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Chemical Kinetics

Course Notes and Exercises
Second Year – Process Engineering

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PREFACE

This handout presents the essential concepts of chemical kinetics, intended for second-year process engineering students. The content is organized into four chapters, accompanied by supplementary exercises:

Chapter 1 serves as an introduction to homogeneous chemical reactions. A series of exercises with detailed solutions is provided to support understanding.

Chapter 2, explores how the rate of a chemical reaction is affected by two key factors: the concentration of reactants and the temperature of the system. Understanding these influences is essential for controlling chemical processes in both laboratory and industrial settings. This chapter is followed by a series of exercises with detailed solutions.

In Chapter 3, we outline some preliminary concepts specific to formal chemical kinetics that are necessary for understanding the remainder of the material. A set of exercises with detailed corrections is included to help clarify the studied phenomena.

Chapter 4 offers an overview of complex reactions and is complemented by applied exercises with detailed solutions.

OBJECTIVES

This document aims to provide a structured and comprehensive overview of the essential principles of chemical kinetics for bachelor-level students in process engineering.

Chemical kinetics is a branch of chemistry that examines **the rates** of chemical reactions and the factors that influence them. This module aims to achieve several objectives:

- Identify the fundamental concepts of chemical kinetics, including reaction rates and their evolution over time;
- Explain the mathematical principles related to reaction rates and influencing parameters; Analyze the factors affecting the rate of a chemical reaction;
- Determine the order of a reaction using physicochemical methods; Calculate both the rate constant and activation energy of a reaction.

To support this learning process, detailed calculations are provided throughout the course, accompanied by practical exercises designed to reinforce and apply the concepts introduced.

PRE-REQUISITE

Students enrolling in this course are expected to have a solid foundation in the following areas:

- Proficiency in mathematics, including derivatives and integrals;
- Ability to express the concentration of a solution;
- Familiarity with unit systems;
- Competence in plotting and interpreting graphs.

Summary

Chemical kinetics is the study of **reaction rates**, the changes in the concentrations of reactants and products with time

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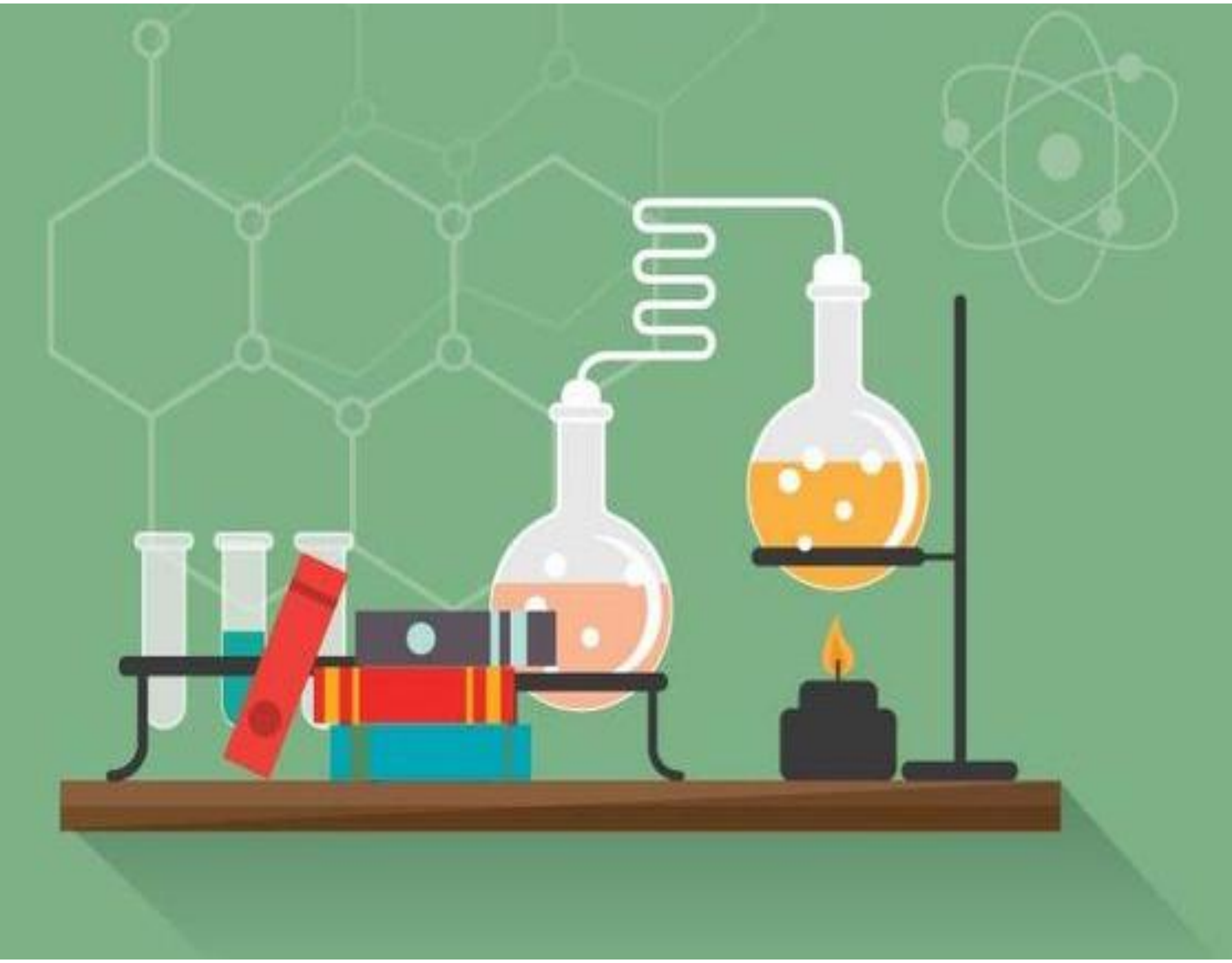
INTRODUCTION

Chemical reactions are fundamental to both natural and industrial processes, shaping the world as we know it. Without them, life would not exist, and essential advancements such as fire, control metal production, synthetic materials, and energy generation would be impossible. Chemical kinetics is the study of reaction rates, the factors that influence them, and the mechanisms by which reactants transform into products.

This field provides a quantitative understanding of how variables such as temperature, pressure, concentration, and catalysts affect the speed and efficiency of chemical reactions. By analyzing these factors, it becomes possible to optimize reaction conditions, improve yields, and develop more efficient and sustainable processes.

The principles of chemical kinetics are widely applied in industries such as **pharmaceuticals**, **energy**, **petrochemicals**, and **environmental science**, where controlling reaction rates is essential for **safety**, **efficiency**, and **reproducibility**. Furthermore, advancements in reactor design and process optimization rely heavily on kinetic studies, enabling large-scale production while minimizing waste and energy consumption.

A thorough understanding of chemical kinetics is therefore crucial for the development of new technologies and the continuous improvement of industrial and scientific applications.



CHAPTER I

HOMOGENEOUS CHEMICAL REACTIONS

CHAPTER I : HOMOGENEOUS CHEMICAL REACTIONS

I.1 Introduction

Chemical kinetics focuses on the study the speed of chemical transformations. When the reaction medium is uniform and consists of a single phase, it is classified as homogeneous kinetics.

Regulating the reaction rate is crucial for the safe and efficient use of chemical substances, as it helps to prevent risks such as runaway reactions and explosions.

By establishing rate laws, chemical kinetics provides a framework for testing and validating hypotheses about reaction mechanisms.

I.2 Reaction Rate (Absolute Rate, Specific Rate)

In a chemical system of constant mass, the instantaneous rate of a chemical species "i" is the variation of the number of moles per unit time.

The rate of a chemical reaction is defined either in terms of the disappearance of a reactant, or of the appearance of a product. The reaction rate is always taken as positive, regardless of whether it is determined from reactants or products.

It is generally expressed in units of concentration per unit of time, typically: $mol \cdot L^{-1} \cdot s^{-1}$.

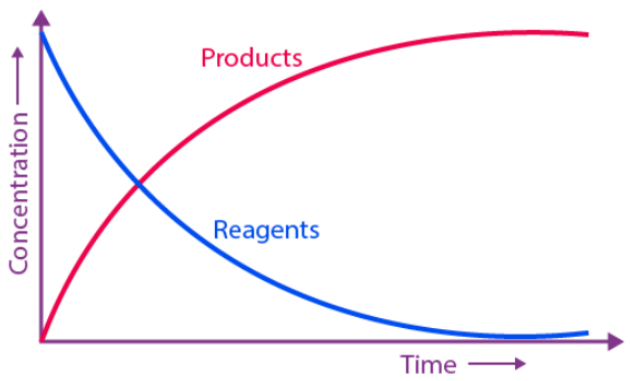


Figure I-1 : Variation over time of the amounts of reactants and products

Consider the general representation of a chemical reaction:

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

The general expression for the reaction rate is defined as the change in the concentration of a given species divided by its stoichiometric coefficients in the balanced chemical equation.

Rate of reaction = Decrease in molar concentration of a reactant per unit time = Increase in molar concentration of a product per unit time.

- The change in reactant concentration in negative (since reactants are consumed);
- The change in product concentration is positive (since products are formed).

$$Rate = \left(-\frac{1}{a}\right)\frac{dn_A}{dt} = \left(-\frac{1}{b}\right)\frac{dn_B}{dt} \quad \text{; rate of disappearance}$$

$$Rate = \left(\frac{1}{c}\right)\frac{dn_C}{dt} = \left(\frac{1}{d}\right)\frac{dn_D}{dt} \text{ ; rate of appearance}$$

I.2.1 Progress of reaction (ξ)

In order to measure the progress of a reaction, it is necessary to define a parameter that quantities the degree of conversion of the reactants. The concept of the extent of reaction or **degree of advancement** is particularly useful for this purpose.

Consider a closed system (i.e., one in which no matter is exchanged with the surroundings) where a single chemical reaction occurs. Initially, there are $n_{i,0}$ moles of a given species present in the system. At a later time, the number of moles of this species is n_i.

At this moment, the molar extent of reaction is represented by the Greek letter ξ (ksi) and is defined by the relation:

$$\zeta = \frac{\left(n_i - n_{i,0}\right)}{\nu_i}$$

n_i: the quantity of species i at the considered of progress;

$n_{i,0}$: is the initial quantity of the species;

ν_i: the stochiometric number (negative for reactants, positive for products), which corresponds to the algebraic value of the stoichiometric coefficient.

If we introduce the degree of progress of the reaction ξ the speed is defined by:

$$R = \frac{d\xi}{dt}$$

We can thus define the specific rate associated with the general expression of a chemical reaction:

$$d\xi = \pm\frac{dn_i}{a_i} \Rightarrow dn_i = \pm a_i d\xi$$

$$R = \pm\frac{dn_i}{dt} = a_i\frac{d\xi}{dt}$$

$$\Rightarrow \quad R = \frac{d\xi}{dt} = \frac{R_A}{a} = \frac{R_B}{b} = \frac{R_C}{c} = \frac{R_D}{d}$$

Giving the following reaction:

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

Applying the previous relation to this reaction:

$$r_A = -\frac{dn_A}{dt} = a\frac{d\xi}{dt}$$

$$r_B = -\frac{dn_B}{dt} = b\frac{d\xi}{dt}$$

$$r_C = +\frac{dn_C}{dt} = c\frac{d\xi}{dt}$$

$$r_D = +\frac{dn_D}{dt} = d\frac{d\xi}{dt}$$

$$R = \frac{d\xi}{dt} = \frac{R_A}{a} = \frac{R_B}{b} = \frac{R_C}{c} = \frac{R_D}{d}$$

I.2.2 Volume rate

In practice, a definition of the reaction rate that is independent of the total amount of material in the system is used:

$$R = \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{d(\frac{n}{V})}{dt} = \frac{1}{\nu_i}\frac{d[C]}{dt}$$

The objective is to establish an expression for the reaction rate based on the knowledge of its reaction mechanism. Since this expression does not involve any empirical factors, it is often referred to as the 'absolute rate'. In the common case of reactions occurring in a systems of constant volume (particularly in solutions), this is called the specific or global volumetric reaction rate.

I.3 Experimental Kinetic Study of a Reaction (Chemical and Physical Methods)

I.3.1 Physical Methods

These methods have the advantage of allowing continuous measurement without disturbing the reaction medium. In addition, they generally require only small quantities of reagents and are often very fast.

a) Pressure Measurement

When a reaction is accompanied by a change in the quantity of gaseous material, the variation in the total pressure of the system can be measured. Assuming the gas mixture behaves as an ideal gas mixture, we have:

$$R = \frac{1}{\Delta V_{gas} R.T} \frac{dP}{dt}$$

Where:

R: rate of the chemical reaction ($mol\cdot L^{-1}\cdot s^{-1}$)

ΔV_{gas} : change in the molar volume of gaseous species during the reaction ($L\cdot mol^{-1}$)

R: universal gas constant (8.314 $J\cdot mol^{-1}\cdot K^{-1}$)

T: absolute temperature (K)

P: total pressure of the system (Pa or atm)

b) Absorbance Measurement

This method is based on directing a beam of monochromatic light of wavelength λ through a cell containing the solution under study and measuring the light intensity at both the entrance and the exit of the cell.

According to the Beer-Lambert law:

$$I = I_0 . e^{-\varepsilon . c . l}$$

where:

l: is the path length of the cell

c: is the concentration of the absorbing species

ε: is the molar absorption coefficient, which depends on the specific species, the incident wavelength, temperature, and possibly the solvent used.

The absorbance or optical density A is defined as:

$$A = log\left(\frac{I_0}{I}\right)$$

This absorbance measurement directly provides the concentration of the absorbing species, allowing for the determination of the reaction rate.

c) Calorimetry

This method is based on measuring the heat released during the reaction.

d) Gravimetry

This technique involves monitoring the weight changing system. If the reaction occurs at a high temperature, a thermobalance is used a highly accurate balance capable of operating under elevated temperatures.

e) Polarimetry

This method is applied in the case of optically active compounds. When polarized light passes through a cell of length l containing an optically active reagent at concentration C, the plane of polarization is rotated by an angle α, given by:

$$\alpha = \alpha_0 . \, l . \, C$$

Where:

α_0: is the specific rotation.

l: length of the polarimeter cell.

C: concentration of the optically active compound.

f) Spectrophotometry

The intensity of the IR, UV, and visible absorption spectra allows for the determination of the concentration of the absorbing species.

I.3.2 Chemical Methods

When pH measurement is employed, the reaction medium remains undisturbed, which offers the same advantages as physical methods.

However, if the analysis requires a titration reaction of the studied species within the reaction medium, successive sampling is necessary, this alters the system. Because, the reaction continues within the collected samples. Therefore, a very rapid titration must be performed, or the sample must be quenched to "freeze" the reaction, either by strong dilution or cooling.

As a result, chemical methods are only used when no other option is available. These methods involve sampling at different reaction times, with the necessary steps outlined as follows:

- Chemical Reaction (Constant Temperature: Thermostat)
- Sampling

- Chemical Quench (Reaction stopped by cooling)
- Titration (Acidimetry, precipitation, complexation, oxidation-reduction, etc.)

