

Chapter 3 Interpretation of Batch Reactor Data

§3-1. Constant-Volume Batch Reactor

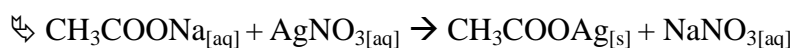
1. Constant-volume Batch Reactor means a constant-density reaction system.

(1) 指 volume of reaction mixture 固定，而非指 the volume of reactor 固定。

(2) 大部分的 liquid-phase reactions
gas-phase reactions in a constant-volume bomb } 為此類型。

① 在一個 1 liter 的 reactor 中，

混合 200 ml, 0.1 M 的 $\text{CH}_3\text{COONa}_{[\text{aq}]}$ 與 200 ml, 0.1 M 的 $\text{AgNO}_3_{[\text{aq}]}$



\hookrightarrow 反應前後的體積未變，為 Constant-volume。

$$r_i = \frac{dC_i}{dt} = \frac{d\left(\frac{N_i}{V}\right)}{dt} = \frac{1}{V} \frac{dN_i}{dt}$$

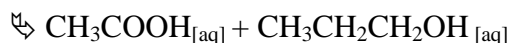
⊙ 請小心代號的意義：

● C \rightarrow concentration，如 mole/L、M、mM ---。

● N \rightarrow mole、mmol ---。

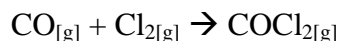
② 在一個 1 liter 的 reactor 中，

混合 200 ml, 1 M 的 $\text{CH}_3\text{COOH}_{[\text{aq}]}$ 與 200 ml, 1 M 的 $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}_{[\text{aq}]}$



\hookrightarrow 反應前後的體積略為改變，但仍可視為 Constant-volume。

③ 在一個 1 liter 的 reactor 中，混合 1 mol 的 CO 和 1 mol 的 Cl_2 進行反應



① 在 constant-volume 下進行反應，

則反應前後的 mole 數改變 \rightarrow 系統壓力改變

$$\hookrightarrow r_i = \frac{dC_i}{dt} = \frac{d\left(\frac{N_i}{V}\right)}{dt} = \frac{1}{V} \frac{dN_i}{dt}$$

\hookrightarrow For ideal gases $\rightarrow C = P/RT$

$$\therefore r_i = \frac{1}{RT} \frac{dP_i}{dt}$$

② 在 constant-pressure 下進行反應，

則反應前後的 mole 數改變 \rightarrow 系統的體積改變

$$\frac{dC_i}{dt} = \frac{d\left(\frac{N_i}{V}\right)}{dt} \neq \frac{1}{V} \frac{dN_i}{dt}$$

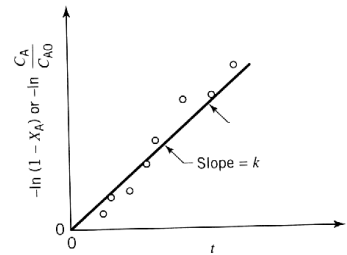
2. The conversion

(1) The conversion of A, X_A

$$X_A = \frac{\text{A 反應掉的 mole 數}}{\text{A 的最初 mole 數}} = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{(N_A/V)}{(N_{A0}/V)} = 1 - \frac{C_A}{C_{A0}}$$

$$\therefore C_A = C_{A0}(1 - X_A); C_{A0} - C_A = C_{A0}X_A$$

$$\begin{aligned} (2) \therefore dX_A &= d\left(1 - \frac{C_A}{C_{A0}}\right) = -\frac{dC_A}{C_{A0}} \\ -r_A &= -\frac{dC_A}{dt} = -\frac{dC_{A0}(1 - X_A)}{dt} \\ &= C_{A0} \frac{dX_A}{dt} \end{aligned}$$



注意：(1)和(2)僅適用於 Constant-Volume Reactor !

4. Integral method of analysis of data:

↳ 主要目的在求出反應過程，time 和 concentration 的關係。

(1) Irreversible unimolecular-type first-order reaction :

Consider the reaction "a A → product" is a first-order reaction

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

$$\therefore \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = -\int_0^t k dt \rightarrow -\ln \frac{C_A}{C_{A0}} = kt$$

❶ 以 $-\ln \frac{C_A}{C_{A0}}$ 對時間 t 作圖 → 得一穿過原點的直線，其 slope = k。

❷ 由 $-\ln \frac{C_A}{C_{A0}} = kt \rightarrow \ln C_A - \ln C_{A0} = -kt$ or $\ln C_A = -kt + \ln C_{A0}$

↳ 以 $\ln C_A$ 對時間 t 作圖 → 得一 slope = -k 的直線，其截距 = $\ln C_{A0}$ 。

❸ $\because X_A = 1 - \frac{C_A}{C_{A0}} \therefore \frac{C_A}{C_{A0}} = 1 - X_A \rightarrow -\ln(1 - X_A) = kt$

以 _____ 對時間 t 作圖 → 得一穿過原點的直線，其 slope = k。

❹ A 的濃度降到原來一半所需的時間 → half-life time, $t_{1/2}$

$$\therefore \text{at } t_{1/2} \rightarrow C_A = \frac{1}{2} C_{A0} \text{ or } X_A = 0.5$$

$$\therefore \ln[(1/2 C_{A0}) / C_{A0}] = -k t_{1/2}$$

$$\Rightarrow t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

⇒ ● First-order reaction 的 half-life time 與初濃度無關。

※ 在化學反應中，有 0、1、2、1/2 --- 階反應；但放射性元素的 decay，皆為 first-order reaction。

◆ 當然，像 $-\frac{dC_A}{dt} = kC_A^{0.6}C_B^{0.4}$ 亦為 first-order reaction，但不適用於上述式子。

(2) Irreversible bimolecular-type second-order reactions

① 此類反應可能是

$$\textcircled{1} nA \rightarrow \text{products} \quad -r_A = -\frac{dC_A}{dt} = kC_A^2$$

$$\textcircled{2} A + B \rightarrow \text{products} \quad -r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B$$

$$\text{or } -r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A^{1.3}C_B^{0.7}$$

$$\textcircled{3} A + 2B \rightarrow \text{products} \quad -r_A = -\frac{dC_A}{dt} = kC_A C_B$$

$$\text{or } -r_A = -\frac{dC_A}{dt} = kC_A^{0.5}C_B^{1.5}$$

④ -----

② 最單純的類型：

$$nA \rightarrow \text{products} \quad -r_A = -\frac{dC_A}{dt} = kC_A^2$$

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = -\int_0^t k dt \Rightarrow \frac{1}{C_A} - \frac{1}{C_{A0}} = kt \quad \text{or} \quad \frac{1}{C_A} = kt + \frac{1}{C_{A0}}$$

① 以 $\frac{1}{C_A}$ 對時間 t 作圖 → 得 slope = k 之直線，截距為 $\frac{1}{C_{A0}}$

② $\therefore C_A = C_{A0}(1 - X_A)$

$$\therefore \frac{1}{C_A} - \frac{1}{C_{A0}} = kt \Rightarrow \frac{1}{C_{A0}(1 - X_A)} - \frac{1}{C_{A0}} = kt \quad \text{or} \quad \frac{1}{C_{A0}} \frac{X_A}{(1 - X_A)} = kt$$

以 _____ 對時間 t 作圖 → 得過原點之直線，其 slope = $C_{A0} k$ 。

③ at $t = t_{1/2}$, $C_A = 1/2 C_{A0}$ or $X_A = 0.5$

$$\therefore t_{1/2} = \frac{1}{k[A]_0}$$

● half-life time 與初濃度的一次方成反比(和 $\frac{1}{[A]_0}$ 成正比)。

(初濃度越高，half-life time 越短)

③ $A + B \rightarrow \text{products}$ $-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B$ 的類型

● A 的最初濃度為 C_{A0} ；B 的最初濃度為 C_{B0}

當 A 的轉化率為 X_A 時，則 A 反應掉 $C_{A0}X_A$ ，而 B 亦反應掉 $C_{A0}X_A$

↳ ■ A 的濃度變成 $C_A = C_{A0}(1-X_A)$

■ B 的濃度變成 $C_B = C_{B0} - C_{A0}X_A = C_{A0}(C_{B0}/C_{A0} - X_A) = C_{A0}(M - X_A)$

$$\therefore -r_A = -\frac{dC_A}{dt} = C_{A0} \frac{dX_A}{dt} = kC_A C_B = k[C_{A0}(1-X_A)][C_{A0}(M - X_A)]$$

$$\text{or } -r_A = C_{A0} \frac{dX_A}{dt} = kC_{A0}^2 (1-X_A)(M - X_A) \quad M = C_{B0}/C_{A0}$$

$$\therefore \int_0^{X_A} \frac{dX_A}{(1-X_A)(M-X_A)} = C_{A0} \int_0^t k dt$$

$$\blacklozenge M = 1 \rightarrow \text{回到 } -r_A = -\frac{dC_A}{dt} = kC_A^2 \rightarrow \frac{1}{C_{A0}} \frac{X_A}{(1-X_A)} = kt$$

$$\blacklozenge M \neq 1 \rightarrow \text{解出 } \int_0^{X_A} \frac{dX_A}{(1-X_A)(M-X_A)} = C_{A0} \int_0^t k dt$$

