

From Rate Laws to Transition States: A Kinetic Journey



"The only true wisdom is in knowing you know nothing."

– Socrates

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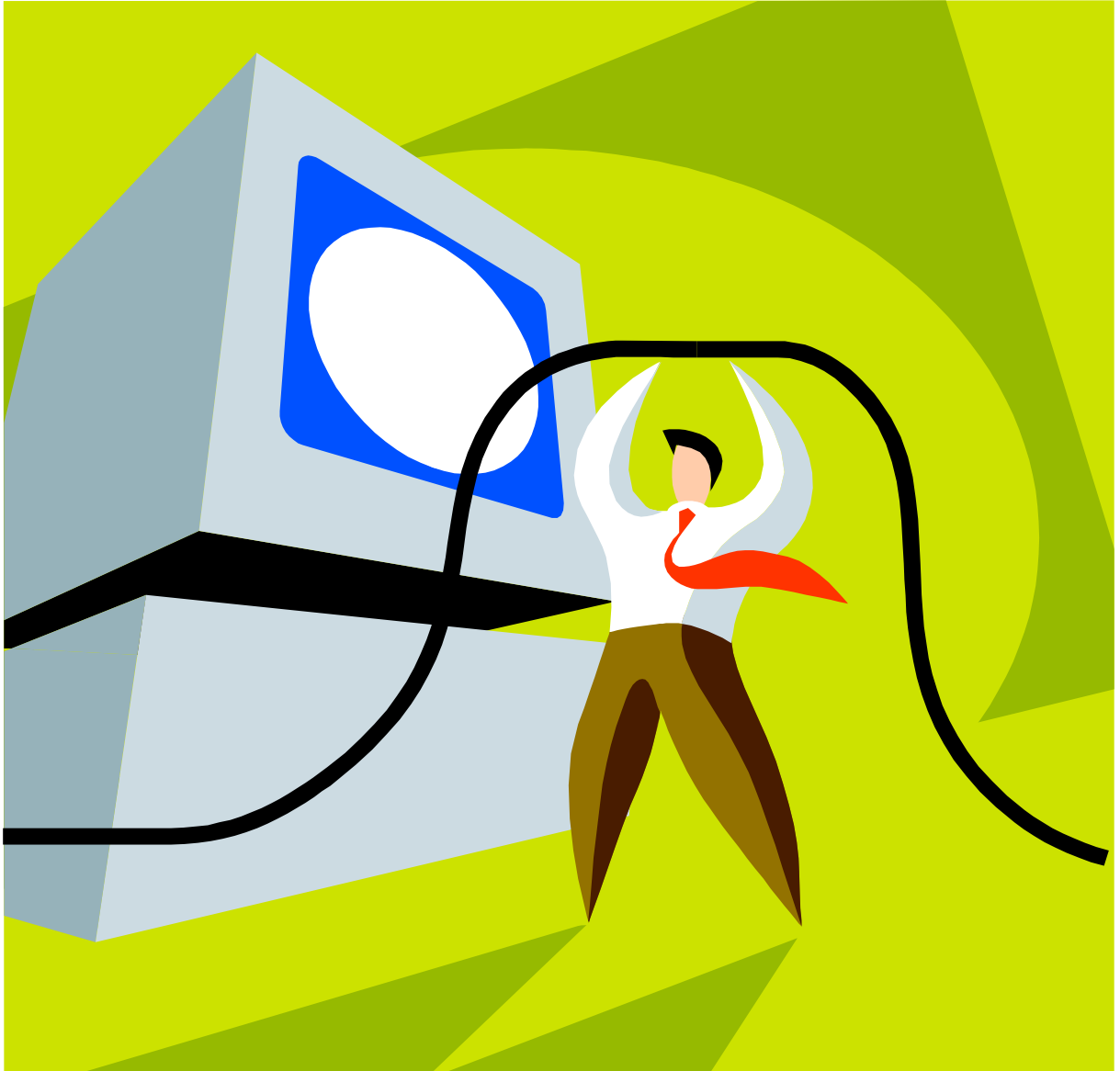


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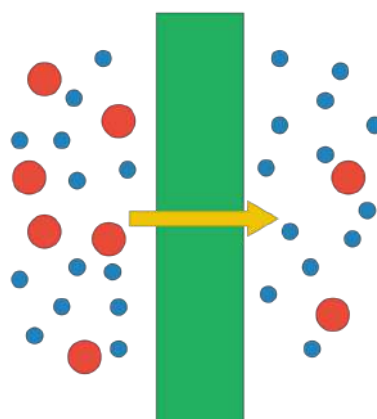
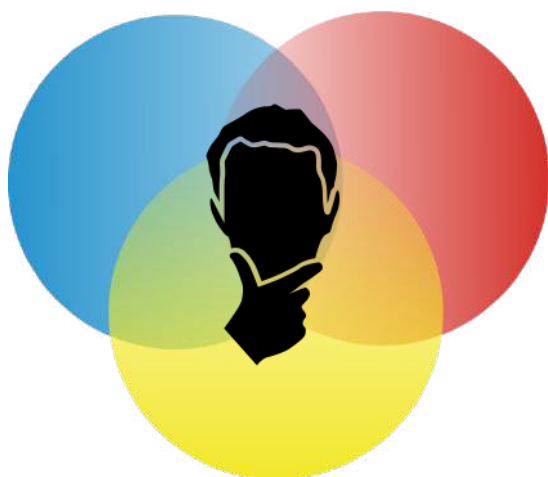
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Abstract:



This study bridges the gap between **chemical kinetics** and **thermodynamics** by developing unified expressions that connect **reaction rate laws**, **temperature dependence**, and **activation parameters**. Using **rate equations** for both simple and complex reactions, it incorporates **stoichiometric coefficients**, **Arrhenius relations**, and **Gibbs free energy changes** to describe how **reaction velocity** varies with **concentration and temperature**. These principles are extended through **Transition State Theory (TST)**, relating the **rate constant** to **kinetic and thermodynamic quantities**. The analysis is further applied to **enzyme catalysis**, deriving **rate equations** that account for **inhibition** and show how **product formation** depends on the rates of enzyme–substrate complex formation and dissociation. The equations also incorporate the **standard Gibbs free energy of activation**, linking **molecular energetics** to **reaction rates**. Overall, this work provides a **unified framework for understanding the kinetic and thermodynamic factors** that govern chemical reactivity in both simple and complex catalytic systems.

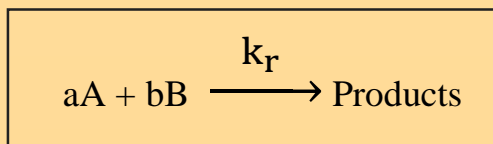


"One thing that you can't fake is chemistry."

 → **Blake Shelton**

- **Rate of Reaction:**

For the reaction:



the rate of reaction is given by the **rate law**:

$$v = k_r [A]^m [B]^n$$

where k_r is the **rate constant**, and $[A]$ and $[B]$ are the **molar concentrations** of the reactants, usually expressed in mol / dm^3 . The **exponents** m and n denote the **order of reaction** with respect to reactants A and B , respectively. If both **reactants** are present at **unit concentrations**, i.e., $[A] = [B] = 1 \text{ mol} / \text{dm}^3$, then:

$$v = k_r$$

This means that the **rate constant** equals the **rate of reaction** when all reactants are at **unit concentration**.

- **Relation with Stoichiometric Coefficients:**

The **rate of reaction** can also be expressed in terms of the **change in concentration** of the reactants over time.

$$v = -\frac{1}{a} \left(\frac{d[A]}{dt} \right) = -\frac{1}{b} \left(\frac{d[B]}{dt} \right)$$

or equivalently,

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

$$-\frac{d[B]}{dt} = b \times v$$

The **negative sign** indicates that the **concentrations of the reactants decrease with time** as the **reaction proceeds**.

- **Time Dependence of the Rate of Reaction:**

Differentiating the **rate law** with respect to time, we get:

$$\frac{dv}{dt} = k_r \left(\frac{d([A]^m)}{dt} \right) [B]^n + \left(\frac{d([B]^n)}{dt} \right) [A]^m$$



$$\frac{dv}{dt} = k_r \ m [A]^{m-1} \left(\frac{d[A]}{dt} \right) [B]^n + n [B]^{n-1} \left(\frac{d[B]}{dt} \right) [A]^m$$

Rearranging terms:

$$\frac{dv}{dt} = m k_r [A]^{m-1} [B]^n \left(\frac{d[A]}{dt} \right) \frac{1}{[A]} + n k_r [A]^m [B]^{n-1} \left(\frac{d[B]}{dt} \right) \frac{1}{[B]}$$

Multiplying both sides by -1 gives:

$$-\frac{dv}{dt} = m k_r [A]^{m-1} [B]^n \left(-\frac{d[A]}{dt} \right) \frac{1}{[A]} + n k_r [A]^m [B]^{n-1} \left(-\frac{d[B]}{dt} \right) \frac{1}{[B]}$$

Since

$$v = k_r [A]^m [B]^n, \quad -\frac{d[A]}{dt} = a \times v, \quad \text{and} \quad -\frac{d[B]}{dt} = b \times v$$

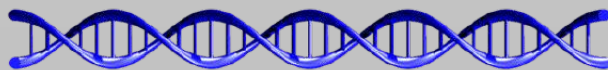
we can substitute to obtain:

$$-\frac{dv}{dt} = \frac{mav^2}{[A]} + \frac{nbv^2}{[B]}$$

or equivalently,

$$-\frac{dv}{dt} = v^2 \left(\frac{ma[B] + nb[A]}{[A][B]} \right)$$

This expression shows that the **reaction rate** decreases over time. The **negative sign** indicates that the **rate of reaction** decreases as the **reactant concentrations** [A] and [B] drop with progress. The v^2 term implies that **faster reactions decelerate more rapidly**. The decrease in reaction velocity depends not only on v but also on the concentrations of the reactants. The terms ma and nb represent the influence of each **reactant's order and stoichiometric coefficient** on this **rate decrease**, where m and n are the **reaction orders** and a and b are the **stoichiometric coefficients**. As fewer reactant molecules remain, there are **fewer effective collisions**, naturally causing the reaction to slow down over time.



1. Case 1: Very high concentration of A compared to B ($[A] \gg [B]$)

- Since $[A] \gg [B]$, the expression simplifies approximately to:

$$-\frac{dv}{dt} \approx v^2 \left(\frac{nb}{[B]} \right)$$

- The decrease in reaction velocity mainly depends on the small concentration of **B**; the reaction slows significantly as **B** is consumed.

2. **Case 2: Very high concentration of B compared to A ([B]»[A])**

- Now [B]»[A], so the expression simplifies approximately to:

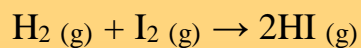
$$-\frac{dv}{dt} \approx v^2 \left(\frac{ma}{[A]} \right)$$

- The decrease in reaction velocity mainly depends on the small concentration of **A**; the reaction slows significantly as **A** is consumed.

When one reactant is in large excess, the **rate of decrease of reaction velocity is controlled by the limiting reactant**, i.e., the one present in lower concentration.



Example: Reaction between Hydrogen and Iodine



Here, $a = b = 1$, and if the reaction is **first-order** with respect to both reactants, then $m = n = 1$.

Substituting into the expression:

$$-\frac{dv}{dt} = v^2 \left(\frac{[I_2] + [H_2]}{[H_2][I_2]} \right)$$

- **Case 1: When $[H_2] \gg [I_2]$**

The **reaction rate** mainly depends on the **smaller concentration** $[I_2]$. As **iodine** is consumed, its concentration decreases rapidly, and the **reaction slows down** significantly.

- **Case 2: When $[I_2] \gg [H_2]$**

The **reaction rate** mainly depends on the **smaller concentration** $[H_2]$. As **hydrogen** is consumed, the number of effective collisions decreases, again causing the **reaction to slow down** over time.

1. Zero-Order:

- Zero-order means the rate does **not depend on concentration** of the reactants.
- So $m = 0$ and $n = 0 \rightarrow$ **rate law:** $v = k_r [A]^0 [B]^0 = k_r$
- Substituting into the expression:

$$-\frac{dv}{dt} = v^2 \left(\frac{0 + 0}{[A][B]} \right) = 0$$

- **Reaction rate** is constant, independent of $[A]$ or $[B]$

2. First-Order:

- First-order in one reactant (say A) $\rightarrow m = 1, n = 0$
- **Rate law:** $v = k_r [A]^1 [B]^0 = k_r [A]$
- Substituting into the expression:

$$-\frac{dv}{dt} = v^2 \left(\frac{(1 \times a)[B] + (0 \times b)[A]}{[A][B]} \right) = \frac{av^2}{[A]}$$

- If the reaction is first-order in B instead ($m = 0, n = 1$):

$$-\frac{dv}{dt} = v^2 \left(\frac{(0 \times a)[B] + (1 \times b)[A]}{[A][B]} \right) = \frac{bv^2}{[B]}$$

3. Second-Order:

- **Second-order in one reactant:** $m = 2, n = 0 \rightarrow v = k_r [A]^2$

$$-\frac{dv}{dt} = v^2 \left(\frac{(2 \times a)[B] + (0 \times b)[A]}{[A][B]} \right) = \frac{2av^2}{[A]}$$

- **First-order in both reactants:** $m = 1, n = 1 \rightarrow v = k_r [A][B]$

$$-\frac{dv}{dt} = v^2 \left(\frac{(1 \times a)[B] + (1 \times b)[A]}{[A][B]} \right) = \frac{v^2(a[B] + b[A])}{[A][B]}$$

$$-\frac{dv}{dt} = v^2 \left(\frac{ma[B] + nb[A]}{[A][B]} \right)$$

- **Case 1:** When the concentration of B is twice that of A:

$$[B] = 2[A]$$

$$-\frac{dv}{dt} = v^2 \left(\frac{2ma + nb}{2[A]} \right)$$

This shows that the **reaction velocity** decreases when B is twice as concentrated as A. The denominator $2[A]$ indicates that a higher concentration of A reduces the rate at which the **reaction velocity** decreases.

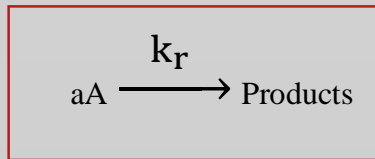
- **Case 2:** When the concentration of A is twice that of B:

$$[A] = 2[B]$$

$$-\frac{dv}{dt} = v^2 \left(\frac{ma + 2nb}{2[B]} \right)$$

This shows that the **reaction velocity** decreases when A is twice as concentrated as B. The denominator $2[B]$ indicates that a higher concentration of B slows down the decrease in **reaction velocity**. In both cases, $-\frac{dv}{dt}$ is proportional to v^2 , meaning the reaction slows down rapidly when the **reaction velocity** is high and more gradually as the **reaction velocity** decreases.

For the reaction:



The **rate of reaction** is given by:

$$v = -\frac{1}{a} \left(\frac{d[A]}{dt} \right) = k_r [A]^m$$

Differentiating $v = k_r [A]^m$ with respect to time:

$$\frac{dv}{dt} = k_r \left(\frac{d([A]^m)}{dt} \right) = k_r m [A]^{m-1} \left(\frac{d[A]}{dt} \right)$$

From this, it follows that:

$$\frac{dv}{dt} = \frac{mv}{[A]} \left(\frac{d[A]}{dt} \right)$$

From the definition of rate:

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

Substituting this:

$$-\frac{dv}{dt} = \frac{mav^2}{[A]}$$

The **negative sign** indicates that the **reaction rate** decreases over time. As the reaction proceeds, the **concentration of A** decreases, leading to **fewer effective molecular collisions**. The **term** ma shows how both the **reaction order** (m) and the **stoichiometric coefficient** (a) of the reactant influence the **rate decrease**, while the v^2 dependence indicates that **faster reactions** slow down more quickly. A plot of $-\frac{dv}{dt}$ versus $\frac{v^2}{[A]}$ is a **straight line**, with a **slope** equal to ma , confirming that the **decrease in reaction rate** depends on both the **reaction order** and the **stoichiometric coefficient**.

1. Zero-Order:

- In a **zero-order reaction**, the **reaction rate** does not depend on the concentration of the reactant.
- So $m = 0 \rightarrow$ **rate law:** $v = k_r [A]^0 = k_r$
- Substituting into the expression:

$$-\frac{dv}{dt} = \frac{0 \times av^2}{[A]} = 0$$

- The **reaction rate** is constant and independent of $[A]$

2. First-Order:

- For a first-order reaction, $m = 1$
- **Rate law:** $v = k_r [A]^1 = k_r [A]$
- Substituting into the expression:

$$-\frac{dv}{dt} = \frac{1 \times av^2}{[A]} = \frac{av^2}{[A]}$$

- The **reaction rate decrease** depends on both the **stoichiometric coefficient** a and the **square of the reaction rate** v^2 , and inversely on $[A]$.

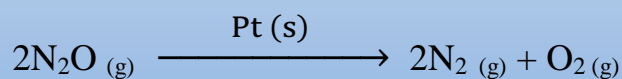
3. Second-Order:

- For a second-order reaction, $m = 2$
- **Rate law:** $v = k_r [A]^2$
- Substituting into the expression:

$$-\frac{dv}{dt} = \frac{2 \times av^2}{[A]} = \frac{2av^2}{[A]}$$

- The **reaction rate** decrease depends on the **stoichiometric coefficient** a and v^2 , and inversely on $[A]$. The **reaction rate decreases more sharply than in lower-order reactions** due to the stronger dependence on concentration.

Example: The **decomposition of nitrous oxide** on a **heated platinum surface** is a well-known example of a **zero-order reaction** in heterogeneous catalysis.



- The **rate of this reaction** is determined by the **available surface area of the platinum catalyst**, rather than the concentration or pressure of N_2O gas.
- Since the **reaction is zero-order** with respect to N_2O , $m = 0$.
- Plugging $m = 0$ into the rate equation gives:

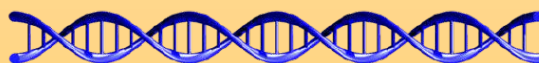
$$-\frac{dv}{dt} = \frac{0 \times av^2}{[A]} = 0$$

- This indicates that the **reaction proceeds at a constant rate**, independent of the reactant concentration.

State of Matter	Rate of Reaction	Explanation
Gaseous State	Highest	<ul style="list-style-type: none"> Gas molecules move rapidly and collide frequently, leading to faster reactions.
Liquid State	Moderate	<ul style="list-style-type: none"> Molecules move slower than in gases but can still collide effectively in solution.
Solid State	Lowest	<ul style="list-style-type: none"> Particles are tightly packed with very limited motion, so collisions occur rarely and reactions are slow.

- Order of decreasing rate of reaction:

Gaseous state > Liquid state > Solid state



"Chemistry: that most excellent child of intellect and art."



Sir Cyril Norman Hinshelwood



- **Factors Affecting Rate of Reaction:**

Factor	Effect on Reaction Rate
Concentration	<ul style="list-style-type: none"> • Higher concentration → Faster reaction rate
Temperature	<ul style="list-style-type: none"> • Higher temperature → Faster reaction rate
Surface Area	<ul style="list-style-type: none"> • More surface area → Faster reaction rate
Pressure (gases)	<ul style="list-style-type: none"> • Higher pressure → Faster reaction rate
Catalyst	<ul style="list-style-type: none"> • Lowers activation energy → Faster reaction rate
Nature of Reactants	<ul style="list-style-type: none"> • Ionic compound reactions are faster • Covalent compound reactions are slower

At **constant temperature**, for gaseous reaction:

Concentration \propto Partial pressure of each reactant

So, **pressure** can be used in the **rate law** instead of **concentration**.

For the **second-order bimolecular gaseous reaction**:

A + B → products , the **rate law** is:

$$v = k_r P_A P_B$$

where:

- v = rate of reaction
- k_r = rate constant
- P_A = partial pressure of reactant A
- P_B = partial pressure of reactant B

- **Temperature Dependence of the Rate of Reaction:**

$$\frac{v}{k_r} = [A]^m [B]^n$$

Differentiating with respect to temperature:

$$\frac{d}{dT} \left(\frac{v}{k_r} \right) = \frac{d}{dT} \left([A]^m [B]^n \right)$$

↓

$$\frac{\left(\frac{dv}{dT} \right) k_r - \left(\frac{dk_r}{dT} \right) v}{k_r^2} = \left(\frac{d([A]^m)}{dT} \right) [B]^n + \left(\frac{d([B]^n)}{dT} \right) [A]^m$$

$$\left(\frac{dv}{dT} \right) \frac{1}{k_r} - \frac{v}{k_r^2} \left(\frac{dk_r}{dT} \right) = m [A]^m [B]^n \left(\frac{d[A]}{dT} \right) \frac{1}{[A]} + n [A]^m [B]^n \left(\frac{d[B]}{dT} \right) \frac{1}{[B]}$$

Multiplying both sides by k_r :

$$\frac{dv}{dT} - v \left(\frac{d \ln k_r}{dT} \right) = m v \left(\frac{d \ln [A]}{dT} \right) + n v \left(\frac{d \ln [B]}{dT} \right)$$

Dividing both sides by v :

$$\frac{d \ln v}{dT} - \left(\frac{d \ln k_r}{dT} \right) = m \left(\frac{d \ln [A]}{dT} \right) + n \left(\frac{d \ln [B]}{dT} \right)$$

The temperature dependence of rate constant k_r is given by the **Arrhenius relation**:

$$\frac{d \ln k_r}{dT} = \frac{E_a}{RT^2}$$

where

- E_a = activation energy and R = universal gas constant.

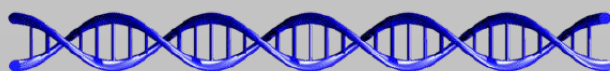
Substituting into the previous equation:

$$\frac{d \ln v}{dT} - \frac{E_a}{RT^2} = m \left(\frac{d \ln [A]}{dT} \right) + n \left(\frac{d \ln [B]}{dT} \right)$$

Finally,

$$\frac{d \ln v}{dT} = m \left(\frac{d \ln [A]}{dT} \right) + n \left(\frac{d \ln [B]}{dT} \right) + \frac{E_a}{RT^2}$$

This equation shows how the **reaction rate changes with temperature**. It indicates that variations in **reactant concentrations** $[A]$ and $[B]$ affect the **rate** according to their **reaction orders** m and n . The term $\frac{E_a}{RT^2}$ reflects the role of activation energy, showing that the **reaction rate increases as temperature rises**. Overall, the equation explains how both **activation energy** and **concentration changes** together control the **temperature dependence of the reaction rate**.



1. Zero-Order Reaction:

- **Rate law:** $v = k_r [A]^0 [B]^0 = k_r$
- Since $m = 0$ and $n = 0$:

$$\frac{d \ln v}{dT} = \frac{E_a}{RT^2}$$

- **Reaction rate changes with temperature and activation energy**, but is independent of concentrations of A and B.

2. First-Order Reaction:

- **Rate law:** $v = k_r [A]^1 [B]^0 = k_r [A]$
- Since $m = 1$ and $n = 0$:

$$\frac{d \ln v}{dT} = \frac{d \ln [A]}{dT} + \frac{E_a}{RT^2}$$

- **Reaction rate** changes with **temperature, activation energy**, and the concentration of A.

- **Rate law:** $v = k_r [A]^0 [B]^1 = k_r [B]$
- Since $m = 0$ and $n = 1$:

$$\frac{d \ln v}{dT} = \frac{d \ln [B]}{dT} + \frac{E_a}{RT^2}$$

- **Reaction rate** changes with **temperature, activation energy**, and the concentration of B.

3. Second-Order Reaction:

- **Rate law:** $v = k_r [A]^2 [B]^0 = k_r [A]^2$
- Since $m = 2$ and $n = 0$:

$$\frac{d \ln v}{dT} = \left(2 \times \frac{d \ln [A]}{dT} \right) + \frac{E_a}{RT^2}$$

- **Reaction rate** changes with **temperature**, **activation energy**, and the concentration of A. Since $m = 2$, changes in [A] have a **squared effect** on the **reaction rate**, while B does not affect the **reaction rate** because $n = 0$.

- **Rate law:** $v = k_r [A]^0 [B]^2 = k_r [B]^2$
- Since $m = 0$ and $n = 2$:

$$\frac{d \ln v}{dT} = \left(2 \times \frac{d \ln [B]}{dT} \right) + \frac{E_a}{RT^2}$$

- **Reaction rate** changes with **temperature**, **activation energy**, and the concentration of B. Since $n = 2$, changes in [B] have a **squared effect** on the **reaction rate**, while A does not influence the **reaction rate** because $m = 0$.

- **Rate law:** $v = k_r [A]^1 [B]^1 = k_r [A] [B]$
- Since $m = 1$ and $n = 1$:

$$\frac{d \ln v}{dT} = \frac{d \ln [A]}{dT} + \frac{d \ln [B]}{dT} + \frac{E_a}{RT^2}$$

- **Reaction rate** changes with **temperature**, **activation energy**, and the **concentrations of A and B**.

