

General Chemistry



Chapter 7: Chemical Kinetics

Chemical Kinetics

- *Chemical Kinetics*
- *Rate of reaction: unit of rate of reaction*
- *Types of rate of reaction: Average and Instantaneous*
- *Equivalent rate expression*
- *Rate Law: rate constant, order of reaction*
- *Zero, 1st, 2nd, 3rd and fractional order*
- *Unit of rate constant for 0, 1, 2, 3 order of reaction*
- *Experimental determination of rate law [order of reaction]*
- *Types of rate law: Differential and Integrated rate law*
- *Elementary and Complex reaction*
- *Reaction mechanism: Molecularity*

Chemical Kinetics

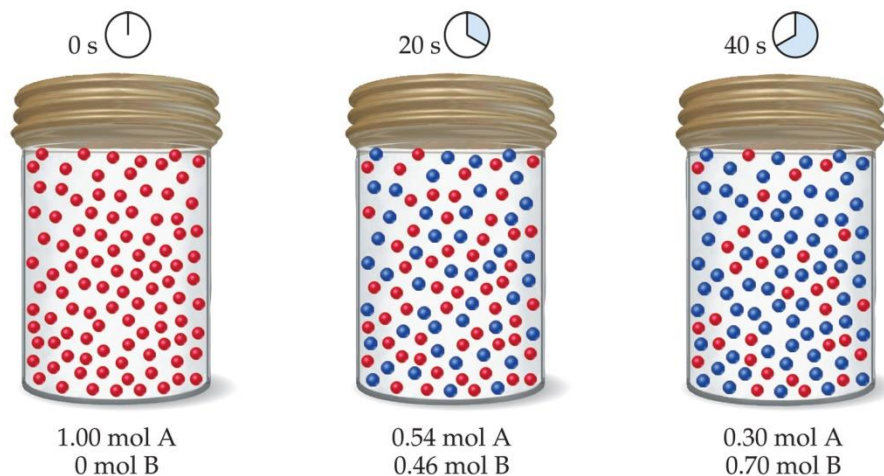
- ❖ *Chemical kinetics, also known as reaction kinetics, is the branch of physical chemistry that is concerned with understanding of **the rates of chemical reactions**.*
- ❖ *Besides information about the speed at which reactions occur, **kinetics also sheds light on the reaction mechanism** (exactly how the reaction occurs).*

Reaction Rates

Rates of reactions can be determined by monitoring the change in concentration of either reactants or products with a change in time.



$$-\frac{\Delta A}{\Delta t} = +\frac{\Delta B}{\Delta t} = \text{rate}$$



rate is always expressed as a positive value

- Reaction rate is measured in terms of the changes in concentrations of reactants or products per unit time.

Rate with respect to **A**

$$\text{Rate} = \frac{\text{Change in concentration of A}}{\text{change in time}} = - \frac{\text{Conc. } A_2 - \text{Conc. } A_1}{t_2 - t_1} = - \frac{\Delta[A]}{\Delta t}$$

- The negative sign is used because the concentration of A is decreasing. This gives the rate a positive value

Rate with respect to **B**

$$\text{Rate} = \frac{\text{Change in concentration of B}}{\text{change in time}} = \frac{\text{Conc. } B_2 - \text{Conc. } B_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}$$

- Square brackets indicate a concentration in moles per liter and time in second . So the unit of rate of reaction is mole/lit-sec

$$\text{Rate} = \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} \dots\dots\dots \text{for simpler reactions}$$



Time (s)	Concentration of O₃ (mol/L)
-----------------	---

0.0	3.20x10 ⁻⁵
-----	-----------------------

10.0	2.42x10 ⁻⁵
------	-----------------------

20.0	1.95x10 ⁻⁵
------	-----------------------

30.0	1.63x10 ⁻⁵
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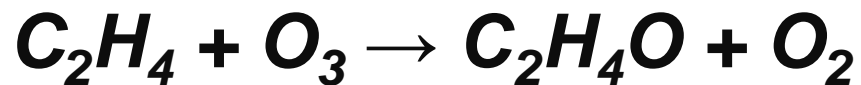
40.0	1.40x10 ⁻⁵
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50.0	1.23x10 ⁻⁵
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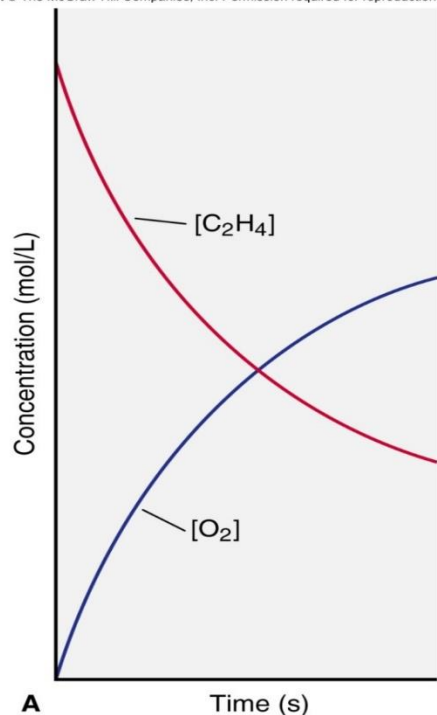
60.0	1.10x10 ⁻⁵
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$$\text{rate} = - \frac{\Delta [\text{C}_2\text{H}_4]}{\Delta t}$$

$$= - \frac{\Delta [\text{O}_3]}{\Delta t}$$



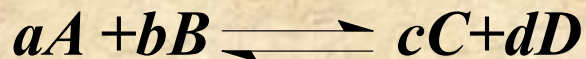
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$[\text{O}_2]$ increases just as fast as $[\text{C}_2\text{H}_4]$ decreases.

$$\begin{aligned} \text{Rate} &= - \frac{\Delta[\text{C}_2\text{H}_4]}{\Delta t} = - \frac{\Delta[\text{O}_3]}{\Delta t} \\ &= \frac{\Delta[\text{C}_2\text{H}_4\text{O}]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t} \end{aligned}$$

□ Equivalent rate expression: For a general reaction



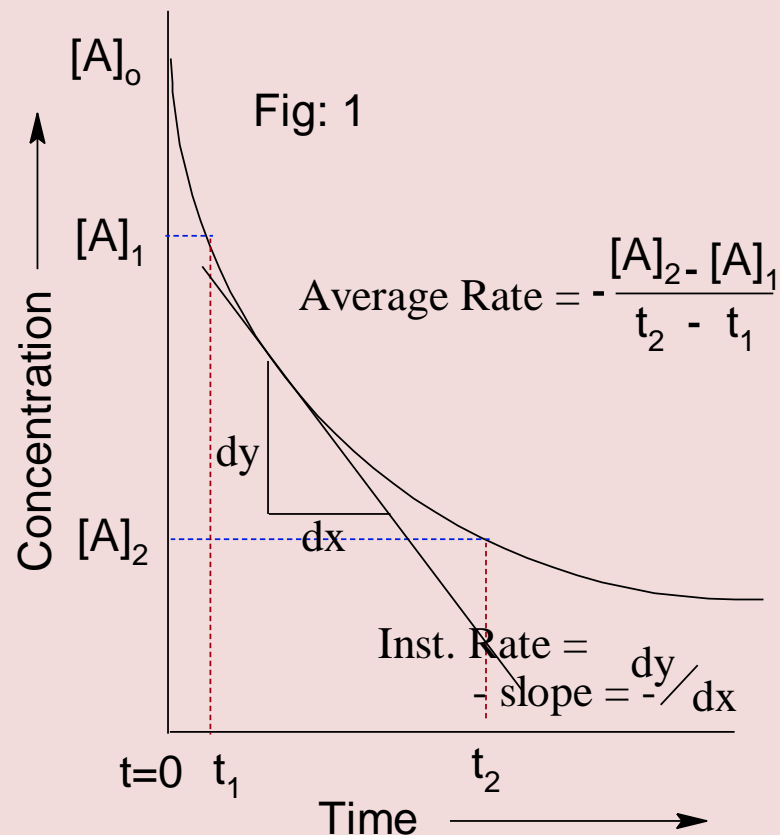
Then, equivalent rate expression is given by;

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c} \frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t}$$

(a) Average rate of reaction:

❑ The rate of change of concentration of reactants or products per unit interval of time is called **average rate of reaction**.

❑ *Note that the average rate decreases as the reaction proceeds. This is because as the reaction goes forward, there are fewer collisions between reactant molecules.*



$$\text{Average rate of reaction} = \frac{|\text{change in concentration of A}|}{\text{time taken}} = \frac{|\text{change in concentration of B}|}{\text{time taken}}$$

$$= \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} \quad \text{where, } \frac{\Delta[A]}{\Delta t}, \text{ represents the decrease of concentration with time}$$

(b) Instantaneous rate of reaction:

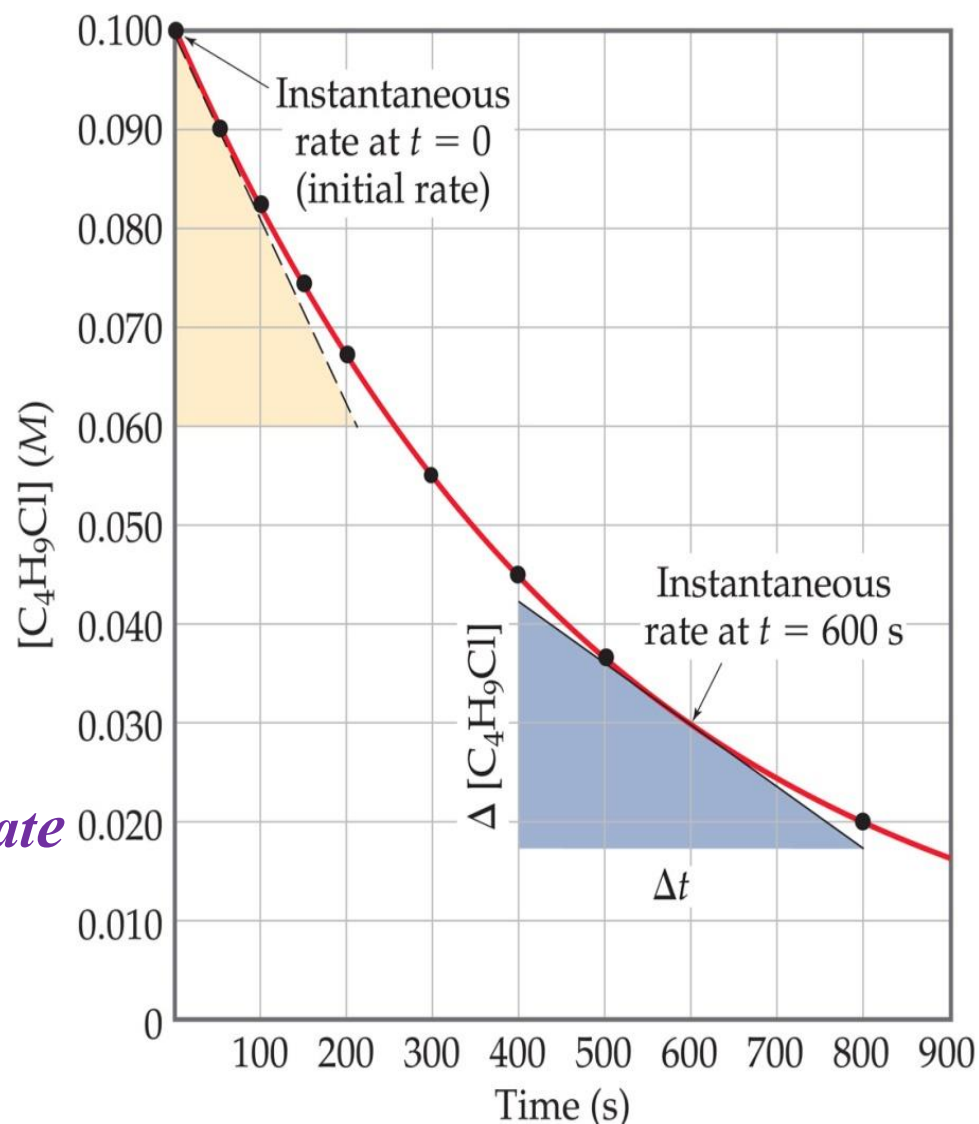
A plot of concentration vs. time for this reaction yields a curve like this.

- The rate of a reaction at a particular instant in time is called **instantaneous rate**.*
- The **slope of the tangent to the curve at any point** is the **instantaneous rate at that instant in time**.*

$$-\frac{\Delta A}{\Delta t} = -\frac{d[A]}{dt} = \text{Instantaneous rate}$$

$\Delta t \rightarrow 0$

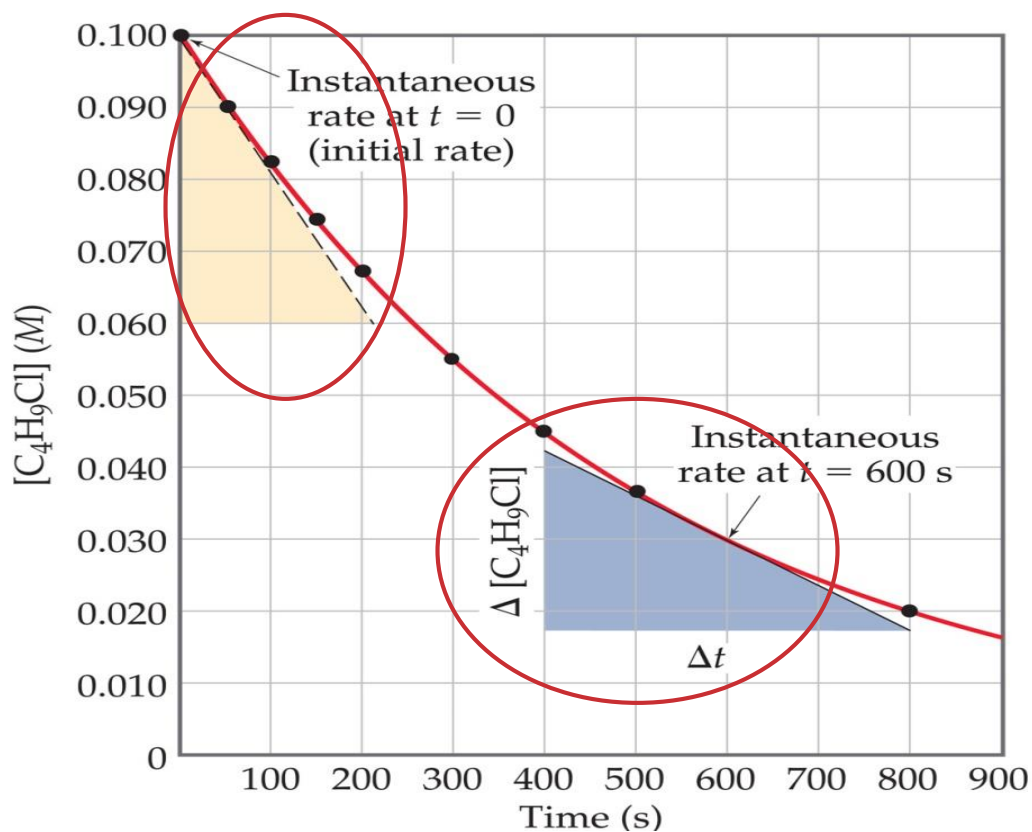
$$\text{Rate} = -\frac{dx}{dt}$$



The reaction slows down with time because the concentration of the reactants decreases.

$$-\frac{\Delta[A]}{\Delta t} = \frac{d[A]}{dt} = \text{Instantaneous rate} = \text{slope}$$

$$\Delta t \rightarrow 0$$



*Instantaneous rate =
(Average rate) $\Delta t \rightarrow 0$*

Factors Influencing Reaction Rates

1. Reactant Concentration: molecular collisions are required for reactions to occur

reaction rate \propto collision frequency \propto concentration

2. Physical State: *molecules must mix to collide*

When reactants are in different phases, the more finely divided a solid or liquid reactant, the greater the surface area per unit volume, the more contact it makes with other reactants, and the faster the reaction.

