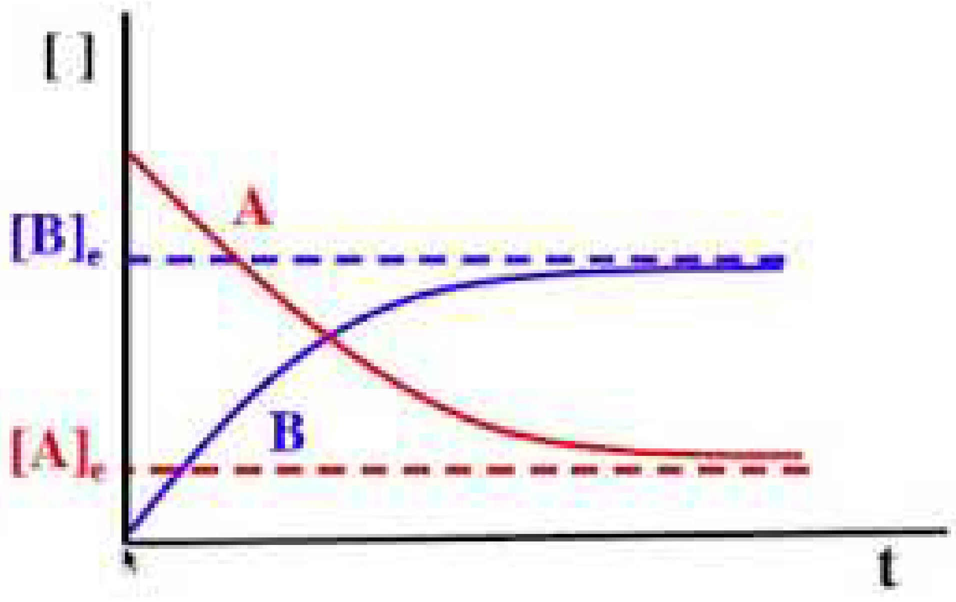
CINÉTICA DE REACCIONES REVERSIBLES



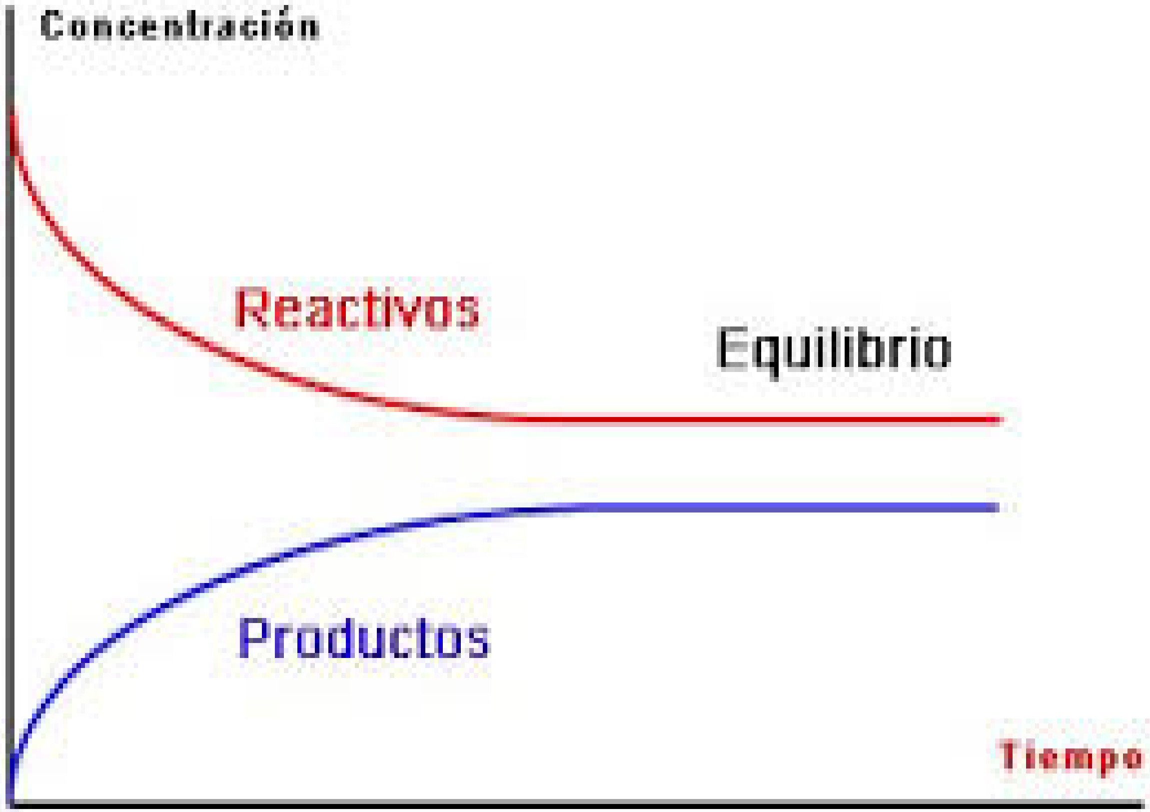
Cinética de reacciones reversibles

Reacciones reversibles de primer orden

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

$[A]_0 = a$
$[B]_0 = 0$
$[A] = a - x$
$[B] = x$

$$-\frac{d[A]}{dt} = k_1[A] - k_2[B]$$



$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

$$\frac{dx}{dt} = k_1(a-x) - k_2x \qquad K = \frac{x_e}{(a-x_e)} = \frac{k_1}{k_2} \;\Rightarrow\; k_2 = \frac{k_1(a-x_e)}{x_e} \quad (\mathbf{1})$$

$$\frac{dx}{dt} = k_1(a-x) - \frac{k_1(a-x_e)x}{x_e}$$

$$\frac{dx}{dt} = k_1\left(\frac{(a-x)x_e - (a-x_e)x}{x_e}\right) = k_1\left(\frac{ax_e \cancel{- xx_e} - ax \cancel{+ x_e x}}{x_e}\right)$$

$$\frac{dx}{dt} = k_1 a\left(\frac{x_e - x}{x_e}\right) \quad (\mathbf{2}) \qquad de\ (\mathbf{1}) \quad k_1 a = x_e(k_2 + k_1)$$

Reemplazando en (**2**) según (**1**):

$$\boldsymbol{\frac{dx}{dt} = (k_1 + k_2)(x_e - x)}$$

Ecuación diferencial de velocidad

$$\int_0^x \frac{dx}{(x_e - x)} = (k_1 + k_2) \int_0^t dt$$

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

$$ln \frac{x_e}{x_e - x} = (k_1 + k_2)t$$

Ecuación integrada de velocidad

$t_{1/2}$: tiempo necesario para que la conversión sea la mitad de la correspondiente al equilibrio

$$ln \frac{x_e}{x_e - \frac{x_e}{2}} = (k_1 + k_2)t_{1/2} \longrightarrow t_{1/2} = \frac{ln2}{(k_1 + k_2)}$$

