People's Democratic Republic of Algeria

Ministry of Higher Education and Scientific Research

Larbi Ben M'Hidi University Oum El Bouaghi



Faculty of Sciences and Applied Sciences

Department of Process Engineering

Course Title

Chemical Kinetics and Homogeneous Catalysis

Course unit level: 2nd Year Engineer

Lecturer: Dr. Ghania MECHERI

Academic Year 2025/2026

Teaching Plan of the Course

Subject: Chemical Kinetics and Homogeneous Catalysis

Field: Process engineering

Semester: 4

Total hours: 67h30 (Lecture :1h30, Tutorial :1h30, Pratical work : 1h30)

Coefficient: 3

Credit: 5

Course main objectives

This course intends to give learners a thorough grasp of the subject of chemical kinetics by covering the following key topics:

- Fundamental concepts: introduce students to the core principles of chemical kinetics, including reaction rates and factors affecting them.
- Reaction order and rate laws: explain the reaction order and guide students through the derivation of rate laws.
- Recognize and identify various types of complex chemical reactions.
- Identify and explain the mechanism of homogeneous catalysis, and how catalysts alter activation energy.
- Examine the benefits, limitations, and environmental effects of a homogeneous catalytic system.

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Introduction

The scientific study of chemical kinetics began in the mid-19th century, when Wilhelmy first established that the rates of chemical reactions follow specific mathematical laws. Despite the significance of his discoveries, which would later form the foundation for the law of mass action developed by Waag and Guldberg, they initially received little attention. It was not until Ostwald revisited and expanded on Wilhemy's ideas toward the end of the century, an evolution detailed by Laidler, that kinetics gained broader recognition. Wilhemy demonstrated that the concentrations of reactants directly influence the rates at which chemical reactions proceed. Before examining specific examples of reaction kinetics, it is essential to understand the classification system used for chemical reactions, as these categories provide the framework for analyzing reaction mechanisms and rates.

Chemical kinetics is the study of reaction rates and the factors that influence them, such as temperature, pressure, catalysts, radiation… . It focuses on understanding how these factors affect reaction speeds and explains the rates of the underlying reaction mechanisms. It is a branch of chemistry that examines the rate of chemical reactions and how these rates can be controlled to maximize efficiency in various applications. The key aspects of chemical kinetics include:

- Factors influencing reaction rates.
- The concept of reaction order, which quantifies the relationship between reactant concentrations and the reaction rate.
- The rate expression is an equation summarizing how the rate depends on reactant concentrations.
- The rate constant, a proportionality factor that encapsulates all necessary information to determine the rate under specific conditions of reaction.
- The effect of temperature on reaction rates, as higher temperatures typically accelerate reactions, provides insights into reaction mechanisms.

Fundamental ideas in chemical kinetics encompass the reaction rate, which measures how quickly reactants are consumed or products are generated with respect to time, as well as the reaction order, which expresses the dependence of this rate on the reactant concentrations. Molecularity describes how many reactant particles take part in the slowest, or rate-limiting,

step of the reaction. The rate law, on the other hand, is an experimentally derived expression that shows how the reaction rate depends on the concentrations of the reactants.

However, kinetics extends beyond physical chemistry, serving as a unifying field across all branches of chemistry, as well as biochemistry and biology. It plays a crucial role in the chemical and pharmaceutical industries, where understanding reaction mechanisms is essential. Additionally, fields such as solid-state chemistry rely heavily on kinetic techniques, surface chemistry, catalysis, analysis, and interpretation.

The study of chemical kinetics has broad applications across both natural and industrial processes. For instance, photochemical kinetics plays a crucial role in understanding photosynthesis and photography, while catalytic kinetics is fundamental to industrial production, environmental safety, and various technological advancements.

Chemical kinetics utilizes mathematical tools, such as integration, differentiation, and inequalities, to fully explore its principles. In analyzing the kinetics of any chemical process, both mathematical and chemical methods are essential for deriving equations that model different reaction stages leading to the final product.

Chapter I: Homogeneous Chemical Reaction

I.1 Type of reaction

Based on the rate, reactions can be classified as slow, moderate, or very fast. From a kinetic perspective, chemical reactions are generally classified into two broad categories: homogeneous and heterogeneous. In homogeneous reactions, all reactants and products exist in the same phase, resulting in a uniform system. For example:

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

$$CH_3COOCH_{3(liq)} + H_2O_{(liq)} \xrightarrow{HCl\ (liq)} CH_3COOH_{(liq)} + CH_3OH_{(liq)}$$

In a heterogeneous reaction, the process occurs at the interface, such as on a catalytic surface or the inner walls of a catalyst, resulting in a non-uniform mixture. For example:

$$C_2H_5OH_{(liq)} \xrightarrow{alumina} C_2H_{4(gas)} + H_2O_{(liq)}$$

$$2NH_{3(gas)} \xrightarrow{tungsten} N_{2(gas)} + 3H_{2(gas)}$$

I.2 Reaction advancement (extent of reaction)

If a reaction is carried out over a short time interval dt, some reactants will be consumed, and some products will be generated. We define the variations in stoichiometric abundances during dt as the differential change $d\xi$ of a specific function, which we refer to as the extent of the reaction.

In a reaction having time-independent stoichiometry, and for any reactant or product, the extent of reaction is defined by :

$$\xi = \frac{n_i - n_{i0}}{\nu_i} \qquad (I.1)$$

Where :

n_{i0} is the initial amount of the species, n_i is the amount at time t, and ν_i is the stoichiometric coefficient for that species in the particular equation. For the general equation.

$$aA + bB + \cdots \rightarrow \cdots + yY + zZ$$

The extent of a reaction is defined as the variation in the number of moles Δn of a substance (a positive quantity for a product generated) or the change in the amount of any reactant (a negative quantity) and its corresponding stoichiometric coefficient :

For the reactants : $\xi = \frac{\Delta n_A}{-a} = \frac{\Delta n_B}{-b}$ $(I.2)$

For the products : $\xi = \frac{\Delta n_Y}{y} = \frac{\Delta Z}{z}$ $(I.3)$

The extent is measured in terms of the amount of substance, specifically in moles.

I.3 Expressing the reaction rate

In a chemical reaction, the rates of consumption and formation of different substances are generally not identical. To simplify comparisons, it is useful to define a reaction rate that remains consistent for all species. For a reaction with time-independent stoichiometry, this can be achieved using the extent of the reaction.

The reaction rate represents the rate of change of the reaction's progress with respect to time, divided by the volume of the system. It is expressed as :

$$r = \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{\nu_i V}\frac{dn_i}{dt} \qquad (I.4)$$

$\frac{dn_i}{V}$ may be replaced by dC_i if the volume remains constant during the reaction. Where C_i is the concentration for the amount i. Then the equation (I.4) becomes :

$$r = \frac{1}{\nu_i}\frac{dC_i}{dt} \qquad (I.5)$$

I.3.1 Rate of disappearance and appearance

An important part of any kinetic investigation is measuring the rates of change in the concentration of reactants and products. Consider the reaction :

$$A + 3B \rightarrow 2Z$$

In this particular reaction, the stoichiometric coefficients vary among three species, and as a result, their concentration changes occur at different rates.

$$r_A = -\frac{1}{3} r_B = \frac{1}{2} r_Z \qquad (I.6)$$

Therefore, a minus sign is included to ensure that the rate is numerically positive. It indicates a decrease in concentration and is always associated with the reactant. The plus sign is always associated with the product because its concentration increases.

If the kinetic experiments begin with a mixture of A and B, initially, we assume that the reaction takes place in a system where the total volume remains constant as the reaction proceeds.

At any time t, the rates of consumption of A and B are defined by :

$$r_{A(initial)} = -\left(\frac{d[A]}{dt}\right)_{(initial)} \qquad (I.7)$$

$$r_{B(initial)} = -\left(\frac{d[B]}{dt}\right)_{(initial)} = 3r_{A(initial)} \qquad (I.8)$$

This rate is the negative of the slope of the tangents to the curve for A and for B at that time.

The rate of formation of Z, is defined as :

$$r_{Z(initial)} = \left(\frac{d[Z]}{dt}\right)_{(initial)} = 2r_{A(initial)} \qquad (I.9)$$

Generally, a rate is a variation of the concentration over time. Its standard international unit is $(mol\,.\,l^{-1}.s^{-1})$. It is expressed more in units of $(mol.dm^{-3}.s^{-1})$ or $mol.cm^{-3}.s^{-1}$. Other units are $g/s, lb/s, kg/day$.

Let us consider the chemical reaction :

$$CO + NO_2 \xrightarrow{200°C} CO_2 + NO$$

The rate of a chemical reaction is described by how the concentration of reactants or products changes over time :

$$Rate = -\frac{d[CO]}{dt} = -\frac{d[NO_2]}{dt} = \frac{d[CO_2]}{dt} = \frac{d[NO]}{dt}$$

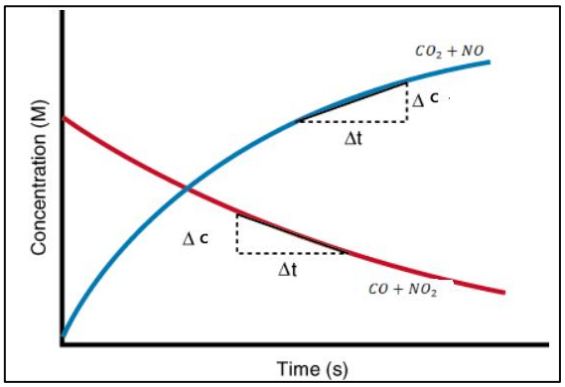


Fig.1 Change in reaction rate over time

A reaction :

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

The consumption rate of HI is twice the formation rate of H_2 or I_2, which relates to the reaction's stoichiometric relationship. According to the international convention, the reaction rate is :

$$Rate = -\frac{1}{2}\frac{d[HI]}{dt} = \frac{d[H_2]}{dt} = \frac{d[I_2]}{dt}$$

I.3.2 Empirical rate equation

The main limitation of using Equation I.5 to estimate the rate of a chemical reaction is its reliance on the expressed chemical equation and its stoichiometry. However, studies have shown that the theoretically derived rate equation does not always match the experimentally determined one. The experimentally obtained rate equation is known as a rate law. The fundamental characteristics of a rate law for a given reaction can be described as follows:

$$r = k[A]^n[B]^m \qquad (I.10)$$

Where :

k is the rate constant with respect to the overall order of reaction,n and m are the orders of reaction with respect to the reactants A and B, respectively. The overall order of the reaction is the sum of the individual or partial orders (n+m) . An experimentally derived equation, such as the one presented in Equation I.10, shows that the rate of the reaction depends on the concentrations of the reactants, each raised to a particular exponent. If the reaction order is 1, 2, 3, ... n, it is classified as first-order, second-order, third-order, and so on. Additionally, reactions can have a zero-order or even a fractional order.

k,n, and m do not depend on concentration or time. In such cases, the rate of consumption of species A can be expressed as :

$$r_A = k_A[A]^n[B]^m \qquad (I.11)$$

The exponents n and m must be identical in both equations. However, since r, generally differs from r_A (as r_A is divided by the negative of the stoichiometric coefficient for A), k differs from k_A by the same factor. The same principle applies to a constant k_Z associated with the product Z. Therefore, if the stoichiometric equation is :

$$A + 2B \rightarrow 3Z$$

The expression relates the rate constants :

$$k = k_A = \frac{1}{2}k_B = \frac{1}{3}k_Z$$

I.4 Experimental kinetic study of a reaction

An experimental kinetic study investigates the rate of a chemical reaction under various conditions to determine the reaction mechanism and rate laws. This process involves monitoring the concentration of reactants and /or products over time and analyzing how various factors influence the reaction.

I.4.1 Chemical methods

Chemical methods involve altering or sampling the reaction mixtures to measure the concentration of reactants or products. These are often destructive, as they involve taking a portion of the reaction sample for analysis.

- *Titration:* used for reactions where an acid, base, or redox species is involved. A small volume of the reaction mixture is periodically removed, quenched (to stop the reaction), and titrated to determine the concentration of a specific component.

Example: monitoring the decomposition of hydrogen peroxide using potassium permanganate titration.

- *Gravimetric analysis:* measures the mass of a precipitate formed in a reaction. Useful for reactions producing solid products.

Example: precipitation of barium sulfate in a reaction involving sulfate ions.

