Analyse des cinétiques bi-moléculaires autocatalytiques du second ordre

Loi de vitesse pour la réaction élémentaire A + B → B + B

$$-\frac{d[A(t)]}{dt} = k[A(t)][B(t)] \tag{1}$$

Posons les conditions initiales $[A(t{=}0)] = [A_o]$ et $[B(t{=}0)] = [B_o]$

Ainsi,

$$[A(t)] + [B(t)] = [A_o] + [B_o] \quad \text{ou} \quad [B(t)] = [A_o] + [B_o] - [A(t)] \tag{2}$$

On substitue cette relation dans (1)

$$\frac{d[A(t)]}{dt} = -k[A(t)]\{[A_o]+[B_o]-[A(t)]\} \tag{3}$$

$$\int_0^t \frac{d[A(t')]}{[A(t')]\{[A_o]+[B_o]-[A(t')]\}} = -k\int_0^t dt' \tag{4}$$

On peut réexprimer le membre de gauche à l'aide de la méthode des fractions partielles :

$$\frac{1}{[A(t)]\{[A_o]+[B_o]-[A(t)]\}} = \frac{\alpha}{[A(t)]} + \frac{\beta}{[A_o]+[B_o]-[A(t)]} = \frac{\alpha([A_o]+[B_o])+(\beta-\alpha)[A(t)]}{[A(t)][A_o]+[B_o]-[A(t)]} \tag{5}$$

Ainsi,

$$\alpha([A_o]+[B_o])+(\beta-\alpha)[A(t)] = 1 \tag{6}$$

Pour obtenir la solution non-triviale (i.e., $[A(t)]\neq 0$), cette relation ne peut être satisfaite que si $\alpha = \beta = \frac{1}{[A_o]+[B_o]}$. On substitue alors dans (5) et réexprime (4) de la façon suivante :

$$\int_0^t \frac{d[A(t')]}{[A(t')]\{[A_o]+[B_o]-[A(t')]\}} = \frac{1}{[A_o]+[B_o]}\int_0^t \left(\frac{d[A(t')]}{[A(t')]} + \frac{d[A(t')]}{\{[A_o]+[B_o]-[A(t')]\}}\right) = -k\int_0^t dt' \tag{7}$$

$$\frac{1}{[A_o]+[B_o]}\{\ln([A(t')])-\ln([A_o]+[B_o]-[A(t')])\}\Big|_0^t = -kt'\Big|_0^t \tag{8}$$

$$\frac{1}{[A_o]+[B_o]}\{\ln([A(t)])-\ln([A_o]+[B_o]-[A(t)])-\ln([A_o])+\ln([A_o]+[B_o]-[A_o])\} = -k(t-0) \tag{9}$$

$$\frac{1}{[A_o]+[B_o]}\ln\left(\frac{[B_o][A(t)]}{[A_o]([A_o]+[B_o]-[A(t)])}\right) = -kt \tag{10}$$

$$\ln\left(\frac{[B_o][A(t)]}{[A_o]([A_o]+[B_o]-[A(t)])}\right) = -([A_o]+[B_o])kt \tag{11}$$

$$\frac{[B_o][A(t)]}{[A_o]([A_o]+[B_o]-[A(t)])} = \exp\{-([A_o]+[B_o])kt\} \tag{12}$$

$$[A(t)] = ([A_o]+[B_o]-[A(t)])\frac{[A_o]}{[B_o]}\exp\{-([A_o]+[B_o])kt\} \tag{13}$$

$$[A(t)]\left[1+\frac{[A_o]}{[B_o]}\exp\{-([A_o]+[B_o])kt\}\right] = ([A_o]+[B_o])\frac{[A_o]}{[B_o]}\exp\{-([A_o]+[B_o])kt\} \tag{14}$$

$$[A(t)] = \frac{[A_o]([A_o]+[B_o])\exp\{-([A_o]+[B_o])kt\}}{[B_o]+[A_o]\exp\{-([A_o]+[B_o])kt\}} \tag{15}$$

