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Ministry of Higher Education and Scientific  
Research



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# COURSE OF

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## Chemical kinetics

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# Foreword

This polycopy is specifically designed for second-year students of Process Engineering, offering a structured and accessible approach to the study of chemical kinetics. Chemical kinetics is essential in understanding the rates of chemical reactions, a critical aspect in the field of process engineering, where optimizing reaction conditions and designing efficient systems are fundamental.

The content provided in this document combines theoretical concepts with practical methodologies, aiming to develop both analytical and problem-solving skills. Students will be equipped with the knowledge to analyze reaction mechanisms, evaluate the impact of various factors on reaction rates, and apply these principles to real-world process engineering challenges.

By bridging academic learning with industrial applications, this polycopy serves as a valuable tool for mastering chemical kinetics and preparing students for future professional endeavors in the field.

# Contents

<b>Foreword</b>	<b>2</b>
<b>General Introduction</b>	<b>5</b>
<b>1 Homogeneous Chemical Reactions</b>	<b>6</b>
1.1 The Rate of a Chemical Reaction . . . . .	7
1.1.1 Definition: Reaction Rate . . . . .	7
1.1.2 The General Reaction Rate . . . . .	8
1.1.3 The Average Reaction Rate . . . . .	9
1.1.4 The Instantaneous Reaction Rate . . . . .	9
1.2 Experimental Study of Reaction Kinetics . . . . .	10
1.2.1 Measuring Reaction Rates . . . . .	10
<b>2 Influence of Concentrations and Temperature on Reaction Rate</b>	<b>12</b>
2.1 Effect of Concentration . . . . .	13
2.2 Molecularity and Stoichiometry of a Reaction . . . . .	15
2.2.1 Molecularity: . . . . .	15
2.2.2 Elementary and Complex Reactions . . . . .	16
2.2.3 Complex Reactions . . . . .	16
2.3 Effect of Temperature . . . . .	16
<b>3 Formal Kinetics: Simple Reactions</b>	<b>19</b>
3.1 Introduction . . . . .	20
3.2 Reactions of Simple Orders . . . . .	20
3.2.1 Zero-Order Reactions . . . . .	20
3.2.2 First-Order Reactions . . . . .	21
3.2.3 Second-Order Reactions . . . . .	22
3.2.4 Higher-Order Reactions . . . . .	22
3.3 Determining Reaction Orders . . . . .	23
3.3.1 Example . . . . .	23
3.3.2 Methods for Determining Reaction Order via Integration . . . . .	23
3.3.3 Differential Method . . . . .	24
3.3.4 Methods Based on Order Degeneracy . . . . .	24
3.3.5 Cases of Order Degeneracy . . . . .	25
<b>4 Complex Reactions</b>	<b>28</b>
4.1 Introduction . . . . .	29
4.1.1 Reversible Reactions (Equilibrium or Opposed Reactions) . . . . .	29
4.1.2 Parallel Reactions . . . . .	29

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4.1.3	Consecutive Reactions (Successive Reactions)	29
4.2	Rate of Reversible (Equilibrated) Reactions	29
4.2.1	General Reversible Reaction	29
4.2.2	Mono-molecular Reversible Reaction	30
4.2.3	Reversible Bi-molecular Reaction	31
4.3	Parallel Reactions	32
4.3.1	Twin Parallel Reactions	32
4.3.2	Competitive Parallel Reactions	33
4.4	Consecutive (Successive) Reactions	33
4.5	Calculation of the Maximum Time	34
4.5.1	Calculation of the Maximum Concentration of $B$	35
4.5.2	Inflection Time for Product $C$ ( $t_{\text{inf}}$ )	35
4.5.3	Inflection Time for Product $B$ ( $t_{\text{inf}}$ )	35

# General Introduction

Chemical kinetics, as a cornerstone of chemical and process engineering, involves the study of reaction rates, the factors that influence them, and the mechanisms that govern chemical transformations. This field is particularly relevant to process engineering, where understanding reaction dynamics is vital for the design and optimization of industrial processes.

This polycopy is organized into four detailed chapters, tailored to the academic level and professional aspirations of second-year Process Engineering students:

## 1. Homogeneous Chemical Reactions

An introduction to reaction rates, the experimental methods for their determination, and the factors influencing reaction speed, providing a solid foundation for further study.

## 2. Influence of Concentration and Temperature on Reaction Rates

A detailed exploration of how changes in reactant concentrations and temperature affect reaction rates, incorporating key concepts such as reaction order, molecularity, stoichiometry, and the Vant't Hoff rule.

## 3. Formal Kinetics of Simple Reactions

Advanced methods for determining reaction rate constants and orders are presented, alongside practical examples and calculations, to help students master the tools needed for analyzing simple reaction systems.

## 4. Complex Reaction Mechanisms

This chapter delves into complex reaction types, including opposing, parallel, and successive reactions, with a focus on their practical implications in industrial processes and process optimization.

Each chapter combines theoretical discussions with illustrative examples and practical applications, ensuring a well-rounded understanding of chemical kinetics. This resource aims to empower second-year Process Engineering students with the skills and knowledge needed to excel academically and contribute to innovation in their field.

# Chapter 1

## Homogeneous Chemical Reactions

Reactions that occur entirely in one phase (liquid or gaseous phase) are referred to as **homogeneous reactions**, while those that occur, at least partially, at the interface of two phases, such as those taking place on the surface of a solid located in a gas or liquid, are described as **heterogeneous reactions**. In this chapter, we will study how to calculate the rate of a **homogeneous chemical reaction**.

## 1.1 The Rate of a Chemical Reaction

### 1.1.1 Definition: Reaction Rate

The rate of a reaction is the quantity of reactants transformed per unit time or the quantity of products formed per unit time.

- The reaction rate can be calculated based on the quantity of products formed:

$$\text{Reaction Rate} = \frac{\text{Quantity of Products Formed}}{\text{Time Interval}} = \frac{\Delta[\text{Product}]}{\Delta t} \quad (1.1)$$

- Alternatively, it can be calculated based on the quantity of reactants consumed:

$$\text{Reaction Rate} = \frac{-\text{Quantity of Reactants Consumed}}{\text{Time Interval}} = \frac{-\Delta[\text{Reactant}]}{\Delta t} \quad (1.2)$$

By convention, reaction rates are expressed as positive values. Since the quantity of reactants decreases (a negative value), a negative sign is placed before this term to yield a positive result. As shown in Figure 1.1, the quantity of reactants decreases proportionally to the increase in the quantity of products as the reaction progresses.

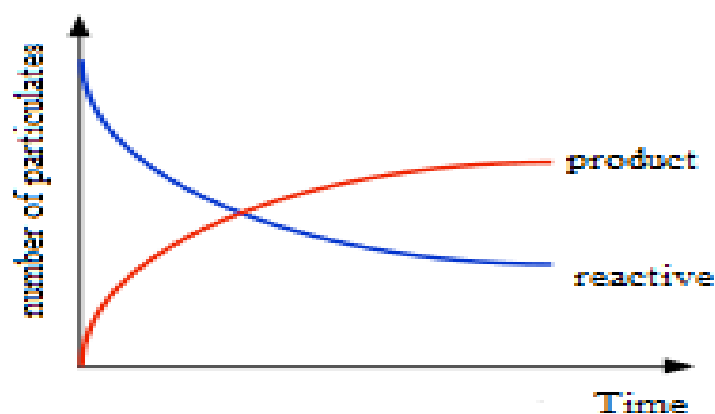
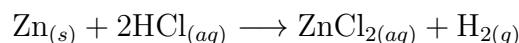


Figure 1.1: The number of particles as a function of reaction time.

**Example Calculation:** A piece of zinc weighing 0.06 g is reacted in 100 mL of a 2 mol/L hydrochloric acid solution, according to the equation:

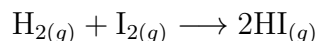


After 142 minutes and 28 seconds, the zinc piece has completely dissolved. Calculate the reaction rate in g/s.