I.4 Experimental Factors Affecting Reaction Rate

Although a balanced chemical equation for a reaction describes the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed, it gives us no information about whether or how fast a given reaction will occur. This information is obtained by studying the chemical kinetics of a reaction, which depend on various factors:

- Temperature is the most important factor because, in many cases, thermal energy allows the system to overcome the energy barrier between its initial state (reactant mixture) and its final state (formed products).
- Quantity of reactants (in solution, the concentration of reactants is crucial) Pressure (for gas-phase reactions).
- Degree of mixing of the reactants (segregation).
- Surface area or contact surface of the reactants in heterogeneous systems.
- The presence of a catalyst, which can speed up the reaction, or an inhibitor, which can slow it down.
- Light intensity (UV or visible), in the case of photochemical reactions.

Exercises

Exercise N°1

Consider the complete oxidation reaction of ammonia by oxygen, which produces nitrogen monoxide (NO) and water vapor from a mixture initially containing 18 moles of ammonia and 20 moles of O2.

1. Write the balanced reaction equation.

2. Let ξ be the corresponding progression. Express the composition of the system as a function of ξ. Apply the numerical solution for $\xi = 3.5$ mol, then 4.2 mol.

3. What is the maximum value of ξ?. What is the composition of the reaction mixture at the end of the reaction?

Exercise N°2

Using the data in the following table, calculate the reaction rate of $SO_{2(g)}$ with $O_{2(g)}$ to give $SO_{3(g)}$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Time (s)	**[SO_2] (M)**	**[O_2] (M)**	**[SO_3] (M)**
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Exercise N°3

Write the rate expressions for the following reaction in terms of the disappearance of the reactants and the appearance of the products:

$$4NO_2 + O_2 \rightarrow 2\ N_2O_5$$

Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.018 M/s.

1. At what rate is being formed?

2. At what rate is reacting?

Exercise N°4

Consider the decomposition reaction of nitrogen pentoxide:

$$4NO_2 + O_2 \rightarrow 2\ N_2O_5$$

The rate of disappearance of N_2O_5 at time t is: r (N_2O_5) = 0.024 mol. $l^{-1}.s^{-1}$.

Calculate the volume rate of the reaction and the rates of formation of NO2 and O2

Exercise N°5

For the reaction:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

The concentration of NO_2 increases by 3.10^{-3} mol/l in 10 seconds What is the rate of the reaction?

Exercise Corrections

Exercise N°1

1- Balanced Reaction Equation

The reaction involves the complete oxidation of ammonia (NH_3) with oxygen (O_2) to form nitrogen monoxide (NO) and water vapor (H_2O). The balanced chemical equation for the reaction is:

$$4NH_{5(g)} + 3O_{2(g)} \rightarrow 2NO_{(g)} + 6H_2O_{(g)}$$

2- Composition as a Function of ξ

Using:

$$\eta_i(\xi) = \eta_{i,0} + \nu_i \xi$$

With stochiometric number $\nu_{NH_3} = -4$, $\nu_{O_2} = -5$, $\nu_{NO} = +4$, $\nu_{H_2O} = +6$:

$$\eta_{NH_3}(\xi) = -18 - 4\xi$$

$$\eta_{O_2}(\xi) = -20 - 5\xi$$

$$\eta_{NO}(\xi) = -0 + 4\xi = 4\xi$$

$$\eta_{H_2O}(\xi) = -0 + 6\xi = 6\xi$$

For ξ = 3.5 mol:

$$\eta_{NH_3}(\xi) = -18 - 4(3.5) = -4\,mol$$

$$\eta_{O_2}(\xi) = -20 - 5(3.5) = 2.5\,mol$$

$$\eta_{NO}(\xi) = 4(3.5) = 14\,mol$$

$$\eta_{H_2O}(\xi) = (3.5) = 21\,mol$$

For ξ= 4.2 mol:

$$\eta_{NH_3}(\xi) = -18 - 4(4.2) = 1.2\,mol$$

$\eta_{O_2}(\xi) = -20 - 5(4.2) = -1\,mol$ (Not physically possible. This means $\xi = 4.2mol$ exceeds the maximum feasible extent))

$$\eta_{NO}(\xi) = 4(4.2) = 16.8\,mol$$

$$\eta_{H_2O}(\xi) = 6(4.2) = 25.2\,mol$$

3- Maximum value of ξ and final composition

Compute the maximum ξ allowed by each reactant (when that reactant is fully consumed):

$$\xi_{max,NH_3} = \frac{\eta_{NH_3,0}}{4} = \frac{18}{4} = 4.5\, mol$$

$$\xi_{max,O_2} = \frac{\eta_{O_2,0}}{5} = \frac{20}{5} = 4\ \ mol$$

The smallest value determines the limiting reagent: $\xi_{max} = 4\, mol$ (O_2 is limiting)

At ξ =4:

$$\eta_{NH_3,final} = -18 - 4(4) = 2\, mol \text{ (excess)}$$

$$\eta_{O_2,final} = -20 - 5(4) = 0\, mol$$

$$\eta_{NO,final} = 4(4) = 16\, mol$$

$$\eta_{H_2O,fimal} = 6(4) = 24\, mol$$

Exercise N°2

The reaction given is:

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

The reaction rate can be expressed in terms of the disappearance of reactants and the appearance of products:

The rate of disappearance of SO_2 is:

$$R = -(\frac{1}{2})\frac{d[SO_2]}{dt} = -\frac{d[O_2]}{dt} = (\frac{1}{2})\frac{d[SO_3]}{dt}$$

The rate of disappearance of SO_2 is:

$$\frac{d[SO_2]}{dt} = \frac{\Delta[SO_2]}{\Delta t} = \frac{[SO_2]_{final} - [SO_2]_{intial}}{t_{final} - t_{intial}}$$

$$= \frac{0.0194 - 0.0270}{720 - 300}$$

$$= -0.0000181 \text{ M/s}$$

$$R = -\left(\frac{1}{2}\right)\frac{d[SO_2]}{dt} = -R = -\left(\frac{1}{2}\right)(-1.8 \times 10^{-5}) = 9.05 \times 10^{-6} \text{ M/s}$$

The rate of disappearance of O_2 is:

$$\frac{d[O_2]}{dt} = \frac{\Delta[O_2]}{\Delta t} = \frac{[O_2]_{final} - [O_2]_{intial}}{t_{final} - t_{intial}}$$

$$= \frac{0.0462 - 0.0500}{720 - 300}$$

$$= -9.05 \times 10^{-6}\ \mathrm{M/s}$$

$$R = -\frac{d[O_2]}{dt} = -(-9.05 \times 10^{-6}) = 9.05 \times 10^{-6}\ \mathrm{M/s}$$

The rate of formation of SO_3 is:

$$\frac{d[SO_3]}{dt} = \frac{\Delta[SO_3]}{\Delta t} = \frac{[SO_3]_{final} - [SO_3]_{intial}}{t_{final} - t_{intial}}$$

$$= \frac{0.0148 - 0.0072}{720 - 300}$$

$$= 1.81 \times 10^{-5}\ \mathrm{M/s}$$

$$R = (\frac{1}{2})\frac{d[SO_3]}{dt} = 2(1.81 \times 10^{-5}) = 9.05 \times 10^{-6}\ \mathrm{M/s}$$

The reaction rate is 9.05×10^{-6} **M/s.**

Exercise N°3

The given balanced chemical reaction is:

$$4NO_2 + O_2 \rightarrow 2N_2O_5$$

The rate of the reaction can be expressed in terms of the disappearance of reactants and the appearance of products as:

$$R = -(\frac{1}{4})\frac{d[NO_2]}{dt} = -\frac{d[O_2]}{dt} = (\frac{1}{2})\frac{d[N_2O_5]}{dt}$$

a- Rate of Formation of N_2O_5

$$R = -\frac{d[O_2]}{dt} = 0.018 M/s$$

$$R = -\frac{d[O_2]}{dt} = = \left(\frac{1}{2}\right)\frac{d[N_2O_5]}{dt}$$

$$=> \frac{d[N_2O_5]}{dt} = 2 \times 0.018 = 0.036\ M/s$$

N_2O_5 is being formed at a rate of 0.036 M/s.

b- Rate of Disappearance of NO_2

$$-(\frac{1}{4})\frac{d[NO_2]}{dt} = -\frac{d[O_2]}{dt}$$

$$=> \ \frac{d[NO_2]}{dt} = 4\frac{d[O_2]}{dt} = 4 \times 0.018 = 0.072 M/s$$

NO_2 is reacting at a rate of 0.072 M/s

Exercise N°4

We are given the decomposition reaction of nitrogen pentoxide:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

The rate of the reaction (R) is related to the rate of disappearance of $\mathbf{N_2O_5}$:

$$R = \left(\frac{1}{2}\right)\frac{d[N_2O_5]}{dt} = \frac{0.024}{2} = 0.012\ M/s$$

Rate of Formation of NO_2

$$R = -(\frac{1}{4})\frac{d[NO_2]}{dt} = -\frac{d[O_2]}{dt} = (\frac{1}{2})\frac{d[N_2O_5]}{dt}$$

$$R_{NO_2} = \left(\frac{4}{2}\right)R_{NO_2} = \left(\frac{4}{2}\right) \times 0.024 = 0.048 M/s$$

$$R_{O_2} = \left(\frac{1}{2}\right)R_{N_2O_5} = \left(\frac{1}{2}\right) \times 0.024 = 0.012 M/s$$

Exercise N°5

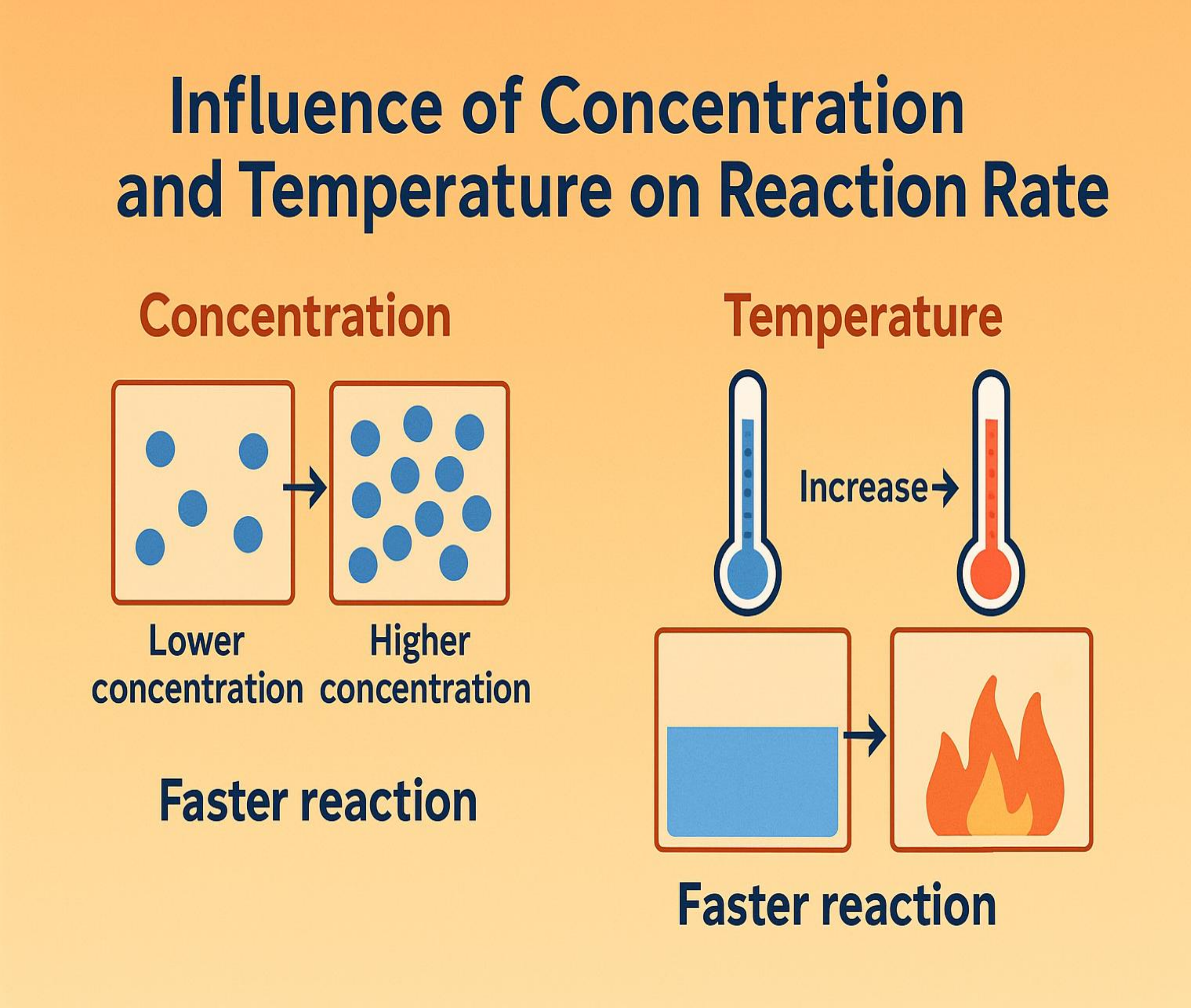
The given balanced chemical reaction is:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

The rate of the reaction can be expressed in terms of the disappearance of reactants and the appearance of products as:

$$R = \left(\frac{1}{4}\right)\frac{d[NO_2]}{dt} = \ \frac{d[O_2]}{dt} = \left(\frac{1}{2}\right)\frac{d[N_2O_5]}{dt}$$

$$=> R = \left(\frac{1}{4}\right)\frac{d[NO_2]}{dt} = \left(\frac{1}{4}\right)\frac{3 \times 10^{-3}}{10} = 7.5 \times 10^{-5}\ mol.l^{-1}.s^{-1}$$



CHAPTER II

INFLUENCE OF CONCENTRATION AND TEMPERATURE ON REACTION RATE

CHAPTER II : INFLUENCE OF CONCENTRATION AND TEMPERATURE ON REACTION RATE

II.1 Introduction

The reaction rate is influenced by several factors, with concentration and temperature being the most significant. Concentration affects the rate through reaction order, molecularity, and stoichiometry, as explained by Vant'Hoff's rule. Temperature impacts reaction kinetics by providing energy to overcome activation barriers, accelerating reactions as described by the Arrhenius equation and collision theory.

II.2 Influence of Concentration

Two substances cannot react with each other unless their constituent particles (molecules, atoms, or ions) come into contact. If there is no contact, the reaction rate will be zero. Conversely, the more frequently reactant particles collide per unit of time, the more likely a reaction is to occur. As a result, the reaction rate generally increases as the concentration of the reactants increases.

An example of this effect is illustrated in the figure below, which shows the evolution of the reaction progress ξ using different initial concentrations of the limiting reagent, where $C_2=2C_1$

- For curve (1), the initial concentration is C_1.
- For curve (2), the initial concentration is C_2.

By plotting the tangents at the origin, we can determine the initial reaction rates at $t_0= 0$. It is observed that as the initial concentration of a reactant increases, the slope of the tangent also increases, indicating a higher initial reaction rate.