3. Temperature: molecules must collide with sufficient energy to react

Higher T translates into more collisions per unit time and into higher-energy collisions

reaction rate \propto collision energy \propto temperature

4. Catalysts: *Speed up reaction by changing mechanism.*

The Rate Law

- ❑ The **rate law** expresses the relationship the rate of reaction and concentration of reactants . It is experimentally determined.
- ❑ The derived rate law for a reaction must be consistent with the postulated chemical mechanism of the reaction!

For a general reaction: $aA + bB \rightarrow cC + dD$

rate law: $\text{rate} = k[A]^m \cdot [B]^n$

The term ***k*** is the **rate constant**, which is specific for a given reaction at a given temperature.

- ❑ The exponents *m* and *n* are reaction orders w.r.t A & B, and are determined by experimentally.
- ❑ The values of *m* and *n* are not necessarily related in any way to the coefficients *a* and *b*.

❑ **The overall order of the reaction** is the sum of individual orders = $n + m$. *Note: In above rate equation n and m are not the stoichiometric coefficients, they are the digits which are experimentally determined, may be 0, 1, 2, 3 or fractional etc.*

❑ **Order of reaction:** Order of reaction can be defined as the number of moles of reactants whose concentration will determine the rate of reaction i.e. (whose concentration will appear in the rate law).

1. If $n + m$ is zero the reaction is termed as zero order reaction,

i.e. rate is independent on concentration of reactants.

Example, $\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl}$ $\text{rate} = -dx/dt = k[\text{H}_2]^0[\text{Cl}_2]^0$.

2. If $n + m$ is one the reaction is termed as first order reaction.

Example $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$ $\text{rate} = -dx/dt = k[\text{N}_2\text{O}_5]$.

3. If $n + m$ is two the reaction is termed as **second order reaction**. Example, $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ rate = $-\text{dx}/\text{dt} = k[\text{H}_2][\text{I}_2]$.

4. If $n + m$ is three the reaction is termed as **third order reaction**. Third order reaction (order = 3): Example,
 $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ rate = $-\text{dx}/\text{dt} = k [\text{NO}]^2[\text{O}_2]$.

5. If $n + m$ is fraction the reaction is termed as **fractional order reaction**. **Fractional order:** Example,
 $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ rate = $-\text{dx}/\text{dt} = k[\text{H}_2]^1[\text{Br}_2]^{1/2}$
overall order = $3/2$.

❑ **Rate constant (k):** The rate of reaction when concentration of every reactant is unity. Rate of reaction = $k [\text{A}]^n[\text{B}]^m = k$; *if both concentrations are unity*. Rate constant remains constant for constant temperature and for the given chemical reaction.

Units of the rate constant, k , for several overall reaction orders

overall reaction order

units of k (t in seconds)

0

mol/L·s (or mol L⁻¹ s⁻¹)

1

1/s (or s⁻¹)

2

L/mol · s (or L mol⁻¹ s⁻¹)

3

L² / mol² · s (or L² mol⁻² s⁻¹)

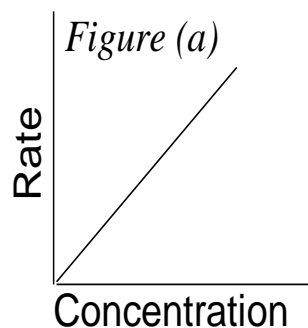
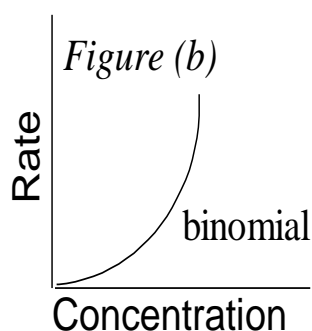
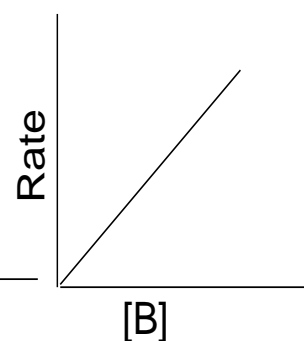
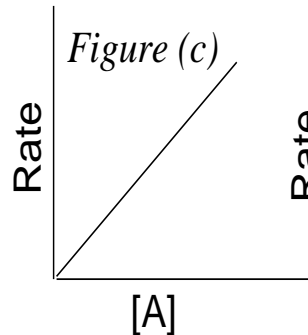
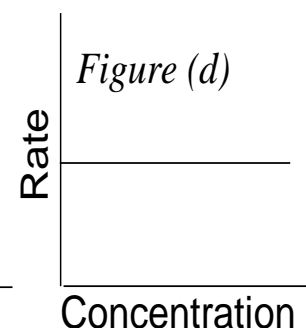
The value of k is easily determined from experimental rate data. The units of k depend on the overall reaction order.

Experimental determination of rate law [order of reaction]:-

For the simple reaction $A \rightarrow \text{products}$:

rate law: $\text{rate} = k[A]^m \dots\dots$

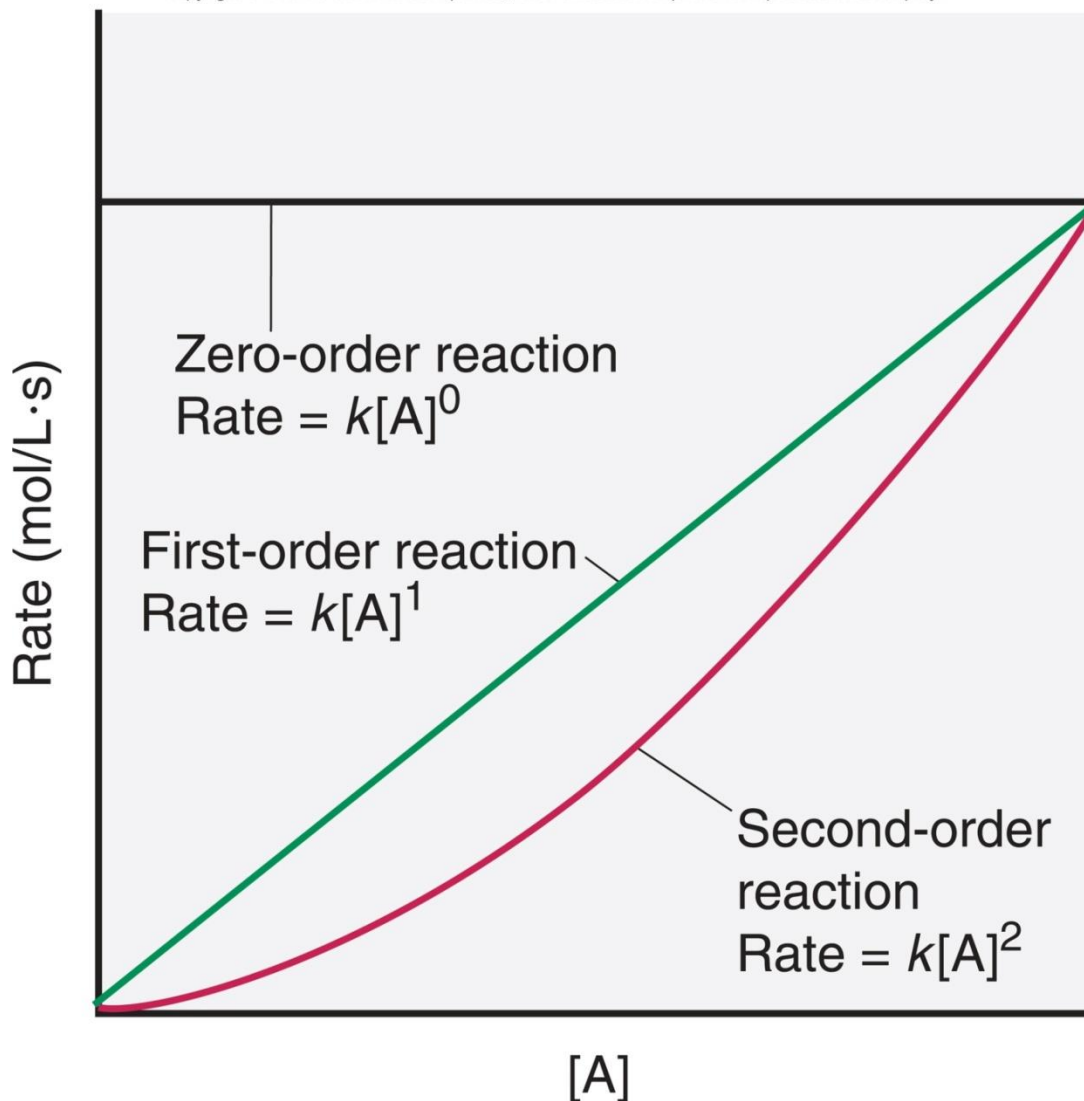
- ☐ *If the rate doubles when $[A]$ doubles, the rate depends on $[A]^1$ and the reaction is first order with respect to A .*
- ☐ *If the rate quadruples when $[A]$ doubles, the rate depends on $[A]^2$ and the reaction is second order with respect to $[A]$.*
- ☐ *If the rate does not change when $[A]$ doubles, the rate does not depend on $[A]$, and the reaction is zero order with respect to A .*

First order**Second order****Overall Second order****Zero order**

- ☐ If rate versus concentration graph is plotted we get the curve as in the figure (a). When the concentration is doubled it will double the rate of the reaction. So it helps to identify whether given reaction is first order or not.
- ☐ If rate versus concentration graph is plotted we get the curve as in the figure (b). When the concentration is doubled it will increase the rate of the reaction by four times. Rate versus concentration curve will be a parabola. So it helps to identify whether given reaction is second order or not.
- ☐ For the reaction $A + B \rightarrow \text{products}$ If the Graph of rate versus concentration with respect to [A] and [B] is plotted separately figure (c) and the total order is calculated. Total order = order w.r.t. A + order w.r.t. B = $1 + 1 = 2$.
- ☐ If rate versus concentration graph is plotted we get the curve as in the figure (d). There is no effect of concentration on the rate of the reaction.

Plots of rate vs. reactant concentration, [A], for first-, second-, and zero-order reactions.

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Experimental determination of rate constant (k):

- Once the order is determined, the rate constant can be calculated from Initial rate of the reaction or the average rate of the reaction is measured from the concentration of particular species at time t.
- It can be measured from spectroscopy, colorimetric measurement or from titration of the quenched solution.

$$k = \frac{\text{measured rate (initial)}}{\text{concentration of reactants with appropriate power}}$$

- It is very difficult to determine initial rate accurately.
- It is better to determine **k** from the integrated rate law.

Types of Rate Laws

- *Differential Rate Law (rate law) – shows how the rate of a reaction depends on concentrations.*
- *Integrated Rate Law – shows how the concentrations of species in the reaction depend on time. It is obtained by taking the integration of differential rate law*

Integrated Rate Law

Consider a simple **1st order rxn**: **$A \rightleftharpoons \text{Product}$**

rate = $k [A]$ **Differential form:** $-\frac{d[A]}{dt} = k [A]$

How much A is left after time t ? Integrate:

Type equation here.

$$-d[A] = k [A] dt$$

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

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

Taking the integration, A_0 at $t=0$ and A_t at time t .

$$\text{or, } \ln [A]_{A_0}^{A_t} = -k [t]_{A_0}^{A_t}$$

$$\text{or, } \ln \frac{A_t}{A_0} = -k t$$

The integrated form of first order rate law:

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

Can be rearranged to give:

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

$[A]_0$ is the initial concentration of A ($t=0$).

*$[A]_t$ is the concentration of A at some time, t ,
during the course of the reaction.*

Manipulating this equation produces...

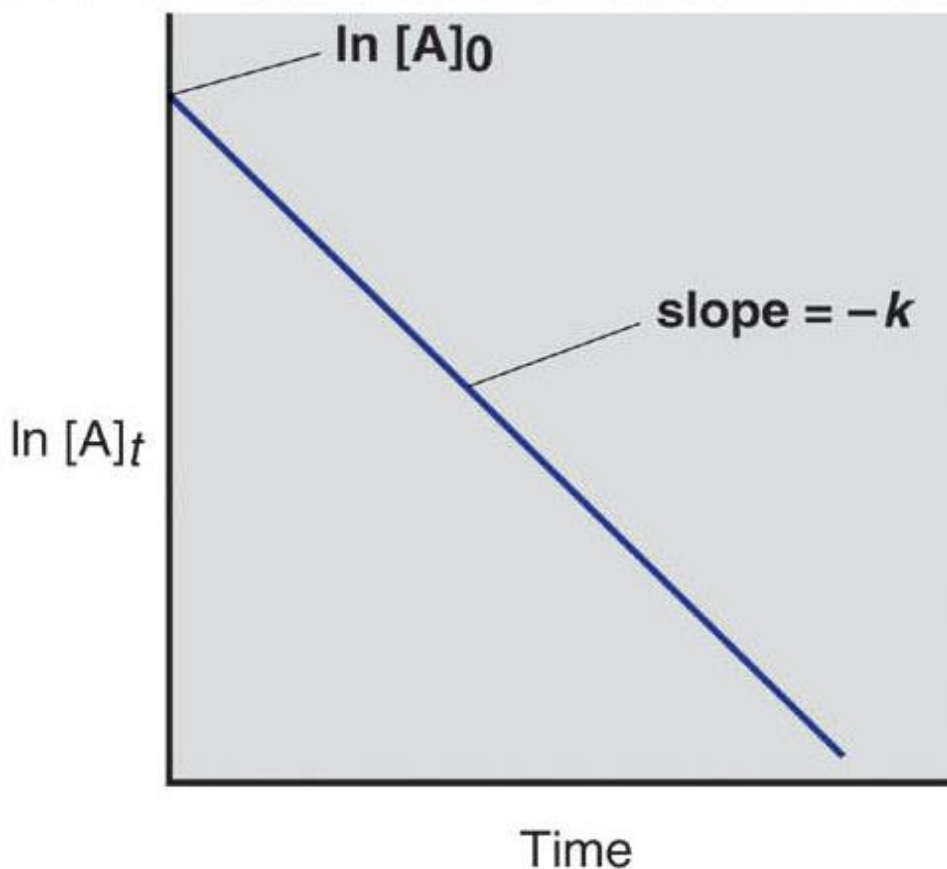
$$\ln \frac{[A]_t}{[A]_0} = -kt$$

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

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

...which is in the form $y = mx + c$

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



integrated rate law

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

straight-line form

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

- *If a reaction is first-order, a plot of $\ln [A]_t$ vs. t will yield a straight line with a slope of $-k$.*
- *For 1st order reaction, logarithm of reactant concentration decreases linearly as time increases.*