● $\int \frac{A}{(X+B)(X+C)} dx$ 一定要拆成 $\int [\frac{S}{(X+B)} + \frac{T}{(X+C)}] dx$ 後，才能各自積分。

● 拆的原則：

以 $\frac{2}{(1-X)(4-X)}$ 為例：

$$\begin{aligned} \text{令 } \frac{2}{(1-X)(4-X)} &= \frac{S}{(1-X)} + \frac{T}{(4-X)} \\ &= \frac{S(4-X) + T(1-X)}{(1-X)(4-X)} = \frac{S(4-X) + T(1-X)}{(1-X)(4-X)} \\ &= \frac{4S - SX + T - TX}{(1-X)(4-X)} = \frac{(4S+T) - (S+T)X}{(1-X)(4-X)} \\ \therefore 4S+T &= 2 \ \& \ S+T = 0 \rightarrow S = \frac{2}{3}; T = -(\frac{2}{3}) \end{aligned}$$

$$\therefore \text{要解出 } \int_0^{X_A} \frac{dX_A}{(1-X_A)(M-X_A)} = C_{A0} \int_0^t k dt$$

$$\begin{aligned} \text{要先拆開 } \frac{1}{(1-X_A)(M-X_A)} &= \frac{S}{(1-X_A)} + \frac{T}{(M-X_A)} \\ &= \frac{S(M-X_A)+T(1-X_A)}{(1-X_A)(M-X_A)} = \frac{SM-SX_A+T-TX_A}{(1-X_A)(M-X_A)} \\ &= \frac{SM+T-(S+T)X_A}{(1-X_A)(M-X_A)} \end{aligned}$$

$$\therefore SM+T=1 \ \& \ S+T=0 \Rightarrow S = \frac{1}{(M-1)} \ ; \ T = -\frac{1}{(M-1)}$$

$$\begin{aligned} \therefore \frac{1}{(1-X_A)(M-X_A)} &= \frac{\left(\frac{1}{M-1}\right)}{(1-X_A)} + \frac{-\left(\frac{1}{M-1}\right)}{(M-X_A)} \\ &= \frac{1}{M-1} \left(\frac{1}{1-X_A} - \frac{1}{M-X_A} \right) \end{aligned}$$

$$\therefore \text{解 } \int_0^{X_A} \frac{dX_A}{(1-X_A)(M-X_A)} = C_{A0} \int_0^t k dt$$

$$\int_0^{X_A} \left(\frac{1}{1-X_A} - \frac{1}{M-X_A} \right) dX_A = (M-1)C_{A0}kt$$

$$-\ln(1-X_A) \Big|_0^{X_A} - [-\ln(M-X_A) \Big|_0^{X_A}] = (M-1)C_{A0}kt$$

$$-\ln(1-X_A) + [\ln(M-X_A) - \ln M] = (M-1)C_{A0}kt$$

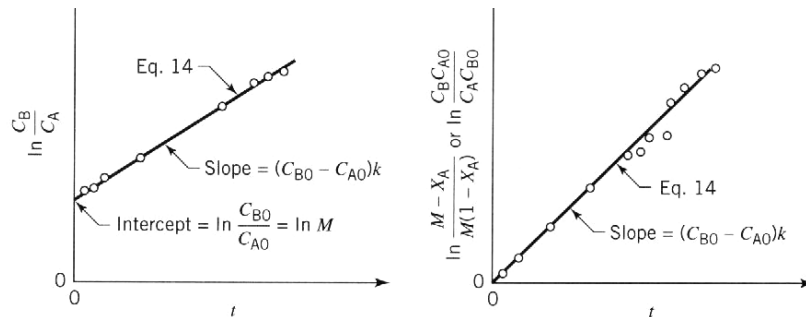
$$\ln \frac{M-X_A}{M(1-X_A)} = (M-1)C_{A0}kt = (C_{B0}-C_{A0})kt$$

$$\begin{aligned} \therefore M = C_{B0}/C_{A0} \Rightarrow M-1 &= (C_{B0}/C_{A0}) - 1 = (C_{B0}-C_{A0})/C_{A0} \\ \therefore (M-1)C_{A0} &= (C_{B0}-C_{A0}) \end{aligned}$$

$$\begin{aligned} \therefore \frac{M-X_A}{M(1-X_A)} &= \frac{\frac{C_{B0}}{C_{A0}} - X_A}{\frac{C_{B0}}{C_{A0}}(1-X_A)} = \frac{C_{B0} - C_{A0}X_A}{C_{B0}(1-X_A)} = \frac{C_B}{C_{B0}(1-X_A)} \\ &= \frac{C_{B0}(1-X_B)}{C_{B0}(1-X_A)} = \frac{(1-X_B)}{(1-X_A)} \end{aligned}$$

$$\therefore \ln \frac{M - X_A}{M(1 - X_A)} = \ln \frac{1 - X_B}{1 - X_A} = \ln \frac{C_B}{MC_A} = (M-1)C_{A0}kt = (C_{B0} - C_{A0})kt \quad \text{---(A)}$$

$$\frac{M - X_A}{M(1 - X_A)} = \frac{C_{A0}}{C_{A0}} \frac{M - X_A}{M(1 - X_A)} = \frac{C_{A0}M - C_{A0}X_A}{MC_{A0}(1 - X_A)} = \frac{C_{B0} - C_{A0}X_A}{MC_A} = \frac{C_B}{MC_A}$$



*** If C_{B0} is much larger than C_{A0} , C_B remains approximately constant at all times, and Eq. (A) approaches equation of the first-order reaction. Thus, the second-order reaction becomes a **pseudo first-order reaction**.

$$\blacksquare -r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B$$

當 $C_{B0} \gg C_{A0} \rightarrow$ 反應過程中, C_B 可視為定值

$$\text{則 } -r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B \doteq k' C_A$$

--- pseudo first-order reaction.

當然, 若 $C_{A0} \gg C_{B0} \rightarrow$ 反應過程中, C_A 可視為定值

$$\text{則 } -r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B \doteq k' C_B$$

--- pseudo first-order reaction.

④ $A + 2B \rightarrow \text{products}$ $-r_A = -\frac{dC_A}{dt} = kC_A C_B$ 的類型

$$\bullet -r_A = C_{A0} \frac{dX_A}{dt} = kC_A C_B = kC_{A0}(1 - X_A)(C_{B0} - 2C_{A0}X_A)$$

$$\text{or } -r_A = C_{A0} \frac{dX_A}{dt} = k C_{A0}^2 (1-X_A)(M-2X_A) \quad M = C_{B0}/C_{A0}$$

$$\therefore \int_0^{X_A} \frac{dX_A}{(1-X_A)(M-2X_A)} = C_{A0} \int_0^t k dt$$

$$\bullet M = 2 \rightarrow \text{回到 } -r_A = -\frac{dC_A}{dt} = 2kC_A^2 \rightarrow \frac{1}{C_{A0}} \frac{X_A}{(1-X_A)} = 2kt = k't$$

• $M \neq 2$

$$\ln \frac{M-2X_A}{M(1-X_A)} = \ln \frac{C_{A0}C_B}{C_{B0}C_A} = \ln \frac{C_B}{MC_A} = \dots = (M-2)C_{A0}kt$$