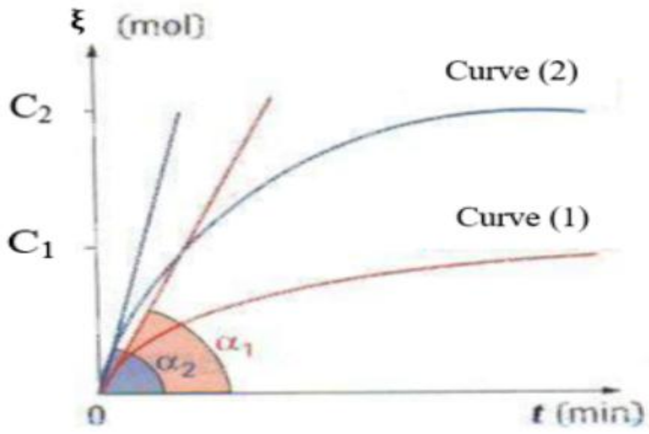


Figure II-1: The variation of the progress ξ with time

II.2.1 Order of a Reaction

The relationship between the reaction rate and the concentrations of all substances present in the reaction medium, along with other factors that may influence the rate, is known as the **rate law**. In general, the rate law can be expressed as:

$$V=k.g(C_i,\ldots.)$$

Where k is a constant value known as the rate constant.

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

Consider the general reaction:

The reaction rate R is given by the variation in the concentrations of A, B, C, or D as a function of time.

$$R = \frac{d\xi}{dt} = \left(-\frac{1}{a}\right)\frac{d[A]}{dt} = \left(-\frac{1}{b}\right)\frac{d[B]}{dt} = \left(\frac{1}{c}\right)\frac{d[C]}{dt} = \left(\frac{1}{d}\right)\frac{d[D]}{dt}$$

Experimentally, it is found that the rate depends on the concentration of the reactants according to the rate law:

$$R = k[A]^x[B]^y$$

***x*:** partial order relative to A;

y: partial order relative to B;

x+y: total or overall order of the reaction;

k: the rate constant (depends on the temperature), its unit depends on the overall order of the reaction.

This law was proposed by Van't Hoff and is based on experimental observations. The reaction order does not necessarily correspond to the stoichiometric coefficients of the chemical equation; it can only be determined experimentally.

⚠ Warning

Under a given set of conditions, the value of the rate constant does not change as the reaction progresses.

II.2.2 Rate Constant Units

The units of the rate constant depend on the form of the rate law in which it appears. For example, a rate constant in a first-order rate law will have different units from a rate constant in a second order or third-order rate law. This follows from the fact that the reaction rate always has the same units of concentration per unit time, which must match the overall units of a rate law, where concentrations may be raised to varying powers. Therefore, it is straightforward to determine the units of a rate constant for any given rate law.

Examples:

- Consider the rate law: $\boldsymbol{R = k[H_2][I_2]}$. If we substitute units into the equation, we obtain:

$$(\text{mol dm}^{-3}\ \text{s}^{-1}) = [k]\ (\text{mol dm}^{-3})\ (\text{mol dm}^{-3})$$

  where the notation [k] means 'the units of k'. We can rearrange this expression to find the units of the rate constant k.

$$[k] = \frac{(\text{mol dm}^{-3}\ \text{s}^{-1})}{(\text{mol dm}^{-3})\ (\text{mol dm}^{-3})} = \text{mol}^{-1}\ \text{dm}^{3}\ \text{s}^{-1}$$

- We can apply the same treatment to a first order rate law, for example $\boldsymbol{R = k[CH_3N_2CH_3]}$.

$$(\text{mol dm}^{-3}\ \text{s}^{-1}) = [k]\ (\text{mol dm}^{-3})$$

$$[k] = \frac{(\text{mol dm}^{-3}\ \text{s}^{-1})}{(\text{mol dm}^{-3})} = \text{s}^{-1}$$

- As a final example, consider the rate law $\boldsymbol{R = k\ [CH_3CHO]^{3/2}}$

$$(\text{mol dm}^{-3}\ \text{s}^{-1}) = [k]\ (\text{mol dm}^{-3})^{3/2}$$

$$[k] = \frac{(\text{mol dm}^{-3}\ \text{s}^{-1})}{(\text{mol dm}^{-3})^{3/2}} = \text{mol}^{-1/2}\ \text{dm}^{3/2}\ \text{s}^{-1}$$

Note

An important point to note is that it is meaningless to try and compare two rate constants unless they have the same units.

II.2.3 Molecularity of reaction

Molecularity refers to the number of species involved in an elementary reaction step, In other words, it is the number of atoms, molecules or ions that simultaneously collide or participate in that step.

Molecularity it always whole number (1, 2 or 3).

It is equal to the sum of the stoichiometric coefficients of the reactants in that elementary step.

Unlike the order of reaction (which is determined experimentally), molecularity is a purely theoretical experimentally), molecularity is a purely theoretical concept, defined only for elementary reactions.

- **Unimolecular reaction** – An elementary step involving the decomposition or rearrangement of a single reactant molecule.

  Example: A → products

- **Bimolecular reaction** – An elementary step involving the collision of two reactant molecules.

  Examples: A + A → products

  A + B → products

- **Termolecular reaction** – An elementary step involving simultaneous collision of three molecules.

  There are rare because the probability of three particles colliding at the same time in very low.

  Example: A + A + A → products

Note

- The overall **order** of an elementary reaction is equal to its **molecularity**, and its **partial orders** correspond to the **stoichiometric coefficients** of the reactants.
- However, the reverse is not necessarily true: the reaction order of a complex (nonelementary) reaction cannot always be determined from its molecularity.
- **Reactions with a molecularity greater than three are rare** because the probability of more than three molecules colliding simultaneously is very low.
- The molecularity of a reaction cannot be **zero**, **negative** or **fractional**. order of a reaction may be zero, negative, positive, fractional, or greater than three. Infinite and imaginary values are not possible.

II.3 Influence of Temperature

For molecules to be transformed from reactants to products, they must pass through an energy state that is higher than that of either the reactants or the products.

Increasing the temperature of a system raises the average kinetic energy of its constituent particles. As their kinetic energy increases, the particles move faster, which results in more frequent collisions per unit time and greater energy during those collisions. Both of these factors contribute to an increase in the reaction rate. Consequently, the reaction rate of nearly all reactions increases with rising temperature and decreases with falling temperature.

For example, refrigeration slows down the growth of bacteria in food by reducing the rates of the biochemical processes necessary for bacterial reproduction.

II.3.1 Signification of Activation Energy and Arrhenius Law

In1889, Arrhenius proposed a quantitative relationship between rate constant and temperature expressed as:

$$k = Ae^{(-E_a/RT)}$$

A: The frequency factor or pre-exponential factor (specific to the reaction under consideration).

R: The gas constant (8.31 J/K·mol). T: The absolute temperature (K).

Ea: The activation energy (J/mol), which has the same unit as RT. (A and Ea are generally considered independent of temperature).

For this law to apply, the reacting species must collide with sufficient energy to initiate the reaction. This phenomenon is explained by collision theory (for gases) or the activated complex theory, which applies to reactions in the gaseous or liquid phase. According to this theory, a reaction occurs only if the reactants gain enough energy potentially facilitated by solvent molecules to reach the transition state and overcome the energy barrier. As shown in the diagram below, there is an energy difference between the reacting molecules and the transition state. This deference, known as activation energy, represents the **minimum energy** required to bring the reactants into the **transition state**, allowing the breaking of existing bonds and the formation of new ones, ultimately leading to the reaction products.

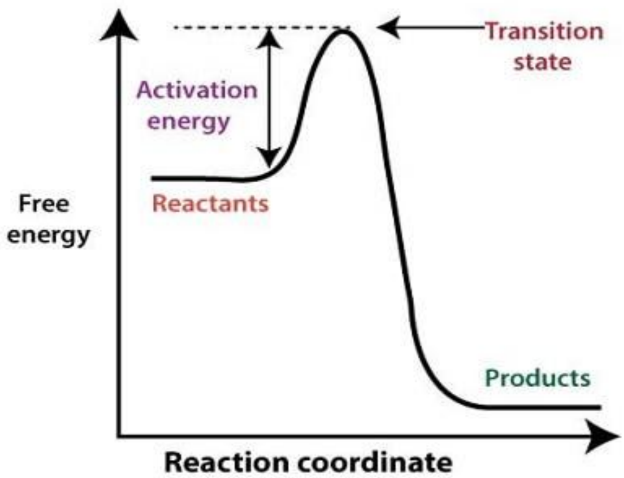


Figure II-2: The energy profile for a chemical reaction

II.3.2 Determination of Activation Energy

A graphical method is used to determine the activation energy:

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

According to this form of the Arrhenius equation, we can conclude the following relationship between activation energy and temperature for a chemical reaction (when the reaction rate is kept constant):

$$\mathbf{E_a \ \alpha \ T}$$

This implies that the activation energy of a chemical reaction varies directly with temperature. If the reaction rate remains constant, the activation energy can be determined based on temperature variations. Since the gas constant **R** is a fixed value and does not change with other reaction parameters, the activation energy is also inversely proportional to the rate coefficient when the temperature is constant.

to determine the activation energy experimentally, it is sufficient to plot ln(k) as a function of 1/T (as shown in the figure below). The Arrhenius equation is given by:

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

This equation corresponds to a straight-line equation of the form y = ax + b, where:

- When x=0, y=b=**ln(A)**
- The slope of the straight line (a) is equal to **-Ea/R**.

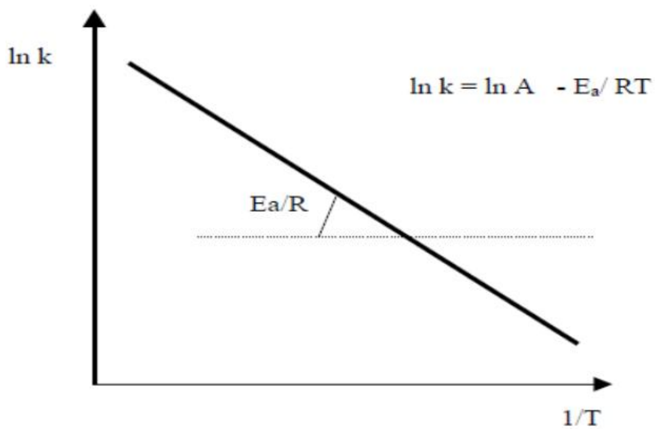


Figure II-3: Variation of ln k as a function of 1/T

Exercises

Exercise N°1:

The reaction of nitric oxide with hydrogen at 1280°C is:

$$2NO_{(g)}+H_{2(g)}\rightarrow N_{2(g)}+2H_2O_{(g)}$$

Determine:

1-The rate law

2-The rate constant

3-The rate of the reaction when [NO] =12x10^{-3} M and [H_2] = 6x10^{-3} M.

Experiment	[NO] (M)	[H_2] (M)	Initial Rate (M/s)
1	5x10^{-3}	2x10^{-3}	1.3x10^{-5}
2	10x10^{-3}	2x10^{-3}	5x10^{-5}
3	10x10^{-3}	4x10^{-3}	10x10^{-5}

Exercise N°2

Express the rate constant k in unit of dm^3 mol^{-1}s^{-1}, if:

1- k = 2.50 × 10^{-9} cm^3 molecule^{-1} s^{-1}

2- k = 2 × 10^{-6} s^{-1}atm^{-1}

Exercise N°3

For a certain reaction, the value of rate constant is 5.0 × 10^{-3} dm^3 mol^{-1}sec^{-1}. Find the value of rate constant in dm^3 molecule^{-1} sec^{-1}, cm^3 mol^{-1}sec^{-1} and cm^{3}molecule^{-1}sec^{-1}.

Exercise N°4

The rate constant for the decomposition of acetaldehyde:

$$CH_3CHO_{(g)} \rightarrow CH_{4(g)} + CO_{(g)}$$

Were measured at five different temperatures.

The data are show in the table:

k(1/M$^{1/2}$)	T(K)
0.011	700
0.035	730
0.105	760
0.343	790

- Plot the ln(k) versus 1/T, and determine the activity energy (in Kj/mol) for the reaction.

Exercise N°5

A reaction has an activation energy of 50 $kJ \cdot mol^{-1}$. Calculate the ratio of the rate constants at 117°C and 127 °C.

Exercise N°6

Calculate the ratio of rate constants of two reactions which have some value of Arrhenius factor and a difference of 5 k mol^{-1} in Ea at 25°C

Exercise Corrections

Exercise N°1

1-**Determine the Rate Law**

The general rate law is:

$$R = [NO]^x[H_2]^y$$

Compare Experiment 1 and Experiment 2, $[H_2]$ is constant, so any rate change is due to [NO].

$$=> \frac{R_2}{R_1} = \frac{5 \times 10^{-5}}{1.3 \times 10^{-5}} \approx 4$$

$$\frac{R_2}{R_1} = \frac{k(10 \times 10^{-3})^x(2 \times 10^{-3})^y}{k(5 \times 10^{-3})^x(2 \times 10^{-3})^y} = 2^x$$

$$2^x = 4 \ => x = 2$$

Compare Experiment 2 and Experiment 3 [NO] is constant, so any rate change is due to $[H_2]$.

$$\frac{R_3}{R_2} = \frac{10 \times 10^{-5}}{5 \times 10^{-5}} = 2$$

$$\frac{R_2}{R_1} = \frac{k(10 \times 10^{-3})^x(4 \times 10^{-3})^y}{k(10 \times 10^{-3})^x(2 \times 10^{-3})^y} = 2^y$$

$$2^y = 2 \ => y = 1$$

$$=> R = [NO]^2[H_2]$$

$$= (260)(12 \times 10^{-3})^2(6 \times 10^{-3}) = \ 2.25 \times 10^{-4}\ \mathrm{M/s}$$

2- Rate constant k

Using experiment (2):

$$5 \times 10^{-5} = k(1 \times 10^{-2})^2(2 \times 10^{-3})$$

$$=> k = \frac{5 \times 10^{-5}}{2 \times 10^{-7}} = 2.5 \times 10^2 M^{-2}s^{-1}$$

3-Reaction rate for [NO]= $12 \times 10^{-3}M, [H_2] = 6 \times 10^{-3}\ M$

$$R = (2.5 \times 10^{-3})(0.012)^2(0.006)$$

$$= 2.16 \times 10^{-4}\ M.s^{-1}$$

Exercise N°2

The expression of k in $dm^3mol^{-1}s^{-1}$ for:

1/ k = 2.50×10^{-9} cm^3 $molecule^{-1}$ s^{-1}

1 dm^3 = 1000 cm^3, i.e. 1 cm^3 = 10^{-3} dm^3

1 mol = 6.02 x 10^{23} molecule

$Molecule^{-1}$ = 6.02 x 10^{23} mol^{-1}

$K=2.50 \times 10^{-9}\ cm^3molecule^{-1}s^{-1}$

$=2.50 \times 10^{-9}\ (10^{-3}\ dm^3)\ (6.02 \times 10^{23}\ mol^{-1})\ s^{-1}$

$= 2.50 \times 6.02 \times 10^{-9+3+23}\ dm^3mol^{-1}s^{-1}$

$= 15.05 \times 10^{11}\ dm^3mol^{-1}s^{-1}$

We know that:

$$P_{(1atm)} = \frac{n}{V}RT = CRT$$

So, we can write:

$$C = \frac{P}{RT} = \frac{1atm}{0.0821\ atm\ dm^3\ mol^{-1}K^{-1} \times 273K}$$

$$=0.0446\ mol\ dm^{-3}$$

Therefore,

1 atm = 0.0446 mol dm^{-3}

1 atm^{-1} = (1/0.0446) $mol^{-1}dm^3$

2/ k = 2×10^{-6} $s^{-1}atm^{-1}$

k= 2 x 10^{-6} $s^{-1}atm^{-1}$

$= 2 \times 10^{-6}\ s^{-1}atm^{-1}$

$= 2 \times 10^{-6}\ s^{-1}\ (1/0.0446)\ mol^{-1}\ dm^3$

$= 44.8 \times 10^{-6}\ dm^3mol^{-1}s^{-1}$

Exercise N°3

The value of rate constant:

In $dm^3mol^{-1}s^{-1}$

$K = 5 \times 10^{-3}\ dm^3mol^{-1}s^{-1}$

$1mol = 6.02 \times 10^{23}$ molecules

$K = 5 \times 10^{-3}\ dm^3\ (6.023 \times 10^{23}\ mol)^{-1}s^{-1}$

$= 0.83 \times 10^{-26}$ dm3molecule$^{-1}s^{-1}$

In $cm^3mol^{-1}s^{-1}$

$1dm^3 = 1000\ cm^3$

$K = 5 \times 10^{-1}\ dm^3mol^{-1}s^{-1}$

$= 5 \times 10^{-3}\ (1000)\ cm^3mol^{-1}s^{-1}$

$= 5\ cm^3mol^{-1}s^{-1}$

In $cm^3molecules^{-1}s^{-1}$

$K = 5\ cm^3\ (6.02 \times 10^{23})^{-1}\ molecules^{-1}s^{-1}$

$= 0.83 \times 10^{-23}\ cm^3molecules^{-1}s^{-1}$

Exercise N°4

To determine the activation energy **(**Ea**)** for the decomposition of acetaldehyde, we use the Arrhenius equation:

$$k = Ae - Ea/RT$$

Taking the natural logarithm on both sides:

$$\ln(k) = -(Ea/R) \cdot (1/T) + lnA$$

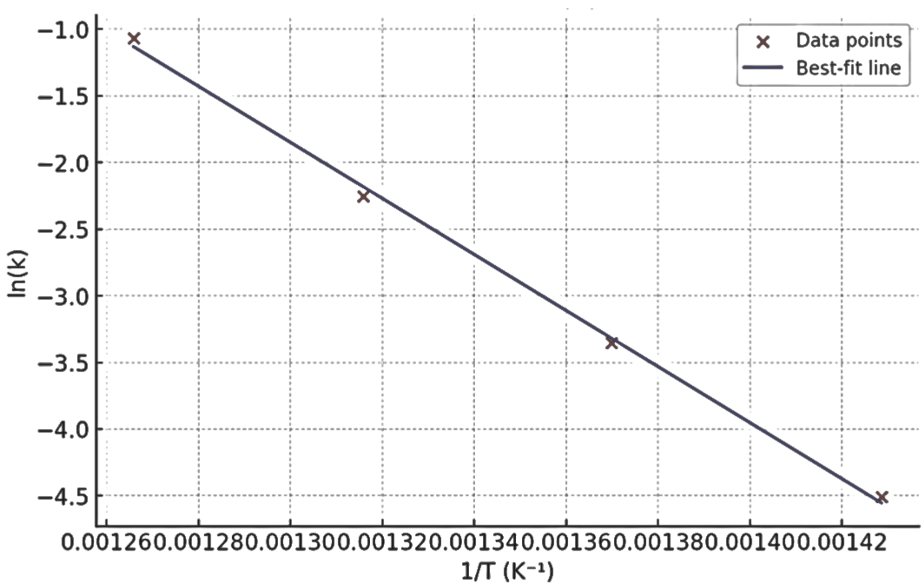
This equation represents a straight-line equation: y=ax+b

where: y=ln(k), x=1/T , slope a=−Ea/R, b=lnA

Calculate 1/T and ln k:

Ln(k)	-4.51	-3.35	-2.254	-1.07	-0.237
1/T	1.43×10^{-3}	1.37×10^{-3}	1.32×10^{-3}	1.27×10^{-3}	1.23×10^{-3}

Plot ln(k) vs. 1/T



Slope a = -Ea/R = -2.09×10^4

⇨ Ea = $(8.314)(2.09 \times 10^4) = 1.74 \times 10^5$ J/mol = 174 kJ/mol.

Exercise N°5

To calculate the ratio of the rate constants at two different temperatures, we use the Arrhenius:

$$k = Ae - Ea/RT$$

Ea=50kJ/mol=50000J/mol

T_1=390K

T_2=400K

Taking the ratio of the rate constants at two different temperatures:

$$\frac{k_2}{k_1} = \frac{e^{-Ea/_{RT_2}}}{e^{-Ea/_{RT_1}}} = e^{-\frac{Ea}{R}(\frac{1}{T_1}-\frac{1}{T_2})}$$

$$\frac{k_2}{k_1} = e^{-\frac{50000}{8.314}(\frac{1}{390}-\frac{1}{400})} = 1.47$$

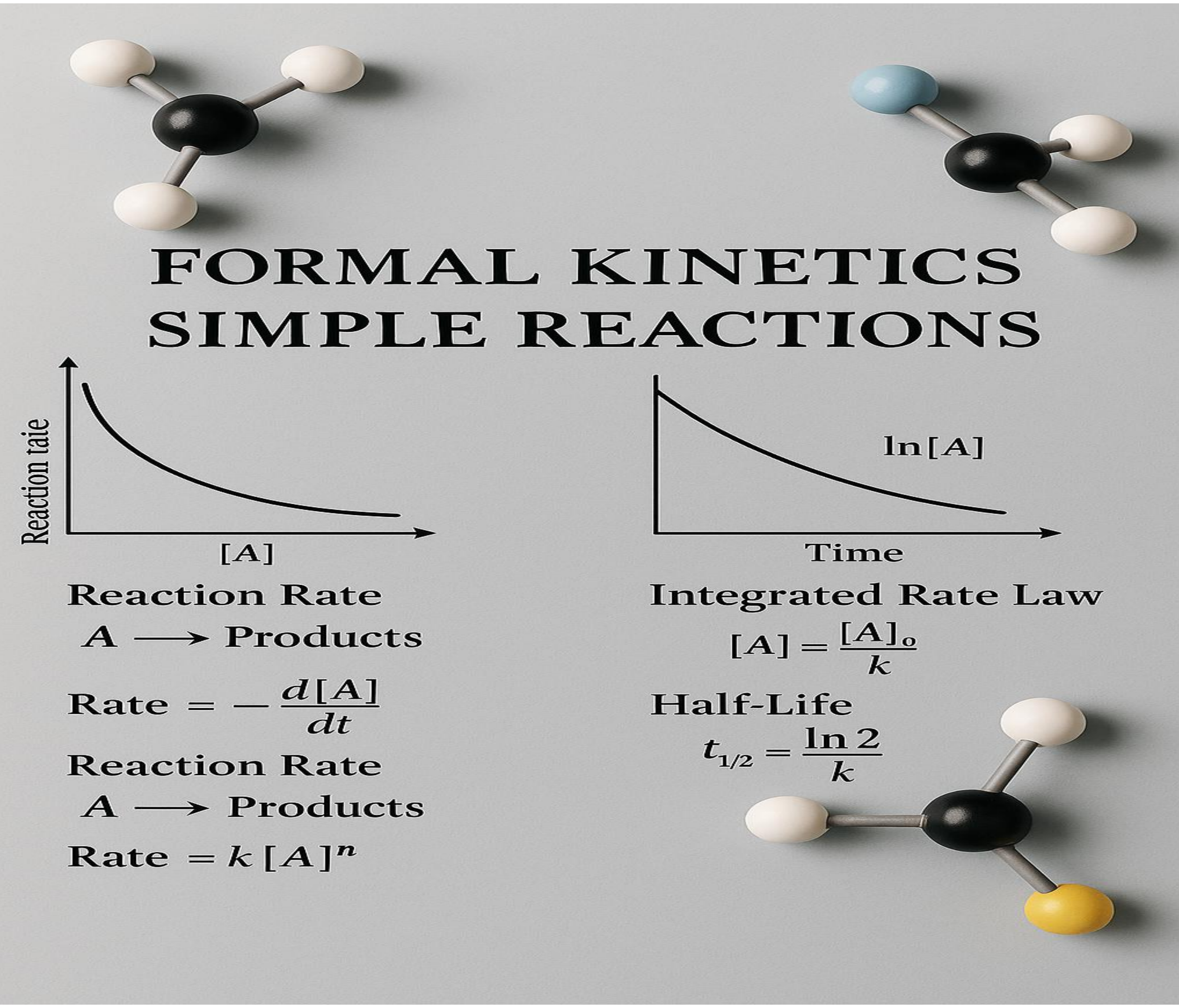
Exercise N°6

We use the Arrhenius equation:

$$k = Ae - Ea/RT$$

the ratio of rate constants:

$$\frac{k_1}{k_2} = \frac{e^{-Ea_1/RT_1}}{e^{-Ea_2/RT_2}} = e^{\frac{1}{RT}(Ea_2 - Ea_1)} = e^{5000/(8.314.298)} = 7.52$$



CHAPTER III

Formal kinetics, simple reaction

CHAPTER III : FORMAL KINETICS, SIMPLE REACTION

III.1 Introduction

The purpose of this section is to provide a mathematically analysis of the relationship between concentration and time (t) in a chemical reaction. This involves deriving equations that describe how the concentrations of reactants and products change over time, based on the reaction order and rate laws. By studying these relationships, we can gain a deeper understanding of reaction kinetics, predict reaction behavior, and determine key parameters such as reaction rate constants and half-life.

III.2 Rate Law and Order of a Reaction

Consider the following reaction:

$$A \xrightarrow{K} B$$

According to its mathematical definition, the rate of a reaction is the instantaneous rate with respect to reactant A:

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

According to Van't Hoff's rate law, the reaction rate is expressed as:

$$R = k[A]^{\alpha}$$

Where:

- α is the partial order of the reaction with respect to A,
- k is the rate constant.

Thus, the reaction rate equation can be rewritten as:

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

Rearranging the equation:

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

By integrating this differential equation, we obtain a mathematical relationship between the concentration of the reactant and time, i.e., [A]=f(t).

III.2.1 First-Order Reaction (α=1)

Let us consider a first-order reaction:

$$A \xrightarrow{K} Products$$

The rate law for this reaction is given by:

$$-\frac{d[A]}{dt} = k[A]^1$$

Rearranging:

$$-\frac{d[A]}{[A]^1} = kdt$$

The integration of this differential equation gives:

$$\int_{[A]_0}^{[A]} -\frac{d[A]}{[A]^1} = \int_0^t k'dt$$

This leads to:

$$-\ln[A] + \ln[A]_0 = kt$$

Simplifying further:

$$ln\frac{[A]_0}{[A]} = kt \qquad (*)$$

The kinetic law for a first-order reaction is:

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

a) Half-Life Period ($t_{1/2}$)

The half-reaction time is defined as the time when:

$$[A] = \frac{[A]_0}{2}$$

Substituting into equation (*):

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

This simplifies to:

$$\ln(2) = kt_{1/2} \quad \Rightarrow t_{1/2} = \ln(2)/k$$

This equation shows that $t_{1/2}$ is independent of the initial concentration [A]. The fact that the half $t_{1/2}$, does not depend on $[A_0]$, implies that the reaction is of first order.

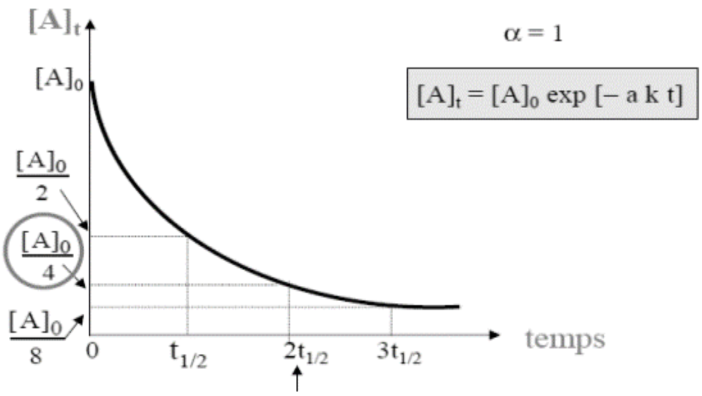


Figure III-1: The variation of [A] with time

b) Rate Constant

The rate constant can be expressed as:

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

Or,

$$k = \frac{1}{t} ln \frac{[A]_0}{[A]}$$

where k has units of t^{-1} (inverse time), typically s^{-1} for first-order reactions.

for a first-order reaction, a plot of $\ln[A]_t$ versus time will always be linear. The rate constant can be determined from the slope of this line, as illustrated in the figure below.

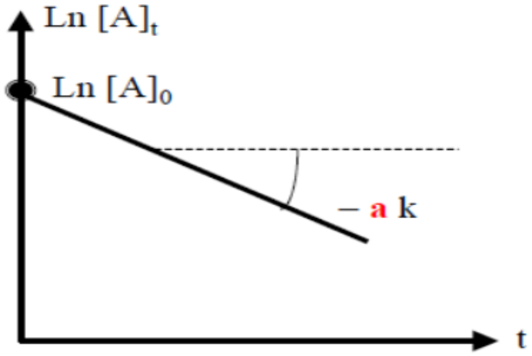


Figure III-2: Plot of $\ln[A]_t$ versus time for a first-order reaction

III.2.2 Second-Order Reaction (α=2)

Let us take a second order reaction:

$$A + B \xrightarrow{k} \text{Products}$$

The rate law for this reaction is expressed as follows:

$$R = -\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

And the rate expression is:

$$R=k[A][B]$$

Given that the partial order of A and B is 1, and assuming [A]=[B], the rate law becomes:

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

Rearranging:

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

Integrating both sides:

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

This leads to:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \qquad (**)$$

Equation (**) represents a straight line with slope k when plotting 1/[A] versus time.

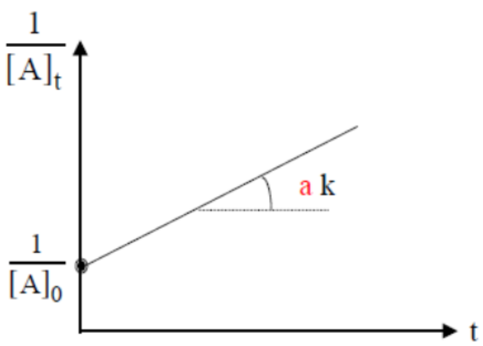


Figure III-3: Variation of $1/[A]_t$ as a function of time

The average rate constant is given by:

$$k_{moy} = \frac{\sum k_i}{n}$$

It can also be calculated using:

$$k = \frac{1}{t}\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) \qquad (k(t^{-1}.[]^{-1})$$

a) Half-Life Period ($t_{1/2}$)

At $t=t_{1/2}$, we have:

$$[A] = \frac{[A]_0}{2}$$

Substituting into equation (**):

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

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

This equation shows that $t_{1/2}$ is inversely proportional to the initial concentration $[A]_0$.

III.2.3 Zero-Order Reaction (α=0)

When the rate of reaction is independent of the concentration of reactants, the rate remains constant throughout the reaction, the reaction is said to be of zero order.

