ALGERIAN DEMOCRATIC AND PEOPLE'S REPUBLIC

Ministry of Higher Education and Scientific Research

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Faculty of Science and Technology

Department of Process Engineering

Chemical kinetics Homogeneous catalysis course and exercises

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Academic year 2024/ 2025

Chapter 3 Experimental methods chemical kinetics studies

Chapter 4 The theory of chemical kinetics

Introduction

Qualitatively, we can see that there are:

- ‘fast’ reactions, such as dosing reactions
- very ‘slow’ reactions, such as the oxidation of most metals in air, the transformation of diamond carbon into graphite carbon, etc.

Chemical kinetics studies the speed at which reactions take place.

The speed depends on a large number of factors, such as temperature, pressure, the chemical composition of the system and the presence of chemicals. a catalyst.

Chemical kinetics is divided into two parts:

- Homogeneous kinetics: the reaction mixture consists of a single phase (liquid or gas)

$$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$$

- Heterogeneous kinetics: the reaction mixture has several phases

(liquid/gas) in the presence of a solid phase, the reaction occurs at the interphases.

$$C_2H_5OH_{(g)} \xrightarrow{Alumine\ (s)} C_2H_{4(g)} + H_2O_{(g)}$$

Objectives of this course :

To know how to define and determine the rates of disappearance of a reactant and of formation of a product.

- Know how to define the rate of reaction and relate it to the rates of disappearance and formation of the different species.
- Know the influence of various kinetic factors:
- Know how to define and determine the order of a chemical reaction, the degeneracy of order
- Arrhenius' empirical law, activation energy
- Know how to express and integrate the corresponding rate law for simple orders. Half-reaction half-reaction time.

Chapter 1

Speed and speed laws

A chemical reaction is the modification of the assembly of atoms making up the **reactant** molecules to lead to new molecules**, the products**.

A complete description of such a transformation requires **three aspects**, two of which depend solely on the **initial** and **final** states (the quantitative and thermodynamic aspects), while the third requires knowledge of the reaction mechanism, the dynamic or kinetic aspect.

1.1 : An overview of chemical kinetics

Chemical kinetics:
The study of reaction rates, the factors that influence them, and the sequence of molecular events, called the reaction mechanism, according to which reactions take place.

Certain variables can speed up or slow down reactions:

- Reagent concentration; speed generally increases with reagent concentration.
- Temperature: the speed of a reaction usually increases with rising temperature.
- Contact surface; the speed of a reaction increases with the size of the contact surface (fine particles).
- Catalysis; the use of catalysts and current to increase the speed of a reaction (enzymes, metal support, etc.).

1.2 : The significance of reaction speed

Speed: variation of a quantity by a unit of time.

- The speed of a chemical reaction *v* is the ratio between the change in

concentration and time :$v = \frac{\Delta C}{\Delta t} = \frac{C_1 - C_2}{t_1 - t_2}$

Where c_2 and c_1 represent the concentrations of a reactant involved in a reaction at times t_2 and t_1 respectively.

In a reaction:

- change in reagent concentration,Δ [reagent], is negative (the reagent disappears)
- change in product concentration,Δ [product], is positive (the product appears)

So

$$v = -\frac{\Delta[reagent]}{\Delta t} = \frac{\Delta[product]}{\Delta t}$$

According to this convention, **the reaction rate is always positive**, whether determined from the reactants or the products. The units most often used are moles/(L,s).

The general speed of a reaction

The **general reaction rate** is defined as the rate of change of the concentration of a given substance divided by its stoichiometric coefficient in the balanced chemical equation. So, for the reaction :

$$2\ HBr(g) \rightarrow H2(g) + Br2(g)$$

the general reaction rate is defined by :

$$v = \frac{\Delta[Br_2]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[HBr]}{2\Delta t}$$

More theoretically: for the reaction

$$aA + bB \rightarrow cC + dD$$

$$v = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t}$$

$$v = -\frac{1}{b}\frac{\Delta[B]}{\Delta t}$$

Average reaction speed

The speed of a reaction is generally not constant. It is therefore necessary to specify when it is measured.

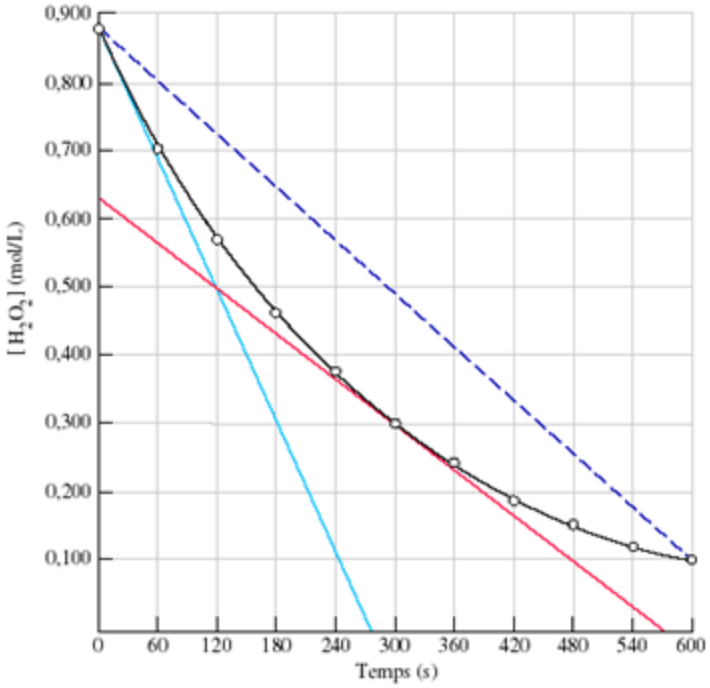
- A reaction speed measured over a given time interval is called **average speed**.

1.3 : Measuring reaction speeds

We have the following hydrogen peroxide degradation reaction:

$$H2O2(aq) \rightarrow H2O(l) + ½\ O2(g)$$

► FIGURE 2.4 $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$



- The black curve represents the rate at which peroxide disappears during the reaction (concentration decreases with time).
- The calculation of the average speed over the whole experiment (between 0 and 600 s) is represented by the dotted line. The numerical value of the velocity is given by the slope of the straight line (which is negative), which we change sign (to give it a positive value) to respect the convention mentioned above.

- To obtain the reaction speed at a precise point on the curve, we need to consider a very short time interval.
- If the time interval in which the reaction speed is measured becomes very short (tends towards zero), the instantaneous speed is approached.

- The **instantaneous velocity** corresponds to the limit of the variation of the reagent in a very short time interval:

$$v = \lim_{\Delta t \to 0} -\frac{\Delta[reagent]}{\Delta t} = -\frac{d[reagent]}{dt}$$

Instantaneous speed =

- Thus, the instantaneous speed can be obtained by the tangent to the curve (derivative) at a given point. This is represented by the red line, which shows the spontaneous reaction speed 300 seconds after the start of the reaction.
- At the start of the reaction, the instantaneous speed is called **the initial reaction speed**. It is represented by the blue (turquoise) straight line in the graph. Again, the numerical value is the value of the slope of the (negative) straight line as it changes sign.

1.4 : The rate law of a chemical reaction

For a reaction involving 2 reactants, A and B :

$$aA + bB \rightarrow \text{products}$$

experimental measurements have shown that the rate of reaction is proportional to the product of the concentrations of the reactants, each assigned an exponent :

$$v = k[\mathrm{A}]^m [\mathrm{B}]^n$$

- The proportionality constant *k* is called the **speed constant.**
- The exponents *m* and *n* are the **reaction orders.**
- The order is usually a small positive integer, but can also be zero, negative or fractional.
- The reaction is said to be of order *m* with respect to A, and of order *n* with respect to B.
- The **sum** of *m* and *n* is the **overall order of** the reaction.
- **Reaction orders are not necessarily the stoichiometric coefficients of the chemical equation.** They can only be determined experimentally.

- **The initial velocity method**

The table above shows the experimental results of initial velocity measurements for the reaction

$$2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$$

- The relative speed method is used to determine the order of reaction with respect to each reactant.
- To do this, we compare initial rates *for the same reaction* by varying the initial
  concentration of one reactant at a time. This is shown in Table 1.

Experience	[NO] initial (mol/L)	$[Cl_2]$ initial (mol/L)	initial speed (mol/L·s)
1	0,0125	0,0255	$2,27 \times 10^{-5}$
2	0,0125	0,0510	$4,55 \times 10^{-5}$
3	0,0250	0,0255	$9,08 \times 10^{-5}$

- Between line 1 and line 3, [NO] doubles, while [Cl2] remains constant.
- Since it's [NO] that's changing, the order of reaction with respect to NO(g) can be found by dividing the initial velocities 3 and 1.
- In general (demonstrated in the volume), the ratio of initial velocities and the order of reaction are linked by the relationship :

$$\frac{(v_0)_3}{(v_0)_1} = 2^m$$

- So, if we calculate the ratio of the initial speeds with the values in the table, we get :

$$\frac{(v_0)_3}{(v_0)_1} = 2^m = 4 = 2^2 \Rightarrow m = 2$$

- Therefore, since $2^m = 4$, m , which is **the order of reaction with respect to NO(g), is equal to 2**.

- Between line 1 and line 2, [NO] remains constant, while [Cl2] doubles.
- Since it's [Cl2] that's changing, the order of reaction with respect to Cl2(g) can be found by dividing the initial velocities 2 and 1.
- Here, the ratio of initial velocities and the order of reaction are linked by the relationship :

$$\frac{(\text{initial velocitie})_2}{(\text{initial velocitie})_1} = 2^n$$

So, if we calculate the ratio of the initial speeds with the values in the table, we get :

$$\frac{(\text{initial velocitie})_2}{(\text{initial velocitie})_1} = \frac{4{,}55\ 10^5}{2{,}27\ 10^5} = 2^n = 2$$

- So: $2^n = 2$, n, which is **the order of reaction with respect to $Cl_{2(g)}$, is equal to 1**.

The overall order of the reaction is therefore (2 + 1) = 3.

IN SUMMARY:

If the concentration of a reagent is doubled, the reaction is :

- if no effect on speed is observed;
- if the speed doubles;
- if speed quadruples;
- if speed increases by a factor of 8.

Once the order of reaction of each reactant is known, the rate constant *k* can be calculated.

It is important to note that **a rate law cannot be determined from the stoichiometry of the reaction.** This can only be done by means of experimental velocity measurements

1.5 : Reactions of order 1

The rate law can also be determined by following the variation of concentrations with time in the same experiment. In this section, we will only consider reactions involving a single reactant (A → products).

Concentration as a function of time: integrated speed law

In reactions of order 1, the speed of reaction is proportional to the concentration of the reactant. $v = -\frac{d[A]}{dt} = k[A]$

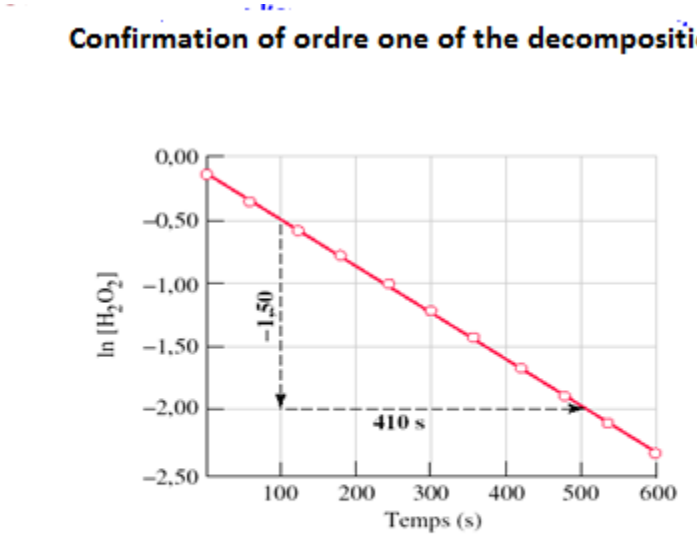
$$\frac{d[A]}{[A]} = -kdt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k\int_0^t dt \Rightarrow \ln\frac{[A]}{[A]_0} = -kt \Rightarrow [A]_t = [A]_0 e^{-kt}$$

Or

$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt$$

This expression takes the form of a straight line (y = b + mx) where -*k* is the slope, *t* is the time in seconds, and ln [A]0 is the y-intercept, as illustrated here:



We can also transform this expression into its exponential form:

$$[A] = [A]_0 e^{-kt}$$

This equation describes an **exponential decrease in** concentration as a function of time. However, the straight-line equation is the one most often used.

1.6 : Zero and second-order reactions

Zero order reactions are those whose rate is **independent of** the concentration of the reactants.

$$v = -\frac{d[A]}{dt} = k[A]^0 = k$$

The last equation is the **differential speed law**, because its expression has the form of a differential equation. We can integrate the expression to obtain the **integrated speed law:**

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

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

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

$$[A] = [A]_0 - kt$$

$$\boxed{[\mathrm{A}] = [\mathrm{A}]_0 - kt}$$

The last expression has the form of the equation of a straight line (y = b + mx) with slope $-k$ and y-intercept $[\mathrm{A}]_0$.

IN SUMMARY:

If we are offered a series of experimental values, to determine the speed law of the reaction

1) First, we plot the concentration of the reagent as a function of time; if this results in a straight line, **the reaction is of zero order.**
2) If it's a curve, then a graph of the natural logarithm of the reagent concentration versus time is constructed. If the result is a straight line,

The reaction is of order 1:

If it's not a straight line, we need to continue the search in another direction.

Reactions of order 2

Again, consider a reaction of the type A → products. Therefore, the reaction rate is proportional to the square of the concentration of A :

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

We then obtain an equation in the form of a straight line (y = b + mx). So, if we plot 1/[A] as a function of time and obtain a straight line, the reaction is of order 2

$$-\frac{d[A]}{dt} = k[A]^2 \Rightarrow \frac{d[A]}{[A]^2} = -kdt$$

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

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

With respect to A. The slope is equal to *k*, and the y-intercept is 1/[A]

II.1. How to find the order a reaction?

If we are offered a series of experimental values, in order to determine the order and rate law of the reaction :

First, we plot the concentration of the reagent as a function of the
If this results in a straight line, **the reaction is of zero order.**

If it's a curve, then a graph of the natural logarithm of the reagent concentration versus time is constructed. If the result is a straight line, **the reaction is of order 1.**

If it's not a straight line, plot 1/[A] against time.

If a straight line results, **the reaction is of order 2**.

II.2. Time to half reaction:

The speed of a reaction can also be expressed by its **half-life**, symbolized $t_{1/2}$.

Definition: Half-reaction time is the time required to consume half of the reagent present.

If the half-life is short, the reaction is *rapid*. According to the

Definition, when t is equal to $t_{1/2}$, [A] is equal to $0.5[A]_0$.
The value of $t_{1/2}$ can be calculated from the integrated speed laws.

The speed of a reaction can also be expressed by its **half-life**, symbolized by $t_{1/2}$

- The half-life is the time after which the concentration of a reagent is halved;

- If the half-life is short, the reaction is rapid.

According to the definition, when *t* is equal to *t1/2*, [A] is equal to 0.5[A]0.

The value of *t1/2* can be calculated from the integrated speed law

For a zero-order :

$$\frac{[A]_0}{2} - [A]_0 = -kt_{1/2}$$

$$-\frac{[A]_0}{2} = -kt_{1/2}$$

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

So, in a zero-order reaction, the half-life depends on the concentration of the reactant.

For a reaction of order 1 :⇒

$$ln\frac{[A]_{0/2}}{[A]_0} = -kt_{1/2} \Rightarrow$$

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

For a reaction of order 2 :

The half-life of second-order reactions can also be found by making the following substitutions:

The half-life of second-order reactions depends on the concentration of A, as in the case of zero-order reactions.

$$\frac{1}{[A]_{0/2}} = \frac{1}{[A]_0} + kt_{1/2}$$

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

IN SUMMARY:

- If the graph of [A] versus *t* shows a straight line, the reaction is of **zero order**.
- If the graph of ln [A] versus *t* shows a straight line, the reaction is of **order 1**.
- If the graph of 1/[A] versus *t* gives a straight line, the reaction is of **order 2**.

Summary table

Ordre	Speed Law	Integrates rate law	Graph of a line	k	Unités k	Half life
0	$v = k$	$[A]_t = -kt + [A]_0$	[A] fonction t	-Slope	mol/L·s	$\frac{[A]_0}{2k}$
1	$v = k[A]$	$\ln\frac{[A]_t}{[A]_0} = -kt$	ln [A] fonction t	–Slope	s^{-1}	$\frac{0{,}693}{k}$
2	$v = k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	1/[A] fonction t	Slope	L/mol·s	$\frac{1}{k[A]_0}$

I. Factors kinetics

The parameters that influence the rate evolution of a chemical system are called kinetic factors:

- ❑ Reagent concentrations
- ❑ Environmental temperature
- ❑ The presence of substances other than reagents (catalysts, initiators)

II.3. Temperature

II.3.1. Speed constant

In the expression for speed : $v = k[A]^{\alpha}[B]^{\beta}$

k is independent of concentration and time

k depends on the reaction studied and the temperature The unit

of ***k*** depends on the overall order of the reaction.

II.3.2. Arrhenius' Law

Experimentally, we can see that the speed of reactions generally increases with temperature. The temperature dependence of the rate is shown by the expression of ***k*** according to *Arrhenius' law*:

$$k = Ae^{-\frac{E_a}{RT}}$$

E_a: activation energy of the reaction in kJ.mol-1

R: perfect gas constant (8.314 J.mol^{-1}.K^{-1})

T: absolute temperature (in K)

A: Arrhenius pre-exponential factor or frequency factor

The activation energy **(Ea)** represents the energy barrier that must be crossed for the reaction to take place. In other words, it's the minimum energy required for a reaction to take place following a collision. If the collision energy is lower than the activation energy, the molecules simply bounce off.

