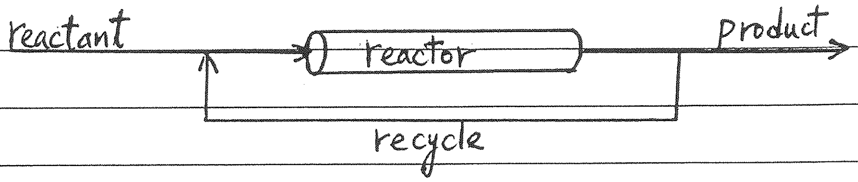
4.8 Recycle Reactors

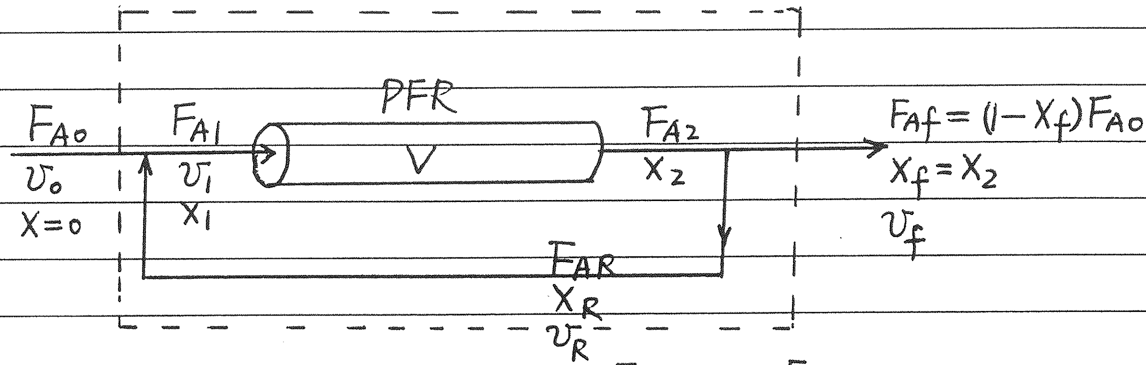


recycle 的目的

1. $A + R \longrightarrow R + R$ autocatalytic rxn

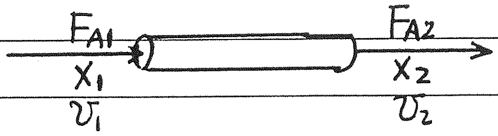
   於發酵反應中，recycle 一些 products（微生物）以促進反應

2. 利用生成物的廢熱 保持反應溫度



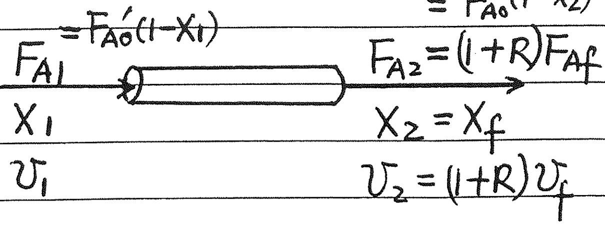
$$\text{Recycle Ratio } R = \frac{v_R}{v_f} = \frac{F_{AR}}{F_{Af}} = \frac{F_{BR}}{F_{Bf}} = \cdots\cdots$$

一般 PFR 之 design eq.



$$V = F_{A0}\int_{X_1}^{X_2}\frac{dX}{-r_A}$$

the PFR in the recycle system

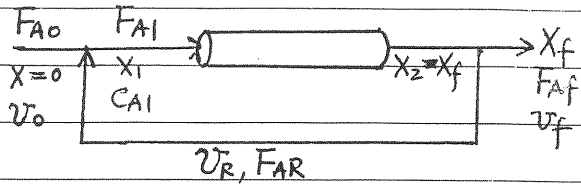


$$V = F'_{A0}\int_{X_1}^{X_2}\frac{dX}{-r_A}$$

$$\because F_{A2} = \underbrace{(1+R)F_{A0}}_{F'_{A0}}(1-X_2) \Longrightarrow F'_{A0} = (1+R)F_{A0}$$

∘ design equation of recycle reactor

$$\frac{V}{F_{A0}} = (1+R)\int_{X_1}^{X_f} \frac{dX}{-r_A}$$



$$\because C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{A0}+RF_{Af}}{v_0+Rv_f}$$