## 1.1.2 The General Reaction Rate

### Definition

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. Consider the reaction of the synthesis of hydrogen iodide, which proceeds according to the following equation:



Under identical measurement conditions, the rate of hydrogen iodide formation is twice the rate of disappearance of each reactant. This is because one molecule of hydrogen and one molecule of iodine produce two molecules of hydrogen iodide. To ensure consistency in reaction rates regardless of the substance chosen, the **general reaction rate** is used and calculated as follows for a hypothetical reaction:



The general reaction rate  $V_g$  is given by:

$$V_g = \frac{V_A}{a} = \frac{V_B}{b} = \frac{V_C}{c} = \frac{V_D}{d} \quad (1.3)$$

where:

- $V_g$ : General reaction rate (in mol/L·s or mol/s).
- $V_A, V_B, V_C, V_D$ : Reaction rates for each substance (in mol/L·s or mol/s).
- $a, b, c, d$ : Stoichiometric coefficients of each substance.

As shown in Figure 1.2, for each molecule of reactants transformed, twice as many molecules of products are formed.

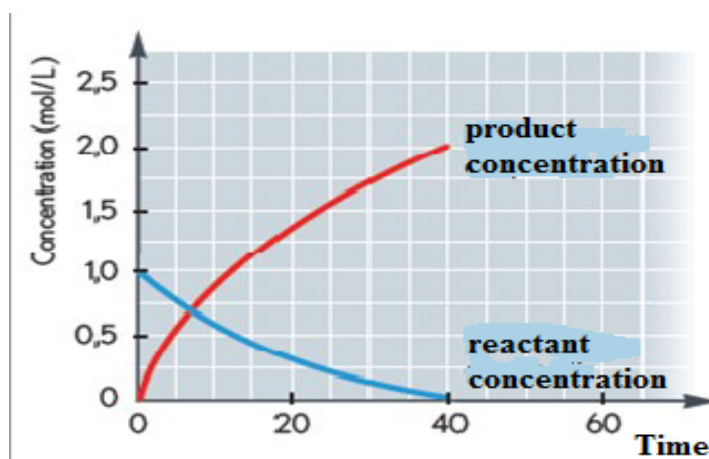
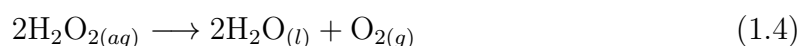


Figure 1.2: Concentration of reactants and products over time.

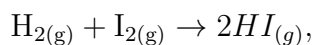
**Example1:** Consider the decomposition of hydrogen peroxide:





If the concentration of hydrogen peroxide decreases from 0.10 mol/L to 0.06 mol/L in 85 seconds, calculate the general reaction rate. What are the rates of reaction with respect to H<sub>2</sub>O and O<sub>2</sub>?

**Example2:** For the reaction:



if the rate of formation of HI is 0.04 mol/L/s, what is the rate of disappearance of H<sub>2</sub> and I<sub>2</sub>?

### 1.1.3 The Average Reaction Rate

**Definition:** The average rate is the rate determined over a specific time interval. It is typically not constant. From Figure 1.3, using the concentrations of reactant *A* at *t*<sub>1</sub> and *t*<sub>2</sub>, the average rate of disappearance of *A* can be calculated as:

$$V_{\text{avg}} = \frac{A_{t_2} - A_{t_1}}{t_2 - t_1} = \frac{\Delta A}{\Delta t}$$

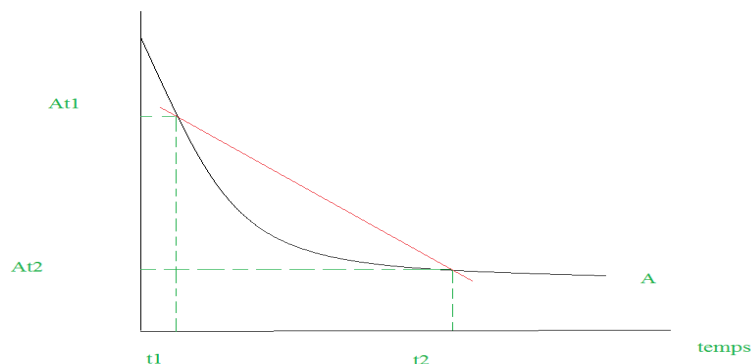


Figure 1.3: The Average Reaction Rate

**Example:** For the reaction:



if the concentration of H<sub>2</sub>O<sub>2</sub> decreases from 0.10 mol/L to 0.06 mol/L in 85 seconds, calculate the average rate of the reaction.

### 1.1.4 The Instantaneous Reaction Rate

**Definition:** The instantaneous reaction rate at a specific time *t* is the rate at that precise moment during the reaction. It is given by:

$$\text{Instantaneous Rate} = \lim_{\Delta t \rightarrow 0} \frac{\Delta[\text{Product}]}{\Delta t} \quad (1.5)$$

**Example:** For the reaction:



if at *t* = 10 s, the slope of the [A] vs *t* curve is -0.02 mol/L/s, what is the instantaneous rate?

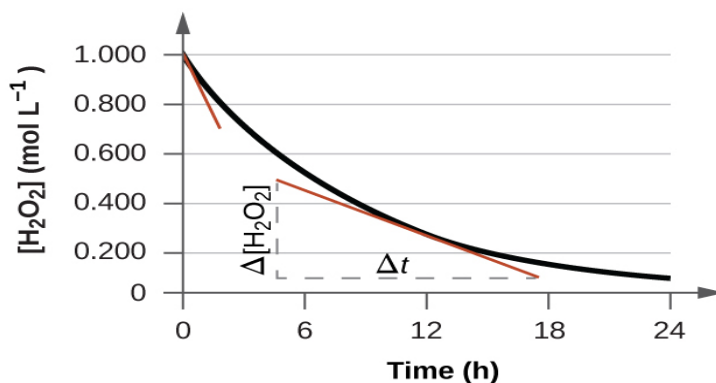


Figure 1.4: The Instantaneous Reaction Rate

## 1.2 Experimental Study of Reaction Kinetics

To study reaction rates experimentally, it is essential to measure changes over time. Parameters influencing these measurements include:

- Initial reactant concentrations.
- Temperature.

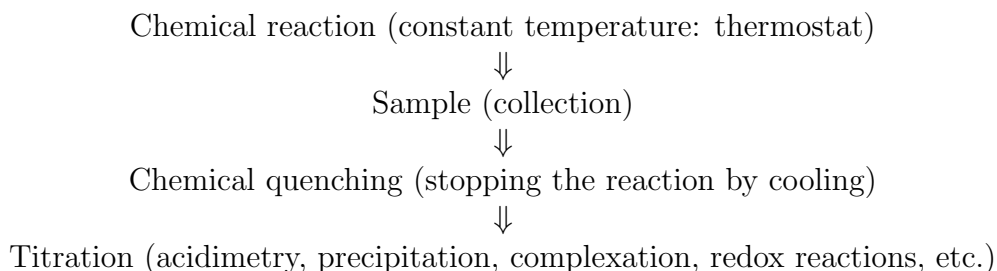
Other factors, such as solvent, impurities, reactor walls, catalysts, and radiation, may also influence reaction rates. The goal is to determine the effect of each parameter on the reaction rate.

### 1.2.1 Measuring Reaction Rates

The kinetic law can be determined by tracking changes in reactant and product concentrations over time at a constant temperature. Tracking the change of one reactant (the most straightforward to see) is enough to determine the reaction's progress and, in turn, all other concentrations if the beginning concentrations are known. To monitor the concentration of a reactant or a product, the following methods can be distinguished:

#### Chemical Methods

These methods involve sampling at different reaction times and determining concentrations through chemical analysis. The necessary steps to perform this sampling are outlined as follows:

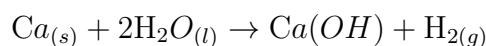


## Physical Methods

These methods involve monitoring physical properties associated with concentration changes, such as:

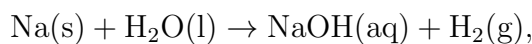
- **Calorimetry:** Measures heat released or absorbed during the reaction.
- **Gravimetry:** Tracks weight changes using a precision balance.
- **Manometry:** Monitors pressure changes in gaseous reactions.
- **Electrical Methods:** Suitable for ionic reactions, such as conductometry and potentiometry.
- **Polarimetry:** Used for optically active compounds.
- **Spectrophotometry:** Measures absorbance in UV, visible, or IR spectra to determine species concentrations.