Consider the reaction:

$$A \xrightarrow{k} \text{Products}$$

The rate law is:

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

For a zero-order reaction, the rate expression becomes:

$$R=k[A]^0 =k$$

Thus, the rate law simplifies to:

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

Integrating both sides:

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

Solving the integral:

$$[A]_0 - [A] = kt \qquad => k = \frac{1}{t}([A]_0 - [A])$$

Half-Reaction Time ($t_{1/2}$)

At $t=t_{1/2}$, we have:

$$[A]=[A_0]/2$$

Substituting into the equation: $[A]_0 - [A] = kt$

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

III.2.4 n-Order Reaction (α=n>0)

The rate law for an n-order reaction is:

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

And the rate expression is:

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

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

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

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

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

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

This equation represents a straight line with slope (n-1)k.

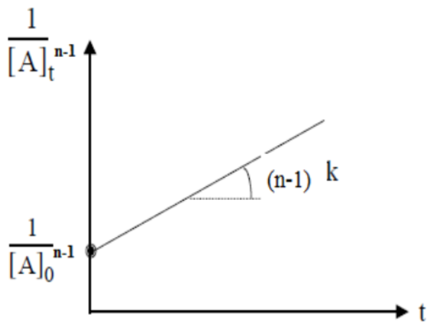


Figure III-2: Variation of $1/[A]_t^{n-1}$ as a function of time

The equation giving the half-life as a function of reaction order and initial concentration can be written in the general form:

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$$

III.2.5 Two-reagent system

Consider the reaction:

$$A + B \longrightarrow C$$

1/ If [A]=[B]

In this case, 1 mole of A reacts with 1 mole of B, and we have $[A_0]=[B_0]$, meaning [A]=[B]. We derive the rate law for a second-order reaction:

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

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

This is the same integrated rate law obtained previously for a second-order reaction with equal initial concentrations.

2/ If [A]#[B]

Let's assume:

- $[A]_0=a$; if x is the amount of A that has reacted, then $[A]=a-x$.
- $[B]_0=b$; if x is the amount of B that has reacted, then $[B]=b-x$.

$$R = \frac{-d(a-x)}{dt} = \frac{-d(b-x)}{dt} = \frac{dx}{dt} = k(a-x)(b-x)$$

$$\frac{dx}{(a-x)(b-x)} = kdt$$

We have

$$\frac{-d(a-x)}{(a-x)} = (b-x)kdt \qquad (1)$$

$$\frac{-d(b-x)}{(b-x)} = (a-x)kdt \qquad (2)$$

(2)-(1) =>

$$kdt = \frac{1}{a-b}\left(\frac{d(a-x)}{a-x} - \frac{d(b-x)}{b-x}\right)$$

Integrating both sides:

$$\int kdt = \frac{1}{a-b}\int \frac{d(a-x)}{a-x} - \int \frac{d(b-x)}{b-x}$$

$$kt + C = \frac{1}{a-b}[\ln(a-x) - \ln(b-x)]$$

At t=0; x=0 =>

$$C = \frac{1}{a-b} ln\frac{a}{b} \qquad => \qquad \ln\left(\frac{a-x}{b-x}\right) = ln\frac{a}{b} + kt(a-b)$$

III.3 Method for Determination of the Reaction Order

The study of reaction kinetics aims to establish the rate law and measure rate constant. The first step involves analyzing the contribution of each reactant or product by identifying its respective reaction order. Several experimental methods can be used to achieve this, but all rely on measuring the concentration of reactants or products at different time intervals.

III.3.1 Differential Method

This method, used by Van't Hoff, is called Van't Hoff's differential method. It consists of plotting the experimental data to analyze the relationship between the reaction rate and the concentration of a. If the experimental data represent the variation of the reaction rate as a function of the concentration of a reactant, the graph will reflect this relationship.

Consider the following reaction:

$$A \xrightarrow{k} \text{Products}$$

The rate of this reaction is given by:

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

By taking the natural logarithm of both sides, we obtain:

$$Ln\ R = Ln\ k + n\ Ln\ [A]$$

A plot of *ln R* versus *ln[A]* allows us to determine the reaction order, which corresponds to the slope of the line, and the rate constant, which is given by the intercept on the y-axis.

Note

- If ln(R) versus ln[A] plot is not linear, the reaction is of complex nature.
- If [A] = f(t) (zero-order), ln[A] = f(t) (first-order), or 1/[A] = f(t) (second-order), the resulting plot will be a straight line. This allows us to determine the overall order of the reaction as 0, 1, or 2, respectively.

III.3.2 Integration Method

In this method, the integrated rate equations are utilized. The concentration of the reactant (a– x) or the product (x) (where $[A]_0$=a and $[A]_t$=a-x) is experimentally measured at different time intervals (t). These values are then substituted into the various rate equations to calculate the rate constant (k) at different time points. he equation which gives
the constant value of rate constant indicates the order of reaction. For example, if the rate constants remain the same over different time intervals in the equation:

$$k = \frac{1}{t}(\frac{1}{a-x} - \frac{1}{a})$$

The order of the reaction will be 2. Thus, this is the trial method and can be used for simple homogenous reactions.

III.3.3 Half-life Period Method

The data for this method represent the variation of $t_{1/2}$ as a function of the initial concentration. Similar to the previous method, the order of the reaction must be assumed before calculating $t_{1/2}$.

- If $t_{1/2}$ is **proportional** to the initial concentration $[A]_0$, then the order of the reaction is 0:

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

- If $t_{1/2}$ is **independent** of the initial concentration $[A]_0$, then the order of the reaction is 1:

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

- If $t_{1/2}$ is **inversely proportional** to the initial concentration $[A]_0$, then the order of the reaction is 2 :

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

III.3.4 Initial Rates Method

This method is applicable when the rate law is expressed as:

$$R = k[A]^{\alpha}[B]^{\beta}$$

By applying the integral form, we obtain:

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

The experimental data represent the variation of the initial rate as a function of the initial concentrations of reactants A and B.

The partial orders α and β are determined using the analytical method (such as division or subtraction). To facilitate the determination of these partial orders, several experiments are typically conducted with different initial concentrations.

- First, a series of experiments is performed to obtain the initial rates as a function of different initial concentrations of one reactant.
- Then, a second series of experiments is carried out, where the concentration of the other reactant is kept constant (equal to the concentration of reactant A).

For the series of experiments in which the concentration of B is constant, we can write:

$$R_1 = k[A]_1^{\alpha}[B]_0^{\beta} \qquad (1)$$

$$R_2 = k[A]_2^{\alpha}[B]_0^{\beta} \qquad (2)$$

Dividing (1) by (2) =>

$$\frac{R_1}{R_2} = \frac{[A]_1^{\alpha}}{[A]_2^{\alpha}}$$

Taking the logarithm:

$$ln\frac{R_1}{R_2} = \alpha ln\frac{[A]_1}{[A]_2}$$

In this way, we can calculate the value of the partial order α. Similarly, the value of B can be determined.

III.3.5 Ostwald Isolation Method (or Order Degeneration Method)

When more than one reactant is involved in the reaction, it is necessary to isolate one of the reactants in order to study its influence on the rate of reaction. The technique of isolating one reactant from rest, developed by Ostwald (1902), is based on the fact that if any reactant is taken in large excess, its concentration virtually constant, and thus it does not affect the rate of reaction.

Let us consider a reaction involving three reactants. A, B and C with reaction orders α, β and γ with respect to A, B and C, respectively. If the reaction is carried out under the conditions where B and C are present in large excess, the reaction rate will be given by:

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

Then apparent order α with respect to A may be determined by any method described earlier. Similarly, the value of β can be determined by taking a large excess of A and C. and the value of γ can be determined by taking a large excess of A and B.

Exercises

Exercise N°1

When studying, at 48°C, the decomposition reaction of benzene diazonium chloride:

$$C_6H_5N_2Cl \rightarrow C_6H_5Cl + H_2$$

It is found that the reactant is half decomposed after 16.4 minutes, regardless of its initial concentration.

1- Order of the reaction – Explain?
2- Rate constant k – Unit?
3- After how much time is the reactant 80% decomposed?

Exercise N°2

A certain reaction has the following general form:

$$aA \rightarrow bB$$

At a specific temperature and starting with an initial concentration of $[A]_0 = 2.10^{-2}$ M, data was collected on the variation of concentration with time. By plotting ln[A] as a function of time, a straight line was obtained with a slope of $(-2.97\times10^{-2}min^{-1})$.
1- Determine the rate law in both differential and integral forms. From this, deduce the rate constant for this reaction.
2- Calculate the half-life. 3- What is the time required for the concentration of A to become equal to 2.5×10^{-3} M?

Exercise N°3

For the reaction: $A + B \rightarrow C + D$

the following data were obtained:

Time (sec)	0	178	275	530	860	1500
$[A] \times 10^3$ ($mol.dm^{-3}$)	9.8	8.9	8.6	8.0	7.3	6.5
$[B] \times 10^3$ ($mol.dm^{-3}$)	4.8	4.0	3.7	3.0	2.3	1.5

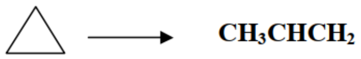
Calculate the rate constant and confirm that reaction is of second order. How the rate constant can be obtained graphically?

Exercise N°4

In a reaction when initial concentration doubles, the half-life is reduced to half. What is the order of reaction?

Exercise N°5

The kinetics of the isomerisation reaction of cyclopropane (A) to propylene (B) is carried out according to the following reaction:



Measuring the rate relative to A at 480°C led to the following table:

[A] (mol/l)	50	46	38	15	12
R (µmol/l)	8.3	7.5	6.33	2.41	1.97

1-Calculate the rate constant k and determine the order of the reaction.

2-After how much time is the concentration reduced to 1/5 of its initial value?

3-If the reaction is carried out at 510°C, and the constant k is equal to $9.47 \times 10^{-4} s^{-1}$, calculate the activation energy Ea of this reaction.

Exercise N°6

$$A_{(g)} \longrightarrow \text{Products}$$

Express the rate laws and kinetic equations for reactions of orders 0, 1, 2, and n that occur in the gas phase. What would be the half-life for each case?

Exercise N°7

The thermal decomposition of tertiary butyl peroxide into acetone and ethane in the gas phase can be monitored by measuring variations in total pressure at constant volume.

$$(CH_3)_3COOC(CH_3) \longrightarrow 2CH_3COCH_3 + C_2H_6$$

The following results were obtained at T=147°C:

Time (min)	0	5	10	20	30	50
P (HPa)	250	272	293	332	368	431

1- Establish the relationship between C_0, P_0, the peroxide concentration at time t(C), and the total pressure P_t, $C = f(C_0, P_0, P_t)$.

2- Assuming first-order kinetics, show that the rate law can be written as:

$$ln \frac{2P_0}{(3P_0 - P_t)} = kt$$

3- Show that the results in the table are consistent with first-order kinetics and calculate the rate constant.

Exercise Corrections

Exercise N°1

1-Order of the Reaction

Since the half-life is constant and does not depend on the initial concentration of benzene diazonium chloride, this confirms that the reaction is **first-order ($t_{1/2}$ = ln2/k).**

2- Rate Constant k

$$t_{1/2} = \frac{\ln(2)}{k} \Rightarrow k = \frac{\ln(2)}{t_{1/2}} = \frac{0.69}{16.4} = 0.042\ min-1$$

3- After How Much Time Is the Reactant 80% Decomposed?

80% of the reactant decomposed => the rest = 100%-80% = 20%

$$[A] = (\frac{20}{100})[A]_0$$

$$Ln(\frac{[A]_0}{[A]}) = kt$$

$$\Rightarrow t = \frac{1}{k} Ln\left(\frac{[A]_0}{[A]}\right) = 40\ min$$

Exercise N°2

1- Rate Law (Differential and Integral Forms)

Differential Form of the Rate Law:

For a reaction of the form: aA→bB

the differential form of the rate law for a first-order reaction is:

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

Integral Form of the Rate Law:

The integrated rate law for a first-order reaction is: $\ln[A] = ln[A]_0 - kt$

Deduction of the Rate Constant:

From the data, the slope of the ln[A] vs. time plot is (-2.97×10^{-2} min^{-1}). The slope is equal to (-k) for a first-order reaction, so: k= 2.97×10^{-2} min^{-1}

2- Half-Life of the Reaction

For a first-order reaction, the half-life $t_{1/2}$ is given by the equation:

$$t_{1/2} = \frac{\ln(2)}{k} = 23.34\,min$$

3- Time Required for $[A]=2.5\times10^{-3}$ M

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

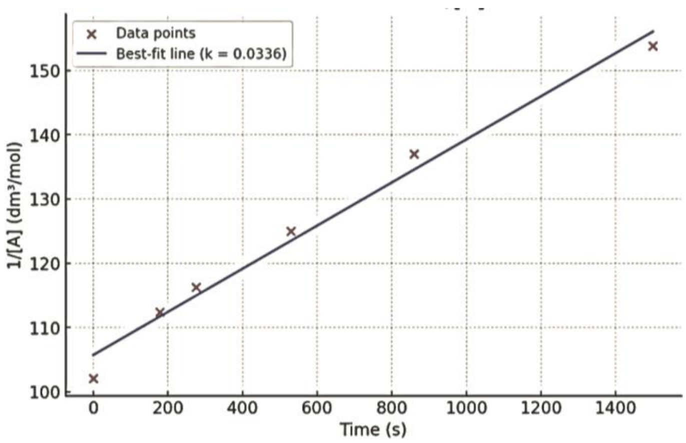
$$t = \frac{1}{k}\ln\left(\frac{[A]_0}{[A]}\right) = 70.03\,min$$

Exercise N°3

If the reaction is second-order, the integrated rate law for A + B → C + D is:

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

So, if we plot 1/[A] vs. time, we should get a straight line with slope k.



The rate constant (k) for the reaction is 0.0336 dm³/mol·s, confirming that the reaction follows second-order kinetics**.**

Note: We can use another method by calculating the rate constant k through different calculations for each experiment.

Exercise N°4

The observation that doubling the initial concentration reduces the half-life to half suggests that the reaction is second-order.

For a second-order reaction, the half-life is given by: $t_{1/2} = \frac{1}{k[A]_0}$

So,

$$t_{1/2} \propto 1/[A]_0$$

This means that the half-life decreases as the initial concentration increases which is consistent with the given observation.

Exercise N°5

1- Calculate the rate constant (k) and determine the order of the reaction

We are given data on the concentration of cyclopropane [A]and the rate of the reaction R. To determine the order of the reaction, we can plot the data and analyze the relationship between [A] and R.

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

$$\ln R = lnk + nln[A]$$

We plot lnR vs. ln[A].

Ln[A]	3.91	3.83	3.64	2.71	2.48
lnR	-11.7	-11.8	-11.97	-12.94	-13.14

Slope = n = 1 => The reaction is the first-order.

The y-intercept = ln(k) = -15.665 => k = 1.57x10^{-7} s^{-1}

2- How long will it take for the concentration to be reduced to 1/5 of its initial value?

