F_{A0} \int_{T_i}^{T_{io}} C_{pi} \theta_{i0} dT - F_{A0} X_A \Delta H_{rxn} = 0$$

移項並整理：

$$X_A = \frac{\sum_i F_{A0} \int_{T_i}^{T_{io}} C_{pi} \theta_{i0} dT}{F_{A0} \Delta H_{rxn}} = \frac{\sum_i \int_{T_{i0}}^{T_i} C_{pi} \theta_{i0} dT}{-\Delta H_{rxn}} = \frac{C_{PA}(T - T_0)}{-\Delta H_{rxn}}$$

(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：

$$k(T) = Ae^{-\frac{E}{RT}}, \text{ where } A \text{ is the pre-exponential factor}$$

代入：

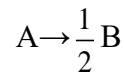$$V = \frac{F_{A0}X_A}{-r_A} = \frac{F_{A0}X_A}{k(T)C_{A0}(1-X_A)} = \frac{v_0 X_A}{Ae^{-\frac{E}{RT}}(1-X_A)}$$

Problem 11
【Solution】

Reaction：

$$A \rightarrow \frac{1}{2}B$$

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 $\sum_i \int_{T_{i0}}^{T_i} C_{pi}\theta_{i0}dT$：

$$\sum_i \int_{T_{i0}}^{T_i} C_{pi}\theta_{i0}dT = C_{PA}\theta_{A0}(T_i - T_{i0}) + C_{PI}\theta_{I0}(T_i - T_{i0})$$
$$= 15(T - 294) + 15(T - 294)$$
$$= 30(T - 294)$$

For $-\Delta H_{rxn}$：

$$-\Delta H_{rxn} = -[\Delta H_{rxn}^\circ(T_R) + \int_{T_R}^{T} \Delta C_{Pi}dT]$$
$$= -[(-50 \times \frac{1}{2}) - (-20) + \int_{T_R}^{T}(30 \times \frac{1}{2} - 15)dT]$$
$$= 5\ (kcal) = 5000(cal)$$

Combine： $X_A = \dfrac{\sum_i \int_{T_{i0}}^{T_i} C_{pi}\theta_{i0}dT}{-\Delta H_{rxn}} = \dfrac{30(T - 294)}{5000} = 0.8$ ，則 __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

$$\lim_{x_1 \to 1} \frac{d\, \hat{f}_1}{dx_1} = f_1$$

(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.)
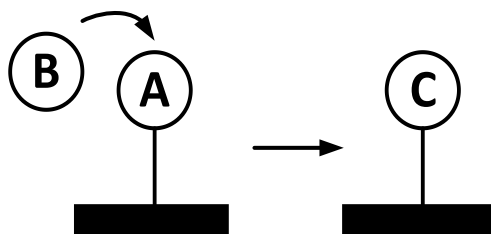

Problem 7
【Solution】

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.)

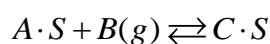## Problem 8
【Solution】

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,

$$A \cdot S + B(g) \rightleftarrows C \cdot S$$

(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 does 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

$$Da \equiv \frac{rate\ of\ reaction\ at\ entrance}{Entering\ flow\ rate\ of\ A} = \frac{-r_{A0}V}{F_{A0}}$$

(本題可參考：**FOGLER, H.** *Elements of Chemical Reaction Engineering*, **4th ed.; p 158.**)

Problem 11

【Solution】

(a)

Initially, according to ideal gas law,

$$PV = nRT \text{ , } P \propto n$$

$$n_{左} : n_{右} = P_{左} : P_{右} = 2 : 1$$

$$n_{左} = 2n_{右}$$

For equilibrium temperatures, by energy balance

(All the gas is considered as one system)

$$\Delta U = \cancel{Q}_{\substack{insulated}} + \cancel{W}_{\substack{no\ external\ work}}$$

$$\Delta U = 0 \text{ , } U_{前} = U_{後}$$

$$n_{左} C_V T_{左} + n_{右} C_V T_{右} = (n_{左} + n_{右})C_V T$$

$$2n_{右} C_V \times (50 + 273) + n_{右} C_V \times (50 + 273) = (2n_{右} + n_{右})C_V T$$

$$\underline{\underline{T = 323K}}$$

(b)

The total volume of the compartment is the same between the initial and final state,

$$\frac{n_{左} R T_{左}}{P_{左}} + \frac{n_{右} R T_{右}}{P_{右}} = \frac{(n_{左} + n_{右})RT}{P}$$

$$\frac{2n_{右} R(50 + 273)}{2} + \frac{n_{右} R(50 + 273)}{1} = \frac{(2n_{右} + n_{右})R(50 + 273)}{P}$$

$$\underline{\underline{P = 1.5\ (bar)}}$$

(c)

$$\Delta S = \cancel{\sum M_k \hat{S}_k}_{\text{closed system}} + \cancel{\frac{Q}{T}}_{\text{adiabatic}} + S_{gen}$$

$$S_{gen} = \Delta S = n_{右}[\,C_p\underbrace{\cancel{\ln(\frac{T_f}{T_i})}}_{T_f=T_i} - R\ln(\frac{P_{f,右}}{P_{i,右}})] + n_{左}[\,C_p\underbrace{\cancel{\ln(\frac{T_f}{T_i})}}_{T_f=T_i} - R\ln(\frac{P_{f,左}}{P_{i,左}})]$$

$$S_{gen} = n_{右}[-R\ln(\frac{P_{f,右}}{P_{i,右}}) - 2R\ln(\frac{P_{f,左}}{P_{i,左}})]$$

$$= \frac{1\times10^5(N/m^2)\times1(m^3)}{8.314\times(50+273)(K)}\times8.314[-\ln(\frac{1.5}{1}) - 2\ln(\frac{1.5}{2})]$$

$$S_{gen} = \underline{\underline{52.6\ (J/K)}}$$
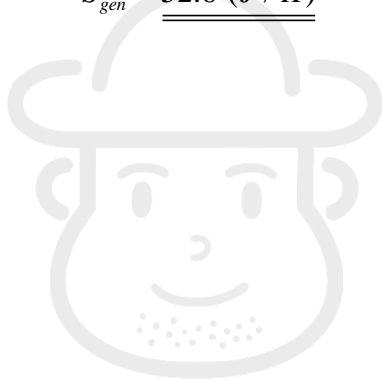
Problem 12
【Solution】

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,

$$0.88 \times 1.72 = r_1 \times 0.6 \times 2$$

$$0.12 \times 1.72 = r_2 \times 0.4 \times 1$$

$$\begin{cases} r_1 = 1.26 \\ r_2 = 0.516 \end{cases}$$

$$\because \Delta \underline{G}_{mix} = \underline{G}^{ex} + \Delta \underline{G}_{mix}^{id}$$

$$\Delta \underline{G}_{mix} = RT[x_1 \ln r_1 + x_2 \ln r_2 + x_1 \ln x_1 + x_2 \ln x_2]$$

$$= 8.314 \times 300[0.6 \ln(1.26 \times 0.6) + 0.4(0.516 \times 0.4)]$$

$$= \underline{\underline{-1992.87}} \ (J / mole)$$

Problem 13

【Solution】

For PFR, design equation,

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

For rate equation,

$$-r_A = k_{(1000K)} C_A = k_{(1000K)} \frac{C_{A0}(1-x_A)}{(1+\varepsilon x_A)} \quad (isobaric)$$

For ε,

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

For $k_{(1000K)}$, by Arrhenius law,

$$\frac{k_{(800K)}}{k_{(1000K)}} = \frac{e^{-\frac{E_a}{R \times 800}}}{e^{-\frac{E_a}{R \times 1000}}} = \frac{0.1}{k_{(1000K)}} = \frac{e^{-\frac{40 \times 10^3}{8.314 \times 800}}}{e^{-\frac{40 \times 10^3}{8.314 \times 1000}}}$$

$$k_{(1000K)} = 0.333 \ s^{-1}$$

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

$$\frac{-dC_A}{dW} = k_1 C_A \text{ , } C_A = c_1 e^{-k_1 W}$$

For $W = 0$, $C_A = C_{A0}$

$$\underline{\underline{C_A = C_{A0} e^{-k_1 W}}}$$

For C_B

$$\frac{dC_B}{dW} = k_1 C_A - k_2 C_B \text{ , 且 } W = 0 \text{ , } C_B = 0 \text{ 代入}$$

$$\underline{\underline{C_B = k_1 C_{A0} (\frac{e^{-k_1 W} - e^{-k_2 W}}{k_2 - k_1})}}$$

For C_B to be maximum, let

$$\frac{dC_B}{dW} = 0$$

$$W_{\max,B} = \frac{\ln\dfrac{k_1}{k_2}}{k_1 - k_2} = \frac{\ln\dfrac{0.1}{0.001}}{0.1 - 0.001} = \underline{\underline{46.51 \ (s)}}$$

代回 C_A

$$C_A = C_{A0} e^{-k_1 W} = C_{A0}(1 - x_A) \text{ , } x_A = 0.99$$

代回 PBR 之 design equation,

$$W = \int_0^{x_A} \frac{F_{A0} dx_A}{-r_A} = \int_0^{0.99} \frac{0.005 \times 2 dx_A}{0.1 \times 0.005 \times (1 - x_A)} = \underline{\underline{92.10 \ (g)}}$$

