



Lecture (3)

Summary:

- The expressions of rate of reaction and types of rates;
- Stoichiometric relationships between the rates of appearance or disappearance of components in a given reaction;
- Determination of rate orders and rate law using the kinetic data of a reaction;
- The graphical method to determine a first-order and second-order reaction.
- The meaning and calculation half-life of a first order reaction;
- Determination of the activation energy, E_a , either graphically or from rate constants at different temperatures.
- Derive rate law from reaction mechanism.
- The role of catalyst

Chemical Kinetics is the study of reaction rates; that is, how fast a given reaction does proceeds. It is a measure of the change of the concentration of reactants (or products) as a function of time.

Reaction rates provide information regarding how fast a chemical process occurs as well as the mechanism by which a reaction occurs at molecular level.

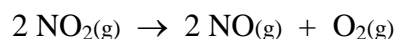
1. Reaction Rates

The rate of reaction is a measure of the change in concentration of reactants or products over time. Rate can be measured at the beginning of the reaction, which is called the *initial rate*, at any point in time while the reaction is in progress, called *instantaneous rate*, or over an interval of time, which is the *average rate*.

In the *initial rate* the change in concentration of a reactant or product as a function of time is measured within minutes (or seconds) the reaction starts. Determination of the dependence of *initial rate* to the concentrations of reactants allows one to derive the *rate law* for the reaction. A *rate law* is a mathematical equation that shows the dependence of reaction rate to the molar concentrations of reactants at constant temperature.

The *instantaneous rate* is calculated from the slope of a *tangent* drawn at any points on the *graph of concentrations versus time*. The slope of tangent taken at the initial point of the graph is assumed to be equal to its *initial rate*.

The *average rate* of reaction is obtained by dividing the change in concentration of a reactant or product that occurs over a longer period of time by the time interval that the change occurs. For example, consider the following reaction at 300°C:



If in the first 150 seconds, the concentration of NO_2 has decreased from 0.0100 mol/L to 0.0055 mol/L, the average rate for the disappearance of NO_2 for first 150 s under this condition is,

$$\frac{-\Delta[\text{NO}_2]}{\Delta t} = \frac{-(0.0055 \text{ mol/L} - 0.0100 \text{ mol/L})}{150 \text{ s}} = \frac{0.0045 \text{ mol/L}}{150 \text{ s}} = 3.0 \times 10^{-5} \text{ mol/(L.s)}$$

Suppose that in the next 150 seconds the concentration of NO_2 decreases from 0.0055 mol/L to 0.0038 mol/L. The average rate during the second 150 s period is

$$\frac{-\Delta[\text{NO}_2]}{\Delta t} = \frac{-(0.0038 \text{ mol/L} - 0.0055 \text{ mol/L})}{150 \text{ s}} = \frac{0.0017 \text{ mol/L}}{150 \text{ s}} = 1.1 \times 10^{-5} \text{ mol/(L.s)}$$

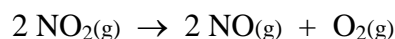


The *average rate* is the *mean* of several *instantaneous rates* taken over a period of time.

Note that *instantaneous rates* of a reaction decreases as time progresses as the concentrations of reactants decrease. Then the average rate taken over a longer period would have a smaller value compared to those taken over a shorter period after the reaction begins.

How is the rate of reaction measured?

The rate of reaction may be determined by measuring the rate of disappearance (decrease in concentration) of one of the reactants or the rate of formation (increase in concentration) of a product. For example, in the reaction:



Various expression of rate can be derived, such as

$$\text{Rate}_1 = \frac{-\Delta[\text{NO}_2]}{\Delta t}; \quad \text{Rate}_2 = \frac{\Delta[\text{NO}]}{\Delta t}; \quad \text{or} \quad \text{Rate}_3 = \frac{\Delta[\text{O}_2]}{\Delta t}$$

The stoichiometric relationships between the different rates are as follows:

$$\frac{-\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t} = \frac{2\Delta[\text{O}_2]}{\Delta t}$$

That is, in this reaction the rate of appearance of NO is the same as the rate of disappearance of NO₂, but double the rate of appearance of O₂.

