2012/1/4

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\begin{aligned} A' &= -k_1 A \\ B' &= k_1 A - k_2 B \\ C &= A_0 - A - B \end{aligned} \quad (1)$$

令

$$\begin{aligned} y_1(t) &= A \\ y_2(t) &= B \end{aligned} \quad (2)$$

$$\begin{aligned} y_1' &= -k_1 y_1 + 0\, y_2 \\ y_2' &= k_1 y_1 - k_2 y_2 \end{aligned} \quad (3)$$

$$\begin{bmatrix} y_1' \\ y_2' \end{bmatrix} = \begin{bmatrix} -k_1 & 0 \\ k_1 & -k_2 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \end{bmatrix}$$

or (4)

$$\mathbf{y}' = \mathbf{C}\mathbf{y}$$

假設

$$\mathbf{y} = \mathbf{x}\, e^{\lambda t}$$

*or* (5)

$$\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} e^{\lambda t}$$

帶入 (4)

$$\begin{aligned} \mathbf{y}' &= \mathbf{x}\, \lambda\, e^{\lambda t} = C\, \mathbf{x}\, e^{\lambda t} \\ C\, \mathbf{x} &= \lambda\, \mathbf{x} \end{aligned} \quad (6)$$

因此，**x** 爲 C 之 eigenvector，λ 爲 eigenvalues

$$(-k_1-\lambda)(-k_2-\lambda)=0$$
$$\lambda=-k_1 \text{ or } -k_2 \tag{7}$$

Eigenvectors 分別爲

$$\begin{bmatrix} 1 \\ \frac{k_1}{k_2-k_1} \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{8}$$

所以此 homogeneous 系統的 general solution 爲

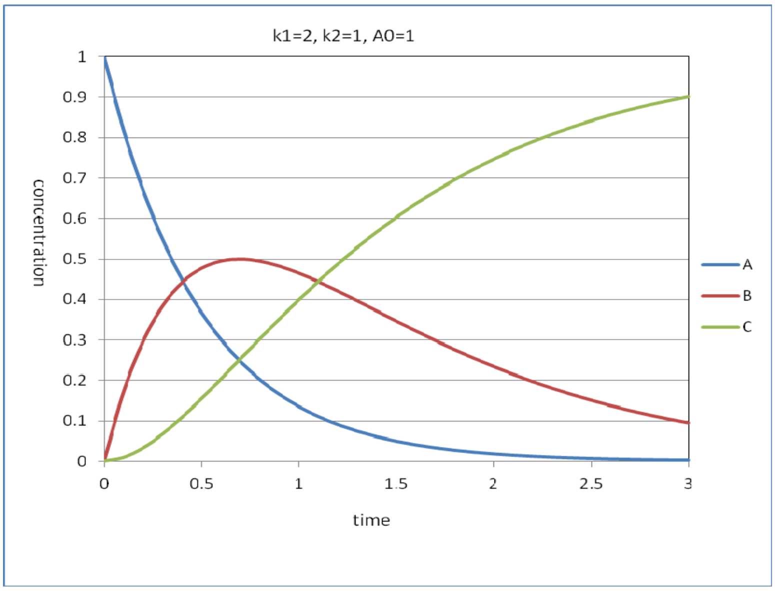
$$\begin{bmatrix} y_1 \\ y_2 \end{bmatrix}=a_1\begin{bmatrix} 1 \\ \frac{k_1}{k_2-k_1} \end{bmatrix}e^{-k_1t}+a_2\begin{bmatrix} 0 \\ 1 \end{bmatrix}e^{-k_2t} \tag{9}$$

$a_1, a_2$ = constants

由起始條件 $A(t=0)=A_0, B(t=0)=0$

$$\begin{bmatrix} A \\ B \end{bmatrix}=A_0\begin{bmatrix} 1 \\ \frac{k_1}{k_2-k_1} \end{bmatrix}e^{-k_1t}-\frac{k_1A_0}{k_2-k_1}\begin{bmatrix} 0 \\ 1 \end{bmatrix}e^{-k_2t} \tag{10}$$

$$A=A_0e^{-k_1t}$$
$$B=\frac{A_0k_1}{k_2-k_1}\left(e^{-k_1t}-e^{-k_2t}\right) \tag{11}$$



如果 $k_1 = k_2$

$$\begin{aligned}&(-k_1-\lambda)(-k_1-\lambda)=0\\&\lambda=-k_1\,,-k_1\end{aligned}\tag{12}$$

Eigenvectors 只有

$$\mathbf{x}=\begin{bmatrix}0\\1\end{bmatrix}\tag{13}$$

除了 $\mathbf{y}=\mathbf{x}\,e^{\lambda t}$ 我們令另外一個解為

$$\begin{aligned}&\mathbf{y}=\mathbf{x}\,te^{\lambda t}+\mathbf{u}\,e^{\lambda t}\\&or\\&\begin{bmatrix}y_1\\y_2\end{bmatrix}=\begin{bmatrix}x_1\\x_2\end{bmatrix}te^{\lambda t}+\begin{bmatrix}u_1\\u_2\end{bmatrix}e^{\lambda t}\end{aligned}\tag{14}$$