(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,

$$r_{E \cdot S} = k_1[E][S] - k_{-1}[E \cdot S] - k_2[S][E \cdot S] + k_{-2}[S \cdot E \cdot S] - k_3[E \cdot S] = 0 - - - - -(1)$$

$$r_{S \cdot E \cdot S} = k_2[S][E \cdot S] - k_{-2}[S \cdot E \cdot S] = 0 - - - - -(2)$$

$$[S \cdot E \cdot S] = \frac{k_2[S][E \cdot S]}{k_{-2}} \; 代回(1)$$

$$[E \cdot S] = \frac{k_1[E][S]}{k_{-1} + k_3}$$

According to enzyme-balance equation,

$$[E_t] = [E] + [E \cdot S] + [S \cdot E \cdot S]$$

$$[E_t] = [E] + \frac{k_1[E][S]}{k_{-1} + k_3} + \frac{k_1 k_2[E][S]^2}{(k_{-1} + k_3)k_{-2}}$$

$$[E_t] = [E](1 + \frac{k_1[S]}{k_{-1} + k_3} + \frac{k_1 k_2[S]^2}{(k_{-1} + k_3)k_{-2}})$$

$$[E] = [E_t](1 + \frac{k_1[S]}{k_{-1} + k_3} + \frac{k_1 k_2[S]^2}{(k_{-1} + k_3)k_{-2}})^{-1}$$

$$[E \cdot S] = \frac{k_1[E][S]}{(k_{-1} + k_3)} = \frac{k_1[S][E_t]}{(k_{-1} + k_3)(1 + \frac{k_1[S]}{k_{-1} + k_3} + \frac{k_1 k_2[S]^2}{(k_{-1} + k_3)k_{-2}})} = \frac{k_1[S][E_t]}{(k_{-1} + k_3 + k_1[S] + \frac{k_1 k_2[S]^2}{k_{-2}})}$$

$$r_p = k_3[E \cdot S] = \frac{k_3 k_1[S][E_t]}{(k_{-1} + k_3 + k_1[S] + \frac{k_1 k_2[S]^2}{k_{-2}})} = \frac{K_I v_{max}[S]}{K_M K_I + K_I[S] + [S]^2} \quad \begin{cases} K_M = \dfrac{(k_{-1} + k_3)}{k_1} \\[2mm] K_I = \dfrac{k_{-2}}{k_2} \\[2mm] v_{max} = k_3[E_t] \end{cases}$$

(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)

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<u>**Problem 1**</u>
【**Solution**】

Space time,

$$\tau = \text{the time require to process one reactor volume of the feed}$$

measured at specified conditions

Space velocity,

$$s = \text{number of reactor volumes of feed}$$

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.**)

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.)

Problem 4

【**Solution**】

Because the water phase and the oil phase are immiscible, the may be two phase 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,

$$f^I(T,P) = f^{II}(T,P) \ 、 \ f^{II}(T,P) = f^{III}(T,P)$$

Therefore,

$$f^I(T,P) = f^{III}(T,P)$$

which means phase I is in equilibrium with phase III.

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，

$$k = 7.80\times10^9 \exp[\frac{-19200}{773}] = 0.127(s^{-1})$$

$$V = \int_0^{0.9} \frac{0.193(1+x_A)dx_A}{0.127(1-x_A)} = 5.616(ft^3)$$

$$V = AL = 5.616 = 0.0388L$$

$$\underline{L = 144.73(ft)}$$

(本題可參考：Davis, M. E. E.; Davis, R. J. J. *Fundamentals of Chemical Reaction Engineering***;**
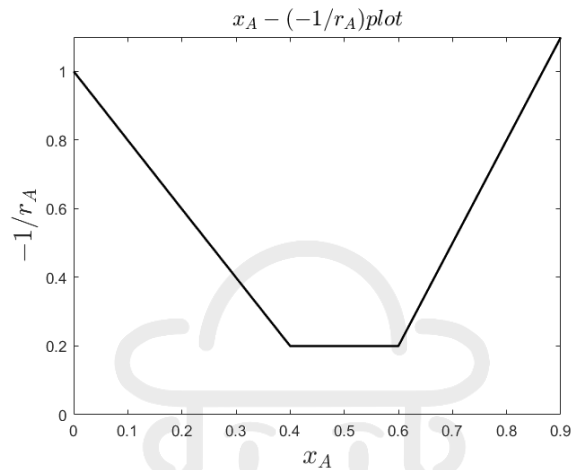
p 78~79, Example 3.4-1.

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 $\dfrac{-1}{r_A}$，作出表格如下：

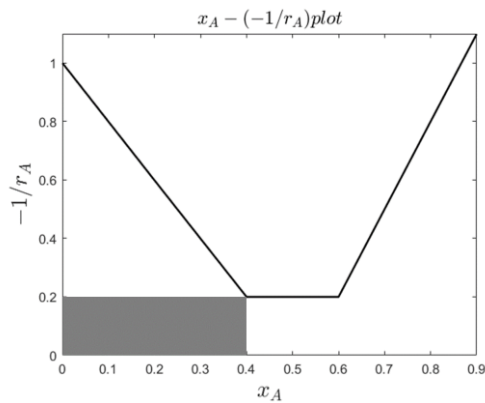| x_A	0	0.2	0.4	0.45	0.5	0.6	0.8	0.9
$-1/r_A$	1	0.6	0.2	0.2	0.2	0.2	0.8	1.1

(假設 x_A 在 Table 未列出的區域呈線性關係)
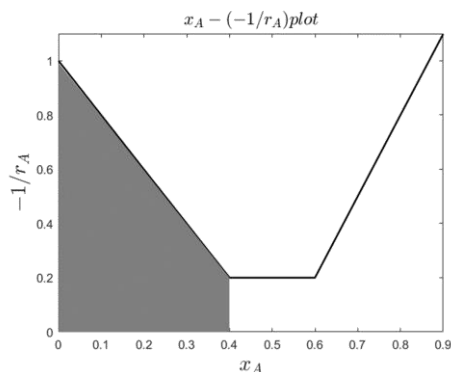
(a)

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：$V_{CSTR} = F_{A0} \times 0.4 \times 0.2 = 300 \times 0.4 \times 0.2 = \underline{\underline{24}} \ (dm^3)$

For PFR, the design equation is,

$$V = \int_0^{x_A} \frac{F_{A0}}{-r_{Af}} dx_A \quad , \text{可作圖如下}$$

其體積可計算為：$V_{PFR} = F_{A0} \times \underbrace{\frac{(0.2+1) \times 0.4}{2}}_{\text{梯形面積}} = 300 \times \frac{(0.2+1) \times 0.4}{2} = \underline{\underline{72 \ (dm^3)}}$

(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

$$V_{CSTR} = F_{A0} \frac{x_A}{-r_A} = F_{A0} x_A (3x_A - 1.6)$$

$$V_{PFR} = F_{A0} \left[\frac{(0.2+1) \times 0.4}{2} + 0.2 \times 0.2 + \frac{(0.2 + 3x_A - 1.6) \times (x_A - 0.6)}{2} \right]$$

$$V_{CSTR} = V_{PFR} \quad , \quad \underline{\underline{x_A = 0.683}}$$

※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)

$$105 = 300 x_A (3x_A - 1.6) \quad , \quad \underline{\underline{x_A = 0.7}}$$

(d)

$72dm^3$ 之 PFR 可達到(a)所計算出之轉化率 $x_{A,PFR} = 0.4$

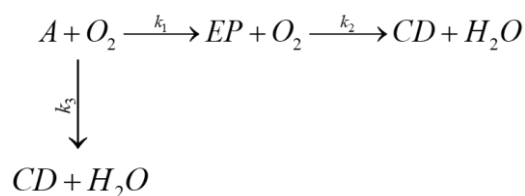$$V_{CSTR} = 300(x_A - 0.4) \times (3x_A - 1.6) = 24 \quad , \quad \underline{\underline{x_A = 0.643}}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*,

4th ed.; p 74, Problem 2-7B.)

Problem 10

【Solution】

(a)

改寫題目所給之方程式：

$$A + O_2 \xrightarrow{k_1} EP + O_2 \xrightarrow{k_2} CD + H_2O$$

$$\Big\downarrow k_3$$

$$CD + H_2O$$

$$\frac{-dC_A}{dt} = k_3 C_A C_{O_2} + k_1 C_A C_{O_2}$$

$$\frac{dC_{EP}}{dt} = k_1 C_A C_{O_2} - k_2 C_{EP} C_{O_2}$$

$$\frac{dC_{CD}}{dt} = k_2 C_{EP} C_{O_2} + k_3 C_A C_{O_2}$$

The percent selectivity to the epoxide (EP) is,

$$S_{EP} = \frac{r_{EP}}{r_{EP} + r_{CD}} = \frac{k_1 C_A C_{O_2} - k_2 C_{EP} C_{O_2}}{k_1 C_A C_{O_2} - k_2 C_{EP} C_{O_2} + k_2 C_{EP} C_{O_2} + k_3 C_A C_{O_2}} = \underline{\underline{\frac{k_1 C_A - k_2 C_{EP}}{k_1 C_A + k_3 C_A}}}$$

(b)

To obtain the maximum selectivity of EP, there must no C_{EP} exists, ($C_{EP} = 0$)

$$S_{EP}^{max} = \frac{k_1 C_A}{k_1 C_A + k_3 C_A} = \underline{\underline{\frac{k_1}{k_1 + k_3}}}$$

(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,

$$P_A^{sat} = 10^{4 - \frac{1170}{49+273-49}} = 0.5179 \ (bar)$$

$$P_B^{sat} = 10^{4 - \frac{1070}{49+273-40}} = 1.6057 \ (bar)$$

$$P_C^{sat} = 10^{5.2 - \frac{1733}{49+273-40}} = 0.1134 \ (bar)$$

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, $z_i = x_i$

$$\begin{cases} y_A = \dfrac{P_A^{sat} x_A}{P} = \dfrac{0.5179 \times \frac{2}{5}}{1} = 0.207 \\\\ y_B = \dfrac{P_B^{sat} x_B}{P} = \dfrac{1.6057 \times \frac{1}{5}}{1} = 0.321 \\\\ y_C = \dfrac{P_C^{sat} x_C}{P} = \dfrac{0.1134 \times \frac{2}{5}}{1} = 0.045 \end{cases}$$

$y_A + y_B + y_C < 1$，not possible for real case

Assume all the three components are not miscible,

$$\begin{cases} y_A = \dfrac{P_A^{sat} x_A}{P} = \dfrac{0.5179 \times 1}{1} = 0.5179 \\[3mm] y_B = \dfrac{P_B^{sat} x_B}{P} = \dfrac{1.6057 \times 1}{1} = 1.6057 \\[3mm] y_C = \dfrac{P_C^{sat} x_C}{P} = \dfrac{0.1134 \times 1}{1} = 0.1134 \end{cases}$$

$y_A + y_B + y_C > 1$ ， 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

$$\begin{cases} y_A = \dfrac{P_A^{sat} x_A}{P} = \dfrac{0.5179 \times \dfrac{2}{2+1}}{1} = 0.3453 \\[5mm] y_B = \dfrac{P_B^{sat} x_B}{P} = \dfrac{1.6057 \times \dfrac{1}{2+1}}{1} = 0.5352 \\[5mm] y_C = \dfrac{P_C^{sat} x_C}{P} = \dfrac{0.1134 \times 1}{1} = 0.1134 \end{cases}$$