1.7: The influence of temperature on reaction speeds

Chemical reactions are sensitive to external factors. Temperature is one such factor. In this section, we'll see that almost all chemical reactions occur more rapidly when the temperature is raised.

The equation

Determines the activation energy of a reaction or process

By introducing the natural logarithm to this expression, we obtain another expression of Arrhenius' law

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln k = \ln Ae^{-\frac{E_a}{RT}}$$

$$\boxed{\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)}$$

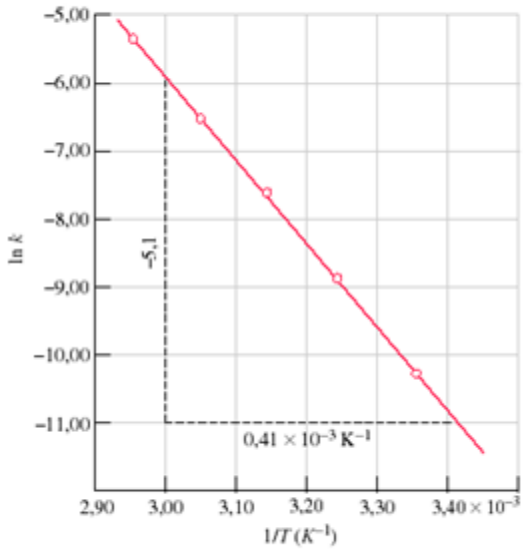
If we plot **ln k= f(1/T)** we obtain a straight line with

slope -Ea/R

This equation takes the form of a straight line (y = b + mx), for which (ln A) is the y-intercept, and (-E(a)/R) is the slope, in a graph of (ln *k*) versus (1/T).

Graphique ln *k* en fonction 1/*T* :

$N_2O_5(g)$: $N_2O_5(g) \longrightarrow 2\ NO_2(g) + \frac{1}{2}O_2(g)$



II. Degeneration of the order of a reaction

III.1. Definition :

It may be that the concentration of an active species is kept virtually constant during the

reaction. In this case, although the concentration of this species plays a part in the rate law, it can be grouped together with the rate coefficient, and the rate law can be simplified.

For example, let's consider a reaction: A+ B= P whose speed law would be

$v = k[A]^{\alpha}[B]^{\beta}$ and global order **n= α+ β** .

If the concentration **[B]**of the species is almost constant and equal to $[B]_0$ during the reaction, then :

$v = k_{obs}[A]^{\alpha}$ with $k_{obs} = k[B]^{\beta}$

The reaction therefore appears to be of order **α** in fact it is of order **α + β** . This is called ***degeneracy of order***.

α is called observed order or apparent order. Similarly, the velocity coefficient k_{obs} is the observed or apparent speed coefficient.

The degeneracy of the order of a reaction may be required to simplify the rate law or particular operating conditions.

III.2 Case of degeneracy order :

It can be observed in the following cases:

1. One reagent is in great excess of the others.

If one reagent is in great excess compared to the others, the quantity that may disappear as a result of the reaction will be small compared to its initial concentration. To a first approximation, its current concentration will therefore remain constant and equal to its initial concentration.

2. A reagent is reformed during the reaction.

If a reactant is reformed during the reaction, it is both a reactant and a product. It is not usually included in the balance equation.

3. The concentration of a reagent is kept constant by the intervention of external factors.

The concentration of an active reagent can be deliberately kept constant to simplify the experimental study by various means.

Example: operating in a buffer solution "a buffer solution is one that maintains approximately the same pH despite the addition of small quantities of an acid or base, or despite dilution. If one of these three criteria is not met, then the solution is a pseudo-buffer solution",

The concentration of H^+ and OH^- ions will remain constant due to the acid-base equilibrium of the buffer couple. If reaction rate law involves one of these ions, degenerate order will result.

Consider the speed law a reaction:$v = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$

In a buffered environment, we observe a velocity law of the form $v = k_{obs}[A]^{\alpha}\,[B]^{\beta} and\ k_{obs} = [OH^-]^{\gamma}$

The real global order **n**= ***α***+ ***β***+ **γ** will therefore be lowered to ***α***+ ***β***

Chapter 2 The mechanisms of reaction

I. The mechanisms of reaction

The mechanism of a chemical reaction is the sequence of steps, on the scale from reactants to products.

Some reactions require only one collision. Others require several, producing intermediates - compounds formed in one step and consumed in a subsequent step.

II. Elementary reactions

An elementary reaction: a reaction taking place in a single step.

Ex: H+ Br_2 → HBr+ Br

In an elementary reaction, the orders of reaction are equal to the stoichiometric coefficients **(VAN'T HOFF's rule)**, which is generally not the case for a multi- step reaction.

aA+ bB → **products**

The law of speed is: single stage.

$v = k[A]^a [B]^b$ if this reaction takes place in one

Molecularity: this is the number of species involved in an elementary reaction. i.e. the number of entities (atoms, molecules, ions, etc.) participating in an elementary reaction. It is therefore also the sum of the stoichiometric coefficients affecting the reactants.

A reaction involving a single molecular entity is said to be **unimolecular.**

A reaction involving two molecular entities is called **bimolecular**.

A reaction involving three molecular entities is called **trimolecular.**

Unimolecular reaction: molecularity= 1.

Example: Gas-phase decomposition of cyclobutane to ethylene

$$C_4H_8 \rightarrow 2\ C_2H_4$$

Bimolecular reaction: molecularity= 2 (most frequent)

$$NO+O_3 \rightarrow NO_2+O_2$$

III. Complex reactions

III.1. Definition: Reactions composed of several reactions elementary operations carried out successively or simultaneously.

Ex: 2 HI + H_2O_2 → I_2 + 2 H_2O step

1: HI+ H_2O_2→ IOH+ H_2O

step 2: HI + IOH → I_2 + H_2O

As IOH is a **reaction intermediate**, it does not appear in the overall balance of reaction.

reaction intermediate: a complex reaction, the intermediates (IR) disappear once the reaction is complete.

Consequence: advancement indirect reaction

$$A \rightarrow C : A \rightarrow \underset{(IR)}{B} \rightarrow C$$

III.2. Kinetically decisive step (limiting step):

The rate of formation of a species produced by a series of successive elementary reactions is determined by the *slowest* step (the limiting step). This step, known as the **kinetically determining step** of the overall reaction, imposes its speed on subsequent steps.

Example 1: 2 NO_2Cl→ 2 NO_2+ Cl_2

Mechanism : NO_2Cl→ NO_2+ Cl

NO_2Cl+ Cl → NO_2+ Cl_2

Velocity law: **v = k[NO_2Cl]**

Example 2 : 2 NO (g)+ F_2 (g)→ 2 ONF (g)

Mechanism: this reaction occurs in two steps:

$NO + F_2 \rightarrow ONF + F$

$NO + F \rightarrow ONF$

- ❑ The sum of the steps gives the overall reaction.
- ❑ The speed law of the slow step is: **v= k [NO][F_2]**
- ❑ However, the speed of the overall reaction is equal to that of the slow step⇒ the speed law of the overall reaction is the same.

III. 3. Types of reactions complex

There are four classes of compound reactions

III. 3. 1. competitive reactions, also known as parallel reactions

They are made up of common reactants, i.e. two reactions with the same reactants but different products. They can be schematized as :

A→B and A→C.

Example:

3 HNO_3+ $NO_2C_6H_5$→ meta $(NO_2)_2C_6H_4$

3 HNO_3+ $NO_2C_6H_5$→ ortho $(NO_2)_2C_6H_4$

They can be schematized as :

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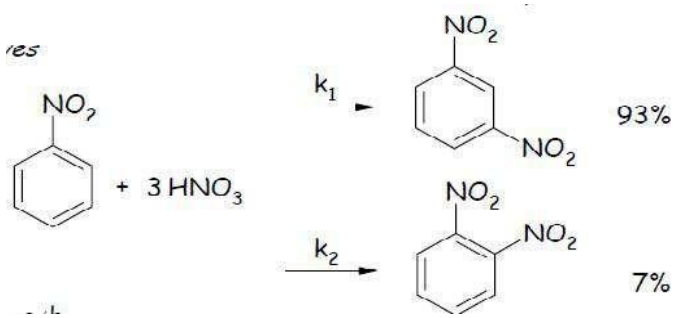


Both reactions are second-order and have rate constants k_1 and k_2. The rate of disappearance of mononitrobenzene is also [2nd] order.

2nd-order reaction with a≠b

$$\frac{dx}{dt} = (k_1 + k_2)(a - x)(b - x)$$

$$(k_1 + k_2)t = \frac{2.303}{b - a}\log\left[\frac{a(b - x)}{b(a - x)}\right]$$

III. 3. 2. reversible or reverse reactions

A reversible reaction occurs when, at the same time and in the same place, reactants are converted into products and products are converted into reactants.

An equilibrium reaction is represented by .⇌

The following equilibrium reaction is considered:

a A+b B⇌ c C+d D

The rate at which reagents disappear from left to right (direction 1) is :

$$v_1 = -\frac{dA}{dt} = \frac{-dB}{dt} = k_1[A]^a[B]^b$$

The rate of product formation (right to left) in direction 2 is :

then, kinetic equilibrium, which is expressed by the fact that, at equilibrium, the velocities of the reactions from left to right and from right to left are equal. Therefore

$$v_2 = \frac{dC}{dt} = \frac{dD}{dt} = k_2[C]^c[D]^d$$

$$v_1 = v_2 = -\frac{dA}{dt} = \frac{-dB}{dt} = \frac{dC}{dt} = \frac{dD}{dt} = k_1[A]^a[B]^b = k_2[C]^c[D]^d$$

From this kinetic equilibrium relationship we can derive the following relationship:

$$\frac{k_1}{k_2} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Knowing that the thermodynamic equilibrium for this reaction expressed by the law of mass action is :

$$k = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K: is the thermodynamic equilibrium constant

From these last two expressions we can deduce that $k = \frac{k_1}{k_2}$

This equation represents the kinetic expression of the thermodynamic equilibrium constant, valid only if the partial orders of the direct (direction 1) and reverse (direction 2) reactions are equal to the stoichiometric coefficients of the reaction.

For example $H_2 + I_2 \underset{k_1}{\overset{k_2}{\leftrightarrows}} 2HI$

Kinetic studies have shown that both the direct reaction and the reverse reaction of this equilibrium are elementary. They therefore follow Van't Hoff's law:

$$v_1 = v_2 = -\frac{d[H_2]}{dt} = \frac{-d[I_2]}{dt} = \frac{d[HI]}{dt} = \frac{d}{dt} = k_1[H_2] \quad [I_2] \quad = k_2[HI]^2$$

$$k = \frac{[HI]^2}{[H_2][I_2]}$$

This result is a specific case, and is only true because reactions in both directions are elementary processes in which order and molecularity merge. Only then does the relationship apply. For example, for the equilibrium involving hydrogen bromide :

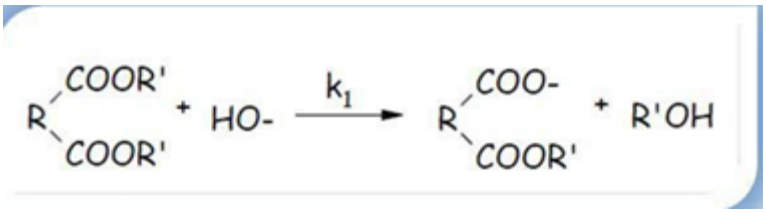
III. 3. 3. consecutive reactions or Consecutive reaction:

Successive (or consecutive) reactions are those in which the products of the first are the reactants of the second. The products of the second can in turn be the reactants of a third, *without ever being regenerated,* and so . Such a sequence of reactions therefore involves.

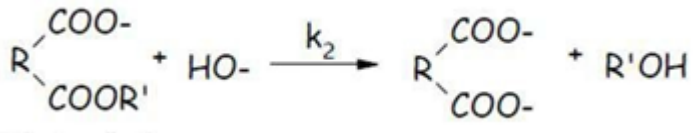
molecules called reaction intermediates, one of whose characteristics is they cannot be isolated, at least not easily.

Example: diester hydrolysis.

- The hydrolysis reaction of a first ester function is represented by



- Reaction followed hydrolysis of second ester function



The example the most simple example is made up of two reactions

Reaction A→ C

Mechanism:

$$A \overset{K_1}{\rightarrow} B \overset{K_2}{\rightarrow} C$$

Initial conditions *$[A]_0$, $[B]_0=[C]_0=0$*

whose kinetic equations are :

$d[A]/dt = -k_1[A]$ (1)

$d[B]/dt = k_1[A] - k_2[B]$ (2)

$d[C]/dt = k_2[B]$ (3)

The velocity equations can be written, bearing in mind that if B is formed from of A, it also disappears to form the final product C :

Equation (1) integrates immediately

$$[A] = [A]_0 e^{k_1 t}_1 \quad (4)$$

By replacing this value in the second differential equation, we obtain

$$\frac{d[B]}{dt} = k_1[A]_0 e^{k_1 t} - k_2[B]$$

$$\frac{\mathrm{d[B]}}{\mathrm{dt}} + \mathrm{k_2[B]} = \mathrm{k_1[A]_0 e^{k_1 t}}$$

Integration equation (2) leads to :

$$\mathrm{[B]} = \frac{[A]_0 \mathrm{k_1}\left(\mathrm{e^{k_1 t}} - \mathrm{e^{k_2 t}}\right)}{k_2 - k_1} \quad (5)$$

Using the mass conservation relation :

$[A]+[B]+[C]=[A]_0+[B]_0+[C]_0=[A]_0 \Rightarrow [C]=[A]_0-[A]-[B]$ therefore

$$\mathbf{[C]= [A]_0\,[1-(k_2\,e^{-k1t} - k_1\,e^{-k2t})\,/\,(k_{(2)}-k_1)]} \text{ ..... } (6)$$

The typical curves showing the concentrations of [A], [B] and [C] during reaction are shown below:

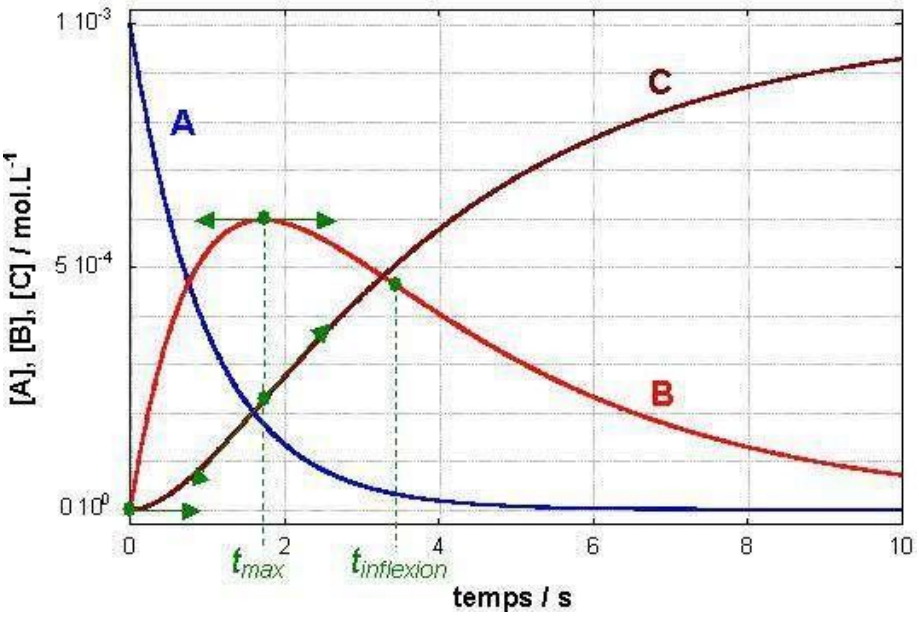
with

[A]: decreasing exponential

[B] bi-exponential with a max at $t_{max}=\ln(k_2/k_1)/(k_{(2)}-k_1)$ and an inflection point at $t_{inflection}=2t_{max}$.

[C] bi-exponential with a minimum at origin (zero slope) and an inflection point at time t_{max} of B's maximum.

($[A]_0=10^{-3}$mol.L^{-1};$[B]_0=[C]_0=0$; $k_1=1$ s^{-1}; $k_2=0.3$ s^{-1})



The evolution curve of [A], ($[A] = [A]_0 e^{-k1t}$), is a decreasing exponential.

That of [B](eq 5), is the sum of two decreasing exponentials. It therefore has a maximum corresponding to the cancellation of the first derivative, i.e. $\mathbf{t_{max}=\ln(k_2/k_1)/(k_{(2)}-k_1)}$ and inflection point corresponding to the cancellation of the second derivative, i.e. $\mathbf{t_{inflection}= \ln(k_2/k_1)^2/(k_2 - k_1) = 2\ t_{max}}$

The evolution curve of **[C]** ,($\mathbf{[C]= [A]_0\ [1-(k_2\ e^{-k1t} - k_1\ e^{-k2t}\ ) / (k_{(2)}-k_{(1)})]}$), is also bi-exponential. Its slope at the origin is zero, corresponding to its extremum. It has an inflection point at $t = \ln(k_2/k_1) / (k_2 - k_1) = t_{max}([B])$, i.e. corresponding to the maximum of [B], where its production rate is maximum. It reaches a level $[C]_e= [A]_0$.

Three particular cases can be represented. The first case,is where k2>> k1. In this case, the slowest reaction is the first step: as B transforms into C faster than it appears, its concentration remains low. In the case where k2 << k1, this is obviously the opposite situation, and the decisive, limiting step being the second step, the concentration of B joins the first.

almost the initial concentration of component A. The final case is where k2=k1. These special cases will be dealt with in greater detail in a tutorial.