Exercise-1:

1. For the reaction: $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}(\text{g}) + \text{O}_2(\text{g})$

(a) write the rate expression in terms of (i) the disappearance of N₂O₅; (ii) the formation of NO; (iii) the formation of O₂. (b) What are the stoichiometric relationships of the various rates for this reaction?

2. For the reaction: $5 \text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6 \text{H}^+(\text{aq}) \rightarrow 3 \text{Br}_2(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$;

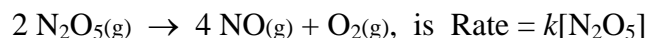
(a) write the expressions of rates in terms of (i) the disappearance of Br⁻; (ii) the disappearance of BrO₃⁻, and (iii) the formation of Br₂. (b) What are the stoichiometric relationships of the various rates for this reaction?

2. Rate Laws

Consider a general reaction: $\text{A} + \text{B} \rightarrow \text{C}$

The rate law is expressed as, $\text{Rate} = k[\text{A}]^x[\text{B}]^y$,

where k is the rate constant; x and y are the *rate orders* with respect to individual reactants. The rate orders x and y are not related to the reaction coefficients. Their values must be experimentally determined from a set of kinetic data. For example, the rate law for reaction:





That is, the rate of the decomposition of N_2O_5 is *first order* with respect to $[\text{N}_2\text{O}_5]$, which means that the rate will double if $[\text{N}_2\text{O}_5]$ is doubled; it will triple if $[\text{N}_2\text{O}_5]$ is tripled.

For the reaction: $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$, the rate law is $\text{Rate} = k[\text{NO}_2]^2$.

That is, the rate of the decomposition of NO_2 is *second order* with respect to $[\text{NO}_2]$. Therefore, the rate will quadruple if $[\text{NO}_2]$ is doubled.

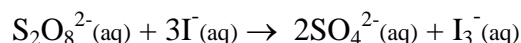
The reaction: $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ is found to be a zero order reaction in the presence of gold catalyst. For this reaction, the rate is independent of $[\text{HI}]$.

3 Determination of the Rate Law

Method of Initial Rates

For many chemical reactions, the expression of rate law contains only the concentrations of reactants, while the concentrations of products do not appear. However, for some reactions that are reversible, the concentration of products may be part of the rate law. To simplify the rate law and avoid the complication that might be contributed by products in reversible reactions, the measurement of rate for rate law determination is normally done at the moment the reactants are mixed. At this point, we can also assume that the effect of product concentration is considered negligible. Therefore, the rates that are measured are the *initial rates*.

Example: Consider the following kinetic data for the reaction:



Expt #	$[\text{S}_2\text{O}_8^{2-}]$ (mol/L)	$[\text{I}^-]$ (mol/L)	Initial Rate, (mol/(L.s))
1	0.038	0.060	1.5×10^{-5}
2	0.076	0.060	2.8×10^{-5}
3	0.038	0.120	2.9×10^{-5}

(a) Calculate the rate order w.r.t. each reactant and write the rate law for this reaction.

(b) Calculate the rate constant and the reaction rate when the concentration of both reactants is 0.050 mol/L?

Solution: The rate law is expressed as $\text{Rate} = k[\text{S}_2\text{O}_8^{2-}]^m[\text{I}^-]^n$, here m and n are rate orders.

(a) Calculation of rate order, m :

$$\frac{k[\text{S}_2\text{O}_8^{2-}]_2^m[\text{I}]^n}{k[\text{S}_2\text{O}_8^{2-}]_1^m[\text{I}]^n} = \frac{k(0.076 \text{ M})^m(0.060 \text{ M})^n}{k(0.038 \text{ M})^m(0.060 \text{ M})^n} = \frac{2.8 \times 10^{-5} \text{ mol/(L.s)}}{1.5 \times 10^{-5} \text{ mol/(L.s)}}$$

$$2^m \sim 2 \Rightarrow m = 1 \text{ (first order w.r.t. } [\text{S}_2\text{O}_8^{2-}])$$

