Chapter 6　Design for Parallel Reactions

(本章為課本的第七章)

§6-1.Qualitative discussion about product distribution

1. Consider the Parallel Reactions

$$A \xrightarrow{k_1} R \quad \text{(desired product)}$$
$$A \xrightarrow{k_2} S \quad \text{(unwanted product)}$$

rate equations:

$$r_R = \frac{dC_R}{dt} = k_1 C_A^{a_1}\ ;\ r_S = \frac{dC_S}{dt} = k_2 C_A^{a_2} \ \rightarrow\ \therefore \frac{r_R}{r_S} = \frac{C_R}{C_S} = \frac{k_1}{k_2} C_A^{a_1 - a_2}$$

- We wish this ratio to be as large possible.
- k_1, k_2, a_1 and a_2 are all constant for a specific system at a given temperature.
  - ↳ C_A is the only factor in this equation which we can adjust and control.

◆If $a_1 > a_2 \rightarrow C_A \uparrow$, $\frac{C_R}{C_S} \uparrow$

↳ A batch or plug flow reactor would favor formation of product R and would require a minimum reactor size.

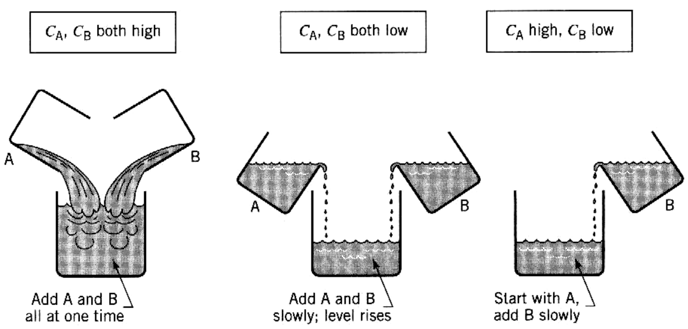
◆If $a_1 < a_2 \rightarrow C_A \uparrow$, $\frac{C_R}{C_S} \downarrow$ or $C_A \downarrow$，所得的 $\frac{C_R}{C_S}$ 相對較高。

↳ Require large mixed flow reactor.

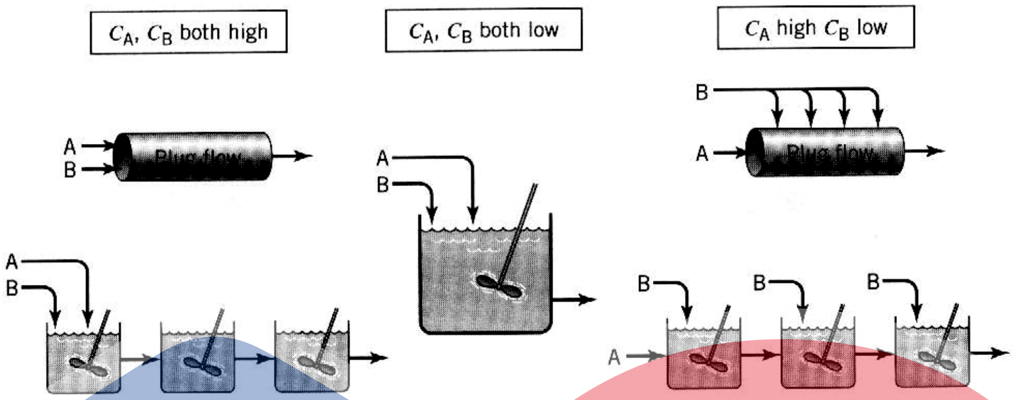
◆If $a_1 = a_2 \rightarrow \frac{r_R}{r_S} = \frac{C_R}{C_S} = \frac{k_1}{k_2}$ = constant

↳ The products distribution is fixed by k_1/k_2 alone and unaffected by types of reactor.

2. By using the correct contacting pattern of reacting fluids, we can control the concentration of reactants.



請參閱課本 Figure 7.1



請參閱課本 Figure 7.2

●●在第二章談到：

$k_1 = k_{10}\exp(-E_1/RT)$

$k_2 = k_{20}\exp(-E_2/RT)$

$$\therefore \frac{r_R}{r_S} = \frac{C_R}{C_S} = \frac{k_1}{k_2} C_A^{a_1-a_2}$$

> 注意：由於 k_1 和 k_2 分別是不同的反應，因此，k_{10} 和 k_{20} 與 E_1 和 E_2 是不同的。

若已經選擇一固定種類的反應器與加料方式

➔ C_A 值的變化已無法再改變

➔ 則改變溫度以調整 $\frac{k_1}{k_2}$ 值亦是重要的方法

由 $\frac{k_2}{k_1} = \frac{k_{20}}{k_{10}}\exp[-(E_2-E_1)/RT]$ or $\frac{k_1}{k_2} = \frac{k_{10}}{k_{20}}\exp[-(E_1-E_2)/RT]$