- *Gas analysis:* involves measuring the volume or pressure of gases produced or consumed in a reaction. It can be performed using a gas burette, a manometer, or a collection over water.

Example: monitoring the evolution of oxygen in the decomposition of potassium chlorate.

I.4.2 Physical methods

Physical methods are typically non-destructive and rely on the measurement of physical properties (e.g., absorbance, conductivity, or pH) that correlate with the concentration of a species in the reactions.

1. Spectrophotometry

Measures the absorbance of light at a specific wavelength by reactants or products. Works well for colored species or reactions involving a color change.

Example: monitoring the reaction between crystal violet and hydroxide ions by observing the decrease in violet color intensity.

2. Electrochemical technique

These approaches are suited for studying reactions that involve ionic species in aqueous solutions. Common examples include conductivity measurement, potential-based analysis, and pH monitoring.

3. Refractometry

Measures the refractive index of the reaction mixture, which changes with concentration. Useful in reactions involving significant changes in solute concentration.

4. Calorimetry

This approach is based on measuring the amount of heat released or consumed during a chemical reaction. Microcalorimetry is the term used when the technique is applied to measure extremely small quantities of heat transfer.

Examples: combustion reactions or neutralization reactions.

5. Polarimetry

Measures the rotation of polarized light by optically active species. Useful for reactions involving chiral molecules.

Example: monitoring the inversion of sucrose to glucose and fructose.

6. Pressure measurement

Used for gaseous reactions to monitor pressure changes over time. Often conducted in a closed system.

Example : decomposition of dinitroge terroxide $N_2O_4 \rightarrow 2NO_2$

Each method (chemical or physical) is chosen based on factors such as :

- The type of reaction (homogeneous/ heterogeneous, fast/slow).
- The nature of reactant/products (ionic, gaseous, optically active).
- Sensitivity and precision requirements.

I.5 Factors influencing reaction rate

Many factors can affect the rate of a reaction, they are :

I.5.1 Effect of concentration

Higher concentrations typically increase the reaction rate because more reactant particles are available to collide and react.

In the reaction between hydrochloric acid (HCl) and sodium thiosulfate ($Na_2S_2O_3$, increasing the concentration of HCl leads to a faster formation of sulfur precipitate.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S(precipate) + H_2O$$

I.5.2 Effect of temperature

It is well known that temperature influences the rate of a chemical reaction. Generally, the reaction rate doubles with every 10°C increase. This acceleration in reaction rate is also reflected in an increase in the rate constant. Different reactions exhibit varying responses to changes in reaction rate with temperature.

Although reaction rate laws can be complicated, graphing experimental data as the logarithm of the reaction rate versus the reciprocal of temperature, referred to as an Arrhenius plot, often results in a linear relationship. This suggests that the reaction follows Arrhenius' law, which can be expressed in (Eq.I.2). However, this apparent linearity can be misleading, often resulting from the strong influence of temperature within a limited range and the inherent linearizing effect of Arrhenius coordinates.

$$k = Aexp\left(-\frac{E_a}{RT}\right) \qquad (I.12)$$

The calculated parameter E_a represents the activation energy of the reaction, which describes the lowest energy required for a reaction to proceed. Where k is the rate constant, T is the temperature, R is the Universal gas constant, and A is the Arrhenius or pre-exponential factor (frequency factor).

I.5.3 Nature of reactants

Chemical reactions involve rearrangement as reactants become products. This process breaks existing bonds and forms new ones. The characteristics and strength of the reactant bonds significantly affect reaction speed. Reactions requiring minimal bond changes typically occur faster than those needing extensive reorganisation.

Reactions between polar ionic compounds, such as double displacement and neutralization reactions, typically occur rapidly. For example :

$$Ag^+ + Cl^- \longrightarrow AgCl\ (s)$$

Electron transfer reactions generally proceed more slowly than ionic reactions. In contrast, the following reaction occurs rapidly :

$$Fe^{2+} + Ce^{4+} \longrightarrow Ce^{3+} + Fe^{3+}$$

Complex reactions are generally slow due to their multiple steps and intermediates. For example :

$$Mg^{2+} + C_2O_4^{2-} \longrightarrow MgC_2O_4(s)$$

I.5.4 Catalyst

A catalyst is a species that accelerates a chemical reaction while remaining unchanged at the end of the process. For any chemical reaction to occur, reactants must first surpass the activation energy barrier, the smallest amount of energy needed to start the process. A catalyst alters the reaction rate by providing an alternative pathway that requires less activation energy.

On its own, the decomposition of hydrogen peroxide H_2O_2 is a relatively slow reaction. However, the use of manganese dioxide MnO_2 as a catalyst causes the reaction to accelerate significantly, releasing oxygen gas considerably faster.

$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2 \quad (Slow\ reaction)$$

Introduce MnO_2 (manganese dioxide) as a catalyst; the reaction speeds up, generating oxygen gas bubbles. MnO_2 is not consumed; it accelerates the reaction by reducing the energy barrier.

I.5.5 Radiation

The rate of certain chemical reactions increases when reacting molecules absorb radiation of specific wavelengths. These are known as photochemical reactions. For instance, hydrogen and chlorine gases can be safely mixed in the dark due to their extremely slow reaction. However, upon exposure to light, the reaction becomes explosive.

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl + 188kJ$$

I.1.6 Reactant surface area

For reactions that include solid substances, increasing the surface area enhances the reaction rate because more solid particles become available to interact and collide with the reactants. For example, finely powdered calcium carbonate ($CaCO_3$)reacts more rapidly with hydrochloric acid than a single large chunk due to its greater surface area.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

Chapter II: Influence of Concentration and Temperature

II.1 Concentration of reactants

It is well known that increasing the concentration of reactants enhances the reaction rate.

The relationship between reaction rate and the concentrations of reactants, products, or catalysts is highly complex and diverse. This complexity is, in fact, advantageous, as it allows rate concentration correlations at a constant temperature to serve as a crucial basis for elucidating reaction mechanisms. In particular, equations of the following type are often observed :

$$rate = k[A_1]^n[A_2]^m \dots\dots[A_i]^x \qquad (II.1)$$

This function depends only on the concentrations of the reactants. In this case, the reaction is said to have an order equal to the sum of the exponents, which represent the partial orders. The constant k depends on the temperature. In closed reactors, it is important to remember that concentrations change only due to the reaction itself and evolve as the reaction progresses. As a result, the influence of concentration involves the extent of reaction progress. However, concentrations can be maintained constant throughout the reaction by using an open reactor with a controlled supply or by conducting the reaction over short periods at high concentrations, where concentration changes become negligible. In such cases, concentration is independent of reaction progress.

II.2 Order of a reaction

II.2.1 Order and molecularity

Chemical reactions can be classified in different ways, one of which is by molecularity, which is defined by the number of reactant molecules involved in a single reaction step. For instance, a reaction $A \longrightarrow P$ involving a single molecule is called unimolecular, while one involving two molecules $A + B \longrightarrow P$ is bimolecular. Reaction involving three molecules $A + B + C \longrightarrow P$, termed termomolecular or trimolecular, are rare.

$$Unimolecular: Cyclopropane \rightarrow Propene, Rate = k[Cyclopropane]$$

$$Bimolecular: NO + O_3 \rightarrow NO_2 + O_2, Rate = k[NO][O_3]$$

$$Trimolecular: 2NO + O_2 \rightarrow 2NO_2, Rate = k[NO]^2[O_2]$$

Reactions can be systematically categorized according to their reaction order, describing the mathematical relationship between reactant concentrations and rate. The rate is directly proportional to a single reactant's concentration in a first-order reaction. Second-order reactions may depend on the product of two different concentrations or the square of a single concentration, and higher orders follow accordingly.

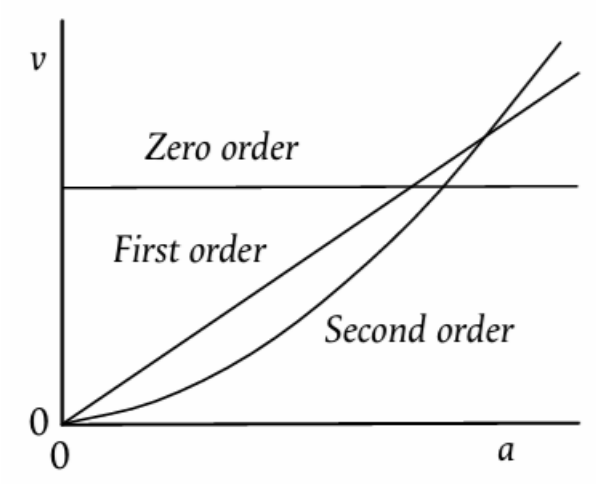


Fig.1 Order of reaction

If a reaction is first-order with respect to reactant A, its rate is directly proportional to the concentration of A. For a second-order reaction, the rate is proportional to A^2. In a zero-order reaction, the rate remains constant and is unaffected by changes in concentrations.

Reaction orders are usually determined experimentally, as they are not necessarily the same as the stoichiometric coefficients in the balanced chemical equation.

The order of a reaction can be an integer (e.g., 0, 1, 2) or a fraction.

Examples :

- Decomposition of NH_3 on a platinum surface :

$$2NH_3 \rightarrow N_2 + 3H_2$$

$$Rate = k[NH_3]^0 = k$$

- Reaction of nitrogen dioxide :

$$2NO_2 \rightarrow 2NO + O_2, Rate = k[NO_2]^2$$

- Decomposition of ethanol on tungsten (fractional order):

$$C_2H_5OH \rightarrow C_2H_4 + H_2O, Rate = k[C_2H_5OH]^{1/2}$$

$$C_2Cl_4 + Cl_2 \rightarrow C_2Cl_6, Rate = k[C_2Cl_4]^0[Cl_2]^{3/2}$$

Molecularity describes the number of molecules in an elementary step and differs from the order of reaction (which is determined experimentally), for example :

The decomposition of azote pentoxide :

$$2N_2O_5 \rightarrow 4NO_2 + O_2, r = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

In this case, the order of the reaction with respect to N_2O_5 is equal to 1, therefore different from the molecularity, which is equal to 2.

II.2.2 Van't Hoff equation (equilibrium constant and temperature)

This principle establishs the relationship between varaiations in the equilibrium constant (k) of a chemical reaction and corresponding changes in temperature (T):

$$lnk_2 - lnk_1 = \frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (II.2)$$

Where:

k_1 and k_2 : Equilibrium constants at temperatures T_1 and T_2 (in Kelvin).

$\Delta H \circ$: Standard enthalpy change of the reaction (in joules per mole).

R: Universal gas constant $(8.314\ J/mol.°K)$.

II.3 Arrhenius equation

The Arrhenius equation became the sole surviving one-parameter model for temperature-dependent reaction rates by approximately 1910. Hood pioneered the first quantitative experimental investigation of this temperature rate relationship, which Svante

Arrhenius later developed and refined. The equation can offer meaningful insights into the mechanisms by which chemical reactions occur.

In 1889, Arrhenius explained the above fact using the van't Hoff equation, which describes how the equilibrium constant varies with temperature. According to Van't Hoff :

$$\frac{dln\, k_c}{dT} = \frac{\Delta E}{RT^2} \qquad (II.3)$$

Or, k_c represents the equilibrium constant, and ΔE denotes the change in energy associated with the reaction. Based on the law of mass action, the equilibrium constant is determined by the ratio between the rate constants of the forward and backward reactions.

Van't Hoff proposed that Equation (II.3) can be separated into two distinct expressions, as follows :

$$\frac{dln\, k_1}{dT} = \frac{E_1}{RT^2} + constant \qquad (II.4)$$

$$\frac{dln\, k_2}{dT} = \frac{E_2}{RT^2} + constant \qquad (II.5)$$

In this context, $\Delta E = E_2 - E_1$, where k_1 and k_2 are the constants for the forward and reverse directions of a reversible reaction at temperature T. The term E refers to the activation energy of the reaction. Arrhenius observed that the pre-exponential constant in the rate expression is independent of temperature and can assume any value, including zero. If this constant is taken to be zero, then Equations II.4 and II.5 can be simplified to the following form :

$$\frac{dln\, k}{dT} = \frac{E_a}{RT^2} \qquad (II.6)$$

Integration of Equation II.3, gives :

$$lnk = -\frac{E_a}{RT} + constant \qquad (II.7)$$

Or it can also be put in the form :

$$k = Ae^{-\frac{E_a}{RT}} \qquad (II.8)$$

It follows from Equation II.7 that a plot of the logarithm of the rate constant versus the reciprocal of temperature gives a straight line with a slope of $-E_a/R$. Alternatively, the activation energy E_a can be determined by measuring the rate constants k_1 and k_2 at two different temperatures T_1 and T_2, respectively.