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

$$t = \frac{1}{k}\ln\left(\frac{[A]_0}{[A]}\right)$$

[A] decrease to 1/5 of its initial concentration => 4/5 of its initial value remains

$$=> [A] = \frac{4}{5}\,[A]_0$$

$$t = \frac{1}{k}\ln\left(\frac{[A]_0}{[A]}\right) = \frac{1}{k}\ln\left(\frac{5 \times [A]_0}{4 \times [A]_0}\right) = 0.14 \times 10^7 s$$

3- Calculate the activation energy (Ea) from the rate constant at a different temperature

We can use the Arrhenius equation to find the activation energy Ea:

$$k = Ae^{-Ea/RT}$$

$$k_1 = Ae^{-Ea/RT_1} \Rightarrow lnk_1 = lnA - \frac{Ea}{RT_1} \qquad (1)$$

$$k_2 = Ae^{-Ea/RT_2} \Rightarrow lnk_2 = lnA - \frac{Ea}{RT_2} \qquad (2)$$

(1)-(2) => $Ea = \frac{Rln\left(\frac{k_1}{k_2}\right)}{\frac{1}{T_2}-\frac{1}{T_1}} = 1247.77\ kJ/mol$

Exercise N°6

Consider the general gas-phase decomposition reaction:

$A_{(g)} \rightarrow$ Products

1- Zero-Order Reaction (n=0)

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

$$PV = nRT \Rightarrow \frac{n}{V} = \frac{P}{RT} = C = [A]$$

$$-\frac{d\left({}^{P}/_{RT}\right)}{dt} = k$$

$$-d\left(\frac{P}{RT}\right) = kdt$$

$$-\left(\frac{1}{RT}\right)\int_{P_0}^{p} dp = k\int_0^t dt$$

$$\frac{1}{RT}(P_0 - P) = kt$$

Half-Life ($t_{1/2}$):

$$[A] = \frac{P}{RT} \Rightarrow [A]_0 = \frac{P_0}{RT}$$

The half-life is the time required for the concentration of A to decrease by half:

$$[A] = \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{P_0}{2kRT}$$

The half-life depends on the initial pressure: the larger P_0, the longer $t_{1/2}$.

2- First-Order Reaction (n=1)

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

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

$$PV = nRT \Rightarrow \frac{n}{V} = \frac{P}{RT} = C = [A]$$

$$-\frac{d\left(P/_{RT}\right)}{P/_{RT}} = kdt$$

$$-\int_{P_0}^{p} \frac{dP}{P} = k\int_0^t dt$$

$$\left(ln\frac{P_0}{P}\right) = kt$$

Half-Life ($t_{1/2}$):

$$t_{1/2} = \frac{ln2}{k}$$

The half-life is constant and independent of the pressure

3- Second-Order Reaction (n=2)

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

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

$$-\frac{d\left(P/_{RT}\right)}{\left(P/_{RT}\right)^2} = kdt$$

$$-\int_{P_0}^{p} \frac{dp}{p^2} = k\frac{1}{RT}\int_0^t dt$$

$$\left(\frac{1}{P_0} - \frac{1}{P}\right) = \frac{k}{RT}t$$

Half-Life ($t_{1/2}$): $t_{1/2} = \frac{RT}{kP_0}$

$t_{1/2}$ decreases as P_0 increases, meaning the reaction proceeds faster at higher initial pressure.

4- General Order Reaction (n)

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

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

$$-\frac{d\left(P/_{RT}\right)}{\left(P/_{RT}\right)^n} = kdt$$

$$-\int_{P_0}^{p}\frac{dp}{p^n} = k\frac{1}{(RT)^{n-1}}\int_0^t dt$$

$$\frac{1}{1-n}\left(P_0^{1-n} - P^{1-n}\right) = \frac{k}{(RT)^{n-1}}t$$

Half-Life ($t_{1/2}$):

$$t_{1/2} = \frac{(RT)^{n-1}(2^{n-1}-1)}{(n-1)kP^{n-1}}$$

The half-life depends on (P_0^{n-1}) and decreases as n increases.

Exercise N°7

1- The relationship between C_0, P_0, the peroxide concentration at time t(C), and the total pressure P_t, C = f (C_0, P_0, P_t).

The form of the thermal decomposition reaction is:

	A →	2B+C	
t_0	C_0, n_0	0	0
t	$n_0(1-x)$	$2x\,n_0$	$x\,n_0$

$$n_t = n_0 + n_0x + 2n_0x + n_0x = n_0(1+2x) \qquad (C = C_0(1-x))$$

$$P_tV = n_tRT \;=>\; \frac{P_tV}{RT} = \frac{P_0V}{RT}(1+2x)$$

$$P_t = P_0(1+2x) \;=>\; \frac{P_t}{P_0} = 1+2x$$

$$=> x = \frac{P_t - P_0}{2P_0}$$

$$C = C_0\left(1 - \frac{P_t - P_0}{2P_0}\right)$$

$$\frac{C}{C_0} = \frac{2P_0 - P_t + P_0}{2P_0} = \frac{3P_0 - P_t}{2P_0}$$

$$=> \frac{C}{C_0} = \frac{3P_0 - P_t}{2P_0} \qquad (1)$$

2- If n=1,

$$R = -\frac{dC}{dt} = kC$$

$$-\int_{C_0}^{C} \frac{dC}{C} = k\int_0^t dt$$

$$=> \ ln\frac{C_0}{C} = kt \qquad (2)$$

By substituting Eq. (1) into Eq. (2):

$$ln\frac{2P_0}{3P_0 - P_t} = kt$$

3- Verify First-Order Kinetics and Calculate k

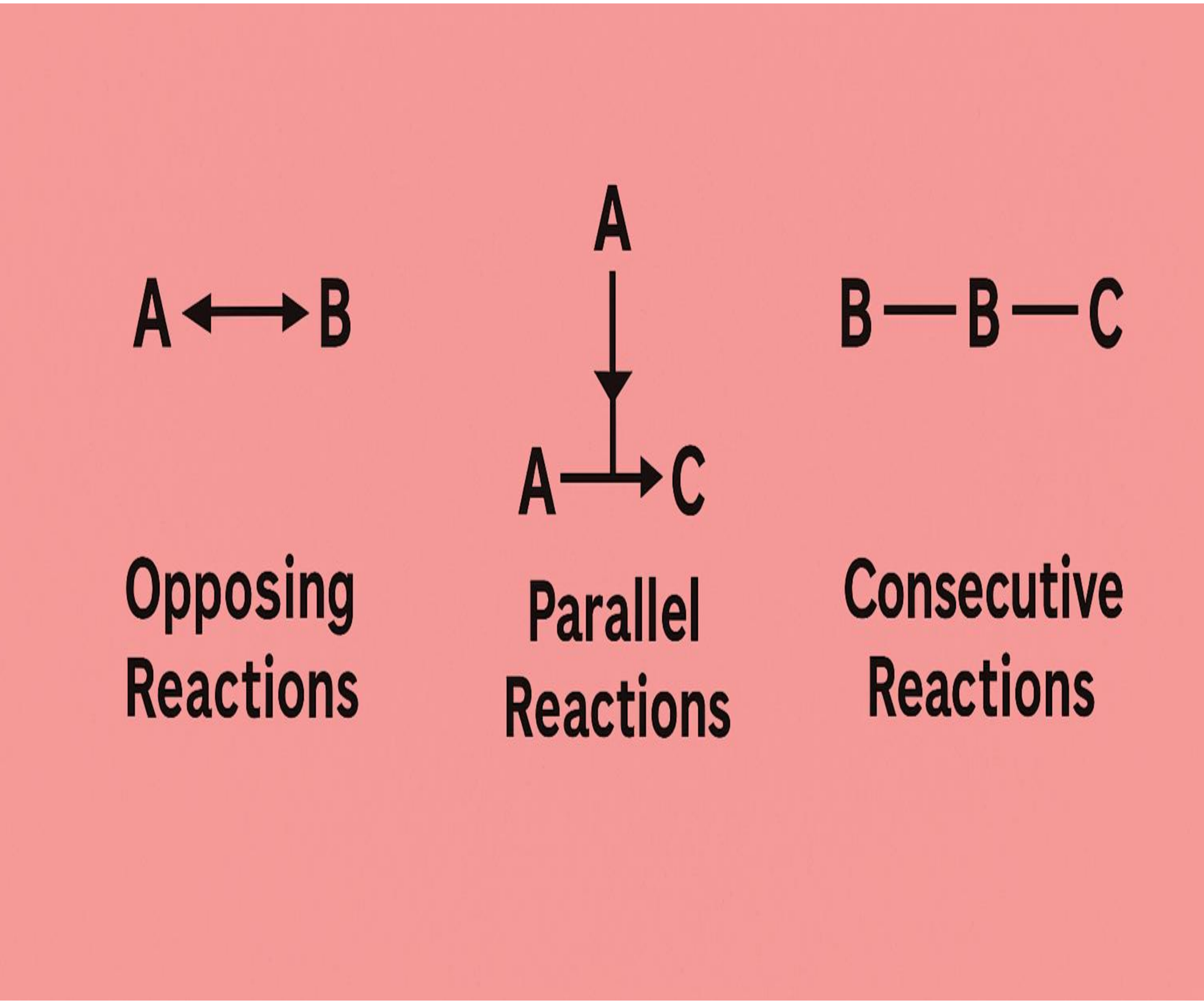
To verify first-order kinetics, we check if plotting ($ln(2P_0/(3P_0-P_t))$) against (t) gives a straight line.

Or, compute ($ln(2P_0/(3P_0-P_t))$) for each time value and determine k.

Time (min)	0	5	10	20	30	50
P (HPa)	250	272	293	332	368	431
k (min^{-1})	/	0.009	0.00899	0.00895	0.00897	0.00898

$$k \approx constant \quad => \quad n = 1$$

$$k = k_{moy} = \frac{\sum k_i}{5} = 9 \times 10^{-3}\ min^{-1}$$



CHAPTER IV

KINETICS OF COMPLEX REACTIONS

CHAPTER IV : KINETICS OF COMPLEX REACTIONS

IV.1 Introduction

In kinetics, a complex reaction refers to a reaction mechanism consists of multiple elementary steps. In this chapter, we will explore various types of complex reactions and the rate laws that can be derived from their kinetic mechanisms. The types of complex reactions discussed include opposing reactions, parallel reactions, and consecutive reactions.

IV.2 Reversible Reactions

In a reversible process, if the rate of backward reaction is much smaller compared to the rate of forward reaction, the equilibrium will be far away from the starting end and the reaction may appear to follow a simple and straightforward path as discussed earlier. However, when the reaction rates are appreciable for both the forward and backward directions, the kinetics must be taken into account.

Let us consider a general reaction:

$$A + B \underset{K_2}{\overset{k_1}{\rightleftharpoons}} C + D$$

Rate of forward reaction (***A+B*** $\longrightarrow$ ***C+D)***: $\boldsymbol{R_1 = k_1[A]^{\alpha 1}[B]^{\beta 1}}$.

Rate of backward reaction (***C+D*** $\longrightarrow$ ***A+B***): $\boldsymbol{R_2 = k_2[A]^{\alpha 2}[B]^{\beta 2}}$.

The overall rate of reaction (net rate) of product formation will be the difference between the two opposing rates **(*R*= *R₁* - *R₂*)**.

The overall reaction rate consists of:

$$R = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$
$$= k_1[A]^{\alpha 1}[B]^{\beta 1} - k_2[C]^{\alpha 2}[D]^{\beta 2}$$

This expression is simplified by assuming simple initial conditions:

$$A + B \underset{K_2}{\overset{k_1}{\rightleftharpoons}} C + D$$

$t=0$	a	a	0	0
t	$a-x$	$a-x$	x	x
$l' \rightleftharpoons$	$a-x_{eq}$	$a-x_{eq}$	x_{eq}	x_{eq}

$$R = \frac{dx}{dt} = k_1(a-x)^{\alpha 1+\beta 1} - k_2(x)^{\alpha 2+\beta 2}$$

At equilibrium, the rate of forward reaction is equal to backward reaction and, therefore, net rate of reaction will be zero. Thus, at equilibrium when: x = x eq (at t $\longrightarrow$ ∞ (equilibrium) => R=0)

$$k_1(a-x_{eq})^{\alpha_1+\beta_1} - k_2\left(x_{eq}\right)^{\alpha_2+\beta_2} = 0$$

$$\frac{K_1}{K_2} = \frac{\left(x_{eq}\right)^{\alpha_2+\beta_2}}{\left(a-x_{eq}\right)^{\alpha_1+\beta_1}} = \frac{[C]_{eq}^{\alpha_2}[D]_{eq}^{\beta_2}}{[A]_{eq}^{\alpha_1}[B]_{eq}^{\alpha_1}} = K_{eq}$$

K_{eq}: is the equilibrium rate constant determined when (t $\longrightarrow$ ∞)

IV.2.1 First-Order Reaction (1)

Let us consider a simple reaction:

$$A \underset{K_2}{\overset{k_1}{\rightleftharpoons}} B$$

At t=0	a	0
t	a-x	x
t_{eq}	$a-x_{eq}$	x_{eq}

The net rate of reaction can be written as:

$$R = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A]^1 - k_2[B]^1 = \frac{dx}{dt}$$

$$R = \frac{dx}{dt} = k_1(a-x) - k_2(x) \qquad (1)$$

At t $\longrightarrow$ ∞ (equilibrium) => R=0

$$k_1(a-x_{eq}) - k_2(x_{eq}) = 0$$

$$k_1 a = (k_1 + k_2)\,(x_{eq}) \qquad (2)$$

We substitute equation (2) into equation (1) and rearrange:

$$\frac{dx}{dt} = (k_1 + k_2)(x_{eq} - x)$$

$$=> \frac{dx}{(x_{eq} - x)} = (k_1 + k_2)\,dt$$

$$=> \int_0^{x_{eq}} \frac{-d(x_{eq} - x)}{(x_{eq} - x)} = (k_1 + k_2)\int_0^t dt$$

By integrating this equation, we obtain:

$$Ln\,\frac{x_{eq}}{(x_{eq} - x)} = (K_1 + K_2)\mathrm{t}$$

At equilibrium, the concentration measurements give:

$$\frac{K_1}{K_2} = \frac{x_{eq}}{(x_{eq} - x)} = \frac{[B]_{eq}}{[A]_{eq}} = K_{eq}$$

IV.2.2 Second-order reaction (2)

Let us consider a general reaction:

$$A + B \underset{K_2}{\overset{k_1}{\rightleftharpoons}} C + D$$

t=0	a	a	0	0
t	a-x	a-x	x	x
t_{eq}	$a-x_{eq}$	$a-x_{eq}$	x_{eq}	x_{eq}

The net rate of reaction can be written as:

$$R = \frac{dx}{dt} = k_1(a - x)^2 - k_2(x)^2 \qquad (3)$$

At t $\longrightarrow$ ∞ (equilibrium) => R=0

$$k_1(a - x_{eq})^2 - k_2\left(x_{eq}\right)^2 = 0$$

$$k_2 = k_1\,\frac{(a - x_{eq})^2}{\left(x_{eq}\right)^2} \qquad (4)$$

We substitute equation (4) into equation (3):

$$R = \frac{dx}{dt} = k_1\left[(a-x)^2 - \frac{(a-x_{eq})^2}{(x_{eq})^2}x^2\right]$$

$$= \frac{k_1}{x_{eq}^2}\left[(a-x)^2x_{eq}^2 - (a-x_{eq})^2x^2\right]$$

$$= \frac{k_1}{x_{eq}^2}\left[((a-x)x_{eq} + (a-x_{eq})x)((a-x)x_{eq} - (a-x_{eq})x)\right]$$

$$= \frac{k_1}{x_{eq}^2}\left[(ax_{eq} - xx_{eq} + ax - xx_{eq})(ax_{eq} - xx_{eq} - ax + xx_{eq})\right]$$

$$= \frac{k_1}{x_{eq}^2}a\left[(ax_{eq} - 2xx_{eq} + ax)(x_{eq} - x)\right]$$

$$= \frac{k_1}{x_{eq}^2}a\left[(ax_{eq} + x(a - 2x_{eq})(x_{eq} - x)\right] \qquad \times (\frac{2x_{eq}-a}{2x_{eq}-a})$$

$$= \frac{k_1}{x_{eq}^2}a(2x_{eq} - a)(\frac{ax_{eq}}{2x_{eq}-a} - x)(x_{eq} - x) \qquad (5)$$