$y_A + y_B + y_C = 0.9939$, feasible result

$$y_B = \underline{\underline{0.5352}}$$

【**Case ②**】B and C are miscible

$$\begin{cases} y_A = \dfrac{P_A^{sat} x_A}{P} = \dfrac{0.5179 \times 1}{1} = 0.5179 \\[3mm] y_B = \dfrac{P_B^{sat} x_B}{P} = \dfrac{1.6057 \times \dfrac{1}{2+1}}{1} = 0.5352 \\[5mm] y_C = \dfrac{P_C^{sat} x_C}{P} = \dfrac{0.1134 \times \dfrac{2}{2+1}}{1} = 0.0756 \end{cases}$$
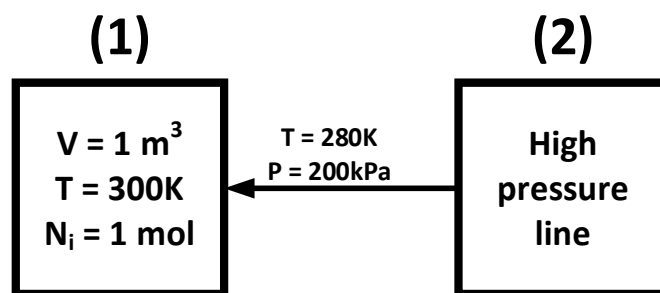
$y_A + y_B + y_C > 1$ ，not possible for real case
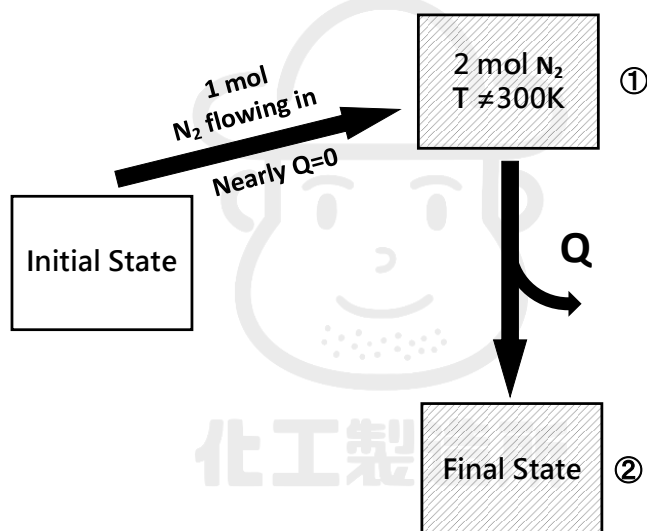
Problem 12

【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)

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

$$\int \underline{H}_{in}\,\dot{n}_{in}\,dt = \int \frac{d}{dt}(n\underline{U})_{sys}dt \quad , \quad \underline{H}_{in}\Delta n = n_f\underline{U}_f - n_i\underline{U}_i$$

$$\begin{cases} \underline{H}_{in} = C_p \times 280 = 29 \times 280 \\ \underline{U}_i = C_V \times 300 = (29 - 8.314) \times 300 \\ \underline{U}_f = C_V \times 300 = (29 - 8.314) \times T_1 \quad (T_{ref} = 0K) \\ n_i = \Delta n = 1 \\ n_f = 2 \end{cases}$$

$$1 \times 29 \times 280 \times (2-1) = 2 \times (29 - 8.314) \times T_1 - 1 \times (29 - 8.314) \times 300$$

$$T_1 = 346.26(K)$$

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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【Solution】

假設初始狀態 A 與 B 達機械平衡(即 $P_A = P_B$)

$$\Delta S = \sum_{i=A,B} \underbrace{(nC_V \ln \frac{T_{2,i}}{T_{1,i}}}_{isothermal} + nR \ln \frac{V_{2,i}}{V_{1,i}}) = nR(\ln \frac{V_A + V_B}{V_A} + \ln \frac{V_A + V_B}{V_B})$$

$$= nR(\ln \frac{n_A + n_B}{n_A} + \ln \frac{n_A + n_B}{n_B}) = \underbrace{-nR(\ln x_A + \ln x_B)}_{entropy\ change\ of\ mixing}$$

$$= -1 \times 8.3145 \times (\ln 0.5 + \ln 0.5) = 11.526 (J/K) \approx \underline{\underline{11.53 (J/K)}}$$

Problem 2：Ans：(b)
【Solution】

By Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H_{transition}}{T \Delta V_{transition}}$$

For most cases,

$$\Delta H_{sublimation} > \Delta H_{vaporization} > \Delta H_{fusion} > 0$$

$$\Delta V_{sublimation} \approx \Delta V_{vaporization} >>> \Delta V_{fusion} > 0$$

因此：

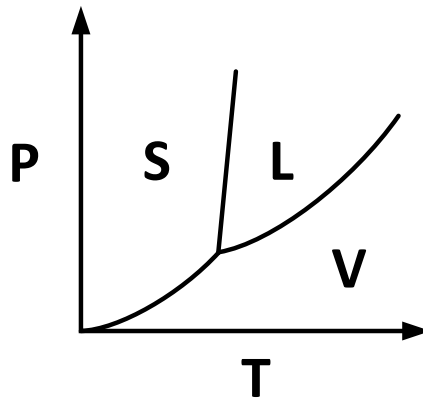$$(\frac{dP}{dT})_{fusion} , (\frac{dP}{dT})_{sublimation} , (\frac{dP}{dT})_{vaporization} > 0 \text{，} \underline{\textbf{選(b)}}$$

(D)

$$\left| (\frac{dP}{dT})_{fusion} \right| \propto (\frac{\Delta H}{\Delta V})_{fusion} \text{、} (\frac{dP}{dT})_{sublimation} \propto (\frac{\Delta H}{\Delta V})_{sublimation}$$

又

$$\Delta V_{sublimation} >>> \Delta V_{fusion}$$

$$\boxed{\left| (\frac{dP}{dT})_{fusion} \right| > (\frac{dP}{dT})_{sublimation}}$$

※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) 同上題討論，對。

(b) $\because \Delta S_{sublimation} > \Delta S_{vaporization}$ ，代表 $(\frac{dP}{dT})_{sublimation} \Delta V_{sublimation} > (\frac{dP}{dT})_{vaporization} \Delta V_{vaporization}$

$\because \Delta V_{sublimation} \approx \Delta V_{vaporization} = \Delta V$

$$(\frac{dP}{dT})_{sublimation} > (\frac{dP}{dT})_{vaporization}$$

which is contradict to the question statement

(c) 同上：

$$\because \Delta S_{vaporization} > \Delta S_{fusion} \text{，代表 } (\frac{dP}{dT})_{vaporization} \Delta V_{vaporization} > (\frac{dP}{dT})_{fusion} \Delta V_{fusion}$$

$$\because \Delta V_{vaporization} > \Delta V_{fusion}$$
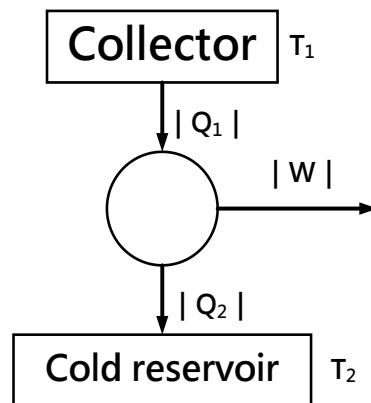
$$(\frac{dP}{dT})_{vaporization} > (\frac{dP}{dT})_{fusion}$$

此結論代入並未違反 $\Delta S_{vaporization} > \Delta S_{fusion}$，對

(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,

$$\Delta S = \underbrace{\sum_{closed\ system} M_k \cancel{S_k}} + \frac{|Q_1|}{T_1} - \frac{|Q_2|}{T_2} + \underbrace{\cancel{S_{gen}}}_{\substack{maximum \\ efficiency}} = 0$$
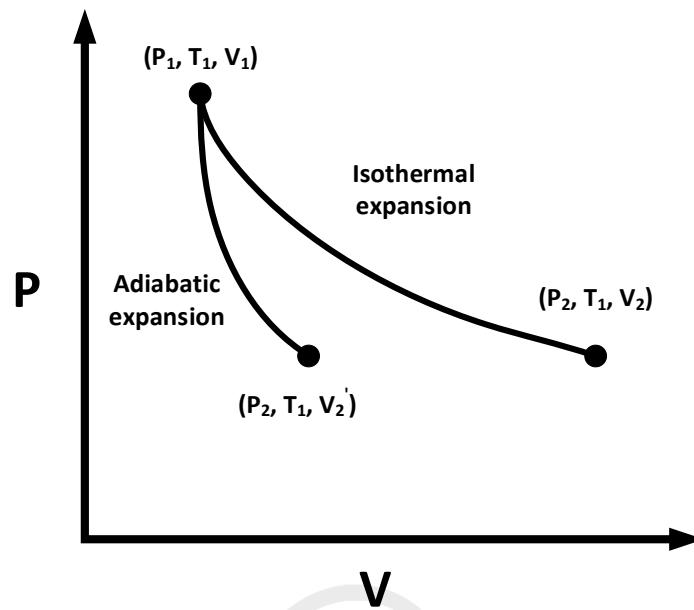
$$\frac{|Q_1|}{|Q_2|} = \frac{T_1}{T_2} \quad 代回$$

$$|W| = |Q_1|(1 - \frac{T_2}{T_1}) = 2 \times \frac{A \times 100^2}{60} \times (1 - \frac{298}{273.15 + 85}) = 1000$$

$$\underline{\underline{A = 17.86 \approx 17.9 m^2}}$$

Problem 5：Ans：(c)

【Solution】

For P_1, P_2, $\because$ expansion, $\underline{\underline{P_1 > P_2}}$

For T_1, T_2, $\because \dfrac{P_2 V_2}{P_2 V_2^{'}} = \dfrac{T_1}{T_2}$, $V_2 > V_2^{'}$, $\underline{\underline{T_1 > T_2}}$

Problem 6：Ans：(e)