Multiplying both sides of the expression:

$$\frac{d \ln v}{dT} = m \left(\frac{d \ln[A]}{dT} \right) + n \left(\frac{d \ln[B]}{dT} \right) + \frac{E_a}{RT^2}$$

by $\frac{dT}{dt}$, we obtain:

$$\frac{d \ln v}{dt} = m \left(\frac{d \ln[A]}{dt} \right) + n \left(\frac{d \ln[B]}{dt} \right) + \left(\frac{dT}{dt} \right) \frac{E_a}{RT^2}$$

Since

$$\frac{d \ln v}{dt} = \frac{1}{v} \left(\frac{dv}{dt} \right), \quad \frac{d \ln[A]}{dt} = \frac{1}{[A]} \left(\frac{d[A]}{dt} \right), \quad \frac{d \ln[B]}{dt} = \frac{1}{[B]} \left(\frac{d[B]}{dt} \right)$$

this gives

$$\frac{dv}{dt} = v \left(\frac{m}{[A]} \left(\frac{d[A]}{dt} \right) + \frac{n}{[B]} \left(\frac{d[B]}{dt} \right) + \left(\frac{dT}{dt} \right) \frac{E_a}{RT^2} \right)$$

The **rate of reaction** is defined as:

$$v = -\frac{1}{a} \left(\frac{d[A]}{dt} \right) = -\frac{1}{b} \left(\frac{d[B]}{dt} \right)$$

or equivalently,

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

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

Substituting this into the previous equation,

$$\frac{dv}{dt} = v \left(\left(-\frac{mav}{[A]} \right) + \left(-\frac{nbv}{[B]} \right) + \left(\frac{dT}{dt} \right) \frac{E_a}{RT^2} \right)$$

If the temperature is constant,

$$\frac{dT}{dt} = 0$$

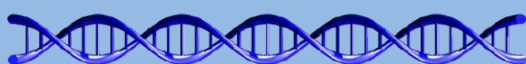
and the expression reduces to:

$$\frac{dv}{dt} = \left(-\frac{mav^2}{[A]} \right) + \left(-\frac{nbv^2}{[B]} \right)$$

or equivalently,

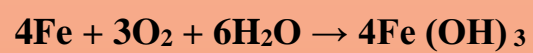
$$-\frac{dv}{dt} = \frac{mav^2}{[A]} + \frac{nbv^2}{[B]}$$

The **negative sign** indicates that the **reaction rate** decreases with time as the **reactant concentration decreases**. At **constant temperature**, the **change in reaction rate** depends on the **reaction orders** m and n, the **stoichiometric coefficients** a and b, the **square of the reaction rate** v^2 , and the **reactant concentrations** [A] and [B]. The v^2 term indicates a **faster decrease in the reaction rate** as the reaction progresses.

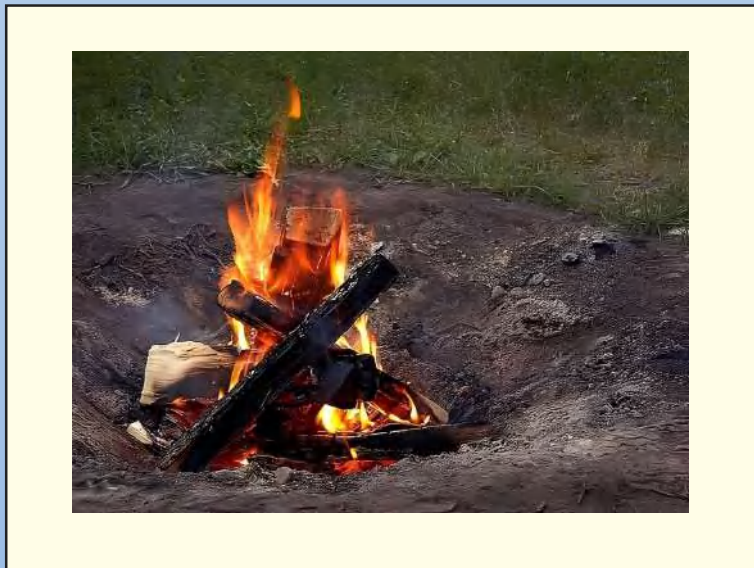




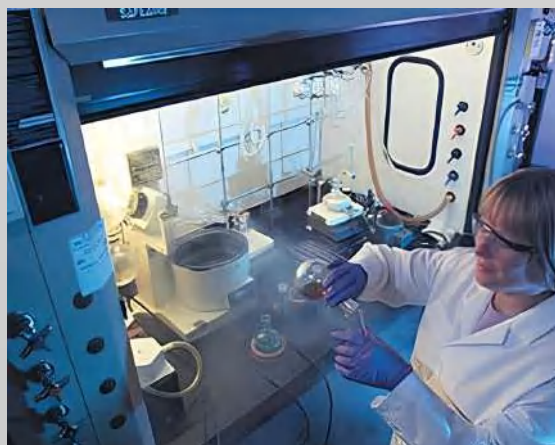
- The **rusting of iron** occurs at a slow rate, indicating a low reaction speed. The overall reaction can be represented as:



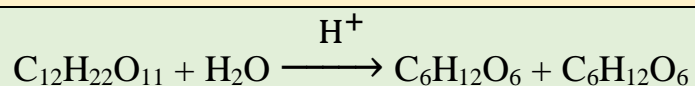
Over time, the **hydrated iron (III) oxide**, $\text{Fe}(\text{OH})_3$, dehydrates to form rust, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.



- The **combustion of wood** occurs rapidly, indicating a **high reaction rate**. It is an **exothermic process** that releases energy in the form of heat and light.



Inversion of cane sugar



(Sucrose breaks into glucose and fructose)

This reaction proceeds with **moderate speed**, meaning it does not occur extremely slowly or extremely fast. It happens at a **noticeable rate** under **standard laboratory conditions**, such as **moderate temperature** and the presence of an **acid catalyst**, allowing the changes to be observed over time. This moderate pace makes it useful for studying reaction rates.

Thermodynamics



- Tells whether a reaction can occur based on energy changes and stability.

Chemical Kinetics



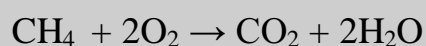
- Tells how fast the reaction occurs by studying reaction rates and mechanisms.

1. Threshold Energy (E_0):

Minimum energy that **colliding reactant molecules** must have for a chemical reaction to occur.

- If **collision energy** $< E_0 \rightarrow$ Reaction **does not occur**
(Molecules lack sufficient energy to overcome the energy barrier)
- If **collision energy** $\geq E_0 \rightarrow$ Reaction **occurs**

Example: Combustion of Methane



- At room temperature \rightarrow methane + oxygen coexist \rightarrow no reaction
(collision energy $< E_0$)
- Spark applied \rightarrow molecules gain energy ($E_{\text{collision}} \geq E_0$) \rightarrow reaction occurs explosively

2. Activation Energy (E_a):

Minimum extra energy required by reactant molecules to reach the **transition state (activated complex)** and start the reaction.

$$E_a = E_0 - E_{av}$$

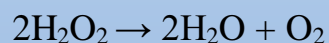
where:

- E_0 = Threshold energy
- E_{av} = Average kinetic energy of reactant molecules at a given temperature

Effect of Catalyst:

- Catalysts **lower** E_a \rightarrow reaction occurs faster
- Do not change the threshold energy E_0

Example: Decomposition of Hydrogen Peroxide



- Room temperature \rightarrow reaction is slow (high E_a)
- With **catalyst** MnO_2 \rightarrow E_a decreases \rightarrow reaction becomes faster

• Photoionization:

Photoionization occurs when a **photon removes an electron** from an atom or molecule.

$$h\nu = E_B + \text{KE}$$

where:

- $h\nu$ = Energy of the photon, E_B = Binding energy of the electron
- KE = Kinetic energy of the ejected electron

- **Photon energy < Binding energy ($h\nu < E_B$)**

- Photon energy **insufficient**
- Electron **cannot escape** \rightarrow **no ionization**

- **Photon energy \geq Binding energy ($h\nu \geq E_B$)**

- Photon energy **sufficient**
- Electron **ejected** with kinetic energy: $\text{KE} = h\nu - E_B$

Reduction of Bromic Acid:



- **Predicted order:**

If the reaction were elementary, the rate law would be:

$$\text{Rate} \propto [\text{HBrO}_3] [\text{HI}]^6$$

Thus, the **predicted overall order = 7**.

- **Experimental rate law:**

Experimentally, the rate is found to follow

$$\text{Rate} \propto [\text{HBrO}_3] [\text{HI}]$$

- **Experimental order:**

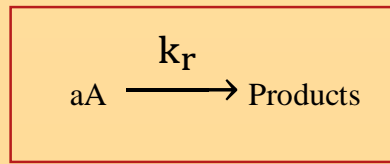
$$\text{Overall order} = 2$$

The disagreement between the predicted and experimental orders shows that the reaction is **not elementary**. It occurs through a **multi-step mechanism**, and the rate is governed by a slow step involving one molecule each of HBrO_3 and HI .



- Reactions of **third and higher order** are very rare, and most reactions are of **first and second order** because the **probability of three or more reactant molecules** colliding simultaneously with **proper orientation** and sufficient energy is extremely low.

For the reaction:



the **rate of reaction (reaction velocity)** is given by:

$$v = k_r [A]^m$$

Differentiating with respect to **temperature T** gives:

$$\frac{dv}{dT} = k_r \left(\frac{d([A]^m)}{dT} \right) + \frac{dk_r}{dT} [A]^m$$



$$\frac{dv}{dT} = k_r m [A]^{m-1} \left(\frac{d[A]}{dT} \right) + \left(\frac{E_a}{RT^2} \right) k_r [A]^m$$



$$\frac{dv}{dT} = \frac{mv}{[A]} \left(\frac{d[A]}{dT} \right) + \frac{vE_a}{RT^2} = mv \left(\frac{d \ln[A]}{dT} \right) + \frac{vE_a}{RT^2}$$

Dividing both sides by v:

$$\frac{d \ln v}{dT} = m \left(\frac{d \ln [A]}{dT} \right) + \frac{E_a}{RT^2}$$

From this, it follows that:

$$\left(\frac{dv}{v} \right) = m \left(\frac{d[A]}{[A]} \right) + \frac{E_a}{RT} \left(\frac{dT}{T} \right)$$

The expression,

$$\frac{d \ln v}{dT} = m \left(\frac{d \ln [A]}{dT} \right) + \frac{E_a}{RT^2}$$

shows how the **reaction rate** v **changes with temperature**. It indicates that the **reaction rate** depends on **two main factors**: the concentration of the reactant A and the activation energy E_a .

- The first term, $m \left(\frac{d \ln [A]}{dT} \right)$, represents the effect of changes in the **reactant concentration** on the **reaction rate**, scaled by the **reaction order** m . For example, in a **first-order reaction** ($m = 1$), doubling the **concentration of A** roughly doubles the **reaction rate**.
- The second term, $\frac{E_a}{RT^2}$, shows how sensitive the **reaction rate** is to temperature, following the **Arrhenius equation**. A **higher activation energy** means that the **reaction rate** increases more sharply with temperature. For example, the **decomposition of hydrogen peroxide** ($2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$) accelerates rapidly with increasing temperature because of its high E_a .

Multiplying both sides of the expression:

$$\frac{d \ln v}{dT} = m \left(\frac{d \ln [A]}{dT} \right) + \frac{E_a}{RT^2}$$

by $\frac{dT}{dt}$, we obtain:

$$\frac{d \ln v}{dt} = m \left(\frac{d \ln [A]}{dt} \right) + \frac{dT}{dt} \left(\frac{E_a}{RT^2} \right)$$

Since

$$\frac{d \ln v}{dt} = \frac{1}{v} \left(\frac{dv}{dt} \right) \quad \text{and} \quad \frac{d \ln [A]}{dt} = \frac{1}{[A]} \left(\frac{d[A]}{dt} \right)$$

this gives

$$\frac{dv}{dt} = v \left(\frac{m}{[A]} \left(\frac{d[A]}{dt} \right) + \left(\frac{dT}{dt} \right) \frac{E_a}{RT^2} \right)$$

The **rate of reaction** is defined as:

$$v = -\frac{1}{a} \left(\frac{d[A]}{dt} \right)$$

or

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

Substituting this into the previous equation,

$$\frac{dv}{dt} = v \left(-\frac{mav}{[A]} + \left(\frac{dT}{dt} \right) \frac{E_a}{RT^2} \right)$$

If the temperature is constant,

$$\frac{dT}{dt} = 0$$

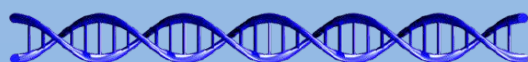
and the expression reduces to:

$$\frac{dv}{dt} = - \left(\frac{mav^2}{[A]} \right)$$

or equivalently,

$$- \frac{dv}{dt} = \frac{mav^2}{[A]}$$

The **negative sign** indicates that the **reaction rate** decreases with time as the **reactant concentration decreases**. At **constant temperature**, the **change in reaction rate** depends on the **reaction order** m , the **stoichiometric coefficient** a , the **square of the reaction rate** v^2 , and the **reactant concentration** $[A]$. The v^2 term indicates a **faster decrease** in the **reaction rate** as the reaction progresses.



In differential form:

$$\left(\frac{dv}{v}\right) = m \left(\frac{d[A]}{[A]}\right) + \frac{E_a}{RT} \left(\frac{dT}{T}\right)$$

this equation quantitatively expresses that **small relative changes** in the **reaction rate** arise from both:

1. **Small relative changes in reactant concentration** $\left(\frac{d[A]}{[A]}\right)$.
2. **Small relative changes in temperature** $\left(\frac{dT}{T}\right)$.

1. Zero-Order Reaction ($m = 0$):

For a **zero-order reaction** (Rate $\propto [A]^0$), the expression becomes:

$$\left(\frac{dv}{v}\right) = \frac{E_a}{RT} \left(\frac{dT}{T}\right)$$

- **Concentration Independence:** The term related to **concentration change**, $m \left(\frac{d[A]}{[A]}\right)$, vanishes because the **reaction order** $m = 0$. This means that variations in the **concentration of reactant** $[A]$ do not influence the **reaction rate** v . The **reaction rate** remains **constant throughout the reaction** until the **reactant** is nearly depleted.
- **Temperature Dependence:** Although the **reaction rate** is independent of concentration, it still increases with temperature. This dependence arises entirely from the term $\frac{E_a}{RT} \left(\frac{dT}{T}\right)$, which reflects how the **rate constant** (k_r) **changes with temperature** according to the **activation energy** (E_a).

2. First-Order Reaction (m = 1):

For a **first-order reaction** (Rate $\propto [A]$), the expression becomes:

$$\frac{dv}{v} = \left(\frac{d[A]}{[A]} \right) + \frac{E_a}{RT} \left(\frac{dT}{T} \right)$$

- **Concentration Dependence:** The term $\frac{d[A]}{[A]}$ illustrates how the **reaction rate** depends on the concentration of A. For a **first-order reaction** (m = 1), the rate is directly proportional to [A]. This means that a 10% decrease in the concentration of A leads to a corresponding 10% decrease in the reaction rate. As the **reaction proceeds** and the reactant is consumed, the **reaction rate** continuously decreases, unlike a **zero-order reaction** where the rate stays constant regardless of the concentration.
- **Temperature Dependence:** The term $\frac{E_a}{RT} \left(\frac{dT}{T} \right)$ represents the effect of temperature on the reaction rate. Even if the **concentration of A** remains **constant**, an **increase in temperature** raises the **reaction rate** because more molecules gain enough energy to overcome the **activation energy** E_a . This term comes from the **Arrhenius equation**, $k_r = A e^{-\frac{E_a}{RT}}$, which shows that the rate constant k_r increases as the temperature rises.

3. Second-Order Reaction (m = 2):

For a **second-order reaction** (Rate $\propto [A]^2$), the expression becomes:

$$\frac{dv}{v} = 2 \left(\frac{d[A]}{[A]} \right) + \frac{E_a}{RT} \left(\frac{dT}{T} \right)$$

- **Concentration Dependence:** The term $2 \left(\frac{d[A]}{[A]} \right)$ illustrates how the reaction rate depends on the concentration of A. For a **second-order reaction** ($m = 2$), the rate is proportional to the square of $[A]$. This means that a 10% decrease in the concentration of A leads to approximately a 20% decrease in the reaction rate. As the **reaction proceeds** and the reactant is consumed, the **reaction rate** decreases more rapidly compared with a **first-order reaction**, unlike a **zero-order reaction** where the rate remains constant regardless of concentration.

- **Temperature Dependence:** The term $\frac{E_a}{RT} \left(\frac{dT}{T} \right)$ shows that the **reaction rate** increases with temperature. This effect arises because the **rate constant** k_r depends on the activation energy E_a and temperature through the exponential factor $e^{-\frac{E_a}{RT}}$. For example, if the **temperature rises from 300 K to 310 K**, **more molecules** acquire **enough energy** to surpass the **activation barrier**, significantly increasing the rate. In general, **even small increases in temperature can lead to noticeable increases in the reaction rate**, especially for reactions with high E_a .

The rate constant of a reaction can be described in two ways: the **Arrhenius equation**

$$k_r = A e^{-\frac{E_a}{RT}}$$

and **collision theory**

$$k_r = \rho Z e^{-\frac{E_a}{RT}}$$

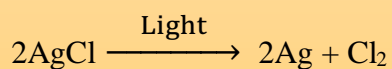
Here, A is the **pre-exponential factor**, Z is the **collision frequency** (how often molecules collide), and ρ is the **steric factor**, which accounts for the correct orientation of molecules during collisions. From these, we see that:

$$A = \rho Z$$

The **steric factor** (ρ) quantifies the probability that **colliding molecules** are correctly oriented to react. It forms part of the **pre-exponential factor** in the **Arrhenius equation**. In **gas-phase reactions**, ρ is typically less than 1 because molecules must align correctly for bonds to break and form; for example, in the reaction $2\text{ClNO} \rightarrow 2\text{Cl} + 2\text{NO}$, $\rho = 0.16$, meaning only 16% of collisions are effective. In **solution-phase reactions**, the solvent can either hinder alignment ($\rho < 1$) or sometimes hold reactants in a favorable orientation, creating a "**solvent cage**," which can make $\rho > 1$ due to entropic effects; for instance, $\text{HOCH}_2\text{CH}_2\text{Cl} + \text{OH}^-$ in water has $\rho = 9.17$. The **overall reaction rate** depends on both sufficient kinetic energy to overcome the **activation energy** E_a and **correct molecular orientation** (ρ). Consequently, reactions like $\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$ with $\rho = 1.7 \times 10^{-6}$ are **extremely slow** despite **frequent collisions** because proper alignment is rare, while reactions with favorable orientation or solvent effects proceed much faster.

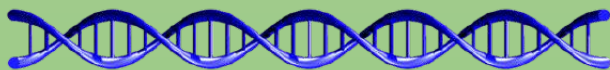
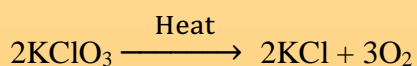
- **Photochemical reaction:** Triggered by light, low activation energy.

Example: The decomposition of silver chloride under sunlight:

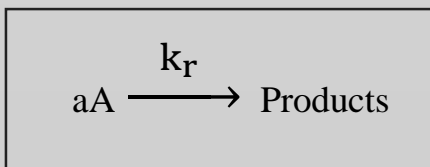


- **Thermal reaction:** Triggered by heat, high activation energy.

Example: Decomposition of potassium chlorate on heating:



For a reaction:



where a moles of A react.

The **rate law** is:

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = k_r [A]^m$$

Here, m is the order of the reaction with respect to A .

Multiplying **both sides by a and** rearranging:

$$\frac{d[A]}{dt} = -ak_r [A]^m \Rightarrow d[A] [A]^{-m} = -ak_r dt$$

Integrating both sides, we get:

$$\frac{[A]^{-m+1}}{(-m+1)} = -ak_r t + C$$

At time $t = 0$, $[A] = [A]_0$, so:

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

Substituting for C , we get:

$$\frac{[A]^{-m+1}}{(-m+1)} = -ak_r t + \frac{[A]_0^{-m+1}}{(-m+1)}$$

Rearranging,

$$\frac{[A]^{-m+1}}{(-m+1)} - \frac{[A]_0^{-m+1}}{(-m+1)} = -ak_r t$$



$$t = \frac{1}{ak_r} \left(\frac{[A]_0^{-m+1} - [A]^{-m+1}}{(-m+1)} \right)$$

At half-life, the **concentration of A** becomes half of its initial value, i.e., $[A] = \frac{[A]_0}{2}$, and

$t = t_{1/2}$. Substituting these values gives:

$$t_{1/2} = \frac{1}{ak_r} \left(\frac{[A]_0^{-m+1} - \left(\frac{[A]_0}{2} \right)^{-m+1}}{(-m+1)} \right)$$

Simplifying,

$$t_{1/2} = \frac{[A]_0^{-m+1} \left(1 - 2^{-(-m+1)} \right)}{ak_r (-m+1)}$$

This shows how the **half-life of a reaction** depends on both the **initial concentration** $[A]_0$ and the **order of the reaction** m . For **reactions of different orders**, the relationship between **half-life and initial concentration** changes significantly. This provides a practical way to determine the **order of a reaction** experimentally – by observing how the **half-life** ($t_{1/2}$) varies with the **initial concentration** $[A]_0$.

- **Zero-order reaction (m = 0):**

Substituting $m = 0$:

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

In **zero-order reactions**, the **half-life** is directly proportional to the **initial concentration of the reactant**. This means that as **more reactant** is present, it takes longer for its concentration to decrease by half. Such reactions usually occur when a **reaction site** becomes saturated, for example, during the decomposition of a substance on a saturated reaction site.

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

Substituting $m = 1$ into the general half-life expression gives $t_{1/2} = \frac{0}{0}$, which is an **indeterminate form**. This occurs because the formula is valid only for $m \neq 1$, and we cannot substitute $m = 1$ into a formula derived under the condition that $m \neq 1$. The **half-life for a first-order reaction** must therefore be derived separately using the **first-order integrated rate law**.

For a **first-order reaction**, the rate law is:

$$-\frac{1}{a} \left(\frac{d[A]}{dt} \right) = k_r [A]$$

Integrating this equation gives the **first-order integrated rate law**:

$$\ln [A] - \ln [A]_0 = -ak_r t$$

To find the **half-life**, we set $[A] = \frac{[A]_0}{2}$ and $t = t_{1/2}$:

$$\ln \left(\frac{[A]_0}{2} \right) - \ln [A]_0 = -ak_r t_{1/2}$$

Simplifying the left-hand side:

$$\ln [A]_0 - \ln 2 - \ln [A]_0 = -ak_r t_{1/2}$$

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

This shows that for a **first-order reaction**, the **half-life** is independent of the initial concentration of the reactant and depends only on the **rate constant** k_r .

- **Second-order reaction (m = 2):**

Substituting $m = 2$:

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

This shows that the **half-life** is inversely proportional to the **initial concentration** of the reactant. As the **initial concentration increases**, the reaction proceeds faster, resulting in a **shorter half-life**.

- Zero E_a → **Fraction of effective collisions is very large** → Most collisions are successful → **Reaction is very fast** (instantaneous)
- High E_a → **Fraction of effective collisions is small** → Fewer collisions are effective → **Slower reaction**
- Low E_a → **Fraction of effective collisions is large** → More collisions are effective → **Faster reaction**.

From the integrated equation,

$$t = \frac{1}{ak_r} \left(\frac{[A]_0^{-m+1} - [A]^{-m+1}}{(-m+1)} \right)$$

it follows that the instantaneous rate of reaction is given by:

$$v = k_r [A]^m = \frac{1}{at} \left(\frac{[A]_0^{-m+1} [A]^m - [A]^{-m+1} [A]^m}{(-m+1)} \right)$$

Since $[A]^{-m+1} [A]^m = [A]$, the expression simplifies to:

$$v = \frac{1}{at} \left(\frac{[A]_0^{-m+1} [A]^m - [A]}{(-m+1)} \right)$$

This equation expresses the relationship between the **reaction rate** and **several key parameters of the reaction**. It connects the **reaction rate** v with the **initial concentration** $[A]_0$ and the **concentration** $[A]$ **at any time** t . The **order of the reaction** m **determines** how strongly the **reaction rate** depends on the concentration of the reactant. The **stoichiometric coefficient** a **accounts** for the proportion of the reactant involved in the reaction. Overall, it shows that the rate of reaction changes as the concentration of the reactant decreases over time.

The **rate of decrease of reaction velocity** is given by:

$$-\frac{dv}{dt} = \frac{mav^2}{[A]} = \frac{m}{[A]at^2} \left(\frac{[A]_0^{-m+1} [A]^m - [A]}{(-m+1)} \right)^2$$

This equation shows that the **rate at which the reaction velocity decreases** depends on the **reaction order** m , the **stoichiometric coefficient** a , and the **concentrations** $[A]_0$ and $[A]$. It indicates that as the **reaction proceeds**, the **change in reactant concentration** significantly influences **how fast the velocity declines**. The presence of $[A]$ in the denominator implies that a **lower reactant concentration** leads to a **faster decrease in reaction velocity**. Overall, the equation connects the kinetic behavior of the reaction to both its order and concentration changes over time.

The **rate of an electrochemical reaction** describes how quickly a chemical reaction occurs at an electrode due to the passage of electric current. It is measured using the equation:

$$v = \frac{I}{nF} \Rightarrow v \propto I$$

- where v = **rate of the electrochemical reaction** (moles per second), I = **current** (amperes), n = **number of electrons transferred per molecule in the reaction**, and F = **Faraday constant** (96,485.3321 C/mol).

Since $v \propto I$, the **rate of an electrochemical reaction** increases as the **current** increases. Conversely, if the **current** decreases, the **electrochemical reaction rate** also decreases.



In the **electrochemical deposition of copper**: $\text{Cu}^{2+}_{(aq)} + 2e^{-} \rightarrow \text{Cu}_{(s)}$ each **copper ion** requires $n=2$ electrons to be reduced and deposited as solid copper. The **rate of deposition** depends on the **current applied**: a higher current deposits more copper per second, while a lower current slows the deposition rate. **For example**, when a current of 1 A is passed, the **rate of copper deposition** can be calculated using $v = \frac{I}{nF} = \frac{1\text{A}}{2 \times (96,485.3321 \text{ C/mol})} = 0.00000518213 \text{ mol/s}$. This illustrates quantitatively how the **applied current** directly controls the **rate of copper deposition**.

The equation:

$$-\frac{dv}{dt} = \frac{mav^2}{[A]} = \frac{m}{[A]at^2} \left(\frac{[A]_0^{-m+1}[A]^m - [A]}{-m+1} \right)^2$$

does not hold for a **first-order reaction** ($m=1$).