Here we'll look at just one of the three cases:

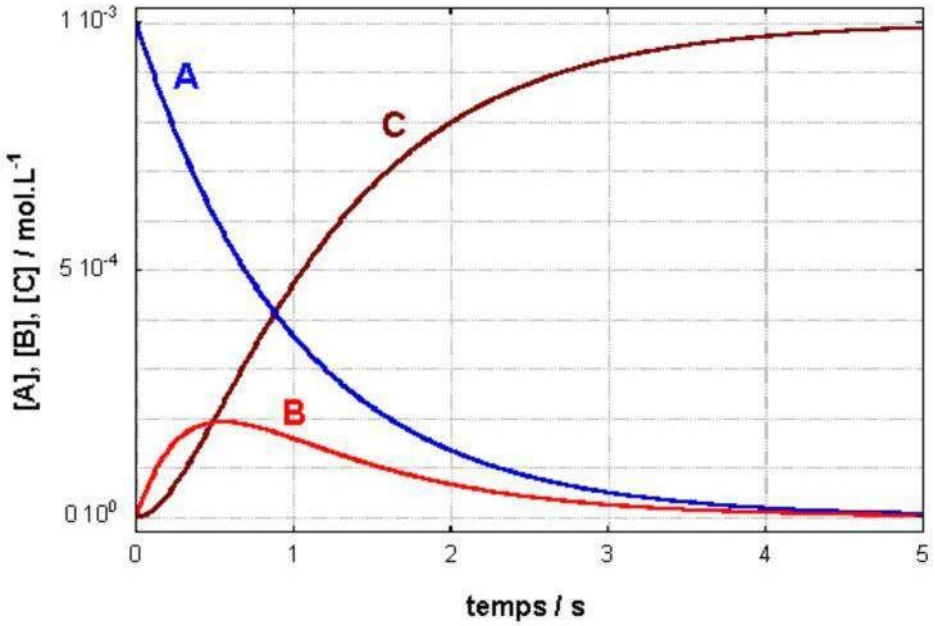
Quasi-stationary state: $k_2>> k_1$

k_2 is much larger than the constant k_1. An equilibrium form of the concentration of intermediate B is reached. Since $k_2>> k_1$, $e^{(-k2)\ t} << e^{-k1\ t}$ and $k_2 - k_1 \approx k_2$. Replacing in the expression for the concentration of B calculated above, we obtain

$$[B]= [A]_0\ k_1\ e^{-k1t} / (k_2) \approx [A]_0\ k_1/ k_2$$

This implies that the formation of C depends on the rate of formation of B. Under these conditions, we say that the A-B step is the determining step. It's the slowest

step, which imposes its speed on the whole reaction.



[B]= reaction intermediate with stationary concentration d[B] /dt ⇒

The formation of **[C]** depends on the rate of formation of B

A→ B is the decisive step, . the slowest step imposes its speed on the reaction set

The concentration of B remains lower and the C curve tends to approach the symmetrical A curve.

Another example:

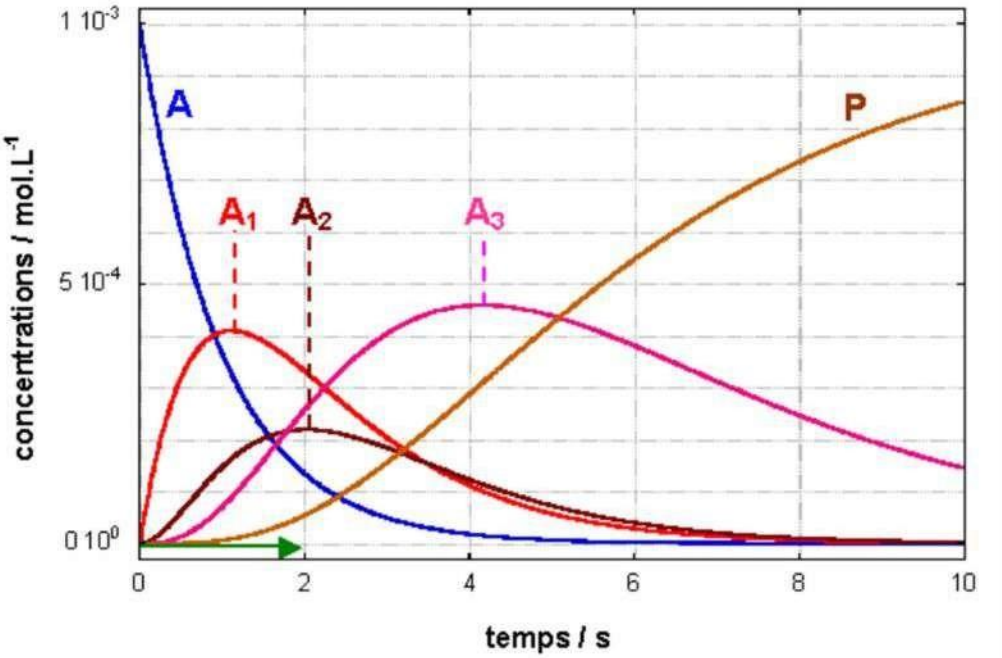
a mechanism comprising any number of successive monomolecular reactions:

$A \rightarrow A_1$ k_1 (r a)

$A_1 \rightarrow A_2$ k_2 (r b)

$A_2 \rightarrow A_3$ $k_{(3)}$ (r c)

$A_{R-1} \rightarrow P$ $k_{(R)}$ (r)



III. *3. 4*. chain reactions:

A chemical chain reaction is one in which an **intermediate** reactive species, often a free radical, catalyzes a series of rapid steps that carry out the overall reaction.

Typical chain reaction stages are *initiation, propagation and termination*:

- initiation: the formation of unstable molecules that act as chain carriers, such as free radicals or reactive ions;
- propagation: a series of steps in which the radical (or other chain carrier) triggers the transformation of reactants into products, with regeneration of the radical. This is equivalent to radical catalysis of the overall reaction;
- termination (or break) of the chain: this is the destruction of the chain carriers, for example through the recombination of free radicals.

Example: the hydrogen synthesis reaction

$$H_2 + Br_2 \xrightarrow{k_1} 2\,HBr$$

We show experimentally that the experimental speed law is of the form :

$$v = \frac{k\,[H_2]\,[Br_2]^{1/2}}{1 + k'\dfrac{[HBr]}{[Br_2]}} = \frac{d[HBr]}{dt}$$

The proposed mechanism is as follows:

Initiation stage:

[1] $Br_2 + M \rightarrow 2\,Br^- + M$ k_1

These three stages are chain propagation stages

[2] $Br^- + H_2 \rightarrow HBr + H^-$ k_2

[3] $H^- + Br_2 \rightarrow HBr + Br^-$ k_3

[4] $H^- + HBr \rightarrow H_2 + Br^-$ k_4

Chain break stage

[5] $2\,Br^- + M \rightarrow Br_2 + M$ k_5

This mechanism is referred to as a chain. Once a few bromine atoms are present (reaction [1]), reaction [2] takes place, forming hydrogen atoms. These, in turn, trigger the third step, which regenerates bromine atoms. This is what is known in programming as a loop, which stops only when one of the reactants disappears. This usually occurs through recombination of the reactive species. Hydrogen and bromine atoms are referred to as chain carriers. To try and recover the experimental speed law, let's apply the principle of quasi-stationarity (also known as the quasi-stationary state approximation) to the two reactive species, bromine and hydrogen atoms.

Another way of presenting the mechanism of this reaction is H_2+ Br_2→ 2 HBr:

- **initiation:** Br_2→ 2 Br-

each Br is a free radical, designated by the symbol "-(representing an unpaired electron);

- **propagation** (here a series or loop of two stages)

Br-+ H_2 → HBr+ H-

H-+ Br_2→ HBr+ Br-

the sum of these two steps corresponds to the overall reaction H_2+Br_2→2HBr, with catalysis by Br- which triggers the first step;

- *slowdown*

H-+ HBr→ H_2+ Br-

step specific to this example, which is the inverse of the first propagation step;

- **termination** 2 Br-→ Br_2

recombination of two radicals, corresponding in this case to opposite of initiation.

IV. Quasi-stationary state approximation (QSSA)

IV.1. Bodenstein's principle: "When, in a reaction sequence, an intermediate species has a much shorter lifetime than the others, we can simplify the solution of the kinetic equations of formation by writing that its rate of formation is equal to its rate of disappearance".

IV.2. The quasi-steady-state approximation, or **QSSA**, is applicable when a reaction intermediate remains at a very low concentration compared to other species, i.e. short-lived or highly reactive.

Let's consider again the mechanism consisting of two successive reactions.

$A \rightarrow B$ $k_{(1)}$ **.....1** **$B \rightarrow C$** $k_{(2)}$ **.....2**

If the second reaction is much faster than the first ($k_2 \gg k_1$), the B's concentration remains negligible **compared with those of A and C**, so that throughout the reaction :

$$[C] \approx [A]_0 - [A]$$

, its derivative is negligible, still ahead of those of [A] and [C], and the equation $d[B]/dt = k_1 [A] - k_2 [B]$ becomes quasi-stationary:

$d[B]/dt = k_1[A] - k_2[B] \approx 0$

Let **$[B] \approx [A]\ k_1/k_2$**

And $d[C]/dt \approx k_1 [A] = -d[A]/dt$

It's as if the mechanism were reduced to a single reaction

$$A \rightarrow C \quad k_1$$

whose rate constant is that of the slowest reaction (**r 1**) (it's always the slowest reaction that determines the overall time scale of a compound reaction).

IV.3. QSSA application example: thermal decomposition of diterbutyl peroxide in the gas phase

$$(CH_3)_3COOC(CH_3)_3 = 2\ CH_3COCH_3 + C_2H_6$$

with experimental kinetics of order 1.

On the other hand, the following mechanism has

$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO^-$ k_1(r a)

$(CH_3)_3CO^- \rightarrow CH_3COCH_3 + CH_3^-$ k_2 (r b)

$2\ CH_3^- \rightarrow C_2H_6$ k_3 (r c)

Let

$A=(CH_3)_3COOC(CH_3)_3$

$P_1=CH_3COCH_3$;$P_2= C_2H_6$

$R_1=(CH_3)_3CO$-; $R_2= CH_{(3)}$-

radical species R_1 and R_2 are a priori highly reactive, i.e. reactions (r b) and (r c) are very fast compared with (r a). Their concentrations, and their derivatives, are therefore very small compared with those of A, P_1 and P_2. AEQS can therefore be applied to R_1 and R_2.

The kinetic equations are :

$d[A]/dt = -k_1[A]$

$\Rightarrow [A] = [A]_0 e^{k_1 t}$

$d[R_1]/dt = 2\ k_1[A] - k_2\ [R_1]$

$d[P_1]/dt = k_2[R_1]$

$d[R_2]/dt = k_2[R_1] - 2\ k_3[R_2]^2$

$d[P_2]/dt = k_3[R_2]^2$

AEQS on R_1: $d[R_1]/dt \approx 0$ $\quad [R_1] \approx 2(k_1/k_2)\,[A]$ (6)

AEQS on R_2: $d[R_2]/dt \approx 0$ $\quad [R_2]^2 \approx k_2/(2k_3)R1 \approx (k_1/k_3)\,[A]$ (7)

We deduce from equations (2) and (6)

$d[P_1]/dt \approx 2\,k_1\,[A] = 2\,k_1\,[A]_0\,e^{-k1t}$

or $\int(0\rightarrow P_1)\,d[P_1] \approx 2k_1\,[A]_0 \int(0\rightarrow t)\,e^{-k1t}\,dt$

$[P_1] \approx 2\,[A]_0\,(1 - e^{-k1t})$ (8)

and, similarly, equations (4) and (7)

$[P_2] \approx [A]_0\,(1 - e^{-k1t})$ (9)

The equations

$$[A] = [A]_0 e^{-k_1 t}$$

$$[P_1] \simeq [A]_0 (1 - e^{-k_1 t})$$

$$[P_2] \simeq [A]_0 (1 - e^{-k_2 t})$$

show that the overall kinetics of this reaction, whether we observe the disappearance of A or the appearance of P_1 or P_2, is of order 1, in agreement with experiment. The global balance is also shown: the amplitude of P_1 is double that of A and P_2.

$(CH_3)_3COOC(CH_3)_3 = 2\,CH_3COCH_3 + C_2H_6$

Note:

QSSA can provide interesting simplifications. However, there is no disadvantage in simulation to using the equations without approximation, with speed constants chosen accordingly. This is even recommended if we are not absolutely sure that the conditions for the correct application of **QSSA** are respected in all situations envisaged during the treatment of a given problem. On the other hand, any type of approximation, at least on crucial species, is to be absolutely avoided in the case of mechanisms with non-linear

characteristics (autocatalysis, for example).

V. Reaction mechanisms and QSSA

When we represent a chemical reaction by a balance equation, we only give a macroscopic view of the reaction, whereas the study of the mechanism of a reaction aims to try and understand what's going on from a microscopic point of view. By studying reaction rates, we can imagine reaction mechanisms and break down the reaction into a series of elementary steps.

Reaction intermediates are species that are neither reagents nor reactants.

products. They are active centers. They can be:

- atoms or radicals obtained by homolytic bond breaking,
  by the action of heat: thermolysis or by absorption a photon: photolysis: Cl^-

  $Cl_{(g)} \rightarrow 2\ Cl^{\cdot}_{(g)}$

- ions: $CH_3^{\cdot}$

ex: $O_2 + hu \rightarrow O^+ + e^-$ $_2$ $_2$ $_2$

Formed by interaction with UV radiation, in the ionosphere.

VI. Hydrogen bromide synthesis

$$H_2 + Br_2 \rightarrow 2\ HBr$$

The experimental speed law is:

$$v = \frac{k\,[H_2]\,[Br_2]^{1/2}}{1 + k'\frac{[HBr]}{[Br_2]}} = \frac{d[HBr]}{dt}$$

The proposed mechanism is as follows:

[1] $Br_2 + M \rightarrow 2\,Br^{\cdot} + M$ k_1

[2] $Br^{\cdot} + H_2 \rightarrow HBr + H^{\cdot}$ k_2

[3] $H^{\cdot} + Br_2 \rightarrow HBr + Br^{\cdot}$ k_3

[4] $H^{\cdot} + HBr \rightarrow H_2 + Br^{\cdot}$ k_4

[5] $2\,Br^{\cdot} + M \rightarrow Br_2 + M$ k_5

$Br^{\cdot}$ and $H^{\cdot}$ radicals are the reaction intermediates

The Quasi Stationary States Approximation, **QSSA**, is applied to , **$H^{\cdot}$ and $Br^{\cdot}$**: "After an initial induction period, during which the **[IR]**↑, intermediate species are considered to disappear as quickly as they occur." The concentration of the active center is then in a quasi-stationary state: **d[IR]/dt = 0**

Since $H^{\cdot}$ and $Br^{\cdot}$ are reaction intermediates then :

$$\frac{d[\dot{B}r]}{dt} = \frac{d[\dot{H}]}{dt} = 0$$

$$\mathbf{d[H^{\cdot}]/dt} = k_2.[Br^{\cdot}].[H_2] - k_3.[H^{\cdot}].[Br_2] - k_4.[HBr].[H^{\cdot}] = \mathbf{0} \qquad (1)$$

$$(1/2)\, d[Br^{\cdot}]/dt = k_1.[Br_2].[M] \quad \mathbf{So} \quad d[Br^{\cdot}]/dt = 2k_1.[Br_2].[M] \quad \mathbf{according\ with\ (1)}$$

$$\mathbf{d[Br^{\cdot}]/dt} = 2k_1.[Br_2].[M] - k_2.[Br^{\cdot}].[H_2] + k_3.[H^{\cdot}].[Br_2] + k_4.[HBr].[H^{\cdot}] - 2k_5.[Br^{\cdot}]^2.[M] = \mathbf{0} \qquad (2)$$

$$(1) + (2): \quad 2k_1.[Br_2].[M] - 2k_5.[Br^{\cdot}]^2.[M] = 0 \quad \text{et } \mathbf{[Br^{\cdot}]} = (k_1/k_5)^{1/2}.[Br_2]^{1/2}$$

$[H^{\cdot}]$ **iscalculated by combining** (1) et $[Br^{\cdot}]$:

$$\mathbf{[H^{\cdot}]} = \{k_2.(k_1/k_5)^{1/2}.[Br_2]^{1/2}.[H_2]\} / \{k_3.[Br_2] + k_4.[HBr]\}$$

$$\mathbf{v = (1/2).d[HBr]/dt} = \{k_2.(k_1/k_5)^{1/2}.[Br_2]^{1/2}.[H_2]\} / \{1 + (k_4.[HBr])/(k_3.[Br_2])\}$$

$$v = 2k_3[\dot{H}][Br_2] \Longrightarrow v = \frac{2k_2k_3[H_2][Br_2]\sqrt{\frac{k_1}{k_5}[Br_2]}}{k_3[Br_2] + k_4[HBr]}$$

$$\boxed{v = \frac{2k_2\sqrt{\frac{k_1}{k_5}}[H_2][Br]^{1/2}}{1 + \frac{k_4}{k_3}\frac{[HBr]}{[Br_2]}}} \quad \textbf{no order}$$

Experimental speed law

$$v = \frac{k\,[H_2]\,[Br_2]^{1/2}}{1 + k'\dfrac{[HBr]}{[Br_2]}}$$

Chapter 3

Experimental methods for chemical kinetics study

I. Experimental methods for kinetic studies chemical

Studies of the dynamics of chemical processes impinge on almost every area of chemistry and biochemistry. It is useful for students even at the general chemistry level to have some understanding of the experimental techniques that have informed what you have already learned about kinetics.

I.1. chemical methods

Concentrations can be measured (at constant temperature) directly using conventional assay methods, or samples can be taken at different times, or different initially identical specimens studied at different times.

The reaction must then be stopped so that it does not continue during the dosing:
can be done by quenching (rapid cooling), strong dilution
elimination a reagent by precipitation or neutralization if it is acidic or alkaline basic.

Chemical dosage methods are often used for substances with acid-base or redox properties. This method is inconvenient for the following reasons:

- The study is carried out in batch mode;
- Samples must be taken from the reaction medium;
- You need to work with relatively large quantities;

I.2. Methods physical

A physical quantity is measured (at constant T°) and related to concentrations. These methods have the advantage of not disturbing the reaction in progress: continuous measurements, low quantities of reagents, very rapid reactions and high sensitivity.