**Example 1:** The rate of the reaction between calcium and water:

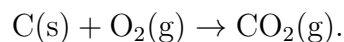


is influenced by the surface area of the calcium. Compare the rate using powdered calcium and a solid block.

**Example 2:** Compare the rate of the following reactions:



and



**Example 3:** The decomposition of  $\text{H}_2\text{O}_2$ :



is significantly faster in the presence of manganese dioxide ( $\text{MnO}_2$ ).

## Chapter 2

# Influence of Concentrations and Temperature on Reaction Rate

**Introduction** The rate of a chemical reaction depends on several factors, including the concentration of reactants and the temperature of the system. Understanding these dependencies is crucial in fields ranging from industrial chemistry to biochemistry.

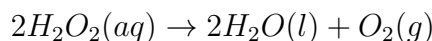
## 2.1 Effect of Concentration

The relationship between the reaction rate and the concentration of reactants is typically described by the rate law:

$$V = k[A]^m[B]^n, (\text{The rule of VAN'THOFF}) \quad (2.1)$$

where  $[A]$  and  $[B]$  are the concentrations of reactants,  $k$  is the rate constant, and  $m$  and  $n$  are the reaction orders with respect to  $A$  and  $B$ .

In The rule of VANT'HOF, if  $m = 1$  and  $n = 2$ , the reaction is of order 1 with respect to  $A$  and of order 2 with respect to  $B$ . The sum of the exponents constitutes the overall order of the reaction, that is, the order for all reactants combined. According to the previous example, the reaction has an overall order of 3. It is worth noting that each exponent is rarely equal to the coefficient of the corresponding substance in the chemical equation. The order of each reactant must be determined experimentally. This allows the calculation of the rate constant. One way to do this is to determine the relationship between the initial rate and the concentrations of the reactants. However, as temperature influences the reaction rate, it is essential to control it during experimentation. Indeed, the rate constant varies with temperature. Let us consider the example of hydrogen peroxide decomposition:



**Table 1.** The initial rate of decomposition of  $H_2O_2$  as a function of its initial concentration.

Experiment	$[H_2O_2]$ Initial (mol/L)	Initial Rate (mol/L.s)
1	0.10	$3.64 \times 10^{-4}$
2	0.20	$7.28 \times 10^{-4}$

By comparing the initial rates of the reaction measured at different hydrogen peroxide concentrations in Table 1, we see that they are directly proportional. In other words, when the peroxide concentration doubles, the reaction rate also doubles. This shows that the reaction is of order 1 with respect to hydrogen peroxide. Thus, the rate law for the decomposition of hydrogen peroxide is expressed as:

$$V = k[H_2O_2]^1$$

**Table 2.** The order of a reactant as a function of the change in rate.

Effect on Rate	Order of Reactant
No effect on rate	0
Rate doubles	1
Rate quadruples	2
Rate increases eightfold	3

This procedure to determine the reaction order is called the method of initial rates. To facilitate the analysis of results, it is preferable to vary the concentration by a simple factor (e.g., 2 or 3). **Table 2** presents the effects on the initial rate when the concentration of a single reactant is doubled, along with the resulting order.

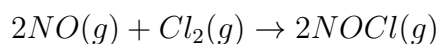
**Table 3.** Units of the rate constant based on reaction order.

Reaction Order	Example Rate Law	Unit of $k$
0	$V = k$	mol/L.s
1	$V = k[A]$	$s^{-1}$
2	$V = k[A]^2$ or $V = k[A][B]$	L/mol.s
3	$V = k[A]^3$ or $V = k[A]^2[B]$	$L^2/mol^2.s$

In conclusion, here are the key aspects to remember about the reaction rate law:

- The reaction rate law can only be determined from experimental results.
- The reaction rate law does not depend on the coefficients of the reaction equation.
- The reaction rate law considers only the concentration of the reactants.
- The units of the rate constant depend on the reaction order.

**Example 1** Consider the following reaction:



The results of three experiments are presented below. In each experiment, only the concentration of one reactant is varied at a time.

**Table 4.** Results of three experiments

Experiment	[NO] Initial (mol/L)	[Cl <sub>2</sub> ] Initial (mol/L)	Initial Rate (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	$9.08 \times 10^{-5}$

What is the rate law for this reaction?

From the data, doubling the concentration of  $Cl_2$  doubles the rate, and doubling the concentration of NO quadruples the rate. This indicates the reaction is first order with respect to  $Cl_2$  and second order with respect to NO.

The rate law is:

$$V = k[NO]^2[Cl_2]^1$$

**Example2:** Using the data from Table 1 for the decomposition of hydrogen peroxide:

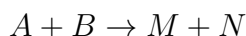
- **Given:**  $[H_2O_2] = 0.10$  M,  $V = 3.64 \times 10^{-4}$  mol/L.s
- **Find:**  $k$

Using the rate law  $V = k[H_2O_2]^1$ , we solve for  $k$ :

$$k = \frac{V}{[H_2O_2]} = \frac{3.64 \times 10^{-4}}{0.10} = 3.64 \times 10^{-3} \text{ s}^{-1}$$

## 2.2 Molecularity and Stoichiometry of a Reaction

A chemical reaction can result from an **elementary reaction**, which occurs in a single step. However, it is often the outcome of a series of elementary reactions. Consider the following elementary reaction:



This implies that the collision of the two particles  $A$  and  $B$  directly produces the species  $M$  and  $N$  in a single step. In this case, the **molecularity** of the reaction is the number of particles (atoms, molecules, radicals, positive or negative ions, etc.) involved in the realization of the reaction. It is a positive, nonzero integer that can only be determined by knowing the reaction mechanism.

### 2.2.1 Molecularity:

The molecularity represents the number of actual particles participating in the chemical act. For an **elementary reaction**, the partial orders with respect to the reactants are equal to their stoichiometric coefficients:



If the reaction is elementary, then  $a = \alpha$  and  $b = \beta$ . However, the converse is not always true.

- A reaction involving a single molecular entity is called **unimolecular**.
- A reaction involving two molecular entities is called **bimolecular**.
- A reaction involving three molecular entities is called **termolecular**.

### Unimolecular Reaction: Molecularity = 1

**Example: Isomerization of cyclopropane into propene:**



$$\text{Rate law: } v = \frac{d[\text{Propene}]}{dt} = k[\text{Cyclopropane}]$$

The rate is proportional to the concentration of cyclopropane, and the partial order with respect to this reactant corresponds to its stoichiometric coefficient in the reaction. Hence, the order equals the molecularity (1 in this case).

### Bimolecular Reaction: Molecularity = 2 (More common)

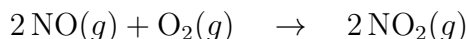
**Example: Decomposition of dinitrogen pentoxide:**



In this case, the order of the reaction with respect to  $\text{N}_2\text{O}_5$  is equal to 1, which differs from the molecularity (which equals 2).

## Termolecular Reaction: Molecularity = 3

**Example: Oxidation of nitric oxide:**



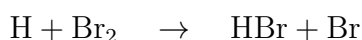
In this case, the order is found to be equal to the molecularity.

### 2.2.2 Elementary and Complex Reactions

#### Elementary Reactions

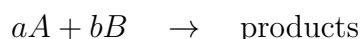
Elementary reactions occur in a single step.

**Example:**



For an elementary reaction, the partial orders with respect to the reactants are equal to their stoichiometric coefficients (*Van't Hoff's Rule*). However, this is generally not the case for a reaction that proceeds in multiple steps.