(3) Irreversible trimolecular-type third-order reactions

① 此類反應可能是

$$\textcircled{1} nA \rightarrow \text{products} \quad -r_A = -\frac{dC_A}{dt} = kC_A^3$$

$$\textcircled{2} A + B + D \rightarrow \text{products} \quad -r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = \dots = kC_A C_B C_D$$

$$\text{or } -r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A^{1.3} C_B^{0.5} C_D^{1.2}$$

$$\textcircled{3} A + 2B \rightarrow \text{products} \quad -r_A = -\frac{dC_A}{dt} = kC_A C_B^2$$

$$\text{or } -r_A = -\frac{dC_A}{dt} = kC_A^{0.8} C_B^{2.2}$$

$$\textcircled{4} A + B \rightarrow \text{products} \quad -r_A = -\frac{dC_A}{dt} = kC_A C_B^2 \quad \text{or } \dots$$

$$\textcircled{5} \dots \dots \dots$$

② 最單純的類型：

$$nA \rightarrow \text{products} \quad -r_A = -\frac{dC_A}{dt} = kC_A^3$$

$$\bullet -\frac{dC_A}{dt} = kC_A^3 \rightarrow \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^3} = -\int_0^t k dt$$

$$-\frac{1}{2} \frac{1}{C_A^2} \Big|_{C_{A0}}^{C_A} = -kt$$

$$\frac{1}{2} \left(\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} \right) = kt \rightarrow \frac{1}{C_A^2} = 2kt + \frac{1}{C_{A0}^2}$$

① 以 _____ 對時間 t 作圖得一斜率為 _____ 的直線，其截距為 _____。

$$\textcircled{2} t_{1/2} = \frac{3}{2k[A]_0^2} \rightarrow \therefore \text{half-life time 和 } [A]_0^2 \text{ 成反比。 (和 } \frac{1}{[A]_0^2} \text{ 成正比)}$$

③ $A + B + D \rightarrow \text{products}$ $-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = \dots = kC_A C_B C_D$ 的類型

●以 X_A 表示，則

$$C_{A0} \frac{dX_A}{dt} = k C_{A0}^2 (1-X_A) \left(\frac{C_{B0}}{C_{A0}} - X_A \right) \left(\frac{C_{D0}}{C_{A0}} - X_A \right)$$

積分得

$$\frac{1}{(C_{A0} - C_{B0})(C_{A0} - C_{D0})} \ln \frac{C_{A0}}{C_A} + \frac{1}{(C_{B0} - C_{D0})(C_{B0} - C_{A0})} \ln \frac{C_{B0}}{C_B} + \frac{1}{(C_{D0} - C_{A0})(C_{D0} - C_{B0})} \ln \frac{C_{D0}}{C_D} = kt$$

④ $A + 2B \rightarrow \text{products}$ $-r_A = -\frac{dC_A}{dt} = kC_A C_B^2$ 的類型

●以 X_A 表示，則

$$\frac{dX_A}{dt} = k C_{A0}^2 (1-X_A) \left(\frac{C_{B0}}{C_{A0}} - 2X_A \right)^2 = k C_{A0}^2 (1-X_A) (M - 2X_A)^2$$

積分得

◆ $M = 2 \rightarrow$ 回到 $-\frac{dC_A}{dt} = kC_A^3$

$$\rightarrow \frac{1}{2} \left(\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} \right) = (4k)t \rightarrow \frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 8kt$$

◆ $M \neq 2$

$$\frac{(2C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0} C_B} + \ln \frac{C_{A0} C_B}{C_{B0} C_A} = (2C_{A0} - C_{B0})^2 kt$$

(4) Zero-order reaction

$$-r_A = -\frac{dC_A}{dt} = k$$

$$\therefore \int_{C_{A0}}^{C_A} dC_A = - \int_0^t k dt \rightarrow C_A - C_{A0} = -kt$$

$$\hookrightarrow C_{A0} - C_A = C_{A0} X_A = kt$$

①以 C_A 對時間 t 作圖 \rightarrow 得一 slope = _____ 的直線，其截距為 _____。

②以 X_A 對時間 t 作圖 \rightarrow 得一穿過原點的直線，其 slope = _____。

③at $t_{1/2} \rightarrow C_A = 1/2 C_{A0} \rightarrow t_{1/2} = \frac{C_{A0}}{2k}$

\hookrightarrow ●Zero-order reaction 的 half-life time 與初濃度成正比。

(5) Empirical rate equations of nth order

※※ 只看 $-r_A = -\frac{dC_A}{dt} = kC_A^n$ 的型式

① $n = 1 \rightarrow -r_A = -\frac{dC_A}{dt} = kC_A \rightarrow -\ln \frac{C_A}{C_{A0}} = kt$

② $n \neq 1 \rightarrow \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^n} = -\int_0^t k dt \rightarrow C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt$

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^n} = \int_{C_{A0}}^{C_A} C_A^{-n} dC_A = \frac{1}{1-n} C_A^{1-n} \Big|_{C_{A0}}^{C_A} = -kt$$
$$\therefore C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt$$

| | order 與作圖的關係 | 半衰期和 C_{A0} 的關係 |
|-----|--------------------|----------------------------|
| 0 級 | C_A 對時間作圖成直線 | $t_{1/2}$ 和 C_{A0} 成正比 |
| 1 級 | $\ln C_A$ 對時間作圖成直線 | $t_{1/2}$ 和 C_{A0} 無關 |
| 2 級 | $1/C_A$ 對時間作圖成直線 | $t_{1/2}$ 和 C_{A0} 成反比 |
| 3 級 | $1/C_A^2$ 對時間作圖成直線 | $t_{1/2}$ 和 C_{A0}^2 成反比 |

Example 3-1:

Acetone 在 600°C 進行 isobaric, thermal decomposition, 已知此反應為 1st-order reaction, half-life time 為 200 sec, 求分解 25% 所需的時間?

Example 3-2:

定溫、定容下, 某化學反應 $A \rightarrow$ 產物 為 3 級反應, 若反應物的 initial concentration 為 10 M, 經 600 sec 後, 發現反應物的為 4 M, 則 300 sec 時, 反應物的濃度為何?

Example 3-3:

A 40-minute experimental run shows that 75% of liquid reactant is converted to product by a $\frac{1}{2}$ -order rate. What would be the fraction converted in a half-hour run?

Example 3-4:

反應 $A + B \rightarrow \text{products}$, $-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B$ 。已知 A 與 B 的 initial concentration 為 $C_{A0} = 0.1 \text{ M}$; $C_{B0} = 0.2 \text{ M}$ 。(1)請導出濃度與時間的關係 (2)當反應 10 分鐘時, 得到 A 的轉化率為 20%, 求達到轉化率 $X_A = 90\%$ 所需之時間。

[解] 時間 = t 時, A 的轉化率為 X_A

$$\text{則 } C_A = C_{A0}(1-X_A) \text{ 且 } C_B = C_{B0} - C_{A0}X_A = C_{A0}(C_{B0}/C_{A0} - X_A) = C_{A0}(2 - X_A)$$

$$\therefore -r_A = -\frac{dC_A}{dt} = C_{A0} \frac{dX_A}{dt} = kC_A C_B = k[C_{A0}(1-X_A)][C_{A0}(2-X_A)]$$

$$\text{or } -r_A = C_{A0} \frac{dX_A}{dt} = k C_{A0}^2 (1-X_A)(2-X_A)$$

$$\therefore \int_0^{X_A} \frac{dX_A}{(1-X_A)(2-X_A)} = C_{A0} \int_0^t k dt$$

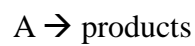
Example 3-5:

After 5 minutes in a batch reactor, reactant ($C_{A0} = 1$ mol/liter) is 47.3% converted; after 20 minutes, conversion is 75.4%. Find a rate equation to represent this reaction.

$$-r_A = -\frac{dC_A}{dt} = 0.2 C_A^{2.3}$$

Example 3-6:

Reactant A decomposes in a batch reactor



The composition of A in the reactor is measured at various times with results shown in the following columns 1 and 2. Find a rate equation to represent the data.

| column 1 | column 2 |
|----------|-------------------|
| Time | Concentration |
| t, s | C_A , mol/liter |
| 0 | 10 |
| 20 | 8 |
| 40 | 6 |
| 60 | 5 |
| 120 | 3 |
| 180 | 2 |
| 300 | 1 |

*熟悉以下基本為微積分：

$$\blacklozenge \frac{de^x}{dx} = e^x \quad \blacklozenge \int e^x dx = e^x \quad \blacklozenge \frac{de^{-5x}}{dx} = \frac{d(-5x)}{dx} \frac{de^{-5x}}{d(-5x)} = -5e^{-5x}$$

$$\blacklozenge \int e^{-5x} dx = \frac{1}{-5} \int e^{-5x} d(-5x) = \frac{1}{-5} e^{-5x}$$

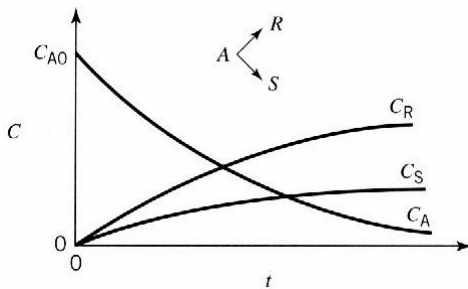
則可解每一個方程式而得到：

$$[R] = \frac{-k_1[A]_0}{k_1+k_2} (e^{-(k_1+k_2)t} - 1) = \frac{k_1[A]_0}{k_1+k_2} (1 - e^{-(k_1+k_2)t})$$

$$[S] = \frac{k_2[A]_0}{k_1+k_2} (1 - e^{-(k_1+k_2)t})$$

② selectivity = $\frac{\text{得到的 R 產物之量}}{\text{得到的 S 產物之量}}$

$$= \frac{[R] - [R]_0}{[S] - [S]_0} = \frac{[R]}{[S]} = \frac{r_R}{r_S} = \frac{k_1[A]}{k_2[A]} = \frac{k_1}{k_2}$$



● Typical concentration-time curve of reactions $A \xrightarrow{k_1} R$ and $A \xrightarrow{k_2} S$ ($k_1 > k_2$, and $[R]_0 = 0$, $[S]_0 = 0$).

