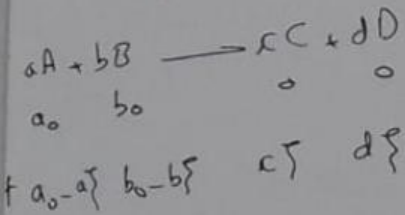


# Cinétique chimique



$$V_R = \frac{1}{V} \frac{d\xi}{dt}$$

$$V_R = -\frac{1}{a} \cdot \frac{1}{V} \cdot \frac{dM_A}{dt} = -\frac{1}{a} \frac{d[A]}{dt} \quad \text{à A}$$

$$V_R = -\frac{1}{b} \cdot \frac{d[B]}{dt}$$

$$V_R = \frac{1}{c} \cdot \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

## Loi de vitesse.

$$V_R = k(T) \cdot [A]^\alpha [B]^\beta$$

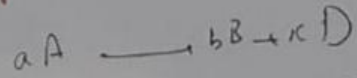
$\alpha$ : ordre cinétique partiel  
à A

$\beta$ : ordre cinétique partiel  
à B

$(\alpha + \beta)$ : ordre global

$k(T)$ : ch. cinétique de la réaction

I. Cinétique chimique par un seul réactif



$$V_R = -\frac{1}{a} \cdot \frac{d[A]}{dt} = k[A]^\alpha$$

$\alpha = 0, 1; 2$

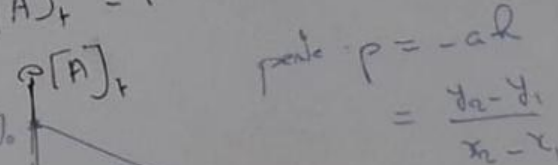
Cinétique d'ordre 0 par rapport à A  
 $\alpha = 0$

$$V_R = -\frac{1}{a} \frac{d[A]}{dt} = k(T)$$

$$\int_{[A]_0}^{[A]_t} d[A] = \int_0^t -a k(T) dt$$

$$[A]_t - [A]_0 = -a k t$$

$$[A]_t = [A]_0 - a k t$$



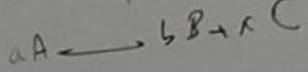
$$k(T) = \frac{[A]_0 - [A]}{a t} : \text{mol.L}^{-1} \cdot \text{s}^{-1}$$

Temps de demi-réaction:  $t_{1/2}$

à  $t_{1/2}$  on  $[A]_{t_{1/2}} = \frac{[A]_0}{2}$  }  $t_{1/2} = \frac{[A]_0}{2ak}$   
 et  $t_{1/2} : \frac{[A]_0}{2} = [A]_0 - a k t_{1/2}$   
 $t_{1/2}$  est proportionnel à  $\frac{1}{[A]_0}$

# Cinétique Chimique

1/ Cinétique d'ordre 1 ( $d=1$ )



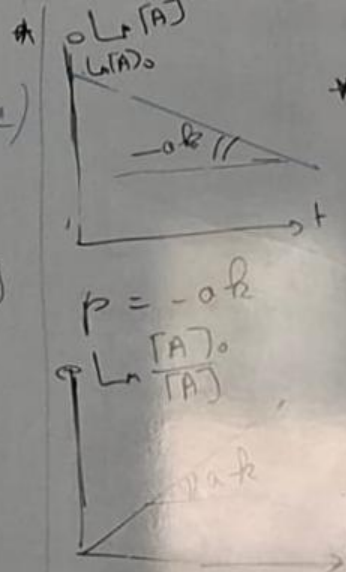
$$v_R = -\frac{1}{a} \frac{d[A]}{dt} = k[A]$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -a k dt$$

$$\ln[A] = \ln[A]_0 - a k t$$

$\ln[A] = f(t)$ : droite affine

$$\ln \frac{[A]_0}{[A]} = a k t$$



$k(t) = \frac{\ln \frac{[A]_0}{[A]}}{t}$   
 $k(t) : (t^{-1})$

\* à  $t_{1/2}$ :  $[A]_{t_{1/2}} = \frac{[A]_0}{2}$   
 $\Rightarrow t_{1/2} = \frac{\ln 2}{a k}$

$t_{1/2}$  indépendant de  $[A]_0$

$v_0 = k[A]_0$

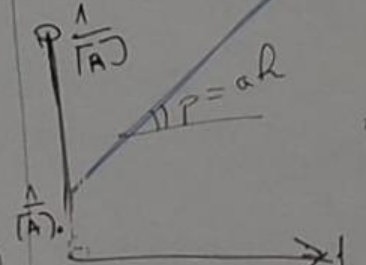
$v_0$  proportionnelle à  $[A]_0$

2/ Cinétique d'ordre 2

$$-\frac{1}{a} \frac{d[A]}{dt} = k[A]^2$$

$$\int_{[A]_0}^{[A]} \frac{-d[A]}{[A]^2} = \int_0^t a k dt$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + a k t$$