Second-Order Processes

Similarly, integrating the rate law for a process that is second-order in reactant A:

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

*Note, $\int 1/x \cdot dx$ or $\int x^{-n} dx$
or $\{(x^{-n+1})/(-n+1)\}$*

Rearrange, integrate:

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

also in the form,

$$y = mx + c$$

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

$[A]$ = concentration of A at time t

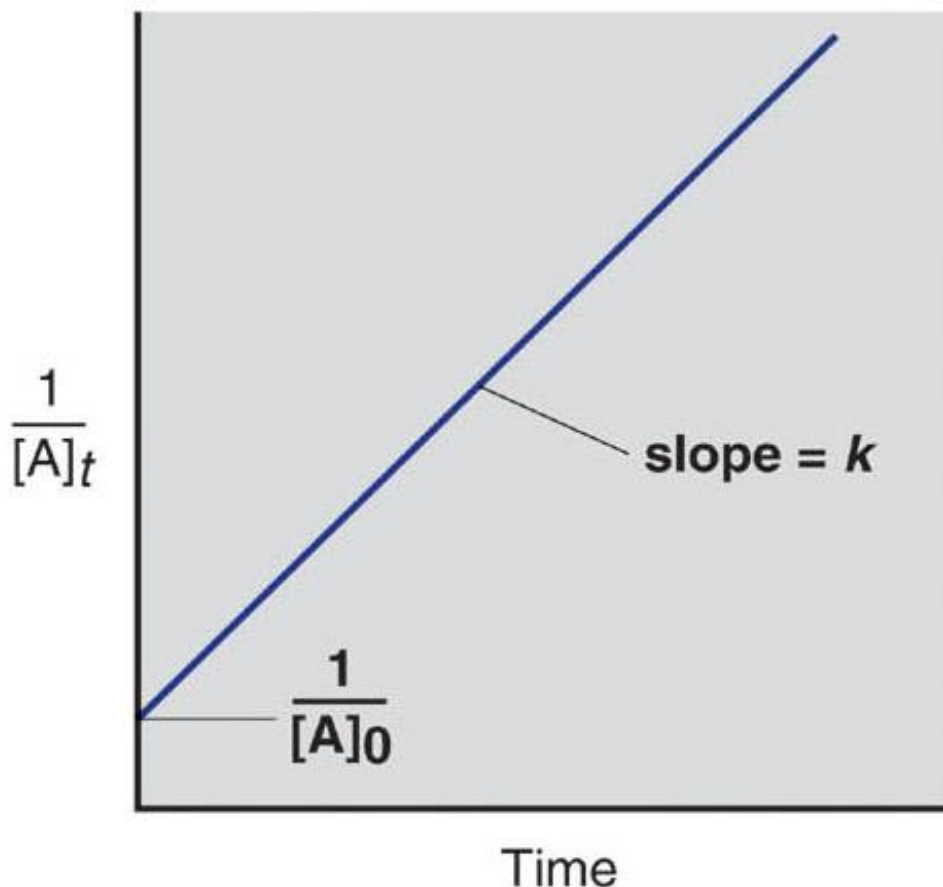
k = rate constant

t = time

$[A]_0$ = initial concentration of A

So if a process is second-order in A, a plot of $1/[A]$ vs. t will yield a straight line with a slope of k .

Second-order reaction



integrated rate law

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

straight-line form,

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

- A plot of $\frac{1}{A}$ vs. time gives a straight line for a second-order reaction.
- For 2nd order reaction, reciprocal of reactant concentration is a linear function of time

Reaction Half-life

- *The half-life ($t_{1/2}$) for a reaction is the time taken for the concentration of a reactant to drop to half its initial value.*
- *For a first-order reaction, $t_{1/2}$ does not depend on the starting concentration.*

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

- *The half-life for a first-order reaction is a constant. Radioactive decay is a first-order process. The half-life for a radioactive nucleus is a useful indicator of its stability.*

first order reaction: $A \rightarrow B$

Integrated rate equation: $\ln \frac{[A]_t}{[A]_0} = -kt$

After one half-life, $t = t_{1/2}$ and $[A]_t = 0.5[A]_0$. Substituting...

$$\ln \frac{0.5 [A]_0}{[A]_0} = -kt_{\frac{1}{2}}$$

$$\ln(0.5) = -kt_{\frac{1}{2}}$$

$$\ln(2) = 0.693 = -kt_{\frac{1}{2}} \qquad \frac{0.693}{k} = t_{\frac{1}{2}}$$

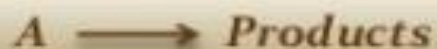
NOTE: For a first-order process, the half-life does not depend on $[A]_0$

Q. N. A first order reaction is 35% complete at the end of 55 minutes. What is the value of k?

$$k = 7.8 \times 10^{-3} \text{ min}^{-1}$$

An overview of zero-order, first-order and simple second-order reactions

	zero order	first order	second order
rate law	$rate = k$	$rate = k[A]$	$rate = k[A]^2$
units for k	$mol/L \cdot s$	$1/s$	$L/mol \cdot s$
integrated rate law in straight-line form	-----	$\ln[A]_t = -kt + \ln[A]_0$	$1/[A]_t = kt + 1/[A]_0$
plot for straight line	---	$\ln[A]_t$ vs t	$1/[A]_t$ VS t
slope, y-intercept	----	$-k, \ln[A]_0$	$k, 1/[A]_0$
half-life	----	$(\ln 2)/k$	----



Reaction Order "n"	Rate variation with Conc.	Differential Rate Law	Integrated Rate Law
1	Rate doubles when [A] doubles	Rate = $k [A]^1$	$\ln [A]_t / [A]_o = -kt$
2	Rate quadruples as [A] doubles	Rate = $k [A]^2$	$1/[A]_t = kt + 1/[A]_o$
0	Rate does not change with [A]	Rate = $k [A]^0$	$[A]_t - [A]_o = -kt$



Rate Law : $k[\text{NO}]^2[\text{H}_2]$

Order of reaction = 3

1st Order wrt $[\text{H}_2]$

2nd Order wrt $[\text{NO}]$

Stoichiometric coefficient of $[\text{H}_2] = 2$

Order with respect to $[\text{H}_2] = 1$

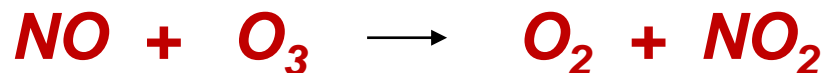


Reaction orders must be determined from experimental data and cannot be deduced from the balanced equation

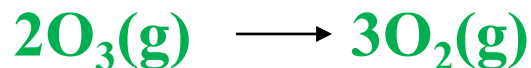
Elementary reaction	Complex reaction
<p><u>Single step</u> reaction</p>	<p>Involves 2 or more steps in the mechanism. Made up of a series of elementary reactions.</p>
<p>Chemical equation represents the actual changes taking place at a molecular level.</p> <p>Can write the rate equation from the stoichiometric equation for the reaction.</p>	<p>Chemical equation merely summarises the overall change involved.</p> <p>Rate equation must be determined experimentally.</p>
<p>For the general elementary reaction $aA + bB \rightarrow \text{products}$</p> <p>rate = $k[A]^a[B]^b$</p> <p>where a and b are the stoichiometric coefficients in the chemical equation and are the orders of the reaction with respect to A and B, respectively.</p> <p>For a first order reaction, $A \rightarrow \text{products}$ rate = $k[A]$</p> <p>For a second order reaction, $A + B \rightarrow \text{products}$ rate = $k[A][B]$</p>	<p>For the general complex reaction $aA + bB \rightarrow \text{products}$</p> <p>rate = $k[A]^m[B]^n$</p> <p>where m and n are the orders of the reaction with respect to A and B, respectively. They often have values 1 or 2, but sometimes take higher values, or even fractional values.</p> <p>The order of reaction with respect to a reactant may sometimes be zero (m = 0).</p> <p>A substance that does not appear in the overall chemical equation may sometimes appear in the rate equation.</p>

Reaction Mechanisms: Complex reaction

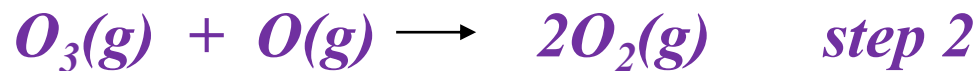
- A complete chemical description of how reactant molecules are converted to products- *reaction mechanism*. An example of a *one step conversion of reactants to products*



- On the other hand, *most chemical reactions do not follow such a simple path from reactants to products.*
- Another example;



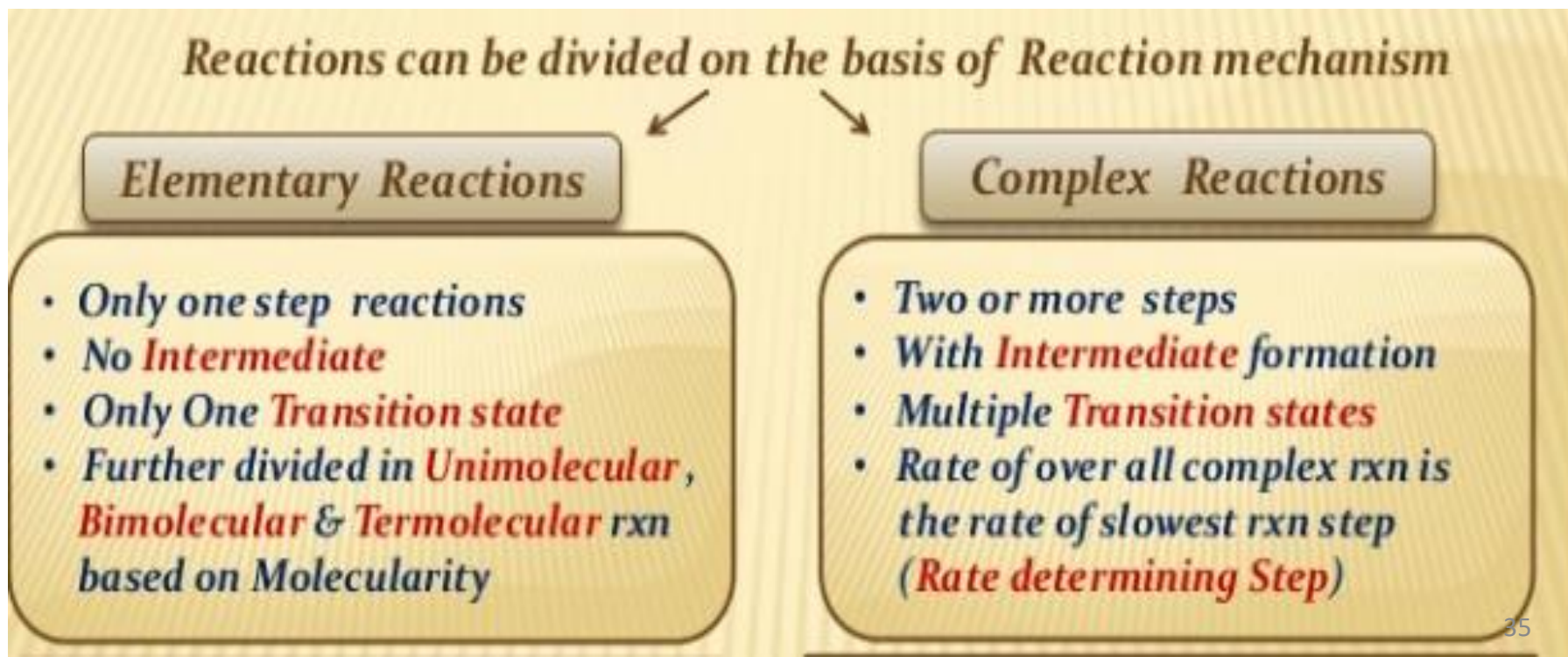
Mechanism



- *An intermediate is formed in one step and used up in a subsequent step and thus is never seen as a product in the overall balanced reaction.*

Reaction Mechanisms

- *Reactions may occur all at once or through several discrete steps. Each of these processes is known as an **elementary reaction** or **elementary process**.*
- *The sequence of events that describes the actual process by which reactants become products is called the **reaction mechanism***



Elementary Reactions and Molecularity

- *An **elementary reaction** is a chemical reaction in which one or more chemical species react directly to form products in a single reaction step and with a single transition state.*
- So, it is one step process in which all reacting species (molecules / atoms) collide simultaneously to give the product.
- *The **molecularity** of the elementary process is the no of molecules coming together once to proceed the reaction.*
- The **rate of such elementary step directly depends on all the reactant molecules.**
- *So, the order of reaction in the elementary process can be predicted from stoichiometric coefficients.*
- In this case, **Molecularity = order of reaction** (for elementary process / step).

Rate Laws for General Elementary Steps

Elementary reactions are single step process and are classified according to the number of molecules which they involve.

Molecularity	Elementary Reaction	Rate Law
Unimolecular	$A \longrightarrow \text{products}$	$\text{Rate} = k[A]$
Bimolecular	$A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^2$
Bimolecular	$A + B \longrightarrow \text{products}$	$\text{Rate} = k[A][B]$
Termolecular	$A + A + A \longrightarrow \text{products}$	$\text{Rate} = k[A]^3$
Termolecular	$A + A + B \longrightarrow \text{products}$	$\text{Rate} = k[A]^2[B]$
Termolecular	$A + B + C \longrightarrow \text{products}$	$\text{Rate} = k[A][B][C]$

The molecularity of a process tells how many molecules are involved in the process.

The rate law for an elementary step is written directly from that step.