◆若 $E_1 < E_2$ ➔ 降低溫度會提高 k_1/k_2 值 ➔ 有利於得到 R。

◆若 $E_1 > E_2$ ➔ 升高溫度可降低 k_1/k_2 值 ➔ 有利於得到 R。

Example 6-1:

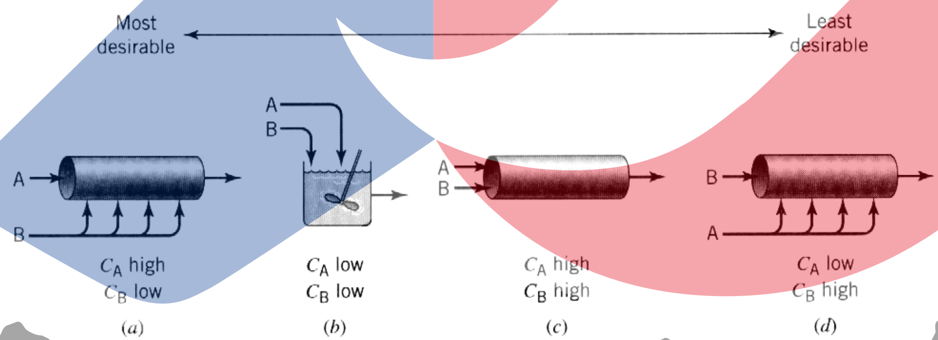
The desired liquid-phase reaction

$$A + B \xrightarrow{k_1} R + T \qquad \frac{dC_R}{dt} = \frac{dC_T}{dt} = k_1 C_A^{1.5} C_B^{0.3}$$

is accompanied by the unwanted side reaction

$$A + B \xrightarrow{k_2} S + U \qquad \frac{dC_S}{dt} = \frac{dC_U}{dt} = k_2 C_A^{0.5} C_B^{1.8}$$

From the standpoint of favorable product distribution, order the contacting schemes of Figure 7.2, from the most desirable to the least desirable.



參閱課本 Figure E7.1

§6-2.Quatitative discussion about product distribution

1.就 parallel reaction 而言：

若 rate equation 為已知

⇘可定量的定出 product distribution and reactor-size requirements。

(1)Define:

❶instantaneous fraction yield of R(R 的瞬間分數產率, φ)

=反應物 A 瞬間消失時，轉變成我們所要的產物 R 的分率。

$$\therefore\ \varphi = \frac{moles\ \ R\ \ formed}{moles\ \ A\ reacted} = \frac{dC_R}{-dC_A}$$

●以微觀來看，

■在 PFR 中 ➔ C_A 值在反應器內隨其位置而有變化，所以，φ 亦變化。

■在 MFR 中 ➔ C_A 值在反應器中是一致的，所以，φ 是一致的。

❷Overall fractional yield of R(R 的總分數產率, Φ)

=反應器內，各點的瞬時分數產率的平均值。

$$\Phi = \frac{all\ R\ formed}{all\ A\ reacted} = \frac{C_{Rf}}{C_{A0}-C_{Af}} = \frac{C_{Rf}}{-\Delta C_A} = \overline{\varphi}_{\text{in reactor}}$$

●For PFR ➔ C_A changes progressively through the reactor

$$\therefore\ \Phi_p = \frac{-1}{C_{A0}-C_{Af}}\int_{C_{A0}}^{C_A}\varphi dC_A = \frac{1}{\Delta C_A}\int_{C_{A0}}^{C_A}\varphi dC_A$$

●For MFR ➔ The composition is C_{Af} everywhere, so φ is likewise constant throughout the reactor

$\therefore\ \Phi_m = \varphi$(在 C_{Af} 求出)

●當 A 的濃度由 C_{A0} 反應到 C_{Af} 時，MFR 與 PFR 有下列的關係：

$$\Phi_m = \left(\frac{d\Phi_p}{dC_A}\right)_{at\ C_{Af}} \qquad \Phi_p = \frac{1}{\Delta C_A}\int_{C_{A0}}^{C_A}\Phi_m dC_A$$

※此式可用來藉一類型的反應器去推測另一類型的反應器。

●N 個 MFR，A 濃度分別為 C_{A1}、C_{A2}、---、C_{AN}，則

overall fractional yields 可由 N 個 reactor 的 instantaneous fraction yield 和其反應量而得：

$$\varphi_1(C_{A0}-C_{A1}) + \varphi_2(C_{A1}-C_{A2}) + \cdots + \varphi_N(C_{A,N-1}-C_{AN}) = \Phi_{N\,mix}(C_{A0}-C_{AN})$$

即

$$\Phi_{N\,mix} = [\varphi_1(C_{A0}-C_{A1}) + \varphi_2(C_{A1}-C_{A2}) + \cdots + \varphi_N(C_{A,N-1}-C_{AN})]/(C_{A0}-C_{AN})$$