II.3.1 Significance of activation energy

Studies indicate that the rate of a chemical reaction approximately doubles for each 10°C rise in temperature. However, early attempts to attribute this sharp increase solely to a rise in the average molecular energy or collision frequency were unsuccessful.

According to Arrhenius, reactant molecules must acquire a specific minimum amount of energy to proceed to the formation of products. This implies that the reactants must first transition through a high-energy, unstable intermediate state known as the activated complex. The energy required to reach this transition state from the initial reactants is termed the activation energy.

This concept is effectively illustrated using a reaction coordinate potential energy diagram, as shown in figure 2.

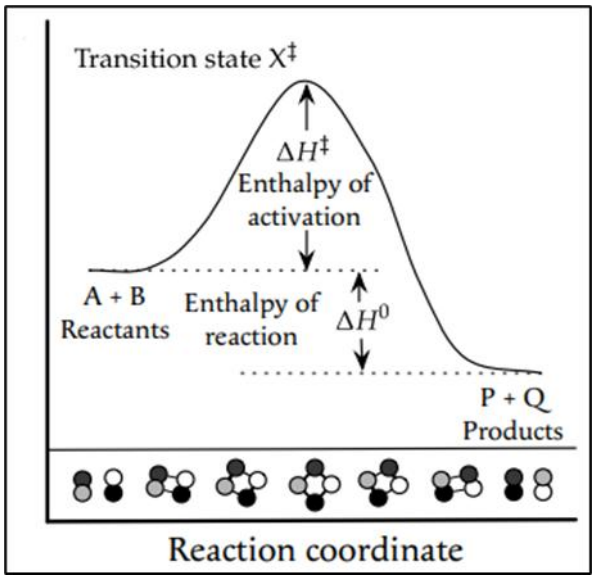


Fig.2 Transition state theory-based reaction profile. The significance of the reaction coordinate in the context of a basic bimolecular reaction

Chapter III: Formal Kinetics, Simple Reactions

III.1 Determination of the rate constant of a reaction

III.1.1 Zero-order kinetics

This type of reaction can be expressed as :

$$A \rightarrow B$$

Where A is the reactant and B is the product. In chemical kinetics, the reaction rate of a zero-order reaction is independent of the concentration of the reactant A. As a result, the concentration of A decreases at a constant rate over time, which means the rate of change of concentration is a constant value.

In other words, the rate does not change; it remains constant regardless of how much reactant is present :

$$Rate = Constant$$

$$-\frac{dC_A}{dt} = k_0 C_A^0 = k_0 \qquad (III.1)$$

Where k_0 is the rate constant of the zero-order reaction.

If x is the concentration of product formed, then :

$$\frac{dx}{dt} = k_0$$

Solving the differential equation gives the following results :

$$x = k_0 t + Constant$$

At the beginning of the reaction (when t equals 0), no product has formed yet, meaning x equals 0. Under these initial conditions, the integration constant becomes zero.

Thus, the final expression represents the rate law for a zero-order reaction, indicating that the reaction occurs at a constant rate, entirely independent of the reactant's concentration.

$$x = k_0 t \qquad (III.2)$$

A plot of x versus t will produce a straight line that passes through the origin, and the slope of this line corresponds to the rate constant k.

A key characteristic of zero-order kinetics is that the half-life is directly proportional to the initial concentration of the reactant.

The half-life is defined as the time required for the concentration of the reactant to decrease to half of its initial value.

By applying the concentration $t = t_{1/2}$ when $x = \frac{a}{2}$, we obtained :

$$t_{1/2} = \frac{a}{2k_0} \qquad (III.3)$$

Where

a: represents the reactant's initial concentration.

This indicates that, for a zero-order reaction, the half-life increases in direct proportion to the reactant's initial concentration.

Zero-order reactions are relatively rare, so the practical application of the zero-order rate law is somewhat limited. However, some heterogeneous reactions that occur on solid surfaces do exhibit zero-order kinetics. A few examples of such reactions are listed below :

$$2N_2O \xrightarrow{hot\ Pt\ wire} 2N_2 + O_2$$

$$2NH_3 \xrightarrow{tungsten} N_2 + 3H_2$$

$$2HI \xrightarrow{gold} H_2 + I_2$$

In such reactions, the process takes place exclusively on the surface of the catalyst. Once the surface becomes saturated with the reactant, the amount of gas adsorbed remains constant.

As a result, increasing the pressure (and thus the gas-phase concentration) does not affect the surface concentration. Therefore, the reaction rate becomes independent of the reactant concentration in the gas phase.

III.1.2 First-order kinetics

A first-order reaction is defined by a rate that depends linearly on the concentration of a single reactant. In mathematical terms, the rate law for such a reaction involves the concentration of one reactant :

$$\frac{dC_A}{dt} = -k_A C_A \qquad (III.4)$$

Where :

C_A represents the concentration of substance A being consumed in the reaction (indicated by the negative sign), and k_A is the specific rate constant for the reaction.

By rearranging the terms, the differential equation can be written as :

$$\frac{dC_A}{C_A} = -kdt$$

This equation can be directly integrated to yield :

$$ln\, C_A = -k_A t + Z$$

Where :

Z is once again the constant of integration, which will be determined by the initial experimental conditions. If the concentration of C_A is C_{A0} at $t = 0$ (which, for convenience, can be set as the reference point), leading to the expression :

$$ln\frac{C_A}{C_{A0}} = -k_A t \qquad (III.5)$$

In exponential form :

$$C_A = C_{A0} e^{-k_A t} \qquad (III.6)$$

The integrated form of the first-order rate equation offers a straightforward graphical method of analysis, as illustrated in Fig. 1, where $ln\, C_A$ is plotted against time t.

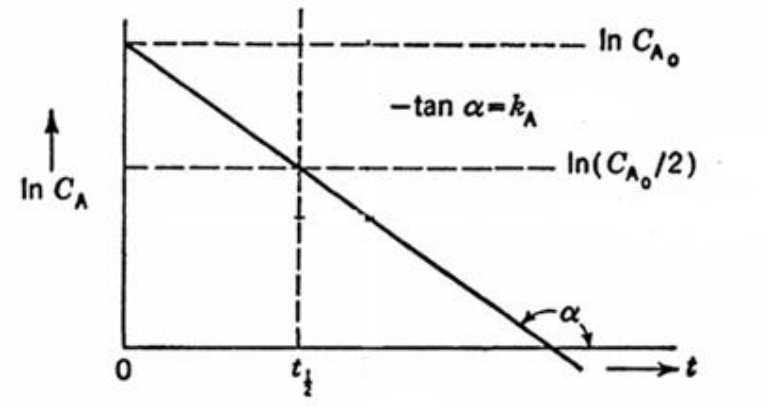


Fig.1 Graphical illustration of first-order reaction kinetics

Another important parameter is the reaction half-life, represented as $t_{1/2}$, which describes the time required for the concentration C_A to decrease to half of its initial value, $\frac{C_{A0}}{2}$.

$$t_{1/2} = \frac{ln\,2}{k_A} \qquad (III.7)$$

It should be noted that $t_{1/2}$ is directly related to the specific rate constant and it is independent of the initial concentration.

A key property of the half-life in equation III.7 has a fundamental characteristic: because the concentration follows an exponential decay pattern, the reaction removes the same proportion of the remaining substance A during each successive half-life period. To illustrate, if we start with an initial concentration C_{A0}, after one half-life period, the concentration becomes $C_{A0}/2$. In the following half-life period, the concentration is further reduced to $C_{A0}/4$, and this proportional reduction continues in the same manner for each subsequent half-life interval.

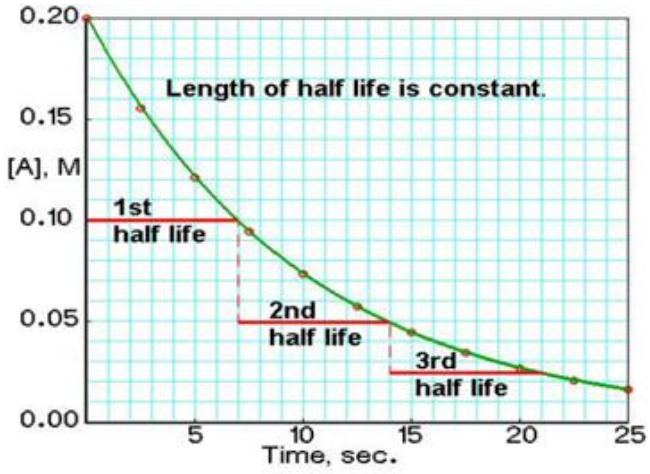


Fig.2 Variation of reactant concentration [A] with time in first-order reaction kinetics

1. Pseudo-unimolecular reactions

Some reactions involve more than one reactant but still follow first-order kinetics. Such reactions are called pseudo-unimolecular reactions. Typical examples include the conversion of cane sugar and the acid-catalyzed hydrolysis of esters.

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$$

$$CH_3COO\,C_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

Although these reactions are fundamentally second-order, involving two reactants (such as water and cane sugar, or water and ester), the rate of reaction is experimentally found to depend only on the concentration of cane sugar or ester.

III.1.3 Second-order kinetics

According to the definition of overall reaction order, second-order reactions can follow two possible forms: the reaction rate can be directly proportional either to the square of a single reactant's concentration or to the product of the concentrations of two distinct reactants. The former occurs when only one reactant is involved, as in the following process :

$$2A \longrightarrow P$$

This behavior is also characteristic of second-order reactions exhibiting the following stoichiometry :

$$A + B \longrightarrow P$$

If the initial concentrations A and B are the same, in such situations, the rate is given as :

$$\frac{dx}{dt} = k_A(a-x)^2 \qquad (III.8)$$

Where x represents the quantity of substance A that has reacted per unit volume at a given time t, while a denotes the initial concentration of A. By applying the method of variable separation, the following expression is obtained :

Which integrates to :

$$\frac{1}{(a-x)} = \frac{1}{a} + k_A t \qquad (III.9)$$

From equation III.8, we can evaluate the half-life. C_A will have the value of $C_{A0}/2$:

$$t_{1/2} = \frac{1}{k_A a} \qquad (III.10)$$

In the second order, the half-life inversely varies with the starting concentration of reactant; higher initial concentrations lead to shorter half-lives, whereas lower concentrations extend the half-life.

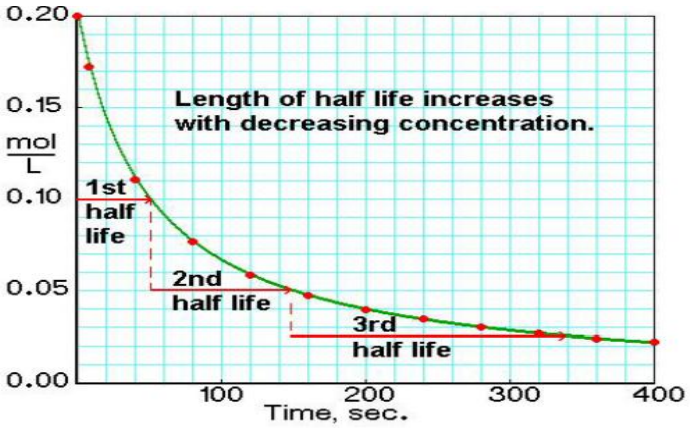


Fig.3 Variation of reactant concentration $[A]$ with time in second-order reaction kinetics

Typical examples of second-order reactions of this type include :

- The thermal decomposition of hydrogen iodide occurring in the gaseous phase

$$2NO_2 \longrightarrow 2NO + O_2$$

- The decomposition of the chlorite ion takes place in the liquid phase

$$2ClO^- \longrightarrow 2Cl^- + O_2$$

- Dimerization of cyclopentadiene (in either the gas or liquid phase)

$$2C_5H_6 \longrightarrow C_{10}H_{12}$$

When the rate of reaction varies in direct proportion to the product of the concentrations of both reactants, and if the initial concentrations of the two reacting substances are different, denoted as a and b, then the reaction rate is given by :

$$\frac{dx}{dt} = k(a-x)(b-x) \qquad (III.11)$$

Where x is the amount of any reactant transformed in time t.

