

Chapter 2 : Chemical kinetics

Chapter 2 : Chemical kinetics :

- I. Definition, rate of reaction, rate laws and order of a reaction
- II. The Change of Concentration with Time :
- III. Factors influencing the rate of reaction
- IV. Speed of reaction, collision theory
- V. Reaction mechanisms

Introduction :

In **chemical kinetics** we study the **speeds** or **rates** of reactions.

Besides information about the speed at which reactions occur, kinetics also sheds light on the reaction mechanism (exactly **how** the reaction occurs).

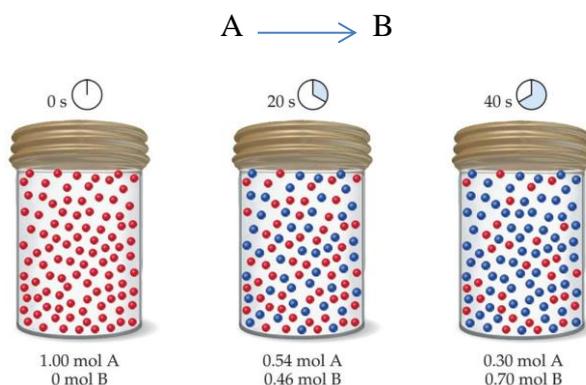
Speed is a type of rate. A rate is a change over time. Speed is the rate defined as a change in distance over time. In chemical reaction we're analyzing a change in concentration over time so we don't use the term speed but speed is a type of rate.

I. Definition, rate of reaction, rate laws and order of a reaction

is the change in the concentration of reactants or products per unit of time. Thus, the units for reaction rate are usually molarity per second (M/s), that is the change in concentration (measured in molarity) divided by a time interval (seconds).

The rate is generally expressed as the decrease in concentration of a reactant or as the increase in concentration of the product. If C the concentration of a reactant at any time t is, the rate is $-d[C]/dt$,

example : consider the reaction :



$$\text{Rate} = d[B]/dt = ([B_2]-[B_1])/(t_2-t_1) = (0.7-0.46)/(40-20) =$$

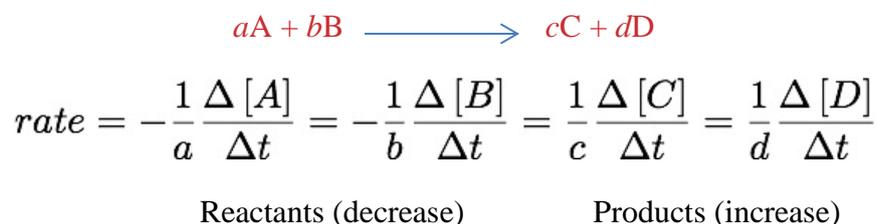
$$\text{Rate} = -d[A]/dt = -([A_2]-[A_1])/(t_2-t_1) = -(30-0.54)/(40-20) = 2.3 \times 10^{-2} \text{ mol/l.s or M/s}$$

Chapter 2 : Chemical kinetics

By convention, rates are always expressed as positive quantities. Because $[A]$ is decreasing with time, $\Delta [A]$ is a negative.

➤ Reaction Rates and Stoichiometry

• To generalize, for the reaction :



Exercise :

How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g})$?

(b) If the rate at which O_2 appears, $\Delta[\text{O}_2]/\Delta t$, is $6.0 \times 10^{-5} \text{ M/s}$ at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[\text{O}_3]/\Delta t$?

Solution

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t}$$

$$-\frac{\Delta[\text{O}_3]}{\Delta t} = \frac{2}{3} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{2}{3} (6.0 \times 10^{-5} \text{ M/s}) = 4.0 \times 10^{-5} \text{ M/s}$$

I.1. RATE LAWS : the Effect of Concentration on rate :

For a general reaction :



The rate law generally has the form

$$\text{rate} = K [A]^m [B]^n$$

The constant k in the rate law is called **rate constant**. k has a specific value for each reaction. The value of k is determined experimentally. The magnitude of k changes with temperature and therefore determines how temperature affects rate.

