Chapter 4　Ideal Reactors for a Single Reaction

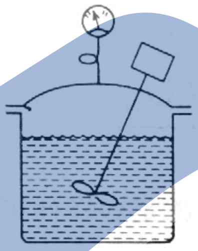
(本章為課本的第四章與第五章)

§4-1.前言

1.在 Chapter 3 所討論的是 batch reactor，但本 chapter 開始討論 PFR 與 MFR。

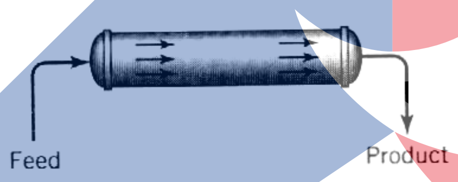
2. Ideal reactor types：

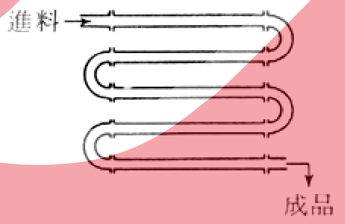
(1) Batch reactor：批式反應器、BR。



(2)連續式反應器(continuous reactor)：反應過程是 stedy state，有 PFR 和 MFR 兩種。

◆Plug flow reactor：塞流式反應器、PFR。





◆Mixed flow reactor：

❶目前最常用的名稱為

混合流動反應器、MFR (Mixed flow reactor)。

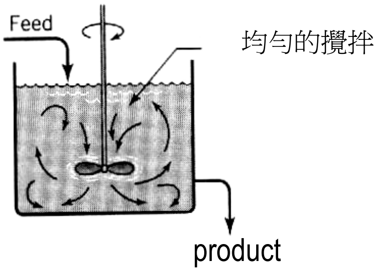
❷其他名稱，依常用情況依序為

① CSTR or CFSTR or C*

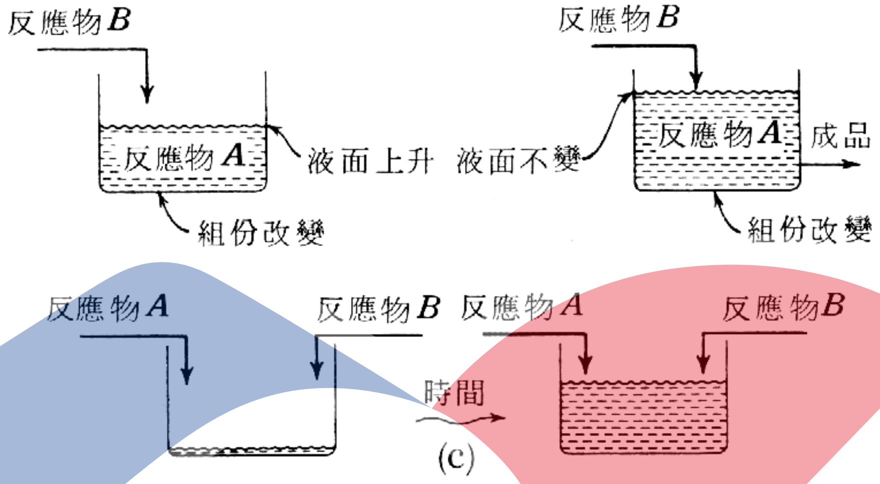
➔ constant flow stirred tank reactor 的簡稱。

② mixed reactor　③ backmix reactor

④the ideal stirred tank reactor

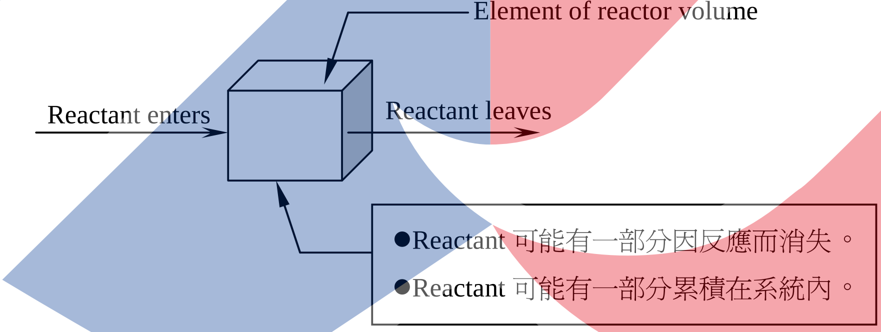


(3)半分批式反應器((semi-batch reactor)