On rearrangement

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

Integration, following decomposition into partial fractions, leads to the expression :

$$\frac{1}{a-b} ln \frac{a-x}{b-x} = \frac{1}{a-b} ln \frac{a}{b} + kt$$

It may also be written as :

$$ln \frac{a-x}{b-x} = ln \frac{a}{b} + (a-b)kt \qquad (III.12)$$

Type II second-order reactions are likely among the most frequently studied reactions overall. A few typical examples include :

- The gas-phase formation of hydrogen iodide

$$H_2 + I_2 \longrightarrow 2HI$$

- Reactions that occur between free radicals and molecular species, such as :

$$H + Br_2 \longrightarrow HBr + Br$$

III.1.4 Third-order kinetics

According to the general definition, third-order reactions are classified into three main categories. When the stoichiometric equation is given as :

$$aA + bB + cC \longrightarrow Products$$

Type I

$$-\frac{dC_A}{dt} = k_A C_A^3 \qquad (III.13)$$

TypeII

$$-\frac{dC_A}{dt} = k_A C_A^2 C_B \qquad (III.14)$$

Type III

$$-\frac{dC_A}{dt} = k_A C_A C_B\, C_C \qquad (III.15)$$

Since the mathematical treatment of these equations closely parallels that of first and second-order reactions, the solution steps will be outlined with type I :

$$-\frac{dC_A}{dt} = k_A C_A^3$$

Upon rearrangement and integration of the equation, the following result is obtained :

$$\frac{1}{C_A^2} = \frac{1}{C_{A0}^2} + 2k_A t \qquad (III.16)$$

This expression may be employed to determine the rate constant of a third-order reaction under the condition that all reactants share the same initial concentration.

The half-life period can be derived from equation (III.16) as follows :

$$t_{1/2} = \frac{3}{2k_A C_{A0}^2}$$

III.1.5 Reactions of nth order kinetics

Consider a reaction of order n that involves either a single reactant with an initial concentration a, or multiple reactants present in equal initial concentrations and participating according to the stoichiometry $A + B + \cdots \longrightarrow P$. If the concentration of A at time t is $(a - x)$ then the rate at which A is consumed is :

$$r_A = \frac{dx}{dt} = k_A (a - x)^n \qquad (III.13)$$

To determine concentration as a function of time, the rate equation must be integrated using the boundary condition x equals 0 at t equals 0. When the reaction order n is not equal to 1, the integrated form of the rate law is:

$$k_A = \frac{1}{t(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] \qquad (III.14)$$

In the case when n is unity, the corresponding solution is expressed by Equation (III.5).

For the half-life, we can calculate :

$$t_{1/2} = \frac{2^{n-1}-1}{k_A C_{A0}^{n-1}(n-1)} \qquad (III.15)$$

Examples of fractional-order reactions :

- The gas-phase formation of phosgene $CO + Cl_2 \longrightarrow COCl_2$, which is overall of $5/3$, being $3/2$ order with respect to Cl_2 and first-order with respect to CO.
- The chlorine catalyzed decomposition of ozone $2O_3 \longrightarrow 3O_2$, which has a $3/2$ order with respect to ozone.

Additionally, many heterogeneous reactions can display fractional-order kinetics under varying experimental conditions.

III.2 Determination of reaction order in elementary systems

We can now take a closer look at how to interpret experimental data using the mathematical frameworks we've built for reaction orders. The first step is to determine how each component influences the reaction, that is, to establish the reaction order with respect to each reactant or product. Although there are various methods to determine the reaction order, all of them fundamentally rely on measuring the concentrations of reactants or products over time.

III.2.1 Integration method

When the concentration of its initial reactants directly influences the rate of a reaction, the process follows a simple rate law :

$$Rate = kC_A^{\alpha} C_B^{\beta} \ldots$$

In this approach, the integrated expressions of different rate equations are applied, and the concentrations of either the reactant or product are experimentally determined at various time intervals. These values of concentrations and time are then substituted into the different rate

equations to calculate the rate constant k at each interval. The equation that yields a consistent value for k indicates the correct reaction order.

Procedure

- Measure the concentration of a reactant over time.
- Plot the data in different ways to check which plot gives a straight line.
- The order is determined based on the type of straight-line plot obtained.

Zero-order integrated rate law :

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

- **A plot of the concentration $[A]$ with time gives a straight line.**
- **The slope is $-k$.**

First-order integrated rate law :

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

- **A plot of logarithmic $ln[A]$ vs . time gives a straight line, with a slope of $-k$.**

Second-order integrated rate law :

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

- **A plot of $\frac{1}{[A]}$ with time gives a straight line, with a slope of k.**

The main advantage of the integration method is that it enables the determination of reaction order from the data obtained in a single experiment.

III.2.2 Half-life period method

The half-life method provides a straightforward and efficient way to estimate the reaction order, especially when only one species is involved in the rate equation.

However, it becomes considerably more complex when applied to reactions involving multiple reactants.

For any chemical reaction, the half-life of a reactant refers to the duration needed for its concentration to decrease to half of its initial value. It is inversely proportional to the reaction's rate constant, meaning faster reactions have shorter half-lives, and it often varies depending on the concentrations of the reactants present.

III.2.3 Initial rate method (differential method)

This approach, introduced by Van't Hoff, is known as Van' Hoff's differential method. Let's examine the following reaction :

$$nA \rightarrow Product$$

The rate of reaction corresponding to two distinct concentrations, C_1 and C_2, can be represented as follows :

$$r_1 = -\frac{dC_1}{dt} = kC_1^n \qquad (III.16)$$

$$r_2 = -\frac{dC_2}{dt} = kC_2^n \qquad (III.17)$$

Dividing equation (III.16) by (III.17), we obtain :

$$\frac{r_1}{r_2} = \left(\frac{C_1}{C_2}\right)^n$$

Taking logarithms and solving for n, we get :

$$n = \frac{log(r_1) - log(r_2)}{log(C_1) - log(C_2)} \qquad (III.18)$$

The differential form of the rate equation may also be written as :

$$-\frac{dC}{dt} = kC^n$$

Or

$$-log\left(\frac{dC}{dt}\right) = logk + nlog(C) \qquad (III.19)$$

Thus, plotting log(rate) versus log(concentration) produces a straight line where the slope equals the reaction order n and the y-intercept equals log(k). This linear relationship allows for

direct determination of the reaction order. If the plot deviates from linearity, however, it suggests the reaction follows a more complex mechanism.

III.2.4 Ostwald isolation method (Degeneration of order)

Esson was the first to observe that when all reactants except one are present in large excess, the reaction appears to follow an order corresponding only to the isolated reactant. This is because the concentrations of the excess reactants remain nearly constant throughout the reaction. Ostwald later generalized this principle: if a reaction is of order α with respect to A, β with respect to B, and γ with respect to C, and if B and C are present in excess relative to A, the apparent reaction order determined by standard kinetic methods will correspond to α. The orders β and γ can be determined similarly by isolating each reactant in turn. However, this method should be used alongside other approaches for determining reaction order, as it can yield misleading results, especially in complex reactions involving multiple steps. In such cases, the reaction mechanism may vary with changes in concentration, leading to different pathways under different isolation conditions

Chapter IV: Complex Reactions

Several gas-phase reactions are classified as complex because they deviate from a single, straightforward reaction mechanism and instead proceed through multiple elementary steps. These reactions typically involve two or more side reactions. In contrast, a simple reaction is characterized by a single rate constant, reflecting the direct conversion of reactants into products. However, certain bimolecular or termolecular reactions proceed through a sequence of steps, each associated with its distinct rate constant. Such reactions exemplify the nature of a complex reaction mechanism. Among the typical examples of complex reactions are :

1. **Reversible or opposing reactions** are those in which the forward and reverse processes occur simultaneously, leading to the establishment of chemical equilibrium:

$$A + B \rightleftharpoons C + D$$

2. **Parallel reactions** are those in which a single reactant produces multiple products through different pathways occurring concurrently.
3. **Consecutive or successive reactions** are those that proceed through a sequence of elementary steps called a reaction mechanism. This type of reaction can be represented as follows :

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

A is a common reactant, and B_1 and B_2 are two specific reactants or co-reactants

It should be noted that, in all cases, it is easy to write the kinetic relationships, that is, the equations describing the evolution of concentrations in their differential form.

IV.1 Kinetics of reversible reactions

When the product of a chemical reaction can react back to form the original reactants, the forward reaction rate decreases as the concentration of the product increases. Eventually, the system reaches dynamic equilibrium, where forward and reverse reaction rates become equal. These reversible reaction systems are particularly important to study because their kinetic behavior provides direct insight into the thermodynamic properties of the equilibrium state.

Consider the following reversible monomolecular reaction:

$$A \rightleftharpoons B$$

The variation in the concentration of B as a function of time is due, on the one hand, to its formation from A at a certain rate $k_1[A]^n$and, on the other hand, to its disappearance at a certain rate $k_2[B]^m$, therefore :

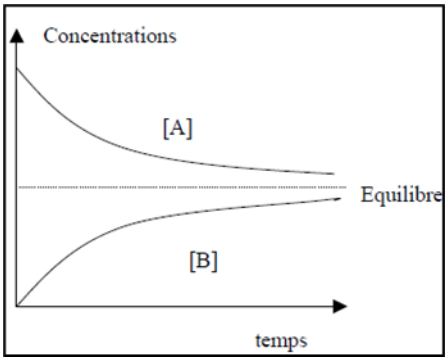
$$r = \frac{d[B]}{dt} = k_1[A]^n - k_2[B]^m = -\frac{d[A]}{dt} \qquad (IV.1)$$

The overall reaction rate at time t is the difference between the two rates :

$$r = r_1 - r_2$$

At equilibrium :

$$r_1 = r_2 \rightarrow r = 0$$



For the reaction: A⇌B

$At\ t = 0 : [A]_0 = a, [B]_0 = 0$

At time t : $[A] = a - x$ and $[B] = x$

At equilibrium : $[A] = a - x_e$ and $[B] = x_e$

$$\left.\begin{array}{l} A \xrightarrow{k_1,n,v_1} B \\ r_1 = k_1[A]^n \\ B \xrightarrow{k_{-1},m,v_2} A \\ r_2 = k_{-1}[B]^m \end{array}\right\} \quad r = r_1 - r_2 = k_1[A]^n - k_{-1}[B]^m$$

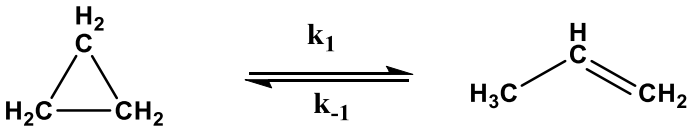
At equilibrium, the rates of the forward and reverse reactions become identical and are given by :

$$r_1 = r_2 \Rightarrow k_1[A]^n_{éq} = k_{-1}[B]^m_{éq} \Rightarrow \frac{k_1}{k_{-1}} = \frac{[B]^m_{éq}}{[A]^n_{éq}} = \frac{(x_e)^m}{(a-x_e)^n} \Rightarrow k_{éq} = \frac{(x_e)^m}{(a-x_e)^n}$$

IV.1.1 Reversible reactions first-order

Such reactions are characterized by first-order kinetics in forward and reverse directions.

It is assumed that the forward (k_1) and reverse (k_{-1}) reactions are of first order, for example, the isomerization reaction of cyclopropane to propene:

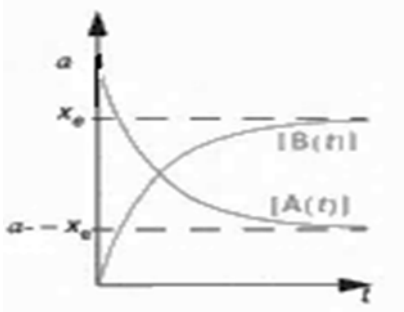


Consider the reaction: $A \rightleftharpoons B$

We can write : $A \xrightarrow{k_1,1,v_1} B$

$B \xrightarrow{k_{-1},1,v_2} A$

$$\Rightarrow r = r_1 - r_2 = k_1[A] - k_{-1}[B] = k_1(a-x) - k_{-1}x = \frac{dx}{dt} \qquad (1)$$



At equilibrium :

$$r_1 = r_2 \Rightarrow k_1(a-x_e) = k_{-1}x_e \Rightarrow k_{-1} = k_1\frac{(a-x_e)}{x_e} \qquad (2)$$

We replace (2) in (1), it gives :

$$r = k_1(a-x) - k_1\left(\frac{a-x_e}{x_e}\right)x = \frac{dx}{dt} \Rightarrow \frac{dx}{(a-x)x_e - (a-x_e)x} = \frac{k_1}{x_e}dt$$
$$\Rightarrow \int_0^x \frac{dx}{a(x_e - x)} = \frac{k_1}{x_e}\int_0^t dt$$

The integrated rate equation becomes :

$$ln\left(\frac{x_e}{x_e - x}\right) = k_1\left(\frac{a}{x_e}\right)t \qquad (IV.2)$$

IV.1.2 Reversible reactions second-order

Or a reversible bimolecular reaction. These are reactions in which both the forward and reverse processes follow second-order kinetics.