【Solution】

At equilibrium,

$$n_{NO} = 2 - 2\varepsilon \qquad\qquad y_{NO} = \frac{2 - 2\varepsilon}{3 - \varepsilon}$$

$$n_{O_2} = 1 - \varepsilon \qquad\qquad y_{O_2} = \frac{1 - \varepsilon}{3 - \varepsilon}$$

$$n_{NO_2} = 2\varepsilon \qquad\qquad y_{NO_2} = \frac{2\varepsilon}{3 - \varepsilon}$$

$$n_T = 3 - \varepsilon$$

Problem 7：Ans：(a)

【Solution】

$$K_P = \frac{P_{NO_2}^2}{P_{NO}^2 P_{O_2}} = \frac{(\frac{2\varepsilon}{3-\varepsilon})^2 P^2}{(\frac{2-2\varepsilon}{3-\varepsilon})^2 P^2 \cdot (\frac{1-\varepsilon}{3-\varepsilon})P}$$

$$K_P = \frac{(3-\varepsilon)\cdot 4\varepsilon^2}{(2-2\varepsilon)^2 \cdot (1-\varepsilon)P} \quad => \quad K_P P = \frac{(3-\varepsilon)\cdot \varepsilon^2}{(1-\varepsilon)^3}$$

$$(1-\varepsilon)^3 = \frac{(3-\varepsilon)\cdot \varepsilon^2}{K_P P}$$

$\because K_P$ is very large, $\varepsilon \to 1$

$$\varepsilon = 1 - \lim_{\varepsilon \to 1} \sqrt[3]{\frac{(3-\varepsilon)\cdot \varepsilon^2}{K_P P}} = 1 - \sqrt[3]{\frac{2}{K_P P}}$$

Problem 8

【Solution】

(a)

$$dA = -PdV - \underbrace{SdT}_{constant\ T} = -PdV$$

$$\because P = \frac{nRT}{V-nb} - \frac{an^2}{V^2 T}$$

$$dA = -PdV = -(\frac{nRT}{V-nb} - \frac{an^2}{V^2 T})dV$$

$$A(T,V) = -\int (\frac{nRT}{V-nb} - \frac{an^2}{V^2 T})dV = -nRT\ln(V-nb) - \frac{an^2}{VT} + f(T)$$

※【補充】倘若題目反而給的是 $V = f(P)$，且難以整理成 $P = f(V)$ 的形式時，可由以下方法嘗試(但示範上一樣代入此題給的方程式)：

$$dA = -PdV = VdP - d(PV)$$

$$\because P = \frac{nRT}{V-nb} - \frac{an^2}{V^2T}$$

$$PV = \frac{nRTV}{V-nb} - \frac{an^2}{VT} \quad , \quad \boxed{d(PV) = d\left(\frac{nRTV}{V-nb} - \frac{an^2}{VT}\right)}$$

$$dP = d\left(\frac{nRT}{V-nb} - \frac{an^2}{V^2T}\right) = \left[\frac{-nRT}{(V-nb)^2} + \frac{2an^2}{V^3T}\right]dV$$

$$\boxed{VdP = \left[\frac{-nRTV}{(V-nb)^2} + \frac{2an^2}{V^2T}\right]dV}$$

$$dA = -nRT\left[\frac{nb}{(V-nb)^2} + \frac{1}{V-nb}\right]dV + \frac{2an^2}{V^2T}dV - d\left(\frac{nRTV}{V-nb} - \frac{an^2}{VT}\right)$$

$$A(T,V) = -nRT\left[\frac{-nb}{V-nb} + \ln(V-nb)\right] - \frac{2an^2}{VT} - \frac{nRTV}{V-nb} + \frac{an^2}{VT} + C(T)$$

$$= \frac{n^2RTb}{V-nb} - nRT\ln(V-nb) - \frac{an^2}{VT} - \frac{nRTV}{V-nb} + C(T)$$

$$= nRT\left(\frac{nb-V}{V-nb}\right) - nRT\ln(V-nb) - \frac{an^2}{VT} + C(T)$$

$$= -nRT - nRT\ln(V-nb) - \frac{an^2}{VT} + C(T)$$

$$\underline{\underline{= -nRT\ln(V-nb) - \frac{an^2}{VT} + f(T)}}$$

(b)

By Maxwell relations,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \underline{\underline{\frac{nR}{V-nb} + \frac{an^2}{V^2T^2}}}$$

(c)

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{nRT}{V-nb} + \frac{an^2}{V^2T} - \frac{nRT}{V-nb} + \frac{an^2}{V^2T} = \underline{\underline{\frac{2an^2}{V^2T}}}$$

Problem 9
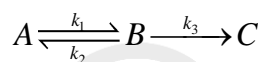
【Solution】

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,

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \overset{k_3}{\longrightarrow} C$$

Pseudo Steady State Approximation：$\underset{small}{\frac{d[B]}{dt}} = \underset{fast}{k_1[A]} - \underset{fast}{k_2[B]} - \underset{fast}{k_3[B]}$

Fast equilibrium Approximation：$\underset{small}{\frac{d[B]}{dt}} = \underset{fast}{k_1[A]} - \underset{fast}{k_2[B]} - \underset{small}{k_3[B]}$

Problem 10

【Solution】

Assume the decomposition reaction is a n-order reaction (usually 1st order reaction)

Initially,
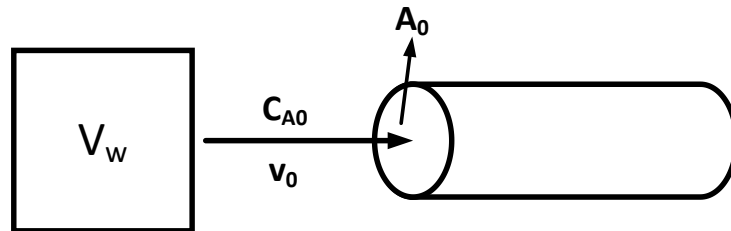
$$\text{Total time} = \frac{V_W}{v_0}$$

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,

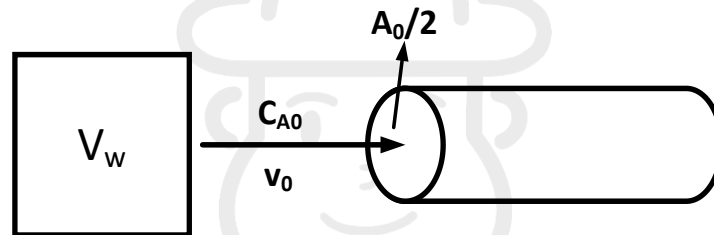$$-r_A = kC_A^n = kC_{A0}^n(1-x_A)^n$$

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,

$$\frac{V_2}{V_1} = \frac{\dfrac{C_{A0}v_0}{k_2 C_{A0}^n} \displaystyle\int_0^{x_A} \dfrac{dx_A}{(1-x_A)^n}}{\dfrac{C_{A0}v_0}{k_1 C_{A0}^n} \displaystyle\int_0^{x_A} \dfrac{dx_A}{(1-x_A)^n}} = \frac{k_1}{k_2} = \frac{1}{2}$$

$$\frac{k_1}{k_2} = \frac{1}{2} = \frac{k_0 e^{\frac{-E_a}{RT_1}}}{k_0 e^{\frac{-E_a}{RT_2}}} = e^{\frac{-E_a}{R}(\frac{1}{T_1}-\frac{1}{T_2})}$$

$$\frac{1}{2} = e^{\frac{-20\times10^3}{1.987}(\frac{1}{350}-\frac{1}{T_2})}, \quad \underline{\underline{T_2 = 358.6\ (K)}}$$

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,

$$[S_1] + [S_2] = [S_1]_0 + [S_2]_0 \quad,\quad [S_2] = [S_1]_0 + [S_2]_0 - [S_1]$$

$$\frac{d[S_1]}{dt} = [N_2][k_1([S_1]_0 + [S_2]_0 - [S_1]) - k_{-1}[S_1]]$$

$$\frac{d[S_1]}{dt} = [N_2]k_1([S_1]_0 + [S_2]_0) - [N_2](k_1 + k_{-1})[S_1]$$

$$\frac{d}{dt}(e^{[N_2](k_1+k_{-1})t}[S_1]) = [N_2]k_1([S_1]_0 + [S_2]_0)e^{[N_2](k_1+k_{-1})t}$$

$$e^{[N_2](k_1+k_{-1})t}[S_1] = \frac{[N_2]k_1([S_1]_0 + [S_2]_0)}{[N_2](k_1+k_{-1})}e^{[N_2](k_1+k_{-1})t} + C$$

$$[S_1] = \frac{k_1([S_1]_0 + [S_2]_0)}{(k_1 + k_{-1})} + Ce^{-[N_2](k_1+k_{-1})t}$$

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)

$$\frac{-d[O_3]}{dt} = k_1[Cl_2][O_3] + k_2[ClO_2\cdot] + k_3[ClO_3\cdot][O_3] - - -(1)$$

By pseudo steady state assumptions,

$$\frac{d[ClO\cdot]}{dt} = k_1[Cl_2][O_3] - k_5[ClO\cdot]^2 = 0 - - -(2)$$

$$\frac{d[ClO_2\cdot]}{dt} = k_1[Cl_2][O_3] - k_2[ClO_2\cdot][O_3] + k_3[ClO_3\cdot][O_3] = 0 - - -(3)$$

$$\frac{d[ClO_3\cdot]}{dt} = k_2[ClO_2\cdot][O_3] - k_3[ClO_3\cdot][O_3] - k_4[ClO_3\cdot]^2 = 0 - - -(4)$$

$(3) + (4)$:

$$k_1[Cl_2][O_3] - k_4[ClO_3\cdot]^2 = 0$$

$$[ClO_3\cdot] = \sqrt{\frac{k_1}{k_4}[Cl_2][O_3]}$$

$(1) + (3)$:

$$\frac{-d[O_3]}{dt} = 2k_1[Cl_2][O_3] + 2k_3[ClO_3\cdot][O_3] = 2k_1[Cl_2][O_3] + 2k_3\sqrt{\frac{k_1}{k_4}[Cl_2][O_3]^3}$$
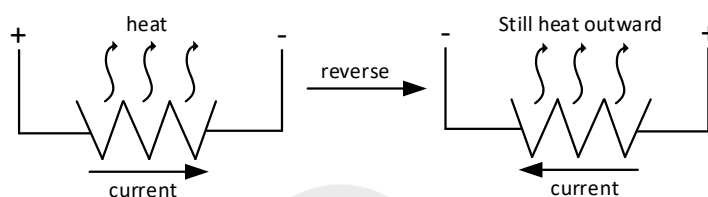
(b) At long time scale, $[O_3]$ is very low

$$\frac{-d[O_3]}{dt} = 2k_1[Cl_2][O_3] + 2k_3\sqrt{\frac{k_1}{k_4}[Cl_2][O_3]^3} \approx 2k_1[Cl_2][O_3]$$

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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 in a cycling process.