Examples include :

- Conductimetry : (measurement of the electrical conductivity of an ionic mixture).: For reaction media containing ions undergoing a transformation, measuring conductivity gives the concentration of these ions using the relationship :

$$\sigma = \sum \lambda_i \, Ci$$

σ: Conductivity of the solution in $S.m^{-1}$

λ_i : Molar ionic conductivity of the ions in $S.m^2.mol^{-1}$

C_i : Molar concentration of ions in mol. L^{-1}

- Spectrophotometry: For a reaction involving a species that absorbs radiation (infrared, visible spectrum or ultraviolet), measuring the absorbance of the solution enables us to measure the concentration of this species and to monitor the reaction, by applying Beer's law.

Lambert : $A = \sum e_i L Ci$

With :

A: Absorbance

ei:Molar extinction (absorption) coefficient of the species in (L. $mol^{-1}.dm^{-1}$). Ci: Molar concentration of the absorbing species i in (mol. L^{-1})

l: tank width in dm

- Polarimetry (measurement of the rotatory power of light).
- Gas density measurement.

Gas pressure measurement (constant volume): In the case of reactions taking place in the gas phase at constant volume and temperature, the system is considered to be an

ideal mixture of perfect gases:

$PV = nRT \Rightarrow P = (n/V)RT = CRT$ so – $\Rightarrow P = CRT$

- Refractometry (refractive index measurement). After calibration, the refractometer can be used to determine the concentration of a solute in a known solvent,

- pH-metry (for acid-base reactions): this is used when the pH of the solution varies during a reaction. In the case of media containing [$H3O^+$] ions, measuring the pH gives access to the concentration of these ions.

$$pH=-Log \quad [H3O^+]$$

- Potentiometry (redox reactions).
- Radiochemical methods (using a radioactive tracer). Study of chemical reactions produced by ionizing radiation
- Microcalorimetry (heat quantities are proportional to the quantity of material reacted), groups together a set of techniques that measure directly enthalpy and the changes of capacity.
  which are involved a chemical reaction

Experimentally, the speed of a reaction can be measured in different ways. In order to choose the most appropriate method, the physical state of the substance to be measured must be taken into account. Table 1 shows the different methods used to measure the quantity of matter transformed or formed and the methods for calculating the rate of reaction as a function of the physical state of the substance being measured.

Table 1: Methods for a quantity of matter as a function of physical state of the substance and formula for calculating the velocity.

Physical condition of the substance	**Measurement of amount of material**	**Speed calculation**	**Speed unit**
Solid	Mass, number of particles	$Speed=\frac{\Delta mass}{\Delta time}$ $Speed=\frac{\Delta number\ of\ particles}{\Delta time}$	g/s mol /s
Liquid	Volume, mass, number of particles	$Speed=\frac{\Delta volume}{\Delta time}$	L/s or ml/s
Gas	Pressure, volume, mass, concentration, number of particles	$Speed=\frac{\Delta pressure}{\Delta time}$	Pa/s
Aqueous solution	Concentration	$Speed=\frac{\Delta Molar\ concentration}{\Delta time}$	mol/L. s

II. Determination of the order

The reaction order represents the influence a reactant on the reaction kinetics. Experience has shown that the speed of reaction increases as the concentration of the reactants increases.

Consider a reaction whose balance equation is: aA+bB→cC+dD
The rate of this reaction can be expressed in a simple form such as :

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

With :
V reaction speed
k: Rate constant; depends on temperature and can be calculated using Arrhenius' law.

n : Partial order of reaction with respect to A
m: Partial order of reaction with respect to B
Generally, the order is a positive integer (1, 2, 3), but it can also be zero or fractional (1/2, 1/3, 3/4, etc.). In the case of a reaction with several reactants, the overall order of the reaction is : $n = \sum_i n_i$
Half-time reaction

II.1. integral method

The aim is to plot a function a concentration C_i, represented in
as a function of time by a straight line, to within the uncertainties of experience . For

example, if: $\ln C_i = f(t)$ is represented by a straight line, the order is 1

A variant of this method involves calculating k on the assumption that the reaction has a given order. We must then check that the values found for k are the same, within the uncertainties of the experiments.

II.2 differential method

The previous method is inefficient when the order is not integer.

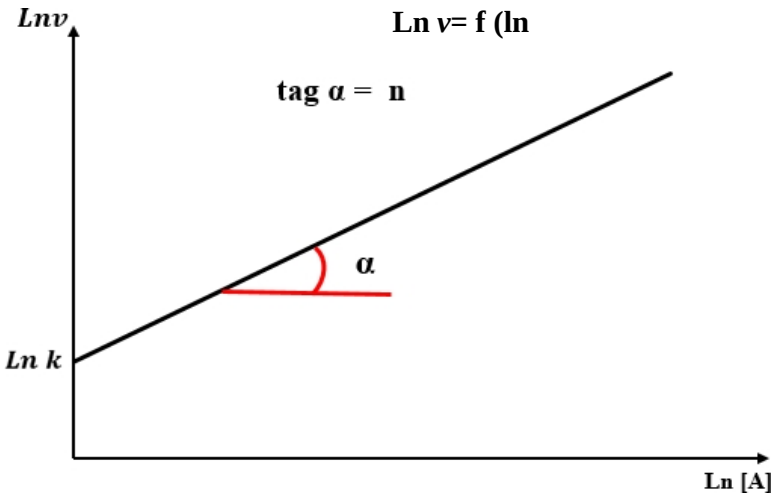
If velocity is of the form **$v= k[A]^{\alpha}$**

we can also write: **$\ln v= \ln k+\alpha \ln[A]$.** First draw the graph representative of [A]= f(t)

By reading this graph, we can deduce the slope v(t)= -d[A]/dt .
It should be noted, however, that this determination is a delicate one.

We then plot the graph representing lnv(t) as a function of ln[A]. The slope of the line will give us **the order α** and the y-intercept **ln(k).**

a) Graphically: Simply plot Ln *v*= f (ln [A]) to obtain a straight line with slope ***n*** and y-intercept ***ln k***.



II.2.1.Initial velocity method

The initial velocity method involves measuring the initial velocity of the reaction for different initial concentrations of reactant **$[A]_0$**. This allows us to plot Ln $_{v0}$ = f (Ln $[A]_0$), which is a straight line with slope ***n*** and y-intercept ***Ln k***.

If there are several reagents : A + B →C+D this method is applied in such a way as to Determine the partial order with respect to one of the reactants (**A).** By measuring a series of initial velocities as a function of the initial concentration of this reactant and holding constant the concentration of the other reactant **([B])**. The graph Ln $_{v0}$ = Ln $[A]_0$ will be a straight line with slope ***α*** representing the partial order with respect to (**A)**.

A second series experiments is then carried out, this time varying the initial concentration of the second reagent **$[B]_0$** while keeping the concentration of the first reagent **[A]** constant.

A curve similar to the previous one can then be used to determine the partial order ***β*** with respect to the second reactant **(B)** and then to determine the overall order of the reaction ***n***, which is the sum of the partial orders.

$$v_0 = k[A]_0^{\alpha}[B]_0^{\beta} \Rightarrow \ln v_0 = \ln k + \alpha \ln[A]_0 + \beta \ln[B]_0$$

The slope of the graph $\ln v_0$ as a function of ***Ln[A]₀*** gives us **α**, and the slope of the straight line $\ln v_0$ as a function of ***Ln[B]₀*** gives us **β**. The overall order of the reaction is: **n= α + β**

III.3. Half-time reaction

The half-reaction time is the time after which the concentration of the reagent is equal to half its initial value.

This is the time $t_{1/2}$ such that **$C(t_{1/2}) = C_i(t = 0)/2$.**

How the half-reaction time depends on initial concentrations ⇒is also characteristic of the reaction order.

- For a reaction of zero order :

  at □=0 we have $[A]_0 = 0$

  and at t½ we have $[A]_{1/2} = \frac{[A]_0}{2}$

  $$[A] = [A]_0 - kt$$

$$t=t_{½} \Rightarrow \frac{[A]_0}{2} = [A]_0 - kt_{1/2} \Rightarrow t_{1/2} = \frac{[A]_0}{2k}$$

- For a reaction of zero order, the half-reaction time is proportional to the initial concentration.

- **First-order reaction (n= 1):**

  Kinetic law: Let the reaction be

  $A \rightarrow B$

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

$$\ln\frac{[A]}{[A]_0} = kt$$

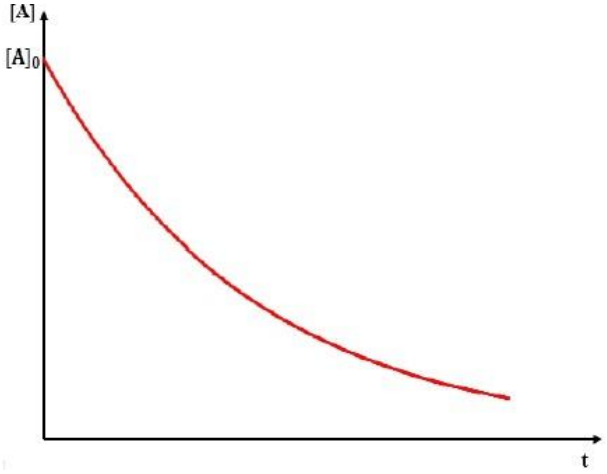
- t=t½ :

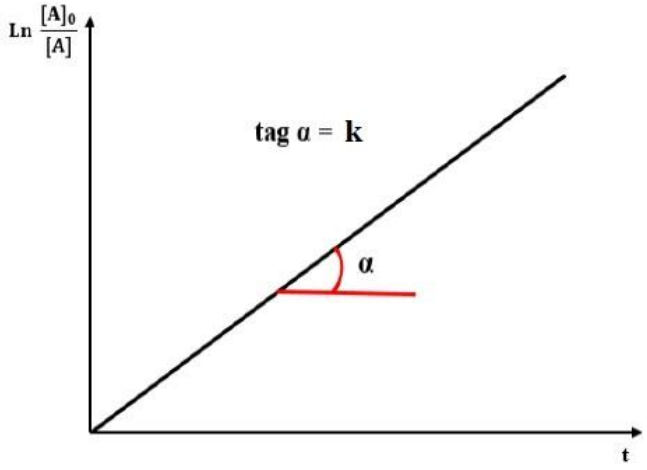
$$\ln\frac{\frac{[A]_0}{2}}{[A]_0} = kt½ \quad \Rightarrow t½ = \frac{ln2}{k}$$

For a reaction of order 1, the half-reaction time is independent of the initial concentration

The graphical representation of $\ln\frac{[A]}{[A]_0}$ as a function of ***t*** takes the form of a straight line (y= a. *x*) or

K :is the slope of the straight line. This expression can also be represented in its exponential form, which describes an exponential decrease in the concentration of the reagent as a function of time:





- **Second-order reaction (n= 2)**

In the case a second-order reaction, there are two possible scenarios:

a) Case 1: □□ → □ (same reagent)

Kinetic law $v = -\frac{d[A]}{dt} = k[A]^2 \Rightarrow \frac{d[A]}{[A]^2} = -kdt \Rightarrow \frac{1}{[A]} = kt + \frac{1}{[A]_0}$

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

For a reaction of order 2, the half-reaction time is inversely proportional to the initial

concentration of reagent A

- **Reaction of order n**

n A → products

$$v = -\frac{1}{n}\frac{d[A]}{dt} = k[A]^n \Rightarrow \frac{d[A]}{[A]^n} = -nkdt \Rightarrow \frac{1}{n-1}\left(\frac{1}{[A]^{n-1}} + \frac{1}{[A]_0^{n-1}}\right) = kt$$

$$t = t_{1/2} = \frac{2^{n-1} - 1}{n(n-1)nk[A]^{n-1}}$$

IV. Degeneration of order

As soon as the overall order becomes greater than 3, the problem of determining the partial orders becomes difficult to solve.

Take, for example, a velocity law of the type: $v = k[A]^{\alpha}[B]^{\beta}$. If we operate with a large **excess of** component **B**, we will have **[B] ≈ cte**.

The speed law is simplified to: $\mathbf{v = k_{app}[A]^{\alpha}}$ with $k_{app} = k[B]^{\beta}$.

All that remains is to determine the partial order **α**. $\mathbf{k_{app} = k[B]^{\beta}}$ is called the apparent constant , since its value depends on the concentration chosen for component B

V. Relaxation techniques

This method, used to study opposing reactions with high rate constants, involves starting with a mixture in chemical equilibrium and subjecting it to a small perturbation. The kinetics of the return to chemical equilibrium are studied.

VI. Initial speed method

A series of experiments is carried out at the same temperature The

evolution of **[A](t)** is studied for a known concentration $\mathbf{[A]_0}$.

The value of the initial velocity can be deduced from this: slope of the tangent at the origin of the

curve [A](t).

For different values of $[A]_0$, we obtain

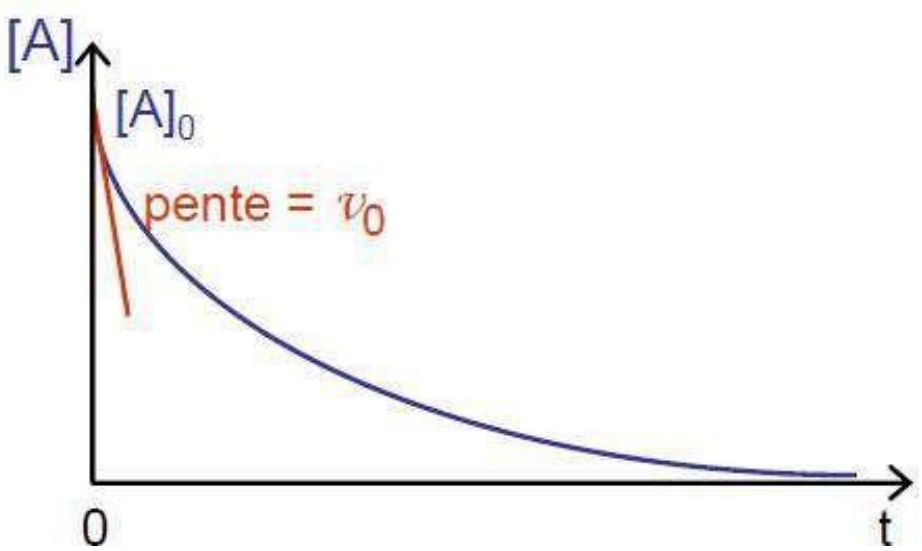
different values of v_0.

Now: **$v_0 = k[A]_0^{\alpha}$**

$\ln v_0 = \ln k + \alpha \ln [A]_0$ Trace

$\ln v_0 = f(\ln [A]_0)$

The result is **a straight line** slope **p** and y-intercept **ln k**



Chapter 3

Chemical kinetics theory

I. Introduction:

Advances in theoretical chemical kinetics have made considerable progress in recent decades. They have been complemented by experimental techniques, in particular molecular beam and modern spectroscopic techniques.

The successes of these advances are the modifications and developments of the original basic theories.

Given the elementary reaction A+B → C, the process leading to C can only take place if A and B are close enough to interact physically and chemically. The two main theories, that of molecular collisions and that of the activated complex, specify the conditions under which bringing A and B together can lead to C.

Chemical reaction theory attempts establish the link between the macroscopic level and the way in which the reaction takes molecular level

II.Collision theory

This theory is based on an assumption: molecules must collide in order to react, so chemical transformation (breaking and forming bonds) can only take place if the molecules meet.

Theory:

- The species are assimilated à to spheres spheres
- They are independent of each other
- The kinetic energy of the colliding species must be sufficient to pass the energy barrier.

II.1.Collision speed or frequency (Z) :

The frequency of collisions (Z) is the number of collisions per between two molecular species. The frequency depends directly on the concentration of the species present.

If we consider bimolecular reactions in the gas phase.

A bimolecular reaction, **A**+ B, can only occur when the two chemical entities **A** and **B** come into contact.

- The speed of the transformation is therefore proportional to the number bimolecular shocks between **A** and **B** per unit time (frequency shocks)

The frequency these shocks is itself proportional to the concentration and each entity.

- If **[A] doubles**, the frequency of collisions between A and B also **doubles**. So the frequency of collisions is proportional to **[A][B]**.

- If the temperature **rises**, the molecules move faster.
  This increases the frequency of collisions between the molecules.

For two different molecules **A** and **B** with diameters d_A and $d_{(B)}$ and masses M_A and M_B , the number of bimolecular shocks **A-B** per unit time, or shock frequency Z_{AB}

This theory considers the molecules of the reactants as rigid, neutral, spherical balls in motion. The number of collisions between A and B per unit time is given by the relation

$$z_A = N_A \sigma_A \sqrt{\frac{8 k_B T}{\pi \mu_A}} [A][B]$$

N_A Avogadro number

σ_{AB} effective cross-section of the reaction $\sigma = \pi . d^2$ and $d = \frac{1}{2}(d_A + d_B)$

k_B Boltzmann constant

μ_{AB} reduced mass of $\mu_A = \frac{M_A M_B}{M_A + M_B}$

$\sqrt{\frac{8 k_B T}{\pi \mu_A}}$ average relative velocity of molecules in a gas

Effective cross-section of a few molecules in nm^2	
Ar	0.36
C_2H_4	0.64
C_6H_6	0.88
CH_4	0.46
Cl_2	0.93
CO_2	0.52
H_2	0.27
He	0.21
N_2	0.43
Ne	0.24
O_2	0.40
SO_2	0.58

II.2.Boltzmann term (*fr*) :

Two factors need to be taken into account:

Firstly, the two molecules must collide with sufficient energy to break the bonds.

Secondly, the molecules must be in a favorable orientation for the reaction to take place.

At the moment of collision, the molecules must possess sufficient energy to cause a rearrangement of chemical bonds (Arrhenius).

If the collision energy is lower than activation , the
molecules are just bouncing around.

