# Reaction kinetics and chemical equilibrium

## *Introduction :*

Enzymatic reactions involve elements of chemical kinetics. Chemical kinetics aims to determine, for a given reaction, the speed at which reactants disappear or products appear. It therefore measures changes in the concentrations (quantities) of reactants or products over time.

## *1. Reaction speed :*

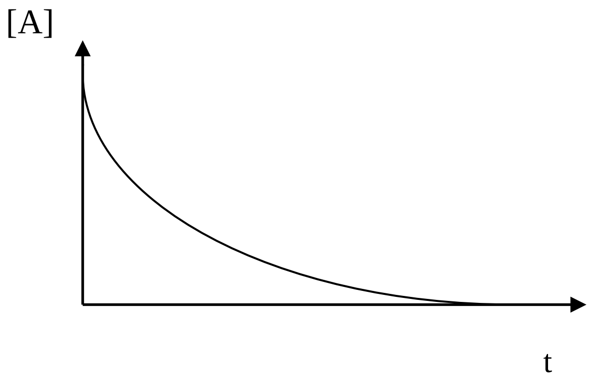
### 1. 1. Definition :

The speed of a reaction is the speed at which a molecular species characteristic of the reaction appears or disappears. It is the change in the quantity of reactants or products over time. It depends mainly on three factors :

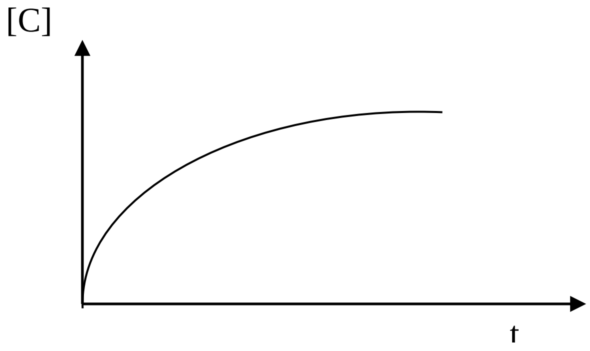
- The concentration of the reactants.
- The temperature.
- The use of catalysts.

### 1. 2. Graphical representation :

Assuming the following simple reaction : $\mathbf{A + B \longrightarrow C}$



Disappearance of A : **[A] = *f* (t)**



Formation of C : **[C] = *g* (t)**

### 1. 3. Mathematical expression of speed :

Consider the following reaction :

$$\mathbf{A + B \longrightarrow C}$$

### *Theoretically :*

During this reaction, the concentration of A changes. Therefore, in the time interval $\Delta t = t_2 - t_1$, $\Delta[A] = [A]_2 - [A]_1$ of reactant A disappears.

The average speed of disappearance of A can be defined as follows :

$$\mathbf{v_m = -\Delta[A] / \Delta t}$$

The instantaneous speed (at instant t) is represented by the derivative of the function : [A] = ƒ (t) at time t or the limit of vm when Δt tends toward 0. Therefore :

$$\mathbf{v_A = -d[A] / dt}$$

An identical relationship can be established for reagent B and product C at instant t :

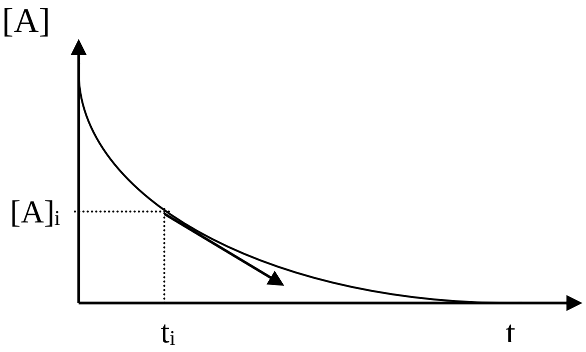
$$\mathbf{v_B = -d[B] / dt} \quad \text{et} \quad \mathbf{v_C = d[C] / dt}$$

It should be noted that the instantaneous speeds $v_A$, $v_B$, and $v_C$ are equal ; we can write :

$$\mathbf{v = -d[A] / dt = -d[B] / dt = d[C] / dt}$$

*Graphically :*

The instantaneous speed is represented by the absolute value of the slope of the tangent at the instant ti considered.