\* à  $t_{1/2}$ :  $[A]_{t_{1/2}} = \frac{[A]_0}{2}$

$$\Rightarrow t_{1/2} = \frac{1}{a k [A]_0}$$

$t_{1/2}$ : inversement proportionnelle à  $[A]_0$

$$v_0 = k[A]_0^2$$

$$k = \frac{\frac{1}{[A]} - \frac{1}{[A]_0}}{a t}$$

$$k : (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{s}^{-1}$$

$$k : \text{mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$$

# Cinética Química

## Método dos reagentes

| t                                                                  | 0                | t <sub>1</sub> | t <sub>2</sub> | ...      |
|--------------------------------------------------------------------|------------------|----------------|----------------|----------|
| [A] <sub>t</sub>                                                   | [A] <sub>0</sub> | ...            | ...            | ...      |
| $R_1 = \frac{d[A]_0 - [A]_t}{dt}$<br>$\alpha = 0$                  |                  | $\alpha$       | $\alpha$       | $\alpha$ |
| $R = \frac{\ln \frac{[A]_0}{[A]_t}}{dt}$<br>$\alpha = 1$           |                  | $\alpha$       | $\alpha$       | ...      |
| $R = \frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{dt}$<br>$\alpha = 2$ |                  |                |                |          |

Appl



$$R(298) = 5 \cdot 10^{-4} \text{ mol. L}^{-1} \text{ min}^{-1}$$

$$3) \text{ a } t_{3/8} : [A]_{3/8} = ?$$

$$v_A = -\frac{1}{2} \frac{d[A]}{dt} = R[A]^{\alpha}$$

$$R_{\text{exp}} = -\frac{1}{2} \frac{d[A]}{dt}$$

$$R(t) = (R_0 L^{1-\alpha}) t^{\alpha-1}$$

$$\text{da } (1-\alpha) = 0 \text{ e } \alpha = 1$$

$$1) \alpha = 1 : v_R = \frac{1}{2} \frac{d[A]}{dt} = R[A]$$

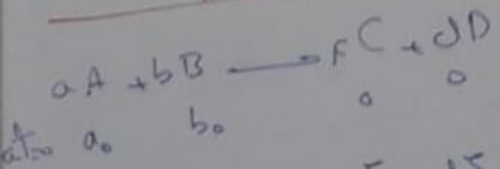
$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -2 R dt$$

$$\ln[A] = \ln[A]_0 - 2 R t$$

$$3) \text{ a } t_{3/8} : \frac{7}{8} [A]_0 \text{ reagiu}$$

$$\text{da } [A]_{3/8} = [A]_0 - \frac{7}{8} [A]_0 = \frac{[A]_0}{8}$$

## II - Cinétique à deux réactifs



at  $a_0 - a\tau$      $b_0 - b\tau$      $c\tau$      $d\tau$

$$[A]_0 = \frac{a_0}{V} ; [B]_0 = \frac{b_0}{V}$$

On suppose  $[B]_0 \gg [A]_0$

A : réactif limitant :  $[B]_t \approx [B]_0$

$$V_R = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^x [B]^y$$

$$= k(\tau) [B]_0^y [A]^x$$

$$-\frac{1}{a} \frac{d[A]}{dt} = k_{app} [A]^x$$

$$[A] = f(t) : d\tau \quad \alpha = 0$$

$$\ln[A] = f(t) : d\tau \quad \alpha = 1$$

$$\frac{1}{[A]} = f(t) : d\tau \quad \alpha = 2$$

On suppose  $\alpha = 1$  (1<sup>re</sup> expérience)

$$\ln[A] = \ln[B]_0 - a k_{app} \tau$$

$$k_{app} = \text{pende.} (\ln[A] = -a k_{app} \tau)$$

$$a k_{app} = k(\tau) [B]_0^y$$

à la m<sup>ème</sup> T

|                            |             |             |
|----------------------------|-------------|-------------|
|                            | $[B]_0$     | $k_{app}$   |
| 1 <sup>re</sup> expérience | $[B]_{0,1}$ | $k_{app,1}$ |
| 2 <sup>de</sup> expérience | $[B]_{0,2}$ | $k_{app,2}$ |

$$k_{app,1} = k(\tau) [B]_{0,1}^y$$

$$k_{app,2} = k(\tau) [B]_{0,2}^y$$

$$k_{app,2} = k(\tau) [B]_{0,2}^y$$

$$\frac{k_{app,1}}{k_{app,2}} = \left( \frac{[B]_{0,1}}{[B]_{0,2}} \right)^y$$

$$\beta = \frac{\ln \frac{k_{app,1}}{k_{app,2}}}{\ln \frac{[B]_{0,1}}{[B]_{0,2}}}$$