帶入(4)

$$\begin{aligned}&\mathbf{y}'=\mathbf{x}\,e^{\lambda t}+\lambda\mathbf{x}\,te^{\lambda t}+\mathbf{u}\,\lambda e^{\lambda t}=C\mathbf{x}\,te^{\lambda t}+C\mathbf{u}\,e^{\lambda t}=\lambda\mathbf{x}\,te^{\lambda t}+C\mathbf{u}\,e^{\lambda t}\\&\mathbf{x}+\lambda\mathbf{u}=C\,\mathbf{u}\\&(C-\lambda\mathbf{I})\,\mathbf{u}=\mathbf{x}\end{aligned}\tag{15}$$

帶入$\lambda$, $\mathbf{x}$ 後可得

$$\mathbf{u}=\begin{bmatrix}\dfrac{1}{k_1}\\0\end{bmatrix}\tag{16}$$

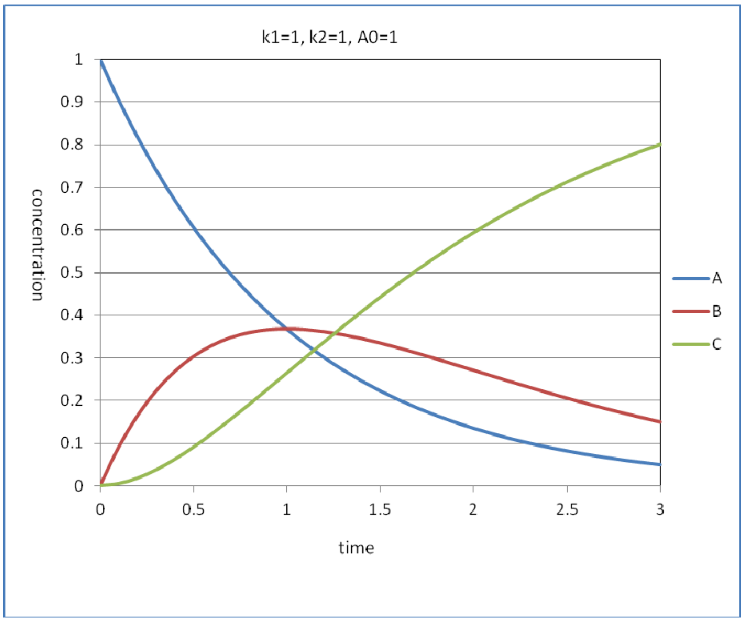
所以一般解為

$$\begin{aligned}&\mathbf{y}=a_1\mathbf{x}e^{\lambda t}+a_2\left(\mathbf{x}\,te^{\lambda t}+\mathbf{u}\,e^{\lambda t}\right)\\&or\\&\begin{bmatrix}y_1\\y_2\end{bmatrix}=a_1\begin{bmatrix}0\\1\end{bmatrix}e^{-k_1t}+a_2\left(\begin{bmatrix}0\\1\end{bmatrix}t+\begin{bmatrix}\dfrac{1}{k_1}\\0\end{bmatrix}\right)e^{-k_1t}\end{aligned}\tag{17}$$

由起始條件 $A(t=0)=A_0, B(t=0)=0$

$$a_2 = k_1 A_0, a_1 = 0 \tag{18}$$

$$A = A_0 e^{-k_1 t}$$
$$B = k_1 A_0 t e^{-k_1 t} \tag{19}$$



所以此 homogeneous 系統的 general solution 為

$$A \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} B \xrightarrow{k_2} C$$

$$A' = -k_1 A + k_{-1} B \qquad (1)$$
$$B' = k_1 A - (k_2 + k_{-1}) B$$
$$C = A_0 - A - B$$

令

$$y_1(t) = A$$
$$y_2(t) = B \qquad (2)$$

$$y_1' = -k_1 y_1 + k_{-1} y_2$$
$$y_2' = k_1 y_1 - (k_2 + k_{-1}) y_2 \qquad (3)$$

$$\begin{bmatrix} y_1' \\ y_2' \end{bmatrix} = \begin{bmatrix} -k_1 & k_{-1} \\ k_1 & -(k_2 + k_{-1}) \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} \qquad (4)$$

$$(-k_1 - \lambda)(-k_2 - k_{-1} - \lambda) - k_1 k_{-1} = 0 \qquad (5)$$

假設 $k_1 = 2, k_2 = k_{-1} = 1$

$$(2 + \lambda)(2 + \lambda) - 2 = 0$$
$$\lambda = -2 \pm \sqrt{2} \qquad (6)$$

Eigenvectors 分別為

$$\begin{bmatrix} 1 \\ \sqrt{2} \end{bmatrix}, \begin{bmatrix} 1 \\ -\sqrt{2} \end{bmatrix} \qquad (7)$$

所以此 homogeneous 系統的 general solution 為

$$\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = a_1 \begin{bmatrix} 1 \\ \sqrt{2} \end{bmatrix} e^{(-2+\sqrt{2})t} + a_2 \begin{bmatrix} 1 \\ -\sqrt{2} \end{bmatrix} e^{(-2-\sqrt{2})t} \tag{8}$$