In cases where the stoichiometric coefficients are different from 1, the reaction is written as :

$$aA + bB \xrightarrow{\qquad} cC$$

This means that a moles of A and b moles of B disappear at the same time that c moles of C appear. These coefficients are entered into the speed formula :

$$v = -d[A] / \boldsymbol{a}\,dt = -d[B] / \boldsymbol{b}\,dt = d(C) / \boldsymbol{c}\,dt$$

Thus, the speed v has the same value regardless of the constituent considered (reagent or product).

***Experimentally :***

Speed can be expressed by the following formula : $\boxed{v = k\,[A]^{\alpha}\,[B]^{\beta}}$

Where : **k** represents the reaction speed constant.

**α** and **β** represent the partial orders with respect to A and B, respectively.

**(α + β)** is the globall order of the reaction.

## 1. 4. Speed unit :

Speed is expressed in moles per liter per second ($mol.\ l^{-1}.\ S^{-1}$).

## 1. 5. Experimental measurement of reaction speeds :

In general, the variables are : the concentration of a constituent, the temperature, and time. Consequently, it is necessary to set the maximum number of parameters to measure the speed.

To monitor the concentration of a reagent or product, we distinguish between :

**The chemical method :**

A method is classified as chemical when the determination of the concentration of the species under study is based on a chemical titration reaction. There must be a means of stopping the reaction at a precise moment $t_n$ (the time required to perform the titration).

**The physical method :**

The concentration of the species being studied is determined by measuring a physical quantity, such as optical absorbance, mechanical pressure, electrical conductance, etc. These methods offer the advantage of continuous measurement without generally disturbing the reaction environment.

The physical quantities that can be measured are :

- ✓ Pressure in gaseous systems (nanometric method);
- ✓ Heat quantity (calorimetric method);
- ✓ Weight (gravimetric method);
- ✓ Conductivity and electrical potential (electrical method);
- ✓ pH (electrical method);
- ✓ Optical rotation (polarimetric method);
- ✓ Absorbance (spectrophotometric method).

## *2. Fundamental concepts :*

### *2.1. Molecularity of a chemical reaction :*

The number of molecules (or particles) involved in a reaction is called molecularity.

### *2.2. Concept of reversibility :*

In chemical kinetics, we usually describe a reaction as reversible or irreversible.

### 2.2.1. Reversible reaction :

It is a reaction that tends toward equilibrium. That is to say, the reaction occurs in both directions. ($A + B \longrightarrow C$ and $C \longrightarrow A + B$).

### 2.2.2. Irreversible reaction :

It is a complete reaction. In this case, regardless of the concentrations of the products formed, the rate of the reverse reaction can be neglected. ($C \longrightarrow A + B$).

## *3. Elementary reactions :*

A reaction is called elementary when it results from the collision between the molecules of its reactants (usually 1 or 2). In this case, the speed is proportional to the concentration of each of the reactants.

### 3. 1. Monomolecular reactions :

- *Total monomolecular reactions :* $A \xrightarrow{k_1} P$
- Monomolecular reactions tending toward equilibrium : $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} P$

### 3. 2. Bimolecular reactions :

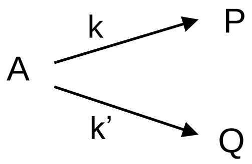
- *Total bimolecular reactions :* $A + B \xrightarrow{k} P$

## *4. Complex reactions :*

Most reactions result from a series of elementary reactions. These are called complex reactions. Complex reactions do not require a collision between the molecules of the reactants to occur. They take place in several steps, and it is the slowest step that determines the overall reaction speed (rate-determining step).

### 4. 1. Simultaneous (parallel) total monomolecular reactions :

Consider the reaction :



Reagent A, in this type of reaction, simultaneously transforms into two different products (P and Q) according to two total monomolecular reactions with speed constants k and k' respectively.