The following reaction serves as an example: $A + B \rightleftharpoons C + D$

At $t = 0$: $[A]_0 = [B]_0 = a$, $[C]_0 = [D]_0 = 0$

At time t : $[A] = [B] = a - x$, $[C] = [D] = x$

At equilibrium : $[A] = [B] = a - x_e$, $[C] = [D] = x_e$

We can write :

$$A + B \xrightarrow{k_1,2,v_1} C + D$$
$$C + D \xrightarrow{k_{-1},2,v_2} A + B$$

$$\Rightarrow r = r_1 - r_2 = k_1[A][B] - k_{-1}[C][D] = k_1(a-x)^2 - k_{-1}x^2 = \frac{dx}{dt} \qquad (1)$$

At equilibrium :

$$r_1 = r_2 \Rightarrow k_1(a-x_e)^2 = k_{-1}x_e^2 \Rightarrow k_{-1} = k_1\frac{(a-x_e)^2}{x_e^2} \qquad (2)$$

We replace (2) in (1), it gives :

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

$$\Rightarrow \frac{dx}{[(a-x)^2x_e^2-(a-x_e)^2x^2]}=\frac{k_1}{x_e^2}dt$$

$$\Rightarrow \frac{dx}{[(a-x)x_e-(a-x_e)x][(a-x)x_e+(a-x_e)x]}=\frac{k_1}{x_e^2}dt$$

$$\Rightarrow \int_0^x \frac{dx}{[a(x_e-x)][(ax_e+x(a-2x_e)]}=\frac{k_1}{x_e^2}\int_0^t dt \qquad (3)$$

We can write the integral (3) as :

$$\Rightarrow \int_0^x \frac{C_1dx}{[a(x_e-x)]}+\int_0^x \frac{C_2dx}{[(ax_e+x(a-2x_e)]}=\frac{k_1}{x_e^2}\int_0^t dt$$

After intégration, we obtain:

$$ln\left[\left(\frac{x_e}{x_e-x}\right)\left(\frac{ax_e}{2x_e-x}-x\right)\right]=ln\left(\frac{ax_e}{2x_e-a}\right)+2a\left(\frac{a-x_e}{x_e}\right)k_1t \qquad (IV.3)$$

IV.1.3 Reversible reactions ($n = 1, m = 2$)

It is postulated that the forward reaction follows first-order kinetics, while the reverse reaction proceeds according to a second-order rate law :

$$A \rightleftharpoons B + C$$

At $t = 0$ $[A]_0 = a, [B]_0 = [C]_0 = 0$

At time t $[A] = a - x, [B] = [C] = x$

At equilibrium $[A] = a - x_e, [B] = [C] = x_e$

The kinetics equation is :

$$r = r_1 - r_2 = k_1[A]^1 - k_{-1}[B]^1[C]^1 = k_1(a-x) - k_{-1}x^2 = \frac{dx}{dt} \qquad (1)$$

At equilibrium :

$$r_1 = r_2 \Rightarrow k_1(a-x_e) = k_{-1}x_e^2 \Rightarrow k_{-1} = k_1\frac{(a-x_e)}{x_e^2} \qquad (2)$$

We replace (2) in (1), it comes :

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

$$\Rightarrow \int_0^x \frac{dx}{[(a-x)x_e^2 - (a-x_e)x^2]} = \frac{k_1}{x_e^2}\int_0^t dt$$

$$\Rightarrow \int_0^x \frac{dx}{[(x_e-x)(ax_e + x(a-x_e)]} = \frac{k_1}{x_e^2}\int_0^t dt \qquad (3)$$

After the integration of equation (3), we obtain :

$$ln\left[\left(\frac{x_e}{x_e-x}\right)\left(\frac{ax_e}{a-x_e}+x\right)\right] = ln\left(\frac{ax_e}{a-x_e}\right) + k_1\left(\frac{2a-x_e}{x_e}\right)t \qquad (IV.4)$$

IV.1.4 Reversible reactions ($n = 2, m = 1$)

Consider the bimolecular reaction versus the monomolecular reaction :

$$A + B \rightleftharpoons C$$

At $t = 0$ $[A]_0 = [B]_0 = a, [C]_0 = 0$

At time t $[A] = [B] = a - x, [B] = x$

At equilibrium $[A] = [B] = a - x_e, [C] = x_e$

The kinetic equation is :

$$r = r_1 - r_2 = k_1[A][B] - k_{-1}[C] = k_1(a-x)^2 - k_{-1}x = \frac{dx}{dt} \qquad (1)$$

At equilibrium:

$$r_1 = r_2 \Rightarrow k_1(a-x_e)^2 = k_{-1}x_e \Rightarrow k_{-1} = k_1\frac{(a-x_e)^2}{x_e} \qquad (2)$$

We replace (2) in (1), it comes :

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

$$\Rightarrow \int_0^x \frac{dx}{[(a-x)^2 x_e - (a-x_e)^2 x]} = \frac{k_1}{x_e}\int_0^t dt \qquad (3)$$

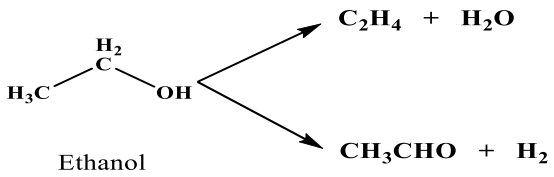
After intégration, we obtain :

$$ln\left[\left(\frac{a^2 - xx_e}{x_e - x}\right)\right] = ln\left(\frac{a^2}{x_e}\right) + k_1\left(\frac{a^2 - x_e^2}{x_e}\right)t \qquad (IV.5)$$

IV.2 Kinetics of parallel reactions

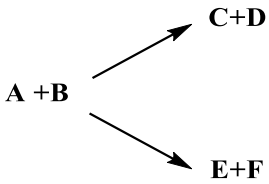
In this case, a reactant leads to two products through two reactions that occur simultaneously. In this type of reaction, the initial reactant(s) can react at the same time and along different pathways, for example :

- *Reaction of decomposition :*



We can distinguish two categories of parallel reactions:

- *Twins' reactions:* the reactants are common, but the products differ.

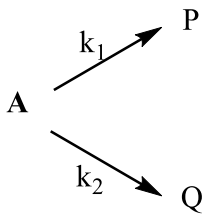


- *Competitive or concurrent reactions :* $A + B_1 \rightarrow C$

$A + B_2 \rightarrow D$

IV.2.1 Kinetics of twin reactions

Consider the reaction :



At $t = 0 \quad [A]_0 = a, [P]_0 = [Q]_0 = 0$

At time $t \qquad [A] = a - x, [P] = y, [Q] = z$

where: $x = y + z$ and $r = r_1 + r_2$

The rate of reactant A is written as :

$$r = -\frac{d[A]}{dt} = -\frac{d(a-x)}{dt} = \frac{dx}{dt} = k_1(a-x)^n + k_2(a-x)^m \qquad (IV.6)$$

$$\begin{cases} \dfrac{dx}{dt} = k_1(a-x)^n + k_2(a-x)^m \\ x = y + z \Rightarrow \dfrac{dx}{dt} = \dfrac{dy}{dt} + \dfrac{dz}{dt} \end{cases}$$

Therefore, it comes :

$$\begin{cases} \dfrac{dy}{dt} = k_1[A]^n \\ \dfrac{dz}{dt} = k_2[A]^m \end{cases}$$

We can deduce the ratios: $\dfrac{dy}{dx}, \dfrac{dy}{dz}, \dfrac{dz}{dx}$

$$\frac{dy}{dx} = \frac{k_1[A]^n}{k_1[A]^n + k_2[A]^m} = \frac{k_1}{k_1 + k_2[A]^{(m-n)}}$$

$$\frac{dy}{dz} = \frac{k_1[A]^n}{k_2[A]^m} = \frac{k_1}{k_2}[A]^{(n-m)}$$

$$\frac{dz}{dx} = \frac{k_2[A]^m}{k_1[A]^n + k_2[A]^m} = \frac{k_2}{k_1[A]^{(n-m)} + k_2}$$

1st case: n=m

$$\frac{dy}{dx} = \frac{k_1}{k_1 + k_2} \Rightarrow \int_0^y dy = \frac{k_1}{k_1 + k_2} \int_0^x dx \Rightarrow y = \frac{k_1}{k_1 + k_2} x$$

$$\frac{dy}{dz} = \frac{k_1}{k_2} \Rightarrow y = \frac{k_1}{k_2} z \Rightarrow [P] = \frac{k_1}{k_2} [Q]$$

In the case where: $\frac{y}{z} = \frac{[P]}{[Q]} = \frac{k_1}{k_2} = cst$ the reaction is twin and $n = m$.

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

2nd case : n≠m

Assume $n = 1$ et $m = 2$

At $t = 0$ $[A]_0 = a$

At time t $[A] = a - x,$
$x = y + z$

At t_∞, $y_\infty + z_\infty = a$

The kinetic law is :

$$r = -\frac{d[A]}{dt} = -\frac{d(a-x)}{dt} = \frac{dx}{dt} = k_1(a-x) + k_2(a-x)^2$$

We have :

$$x = y + z \Rightarrow \frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt}$$

$$\left.\begin{aligned} \frac{dy}{dt} &= k_1[A] = k_1(a-x) \\ \frac{dz}{dt} &= k_2[A]^2 = k_2(a-x)^2 \end{aligned}\right\} \quad \frac{dx}{dt} = k_1(a-x) + k_2(a-x)^2$$

$$\Rightarrow \int_0^x \frac{dx}{(a-x)(k_1 + k_2(a-x))} = \int_0^t dt \qquad (1)$$

After intégration of equation (1), we obtain :

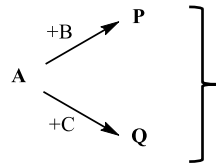
$$ln\left(\frac{a}{a-x}\right) = ln\left(\frac{\frac{k_1}{k_2}+a}{\frac{k_1}{k_2}+(a-x)}\right) + k_1 t \qquad (IV.7)$$

$$\frac{dy}{dx} = \frac{k_1(a-x)}{k_1(a-x)+k_2(a-x)^2} = \frac{k_1}{k_1+k_2(a-x)}$$

$$\Rightarrow \int_0^y dy = \int_0^x \frac{k_1 dx}{k_1+k_2(a-x)} \Rightarrow y = \frac{k_1}{k_2} ln\left(\frac{k_1+k_2 a}{k_1+k_2(a-x)}\right) = [P]$$

IV.2. 2 Kinetics of competitive reactions

Consider the following competitive reaction:



$$\neq A + B + C \rightarrow P + Q$$

At $t = 0$ $[A]_0 = a, [B]_0 = b, [C]_0 = c, [P]_0 = 0, [Q]_0 = 0$

At time t $[A] = a - x, [B] = b - y, [C] = c - z, [P] = y, [Q] = z$

Where: $x = y + z$ and $r = r_1 + r_2$

The rate of reaction :

$$r = r_1 + r_2 = k_1[A]^n[B]^m + k_2[A]^{n'}[C]^{m'} = k_1(a-x)^n(b-y)^m + k_2(a-x)^{n'}(c-z)^{m'}$$
$$= -\frac{d(a-x)}{dt} = \frac{dx}{dt} \qquad (IV.8)$$

We have :

$$x = y + z \Rightarrow \frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt}$$

$$\begin{cases} \frac{dx}{dt} = k_1(a-x)^n(b-y)^m + k_2(a-x)^{n'}(c-z)^{m'} & (1) \\ \frac{dy}{dt} = k_1(a-x)^n(b-y)^m & (2) \\ \frac{dz}{dt} = k_2(a-x)^{n'}(c-z)^{m'} & (3) \end{cases}$$