Uso de propiedades proporcionales a la concentración

$P = \alpha[A] + \beta[B]$

$t = 0 \qquad P_0 = \alpha a$

$t = t \qquad P_t = \alpha(a - x) + \beta x$

$t = \infty \qquad P_\infty = \alpha(a - x_e) + \beta x_e$

$$A \rightleftharpoons B$$

$$ln\frac{x_e}{x_e - x} = (k_1 + k_2)t$$

$$\boldsymbol{ln\frac{(P_0 - P_\infty)}{(P_t - P_\infty)} = (k_1 + k_2)t}$$

$P_0 - P_\infty = x_e(\alpha - \beta) \rightarrow$

$$x_e = \frac{P_0 - P_\infty}{\alpha - \beta}$$

$P_t - P_\infty = \alpha(a - x) + \beta x - \alpha(a - x_e) - \beta x_e$

$P_t - P_\infty = \alpha(x_e - x) - \beta(x_e - x) \rightarrow$

$$(x_e - x) = \frac{P_t - P_\infty}{(\alpha - \beta)}$$

Reacciones reversibles de segundo orden

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D$$

$[A]_0 = [B]_0$
$[C]_0 = [D]_0 = 0$
$[A] = [B] = [A]_0 (1 - x_A)$
$[C] = [D] = [A]_0 x_A$

$$-\frac{d[A]}{dt} = k_1[A][B] - k_2[C][D]$$

$$\frac{dx_A}{dt} = k_1[A]_0(1 - x_A)^2 - k_2[A]_0 x_A^2 \quad (3)$$

$$\frac{dx_A}{dt} = (k_1 - k_2)[A]_0(m_1 - x_A)(m_2 - x_A) \quad (4)$$

Ecuación diferencial de velocidad

$$m_1 = \frac{K_e + \sqrt{K_e}}{K_e - 1}$$

$$\frac{1}{(m_2 - m_1)} \ln\left(\frac{m_1(m_2 - x_A)}{m_2(m_1 - x_A)}\right) = (k_1 - k_2)[A]_0 t$$

$$m_2 = \frac{K_e - \sqrt{K_e}}{K_e - 1}$$

Ecuación integrada de velocidad

Cómo pasamos de (3) a (4)?

$$\frac{dx_A}{dt} = k_1[A]_0(1 - x_A)^2 - k_2[A]_0 x_A^2 \quad (3)$$

$$\frac{dx_A}{dt} = [A]_0[k_1 - 2k_1 x_A + k_1 x_A^2 - k_2 x_A^2]$$

$$\frac{dx_A}{dt} = [A]_0[k_1 - 2k_1 x_A + (k_1 - k_2) x_A^2]$$

$$\frac{dx_A}{dt} = (k_1 - k_2)[A]_0 \left[\frac{\frac{k_1}{k_2}}{\frac{k_1 - k_2}{k_2}} - \frac{\frac{2k_1}{k_2}}{\frac{k_1 - k_2}{k_2}} x_A + x_A^2 \right] = (k_1 - k_2)[A]_0 \left[\frac{K_e}{K_e - 1} - \frac{2K_e}{K_e - 1} x_A + x_A^2 \right]$$

$$\textit{raíces de la expresión cuadrática:}\; m_{1,2} = \frac{K_e \mp \sqrt{K_e}}{K_e - 1};\; (m_1 - x_A)(m_2 - x_A)$$

$$\frac{dx_A}{dt} = (k_1 - k_2)[A]_0 (m_1 - x_A)(m_2 - x_A) \quad (4)$$

Reacciones reversibles de segundo orden para la reacción directa y Primer orden para la reacción inversa

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$$

$[A]_0 = [B]_0$
$[C]_0 = 0$
$[A] = [B] = [A]_0\,(1 - x_A)$
$[C] = [A]_0\,x_A$

$$-\frac{d[A]}{dt} = k_1[A][B] - k_2[C]$$

$$\frac{dx_A}{dt} = k_1[A]_0(1 - x_A)^2 - k_2 x_A$$

$$\frac{dx_A}{dt} = k_1[A]_0(m_1 - x_A)(m_2 - x_A)$$

Ecuación diferencial de velocidad

$$m_1 = \left(\frac{2K_e[\text{A}]0 + 1}{K_e[\text{A}]0} + \sqrt{(\frac{2K_e[\text{A}]0 + 1}{K_e[\text{A}]0})^2 - 4} \right)/2$$

$$m_2 = \left(\frac{2K_e[\text{A}]0 + 1}{K_e[\text{A}]0} - \sqrt{(\frac{2K_e[\text{A}]0 + 1}{K_e[\text{A}]0})^2 - 4} \right)/2$$

$$\frac{1}{(m_2 - m_1)} \ln \left(\frac{m_1(m_2 - x_A)}{m_2(m_1 - x_A)} \right) = k_1[\text{A}]0t$$