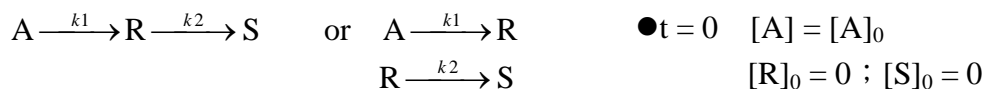
Example 3-7:

— 1st-order reaction $A \xrightarrow{k_1} R$ 且 $A \xrightarrow{k_2} S$ ， $[A]_0 = 1.5 \text{ M}$ 且 $[R]_0 = [S]_0 = 0$ 。在一反應器中進行反應，若 A 的轉化率 $X_A = 0.4$ 時， $[R] = 0.2 \text{ mol/l}$ ，求

- (A) $\frac{[R]}{[S]}$ (B) 若反應 20 分鐘時， $X_A = 0.75$ ，求 rate constant k_1 及 k_2 。

(2) Irreversible reactions in series

● Consider consecutive unimolecular-type first-order reactions



$$\textcircled{1} -\frac{d[A]}{dt} = k_1[A] \rightarrow \frac{d[A]}{dt} = -k_1[A] \quad \begin{array}{l} \bullet t = t \quad [A] = [A] \\ \quad \quad \quad [R] = [R] \\ \quad \quad \quad [S] = [S] \end{array}$$

$$\textcircled{2} \frac{d[R]}{dt} = R \text{ 之生成} - R \text{ 之消耗} = k_1[A] - k_2[R]$$

$$\textcircled{3} \frac{d[S]}{dt} = k_2[R]$$

由 $\textcircled{1}$ 知 $\frac{d[A]}{[A]} = -k_1 dt \rightarrow \int \frac{d[A]}{[A]} = \int -k_1 dt \rightarrow \ln[A] = -k_1 t + C$

而條件 $t = 0$ 時, $[A] = [A]_0 \rightarrow \ln[A]_0 = -k_1 \times 0 + C \therefore C = \ln[A]_0$

$\therefore \ln[A] = -k_1 t + \ln[A]_0 \rightarrow \ln[A] - \ln[A]_0 = -k_1 t$

$\therefore \ln([A]/[A]_0) = -k_1 t \rightarrow [A]/[A]_0 = e^{-k_1 t} \rightarrow [A] = [A]_0 e^{-k_1 t}$ 代入 $\textcircled{2}$ 式得

$$\frac{d[R]}{dt} + k_2[R] = k_1[A]_0 e^{-k_1 t}$$

◆ $\frac{d[R]}{dt} + k_2[R] = k_1[A]_0 e^{-k_1 t}$ 是符合 first-order linear differential eq. 的 $\frac{dy}{dx} + Py = Q$ 的形式。解題時先找出積分因子 $e^{\int P dx}$ ，而解為

$$y e^{\int P dx} = \int Q e^{\int P dx} dx + C$$

◆ 以 $\frac{dy}{dx} + 2xy - 6x = 0$ 為例：

$$\frac{dy}{dx} + 2xy = 6x \rightarrow \text{積分因子 } e^{\int P dx} = e^{\int 2x dx} = e^{x^2}$$

所以答案是 $y e^{x^2} = \int (6x) e^{x^2} dx + C = \int 3 e^{x^2} dx^2 + C = 3 e^{x^2} + C$

即 $y = 3 + C/e^{x^2} = 3 + C e^{-x^2}$

$[dx^2 = 2x dx ; dx^3 = 3x^2 dx \rightarrow \text{所以 } (6x) e^{x^2} dx = 3 e^{x^2} (2x) dx = 3 e^{x^2} dx^2]$

$$\begin{aligned}
 \bullet \text{驗算: } \frac{dy}{dx} + 2xy &= \frac{d(3 + Ce^{-x^2})}{dx} + 2x(3 + Ce^{-x^2}) \\
 &= \frac{d(Ce^{-x^2})}{dx} + 2x(3 + Ce^{-x^2}) = C \frac{d(-x^2)}{dx} \frac{de^{-x^2}}{d(-x^2)} + 2x(3 + Ce^{-x^2}) \\
 &= -2xCe^{-x^2} + 6x + 2xCe^{-x^2} = 6x
 \end{aligned}$$

$$\therefore \text{解 } \frac{d[R]}{dt} + k_2[R] = k_1[A]_0 e^{-k_1 t}$$

$$\text{積分因子 } e^{\int k_2 dt} = e^{k_2 t}; \quad Q = k_1[A]_0 e^{-k_1 t}$$

$$\therefore \text{正解是 } e^{k_2 t} [R] = \int (k_1[A]_0 e^{-k_1 t}) e^{k_2 t} dt + C$$

$$= k_1[A]_0 \int e^{(k_2 - k_1)t} dt + C = \frac{k_1[A]_0}{k_2 - k_1} e^{(k_2 - k_1)t} + C$$

而 $t = 0$ 時, $[R] = 0$

$$\therefore e^0 \times 0 = \frac{k_1[A]_0}{k_2 - k_1} e^0 + C \rightarrow C = -\frac{k_1[A]_0}{k_2 - k_1}$$

$$\therefore e^{k_2 t} [R] = \frac{k_1[A]_0}{k_2 - k_1} e^{(k_2 - k_1)t} - \frac{k_1[A]_0}{k_2 - k_1}$$

$$\text{整理得 } [R] = \frac{k_1[A]_0}{k_2 - k_1} \left(\frac{e^{(k_2 - k_1)t}}{e^{k_2 t}} - \frac{1}{e^{k_2 t}} \right) = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

◆ 注意: $e^{-k_1 t} - e^{-k_2 t} \neq e^{(k_2 - k_1)t}$

◆ $\therefore [A]_0 = [A] + [R] + [S]$

$$\therefore [S] = [A]_0 - [A] - [R] = [A]_0 - [A]_0 e^{-k_1 t} - \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$= [A]_0 \left(1 - e^{-k_1 t} - \frac{k_1}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right)$$

$$= [A]_0 \left[1 - \left(\frac{k_2 - k_1}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_1 t} \right) + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right]$$

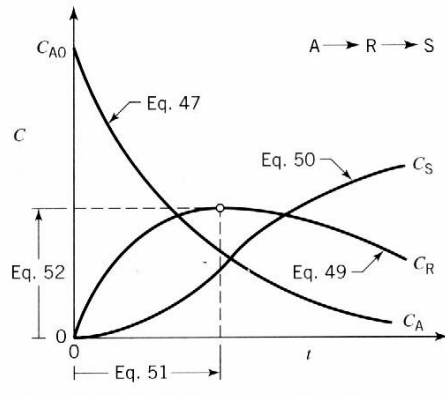
$$= [A]_0 \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right)$$

$$= [A]_0 \left(1 + \frac{k_2}{k_1 - k_2} e^{-k_1 t} - \frac{k_1}{k_1 - k_2} e^{-k_2 t} \right)$$

$$\ast k_2 \gg k_1 \rightarrow [S] = [A]_0 (1 - e^{-k_1 t})$$

$$\ast k_1 \gg k_2 \rightarrow [S] = [A]_0 (1 - e^{-k_2 t})$$

◆ A、R、S 的 concentration-time curve 為



* Obviously, there existed the maximum concentration of R. The time

at which the maximum concentration of R occurs at $\frac{d[R]}{dt} = 0$.

