TP CH5
Aspects théoriques

2.1. Dégénérescence de l'ordre.

Ordre β par rapport à H_2O_2

$\Rightarrow [H_2O_2]_0 \ll [I^-]_0 , [H^+]_0$

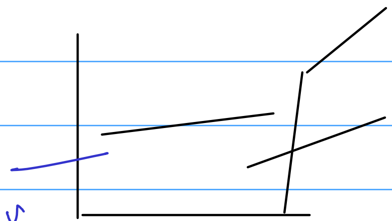
2.2. $\Rightarrow [I^-] \approx [I^-]_0$ et $[H^+] \approx [H^+]_0$

D'où :

$$v = k [I^-]^{\alpha} [H_2O_2]^{\beta} [H^+]^{\gamma}$$

$$\approx \underbrace{k [I^-]_0^{\alpha} [H^+]_0^{\gamma}}_{k_{app.}} [H_2O_2]^{\beta}$$

3.1.



$V = v + v_1 + v_2 + v_3 = 100 \text{ mL}$

$v = 80 \text{ mL}$ $H_2O(l)$

$v_1 = 5 \text{ mL}$ de H_2SO_4 à $C_1 = 1 \text{ mol.L}^{-1}$ ← 1 apport de H^+

$v_2 = 5 \text{ mL}$ de K^+, I^- à $c_2 = 200 \text{ g.L}^{-1}$

v_3 10 mL de H_2O_2 à $c_3 = 10^{-2} \text{ mol.L}^{-1}$

Concentrations initiales :

* $[H^+]_0 = \dfrac{n_{H^+}}{V} = \dfrac{c_1 \times v_1}{V} \approx \dfrac{1 \times 5 \times 10^{-3}}{10^{-1}} \sim 5 \times 10^{-2} \text{ mol.L}^{-1}$

$KI = K^+ + I^-$

* $[I^-]_0 = \dfrac{n_{I^-}}{V} = \dfrac{n_{KI}}{V} = \dfrac{m_{KI}/M_{KI}}{V} = \dfrac{c_2 v_2}{V \times M_{KI}}$

$$\approx \frac{5 \times 10 \times 5 \times 10^{-3}}{10^{-1} \times 1\ 5 \times 10} \sim \frac{25}{15} \times \frac{10^{-2}}{1} \sim 1{,}2 \times 10^{-} \text{ mol.L}^{-1}$$

* $[H_2O_2]_0 \approx \dfrac{n_{H_2O_2}}{V} = \dfrac{c_3 v_3}{V} \sim \dfrac{10^{-2} \times 10^{-2}}{0{,}1} \sim 10^{-3} \text{ mol.L}^{-1}$

Donc $[I^-]_0 , [H^+]_0 \gg [H_2O_2]_0 \Longrightarrow$ dégénérescence de l'ordre.

3.1.

$2H_2O_2(aq)$	$+ 6I^-(aq)$	$+ 4H_3O^+(aq)$	$= 8H_2O(l)$	$+ 2I_3^-(aq)$
C_0	x	x	excès	0
$C_0 - 2x$	x	x	excès	$2x$

D'où $[H_2O_2] = C_0 - 2x$
$[I_3^-] = 2x$

D'où : $\boxed{[I_3^-] = C_0 - [H_2O_2]}$

3.2. Loi de Beer-Lambert :
$A = \varepsilon(\lambda)\,l\,[I_3^-]$

$\Rightarrow \boxed{A = \varepsilon(\lambda)\,l\,(C_0 - [H_2O_2])}$

3.3. $t \longrightarrow +\infty \quad > \quad [H_2O_2]_\infty = 0$

D'où $\underline{A_\infty = \varepsilon(\lambda)\,l\,C_0.}$

$A = \underbrace{\varepsilon(\lambda)\,l\,C_0}_{A_\infty} - \varepsilon(\lambda)\,l\,[H_2O_2]$

$\Leftrightarrow \boxed{[H_2O_2] = \dfrac{A_\infty - A}{\varepsilon(\lambda)\,l.}}$

3.3. ① $\beta = 0$? $[H_2O_2](t)$?

$v = \dfrac{1}{-2}\dfrac{d[H_2O_2]}{dt}$ et $v = k_{app}$

$\Rightarrow$ d'où $-\dfrac{1}{2}\dfrac{d[H_2O_2]}{dt} = k_{app}$

$\Leftrightarrow d[H_2O_2] = -2k_{app}\,dt$

$$\Rightarrow \int_{C_0}^{[H_2O_2](t)} d[H_2O_2] = -2\,k_{app}\int_0^t dt$$

$$\Rightarrow [H_2O_2] - C_0 = -2k_{app}\,t$$

$$\Rightarrow \boxed{[H_2O_2] = C_0 - 2k_{app} \times t}$$

Or $A = A_\infty - \varepsilon(\lambda)\,\ell\,[H_2O_2]$

$$\Rightarrow A = \cancel{A_\infty} - \underbrace{\varepsilon \ell C_0}_{\cancel{A_\infty}} + 2\varepsilon\ell\,k_{app}'\,t$$

$$\boxed{A = 2\,\varepsilon\ell\,k_{app}\,t}$$

② $\beta = 1$? $[H_2O_2](t)$?

$$v = -\frac{1}{2}\frac{d[H_2O_2]}{dt} \quad \text{et} \quad v = k_{app}[H_2O_2]$$

$$\Rightarrow \frac{d[H_2O_2]}{dt} = -2\,k_{app}[H_2O_2]$$

$$\Leftrightarrow \frac{d[H_2O_2]}{[H_2O_2]} = -2\,k_{app}\,dt$$

$$\Rightarrow \int_{C_0}^{[H_2O_2](t)} \frac{d[H_2O_2]}{[H_2O_2]} = -2\int_0^t k_{app}\,dt$$

$$\Leftrightarrow \boxed{\ln\left(\frac{[H_2O_2]}{C_0}\right) = -2\,k_{app}\,t}$$

Or $[H_2O_2] = \frac{1}{\varepsilon\ell}\left(A_\infty - A(t)\right)$ et $C_0 = \frac{A_\infty}{\varepsilon\ell}$

$$\Rightarrow \boxed{\ln\left(\frac{A_\infty - A}{A_\infty}\right) = -2\,k_{app}\,t}$$

③ $\beta = ?$

$$v = -\frac{1}{2}\frac{d[H_2O_2]}{dt} \quad \text{et} \quad v = k_{app}[H_2O_2]^2$$

$$\Rightarrow \frac{d[H_2O_2]}{dt} = -2k_{app}[H_2O_2]^2$$

$$\Rightarrow \int_{C_0}^{[H_2O_2]} \frac{d[H_2O_2]}{[H_2O_2]^2} = \int_0^t -2k_{app}\,dt$$

$$\Leftrightarrow -\frac{1}{[H_2O_2]} + \frac{1}{C_0} = -2k_{app}t$$

Avec $[H_2O_2] = \frac{1}{\varepsilon l}(A_\infty - A(t))$ et $C_0 = \frac{A_\infty}{\varepsilon l}$

$$\Rightarrow -\frac{\varepsilon l}{A_\infty - A(t)} + \frac{\varepsilon l}{A_\infty} = -2k_{app}t \Rightarrow \boxed{\frac{1}{A_\infty - A(t)} + \frac{1}{A_\infty} = -\frac{2k_{app}}{\varepsilon l}t}$$