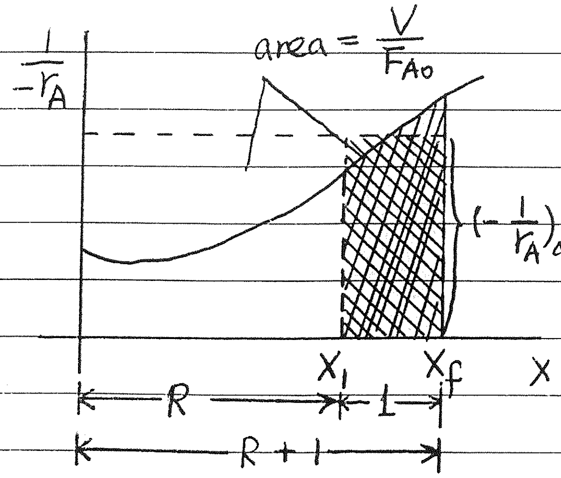
$$= \frac{F_{A0}+RF_{A0}(1-X_f)}{v_0+Rv_0(1+\varepsilon X_f)}$$

$$= C_{A0}\,\frac{1+R-RX_f}{1+R+\varepsilon R X_f}$$

$$= C_{A0}\,\frac{1-\frac{R}{1+R}X_f}{1+\varepsilon\frac{R}{1+R}X_f}$$

but $C_{A1} = C_{A0}\,\dfrac{1-X_1}{1+\varepsilon X_1}$

by comparison $\quad X_1 = \dfrac{R}{1+R}X_f \quad$ or $\quad \dfrac{X_1}{X_f-X_1} = \dfrac{R}{1}$

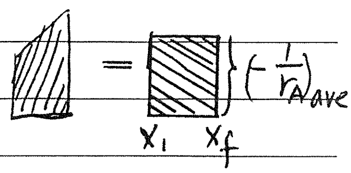


$$\frac{V}{F_{A0}} = (1+R)\int_{X_1}^{X_f}\frac{dX}{-r_A}$$

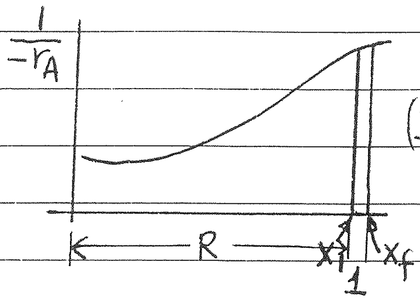
$$= (1+R)(X_f-X_1)\,\frac{\int_{X_1}^{X_f}\frac{dX}{-r_A}}{(X_f-X_1)}$$

$$= (1+R)(X_f-X_1)\left(\frac{1}{-r_A}\right)_{ave}$$

$$= X_f\cdot\left(\frac{1}{-r_A}\right)_{ave}$$



if $R \longrightarrow \infty$



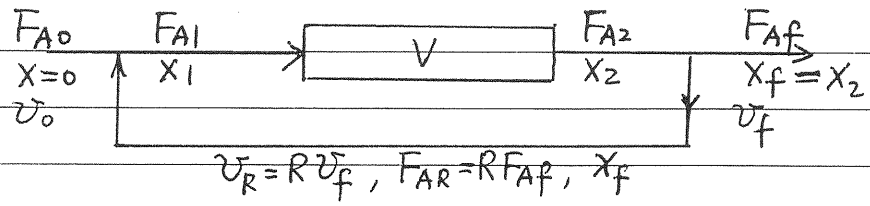
$$\left(\frac{1}{-r_A}\right)_{ave} \approx \frac{1}{-r_{Af}}$$

$$\therefore \quad \frac{V}{F_{A0}} = (1+R)(X_f - X_1)\cdot\frac{1}{(-r_A)_f}$$

$$= \frac{X_f}{(-r_A)_f} \qquad \text{CSTR 之 design eq.}$$

Summary :

Recycle Reactor



$$\frac{V}{F_{A0}} = (1+R)\int_{\frac{R}{1+R}X_f}^{X_f} \frac{dX}{-r_A}$$

$\Longrightarrow$ $R = 0$: $$\frac{V}{F_{A0}} = \int_0^{X_f} \frac{dX}{-r_A} \qquad \text{PFR}$$