(c)

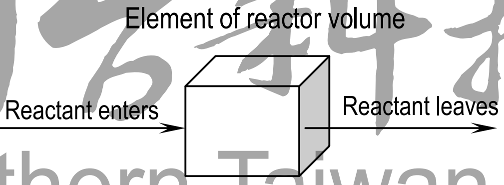
§4-2. Material balance



●Reactant 可能有一部分因反應而消失。

●Reactant 可能有一部分累積在系統內。

✸Material balance or Energy balance 的基本概念✸



(1) Input ➔ 10 mol/hr 的 A。

(2) Output ➔ 2 mol/hr 的 A。

(3)累積在反應器(system)中 ➔ 1 mol/hr 的 A。

(4) 因反應而消失的 A ➔ ____ mol/hr。

◆ 1 = 10 – 2 – 7 ➔❶ accumulation = Input – Output – disappearance

∵disappearance 前面已經取負號

➔消失的量是取正值。

❷ accumulation = Input – Output + disappearance

∵disappearance 前面已經取正號

➔消失的量是取負值。

◆ 10 = 2 + 7 + 1 ➔ Input = output + disappearance + accumulation

●明顯的，此表示法的消失的量是取正值。

§4-3. Ideal batch reactor

1.在第三章(§3-1)，我們探討的 Constant-Volume Batch Reactor，

A ➔ product，進行 n-order 的反應：

(1) 則 $-r_A = -\dfrac{dC_A}{dt} = kC_A^n$ ➔ $\displaystyle\int_{C_{A0}}^{C_A}\frac{dC_A}{C_A^n} = -\int_0^t kdt$

❶ n = 1 ➔ $-r_A = -\dfrac{dC_A}{dt} = kC_A$ ➔ $-\ln\dfrac{C_A}{C_{A0}} = kt$

❷ n≠1 ➔ $\displaystyle\int_{C_{A0}}^{C_a}\frac{dC_A}{C_A^n} = -\int_0^t kdt$ ➔ $C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt$

(2)但是若以 $-r_A = -\dfrac{dC_A}{dt}$ 的觀點來看，則

$\displaystyle\int_0^t dt = -\int_{C_{A0}}^{C_A}\frac{dC_A}{-\gamma_A}$ or $\displaystyle t = -\int_{C_{A0}}^{C_A}\frac{dC_A}{-\gamma_A}$

❶ n = 1 ➔ $-r_A = kC_A$ ➔ $-\ln\dfrac{C_A}{C_{A0}} = kt$

❷ n≠1 ➔ $-r_A = kC_A^n$ ➔ $C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt$

所以，Constant-Volume Batch Reactor ➔ $\displaystyle t = -\int_{C_{A0}}^{C_A}\frac{dC_A}{-\gamma_A}$ --- 另一種通式

2.以 mass balance 的角度來看 batch reactor：

(1)在反應過程 ➔ no reactant enters or leaves the batch reactor.

$$\overset{0}{\cancel{\text{Input}}} = \overset{0}{\cancel{\text{output}}} + \text{disappearance} + \text{accumulation}$$

or

Rate of reactant loss due to chemical reaction within the element of reactor volume	= -	Rate of accumulation of reactant in the element of reactor volume

(2) $$\boxed{\begin{array}{c}\text{Disappearance of}\\ \text{A by reaction}\\ \text{(mole/time)}\end{array}} = (-\gamma_A)\,V = \frac{\text{moles A reacting}}{\text{(time)(volume of fluid)}} \text{ x volume of fluid}$$

$$\boxed{\begin{array}{c}\text{accumulation of A}\\ \text{(mole/time)}\end{array}} = \frac{dN_A}{dt} = \frac{d[N_{A0}(1-X_A)]}{dt} = -N_{A0}\frac{dX_A}{dt}$$

$$\therefore\ (-\gamma_A)\,V = -(-N_{A0}\frac{dX_A}{dt}) \Rightarrow t = \int_0^t dt = N_{A0}\int_0^{X_A}\frac{dX_A}{(-\gamma_A)V} \quad \text{------通式------Eq. 3}$$