Consider the reaction:



The rate law is given by:

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

If the reaction is elementary, then  $a = \alpha$  and  $b = \beta$ . However, the reverse is not always true.

### 2.2.3 Complex Reactions

Most chemical reactions are complex. This means that their overall equation does not provide information about the mechanism.

A complex reaction occurs through a series of elementary reactions, where each step has its own rate. The overall rate of the complex reaction (mechanism rate) is determined by the slowest step.

**Example:**

**Nucleophilic Substitution Reaction (SN1) in Organic Chemistry:**

Mechanism: This complex reaction is the sum of two elementary reactions (the first of which is an equilibrium).

## 2.3 Effect of Temperature

Temperature affects reaction rates exponentially, as described by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \quad (2.2)$$

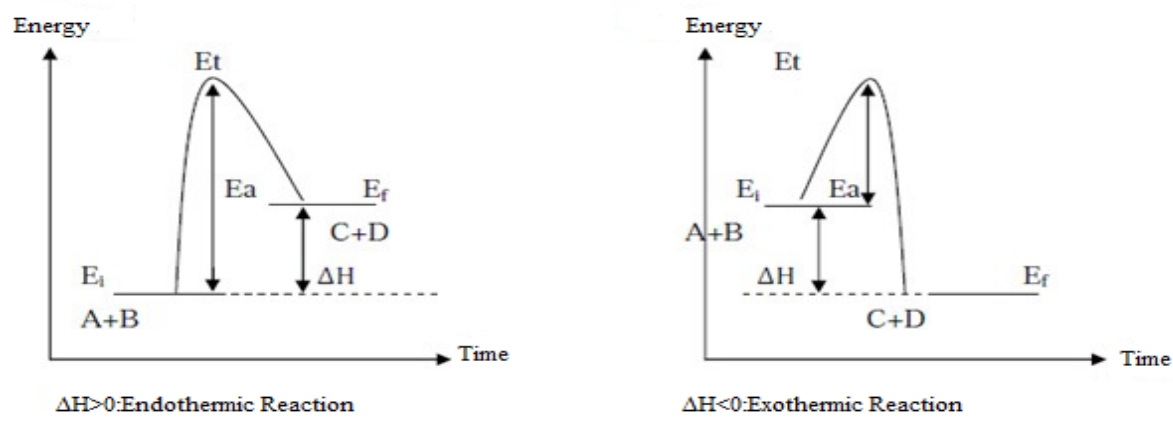
where

- $k$  is the rate constant,



- A is the pre-exponential factor,
- $E_a$  is the activation energy,
- R is the gas constant,
- T is the temperature in Kelvin.

The activation energy  $E_a$ , represents the energy barrier to be crossed for the reaction to take place. In other words, it is the minimum energy required for a reaction to take place following a collision. If the energy during the collision is lower than the activation energy, the molecules only bounce



The arrangement of molecules at the top of the energy barrier is called the **activated complex**. It is a transition state, unstable, and has a very short lifetime.

By introducing the natural logarithm ( $\ln$ ) to the Arrhenius equation, we obtain another form of the Arrhenius law:

$$\ln K = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$$

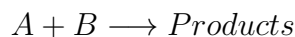
If we plot  $\ln K$  as a function of  $1/T$ , we obtain a straight line with a slope of  $-E_a/R$ .

The reaction rate constant is directly proportional to reactant concentration and increases exponentially with temperature. These principles are essential for optimizing chemical reactions in various applications.

## Exercises

### 1. Effect of Concentration

Given the following experimental data for the reaction:



Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.1	0.1	$2.0 \times 10^{-4}$
2	0.2	0.1	$4.0 \times 10^{-4}$
3	0.1	0.2	$2.0 \times 10^{-4}$

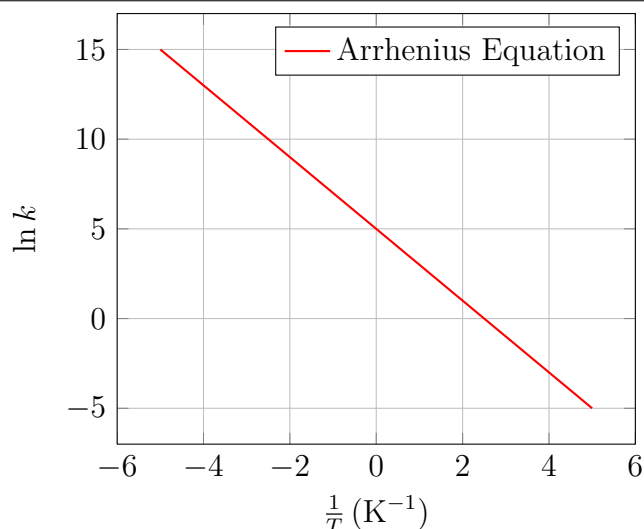


Figure 2.1: Arrhenius plot showing the relationship between  $\ln k$  and  $1/T$ .

- Determine the reaction order with respect to  $A$  and  $B$ .
- Write the rate law for the reaction.
- Calculate the rate constant ( $k$ ) with appropriate units.

## 2. Effect of Temperature

- The rate constant for a reaction at 300 K is  $1.5 \text{ s}^{-1}$ , and at 350 K it is  $5.0 \text{ s}^{-1}$ . Assuming the gas constant  $R = 8.314 \text{ J/mol}\cdot\text{K}$ :
  - Calculate the activation energy ( $E_a$ ) using the Arrhenius equation.
  - What is the rate constant at 400 K?
- Plot  $\ln k$  vs.  $1/T$  for the following data:

Temperature (K)	$k(\text{s}^{-1})$
300	0.5
320	1.2
340	3.0
360	7.5

- Determine the slope of the line and calculate the activation energy ( $E_a$ ).
- Interpret the graph in terms of temperature dependence.

## Challenge Problem: Designing a Reaction

You are tasked with optimizing the production rate of a chemical reaction. The reaction rate is influenced by both the reactant concentration and temperature.

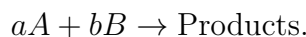
- Propose experimental conditions (reactant concentration and temperature range) to maximize the rate.
- Explain how you would test your proposal experimentally.

## Chapter 3

# Formal Kinetics: Simple Reactions

## 3.1 Introduction

The irreversible reactions studied here are either unimolecular or bimolecular and proceed in only one direction. Generally, these reactions can be represented as:



The objective of formal kinetics is to describe the progression of a chemical reaction over time. It provides an analytical representation of macroscopic variables of the reaction system as functions of time, such as:

$$[A] = f(t), [B] = g(t), \text{ etc..}$$

For simplicity, this course focuses on homogeneous and isothermal systems, assuming a simple kinetic law applies. This allows us to determine how the concentrations of the various reactants change over time.

## 3.2 Reactions of Simple Orders

### 3.2.1 Zero-Order Reactions

For the reaction:



the rate of the reaction is given by:

$$-\frac{d[A]}{dt} = k[A]^0 \quad \text{or simply} \quad -\frac{d[A]}{dt} = k.$$

This equation allows us to conclude that the reaction rate does not depend on the concentration. By integrating this equation, we obtain:

$$\int_{[A]_0}^{[A]_t} d[A] = \int_{t_0}^t k dt.$$

The integration of this formula gives:

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

The plot of  $[A]_t$  as a function of time  $t$  is a straight line with a negative slope  $-k$  and an intercept at the origin  $[A]_0$ . The unit of the rate constant  $k$  for zero-order reactions is mol/L.s.