For a **first-order reaction** ($m = 1$):

$$-\frac{dv}{dt} = \frac{av^2}{[A]} = \frac{a(k_r[A])^2}{[A]} = ak_r^2 [A]$$

Since

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

we obtain:

$$-\frac{dv}{dt} = ak_r^2 [A]_0 e^{-ak_r t}$$

This expression shows that the rate at which the reaction velocity **decreases** falls exponentially with time. As the concentration $[A]$ decreases during a **first-order reaction**, the value of $-\frac{dv}{dt}$ also becomes smaller. The term $[A]_0 e^{-ak_r t}$ represents this exponential decay, indicating that the reaction steadily slows down as the reactant is consumed. The factors ak_r^2 set the overall **magnitude** of this decrease, while the exponential term determines how quickly the **reaction rate** drops with time.

For the reaction $aA \xrightarrow{k_r} \text{Products}$, the change in the extent of reaction is defined as:

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

- where n_A denotes the number of moles of the reactant A, and a is the stoichiometric coefficient of the reactant.
- The **negative sign** indicates that the **number of moles of the reactant A** decreases as the reaction proceeds.

Since $n_A = C_A V$, where C_A is the concentration and V is the volume of the reactant, the differential form is:

$$dn_A = VdC_A + C_A dV$$

Substituting this expression into the equation for $d\xi$:

$$d\xi = -\frac{1}{a} \left[VdC_A + C_A dV \right]$$

This shows that when the volume of the reactant changes, both the **change in concentration** (dC_A) and the **change in volume** (dV) contribute to the change in the extent of reaction. If the **volume is constant** ($V = \text{constant}$), then $dV = 0$, and the equation simplifies to:

$$d\xi = -\frac{1}{a} \left[VdC_A \right]$$

In this case, only the **change in concentration** (dC_A) affects the **extent of reaction**, as the volume remains unchanged.

From the expression for the extent of reaction, it follows that:

$$\frac{d\xi}{dt} = V \left(-\frac{1}{a} \frac{dC_A}{dt} \right) - \frac{C_A}{a} \left(\frac{dV}{dt} \right)$$

Since the **rate of reaction** is defined as:

$$v = -\frac{1}{a} \frac{dC_A}{dt}$$

we can rewrite the equation as:

$$\frac{d\xi}{dt} = (V \times v) - \frac{C_A}{a} \left(\frac{dV}{dt} \right)$$

Rearranging gives the **rate of reaction** in terms of the **extent of reaction**:

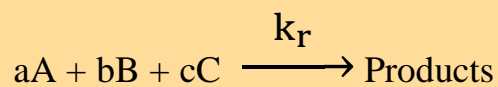
$$v = \frac{1}{V} \left(\frac{d\xi}{dt} + \frac{C_A}{a} \left(\frac{dV}{dt} \right) \right)$$

The **rate of decrease of reaction velocity** can then be expressed as:

$$-\frac{dv}{dt} = \frac{mav^2}{C_A} = \frac{ma}{n_A V} \left(\frac{d\xi}{dt} + \frac{C_A}{a} \left(\frac{dV}{dt} \right) \right)^2$$

This expression shows that the **rate of decrease of reaction velocity** ($-\frac{dv}{dt}$) depends on both the **rate of reaction progress** ($\frac{d\xi}{dt}$) and the **rate of change in reactant volume** ($\frac{dV}{dt}$). As the reaction proceeds, the consumption of reactant affects the reaction rate, while any change in the volume of the reactant alters its concentration, further influencing the rate of decrease of velocity.

For the reaction:



the **rate of reaction** is given by the **rate law**:

$$v = k_r [A]^m [B]^n [C]^p$$

The **rate of reaction** can also be expressed in terms of the rate of change of the reactant concentrations over time:

$$v = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = -\frac{1}{c} \frac{d[C]}{dt}$$

or equivalently,

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

$$-\frac{d[B]}{dt} = b \times v$$

$$-\frac{d[C]}{dt} = c \times v$$

Dividing the rate law by $[C]^p$:

$$\frac{v}{[C]^p} = k_r [A]^m [B]^n$$

Taking the time derivative of both sides:

$$\frac{d}{dt} \left(\frac{v}{[C]^p} \right) = k_r \frac{d}{dt} \left([A]^m [B]^n \right)$$

This can also be written as:

$$\frac{d}{dt} \left(v [C]^{-p} \right) = k_r \frac{d}{dt} \left([A]^m [B]^n \right)$$

- Applying the product rule to the left-hand side, we get:

$$\left(\frac{dv}{dt} \right) [C]^{-p} + \left(\frac{d([C]^{-p})}{dt} \right) v$$

↓

$$\left(\frac{dv}{dt} \right) [C]^{-p} - p [C]^{-p-1} \left(\frac{d[C]}{dt} \right) v$$

↓

$$\frac{dv}{dt} \left(\frac{1}{[C]^p} \right) + \frac{p}{[C]^p [C]} \left(- \frac{d[C]}{dt} \right) v$$

↓

$$\frac{dv}{dt} \left(\frac{1}{[C]^p} \right) + \frac{cpv^2}{[C]^p [C]}$$

- Applying the product rule to the right-hand side, we get:

$$\left(\frac{d([A]^m)}{dt} \right) [B]^n + \left(\frac{d([B]^n)}{dt} \right) [A]^m$$

↓

$$\left(\frac{m}{[A]} \right) [A]^m [B]^n \left(\frac{d[A]}{dt} \right) + \left(\frac{n}{[B]} \right) [A]^m [B]^n \left(\frac{d[B]}{dt} \right)$$

↓

$$\left(\frac{-mav}{[A]} \right) [A]^m [B]^n + \left(\frac{-nbv}{[B]} \right) [A]^m [B]^n$$

From the equation,

$$\frac{d}{dt} \left(v [C]^{-p} \right) = k_r \frac{d}{dt} \left([A]^m [B]^n \right)$$

it follows that:

$$\frac{dv}{dt} \left(\frac{1}{[C]^p} \right) + \frac{cpv^2}{[C]^p [C]} = \left(\frac{-mav}{[A]} \right) k_r [A]^m [B]^n + \left(\frac{-nbv}{[B]} \right) k_r [A]^m [B]^n$$

or equivalently,

$$\frac{dv}{dt} = \left(\frac{-mav^2}{[A]} \right) + \left(\frac{-nbv^2}{[B]} \right) + \left(\frac{-pcv^2}{[C]} \right)$$

The equation

$$-\frac{dv}{dt} = \frac{mav^2}{[A]} + \frac{nbv^2}{[B]} + \frac{pcv^2}{[C]}$$

means that the reaction rate v **decreases with time**, and the rate of this decrease ($-\frac{dv}{dt}$) depends on the concentrations of the reactants A, B, and C.

Each term on the right-hand side shows how a **specific reactant** contributes to slowing down the reaction. The constants a, b, and c are the **stoichiometric coefficients**, showing how much of each reactant is involved, while m, n, and p are the **reaction orders**, describing how strongly the rate depends on each reactant's concentration.

The presence of v^2 indicates that as the reaction proceeds and v becomes smaller, the rate decreases faster – showing a **self-limiting behavior**. In simple terms, this equation expresses how the reaction naturally slows down as reactants are used up.

Type of Reaction	Rate Constant	Half-Life	Description
Slow	Very low	Very long	These reactions proceed very slowly and may take hours, days, or even years to complete.
Moderate	Intermediate	Moderate	These reactions occur at a noticeable rate and are commonly observed in laboratory conditions.
Fast	High	Short	These reactions take place quickly, often within seconds or less, and require rapid measurement techniques.
Ultrafast	Extremely high	Extremely short	These reactions happen almost instantaneously, often in picoseconds or femtoseconds, and are studied using laser spectroscopy.

$$-\frac{dv}{dt} = \frac{mav^2}{[A]} + \frac{nbv^2}{[B]} + \frac{pcv^2}{[C]}$$

It can be simplified to:

$$-\frac{dv}{dt} = v^2 \left(\frac{(ma[B][C] + nb[A][C] + pc[A][B])}{[A][B][C]} \right)$$

This equation shows that the **rate of decrease of v** depends on the **combined effects of reactants A, B, and C**, each weighted by the **reaction orders m, n, p** and the **stoichiometric coefficients a, b, and c**. The denominator $[A][B][C]$ indicates that the **rate of decrease of v** is inversely related to the concentrations of all three species.

Condition	Rate Equation
$m = 0$ (Zero order with respect to A)	$-\frac{dv}{dt} = v^2 \left(\frac{(nb[A][C] + pc[A][B])}{[A][B][C]} \right)$
$n = 0$ (Zero order with respect to B)	$-\frac{dv}{dt} = v^2 \left(\frac{(ma[B][C] + pc[A][B])}{[A][B][C]} \right)$

<p style="text-align: center;">$p = 0$ (Zero order with respect to C)</p>	$-\frac{dv}{dt} = v^2 \left(\frac{ma[B][C] + nb[A][C]}{[A][B][C]} \right)$
<p style="text-align: center;">$m = 0, n = 0$</p> <div style="border: 1px solid red; padding: 5px; width: fit-content; margin: auto;"> <p style="text-align: center;">(Zero order with respect to A and B)</p> </div>	$-\frac{dv}{dt} = v^2 \left(\frac{pc}{[C]} \right)$
<p style="text-align: center;">$n = 0, p = 0$</p> <div style="border: 1px solid red; padding: 5px; width: fit-content; margin: auto;"> <p style="text-align: center;">(Zero order with respect to B and C)</p> </div>	$-\frac{dv}{dt} = v^2 \left(\frac{ma}{[A]} \right)$
<p style="text-align: center;">$m = 0, p = 0$</p> <div style="border: 1px solid red; padding: 5px; width: fit-content; margin: auto;"> <p style="text-align: center;">(Zero order with respect to A and C)</p> </div>	$-\frac{dv}{dt} = v^2 \left(\frac{nb}{[B]} \right)$

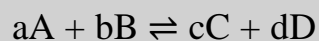
"Living organisms are created by chemistry. We are huge packages of chemicals."



David Christian

- **Interpreting ΔG Through Reaction Rate Ratios:**

For a reversible elementary reaction:



the Gibbs free energy change is expressed as:

$$\Delta G = \Delta G^0 + RT \ln Q$$

where:

- R is the gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$),
- T is the temperature in Kelvin,
- ΔG^0 is the standard Gibbs free energy change,
- Q is the reaction quotient given by $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

At equilibrium, $\Delta G = 0$ and $Q = K_{eq}$, so the **standard Gibbs free energy change** can be written as:

$$\Delta G^0 = - RT \ln K_{eq}$$

Substituting this into the first equation, we get:

$$\Delta G = - RT \ln K_{eq} + RT \ln Q$$

According to the **Law of Mass Action**, at a **constant temperature**, the **rate of a chemical reaction** is directly proportional to the product of the **molar concentrations** of the reactants, with **each concentration** raised to the power of its **stoichiometric coefficient** in the balanced equation.

For the forward reaction:

$$v_1 = k_1 [A]^a [B]^b$$

where:

- k_1 is the rate constant for the forward reaction,
- $[A]$ and $[B]$ are the molar concentrations of A and B,
- a and b are their respective stoichiometric coefficients.

For the backward reaction:

$$v_2 = k_2 [C]^c [D]^d$$

where:

- k_2 is the rate constant for the backward reaction,
- $[C]$ and $[D]$ are the molar concentrations of C and D,
- c and d are their respective stoichiometric coefficients.

Taking their ratio:

$$\frac{v_1}{v_2} = \frac{k_1 [A]^a [B]^b}{k_2 [C]^c [D]^d}$$

Since the **equilibrium constant** K_{eq} is defined as the **ratio of the rate constants** ($\frac{k_1}{k_2}$),

and the reaction quotient Q is given by $\frac{[C]^c [D]^d}{[A]^a [B]^b}$, substituting these expressions into the **rate ratio equation** provides a relationship between the **reaction rates** and **thermodynamic quantities**:

$$\frac{v_1}{v_2} = \frac{K_{eq}}{Q}$$

Taking the natural logarithm of both sides gives:

$$\ln \left(\frac{v_1}{v_2} \right) = \ln K_{eq} - \ln Q$$

Multiplying through by $-RT$:

$$-RT \ln \left(\frac{v_1}{v_2} \right) = -RT \ln K_{eq} + RT \ln Q$$

By comparing this expression with the earlier equation for ΔG , we find that:

$$\Delta G = -RT \ln \left(\frac{v_1}{v_2} \right)$$

- When the forward reaction is favored ($v_1 > v_2$), the **rate ratio** $\frac{v_1}{v_2} > 1$. This makes $\ln \left(\frac{v_1}{v_2} \right)$ positive, giving $\Delta G < 0$. A **negative ΔG** indicates that the **forward reaction** is **spontaneous** and will generate more products.
- When the backward reaction is favored ($v_2 > v_1$), the rate ratio $\frac{v_1}{v_2} < 1$. In this case, $\ln \left(\frac{v_1}{v_2} \right)$ is negative, resulting in $\Delta G > 0$. This means the **forward reaction** is **non-spontaneous**, and the backward reaction predominates.
- At **equilibrium** ($v_1 = v_2$), the **rate ratio** is 1. Since $\ln(1) = 0$, $\Delta G = 0$, indicating **no net change** in the concentrations of reactants or products.

In an **elementary reaction**, each **molecular event** occurs exactly as written in the **chemical equation**, so the **reaction order** equals the **stoichiometric coefficients** of the reactants. For a **general reaction** $aA + bB \rightleftharpoons cC + dD$, the **forward and reverse reaction rates** are given by $v_1 = k_1 [A]^a [B]^b$ and $v_2 = k_2 [C]^c [D]^d$, where k_1 and k_2 are the respective rate constants. The **Gibbs free energy change** is related to the **ratio of the forward and reverse rates** by:

$$\Delta G = -RT \ln \left(\frac{v_1}{v_2} \right)$$

The **reaction quotient**, derived from the **stoichiometric coefficients**, is expressed as:

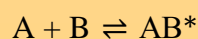
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

For example, in the reaction $H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$, the **forward and reverse rates** are given by $v_1 = k_1 [H_2] [I_2]$ and $v_2 = k_2 [HI]^2$, respectively, and the **reaction quotient** is $Q = \frac{[HI]^2}{[H_2][I_2]}$.

Several reactions are **considered elementary**, meaning each molecular event occurs exactly as written in the chemical equation and the **molecularity is equal to the reaction order**.

Such reactions obey the relation:
$$\frac{v_1}{v_2} = \frac{K_{eq}}{Q}$$

For instance,



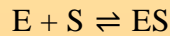
is a **bimolecular reaction** representing the direct association of two molecules to form an **activated complex**. This step is common in **transition-state theory**, where reactants combine in a single elementary step to form a transient species.

It obeys:

$$v_{\text{activation}} = k_1 [A] [B], \quad v_{\text{deactivation}} = k_2 [AB^*], \quad Q = \frac{[AB^*]}{[A][B]}, \quad \frac{v_{\text{activation}}}{v_{\text{deactivation}}} = \frac{K^*}{Q},$$

$$\Delta G^* = -RT \ln \left(\frac{v_{\text{activation}}}{v_{\text{deactivation}}} \right)$$

Similarly,



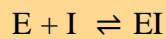
is a bimolecular step in **Michaelis–Menten kinetics**, where the **enzyme** (E) binds the **substrate** (S) to form an **enzyme–substrate complex**.

It obeys:

$$v_{\text{binding-S}} = k_1 [E] [S], \quad v_{\text{unbinding-S}} = k_2 [ES], \quad Q_S = \frac{[ES]}{[E][S]}, \quad \frac{v_{\text{binding-S}}}{v_{\text{unbinding-S}}} = \frac{K_S^*}{Q_S},$$

$$\Delta G_S^* = -RT \ln \left(\frac{v_{\text{binding-S}}}{v_{\text{unbinding-S}}} \right)$$

The reaction



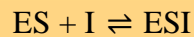
represents **enzyme inhibition**, where the **inhibitor** (I) binds to the **enzyme** (E) and blocks **substrate binding** or **catalysis**.

It obeys:

$$v_{\text{binding-I}} = k_1 [E] [I], \quad v_{\text{unbinding-I}} = k_2 [EI], \quad Q_I = \frac{[EI]}{[E][I]}, \quad \frac{v_{\text{binding-I}}}{v_{\text{unbinding-I}}} = \frac{K_I^*}{Q_I},$$

$$\Delta G_I^* = -RT \ln \left(\frac{v_{\text{binding-I}}}{v_{\text{unbinding-I}}} \right)$$

The step



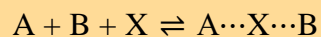
describes the binding of **inhibitor** (I) to the **enzyme–substrate complex** (ES), forming a **ternary enzyme–substrate–inhibitor complex**.

It obeys:

$$v_{\text{binding-SI}} = k_1 [ES] [I], \quad v_{\text{unbinding-SI}} = k_2 [ESI], \quad Q_{SI} = \frac{[ESI]}{[ES][I]}, \quad \frac{v_{\text{binding-SI}}}{v_{\text{unbinding-SI}}} = \frac{K_{SI}^*}{Q_{SI}}$$

$$\Delta G_{SI}^* = -RT \ln \left(\frac{v_{\text{binding-SI}}}{v_{\text{unbinding-SI}}} \right)$$

The **termolecular reaction**



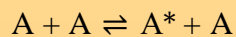
involves a **catalyst** X that temporarily binds both **reactants** to form a **catalytic activated complex**. This step models a **rare three-body collision** that facilitates product formation.

It obeys:

$$v_{\text{activation}} = k_1 [A] [B][X], \quad v_{\text{deactivation}} = k_2 [A \cdots X \cdots B], \quad Q = \frac{[A \cdots X \cdots B]}{[A][B][X]},$$

$$\frac{v_{\text{activation}}}{v_{\text{deactivation}}} = \frac{K^*}{Q}, \quad \Delta G^* = -RT \ln \left(\frac{v_{\text{activation}}}{v_{\text{deactivation}}} \right)$$

The collisional-activation reaction



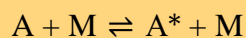
is bimolecular: **one molecule transfers energy to another during a collision**, exciting it to a **higher-energy state** A*. This is a key step in the **Lindemann mechanism**.

It obeys:

$$v_{\text{activation}} = k_1 [A]^2, \quad v_{\text{deactivation}} = k_2 [A^*] [A], \quad Q = \frac{[A^*][A]}{[A]^2},$$

$$\frac{v_{\text{activation}}}{v_{\text{deactivation}}} = \frac{K^*}{Q}, \quad \Delta G^* = -RT \ln \left(\frac{v_{\text{activation}}}{v_{\text{deactivation}}} \right)$$

The reaction



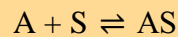
is another **bimolecular activation step**, where M acts as the **energy-transfer partner** that either donates or absorbs excess energy.

It obeys:

$$v_{\text{activation}} = k_1 [A] [M], \quad v_{\text{deactivation}} = k_2 [A^*] [M], \quad Q = \frac{[A^*][M]}{[A][M]},$$

$$\frac{v_{\text{activation}}}{v_{\text{deactivation}}} = \frac{K^*}{Q}, \quad \Delta G^* = -RT \ln \left(\frac{v_{\text{activation}}}{v_{\text{deactivation}}} \right)$$

The surface-adsorption reaction



describes binding of molecule A to a **surface site** S, forming the **adsorbed complex** AS. Adsorption may occur through **physisorption** or **chemisorption**.

It obeys:

$$v_{\text{binding-1}} = k_1 [A] [S], \quad v_{\text{unbinding-1}} = k_2 [AS], \quad Q = \frac{[AS]}{[A][S]}, \quad \frac{v_{\text{binding-1}}}{v_{\text{unbinding-1}}} = \frac{K_{\text{eq}}}{Q},$$

$$\Delta G_1 = -RT \ln \left(\frac{v_{\text{binding-1}}}{v_{\text{unbinding-1}}} \right)$$

Likewise,



describes the **adsorption of molecule** B on the **same surface site** type, forming the **adsorbed complex** BS.

It obeys:

$$v_{\text{binding-2}} = k_1 [B] [S], \quad v_{\text{unbinding-2}} = k_2 [BS], \quad Q = \frac{[BS]}{[B][S]}, \quad \frac{v_{\text{binding-2}}}{v_{\text{unbinding-2}}} = \frac{K_{\text{eq}}}{Q},$$

$$\Delta G_2 = -RT \ln \left(\frac{v_{\text{binding-2}}}{v_{\text{unbinding-2}}} \right)$$

Every reaction listed above is treated as an **elementary step**, meaning that the **forward reaction rate** v_1 depends directly on the concentrations of the reactants exactly as written, while the **reverse reaction rate** v_2 depends on the concentrations of the products exactly as written. In each case, the **reaction quotient** Q is defined as the ratio of product terms to reactant terms, and the equilibrium constant satisfies $K_{eq} = \frac{k_1}{k_2}$. Therefore, every individual reaction – whether $A + B \rightleftharpoons AB^*$ describing **formation of an activated complex**, $E + S \rightleftharpoons ES$ representing **enzyme–substrate binding**, $E + I \rightleftharpoons EI$ illustrating **enzyme–inhibitor binding**, $ES + I \rightleftharpoons ESI$ showing formation of a **ternary inhibitory complex**, $A + B + X \rightleftharpoons A \cdots X \cdots B$ describing **catalyst-assisted termolecular activated-complex formation**, $A + A \rightleftharpoons A^* + A$ and $A + M \rightleftharpoons A^* + M$ representing collisional activation in the **Lindemann mechanism**, or $A + S \rightleftharpoons AS$ and $B + S \rightleftharpoons BS$ modeling **adsorption of reactants onto surface sites** — individually obeys

$$\frac{v_1}{v_2} = \frac{K_{eq}}{Q}$$

Finally, **ligand-binding reactions** such as $P + L \rightleftharpoons PL$ and $PL + L \rightleftharpoons PL_2$ are additional examples of **bimolecular elementary steps** in which ligands bind sequentially. Although the overall process $P + 2L \rightleftharpoons PL_2$ has **termolecular stoichiometry**, it is not an elementary reaction because it does not arise from a **single three-body collision** but instead proceeds through two separate bimolecular association steps.

"It's more interesting to work on challenges where you don't know the answer.

In chemistry, you should enter into an adventure with molecules."



Ben Feringa



Non-elementary reactions are chemical reactions that occur through **multiple steps** rather than a single event. In these reactions, the **molecularity** based on the overall balanced equation does not match the **experimentally determined reaction order**, showing that intermediates are involved. For example, in the reaction $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$, the **molecularity** is two, but the rate law $\text{Rate} = k_r [\text{H}_2][\text{Br}_2]^{\frac{1}{2}}$ gives an overall order of 1.5, indicating a complex mechanism involving intermediate radicals. Similarly, in $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, the **molecularity** is four, while the rate law $\text{Rate} = k_r [\text{NO}]^2 [\text{H}_2]$ shows a third-order reaction, which cannot occur in a single step, proving it is multi-step. Another case is $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$, where the rate law $\text{Rate} = k_r [\text{CO}] [\text{Cl}_2]^{\frac{3}{2}}$ gives a fractional order of 2.5, showing that it proceeds through a radical chain mechanism. In the **decomposition of PH_3 on tungsten (W)**, the rate law $\text{Rate} = k_r [\text{PH}_3]^0 = k_r$ indicates a zero-order reaction, typical of **surface-catalyzed processes** where the rate becomes independent of concentration once the surface is saturated. Thus, **non-elementary reactions** demonstrate that real chemical processes often occur through several intermediate stages, and their **rate laws** must be determined experimentally rather than directly from **stoichiometry**.

- **Temperature Coefficient of a Reaction:**

The **temperature coefficient (μ)** is the **ratio of the rate constant (k_r)** of a reaction at a temperature $T + 10^\circ\text{C}$ to that at $T^\circ\text{C}$.

$$\mu = \frac{k_{T+10}}{k_T}$$

It indicates **how much the rate constant (and thus the reaction rate)** changes when the temperature is increased by 10°C .

From the **Arrhenius equation**:

$$k_r = A e^{-\frac{E_a}{RT}}$$

The rate constant k_r increases **exponentially** with an increase in **temperature** (T).

- When **T** increases, the value of $-\frac{E_a}{RT}$ becomes **less negative**, so $e^{-\frac{E_a}{RT}}$ increases, and therefore **k_r increases**.
- This explains why reactions proceed faster at higher temperatures.

- ✓ Increasing **temperature** increases k_r (and reaction rate).
- ✓ Increasing **activation energy** (E_a) decreases k_r .

So,

$$\mu = \frac{k_{T+10}}{k_T} = \frac{A e^{-\frac{E_a}{R(T+10)}}}{A e^{-\frac{E_a}{RT}}} = e^{-\frac{E_a}{R} \left(\frac{1}{T+10} - \frac{1}{T} \right)}$$

A (**the pre-exponential factor**) and E_a (**the activation energy**) in the **Arrhenius equation** are generally assumed to remain constant over the small temperature ranges typically studied, such as the 10 °C range.



This equation shows that the **temperature coefficient** (μ) depends on both **activation energy** (E_a) and **temperature** (T).

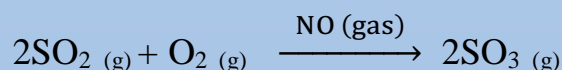


For most reactions, the **temperature coefficient** (μ) ranges between 2 and 3, meaning the **rate constant** approximately doubles or triples for every 10 °C increase in temperature. A value of $\mu=2$ indicates that when the temperature rises by 10 °C, the rate constant doubles. This happens because a **higher temperature** increases the fraction of molecules possessing energy equal to or greater than the **activation energy** (E_a), resulting in a greater number of successful collisions and, consequently, a faster reaction rate.