The exponents m and n are typically small whole numbers (usually 0, 1, or 2). m and n in a rate law are called **reaction orders or partial orders**.

Chapter 2 : Chemical kinetics

The **overall reaction order** is the sum of the partial orders (m, n)

A rate law shows the relationship between the reaction rate and the concentrations of reactants. (For gas-phase reactants use P_A instead of $[A]$).

A reaction has an **individual order** “with respect to” or “in” each reactant.

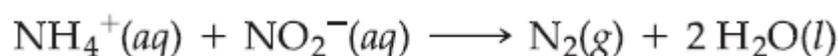
For the simple reaction $A \rightarrow$ products:

If the rate doubles when $[A]$ doubles, the rate depends on $[A]^1$ and the reaction is **first order** with respect to A.

If the rate quadruples when $[A]$ doubles, the rate depends on $[A]^2$ and the reaction is **second order** with respect to $[A]$.

If the rate does not change when $[A]$ doubles, the rate does not depend on $[A]$, and the reaction is **zero order** with respect to A.

Example :



$$\text{Rate} = K [\text{NH}_4^+]^m [\text{NO}_2^-]^n$$

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

- If we compare Experiments 1 and 2, we see that when $[\text{NH}_4^+]$ doubles while $[\text{NO}_2^-]$ hold constant, the initial rate doubles.
- Likewise, when we compare. experiments 5 and 6, we see that when $[\text{NO}_2^-]$ doubles while $[\text{NH}_4^+]$ hold constant, the initial rate doubles.
- If $[\text{NH}_4^+]$ is increased by a factor 4 with $[\text{NO}_2^-]$ left unchanged (Experiments 1 and 3), the rate changes by a factor of 4, and so forth.

The **overall reaction order** is $1 + 1 = 2$

Determining a Rate Law from Initial Rate Data : The initial rate of a reaction

$A + B \rightarrow C$ was measured for several different starting concentrations of A and B, and the results are as follows:

Chapter 2 : Chemical kinetics

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Using these data, determine

- the rate law for the reaction,
- the rate constant
- the rate of the reaction when [A] = 0.050 M and [B] = 0.100 M.

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{4.0 \times 10^{-5} \text{ M/s}}{4.0 \times 10^{-5} \text{ M/s}} = 1$$

$$1 = \frac{\text{rate 2}}{\text{rate 1}} = \frac{k[0.100 \text{ M}]^m [0.200 \text{ M}]^n}{k[0.100 \text{ M}]^m [0.100 \text{ M}]^n} = \frac{[0.200]^n}{[0.100]^n} = 2^n$$

$$n = 0$$

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{16.0 \times 10^{-5} \text{ M/s}}{4.0 \times 10^{-5} \text{ M/s}} = 4$$

$$4 = \frac{\text{rate 3}}{\text{rate 1}} = \frac{k[0.200 \text{ M}]^m [0.100 \text{ M}]^n}{k[0.100 \text{ M}]^m [0.100 \text{ M}]^n} = \frac{[0.200]^m}{[0.100]^m} = 2^m$$

Because $2^m = 4$, we conclude that : $m = 2$

$$\text{rate} = K [A]^2 [B]^0 = K [A]^2$$

b) Using the rate law and the data from experiment 1, we have :

$$K = \frac{\text{rate}}{[A]^2}$$

$$K_1 = \frac{\text{rate}_1}{[A]_1^2} = \frac{4.0 \times 10^{-5} \text{ M/s}}{(0.1 \text{ M})^2} = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$K_2 = \frac{\text{rate}_2}{[A]_2^2} = \frac{4.0 \times 10^{-5} \text{ M/s}}{(0.1 \text{ M})^2} = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$K_3 = \frac{\text{rate}_3}{[A]_3^2} = \frac{16.0 \times 10^{-5} \text{ M/s}}{(0.2 \text{ M})^2} = 4.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