### 4. 2. Successive monomolecular reactions :

Consider the reaction :

$$A \xrightarrow{\mathbf{k_1}} B \xrightarrow{\mathbf{k_2}} C$$

## *5. Order of reactions :*

### 5. 1. Definition :

The speed of a reaction depends on the concentrations of its reactants. For this reason, the concept of reaction order was introduced to describe variations in speed (speeds) as a function of these concentrations. In other words, determining the order of a reaction means defining, by a number, how each reactant affects the speed.

The partial order is defined in relation to one reactant (the other reactants being kept constant). It is often equal to the stoichiometric coefficient of the reactant in question.

### 5. 2. Determination of the reaction order :

The order value is established experimentally based on a series of speed determinations using two methods :

1. The first consists of studying the speed as a function of concentrations in order to determine the partial order for each of the reactants.

2. The second consists of studying the variation in concentrations over time, which makes it possible to determine the global order of the reaction with respect to all the reactants.

In fact, the order of a reaction can be deduced from the experimental curves [Reactant] = f ( t ).

If we consider the following reaction : $aA + bB \xrightarrow{k} cC + dD$

$$v = -d[A] / a dt = -d[B] / b dt = d[C] / c dt = d[D] / d dt$$

$$\mathbf{v = k\,[A]^{\alpha}\,[B]^{\beta}}$$

Where :

**α** and **β** are the partial orders with respect to A and B, respectively,
and **(α + β)** is the global order of the reaction.

### 5. 3. Study of order as a function of concentration and time :

In this course, we will limit the study of chemical reactions with entire orders : zero-, first- and second-order reactions.

### *5. 3. 1. Zero-order reactions "0" :*

In this reaction, the speed remains constant as the reagent is consumed. It is independent of the reagents concentration, the amount of which is transformed in proportion to the reaction duration.

The observation of zero order suggests that the authentic substrate has not been chosen.

If we consider the reaction :

$$A \xrightarrow{\mathbf{k}} p$$

We will have : $v = k\,[A]^0$ therefore $\mathbf{v = k}$

As : $v = -d[A] / dt$

Therefore $-d[A] / dt = k \Longrightarrow d[A] = -\,k\,dt$

$\Longrightarrow \int d[A] = \int -\,k\,dt$

$\Longrightarrow [A] - [A]_0 = -\,k\,t$

This gives the equation : $\boxed{\mathbf{[A] = -\,k\,t + [A]_0}}$

<u>The unit of k :</u>

The speed constant k is expressed in concentration/time ($mol.l^{-1}.S^{-1}$).

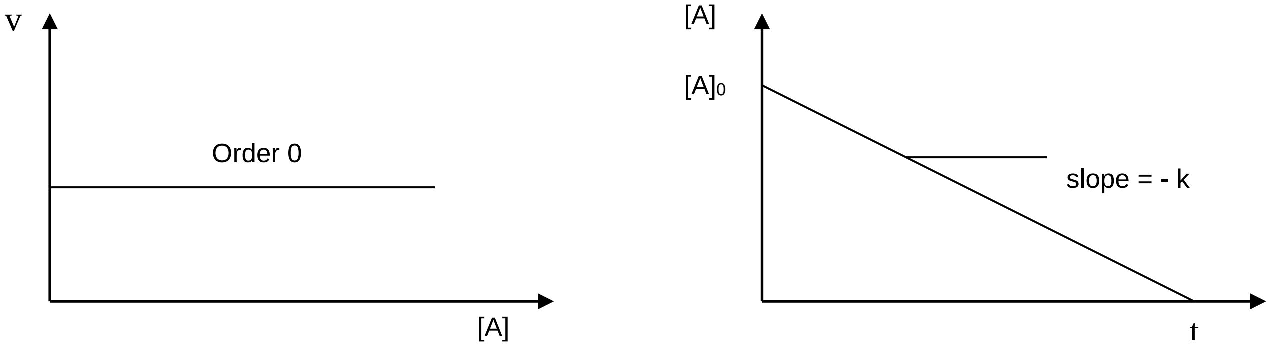
*<u>Half-reaction time :</u>*

The half-reaction time or period ($t_{0.5}$ or $t_{1/2}$) is the time required for half of the reactant ($[A]_0/2$) to be converted.