Only collisions involving a kinetic energy above the reaction potential barrier are effective. The probability of such a collision is given by the **Boltzmann term**:

$$f_r = e^{-\frac{E_a}{RT}}$$

The fraction f_r is between 0 and 1. $f_r$increases as T increases.

reaction speed= collision speed(Z_{AB})/N_A . $e^{-Ea/RT}$

$$v = \sigma_{AB}\sqrt{\frac{8k_bT}{\pi\mu_{AB}}}[A][B]e^{-\frac{E_a}{RT}}$$

By comparing this relationship with that of the second-order speed law

$v=k\ [A][B]$, we deduce that, in the context of this theory, the coefficient of speed k takes the form :

$$k = \sigma_{AB}\sqrt{\frac{8k_bT}{\pi\mu_{AB}}}e^{-\frac{E_a}{RT}}$$

In first approximation, this relation is compatible with the equation empirical Arrhenius: $k= Ae^{\frac{-E_a}{R}}$ provided that the exponential factor outweighs the variation $\sqrt{T}$ in which the pre-exponential factor would be involved.

II.3.Effective collisions (Hinshelwood) The steric factor p :

The effectiveness of a collision depends on :

- The energy involved, which must be greater than *Ea*,
- The orientation of the molecules at the moment of impact: this must be favourable, - The theoretical rate of reaction is given by : v=ZAB e(-E_a)/RT)

If we compare $_{ZAB}$ to the speed of the reaction, if we compare the number of collisions to the number of particles actually transformed, we see that Z_{AB} is always very large compared to the speed of the reaction (*v*), ($_{ZAB}$≫ *v* (≃ 10^7 to 10^8 times). This means that of all the theoretical collisions

only some of them lead to a chemical transformation.

These shocks are called effective shocks: Zeff=ZAB e(-E_a)/RT)

However, the experimental results are often inferior to the theoretical results. This difference is linked to the importance of the point impact of the shock. The reaction does not occur even if the shock has a high energy level if it does not occur at the desired point (sensitive point). This leads to the introduction of a corrective term called the efficiency or steric factor or Hinshelwood factor, which is between 0 and 1.

Not all collisions whose energy exceeds E_a lead to the formation of products; they are said to be inefficient. The orientation of the atoms during the collision can influence product formation, or the return to the reactants.

The steric factor, p, can be included in the expression of the speed law

theoretical. Its value lies between 0 and 1.

$$v = \text{collision velocity}(Z) \cdot e^{-Ea/RT} \cdot P$$

II.4.Limitations of collision theory

- ✓ no P modeling: limited to sphere models
- ✓ valid for bimolecular reactions
- ✓ valid for gas phase

Collision theory does not go into the details of the interaction between reacting molecules, nor how energy is distributed within each molecule. As a result, it cannot adequately account for the differences in velocities observed for different reactions, or even for different molecules participating in the same class of reactions.

III. The theory of the activated complex (the transition state)

III.1. Definition

The so-called "activated complex" theory, developed mainly by H. Eyring and M. Polanyi in the 1930s, is based on the same conceptual framework as collision theory, but goes into detail about the interactions between the reacting species to describe the formation of a high-energy intermediate complex or "activated complex", which decomposes to give the reaction products.

The theory of the activated complex allows the calculation of the velocity constant of a reaction between two molecules A and from properitie of these molecules namely namely

1. The arrangement of atoms within molecules A and B
2. The moments inertia of molecules A and B about their axes of rotation,
3. The vibrational frequencies of the various bonds between atoms

The theory of the activated complex posits that molecules **A** and **B** will move towards

each other through their own motion. The free energy of the system increases as a result of the interactions, which become more and more pronounced at short distances, until the molecules **A** and **B** can no longer be distinguished as individuals, forming a high-energy complex labelled **AB**$^{\#}$.

This complex can decompose, giving back the reactants and/or the products of the reaction.

The reaction (figure below) is described by two steps:

1. Formation of the complex activated by a rapid equilibrium reaction:

$$A + B \rightleftarrows AB^{\#}$$

2. limiting stage product formation $AB^{\#} \rightarrow C + D$

3-stage mechanism: $A + B \rightleftarrows AB^{\#} \rightarrow C + D$

III.2. The speed of the reaction

The rate of reaction is equal to the rate of formation of the products, i.e. the rate of transformation of the complex: $v = k^{\#}.C_{AB^{\#}}$

Wit$C_{AB^{\#}} = K_C^{\#}.C_A.C_B$

$K_C^{\#}$ the equilibrium constant relative to the concentrations between the reactants and the activated complex

the speed of reaction is expressed by $v = \kappa \frac{k_B.T}{h} C_{AB^{\#}}$

k_B is Boltzmann's constant (1.381 10^{-23} J K^{-1}),

h Planck's constant (6.626 10^{-34} J s)

κ, the transmission factor, represents the proportion of activated molecules which, crossing the top of the energy barrier, actually transform to give the reaction products. In most cases, **this factor is**

equal to 1

the expression for the **speed coefficient** becomes :

$$\mathbf{k} = \frac{\mathbf{k_B}.\mathbf{T}}{\mathbf{h}} \cdot \exp\left(\frac{-\Delta^{\#}\mathbf{S}^{\circ}}{\mathbf{R}}\right).\exp\left(\frac{-\Delta^{\#}\mathbf{H}^{\circ}}{\mathbf{R}.\mathbf{T}}\right)$$

With $\Delta^{\#}G^{\circ} = -R.T.\ln K^{\#}$ $\Delta^{\#}G^{\circ} = \Delta^{\#}H^{\circ} - T.\Delta^{\#}S^{\circ}$

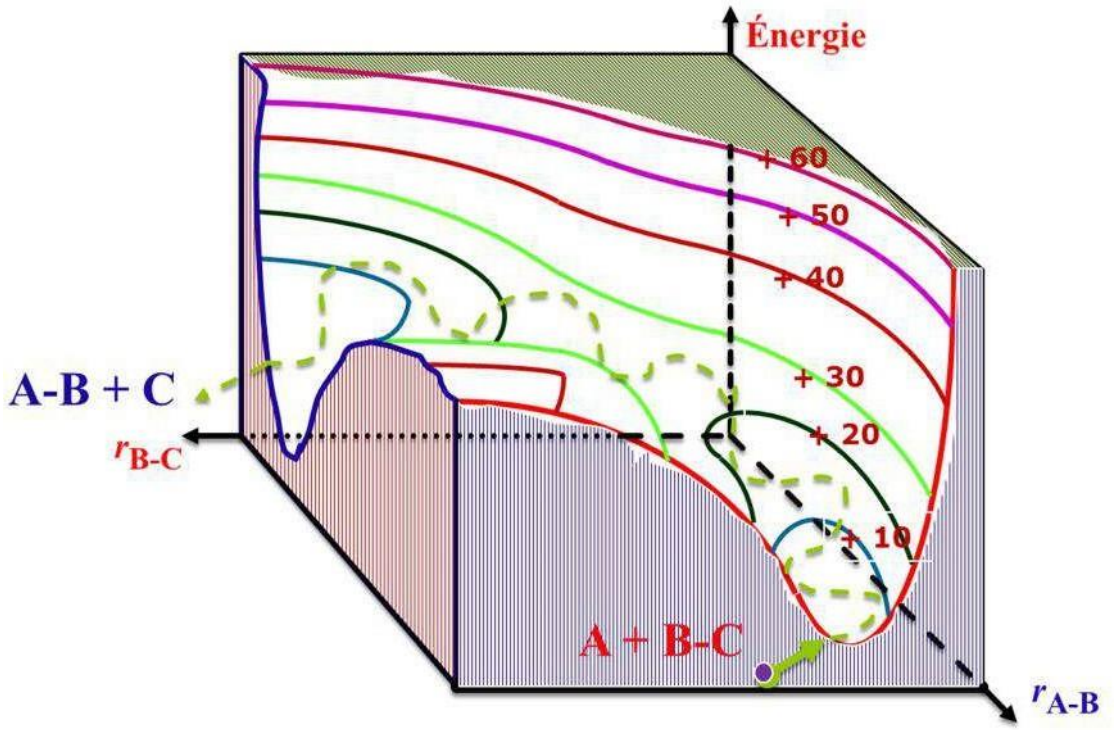
To illustrate more precisely the notion of reaction path and transition state, we'll construct **the potential energy surface** in the simplest case where an **atom A** reacts with a **molecule BC** to replace one of its atoms **(C)**.

The reaction under consideration is written:

$$A + B\text{–}C \Leftrightarrow (A - - B - - C)^* \rightarrow A\text{–}B + C$$

III.3. The path on potential energy surface

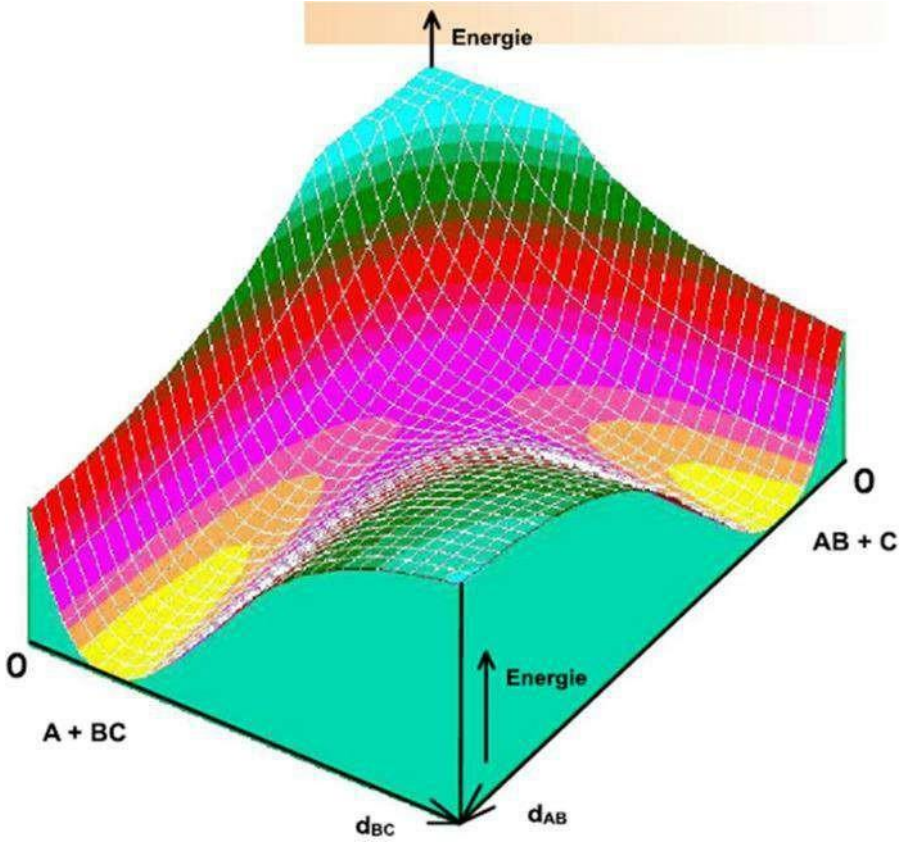
The reaction path has been defined as the sequence of states of the system that allows it to pass from the initial state (reactants) to the final state (products) with the minimum input of energy to cross the potential energy barrier. As its name suggests, the potential energy surface represents only the potential energy to which we must add the kinetic energy (translation, rotation, vibration) of all the system's constituents to obtain its total energy. If we consider the system in its initial state **(A+ BC),** the molecule **BC** has a vibratory motion that gives it vibratory kinetic energy. Taking this motion into account, the representative point of the system is no longer fixed, but moves to either side of the equilibrium position.



If we now consider the approach of the two reactants (**A and BC**) along **the BC axis**, we must add a kinetic energy term that places the representative point of the system at a certain height with respect to the energy surface

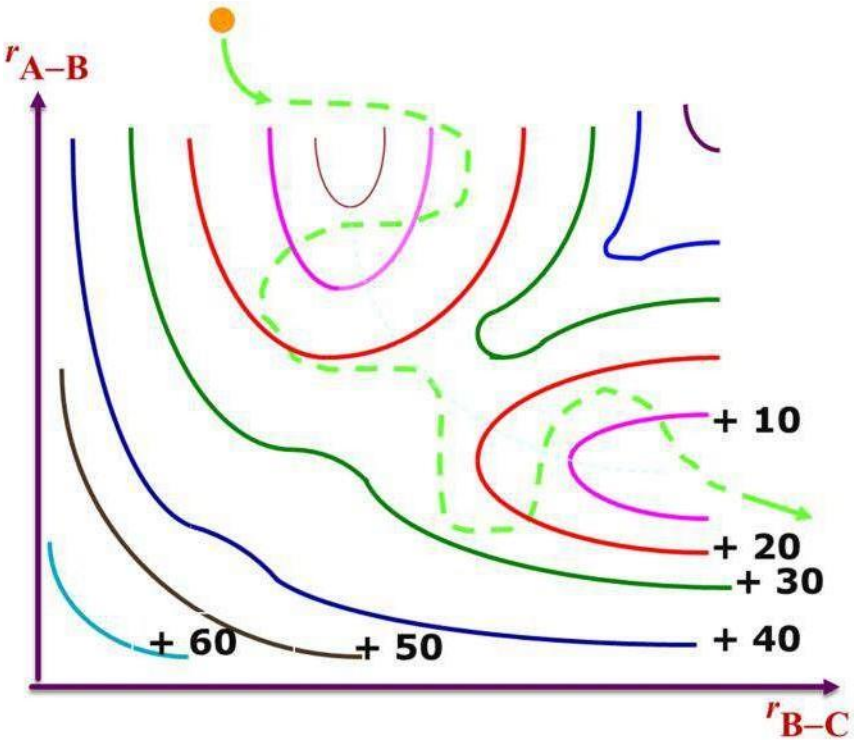
potential. As the reactants approach each other, the projection of the system's representative point on the plane will move as shown in the animation.

As the system **"climbs"** towards **the pass**, its **potential energy increases** and it **loses kinetic energy** (or its kinetic energy decreases accordingly).



➢ *Passage not successful*

If the system's kinetic energy is insufficient, it will not be able to reach the transition state. It will therefore "go back" and the reactants will separate without having reacted.



III.4. Conclusion

As soon as we're dealing with more complex systems with more than three atoms, it becomes impossible to represent the potential energy surface. But the concepts developed above remain valid. We therefore need to imagine the reaction path and validate it by performing point calculations at a series of characteristic points along the path. One of the trickiest points is characterizing the transition state and its vibrational modes.

In reactions involving more complex reactants, the vibration corresponding to the transition state may involve many atoms and cannot always be easily associated with a particular bond. However, the concept of transition state vibration taking place "along the reaction path" remains.

Chapter 4

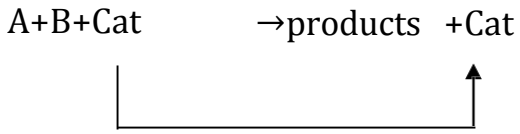
Homogeneous Catalysis

I. Introduction:

For a thermodynamically feasible reaction, the catalyst is the third most important factor after concentration and temperature, making it possible to favourably modify the speed of the reaction by a considerable . gain in reaction timeIt also significantly the activation energy, thereby favouring the formation of the activated complex.reduces

II. Definitions:

A catalyst is a substance that modifies the rate of a chemical reaction without itself undergoing any modification (is not consumed in the reaction). When the catalyst in question increases the speed of the reaction, it is said to be a positive catalyst or promoter; when it does not, it is said to be a negative catalyst or inhibitor.



Catalysis is homogeneous when the catalyst and the reaction medium are in the same phase, heterogeneous when the reactions take place at the interface of 2 media. The catalyst acts in infinitesimal doses. The action of the catalyst is interpreted by admitting that it carries out the chemical transformation according to a reaction whose resulting activation energy is less than that of the normal reaction. Figure I. 14 shows the variation in the activation energy of a catalysed or non-catalysed system.

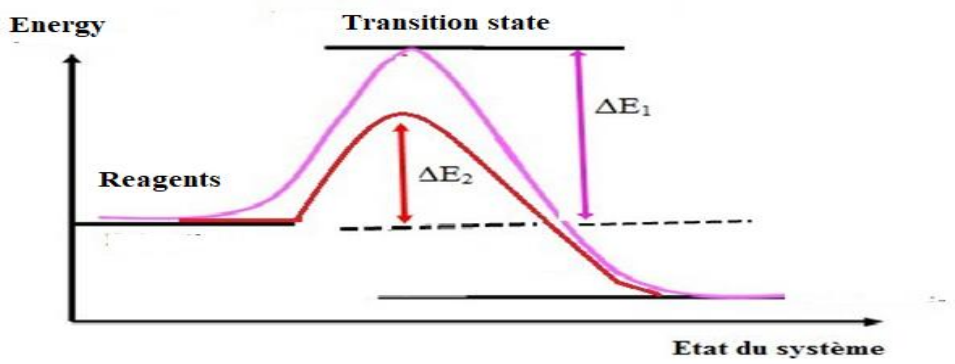


Figure I. 14: Variation in the activation energy of a catalysed or non-catalysed system. $\Delta E2 < \Delta E1$ with :

ΔE_1: activation energy of the normal reaction

ΔE_2:activation energy of the catalysed reaction

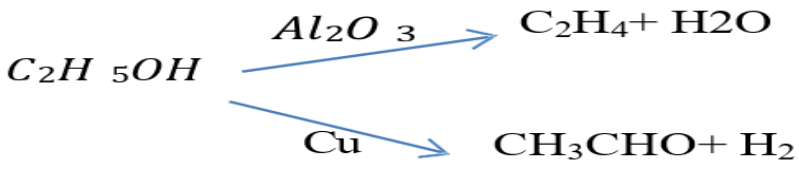
It is possible for one of the products formed during a reaction to be a catalyst for that reaction, in which case it is referred to as an autocatalytic reaction.

III. Properties of catalysts:

III.1. Selectivity:

A catalyst can direct (or favour) reactions. For example, at 400°C, the alcohol C_2H_5OH leads to two different products depending on the catalyst: there an orientation effect.