Chapter 2 : Chemical kinetics

$$K = \frac{K_1 + K_2 + K_3}{3} = 4.0 \cdot 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

c) Using the rate law from part (a) and the rate constant from part (b), we have :

$$\text{rate} = K [A]^2 = 4.0 \cdot 10^{-3} (0.05)^2 = 1 \cdot 10^{-5}$$

1.2. Reaction order :

The order of reaction can be defined as the power dependence of rate on the concentration of all reactants. For example, the rate of a first-order reaction is dependent solely on the concentration of one species in the reaction. Some characteristics of the reaction order for a chemical reaction are listed below.

- Reaction order represents the number of species whose concentration directly affects the rate of reaction.
- It can be obtained by adding all the exponents of the concentration terms in the rate expression.
- The order of reaction does not depend on the stoichiometric coefficients corresponding to each species in the balanced reaction.
- The reaction order of a chemical reaction is always defined with the help of reactant concentrations and not with product concentrations.
- The value of the order of reaction can be in the form of an integer or a fraction. It can even have a value of zero.

For a general reaction :



The rate law generally has the form

$$\text{rate} = K [A]^m [B]^n$$

K : is the rate constant of the reaction,

[A] and [B] : are the concentrations of the reactants. The exponents of the reactant concentrations

m and n : are referred to as partial orders of the reaction. Therefore, the sum of all the partial orders of the reaction yields the overall order of the reaction.

Chemical reactions can be classified into the following types based on the dependence of the rate on the concentration.

The **overall reaction order** is the sum of the orders with respect to each reactant in the rate law.

Chapter 2 : Chemical kinetics

For the **first order** reactions in a reactant [A], changes in the concentration of that reactant will produce proportional changes in the rate. Thus, doubling or tripling the reactant concentration, doubles or triples the rate, and so forth.

If the rate law is **second order** in a particular reactant $[A]^2$, then doubling the concentration of that substance causes the reaction rate to quadruple ($[2]^2 = 4$), whereas tripling the concentration causes the rate to increase ninefold ($[3]^2 = 9$), and so forth.

If a reaction is **zero order** in a particular reactant $[A]^0$, changing its concentration will have no effect on rate, any concentration raised to the power zero equals 1 (catalytic reaction).

II. The Change of Concentration with Time :

In order to determine the reaction order, the power-law form of the rate equation is generally used.

The expression of this form of the rate law is given for a simple reaction ($A \longrightarrow$ products), by

$$\text{rate} = k[A]^m.$$

These rate laws can also be converted into equations that show the relationship between the concentrations of the reactants or products and time.

$$\int \text{rate} = - \int \frac{d[A]}{dt}$$

$$\text{So : } k[A]^m = - \frac{\Delta[A]}{\Delta t}$$

Zero-order rate equation:

$$k[A]^0 = - \int \frac{d[A]}{dt} \Rightarrow k \int_0^t dt = - \int_{[A]_0}^{[A]_t} d[A]$$

$$\Rightarrow [A]_t - [A]_0 = -kt$$

Note : zero order process; rate = k

Half-life equation : $t_{1/2}$ is **directly** proportional to the initial concentration

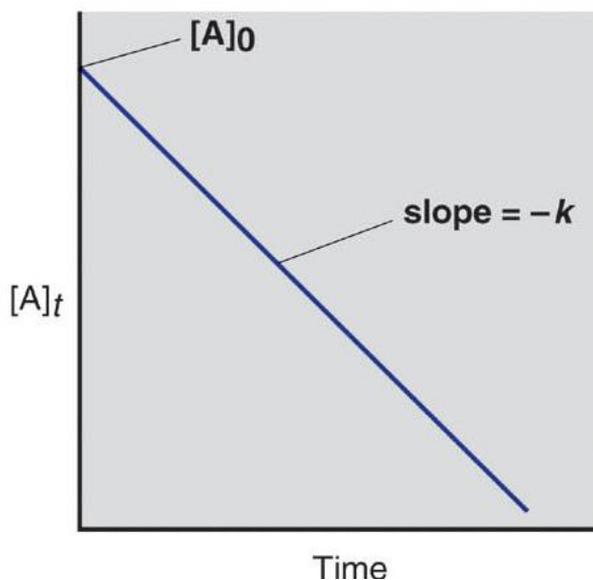
$$\text{At } t_{1/2} [A] = \frac{1}{2} [A]_0 \Rightarrow t_{1/2} = \frac{1/2[A]_0}{k} = \frac{[A]_0}{2k}$$