To simplify equation (1), we assume the following cases :

If : $\begin{cases} n = n' \\ m = m' = 1 \end{cases}$

$$\frac{dy}{dz} = \frac{k_1 (a-x)^n (b-y)^m}{k_2 (a-x)^{n'} (c-z)^{m'}} \Rightarrow \int_0^y \frac{dy}{(b-y)} = \frac{k_1}{k_2} \int_0^z \frac{dz}{(c-z)} \Rightarrow \ln\left(\frac{b}{b-y}\right) = \frac{k_1}{k_2} \ln\left(\frac{c}{c-z}\right) \Rightarrow \ln \frac{[B]_0}{[B]} = \frac{k_1}{k_2} \ln \frac{[C]_0}{[C]}$$

If we plot the curve $\ln \frac{[B]_0}{[B]} = f\left(\ln \frac{[C]_0}{[C]}\right)$, we obtain a straight line with a slope of $\frac{k_1}{k_2}$

If : $\begin{cases} n = n' \\ m = m' = 2 \end{cases}$

$$\frac{dy}{dz} = \frac{k_1 (a-x)^n (b-y)^m}{k_2 (a-x)^{n'} (c-z)^{m'}} = \frac{k_1}{k_2} \left(\frac{b-y}{c-z}\right)^2 \Rightarrow \int_0^y \frac{dy}{(b-y)^2} = \frac{k_1}{k_2} \int_0^z \frac{dz}{(c-z)^2} \Rightarrow \frac{1}{(b-y)} - \frac{1}{b} = \frac{k_1}{k_2} \left(\frac{1}{c-z} - \frac{1}{c}\right)$$

$$\Rightarrow \frac{1}{[B]} - \frac{1}{[B]_0} = \frac{k_1}{k_2} \left(\frac{1}{[C]} - \frac{1}{[C]_0}\right)$$

If : $\begin{cases} n = n' \\ m \neq m', m = 1, m' = 2 \end{cases}$

$$\frac{dy}{dz} = \frac{k_1 (a-x)^n (b-y)^m}{k_2 (a-x)^{n'} (c-z)^{m'}} = \frac{k_1}{k_2} \frac{(b-y)}{(c-z)^2} \Rightarrow \int_0^y \frac{dy}{(b-y)} = \frac{k_1}{k_2} \int_0^z \frac{dz}{(c-z)^2} \Rightarrow \ln\left(\frac{b}{b-y}\right) = \frac{k_1}{k_2} \left(\frac{1}{c} - \frac{1}{c-z}\right)$$

$$\Rightarrow \ln\left(\frac{[B]_0}{[B]}\right) = \frac{k_1}{k_2} \left(\frac{1}{[C]_0} - \frac{1}{[C]}\right)$$

IV.3 Kinetics of successive reactions

It is often the case that reactants in the system do not combine directly to form the final products. Instead, they first generate intermediate species, which may subsequently react either with each other or with the original reactants.

They fall into two categories depending on whether or not an initial reactant participates in the subsequent steps:

- *Competitive successive reactions* in the form of

$$A \xrightarrow{+B} C \xrightarrow{+B} D \xrightarrow{+B} E \ldots$$

- *Non-competitive successive reactions* in the form of

$$A \rightarrow B \rightarrow C \rightarrow D \ldots$$

IV.3.1 Kinetics of non-competitive successive reactions

Consider the reaction:

$$A \xrightarrow{k_1,n} B \xrightarrow{k_2,m} C$$

with $n = m = 1$

At $t = 0$ $[A]_0 = a, [B]_0 = 0, [C]_0 = 0$

At time t $[A] = a - x, [B] = y, [C] = z$

where: $x = y + z$

For the constituent A :

$$r = -\frac{d[A]}{dt} = k_1[A] \Longrightarrow ln[A] = ln[A]_0 - k_1 t \Longrightarrow [A] = ae^{-k_1 t} \qquad (IV.9)$$

For the constituant B :

We have the formation of constituent B in the first reaction and its disappearance in the second reaction. The rate of the reaction is:

$$r = \frac{dy}{dt} = r_1 - r_2 = k_1[A] - k_2[B] = k_1[A] - k_2 y \Longrightarrow \frac{dy}{dt} + k_2 y = k_1[A] = k_1 a e^{-k_1 t} \quad (1)$$

Multiplying equation (1) by $e^{k_2 t}$, we get :

$$\left(\frac{dy}{dt} + k_2 y\right) e^{k_2 t} = k_1 a\left(e^{(k_2 - k_1)t}\right) \qquad (2)$$

We know that:

$$\left(\frac{d}{dt}(y e^{k_2 t})\right) = \frac{dy}{dt}(e^{k_2 t}) + \frac{d}{dt}(y e^{k_2 t}) \qquad (3)$$

By comparing (2) and (3), we find:

$$\left(\frac{d}{dt}(y e^{k_2 t})\right) = k_1 a\left(e^{(k_2 - k_1)t}\right)$$

The integration of this equation gives :

$$ye^{k_2 t} = \frac{k_1 a}{k_2 - k_1}\left(e^{(k_2-k_1)t} - 1\right)$$

$$\Longrightarrow y = [B] = \frac{k_1 a}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

For the constituent C :

At time t :

$$[C] = z \Longrightarrow \frac{dz}{dt} = k_2[B] = \frac{k_2 k_1 a}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

$$\Longrightarrow \int_0^z dz = \frac{k_2 k_1 a}{k_2 - k_1}\int_0^t (e^{-k_1 t} - e^{-k_2 t})\, dt$$

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

IV.3.1.1 The maximum concentration of B

At t_{max}, the concentration of B reaches a maximum value. To obtain t_m, it is necessary to solve :

$$\frac{dy}{dt} = \left(\frac{d[B](t)}{dt}\right)_{t=t_m} = 0$$

$$\frac{dy}{dt} = 0 \Rightarrow \frac{k_1 a}{k_2 - k_1}\left(-k_1 e^{-k_1 t_m} + k_2 e^{-k_2 t_m}\right) = 0 \Rightarrow \left(-k_1 e^{-k_1 t_m} + k_2 e^{-k_2 t_m}\right) = 0$$

$$\Rightarrow \frac{k_1}{k_2} = \frac{e^{-k_2 t_m}}{e^{-k_1 t_m}} = e^{(k_1 - k_2)t_m} \Rightarrow t_m = \frac{\ln\left(\frac{k_1}{k_2}\right)}{(k_1 - k_2)}$$

Where t_m corresponds to the maximum time for the disappearance of B.

$[B]_{max}$ =?

We have : $\frac{d[B]}{dt} = k_1[A] - k_2[B] = 0 \Rightarrow k_1[A]_0 e^{-k_1 t} = k_2[B] \Rightarrow [B]_m = \frac{k_1}{k_2}[A]_0 e^{-k_1 t_m}$

We substitute t_m into this equation, and we get:

$$[B]_m = \frac{k_1}{k_2}[A]_0 \, e^{\frac{-k_1}{(k_1-k_2)}\ln\left(\frac{k_1}{k_2}\right)} = [A]_0\left(\frac{k_1}{k_2}\right)^{\frac{k_2}{(k_2-k_1)}}$$

$$\text{At } t_\infty \begin{cases} [A] = 0 \\ [B] = 0 \\ [C] = a = [A]_0 \end{cases}$$

The variation of [A], [B], and [C] with respect to time is shown in the figure.1:

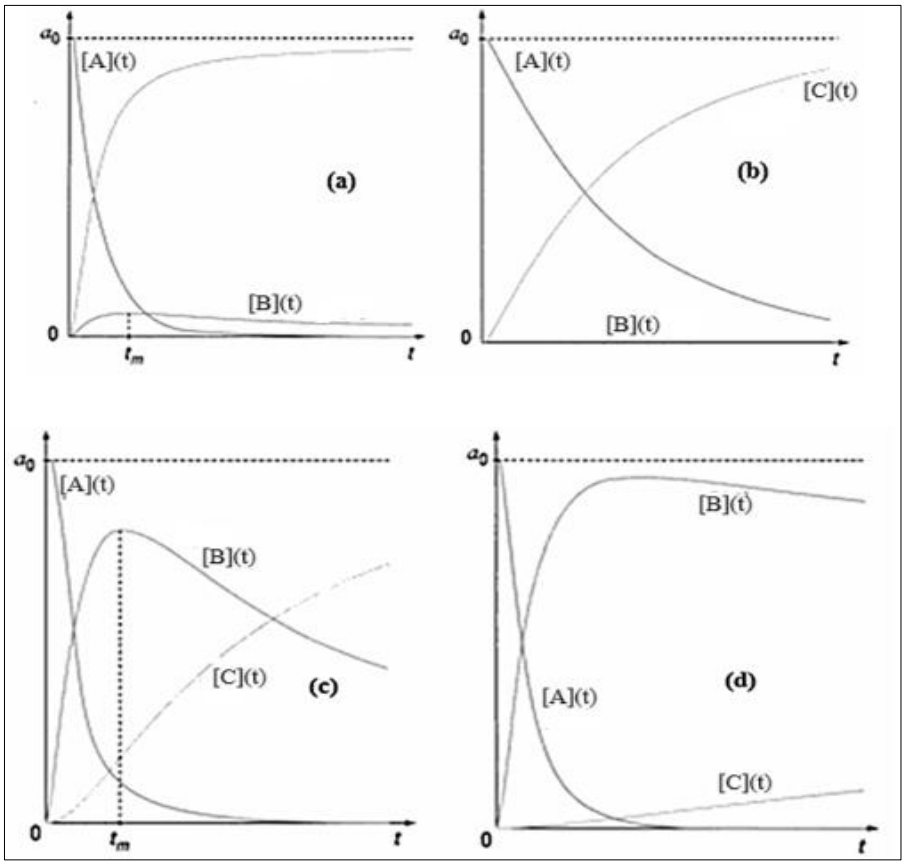


Fig.1 Evolution of the concentrations of A, B, and C over time

- **(a) $k_2 > k_1$**

It is observed that the concentration of the intermediate B remains very low, even at time t_m, so we can write: $[B](t) = 0$, When entity B is formed, it disappears very quickly to form C. The mechanism approaches the limiting mechanism $A \xrightarrow{k_1} C$, this step appears as the kinetically determining step.

- **(b) $k_2 >>> k_1$**

In this limiting case, the concentration of B remains very low and practically constant, so we can write: $\frac{d[B]}{dt} \cong 0$, this assumption corresponds to the quas-state approximation applied to an intermediate.

- **(c)$k_1 > k_2$**

The concentration of [B] attains its highest level at a specific point in time before subsequently decreasing $t_m = \frac{1}{(k_1 - k_2)} \ln\left(\frac{k_1}{k_2}\right)$, and the intermediate B begins to accumulate in the medium before forming C.

- **(d) $k_1 >>> k_2$**

The maximum concentration of the intermediate compound B appears very quickly after the start of the reaction and almost reaches that of the reactant A. The mechanism thus approaches the mechanism of $A \xrightarrow{k_2} C$.

The rate of the slowest step, referred to as the kinetically determining step, dictates the rate of appearance or formation of C.

Chapter V : Homogeneous Catalysis

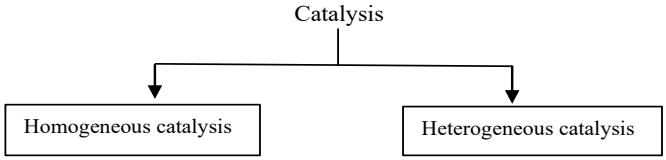
Most chemical reactions require the input of energy in the form of activation energy. However, some substances can reduce this activation energy, thus promoting the reaction. At the end of the reaction, these substances, also called catalysts (or substrates and reactants), are recovered.

V.1 Generalities

Catalysis is a multidisciplinary field with applications in chemistry, biology, and various industrial sectors. The study of catalysis is crucial for understanding and optimizing chemical processes, and it remains an area of active research and development.