(b) **False.** If the concentration, pressure, or temperature, etc., of the species change in a way largen 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) <u>**False.**</u> It depends on the type of process. According to the Kelvin-Planck statement of the second law of thermodynamics, it is impossible to construct a device that **<u>operates *cyclically* and converts heat completely into work *without other effects*.</u>** However, the reverse process is possible.

(本題可參考：**Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 106~107, Illustration 4.1-2;以及 Smith, J.; Van Ness, H.; Abbott, M.; Hwalek, J. *Introduction to Chemical Engineering Thermodynamics*, 7th ed.; p 160.)**

事實上，第二定律闡述的是我們不可能搭建一個程序，使得這個程序在<u>不改變系統與外界狀態的條件下，將熱 100%轉成功</u>。例如 cycling processes，其特色為經歷一個完整的 cycle 後，系統與環境的狀態可視為不變(比如溫度、壓力、體積皆回到原初始狀態)。因此在這樣的情況下，就不可能將吸收的熱 100%轉為淨功。然而如果考慮單次的理想氣體恆溫可逆膨脹：

$$
\boxed{
\begin{array}{c}
P_0 \\ V_0 \\ T_0
\end{array}
}
\quad\longrightarrow\quad
\boxed{
\begin{array}{c}
P_1 \\ V_1 \\ T_0
\end{array}
}
$$
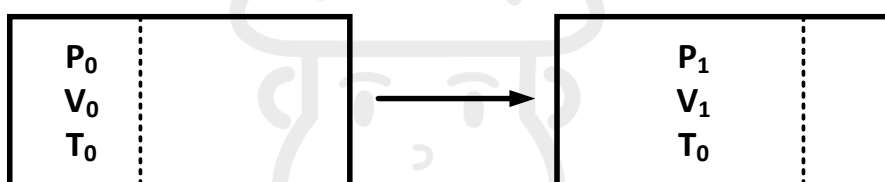
根據第一定律：

$$\Delta\!\!\!/\,U = Q + W \ , \ \underline{\underline{Q = -W}}$$

亦即吸了多少熱，確實能將其全部轉為功，<u>然而其系統內狀態改變了</u>。

(e) <u>**False.**</u> The entropy of an isolated system can only increase, which is,

$$\Delta S_{isolated} = \underset{isolated}{\cancel{\frac{Q}{T}}} + S_{gen} \geq 0$$

But if we consider a reversible isothermal compression process of ideal gas,

$$\underset{isothermal}{\cancel{\Delta U}} = Q + W \ , \ Q = -W < 0$$

$$\Delta S = \frac{Q}{T} + \underset{reversible}{\cancel{S_{gen}}} < 0$$

Problem 2

【Solution】

If the mixture is a system of ideal solution, consider the process,

W_{min}

| $N_A + N_B = 1$ | → | $N_A = x_A$ mole |
| | | $N_B = x_B$ mole |

state①   state②
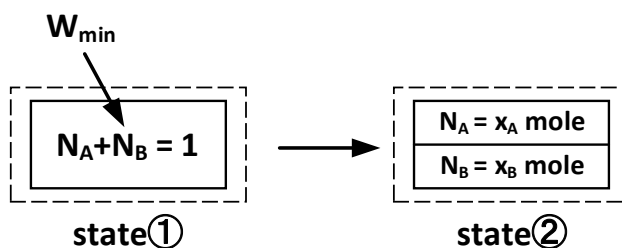
System = separator + its content

By energy balance of the closed system,

$$U_2 - U_1 = Q + W_s - (P_2 V_2 - P_1 V_1) \text{ , } P_2 = P_1 (constant \ P)$$

By entropy balance,

$$\Delta S_{sys} = \frac{Q}{T} + \underset{minimum \ work}{\cancel{S_{gen}}} = S_2 - S_1$$

$Q = T(S_2 - S_1)$ 代回(定溫)：

$$U_2 - U_1 = TS_2 - TS_1 + W_s - P_2 V_2 - P_1 V_1$$

$$W_s = (U_2 + P_2 V_2 - TS_2) - (U_1 + P_1 V_1 - TS_1) = G_2 - G_1$$

$$W_{min} = -\Delta G_{mix}^{id} = -nRT(\underset{讀圖}{x_A \ln x_A + x_B \ln x_B})$$

$$= -1 \times 8.314 \times 300 (0.8 \ln 0.8 + 0.2 \ln 0.2) = \underline{\underline{1248.1 \ (J)}}$$

<u>Problem 3</u>

【**Solution**】

(a)

$\because dU = TdS - PdV$, for the dS term, we need,

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

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

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

For $(\frac{\partial S}{\partial V})_T$, by Maxwell relation,

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

$$dU = T[\frac{C_V}{T}\, dT + (\frac{\partial P}{\partial T})_V\, dV] - PdV = C_V dT + [-P + T(\frac{\partial P}{\partial T})_V]dV$$

(**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,

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

在固定 V 下，再對 T 微分：

$$\frac{\partial}{\partial T}[(\frac{\partial U}{\partial V})_T]_V = \frac{\partial}{\partial T}[T(\frac{\partial P}{\partial T})_V - P]_V = (\frac{\partial P}{\partial T})_V + T(\frac{\partial^2 P}{\partial T^2})_V - (\frac{\partial P}{\partial T})_V = T(\frac{\partial^2 P}{\partial T^2})_V$$

Because U is an exact function,

$$\frac{\partial}{\partial T}[(\frac{\partial U}{\partial V})_T]_V = \frac{\partial}{\partial V}[(\frac{\partial U}{\partial T})_V]_T = [\frac{\partial C_V(T,V)}{\partial V}]_T$$

$$(\frac{\partial C_V}{\partial V})_T = T\underbrace{(\frac{\partial^2 P}{\partial T^2})_V}_{ideal\ gas=0} = 0 \quad , \quad C_V(T,\cancel{V}) = C_V(T)$$

which shows **<u>heat capacity depends only on temperature.</u>**

To prove $U = U(T)$ for an ideal gas, we start by,

Because U is an exact function,

$$dU = C_V(T)dT + [-P + T\underbrace{(\frac{\partial P}{\partial T})_V}_{PV=RT}]dV$$

$$= C_V dT + [\frac{RT}{\cancel{V}} - P]dV = \underline{\underline{C_V(T)dT}}$$

which shows **<u>internal energy depends only on temperature.</u>**

(**本題可參考**：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.;
p 200/212.)

(c)

For general case,

$$dU = C_V dT + [\cancel{-P} + T(\frac{\partial P}{\partial T})_V]dV = TdS - \cancel{PdV}$$

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

$$dS = \frac{C_V}{T}dT + [\frac{1}{T}\cdot\underbrace{(\frac{\partial P}{\partial T})_V}_{PV=RT}]dV = \frac{C_V}{T}dT + \frac{R}{V}dV$$

$$S(T_2,V_2) - S(T_1,V_1) = \int_{V_1}^{V_2}\frac{R}{V}dV + \int_{T_1}^{T_2}\frac{C_V}{T}dT = \underline{\underline{C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}}}$$

(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,

$$\Delta U = \cancel{Q}_{adiabatic} + W \quad , \quad C_V(T_2 - T_1) = P_{ext}(V_1 - V_2)$$

$$\underline{\underline{T_2 = \frac{P_{ext}(V_1 - V_2)}{C_V} + T_1}}$$

(不可直接使用 $\frac{T_1}{T_2} = (\frac{V_2}{V_1})^{\gamma - 1}$，非可逆程序)

(f)

By entropy balance,

$$\Delta S = \cancel{\frac{Q}{T}}_{adiabatic} + S_{gen}$$

$$S_{gen} = \Delta S = C_V \ln[\frac{\frac{P_{ext}(V_1 - V_2)}{C_V} + T_1}{T_1}] + R \ln\frac{V_2}{V_1} = \underline{\underline{C_V \ln[\frac{P_{ext}(V_1 - V_2)}{C_V T_1} + 1] + R \ln\frac{V_2}{V_1}}}$$

Problem 4

【Solution】

(a)
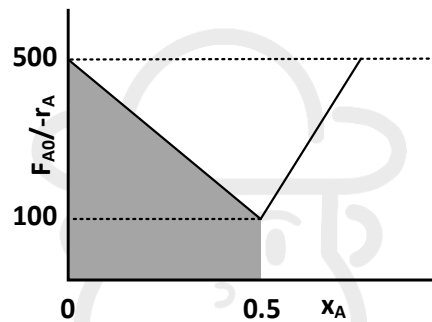
$$\varepsilon = \delta\, y_{A0} = (\frac{2-2-1}{2}) \times \frac{1}{2} = \underline{\underline{\frac{-1}{4}}}$$

(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,

$$V = \frac{(100+500)\times 0.5}{2} = \underline{\underline{150\ (dm^3)}}$$

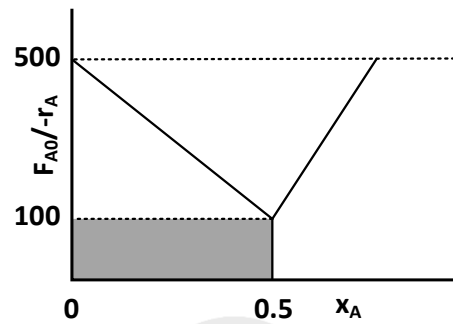**(c)**

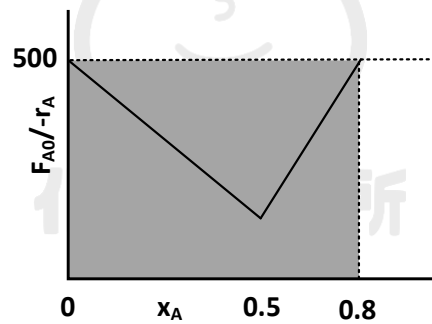By the design equation of CSTR,

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

We need to calculate the rectangular area from the figure below,

$$V = 100 \times 0.5 = \underline{\underline{50}} \ (dm^3)$$
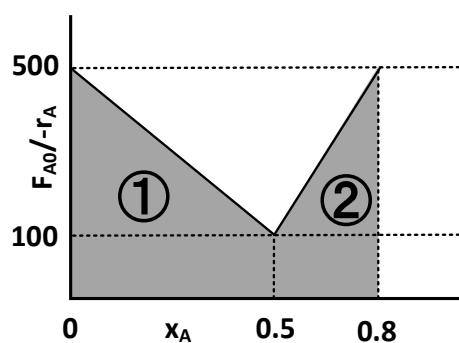
(d)