$a_1, a_2 = \text{constants}$

由起始條件 $A(t = 0) = A_0$, $B(t = 0) = 0$, $a_1 = a_2 = 1/2\ A_0$

$$\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \frac{A_0}{2} \begin{bmatrix} 1 \\ \sqrt{2} \end{bmatrix} e^{(-2+\sqrt{2})t} + \frac{A_0}{2} \begin{bmatrix} 1 \\ -\sqrt{2} \end{bmatrix} e^{(-2-\sqrt{2})t} \tag{9}$$

$$\begin{aligned} A &= \frac{A_0}{2}\left(e^{(-2+\sqrt{2})t} + e^{(-2-\sqrt{2})t}\right) \\ B &= \frac{A_0\sqrt{2}}{2}\left(e^{(-2+\sqrt{2})t} - e^{(-2-\sqrt{2})t}\right) \end{aligned} \tag{10}$$

$$A + B \underset{k-1}{\overset{k_1}{\leftrightarrow}} C$$

$$t = 0, A = B = A_0 = 1.0M, C = 0$$

$$\frac{d[A]}{dt} = -k_1[A]^2 + k_{-1}[C]$$

$$[C] = A_0 - A$$

$$\frac{d[A]}{dt} = -k_1[A]^2 + k_{-1}(A_0 - [A]) = -(k_1[A]^2 + k_{-1}[A] - k_{-1}A_0)$$

$$= -([A] - a)([A] - b)$$

$$a, b = \frac{-k_{-1} \pm \sqrt{k_{-1}{}^2 + 4k_1k_{-1}}}{2k_1}$$

$$\frac{d[A]}{dt} = -k_1[A]^2 + k_{-1}(A_0 - [A]) = -(k_1[A]^2 + k_{-1}[A] - k_{-1}A_0)$$

$$= -k_1([A] - a)([A] - b)$$

$$a, b = \frac{-k_{-1} \pm \sqrt{k_{-1}{}^2 + 4k_1k_{-1}A_0}}{2k_1}$$

$$\frac{d[A]}{([A] - a)([A] - b)} = \frac{1}{a - b}\left(\frac{1}{[A] - a} - \frac{1}{[A] - b}\right)d[A] = -k_1 dt$$

$$\frac{1}{a - b}\left(\ln\frac{[A] - a}{[A] - b}\right) = -k_1 t + c,\ c = \frac{1}{a - b}\left(\ln\frac{A_0 - a}{A_0 - b}\right)$$

$$\frac{[A] - a}{[A] - b} = 1 + \frac{b - a}{[A] - b} = e^{(a-b)(-k_1 t + c)}$$

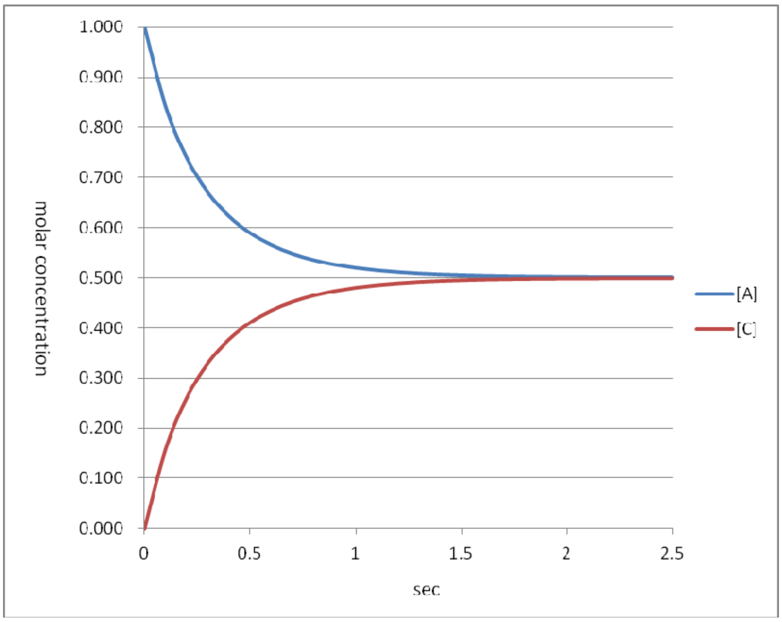
$$\frac{1}{[A] - b} = \frac{e^{(a-b)(-k_1 t + C)} - 1}{b - a}$$

$$[A] = \frac{b - a}{e^{(a-b)(-k_1 t + c)} - 1} + b$$

If $k_1$=2.0 $M^{-1}$ $s^{-1}$, $k_{-1}$ = 1.0 $s^{-1}$

$a$ = 0.5M, $b$ = –1 M, $c$ = –0.9242 M

$$[A] = \frac{-1.5}{e^{(1.5)(-2t-0.9242)} - 1} - 1$$


1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
molar concentration
0
0.5
1
1.5
2
2.5
sec
[A]
[C]