●Constant-Volume Batch Reactor

$$\Rightarrow t = N_{A0}\int_0^{X_A}\frac{dX_A}{(-\gamma_A)V} = \frac{N_{A0}}{V}\int_0^{X_A}\frac{dX_A}{-\gamma_A} = C_{A0}\int_0^{X_A}\frac{dX_A}{-\gamma_A} = -\int_{C_{A0}}^{C_A}\frac{dC_A}{-\gamma_A} \quad \text{---Eq. 4}$$

●Varying-Volume Batch Reactor

◆根據§3-2 Varying-Volume Batch Reactor ➔ $V=V_0(1+\varepsilon_A X_A)$

$$\therefore t = N_{A0}\int_0^{X_A}\frac{dX_A}{(-\gamma_A)V} = N_{A0}\int_0^{X_A}\frac{dX_A}{(-\gamma_A)V_0(1+\varepsilon_A X_A)} = C_{A0}\int_0^{X_A}\frac{dX_A}{(-\gamma_A)(1+\varepsilon_A X_A)}$$

-----Eq. 5

❈❈Eq. 3～5 are applicable to both isothermal and nonisothermal operations.

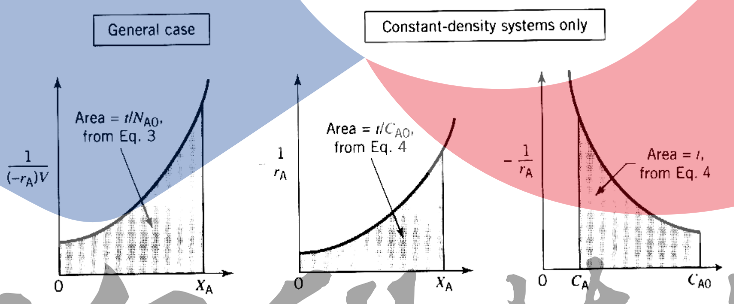


Figure 5.2 Graphical representation of the performance equations for batch reactors, isothermal or nonisothermal.

§4-4.Space-time and space-velocity

●在 batch reactor 中 ➔ 計算反應所進行的時間是理所當然的。

●在 continuous reactor 中 ➔ 反應時間不易計算。

∴便用 Space-time and space-velocity 作為衡量的方式。

1. Space-time:

$$\tau = \frac{1}{s} = \boxed{\begin{array}{l}\text{Time required to process one reactor volume}\\ \text{of feed measured at specified conditions}\end{array}} = \text{[time]}$$

∴ τ = 2 min. ➔在某條件下，處理一個反應器體積的進料需 2 分鐘。

2. Space-velocity:

$$s = \frac{1}{\tau} = \boxed{\begin{array}{l}\text{Number of reactor volumes of feed at specified} \\ \text{conditions which can be treated in unit time}\end{array}} = [\text{time}^{-1}]$$

∴ $s = 5\ \text{hour}^{-1}$ ➔在某條件下，每小時可處理 5 個反應器體積的進料。

$\tau = \frac{1}{s} = 0.2$ hour ➔處理一個反應器體積的進料需 0.2 小時。

3. V = volume of reactor (例如 100 liters)

N_{A0} = A 的進料 mole 數 = mole

C_{A0} = A 的進料濃度 = (moles A entering)/(volume of feed)

[如：C_{A0} = 5 M = 5 mol/liter]

F_{A0} =單位時間，A 的進料 mole 數。(molar feed rate of A，如：10 mol/min.)

v_o =單位時間，A 的進料體積。(volumetric feed rate of A, 其單為是 liter/min, ft^3/sec -------等。)

$$\therefore\ F_{A0} = C_{A0}\, v_o \Rightarrow\ v_o = \frac{F_{A0}}{C_{A0}} \Rightarrow\ v_o = \frac{10\,\frac{mol}{\min}}{5\,\frac{mol}{\ell}} = 2\,\frac{\ell}{\min}$$