$$\frac{d[R]}{dt} = 0 = \frac{d}{dt} \left\{ \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \right\}$$

$$\Rightarrow \frac{d}{dt} (e^{-k_1 t} - e^{-k_2 t}) = 0 \Rightarrow -k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0$$

$$\Rightarrow k_1 e^{-k_1 t} = k_2 e^{-k_2 t} \Rightarrow \ln k_1 + \ln e^{-k_1 t} = \ln k_2 + \ln e^{-k_2 t}$$

$$\Rightarrow \ln k_1 + (-k_1 t) = \ln k_2 + (-k_2 t)$$

$$\therefore t = \frac{\ln k_2 - \ln k_1}{k_2 - k_1} = \frac{\ln(k_2 / k_1)}{k_2 - k_1} = t_{\max} \text{ ----- 達到最大值[R]所需的時間。}$$

將此 t_{\max} 代入 $[R] = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$ 得最大的[R]值

$$[R]_{\max} = \frac{k_1[A]_0}{k_2 - k_1} \left\{ \exp\left[\frac{-k_1}{k_2 - k_1} \ln(k_2 / k_1)\right] - \exp\left[\frac{-k_2}{k_2 - k_1} \ln(k_2 / k_1)\right] \right\}$$

$$= \frac{k_1[A]_0}{k_2 - k_1} \left\{ \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_1}{k_2 - k_1}\right)} - \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2 - k_1}\right)} \right\}$$

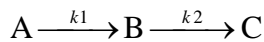
$$= \frac{k_1[A]_0}{k_2 - k_1} \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2 - k_1}\right)} \left\{ \frac{\left(\frac{k_1}{k_2}\right)^{\left(\frac{k_1}{k_2 - k_1}\right)}}{\left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2 - k_1}\right)}} - 1 \right\}$$

$$= \frac{k_1[A]_0}{k_2 - k_1} \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2 - k_1}\right)} \left\{ \left(\frac{k_1}{k_2}\right)^{\left[\left(\frac{k_1}{k_2 - k_1}\right) - \left(\frac{k_2}{k_2 - k_1}\right)\right]} - 1 \right\}$$

$$\begin{aligned}
&= \frac{k_1[A]_0}{k_2 - k_1} \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2 - k_1}\right)} \left\{ \left(\frac{k_1}{k_2}\right)^{-1} - 1 \right\} \\
&= \frac{k_1[A]_0}{k_2 - k_1} \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2 - k_1}\right)} \left\{ \frac{k_2}{k_1} - 1 \right\} \\
&= \frac{k_1[A]_0}{k_2 - k_1} \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2 - k_1}\right)} \left(\frac{k_2 - k_1}{k_1}\right) \\
\therefore \frac{[R]_{\max}}{[A]_0} &= \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2 - k_1}\right)}
\end{aligned}$$

Example 3-8:

Consider the series of the first-order irreversible reactions



The initial concentration of A is $[A]_0$. Neither B nor C is present initially.

(A) Derive the expressions for the variations of $[A]$, $[B]$ and $[C]$ with time.

(B) At what time does the concentration of B reach a maximum?

Sol:

$$(A) \textcircled{1} -\frac{d[A]}{dt} = k_1[A] \rightarrow \frac{d[A]}{dt} = -k_1[A]$$

$$\textcircled{2} \frac{d[B]}{dt} = \text{B 之生成} - \text{B 之消耗} = k_1[A] - k_2[B]$$

$$\textcircled{3} \frac{d[C]}{dt} = k_2[C]$$

$$(B) t = \frac{\ln k_2 - \ln k_1}{k_2 - k_1} = \frac{\ln(k_2/k_1)}{k_2 - k_1} = t_{\max}$$

Example 3-9:

For the first-order reactions in series $P \xrightarrow{k_1} Q \xrightarrow{k_2} R$ with $k_1 = k_2 = 0.25 \text{ min}^{-1}$, find the time required to reach the maximum concentration of Q.

$$t_{\max} = 1/k_1 = 4 \text{ min.}$$

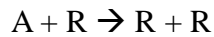
Sol: 與上題一模一樣的解法，但把 k_2 改成 k_1 ，最後得 $t_{\max} = 1/k_1$ 。不可將 $k_1 = k_2$

$$\text{得數值代入 } t_{\max} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

(3) Autocatalytic reaction

❶ A reaction in which one of the products of reaction acts as a catalyst is called an autocatalytic reaction.

❷ The simplest such reaction is



$$\text{Rate equation } -r_A = -\frac{dC_A}{dt} = kC_A C_R$$

∵ 反應過程，系統的總 mol 數不變(why?)

$$\therefore C_0 = C_{A0} + C_{R0} = C_A + C_R = \text{constant}$$

$$\therefore -r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$$

$$-\frac{dC_A}{C_A(C_0 - C_A)} = kdt$$

$$\therefore \int_{C_{A0}}^{C_A} \left[-\frac{1}{C_0} \left(\frac{1}{C_A} + \frac{1}{C_0 - C_A} \right) \right] dC_A = \int_0^t kdt$$

$$\ln \frac{C_A}{C_{A0}} + \ln \frac{C_0 - C_{A0}}{C_0 - C_A} = -C_0 kt \quad \rightarrow \quad -\ln \frac{C_A}{C_{A0}} - \ln \frac{C_0 - C_{A0}}{C_0 - C_A} = C_0 kt$$

$$\text{or } \ln \frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = \ln \frac{C_{A0}C_R}{C_A C_{R0}} = \ln \frac{C_R/C_{R0}}{C_A/C_{A0}} = C_0 kt = (C_{A0} + C_{R0})kt$$

●若初濃度比 $M = C_{R0}/C_{A0}$ ，則上式可變成 $\ln \frac{M + X_A}{M(1 - X_A)} = (C_{A0} + C_{R0})kt$

$$\begin{aligned} \ln \frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} &= \ln \frac{C_{A0}C_R}{C_A C_{R0}} = \ln \frac{C_{A0}(C_{A0} + C_{R0} - C_A)}{C_{R0}C_{A0}(1 - X_A)} \\ &= \ln \frac{(C_{A0} + C_{R0} - C_A)}{C_{R0}(1 - X_A)} = \ln \frac{(C_{A0} + C_{R0} - C_A)}{C_{R0}(1 - X_A)} = \ln \frac{(C_{A0}X_A + C_{R0})}{C_{R0}(1 - X_A)} \\ &= \ln \frac{(X_A + C_{R0}/C_{A0})}{(C_{R0}/C_{A0})(1 - X_A)} = \ln \frac{M + X_A}{M(1 - X_A)} \end{aligned}$$

別忘了！ Constant-volume system 下：

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{C_A}{C_{A0}} ; C_A = C_{A0}(1 - X_A) ; C_{A0} - C_A = C_{A0}X_A$$

◆反應物 A 加入少量 R 進行 $A + R \rightarrow R + R$ 的 Autocatalytic reaction：

●時段一 → 起使期，反應速率較慢，單位時間的轉化率低。

原因：_____

●時段二 → 增速期，反應速率變快，單位時間的轉化率高。

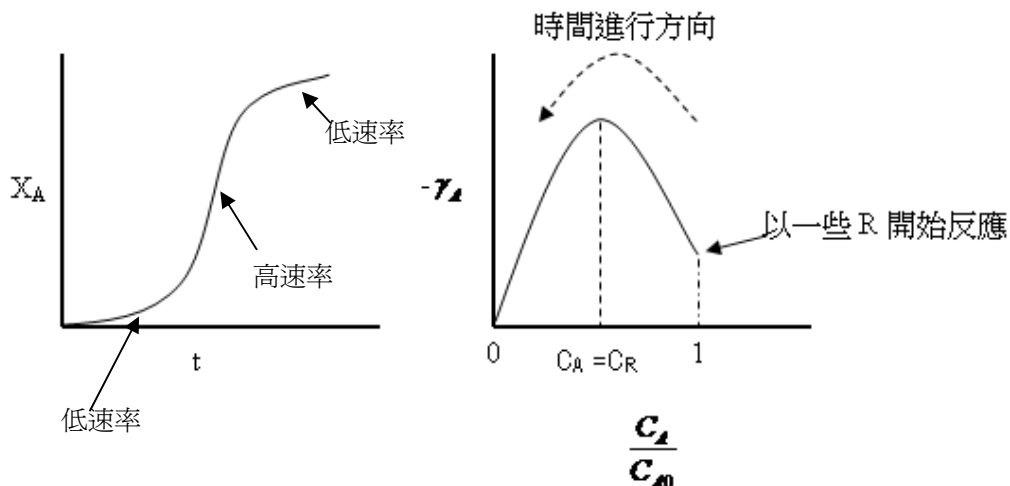
原因：_____

●時段三 → 速率達最高值後，進入衰減期，反應速率逐漸變慢(但仍算快速反應)，單位時間的轉化率仍高。

原因：_____

●時段四 → 反應速率很慢，單位時間的轉化率又很低。

原因：_____



◆因為反應速率存在著最大值，因此，假設時間為 t_{\max} 時，反應速率達最

大值 \rightarrow 則 $\frac{d(-\gamma_A)}{dt} = 0$ 求出 t_{\max} 與 $(-\gamma_A)_{\max}$ 。