Molecularity

Number of colliding molecular entities that are involved in a single reaction step
 Depending on the number of colliding species in elementary step it can be of different types

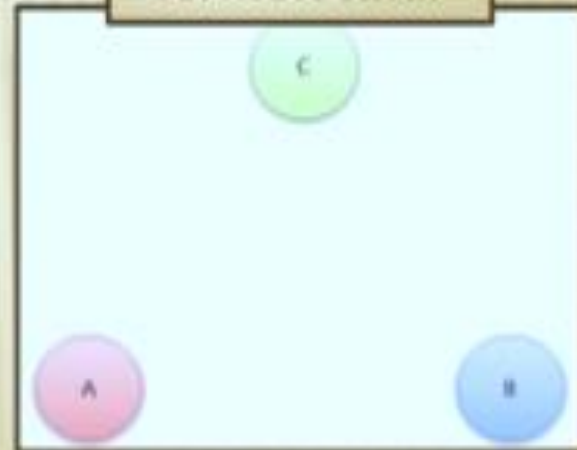
Unimolecular



Bimolecular



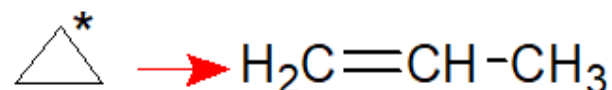
Termolecular



Molecularity	Elementary Step	Rate law	Examples
Unimolecular	$A \longrightarrow \text{Products}$	$\text{rate} = k [A]$	$\text{N}_2\text{O}_4(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$
Bimolecular	$A + A \longrightarrow \text{Products}$ $A + B \longrightarrow \text{Products}$	$\text{rate} = k [A]^2$ $\text{rate} = k [A][B]$	$2\text{NOCl} \longrightarrow 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$ $\text{CO}(\text{g}) + \text{NO}_3(\text{g}) \longrightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$
Termolecular	$A + A + A \longrightarrow \text{Products}$ $A + A + B \longrightarrow \text{Products}$ $A + B + C \longrightarrow \text{Products}$	$\text{rate} = k [A]^3$ $\text{rate} = k [A]^2 [B]$ $\text{rate} = k [A][B][C]$	$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$ $\text{H} + \text{O}_2(\text{g}) + \text{M} \longrightarrow \text{HO}_2(\text{g}) + \text{M}$

Other examples

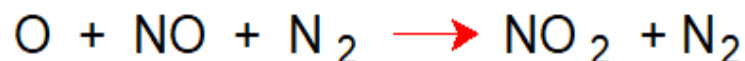
Type I: Unimolecular elementary process: Involves only one molecule as reactant in the elementary process. It may get collide with wall of vessel or with the catalyst.
e.g., dissociation and rearrangement reactions.



II: Bimolecular elementary process: Involves two molecules in the elementary process. For
e.g.,



III: Termolecular elementary process: Involves three molecules in the elementary process, which collide together and give the products. e.g.,



The third molecule (N_2) provides only the reaction site and helps to transfer the energy.

Elementary processes with Molecularity above three are very rare

- *Simultaneous collision of more than three species with proper orientation and sufficient energy (effective collision) to give the product is not favorable.*
- *In the elementary process all the species giving the product must collide at once. The probability of collision of these species is directly proportional to their individual concentration. Thus the reaction must be first order w. r. t. all individual species. Hence the total order will be equal to the number of colliding particles.*
- ***Note I:** if two molecules of same species are colliding order w. r. t. both should be considered.*
- ***Note II:** In elementary process, molecularity = order. But for the non elementary process molecularity \neq order.*
- *For example in $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ **Order** = 1 and **molecularity** = 1 or 2. The molecularity in a complex reaction is generally considered to be equal to the molecularity of the slowest elementary step.*

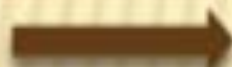
Molecularity

- Number of reacting species which collide to result in reaction
- Only positive integral values e.g 1,2,3 & never -ve
- Theoretical concept & value is derived from mechanism of reaction

Order

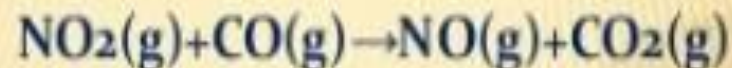
- Sum of powers to which concentrations are raised in the rate law expression
- Zero, fractional or even be -ve
- Experimental fact & derived from rate law

Rate
Determining
Step

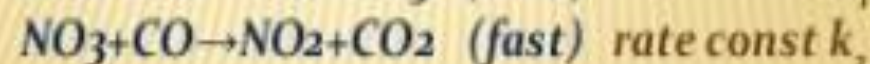
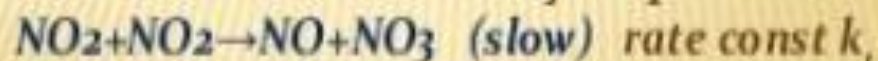


Slowest step of a chemical reaction that determines the speed (rate) at which the overall reaction proceeds

Eg: A complex reaction



occur in two elementary steps :



$$\text{Rate} = k_1 [\text{NO}_2][\text{NO}_2] = k_1 [\text{NO}_2]^2$$

Differences between order and Molecularity:-

Order of reaction	Molecularity of reaction
<ol style="list-style-type: none">1. It is the sum of concentration terms on which the rate of reaction actually depends or the sum of exponents of concentrations of reactants in the rate law equation.2. Cannot be calculated from stoichiometric coefficient of the reactants.3. It is experimentally determined.4. It may or may not be a whole number.[0, and fractional]]5. While writing order of reaction only molecules are raised to some exponent.6. May be changed depending on condition7. Should be calculated for a complex reaction	<ol style="list-style-type: none">1. It is the number of atoms/ molecules present in the reactant side of the elementary step, or in the rate determining step of the complex reaction.2. Can be calculated from the stoichiometric coefficient.3. Determined by simple calculation .4. It must be the whole number.5. Molecularity is calculated from no of atoms/molecules/ions.6. It is always constant for a given reaction7. Molecularity of the slowest rate determining step is the molecularity of complex reaction.

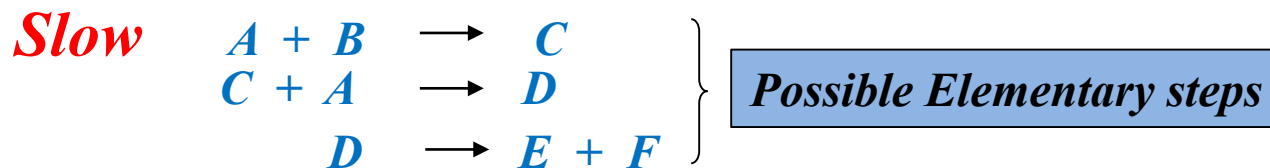
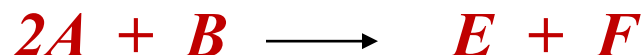
Give resonable explanations:

- ❖ *Elementary processes with molecularity greater than three are not known.*
- ❖ *The order of a reaction cannot, in general, be predicted from the stoichiometry of the overall reaction . However, the order of an elementary process is predictable.*

Reaction Mechanisms and Rate Law

- ❑ The experimentally observed order and rate of an overall reaction are related to the order and rate of elementary processes which comprise its mechanism.

Consider, a reaction as:



- ❑ Here the **products E and F** are the result of a sequence of three elementary steps and can be formed **no faster than the rate of slowest step in this sequence**. So, if any **one of the steps is much slower than all the others**, the rate of **overall reaction will be limited** by, and be exactly equal to the rate of this slow step. Here, **the slowest elementary step in a sequence** is called the **rate-determining step**. Suppose, first step in reaction mechanism is slowest one with the rate constant k_1 , then

$$\text{Rate} = -\frac{1}{2} \frac{d[A]}{dt} = k_1 [A] \cdot [B] \quad \{\text{Overall order is 2, wrt } A=1 \text{ and wrt } B=1\}$$

Determining molecularity and rate laws for elementary steps

PROBLEM: *The following two reactions are proposed as elementary steps in the mechanism of an overall reaction:*



- (a) *Write the overall balanced equation.*
- (b) *Determine the molecularity of each step.*
- (c) *Write the rate law for each step.*

PLAN:

We find the overall equation from the sum of the elementary steps. The molecularity of each step equals the total number of reactant particles. We write the rate law for each step using the molecularities as reaction orders.

SOLUTION:

(a) Writing the overall balanced equation:



***(b) Step(1) is unimolecular.
Step(2) is bimolecular.***

$$(c) \quad \text{rate}_1 = k_1[\text{NO}_2\text{Cl}]$$

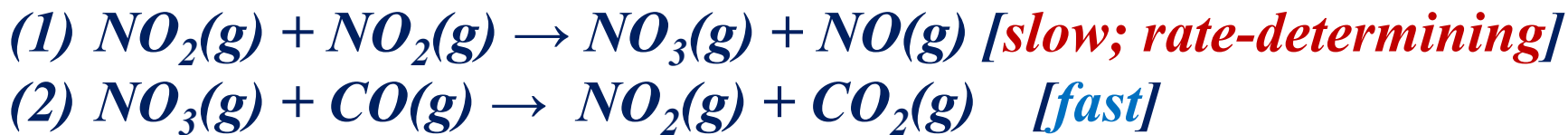
$$\text{rate}_2 = k_2[\text{NO}_2\text{Cl}] [\text{Cl}]$$

The Rate-Determining Step of a Reaction Mechanism

□ *All of the elementary steps of a mechanism do not occur at the same rate. Usually **one step** is much slower than the **others**. This step is called the **rate-determining (or rate-limiting) step**.*

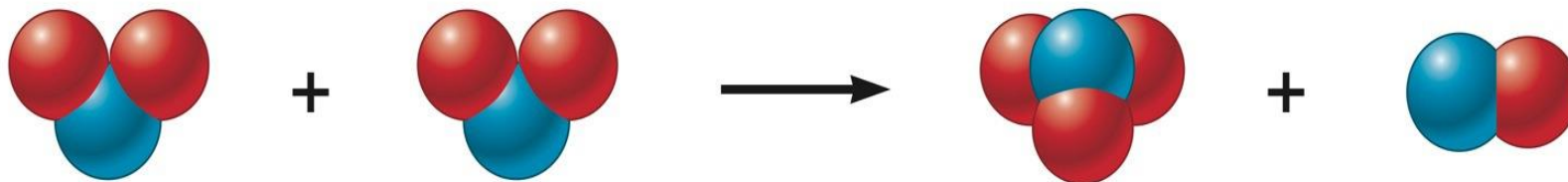
An example:

The reaction $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$ has been proposed to occur by a two-step mechanism:

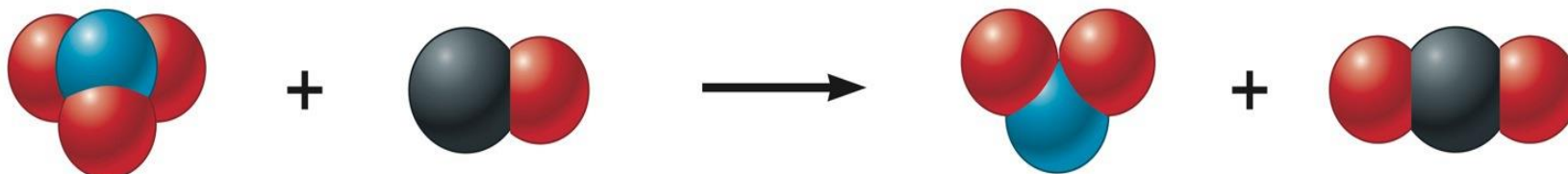




Step 1



Step 2



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Experimental rate law: $rate = k [NO_2]^2$



- In the above mechanism, Step 1 is **slow and rate-determining**; Step 2 is **fast**.

NO_3 is an **intermediate**!

- Thus, if $k_1 = k$, the rate law for Step 1 (rate-determining) is the same as the experimental rate law!

- Thus, the **rate law for the rate-determining step becomes the rate law for the overall reaction**.

Correlating the Mechanism with the Rate Law

- *A mechanism is a hypothesis –we cannot prove it is correct, but if it is consistent with the data, and can be used to predict results accurately, it is a useful model for the reaction.*

A valid mechanism must meet three criteria:

- 1. The elementary steps must add up to the overall equation.*
- 2. The elementary steps must be physically reasonable.*
- 3. The mechanism must correlate with the observed rate law.*

Reaction Energy Diagram for the two-step NO₂ - F₂ reaction

➤ *The overall reaction $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{NO}_2\text{F}(\text{g})$ has an experimental rate law,*

$$\text{Rate} = k[\text{NO}_2][\text{F}_2].$$

The accepted mechanism is,



The elementary steps sum to the overall balanced equation:

Both steps are bimolecular and are therefore reasonable.

$$\text{rate}_1 = k_1[\text{NO}_2][\text{F}_2]$$

$$\text{rate}_2 = k_2[\text{NO}_2][\text{F}]$$

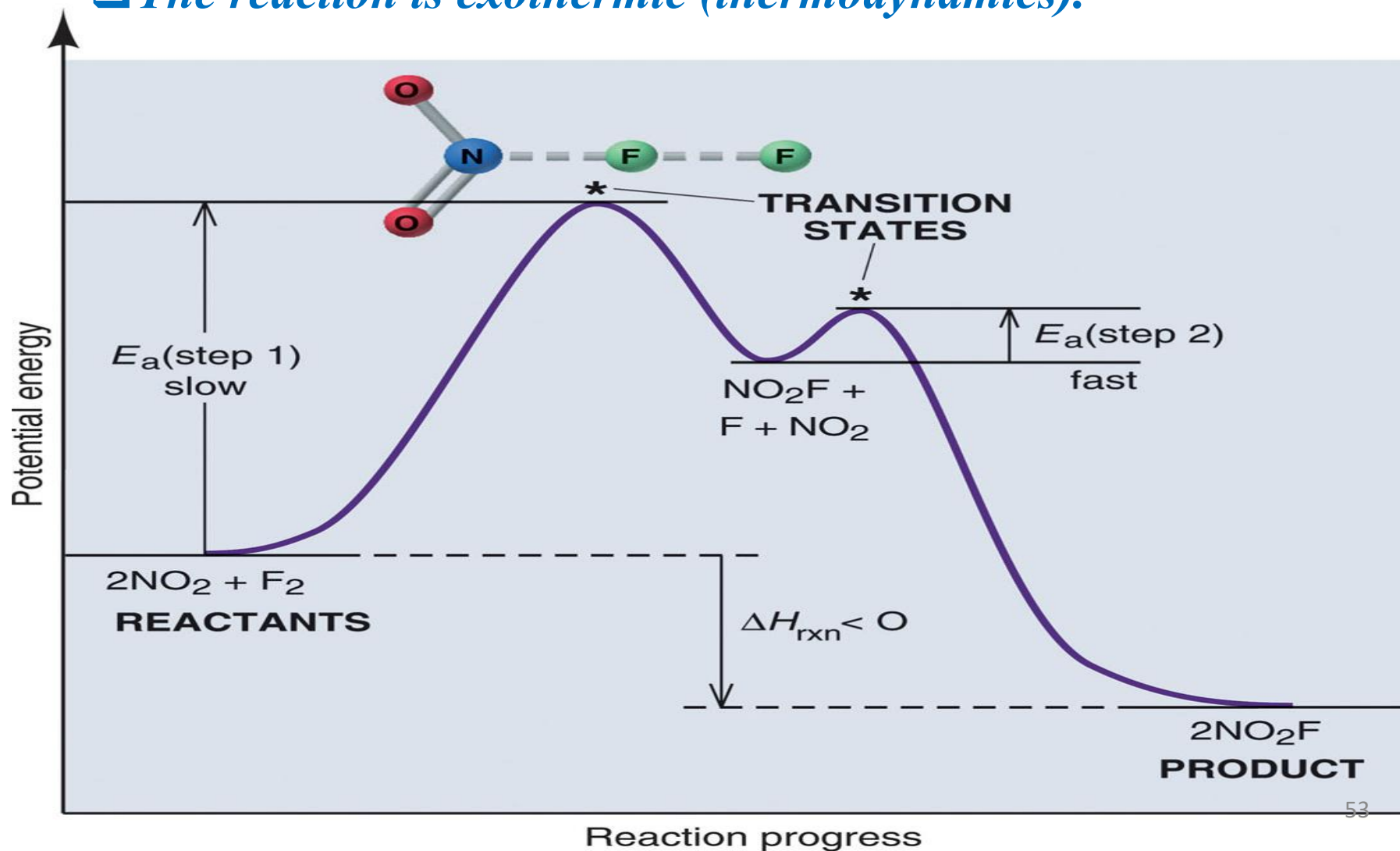
Step 1 is the slow step, and rate₁ correlates with the observed rate law.