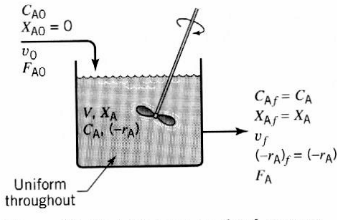
$$\because\ \tau = \frac{1}{s} = \frac{V}{v_o} = \frac{C_{A0}V}{F_{A0}}$$

$$\Rightarrow \tau = \frac{5\,\frac{mol}{\ell}\ \text{x}\ 100\,\ell}{10\,\frac{mol}{\min}} = 50\ \text{min.} = \frac{V}{v_o} = \frac{100\ell}{2\,\frac{\ell}{\min}}$$

§4-5. Steady-state mixed flow reactor

1.Steady-state mixed flow reactor

(1) Input = output + disappearance + $\overset{0}{\cancel{\text{accumulation}}}$



- ●input of A = $F_{A0}(1-X_{A0}) = F_{A0}$ (moles/time)
- ●output of A = $F_{A0}(1-X_A) = F_A$ (moles/time)
- ●disappearance of A by reaction

  = $(-\gamma_A)$ V (moles/time) ---可參看 page 4-2

(2).∴$F_{A0} = F_{A0}(1-X_A) + (-\gamma_A)\, V$ ➔ $F_{A0}X_A = (-\gamma_A)\, V$

$$\therefore \frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{X_A}{-\gamma_A}$$

$$\therefore \tau = \frac{1}{s} = \frac{V}{v_0} = \frac{C_{A0}V}{F_{A0}} = \frac{C_{A0}X_A}{-\gamma_A}$$ --------------------any ε_A

❈X_A and $-\gamma_A$ are measured at exit stream conditions, which are the same as the conditions within the reactor.

❈若進料的轉化率不是 0 ➔ 則以 X_{Ai} 表示。

而出口的轉化率不以 X_A 表示➔ 而以 X_{Af} 表示。

則 $\frac{V}{F_{A0}} = \frac{X_A}{-\gamma_A}$ 應寫成更廣泛的式子：

◆ $\frac{V}{F_{A0}} = \frac{X_{Af} - X_{Ai}}{(-\gamma_A)_f}$ ◆ $\tau = \frac{C_{A0}V}{F_{A0}} = \frac{C_{A0}(X_{Af} - X_{Ai})}{(-\gamma_A)_f}$

❈Special case of constant-density systems (即 $\varepsilon_A = 0$) ➔ $X_A = 1 - C_A/C_{A0}$

∴◆ $\frac{V}{F_{A0}} = \frac{X_A}{-\gamma_A} = \frac{C_{A0} - C_A}{C_{A0}(-\gamma_A)}$ ◆ $\tau = \frac{C_{A0}V}{F_{A0}} = \frac{C_{A0}X_A}{-\gamma_A} = \frac{C_{A0} - C_A}{-\gamma_A}$

①for first-order reaction ➔ $-\gamma_A = -\frac{dC_A}{dt} = kC_A$

$\therefore \tau = \frac{C_{A0} - C_A}{kC_A}$ ➔ $k\tau = \frac{C_{A0} - C_A}{C_A} = \frac{X_A}{1 - X_A}$

當然，若是要選廣泛的 first-order reaction

則 $V = V_0(1+\varepsilon_A X_A)$ & $C_A = C_{A0}\frac{(1 - X_A)}{(1 + \varepsilon_A X_A)}$

∴ $k\tau = \frac{X_A(1 + \varepsilon_A X_A)}{1 - X_A}$ for any ε_A

②for second-order reaction ➔ $-\gamma_A = -\frac{dC_A}{dt} = kC_A^2$

∴ $k\tau = \frac{C_{A0} - C_A}{C_A^2}$ or $C_A = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau}$

Example 4-1:

以 2 liters/hr 的速率輸送初濃度為 100 mol/L 的氣體反應物 A 到一個 mixed flow reactor 中進行 2A → R ($-r_A = 0.2C_A^2$)的反應，若測得出口尚有 A 氣體 10 mol/L 且反應系統是 constant-pressure system，則此 MFR 的體積應是多少？

Example 4-2:

Pure gases reactant A (C_{A0} = 100 millimol/liter) is fed at a steady rate into a mixed flow reactor (V = 0.1 liter) where it dimerizes (2 A → R). For different gas feed rates the following data are obtained:

Run number	1	2	3	4
v_o, liter/hr	10	3	1.2	0.5
C_{af}, millimol/liter	85.7	66.7	50	33.4

Find a rate equation for this reaction.

Sol: $-r_A = -\frac{dC_A}{dt} = kC_A^n$ → $\log(-r_A) = \log k + n \log C_A$

或 $\ln(-r_A) = \ln k + n \ln C_A$

∴以 $\log(-r_A)$ 對 $\log C_A$ 作圖[或 $\ln(-r_A)$ 對 $\ln C_A$ 作圖]

得一直線，其 slope 為 n；截距 = log k (或 ln k)

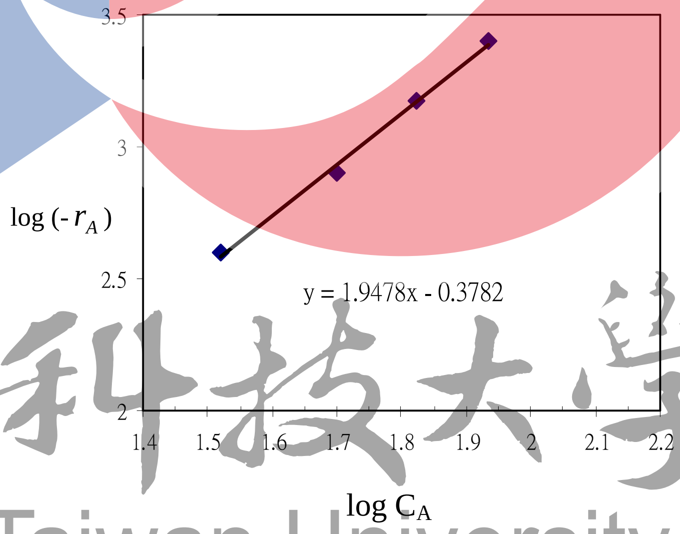
∴先求 $-r_A$

由 $\tau = \frac{V}{v_0} = \frac{C_{A0}V}{F_{A0}} = \frac{C_{A0}X_A}{-\gamma_A}$ → $-r_A = \frac{C_{A0}X_A}{\tau}$

再由 $C_A = C_{A0}\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)$ & $\varepsilon_A = \frac{1-2}{2} = -\frac{1}{2}$

$$\text{得 } C_A = C_{A0}\left(\frac{1-X_A}{1-\frac{1}{2}X_A}\right) \rightarrow X_A = \frac{1-\frac{C_A}{C_{A0}}}{1-\frac{C_A}{2C_{A0}}}$$

No.	1	2	3	4
τ			0.0833	0.2
X_A			0.667	0.8
$-r_A$			800	400
$\log(-r_A)$			2.903	2.602
$\log C_A$			1.699	1.522



Example 4-3:

The elementary liquid-phase reaction

$$A + 2B \underset{k_2}{\overset{k_1}{\rightleftarrows}} R$$

with rate equation

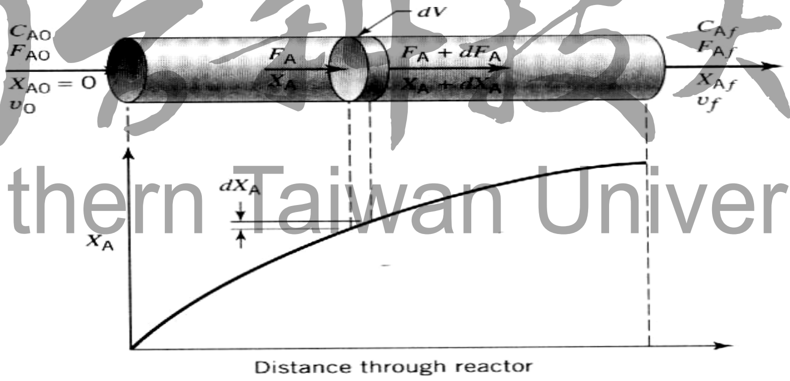
$$-\gamma_A = -\frac{1}{2}\gamma_B = (12.5\ \text{liter}^2/\text{mol}^2.\text{min})C_AC_B^{2} - (1.5\ \text{min}^{-1})C_R, \quad [\ \text{mol}/(\text{liter}\cdot\text{min})]$$