Order of Reaction	Molecularity of Reaction
The sum of the powers of concentration terms in the experimentally determined rate law.	The number of reactant molecules that collide at the same time in a single elementary step to bring about a chemical reaction.
Determined experimentally from the rate law.	Determined theoretically from the reaction mechanism.
May be 0, 1, 2, or fractional , etc.	Always a whole number – 1 (unimolecular), 2 (bimolecular), or 3 (trimolecular).
Depends on the experimentally observed rate law .	Depends on the mechanism of the reaction .
For the reaction $\text{H}_2 + \text{Br}_2 \rightarrow \text{HBr}$, the experimentally determined order is $\frac{3}{2}$.	For the same reaction $\text{H}_2 + \text{Br}_2 \rightarrow \text{HBr}$, one molecule of H_2 and one molecule of Br_2 collide – hence it is bimolecular .

1. Homogeneous Catalysis:

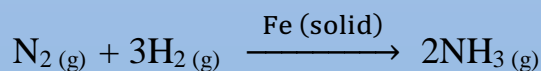
- Catalyst and reactants are in the same phase (usually liquid or gas).
- **Example:**



Nitric oxide (NO) acts as a homogeneous catalyst in the oxidation of sulfur dioxide.

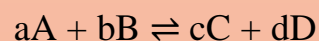
2. Heterogeneous Catalysis:

- Catalyst and reactants are in different phases (usually solid catalyst with gaseous or liquid reactants).
- **Example:**



Iron acts as a heterogeneous catalyst in the Haber process for ammonia synthesis.

- **Reversible non-elementary reaction:**



Reaction quotient: $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

Rate laws (non-elementary, orders need not equal stoichiometric coefficients):

$$v_1 = k_1 [A]^m [B]^n \text{ (forward)}, \quad v_2 = k_2 [C]^x [D]^y \text{ (backward)}$$

Since $\frac{k_1}{k_2} = K_{eq}$. Then

$$\frac{v_1}{v_2} = \frac{k_1}{k_2} \frac{[A]^m [B]^n}{[C]^x [D]^y} = K_{eq} \frac{[A]^m [B]^n}{[C]^x [D]^y}$$

Taking natural logs:

$$\ln \left(\frac{v_1}{v_2} \right) = \ln K_{eq} + \ln \left(\frac{[A]^m [B]^n}{[C]^x [D]^y} \right)$$

Multiplying by $-RT$:

$$-RT \ln \left(\frac{v_1}{v_2} \right) = -RT \ln K_{eq} - RT \ln \left(\frac{[A]^m [B]^n}{[C]^x [D]^y} \right)$$

Using the standard relation

$$\Delta G^0 = -RT \ln K_{eq}$$

we can write:

$$-RT \ln \left(\frac{v_1}{v_2} \right) = \Delta G^0 - RT \ln \left(\frac{[A]^m [B]^n}{[C]^x [D]^y} \right)$$

Rearranging, we get:

$$\Delta G^0 = -RT \ln \left(\frac{v_1}{v_2} \right) + RT \ln \left(\frac{[A]^m [B]^n}{[C]^x [D]^y} \right)$$

Substituting this expression for ΔG^0 into the relation

$$\Delta G = \Delta G^0 + RT \ln Q$$

we obtain:

$$\Delta G = -RT \ln \left(\frac{v_1}{v_2} \right) + RT \ln \left(\frac{[A]^m [B]^n}{[C]^x [D]^y} \right) + RT \ln Q$$

Substituting $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$, we get:

$$\Delta G = -RT \ln \left(\frac{v_1}{v_2} \right) + RT \ln \left(\frac{[A]^m [B]^n}{[C]^x [D]^y} \times \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

Simplifying,

$$\Delta G = -RT \ln \left(\frac{v_1}{v_2} \right) + RT \ln \left([A]^{m-a} [B]^{n-b} [C]^{c-x} [D]^{d-y} \right)$$

This result shows the relationship between the Gibbs free energy change (ΔG), the ratio of the forward and reverse reaction rates $\left(\frac{v_1}{v_2} \right)$, and the concentrations of reactants and

products in a **non-elementary reversible reaction**. The first term, $-RT \ln \left(\frac{v_1}{v_2} \right)$,

represents the contribution of the reaction rates to the free energy change, showing how the **kinetic behavior** influences the **thermodynamic state**. The second term,

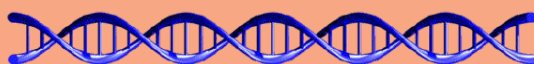
$$\left([A]^{m-a} [B]^{n-b} [C]^{c-x} [D]^{d-y} \right),$$

accounts for deviations from the **stoichiometric proportions of the reactants and products**. Together, these terms indicate that ΔG depends not only on the **intrinsic reaction rates** but also on how the **actual reaction orders** differ from the **stoichiometric coefficients**.



If the rate orders are equal to the **stoichiometric coefficients** (i.e., $m=a$, $n=b$, $x=c$, $y=d$), the second term vanishes, giving $\Delta G = -RT \ln \left(\frac{v_1}{v_2} \right)$. At equilibrium, $v_1 = v_2$, so $\Delta G=0$

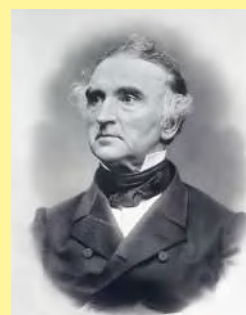
as expected. However, if the **forward and reverse reaction rates** are equal ($v_1 = v_2$) but the reaction orders differ from the **stoichiometric coefficients**, the **Gibbs free energy change** (ΔG) will not necessarily be zero. In this situation, the deviation term determines the value of ΔG . This shows that having **equal forward and reverse rates** does not always mean the system is at **thermodynamic equilibrium** – **true equilibrium** occurs only when the reaction also satisfies **microscopic reversibility**, meaning the reaction orders match the stoichiometric coefficients.



"Chemistry, in its application to animals and vegetables. Endeavours jointly with physiology to enlighten us respecting the mysterious processes and sources of organic life."



Justus von Liebig



Differentiating $\Delta G^0 = -RT \ln K_{eq}$ with respect to temperature, we get:

$$\frac{d(\Delta G^0)}{dT} = -R \ln K_{eq} - RT \frac{d \ln K_{eq}}{dT} \Rightarrow \frac{d(\Delta G^0)}{dT} = \frac{\Delta G^0}{T} - RT \frac{d \ln K_{eq}}{dT}$$

From the **van't Hoff relation**:

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H^0}{RT^2}$$

and since

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

we get:

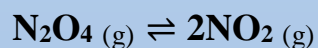
$$\frac{d(\Delta G^0)}{dT} = \frac{\Delta H^0}{T} - \Delta S^0 - \frac{\Delta H^0}{T} \Rightarrow \Delta S^0 = -\frac{d(\Delta G^0)}{dT}$$

This relation shows that the **standard entropy change** is equal to the **negative temperature derivative of the standard Gibbs free energy change**. In other words, the slope of ΔG^0 versus **temperature** directly corresponds to $-\Delta S^0$ connecting the **extensive property of entropy** to the observable changes in the **standard Gibbs free energy** with the **intensive property of temperature**.

$$\Delta S^0 = - \frac{d(\Delta G^0)}{dT}$$

So:

- If ΔG^0 decreases quickly as temperature increases, then ΔS^0 is large and positive.
- If ΔG^0 hardly changes with temperature, then ΔS^0 is small.



This reaction increases the number of gas molecules:

- **Left side:** 1 gas molecule
- **Right side:** 2 gas molecules

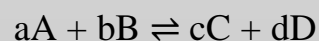
More gas molecules mean more disorder $\rightarrow \Delta S^0 > 0$.

If $\Delta S^0 > 0$, then $\frac{d(\Delta G^0)}{dT} < 0$:

- **As temperature increases**, the **effect of disorder** becomes more important.
- A **positive ΔS^0** means the reaction producing more gas becomes more favorable at high temperature.
- Therefore, **ΔG^0 becomes more negative as temperature increases.**

So, the **Gibbs free energy** becomes **more negative** with increasing temperature. This matches what we observe: **the reaction shifts toward NO_2 at higher temperature.**

For the reversible reaction:



the **rate of the forward reaction** in terms of **concentration change** is:

$$v_1 = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$

and the **rate of the backward reaction** is:

$$v_2 = -\frac{1}{c} \frac{d[C]}{dt} = -\frac{1}{d} \frac{d[D]}{dt} = +\frac{1}{a} \frac{d[A]}{dt} = +\frac{1}{b} \frac{d[B]}{dt}$$

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

- **The Rate of Increase of Q ($+\frac{dQ}{dt}$):**

Taking the Natural Logarithm:

$$\ln Q + a \ln[A] + b \ln[B] = c \ln[C] + d \ln[D]$$

Differentiating with respect to time:

$$\frac{d \ln Q}{dt} + a \left(\frac{d \ln[A]}{dt} \right) + b \left(\frac{d \ln[B]}{dt} \right) = c \left(\frac{d \ln[C]}{dt} \right) + d \left(\frac{d \ln[D]}{dt} \right)$$

Rearranging:

$$\frac{d\ln Q}{dt} = c \left(\frac{d\ln[C]}{dt} \right) + d \left(\frac{d\ln[D]}{dt} \right) - a \left(\frac{d\ln[A]}{dt} \right) - b \left(\frac{d\ln[B]}{dt} \right)$$

Expanding in terms of concentration changes:

$$\frac{d\ln Q}{dt} = \frac{c}{[C]} \left(\frac{d[C]}{dt} \right) + \frac{d}{[D]} \left(\frac{d[D]}{dt} \right) + \frac{a}{[A]} \left(-\frac{d[A]}{dt} \right) + \frac{b}{[B]} \left(-\frac{d[B]}{dt} \right)$$

From this, the rate of increase of Q with time can be expressed as:

$$+ \left(\frac{dQ}{dt} \right) = Q v_1 \left(\frac{c^2}{[C]} + \frac{d^2}{[D]} + \frac{a^2}{[A]} + \frac{b^2}{[B]} \right)$$

- **The Rate of Decrease of Q ($-\frac{dQ}{dt}$):**

Starting with the relation:

$$\frac{d\ln Q}{dt} + a \left(\frac{d\ln[A]}{dt} \right) + b \left(\frac{d\ln[B]}{dt} \right) = c \left(\frac{d\ln[C]}{dt} \right) + d \left(\frac{d\ln[D]}{dt} \right)$$

If we multiply through by -1 , we get:

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

Rearranging:

$$-\left(\frac{d\ln Q}{dt}\right) = -c \left(\frac{d\ln[C]}{dt}\right) - d \left(\frac{d\ln[D]}{dt}\right) + a \left(\frac{d\ln[A]}{dt}\right) + b \left(\frac{d\ln[B]}{dt}\right)$$

Expanding in terms of concentration changes:

$$-\left(\frac{d\ln Q}{dt}\right) = \frac{c}{[C]} \left(-\frac{d[C]}{dt}\right) + \frac{d}{[D]} \left(-\frac{d[D]}{dt}\right) + \frac{a}{[A]} \left(\frac{d[A]}{dt}\right) + \frac{b}{[B]} \left(\frac{d[B]}{dt}\right)$$

From this, the rate of decrease of Q with time can be expressed as:

$$-\left(\frac{dQ}{dt}\right) = Q v_2 \left(\frac{c^2}{[C]} + \frac{d^2}{[D]} + \frac{a^2}{[A]} + \frac{b^2}{[B]}\right)$$

The **net change in Q** can be written as:

$$\frac{dQ}{dt} = Q (v_1 - v_2) \left(\frac{c^2}{[C]} + \frac{d^2}{[D]} + \frac{a^2}{[A]} + \frac{b^2}{[B]}\right)$$

This shows that the **reaction quotient Q** changes in proportion to:

- Q itself
- The difference between forward and reverse rates ($v_1 - v_2$)
- A factor depending on the stoichiometric coefficients and concentrations.

1. **At equilibrium** ($v_1 = v_2$):

$$\frac{dQ}{dt} = 0$$

- Q reaches the **equilibrium constant** K_{eq} and no longer changes.

2. **Forward reaction dominates** ($v_1 \gg v_2$):

$$\frac{dQ}{dt} \approx Q v_1 \left(\frac{c^2}{[C]} + \frac{d^2}{[D]} + \frac{a^2}{[A]} + \frac{b^2}{[B]} \right) > 0$$

- Reaction shifts toward products; Q increases.

3. **Reverse reaction dominates** ($v_2 \gg v_1$):

$$\frac{dQ}{dt} \approx -Q v_2 \left(\frac{c^2}{[C]} + \frac{d^2}{[D]} + \frac{a^2}{[A]} + \frac{b^2}{[B]} \right) < 0$$

- Reaction shifts toward reactants; Q decreases.

4. **Very dilute system** ($[A], [B], [C], [D] \rightarrow 0$)

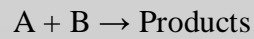
- Denominators are small \rightarrow the factor $\left(\frac{c^2}{[C]} + \frac{d^2}{[D]} + \frac{a^2}{[A]} + \frac{b^2}{[B]} \right)$ becomes **large**.
- Even **small differences** between v_1 and v_2 cause **large changes** in Q.

5. **Very concentrated system** ($[A], [B], [C], [D] \rightarrow \infty$)

- Denominators are large \rightarrow the factor $\left(\frac{c^2}{[C]} + \frac{d^2}{[D]} + \frac{a^2}{[A]} + \frac{b^2}{[B]} \right)$ becomes **small**.
- Even **large differences** between v_1 and v_2 cause **small changes** in Q.

- **Transition State Theory:**

For the **bimolecular reaction**:



the process proceeds through the formation of an **activated complex** AB*:



The **rate of reaction** is expressed as:

$$v = k_r [A] [B] = \frac{\kappa k_B T}{h} [AB^*]$$

Thus, the **rate constant** can be written as:

$$k_r = \frac{\kappa k_B T}{h} \frac{[AB^*]}{[A][B]}$$

Since:

$$\Delta G^* = (\Delta G^*)^0 + RT \ln \frac{[AB^*]}{[A][B]}$$

and

$$v_{\text{activation}} = v_{\text{deactivation}} e^{-\frac{\Delta G^*}{RT}}$$

Therefore:

$$k_r = \frac{\kappa k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

Since $(\Delta G^*)^0 = (\Delta H^*)^0 - T (\Delta S^*)^0$, we can rewrite the equation as:

$$k_r = \kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0}{RT}} e^{\frac{(\Delta S^*)^0}{R}}$$

- $(\Delta H^*)^0$ = standard enthalpy of activation
- $(\Delta S^*)^0$ = standard entropy of activation

Expressing k_1 and k_2 using the above equation:

$$k_1 = \left(\kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0}{RT}} e^{\frac{(\Delta S^*)^0}{R}} \right) \text{Forward reaction}$$

$$k_2 = \left(\kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0}{RT}} e^{\frac{(\Delta S^*)^0}{R}} \right) \text{Backward reaction}$$

Ratio gives the equilibrium constant:

$$K_{\text{eq}} = \frac{k_1}{k_2} = \frac{\left(\kappa \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0}{RT}} e^{\frac{(\Delta S^*)^0}{R}} \right) \text{Forward reaction}}{\left(\kappa \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0}{RT}} e^{\frac{(\Delta S^*)^0}{R}} \right) \text{Backward reaction}}$$

Expressing k_1 and k_2 using the **Arrhenius equation**:

$$k_1 = A_1 e^{-\frac{E_1}{RT}}$$

$$k_2 = A_2 e^{-\frac{E_2}{RT}}$$

- E_1 and E_2 denote the **activation energies** of the forward and backward reactions.
- A_1 and A_2 denote the **Arrhenius frequency factors** for the forward and backward reactions.

The **ratio of the rate constants** gives the **equilibrium constant**:

$$K_{\text{eq}} = \frac{k_1}{k_2} = \frac{A_1}{A_2} e^{\frac{E_2 - E_1}{RT}}$$

Collision theory expressions for forward and backward reactions:

$$k_1 = \rho_1 Z_1 e^{-\frac{E_1}{RT}}$$

$$k_2 = \rho_2 Z_2 e^{-\frac{E_2}{RT}}$$

- Z_1 and Z_2 = collision frequencies for forward and backward reactions
- ρ_1 and ρ_2 = steric factors for forward and backward reactions
- E_1 and E_2 = activation energies for forward and backward reactions

Equilibrium constant:

$$K_{\text{eq}} = \frac{k_1}{k_2} = \frac{\rho_1 Z_1}{\rho_2 Z_2} e^{\frac{E_2 - E_1}{RT}}$$

The net change in **concentration of AB*** is given by:

$$\frac{d[AB^*]}{dt} = (\text{rate of appearance of } AB^* - \text{rate of disappearance of } AB^*)$$

$$\frac{d[AB^*]}{dt} = V_{\text{activation}} - (V_{\text{deactivation}} + V_{\text{decomposition}})$$

where

- $V_{\text{activation}}$ = rate of activation
- $V_{\text{deactivation}}$ = rate of deactivation
- $V_{\text{decomposition}}$ = rate of decomposition of AB^* to products

Since

$$V_{\text{activation}} = V_{\text{deactivation}} e^{-\frac{\Delta G^*}{RT}}$$

we have

$$\frac{d[AB^*]}{dt} = V_{\text{deactivation}} e^{-\frac{\Delta G^*}{RT}} - V_{\text{deactivation}} - V_{\text{decomposition}}$$

↓

$$\frac{d[AB^*]}{dt} = V_{\text{deactivation}} \left(e^{-\frac{\Delta G^*}{RT}} - 1 \right) - V_{\text{decomposition}}$$

$$\frac{d[AB^*]}{dt} = k_{\text{deactivation}} [AB^*] \left(e^{-\frac{\Delta G^*}{RT}} - 1 \right) - k_{\text{decomposition}} [AB^*]$$



$$\frac{d \ln[AB^*]}{dt} = k_{\text{deactivation}} \left(e^{-\frac{\Delta G^*}{RT}} - 1 \right) - k_{\text{decomposition}}$$

This equation describes how the logarithm of the **concentration of the activated complex** AB^* changes over time. The **first term**, $k_{\text{deactivation}} \left(e^{-\frac{\Delta G^*}{RT}} - 1 \right)$, represents the balance between activation and deactivation, which is controlled by the free energy barrier ΔG^* . The **second term**, $k_{\text{decomposition}}$, accounts for the loss of AB^* as it decomposes into products. Overall, the equation shows the interplay between the **formation and decay of the activated complex** during the reaction.

- **Quasi-equilibrium assumption:**

$$v_{\text{activation}} = v_{\text{deactivation}}, \quad -\frac{d[AB^*]}{dt} = v_{\text{decomposition}}$$

This means the **activated complex** AB^* is in **rapid equilibrium** with reactants, while its **slow decomposition** drives product formation.

- **Steady-state assumption:**

$$\frac{d[AB^*]}{dt} = 0$$

Here, the **rate of appearance** of AB^* equals its **rate of disappearance**, so the concentration of AB^* remains nearly constant during the reaction.

The **rate constant for a bimolecular reaction**, as predicted by **Arrhenius Equation** is:

$$k_r = A e^{-\frac{E_a}{RT}}$$

where:

- E_a = **activation energy of the reaction**.
- A = **Arrhenius frequency factor (pre-exponential factor)**, representing the frequency of effective collisions between reactant molecules that have the correct orientation to form products.
- R = gas constant, T = absolute temperature.

According to **transition state theory**, the **rate constant** can also be written as:

$$k_r = \kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0}{RT}} e^{\frac{(\Delta S^*)^0}{R}}$$

Comparing the **Arrhenius form** with the **TST form**, the **pre-exponential factor A** can be expressed as:

$$A e^{-\frac{E_a}{RT}} = \kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0}{RT}} e^{\frac{(\Delta S^*)^0}{R}}$$



$$A = \kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{\frac{-(\Delta H^*)^0 + E_a}{RT}} e^{\frac{(\Delta S^*)^0}{R}}$$

- $k_r = \rho Z e^{-\frac{E_a}{RT}}$ (**Collision Theory**)
- $k_r = \kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0}{RT}} e^{\frac{(\Delta S^*)^0}{R}}$ (**Transition State Theory**)

Connecting the two forms:

$$\rho Z e^{-\frac{E_a}{RT}} = \kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0}{RT}} e^{\frac{(\Delta S^*)^0}{R}}$$



$$Z = \kappa \frac{k_B T}{\rho h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0 + E_a}{RT}} e^{\frac{(\Delta S^*)^0}{R}}$$

This shows how the **collision frequency** Z , which represents how often reactant molecules collide effectively in **collision theory**, can be interpreted using **transition state theory** (TST) parameters.

The **reaction rate** can be expressed as the product of three factors:

$$\text{Rate} = \text{Collision frequency} \times \text{Energy factor} \times \text{Orientation factor}$$

- **Collision frequency** = Total number of collisions per unit volume per second.
- **Energy factor** = Fraction of collisions where molecules have energy \geq activation energy (E_a).
- **Orientation factor** = Fraction of collisions with the correct molecular orientation.

$$\text{Fraction of molecules with energy } \geq E_a = \frac{n}{n_0} = e^{-\frac{E_a}{RT}}$$

- n_0 = total number of molecules
- n = number of molecules with energy $\geq E_a$
- R = gas constant, T = absolute temperature

So the number of molecules capable of reacting is:

$$n = n_0 e^{-\frac{E_a}{RT}}$$



"**Chemistry** works with an enormous number of substances, but cares only for some few of their properties; it is an extensive science. **Physics** on the other hand works with rather few substances, such as mercury, water, alcohol, glass, air, but analyses the experimental results very thoroughly; it is an intensive science. **Physical chemistry** is the child of these two sciences; it has inherited the extensive character from chemistry. Upon this depends its all-embracing feature, which has attracted so great admiration. But on the other hand it has its profound quantitative character from the **science of physics.**"



Svante Arrhenius



Given quasi-equilibrium conditions:

$$V_{\text{activation}} = V_{\text{deactivation}}, \quad \Delta G^* = 0$$

At equilibrium:

$$0 = \Delta H^* - T\Delta S^* \Rightarrow T = \frac{\Delta H^*}{\Delta S^*}$$

$$(\Delta G^*)^0 = (\Delta H^*)^0 - T (\Delta S^*)^0$$



$$(\Delta G^*)^0 = (\Delta H^*)^0 - \frac{\Delta H^*}{\Delta S^*} (\Delta S^*)^0$$

Expressing in terms of ratios:

$$\alpha_1 = \frac{(\Delta S^*)^0}{\Delta S^*}$$

$$\alpha_2 = \frac{(\Delta H^*)^0}{\Delta H^*}$$

Then:

$$(\Delta G^*)^0 = \Delta H^* (\alpha_2 - \alpha_1)$$

$$k_r = \kappa \frac{k_B T}{h} e^{-\frac{(\Delta G^*)^0}{RT}} \Rightarrow k_r = \kappa \frac{k_B T}{h} e^{-\frac{\Delta H^* (\alpha_2 - \alpha_1)}{RT}}$$

$$k_r = \kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$



$$k_r = \kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} K^*$$

Taking the **natural logarithm** of both sides:

$$\ln k_r = \ln \kappa + \ln\left(\frac{k_B}{h}\right) + \ln T + \ln(v_{\text{deactivation}}) - \ln(v_{\text{activation}}) + \ln K^*$$

Differentiating with respect to **temperature T**:

$$\frac{d \ln k_r}{dT} = \frac{d \ln \kappa}{dT} + \frac{d \ln T}{dT} + \frac{d \ln(v_{\text{deactivation}})}{dT} - \frac{d \ln(v_{\text{activation}})}{dT} + \frac{d \ln K^*}{dT}$$

Now, using known **thermodynamic relations**:

$$\frac{d \ln k_r}{dT} = \frac{E_a}{RT^2}$$

(**Arrhenius relation** between the rate constant and the activation energy)

$$\frac{d \ln K^*}{dT} = \frac{(\Delta H^*)^0}{RT^2}$$

(**Van't Hoff relation** for equilibrium constant and standard enthalpy of activation)

Substituting these into the **derivative expression**:

$$\frac{E_a}{RT^2} = \frac{d \ln \kappa}{dT} + \frac{1}{T} + \frac{d \ln(v_{\text{deactivation}})}{dT} - \frac{d \ln(v_{\text{activation}})}{dT} + \frac{(\Delta H^*)^0}{RT^2}$$

In the **quasi-equilibrium approximation** ($v_{\text{activation}} = v_{\text{deactivation}}$), the relation reduces to:

$$\frac{E_a}{RT^2} = \frac{d \ln \kappa}{dT} + \frac{1}{T} + \frac{(\Delta H^*)^0}{RT^2}$$



$$\frac{d \ln \kappa}{dT} = \frac{E_a - (\Delta H^*)^0}{RT^2} - \frac{1}{T}$$



"It is sometimes easier to circumvent prevailing difficulties
[in science] rather than to attack them."