Example 3-10:

乙酸甲酯的水解： $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$

產生的乙酸會產生 H^+ 來催化反應而加速水解。若乙酸甲酯和乙酸的出濃度分別為 500 及 5 mmol/L。經 5.4×10^3 秒後，conversion 為 70%。求此反應之最大速率和達此值之時間。

[解] $\text{A} + \text{R} \rightarrow \text{R} + \text{S} \rightarrow$ 可視為 $\text{A} + \text{R} \rightarrow \text{R} + \text{R}$

(因為隨著反應時間的增加，R 的濃度將幾乎等於 S 的濃度。)

$$C_0 = C_{A0} + C_{R0} = 0.5 + 0.005 = 0.505 \text{ mol/L}$$

$$M = C_{R0}/C_{A0} = 0.005/0.5 = 0.01$$

$$-r_A = -\frac{dC_A}{dt} = kC_A C_R = kC_A(C_0 - C_A)$$

$$-\frac{dC_A}{C_A(C_0 - C_A)} = kdt \rightarrow \int_{C_{A0}}^{C_A} \left[-\frac{1}{C_0} \left(\frac{1}{C_A} + \frac{1}{C_0 - C_A} \right) \right] dC_A = \int_0^t kdt$$

$$\therefore \ln \frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = C_0 kt$$

$$\text{or } \frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = e^{C_0 kt} \rightarrow \frac{C_{A0}}{C_A C_{R0}} (C_0 - C_A) = e^{C_0 kt}$$

$$\frac{1}{C_A M} (C_0 - C_A) = e^{C_0 kt} \rightarrow C_0 - C_A = C_A M e^{C_0 kt}$$

$$C_A = \frac{C_0}{1 + M e^{C_0 kt}}$$

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A) = kC_A C_0 - C_A^2$$

$$= kC_0^2 \left[\frac{1}{1 + M e^{C_0 kt}} - \frac{1}{(1 + M e^{C_0 kt})^2} \right]$$

$$\therefore \text{最大速率} \rightarrow \frac{d(-\gamma_A)}{dt} = 0 = \frac{d}{dt} \left\{ kC_0^2 \left[\frac{1}{1 + M e^{C_0 kt}} + \frac{1}{(1 + M e^{C_0 kt})^2} \right] \right\}$$

$$0 = kC_0^3 M e^{C_0 kt_{\max}} \left[\frac{-1}{(1 + M e^{C_0 kt_{\max}})^2} + \frac{2}{(1 + M e^{C_0 kt_{\max}})^3} \right]$$

$$\therefore 1 + M e^{C_0 kt_{\max}} = 1 \rightarrow e^{C_0 kt_{\max}} = 1/M$$

$$\rightarrow t_{\max} = \frac{1}{C_0 k} \ln \frac{1}{M} \rightarrow \text{需要 } k \text{ 值才能求得 } t_{\max}$$

再把 $1 + Me^{C_0kt_{\max}} = 1$ 代入

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A) = kC_0^2 \left[\frac{1}{1 + Me^{C_0kt}} - \frac{1}{(1 + Me^{C_0kt})^2} \right]$$

$$\text{得 } (-\gamma_A)_{\max} = kC_0^2 \left[\frac{1}{2} - \frac{1}{(2)^2} \right] = \frac{1}{4} kC_0^2$$

→ 需要 k 值才能得 $(-\gamma_A)_{\max}$

由於 $t = 5.4 \times 10^3 \rightarrow X_A = 70\%$ ，即 $C_A = C_{A0}(1 - X_A) = 0.15 \text{ M}$ 代入

$$\ln \frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = C_0kt \text{ (或其他式子亦可)}$$

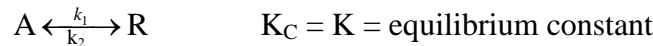
$$\text{得 } \ln \frac{0.5(0.505 - 0.15)}{0.15(0.505 - 0.5)} = 0.505 \times k \times 5400 \rightarrow k = 2 \times 10^{-3}$$

$$\therefore t_{\max} = \frac{1}{C_0k} \ln \frac{1}{M} = \frac{1}{0.505 \times 2 \times 10^{-3}} \ln \frac{1}{0.01} = 4560 \text{ sec}$$

$$(-\gamma_A)_{\max} = \frac{1}{4} kC_0^2 = \frac{1}{4} \times 2 \times 10^{-3} \times 0.505^2 = 1.28 \times 10^{-4} \text{ (mol/L)s}^{-1}$$

(4) First-order reversible reactions:

● The simplest case is:



$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = k_1C_A - k_2C_R \quad (\text{或 } \frac{dC_A}{dt} = -k_1C_A + k_2C_R)$$

① Start with a concentration ratio $M = C_{R0}/C_{A0}$

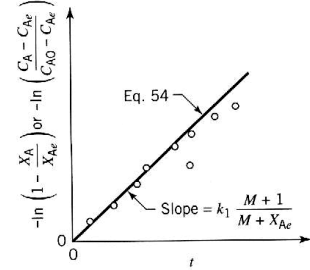
$$\begin{aligned} \therefore \frac{dC_R}{dt} = -\frac{dC_A}{dt} &= C_{A0} \frac{dX_A}{dt} = k_1C_A - k_2C_R \\ &= k_1(C_{A0} - C_{A0}X_A) - k_2(C_{R0} + C_{A0}X_A) \\ &= k_1(C_{A0} - C_{A0}X_A) - k_2(MC_{A0} + C_{A0}X_A) \end{aligned}$$

② At equilibrium → $K_C \equiv \frac{k_1}{k_2} \equiv \frac{C_{Re}}{C_{Ae}} = \frac{C_{R0} + C_{A0}X_{Ae}}{C_{A0}(1 - X_{Ae})} = \frac{M + X_{Ae}}{1 - X_{Ae}}$

$$\begin{aligned} \therefore C_{A0} \frac{dX_A}{dt} &= k_1(C_{A0} - C_{A0}X_A) - k_2(MC_{A0} + C_{A0}X_A) \\ \therefore \frac{dX_A}{dt} &= k_1(1 - X_A) - k_2(M + X_A) = k_1 \left[(1 - X_A) - \frac{k_2}{k_1} (M + X_A) \right] \\ &= k_1 \left[(1 - X_A) - \frac{1 - X_{Ae}}{M + X_{Ae}} (M + X_A) \right] \\ &= k_1 \left[\frac{M + X_{Ae} - MX_{Ae} - X_A X_{Ae} - M - X_A + MX_{Ae} + X_{Ae} X_A}{M + X_{Ae}} \right] \end{aligned}$$

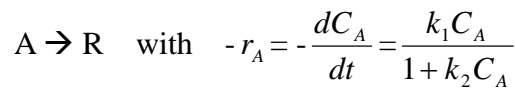
$$\begin{aligned}
&= k_1 \left[\frac{X_{Ae} - MX_{Ae} - X_A + MX_{Ae}}{M + X_{Ae}} \right] \\
&= \frac{k_1}{M + X_{Ae}} [X_{Ae}(1+M) - X_A(1+M)] = \frac{k_1(1+M)}{M + X_{Ae}} [X_{Ae} - X_A] \\
\therefore -\frac{1}{X_A - X_{Ae}} dX_A &= \frac{k_1(1+M)}{M + X_{Ae}} dt \\
\int_0^{X_A} \frac{1}{X_A - X_{Ae}} dx &= -\frac{(1+M)}{M + X_{Ae}} \int_0^t k_1 dt \\
\ln(X_A - X_{Ae}) \Big|_0^{X_A} &= -\frac{(1+M)}{M + X_{Ae}} k_1 t \\
\Rightarrow \ln \frac{X_A - X_{Ae}}{-X_{Ae}} &= -\frac{(1+M)}{M + X_{Ae}} k_1 t \Rightarrow \ln \frac{X_{Ae} - X_A}{X_{Ae}} = -\frac{(1+M)}{M + X_{Ae}} k_1 t \\
\therefore -\ln \frac{X_{Ae} - X_A}{X_{Ae}} &= -\ln \left(1 - \frac{X_A}{X_{Ae}} \right) = -\ln \frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = \frac{(1+M)}{M + X_{Ae}} k_1 t
\end{aligned}$$

* 別忘了! $X_{Ae} = (C_{A0} - C_{Ae})/C_{A0}$; $X_A = (C_{A0} - C_A)/C_{A0}$



(5) Reaction of shifting order:

- 有的反應可能在 high concentrations 時為一種 reaction order，在 low concentrations 時為另一種 reaction order。
- ① Consider the reaction:



① At high C_A (or $k_2 C_A \gg 1$)

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A} =$$

↳ the reaction is of zero order with rate constant k_1/k_2 .