●任何 reactor，R 的出口濃度： $C_{Rf} = \Phi(C_{A0}-C_{Af})$

Example 6-2:

Consider the aqueous reactions

$$A + B \xrightarrow{k_1} R \quad \text{(desired product)} \qquad \frac{dC_R}{dt} = 1.0\, C_A^{1.5} C_B^{0.3}, \ \text{mol/min}\cdot\ell$$

$$A + B \xrightarrow{k_2} S \quad \text{(unwanted product)} \qquad \frac{dC_S}{dt} = 1.0\, C_A^{0.5} C_B^{1.8}, \ \text{mol/min}\cdot\ell$$

Equal volumetric flow rates of A and of B streams are fed to the reactor, and each stream has a concentration of 20 mol/liter of reactant. For 90% conversion of A, find the concentration of R in the product stream.

The flow in the reactor follows.

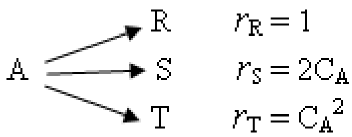
(A)Plug flow

(B)Mixed flow

(C)The best of the four plug-mixed contacting schemes of Example 6.1.

Example 6-3:

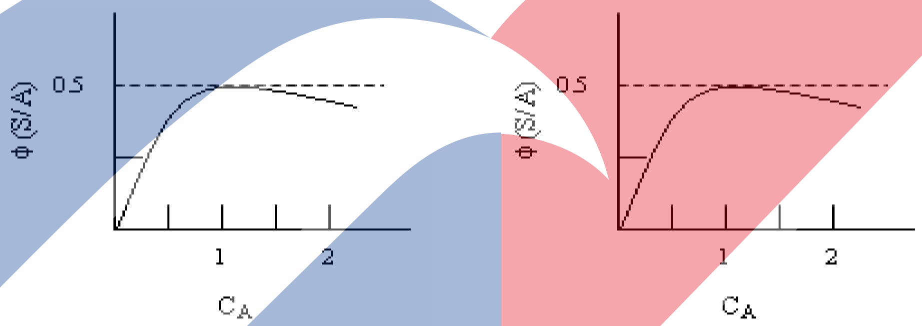
The parallel decompositions of A, $C_{A0} = 2$ M,



Find the maximum expected CS for isothermal operations

(a) in a mixed flow reactor

(b) in a plug flow reactor



Sol: $$\varphi(S/A) = \frac{dC_S}{-dC_A} = \frac{dC_S}{dC_R + dC_S + dC_T} = \frac{2C_A}{1 + 2C_A + C_A^2} = \frac{2C_A}{(1+C_A)^2}$$

∴以 φ (S/A)對 CA 作圖而得到上圖，而曲線的最高點發生在

$$\frac{d\varphi}{dC_A} = 0 = \frac{d}{dC_A}\left[\frac{2C_A}{(1+C_A)^2}\right] = \frac{(1+C_A)^2 - C_A[2(1+C_A)]}{(1+C_A)^4}$$

∴ $C_A = 1$ M 時 ➔ 得 φ(S/A) = 0.5 的最大值

(A)mixed flow reactor ➔ 由上圖知 C_A 不同，矩形面積(即 C_{Sf})不同，但

$$C_{Sf} = \varphi(S/A) \times (-\Delta C_A) = \frac{2C_A}{(1+C_A)^2} x (C_{A0} - C_A) = \frac{2C_A}{(1+C_A)^2}(2 - C_A)$$

∴ C_{Sf} 是隨著 C_A 的大小而變(此和前 2 行，用圖形分析的結論相同)，但最大值出現在

$$\frac{dC_{Sf}}{dC_A} = 0 = \frac{d}{dC_A}\left[\frac{2C_A}{(1+C_A)^2}(2 - C_A)\right] = \frac{d}{dC_A}\left[\frac{(4C_A - 2C_A^2)}{(1+C_A)^2}\right]$$

$$0 = \frac{(4 - 4C_A)(1+C_A)^2 - (4C_A - 2C_A^2)2(1+C_A)}{(1+C_A)^4}$$

$\therefore\ C_A = \frac{1}{2}$ 時，得最大的 $C_{Sf} = \frac{2}{3}$

(B) plug flow reactor ➔ 由上圖知 C_A 降到 0 時，曲線下的面積(即 C_{Sf})最大

$$\therefore C_{Sf} = -\int_{C_{A0}}^{C_{Af}} \varphi(S/A)dC_A = \int_0^2 \frac{2C_A}{(1+C_A)^2}dC_A$$

C_{Sf} = 0.867

$$\int \frac{2C_A}{(1+C_A)^2}dC_A$$

令 $1 + C_A = y$ ➔ $C_A = y-1$ 且 $dC_A = dy$

$$\therefore \int \frac{2C_A}{(1+C_A)^2}dC_A = \int \frac{2(y-1)}{y^2}dy = 2\int (\frac{y}{y^2} - \frac{1}{y^2})dy = ---$$