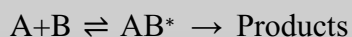


~~~~~~> **Jacobus Henricus Van't Hoff**

The quote illustrates **Van't Hoff's belief** that scientific progress often relies on unconventional thinking and creative detours, suggesting that innovative, indirect approaches are often more effective than directly confronting a problem.

$$k_r = \kappa \frac{k_B T}{h} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta H^*)^0}{RT}} e^{\frac{(\Delta S^*)^0}{R}}$$

In most textbooks, it is assumed that  $\kappa = 1$ . For the reaction



this assumption means that once the **activated complex**  $AB^*$  is formed, it always proceeds to products and never reverts back to the reactants. Such an assumption **oversimplifies the reaction** because, in reality, part of the **activated complex** can fall back to  $A+B$ . The **transmission coefficient**  $\kappa$  measures the fraction of the **activated complex** that successfully converts to products without recrossing. Therefore, while  $\kappa = 1$  represents the **ideal no-recrossing case**, in practice  $\kappa$  is usually less than one.

Since:

$$(\Delta S^*)^0 = -\frac{d(\Delta G^*)^0}{dT}$$

$$\frac{d[AB^*]}{dt} = v_{\text{deactivation}} \left( e^{-\frac{\Delta G^*}{RT}} - 1 \right) - v_{\text{decomposition}}$$

Therefore:

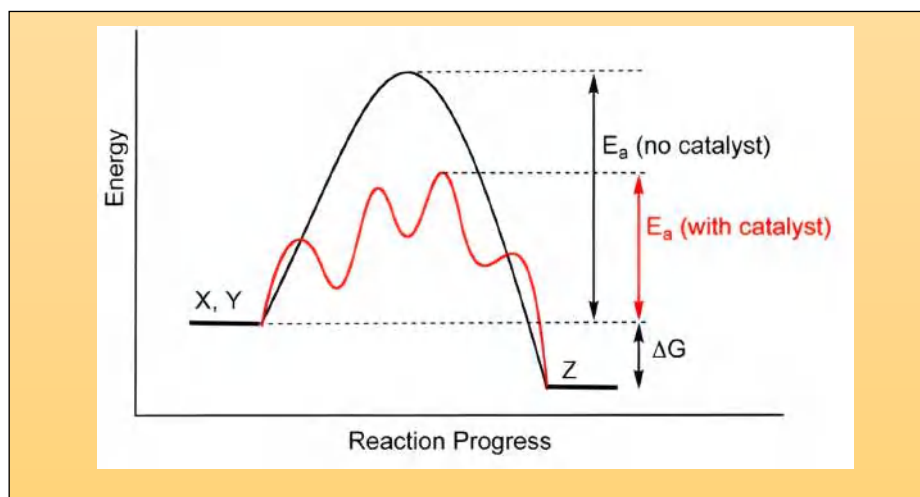
$$k_r = \kappa \frac{k_B T}{h} \frac{\left( \frac{d[AB^*]}{dt} + v_{\text{decomposition}} \right)}{v_{\text{activation}} \left( e^{-\frac{\Delta G^*}{RT}} - 1 \right)} e^{-\frac{(\Delta H^*)^0}{RT}} e^{-\frac{d(\Delta G^*)^0}{RdT}}$$

$$\text{Rate of radioactive decay} = -\frac{dN}{dt} = \lambda \times N$$

where N is the number of radioactive nuclei and  $\lambda$  is the decay constant.

**Radioactive decay** always follows **first-order kinetics** because it depends only on the number of radioactive nuclei present, not on anything else.

| Type                             | Reaction                                                                              | Catalyst                         | Effect                                     |
|----------------------------------|---------------------------------------------------------------------------------------|----------------------------------|--------------------------------------------|
| Positive Catalyst<br>(Promoter)  | $\text{C}_2\text{H}_4 + \text{H}_2 \xrightarrow{\text{Pt}} \text{C}_2\text{H}_6$      | Platinum<br>(Pt)                 | Speeds up the reaction<br>(hydrogenation)  |
| Negative Catalyst<br>(Inhibitor) | $2\text{H}_2\text{O}_2 \xrightarrow{\text{Pb}^{2+}} 2\text{H}_2\text{O} + \text{O}_2$ | Lead ions<br>(Pb <sup>2+</sup> ) | Slows down the reaction<br>(decomposition) |

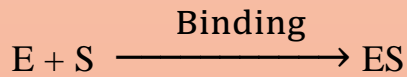


The diagram shows that a catalyst lowers the activation energy ( $E_a$ ) of a reaction without changing the **overall Gibbs free energy** ( $\Delta G$ ). The **black curve** represents the uncatalyzed reaction with a high energy barrier, while the **red curve** shows the catalyzed reaction with a lower barrier. **A higher energy barrier means a slower reaction, and lowering it allows more reactant molecules to convert into products faster.**

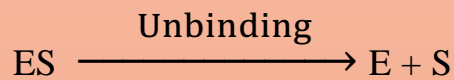
Consider a reaction:



- E = Free enzyme, S = Substrate, ES = Enzyme–substrate complex, P = Product.



The **enzyme** (E) binds the **substrate** (S) to form the **enzyme–substrate complex** (ES).

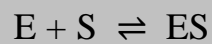


The **enzyme–substrate complex** (ES) can break apart back into **free enzyme** (E) and **substrate** (S).



The **enzyme–substrate complex** (ES) converts the **substrate** (S) into **product** (P) and releases the **enzyme** (E) for reuse.

The **Gibbs free energy change** for the reaction



can be written as:

$$\Delta G^* = (\Delta G^*)^0 + RT \ln \frac{[ES]}{[E][S]}$$

From the above equation:

$$\frac{[ES]}{[E][S]} = e^{\frac{\Delta G^*}{RT}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

↓

$$\frac{[ES]}{[E][S]} = \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

Since the **total enzyme concentration** equals the sum of **free and bound enzyme**:

$$[E_T] = [E] + [ES]$$

Substituting for  $[E] = [E_T] - [ES]$ , we get:

$$\frac{[ES]}{([E_T] - [ES])[S]} = \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

↓

$$[ES] = ([E_T] - [ES])[S] \left( \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}} \right)$$

From this, it follows that:

$$[ES] = \frac{[E_T][S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}}}{\left( 1 + [S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}} \right)}$$

The **rate of product formation** is given by:

$$v = k_{\text{cat}} \times [ES]$$

The **maximum rate of product formation** occurs when all enzyme molecules are bound to the substrate:

$$v_{\text{max}} = k_{\text{cat}} \times [E_T]$$

where  $k_{\text{cat}}$  is the **rate constant for product formation**, also known as the **turnover number**.

- **Higher turnover number** → The enzyme is more efficient
- **Lower turnover number** → The enzyme is less efficient

$$v = \frac{v_{\text{max}}[S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}}}{\left( 1 + [S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}} \right)}$$

This equation shows that the **rate of product formation** ( $v$ ) is influenced by several factors: the **substrate concentration** ( $[S]$ ), the **maximum rate** ( $v_{\text{max}}$ ), the **rates of enzyme–substrate binding and unbinding**, and the **standard Gibbs free energy change** ( $\Delta G^0$ ). Together, these factors determine how efficiently the **enzyme converts substrate into product** under different conditions, reflecting both **kinetic and thermodynamic contributions** to the reaction.

- **Case 1: Low substrate or weak binding**

If

$$[S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}} < 1$$

then

$$v \approx V_{\text{max}} [S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

- This occurs when the **substrate concentration** is low or the binding is weak.
- The **rate of product formation** is directly proportional to the **substrate concentration** [S] and increases linearly as [S] rises.

- **Case 2: High substrate or strong binding**

If

$$[S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}} > 1$$

then

$$v \approx V_{\text{max}}$$

- This occurs when the **substrate concentration** is high or binding is very strong.
- The **enzyme is saturated with substrate**, so the **rate of product formation** reaches its maximum, independent of [S].

### Catalytic rate enhancement (CRE):

- The **ratio of the catalyzed to uncatalyzed rate constants** is called the **catalytic rate enhancement**:

$$\text{CRE} = \frac{k_{\text{catalyzed}}}{k_{\text{uncatalyzed}}}$$

- $k_{\text{catalyzed}}$  = rate constant for the enzyme-catalyzed reaction.
- $k_{\text{uncatalyzed}}$  = rate constant for the uncatalyzed reaction.

- **CRE** indicates how many times faster the **catalyzed reaction** occurs compared to the **uncatalyzed one**.

### Arrhenius expressions:

$$k_{\text{catalyzed}} = A_{\text{catalyzed}} e^{-\frac{E_{\text{catalyzed}}}{RT}}$$

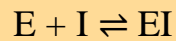
$$k_{\text{uncatalyzed}} = A_{\text{uncatalyzed}} e^{-\frac{E_{\text{uncatalyzed}}}{RT}}$$

$$\text{CRE} = \frac{k_{\text{catalyzed}}}{k_{\text{uncatalyzed}}} = \frac{A_{\text{catalyzed}}}{A_{\text{uncatalyzed}}} e^{\frac{(E_{\text{uncatalyzed}} - E_{\text{catalyzed}})}{RT}}$$

- **Substrate binding and catalysis:**

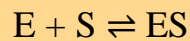


- **Competitive inhibitor binding to free enzyme:**



Here, the **inhibitor (I)** competes with the **substrate** for the same **active site on the enzyme**, forming an **enzyme–inhibitor complex (EI)** that prevents substrate binding.

- **For the substrate binding reaction:**

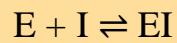


The **reaction quotient** for substrate binding ( $Q_s$ ) is given by:

$$Q_s = \frac{[ES]}{[E][S]} = \frac{v_{\text{unbinding-S}}}{v_{\text{binding-S}}} e^{-\frac{(\Delta G_S^*)^0}{RT}}$$

- $v_{\text{binding-S}}$  corresponds to the rate at which the **enzyme** and **substrate** combine to form the **enzyme–substrate complex (ES)**.
- $v_{\text{unbinding-S}}$  corresponds to the rate at which the **enzyme–substrate complex** dissociates back into **free enzyme (E)** and **substrate (S)**.
- $(\Delta G_S^*)^0$  is the **standard free energy of activation** for the **substrate binding reaction**.

- **For the inhibitor binding reaction:**



The **reaction quotient** for inhibitor binding ( $Q_I$ ) is given by:

$$Q_I = \frac{[EI]}{[E][I]} = \frac{v_{\text{unbinding-I}}}{v_{\text{binding-I}}} e^{-\frac{(\Delta G_I^*)^0}{RT}}$$

- $v_{\text{binding-I}}$  corresponds to the rate at which the **enzyme (E)** and **inhibitor (I)** combine to form the **enzyme-inhibitor complex (EI)**.
- $v_{\text{unbinding-I}}$  corresponds to the rate at which the **enzyme-inhibitor complex (EI)** dissociates back into **free enzyme (E)** and **inhibitor (I)**.
- $(\Delta G_I^*)^0$  is the **standard free energy of activation** for the **inhibitor binding reaction**.

The **total enzyme concentration** is the sum of **free enzyme** and all **enzyme bound** in complexes:

$$[E_T] = [E] + [ES] + [EI]$$

Since:

$$[ES] = Q_S [E] [S] \quad \text{and} \quad [EI] = Q_I [E] [I],$$

substituting these into the **total enzyme expression**:

$$[E_T] = [E] (1 + Q_S [S] + Q_I [I])$$

Rearranging gives:

$$[E] = \frac{[E_T]}{(1 + Q_S [S] + Q_I [I])}$$

$$[ES] = Q_S [E] [S] = \frac{[E_T] Q_S [S]}{(1 + Q_S [S] + Q_I [I])}$$

**Rate of product formation:**

$$v = k_{cat} [ES] = \frac{k_{cat} [E_T] Q_S [S]}{(1 + Q_S [S] + Q_I [I])}$$

From this, it follows that:

$$v = \frac{v_{max} Q_S [S]}{(1 + Q_S [S] + Q_I [I])}$$



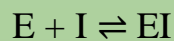
$$v = \frac{v_{max} \left( \frac{v_{unbinding-S}}{v_{binding-S}} e^{-\frac{(\Delta G_S^*)^0}{RT}} \right) [S]}{1 + \left( \frac{v_{unbinding-S}}{v_{binding-S}} e^{-\frac{(\Delta G_S^*)^0}{RT}} \right) [S] + \left( \frac{v_{unbinding-I}}{v_{binding-I}} e^{-\frac{(\Delta G_I^*)^0}{RT}} \right) [I]}$$

This equation describes the **rate of product formation** in the presence of a **competitive inhibitor**. It shows how **substrate** and **inhibitor** binding rates, together with their **standard Gibbs activation free energies**, influence enzyme activity. A **lower activation free energy** or **stronger substrate binding** increases the reaction rate, whereas a **higher inhibitor concentration** or **stronger inhibitor** binding reduces it.

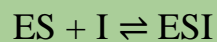
- **Substrate binding and catalysis:**



- **Competitive inhibitor binding to free enzyme:**

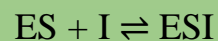
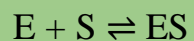


- **Inhibitor binding to enzyme–substrate complex:**



This reaction represents the formation of a **non-productive ternary complex** between the **enzyme–substrate complex (ES)** and the **inhibitor (I)**, resulting in ESI.

- **For the reactions:**



the **reaction quotients** are defined as:

$$Q_S = \frac{[ES]}{[E][S]} = \frac{v_{\text{unbinding-S}}}{v_{\text{binding-S}}} e^{-\frac{(\Delta G_S^*)^0}{RT}}$$

$$Q_I = \frac{[EI]}{[E][I]} = \frac{v_{\text{unbinding-I}}}{v_{\text{binding-I}}} e^{-\frac{(\Delta G_I^*)^0}{RT}}$$

$$Q_{SI} = \frac{[ESI]}{[ES][I]} = \frac{v_{\text{unbinding-SI}}}{v_{\text{binding-SI}}} e^{-\frac{(\Delta G_{SI}^*)^0}{RT}}$$

**Based on these definitions**, the **concentrations of the enzyme complexes** can be expressed as:

$$[ES] = Q_S [E] [S]$$

$$[EI] = Q_I [E] [I]$$

$$[ESI] = Q_{SI} [ES] [I] = Q_{SI} Q_S [E] [S] [I]$$

**Total enzyme concentration:**

$$[E_T] = [E] + [ES] + [EI] + [ESI]$$

$$[E_T] = [E] \left( 1 + Q_S [S] + Q_I [I] + Q_{SI} Q_S [S] [I] \right)$$



$$[E] = \frac{[E_T]}{[1 + Q_S [S] + Q_I [I] + Q_{SI} Q_S [S][I]]}$$

$$[ES] = Q_S [E] [S] = \frac{[E_T] Q_S [E] [S]}{[1 + Q_S [S] + Q_I [I] + Q_{SI} Q_S [S][I]]}$$

**Rate of product formation:**

$$v = k_{cat} [ES] = \frac{k_{cat} [E_T] Q_S [E] [S]}{[1 + Q_S [S] + Q_I [I] + Q_{SI} Q_S [S][I]]}$$

From this, it follows that:

$$v = \frac{v_{max} Q_S [E] [S]}{1 + Q_S [S] + Q_I [I] + Q_{SI} Q_S [S][I]}$$

where:

- $Q_S = \frac{v_{unbinding-S}}{v_{binding-S}} e^{-\frac{(\Delta G_S^*)^0}{RT}}$
- $Q_I = \frac{v_{unbinding-I}}{v_{binding-I}} e^{-\frac{(\Delta G_I^*)^0}{RT}}$
- $Q_{SI} = \frac{v_{unbinding-SI}}{v_{binding-SI}} e^{-\frac{(\Delta G_{SI}^*)^0}{RT}}$

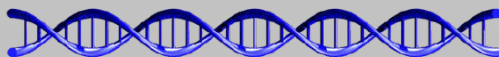


This equation describes the **enzyme reaction rate** considering all **possible binding interactions**:  $E + S \rightleftharpoons ES$ ,  $E + I \rightleftharpoons EI$ , and  $ES + I \rightleftharpoons ESI$ . It shows how the distribution of the enzyme among **free, substrate-bound, inhibitor-bound, and ternary complex (ESI) forms** determines the **rate of product formation**. Increasing **substrate concentration** increases the rate, while **higher inhibitor concentration** or **formation of the ternary complex** decreases it. The Q terms reflect binding affinities, linking **kinetics** to **thermodynamic** properties.

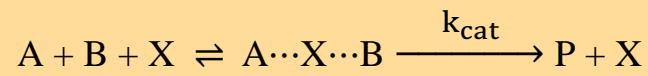
"It was obvious – to me at any rate – that the answer was to why an **enzyme** is able to speed up a **chemical reaction** by as much as **10 million times**. It had to do this by lowering the **energy of activation** – the **energy of forming the activated complex**. It could do this by forming strong bonds with the **activated complex**, but only weak bonds with the reactants or products."



**Linus Pauling**

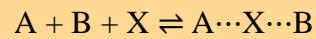


- Consider the reaction:



where **X** is the free catalyst, **A** and **B** are the reactants, **A···X···B** is the activated complex, and **P** is the product.

- The **Gibbs free energy change** for the reaction



can be expressed as:

$$\Delta G^* = (\Delta G^*)^0 + RT \ln \frac{[A \cdots X \cdots B]}{[A][B][X]}$$

Rearranging, we get:

$$\frac{[A \cdots X \cdots B]}{[A][B][X]} = \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

The **total catalyst concentration** equals the sum of the **free and bound** catalyst:

$$[X_T] = [X] + [A \cdots X \cdots B]$$

Substituting  $[X] = [X_T] - [A \cdots X \cdots B]$ , we obtain:

$$\frac{[A \cdots X \cdots B]}{[A][B]([X_T] - [A \cdots X \cdots B])} = \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

$$[A \cdots X \cdots B] = \frac{[X_T][A][B] \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}}{1 + [A][B] \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}}$$

The **rate of product formation** can be expressed as:

$$v = k_{\text{cat}} \times [A \cdots X \cdots B]$$

where  $k_{\text{cat}}$  is the rate constant for the formation of the product.

The **maximum rate** of product formation is reached when all catalyst molecules are bound to reactants A and B:

$$v_{\text{max}} = k_{\text{cat}} \times [X_T]$$

where  $[X_T]$  represents the total concentration of the catalyst.

$$v = \frac{v_{\text{max}} \left( [A][B] \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}} \right)}{\left( 1 + [A][B] \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}} \right)}$$

This equation shows that the **rate of product formation** ( $v$ ) depends on several factors: the concentrations of **reactants A and B**, the **maximum rate** ( $v_{\max}$ ), the **rates of catalyst–reactant binding and dissociation**, and the **standard Gibbs free energy of activation** ( $(\Delta G^*)^0$ ). Together, these factors determine how effectively the catalyst converts **A and B** into the **product** under varying conditions, reflecting both **kinetic and thermodynamic** influences on the reaction.

- The rate constant for the **catalyzed reaction** is given by:

$$k_{\text{catalyzed}} = \kappa_{\text{catalyzed}} \frac{k_{\text{B}}T}{h} \left( \frac{v_{\text{deactivation}}}{v_{\text{activation}}} \right)_{\text{catalyzed}} e^{-\frac{(\Delta G^*)^0_{\text{catalyzed}}}{RT}}$$

- The rate constant for the **uncatalyzed reaction** is given by:

$$k_{\text{uncatalyzed}} = \kappa_{\text{uncatalyzed}} \frac{k_{\text{B}}T}{h} \left( \frac{v_{\text{deactivation}}}{v_{\text{activation}}} \right)_{\text{uncatalyzed}} e^{-\frac{(\Delta G^*)^0_{\text{uncatalyzed}}}{RT}}$$

$$\text{CRE} = \frac{\kappa_{\text{catalyzed}} \left( \frac{v_{\text{deactivation}}}{v_{\text{activation}}} \right)_{\text{catalyzed}} e^{-\frac{(\Delta G^*)^0_{\text{catalyzed}}}{RT}}}{\kappa_{\text{uncatalyzed}} \left( \frac{v_{\text{deactivation}}}{v_{\text{activation}}} \right)_{\text{uncatalyzed}} e^{-\frac{(\Delta G^*)^0_{\text{uncatalyzed}}}{RT}}}$$

For the bimolecular reaction



where A and B are **ionic species** present in solution, and  $AB^*$  is the **activated complex**, the **reaction quotient** ( $Q^*$ ) for the formation of the activated complex is defined using **activities** rather than **concentrations**:

$$Q^* = \frac{a_{AB^*}}{a_A a_B} = \frac{\gamma_{AB^*}}{\gamma_A \gamma_B} \frac{[AB^*]}{[A][B]}$$

or equivalently,

$$Q^* = \frac{\gamma_{AB^*}}{\gamma_A \gamma_B} Q$$

where

- $Q^*$  — reaction quotient based on **activities**,
- $Q$  — reaction quotient based on **concentrations**,
- $\gamma_A, \gamma_B, \gamma_{AB^*}$  — **activity coefficients** that account for ionic interactions in solution.

From this, it follows that

$$Q^* = \frac{\gamma_{AB^*}}{\gamma_A \gamma_B} \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

In experimental studies, the **activity coefficients** ( $\gamma$ ) are often assumed to be **unity** or remain **unknown**, because it is difficult to measure them directly. As a result, reaction quotients and equilibrium constants are usually expressed in terms of **concentrations** rather than **activities**, introducing a small approximation for ionic systems.

The relationship between the **activity coefficient** and **ionic strength** is given by the **Debye–Hückel Limiting Law** as:

$$\log_{10} \gamma_i = -A Z_i^2 \sqrt{I}$$

where

- A is the **Debye–Hückel parameter**, which depends on temperature and the solvent,
- $Z_i$  is the **charge** of ion i, and
- I is the **ionic strength** of the solution.

For the reacting ions A and B, and the activated complex AB\*:

- $\log_{10} \gamma_A = -A Z_A^2 \sqrt{I}$
- $\log_{10} \gamma_B = -A Z_B^2 \sqrt{I}$
- $\log_{10} \gamma_{AB^*} = -A Z_{AB^*}^2 \sqrt{I}$

Since the charge on the activated complex is the sum of the charges of the reacting ions:

$$Z_{AB^*} = Z_A + Z_B$$

Therefore,

$$\log_{10} \gamma_{AB^*} = -A (Z_A + Z_B)^2 \sqrt{I}$$

$$\log_{10} \left( \frac{\gamma_{AB^*}}{\gamma_A \gamma_B} \right) = \log_{10} \gamma_A + \log_{10} \gamma_B - \log_{10} \gamma_{AB^*}$$

Substituting the Debye–Hückel expressions:

$$\log_{10} \left( \frac{\gamma_{AB}^*}{\gamma_A \gamma_B} \right) = -A Z_A^2 \sqrt{I} - A Z_B^2 \sqrt{I} + A (Z_A + Z_B)^2 \sqrt{I}$$

Simplifying:

$$\log_{10} \left( \frac{\gamma_{AB}^*}{\gamma_A \gamma_B} \right) = 2A Z_A Z_B \sqrt{I}$$

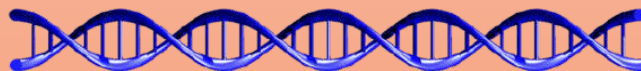
From this, it follows that:

$$\frac{\gamma_{AB}^*}{\gamma_A \gamma_B} = e^{2AZ_A Z_B \sqrt{I} \ln(10)}$$

Substituting this into the expression for the **reaction quotient** ( $Q^*$ ):

$$Q^* = e^{2AZ_A Z_B \sqrt{I} \ln(10)} \left( \frac{v_{\text{deactivation}}}{v_{\text{activation}}} \right) e^{-\frac{(\Delta G^*)^0}{RT}}$$

When  $Z_A Z_B = 0$ , one reactant is neutral and  $Q^*$  does not depend on ionic strength.  
When  $Z_A Z_B > 0$ , both reactants have the same charge and  $Q^*$  increases with ionic strength. When  $Z_A Z_B < 0$ , the reactants have opposite charges and  $Q^*$  decreases with ionic strength.



- **Kinetic Isotope Effect (KIE):**

The **kinetic isotope effect (KIE)** is the change in the **reaction rate** when one atom in a molecule is replaced by one of its isotopes. It is given by the equation:

$$\text{KIE} = \frac{k_L}{k_H}$$

where

- $k_L$  = rate constant for the reaction **involving the lighter isotope** (e.g., hydrogen)
- $k_H$  = rate constant for the reaction **involving the heavier isotope** (e.g., deuterium)


- **Example:**


If

$$\text{KIE} = \frac{k_L}{k_H} = 2$$

it means the reaction **involving the lighter isotope (hydrogen)** is **twice as fast** as the reaction **involving the heavier isotope (deuterium)**.

- **Thermodynamic and Kinetic Reaction Control:**

| Type of Control                                                                                                                                                                                    | Determining Factor                                                                            | Reaction Speed                                   | Product Stability                           | Favored Conditions                                                               |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|--------------------------------------------------|---------------------------------------------|----------------------------------------------------------------------------------|
| <div style="border: 1px solid black; padding: 5px; display: inline-block;"> <b>Kinetic Control</b><br/>  </div> | Controlled by <b>activation energy (<math>E_a</math>)</b> – the pathway with the <b>lower</b> | <b>Fast</b><br>(forms quickly due to low $E_a$ ) | <b>Less stable</b><br>(higher final energy) | <b>Low temperature and short reaction time</b> – reaction is <b>irreversible</b> |

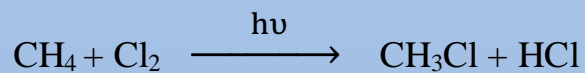
|                                                                                                                   |                                                                                                                          |                                  |                                            |                                                                                |
|-------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|----------------------------------|--------------------------------------------|--------------------------------------------------------------------------------|
|                                                                                                                   | <b>energy barrier</b><br>forms first                                                                                     |                                  |                                            |                                                                                |
| <b>Thermodynamic Control</b><br> | Controlled by <b>Gibbs free energy (<math>\Delta G</math>)</b> – the <b>more stable product</b> has lower overall energy | <b>Slow</b><br>(forms gradually) | <b>More stable</b><br>(lower final energy) | <b>High temperature and long reaction time</b> – reaction is <b>reversible</b> |

- **Chain Reaction:**

A **chemical reaction** in which reactive intermediates (such as free radicals, ions, or atoms) are continuously formed and consumed, making the reaction self-sustaining until it is stopped.

**Example:**

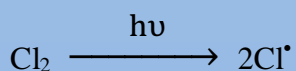
**Chlorination of Methane under UV light**



**Steps of the Chain Reaction:**

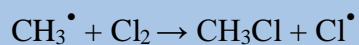
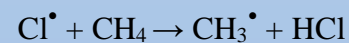
**1. Initiation**

Reactive species (free radicals) are **produced** to start the reaction.



### 1. Propagation

Radicals **react with stable molecules** to form **new radicals**, allowing the chain to **continue**.



### 3. Termination

Two radicals combine to form a stable molecule, ending the chain.



- **Initiation:** Generates radicals.
- **Propagation:** Radicals react and regenerate (chain continues).
- **Termination:** Radicals combine, stopping the reaction.



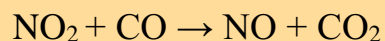
- **Rate-Determining Step (RDS):**

The **rate-determining step** is the slowest step in a **multi-step chemical reaction** that determines the rate of the overall reaction.

The **reaction rate** depends only on the **slowest step**, not the faster ones.

### Example: Rate-Determining Step in the Reaction Between NO<sub>2</sub> and CO

Overall Reaction:



If the Reaction Occurred in a Single Step

The reaction rate would depend on collisions between NO<sub>2</sub> and CO molecules:

$$\text{Rate} = k_r [\text{NO}_2] [\text{CO}]$$

However, **experimental data** shows that the rate law is:

$$\text{Rate} = k_r [\text{NO}_2]^2$$

This means the reaction is **second-order in NO<sub>2</sub>** and **zero-order in CO**.

**Proposed Mechanism**

**Mechanism 1**

1.  $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$  (fast step)
2.  $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$  (slow, rate-determining step)

This mechanism **does not fit** the observed rate law:

$$\text{Rate} = k_r [\text{NO}_2]^2$$

**Does not match experimental data.**

**Mechanism 2**

1.  $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$  (slow, rate-determining step)
2.  $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$  (fast step)

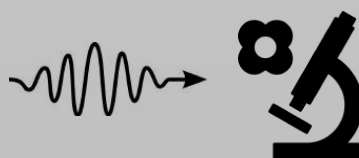
This mechanism **fits** the observed rate law:

$$\text{Rate} = k_r [\text{NO}_2]^2$$

Matches experimental data; hence, this mechanism is correct for this reaction.

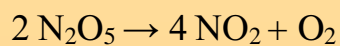


- **Antoine Lavoisier** proposed that **combustion** is a chemical reaction involving oxygen. His work replaced the **old phlogiston theory** and laid the foundation for modern chemistry.



- **Decomposition of Dinitrogen Pentoxide:**

The reaction is:



This is a **first-order reaction** with respect to  $\text{N}_2\text{O}_5$ .

The **rate of reaction** is given by:

$$v = k_r [\text{N}_2\text{O}_5]^1$$

where

- $v$  = rate of reaction,
- $k_r$  = rate constant,
- $[\text{N}_2\text{O}_5]$  = concentration of dinitrogen pentoxide.

**Given Parameters**

- $a = 2 \rightarrow$  stoichiometric coefficient of  $\text{N}_2\text{O}_5$
- $m = 1 \rightarrow$  order of reaction with respect to  $\text{N}_2\text{O}_5$

The general formula for the rate of decrease of  $v$  is:

$$-\frac{dv}{dt} = \frac{mav^2}{[A]}$$

where  $[A]$  is the concentration of the reactant.

Substituting the known values  $a = 2$ ,  $m = 1$ , and  $[A] = [N_2O_5]$ :

$$-\frac{dv}{dt} = \frac{(1 \times 2) v^2}{[N_2O_5]} = \frac{2v^2}{[N_2O_5]}$$

Since  $v = k_r [N_2O_5]$ , we can substitute this into the above equation:

$$-\frac{dv}{dt} = \frac{2 (k_r [N_2O_5])^2}{[N_2O_5]}$$

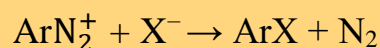
Simplifying:

$$-\frac{dv}{dt} = 2k_r^2 [N_2O_5] \Rightarrow -\frac{dv}{dt} \propto [N_2O_5]$$

The **rate of decrease of the reaction velocity** is directly proportional to the concentration of  $N_2O_5$ . The **proportionality constant** for this relationship is  $2k_r^2$ . As the reaction progresses and the concentration of  $N_2O_5$  decreases, the **reaction rate**  $v$  also decreases accordingly. Therefore, in the **first-order decomposition of dinitrogen pentoxide**, the **rate of decrease of the reaction velocity** varies linearly with the **reactant concentration**, showing that the decline in rate directly follows the reduction in  $N_2O_5$  concentration.

- **SN1 Reaction (Nucleophilic Substitution)**

**Reaction:**



This is a **first-order reaction** with respect to the aryldiazonium ion ( $\text{ArN}_2^+$ ) and **zero-order** with respect to the nucleophile ( $\text{X}^-$ ).

### Rate Law

$$v = k_r [\text{ArN}_2^+]^1 [\text{X}^-]^0 = k_r [\text{ArN}_2^+]$$

where

- $v$  = rate of reaction,
- $k_r$  = rate constant,
- $[\text{ArN}_2^+]$  = concentration of the aryldiazonium ion.

### Given Parameters

| Symbol | Meaning                                  | Value | Corresponds to   |
|--------|------------------------------------------|-------|------------------|
| a      | Stoichiometric coefficient of reactant A | 1     | $\text{ArN}_2^+$ |
| b      | Stoichiometric coefficient of reactant B | 1     | $\text{X}^-$     |
| m      | Order of reaction w.r.t. A               | 1     | $\text{ArN}_2^+$ |
| n      | Order of reaction w.r.t. B               | 0     | $\text{X}^-$     |

### General Formula for the Rate of Decrease of v:

$$-\frac{dv}{dt} = v^2 \left( \frac{ma[B] + nb[A]}{[A][B]} \right)$$

where

- $[A]$  = concentration of reactant A,
- $[B]$  = concentration of reactant B.

## Substitution

Given:

$$a = 1, b = 1, m = 1, n = 0,$$

$$[A] = [\text{ArN}_2^+], [B] = [\text{X}^-]$$

Substituting into the formula:

$$-\frac{dv}{dt} = v^2 \left( \frac{(1 \times 1)[\text{X}^-] + (0 \times 1)[\text{ArN}_2^+]}{[\text{ArN}_2^+][\text{X}^-]} \right) = \frac{v^2}{[\text{ArN}_2^+]}$$

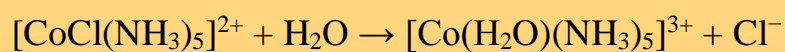
Substituting  $v = k_r [\text{ArN}_2^+]$

$$-\frac{dv}{dt} = \frac{[k_r [\text{ArN}_2^+]]^2}{[\text{ArN}_2^+]} = k_r^2 [\text{ArN}_2^+]$$

The **rate of decrease of the reaction rate** is directly proportional to the concentration of  $\text{ArN}_2^+$ . The proportionality constant is  $k_r^2$ . As the reaction proceeds and  $[\text{ArN}_2^+]$  decreases, the **reaction rate**  $v$  also decreases accordingly. Thus, for this **first-order SN1 reaction**, the rate of decrease of  $v$  depends linearly on the concentration of the aryldiazonium ion.

- **Hydrolysis of Pentaamminechloridocobalt(III) Ion:**

**Reaction:**



In this reaction, the **chloride ligand** in the **cobalt complex** is replaced by a water molecule. Since **water acts as a solvent** and is present in large excess, its concentration remains effectively constant during the reaction. Therefore, the rate depends only on the concentration of the cobalt complex ion, making the reaction **first-order** with respect to  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ .

**Rate Law:**

$$v = k_r [[\text{CoCl}(\text{NH}_3)_5]^{2+}]^1 [\text{H}_2\text{O}]^0 = k_r [[\text{CoCl}(\text{NH}_3)_5]^{2+}]$$

This shows that the **reaction rate** is directly proportional to the concentration of the cobalt complex ion only.

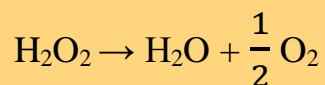
**Rate of Decrease of the Reaction Velocity:**

$$-\frac{dv}{dt} = \frac{[k_r [[\text{CoCl}(\text{NH}_3)_5]^{2+}]]^2}{[[\text{CoCl}(\text{NH}_3)_5]^{2+}]} = k_r^2 [[\text{CoCl}(\text{NH}_3)_5]^{2+}]$$

This equation represents that the **rate of decrease of the reaction velocity** is directly proportional to the concentration of the cobalt complex ion.

- **Decomposition of Hydrogen Peroxide:**

**Reaction:**



**Hydrogen peroxide** slowly decomposes into water and oxygen. The rate of decomposition depends only on the concentration of **hydrogen peroxide**, making it a **first-order reaction**.

**Rate Law:**

$$v = k_r [\text{H}_2\text{O}_2]$$

This means the **rate of reaction** decreases proportionally as the concentration of  $\text{H}_2\text{O}_2$  decreases.

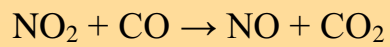
**Rate of Decrease of the Reaction Velocity:**

$$-\frac{dv}{dt} = \frac{[k_r[\text{H}_2\text{O}_2]]^2}{[\text{H}_2\text{O}_2]} = k_r^2 [\text{H}_2\text{O}_2]$$

This equation represents that the **rate of decrease of the reaction velocity** is directly proportional to the concentration of the hydrogen peroxide.

These reactions follow **first-order kinetics**, meaning the **rate of decrease of the reaction velocity** depends only on the concentration of a single reactant. As the reaction proceeds, the **concentration of this reactant** gradually decreases, causing a proportional **decrease in the reaction velocity**. This shows a direct and linear relationship between concentration and rate of decrease of  $v$ . In **first-order reactions**, only one reactant determines how quickly the reaction slows down. Thus, the **rate of decrease of the reaction velocity** clearly reflects the influence of a single reactive species on the overall reaction progress.

- **Reaction Between Nitrogen Dioxide and Carbon Monoxide:**



This is a **second-order reaction** with respect to  $\text{NO}_2$  and **zero order** with respect to  $\text{CO}$ .

**Rate Law:**

$$v = k_r [\text{NO}_2]^2 [\text{CO}]^0 = k_r [\text{NO}_2]^2$$

where:

- $v$  = rate of reaction
- $k_r$  = rate constant
- $[\text{NO}_2]$  = concentration of nitrogen dioxide
- $[\text{CO}]$  = concentration of carbon monoxide

Since the order with respect to  $\text{CO}$  is zero, the reaction rate is **independent of  $\text{CO}$  concentration** and depends **only on  $[\text{NO}_2]^2$** .

**Given Parameters:**

| Symbol | Meaning                                     | Value |
|--------|---------------------------------------------|-------|
| a      | Stoichiometric coefficient of $\text{NO}_2$ | 1     |
| m      | Order with respect to $\text{NO}_2$         | 2     |
| b      | Stoichiometric coefficient of $\text{CO}$   | 1     |
| n      | Order with respect to $\text{CO}$           | 0     |

**General Formula for the Rate of Decrease of Reaction Velocity:**

$$-\frac{dv}{dt} = v^2 \left( \frac{ma[B] + nb[A]}{[A][B]} \right)$$

Here:

- $v$  = reaction rate
- $[A]$  and  $[B]$  = concentrations of the two reactants
- $m$  and  $n$  = respective reaction orders
- $a$  and  $b$  = stoichiometric coefficients

Substituting:

$$A = [\text{NO}_2], \quad B = [\text{CO}], \quad m = 2, \quad n = 0, \quad a = 1, \quad b = 1$$

we get:

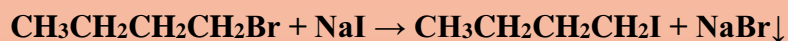
$$-\frac{dv}{dt} = v^2 \left( \frac{(2 \times 1)[\text{CO}] + (0 \times 1)[\text{NO}_2]}{[\text{NO}_2][\text{CO}]} \right) = \frac{2v^2}{[\text{NO}_2]}$$

Substituting the rate law  $v = k_r [\text{NO}_2]^2$ ,

$$-\frac{dv}{dt} = \frac{2 (k_r [\text{NO}_2]^2)^2}{[\text{NO}_2]} = 2k_r^2 [\text{NO}_2]^3$$

This equation shows that the **rate of decrease of the reaction velocity** is directly proportional to the cube of the concentration of  $\text{NO}_2$ . As the concentration of  $\text{NO}_2$  decreases during the reaction, the **reaction velocity** drops sharply. This strong dependence of rate on  $[\text{NO}_2]$  demonstrates the behavior typical of a second-order reaction, where small changes in reactant concentration lead to large changes in **reaction velocity**.

Another important category of second-order reactions is the **SN2 (bimolecular nucleophilic substitution)** reaction. A typical example is the reaction between **n-butyl bromide** and **sodium iodide** in acetone:



In this reaction, the **reaction rate** depends on the concentrations of both the alkyl halide and the nucleophile, making it second order overall.

**Rate law:**

$$v = k_r [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}] [\text{NaI}]$$

**Rate of decrease of reaction velocity:**

$$-\frac{dv}{dt} = v^2 \left( \frac{(1 \times 1)[\text{NaI}] + (1 \times 1)[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}]}{[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}] [\text{NaI}]} \right)$$

From this, it follows that:

$$-\frac{dv}{dt} = v^2 \left( \frac{[\text{NaI}] + [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}]}{[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}] [\text{NaI}]} \right)$$

Substituting the rate law  $v = k_r [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}] [\text{NaI}]$ :

$$-\frac{dv}{dt} = k_r^2 [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}] [\text{NaI}] \left( [\text{NaI}] + [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}] \right)$$

This shows that the **rate of decrease of the reaction velocity** depends directly on the concentrations of both reactants. As the concentration of either reactant decreases, the reaction rate correspondingly slows down — a key characteristic of **second-order kinetics**.

The same compound can also undergo a **bimolecular elimination (E2) reaction**, which is another example of a **second-order process**. This occurs when sodium iodide and acetone are replaced with **sodium tert-butoxide** and **tert-butanol** as the solvent:



**Rate law:**

$$v = k_r [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}] [\text{NaOt-Bu}]$$

**Rate of decrease of reaction velocity:**

$$-\frac{dv}{dt} = k_r^2 [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}] [\text{NaOt-Bu}] \left( [\text{NaOt-Bu}] + [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}] \right)$$

In this case, the **reaction proceeds** through a single concerted step, where the base abstracts a proton while the leaving group departs simultaneously. The reaction rate depends on the concentrations of both reactants, confirming the **second-order kinetics**

characteristic of the **E2 process**. A larger value of  $\left( -\frac{dv}{dt} \right)$  indicates that the reaction velocity decreases more rapidly. When the **concentration of the base**, [NaOt-Bu], is much greater than that of the **alkyl halide**, the term  $[\text{NaOt-Bu}] + [\text{alkyl halide}] \approx [\text{NaOt-Bu}]$ , and the expression simplifies to:

$$-\frac{dv}{dt} \approx k_r^2 [\text{alkyl halide}] [\text{NaOt-Bu}]^2$$

, showing that the base concentration dominates the rate behavior. Conversely, if the concentration of the alkyl halide greatly exceeds that of the base, then

$$-\frac{dv}{dt} \approx k_r^2 [\text{alkyl halide}]^2 [\text{NaOt-Bu}]$$

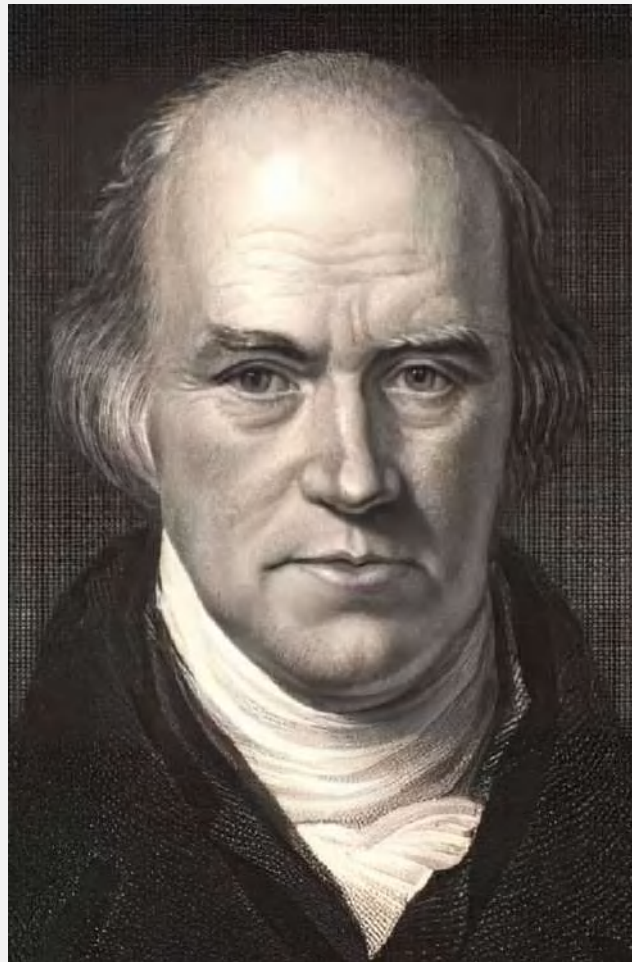
, indicating that the alkyl halide concentration dominates the reaction rate. For example, the **pyrolysis of acetaldehyde** obeys the rate law  $v = k_r [\text{CH}_3\text{CHO}]^{3/2}$ , so it is **1.5 order** with respect to acetaldehyde. Differentiating this expression with respect to  $[\text{CH}_3\text{CHO}]$ , we obtain:

$$\frac{dv}{d[\text{CH}_3\text{CHO}]} = \frac{3k_r}{2} [\text{CH}_3\text{CHO}]^{1/2}$$

This shows that the **rate of change of the reaction velocity** with respect to **acetaldehyde concentration** is proportional to the square root of its concentration, indicating that as  $[\text{CH}_3\text{CHO}]$  decreases, the reaction slows down but not linearly. The **decomposition of phosgene** ( $\text{COCl}_2$ ) follows the **rate law**  $v = k_r [\text{COCl}_2]^1 [\text{Cl}_2]^{1/2}$ , making it first order with respect to  $\text{COCl}_2$  and half order with respect to  $\text{Cl}_2$ , giving an overall order of 1.5. This **fractional order** indicates a complex mechanism involving chlorine free radicals, where the concentration of the reactive intermediate ( $\text{Cl}^\bullet$ ) depends on the square root of the chlorine concentration. In contrast, the **conversion of ozone ( $\text{O}_3$ ) to oxygen ( $\text{O}_2$ )** follows the **rate law**  $v = k_r [\text{O}_3]^2 [\text{O}_2]^{-1}$ , showing second order in ozone and negative one order in oxygen, resulting in an overall order of 1. The **negative order** implies that increasing oxygen concentration decreases the **reaction rate**, a phenomenon known as **product inhibition**, where the product interferes with or deactivates the reactive intermediate needed for the main reaction step.



"**Experimental science** hardly ever affords us more than **approximations to the truth**; and whenever many agents are concerned we are in great danger of being mistaken."



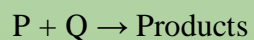
 **Humphry Davy** 

This **quote** means that **experimental science** rarely gives exact or **absolute truth**, but only **close approximations**. When **many factors or variables** are involved, the **chances of error or misunderstanding** increase, so experimental results must be interpreted carefully.



- **Pseudo First-Order Reaction:**

For the reaction:



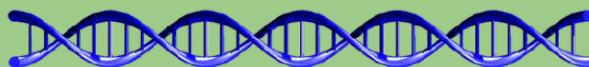
The **rate law** is:

$$v = k_r [P] [Q]$$

If the concentration of one reactant, **Q**, is taken in excess:

- The change in the concentration of **Q** is negligible during the reaction.
- Therefore, **[Q] can be treated as constant**.
- As a result, the **reaction rate** depends only on the concentration of **P**.

Thus, the **second-order reaction** behaves like a **first-order reaction**, and it is called a **pseudo first-order reaction**.



"**Chemistry** has been termed by the physicist as the **messy part of physics**, but that is no reason why the physicists should be permitted to make a mess of chemistry when they invade it."



