

**MOHAMED KHIDER UNIVERSITY OF BISKRA.**

**FACULTY OF EXACT SCIENCES AND NATURAL AND LIFE SCIENCES**

**DEPARTMENT OF BIOLOGY**

**Semester2: THERMODYNAMICS AND CHEMISTRY OF  
MINERAL SOLUTIONS**

**CHAPTER II**

**Level: 1<sup>st</sup> year LMD**

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## 6. Chemical kinetics

### 6.1. Definition

Chemical kinetics is the field of chemistry that studies the rate of chemical reactions as a function of time. Qualitatively, we notice that there are different types of reactions:

- Very rapid or even violent reactions: for example explosion reactions.
- Very slow reactions, they last several years (like the formation of rust), or even several centuries (like the formation of coal or oil).

Some are even so slow that the starting reagents are considered stable, for example the transformation of carbon diamond into graphite. We then speak of “metastable” states.

The types of reactions depend on certain factors (parameters) which can accelerate or slow them down, for example:

The concentration of the reactants: the speed generally increases as a function of the concentration of the reactants.

Temperature: The speed of a reaction increases with increasing temperature.

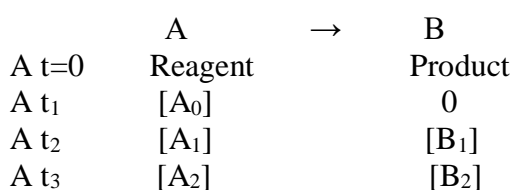
The contact surface: the speed of a reaction increases with the extent of the contact surface.

Catalysis: the use of catalysts is common to increase the speed of a reaction (in the case of enzymes).

### 6.2. Reaction speed

Knowing that the first importance in all applications of chemistry is to know the speed of chemical reactions.

For a reaction like:



We determine the average reaction speed  $V_{avg}$  between 2 times  $t_1$  and  $t_2$  for the products and the reactants.

According to the expressions:

$$V_{Averg} = \frac{[B_2] - [B_1]}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t} \quad \text{Or : } V_{Averg} = \frac{[B_2] - [B_1]}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}$$

$$V_{Averg} = \frac{d[B]}{dt} = -\frac{d[A]}{dt} \quad V_{Averg} = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$



The speed of the reaction at any moment is:

$$v = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

In the case where a reaction takes place in the gas phase then:  $[A] = -\frac{P_A}{RT}$

### **6.3. Expression of the law of speed and order of a reaction**

An equation depends on the total order of the reaction:  $\alpha A + \beta B \rightarrow \gamma C$

$$v = k[A]^\alpha [B]^\beta$$

K: is the speed constant.

$\alpha + \beta$ : is the total order of the reaction.

$\alpha$  and  $\beta$ : partial order with respect to reactants A and B.

Note: The order of the reaction is always determined experimentally.

#### **6.3.1. Order 0 reactions:**

For a reaction like:



The speed is expressed by:  $v = -\frac{d[A]}{dt} = k[A]^0 = k$

Speed is a constant independent of concentration:  $\int_{[A_0]}^{[A]} -d[A] = k \int_0^t dt$

Hence:  $[A] = -kt + [A_0]$ : this equation represents a line with a slope opposite the speed constant k. k: expressed in mol/Ls

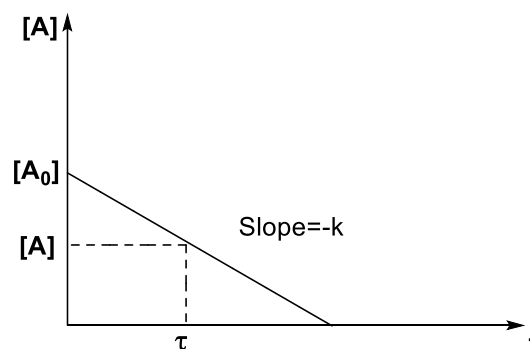
$$t = \frac{1}{k} ([A_0] - [A])$$

If:  $t = t_{1/2} = \tau =$  half-life: the half-reaction time, i.e.: the time after which half of the reactant