Ecuación integrada de velocidad

$$\frac{dx_A}{dt} = k_1[\mathrm{A}]_0(1 - x_A)^2 - k_2 x_A$$

$$\frac{dx_A}{dt} = k_1[\mathrm{A}]_0 - 2k_1[\mathrm{A}]_0\, x_A + k_1[\mathrm{A}]_0 x_A^2 - k_2 x_A$$

$$\frac{dx_A}{dt} = k_1[\mathrm{A}]_0 - (2k_1[\mathrm{A}]_0 + k_2)x_A + k_1[\mathrm{A}]_0 x_A^2$$

$$\frac{dx_A}{dt} = k_1[\mathrm{A}]_0\left(1 - \left(2 + \frac{\boldsymbol{k_2}}{\boldsymbol{k_1}[\mathrm{A}]_0}\right)x_A + x_A^2\right) = k_1[\mathrm{A}]_0\left(1 - \left(2 + \frac{1}{\boldsymbol{K_e}\,[\mathrm{A}]_0}\right)x_A + x_A^2\right)$$

$$\textit{raíces de la expresión cuadrática:}\;\; m_{1,2} = \left(\frac{2K_e[\mathrm{A}]_0 + 1}{2K_e[\mathrm{A}]_0} \mp \frac{\sqrt{\left(\frac{2K_e\,[\mathrm{A}]_0 + 1}{K_e\,[\mathrm{A}]_0}\right)^2 - 4}}{2}\right)$$

$$\boldsymbol{\frac{dx_A}{dt} = k_1[\mathrm{A}]_0(m_1 - x_A)(m_2 - x_A)}$$

Reacción reversible de segundo orden en ambas direcciones

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B + C$$

$[A]_0$

$[C]_0 = [B]_0 = 0$

CINÉTICA DE REACCIONES EN SERIE

Reacciones en Serie

$$A \xrightarrow[n=1]{k_1} B \xrightarrow[n=1]{k_2} C$$

$$-\frac{dC_A}{dt} = k_1 C_A \Rightarrow ln\frac{C_{A0}}{C_A} = k_1 t \text{ ó } \boldsymbol{C_A = C_{A0}e^{-k_1 t}}$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B = k_1 C_{A0} e^{-k_1 t} - k_2 C_B$$

$$dC_B + k_2 C_B dt = k_1 C_{A0} e^{-k_1 t} dt$$

$f\!actor\ de\ integración$: $\boldsymbol{e^{k_2 t}}$ => $\int_{0,0}^{C_B,t} d(C_B \boldsymbol{e^{k_2 t}}) = k_1 C_{A0} \int_0^t \boldsymbol{e^{(k_2 - k_1)t}}\, dt$