### Half-Life Time $t_{1/2}$ for Zero Order

The half-life time, defined as the time to consume half of the initial quantity, follows:

$$[A]_{t_{1/2}} - [A]_0 = -kt_{1/2}$$

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

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

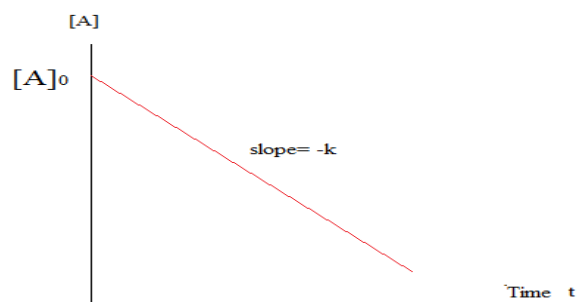


Figure 3.1: Graphical presentation of a zero-order reaction

### 3.2.2 First-Order Reactions

For the reaction:



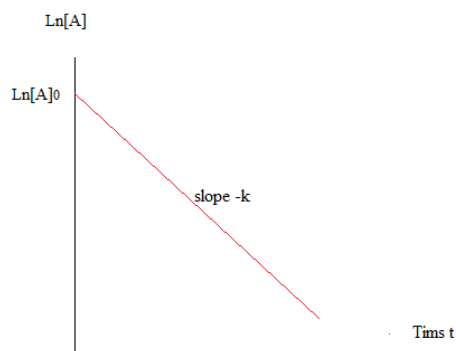
the rate is expressed as:

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

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_{t_0}^t dt$$

Integrating this gives:

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



The plot of  $\ln [A]$  versus  $t$  yields a straight line with a negative slope  $-k$ . The unit of the rate constant  $k$  for first-order reactions is  $s^{-1}$ .

### Half-Life Time $t_{1/2}$ for First Order

For a first-order reaction, the half-life time is derived as:

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

Since  $[A]_{t_{1/2}} = \frac{[A]_0}{2}$ , we have:

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

### 3.2.3 Second-Order Reactions

For the reaction:



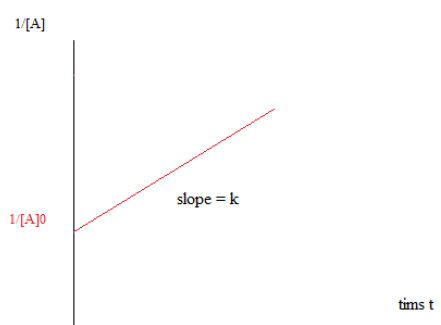
the rate is given by:

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

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

Integration leads to:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt.$$



The plot of  $\frac{1}{[A]_t}$  versus  $t$  is a straight line with a slope  $+k$  and an intercept  $\frac{1}{[A]_0}$ . The unit of the rate constant  $k$  for second-order reactions is  $L/mol.s$ .

### Half-Life Time $t_{1/2}$ for Second Order

The half-life time for a second-order reaction follows:

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

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

### 3.2.4 Higher-Order Reactions

For a reaction of order  $n$ :



the rate is expressed as:

$$-\frac{d[A]}{dt} = k[A]^n.$$

Integration gives:

$$\frac{1}{1-n} ([A]_0^{1-n} - [A]_t^{1-n}) = kt.$$

The half-life is derived as:

$$t_{1/2} = \text{constant} \cdot [A]_0^{1-n}.$$

The table below summarizes the orders studied:

Order	Equation	Integration	Slope	Unit of K	$t_{1/2}$
0	$-\frac{d[A]}{dt} = k$	$[A]_t - [A]_0 = -kt$	$-k$	mol/L.s	$t_{1/2} = \frac{[A]_0}{2k}$
1	$-\frac{d[A]}{dt} = k[A]^1$	$\ln \frac{[A]_t}{[A]_0} = -kt$	$-k$	$s^{-1}$	$t_{1/2} = \frac{\ln 2}{k}$
2	$-\frac{d[A]}{dt} = k[A]^2$	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$	$k$	L/mol.s	$t_{1/2} = \frac{1}{k[A]_0}$
n	$-\frac{d[A]}{dt} = k[A]^n$	$\frac{1}{1-n} ([A]_0^{1-n} - [A]_t^{1-n}) = kt$	$k$	L/mol.s	$t_{1/2} = \text{constant} \cdot [A]_0^{1-n}$

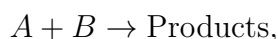
Table 3.1: Summary of the reaction orders studied.

### 3.3 Determining Reaction Orders

In certain cases, the reaction order can be simplified if the concentration of one reactant remains constant. This occurs when one reactant is in excess compared to others. The limiting reactant determines the reaction's progression.

#### 3.3.1 Example

For the reaction:



if  $[B]$  is in large excess, its concentration remains constant over time. The rate law simplifies to:

$$V = k'[A], \quad \text{where } k' = k[B]_0.$$

#### 3.3.2 Methods for Determining Reaction Order via Integration

##### Variation of Concentrations as a Function of Time

In this method, we make an assumption about the reaction order and integrate the resulting differential equation. If the reaction is:  $A \rightarrow \text{Products}$

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

We determine the function  $f([A])$ , whose representation as a function of time is expected to be linear. Using experimental values, we plot the corresponding curve; the assumption is verified if the curve is a straight line.

Order	Graph	Slope Calculation
0	$[A] = f(t)$	Slope = $-k$ , $\frac{[A]_0 - [A]_t}{t} = k$
1	$\ln[A] = f(t)$	Slope = $-k$ , $\ln[A]_0 - \ln[A]_t = kt$
2	$\frac{1}{[A]} = f(t)$	Slope = $+k$ , $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$
n	$\frac{1}{(n-1)[A]^{n-1}} = f(t)$	Slope = $(n-1)k$ , $\frac{[A]_0^{1-n} - [A]_t^{1-n}}{t} = k$

Table 3.2: Graphical representations and slope calculations for different reaction orders.

## Partial Reaction Times Method

This method relies on the concept that the time required to reduce the concentration of a reactant by half, three-quarters, one-quarter, or one-third contains information about the reaction order. For the reaction  $A \rightarrow \text{Products}$ , the ratio of times needed to reduce the concentration by specific fractions is provided in the following table:

Order of Reaction	$\frac{t_{3/4}}{t_{1/2}}$	$\frac{t_{1/2}}{t_{1/4}}$	$\frac{t_{1/2}}{t_{1/3}}$	$\frac{t_{3/4}}{t_{1/4}}$
1	2	2.41	1.71	4.82
2	3	3	2	9
3	5	3.86	2.4	19.3

Table 3.3: Ratios of reaction times for different orders.

### 3.3.3 Differential Method

For the reaction  $A \rightarrow \text{Products}$ : If  $[A] = f(t)$  is known, the curve is plotted, and the rate of disappearance of  $A$  is determined at different times.

If the reaction has an order:

$$v = k[A]^n$$

Taking the natural logarithm:

$$\ln v = \ln k + n \ln[A]$$

If the reaction order  $n$  exists, the curve of  $\ln v$  as a function of  $\ln[A]$  is a straight line with a slope equal to  $n$  and an intercept equal to  $\ln k$ .

This method can also be applied by considering initial rates, as in the following example: For the reaction  $A + B \rightarrow \text{Products}$ :

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

At  $t = 0$ :

$$v_0 = k[A]_0^\alpha[B]_0^\beta$$

**Protocol:** Perform several experiments with  $[B]_0$  fixed, and measure  $v_0$  for various values of  $[A]_0$ :

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

Repeat the procedure to determine  $\beta$ . The graphical determination of the intercept allows for the calculation of  $k$ .

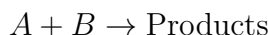
### 3.3.4 Methods Based on Order Degeneracy

#### Definition

It may happen that the concentration of an active species remains practically constant during the course of the reaction. In this case, although the concentration of this



species appears in the rate law, it can be grouped with the rate constant, simplifying the rate law. For example, consider the reaction:



with the rate law:

$$v = k[A]^\alpha[B]^\beta \quad \text{and the global order } n = \alpha + \beta.$$

If the concentration of the species  $[B]$  remains nearly constant and equals  $[B]_0$  during the reaction, the rate becomes:

$$v = k_{\text{obs}}[A]^\alpha \quad \text{with } k_{\text{obs}} = k[B]_0^\beta.$$

The reaction therefore appears to be of order  $\alpha$  when, in reality, it is of order  $\alpha + \beta$ . This phenomenon is referred to as order degeneracy.  $\alpha$  is called the observed or apparent order. Similarly, the rate constant is referred to as the observed or apparent rate constant.