$\Longrightarrow$ $R = \infty$: $$\frac{V}{F_{A0}} = \frac{X_f}{(-r_A)_f} \qquad \text{CSTR}$$

一 elementary reaction A + R ---> R + R, rate constant k = 1 liter / (mol min)。我們將以不同的反應器進行實驗。在各個實驗中，進料之體積流率均爲 1 liter/min，且含99% A和1% R，而出口產物含 10% A和90% R。由於反應過程中總莫耳數不變，所以保持總濃度 $C_0 = C_{A0} + C_{R0} = C_A + C_R = 1$ mol/liter。

a) 試求出反應速率之最高值以及當 時之 C_A，並以 $1/(-r_A)$ 爲縱軸，C_A 爲橫軸，簡略繪出關係圖。(5%)

b) 若反應於 PFR 內進行，求其反應器體積。 (5%) [Hint: $\frac{V}{v_0} = -\int_{C_{Ai}}^{C_{Af}} \frac{dC_A}{-r_A}$ for PFR]

c) 若反應於 CSTR 內進行，求其反應器體積。 (5%)

d) 若可併用 PFR 和 CSTR，但不使用 Recycle 和 Separator，試以 a) 之關係圖描述最佳操作系統，並求出此系統之反應器總體積。 (8%)

e) 若使用 Recycle Reactor，且 Recycle Ratio R = 0.5。求進入反應器前之 C_{A1} 值，以及反應器體積。 (7%)

$$A + R \xrightarrow{k} R + R$$

$$-r_A = k C_A C_R = \left[1 \frac{l}{mol \cdot min}\right] \cdot C_A C_R$$

$$C_{A0} + C_{R0} = C_A + C_R = 1 \ mol/l$$

$v_0 = 1 \frac{l}{min}$ → Reactor →

$C_{Ai} = 0.99 \frac{mol}{l}$ $\qquad$ $C_{Af} = 0.1$

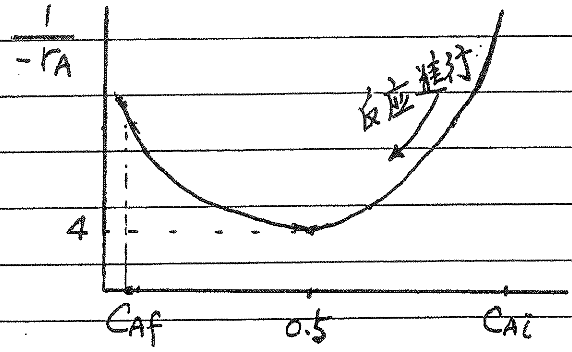
$C_{Ri} = 0.01 \frac{mol}{l}$ $\qquad$ $C_{Rf} = 0.9$

a) $-r_A = k C_A C_R = k C_A (1 - C_A)$

At maximum $-r_A$

$$\frac{d(-r_A)}{d C_A} \overset{set}{=} 0 = k - 2k C_A \Longrightarrow C_A^* = 0.5, \quad -r_{A,max} = 1 \times 0.5 \times 0.5 = 0.25$$

$\therefore$ At $C_A = 0.5 \frac{mol}{l}$, $-r_A = -r_{A,max} = 0.25 \frac{mol}{l \cdot min}$ ※



b)

$$\frac{V_p}{v_0} = -\int_{C_{Ai}}^{C_{Af}} \frac{dC_A}{-r_A} = \int_{C_{Af}}^{C_{Ai}} \frac{dC_A}{-r_A}$$

$$= \int_{0.1}^{0.99} \frac{dC_A}{C_A(1-C_A)}$$

$$= \left[\int_{0.1}^{0.99} \frac{dC_A}{C_A} + \int_{0.1}^{0.99} \frac{dC_A}{1-C_A}\right]$$

$$= \ln \frac{0.99}{0.1} + \ln \frac{0.9}{0.01} = 6.8$$

$\therefore V_p = 6.8 \times v_0 = 6.8$ liters ※

c)