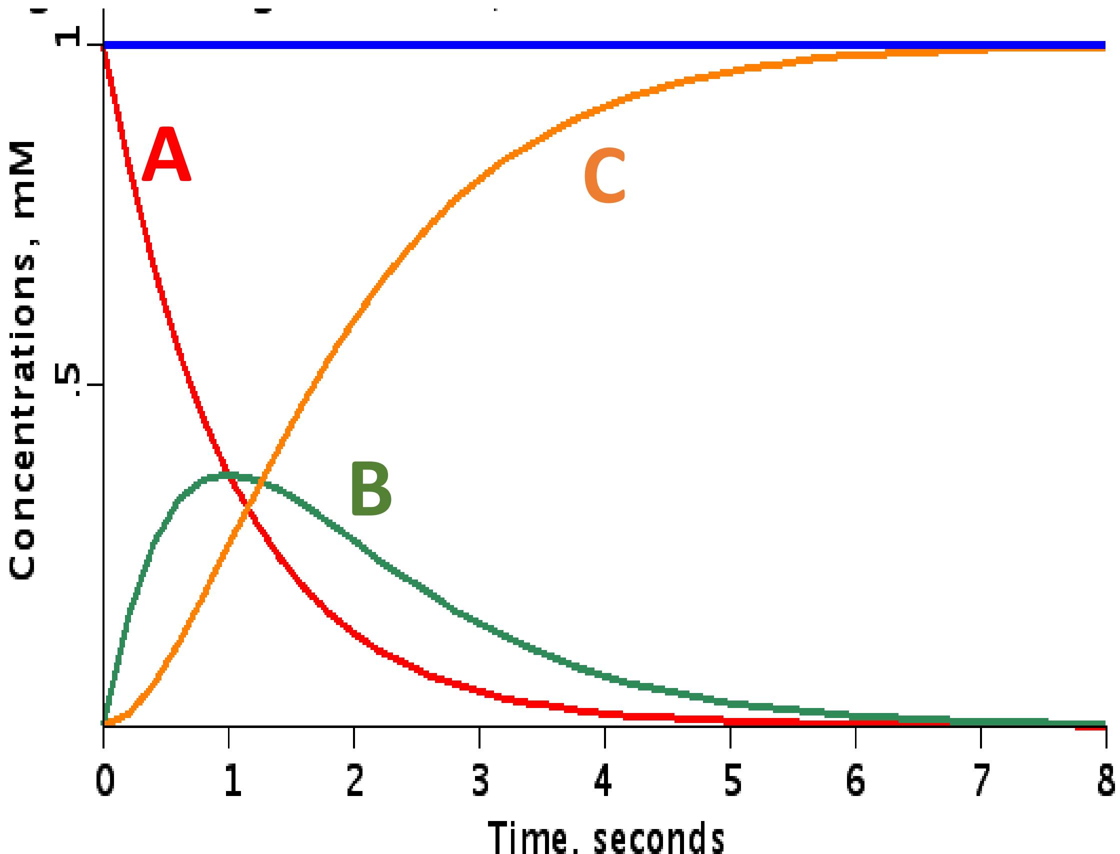
$$\boxed{\boldsymbol{C_B = C_{A0}\frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)}}$$

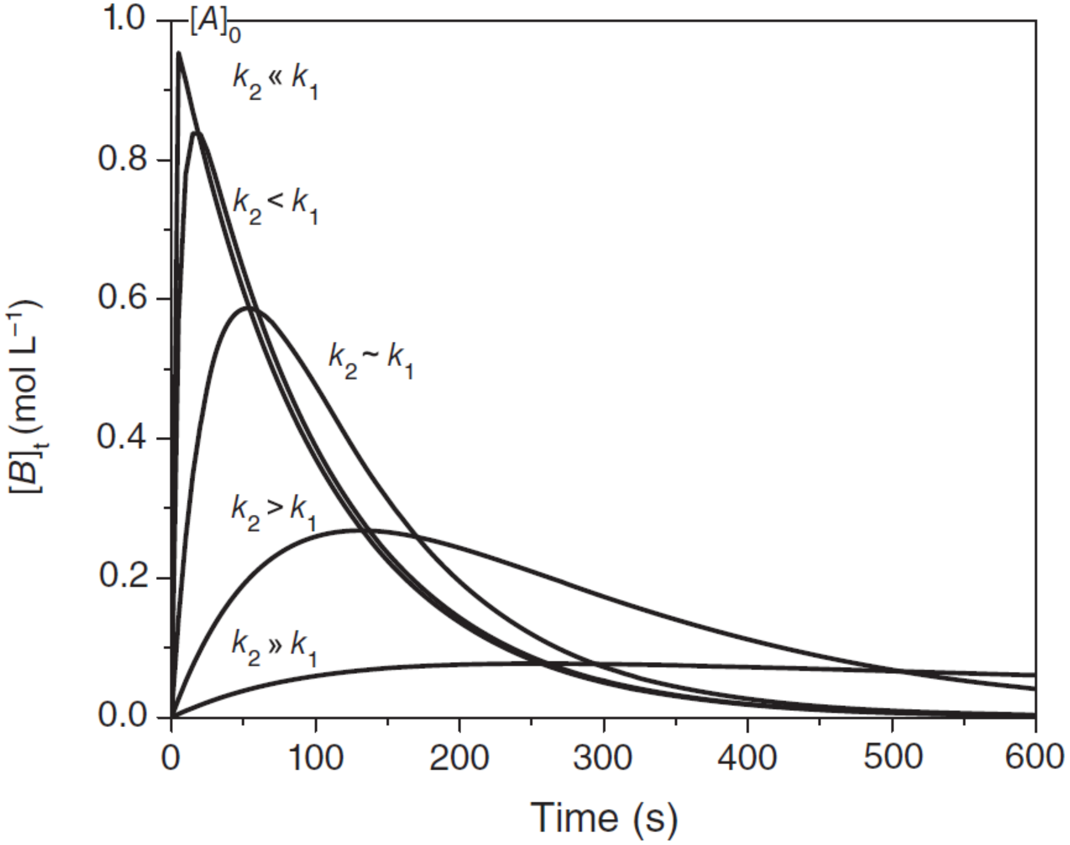
$$\boxed{\boldsymbol{C_C = C_{A0}\left(1 - \frac{k_2}{k_2 - k_1}e^{-k_1 t} + \frac{k_1}{k_2 - k_1}e^{-k_2 t}\right)}}$$