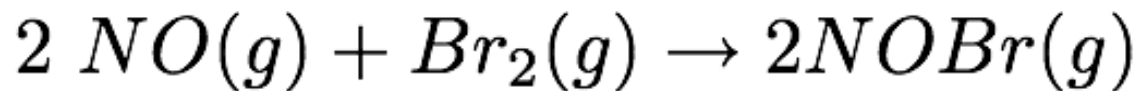
The mechanism is therefore reasonable.

❑ *Two transition states and one intermediate are involved.*

❑ *The first step is rate-determining.*

❑ *The reaction is exothermic (thermodynamics).*



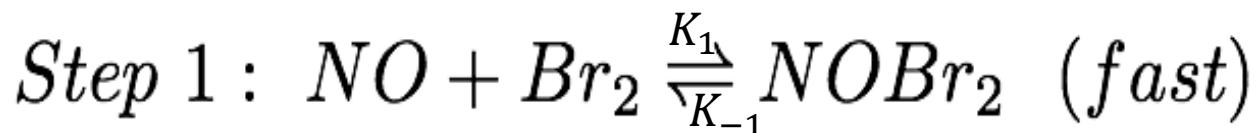


- *The rate law for this reaction is found (experimentally) to be*

$$\text{rate} = k [\text{NO}]^2 [\text{Br}_2]$$

- *Because termolecular processes are rare, this rate law suggests a two-step mechanism.*

A proposed mechanism is



Step 1 is an equilibrium- it includes the forward and reverse reactions.

- The rate of the overall reaction depends upon the rate of the slow step.*
- The rate law for that step would be*

$$\text{rate}_2 = k_2 [\text{NOBr}_2] [\text{NO}]$$

- But how can we find $[\text{NOBr}_2]$?*

- *NOBr_2 can react two ways:*
 - *With NO to form NOBr*
 - *By decomposition to reform NO and Br_2*
- *The reactants and products of the first step are in equilibrium with each other.*
- *Therefore,* $\text{Rate}_f = \text{Rate}_r$

$$k_1 [\text{NO}] [\text{Br}_2] = k_{-1} [\text{NOBr}_2]$$

Solving for $[\text{NOBr}_2]$ gives us

$$\frac{k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] = [\text{NOBr}_2]$$

Substituting this expression for $[NOBr_2]$ in the rate law for the rate-determining step gives

$$\begin{aligned} \text{rate} &= \frac{k_2 k_1}{k_{-1}} [NO] [Br_2] [NO] \\ &= \frac{k_2 k_1}{k_{-1}} [NO]^2 [Br_2] \end{aligned}$$

$$\text{rate} = k [NO]^2 [Br_2]$$

Steady State Approximation(SSA)

- ❑ *When **more than two steps** are involved in a mechanism, the rate law equation may be very complicated*
- *Multiple intermediates may form and their concentrations depend on each other.*
- *Some time intermediates react with other species (reactants, intermediates)*
- ❑ *If the intermediate is fairly reactive then they do not attain an appreciable concentration.*
- *If **an intermediate concentration is always small** , then **its change in concentration is also small** throughout the experiment*

$$\text{i.e. } \frac{d[I]}{dt} = 0$$

- *Key assumption: production and consumption of the intermediate occur at the same rate, so the rate of change in concentration of the intermediate with respect to time is zero.*

$$\text{i.e. } \frac{d[I]}{dt} = 0$$

- *The steady state approximation consists of selecting an intermediate in the reaction mechanism and calculating its concentration by assuming that it is destroyed as rapidly as it is formed.*
- *Therefore, according to the steady state approximation;*

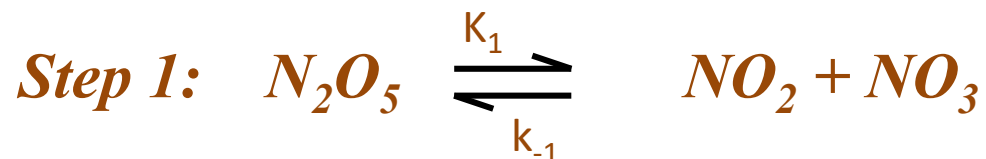
“Rate of production of Intermediate = Rate of destruction of Intermediate”

➤ *As a practical example of the application of SSA, let us consider the decomposition of gaseous N_2O_5 :*



The experimental rate law is: $\frac{d[O_2]}{dt} = k[N_2O_5]$

The mechanism is:



NO_3 and NO are the intermediates . let us find their steady state concentrations by using SSA.

For NO , we proceed as follows:

$$\begin{aligned}
 \text{Rate of production of NO} &= \text{Rate of destruction of NO} \\
 K_2 [\text{NO}_2][\text{NO}_3] &= k_3 [\text{NO}][\text{NO}_3] \\
 [\text{NO}] &= k_2/k_3 [\text{NO}_2] \dots \dots \dots (1)
 \end{aligned}$$

For NO_3 ,

$$\text{Rate of production of } \text{NO}_3 = \text{Rate of destruction of } \text{NO}_3$$

$$K_1 [\text{N}_2\text{O}_5] = K_{-1} [\text{NO}_2][\text{NO}_3] + K_2 [\text{NO}_2][\text{NO}_3] + K_3 [\text{NO}][\text{NO}_3]$$

$$K_1 [\text{N}_2\text{O}_5] = (K_{-1} [\text{NO}_2] + K_2 [\text{NO}_2] + K_3 [\text{NO}]) [\text{NO}_3] \dots \dots \dots (2)$$

Substituting the value of [NO] and solving for NO₃, equation (2) reduces to the form:

$$[NO_3] = \frac{K_1[N_2O_5]}{K_{-1}[NO_2] + 2 K_2[NO_2]} \dots\dots\dots(3)$$

The rate of reaction is also the rate of formation of oxygen,

$$\frac{d[O_2]}{dt} = K_2[NO_2]/[NO_3] \dots\dots\dots(4)$$

Using eqn.3 in eqn.4 and solving produces,

$$\frac{d[O_2]}{dt} = \frac{K_1 K_2 [N_2O_5]}{K_{-1} + 2 K_2} \dots\dots\dots(5)$$

This is as the same form as the experimental rate law. The relation between the experimental rate constant K and rate constants for the individual elementary steps is:

$$K = \frac{K_1}{K_{-1} + 2 K_2}$$

Chain reaction:

- ❑ In many of **the reactions occurring in gaseous phase** (flame, explosion and nuclear) or **in liquid phase** (like polymerization, natural/ synthesis) *an reactive intermediate* produced in the first step generates one or more intermediates in sequence of subsequent steps, so that the reaction proceeds continuously.
- ❑ The reactions occurring in this process are generally chain reactions.
- ❑ **The reactions proceeding in a series of successive steps once initiated by a suitable primary process is called chain reaction i.e. the reaction is continued after initiation.**

❑ The main steps of the chain reaction are:

1. The chain initiating step:

It is the first step in which *reactive intermediate species / chain carriers* are produced. These reactions are *mostly catalyzed by light (photolysis) and heat (thermolysis)*. It is generally *slow step so is the rate determining step*. Chain carriers are reactive species like, ions, free radicals, neutrons (in nuclear reaction) etc.

2. The chain propagation step:

Those steps in which *reactive intermediate reacts to give product and a new intermediate again*. That it produces *more and more reactive species successively*.

- *If two intermediates are produced by the loss of one, the reaction is termed as branching.*

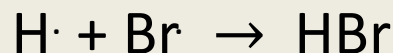


3. The chain termination step:

Those steps in which *two reactive intermediate combine (will decay/die) to give the product or non reactive species* and *ends the reaction are chain termination steps*.

4. Retardation:

- If *carrier strikes the product* and reduces the *rate of formation of product* is *the retardation step*.

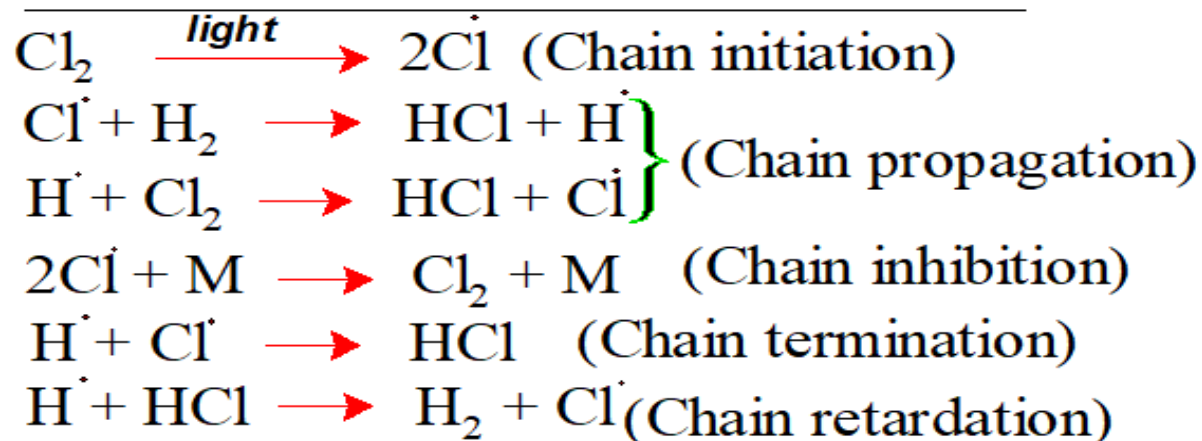


5. Chain inhibition step:

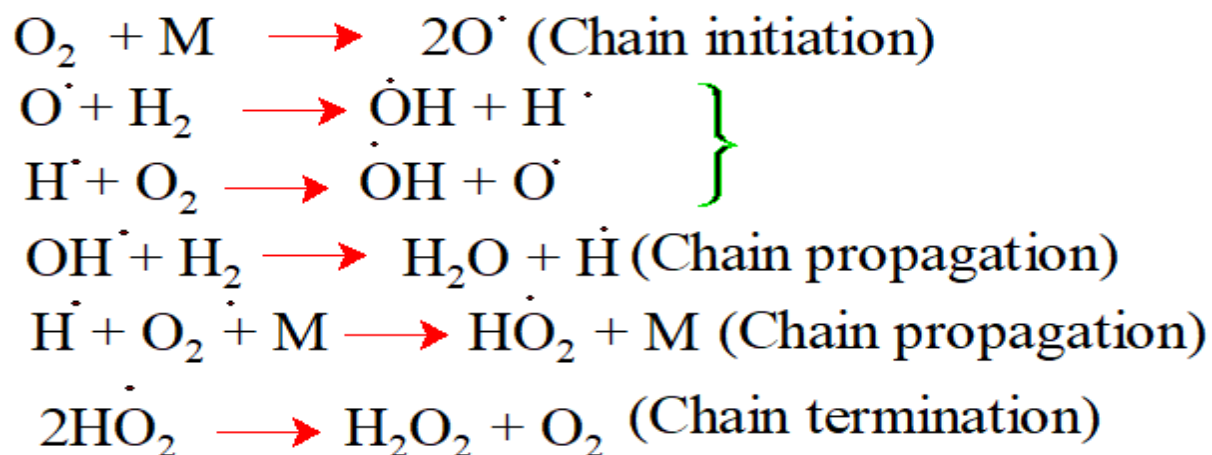
Those steps where radicals are removed by other away chain termination (i.e. with wall/foreign radicals) for example, NO molecule with odd electron is a better inhibitor, can also quench the reaction if present in excess.

Some common examples

1. $\text{H}_2 + \text{Cl}_2$ Reaction, $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$



2. $\text{H}_2 + \text{O}_2$ Reaction, $\text{H}_2 + \text{O}_2 \longrightarrow \text{H}_2\text{O}_2$



Polymerization of *ethylene* or *vinyl chloride* also follows chain mechanism.

- Polymerization is the process in which monomers (small compounds) combine to give long chain compounds (polymers).

Example; $2n \text{ (CH}_2\text{CHCl)} \rightarrow \{-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CHCl}-\}_n$

Vinyl chloride

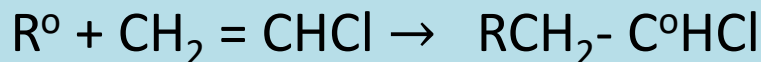
Polyvinyl chloride.

1. Chain initiation steps: Organic peroxides are easily split into free radicals in presence of light.

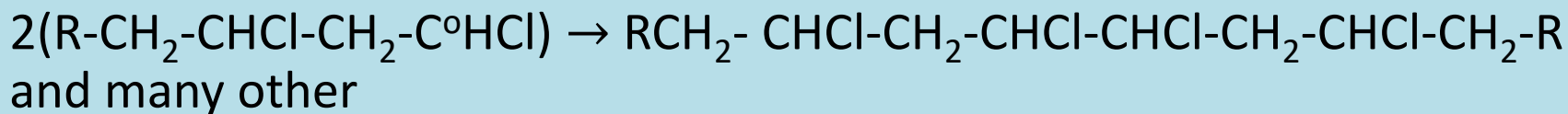


Benzoyl peroxide Consider R^\bullet = free radical.

2. Chain propagation: Free radicals combine with vinyl chloride and long chain free radical is formed.



3. Chain termination: Chain may terminate in any step.



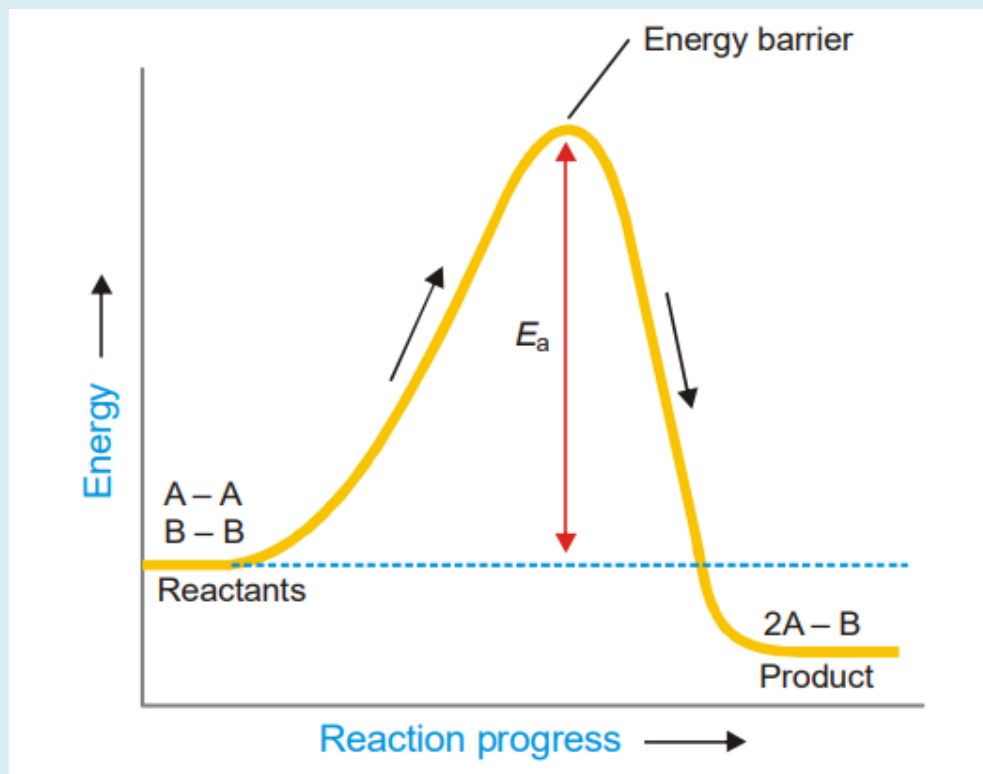
Collision Theory of Gaseous Reactions

- According to this theory, reactant molecules must undergo **collision to give the products** and **rate of reaction will depend** on the rate of collision.
- But **not all collisions are effective**. Only a small **fraction of the collisions produce a reaction**.
- The **two main conditions for a collision** between the reacting molecules **to be productive** are :
 - The **colliding molecules must possess sufficient kinetic energy** to cause a reaction.
 - The reacting **molecules must collide with proper orientation**.