The solution of the differential equation (5) is of type:

$$\frac{dx}{dt} = k'(a'-x)(b'-x)$$

Where:

$$a' = \frac{ax_{eq}}{2x_{eq}-a}\ ,\ b' = x_{eq}, k' = k_1\frac{a}{x_{eq}^2}(2x_{eq} - a)$$

Integration and initial conditions (t = 0, x = 0) give the following kinetic equation:

$$\frac{dx}{dt} = k'(a'-x)(b'-x)$$

Separating the variables gives:

$$\frac{dx}{(a'-x)(b'-x)} = k'dt$$

Integrating both sides between the limits x=0 and t=0:

$$\int_0^x \frac{dx}{(a'-x)(b'-x)} = \int_0^t k'dt = k't$$

Using partial fraction decomposition:

$$\frac{1}{(a'-x)(b'-x)} = \frac{1}{b'-a'}(\frac{1}{a'-x} - \frac{1}{b'-x})$$

$$\frac{1}{b' - a'}\left[ln\left(\frac{b' - x}{a' - x}\right)\right]_0^x = \frac{1}{b' - a'}\left(ln\frac{b' - x}{a' - x} - ln\frac{b'}{a'}\right)$$

Simplifying, we obtain:

$$ln\left(\frac{b' - x}{a' - x}.\frac{a'}{b'}\right) = (b' - a')k't$$

Substituting the expressions for a', b' and k' into this equation, we obtain:

$$ln\left(\frac{a(x_{eq} - x)}{(2x_{eq} - a)(\frac{ax_{eq}}{2x_{eq} - a} - x)}\right) = \frac{2ak_1(x_{eq} - a)}{x_{eq}}t$$

At equilibrium, the concentration measurements give:

$$\frac{K_1}{K_2} = \frac{x_{eq}^2}{(a - x_{eq})^2} = K_{eq}$$

IV.2.3 Reaction of order (2/1)

Consider the following reaction:

$$A + B \underset{K_2}{\overset{k_1}{\rightleftharpoons}} C$$

t=0	a	a	0
t	a-x	a-x	x
t_{eq}	a-x_{eq}	a-x_{eq}	x_{eq}

The net rate of reaction can be written as:

$$R = \frac{dx}{dt} = k_1(a - x)^2 - k_2x \qquad (6)$$

At equilibrium:

$$R = \frac{dx}{dt} = k_1(a - x_{eq})^2 - k_2x_{eq} = 0$$

$$k_2 = k_1\frac{(a-x_{eq})^2}{x_{eq}} \qquad (7)$$

We substitute equation (7) into equation (6):

$$R = \frac{dx}{dt} = k_1(a-x)^2 - k_1\frac{(a-x_{eq})^2}{x_{eq}}x$$

$$\frac{dx}{dt} = k_1\left[(a-x)^2 - \frac{(a-x_{eq})^2}{x_{eq}}x\right]$$

$$= \frac{k_1}{x_{eq}}\left[(a-x)^2 x_{eq} - (a-x_{eq})^2 x\right]$$

$$= \frac{k_1}{x_{eq}}\left[(a^2-2ax+x^2)x_{eq} - \left(a^2-2ax_{eq}+{x_{eq}}^2\right)x\right]$$

$$= \frac{k_1}{x_{eq}}\left[a^2x_{eq} - 2axx_{eq} + x^2x_{eq} - a^2x + 2axx_{eq} - {x_{eq}}^2x\right]$$

$$= \frac{k_1}{x_{eq}}\left[a^2(x_{eq}-x) + xx_{eq}(x-x_{eq})\right]$$

$$= k_1(\frac{a^2}{x_{eq}} - x)(x_{eq}-x)$$

This differential equation can be written as follows:

$$\frac{dx}{dt} = k'(a'-x)(b'-x) \qquad (6)$$

The solution of the differential equation (6) is of type:

$$Ln\left[\frac{a'(b'-x)}{b'(a'-x)}\right] = K'(b'-a')t$$

Where:

$$K' = K_1, a' = \frac{a^2}{x_{eq}}, \; b' = x_{eq}$$

Integration with the initial conditions (t=0, x=0) yields the following kinetic equation:

$$ln\left[\frac{\frac{a^2}{x_{eq}}(x_{eq}-x)}{x_{eq}(\frac{a^2}{x_{eq}}-x)}\right] = k_1\left(x_{eq} - \frac{a^2}{x_{eq}}\right)t$$

$$ln\left[\frac{a^2(x_{eq}-x)}{x_{eq}(a^2-xx_{eq}}\right] = k_1\left(\frac{x_{eq}^2-a^2}{x_{eq}^2}\right)t$$

$$\left(\frac{x_{eq}}{x_{eq}^2-a^2}\right) ln\left[\frac{a^2(x_{eq}-x)}{x_{eq}(a^2-xx_{eq}}\right] = k_1 t$$

$$\left(-\frac{x_{eq}}{x_{eq}^2 - a^2}\right) ln\left[\frac{x_{eq}(a^2 - xx_{eq})}{a^2(x_{eq} - x)}\right] = k_1 t$$

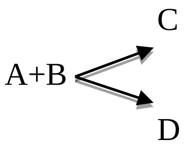
$$\left(\frac{x_{eq}}{a^2 - x_{eq}^2}\right) ln\left[\frac{x_{eq}(a^2 - xx_{eq})}{a^2(x_{eq} - x)}\right] = k_1 t$$

At equilibrium, the concentration measurements give:

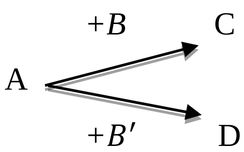
$$\frac{k_1}{k_2} = \frac{x_{eq}}{(a - x_{eq})^2} = k_{eq}$$

IV.3 Parallel (or side) reactions

The term parallel reactions describe situations in which reactants can undergo two or more reactions independently and concurrently. These reactions may be reversible or irreversible. They include cases where one or more species may react through alternative pathways to produce two or more different products (simple parallel reactions).



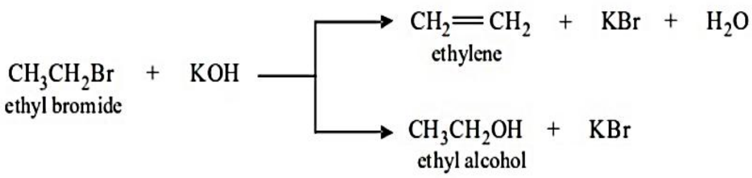
As well as cases where one reactant may not be common to both reactions (competitive parallel reactions).



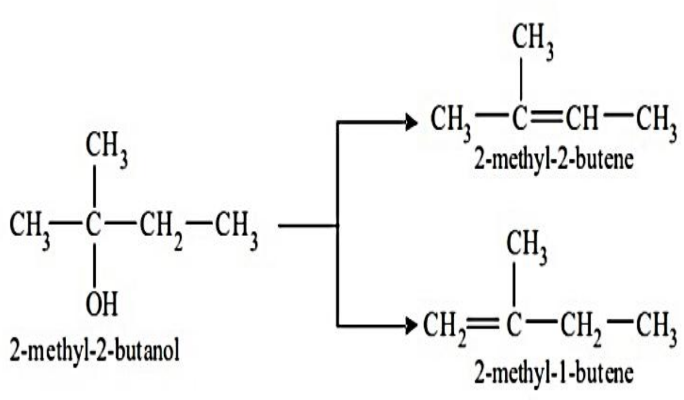
In this section we will consider the kinetic implications of both general classes of parallel reactions.

Examples of Parallel or Side Reactions:

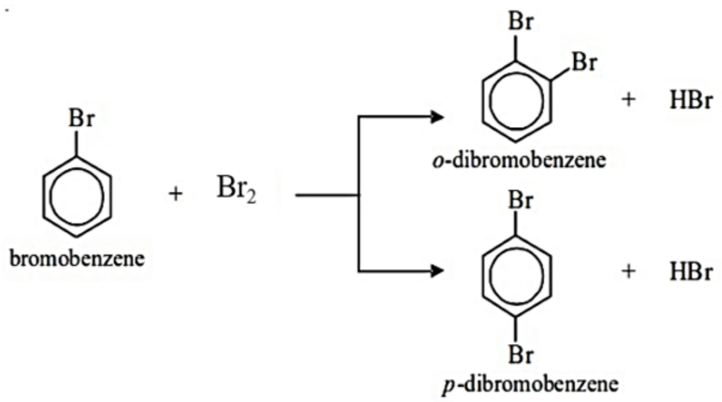
(a) Reaction of ethyl bromide with potassium hydroxide



(b) Dehydration of 2-methyl–2–butanol



(c) Bromination of bromobenzene



IV.3.1 Twin Parallel Reactions

Consider the following reaction: Br_2

$$A+B \xrightarrow{K_1} C$$
$$A+B \xrightarrow{K_2} D$$

In the above reaction, the reactants A and B give two products C and D, in two separate reactions different reactions with rate constants K_1 and K_2 respectively. If $K_1 > K_2$ the reaction A + B → C will be the major reaction while A + B→ D will be the side or parallel reaction.

The material balance is:

	A	B	C	D
t=0	a	a	0	0
t	a-x	a-x	y	z

Where: x=y+z

The rate of disappearance of A (or B) is:

$$R_{dis(A)} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -\frac{d(a-x)}{dt}$$

$$= -\frac{d(a-x)}{dt} = k_1(a-x)^{\alpha} + k_2(a-x)^{\beta} = \frac{dx}{dt}$$

The rate of appearance of C (or D) is:

$$R_{app(c)} = \frac{d[C]}{dt} = \frac{dy}{dt} = k_1(a-x)^{\alpha}$$

$$R_{app(D)} = \frac{d[D]}{dt} = \frac{dz}{dt} = k_2(a-x)^{\beta}$$

And we have:

$$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt}$$

$$\frac{(\frac{dy}{dt})}{(\frac{dx}{dt})} = \frac{dy}{dx} = \frac{k_1(a-x)^{\alpha}}{k_1(a-x)^{\alpha} + k_2(a-x)^{\beta}}$$

$$\frac{(\frac{dz}{dt})}{(\frac{dx}{dt})} = \frac{dz}{dx} = \frac{k_2(a-x)^{\beta}}{k_1(a-x)^{\alpha} + k_2(a-x)^{\beta}}$$

In the case of: $\alpha = \beta$

$$\frac{dy}{dx} = \frac{k_1}{k_1 + k_2} \Rightarrow y = \frac{k_1}{k_1 + k_2}x$$

$$\frac{dz}{dx} = \frac{k_2}{k_1 + k_2} \Rightarrow z = \frac{k_2}{k_1 + k_2}x$$

$$\frac{y}{z} = \frac{k_1}{k_2} = constant$$

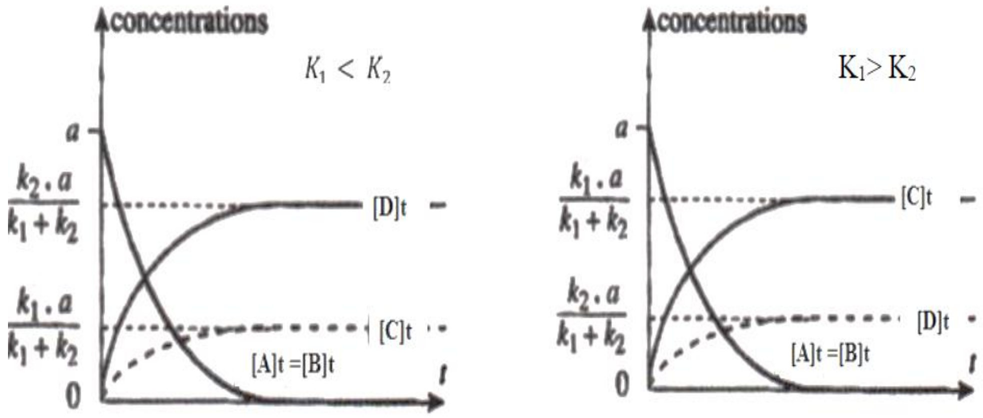


Figure IV-1: Variation of concentration with time

IV.3.2 Concurrent Reactions

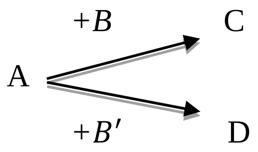
The mathematical treatment of this type of parallel reaction is generally more complex than the previous one because in this case there is only one common reactant.

Example:

$$CH_3CH_2Cl + OH^- \xrightarrow{k_1} CH_3CH_2OH + Cl^-$$

$$(CH_3)_2CHCl + OH^- \xrightarrow{k_2} (CH_3)_2CHOH + Cl^-$$

Let us consider a general reaction:



The rate constants of these two competitive reactions are k_1 and k_2.

The material balance is:

	A	B	B'	C	D
At t=0	a	b	b'	0	0
t	a-x	b-y	b'-z	y	z

x represents the concentration of A consumed at time t (x=y+z).

Let us assume that both these reactions are of first order. The differential rate expressions are:

$$-\frac{d[A]}{dt} = k_1(a-x)(b-y) + k_2(a-x)(b'-z)$$

$$\frac{d[C]}{dt} = \frac{dy}{dt} = k_1(b-y)(a-x)$$

$$\frac{d[D]}{dt} = \frac{dz}{dt} = k_2(b'-z)(a-x)$$

adding these two equations gives:

$$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt} = (a-x)[k_1(b-y) + k_2(b'-z)]$$

knowing that at t=0, y=z=0, by eliminating time as an independent variable we obtain:

$$\frac{dy}{dz} = \frac{k_1}{k_2}(\frac{b-y}{b'-z})$$

By integrating this equation, we get::

$$\int_0^y \frac{dy}{b-y} = \frac{k_1}{k_2}\int_0^z \frac{dz}{b'-z}$$

$$-ln\frac{b-y}{b} = -\frac{k_1}{k_2}\ln(\frac{b'-z}{b'})$$

$$ln\frac{b}{b-y} = -\frac{k_1}{k_2}\ln(\frac{b'}{b'-z})$$

$$\frac{b}{b-y} = \left(\frac{b'}{b'-z}\right)^{\frac{k_1}{k_2}}$$

The ratio k_1/k_2 can be determined by plotting ln[b/(b-y)] as a function of ln[b'/(b'-z)] (the slope of the straight line obtained).

IV.4 Consecutive Reactions

Reactions in which the reactants are converted to products through one or more intermediate stages are called consecutive reactions. The overall reaction is a result of several consecutive steps. Every stage has its own reactant and rate constant.

The simplest case is that of two successive reactions of first order, with rate constants k_1 and k_2.