$$C_C = C_{A0}\left(1 - \frac{k_2}{k_2-k_1}e^{-k_1 t} + \frac{k_1}{k_2-k_1}e^{-k_2 t}\right)$$

$$C_B = C_{A0}\frac{k_1}{k_2-k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$\frac{dC_B}{dt} = C_{A0}\frac{k_1}{k_2-k_1}\left(-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right) = 0 \Rightarrow t_{max} = \frac{\ln\frac{k_1}{k_2}}{k_1 - k_2}$$

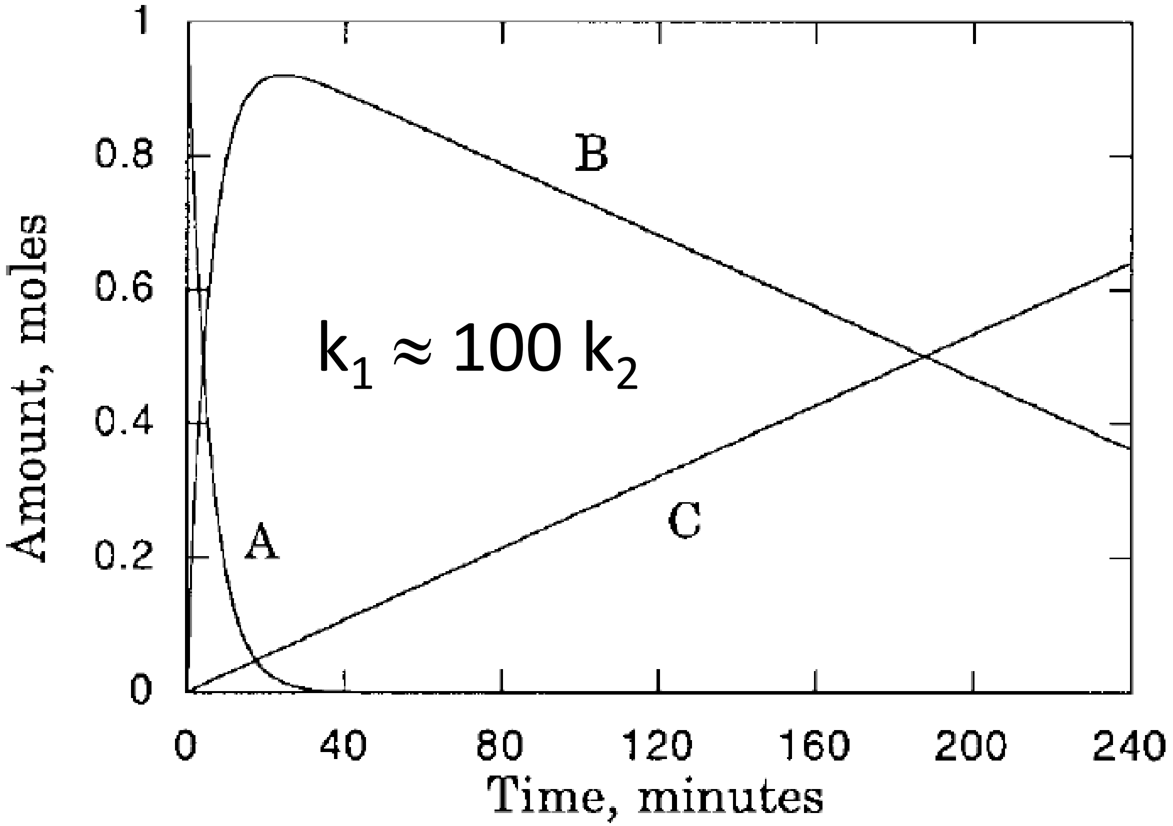




$$A \xrightarrow[n=1]{k_1} B \xrightarrow[n=0]{k_2} C$$

$$-\frac{dC_A}{dt} = k_1 C_A \Rightarrow ln\frac{C_{A0}}{C_A} = k_1 t \text{ ó } \boldsymbol{C_A = C_{A0}e^{-k_1 t}}$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 = k_1 C_{A0} e^{-k_1 t} - k_2$$