(1) The molecules must collide with sufficient kinetic energy.

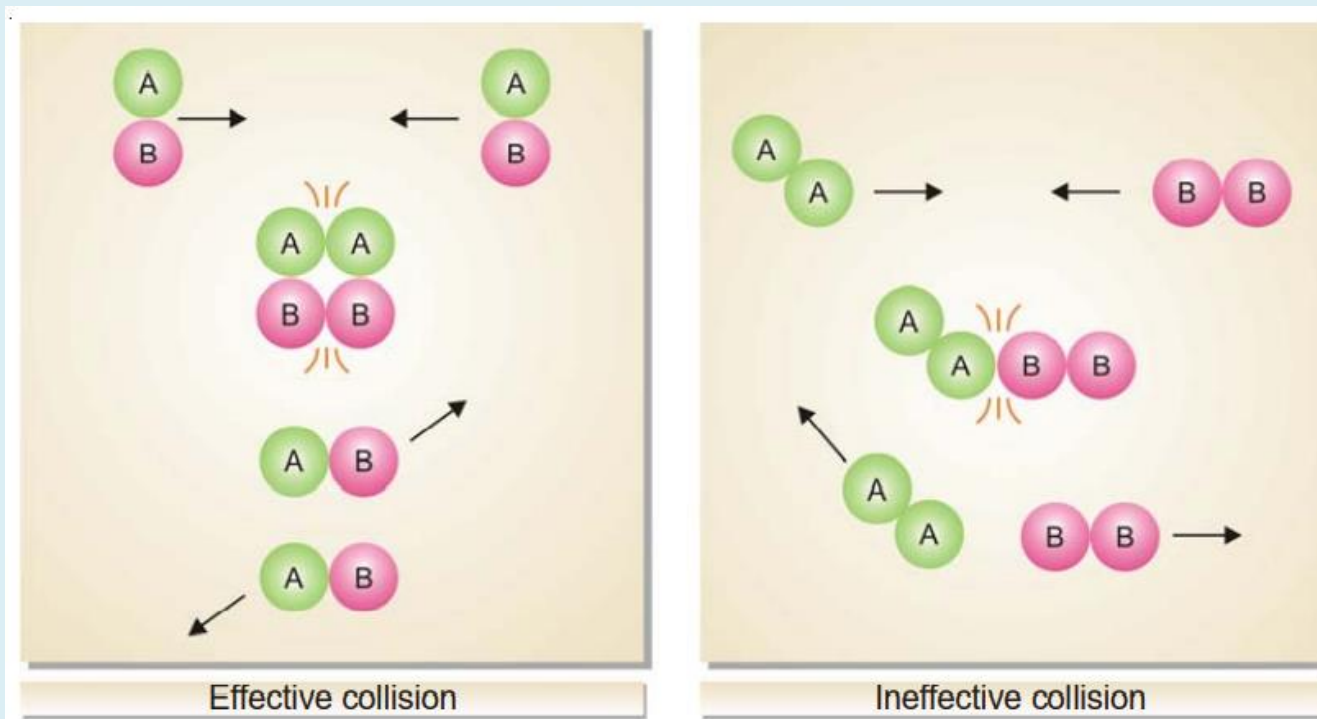
- Let us consider a reaction: $A - A + B - B \longrightarrow 2A - B$

- Activation energy, (E_a) is the minimum energy necessary to cause a reaction between the colliding molecules.
- Only the molecules that collide with a kinetic energy greater than E_a , are able to get over the barrier and react.



The energy of the colliding molecules as the reaction $A_2 + B_2 \rightarrow 2AB$ proceeds. The activation energy E_a provides the energy barrier.

(2) The molecules must collide with correct orientation.



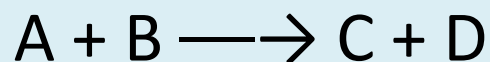
Orientations of reacting molecules A_2 and B_2 which lead to an effective and ineffective collision.

- The reactant molecules must collide with favourable orientation (relative position).
- The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming of bonds.

Only the molecules colliding with kinetic energy greater than E_a and with correct orientation can cause reaction

Collision Theory and Reaction Rate Expression

- Taking into account the two postulates of the collision theory,
- The reaction rate for the elementary process.



is given by the expression

- **rate = $f \times p \times z$**

- where

f = fraction of molecules which possess sufficient energy to react;

p = probable fraction of collisions with effective orientations, and

z = collision frequency

Temperature and Reaction Rate

*Increased $T \rightarrow$ Increased Average Speed Of Particles \rightarrow
Increased Collision Frequency \rightarrow Increased Reaction Rate*

*But,
most collisions fail to yield products!*

Significance of activation energy: *only those collisions with energy equal to, or greater than, E_a can yield products.*

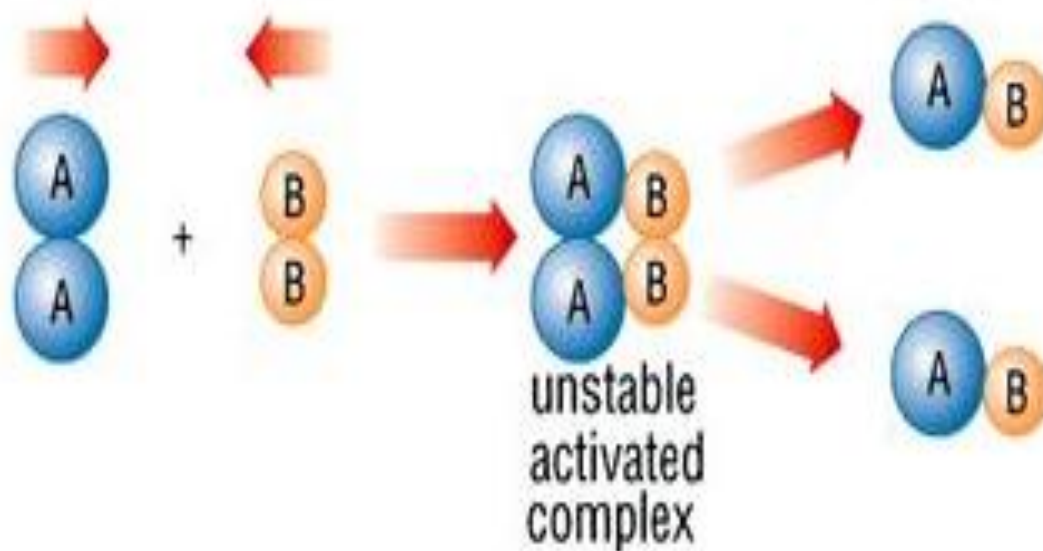
Increasing T enhances the fraction of productive collisions, f .

$$f = e^{-E_a/RT}$$

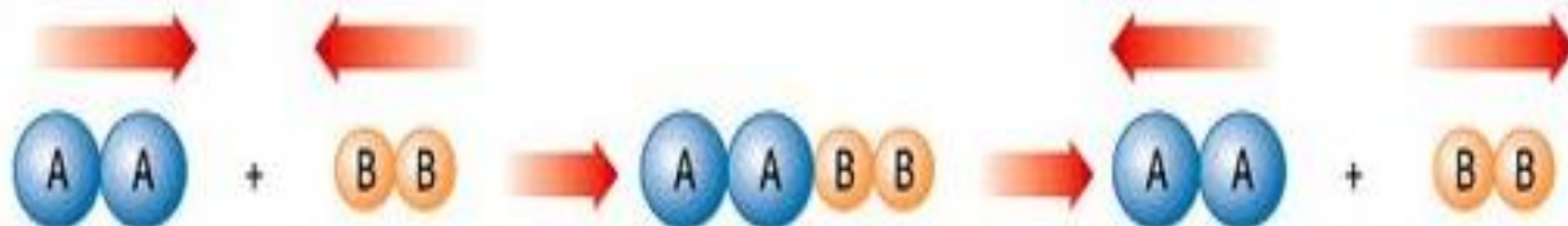
From this equation, we can see that both E_a and T affect f , which in turn influences reaction rate.

Generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by 10°C doubles the reaction rate.

a fruitful collision



an unfruitful collision



Effective Collisions

- ❑ *Not all collisions that occur with energy equal to, or exceeding, the activation energy lead to products.*

Molecular orientation is critical!

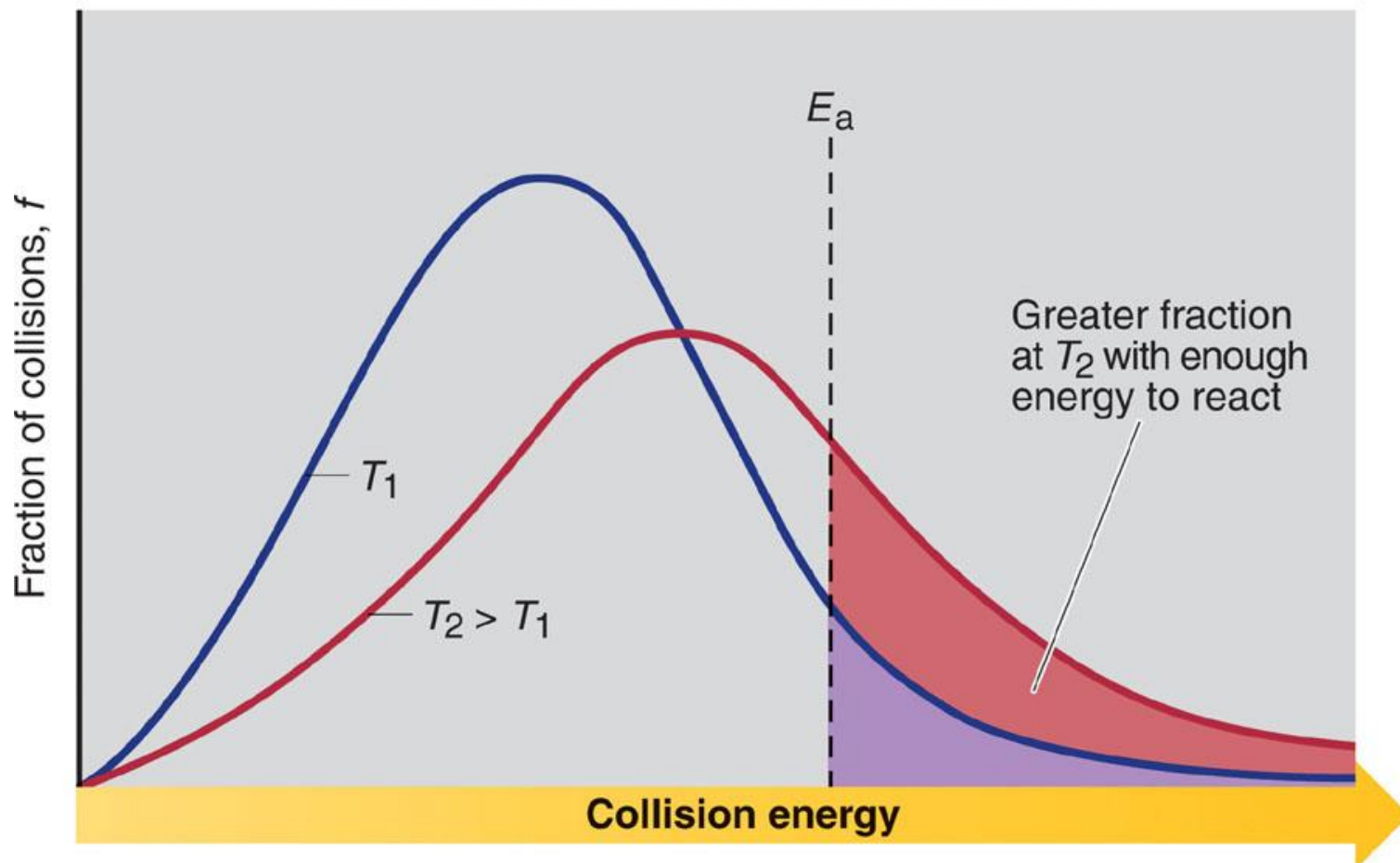
$$k = A e^{-E_a/RT}$$



- ❑ *The frequency factor = product of collision frequency Z and an orientation probability factor p ($A = Zp$)*

The effect of temperature on the distribution of collision energies

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Dependence of rate constant on temperature

□ **Arrhenius Equation:** Svante Arrhenius developed a mathematical relationship between k and E_a :

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

A = frequency factor

E_a = activation energy

R = gas constant (8.3145 J/K·mol)

T = temperature (in K)

k = rate constant of the reaction

Linear Form of Arrhenius Equation:

- *Taking the natural logarithm of both sides, the equation becomes*

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

$$y = mx + c$$

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

□ *The activation energy = the minimum energy that the molecules must possess in order for reaction to occur*

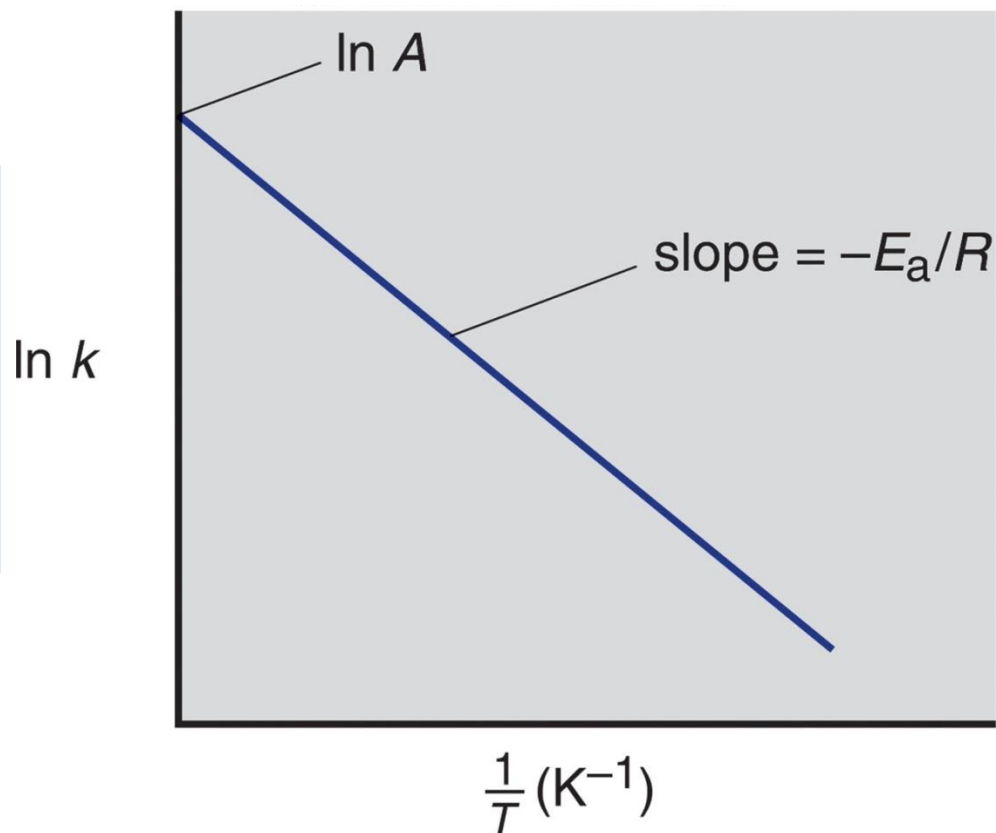
□ *The negative exponent suggests that, as T increases, the negative exponent becomes smaller (less negative), the value of k increases, and thus the reaction rate increases.*

higher T → larger k → increased rate

Graphical determination of the activation energy, E_a


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

- If the activation energy and value of the rate constant at one temperature are known, then it is possible to calculate the rate constant for any other temperature.