Figure : Graphical method for finding the reaction order from the integrated rate law.

(straight-line form $[A]_t = -kt + [A]_0$)

Zero-order reaction

Chapter 2 : Chemical kinetics



A plot of $[A]$ vs. time gives a straight line for a zero-order reaction.

$$k = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_t - [A]_0}{t}$$

Units of rate constant : $\text{mol.l}^{-1}\text{time}^{-1}$

First-order rate equation:

$$k[A]^1 = -\int \frac{d[A]}{dt} \Rightarrow k \int_0^t dt = -\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]_t}$$

$$\Rightarrow \ln \frac{[A]_t}{[A]_0} = -kt \Rightarrow [A]_t = [A]_0 e^{-kt}$$

Half-life equation : for a reaction is the time taken for the concentration of a reactant to drop to **half its initial value**.

$$\Rightarrow t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

For a **first-order** reaction, $t_{1/2}$ does not depend on the starting concentration.

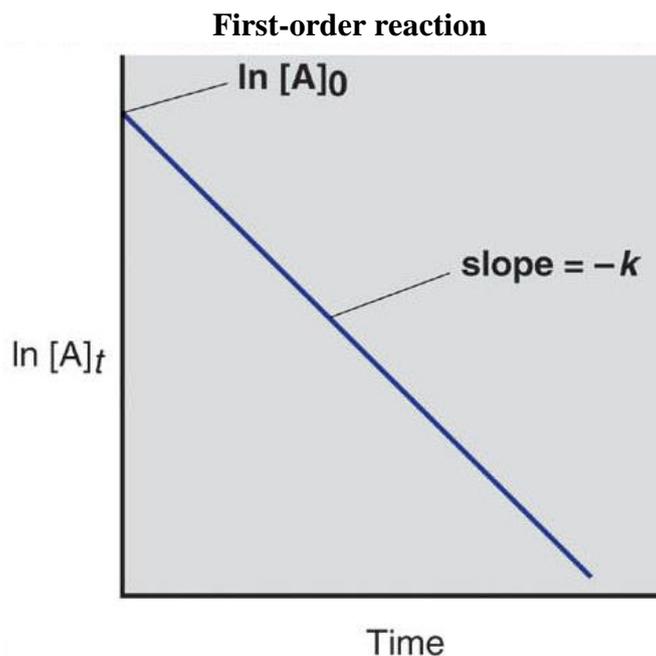
Note : The half-life for a first-order reaction is a **constant**. Radioactive decay is a first-order process.

The half-life for a radioactive nucleus is a useful indicator of its stability.

Figure : Graphical method for finding the reaction order from the integrated rate law.

(straight-line form $\ln[A]_t = -kt + \ln[A]_0$)

Chapter 2 : Chemical kinetics



A plot of $[A]$ vs. time gives a straight line for a first-order reaction.

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

Units of rate constant : time^{-1}

second-order rate equation:

firste case : $A + A \longrightarrow \text{produces}$

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

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

Half-life equation : for a reaction is the time taken for the concentration of a reactant to drop to **half its initial value**.