Catalysis is a fundamental concept in chemistry that describes the phenomenon in which a substance, known as a catalyst, enhances the rate of a chemical reaction while remaining unchanged upon completion of the process. Here are some key aspects of catalysis :

- ***Acceleration of reactions:*** The main role of catalysis is to increase the rate of chemical reactions. By lowering the activation energy, a catalyst allows reactant molecules to overcome the energy barrier more easily, leading to faster reaction rates.
- ***Catalyst specificity:*** Different catalysts are often needed for different reactions. Catalysts can be very specific to certain types of chemical transformations, contributing to the selectivity of the reaction.
- ***Reversibility:*** Catalysis can be reversible, allowing a catalyst to facilitate both forward and reverse reactions in a dynamic equilibrium. This is particularly important in reactions that reach a state of equilibrium between reactants and products.
- ***Homogeneous and heterogeneous catalysis:*** Catalysis can occur in the same phase as the reactants (homogeneous catalysis) or in a different phase (heterogeneous catalysis). In homogeneous catalysis, the catalyst is usually part of the same solution or gas phase as the reactant, while in heterogeneous catalysis, the catalyst is usually solid.



Catalysts and reactants in the same phase

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO(g)} 2SO_{3(g)}$$

$$CH_3CHO_{(vapor)} \xrightarrow{I_2(vapor)} CH_{4(g)} + CO_{(g)}$$

$$Ester_{(l)} + H_2O_{(l)} \xrightarrow{H^+(l)} Acid_{(l)} + Alcohol_{(l)}$$

Catalysts and reactants in different phases

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{Pt(s)} 2SO_{3(g)}$$

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_{3(g)}$$

$$CH_2 = CH_{2(g)} \xrightarrow{Ni(s)} CH_3 - CH_{3(g)}$$

$$2H_2O_{2(l)} \xrightarrow{Pt(s)} 2H_2O_{(l)} + O_{2(g)}$$

- ***Catalyst poisoning:*** Some catalysts may be sensitive to certain substances that can deactivate or poison them, reducing their catalytic activity.
- ***Industrial significance:*** Catalysis plays a vital role in many industrial processes, enhancing performance, lowering energy use, and facilitating the production of desired products.
- ***Biocatalysts (Enzymatic):*** In biological systems, enzymes act as natural catalysts, accelerating biochemical reactions essential to life processes. Enzymatic catalysis is very specific and often occurs under mild conditions.
- ***Environmental impact:*** Catalysis can contribute to green chemistry by reducing the environmental impact of chemical processes. The utilization of efficient catalytic systems often enables the reaction to proceed under milder operating conditions, thereby reducing energy consumption, while simultaneously minimizing the formation of undesirable by-products.
- ***Catalyst regeneration:*** represents a significant advantage in catalytic processes, as many catalysts can be restored and reutilized in successive reactions, which contributes to greater sustainability and improved economic efficiency.

V.2 Catalyst concepts

A catalyst is defined as a substance that alters the kinetics of a chemical reaction while remaining chemically unchanged throughout the reaction process, typically effective even when present in minimal concentrations. The process by which catalysts influence reaction rates is termed catalysis. Catalysts may be classified based on their effect on reaction kinetics: those that increase the rate of reaction are designated as positive catalysts or promoters. For example:

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_3$$

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

$$H_2O_2 \xrightarrow{Pt} H_2O + O$$

In contrast, those that decrease the reaction rate are classified as negative catalysts or inhibitors. For example:

$$2H_2O_2 \xrightarrow{Acetanilide} 2H_2O + O_2$$

$$4CHCl_3 + 3O_2 \xrightarrow{Alcohol} 4COCl_2 + 2H_2O + 2Cl_2$$

Catalysts generally affect reaction kinetics by altering the activation energy barrier. In particular, positive catalysts lower this energy, thereby reducing both the energy requirement and the time needed for reactant molecules to progress from their ground vibrational state to the activated complex.

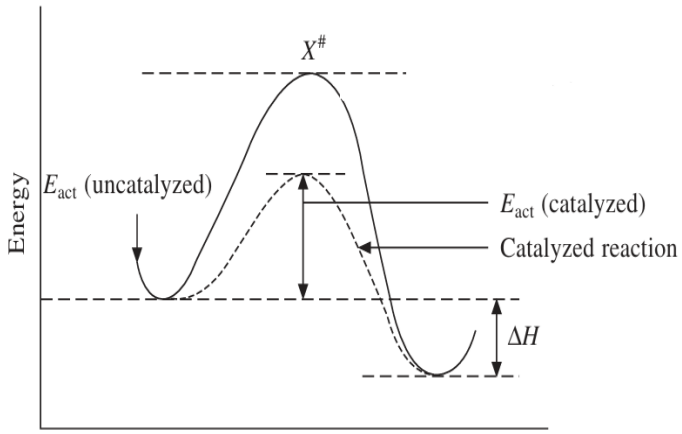


Fig.1 Activation energy for reactions catalyzed and uncatalyzed

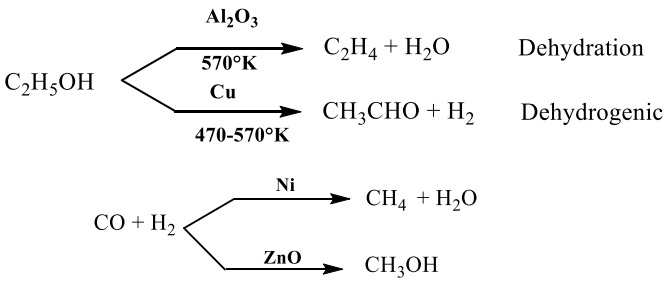
Catalytic processes demonstrate distinctive kinetic and thermodynamic properties relative to their non-catalytic counterparts and may be characterized through the following parameters :

- ✓ A catalyst retains its quantity and chemical composition upon completion of the reaction, although its physical characteristics, such as particle size or surface morphology, may undergo modification.

- ✓ Even a very minimal quantity catalyst can be sufficient to alter the reaction rate. For example, as little as 10^{-3} gram-ions per liter of Cu^{2+} can accelerate the oxidation of sodium sulfate by oxygen in aqueous solution :

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

- ✓ A catalyst does not possess the capacity to initiate thermodynamically unfavorable reactions; instead, it facilitates alternative reaction pathways that reduce the activation energy barrier, subsequently enhancing reaction kinetics. In this sense, it acts as an agent that provides an alternative mechanism for the process.
- ✓ Each catalyst exhibits a specific mode of action, as catalysts are often highly selective in their activity. A catalyst that is effective for one type of reaction may prove ineffective for another :



V.3 General catalytic mechanism

To accelerate the rate of a reaction, a catalyst combines with a reactant to produce an intermediate complex, which subsequently decomposes to yield the final products while regenerating the catalyst. The reactant that associates with the catalyst is usually called the substrate. A common mechanism that explains catalytic reactions can be shown as follows :

$$S + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X + Y$$

$$X + W \xrightarrow{k_3} P + C$$

S represents the substrate or reactant, and C denotes the catalyst, while X signifies the intermediate complex formed during the reaction. The term Y refers to an additional species formed alongside X, and W designed a molecule that subsequently reacts with the complex to yield the product P, accompanied by the release of the catalyst. In the case of surface catalysis, where X represents an adsorption complex and the entities Y and W are absent, the mechanism can be expressed in the following simplified form :

$$S + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X$$

$$X \xrightarrow{k_3} P + C$$

In such cases, the concentration of the intermediate complex is evaluated using the steady-state approximation.

The product formation rate is defined by :

$$\frac{d[P]}{dt} = k_3[X] \qquad (V.1)$$

The concentration of intermediate complex X can be determined using the steady-state conditions, that is :

$$\frac{d[X]}{dt} \cong 0$$

$$\frac{d[X]}{dt} = k_1[S][C] - k_2[X] - k_3[X] = 0 \Longrightarrow k_1[S][C] - (k_2 + k_3)[X] = 0$$

$$\Longrightarrow [X] = \frac{k_1}{k_2 + k_3}[S][C] \qquad (V.2)$$

By substituting Eq (V.2) into the rate expression provided in Eq (V.1), one yields :

$$\frac{d[P]}{dt} = \frac{k_1 k_3}{k_2 + k_3}[S][C] = k_c[S][C] \qquad (V.3)$$

k_c is the catalytic coefficient.

Equation (V.3) indicates that the reaction rate varies with the catalyst concentration. When the catalyst concenration is held constant, the effective rate constant can be expressed as :

$$k_{obs} = \frac{k_1 k_3}{k_2 + k_3}[C] \qquad (V.4)$$

If $k_3 \ll k_2$, its contribution in the denominator of equation (V.4) can be neglected. Consequently :

$$k_{obs} = \frac{k_1}{k_2} k_3[C] = k_{eq}\,[C] \qquad (V.5)$$

V.4 Homogeneous catalysis

A homogeneous catalyst refers to a catalytic substance that exists in the same physical phase as the reactants involved in the reaction. In such systems, both the catalyst and the reactants are present in a shared phase, whether gaseous, liquid, or solid. Homogeneous catalysts are commonly used in liquid-phase reactions.

The following section presents general characteristics of homogeneous catalysts :

- ***Solubility:*** homogeneous catalysts exhibit complete miscibility within the reaction medium, a critical property that ensures uniform distribution throughout the reaction mixture and facilitates molecular-level interactions between catalyst and reactants.
- ***Homogeneous distribution:*** since the catalyst exists within the same phase as the reactants, it can readily interact with reactive molecules at the molecular level. This intimate contact typically results in enhanced reaction rates compared to heterogeneous catalysis, where the catalyst occupies a distinct phase from the reactants.
- ***Specifity:*** homogeneous catalysts frequently demonstrate exceptional selectivity toward particular reactions. They can be rationally designed and selected to catalyze specific transformations with high selectivity.
- ***Catalyst recovery:*** A major challenge associated with homogeneous catalysts is their separation and recovery from the reaction mixture. Techniques such as extraction or distillation are frequently employed to isolate the catalyst for subsequent reuse.
- ***Sensitivity to reaction conditions:*** homogeneous catalysts exhibit considerable sensitivity to variations in reaction parameters, including temperature, pressure, and reactant concentration. Precise maintenance of optimal reaction conditions is essential to ensure maximum catalytic efficiency and prevent catalyst deactivation.

Examples: Some common examples of homogeneous catalysts include transition metal complexes, acids, and bases dissolved in a reaction solvent.

1. ***Transition metal catalysts***

- ✓ Ruthenium-based catalysts

Exemple: the complex $[RuCl_2(p-cymene)_2)$, commonly employed in hydrogenation reactions.

- ✓ Palladium-based catalysts

Example: the complex $[Pd(PPh_3)_4]$, widely used in carbon-carbon bond forming reactions, particulary cross coupling reactions.

- ✓ Nickel-based catalysts

Example: the complex $[Ni(dppe)Cl_2]$, which catalyzes a variety of addition and coupling reaction.

2. Acid catalysts

- ✓ Sulfuric acid (H_2SO_4)

Example: frequently used as an acid catalyst in esterification reactions.

- ✓ Triflic acid

Example: a strong Lewis acid employed in Friedel-Crafts reactions.

3. Basic catalysts

- ✓ Sodium hydroxide $(NaOH)$

Example: used as a basic catalyst in the saponification of esters.

- ✓ Triethylamine (NEt_3)

Example: a basic organic catalyst used in condensation and alkylation reactions.

4. Reaction solvents

- ✓ Dimethyl sulfoxide $(DMSO)$

Example: widely used as a reaction solvent in organic transformations, especially in nucleophilic substitution reactions.

- ✓ Acetonitrifile (CH_3CN)

Example: a commonly employed solvent in transition metal-catalyzed reactions, especially in organometallic chemistry.

It is important to note that these represent only a small portion of the wide range of homogeneous catalysts available. The selection of a homogeneous catalyst is closely determined by the specific chemical reaction to be catalyzed and the corresponding reaction

conditions. Moreover, constant advances in catalytic chemistry are leading to the development of new, more efficient, and selective catalysts.

Homogeneous catalysis finds extensive application in numerous industrial processes and laboratory syntheses due to the benefits it provides regarding reaction control and selectivity. Nevertheless, challenges associated with catalyst recovery and potential sensitivity to reaction conditions remain active areas of ongoing research and development.

V.4.1 Homogeneous acid-base catalysis

The acceleration of chemical reactions through the addition of an acidic or basic species into reaction mixtures represents one of the most widely used approaches in mechanism studies, known as acid-base catalysis. Numerous chemical reactions, especially in organic chemistry, proceed under the influence of either acidic or basic species, or both. When reactions are catalyzed exclusively by H^+ ions, it is known as specific hydrogen ion catalysis. Conversely, when any acidic species can facilitate the reaction, the mechanism is classified as general acid catalysis. Analogously, reactions that are accelerated solely by hydroxide ions, OH^-, are categorized as specific hydroxyl ion catalysis. When any basic species can promote the reaction, the process is termed general base catalysis.