$$\int_0^{C_B} dC_B = k_1 C_{A0}\int_t^t \boldsymbol{e^{-k_1 t}}\, dt - k_2 \int_0^t dt$$

$$\boxed{C_B = C_{A0}(1 - e^{-k_1 t}) - k_2 t}$$

$$\boldsymbol{\frac{dC_B}{dt} = 0 \Rightarrow t_{max} = \frac{ln\frac{C_{A0}k_1}{k_2}}{k_1}}$$

$$A \xrightarrow[n=0]{k_1} B \xrightarrow[n=1]{k_2} C$$

$$-\frac{dC_A}{dt} = k_1 \Rightarrow \boldsymbol{C_A = C_{A0} - k_1\, t}$$

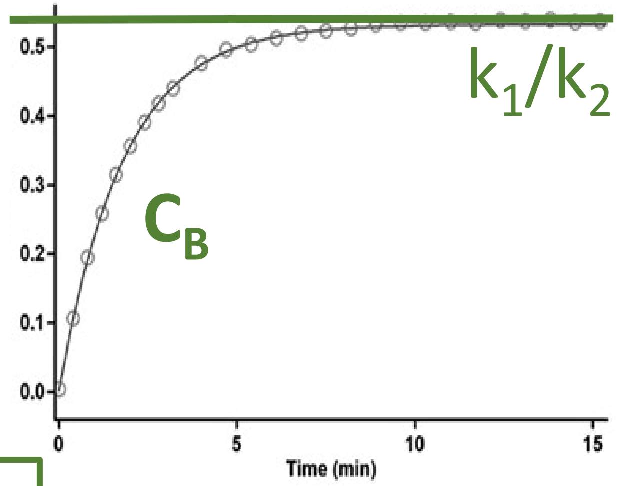
$$\frac{dC_B}{dt} = k_1 - k_2 C_B \qquad dC_B = k_1 dt - k_2 C_B dt$$

$$e^{k_2 t}(dC_B + k_2 C_B dt = k_1 dt)$$

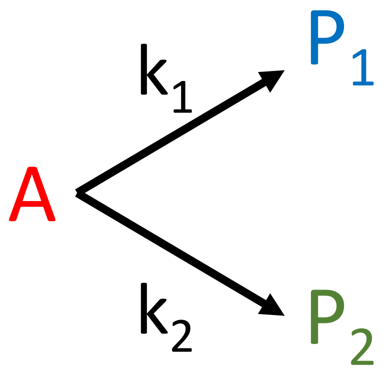
$$\int_{0,0}^{C_B,t} d(C_B e^{k_2 t}) = k_1 \int_0^t e^{k_2 t}\, dt$$