For example



III.2. Specificity:

- A type of catalyst is specific 1 reaction. For example, among the catalysts for the hydrogenation of double or triple bonds:
- (Pd) catalysts are specifically designed hydrogenation C≡C In C= C.
- (Pt) or (Ni) catalysts are specific hydrogenation C≡Cor C=C in C−C.

IV. Order of reaction in relation to the catalyst

Consider the reaction A→p+ q in the presence of catalyst **C**, an intermediate compound, **I,** is formed between **A** and **C**.

$$A + C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} I \xrightarrow{k_2} P + q + C$$

If ***I*** is highly reactive (k_2 is large), it can be considered an active centre and the AEQS can be applied to it.

$$\frac{d[I]}{dt} = k_1[A][C] - k_{-1}[I] - k_2[I] = 0 \Rightarrow [I] = \frac{k_1}{k_2 + k_{-1}}[A][C]$$

$$v = \frac{d[P]}{dt} = k_2[I] \Rightarrow \frac{k_1 k_2}{k_2 + k_{-1}}[A][C]$$

The reaction is of order 1 with respect to the catalyst

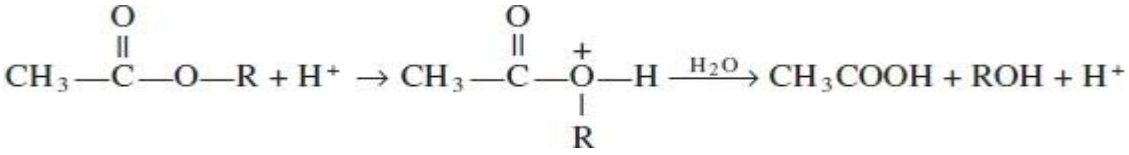
V. Acid-base catalysis

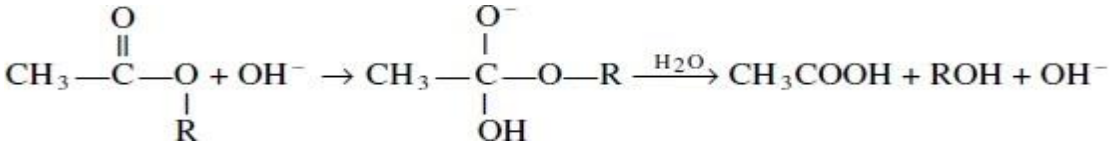
Acids and bases are the simplest and oldest known catalysts in the liquid phase. Catalysis is said to be acid-base if the chemical reaction is catalysed by an acid (presence H^+ ions) or by a base (presence HO^- ions). There are two types of acid-base catalysis:

a) Specific acid-base catalysis: in this type of catalysis, the speed of the reaction is proportional to the concentration of ionised solvent molecules, and the observable catalytic effects are due to those formed from the solvent itself. In this case, the acid or base catalyst helps to speed up the reaction by encouraging the chemical equilibrium shift in the direction of ionised solvent formation:

$$S+AH \rightarrow SH^{+}+A^{-}$$

Ester hydrolysis is an example where H^{+} and OH^{-} ions act as catalysts





The reaction rate is

$$v = k[S]$$

$[S]$: Concentration of the ester

k is the apparent rate constant, which depends on the pH, as the reaction is catalysed by H^+ or OH^-.

If k_0 is the rate constant of the spontaneous process (in the absence H^+ and OH^- ions), the constant of speed k is written :

- In acid medium: $K_A = K_0 + K_{H^+}[H_3O^+]$
- In a basic medium: $K_B = K_0 + K_{OH}[OH^-]$

If catalysis is carried out simultaneously by the ions H^+ and OH^- and the reaction also occurs in the absence of these ions, the apparent rate constant can be written as follows:

$$k = k_o + k_{H^+}[H_3O^+] + k_{OH^-}[OH^-]$$

The speed of reaction is written as :

$$v = k_0[S] + k_{H^+}[H_3O^+][S] + k_{OH^-}[OH^-][S]$$

To illustrate the variations in k as a function of pH, let's assume that k_0 is very small compared with either of the two terms as soon as the pH differs significantly from the minimum value $(pH)_m$ corresponding to $[H3O^+]_m$. In this case, in an acidic environment, log k will vary linearly with pH along a straight line with slope (-1) and in a basic environment, it will be the same along a straight line with slope (+1), graphically obtaining the shape of curve (a) in Fig I. 15.

The three other cases frequently encountered are shown in Fig I. 15 :

- Curve (b) is encountered in the case where the constant k_0 is not at all negligible over a certain pH range.
- Curve (c) occurs OH^- ions do not catalyse the reaction.
- Curve (d) occurs when H_3O^+ do not catalyse the reaction.

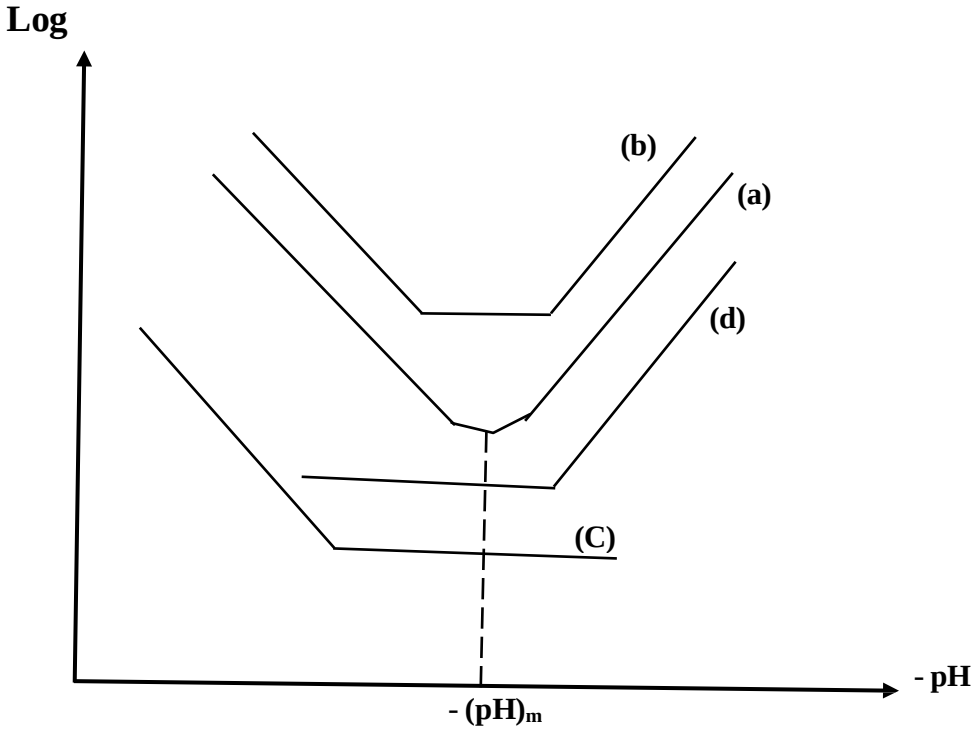


Figure I. 15: Schematic variation of log k as a function of pH in the case of catalysis by H_3O^+ and OH^- ions.

b) General acid-base catalysis

In general acid-base catalysis, all species capable of donating H^+ protons or $OH^{(-)}$ contribute speeding up the reaction. The strongest acids and bases are the most effective. In this case, it is not only the H_3O^+ and OH^- ions resulting the reaction of the weak acid or base with water that are responsible for the catalytic effect. In fact, even the acidic form AH and the basic form A^- have catalytic power.

VI. Autocatalysis:

A reaction is autocatalysed when one of the reaction products is involved in the rate equation.

Example: oxidation of oxalic acid by potassium .permanganate

$$2MnO_4^- + 2C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 4CO_2 + 8H_2O$$

The decolourisation of the permanganate is slow at the start of the reaction and

becomes faster. The kinetic study shows that the speed of the reaction is of the form:

$$v = k[C_2O_4{}^{2-}][Mn^{2+}]$$

Therefore Mn^{2+}autocatalyses the reaction.

Another example isthe hydrolysis of esters autocatalysed by the acid weak released during reaction.

$$HCOOC_2H_5 + H_2O \rightarrow HCOOH + C_2H_5OH$$

□= K[Ester]. [HCOOH]

VII. heterogeneous catalysis :

The catalyst is solid, the products and reagents are in the liquid phase or in the liquid gas. The reaction takes place at the surface of the catalyst. The larger the surface, greater the efficiency is high

In industrial terms, heterogeneous catalysis has gained considerable momentum in recent decades, which is why there is a research being carried out in this field.great deal of

VII.1. Mechanism of heterogeneous :catalysis

The important stages involved inthe mechanism are:

a. Diffusion of reagents from the homogeneous phase towards the surface of the catalyst.
b. Adsorption of reagents to the surface.
c. The chemical reaction between the different species adsorbed on the surface of the catalyst is often the slowest stage and the one that determines the speed of the reaction.
d. Desorption of the products formed on the surface of the catalyst.

EXERCISES WITH SOLUTIONS

EXERCISE 1 :

When of the decomposition by the heat, in volume constant, the vanadium to nitrogen, in phase

gaseous and following the reaction : $\mathbf{N_2O_5 \xrightarrow{k} 2NO_2 + ½\ O_2}$

It is found that the time t_1 at the end of which one-half of N_2O_5 original has disappeared is independent of the initial pressure.

1) In deducing the order of the reaction.

2) A 55°C, one finds that the time t_1 is of 460 seconds. Calculate the constant of speed k of decomposition of N_2O_5**.**

EXERCISE 2 :

The bromo-2 octane optically active substance is subjected to the action of the potash in a solvent containing a volume of 60% water and 40% ethyl alcohol. It will form the corresponding alcohol with inversion of configuration, and bromide of potassium. The kinetic study of this reaction gives the following results at a given temperature :

$[Br^-] .10^3$ mol.l^{-1}	202	288	336	366	436
t in seconds	1000	2000	3000	4000	10000

Knowing that this was a party of 1 liter of a solution containing 0.5 mol of bromo-2 octane and 0.5 mole of potash, show that the reaction is second order and calculate the rate constant.

EXERCISE 3 :

It assumes that the reaction of the pyrolysis of a compound Has the equation : **A (g) → B (g)** admits an order. It was obtained at 298 K, the following results :

[A] (10^{-3}mol.L-1)	16	12,8	9,6	6,4	3,2
- Time in seconds	0	4	10,68	24	64

Determine the order of this reaction and that the constant of speed k.

EXERCISE 4 *:*

One introduces the ethylamine into an empty container of air at 500 °C. The pressure is 55 mm of mercury at time t = 0.

The decomposition of the body has been held at this temperature and gives C_2H_4 and NH_3.

The volume of the container will remain constant for the duration of the reaction, measure the gas pressure **to total P** at various time intervals. The results obtained are

P (mm of Hg)	T (mn)
55	0
60	1
72,5	4
89	10

recorded in the following table ~~: *The gas are assumed to be perfect*~~

1) Show, by calculating the rate constant k, for the reaction of decomposition of ethylamine is of the first order.

2) Has 1000 K, what is the time required to make it go away 80% of the ethylamine ?

3) In deduct the factor pre-exponential of the reaction.

Data : E_a = 600 J. mol^{-1} R = 8,32 J. mol^{-1}.K^{-1} = 62,3 mmHg.l.mol^{-1}.K^{-1}

Exercise 5 :

The decomposition of nitric nitrogen in the gas phase has been proposed to obtain an atmosphere suitable in space capsules :

$$2N_2O \rightarrow 2N_2 + O_2 \text{ (k)}$$

This reaction has been studied by introducing it in a container of volume V constant, draining, a certain amount of monoxide, dinitrogen, and by measuring the total pressure P_t in the course of time. The following results were obtained at 800 K, the pressures are measured in units of mmHg :

t / min	**0**	**12**	**26**	**45**
P_t / mmHg	**100**	**106,2**	**112,5**	**119,5**

1) Give the expression for the rate of disappearance of N_2O and formation of N_2. To establish a relationship between them.

2) If it is assumed that the unit of the rate constant of the reaction is min^{-1}, what will be the order of the reaction ?

3) We want to verify, from the data in the table relating to T_1 = 800 K, the reaction is indeed not simple. The monoxide dinitrogen is pure to the initial state and the gas are assumed to be perfect.

In assuming that the order of the reaction is a whole number belonging to the interval]3 , 0[Prove the following equality : $$2k.t = Ln\frac{P_0}{3P_0 - 2P_t}$$

With : k : constant of speed of the Reaction reaction.

t : time.

P_0 : pressure initial of N_2O.

P_t : pressure total in the enclosure to the date t.

4) By the method of calculation, calculate the constant of speed k for the reaction at this temperature T_1.

5) Always at the same temperature T_1, calculate the time, t, after which 20% of N_2O was not consumed. What is the total pressure reign, and in the compound at $t_{80\%}$?

6) Knowing that the rate constant for the reaction above at T_2 = 600 K shows the 1/3 of the rate

constant at T_1 = 800 K, determine the activation energy and the frequency factor of the reaction. (R constant of an ideal gas is equal to 2 cal.mol^{-1}K^{-1}).

Correction of the Series 1

EXERCISE 4 :

1) The time t_1 is independent of the pressure wants to say that it is independent of the concentration , therefore, the order of the reaction is a.

2) t_1 is equivalent to $t_{1/2}$, and since the reaction is of first order , therefore :

$$Ln\frac{[N_2O_5]_0}{[N_2O_5]} = k.t \Rightarrow Ln\frac{[N_2O_5]_0}{\left(\frac{1}{2}\right).[N_2O_5]_0} = k.t_{1/2}$$

So

$$k = \left(\frac{1}{t_{1/2}}\right)Ln2 = \left(\frac{1}{460}\right)Ln2 = 1{,}5.10^{-3}\,s^{-1}$$

EXERCISE 5 :

Bromo-2 octane + OH^- $\xrightarrow{k}$ Octane-2 - ol + Br^-

Law of speed : -d[Bromo-2 octane]/dt = k[Bromo-2 octane]$^{\alpha}$. $[OH^-]^{\beta}$

Since the concentrations initials are equal , and since it was asked in the year to demonstrate that the order is 2, so the equation kinetics becomes :

-d[Bromo-2 octane]/dt = k[Bromo-2 octane]^1. $[OH^-]^1$= k[Bromo-2 octane]^2

So: $-\frac{d[\text{Bromo}-2\text{ octane}]}{d[\text{Bromo}-2\text{ octane}]} = kdt$

After integration, one obtains:

$$\frac{1}{[\text{Bromo - 2 octane}]} - \frac{1}{[\text{Bromo - 2 octane}]_0} = k.t$$

It is to be noted that in the year it gives the amount of Br- formeé, so :

[Bromo-2 octane] $_{remaining}$ = [Bromo-2 octane]$_0$- [Br^-]$_{formed}$

To demonstrate that the order is 2 , and derive the constant of speed of two methods are presented (calculation method or graphical method) :

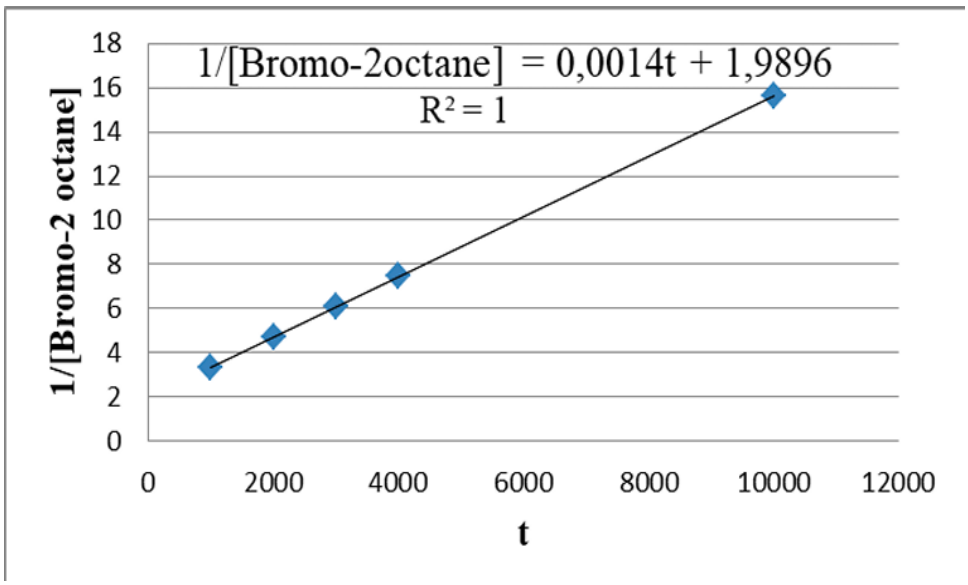
- Method of calculation :

t en secondes	1000	2000	3000	4000	10000
$[Br^-]$ mol.l^{-1}	0,202	0,288	0,336	0,366	0,436
[Bromo-2 octane] mol.l^{-1} = 0,5 – $[Br^-]$	0,298	0,212	0,164	0,134	0,064
$\left(\frac{1}{t}\right).\left(\frac{1}{[\text{Bromo - 2 octane}]} - \frac{1}{[\text{Bromo - 2 octane}]_0}\right) = k$	1,35.10^{-3}	1,36.10^{-3}	1,36.10^{-3}	1,36.10^{-3}	1,36.10^{-3}

The constant of speed, k is constant , therefore, the order is well - 2 and k_{avg} = 1,36.10^{-3} mol^{-1}.L.s^{-1}

- Method graph :

$\frac{1}{[Bromo-2octane]} - \frac{1}{[Bromo-2octane]_0}$In bearing in function of the time and it checks to see line .



It is clear based on the table that It is a right of coefficient of correlation R^2=1 , so the reaction is second-order and k=1,4.10^{-3} mol^{-1}.L.s^{-1}.

EXERCISE 6:

To determine the order as well as the constant of speed of the reaction of pyrolysis

Has $\xrightarrow{k}$ Products , using the integral method, which is to make guesses orders.