is to take place in a 6-liter steady-state mixed flow reactor. Two feed streams, one containing 2.8 mol A/liter and the other containing 1.6 mol B/liter, are to be introduced at equal volumetric flow rates into the reactor, and 75% conversion of limiting component is desired . What should be the flow rate of each stream? Assume a constant density throughout.

§4-6.Steady-state plug flow reactor

1.(1)In a plug flow reactor, the composition of the fluid varies from point to point along a flow path.

(2)Material balance ➔ 選一個 differential element of volume dV 作分析。



2. (1) Input = output + disappearance + $\cancelto{0}{\text{accumulation}}$

●input of A = F_A (moles/time)

●output of A = $F_A + dF_A$ (moles/time)

●disappearance of A by reaction = $(-\gamma_A)\,dV$ (moles/time)

☹☹注意左三式與 MFR(page 4-5) 的不同。

(2) Material balance ➔ $F_A = (F_A + dF_A) + (-\gamma_A)\,dV$

∵ $dF_A = d[F_{A0}(1-X_A)] = -F_{A0}dX_A$

∴$F_{A0}dX_A = (-\gamma_A)\,dV$ -----------這只是對一個微量體積 dV 作分析，若考慮整個反應器，當然要做積分。

$$\therefore \int_0^V \frac{dV}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-\gamma_A} \rightarrow \frac{V}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-\gamma_A} = \frac{\tau}{C_{A0}}$$

$$\therefore \tau = \frac{V}{v_0} = \frac{C_{A0}V}{F_{A0}} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-\gamma_A} \quad \text{----- any } \varepsilon_A$$

●與 MFR(page 4-4)的差異在哪裡？

■MFR 的γ_A在 reactor 中的任何位置是相同的定值。

■PFR 的γ_A在 reactor 中，隨著離進料處的距離遠近而變，所以，需用積分的方式。

✵若進料的轉化率不是 0 ➔ 則以 X_{Ai} 表示。
而出口的轉化率不以 X_A 表示➔ 而以 X_{Af} 表示。

$$\text{則}\quad \frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-\gamma_A} \quad \text{or} \quad \tau = \frac{V}{v_0} = \frac{C_{A0}V}{F_{A0}} = C_{A0}\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-\gamma_A}$$

✵Special case of constant-density systems (即 ε_A=0)

$$X_A = 1 - C_A/C_{A0} \rightarrow dX_A = -\frac{dC_A}{C_{A0}}$$

$$\therefore ◆ \frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-\gamma_A} = -\frac{1}{C_{A0}}\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-\gamma_A}$$

$$◆ \tau = \frac{C_{A0}V}{F_{A0}} = \frac{V}{v_0} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-\gamma_A} = -\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-\gamma_A}$$

①for zero-order homogeneous reaction ➔ $-\gamma_A = -\frac{dC_A}{dt} = k$

$$\therefore \tau = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-\gamma_A} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{k} = C_{A0}\frac{X_A}{k}$$

$$\therefore k\tau = C_{A0}X_A$$

②First-order irreversible reaction, any ε_A

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = kC_A = kC_{A0}\frac{(1-X_A)}{(1+\varepsilon_A X_A)}$$

$\therefore k\tau = -(1+\varepsilon_A)\ln(1-X_A) - \varepsilon_A X_A$ 若 $\varepsilon_A = 0$ ➔ $\tau = -\ln(1-X_A)/k$

●在 PFR 中，若 $\varepsilon_A = 0$
- ■ zero-order reaction $\tau = C_{A0}X_A/k$
- ■ first-order reaction $\tau = -\ln(1-X_A)/k$

●在 chapter 3 的 batch reactor 中，若 $\varepsilon_A = 0$
- ■ zero-order reaction $t = C_{A0}X_A/k$ (pgae 3-7)
- ■ first-order reaction $t = -\ln(1-X_A)/k$ (pgae 3-3 的❸)

●For system of constant density:
↳τ for plug flow reactor is equivalent to t for the batch rector.