### Cases of Order Degeneracy

- **A Buffer Solution:** Operating in a buffer solution—“a solution that maintains approximately the same pH despite the addition of small amounts of acid or base or despite dilution”—ensures that the concentrations of  $H^+$  and  $OH^-$  ions remain constant due to the acid-base equilibrium of the buffer system. If the rate law of the reaction involves one of these ions, it will result in order degeneracy.
- **Example:** Consider the reaction:



The rate law is:

$$v = k[H_2O_2]^1[Br^-]^1[H^+]^1 \quad \text{thus } n = 3.$$

### 3.3.5 Cases of Order Degeneracy

#### Buffer Effect

In a buffer solution (a solution that maintains approximately the same pH despite the addition of small amounts of acid or base, or dilution), the concentrations of  $H^+$  and  $OH^-$  ions remain constant due to the acid-base equilibrium of the buffer. If one of these ions appears in the rate law, order degeneracy will occur.

#### Example:

For the reaction:



the rate law is:

$$v = k[H_2O_2]^1[Br^-]^1[H^+]^1, \quad \text{thus } n = 3.$$

If  $[H^+]$  is constant, the rate becomes:

$$v = k_{\text{obs}}[H_2O_2]^1[Br^-]^1, \quad \text{where } k_{\text{obs}} = k[H^+]^1.$$

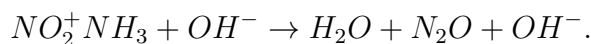
The reaction behaves like a second-order reaction ( $n' = 2$ ) even though it is actually a third-order reaction. In conclusion, the buffer effect leads to order degeneracy.

## Use of a Catalyst

A catalyst is a substance that is regenerated during the reaction and whose concentration remains constant. It acts as both a reactant and a product, and it is generally not included in the overall equation.

### Example:

Consider the reaction:



The rate law is:

$$v = k[\text{NO}_2][\text{NH}_3][\text{OH}^-]^1.$$

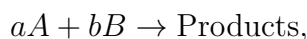
Since  $[\text{OH}^-]$  is a catalyst:

$$v = k_{\text{obs}}[\text{NO}_2][\text{NH}_3], \quad \text{where } k_{\text{obs}} = k[\text{OH}^-]^1.$$

The reaction is actually second-order but follows the kinetics of a first-order reaction.

## Excess of One Reactant Over Another

One reactant is considered in excess if its concentration is at least 5 times greater than that of the other reactant. For the reaction:



the rate law is:

$$v = k[A]^\alpha[B]^\beta, \quad \text{with global order } n = \alpha + \beta.$$

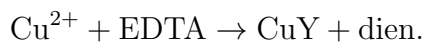
If  $[B]_0 \gg [A]_0$ , then:

$$v = k[A]^\alpha[B]^\beta \approx k'[A]^\alpha, \quad \text{where } k' = k[B]_0^\beta.$$

## Examples and Exercises

### Exercise 1

The reaction involves EDTA (ethylenediaminetetraacetic acid) and  $\text{Cu}^{2+}$  ions. The reaction studied is:



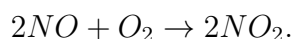
### Data:

- $T = 25^\circ\text{C}$ ,  $pH = 4.0$  constant.
- Initial concentrations:  $[\text{Cu}^{2+}]_0 = 1.0 \times 10^{-3} \text{ mol.L}^{-1}$ ,  $[\text{EDTA}]_0 = 6.0 \times 10^{-4} \text{ mol.L}^{-1}$ .
- Time (s): 10, 20, 30, 40, 50.

- $C$  (mol.L<sup>-1</sup>):  $1.50 \times 10^{-3}, 1.10 \times 10^{-3}, 0.80 \times 10^{-3}, 0.60 \times 10^{-3}, 0.43 \times 10^{-3}$ .
1. Write the rate law assuming the reaction has partial orders  $\alpha$  and  $\beta$  with respect to Cu<sup>2+</sup> and EDTA, respectively.
  2. Show how the initial conditions allow determination of one partial order, and deduce the apparent rate constant  $k_{\text{app}}$ .
  3. Determine the partial order of the reaction with respect to Cu<sup>2+</sup> graphically.
  4. Calculate the apparent rate constant  $k_{\text{app}}$  and the half-life  $t_{1/2}$ .

## Exercise 2

The oxidation of NO by O<sub>2</sub> is described by the reaction:



## Data:

Two series of measurements are carried out to determine the order and rate constant:

- **Series 1:** Excess O<sub>2</sub> over NO. Measure the variation of NO concentration over time.

$$[O_2] = 5 \times 10^{-3} \text{ mol.L}^{-1}, [NO]_0 = 10^{-5} \text{ mol.L}^{-1}.$$

Time (min): 1, 2, 4, 8, 12, 20, 30;  $[NO](10^{-6} \text{ mol.L}^{-1})$ : 9.6, 9.2, 8.5, 7.4, 6.5, 5.3, 4.3.

- **Series 2:** Excess NO over O<sub>2</sub>. Measure the variation of O<sub>2</sub> concentration over time.

$$[NO] = 10^{-3} \text{ mol.L}^{-1}, [O_2]_0 = 10^{-5} \text{ mol.L}^{-1}.$$

Time (s): 10, 20, 30, 60, 120, 240, 360;  $[O_2](10^{-6} \text{ mol.L}^{-1})$ : 9.3, 8.6, 8.0, 6.4, 4.1, 1.7, 0.7.

1. Compare the initial concentrations for each series and deduce the method used.
2. Determine the orders of the reaction with respect to NO and O<sub>2</sub>, and calculate the rate constants for each series.

# Chapter 4

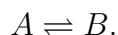
## Complex Reactions

## 4.1 Introduction

The realization of complex reactions involves reaction mechanisms where elementary reactions combine in different ways. In this context, we distinguish the following types:

### 4.1.1 Reversible Reactions (Equilibrium or Opposed Reactions)

These reactions are represented by two arrows in opposite directions:

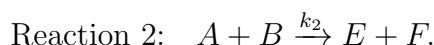
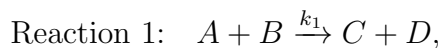


### 4.1.2 Parallel Reactions

There are two types of parallel reactions:

#### Coupled Reactions (Twin Reactions)

These are reactions that share the same reactants but yield different products:



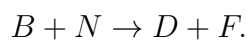
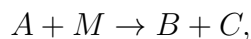
#### Competitive Parallel Reactions

These are reactions that share a common reactant:



### 4.1.3 Consecutive Reactions (Successive Reactions)

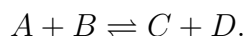
These are reactions composed of a series of elementary reactions:



## 4.2 Rate of Reversible (Equilibrated) Reactions

### 4.2.1 General Reversible Reaction

Let us consider the following reversible reaction:



The reactions in both directions are elementary, which means that the partial orders with respect to the reactants are equal to the stoichiometric coefficients.

- The reaction rate in the forward direction (1) is given by:

$$V_1 = k_1[A][B].$$

- The reaction rate in the reverse direction (-1) is given by:

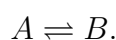
$$V_{-1} = k_{-1}[C][D].$$

- The net reaction rate is:

$$V = V_1 - V_{-1}.$$

### 4.2.2 Mono-molecular Reversible Reaction

Consider the simpler reversible reaction:



The rate of this reaction is:

$$V = k_1[A] - k_{-1}[B] = -\frac{d[A]}{dt}.$$

Considering the initial conditions and concentrations at a given time  $t$ : - At  $t = 0$ , the concentrations are  $[A]_0 = a_0$  and  $[B]_0 = 0$ . - At time  $t$ , the concentrations become  $[A] = a_0 - x$  and  $[B] = x$ .