In a zero-order reaction, $t_{1/2}$ is equal to. $\boxed{\mathbf{t_{1/2} = [A]_0 / 2k}}$

*<u>Graphically :</u>*

The representation of speed as a function of reagent A concentration is a straight line parallel to the x-axis, while that of the function [A] = f (t) is a straight line with a negative slope equal to the speed constant (- k).



*Examples of zero-order reactions :*

These are certain cases where :

- ✓ The reagent is strongly absorbed on a surface.
- ✓ The reagent is gaseous.
- ✓ The concentration of the reagent is in excess ($[A] \approx$ constant).
- ✓ The reagent is not very reactive.

### *5. 3. 2. First-order reactions (1) :*

Such a reaction generally corresponds to the transformation of a single reactant into a product (transformation of one molecule into another molecule). In this case, the speed is proportional to the concentration of the reactant [A].

If we consider the reaction : $A \xrightarrow{k} P$

We have : $v = -d[A] / dt$ and $\mathbf{v = k\,[A]^1}$

Therefore : $-d[A] / dt = k\,(A) \Longrightarrow d[A] / [A] = -k\,dt$

$$\Longrightarrow \int d[A] / [A] = \int -k\,dt$$

$$\Longrightarrow \ln[A]| = -k\,t|$$

$$\Longrightarrow \ln[A] - \ln[A]_0 = -k\,t$$

$$\Longrightarrow \ln[A] / [A]_0 = -k\,t \ldots\ldots\ldots\ldots \mathbf{(6)}$$

Equation (6) can be expressed in exponential form : $\boxed{\mathbf{[A] = [A]_0\, e^{-k\,t}}}$

*The unit of k :*

The speed constant k is expressed in time$^{-1}$. (S $^{-1}$).

*Half- time reaction :*

At $t_{1/2}$, $[A] = [A]_0 / 2$

Replacing [A] with its value in equation (6), we obtain :

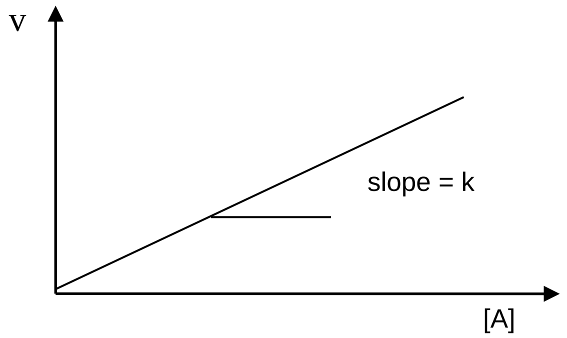
$$\ln([A]_0 / 2[A]_0) = -k\,t_{1/2} \Longrightarrow \ln(1/2) = -k\,t_{1/2}$$

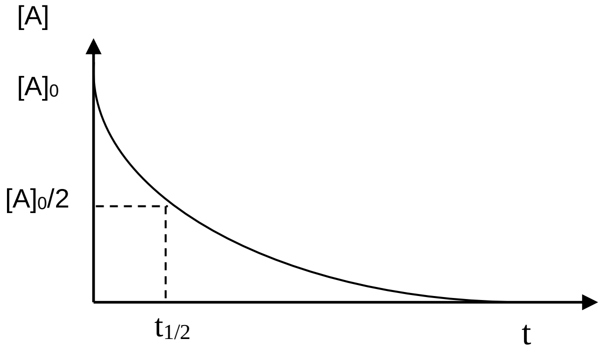
$$\Longrightarrow -\ln 2 = -k\,t_{1/2}$$

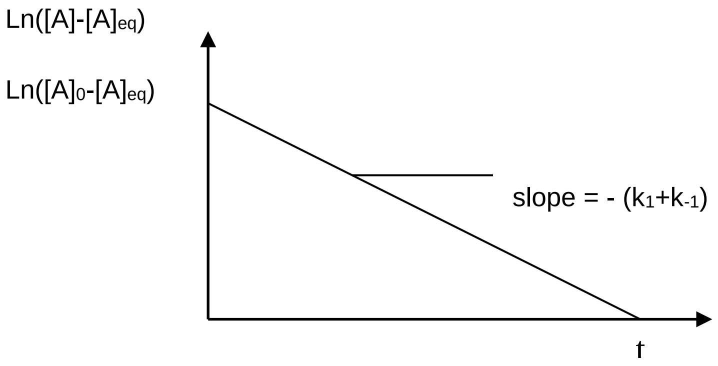
$$\Longrightarrow t_{1/2} = \ln 2 / k \quad \text{thus} \quad \boxed{\mathbf{t_{1/2} = 0.69 / k}}$$