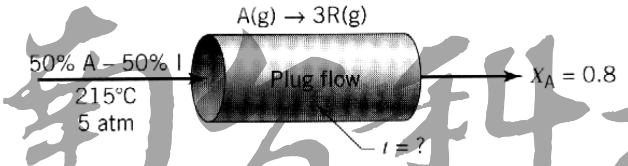
●For system of changing density:
↳The correct eq. must be used for each particular situation.

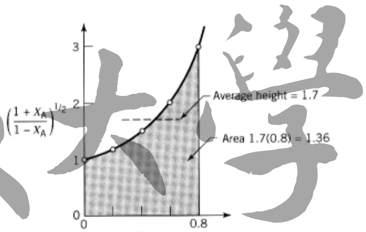
Example 4-4:

A homogeneous gas reaction A→ 3R has a reported rate at 215℃

$$-r_A = 10^{-2}C_A^{1/2} \quad [\text{mol/liter·sec}]$$

Find a space time needed for 80% conversion of a 50% A & 50% inert feed to a plug flow reactor operating at 215℃ and 5 atm(C_{A0} = 0.0625 mol/liter).





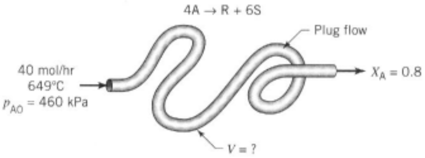
Example 4-5:

The homogeneous gas decomposition of phosphine

$$4\,PH_{3(g)} \rightarrow P_{4(g)} + 6\,H_{2(g)}$$

prcceeds at 649℃ with the first-order rate

$$-r_A = (10/\text{hr})C_{PH3}$$



What size of plug flow reactor operating at 649℃ and 460 kPa can produce 80% conversion of a feed consisting of 40 mol of pure phosphine per hour?

※1 atm = 101325 pa = 101.325 kpa

§4-7. Holding time and space time for flow reactors

1.Define:

(1)space time:

$$\tau = \frac{1}{s} = \boxed{\text{Time required to process one reactor volume of feed measured at specified conditions}} = \frac{V}{v_0} = \frac{C_{A0}V}{F_{A0}}$$

(2)holding time:

$$\bar{t} = \boxed{\text{Mean residence time of flowing material in the reactor}} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-\gamma_A(1+\varepsilon_A X_A)}$$

2.For constant density system (all liquids and constant density gases)

$$\Rightarrow \tau = \bar{t} = \frac{V}{v_0}$$

3.For changing density system

$$\Rightarrow \tau \neq \bar{t} \quad \text{and} \quad \bar{t} \neq \frac{V}{v_0}$$

4.如圖所示：

●將玉米花原料以 1 liter/min 的進料送入一個體積為 1 liter 的加熱器(反應器)中，由於玉米花原料遇熱會膨脹，所以，若以爆開的玉米花來看，其前進的體積流率為 28 liters/min。假設玉米花爆開的位置如下圖所示，則：