$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad (\text{I})$$

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad (\text{II})$$

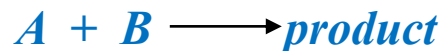

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (\text{III})$$

Catalysis: Enhancing Reaction Rates

- ☐ *Catalyst: A substance that speeds up a reaction without being consumed itself.*
- ☐ *Catalysts provide New faster paths by which reaction can proceed. This can be done in a variety of ways:*
 - ☐ *Provides a new pathway for the reaction with a lower activation energy.*
 - ☐ *The catalyzed reaction proceeds via a different mechanism than the uncatalyzed reaction.*
 - ☐ *Catalysts change the mechanism by which the process occurs.*

Energy diagram of an uncatalyzed and catalyzed reaction

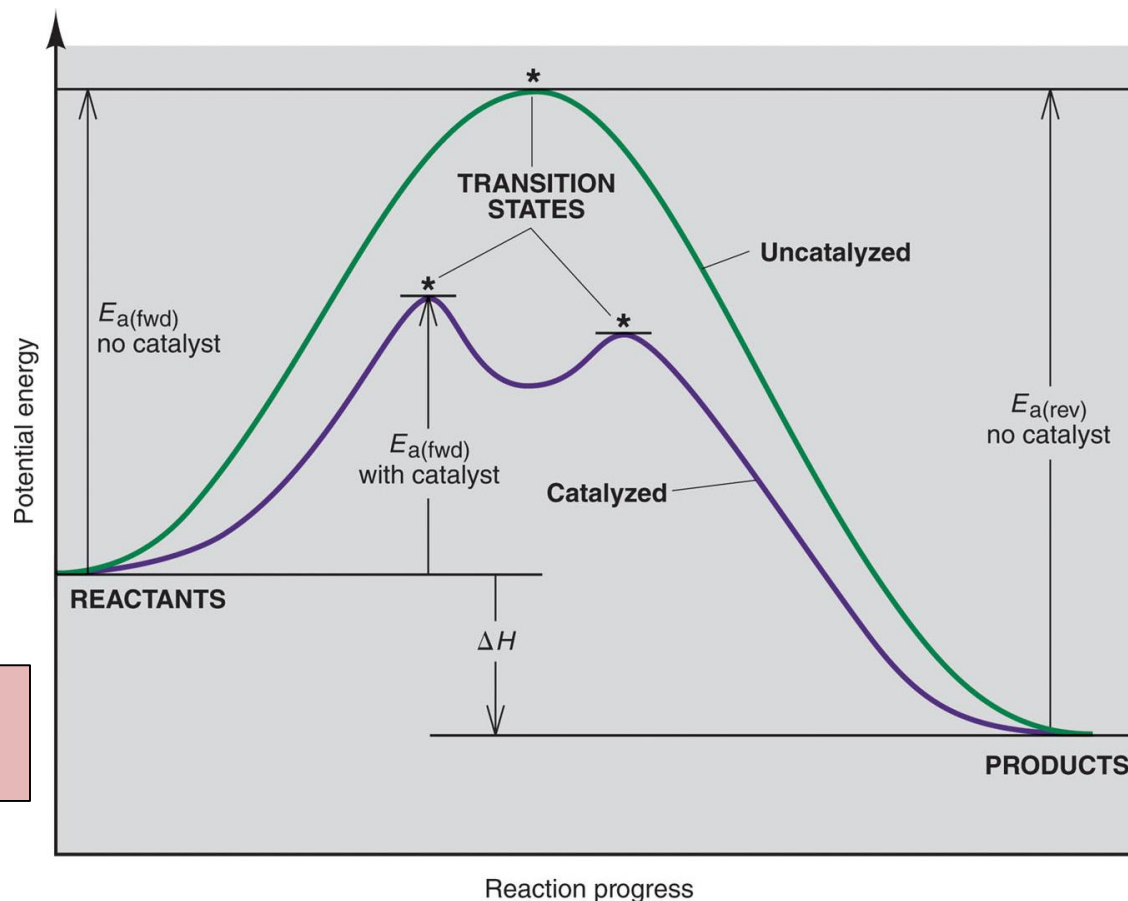
Uncatalyzed reaction:



Catalyzed reaction:



Note that both reactions exhibit the same thermodynamics!



A catalyst does not affect either ΔH or the overall yield for a reaction.

The catalyzed and uncatalyzed reactions occur via different pathways.

Types of Catalysts

- *Homogeneous catalysis:* *Exists in the same phase as the reacting molecules.*
- *Heterogeneous catalysis:* *catalyst and reaction mixture are in different phases*

□ *Homogeneous catalysis:*

*(1) Catalyst can act by modifying the electronic structure of the reactants. For example, the conversion of an alcohol to an organic halide is catalyzed by **hydrogen ion**. Find the role of hydrogen ion?*



□ *The presence of the proton on the hydroxyl group of the alcohol apparently lowers the activation energy of the second slow step*



*The above reaction is **slow**. Now the reaction is catalyzed by **Mn⁺⁺**, which acts in the following ways*

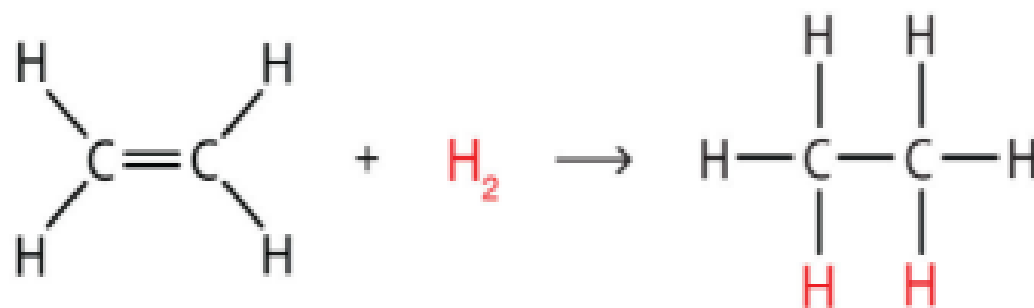
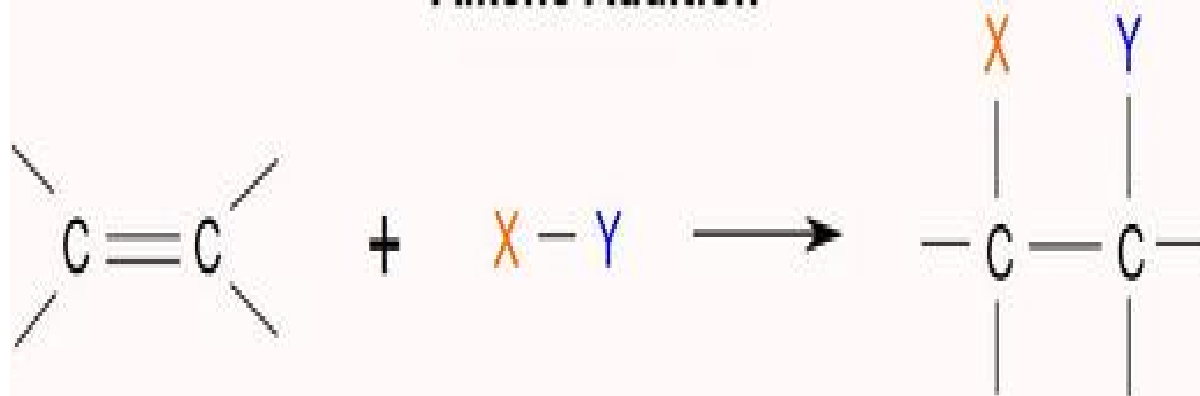


➤ ***Mn⁺⁺** permits a new mechanism whereby the single slow termolecular process is replaced by three Faster bimolecular elementary reactions*

Heterogeneous Catalyst

- 1. Most often involves gaseous reactants being adsorbed on the surface of a solid catalyst.*
- 2. Adsorption and activation of the reactants.*
- 3. Migration of the adsorbed reactants on the surface.*
- 4. Reaction of the adsorbed substances.*
- 5. Escape, or desorption, of the products.*

Alkene Addition



Ethylene

Hydrogen

Ethane

One of the outstanding example of the heterogeneous catalysis is the hydrogenation of unsaturated organic compounds.



The reaction is slow at moderate temperature in the gas phase. The same reaction is fast if carried out at the surface of the metal because these metal can absorb large quantities of hydrogen , apparently by incorporating it in the metallic lattice as hydrogen atoms. The process is represented by:



Where $M \cdot H$ represents the pool of atomic hydrogen in the metallic lattice. Thus hydrogenation takes place as:



In effect, the metal provides a new reaction path of low activation energy by dissociating the molecular hydrogen to atoms.

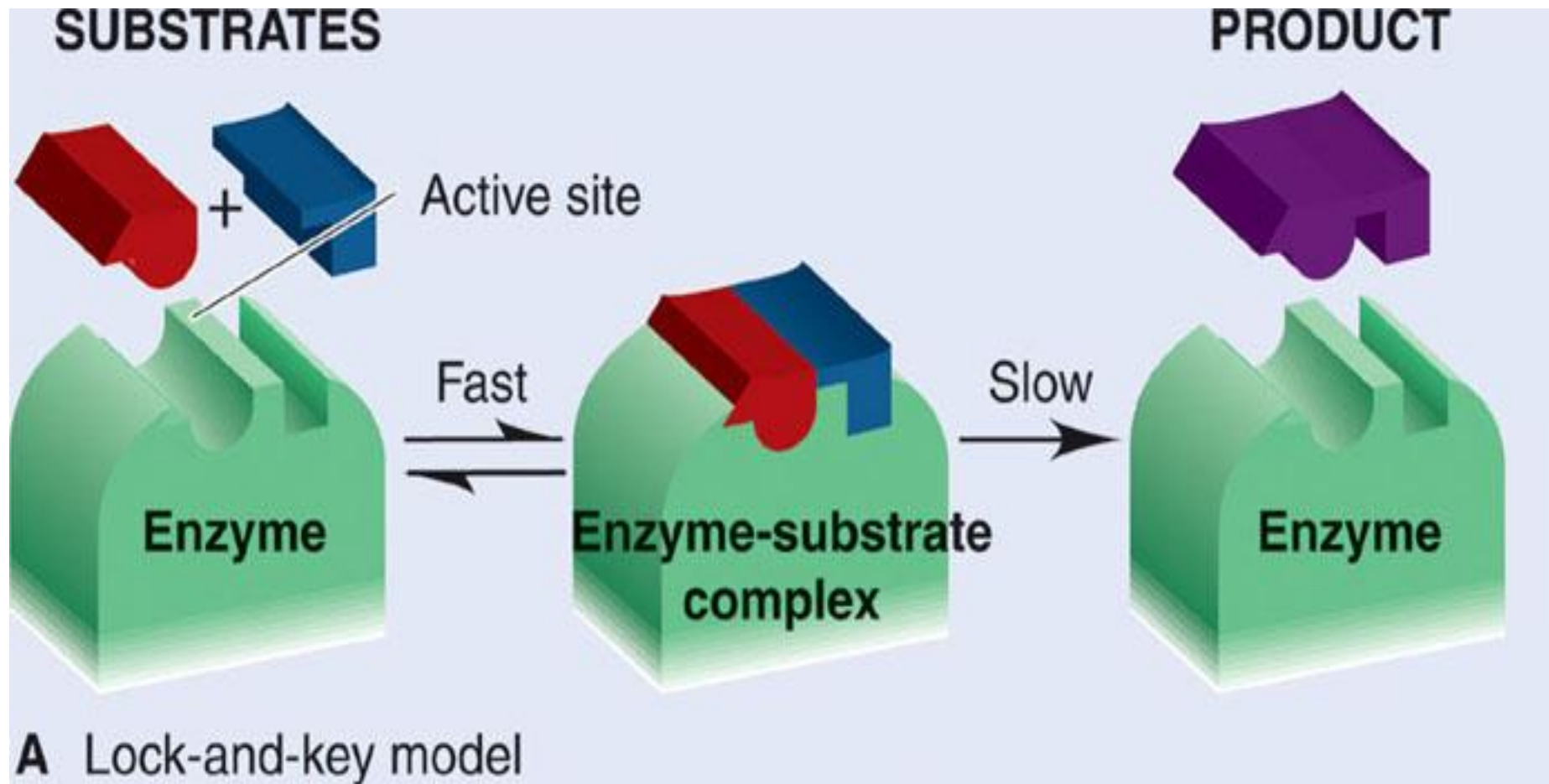
Enzyme Catalysis

- ❑ *Enzymes are **biological catalysts**. Catalysts are substances that increase the rate of chemical reactions without being used up. Enzymes are also proteins that are folded into complex shapes that allow smaller molecules to fit into them. The place where these substrate molecules fit is called the **active site**. Examples are **lactase**, **alcohol dehydrogenase** and **DNA polymerase**.*
- ❑ *On a molecular level, most catalysts (or most substances really) are not just flat surfaces, **they have complex three-dimensional shapes**. The substrate often has to bind to the catalyst in a very specific way in order for the catalyzed reaction to take place - this is the **active centre**.*