Assume that the order is zero and check the compatibility of data experimental with the law kinetics.

-d[A]/dt = k[A]^0=k $\Rightarrow$[A]-[A]$_0$=k. t

Verification of the compatibility of this relationship with the data - experimental.

Time in seconds	0	4	10,68	24	64
[A] (10^{-3}mol.L^{-}1)	16	12,8	9,6	6,4	3,2
(1/t).([A]-[A]$_0$)=k	-	0,8.10^{-3}	and 0.6.10^{-3}	to 0.4.10^{-3}	to 0.2.10^{-3}

According to the table the value of the constant of the speed is not constant , therefore, it n there was not of compatibility.

We continue , therefore, the assumptions , and we assume this time that the order is two and we redid the same thing.

$$-d[A]/dt = k[A]^2 = k \Rightarrow \frac{1}{[A]} - \frac{1}{[A]_0} = k.t$$

Temps en seconde	0	4	10,68	24	64
[A] (10^{-3}mol.L^{-}1)	16	12,8	9,6	6,4	3,2
$\left(\frac{1}{t}\right).\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) = k$	-	3,9	3,9	3,9	3,9

According to the table the value of the rate constant is constant, therefore there has to be compatibility between the law kinetics and the experimental data so the order is 2, and k=a 3.9 mol^{-1}.L.s^{-1}.

EXERCISE 7 :

1) Is the reaction : $C_2H_5NH_2 \xrightarrow{k} C_2H_4 + NH_3$

Progress	**$C_2H_5NH_{2(g)}$**	**$C_2H_{4(g)}$**	**$NH_{3(g)}$**
t=0	**n_o = PoV/RT**	**0**	**0**
t any	**$n_0 - \alpha = P_{(C2H5NH2)}$ .V/RT**	**α**	**α**

The number of mol total to the date t is $n_o+\alpha$ = PV/RT (1)

$n_o - \alpha = P_{(C2H5NH2)}$ .V/RT (2) By adding up the two equations (1) and (2) one obtains : $P_{(C2H5NH2)}$=2-P ($P_{(C2H5NH2)}$: partial pressure of $C_2H_5NH_2$, and P is total pressure).

Reaction order 1 :

$$Ln\frac{[C_2H_5NH_2]_0}{[C_2H_5NH_2]} = k.t = Ln\frac{P_0/RT}{P_{(C_2H_5NH_2)}/RT} = Ln\frac{P_0}{(2P_0 - P_t)}$$

Conformity of the data with the experimental with the relationship of theoretical previous :

Time in (min)	0	1	4	10
Pressure in (mmHg)	55	60	72,5	89
$k = \frac{1}{t} Ln \frac{P_0}{(2P_0 - P)}$	-	**9,53.10^{-2}**	**9,57.10^{-2}**	**9,62.10^{-2}**

It turns out that one has obtained the same value of the rate constant, the reaction is of first order and $\mathbf{k_{avg} = 9{,}57.10^{-2}\ min^{-1}}$.

- Calculate first the constant of speed to 1000 K,

Arrhénius $k_T = A.e^{\frac{-Ea}{R.T}}$

- T_1= 773K and T_2= 1000K. Based on the equation of Arrhenius it has

$k_{T2} = k_{T1}.e^{\frac{Ea}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$ AN : $k_{T2} = 9{,}57.10^{-2}.e^{\frac{600}{8{,}314}\left(\frac{1}{773}-\frac{1}{1000}\right)} = 9{,}77.10^{-2}\ min^{-1}$.

- The time necessary to make it disappear 80% of The ethylamine is :

$$t_{80\%} = \left(\frac{1}{k}\right) Ln \frac{[C_2H_5NH_2]_0}{20\%.[C_2H_5NH_2]_0} = \left(\frac{1}{k}\right).Ln(5) = \left(\frac{1}{(9{,}77.10^{-2})}\right).Ln(5) = 16{,}47 \ \text{min}$$

$$t_{1/2} = t80\% = 16{,}47 \text{ minutes.}$$

Exercise :

1) $Vd_{(N2O)} = -\frac{1}{2}d[N_2O]/dt = k[N_2O]^p$ $Vf_{(N2)} = \frac{1}{2}d[N_2] = k[N_2O]^p$ $Vd_{(N2O)} = Vf_{(N2)}$

2) If the unit of the constant of speed is $time^{-1}$ (min^{-1}) then the reaction is of first order.

3) The reaction is not simple wants to say that the order is not 2, not 0 and 3 because the order belongs to interval]3,0[. It remains to assume that the order is 1 and demonstrate the relationship $2kt = \ln\frac{P_0}{3P_0-P_t}$ $2k.t = Ln\frac{P_0}{3P_0-2P_t}$

Progress	$\mathbf{2N_2O_{(g)}}$	$\mathbf{2N_{2(g)}}$	$\mathbf{O_{2(g)}}$
t=0	$\mathbf{n_o = PoV/RT}$	**0**	**0**
t any	$\mathbf{n_o - 2\alpha = P_{(N2O)}.V/RT}$	$\mathbf{2\alpha}$	$\mathbf{\alpha}$

The number of mol total to the date t is $n_o+\alpha = P_tV/RT$

(1) $n_o - 2\alpha = P_{(N2O)}.V/RT$

By multiplying the equation (1) by a factor of 2 , and by adding up the two equations (1) and (2) one obtains : $P_{(N2O)}=3P_0-2P_t$

($P_{(N2O)}$: partial pressure of N_2O and P_t total pressure).

Reaction order 1 : $\ln \frac{[N_2O]_0}{[N_2O]} = 2kt = \ln \frac{P_0/_{RT}}{P_{N2O}/_{RT}} = \ln \frac{P_0}{3P_0 - 2P_t}$

2

4) Compliance of data with the experimental with the relationship of theoretical previous :

Time in (min)	0	12	26	45
Pressure P_t in (mmHg)	100	106,2	112,5	119,5
$k = \frac{1}{2.t} Ln \frac{P_0}{(3P_0 - 2P_t)}$	-	**5,51.10^{-3}**	**5.53.10^{-3}**	**5,49.10^{-3}**

It turns out that one has obtained the same value of the rate constant, the reaction is of first order and

k_{avg} = 5,5.10^{-3} min^{1}.

Reaction order 1 : $\ln \frac{[N_2O]_0}{[N_2O]} = 2kt$

$$t_{80\%} = \left(\frac{1}{2k}\right) Ln \frac{[N_2O]_0}{20\%.[N_2O]_0} = \left(\frac{1}{2k}\right).Ln(5) = \left(\frac{1}{(2).(5{,}5.10^{-3})}\right).Ln(5) = 146{,}3 \text{ min}$$

$$* \; 2k.t = Ln\frac{P_0}{(3P_0 - 2P_t)} \Rightarrow -2k.t = Ln\frac{(3P_0 - 2P_t)}{P_0} \Rightarrow e^{-2k.t} = \frac{(3P_0 - 2P_t)}{P_0} \Rightarrow$$

$$P_t = \frac{P_0}{2}(3 - e^{-2k.t_{80\%}}) = \frac{100}{2}(3 - e^{-(2.)\,(5{,}5.10-3).(146{,}3)}) = \mathbf{140 \text{ mmHg}}$$

5) $k_{600}=1/3.k_{800}$ calculate the energy of activation and the factor pre-exponential :

k= $A.e^{\frac{-Ea}{RT}}$ (Equation d'Arrhénius) $\frac{k_{800}}{k_{600}} = 3 = \frac{e^{(\frac{-Ea}{R.800})}}{e^{(\frac{-Ea}{R.600})}} = e^{\frac{Ea}{R}(\frac{1}{600} - \frac{1}{800})} \Rightarrow Ln(3) = \frac{Ea}{R}(\frac{1}{600} - \frac{1}{800})$

C'est-à-dire Ea = R.Ln(3). $\left[\frac{1}{600} \frac{1}{800}\right]^{-1}$ = 2.Ln(3). $\left[\frac{1}{600} - \frac{1}{800}\right]^{-1}$ = **5,27 kcal.mol^{-1}.**

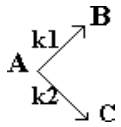
k_{800} = $A.e^{\frac{-Ea}{R.800}}$ donc A = $5{,}5.10^{-3}.e^{\frac{5270}{(2).(800)}}$

A = 1,48.10^{-1} min^{-1}

Series 2

EXERCISE 1 :

Is the reaction of decomposition of a species chemical Has in two compounds B and C.



1) Of what type of reaction is it ?

2) To establish a relationship between the constant of speed k_1 and the concentrations bet in the game for the reaction above, which is supposed to the first order.

([A], [B] and [C] denote , respectively, the concentrations of A, B and C at a time t given , and $[A]_o$ the concentration of A at t = zero).

- Knowing this time that C is the product obtained at from B,

3) Define the type of reaction

4) Give the concentration of A, B and C in function of time as well as time maximum training of B.

EXERCISE 2 :

It focuses on a balance of order a : $A \underset{k2}{\overset{k1}{\rightleftharpoons}} B$

Has t = 0, the concentration of A is a, that of B is b. Has the time t, that of B is b-x.

1) To establish a relationship between x and the time.

2) On the curve experimental, it falls within the values x_1 and x_2 to the instants t_1 and t_2 in the case where

$t_2 = 2t_1$. In deducing an expression in the report $\theta = \frac{k_1+k_2}{K_2 b+ak_1}$

3) Calculate the constants k_1 and k_2, it gives : a = 0,083 $mol.l^{-1}$; b = 1,767 $mol.l^{-1}$; x_1 = 0,23 $mol.l^{-1}$; x_2 = 0,424 $mol.l^{-1}$ and $t_1 = 50.10^3$ s.

EXERCISE 3 **:**

It is proposed to study the kinetics of the reaction of decomposition of

Ethanal :

To interpret the facts , experimental, we postulate the mechanism following :

$$CH_3CHO \xrightarrow{k1} CH_3^{\bullet} + CHO^{\bullet}$$

$$CHO^{\bullet} \xrightarrow{k2} CO + H^{\bullet}$$

$$H^{\bullet} + CH_3CHO \xrightarrow{k3} H_2 + CH_3CO^{\bullet}$$

$$CH_3CO^{\bullet} \xrightarrow{k4} CH_3^{\bullet} + CO$$

$$CH_3^{\bullet} + CH_3CHO \xrightarrow{k5} CH_4 + CH_3CO^{\bullet}$$

$$2CH_3^{\bullet} \xrightarrow{k6} C_2H_6$$

1) Show that this mechanism is compatible with the equation, the stoichiometric proposed previously.

2) Describe the different phases of the mechanism, in specifying the role that will play Mr.

3) Give the expression for the rate of formation of CH_4 as a function of the different rate constants of the elementary steps and the concentrations of the species stable (it will be assumed that the steady-state radical $H^{\bullet}$, $CHO^{\bullet}$, $CH_3CO^{\bullet}$ and $CH_3^{\bullet}$ is reached).

4) Deduce the order and the activation energy of the overall reaction predicted by this mechanism, it gives (E_1 = 76 kcal.mol^{-1} , E_5 = a 7.8 kcal.mol^{-1}, E_6 = 0,02 kcal.mol^{-1}).

Exercise 4 :

The mixture stoichiometric H_2 + 1/2 O_2 is a mixture of a gas in a certain area of temperature and of pressure. $H_2 + 1/2\ O_2 \xrightarrow{K} H_2O$

The experimental conditions suggest the existence of a process of radical chain divergent; Hinshelwood proposed the following mechanism :

Initiation : shocks on wall :	H_2	$\rightarrow 2\ H^{\bullet}$	k1	**(1)**
Spread :	$H^{\bullet} + O_2$	$\rightarrow OH^{\bullet} + O^{\bullet}$	k2	**(2)**
	$O^{\bullet} + H_2$	$\rightarrow OH^{\bullet} + H^{\bullet}$	k3	**(3)**
	$OH^{\bullet} + H_2$	$\rightarrow H_2O + H^{\bullet}$	k4	**(4)**
Terminator: shock on wall and possibly the appearance of water :				
	$H^{\bullet}$	$\rightarrow H^{\bullet}$fixed	k5	**(5)**
	$OH^{\bullet}$	$\rightarrow OH^{\bullet}$set	k6	**(6)**

1) Write the speed of synthesis of the water - v according to the reaction (4).

2) Knowing that, for each process, elementary, the order identifies itself to the molécularité, and that after an induction phase is very brief, the principle of the stationary condition is satisfied, show that v can be put under the form:

$$v = \frac{\alpha[H_2]^2.[O_2]}{\beta + \gamma[H_2] + \theta[H_2].[O_2]}$$

Identify α, β, γ and θ in function of k_i. $(1 \leq i \leq 6)$

3) In the case where $\beta + \gamma[H_2] + \theta[H_2].[O_2] = 4/k_{-5}$, in deducing the order total and an expression of the rate constant K of the reaction of synthesis of water.

Correction of the series 2 :

1) It is a reaction parallel (twin)

2) -d[A]/dt = k_1[A] + k_2[A] = (k_1 + k_2).[A] this , which implies that -d[A]/[A] = (k_1 + k_2).dt.

After integration, one obtains : $\ln\frac{[A]_0}{[A]} = (k_1 + k_2)$ (1)

d[B]/dt = k_1[A] (2)

d[C]/dt = k_2[A] (3)

$$(2)/(3) \Rightarrow \frac{d[B]}{d[C]} = \frac{k_1}{k_2} \Rightarrow d[B] = \frac{k_1}{k_2} d[C] \Rightarrow \int_{[B]0}^{[B]} d[B] = \frac{k_1}{k_2}\int_{[C]0}^{[C]} d[C] \Rightarrow k_2 = \frac{k_1[C]}{[B]}$$

It is to note that at t=0 : $[B]_0 = [C]_0 = 0$

Replaced in (1) it leads to $\boldsymbol{t\left(k_1 + \frac{K_1[C]}{[B]}\right) = \ln\frac{[A]_0}{[A]}}$ where finally $\boldsymbol{k_1 = \frac{[B]\ln\frac{[A]_0}{[A]}}{t([B]+[C])}}$

3- It is a reaction consecutive or successive.

4-

$$[A] = [A]_0 . e^{-k_1 t}$$

$$[B] = [A]_0 . \frac{k_1}{k_2 - k_1} . (e^{-k_1 t} - e^{-k_2 t})$$

$$[C] = [A]_0 - [B] - [A] = [A]_0 \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t}\right)$$

3) B passes <u>by a maximum of concentration</u> corresponding to d[B]/dt = 0

$$\Rightarrow t_{max} = \frac{1}{k_2 - k_1} Ln \frac{k_2}{k_1}$$

EXERCISE 2 :

1. **It is to study the equilibrium between two bodies A and B**

$$A \underset{k2}{\overset{k1}{\rightleftarrows}} B$$

According to the statement at t= 0 [A] = a and [B] = b and a to t in any

[A] = a+x and [B] = b-x Equation kinetics that governs the balance :

$-d[A]/dt = k_1[A]-k_2[B] = k_1(a+x)-k_2(b-x)$, therefore :

$-d(a+x)/dt = -dx/dt = k_1(a+x)-k_2(b-x) \Rightarrow dx/dt=k_2b\ k_{-1}(a - (k_{1+}\ k_2).x$ Therefore :

$$\frac{dx}{(k_2b-k_1a)-(k_1+k_2).x} = dt \Rightarrow \int_0^x \frac{dx}{(k_2b-k_1a)-(k_1+k_2).x} = \int_0^t dt \Rightarrow$$

$$\left[\frac{Ln((k_2b-k_1a)-(k_1+k_2).x)}{-(k_1+k_2)}\right]_0^x = t \ \Rightarrow\ \left[Ln((k_2b-k_1a)-(k_1+k_2).x)\right]_0^x = -(k_1+k_2)t$$

$$\Rightarrow Ln\frac{(k_2b-k_1a)-(k_1+k_2).x}{(k_2b-k_1a)} = -(k_1+k_2).t \Rightarrow Ln(1-\frac{(k_1+k_2)}{(k_2b-k_1a)}.x) = -(k_1+k_2).t \Rightarrow$$

$$x = \frac{(k_2b-k_1a)}{(k_1+k_2)}(1-e^{-(k_1+k_2).t})$$

At t_1 : $Ln(1-\theta.x_1) = -(k_1+k_2)t_1$……(1)

At t_2 : $Ln(1-\theta.x_2) = -(k_1+k_2)t_2$……(2)

(2 /1) : and since $t_2 = 2t_1$

$$\frac{Ln(1-\theta x_2)}{Ln(1-\theta x_1)} = 2 \Rightarrow \ln(1-\theta x_2) = (1-\theta x_1)^{2}$$

Equation of the second degree in θ : Resolution of the equation leads to

$$\theta = \frac{2x_1 - x_2}{x_1^2}$$

a= 0,083 , b=1,767, x_1=0,23 , x_2=0,424 et t_1=50.103 secondes

$$\theta = \frac{2x_1 - x_2}{x_1^2}$$

$$\theta = \frac{2x_1 - x_2}{x_1^2} = \frac{k_1 + k_2}{k_2 b - k_1 a} \Rightarrow \frac{K_1}{K_2} = \frac{\theta b - 1}{1 + \theta a} = 0{,}19$$

We know that :

$$Ln(1 - \theta x_1) = -(k_1+)t_1 \Rightarrow Ln(1 - \theta x_1) = -k_2(1 + 0{,}19)t_1$$

Therefore, $k_2 = \frac{-Ln(1-\theta x_1)}{(1+0{,}19)t_1}$ et $k_1 = 0{,}19k_2 = 1{,}5.10^{-5} \Rightarrow k_2 = 2{,}86.10^{-6}s^{-1}$

EXERCISE 3 :

1) At the level of the mechanism, if one multiplies the reaction 4 with a coefficient of 2 and is the sum of the reactants and the sum of the products, on the other hand, we reproduced the overall reaction.