Same as problem (c), by the figure below,

$$V_{CSTR, x_A=0.8} = 500 \times 0.8 = 400 \ (dm^3)$$

$$\Delta V = 400 - 50 = \underline{\underline{350}} \ (dm^3)$$

(e)

※題目也許改為 Part (b)較為合適

Same as problem (b), by the figure below,

$$\Delta V_{PFR} = [(1)+(2)]-(1) = (2)$$

$$\Delta V_{PFR} = \frac{(100+500)\times(0.8-0.5)}{2} = \underline{\underline{90 \ (dm^3)}}$$

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,

$$-r_X = kC_X^2 = kC_{X0}^2[\frac{(1-x_X)}{(1+\varepsilon x_X)}]^2$$

Combine,

$$V = \int_0^{x_X} \frac{F_{X0}dx}{kC_{X0}^2[\frac{(1-x_X)}{(1+\varepsilon x_X)}]^2} = \int_0^{x_X} \frac{F_{X0}(1+\varepsilon x_X)^2}{kC_{X0}^2(1-x_X)^2} dx$$

$$\because \varepsilon = \frac{(1-2)}{2} \cdot y_{X0} = \frac{-1}{2} y_{X0}$$

If y_{X0} increases, the $(1+\varepsilon x_X)^2$ term would be lowered, so does the volume of PFR

<u>也就是反應物濃度越高，反應速率越快，需要的體積就小</u>

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Problem 6
【Solution】

The pressure drop rate can be calculated as,

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{T}{T_0}\frac{F_T}{F_{T0}}$$

$$\alpha = \frac{2\beta_0}{A_c \rho_{cat}(1-\phi)P_0} \quad , \quad \beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3}[\frac{150(1-\phi)\mu}{D_P}+1.75G]$$

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,

$$\frac{dP}{dz} = \frac{-G(1-\phi)}{\rho g_c D_P \phi^3}[\frac{150(1-\phi)\mu}{D_P}+1.75G] \begin{cases} \phi = bed\ porosity \\ \rho = gas\ density \\ D_P = diameter\ of\ particles \\ G = \sup erfacial\ mass\ velocity = \frac{\dot{m}}{A_c} \end{cases}$$

$$\because \rho = \frac{\rho_0 v_0}{v} = \rho_0(\frac{P}{P_0})(\frac{T_0}{T})(\frac{F_{T0}}{F_T})\ 代入:$$

$$\frac{dP}{dz} = -\underbrace{\frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3}[\frac{150(1-\phi)\mu}{D_P}+1.75G]}_{\beta_0}(\frac{P_0}{P})(\frac{T}{T_0})(\frac{F_T}{F_{T0}}) = -\beta_0(\frac{P_0}{P})(\frac{T}{T_0})(\frac{F_T}{F_{T0}})$$

From z = 0 to z = z, the total weight of catalyst is,

$$W = (1 - \phi) A_c z \rho_{cat}$$

$$dW = (1 - \phi) \rho_{cat} A_c dz \text{ 代回 } \frac{dP}{dz}$$

$$\frac{dP}{dW} = -\frac{\beta_0}{(1 - \phi) A_c \rho_{cat}} (\frac{P_0}{P})(\frac{T}{T_0})(\frac{F_T}{F_{T0}})$$

令 $y = \dfrac{P}{P_0}$ 代入：

$$\frac{dy}{dW} = -\frac{\beta_0}{(1 - \phi) A_c \rho_{cat} P_0} (\frac{1}{y})(\frac{T}{T_0})(\frac{F_T}{F_{T0}})$$

$$\underline{\underline{\frac{dy}{dW} = -\frac{\alpha}{2y} (\frac{T}{T_0})(\frac{F_T}{F_{T0}})}} \quad , \quad \alpha = \frac{2\beta_0}{A_c (1 - \phi) \rho_{cat} P_0})$$

For isothermal operation with $\varepsilon = 0$

$$\frac{dy}{dW} = -\frac{\alpha}{2y} \quad , \quad y = (1 - \alpha W)^{1/2} = \frac{P}{P_0}$$

(本題可參考：FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 177~181)

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Part I. Short-Answer Questions
【Solution】

(1)

The gas-hourly space velocity (GHSV) is the space velocity of gas reported at **standard temperature and pressure**, that is,

$$GHSV = \frac{v_0|_{STP}}{V}$$

※類似定義的還有 **liquid-hourly space velocity**，為液體進料於 60℉或 75℉下所測量之 **space velocity**：

$$LHSV = \frac{v_0|_{liquid}}{V}$$

與 **space velocity** 相對的參數為 **space time**，定義為：

$$\tau = \frac{V}{v_0}$$

(本題可參考：**FOGLER, H.** *Elements of Chemical Reaction Engineering*, **4th ed.; p 68**)

(2)

The turnover frequency (TOF) is **the number of molecules reacting per active site per second at the conditions of the experiment.**

※另一個用於觸媒反應的類似參數為 **turnover number** k_{act}，為當所有觸媒皆充滿反應物時，單個觸媒反應位在單位時間內可以轉化多少反應物(**the number of substrate molecules converted to product in a given time on a single-enzyme molecule when the enzyme is saturated with substrate.**)

(本題可參考：**FOGLER, H.** *Elements of Chemical Reaction Engineering*, **4th ed.;**

p 399~400/651~652)

(3)

The rate-limiting step is the critical reaction within a series of reactions, dictating the overall reaction rate.

(4)

The parallel reactions are reactions where the reactant is consumed by different reaction pathways to form different products, which can be illustrated as,

$$A \overset{B}{\underset{C}{\diagdown}}$$
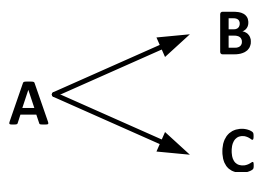
(5)

$$W = \frac{F_{A0} X_A}{-r_A}$$

(6) False

$$W = \frac{F_{A0} X_A}{-r_A}$$

(7) False

For a steam-water mixture, the *mass fraction of the steam* is termed as the quality, that is,

$$quality = \frac{mass \ of \ steam}{total \ mass \ of \ the \ mixture}$$

(8) True

For a reversible Carnot cycle, the efficiency is derived as,

$$\eta = 1 - \frac{T_c}{T_h} < 100\%$$

(9)

Joule-Thomson process refers to an **adiabatic** and **isenthalpic** process.

(10) False

By the definition of fugacity,

$$d\underline{G} = RTd(\ln f)$$

it can be considered the measure of **the molar Gibbs energy of a real fluid**.

Fugacity coefficient is a measure of **the difference** between the real and ideal gas

Gibbs energies,

$$\phi = \frac{f}{P} = \exp[\frac{\underline{G} - \underline{G}^{IG}}{RT}]$$

※fugacity 在定義上，可以視為一個真實流體(real fluid)，包含氣體、液體、甚至固體的 molar

Gibbs energy 的度量(由上式可知)，而 fugacity coefficient 則可以視為真實流體與理想氣體(氣體

為一種流體)的差異。因此與題目所指的情況剛好相反，所以選 False。

(11)

From the criteria of a stable equilibrium, we need,

$$(\frac{\partial P}{\partial V})_T < 0$$

If we follow the isotherm T_3, from V_3 to V_2 ((1) to (2)),
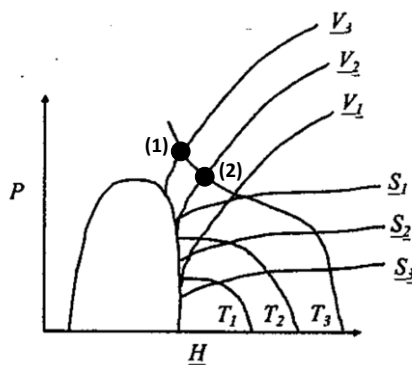
$$\Delta V = V_2 - V_3 < 0 \text{，} \Delta P = P_2 - P_3 < 0$$

$(\frac{\partial P}{\partial V})_T > 0$, which is not consistent with the requirements for a stable equilibrium.

※在 Sandler 原文書中，對於一個熱力學系統的穩定標準，有主要兩個形式：

(1) $C_V > 0$ (first or thermal stability criterion)

(2) $(\frac{\partial P}{\partial V})_T < 0$ (second or mechanical stability criterion)

皆是由一連串不太好做的數學得出，然而第二點可根據一般的 P-V diagram 的相平衡區幫助記憶，也就是在相平衡區時，P-V 曲線在虛線區域的斜率>0，在真實世界並不存在，因此才引申為兩端各代表液氣相，且兩相平衡的概念。
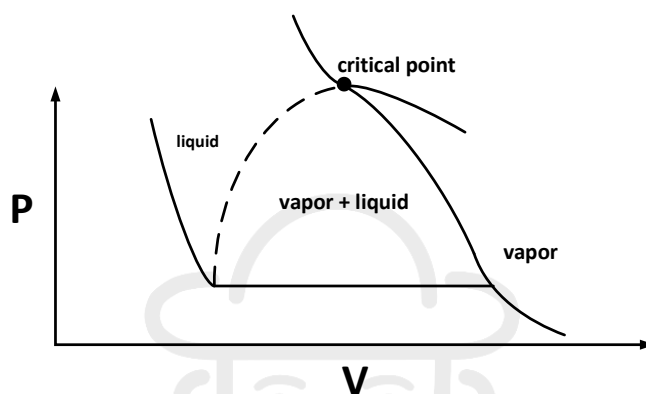
(本題改編自：Sandler, S. *Chemical, Biochemical and Engineering Thermodynamics*, 5th ed.; p 352, Problem 7.68.