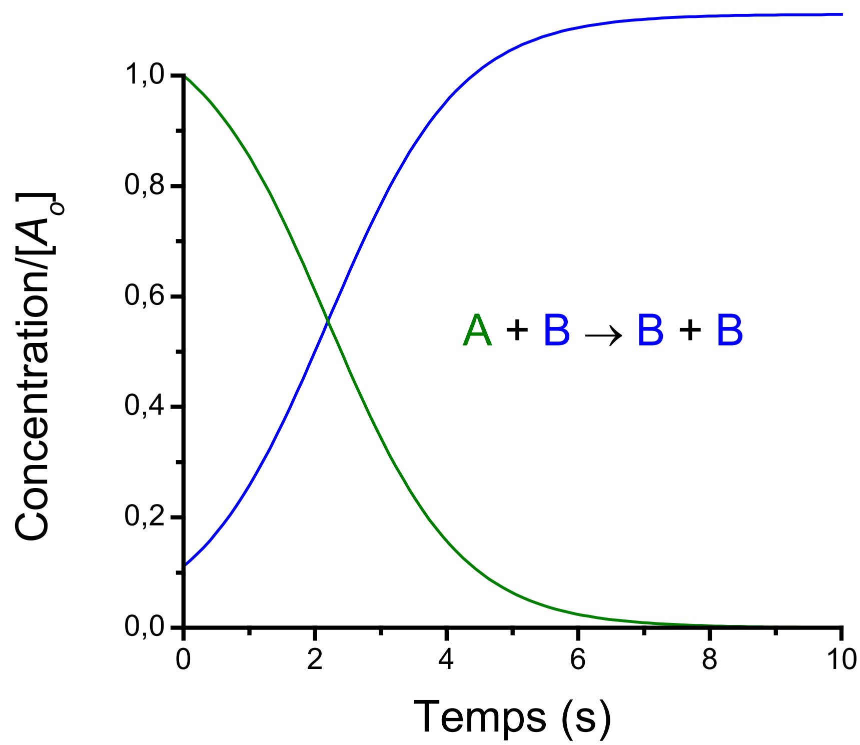
On peut maintenant utiliser (2) pour obtenir

$$[B(t)] = [A_o]+[B_o]-\frac{[A_o]([A_o]+[B_o])\exp\{-([A_o]+[B_o])kt\}}{[B_o]+[A_o]\exp\{-([A_o]+[B_o])kt\}} \tag{16}$$

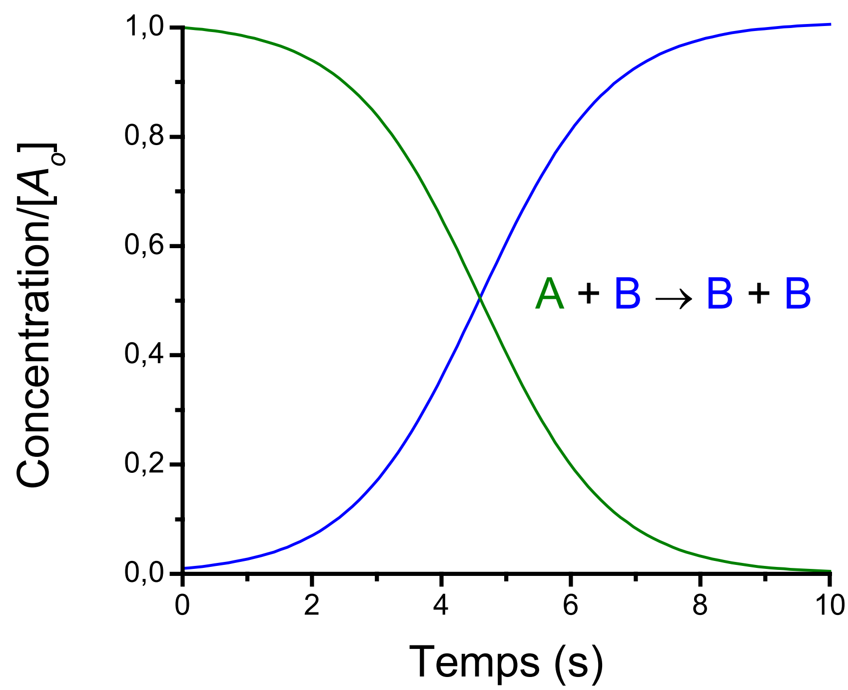
$$[B(t)] = \frac{[B_o]([A_o]+[B_o])+[A_o]([A_o]+[B_o])\exp\{-([A_o]+[B_o])kt\}-[A_o]([A_o]+[B_o])\exp\{-([A_o]+[B_o])kt\}}{[B_o]+[A_o]\exp\{-([A_o]+[B_o])kt\}} \tag{17}$$

$$[B(t)] = \frac{[B_o]([A_o]+[B_o])}{[B_o]+[A_o]\exp\{-([A_o]+[B_o])kt\}} = \frac{([A_o]+[B_o])}{1+\frac{[A_o]}{[B_o]}\exp\{-([A_o]+[B_o])kt\}} \tag{18}$$

Graphiquement, on obtient pour k = 1 L mole^{-1} s^{-1}, $[A_o]=9[B_o]$



Alors que pour k = 1 L mole^{-1} s^{-1}, $[A_o]=99[B_o]$, on obtient



Et pour $k = 1$ L mole^{-1} s^{-1}, $[A_o]=999[B_o]$, on obtient