~~~~~→ **Frederick Soddy** 

- This quote says, "Just because chemistry is complex doesn't give physicists the right to misuse or misrepresent it."

Reaction:

This is a **redox reaction** because **bromide ions** are oxidized to **bromine** and **bromate ions** are reduced.

Rate Law

$$v = k_r [\text{Br}^-] [\text{BrO}_3^-] [\text{H}^+]^2$$

where:

- v = rate of reaction
- k_r = rate constant
- $[\text{Br}^-]$, $[\text{BrO}_3^-]$, $[\text{H}^+]$ = concentrations of reactants

- The reaction is **first order with respect to Br^- and BrO_3^-** , and **second order with respect to H^+** .
- Overall order of reaction = $1 + 1 + 2 = 4$.

Given Parameters

| Symbol | Meaning | Value | Corresponds To |
|----------|--|-------|--|
| a | Stoichiometric coefficient of reactant A | 5 | Br^- in the reaction |
| b | Stoichiometric coefficient of reactant B | 1 | BrO_3^- in the reaction |
| c | Stoichiometric coefficient of reactant C | 6 | H^+ in the reaction |
| m | Order of reaction w.r.t. A | 1 | Order with respect to Br^- |
| n | Order of reaction w.r.t. B | 1 | Order with respect to BrO_3^- |
| p | Order of reaction w.r.t. C | 2 | Order with respect to H^+ |

General Formula for the Rate of Decrease of v:

$$-\frac{dv}{dt} = v^2 \left(\frac{(ma[B][C] + nb[A][C] + pc[A][B])}{[A][B][C]} \right)$$

where

- [A] = concentration of reactant A,
- [B] = concentration of reactant B,
- [C] = concentration of reactant C.

Substitution

Given:

$$a = 5, b = 1, c = 6, m = 1, n = 1, p = 2,$$

$$[A] = [\text{Br}^-], [B] = [\text{BrO}_3^-], [C] = [\text{H}^+]$$

Substituting into the formula:

$$-\frac{dv}{dt} = v^2 \left(\frac{(1 \times 5)[\text{BrO}_3^-][\text{H}^+] + (1 \times 1)[\text{Br}^-][\text{H}^+] + (2 \times 6)[\text{Br}^-][\text{BrO}_3^-]}{[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]} \right)$$

Simplifying the multiplication:

$$-\frac{dv}{dt} = v^2 \left(\frac{5[\text{BrO}_3^-][\text{H}^+] + [\text{Br}^-][\text{H}^+] + 12[\text{Br}^-][\text{BrO}_3^-]}{[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]} \right)$$

This equation shows that the **rate of decrease of the reaction velocity**, proportional to v^2 , depends on the **concentrations** of Br^- , BrO_3^- , and H^+ , with each term weighted by **stoichiometric coefficients** and **reaction orders**.

- **Different reactants react at different rates.**



$\text{Rate} \propto \text{Reactivity of Reactants}$

- More Reactive Substances \rightarrow Faster Reaction Rate
- Less Reactive Substances \rightarrow Slower Reaction Rate

Sodium, being **more reactive**, reacts **faster** with water,
while iron, being **less reactive**, reacts **slowly**.



- **Exothermic:** Heat is released to the surroundings ($\Delta H < 0$)

Energy of products < Energy of reactants

- **Endothermic:** Heat is absorbed from the surroundings ($\Delta H > 0$)

Energy of products > Energy of reactants

$$T = \frac{\Delta H^* - \Delta G^*}{\Delta S^*}$$

$$T = \frac{(\Delta H^*)^0 - (\Delta G^*)^0}{(\Delta S^*)^0}$$

By equating both forms of T:

$$\frac{\Delta H^* - \Delta G^*}{\Delta S^*} = \frac{(\Delta H^*)^0 - (\Delta G^*)^0}{(\Delta S^*)^0}$$

Rearranging for ΔS^* :

$$\Delta S^* = (\Delta S^*)^0 \times \frac{\Delta H^* - \Delta G^*}{(\Delta H^*)^0 - (\Delta G^*)^0}$$

Since thermodynamically

$$(\Delta S^*)^0 = - \frac{d(\Delta G^*)^0}{dT}$$

we substitute this relation to obtain:

$$\Delta S^* = - \frac{d(\Delta G^*)^0}{dT} \times \frac{\Delta H^* - \Delta G^*}{(\Delta H^*)^0 - (\Delta G^*)^0}$$

Using the relations:

$$\Delta G^* = -RT \ln \left(\frac{v_{\text{activation}}}{v_{\text{deactivation}}} \right)$$

and

$$(\Delta G^*)^0 = -RT \ln K^*$$

the final expression becomes:

$$\Delta S^* = - \frac{d(\Delta G^*)^0}{dT} \times \frac{\Delta H^* + RT \ln \left(\frac{v_{\text{activation}}}{v_{\text{deactivation}}} \right)}{(\Delta H^*)^0 + RT \ln K^*}$$

This equation shows that the **entropy of activation** (ΔS^*) is governed by the **negative temperature derivative of the standard Gibbs free energy of activation** $(\Delta G^*)^0$ and the balance between **enthalpic and kinetic factors**. It highlights how changes in temperature and reaction energetics affect the organization of molecules as they reach the **transition state**. By linking **thermodynamic and kinetic aspects of activation**, the equation provides insight into how energy barriers, rate ratios, and molecular motion together determine the degree of disorder and probability of successful **activation during a reaction**.

"Chemistry is a game that electrons play."



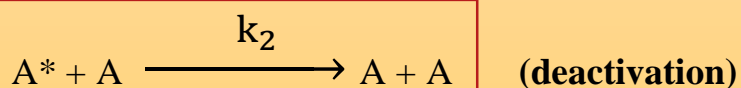
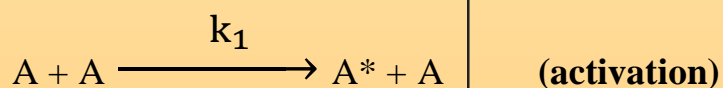
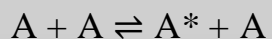
Joseph J. W. McDouall



The unimolecular reaction



proceeds through the following mechanism:



The **Gibbs free energy change** for the reaction



$$\Delta G^* = (\Delta G^*)^0 + RT \ln \frac{[A^*][A]}{[A]^2}$$

Simplifying, we get:

$$\frac{[A^*]}{[A]} = \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

Hence,

$$[A^*] = [A] \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

The **rate of product formation** is given by:

$$v = k_3[A^*]$$

Substituting the value of $[A^*]$, we get:

$$v = k_3 [A] \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

The derived result shows that the rate of product formation depends on both the activation and deactivation processes of the **reactant** molecules. The expression

$$v = k_3 [A] \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

indicates that the rate of product formation increases with the **concentration of reactant A** and the ease of activation of its molecules. The exponential term

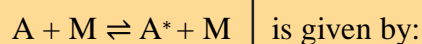
$e^{-\frac{(\Delta G^*)^0}{RT}}$ represents the **thermodynamic barrier for activation** – lower values of $(\Delta G^*)^0$ mean easier formation of the activated species A^* , leading to a faster reaction. Thus, the **rate of product formation** is controlled by how readily **A** molecules acquire **sufficient energy** to become activated and then decompose into products.