關於 first 與 second stability criterion 的推導，可參考同本書之 p 293~297；關於 PV 相圖的討論，可參考 p 300~p 302。)

Part II. Short-Answer Questions

【Solution】

12.

According to the ***uncompetitive-inhibition*** reaction mechanism, we have,

$$-r_s = k_1[E][S] - k_2[E \cdot S]$$

Assume PSSH,

$$r_{E \cdot S} = k_1[E][S] - k_2[E \cdot S] - k_3[E \cdot S] - k_4[I][E \cdot S] + k_5[I \cdot E \cdot S] = 0$$

$$r_{I \cdot E \cdot S} = k_4[E \cdot S][I] - k_5[I \cdot E \cdot S] = 0$$

Add the two equations together, we have,

$$[E \cdot S] = \frac{k_1[E][S]}{k_2 + k_3}$$

$$[I \cdot E \cdot S] = \frac{k_4}{k_5}[E \cdot S][I] = \frac{k_1 k_4[E][S][I]}{k_5(k_2 + k_3)}$$

By enzyme balance,

$$[E_t] = [E] + [E \cdot S] + [I \cdot E \cdot S] = [E][1 + \frac{k_1[S]}{k_2 + k_3} + \frac{k_1 k_4[S][I]}{k_5(k_2 + k_3)}]$$

$$[E] = \frac{[E_t]}{[1 + \frac{k_1[S]}{k_2 + k_3} + \frac{k_1 k_4[S][I]}{k_5(k_2 + k_3)}]}$$

代回：

$$-r_s = k_1[E][S] - k_2[E \cdot S] = k_1[E][S] - \frac{k_1 k_2[E][S]}{k_2 + k_3} = [E](k_1[S] - \frac{k_1 k_2[S]}{k_2 + k_3}) = k_1[E](\frac{k_3[S]}{k_2 + k_3})$$

$$-r_s = k_1[E](\frac{k_3[S]}{k_2 + k_3}) = \frac{k_1 k_3[E_t][S]}{[k_2 + k_3 + k_1[S] + \frac{k_1 k_4[S][I]}{k_5}]}$$

同除 k_1

$$-r_s = \frac{k_3[E_t][S]}{[\frac{k_2 + k_3}{k_1} + [S] + \frac{k_4[S][I]}{k_5}]}$$

定義

$$V_{\max} = k_3[E_t]、\quad K_M = \dfrac{k_2 + k_3}{k_1}、\quad K_I = \dfrac{k_5}{k_4}$$

$$-r_s = \dfrac{V_{\max}[S]}{[K_M + [S](1 + \dfrac{[I]}{K_I})]}$$

變更為 Lineweaver-Burk plot 的形式：

$$\dfrac{1}{-r_s} = \dfrac{1}{[S]}\dfrac{K_M}{V_{\max}} + \dfrac{1}{V_{\max}}(1 + \dfrac{[I]}{K_I})$$

(本題可參考：**FOGLER, H.** *Elements of Chemical Reaction Engineering*, **4th ed.; p 412~413**)

13.

(1) 根據題目附圖關係：

① 反應速率與 A 呈線性關係，$-r_A \propto P_A$

② 反應速率與 B 呈現先線性後無關關係，$-r_A \propto \dfrac{P_B}{1 + K_B P_B + ...}$

③ 反應速率與 C 呈現反比關係，$-r_A \propto \dfrac{1}{1 + K_C P_C + ...}$

④ 反應速率與 D 無關，綜合以上：

$$-r_A = \dfrac{k P_A P_B}{1 + K_B P_B + K_C P_C}$$

(2)

根據上題結論，可知：

①A 出現在速率決定步驟上，但無吸附於觸媒上

②B 出現於速率決定步驟上，且有吸附於觸媒上 (在分母)

③ 速率決定步驟為單向，因此 C 無出現在分子，但有吸附於觸媒上

④D 無吸附於觸媒上

因有反應物不吸附於觸媒上就可反應，因此應為 **Eley-Rideal 反應機制**。

(本題可參考：**FOGLER, H.** *Elements of Chemical Reaction Engineering*, **4th ed.; p 666~668**)

(3)

Yes, the reactant A and product C compete each other for the catalytic surface.

14.

(1)

For one CSTR with optimal space time that maximizing the concentration of B,

by the design of CSTR,

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

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

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

To determine the optimal space time,

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

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

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

Put $k_1 = 0.4$ and $k_2 = 0.1$ into the relation,

$$\tau = \frac{1}{\sqrt{k_1 k_2}} = \frac{1}{\sqrt{0.4 \times 0.1}} = \frac{6}{v_0} \quad , \quad \underline{\underline{v_0 = 1.2 \ (L/\min)}}$$

15.

(1)

By energy balance for the tank and its content (steady state),

$$\Delta H + \underbrace{\frac{\Delta v^2}{2g_c} + \frac{g}{g_c}\Delta z}_{negligible} = \cancel{Q} + \cancel{W}$$

$$\Delta H = \dot{M}_{out}H_{out} - \dot{M}_{in,1}H_{in,1} - \dot{M}_{in,2}H_{in,2} = 0$$

$$10 \times \cancel{C_P}T_{out} - 5 \times \cancel{C_P}T_{in,1} - 5 \times \cancel{C_P}T_{in,2} = 0$$

$$T_{out} = \frac{5(T_{in,1} + T_{in,2})}{10} = \frac{50 + 80}{2} = \underline{\underline{65}} \ (^\circ C)$$

(2)

By energy balance for the tank and its content (unsteady state),

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

$$H_{in,1}\frac{dM_{in,1}}{dt} + H_{in,2}\frac{dM_{in,2}}{dt} - H_{out}\frac{dM_{out}}{dt} = \frac{d}{dt}[M(\underline{U})]_{sys} = M_{sys}\frac{dU_{sys}}{dt}$$

$$5\cancel{C_P}T_{in,1} + 5\cancel{C_P}T_{in,2} - 10\cancel{C_P}T_{out} = 50\cancel{C_V}\frac{dT_{out}}{dt}$$

$$5(50 + 80) - 10T_{out} = 50\frac{dT_{out}}{dt}$$

$$T_{out} = Ae^{-\frac{10t}{50}} + C \begin{cases} T = 0, \ T_{out} = 25 \\ T \to \infty, \ T_{out} = 65 \end{cases}, \quad \begin{cases} A = -40 \\ C = 65 \end{cases}$$

$$\boxed{T_{tank} = T_{out} = -40e^{-\frac{t}{5}} + 65}$$

16.

Consider the heating process, by energy balance, we have,

$$\Delta U = Q - W = Q - P\Delta V = NC_V(T_2 - T_1)$$

For the number of gases being lifted,

$$N = \frac{PV}{RT} = \frac{(1.013\times10^5 + \dfrac{4000\times9.8}{2.5})\times25}{8.314\times(273.15+20)} = 1200\ mole$$

For the temperature after lifted,

$$N = 1200 = \frac{PV_2}{R(T_2 + 273.15)} = \frac{(1.013\times10^5 + \dfrac{4000\times9.8}{2.5})\times(25 + 2.5\times3)}{8.314\times(T_2 + 273.15)}$$

$$\boxed{T_2 = 107.9\ (°C)}$$

代回：

$$Q - P\Delta V = NC_V(T_2 - T_1)$$

$$1200\times(30 - 8.314)(107.9 - 20) = Q - (1.013\times10^5 + \frac{4000\times9.8}{2.5})\times(2.5\times3)$$

$$\boxed{Q = 3.16\times10^6\ (J)}$$

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

p 95, Problem 3.20.)

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True or False Questions

(1) <u>False</u>

For zero-order reaction, the rate law is,

$$rate = k$$

which is independent of concentration but **<u>dependent on temperature</u>** according to

Arrhenius law.

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

(2) <u>True</u>

True, the selectivity between the two reactions is,

$$S_{DU} = \frac{r_D}{r_U}$$

(3) <u>False</u>

The entropy of an ***<u>isolated</u>*** system is always maximized at equilibrium.

$$\Delta S_{isolated} = \cancel{\frac{Q}{T}}_{isolated} + S_{gen} \geq 0$$

(4) <u>True</u>

(5) <u>True</u>

According to the Kelvin-Planck statement of the second law of thermodynamics, it is impossible to construct a device that **<u>operates *cyclically* and converts heat completely into work *without other effects*.</u>** However, the reverse process is possible.

Short Answer Questions

(6)

When choosing the appropriate gas phase reaction catalyst, several factors could be considered:

(1) Catalyst particle size: For example, if the catalyst particles are small, they provide a high surface area-to-volume ratio, which can enhance reaction efficiency. However, this may also lead to a significant pressure drop, which is undesirable for gas-phase reactions.

(2) Adsorption properties: The catalyst should effectively adsorb reactant gases to enhance gas-solid interface catalysis and improve reaction efficiency. Ideally, it should exhibit minimal adsorption of toxic substances, as their accumulation on the catalyst surface can lead to deactivation and reduced performance.

(3) Selectivity: High selectivity toward the desired reaction is essential to minimize unwanted side reactions, which could generate byproducts requiring complex and energy-intensive separation processes. A well-optimized catalyst ensures maximum product yield while maintaining efficiency in industrial applications.

(7)

Deactivation refers to the decline in a catalyst's activity over time, which may be caused by:

(1) **Aging**: Gradual changes in pore structure or crystal structure over time.

(2) **Poisoning**: The irreversible deposition of a substance on the active site, preventing catalytic activity.

(3) **Coking**: The accumulation of carbonaceous or other materials on the entire surface.