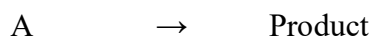
has transformed into product;  $[A] = \frac{[A_0]}{2}$

$$\frac{[A_0]}{2} = -kt_{1/2} + [A_0] \quad t_{1/2} = \tau = \frac{[A_0]}{2k}$$

Hence:  $\Rightarrow k$ : expressed in mol L<sup>-1</sup>s<sup>-1</sup>



### 6.3.2. Order 1 reaction:



$$v = -\frac{d[A]}{dt} = k[A]$$

$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]} = k \int_0^t dt \quad \text{Ln} \frac{[A_0]}{[A]} = kt$$

$$\Rightarrow t = \frac{1}{k} \text{Ln} \frac{[A_0]}{[A]} \quad (1)$$

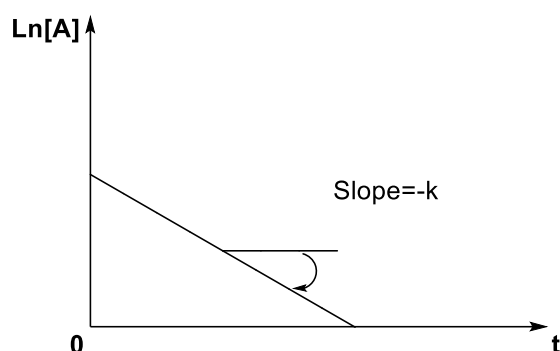
$$\text{Ln}[A] = -kt + \text{Ln}[A_0] \quad (2)$$

k: expressed in time<sup>-1</sup> i.e. : s<sup>-1</sup> or min<sup>-1</sup> or h<sup>-1</sup>

Half-reaction time:  $t = t_{1/2} = \tau = \text{half-life} \Rightarrow [A] = \frac{[A_0]}{2}$

$$t_{1/2} = \frac{1}{k} \text{Ln} \frac{[A_0]}{[A_0]/2} \quad \Rightarrow \quad t_{1/2} = \frac{\text{Ln}2}{k}$$

The order of the reaction can be determined experimentally by plotting:  $\text{Ln}[A] = f(t)$



### 6.3.3. Order 2 reactions:

In a general case:  $A + B \rightarrow \text{Product}$

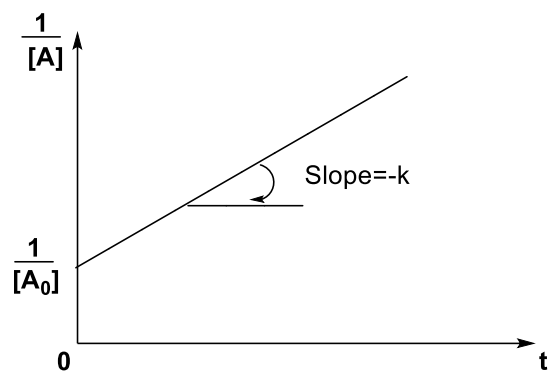
1<sup>st</sup> Case: If we have  $[A] = [B]$

The speed is expressed by:  $v = -\frac{d[A]}{dt} = k[A][A] = k[A]^2$

$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]^2} = k \int_0^t dt$$

$$\frac{1}{[A]} - \frac{1}{[A_0]} = kt \quad \text{Or:} \quad k = \frac{1}{t} \left( \frac{1}{[A]} - \frac{1}{[A_0]} \right) \quad \text{k: expressed in mol}^{-1}\text{liter t}^{-1}$$

Graphical method: then we plot:  $\frac{1}{[A]} = f(t)$



2<sup>nd</sup> Case: If we have:  $[A] \neq [B]$

	A	+	B	→	Product
t=0	a		b		0
t>0	a-x		b-x		x

The speed is expressed by:  $v = -\frac{d[A]}{dt} = k[A][B]$

$$[A]_0 = a \quad [A]_t = a-x$$

$$[B]_0 = b \quad [B]_t = b-x$$

The speed of disappearance and appearance:

$$v = \frac{-d(a-x)}{dt} = \frac{-d(b-x)}{dt} = \frac{dx}{dt} = k[A][B] = k(a-x)(b-x) \Rightarrow \frac{dx}{(a-x)(b-x)} = kdt \Rightarrow$$

But it is clear that:  $\frac{1}{(a-x)(b-x)} = \frac{1}{(b-a)} \left( \frac{1}{a-x} - \frac{1}{b-x} \right)$

$$\int_0^x \left( \frac{1}{a-x} - \frac{1}{b-x} \right) dx = \int_0^t kdt \Rightarrow \frac{1}{(b-a)} [-\ln(a-x) + \ln(b-x)]_0^x = kt$$

$$\Rightarrow \frac{1}{(b-a)} [\ln \frac{b-x}{a-x}]_0^x = kt$$

$$\frac{1}{(b-a)} \left( \ln \frac{b-x}{a-x} - \ln \frac{b}{a} \right) = kt \Rightarrow \frac{1}{(b-a)} \left( \ln \frac{a(b-x)}{b(a-x)} \right) = kt$$