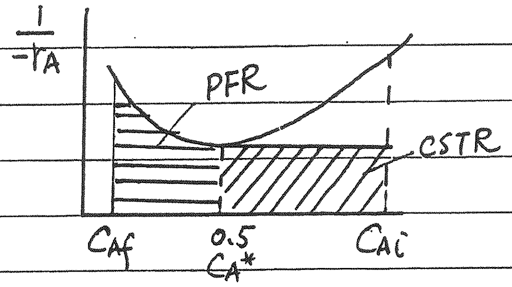
$$\frac{V_m}{v_0} = \frac{C_{Ai} - C_{Af}}{-r_{Af}}$$

$$= (0.99 - 0.1) \cdot \frac{1}{(0.1)(1-0.1)}$$

$$= 9.9 \text{ min}$$

$\therefore V = 9.9 \times v_0 = 9.9$ liters

d) minimum-size setup without recycle



$$\frac{V_m}{v_0} + \frac{V_p}{v_0} = \frac{C_{Ai} - C_A^*}{-r_{A,max}} + \int_{C_A^*}^{C_{Af}} \frac{-dC_A}{-r_A}$$

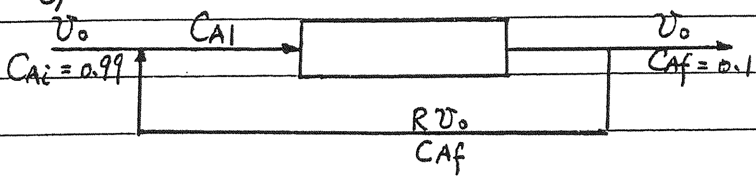
$$= \frac{0.99 - 0.5}{0.25} + \int_{0.1}^{0.5} \frac{dC_A}{C_A(1-C_A)}$$

$$= 1.96 + \left[\ln\frac{0.5}{0.1} + \ln\frac{0.9}{0.5}\right]$$

$$= 4.2$$

$\therefore V_m + V_p = v_0 \cdot 4.2$
$= 4.2$ liters ※

e)



$$C_{A1} = \frac{C_{Ai} v_0 + C_{Af} \cdot R v_0}{(1+R) v_0}$$

$$= \frac{C_{Ai} + R C_{Af}}{1+R}$$

$$= \frac{0.99 + (0.5)(0.1)}{1+0.5}$$

$$= 0.693 \ \frac{mol}{l}$$

※

$$\frac{V}{v_0} = (1+R)\int_{C_{A1}}^{C_{Af}} \frac{-dC_A}{-r_A} = (1+R)\int_{C_{Af}}^{C_{A1}} \frac{dC_A}{C_A(1-C_A)}$$

$$= (1+R)\int_{0.1}^{0.693} \frac{dC_A}{C_A(1-C_A)}$$

$$= (1.5)\left[\ln\frac{0.693}{0.1} + \ln\frac{0.9}{0.307}\right]$$

$$= 4.5$$

$\therefore V = 4.5 \times v_0 = 4.5$ liters ※

c. Polynomial Fit

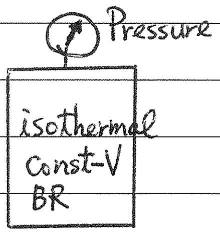
C_A vs. time $\xrightarrow{PC}$ $C_A = \underbrace{a_0 + a_1 t + a_2 t^2 + \cdots + a_n t^n}_{\text{order 的選定很重要}}$

$$\therefore \frac{dC_A}{dt} = a_1 + 2a_2 t + 3a_3 t^2 + \cdots + n a_n t^{n-1}$$

Ex. 5-1

gas-phase decomposition of di-tert-butyl peroxide

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow C_2H_6 + 2\ CH_3COCH_3$$



pure A initially

time (min)	total pressure (mmHg)
0	7.5
2.5	10.5
5.0	12.5
10.0	15.8
15.0	17.9
20.0	19.4

find rate law $-r_A = k\,C_A^{\alpha}$

Sol.