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

	A	B	C	
At t=0	a	0	0	
t	a-x	x-y	y	*([A]₀ = [A]+[B]+[C])*

The differential rate expressions are:

$$-\frac{d[A]}{dt} = k_1[A] \quad or \quad \frac{dx}{dt} = k_1(a-x) \qquad (1)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad (2)$$

$$\frac{d[C]}{dt} = k_2[B] \qquad (3)$$

The solution to the first equation (1) is:

$$[A] = [A]_0 e^{-k_1 t} \quad \text{or} \quad x = a(1 - e^{-k_1 t})$$

This result can be substituted into the second equation (2):

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

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

It is a first-order differential equation with a non-homogeneous second member. Its general solution is the sum of the particular solution and the solution of the homogeneous equation (S = Sh+Sp).

This reaction has a general solution of the form:

$$[B] = Cst(e^{-k_1 t} - e^{-k_2 t})$$

Solving the differential equation leads to:

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

Graphic study

The concentration of A decreases over time following an exponential law (first-order kinetics). B does not accumulate indefinitely, as it is gradually transformed into C. Therefore, a maximum concentration of B is observed, which corresponds to the point where d[B]/dt=0.

C begins to appear slowly at the start of the reaction (induction period), which is the time it takes for B to start forming.

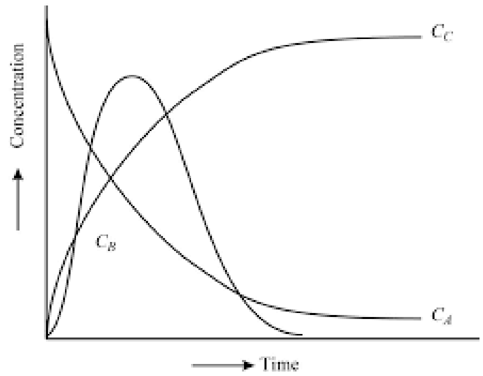


Figure IVV-2: Time dependence of species concentrations for the consecutive reactions

IV.4.1 Consecutive Reversible Reactions

Let us consider a general reaction:

$$A \xrightarrow{k_1} B \underset{k_3}{\overset{k_2}{\rightleftharpoons}} C$$

	A	B	C
At t=0	a	0	0
t	a-x	y	z

x represents the concentration of A consumed at time t. $\left\{\begin{matrix} x = y + z \\ => y = x - z \end{matrix}\right\}$

$$\frac{d[A]}{dt} = \frac{dx}{dt} = k_1(a - x) \qquad (1)$$

$$\frac{d[B]}{dt} = \frac{dy}{dt} = k_1(a - x) - k_2 y + k_3 z \qquad (2)$$

$$\frac{d[C]}{dt} = \frac{dZ}{dt} = k_2 y - k_3 z \qquad (3)$$

Replacing *y* by *(x-z)* in equation (3) gives:

$$\frac{dz}{dt} = k_2(x - z) - \ k_3 z$$

$$\frac{dz}{dt} + Kz = k_2 x \qquad (K = k_2 + k_3)$$

The differential equation obtained is non-homogeneous and linear. its integration, taking into account the initial conditions, leads to:

$$z = \frac{k_2 a}{K}(1 - e^{-Kt}) + \frac{k_2 a}{K - k_1}(e^{-Kt} - e^{-k_1 t})$$

$$x = a(1 - e^{-k_1 t})$$

$$y = x - z$$

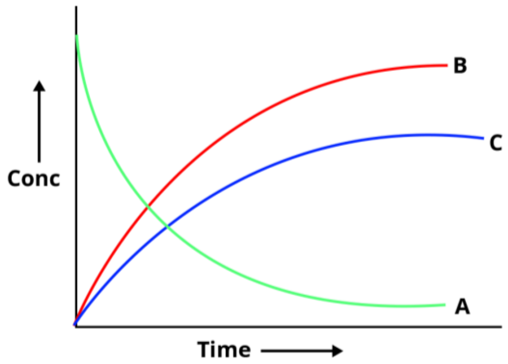
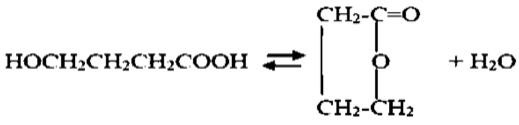


Figure IVV-3: Time dependence of species concentrations for the consecutive reversible reactions

Exercises

Exercise N°1

γ-hydroxybutyric acid converts into lactone (L): 

The following data is recorded:

t(sec)	1260	3000	6000	7200	9600	13200	∞
(L)	2.42	4.96	8.11	8.90	10.35	11.55	13.28

- Calculate k_1+k_{-1}

Exercise N°2

At 8°C, the concentration balances for the following estirification reaction are:

$$CH_3COOH + CH_3CH_2OH \underset{K_2}{\overset{K_1}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

Time (days)	CH_3COOH (mol/l)	C_2H_5OH (mol/l)	$CH_3COOC_2H_5$ (mol/l)	H_2O (mol/l)
0	1	1	0	0
190	0.5	0.5	0.5	0.5
300	0.417	0.417	0.583	0.583
Equilibrium	0.333	0.333	0.666	0.666

1/ Calculate the equilibrium constant K.

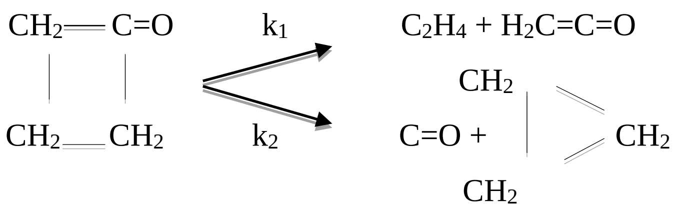
2/ Establish the kinetic law x=f(t).

3/ Calculate k_1 and k_2.

4/ Calculate R_1, R_2 and R at t=300 days.

Exercise N°3

During the thermal decomposition of pure cyclobutanone, four products are obtained in the following two parallel reactions:



The concentrations of ethylene and cyclopropane are obtained experimentally at 383°C for an initial cyclobutanone concentration of 6.5 10^{-3} mol/l.

Time(min)	0	0.5	1	3	6
$[C_2H_4]$ x10^6 (mol/l)	0	4.5	9.1	27.2	54.3
$[C_3H_6]$ x 10^8 mol/l	0	3.8	7.6	22.7	45.2

Determine the values of the constants k_1 and k_2 from these results.

Exercise N°4

Consider two successive reactions:

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

which exhibit the following rate constants: k_1 = 0,1 min^{-1} and k_2 = 0,05 min^{-1}

a) Plot the curves of concentrations (A), (B), and (C) as a function of time. Should we take $[A]_0$= 1 mole/l?

b) Calculate $[B]_{max}$. At what value of t do we obtain this maximum concentration?

Exercise Corrections

Exercise N°1

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

$$\frac{\mathrm{dx}}{\mathrm{dt}} = k_1(a-x) - k_{-1}x \qquad (1)$$

$$0 = k_1(a-x_\infty) - k_{-1}x_\infty \qquad (2)$$

$$\frac{\mathrm{dx}}{\mathrm{dt}} = k_1(a-x-a+x_\infty) - k_{-1}(x-x_\infty)$$

$$\frac{\mathrm{dx}}{\mathrm{dt}} = k_1(x_\infty - x) - k_{-1}(x-x_\infty)$$

$$\frac{\mathrm{dx}}{\mathrm{dt}} = k_1x_\infty - k_1x - k_{-1}x + k_{-1}x_\infty)$$

$$\frac{\mathrm{dx}}{\mathrm{dt}} = (k_1 + k_{-1})(x_\infty - x)$$

$$=> \quad \frac{\mathrm{dx}}{(x_\infty - x)} = (k_1 + k_{-1})\mathrm{dt}$$

$$=> \quad ln\frac{x_\infty}{(x_\infty - x)} = (k_1 + k_{-1})\mathrm{t}$$

To determine $(k_1 + k_{-1})$, one can plot $ln\frac{x_\infty}{(x_\infty - x)}$ as a function of time t; the slope of the resulting straight line gives the value of $(k_1 + k_{-1})$.

Alternatively, from a single data point, $(k_1 + k_{-1})$ can be calculated directly using the relation:

$$(k_1 + k_{-1}) = \frac{1}{t} ln\frac{x_\infty}{(x_\infty - x)}$$

t(sec)	1260	3000	6000	7200	9600	13200
(L)	2.42	4.96	8.11	8.90	10.35	11.55
$(k_1 + k_{-1}) \times 10^{-4}s^{-1}$	1.596	1.558	1.572	1.540	1.574	1.544

$$=> (k_1 + k_{-1})_{moy} = 1.564 \times 10^{-4}s^{-1}$$

Exercise N°2

1- The equilibrium constant K.

$$K = \frac{\pi[Pruducts]}{\pi[Reactifs]}$$

At equilibrium:

$$K = \frac{[C][D]}{[A][B]} = 4$$

2- The kinetic law x=f(t).

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C+D$$

At t 1-x 1-x x x

$$R = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = -\frac{d[D]}{dt}$$

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

$$\frac{dx}{dt} = k_1(1-x)^2 - k_2(x)^2$$

At equilibrium R=0 => $k_1[A][B] = k_2[C][D]$

$$=> \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]} = 4$$

$$=> k_1 = 4k_2$$

Substitute $k_1 = 4k_2$ into the rate equation:

$$\frac{dx}{dt} = 4k_2(1-x)^2 - k_2(x)^2 = k_2[4(1-x)^2 - (x)^2]$$

$$= k_2[(2-x)(2-3x)]$$

$$=> \int \frac{dx}{(2-x)(2-3x)} = k_2 \int dt$$

$$\ln\left(\frac{2-x}{2-3x}\right) = 4k_2 t = k_1 t$$

3- Calculate k_1 and k_2

Plot: $\ln\left(\frac{2-x}{2-3x}\right) = f(t)$

Slope = $4k_2 = k_1$

$\Rightarrow k_1 = 5.78 \times 10^{-3}\ Day^{-1}$

$k_2 = \frac{k_1}{4} = 1.445 \times 10^{-3}\ Day^{-1}$

4- Calculate R_1, R_2 and R at t=300 days.

$$R_1 = k_1[A][B]$$

$$= 5.78 \times 10^{-3}\ (0.417)^2 = 10^{-3}\ mol.l^{-1}.day^{-1}$$

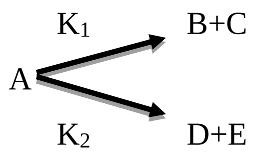
$$R_2 = k_2[C][D]$$

$$= 1.445 \times 10^{-3}\ (0.583)^2 = 4.9 \times 10^{-4}\ mol.l^{-1}.day^{-1}$$

$$R = R_1 - R_2$$

$$= 10^{-3} - 4.9 \times 10^{-4} = 5.1 \times 10^{-4}\ mol.l^{-1}.day^{-1}$$

Exercise N°3



To determine the rate constants k_1 and k_2 for the two parallel reactions, the rate law:

$$R = R_1 - R_2$$

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

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

$$ln\frac{[A]_0}{[A]} = (k_1 + k_2)t$$

The material balance is:

	A	B	C	D	E
t_0	$[A]_0$	0	0	0	0
t_{eq}	$[A]_0$-x	y	y	z	z

Where:

$$x=y+z$$

We have:

$$ln\frac{[A]_0}{[A]} = (k_1 + k_2)t$$

Time(min)	0	0.5	1	3	6
y=[C_2H_4] (x10^{-6} mol/l)	0	4.5	9.1	27.2	54.3
z=[C_3H_6] (x 10^{-8} mol/l)	0	3.8	7.6	22.7	45.2
x=y+z (x10^{-6} mol/l)	0	4.538	9.176	27.427	54.752
Ln($[A]_0$/($[A]_0$-x))	0	0.0865	0.1834	0.6950	∞

To find (k_1+k_2), we plot (ln($[A]_0$/($[A]_0$-x)) against (t).

⇨ $k_1+k_2 = 1.3x10^{-3}$ min^{-1}

(Or compute k_1+k_2 for each time value)

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] \qquad (1)$$

$$\frac{d[B]}{dt} = \frac{dy}{dt} = k_1[A] \qquad (2)$$

$$\frac{d[D]}{dt} = \frac{dz}{dt} = k_2[A] \qquad (3)$$

By dividing Eq. (2) by Eq. (3):

$$\frac{k_1}{k_2} = \frac{d[B]}{d[D]} = \frac{dy}{dz}$$

$$=> \frac{k_1}{k_2} = \frac{y}{z} \approx 120$$

$$=> k_1 = 1.38 \times 10^{-3}\, min^{-1}$$

$$k_2 = 1.15 \times 10^{-5}\, min^{-1}$$

Exercise N°4

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

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

$$[A] = e^{-k_1 t} = e^{-0.1t}$$

T	0	6.9	13.8
[A]	1	0.5	0.25

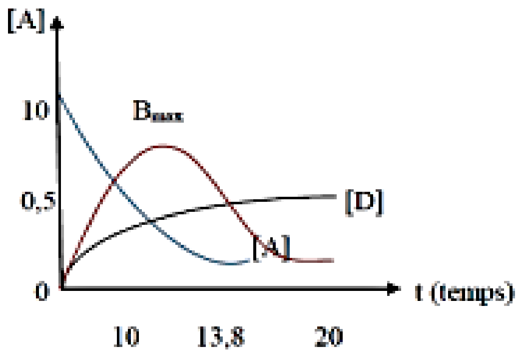
$$0 = e^{-0.1t}$$

$$\ln\left(\frac{1}{2}\right) = -0.1t \;\; => t = 6.9\, min$$

$$\ln\left(\frac{1}{4}\right) = -0.1t \;\; => t = 13.8\, min$$

$$\ln 10^{-1} = -0.1t \;\; => t = 23\, min$$

We plot the curve [A]=f(t) :



$$=> [B]_{max} = y = \frac{0.1}{0.1 - 0.05}(e^{-0.05t} - e^{-0.1t})$$

$$=> y = 2(e^{-0.05t} - e^{-0.1t})$$

$$=> e^{-0.1t} = 2(e^{-0.05t} - e^{-0.1t}) => t = 8.1\, min$$

We have: $e^{-0.1\,(8.1)} = 0.44$

$$\frac{dy}{dt} = 0 = -0.05e^{-0.05t} + 0.1e^{-0.1t} + 0.05e^{-0.05t} = 0.1e^{-0.1t}$$

$$=> \frac{e^{-0.05t}}{e^{-0.1t}} = \frac{0.1}{0.05} = 2 \; => t_{max} = 13.8\, min$$

$$z = 1 + \frac{0.05e^{-0.1t} - 0.1e^{-0.05t}}{0.05}$$

$$=> \; e^{-0.1t} = \; \frac{0.05 + 0.05e^{-0.1t} - 0.1e^{-0.05t}}{0.05}$$

$$0.1e^{-0.05t} = 0.05 \; => \; e^{-0.05t} = \frac{0.05}{0.1} = \frac{1}{2}$$

$$-0.05t = -\ln(2) => t_{max} = 13.8\, min$$

$$y = [B]_{max} = 2(e^{-0.05t} - e^{-0.1t})$$

By substituting $t_{max} = 13.8\, min$ into the equation, we obtain:

$$[B]_{max} = 0.5\, mol/l$$

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REFERENCES

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