

Exercices Supplémentaires de cinétique

Exercice 1

12 Ester + Dode $\rightarrow$...



$$V_e [\text{ester}] = [\text{dode}]$$

$$v = k [\text{ester}] [\text{dode}]$$

$$= k [\text{dode}]^2 = - \frac{d[\text{dode}]}{dt}$$

$$\frac{1}{[\text{dode}]} - \frac{1}{[\text{dode}]_0} = kt$$

3/4 disparu $\Rightarrow$ il reste $1/4 \times 0,01$

$$\frac{1}{0,01} - \frac{1}{0,01} = kt_{3/4}$$

$$\frac{3}{0,01} = k \times 2$$

$$k = \frac{3}{0,02} = 150 \text{ h}^{-1} \text{ mol}^{-1} \text{ L}$$

$$t_{1/2} = \frac{1}{k[\text{A}]_0} = \frac{1}{150 \times 0,01} = 0,66 \text{ h}$$

$$= 40 \text{ minutes}$$

22 $k' = 4k = 4 \times 150 = 600 \text{ mol}^{-1} \text{ L h}^{-1}$

$$t_{1/2}' = \frac{1}{600 \times 0,01} = 0,16 \text{ h} = 10 \text{ minutes}$$

$$E_n k' (400) \quad E_n k (300) = \frac{E_a}{R} \left(\frac{1}{400} - \frac{1}{300} \right)$$

$$(E_n 4) \times \frac{8,31}{300} - \frac{1}{400} = E_a = 13,8 \text{ kJ mol}^{-1}$$

Exercice 2

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

12 temps de fin de réaction $[\text{A}]_0 = 0,01 [\text{A}]$

$$\frac{1}{0,01 [\text{A}]_0} - \frac{1}{[\text{A}]_0} = \frac{q_1}{[\text{A}]_0} = k t_q$$

$$t_q = \frac{q_1}{k[\text{A}]_0} \quad \text{or } t_{1/2} = \frac{1}{k[\text{A}]_0}$$

$$t_q = q_1 t_{1/2} = q_1 h$$

22 On veut $t_q = 1 \text{ h} = \frac{q_1}{k[\text{A}]_0}$

$$k([\text{I}']) = \frac{q_1}{[\text{A}]_0}$$

$$\text{or } k(300) = \frac{1}{[\text{A}]_0}$$

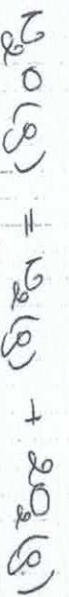
$$E_n k([\text{I}']) - E_n k(300) = \frac{E_a}{R} \left(\frac{1}{T'} - \frac{1}{T} \right)$$

$$- \frac{R}{E_a} \left(E_n 991 + \frac{1}{300} - \frac{1}{T'} \right)$$

$$\Rightarrow \frac{8,31}{23000} \ln 99 + \frac{1}{300} = \frac{1}{T'}$$

$$\frac{1}{T'} = 1,67 \times 10^{-3} \Rightarrow T' = 599,7 \text{ K}$$

Exercice 3



$$n_0 \quad \xi \quad 2\xi \quad n_T = n_0 + 2\xi$$

Ordre 1

$$\ln [\text{H}_2\text{O}]_0 - \ln [\text{H}_2\text{O}]_t = -kt$$

$$\ln \frac{n_0 - \xi}{n_0} = -kt$$

$$\xi = n_0 (1 - e^{-kt})$$

$$P_T = n_T \frac{RT}{V}$$

$$= (n_0 + 2\xi) \frac{RT}{V}$$

$$= P_0 + 2P_0 (1 - e^{-kt})$$

$$= 3P_0 - 2P_0 e^{-kt}$$

$$\frac{3P_0 - P_T}{2P_0} = e^{-kt}$$

$$-kt = \ln \left(\frac{3P_0 - P_T}{2P_0} \right)$$

Calcul de k : $k = -\frac{1}{26,5} \ln \left(\frac{3 \times 37,43 - 41,5}{2 \times 37,43} \right)$

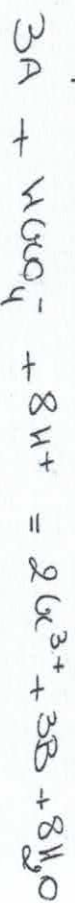
$$= 2,13 \times 10^{-3} \text{ s}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{2,13 \times 10^{-3}}$$

$$= 325,3 \text{ s}$$

Exercice 4

Barque PT 2023



$$v = k [\text{A}]^\alpha [\text{HCO}_3^-]^\beta [\text{H}^+]^\gamma$$

2^e Tableau 1 :

$$b \ll a \quad \text{or} \quad b \ll [\text{H}^+]$$

dégénérescence de l'ordre

$$v = k_1 [\text{HCO}_3^-]^\beta$$

$$\text{avec } k_1 = k a^\alpha [\text{H}^+]_0^\gamma$$

$$3^{\text{e}} \quad v = -\frac{1}{2} \frac{d[\text{HCO}_3^-]}{dt} = k_1 [\text{HCO}_3^-]^\beta$$

$$\text{Si } \beta = 1 \quad \ln [\text{HCO}_3^-]_0 - \ln [\text{HCO}_3^-]_t = -2k_1 t$$

En traçant $\ln [\text{HCO}_3^-] = f(t)$, on obtient une droite : ordre 1

Vérifié et

$$k_1 = \frac{2,38 \times 10^{-2}}{2} = 1,19 \times 10^{-2} \text{ min}^{-1}$$

4^e Tableau 2 : Proportions

stoechiométriques pour A et HCO_3^-

$$\frac{a'}{3} = \frac{b'}{2} \quad \text{et excès de } \text{H}^+$$

$$62 \quad k_2 = k \times (0,08) (0,240)^Y = 1,1910^{-2}$$

$$k_2 = k \times \left(\frac{2}{2}\right) (0,405)^Y = 0,5$$

$$\frac{0,5}{1,1910^{-2}} = \frac{2}{2} \left(\frac{0,405}{0,240} \right)^Y \times \frac{1}{0,08}$$

$$\ln \left(\frac{2}{3} \frac{0,5}{1,1910^{-2}} \times 0,08 \right) = Y \ln \left(\frac{0,405}{0,240} \right)$$

$$Y = \frac{\ln \frac{2}{3} \times \frac{0,5}{1,1910^{-2}} \times 0,08}{\ln \frac{0,405}{0,240}}$$

$$Y = 2$$

On peut en déduire k

$$k = 0,5 \times \frac{2}{3} \times \frac{1}{(0,405)^2}$$

$$= 2 \text{ mol}^3 \text{ L}^{-3} \text{ min}^{-1}$$