$$C_B e^{k_2 t} = \frac{k_1}{k_2}(e^{k_2 t} - 1)$$

$$\boxed{\boldsymbol{C_B = \frac{k_1}{k_2}(1 - e^{-k_2 t})}}$$



CINÉTICA DE REACCIONES EN PARALELO



$v_1 = k_1\,[A]$

$v_2 = k_2\,[A]$

$$-\frac{dC_A}{dt} = (k_1+k_2)C_A$$

$$\frac{v_1}{v_2} = \frac{C_{P1}}{C_{P2}} = \frac{k_1}{k_2}$$

$k_{exp} = k_1 + k_2$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = (k_1+k_2)\int_0^t dt \quad \Rightarrow \quad \boldsymbol{C_A = C_{A0}e^{-(k_1+k_2)t}}$$

$$v_1 = \frac{dC_{P1}}{dt} = k_1 C_A = k_1 C_{A0} e^{-(k_1+k_2)t}$$

$$\int_0^{C_{P1}} dC_{P1} = k_1 C_{A0}\int_0^t e^{-(k_1+k_2)t}\,dt \quad \Rightarrow \quad \boldsymbol{C_{P1} = \frac{k_1 C_{A0}}{k_1+k_2}\left(1 - e^{-(k_1+k_2)t}\right)}$$

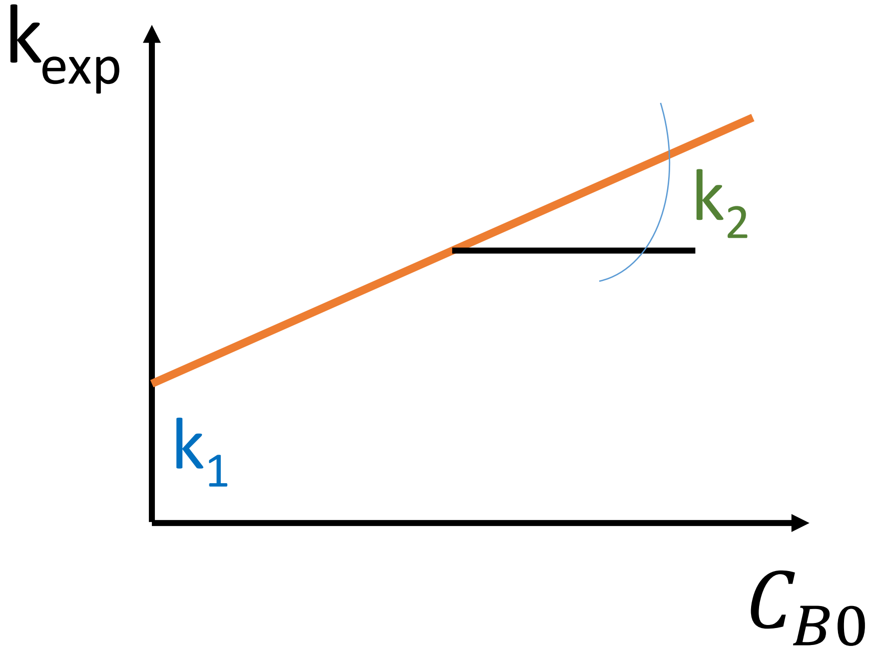
$$\boldsymbol{C_{P2} = \frac{k_2 C_{A0}}{k_1+k_2}\left(1 - e^{-(k_1+k_2)t}\right)}$$

$$A \xrightarrow{k_1} P_1 \quad v_1 = k_1 [A]$$

$$-\frac{dC_A}{dt} = k_1 C_A + k_2 C_A C_{B0} = (k_1 + k_2 C_{B0}) C_A$$

$$A + B_{ex} \xrightarrow{k_2} P_2 \quad v_2 = k_2 [A][B]_0$$

$$k_{exp} = k_1 + k_2 C_{B0}$$



$$\frac{v_1}{v_2} = \frac{C_{P1}}{C_{P2}} = \frac{k_1}{k_2 C_{B0}}$$