This mechanism provides a systematic approach to understanding the role of acid-base interactions in chemical transformations and offers valuable insights into reaction optimization.

In the mechanism of acid-base-catalyzed reactions, the initial sequence involves the transfer of a proton, either from an acid to the substrate or from the substrate to a base. Accordingly, the interaction between an acid HA and a substrate can be expressed as follows :

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^+ + H_2O \overset{k_2}{\rightarrow} P + H_3O^+$$

P is the reaction product.

The product formation rate P is given by the expression :

$$\frac{d[P]}{dt} = k_2[SH^+] \qquad (V.6)$$

By applying the steady-state approximation to species SH^+, we obtain :

$$\frac{d[SH^+]}{dt} = k_1[S][HA] - k_{-1}[SH^+][A^-] - k_2[SH^+] = 0$$

$$\Longrightarrow [SH^+] = \frac{k_1[S][HA]}{k_{-1}[A^-] + k_2} \qquad (V.7)$$

Then, equation (V.6) can be written as :

$$\frac{d[P]}{dt} = \frac{k_1 k_2[S][HA]}{k_{-1}[A^-] + k_2} \qquad (V.8)$$

From the last equation, if $k_2 \gg k_{-1}[A^-]$, then we get :

$$\frac{d[P]}{dt} = k_1[S][HA]$$

In this case, it can be said that the mechanism corresponds to general acid catalysis, and the reaction rate becomes directly dependent on the concentrations of both the catalyst and the reactants.

The assumption that hydrogen and hydroxide ions are the sole catalytic species in acid-base catalysis requires revision. It is, however, useful to begin by considering the kinetic equation applicable to cases in which these ions act as the only effective catalysts.

When a reaction is conducted in aqueous solution under strongly acidic conditions at low pH, the concentration of hydroxide ions is diminished to the point where they exert negligible catalytic influence. In such cases, hydrogen ions may serve as the sole effective catalysts, and the rate expression takes the form :

$$r = k_0[S] + k_{H^+}[S][H^+] \qquad (V.9)$$

Here, S denotes the substrate, k_{H^+}represent the catalytic constant for hydrogen ions, while k_0 corresponds to the rate constant in the absence of a catalyst.

Under conditions where hydroxide ions also contribute to the catalysis, the rate equation can be expressed as :

$$r = k_0[S] + k_{H^+}[S][H^+] + k_{OH^-}[S][OH^-] \qquad (V.10)$$

We may express the first-order rate constant for the reaction through the following equation :

$$k = \frac{r}{[S]}$$

So,

$$k = k_0 + k_{H^+}[H^+] + k_{OH^-}[OH^-] \qquad (V.11)$$

k_{OH^-} represent the catalytic constant for hydroxide ions.

Within protonic solvents, the levels of protons and hydroxide ions are interdependent rather than independent variables. In an aqueous system, the apparent rate constant described in equation (V.11) may therefore be represented as :

$$k = k_0 + k_{H^+}\left(\frac{K_e}{[OH^-]}\right) + k_{OH^-}[OH^-] \qquad (V.13)$$

If k_{OH^-} is very low, the reaction predominantly proceeds through specific hydrogen catalysis. Conversely, if k_{H^+} is negligible, the reaction is governed by specific hydroxide ion catalysis.

Under acidic conditions, hydroxide-catalyzed reactions become negligible, and the reaction rate exhibits a linear dependence on hydrogen ion concentration. This allows for straightforward determination of the acid-catalysis constant k_{H^+}. Therefore, from Eq (V.12), the rate constant is given as :

$$log(k) = log(k_0) + log(k_{H^+}[H^+]\,)$$

$$log(k) = log(k_0) + log(k_{H^+}) - pH \qquad (V.14)$$

A plot of ln(k) vs. pH gives a straight line, with slope -1.

Under basic conditions, the opposite occurs: hydrogen ion catalysis becomes insignificant, the rate shows linear dependence on hydroxide ion concentration, and the base catalysis constant k_{OH^-}, can be readily determined, therefore :

$$k = k_0 + k_{OH^-}\left(\frac{K_e}{[H^+]}\right)$$

$$log(k) = log(k_0) + log(k_{OH^-}.K_e) + pH \qquad (V.15)$$

For a basic solution, a plot of ln(k) vs. pH gives a straight line, and the slope is +1.

V.5 Enzymatic catalysis

Biological processes, whether occurring at the cellular level or within complex multicellular organisms, represent some of the most sophisticated and challenging phenomena

in chemistry and chemical kinetics. The extensive research conducted to elucidate elementary kinetic pathways in biological systems has yielded several important generalizations. A fundamental principle that has emerged is that the majority of discrete structural transformations in biomedical processes are catalyzed by macromolecular proteins known as enzymes.

Enzymes are protein molecules that function as catalysts in a wide range of biologically and biochemically significant reactions. Owing to their efficiency, they are effective even at very low concentrations, typically in the range of 10^{-8} to 10^{-10} mol.dm^{-3}. The molecule undergoing the reaction is referred to as the substrate (S), which is usually present at concentrations of 10^{-6}mol.dm^{-3} or higher. Consequently, the substrate is always present in large excess relative to the enzyme.

Enzymes function by means of an active site, a specialized region of the protein that is precisely structured to recognize and bind a specific reactant molecule or substrate. The enzyme activity depends on the concentrations of substrate, enzyme, acidity, and temperature.

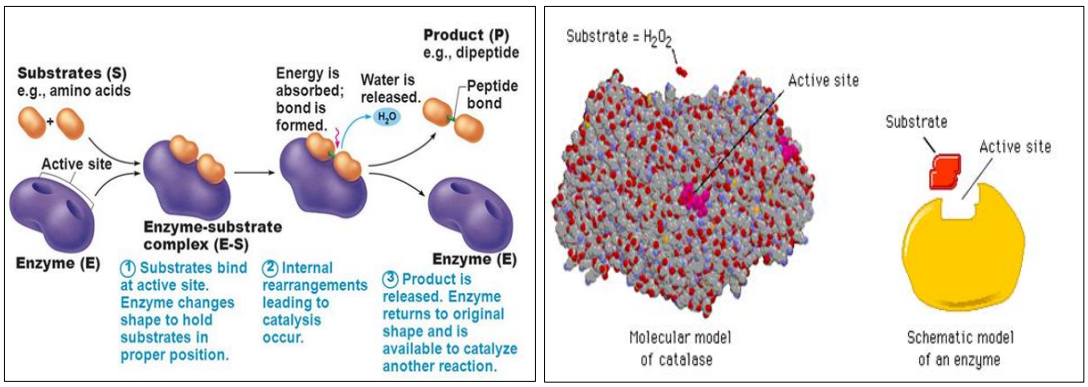


Fig.2 Schematic of enzyme action

V.5.1 Kinetics of enzyme-catalyzed reactions

Studying the kinetics of enzyme-catalyzed reactions can present considerable challenges. However, many enzyme systems can be explained with simple kinetic models that work quite well in practice. Enzyme-catalyzed reactions are also classified as a type of homogeneous catalysis. In an enzyme-catalyzed reaction, the reacting molecule (substrate, S) binds reversibly to a specific site on the enzyme E, forming a stable enzyme-substrate complex (ES). The subsequent breakdown of this complex into products is the rate-determining step. The kinetic role of enzymes was first formally described by Michaelis and Menten (1913). This

mechanism, which resembles the model proposed by Langmuir for surface catalysis, can be represented as :

$$E+S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \overset{k_2}{\rightarrow} P + E$$

Where, ES is an activated complex.

The rate of reaction is :

$$r = \frac{d[P]}{dt} = k_2[ES] \qquad (V.16)$$

In this case, the steady-state assumption is made, with the relevant constants k_1, k_{-1}, and k_2 :

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0 \qquad (V.17)$$

$$[ES] = \frac{k_1}{k_{-1} + k_2}[E][S]$$

And therefore,

$$r = \frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2}\ [E][S]$$

During the examination of enzyme-catalyzed reactions, the amount of substrate is generally present in significant excess over that of the enzyme. As a result, only a small fraction of the substrate becomes bound to the enzyme. Thus, the overall enzyme concentration, represented as E_0, equals the combined concentrations of free enzyme and the enzyme-substrate complex :

$$[E_0] = [E] + [ES] \qquad (V.18)$$

The equation (V.17) is given by :

$$k_1([E_0] - [ES])[S] - (k_{-1}+k_2)[ES] = 0$$

$$[ES] = \frac{k_1[E_0][S]}{k_{-1}+k_2 + k_1[S]}$$

From the Eq (V.16) the rate of reaction is :

$$r = \frac{d[P]}{dt} = k_2 \frac{[E_0][S]}{\frac{k_{-1}+k_2}{k_1} + [S]}$$

$$r = k_2 \frac{[E_0][S]}{k_M + [S]} = k\,[E_0] \qquad (V.19)$$

Or

$$k = \frac{k_2[S]}{k_M + [S]}$$

The equation (V.19) is called as a Michaelis-Menten equation, and k_M is known as the Michaelis constant in $mol.dm^{-3}$.

From the above analysis, it is evident that the rate of an enzyme-catalyzed reaction (enzymolysis) increases linearly with enzyme concentration, while its dependence on substrate concentration is more complex. However, under certain conditions, the relationship with substrate concentration becomes simplified.

- **If $[S] \gg k_M$:**

The reaction rate is $r = k_2[E_0]$, when the substrate is supplied in substantial excess, the overall rate of the reaction no longer depends on substrate concentration. In this situation, the substrate concentration remains effectively constant throughout the reaction. Under such conditions, the reaction achieves its maximum rate ($r = r_{max}$), since all enzyme active sites are occupied by substrate molecules.

- **If $[S] \ll k_M$:**

The reaction rate is :

$$r = \frac{k_2}{k_M}[E_0][S]$$

In this case, the reaction rate is first order with respect to both the initial enzyme concentration and the substrate concentration.

- **If $[S] = k_M$:**

The rate of the enzymatic reaction simplifies significantly. The Michaelis-Menten equation is :

$$r = k_2 \frac{[E_0][S]}{k_M + [S]} = \frac{r_{max}[S]}{[S] + [S]} = \frac{r_{max}}{2}$$

k_M corresponds to the substrate concentration at which the reaction rate attains half of its maximum value, as illustrated in the figure

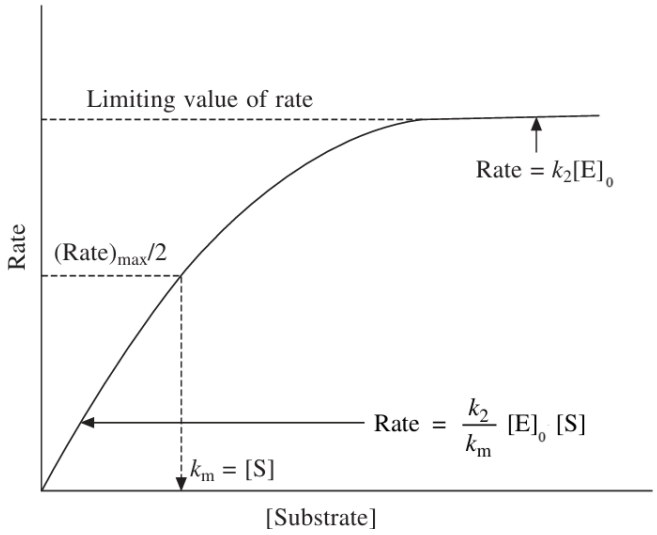


Fig.3 Reaction rate vs. substrate concentration in enzymatic catalysis

To evaluate k_2 and k_M from experimental rate data, the Michaelis-Menten equation must be rearranged into an inverse form. The common linearization method is :

$$k = \frac{k_2[S]}{k_M + [S]} \Rightarrow \frac{1}{k} = \frac{k_M}{k_2[S]} + \frac{1}{k_2}$$

A plot of $\frac{1}{k}$ against $\frac{1}{[S]}$, form a linear graph with a slope of $\frac{k_M}{k_2}$, and an intercept of $\frac{1}{k_2}$. In experimental applications, the initial rates method is commonly used to determine reaction rate, as it reduces interference from subsequent product-related reactions.

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