For the reaction:



- Here, **M** is the collision partner, which is not similar to **A**.

The **Gibbs free energy relation** for the reaction



$$\Delta G^* = (\Delta G^*)^0 + RT \ln \left(\frac{[A^*][M]}{[A][M]} \right)$$

or equivalently,

$$\frac{[A^*][M]}{[A][M]} = \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

Hence, the **concentration of the activated species** is:

$$[A^*] = [A] \frac{v_{\text{deactivation}}}{v_{\text{activation}}} e^{-\frac{(\Delta G^*)^0}{RT}}$$

This expression is **mathematically identical** to the case where **A** collides with itself ($A + A \rightleftharpoons A^* + A$). However, the **physical meaning differs** – when **M** is not the same as **A**, the **activation and deactivation** of **A** depend on both **[A]** and **[M]**, whereas in self-collisions ($A + A$), these processes depend only on **[A]**.



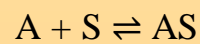
Enzymatic browning occurs when a banana is cut or bruised. The enzyme **polyphenol oxidase (PPO)** reacts with **phenolic compounds** and **oxygen (O₂)**, converting the **phenolic compounds** into **quinones** that form brown pigments, turning the **banana brown**. It is a **redox reaction** because the **phenolic compounds** are oxidized (lose electrons) while **oxygen** is reduced (gains electrons).

- **Types of Photochemical Reactions:**

| Reaction | Equation | Description |
|------------------------------------|-----------------------------------|---|
| Photo-dissociation | $AB + h\nu \rightarrow A^* + B^*$ | Light energy ($h\nu$) breaks a molecule into two excited fragments. |
| Photo-induced Isomerization | $A + h\nu \rightarrow B$ | Light causes a structural change (rearrangement of atoms) in A, forming an isomer B. |

| | | |
|-----------------------------|--------------------------------------|--|
| Photo-addition | $A + B + h\nu \rightarrow AB$ | Light helps two molecules (A and B) combine to form a single new product (AB). |
| Photo-substitution | $A + BC + h\nu \rightarrow AB + C$ | Light replaces one atom or group (C) in a molecule (BC) with another (A). |
| Photo-redox Reaction | $A + B + h\nu \rightarrow A^- + B^+$ | Light causes electron transfer between molecules: A is reduced (A^-) and B is oxidized (B^+). |

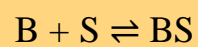
1. Binding of A to the site S:



$$\frac{[AS]}{[A][S]} = \frac{v_{\text{unbinding-1}}}{v_{\text{binding-1}}} e^{-\frac{(\Delta G^0)_1}{RT}}$$

- [AS] is the concentration of AS.
- [A] and [S] are the concentrations of A and S, respectively.
- $v_{\text{binding-1}}$ and $v_{\text{unbinding-1}}$ are the binding and unbinding rates.
- $(\Delta G^0)_1$ is the standard Gibbs free energy of binding.

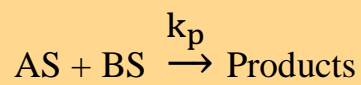
2. Binding of B to the site S:



$$\frac{[BS]}{[B][S]} = \frac{v_{\text{unbinding-2}}}{v_{\text{binding-2}}} e^{-\frac{(\Delta G^0)_2}{RT}}$$

- [BS] is the concentration of BS.
- [B] and [S] are the concentrations of A and S, respectively.
- $v_{\text{binding-2}}$ and $v_{\text{unbinding-2}}$ are the binding and unbinding rates.
- $(\Delta G^0)_2$ is the standard Gibbs free energy of binding.

3. Reaction between AS and BS to form products:



The **rate of product formation** is:

$$v = k_p [AS] [BS]$$



$$v = k_p [A] [B] [S]^2 \left(\frac{v_{\text{unbinding-1}}}{v_{\text{binding-1}}} e^{-\frac{(\Delta G^0)_1}{RT}} \right) \left(\frac{v_{\text{unbinding-2}}}{v_{\text{binding-2}}} e^{-\frac{(\Delta G^0)_2}{RT}} \right)$$

This equation shows that the **rate of product formation** depends on both the **concentrations of the reactants** and the **binding dynamics of A and B** to the site S. The factors $[A][B][S]^2$ indicate that the reaction is **second-order** with respect to the site S and **first-order** with respect to each reactant. The exponential terms reflect the **thermodynamic favorability of binding** through the **standard Gibbs free energy changes** ($(\Delta G^0)_1$ and $(\Delta G^0)_2$). Finally, the ratios of unbinding to binding velocities account for the **kinetic influence of the association and dissociation reactions**. Overall, this equation combines both **thermodynamic and kinetic contributions** to determine the **rate of product formation**.

The **rate of a photochemical reaction** is given by:



$$\text{Rate} = I_{\text{abs}} \times \Phi$$

- I_{abs} = **intensity of absorbed light**
- Φ (quantum yield) = **number of molecules reacting per photon absorbed**.

The **reaction rate** equals the **intensity of absorbed light** multiplied by the **efficiency of converting photons into chemical reactions**.

- $\Phi=1$: **Every absorbed photon produces a reaction**, meaning the reaction is **100% efficient**.
- $\Phi<1$: **Not every absorbed photon leads to a reaction**, so the efficiency is less than 100%. This can occur due to **competing processes** like **fluorescence**, **internal conversion**, or **non-productive relaxation**.

Φ quantifies **how effectively light energy drives the chemical reaction**.

| Photochemical Law | Description | Example |
|--|---|---|
| Grotthuss–Draper Law
 | Light must be absorbed for a photochemical reaction to happen. | Photosynthesis happens only when chlorophyll absorbs light. |
| Stark–Einstein Law
 | Each absorbed photon activates one molecule for reaction. | One photon activates one Cl ₂ molecule during its photochemical decomposition . |

- **Thermal Reactions vs. Photochemical Reactions:**

| Feature | Thermal Reaction | Photochemical Reaction |
|-----------------------------|---|---|
| Energy Source | Heat (thermal energy) | Light (photons) |
| Activation | Molecules gain energy from heat; requires higher activation energy ; usually slower. | Molecules gain energy by absorbing light; can be fast even with low activation energy . |
| Reaction Requirement | Does not require light. | Requires light to proceed. |
| Speed | Often slower | Can be very fast if photons are absorbed |
| Example | Combustion of methane:
$\text{CH}_4 + 2\text{O}_2 \xrightarrow{\Delta} \text{CO}_2 + 2\text{H}_2\text{O}$ | Photosynthesis:
$6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{h\nu} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ |

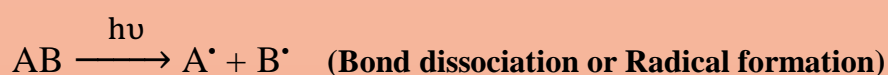
| Reaction | Quantum Yield (Φ) | Description |
|---|---|--|
| Formation of HCl:
$\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl}$ | $\Phi \approx 10^4 \text{ to } 10^6$
High
$(\Phi > 1)$ | One photon produces many radicals, leading to chain reactions that form thousands to millions of HCl molecules. |
| Dimerization of anthracene:
$2\text{C}_{14}\text{H}_{10} \xrightarrow{h\nu} \text{C}_{28}\text{H}_{20}$ | $\Phi \approx 0.5$
Low
$(\Phi < 1)$ | Product is unstable and breaks back into reactants, so reverse reactions reduce the overall yield. |

- **Primary Photochemical Process (Activation Step):**

This is the **light-dependent step** in which a **molecule absorbs radiant energy** and becomes activated.



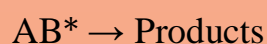
Or



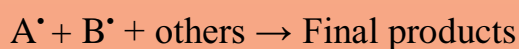
The molecule **AB** absorbs a **photon of energy** ($h\nu$), becoming an **excited species** (AB^*); in some cases, this energy is high enough to **break a chemical bond**, directly forming **free radicals** (A^{\bullet} and B^{\bullet}). This step **strictly requires light** and **does not produce final products**, yielding **only highly reactive intermediates**. Its purpose is to **activate the molecule** by providing the energy needed to overcome activation barriers for subsequent chemical reactions.

- **Secondary Photochemical Process (Reaction Step):**

This is the **light-independent step** in which the **activated species** undergoes chemical reactions to form stable products.



Or



After activation, the **excited molecule** (AB^*) or the **radicals** (A' and B') react further through rearrangement, combination, or reaction with other molecules. These reactions **do not involve light** and proceed by normal **thermal chemical pathways**, even in the dark. This stage **produces stable final products**, converting short-lived, highly reactive species into **stable chemical compounds**.

For the reaction:



- **Predicted order:**

If the reaction were an **elementary reaction**, the rate law would be written directly from the stoichiometry:

$$v \propto [\text{ClO}^-]^3$$

So, the **predicted order = 3**.

- **Experimental order:**

Experimentally, the rate law is:

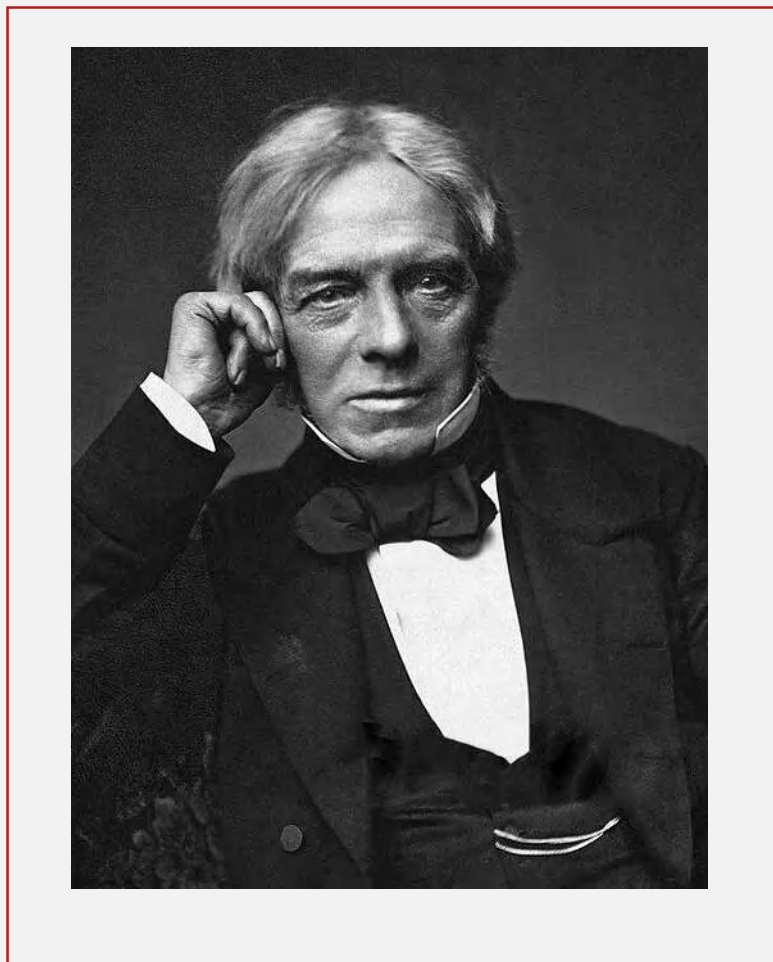
$$v \propto [\text{ClO}^-]^2$$

Hence, the **experimental order = 2**.

- **Predicted order: 3**
- **Experimental order: 2**

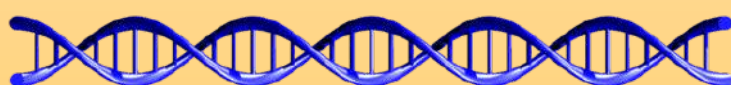
Since the **predicted order** does not match the **experimental order**, the reaction is not an **elementary reaction** and proceeds through a **multi-step mechanism**.






"**Chemistry** is necessarily an **experimental science**: its conclusions are drawn from data, and its principles supported by evidence from facts."



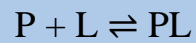
~ ~ ~ ~ ~ → **Michael Faraday** 

This **quote** means that **chemistry** depends on experiments and observations, not just theory or assumptions. All **conclusions in chemistry** are based on experimental data, and chemical laws and principles are validated by factual evidence obtained through experiments.



| Aspect
 | Arrhenius Equation Theory
 | Transition State Theory (TST)
 | Collision Theory
 |
|--|---|--|--|
| Originator | Svante Arrhenius | Henry Eyring | Max Trautz and William Lewis |
| Time Period | Late 19th century | 1930s | Early 20th century |
| Main Concept
 | Reaction rate increases exponentially with temperature | Reactions proceed via a high-energy transition state | Reactions occur through effective molecular collisions |
| Key Idea | Temperature affects rate by overcoming activation energy | Rate depends on formation of an activated complex | Rate depends on collision energy and orientation |
| Role of Temperature | Higher temperature increases the number of molecules with enough energy to react | Higher temperature increases the probability of reaching the transition state | Higher temperature increases molecular speed and collision frequency |
| Mathematical Basis | Arrhenius equation relates rate constant to temperature and activation energy | Uses energy profiles and partition functions | Based on kinetic theory of gases |
| Molecular Insight | Limited molecular detail | Detailed molecular-level explanation | Focuses on physical collisions |
| Strength | Simple and widely applicable | Provides deeper insight into reaction mechanisms | Intuitive explanation of reaction rates |
| Limitation | Does not explain reaction mechanism | More complex and theoretical | Less accurate for complex reactions |
| Relevance to Temperature Study | Predicts rate changes with temperature | Explains how temperature affects reaction pathway | Explains how temperature increases effective collisions |

For the binding reaction:



- **P** → The protein.
- **L** → The ligand that binds to the protein.
- **PL** → The complex formed when the protein binds with the ligand.

The **reaction quotient** is:

$$Q = \frac{[PL]}{[P][L]}$$

Rearranging:

$$[P] = \frac{[PL]}{Q[L]}$$

The **total protein concentration** is the sum of free and bound forms:

$$[P_T] = [P] + [PL] \Rightarrow [P] = [P_T] - [PL]$$

Substituting for [P]:

$$[P_T] = [PL] \left(\frac{1}{Q[L]} + 1 \right) \Rightarrow [P_T] = [PL] \left(\frac{1+Q[L]}{Q[L]} \right)$$

Therefore, the **fraction of bound protein** (θ) is given by:

$$\theta = \frac{[PL]}{[P_T]} = \frac{Q[L]}{(1+Q[L])}$$

Since

$$Q = \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^0)_B}{RT}}$$

we can write:

$$\theta = \frac{\frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^0)_B}{RT}} [L]}{\left(1 + \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^0)_B}{RT}} [L]\right)}$$

This equation describes how the **fraction of bound protein** (θ) varies with the **ligand concentration** ($[L]$), the **standard Gibbs free energy of binding** $(\Delta G^0)_B$, and the **ratio of unbinding to binding rates**, providing a measure of the **protein–ligand interaction** affinity. A more negative $(\Delta G^0)_B$ signifies a stronger and more spontaneous binding between the protein and ligand.

- **Low ligand (or weak binding) limit:**

If $\frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^0)_B}{RT}} [L] \ll 1$, then

$$\theta \approx \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^0)_B}{RT}} [L]$$

In this case, only a small fraction of protein is bound. θ increases with $[L]$, and binding is rare due to either **low ligand concentration** or **weak binding**.

- **High ligand (or saturation) limit:**

$$\text{If } \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^0)_B}{RT}} [L] \gg 1, \text{ then}$$

$$\theta \approx 1$$

Nearly **all protein is bound**, indicating saturation.

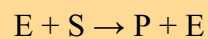
- **Half-occupancy (midpoint):**

$$\text{If } \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^0)_B}{RT}} [L] = 1, \text{ then}$$

$$\theta \approx 0.5$$

At this point, **half of the total protein is bound to the ligand**, representing the midpoint of the binding process.

For the **enzyme-catalyzed** reaction:



- **Instantaneous rate at time t:**

$$v = k_r [E] [S]$$

[E]: Enzyme concentration at time t and [S]: Substrate concentration at time t

- **Initial rate (v_0):**

$$v_0 = k_r [E_0] [S_0]$$

- v_0 : rate at $t = 0$ (before the substrate or enzyme concentrations have changed significantly)
- $[E_0]$: initial enzyme concentration
- $[S_0]$: initial substrate concentration

At $t = 0$ (under initial rate conditions), no significant amount of **product or enzyme-substrate (ES) complex** has formed. Therefore, the **initial enzyme concentration** $[E_0]$ is equal to the **total enzyme concentration** $[E_T]$.

- $v = k_r [E] [S] \rightarrow$ rate at any time t
- $v_0 = k_r [E_T] [S_0] \rightarrow$ initial rate when $t = 0$

- **Ratio of Instantaneous Rate to Initial Rate:**

$$\frac{v}{v_0} = \frac{k_r [E][S]}{k_r [E_T][S_0]}$$

At time t the unreacted **substrate concentration** is given by:

$$[S] = [S_0] - [X] - [ES]$$

where:

- $[X]$ = concentration of the substrate converted into product
- $[ES]$ = concentration of the substrate bound to the enzyme

Defining the **fraction of substrate reacted** as:

$$\theta_1 = \frac{[X]}{[S_0]}$$

Then, the **fraction of substrate remaining** is:

$$\frac{[S]}{[S_0]} = \left(1 - \theta_1 - \theta_2 \right)$$

where:

- θ_1 = fractional amount of substrate converted into product
- θ_2 = fractional amount of substrate bound to the enzyme

Substituting this into the rate ratio gives:

$$\frac{v}{v_0} = \frac{[E]}{[E_T]} \times \left(1 - \theta_1 - \theta_2 \right)$$

The **rate ratio** $\left(\frac{v}{v_0} \right)$ is determined by the **fraction of free enzyme** $\left(\frac{[E]}{[E_T]} \right)$ and the **fraction of remaining substrate** $(1 - \theta_1 - \theta_2)$. As the reaction proceeds, more substrate molecules are bound to **enzymes or converted into products**, reducing the **available substrate** and causing the reaction rate to decline. For instance, **during starch conversion to glucose by amylase**, the reaction starts fast when starch is abundant but gradually slows as starch is consumed and fewer substrate molecules remain for the enzyme to act upon.

The **total enzyme concentration** is the sum of free and bound enzyme:

$$[E_T] = [E] + [ES] \Rightarrow [E] = [E_T] - [ES]$$

Hence, the **fraction of free enzyme** is:

$$\frac{[E]}{[E_T]} = \left(1 - \frac{[ES]}{[E_T]} \right)$$

Substituting this expression:

$$\frac{v}{v_0} = \left(1 - \frac{[ES]}{[E_T]} \right) \times (1 - \theta_1 - \theta_2)$$

The term $\left(1 - \frac{[ES]}{[E_T]} \right)$ accounts for **enzyme saturation** – as more enzyme forms the **ES complex**, less remains free to catalyze new substrate molecules.

- **Product formation rate:** $v_p = k_3 [ES]$
- **Maximum velocity** (when every enzyme molecule is in the ES complex, $[ES] = [E_T]$): $v_{\max} = k_3 [E_T]$

Dividing these two expressions:

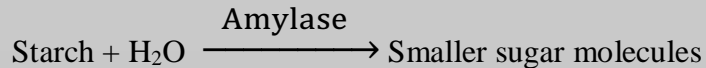
$$\frac{v_p}{v_{\max}} = \frac{[ES]}{[E_T]}$$

Substituting into the previous expression:

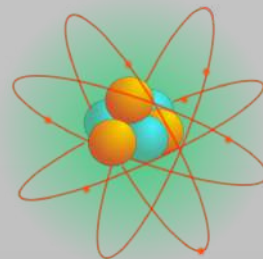
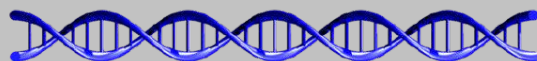
$$\frac{v}{v_0} = \left(1 - \frac{v_p}{v_{\max}} \right) \times (1 - \theta_1 - \theta_2)$$

The expression shows that the **ratio of the current reaction rate to the initial rate** depends on three key factors – the **ratio of the product formation rate to the maximum rate of product formation**, the fraction of substrate bound to the enzyme, and the fraction of substrate already converted into product. As the **reaction continues**, more substrate molecules are either consumed or bound to enzyme molecules, reducing the available free substrate ($1 - \theta_1 - \theta_2$). This decrease causes **the overall reaction rate** v to drop compared to the **initial rate** v_0 .

For example, in the enzymatic hydrolysis of starch by amylase:



At first, when the **starch concentration** is high, the enzyme acts rapidly. As the reaction progresses and **more starch is converted into smaller sugar molecules such as maltose and glucose**, the number of available starch molecules for enzyme binding decreases. This reduction in **free substrate leads to a gradual decline in the reaction rate** due to substrate depletion and the accumulation of products.



Since

$$\frac{[ES]}{[E_T]} = \frac{\left[[S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}} \right]}{1 + \left[[S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}} \right]}$$

Therefore,

$$\frac{v}{v_0} = \left(1 - \frac{[ES]}{[E_T]} \right) \times (1 - \theta_1 - \theta_2)$$

can be written as:

$$\frac{v}{v_0} = 1 - \left(\frac{[S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}}}{1 + [S] \frac{v_{\text{unbinding}}}{v_{\text{binding}}} e^{-\frac{(\Delta G^*)^0}{RT}}} \right) \times (1 - \theta_1 - \theta_2)$$

The equation indicates that the **reaction rate** rises with increasing substrate concentration and reaches its **maximum value** v_{max} at high $[S]$.

The **rate ratio** $\left(\frac{v}{v_0} \right)$ is influenced by the **substrate concentration**, the balance between unbinding and binding rates, and the **standard Gibbs activation energy** represented by the exponential term $e^{-\frac{(\Delta G^*)^0}{RT}}$. As the **reaction continues**, more substrate is either converted into product or bound to the enzyme, decreasing the fraction $(1 - \theta_1 - \theta_2)$ and causing the **reaction rate** to gradually slow down due to **substrate depletion**.

Considering the reaction:



- The **rate of formation** of the enzyme–substrate complex (ES) is:

$$\text{Rate of ES formation} = k_1 [E] [S]$$

- The **rate of disappearance of the complex** (due to its breakdown into either enzyme and substrate or enzyme and product) is:

$$\text{Rate of ES disappearance} = k_2 [ES] + k_3 [ES]$$

- According to the **steady-state assumption**, the formation and disappearance of the ES complex rapidly reach a balance, so:

$$\frac{d[ES]}{dt} = 0 = k_1 [E] [S] - \left(k_2 [ES] + k_3 [ES] \right)$$

Rearranging this gives:

$$k_1 [E] [S] = (k_2 + k_3) [ES]$$

- The **Michaelis constant** (K_M) is defined as:

$$K_M = \frac{(k_2 + k_3)}{k_1}$$

Therefore,

$$[E] [S] = K_M [ES]$$

Since

$$[S] = [S_0] - [X] - [ES]$$

therefore,

$$[E] \left([S_0] - [X] - [ES] \right) = K_M [ES]$$

Expanding the terms:

$$[E] [S_0] - [E] [X] - [E] [ES] = K_M [ES]$$

Rearranging gives:

$$[E] [S_0] - [E] [X] = [ES] \left(K_M + [E] \right)$$

Substituting $[X] = \theta_1 [S_0]$, we obtain:

$$[E] [S_0] - [E] \theta_1 [S_0] = [ES] \left(K_M + [E] \right)$$

Simplifying:

$$[ES] = \frac{[E][S_0](1-\theta_1)}{[K_M + [E]]}$$

- The **rate of product formation** (v_p) is proportional to the breakdown of the ES complex to form product: $v_p = k_3[ES]$

Substituting the expression for [ES]:

$$v_p = \frac{k_3[E][S_0](1-\theta_1)}{K_M + [E]}$$

This equation shows that the **product formation rate** depends on the free enzyme concentration, the initial substrate concentration, substrate availability, and the **Michaelis constant** (K_M). The **Michaelis constant** represents the apparent affinity of the enzyme for its substrate. A **lower K_M value** indicates **stronger enzyme–substrate binding**, meaning the enzyme can achieve a high product formation rate even at low substrate concentrations. Conversely, a **higher K_M value** suggests weaker binding and requires higher substrate levels to reach the same product formation rate.

- **Case 1: Low enzyme concentration ($[E] \ll K_M$)**

When the free enzyme concentration is much smaller than K_M , the denominator is dominated by K_M . The equation simplifies to:

$$v_p \approx \frac{k_3[E][S_0](1-\theta_1)}{K_M}$$

The **product formation rate** increases almost linearly with enzyme concentration. The reaction is enzyme-limited because there is not enough enzyme available to bind most of the substrate.

- **Case 2: High enzyme concentration ($[E] \gg K_M$)**

When enzyme concentration is much higher than K_M , the denominator is dominated by $[E]$. The equation simplifies to:

$$v_p \approx k_3[S_0](1 - \theta_1)$$

The **product formation rate** becomes independent of [E] and approaches a maximum value. The enzyme is now in excess, so nearly all the substrate is bound and converted rapidly.

$$v_p = \frac{k_3[E][S_0](1-\theta_1)}{[K_M + [E]]} \Rightarrow v_p = \frac{k_3([E_T] - [ES])[S_0](1-\theta_1)}{[K_M + [E]]}$$

$$v_p = \frac{(k_3[E_T] - k_3[ES])[S_0](1-\theta_1)}{[K_M + [E]]} \Rightarrow v_p = \frac{(v_{\max} - v_p)[S_0](1-\theta_1)}{[K_M + [E]]}$$

Rearranging, we get:

$$\frac{(v_{\max} - v_p)}{v_p} = \frac{K_M + [E]}{[S_0](1-\theta_1)}$$

Finally, solving for v_p :

$$v_p = \frac{v_{\max}}{\left(\frac{K_M + [E]}{[S_0](1-\theta_1)} \right) + 1}$$

When $v_p = \frac{v_{\max}}{2}$, it means the reaction is proceeding at **half of its maximum rate**.