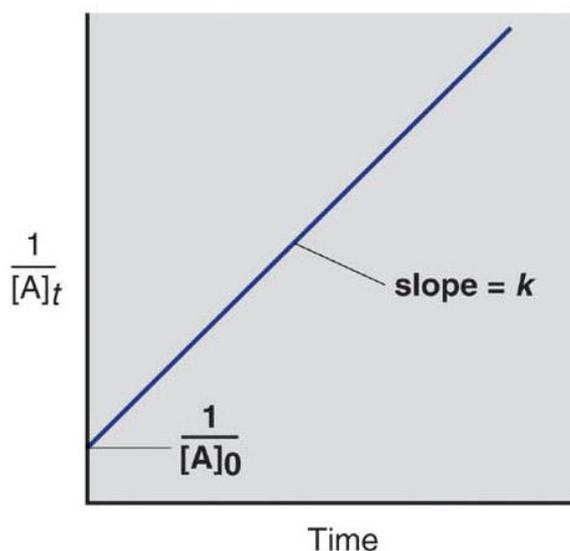
For a **second-order** reaction, $t_{1/2}$ is **inversely** proportional to the initial concentration:

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

Figure : Graphical method for finding the reaction order from the integrated rate law.

(straight-line form $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$)

Second-order reaction



A plot of $\frac{1}{[A]}$ vs. time gives a straight line for a second-order reaction.

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

Units of rate constant : $\text{mol}^{-1} \text{time}^{-1}$

Second case : $A + B \longrightarrow \text{products}$

If $[A] = [B]$, so we have : $\text{rate} = k [A] [B] = k [A]^2$ and we retourne to a firste case

If $[A] \neq [B]$ and $[A] \llll [B]$, so the B concentration does not get altered much during the course of the reaction so $[B]$ can be taken as constant $\Rightarrow k [B] = \text{constante} = k' \Rightarrow \text{rate} = k' [A]$

And the reaction beleaves as firste order reaction (called pseudo first reaction)

III. Factors that Affect the Reaction Rate Constant

- **Temperature:** At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy
- **Collision Theory:** When two chemicals react, their molecules have to collide with each other (in a particular orientation) with sufficient energy for the reaction to take place.
- **Kinetic Theory:** Increasing temperature means the molecules move faster.
 - **Concentrations of reactants :** As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.
 - **Catalysts :** Speed up reactions by lowering *activation energy*
 - **Surface area of a solid reactant :** More area for reactants to be in contact
 - **Pressure of gaseous reactants or products :** Increased number of collisions

Chapter 2 : Chemical kinetics

IV. Speed of reaction, collision theory

In a chemical reaction, **bonds** are **broken** and new bonds are **formed**.

- Molecules can only react if they **collide** with each other (molecules must collide to react).
The greater the number of collisions, the greater is the reaction rate.
- The basic principle of **collision theory** is that particles must collide in order to react.
- Furthermore, molecules must collide with the correct **orientation** and with enough **energy** to cause bond breakage and formation.
- As the **concentration** of reactant molecules increases, the number of collisions increases, leading to an increase in reaction rate.
- Increasing the **temperature** increases molecular speed. Then collide more forcefully (with more energy) and more frequently, increasing reaction rates.

• **Activation energy, E_a** , is the minimum energy required to initiate a chemical reaction.

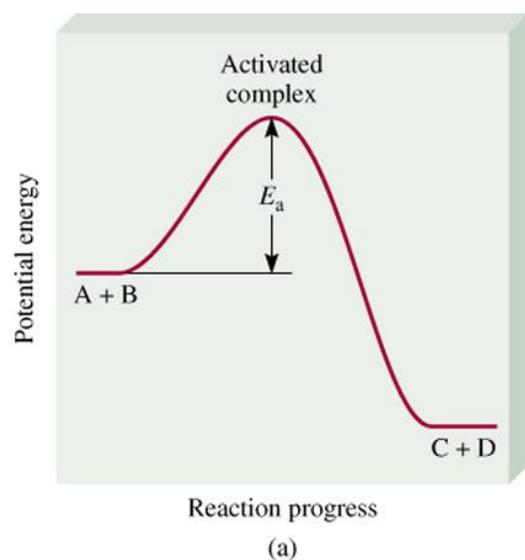
E_a will vary with the reaction :

The **activation energy E_a** is the difference in energy between reactants, and the transition state.

