

Chemical kinetics

Introduction

In all what we have studied in the previous chapter (chemical equilibria) we did not take time into account. This chapter concerns the kinetic aspect of chemical reactions, that is to say the evolution of chemical systems over time.

We will interpret this evolution at the molecular level. The subject of this course is to study speed of chemical reactions.

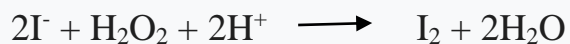
1. Slow reactions and fast reactions

- If we mix, at ordinary temperature, two colorless aqueous solutions of AgNO_3 and NaCl , we immediately obtain a white precipitate of silver chloride AgCl .



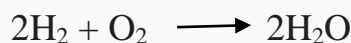
Such reaction is instantaneous.

- On the other hand, if we mix at ordinary temperature, potassium iodide solution and hydrogen peroxide in the presence of acid, the brown color of the iodine gradually appears



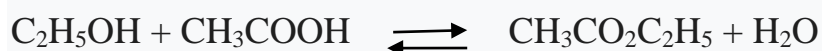
The reaction is slow.

- Even after a century, a mixture of oxygen and hydrogen, taken at ordinary temperature, will not have produced appreciable quantities of water.



Such reaction is extremely slow.

However, reaction rates vary greatly with conditions. So, the reaction:



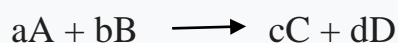
(Ethanol) (Acetic acid)

Acidic alcohol

is without appreciable speed at ordinary temperature, accelerates if the mixture is heated.

2. Reaction speed

Let be the chemical reaction:



A,B: reagents

C,D: products

During the evolution of the previous reaction, the quantities of reactants decrease over time, but those of the products increase. We can represent these variations using molar concentrations or number of moles (fig1)

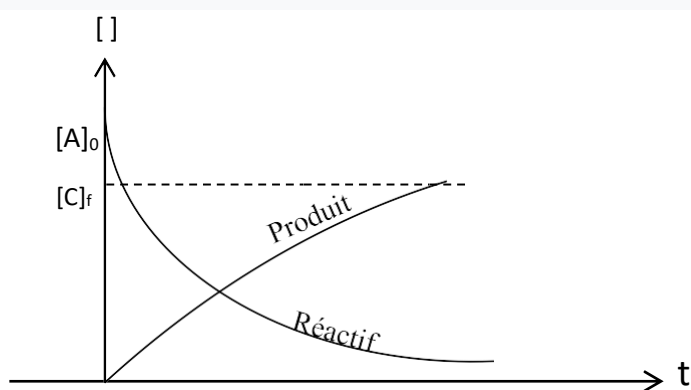


Fig1: evolution of reagents and products quantities .

• Definition of reaction speed

Reaction rate is an experimental quantity of the number of moles which react in the unit of time. At a given temperature, this speed is equal to the variation of the concentration of a species with respect to time (reactants or products)

For the reaction: $aA + bB \rightarrow cC + dD$

$$V = (-1/a)d[A]/dt = (-1/b) d[B]/dt = (+1/c) d[C]/dt = (+1/d) d[D]/dt$$

The – sign means the disappearance of the reactants and the + sign means the appearance of the products.

V is expressed in mole/l. time

3. Kinetic factors:

Speed of chemical reaction depends on several parameters called kinetic factors.

- the concentration of the reagents
- temperature
- the possible presence of a catalyst

4. Influence of concentration on the speed of reaction

Concept of order of a reaction

The speed depends on the concentrations of reacting species:

$$V = K[A]^\alpha [B]^\beta$$

K: speed constant

α : partial order with respect to A ; β : partial order with respect to B

$$\alpha + \beta = \text{overall order of the reaction.}$$

Order of reaction is determined experimentally. The order is not the stoichiometric coefficient except in the case of an elementary reaction.

The expressions of speed law for different orders are :

Zero order: $V = k$ (constant independent of concentration)

First global order: $V = k[A]$ or $k[B]$

Second global order: $V = k[A].[B]$ or $k[A]^2$ or $k[B]^2$

Third order global: $V = k[A].[B].[C]$ or $k[A]^2.[B]$... etc.

a. Zero order reaction: $A \longrightarrow C$

A zero-order reaction is one such that the number of moles (or grams) of initial product are consumed consistently over time. (A candle burning in air is a good example of a zero-order reaction).

If the reaction speed is expressed by the relation:

$$V = -1/a \, d[A]/dt = k \longrightarrow \int_{t=0}^t d[A] = -Ka \int_{t=0}^t dt$$

The reaction is then said to be of zero order, the speed is constant as a function of time. To know the evolution of the concentration as a function of time, we must integrate this differential equation:

Concentration variation law is:

$$[A]_t - [A]_0 = -aKt \quad \text{Hence: } [A]_t = -aKt + [A]_0 \text{ (fig2)}$$

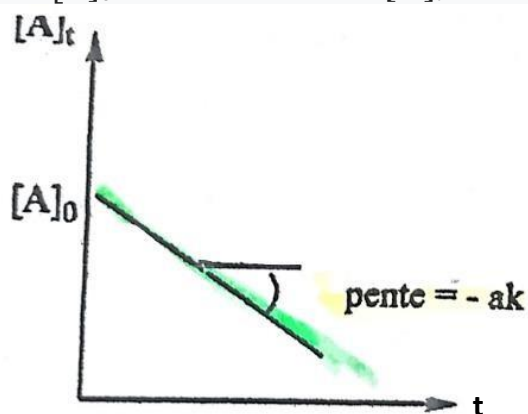


Fig2: variation in the concentration of the reactant of a zero-order reaction.