By substituting  $[A]$  and  $[B]$  into the rate equation:

$$-\frac{d(a_0 - x)}{dt} = k_1(a_0 - x) - k_{-1}x,$$

$$\frac{dx}{dt} = k_1(a_0 - x) - k_{-1}x,$$

$$\frac{dx}{dt} = x(k_1 - k_{-1}) + k_1a_0.$$

At equilibrium, the reaction rate is zero ( $V = 0$ ), which implies:

$$V_1 = V_{-1}.$$

The equilibrium constant  $K_e$  is defined as:

$$K_e = \frac{x_e}{a_0 - x_e} = \frac{k_1}{k_{-1}},$$

where  $x_e$  is the concentration of  $B$  at equilibrium.

Rearranging for  $k_{-1}$ , we obtain:

$$k_{-1} = k_1 \frac{a_0 - x_e}{x_e}.$$

Substituting this expression into the rate equation:

$$V = \frac{dx}{dt} = k_1(a_0 - x) - k_1 \frac{a_0 - x_e}{x_e} x,$$

$$\frac{dx}{dt} = k_1 a_0 - k_1 x - k_1 a_0 \frac{x}{x_e} + k_1 x,$$

$$\frac{dx}{dt} = k_1 a_0 - k_1 a_0 \frac{x}{x_e},$$

$$\frac{dx}{dt} = k_1 a_0 \left( 1 - \frac{x}{x_e} \right).$$

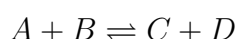
Let  $k_1 a_0 = k'$ , so the equation becomes:

$$\frac{dx}{\left( 1 - \frac{x}{x_e} \right)} = k' dt.$$

This equation is similar to that of a first-order reaction.

### 4.2.3 Reversible Bi-molecular Reaction

Consider the reaction:



The rate of this reaction is given by:

$$V = k_1[A][B] - k_{-1}[C][D] = -\frac{d[A]}{dt}.$$

**Reaction Progress** - At  $t = 0$ , the concentrations are:  $[A]_0 = a_0$ ,  $[B]_0 = b_0$ ,  $[C]_0 = 0$ ,  $[D]_0 = 0$ . - At time  $t$ , the concentrations become:

$$[A] = a_0 - x, \quad [B] = b_0 - x, \quad [C] = x, \quad [D] = x.$$

- At equilibrium, these concentrations are:

$$[A] = a_0 - x_e, \quad [B] = b_0 - x_e, \quad [C] = x_e, \quad [D] = x_e.$$

For simplicity, let us assume  $a_0 = b_0$ . The rate expression becomes:

$$-\frac{d(a_0 - x)}{dt} = k_1(a_0 - x)^2 - k_{-1}x^2.$$

At equilibrium, replacing  $k_{-1}$  with its expression:

$$k_{-1} = k_1 \frac{(a_0 - x_e)^2}{x_e^2},$$

we obtain:

$$\frac{dx}{\left( 1 - \frac{x}{x_e} \right)^2} = k' dt,$$

where  $k' = k_1(a_0)^2$ . This equation corresponds to a second-order reaction.

## 4.3 Parallel Reactions

Parallel reactions occur when a single reactant undergoes multiple competing reactions to form different products. These reactions are represented as:



Rate laws:

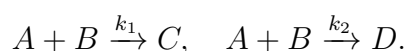
$$-\frac{d[A]}{dt} = k_1[A] + k_2[A]$$

Product ratio:

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

### 4.3.1 Twin Parallel Reactions

Consider the following twin reactions:



- At  $t = 0$ , the concentrations are:  $[A]_0 = a_0$ ,  $[B]_0 = b_0$ ,  $[C]_0 = 0$ ,  $[D]_0 = 0$ . - At time  $t$ , the concentrations become:

$$[A] = a_0 - z, \quad [B] = b_0 - z, \quad [C] = x, \quad [D] = y,$$

where  $z = x + y$ .

The overall rate of consumption of  $A$  is:

$$-\frac{d[A]}{dt} = V_1 + V_2 = k_1[A][B] + k_2[A][B],$$

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A][B].$$

Substituting  $[A] = a_0 - z$  and  $[B] = b_0 - z$ :

$$-\frac{d(a_0 - z)}{dt} = (k_1 + k_2)(a_0 - z)(b_0 - z).$$

If  $a_0 = b_0$ , this equation simplifies to:

$$\frac{dz}{(a_0 - z)^2} = k' dt,$$

where  $k' = k_1 + k_2$ . This equation corresponds to a second-order reaction.

Rates with respect to  $C$  and  $D$ :

$$\frac{d[C]}{dt} = k_1[A][B], \quad \frac{d[D]}{dt} = k_2[A][B].$$

Dividing the two equations:

$$\frac{d[C]}{d[D]} = \frac{k_1}{k_2}.$$

Integration yields:

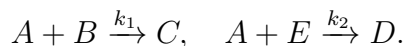
$$[C] = \frac{k_1}{k_2}[D].$$

**Graphical Interpretation:** The plots of the following equations give straight lines: - For  $\frac{dz}{(a_0 - z)^2} = k' dt$ : slope  $(k_1 + k_2)$ . - For  $\frac{d[C]}{d[D]} = \frac{k_1}{k_2}$ : slope  $\frac{k_1}{k_2}$ .



### 4.3.2 Competitive Parallel Reactions

Consider the following competitive reactions:



- At  $t = 0$ , the concentrations are:

$$[A]_0 = a_0, \quad [B]_0 = b_0, \quad [E]_0 = e_0, \quad [C]_0 = 0, \quad [D]_0 = 0.$$

- At time  $t$ , the concentrations become:

$$[A] = a_0 - x, \quad [B] = b_0 - x_1, \quad [E] = e_0 - x_2, \quad [C] = x_1, \quad [D] = x_2.$$

The rates are:

$$\frac{dx_1}{dt} = k_1(a_0 - x)(b_0 - x_1), \quad \frac{dx_2}{dt} = k_2(a_0 - x)(e_0 - x_2).$$

Dividing the two:

$$\frac{dx_1}{dx_2} = \frac{k_1(b_0 - x_1)}{k_2(e_0 - x_2)}.$$

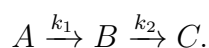
Integration yields:

$$\ln \left( \frac{b_0 - x_1}{b_0} \right) = \frac{k_1}{k_2} \ln \left( \frac{e_0 - x_2}{e_0} \right).$$

The plot of  $\ln(x_1)$  versus  $\ln(x_2)$  gives a straight line with slope  $\frac{k_1}{k_2}$ .

## 4.4 Consecutive (Successive) Reactions

A consecutive reaction consists of multiple successive steps:



Concentrations at time  $t$ : - For  $A$ :

$$-\frac{d[A]}{dt} = k_1[A],$$

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

- For  $B$ :

$$\frac{d[B]}{dt} = k_1[A] - k_2[B].$$

Substituting  $[A]$ :

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

Solving this differential equation yields:

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

- For  $C$ :

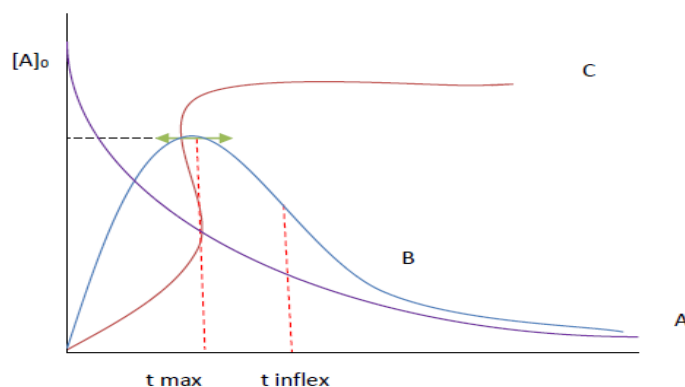
$$\frac{d[C]}{dt} = k_2[B].$$

Integrating and substituting  $[B]$ :