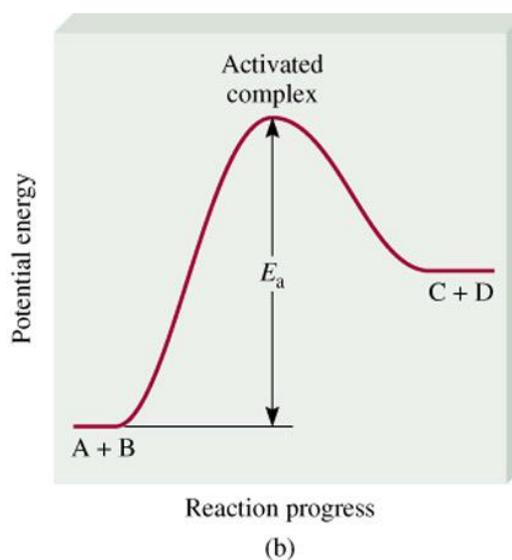
The rate depends on E_a . If the “hill” is taller, the reaction rate is slower. If the “hill” is shorter the rate is faster.

- From kinetic molecular theory, we know that as temperature increases, the total kinetic energy increases and the number of molecules with energy greater than E_a increases.

Exothermic Reaction



Endothermic Reaction



Chapter 2 : Chemical kinetics

Arrhenius Equation :

Svante Arrhenius developed a mathematical relationship between k and E_a :

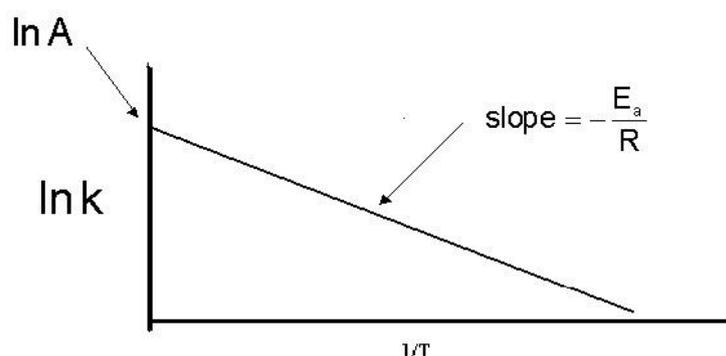
$$k = Ae^{-\frac{E_a}{RT}}$$

where A is the frequency factor, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Taking the natural logarithm of both sides, the equation becomes :

$$\ln(k) = -\frac{E_a}{RT} + \ln A$$
$$y = mx + b$$

Plot of Arrhenius Equation



When k is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of $\ln(k)$ vs. $1/T$.

k : is the rate constant

E_a : is the activation energy (J/mol)

R : is the gas constant (8.314 J/K•mol)

T : is the Kelvin temperature

A : is the frequency factor

If data is available at 2 different temperature :

Chapter 2 : Chemical kinetics

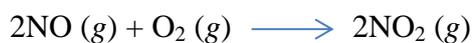
$$\ln \frac{k_2}{k_1} = - \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

V. Reaction Mechanisms

The overall progress of a chemical reaction can be represented **at the molecular level** by a series of simple *elementary steps* or *elementary reactions*.

The **sequence of elementary steps** that leads to product formation is the *reaction mechanism*.

Example :



N_2O_2 is detected during the reaction!



Rate Laws and Rate Determining Steps

Writing plausible reaction mechanisms:

- The **sum** of the elementary steps must give the overall **balanced** equation for the reaction.
- The rate-determining step should predict the **same** rate law that is determined experimentally.

The *rate-determining step* is the **slowest** step in the sequence of steps leading to product formation.