(本小題可參考：**FOGLER, H.** *Elements of Chemical Reaction Engineering*, **4th ed.; p 650.**)

(8)

這邊所討論的 residence time distribution (RTD)是考慮反應物在不同反應器中，其每個部份會因為在不同反應器中的流動情況不同，而有不同的出料時間。可以想像成若是在一個有一定阻力，會在反應器內產生明顯速度分布的流動情況下，速度快的部分會先出來反應器，而在反應器出口部份會先測定到一部分濃度，再根據不同速度所佔的部份的濃度測定到出口濃度相對應的變化。

一種典型的實驗為在反應器進口<u>瞬間注入</u>一小段進料(impulse)來觀察反應器出口濃度的情況：

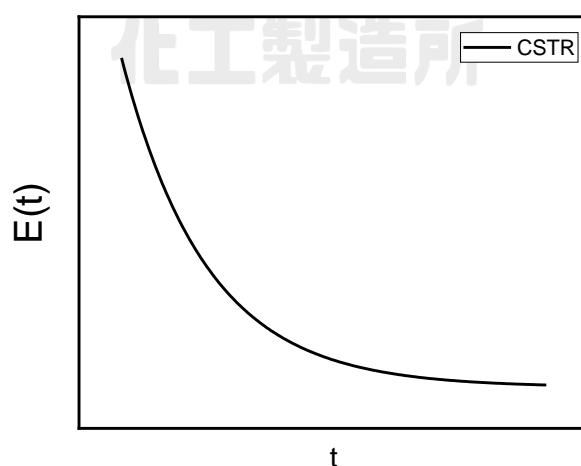**(1) CSTR**：理想 **CSTR** 為完美攪拌的情況，因此根據其反應器特性，假設注入濃度後，其反應器內的濃度可由質量平衡方式推導，亦即：

$$0 - vC = V\frac{dC}{dt}$$

整理後積分：

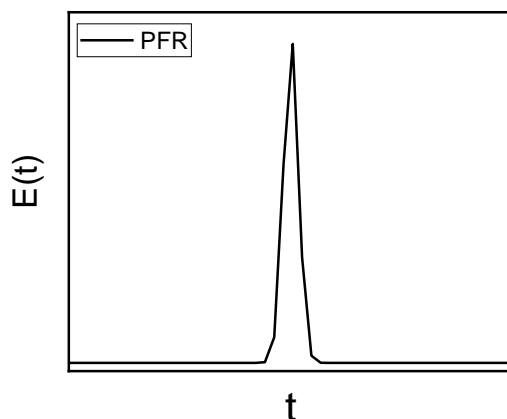$$-\int_0^t \frac{v}{V}dt = \int_{C_0}^C \frac{dC}{C} \ , \ C = C_0 e^{-\frac{v}{V}t} = C_0 e^{-\frac{t}{\tau}}$$

定義 E(t)為在時間為 t 時出來的瞬間濃度與總體濃度的比例，因此：

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} = \frac{C_0 e^{-\frac{t}{\tau}}}{\int_0^\infty C_0 e^{-\frac{t}{\tau}}dt} = \frac{e^{-\frac{t}{\tau}}}{\tau}$$

此即為 **CSTR** 的 **residence time distribution**

(2) PFR：理想 PFR 為 plug flow，沒有速度差，因此原先濃度怎麼進入，濃度就怎麼出來，其出

口端測定到的濃度-時間關係大概為

(※基本上遵照 delta function 的形狀。)

本題因牽涉到非理想反應器相關的概念，大部分大學部課程可能很少談到，因此在此只簡單整

理一些重點，實際的理論推導與概念請參考原文書：

(1) FOGLER, H. *Elements of Chemical Reaction Engineering*, 4th ed.; p 867~888.

(2) Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; p 257~266.

(9)

在半批式反應器 (semi-batch reactor)中進行高度放熱反應時，與一次性加入所有

反應物的批式反應器 (batch reactor) 相比，透過逐步加入反應物，半批式反應器

能夠維持較低且穩定的反應物濃度，避免因濃度過高導致反應速率過快，進而產

生熱量移除困難的問題，有助於防止熱失控 (thermal runaway)，提升反應的安全

性。

(10)

此系統**並非平衡**。因一般多相平衡來說，其標準為：

$$\mu_i^\alpha(T, P, x_{i,\alpha}) = \mu_i^\beta(T, P, x_{i,\beta})$$

若系統已達成相平衡，則在**同溫壓下，各相的組成應不會改變**。假設此時總組成改變，此時會改變的應該是 α 與 β 相的相對比例(即 lever rule)。

Calculation and Derivation Questions

(11)

By the design equation of isothermal batch reactor ($V \neq constant$):

$$-\frac{dN_A}{dt} = (-r_A)V \quad , \quad N_{A0}\frac{dx_A}{dt} = (-r_A)V_0(1+\varepsilon x_A)$$

$$C_{A0}\frac{dx_A}{dt} = (-r_A)(1+\varepsilon x_A)$$

For the rate equation,

$$-r_A = kC_A^2 = \frac{kC_{A0}^2(1-x_A)^2}{(1+\varepsilon x_A)^2}$$

Combine,

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

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

$$-r_A = kC_A^2 = \frac{kC_{A0}^2(1-x_A)^2}{(1+0.5x_A)^2}$$

For the target conversion, we have,

$$C_A = \frac{C_{A0}(1-x_A)}{(1-0.5x_A)} \quad , \quad 0.2 = \frac{1.0\times(1-x_A)}{(1-0.5x_A)} \quad , \quad x_A = 0.889$$

$$t = \int_0^{0.889} \frac{(1-0.5x_A)}{0.05\times 1.0\times(1-x_A)^2}\, dx_A = \underline{\underline{102.07 \text{ (min)}}}$$

(12)

For CSTR, the design equation is,

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

The rate law is,

$$-r_A = (k_1 + k_2)C_A = (k_1 + k_2)C_{A0}(1 - x_A)$$

Combine,

$$V = \frac{F_{A0} x_A}{(k_1 + k_2)C_{A0}(1 - x_A)} = \frac{1 \times 0.8}{(0.5 + 0.2) \times 2 \times (1 - 0.8)} = \underline{\underline{2.86\ (L)}}$$

The selectivity of B to C is,

$$S_{B/C} = \frac{k_1}{k_2} = \frac{0.5}{0.2} = \underline{\underline{2.5}}$$

(13)

※這裡的 performance equation 為 Levenspiel 原文書的稱呼，即為 design equation。本題因為配分比較重，因此推薦要先從 CSTR 的莫爾平衡推導出 design equation，再將反應速率結合，本解答會略過這段，直接挑重點寫。

By the design equation of CSTR,

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

By the rate law,

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

代回：

$$V = \frac{F_{A0} X}{kC_{A0}^2 (1 - X)^2} \quad, \quad \tau = \frac{X}{kC_{A0}(1 - X)^2}$$

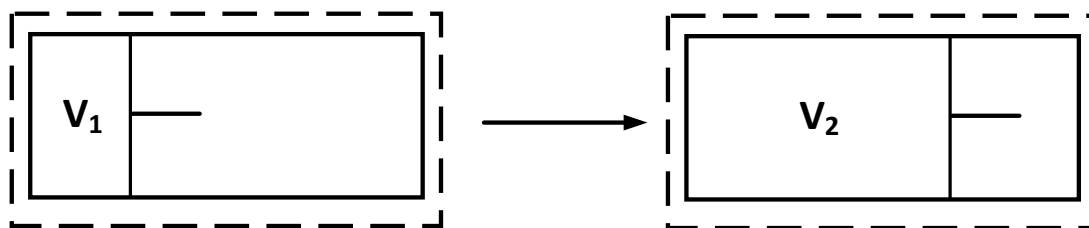$$kC_{A0}\tau(1 - X)^2 - X = 0 \quad, \quad kC_{A0}\tau X^2 - (2kC_{A0}\tau + 1)X + 1 = 0$$

$$\boxed{X = \frac{(2kC_{A0}\tau + 1) \pm \sqrt{(2kC_{A0}\tau + 1)^2 - 4kC_{A0}\tau}}{2kC_{A0}\tau} = \frac{(2kC_{A0}\tau + 1) - \sqrt{(2kC_{A0}\tau + 1)^2 - 4kC_{A0}\tau}}{2kC_{A0}\tau}}$$

(※取正會使轉化率>1，因此取負)

(14)

(1)

假設整個(容器+氣體)視為一個系統(虛線)，則根據第一定律：

$$\Delta U = \cancel{Q} + \cancel{W} = 0$$

對於理想氣體來說，其內能只與溫度有關，因此：

$$\Delta U \propto \Delta T = 0 \text{，} \underline{T = 300 \ (K)}$$

(2)

假設整個(容器+氣體)視為一個系統(虛線)，則根據第一定律：

$$\Delta U = \cancel{Q} + \cancel{W} = 0$$

對於凡德瓦氣體：

$$d\cancel{U} = C_V dT + [T(\frac{\partial P}{dT})_{V_m} - P]dV_m$$

For $T(\frac{\partial P}{dT})_V - P$

$$T(\frac{\partial P}{dT})_{V_m} - P = T(\frac{R}{V_m - b}) - (\frac{RT}{V_m - b} - \frac{a}{V_m^2}) = \frac{a}{V_m^2}$$

代回：

$$0 = C_V dT + [T(\frac{\partial P}{dT})_{V_m} - P]dV_m = C_V dT + \frac{a}{V_m^2}dV_m$$

$$C_V dT + \frac{a}{V_m^2}dV_m = \int_{300}^{T} 12.47 \times dT + \int_{2.8 \times 10^{-3}}^{2.8 \times 10^{-3}} \frac{a}{V_m^2}dV_m = 12.47(T - 300) + 0.2355(\frac{1}{2.8} - \frac{1}{24}) \times 1000 = 0$$

$$\underline{\underline{T = 294.04 \ (K)}}$$

(15)

(1)

Assume:

[1] The liquid solution contains mostly component B, so the liquid phase can be treated as ideal solution.

[2] Due to the low pressure, the gas phase can be treated as ideal gas mixture.

Therefore, **assume Henry's law and Raoult's law can be applied to component A and B, respectively**.

For A:

$$Py_A = H_A x_A \text{ , } 1 \times y_A = 300 x_A$$

For B:

$$Py_B = P_B^* x_B \text{ , } 1 \times y_B = 0.1 x_B$$

二式相加：

$$1 = 300 x_A + 0.1 x_B = 300 x_A + 0.1(1 - x_A) \text{ , } \underline{x_A = 0.003}$$

因在此假設下，A 的莫耳分率非常小，與題意相符，因此上述假設合理。

(2)

代回 A 的關係式：

$$y_A = 300 x_A = 300 \times 0.003 = \underline{0.9}$$

【驗證】

按此結論下，$x_B = 1 - 0.003 = 0.997$ ，$y_B = 0.1$

$$1 \times 0.1 \approx 0.1 \times 0.997 \text{ ，假設也算合理。}$$