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

This final equation can also be derived from mass conservation:

$$[C] = [A]_0 - [A] - [B].$$



## 4.5 Calculation of the Maximum Time

Graphically, the maximum time corresponds to the maximum of  $B$ , defined as:

$$t_{\max} : \frac{d[B]}{dt} = 0$$

To calculate this time:

$$\frac{d[B]}{dt} = k_1[A]_0(k_2 - k_1)(e^{-k_1 t} - e^{-k_2 t}) = 0$$

This implies:

$$\frac{d[B]}{dt} = k_1[A]_0(k_2 - k_1)(-k_1 e^{-k_1 t_{\max}} + k_2 e^{-k_2 t_{\max}}) = 0$$

$$k_1 e^{-k_1 t_{\max}} = k_2 e^{-k_2 t_{\max}}$$

Taking the logarithm:

$$e^{(k_2 - k_1)t_{\max}} = \frac{k_2}{k_1}$$

$$t_{\max} = \frac{1}{k_2 - k_1} \ln \left( \frac{k_2}{k_1} \right)$$

### 4.5.1 Calculation of the Maximum Concentration of $B$

The maximum concentration is represented graphically as the peak, defined mathematically as:

$$\begin{aligned}\frac{d[B]}{dt} &= k_1[A] - k_2[B] = 0 \\ k_1[A]_0 e^{-k_1 t_{\max}} &= k_2[B]_{\max} \\ [B]_{\max} &= \frac{k_1[A]_0 e^{-k_1 t_{\max}}}{k_2}\end{aligned}$$

Substituting  $t_{\max}$ :

$$[B]_{\max} = \frac{k_1[A]_0 e^{-\frac{k_1}{k_2 - k_1} \ln \frac{k_2}{k_1}}}{k_2}$$

Using the property  $e^{-\ln x} = \frac{1}{x}$ :

$$[B]_{\max} = \frac{k_1[A]_0 \left(\frac{k_1}{k_2}\right)}{k_2(k_2 - k_1)}$$

Simplifying:

$$[B]_{\max} = \frac{[A]_0 k_1}{k_2(k_2 - k_1)}$$

### 4.5.2 Inflection Time for Product $C$ ( $t_{\text{inf}}$ )

The inflection time corresponds to the point where the second derivative of  $C$ 's formation rate is zero:

$$\begin{aligned}\frac{d[C]}{dt} &= k_2[B] \\ \frac{d^2[C]}{dt^2} &= k_2 k_1 [A]_0 (k_2 - k_1) (-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}) = 0 \\ k_1 e^{-k_1 t_{\text{inf}}} &= k_2 e^{-k_2 t_{\text{inf}}}\end{aligned}$$

Taking the logarithm:

$$t_{\text{inf}} = \frac{1}{k_2 - k_1} \ln \left( \frac{k_2}{k_1} \right)$$

This shows that  $t_{\text{inf}}$  for  $C$  is equal to  $t_{\text{max}}$  for  $B$ , implying:

$$[B]_{\max} = [C]_{\text{inf}}$$

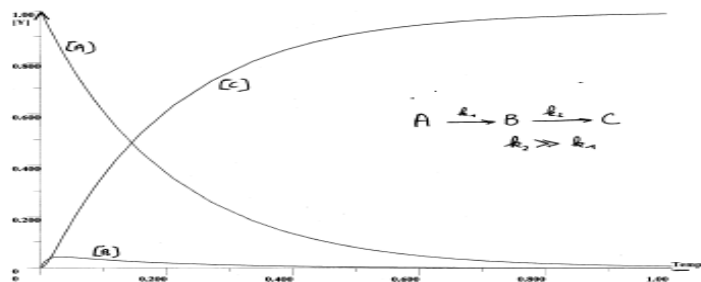
### 4.5.3 Inflection Time for Product $B$ ( $t_{\text{inf}}$ )

For  $B$ :

$$\begin{aligned}\frac{d^2[B]}{dt^2} &= k_1 [A]_0 (k_2 - k_1) (k_1^2 e^{-k_1 t_{\text{inf}}} - k_2^2 e^{-k_2 t_{\text{inf}}}) = 0 \\ k_1^2 e^{-k_1 t_{\text{inf}}} &= k_2^2 e^{-k_2 t_{\text{inf}}}\end{aligned}$$

Taking the logarithm:

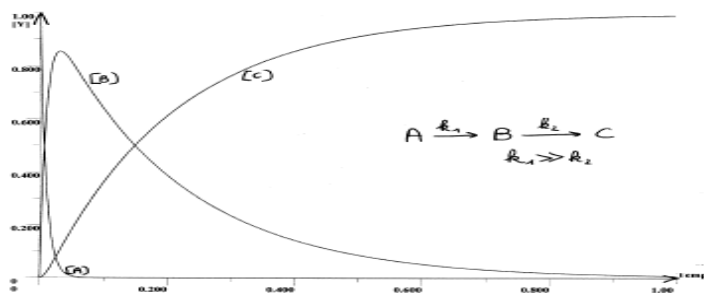
$$t_{\text{inf}} = \frac{2}{k_2 - k_1} \ln \left( \frac{k_2}{k_1} \right)$$



Thus,  $t_{\text{inf}}$  for  $B$  is twice  $t_{\text{max}}$ :

$$t_{\text{inf}} = 2t_{\text{max}}$$

**Note:** The behavior of this consecutive reaction changes significantly if  $k_1 \ll k_2$ .  
And when  $k_2 \ll k_1$



# Bibliography

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**Semestre :4**

**Unité d'enseignement : UEF 2.2.3**

**Matière1: Cinétique chimique**

**VHS: 22h30 (Cours: 1h30)**

**Crédits : 2**

**Coefficient: 1**

**Objectifs de la matière:**

Fournir à l'étudiant les bases indispensables à toute étude cinétique d'un processus chimique et touche aussi bien les notions élémentaires de la cinétique formelle et les bases mathématiques concernant la notion de vitesse d'une réaction chimique et son évolution au cours du temps, les paramètres influençant sur la vitesse d'une réaction, la détermination de l'ordre d'une réaction par les méthodes physico-chimiques, la constante de vitesse et l'énergie d'activation.

**Connaissances préalables recommandées:**

Mathématiques (dérivée, intégrale), savoir exprimer la concentration d'une solution, maîtriser les systèmes d'unités, savoir tracer et exploiter les graphiques.

**Contenu de la matière:**

**Chapitre I. Réactions chimiques homogènes**

**(1 semaine)**

I. Vitesse de réaction (Vitesse absolue, vitesse spécifique)

II. Etude cinétique expérimentale d'une réaction (Méthodes chimiques et physiques)

III. Facteurs expérimentaux influençant la vitesse

**Chapitre II. Influence des concentrations et de la température sur la vitesse**

**(2 semaine)**

I. Influence de la concentration (Ordre d'une réaction, Molécularité et Stœchiométrie d'une réaction, Règle de VANT'HOFF)

II. Influence de la température

**Chapitre III. Cinétique formelle, réaction simple**

**(6 semaines)**

I. Détermination de la constante de vitesse d'une réaction d'ordre donné (Ordre 0,1,2,3 et n)

II. Détermination des ordres de réactions

- Méthodes de détermination de l'ordre par Intégration (variation des concentrations en fonction du temps, méthodes des temps de réaction partiels), exemple de calcul

- Méthode différentielle, exemple de calcul

- Méthodes basées sur la dégénérescence de l'ordre, exemple de calcul

- Méthode utilisant les paramètres sans dimension, exemple de calcul

**Chapitre IV. Réactions composées**

**(6 semaines)**

**1. Réactions opposées ou équilibrées**

- Généralités

- Exemples de réactions opposées (les deux réactions opposées sont d'ordre 1, d'ordre 2, réactions d'ordre 2 opposée à réaction d'ordre 1, réactions d'ordre 1 opposée à réaction d'ordre 2)

- Equilibre et vitesse de réactions

- Principe de microréversibilité

**2. Réactions parallèles** : généralités, réactions jumelles, réactions concurrentes, exemple,

**3. Réactions successives** : détermination des constantes de vitesse, équilibre radioactif, exemple de calcul.

**Modé d'évaluation:** Examen final: 100%.