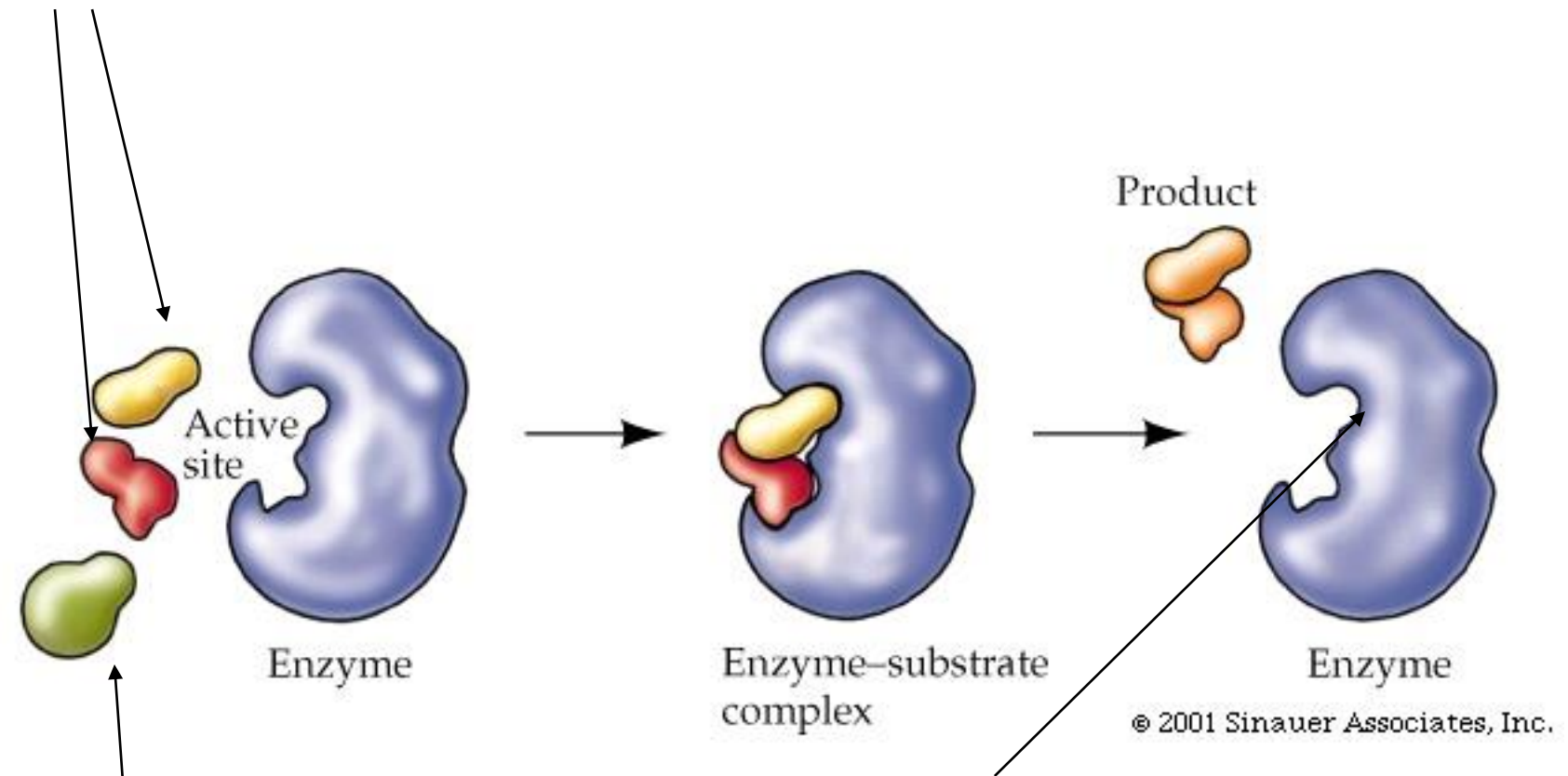
Characteristics of enzymes

- ❑ *Enzymes possess great catalytic power.*
- ❑ *Enzymes are highly specific.*
- ❑ *Enzymes show varying degree of specificities.*
- ❑ *Absolute specificity where the enzymes react specifically with only one substrate.*
- ❑ *The mechanism by which enzymes catalyzed chemical reactions begins with the binding of the substrates to the active site on the enzyme.*
- ❑ *The substrate fits into the active site of the enzyme much like a key fits into a lock.*

Model of Enzyme Action



Reactants: *Reactants in an enzyme-catalyzed reaction = “substrates”*



Not a substrate

Active site
or
substrate binding site
(not always exactly synonymous,
latter could be just a part of the active site)

Michaelis-Menten equation

- In 1913, Michaelis-Menten proposed a mathematical model of the reaction. It involves an enzyme, **E**, binding to a substrate, **S**, to form a complex, **ES**, which in turn releases a product, **P**, regenerating the original enzyme. This may be represented schematically as



- The double arrows between **S** (substrate) and **ES** (enzyme-substrate complex) represent the fact that **enzyme-substrate binding** is a reversible process, and the single forward arrow represents the formation of **P** (product).

- Let ***V*** be the rate at which product appears

$$V = k_2 [ES] \dots \dots \dots (1)$$

- To derive the equation for kinetics of enzyme catalyzed reaction, we use **steady state approximation** for the intermediate, ***ES***.

$$K_1 [E][S] = k_{-1} [ES] + k_2 [ES]$$

$$K_1 [E][S] = (k_{-1} + k_2) [ES] \dots \dots \dots (2)$$

- This equation might be solved for ***[ES]***, but it also contains , which is unknown. We **can write the enzyme conservation equation**.

$$[E_0] = [E] + [ES] \dots \dots \dots (3)$$

- Where ***[E₀]*** is the total concentration of the enzyme material. Solving this equation for ***[E]*** and substituting the result in equation(2), yields ***[ES]*** as follows:

$$K_1[S] \{[E_0] - [ES]\} = (k_{-1} + k_2)[ES]$$

$$K_1[E_0][S] - K_1[S][ES] = (k_{-1} + k_2)[ES]$$

$$(k_{-1} + k_2)[ES] + K_1[S][ES] = K_1[E_0][S]$$

$$[ES] \{(k_{-1} + k_2) + K_1[S]\} = K_1[E_0][S]$$

$$[ES] = \frac{K_1[E_0][S]}{k_{-1} + k_2 + K_1[S]} \dots\dots\dots(4)$$

Substituting this in equation (1), we find the rate of reaction given by

$$V = \frac{k_2 K_1[E_0][S]}{k_{-1} + k_2 + K_1[S]}$$

Divide the numerator and denominator by K_1 , the result is:

$$V = \frac{k_2 [E_0] [S]}{k_m + [S]} \dots\dots\dots (5)$$

This expression is known as the Michaelis—Menten equation.

Understanding k_m

$$k_m = \frac{k_{-1} + k_2}{k_1}$$

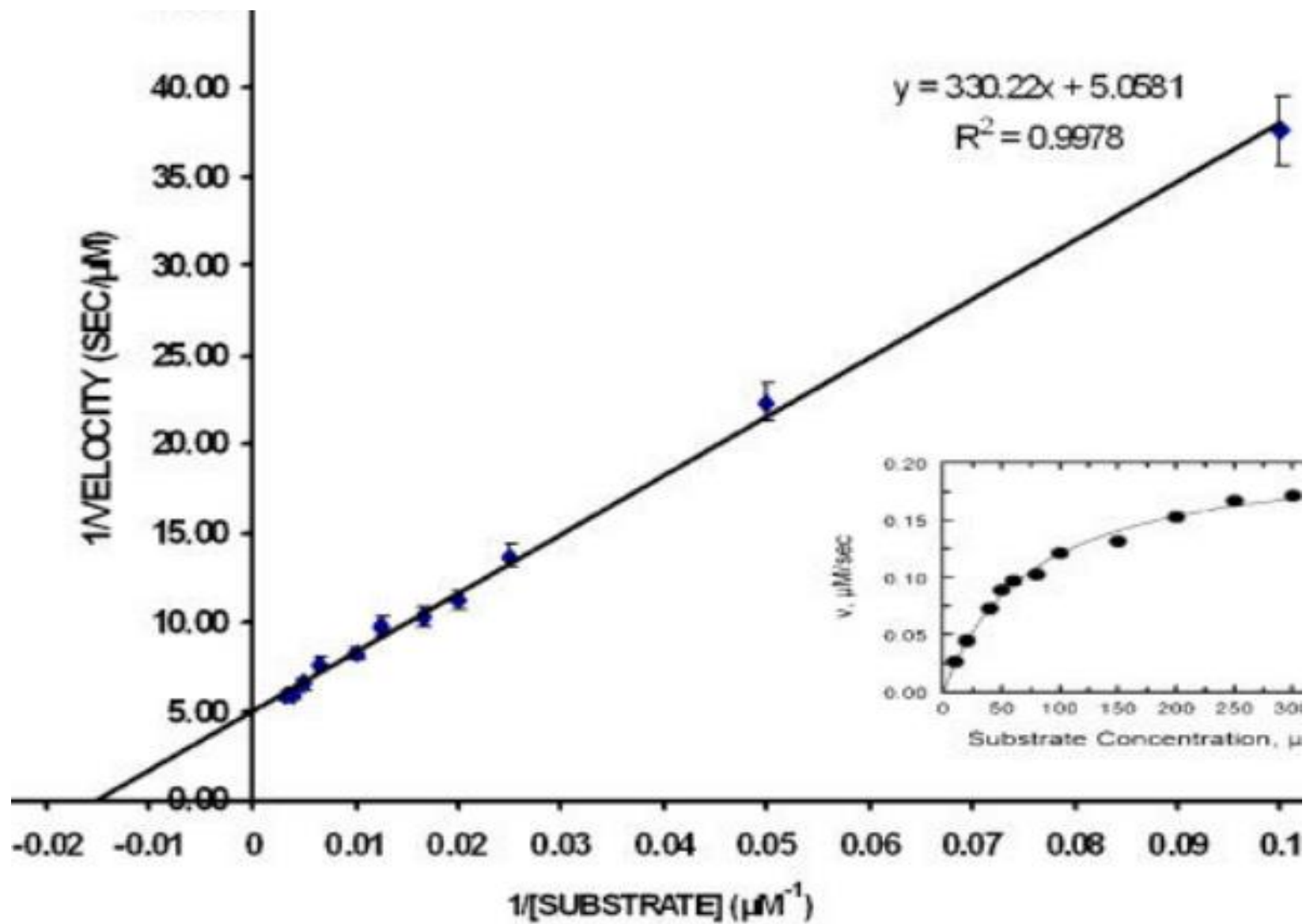
*The **lower the K_m** , the **more poorly it dissociates**. That is, the more **TIGHTLY** it is held by the enzyme*

*And **the greater the K_m** , the **more readily the substrate dissociates**, so **the enzyme is binding it poorly***

□ *From equation (5), by taking the reciprocal of both sides, we have the another common form of the Michaelis-Menten rate law:*

$$\frac{1}{V} = \frac{1}{k_2[E_0]} + \frac{k_m}{k_2[E_0][S]} \dots\dots\dots(6)$$

□ *Thus the reciprocal of the reaction rate is a linear function of the reciprocal of the substrate concentration when the total amount of the enzyme is held constant.*



We have, Michaelis—Menten equation as:

$$V = \frac{k_2 [E_0] [S]}{k_m + [S]} \dots (a)$$

Let us analyze the dependence of reaction rate on the concentration of the substrate given by this equation.

□ Condition 1

At sufficiently low substrate concentration: $[S] \ll K_m$

Hence the concentration of substrate can be neglected compared to K_m

And equation(a) reduces to the form as given below:

$$V = \frac{k_2 [E_0] [S]}{k_m}$$

- *This rate law equation shows that the rate is first order with respect to substrate concentration.*

□ Condition 2

At sufficiently high substrate concentration: $K_m \ll [S]$

- *Hence K_m is neglected compared to concentration of substrate and equation(a) reduces to the form as given below:*

$$V = k_2 [E_0]$$

- *This rate law equation shows that the rate is zero order with respect to substrate concentration.*

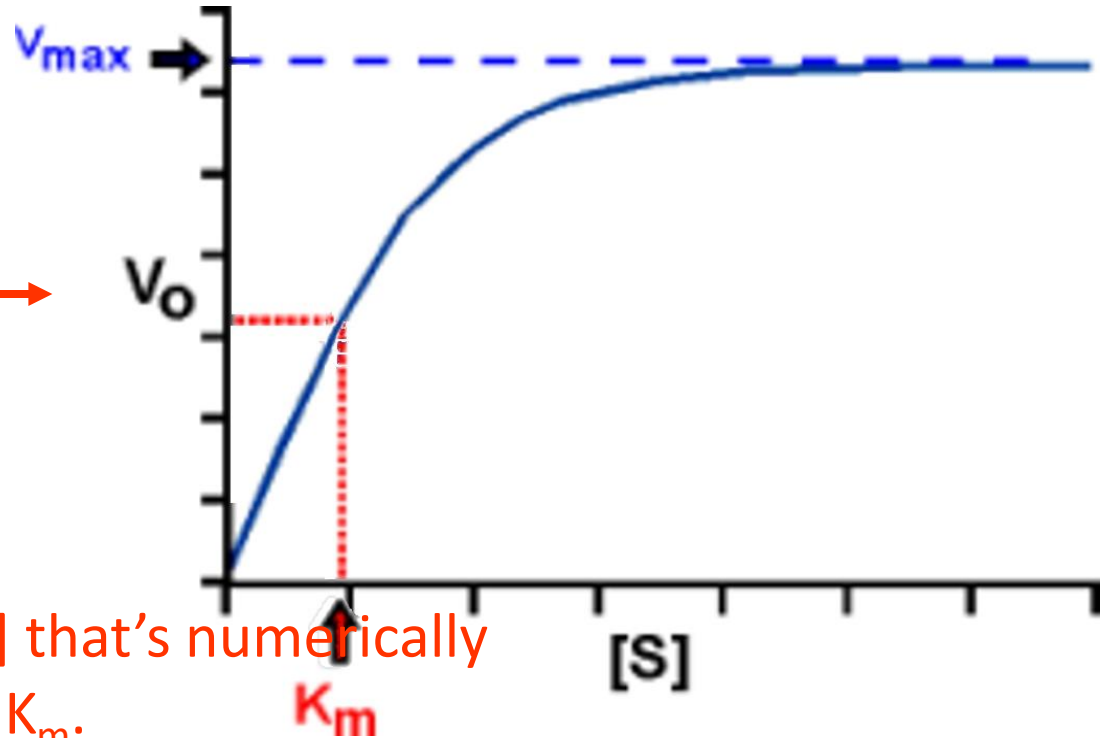
Question

???????

Give the physical reason behind reaction rate which changes from first to zero order with respect to substrate concentration as the substrate concentration is increased.

Understanding K_m

Consider the \longrightarrow
 V_o that is equal
to 50% of V_{max}



$V_{max}/2$ is reached at a $[S]$ that's numerically
equal to K_m .

Try it (Set $V_o = \frac{1}{2} V_{max}$ in M.M. equation and
solve for $[S]$).

So, K_m is numerically equal to the concentration of substrate
required to drive the reaction at $\frac{1}{2}$ the maximal velocity