(1) + (2) + (3) + 2.(4) + (5) + (6) $\Rightarrow$ $3CH_3COH \rightarrow CH_4 + 3CO + C_2H_6 + H_2$

2) - Induction Phase (1) this is the stage in which one generates the first holder of the chain it is a slow step that requires a lot of energy.

- Phase of propagation (2), (3), (4) and (5) it is the step in which it consumes the bearer of the string and it refreshes others, it is a fast stage.

- Phase termination or breach (6) it is the judgment of the chain, it is a step that requires the absorption of the excess of the energy provided at the level of initiation to prevent a new dissociation.

M plays the role of the absorption of the excess of energy provided at the level of the phase of initiation.

3) $V_{f(CH4)} = k_5[CH_3^\bullet].[CH_3CHO]$

Apply the AEQS to $CH_3^\bullet$, $CHO^\bullet$, $H^\bullet$, $CH_3CO^\bullet$:

* $d[CH_3^\bullet]/dt = 0 = k_1[CH_3CHO]+k_4[CH_3CO^\bullet]-k_5[CH^\bullet][CH_3CHO]-2k_6[CH_3^\bullet]^2$ **(1)**

* $d[CHO^\bullet]/dt = 0 = k_1[CH_3CHO]-k_2[CHO^\bullet]$ **(2)**

* $d[H^\bullet]/dt = 0 = k_2[CHO^\bullet]-k_3[H^\bullet][CH_3CHO]$ **(3)**

* $d[CH_3CO^\bullet]/dt = 0 = k_3[H^\bullet][CH_3CHO]-k_4[CH_3CO^\bullet]+k_5[CH_3^\bullet][CH_3CHO]$ **(4)**

$$(1) + (2) + (3) + (4) \Rightarrow 2k_1[CH_3CHO]-2k_6[CH_3^\bullet]^2=0 \Rightarrow [CH_3^\bullet]=\sqrt{\frac{k_1}{k_6}[CH_3CHO]}$$

$$\Rightarrow Vf_{(CH4)} = k_5\sqrt{\frac{k_1}{k_6}[CH_3CHO]}[CH_3CHO] = k_5\sqrt{\frac{k_1}{k_6}}[CH_3CHO]^{3/2}$$

We pose : $k = k_5\sqrt{\frac{k_1}{k_6}}$, Equation Arrhenius : $Ae^{\frac{-E_a}{RT}} = A_5e^{\frac{-Ea_5}{RT}}\sqrt{\frac{A_1e^{\frac{-E_{a1}}{RT}}}{A_1e^{\frac{-E_{a6}}{RT}}}}$

$$e^{\frac{-Ea}{RT}} = e^{\frac{-Ea_5}{RT}}\sqrt{\frac{e^{\frac{-Ea_1}{RT}}}{e^{\frac{-Ea_6}{RT}}}} \Rightarrow E_a = E_{a5} + ½\ (E_{a1}\text{-}E_{a6}) = 7{,}8+1/2\ (76\text{-}0{,}02) = 45{,}79\ \text{kcal.mol}^{-1}.$$

Exercise :

1) $V_{f(H2O)} = k_4.[OH^\bullet].[H_2]$

2) Apply the AEQS to $[OH^\bullet]$

* $d[OH^\bullet]/dt = 0 = k_2.[H^\bullet].[O_2] + k_3.[O^\bullet].[H_2] – k_4.[OH^\bullet].[H_2] – k_{-6}.[OH^\bullet]$ **(1)**

The expression (1) is a function also of other species labile, so it is necessary to establish the AEQS to $[H^\bullet]$and $[O^\bullet]$

* $d[H^\bullet]/dt = 0 = 2k_1.[H_2] – k_2.[H^\bullet].[O_2] + k_3.[O^\bullet].[H_2] + k_4.[OH^\bullet].[H_2] – k_5.[H^\bullet]$ **(2)**

* $d[O^\bullet]/dt = 0 = k_2.[H^\bullet].[O_2] – k_3.[O^\bullet].[H_2]$ **(3)**

(2) + **(3)** $\Rightarrow 2k_1.[H_2] + k_4.[OH^\bullet].[H_2] – k_5.[H^\bullet] = 0$ **(4)**

(2) $\Rightarrow$ $[O^\bullet] = k_2.[H^\bullet].[O_2] / k_3.[H_2]$ replaced, in the expression **(1)** we obtain :

$2\ k_2.[H^\bullet].[O_2] – k_4.[OH^\bullet].[H_2] – k_{-6}.[OH^\bullet] = 0$ **(5)**

$$\textbf{(4)} \Rightarrow [H^\bullet] = \frac{2k_1.[H_2] + k_4.[OH^\bullet].[H_2]}{k_5}$$

Replaced in **(5)** we obtain an equation in a single unknown $[OH^\bullet]$.

$$\frac{4k_1.k_2.[H_2].[O_2]}{k_5} + \frac{2k_2.k_4.[OH^\bullet].[H_2].[O_2]}{k_5} - k_4.[OH^\bullet].[H_2] - k_6.[OH^\bullet] = 0$$

$$[OH^{\bullet}] = \frac{\frac{4k_1.k_2.[H_2].[O_2]}{k_5}}{-\frac{2k_2k_4.[H_2].[O_2]}{k_5} + k_4.[H_2] + k_6}$$

Expression of the speed of formation of H_2O:

$$V_{fH2O} = \frac{4k_1k_2k_4.[H_2]^2.[O_2]}{-2k_2k_4.[H_2].[O_2] + k_4k_5.[H_2] + k_5k_6}$$

$$v = \frac{\alpha[H_2]^2.[O_2]}{\beta + \gamma[H_2] + \theta[H_2].[O_2]} \quad \textbf{with} \quad \alpha = 4k_1k_2k_4 \; ; \; \beta = k_5k_6 \; ; \; \gamma = k_4k_5 \text{ et } \theta = -2k_2k_4$$

3) In the case where $\beta + \gamma[H_2] + \theta[H_2].[O_2] = 4/k_5$ so $v=K.[H_2]^m.[O_2]^n = k_1.k_2.k_4.k_5.[H_2]^2.[O_2]^1$

$\Rightarrow$ global order is 3, and the rate constant K is equal to $k_1.k_2.k_4.k_5$.

Exercises

Kinetics Chemical : Series of TD N°1

Exercise N°1 :

Is the reaction hypothetical follows : aA + bB cC+→ dD + eE

Give the different expressions of the speed of this reaction in function of the concentration, the number of moles or partial pressure, assuming that it is carried out at room temperature and volume constant.

Exercise N°2 :

Is the transformation following : Ester + base → Salt + alcohol. At the dose of the base remaining in solution, and on trpreffered this :

Time (S)	0	150	300	450	600	750
[Base] mole/l	10^{-2}	7.710^{-3}	6.2510^{-3}	5.2510^{-3}	4.5510^{-3}	410^{-3}

1°) Draw the curve giving [Base] in function of the (Time)

2°) Determine the speed average between the instants t=150 s and t= 450 s

3°) Calculate the instantaneous velocity at t=600 s.

Exercise N°3 :

In the course of the reaction : $2N_2O_5 \longrightarrow 4NO_2 + O_2$, the speed of disappearance of N_2O_5 is, at time t_1 given $v_{d1}(N_2O_5) = 2.10^{-2}$ mol. $L^{-1}.s^{-1}$.

In infer (at this moment) the value of v_1, the speed overall of the reaction, as well as those of $v_{f1}(NO_2)$ and $v_{f1}(O_2)$, formation rates (of appearance) of the two products.

Exercise N°4 :

The peroxide liquid hydrogen (H_2O_2) decomposes into water and dioxygen in the presence of $FeCl_3$ (catalyst) according to the reaction as follows : $2H_2O_{2(l)} \rightarrow 2\ H_2O_{(l)} + O_{2(g)}$. In the un container, introduced on the peroxide and the catalyst and on the measure in the course of time the volume of O_2 released.

Time in minutes	0	2	4	6	10	15	20	25
n of O_2 (10^{-5} mol)	0	2	4	6	20	30	40	48
Conc of H_2O_2 (10^{-4} mol/L)	40	39.6	39.2	38.8		34	32	30.4

a) Calculate the speed average of formation of O_2 between 4 and 10 minutes.

b) Calculate the concentration of H_2O_2 at time t = 10 min

c) Draw the graph of the evolution of the concentration of H_2O_2 as a function of time.

d) Determine graphically the time after which the 1/8 of H_2O_2 has been decomposed.

Exercise # 5 :

Having to make it on double leaf

$$H_2+I_2 \text{ give } 2\ HI$$

On the door at a temperature of 350°C, four balloons of 1L: A, B, C and D containing each of 0.50 mmol of H_2. The balloons are maintained at this temperature during different periods of time, and then they are cooled suddenly. The diiode remaining in each balloon is first dissolved in a solution of potassium iodide (which takes on a yellow color),and then it is dosed par a solution of sodium thiosulfate formula $Na_2S_2O_3$ and the molar concentration C=0,050 $mol.L^{-1}$.

1. The end of the dosing est indicated by discoloration of the solution diiode. Either Vss the volume of the solution of thiosulphate of sodium necessary to pour obtain the discoloration.

(It gives couples the redox following: (I_2/I^- = 0,62 V; $S_3O_6^{2-}/S_2O_3^{2-}$ = 0,09 V)

2. Explain the general principle of the manipulation.
3. Explain the principle of the assay of diiode in the solution and write the equation for the reaction corresponding.
4. Complete the table after grouping the results of experimental obtained:

e)

balloon	A	B	C	D
t (min)	50	100	150	200
Vdss (mL)	16,6	13,7	11,4	9,4
N_2O_3 (mmol)				
n(I_2) remaining (mmol)				

1. Draw of the curve representing the amount of diiode remaining in the community reaction as a function of time. Deduce the instantaneous speed of the disappearance of the diiode at t=100 min. Deduce the instantaneous speed of formation of the iodide of hydrogen at the same time.

Kinetic Chimigeu : Series of TD N°2

Exercise N°1 :

Is the following reaction : $2NO + 2H_2 \longrightarrow 2H_2O + N_2$

1) Express the speed of formation of the products, of disappearance of the reactants and the reaction rate.
2) On met H_2 en excesses in front of NOT : The reaction admits of the united nations in order to be equal to " 2 ". On met NOT in excess in front of H_2 : The reaction admits of the united nations in order to be equal to " 1 ".
   a) What is the est, the order total of the reaction ? Quelle est sa molécularité ? The reaction is elementary ?
   b) Express the speed of this reaction function of the concentrations of the 2 reagents.
3) Imagine the mechanism of this reaction in knowing :
   - He was a step slow and a fast one.
   - It is the form of the peroxide of hydrogen, H_2O_2 as an intermediate.

Exercise N°2 :

The decomposition of water to hydrogen peroxide (H_2O_2 est catalyzed by the ion - iodides (I^- and the mechanism of this reaction in solution is:

$H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (slow reaction) $IO^- +$
$H_2O_2 \longrightarrow H_2O + I^- + O_2$ (reaction fast)

1°) Write the equation-balance sheet of this reaction. 2°) Express the rate of this reaction.
3°) What can we say of the ion-IO^-.

Exercise N°3 :

Is the reaction : $CH_3I + C_2H_5ONa \longrightarrow CH_3OC_2H_5 + NaI$. It est d'ordre world '2' and K is its constant speed. On a bench the experimental results, the following : (R = 8,31 $J.K^{-1}.mol^{-1}$)

T (°C)	0	6	12	18	24	30
K ($mol^{-1}.The.s^{-1}$)	$5,60.10^{-5}$	$11,8.10^{-5}$	$24,5.10^{-5}$	$48,8.10^{-5}$	100.10^{-5}	208.10^{-5}

In deducing the energy of activation of this reaction, as well as son-factor of frequency.

Exercise N°4 :

a) The constant of speed of the reaction $2\ N_2O_{5(g)} \rightarrow 4\ No_{2(g)} + O_{2(g)}$ double when on password

22.50°C to 27,47°C. Determine the activation energy of the reaction.
A reaction has an energy of activation of 70 kJ. What is the est the value of the ratio of the speeds of 40°C and 60°C?

Kinetics Chemical : Series of TD N°3

Exercise N°1 :

Pour the reaction : $N_2O_5(g) \rightarrow 2\ N_2(g) + ½\ O_2(g)$ on the united nations , the results of experimental the following :

Experience	[N2O5] in mol/L of	Speed in mol/(L. min)
1	0,01	0,018
2	0,02	0,036
3	0,04	0,072

a) Determine the order of the reaction in justifying.
b) Calculate the constant speed and the half-life of this reaction.

Exercise N°2 :

Is a reaction of the type : A + B ⟶ C. Three experiments lead to the following results :

	experiment 1	experiment 2	experiment 3
[A] (mol /L)	2	6,1	8,1
[B] (mol /L)	2	2	6
-d[A] / dt (mol /L. s)	0,032	0,29	1,5

a) Give the general expression of the speed of this reaction ?
b) In deduct the orders partial , by report to the reagents ?
c) Calculate the constant speed **in specifying the units** ?
d) The speed of the reaction est multiplied by 4 when the temperature goes from 27°C to 127°C. Calculate son activation Energy?

Exercise N°3 :

In the course of time, the water of Bleach loses son power cleaner to the cause of the decrease of the concentration of ions, hypochlorite, ClO^- . Of these ions, the origin of the oxidizing properties of the Bleach, undergo disproportionation slow. The kinetics of this reaction is studied in aqueous solution at 343 K.

$$ClO^-(aq) \rightarrow 1/3\ ClO_3^-(aq) + 2/3\ Cl^-(aq)$$

The order total of the reaction considered hne be equal to 2. The concentration

initial of ClO^- est equal to 0.10 mol.L^{-1}.

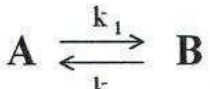
1) Give the expression of the law of the speed of the reaction considered.
2) Determine the expression for the concentration in *ClO*- in function of the time.
3) The un 343 K, the constant of speed of the reaction considered hne equal to the 3.1.10^{-3}mol^{-1}.The.s^{-1}. Calculate the half-time of reaction of the reaction considered to 343 K.
4) The activation energy of the reaction considered hne equal to 47 kJ.mol^{-1}.

   Calculate the constant of speed of the reaction is considered to 363 K.

   Calculate the time *t1* is necessary to pay to consume 30 % of the initial amount of ClO^- at 363 K.

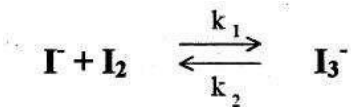
   1) Why work at constant temperature and volume?
   2) How many necessary and sufficient variables are needed to describe this system?
   3) Give the conservation relationships
   4) Would it be possible to offer a single instant assessment

Exercise 4:

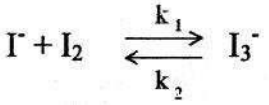


1. Expres in the concentrations of species A and B over time. Note λ, the reduced advance $\xi_{(1)}$ and $\xi_{(2)}$ ($\lambda = \xi_{(12)} = \xi_{(1)} - \xi_{(2)}$).
2. We will note **ε** the difference in chemical advance $\lambda - \lambda_{(eq)}$ (where $\lambda = \xi_{(1)} - \xi_{(2)}$). Demonstrate that**(t)** can be written as an exponential
3. Express **τ** relaxation time of this equilibrium as a function of the rate constants $\mathbf{k_i}$, ($\varepsilon\mathbf{(t)} = \varepsilon_0\, \mathbf{e}^{(-t/\tau)}$).

Exercise 5:

Balance 

When studying the return to equilibrium after a temperature change under laser illumination, the relaxation time **τ** at 25 °C of the reaction :



depends on iodide and iodine ion concentrations

Exp.	$[I^-]$ / 10^{-3} mol.dm^{-3}	$[I_2]$ / 10^{-3} mol.dm^{-3}	τ / ns
1	0,57	0,36	71
2	1,58	0,24	50
3	2,39	0,39	39
4	2,68	0,16	38
5	3,45	0,14	32

1. $\boldsymbol{\varepsilon} = \lambda - \lambda_{(eq)}$, Give the expression of $\varepsilon\mathbf{(t)}$ as a function of $[I^-]$, $[I_2]$ and the rate constants $k_1$and k_2**,** Express **τ** relaxation time of this equilibrium as a function of the rate constants k_1, k_2 and the concentrations of I^- and I_2.
2. Plot τ as a function of $([I^-]+[I_2])$; deduce the speed constants $k_1$and k_2 (don't forget to mention the units).
3. from the result of question 1
   a) show that k_1 can be expressed as :

$$k_1 = \tau^{-1}\left([I^-] + [I_2] + K^{-1}\right)^{-1}$$

   where K is the equilibrium constant of the reaction and is equal to k_1/k_2

   b) using the data from the first 2 experiments experiments (1 and 2), find the value of K (constant depends only on temperature)

deduce k_1 for each experiment and give its mean value

Exercise 1:

a) Let the reaction be: 1 A→ 2 B
   1- Establish the speed law
   2- Draw the composition diagram

b) Consider the reaction: 1 A→ 1 B+ 2 C
   1- Write the mass conservation relations
   2- Graphical representation of concentration variations over time

Exercise 2:

Consider the following chemical reaction:

$$2\ \mathbf{N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2\ (g)}$$

For which the N_2O_5 concentration as a function of time is available:

t (min)	0	10	20	30	40	50	60	70	80	90	100
$[N_2O_5]$ 10^{-2}mol/L	1.24	0.92	0.68	0.5	0.37	0.28	0.20	0.15	0.11	0.08	0.06

2. On the basis of the experimental values, determine whether the order with respect to N_2O_5 is 1 or 2 (for each of these two cases, write down the speed law and draw the "good lines").

3. deduce the value of k

4. calculate the value of $t_{1/2}$

Exercise 3:

The following parallel reactions are studied at constant T and V :

A→B

A→C

1) Why work at constant temperature and volume?
2) How many necessary and sufficient variables are needed to describe this system?
3) Give the conservation relationships
4) Would it be possible to offer a single instant assessment