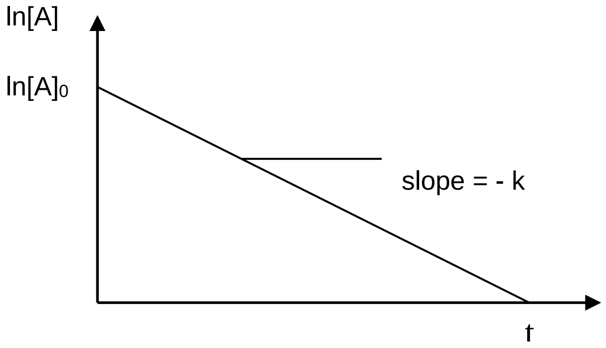
*Graphically :*

The representation of speed as a function of reagent concentration is a straight line passing through the origin. The graph representing $\ln[A] = f(t)$ is a straight line with a negative slope ($-k$) and an ordinate at the origin ($\ln[A]_0$).









If the reaction is first order and tends toward equilibrium, the graph will show $\text{Ln}|[A] - [A]_{eq}|$ as a function of time (linear function).

Examples of first-order reactions :

- Thermal denaturation of enzymes.
- Racemization of amino acids (dextrorotatory and levorotatory).
- Hydrolysis reactions.
- Radioactive decay.

### *5. 3. 3. Second-order reactions :*

It is a reaction in which two substrates react with each other to produce one or more products. Thus, the reaction speed is proportional to the concentration of each substrate.

If we consider the reaction : $A + B \xrightarrow{k} P$

If the reaction is total, it behaves like a total bimolecular reaction. Therefore, the rate is expressed by :

$$v = - d[A] / dt = - d[B] / dt = d[P] / dt$$

$$\mathbf{v = k [A]^1 [B]^1 = k [A_0 – P] [B_0 – P]}$$

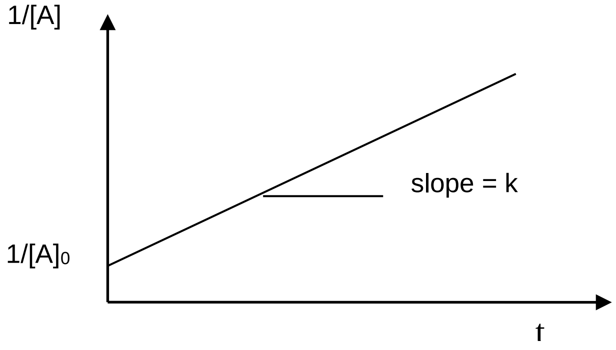
There are two cases :

**<u>1st case :</u>** $[A]_0 = [B]_0$

The experimentally determined speed is then : $v = k [A]^2$

Therefore : $$\boxed{\mathbf{1/[A] = k\, t + 1/[A]_0}}$$

The representation of (1/[A]) as a function of time is linear with a positive slope (k).



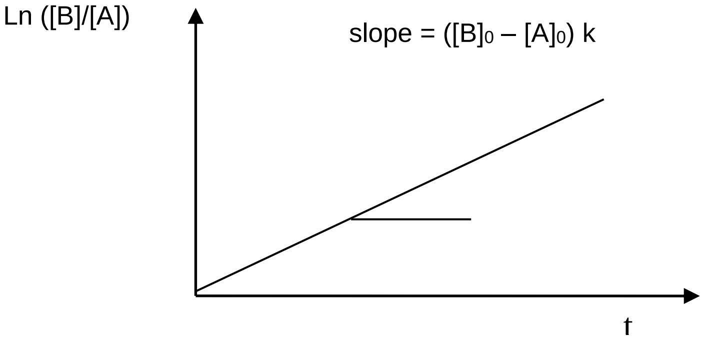
**<u>2nd case :</u>** $[A]_0 \neq [B]_0$

Speed is expressed by : $v = k [A] [B]$

After integration, we will have the following formula :

$$\boxed{\mathbf{Ln([A]_0[B] / [B]_0[A]) = ([B]_0 – [A]_0)k\, t}}$$

In this case, the representation of ln([B]/[A]) as a function of time is a straight line with a slope equal to : ***k ([B]0 – [A]0)***.