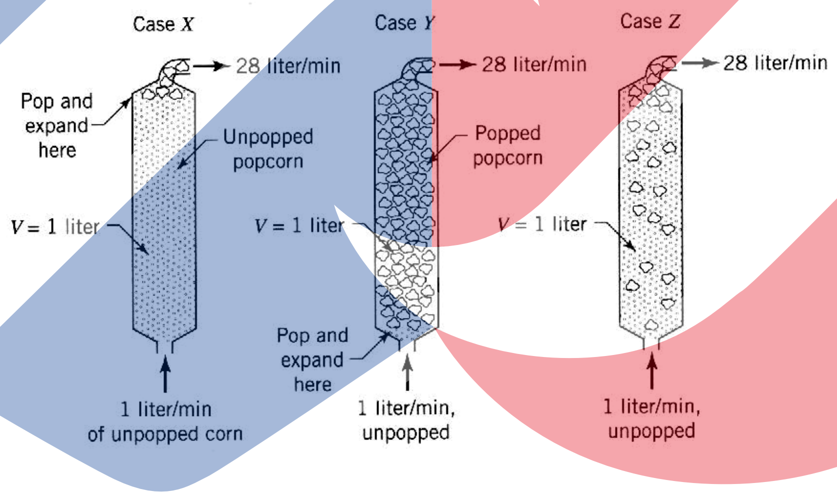
(1)space-time $\tau_X = \tau_Y = \tau_Z = \frac{V}{v_0}$ = 1 liter/(1 liter/min.) = 1 min. = 60 sec.

(2)holding time:

$\bar{t}_X$ = 60 sec

$\bar{t}_Y$ = 1 liter/(28 liter/min.) = 0.0357 min. = 2.14 sec.

$\bar{t}_Z$ = 2.14 ~ 60 sec 之間



Example 4-6:

A pure gas A (reaction A→ 2 R) with volumetric flow rate 0.1 m^3/min is introduced into a mixed flow reactor. The reactor volume needed for 50% conversion of A is 0.5 m^3. Find the corresponding

(A) space-time

(B) mean residence time for this system.

Example 4-7:

均勻液相反應：$A \rightarrow R$，$-r_A = kC_A^2$，in CSTR，$X_A = 0.5$

(A)若改成一 6 倍大的 CSTR，條件不變，$X_A =$ ？

(B)若為一相等大小的 PFR，條件不變，$X_A =$ ？

Example 4-8:

Ethylene is produced by the dehydrogenation of ethane

$C_2H_{6(g)} \rightarrow C_2H_{4(g)} + H_{2(g)}$

Determine the plug flow reactor volume necessary to produce 100 million kilograms of ethylene a year from the above reaction. The reaction is irreversible and elementary. We want to achieve 80% conversion of ethane, operating the reactor isothermally at 1100 K and a pressure of 6 atm. The rate constant k at 1100 K is 3.07 sec^{-1}.

<Hint> $\int_0^X \left(\frac{1+\varepsilon X}{1-X}\right) dX = (1+\varepsilon)\ln[1/(1-X)] - \varepsilon X$

Example 4-9:

Consider the following batch, elementary reaction of ethyl acetate in an aqueous solution of sodium hydroxide at 25℃:

$CH_3COOC_2H_5 + NaOH \xrightarrow{k} CH_3COONa + C_2H_5OH$ where k equals 6.48 ℓ/mol·min. The reaction is commenced with equal concentration (0.01 mol/ℓ) of ethyl acetate and sodium hydroxide. Please calculate concentration of ethyl acetate 25 minutes after the start of the reaction.

Example 4-10:

An irreversible reaction A→ R was carried out in a plug flow reactor. The rate equation is

$$\frac{1}{-\gamma_A} = \frac{C_A}{(1+C_A)^2}$$

The flow rate of feed is 0.2 m^3/sec. The concentration of A in the feed is 10 kmol/m^3. What is the reactor volume to get the 99% conversion of A?

Hint: $\int \frac{x\,dx}{(a+bx)^2} = \frac{1}{b^2}[\ln(a+bx) + \frac{a}{a+bx}]$

Example 4-11:

A second-order liquid phase reaction takes place with 50% conversion in a CSTR. What will be the conversion if this reactor is replaced by one PFR twice as large as CSTR? All else remain unchanged? 80%

Example 4-12:

A first order irreversible gas-phase reaction $A \rightarrow B + 2\,C$ take place in a CSTR. The operation is isothermal and isobaric. The reaction rate constant is 0.2 min^{-1}, and the reactor volume is 500L. The feed contains a 60 mol% of A and a 40 mol% of an inert compound. The molar flow rate of the reactant A is 400 mol/min. and the initial concentration of the reactant A is 4 mol/L. What is the conversion at the exit of this CSTR?