From the given equation

$$v_p = \frac{v_{\max}}{\frac{K_M + [E]}{[S_0](1-\theta_1)} + 1}$$

setting $v_p = \frac{v_{\max}}{2}$ gives

$$\left(\frac{K_M + [E]}{[S_0](1-\theta_1)} \right) + 1 = 2$$

Simplifying this yields

$$K_M + [E] = [S_0](1-\theta_1)$$

So, the **product formation rate** becomes half of v_{\max} when the **initial substrate concentration** minus the **reacted substrate concentration** equals the sum of the **Michaelis constant** and the free enzyme concentration.

"**Enzymes are masters of chemistry**. They evolved over billions of years to perform **specific biological functions**. They make complex materials with virtually no waste."



 **Frances Arnold**

For an **enzyme-catalyzed reaction**:



The **Michaelis constant** is given by:

$$K_M = \frac{k_2+k_3}{k_1}$$

Using the **Arrhenius equation** for each rate constant:

$$K_M = \frac{A_2 e^{-\frac{E_2}{RT}} + A_3 e^{-\frac{E_3}{RT}}}{A_1 e^{-\frac{E_1}{RT}}}$$

From this it follows that:

$$K_M = \frac{1}{A_1} \left(A_2 e^{-\frac{(E_2-E_1)}{RT}} + A_3 e^{-\frac{(E_3-E_1)}{RT}} \right)$$

The equation shows that K_M is influenced by the **activation energies** (E_1 , E_2 , E_3) and **frequency factors** (A_1 , A_2 , A_3) of each reaction step. If the energy required for **complex breakdown** or **catalysis** (E_2 or E_3) is higher than that for **substrate binding** (E_1), K_M increases, indicating weaker enzyme–substrate binding. If **substrate binding** requires less energy (E_1 is smaller), K_M decreases, showing **stronger enzyme–substrate affinity**. The K_M values show **enzyme–substrate binding** strength. **Fumarase** has the lowest K_M (5.0×10^{-6} M), indicating very strong binding. **Pepsin** (3.0×10^{-4} M) and **tRNA synthetase** (9.0×10^{-4} M) also show strong affinity. **Chymotrypsin** (1.5×10^{-2} M) and **ribonuclease** (7.9×10^{-3} M) have moderate binding, while **carbonic anhydrase** has the highest K_M (2.6×10^{-2} M), showing the weakest binding.

$$K_M k_1 = (k_2 + k_3)$$

Differentiating both sides with respect to temperature T:

$$\frac{d}{dT} (K_M k_1) = \frac{d}{dT} (k_2 + k_3)$$

From this, it follows that:

$$K_M \left(\frac{dk_1}{dT} \right) + k_1 \left(\frac{dK_M}{dT} \right) = \frac{dk_2}{dT} + \frac{dk_3}{dT}$$

Or equivalently, it can be written as:

$$\frac{dK_M}{dT} = \frac{1}{k_1} \left(\frac{dk_2}{dT} + \frac{dk_3}{dT} - K_M \left(\frac{dk_1}{dT} \right) \right)$$

Since:

$$\frac{dk_2}{dT} = \frac{k_2 E_2}{RT^2}$$

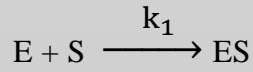
$$\frac{dk_3}{dT} = \frac{k_3 E_3}{RT^2}$$

$$\frac{dk_1}{dT} = \frac{k_1 E_1}{RT^2}$$

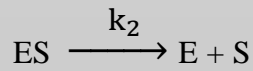
Therefore,

$$\frac{dK_M}{dT} = \frac{1}{k_1} \left(\frac{k_2 E_2}{RT^2} + \frac{k_3 E_3}{RT^2} - \frac{K_M k_1 E_1}{RT^2} \right)$$

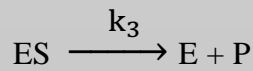
- $E_1 \rightarrow$ Activation energy for the **formation of the enzyme–substrate complex (ES)**



- $E_2 \rightarrow$ Activation energy for the **dissociation of the complex back to enzyme and substrate**



- $E_3 \rightarrow$ Activation energy for the **conversion of the complex into enzyme and product**



- E_1 controls how easily the substrate binds to the enzyme.
- E_2 determines how readily the complex breaks apart without forming product.
- E_3 reflects the energy barrier for the **catalytic step**, where product formation occurs.

Substituting $K_M k_1 = (k_2 + k_3)$ into the previous equation gives:

$$\frac{dK_M}{dT} = \frac{1}{k_1} \left(\frac{k_2 E_2}{RT^2} + \frac{k_3 E_3}{RT^2} - \frac{(k_2 + k_3) E_1}{RT^2} \right)$$

Simplifying, we obtain:

$$\frac{dK_M}{dT} = \frac{k_2(E_2 - E_1) + k_3(E_3 - E_1)}{k_1 RT^2}$$

This equation expresses how the **temperature dependence of the Michaelis constant K_M** is governed by the **differences in activation energies** between the individual reaction steps.

- The terms $(E_2 - E_1)$ and $(E_3 - E_1)$ indicate how much higher or lower the activation energies of the reverse and product-forming steps are compared to the forward binding step.
- If $E_2, E_3 > E_1$ then $(E_2 - E_1) > 0$ and $(E_3 - E_1) > 0$

Therefore

$$k_2(E_2 - E_1) + k_3(E_3 - E_1) > 0$$

So

$$\frac{dK_M}{dT} > 0$$

Hence K_M **increases with temperature**, which means the **enzyme-substrate binding** becomes weaker as temperature rises.

- If E_1 is higher than E_2 and E_3 , then $(E_2 - E_1) < 0$ and $(E_3 - E_1) < 0$

Therefore

$$k_2(E_2 - E_1) + k_3(E_3 - E_1) < 0$$

So

$$\frac{dK_M}{dT} < 0$$

Hence K_M **decreases with temperature**, indicating that **enzyme-substrate binding** becomes stronger at higher temperatures.

Thus, the equation links **enzyme kinetics** to **thermal sensitivity** through the differences in activation energies of the individual steps.

1. Temperature:

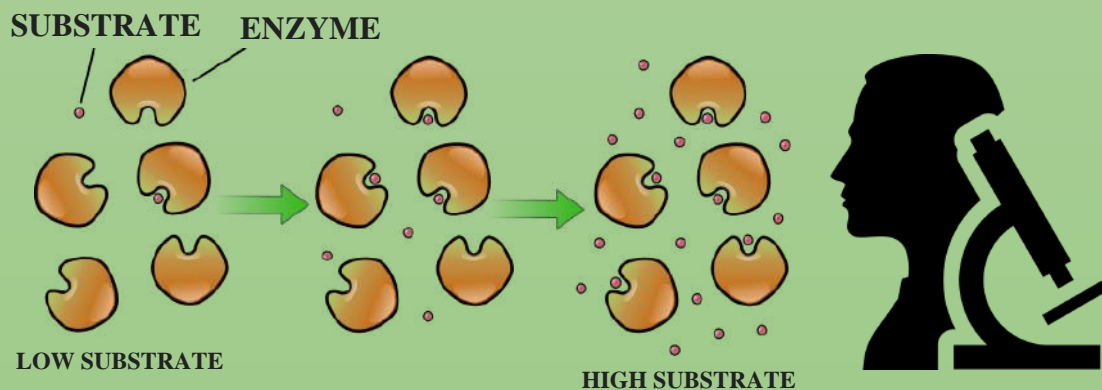
- **Reaction rate** \propto Temperature (up to optimum)
- **Reaction rate** decreases when temperature exceeds optimum (enzyme denatures)
- **Example:** Catalase activity decreases above 40°C.

2. pH

- **Reaction rate** decreases when pH deviates from the optimum (as enzyme shape and active site are altered).
- **Example:** Pepsin works best at pH 2 and loses activity at pH 7.

3. Inhibitors

- **Reaction rate** decreases in the presence of inhibitors.
- **Example:** Cyanide inhibits cytochrome oxidase, stopping cellular respiration.



As substrate concentration increases, the reaction rate rises until the enzymes become saturated,



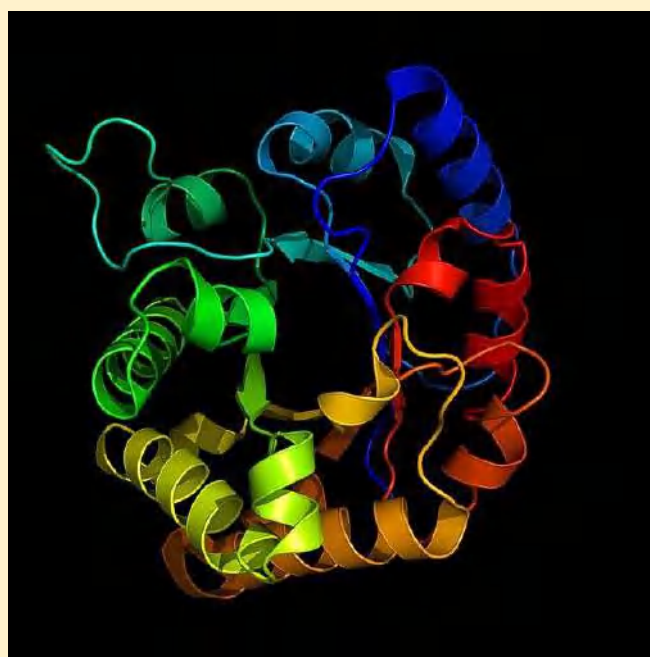
after which the rate no longer increases.





- **Chemical-Catalysed Reaction vs. Enzyme-Catalysed Reaction:**

| Aspect | Chemical-Catalysed Reaction | Enzyme-Catalysed Reaction |
|---------------------------|---|---|
| Catalyst type | Inorganic (metals, acids, bases) | Organic (globular proteins) |
| Nature | Non-biological | Biological |
| Specificity | Low: one catalyst often triggers many reactions | Highly specific: "lock-and-key" fit; acts on one substrate |
| Temperature | Often requires high temperature | Operates at mild temperatures ($\approx 37\text{ }^{\circ}\text{C}$ in humans) |
| pH sensitivity | Works over a wide pH range | Very sensitive to pH; may denature |
| Reaction rate | Significant increase in speed | Massive increase ($10^6 - 10^{12}$ times faster) |
| Regulation | Difficult to control once started | Highly regulated by activators and inhibitors |
| Reaction (example) | $2\text{H}_2\text{O}_2 \xrightarrow{\text{MnO}_2} 2\text{H}_2\text{O} + \text{O}_2$ | Amylase breaking down starch into smaller sugar molecules |



The ribbon diagram of **triose-phosphate isomerase** shows a precisely folded protein whose active site binds the substrate and stabilises the transition state. This **structural perfection** allows the enzyme to catalyse the **interconversion** of **dihydroxyacetone phosphate** and **glyceraldehyde-3-phosphate** with near-maximum efficiency in **glycolysis**.

For the reversible enzymatic reaction:



Reaction quotients:

$$Q_1 = \frac{[ES]}{[E][S]}$$

This is the **reaction quotient** for the reaction $E+S \rightleftharpoons ES$.

Q_1 tells us how much ES complex forms relative to the amounts of free enzyme and substrate.

- A large Q_1 means ES formation is favored.
- A small Q_1 means ES formation is not favored.

Rearranging:

$$[ES] = Q_1 [E] [S]$$

$$Q_2 = \frac{[E] [P]}{[ES]}$$

This is the **reaction quotient** for the reaction $ES \rightleftharpoons E + P$.

Q_2 describes how strongly ES tends to break down into free enzyme and product.

- A large Q_2 means ES readily converts to E + P.
- A small Q_2 means ES tends to stay as ES (little product formed).

Rearranging:

$$[ES] = \frac{[E] [P]}{Q_2}$$

$$[ES] \times [ES] = Q_1 [E] [S] \times \frac{[E] [P]}{Q_2}$$

$$[ES]^2 = [E]^2 \left(\frac{Q_1}{Q_2} \times [S] [P] \right)$$

Taking the square root of both sides:

$$[ES] = [E] \sqrt{\frac{Q_1}{Q_2} \times [S] [P]}$$

Solving for free enzyme [E]:

$$[E] = \frac{[ES]}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]}}$$

Total enzyme concentration:

$$[E_T] = [E] + [ES] \Rightarrow [E] = [E_T] - [ES]$$

Substituting the expression for [E] into the equation:

$$[E_T] - [ES] = \frac{[ES]}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]}}$$

From this, it follows that:

$$[E_T] = [ES] \left(\frac{1}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]}} + 1 \right)$$

The fraction of bound enzyme is given by:

$$\theta = \frac{[ES]}{[E_T]} = \frac{1}{\left(\frac{1}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]}} + 1 \right)}$$

The expression for θ shows **what fraction of the total enzyme is present in the bound form ES**. It increases when the combination of substrate concentration, product concentration, and the **tendency of the enzyme to form ES** (captured by $\frac{Q_1}{Q_2}$) is large. In this situation, the enzyme is mostly bound. **When these factors are small**, θ becomes small, meaning most enzyme remains unbound. Overall, the formula describes **how strongly the system favors the enzyme being in the ES state** based on substrate, product, and the reaction quotients.

The **net rate of change of product concentration** is:

$$\frac{d[P]}{dt} = \text{Rate of formation of product} - \text{Rate of disappearance of product}$$

$$\text{Rate of formation} = k_3 [ES]$$

Here, **k₃** is the **rate constant for the conversion of the enzyme–substrate complex (ES) into product (P) and free enzyme (E)**.

$$\text{Rate of disappearance} = k_4 [E] [P]$$

Here, **k₄** is the **rate constant**, describing how enzyme (E) and product (P) recombine to form ES again.

$$\frac{d[P]}{dt} = k_3 [ES] - k_4 [E] [P]$$

Since:

$$[E][P] = Q_2 [ES]$$

Substituting:

$$\frac{d[P]}{dt} = k_3 [ES] - k_4 Q_2 [ES]$$

Factoring out [ES]:

$$\frac{d[P]}{dt} = [ES] (k_3 - k_4 Q_2)$$

- If $k_3 > k_4 Q_2$, then

$$\frac{d[P]}{dt} > 0$$

Net product formation occurs.

The forward catalytic step (conversion of $ES \rightarrow E + P$) is stronger than the reverse step.

- If $k_3 < k_4 Q_2$, then

$$\frac{d[P]}{dt} < 0$$

Net product consumption occurs (reverse flux).

The reverse reaction ($E + P \rightarrow ES$) dominates over the forward step.

- If $k_3 = k_4 Q_2$, then

$$\frac{d[P]}{dt} = 0$$

The system is at equilibrium.

Forward and reverse rates are exactly balanced, so there is no net change in product concentration.

Using:

$$[ES] = \frac{[E_T]}{\left(\frac{1}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]} + 1} \right)}$$

Substituting:

$$\frac{d[P]}{dt} = \frac{[E_T] (k_3 - k_4 Q_2)}{\left(\frac{1}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]} + 1} \right)}$$

1. **When substrate [S] and product [P] concentrations are high**, the term

$$\frac{1}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]}} \ll 1$$

This makes the denominator in

$$\frac{d[P]}{dt} = \frac{[E_T] (k_3 - k_4 Q_2)}{\left(\frac{1}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]} + 1} \right)}$$

approximately equal to 1. So the net rate simplifies to

$$\frac{d[P]}{dt} \approx [E_T] (k_3 - k_4 Q_2)$$

2. When substrate [S] and product [P] concentrations are low, the term

$$\frac{1}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]}} \gg 1$$

This makes the denominator in

$$\frac{d[P]}{dt} = \frac{[E_T] (k_3 - k_4 Q_2)}{\left(\frac{1}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]}} + 1 \right)}$$

approximately equal to $\frac{1}{\sqrt{\frac{Q_1}{Q_2} \times [S] [P]}}$. So the net rate simplifies to

$$\frac{d[P]}{dt} \approx [E_T] (k_3 - k_4 Q_2) \sqrt{\frac{Q_1}{Q_2} \times [S] [P]}$$

$$\text{Turnover Frequency (TOF)} = \frac{\text{Number of product molecules formed}}{\text{Number of active sites} \times \text{time}}$$

- **Turnover Frequency (TOF)** tells how fast a catalyst works. It shows how many product molecules are formed by each active site in a given amount of time. A **higher TOF** means the catalyst is working more efficiently.

- **Which Theory When?**

| Scenario | Best Theory to Use |
|--------------------------------|---|
| Simple laboratory calculations | Arrhenius Equation
(fastest and easiest to apply) |
| Explaining gas-phase reactions | Collision Theory
(effective for pressure and concentration effects) |
| Mapping a reaction mechanism | Transition State Theory (TST)
(explains transition-state geometry) |

- **Examples of Chemical Reactions in Everyday Life:**

| Everyday Activity | Chemical Reaction Involved |
|----------------------|--|
| Cooking food | Heat causes chemical changes in proteins and starches |
| Rusting of iron | Iron reacts with oxygen and moisture to form rust |
| Digestion of food | Enzymes break complex food into simpler substances |
| Burning of fuel | Combustion produces energy, carbon dioxide, and water |
| Photosynthesis | Plants convert carbon dioxide and water into food

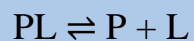
$6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ |
| Respiration | Glucose reacts with oxygen to release energy

$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{Energy}$ |
| Milk turning sour | Bacterial fermentation produces lactic acid |
| Baking bread or cake | Yeast fermentation releases carbon dioxide

$\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$ |
| Tarnishing of silver | Silver reacts with sulfur compounds in air

$4\text{Ag} + 2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{Ag}_2\text{S} + 2\text{H}_2\text{O}$ |
| Battery operation | Redox reactions generate electrical energy |

For the reaction:



the reaction quotient is:

$$Q = \frac{[PL]}{[P][L]}$$

or equivalently,

$$Q [PL] = [P] [L]$$

By substituting

$$\begin{aligned} [PL] &= [P_T] - [P], \\ [L] &= [L_T] - [PL], \\ [P] &= [P_T] - [PL], \end{aligned}$$

we obtain

$$Q ([P_T] - [P]) = ([P_T] - [PL]) ([L_T] - [PL])$$

Expanding and simplifying gives:

$$Q [P_T] - Q [P] = [P_T] [L_T] - [P_T] [PL] - [PL] [L_T] + [PL]^2$$

Rearranging:

$$Q [P_T] - [P_T] [L_T] + [P_T] [PL] = - [PL] [L_T] + [PL]^2 + Q [P]$$

$$[P_T] (Q - [L_T] + [PL]) = [PL] (- [L_T] + [PL]) + Q [P]$$

Since $[L_T] = [L] + [PL]$, then

$$[P_T] (Q - [L]) = - [PL] [L] + Q [P]$$

which simplifies to:

$$Q - [L] = Q \left(\frac{[P]}{[P_T]} \right) - \left(\frac{[PL]}{[P_T]} \right) [L]$$

Let

- $F_{FP} = \frac{[P]}{[P_T]}$ (fraction of free protein),
- $F_{BP} = \frac{[PL]}{[P_T]}$ (fraction of bound protein)

then the equation becomes:

$$Q - [L] = Q F_{FP} - F_{BP} [L]$$

- When $F_{FP} = F_{BP} = 1$, the left and right sides are equal, and the equation holds true.
- When $F_{FP} = F_{BP} \neq 1$, the two sides are not equal, making the equation invalid.

According to the **law of conservation of protein**:

$$[P_T] = [P] + [PL] \Rightarrow 1 = F_{FP} + F_{BP}$$

If both F_{FP} and F_{BP} are assumed to be 1, it leads to $1=2$, which is not possible.

Therefore, the condition $F_{FP} = F_{BP} = 1$ is invalid, and the derived equation does not hold.

If we substitute $[PL] = [P_T] - [P]$, $[L] = [L_T] - [PL]$, and $[P] = [P_T] - [PL]$, then the **relationship** $Q [PL] = [L] [P]$ results in $Q F_{FP} - F_{BP} [L]$, which is a **wrong result**. Therefore, substitution for $[PL]$ along with those for $[L]$ and $[P]$ should be avoided to prevent the derivation of incorrect expressions and maintain the validity of the relationship.

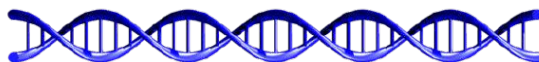
"I can live with doubt and uncertainty. I think it's much more interesting to live not knowing than to have answers which might be wrong."



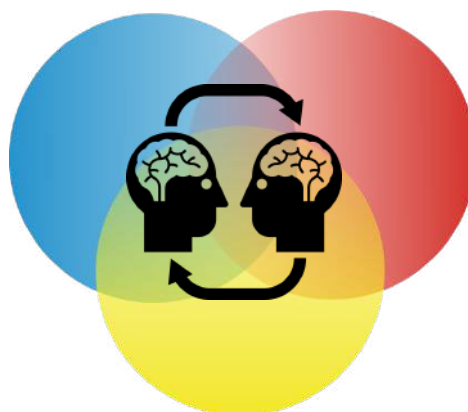
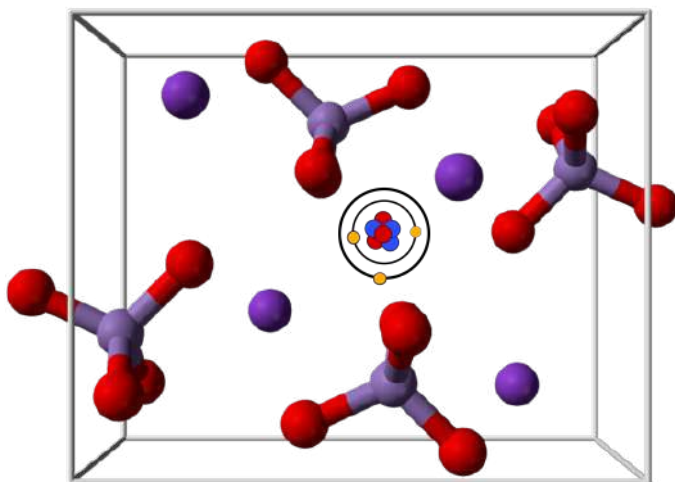
 **Richard P. Feynman**



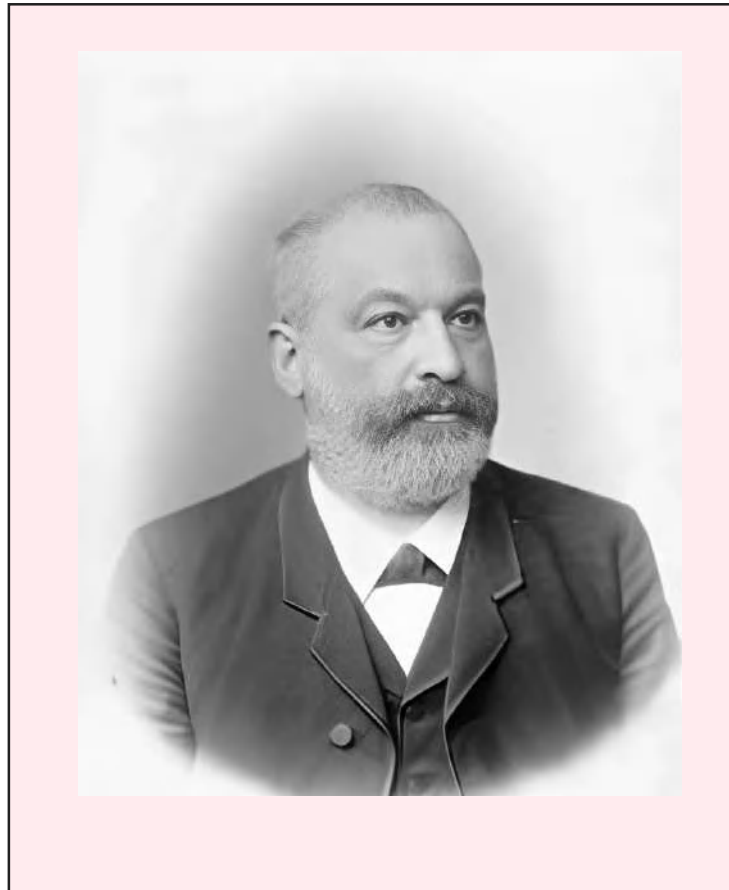
Conclusion:



The **theoretical and mathematical derivations** presented establish a comprehensive framework for understanding and predicting **reaction rate dynamics**. Key relationships quantify the **natural slowing of reaction velocity over time**, showing it is inversely dependent on **reactant concentrations** and **proportional to the square of the initial rate** (v^2), emphasizing the critical role of the **limiting reactant**. The **temperature dependence equation** demonstrates how both **activation energy** (E_a) and **temperature-driven changes in reactant concentrations** influence overall reaction rates. By integrating the **Arrhenius equation** with **Transition State Theory** and **Gibbs free energy change** (ΔG), the work links **kinetic behavior** to **thermodynamic stability and energy barriers**, highlighting how **activation parameters** govern both **reaction speed** and **spontaneity**. Application to **enzyme kinetics** illustrates practical utility, explaining how **catalysts** enhance rates by lowering activation energy. Overall, the study shows how **concentration, temperature, and activation parameters** collectively determine **reaction dynamics**, offering a unified understanding of **chemical reactivity, catalysis, and energy landscapes**.



"The world of chemical reactions is like a stage, on which scene after scene is ceaselessly played. The actors on it are the elements."



~ ~ ~ ~ ~ → **Clemens Winkler**