② At low C_A (or $k_2 C_A \ll 1$)

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A} =$$

↳ the reaction is of first order with rate constant k_1 .

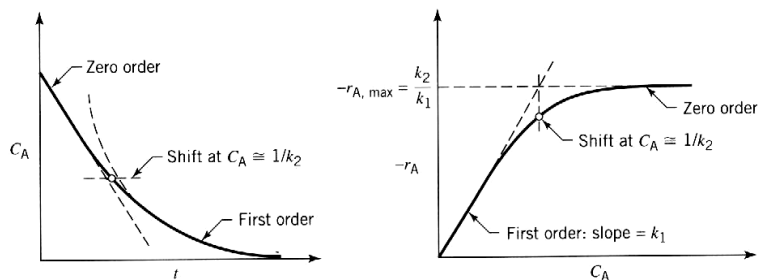


Figure 3.15 Behavior of a reaction that follows Eq. 57.

$$\textcircled{2} \text{ 由 } -r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1+k_2 C_A} \rightarrow \int_{C_{A0}}^{C_A} \frac{1+k_2 C_A}{C_A} dC_A = -\int_0^t k_1 dt$$

$$\therefore \ln \frac{C_A}{C_{A0}} + k_2(C_A - C_{A0}) = -k_1 t$$

$$\text{or } \ln \frac{C_{A0}}{C_A} + k_2(C_{A0} - C_A) = k_1 t$$

●從 page 3-2 至此都是在介紹 Integral method of analysis of data。

5. Differential method of analysis of data:

(1) 以 C_A 對時間 t 作圖。

(2) 求出每個點的切線及其斜率(需利用微分方式)，此斜率為 dC_A/dt ，加個負號即為每個點的瞬間反應速度 $-r_A = -\frac{dC_A}{dt}$ 。

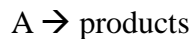
$$(3) \because -r_A = -\frac{dC_A}{dt} = kC_A^n \rightarrow \ln(-r_A) = \ln k + n \ln C_A$$

\therefore 再以 $\ln(-r_A)$ 對 $\ln C_A$ 作圖(用 \log 亦可) \rightarrow 其 slope 為 n ；截距為 $\ln k$

$$\therefore -r_A = -\frac{dC_A}{dt} = kC_A^n \text{ 即可順利求出來}$$

Example 3-11:

Reactant A decomposes in a batch reactor



The composition of A in the reactor is measured at various times with results shown in the following columns 1 and 2. Find a rate equation to represent the data.

| column 1 | column 2 |
|--------------|------------------------------------|
| Time t, s | Concentration C_A , mol/liter |
| 0 | 10 |
| 20 | 8 |
| 40 | 6 |
| 60 | 5 |
| 120 | 3 |
| 180 | 2 |
| 300 | 1 |

[解] (1) 以 C_A 對時間 t 作圖得 Fig. A。

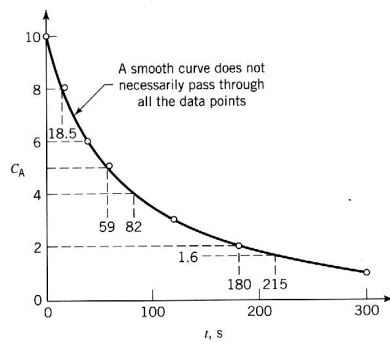


Fig. A

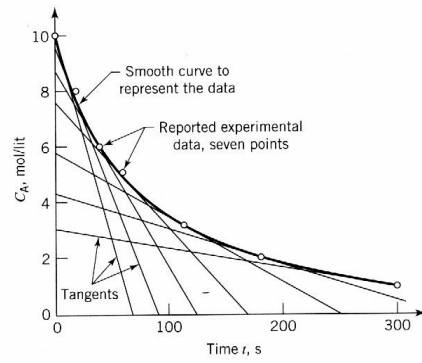


Fig. B

(2) 求出每個點的切線(Fig. B)及其斜率(需利用微分方式)，此斜率為

dC_A/dt ，加個負號即為每個點的瞬間反應速度 $-r_A = -\frac{dC_A}{dt}$ (Table I)。

| Column 1 | Column 2 | Column 3 | Column 4 | Column 5 |
|----------------|--|---------------------------------------|-----------------------|-----------------|
| Time t, s | Concentration $C_A, \text{mol/liter}$ | Slope, from Fig. E3.2a (dC_A/dt) | $\log_{10}(-dC_A/dt)$ | $\log_{10} C_A$ |
| 0 | 10 | $(10 - 0)/(0 - 75) = -0.1333$ | -0.875 | 1.000 |
| 20 | 8 | $(10 - 0)/(-3 - 94) = -0.1031$ | -0.987 | 0.903 |
| 40 | 6 | $(10 - 0)/(-21 - 131) = -0.0658$ | -1.182 | 0.778 |
| 60 | 5 | $(8 - 0)/(-15 - 180) = -0.0410$ | -1.387 | 0.699 |
| 120 | 3 | $(6 - 0)/(-10 - 252) = -0.0238$ | -1.623 | 0.477 |
| 180 | 2 | $(4 - 1)/(24 - 255) = -0.0108$ | -1.967 | 0.301 |
| 300 | 1 | $(3 - 1)/(-10 - 300) = -0.0065$ | -2.187 | 0.000 |

Table I

(3) 求出 $\log(-r_A)$ 與 $\log C_A$ 的值(Table I)。

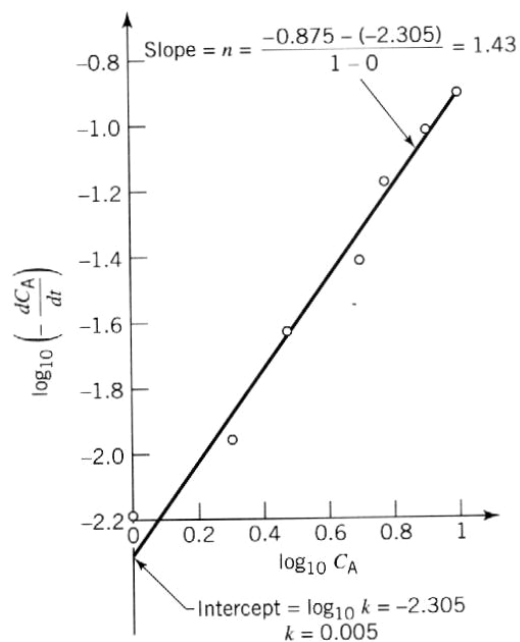
(4) 以 $\log(-r_A)$ 對 $\log C_A$ 作圖(Fig. C) \rightarrow 其 slope 為 n ；截距為 $\ln k$ 。

由右圖(Fig. C)知：

$$\text{slope} = 1.43$$

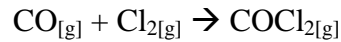
$$\log k = -2.305 \rightarrow k = 0.00495$$

$$\therefore -r_A = -\frac{dC_A}{dt} = 0.00495 C_A^{1.43}$$



§3-2. Varying-Volume Batch Reactor

1. 如前所述，在一個 1 liter 的 reactor 中，混合 1 mol 的 CO 和 1 mol 的 Cl₂ 在 isothermal, constant-pressure 下進行反應



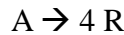
∴ 則反應前後的 mole 數改變 → 系統的體積改變

● Consider a isothermal and isobaric gas-phase reaction:

① Define: ϵ_A = the fractional change in volume of the system between no conversion and complete conversion of reactant A.

$$\therefore \epsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}$$

● For example: A isothermal and isobaric gas-phase reaction:



① Start with pure reactant A of 1 mole:

| | | | |
|--------------------|-------|---|-------|
| | A | → | 4 R |
| X _A = 0 | 1 mol | | 0 |
| X _A = 1 | 0 | | 4 mol |

$$\therefore \epsilon_A = \frac{4-1}{1} = 3$$

$$\epsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} = \frac{4RT/P - 1RT/P}{1RT/P} = \frac{4-1}{1}$$

◆ 若 X_A = 0.4 → 系統的體積變成多少？

| | | | |
|----------------------|-------|---|---------|
| | A | → | 4 R |
| X _A = 0 | 1 mol | | 0 |
| X _A = 0.4 | 0.6 | | 1.6 mol |

$$X_A = 0 \rightarrow n_{\text{total}} = 1 \text{ mol} \rightarrow V_0 = 1RT/P$$

$$X_A = 0.4 \rightarrow n_{\text{total}} = 2.2 \text{ mol} \rightarrow V = 2.2RT/P = 2.2 V_0 = V_0(1 + 3 \times 0.4) = V_0(1 + \epsilon_A \times X_A)$$

◆ 若 X_A = 0.85 → 系統的體積變成多少？

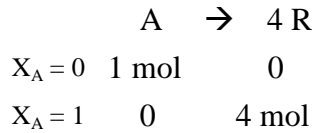
| | | | |
|-----------------------|-------|---|---------|
| | A | → | 4 R |
| X _A = 0 | 1 mol | | 0 |
| X _A = 0.85 | 0.15 | | 3.4 mol |

$$X_A = 0 \rightarrow n_{\text{total}} = 1 \text{ mol} \rightarrow V_0 = 1RT/P$$

$$X_A = 0.85 \rightarrow n_{\text{total}} = 3.55 \text{ mol}$$

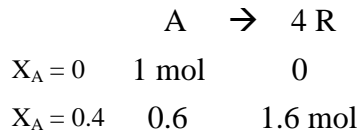
$$\hookrightarrow V = 3.55RT/P = 3.55 V_0 = V_0(1 + 3 \times 0.85) = V_0(1 + \varepsilon_A \times X_A)$$

② Start with pure reactant A of 1 mole and inert gas of 1 mole:



$$\therefore \varepsilon_A = \frac{(4+1)-(1+1)}{1+1} = 1.5$$

◆ 若 $X_A = 0.4 \rightarrow$ 系統的體積變成多少？



$$X_A = 0 \rightarrow n_{\text{total}} = (1+1) \text{ mol} \rightarrow V_0 = 2RT/P$$

$$X_A = 0.4 \rightarrow n_{\text{total}} = (2.2+1) \text{ mol}$$

$$\hookrightarrow V = 3.2RT/P = 1.6 V_0 = V_0(1 + 1.5 \times 0.4) = V_0(1 + \varepsilon_A \times X_A)$$

結論

$$\bullet V = V_0(1 + \varepsilon_A X_A)$$

$$\bullet X_A = \frac{V - V_0}{V_0 \varepsilon_A}$$

V_0 = initial volume of the reactor
 V = the volume at time t (X_A)

2. 因此，即使是含有 inert gas 的反應：

$$N_A = N_{A0}(1 - X_A) \quad \text{----- 為何與 inert gas 的存在、壓力、體積的變化無關？}$$

$$\text{但 } C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X_A)}{V_0(1 + \varepsilon_A X_A)} = C_{A0} \frac{(1 - X_A)}{(1 + \varepsilon_A X_A)}$$

$$\therefore \frac{C_A}{C_{A0}} = \frac{(1 - X_A)}{(1 + \varepsilon_A X_A)} \quad \text{or} \quad X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A C_A/C_{A0}} \quad \text{or} \quad dX_A = \frac{dV}{V_0 \varepsilon_A}$$

$$\begin{aligned} \therefore -r_A &= -\frac{1}{V} \frac{dN_A}{dt} = -\frac{1}{V_0(1 + \varepsilon_A X_A)} \frac{dN_{A0}(1 - X_A)}{dt} = \frac{C_{A0}}{(1 + \varepsilon_A X_A)} \frac{dX_A}{dt} \\ &= \frac{C_{A0}}{(1 + \varepsilon_A X_A)} \frac{1}{V_0 \varepsilon_A} \frac{dV}{dt} = \frac{C_{A0}}{\varepsilon_A} \frac{1}{V_0(1 + \varepsilon_A X_A)} \frac{dV}{dt} = \frac{C_{A0}}{\varepsilon_A} \frac{1}{V} \frac{dV}{dt} \\ &= \frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} \end{aligned}$$

2. Integral method of analysis

● 只考慮簡單的類型，即 $nA \rightarrow \text{product}$ ， $-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A^n$

(1) Zero-order reaction:

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = k$$

※ 以轉化率來分析：

$$\frac{C_{A0}}{(1 + \varepsilon_A X_A)} \frac{dX_A}{dt} = k \rightarrow \frac{C_{A0}}{\varepsilon_A} \ln(1 + \varepsilon_A X_A) = kt$$

※ 以 volume 來分析：

$$\frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} = k \rightarrow \frac{C_{A0}}{\varepsilon_A} \ln \frac{V}{V_0} = kt$$

(2) First-order reaction:

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

※ 以轉化率來分析：

$$\frac{C_{A0}}{(1 + \varepsilon_A X_A)} \frac{dX_A}{dt} = kC_{A0} \frac{(1 - X_A)}{(1 + \varepsilon_A X_A)} \rightarrow -\ln(1 - X_A) = kt$$

※ 以 volume 來分析：

$$\frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} = kC_{A0} \frac{(1 - X_A)}{(1 + \varepsilon_A X_A)} \quad \blacklozenge \quad X_A = \frac{V - V_0}{V_0 \varepsilon_A}$$

$$\therefore \frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} = kC_{A0} \frac{(1 - \frac{V - V_0}{V_0 \varepsilon_A})}{(1 + \varepsilon_A \frac{V - V_0}{V_0 \varepsilon_A})} = kC_{A0} \frac{[(\varepsilon_A + 1)V_0 - V] / \varepsilon_A V_0}{V / V_0}$$

$$\therefore \frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} = kC_{A0} \frac{[(\varepsilon_A + 1)V_0 - V] / \varepsilon_A V_0}{V / V_0} = kC_{A0} \frac{[(\varepsilon_A + 1)V_0 - V]}{\varepsilon_A V}$$

$$\frac{C_{A0}}{\varepsilon_A} \frac{1}{V} \frac{dV}{dt} = kC_{A0} \frac{[(\varepsilon_A + 1)V_0 - V]}{\varepsilon_A V} \rightarrow \frac{dV}{dt} = k[(\varepsilon_A + 1)V_0 - V]$$

$$\frac{1}{(\varepsilon_A + 1)V_0 - V} dV = k dt \rightarrow -\int_{V_0}^V \frac{1}{(\varepsilon_A + 1)V_0 - V} d[(\varepsilon_A + 1)V_0 - V] = \int_0^t k dt$$

$$-\ln[(\epsilon_A+1)V_0-V] \Big|_{V_0}^V = kt \quad \rightarrow \quad -\ln[(\epsilon_A+1)V_0-V] - \{-\ln[(\epsilon_A+1)V_0-V_0]\} = kt$$

$$-\ln \frac{\epsilon_A V_0 + V_0 - V}{\epsilon_A V_0} = kt \quad \rightarrow \quad -\ln \left(1 - \frac{\Delta V}{\epsilon_A V_0}\right) = kt \quad \text{其中 } \Delta V = V - V_0$$

(3) Second-order reaction:

● 考慮最單純的

$nA \rightarrow \text{products}$

or $A + B \rightarrow \text{products}$ 而 $C_{A0} = C_{B0}$

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A^2 = kC_{A0}^2 \left[\frac{(1-X_A)}{(1+\epsilon_A X_A)} \right]^2$$

※ 以轉化率來分析：

$$\frac{(1+\epsilon_A)\Delta V}{V_0\epsilon_A - \Delta V} + \epsilon_A \ln \left(1 - \frac{\Delta V}{V_0\epsilon_A}\right) = kC_{A0}t$$

※ 以 volume 來分析：

Example 3-12:

定溫下， $A_{(g)} \rightarrow 5 B_{(g)}$ 為 zero-order reaction。已知 reactant A 的初濃度為 3 M，反應 100 分鐘後，發現 A 的濃度是 0.6 M。

(1) 若反應是在 constant-volume 下進行，請導出轉化率對時間的關係式並求出反應 45 分鐘時，reactant A 的濃度。

(2) 若反應是在 constant-pressure 下進行，請導出轉化率對時間的關係式並求出反應 45 分鐘時，reactant A 的濃度。