*<u>The unit of k :</u>*

In a second-order reaction, the speed constant k is expressed in concenration$^{-1}$ time$^{-1}$. ($mol^{-1}.l.S^{-1}$).

*<u>Half- time reaction :</u>*

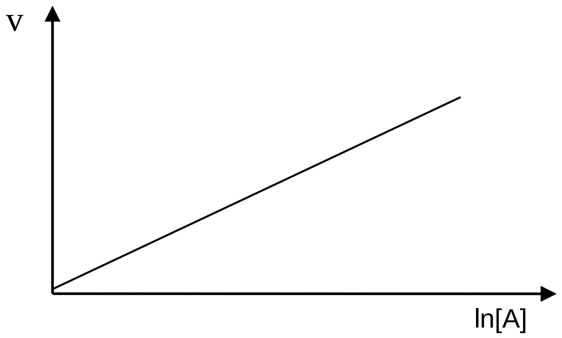
If $[A]_0 = [B]_0$ at $t_{1/2}$, $[A] = [A]_0/2$ or $1/[A] = 2/[A]_0$

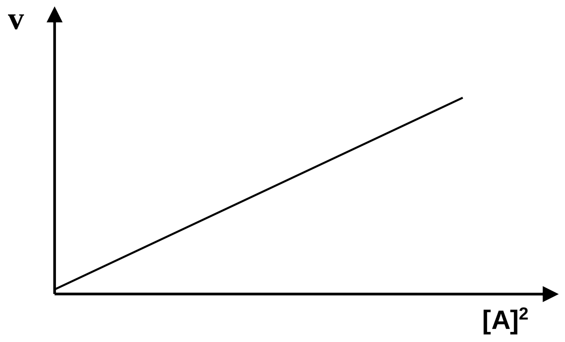
Therefore : $1/[A]_0 = k\ t_{1/2}$ thus $\boxed{t_{1/2} = 1/k\ [A]_0}$

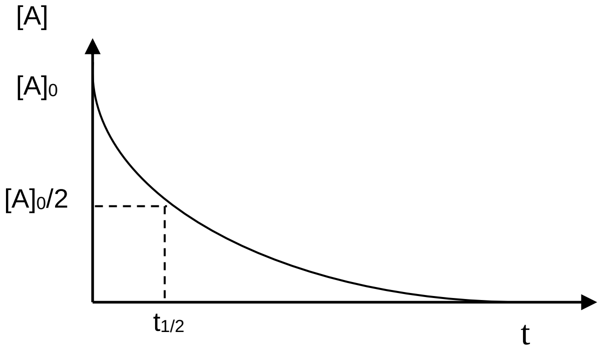
It can be seen that, in a second-order reaction, $t_{1/2}$ depends on the initial concentration of the reactants.

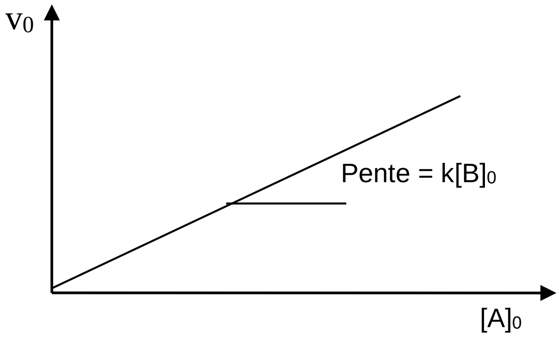
*Graphically :*

The representation of the initial speed (v0) as a function of the square of the reactant A concentration ($[A]^2$) (or as a function of ln[A]) is a straight line that passes through the origin.









*Examples of second-order reactions :*

- ✓ Esterification reactions (methanol + acetic acid).
- ✓ Dimerization reactions.