Const-V BR $\Longrightarrow$ $C_A = C_{A0}(1-X)$

$$= \frac{N_{A0}}{V}(1-X)$$

$$= \frac{P_0 y_{A0}}{RT}(1-X) = \frac{P_0}{RT}(1-X)$$

need X in terms of P

$$N = N_0(1+\varepsilon X) = N_0(1+y_{A0}\delta X) \quad (\delta = 1+2-1 = 2)$$

$$= N_0(1+2X)$$

$$\Rightarrow \frac{PV}{RT} = \frac{P_0 V}{RT}(1+2X)$$

$$\Rightarrow P = P_0(1+2X)$$

$$\Rightarrow X = \frac{1}{2}\left(\frac{P}{P_0}-1\right)$$

$$\therefore C_A = \frac{P_0}{RT}\left[1-\frac{1}{2}\left(\frac{P}{P_0}-1\right)\right] = \frac{3P_0-P}{2RT}$$ 代入 rate law

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

$$\Rightarrow \frac{1}{2RT}\frac{dP}{dt} = k\left(\frac{3P_0-P}{2RT}\right)^{\alpha}$$

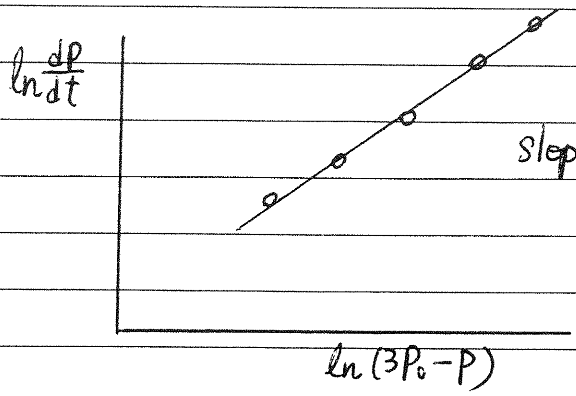
$$\Rightarrow \frac{dP}{dt} = k'(3P_0-P)^{\alpha}$$ 其中 $k' = k(2RT)^{1-\alpha}$

$$\Rightarrow \ln\frac{dP}{dt} = \alpha\ln(3P_0-P) + \ln k'$$

plot $\ln\frac{dP}{dt}$ vs. $\ln(3P_0-P)$

dP/dt 的求法有 { graphical, numerical, Polynomial

詳見課本



slope $= \alpha = 1$

$$k' = k(2RT)^{1-\alpha} = k$$

$$\therefore -r_A = k C_A$$

而 $k = k' = \dfrac{(dP/dt)_p}{(3P_0 - P)_p}$ 在 linear fit 上任取一點

$(3P_0 - P) = 5$ mmHg

$(dP/dt) = 0.4$ mmHg/min

$$\therefore k = \frac{0.4 \text{ mmHg/min}}{5 \text{ mmHg}} = 0.08 \text{ min}^{-1}$$

the rate law is :

$$-r_A = \frac{0.08}{\text{min}} \cdot C_A$$

Ex 5-2 :

Use the integral method to firm that the rxn order for the di-tert-butyl peroxide decomposition in Ex 5-1 is first order

Sol.

in Ex 5-1

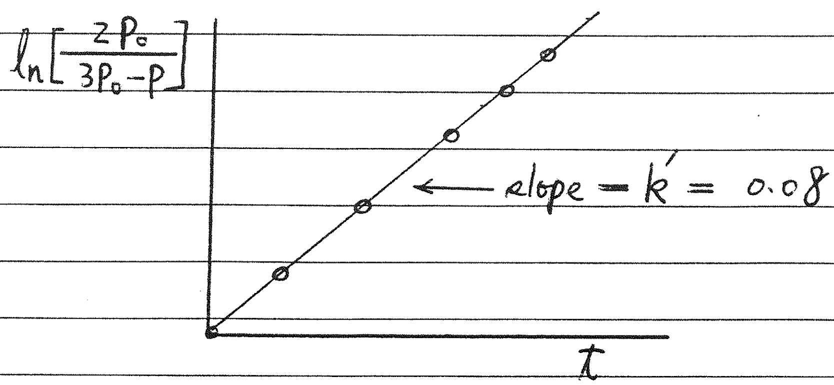
$$\frac{dP}{dt} = k'(3P_0 - P)^{\alpha}$$ from mole balance for a const-V batch reactor

for $\alpha = 1$

$$\frac{dP}{dt} = k'(3P_0 - P) \qquad P = P_0 \text{ at } t = 0$$

$$\xrightarrow{\text{integ.}} \ln\frac{2P_0}{3P_0 - P} = k't$$

t (min)	P (mmHg)	$\ln[2P_0/(3P_0-P)]$
0	7.5	⋮
⋮	⋮	⋮



的確是 linear plot, 可確認為 first order rxn.