Concentration of A decreases linearly and reaches zero after a limited time.

The constant $k = ([A]_0 - [A])/at$ is expressed in mole/l.s

The half-reaction time is the time necessary for the transformation of Half quantity of reactant A to products. The concentration is then $[A] = [A]_0/2$.

It follows that $t_{1/2} = [A]_0/2ka$ is proportional to the initial concentration.

b. First order reaction:

if the speed is expressed by the relation:

$$V = (-1/a) d[A]/dt = k[A] \longrightarrow d[A]/[A] = -akdt$$

The speed is said to be of order one with respect to the reactant A.

By integration $\int_{t=0}^t d[A]/[A] = -Ka \int_{t=0}^t dt \longrightarrow \text{Ln}[A]_t - \text{Ln}[A]_0 = -akt$

Concentration variation law is a function of time:

$$\text{Ln}([A]_t/[A]_0) = -akt \quad (\text{fig 3a}) \quad \text{or} \quad [A]_t = [A]_0 e^{-akt} \quad (\text{fig 3b})$$

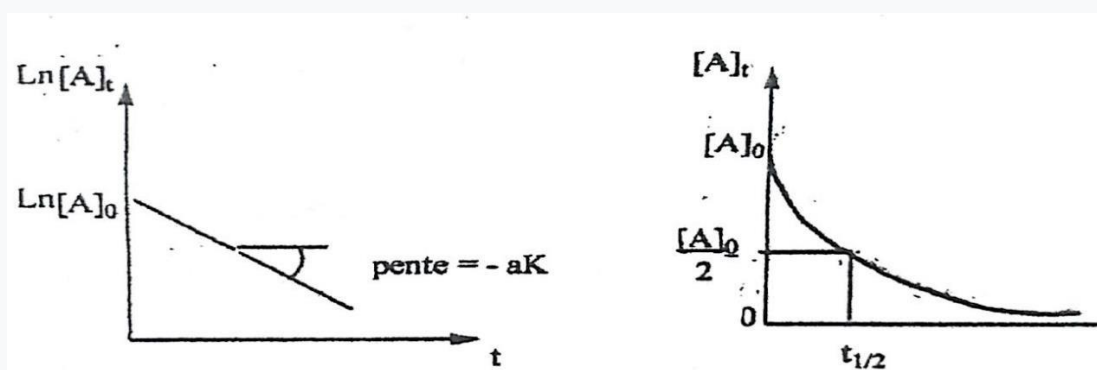


fig 3: variation in the concentration of the reactant of a reaction of order one.

Concentration of A decreased exponentially. The half-reaction time: $t_{1/2}$, necessary to consume half concentration of initial reagent.

at $t = t_{1/2}$: $[A] = [A]_0/2$ and $t_{1/2} = (\ln 2)/ak$, is independent of the initial concentration.

c. Second order reaction:

In the case of a type reaction: $A+B \rightarrow$ products

The speed is expressed by: $V = (-1/a)d[A]/dt = k[A][B]$

If $[A] = [B] \Rightarrow V = (-1/a)d[A]/dt = k[A]^2$, after integration:

$$\int_{t=0}^t d[A]/[A]^2 = -ak \int_{t=0}^t dt \longrightarrow -1/[A]_t - (-1/[A]_0) = -akt$$

Then ,we obtain : $1/[A]_t - 1/[A]_0 = akt$ and the law of variation of

Concentration of reagent is a function of time given by:

$$1/[A]_t = 1/[A]_0 + akt$$

Or : $[A]_t = [A]_0 / (1 + ak[A]_0 t)$ (fig 4)

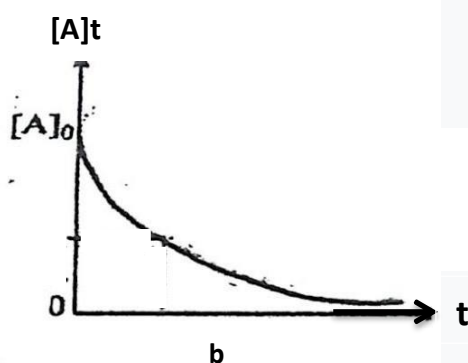


Fig 4: variation in concentration of the reactant of a second-order reaction

Half-reaction time: $t_{1/2} = 1/[A]_0$, is inversely proportional to the initial concentration.

d. Degeneration order of a reaction: $A + B \longrightarrow C$

if for example reagent B is in great excess compared to A $\Rightarrow [B]_0 \gg [A]_0$

then we set $[B] = [B]_0$ (constant) .

$V = k[A]^\alpha [B]^\beta$ with k = real speed constant $\Rightarrow V = k'[A]^\alpha$ or k' is an apparent rate constant $\Rightarrow k' = k [B]^\beta$

The actual rate constant k depends on the initial concentration of B .

The global order is $\alpha + \beta$ and the apparent order is α (degeneracy of the order) .

This method is used to determine the partial order with respect to a given reactant.