Calculation of rate order, n :

$$\frac{k[\text{S}_2\text{O}_8^{2-}]^m[\text{I}]_3^n}{k[\text{S}_2\text{O}_8^{2-}]^m[\text{I}]_1^n} = \frac{k(0.038 \text{ M})^m(0.120 \text{ M})^n}{k(0.038 \text{ M})^m(0.060 \text{ M})^n} = \frac{2.9 \times 10^{-5} \text{ mol/(L.s)}}{1.5 \times 10^{-5} \text{ mol/(L.s)}}$$

$$2^n \sim 2 \Rightarrow n = 1 \text{ (first order w.r.t. } [\text{I}^-])$$



The rate law is expressed as: $\text{Rate} = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$

The rate constant, k , can be calculated using data of any one run, such as:

$$R_1 = k(0.038 \text{ mol/L})(0.060 \text{ mol/L}) = 1.5 \times 10^{-5} \text{ mol/(L.s)};$$

$$k = \frac{1.5 \times 10^{-5} \text{ mol/L}}{(0.038 \text{ mol/L})(0.060 \text{ mol/L})} = 6.6 \times 10^{-3} \text{ L.mol}^{-1}.\text{s}^{-1}$$

$$\begin{aligned} \text{When } [\text{S}_2\text{O}_8^{2-}] = [\text{I}^-] = 0.050 \text{ mol/L, Rate} &= (6.6 \times 10^{-3} \text{ L/mol.s})(0.050 \text{ mol/L})(0.050 \text{ mol/L}) \\ &= 1.6 \times 10^{-5} \text{ mol/(L.s)} \end{aligned}$$

Exercise-2:

1. Kinetic data for the following reaction are summarized below.



Expt #	$[\text{H}_2\text{O}_2]$ (mol/L)	$[\text{I}^-]$ (mol/L)	$[\text{H}^+]$ (mol/L)	Initial Rate mol/(L.s)
1	0.010	0.010	0.00050	1.15×10^{-6}
2	0.020	0.010	0.00050	2.30×10^{-6}
3	0.010	0.020	0.00050	2.35×10^{-6}
4	0.010	0.010	0.00100	1.14×10^{-6}

Determine the rate order with respect to each reactant and derive the rate law, expressed as: $\text{Rate} = k[\text{H}_2\text{O}_2]^m[\text{I}^-]^n[\text{H}^+]^p$. Calculate the rate constant, k .

The Graphical Method for determining Zero-order, First-order and Second-order Rates

Consider a reaction: $\text{R} \rightarrow \text{Products}$.

(i) If the reaction is *zero-order* with respect to R, $\text{Rate} = \frac{-\Delta[\text{R}]}{\Delta t} = k$

This gives $\Delta[\text{R}] = -k\Delta t$, and $[\text{R}]_t = [\text{R}]_0 - kt$;

a plot of $[\text{R}]$ versus t yields a straight line with slope $= -k$

(ii) If the rate is *first-order* in $[\text{R}]$, $\text{Rate} = \frac{-\Delta[\text{R}]}{\Delta t} = k[\text{R}]$, which also gives $\frac{\Delta[\text{R}]}{[\text{R}]} = -k\Delta t$,

Integrating this equation from time $t = 0$ to $t = t$, yields the expression: $\ln[\text{R}]_t = \ln[\text{R}]_0 - kt$; or

$\ln([\text{R}]_t/[\text{R}]_0) = -kt$; If the common log is used, the integrated expression for first rate would be:

$\log[\text{R}]_t = \log[\text{R}]_0 - kt/2.30$; where, $[\text{R}]_0$ = concentration at $t = 0$, and $[\text{R}]_t$ = concentration at time t .

Plotting $\ln[\text{R}]_t$ versus t yields a straight line with slope $= -k$; (slope $= -k/2.30$ if $\log[\text{R}]_t$ is plotted).



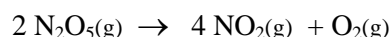
(iii) If the rate is *second-order* with respect to R, $\text{Rate} = \frac{-\Delta[R]}{\Delta t} = k[R]^2$ or $\frac{\Delta[R]}{[R]^2} = k\Delta t$;

Integrating the equation from time $t = 0$ to $t = t$ yields the expression: $\frac{1}{[R]_t} = kt + \frac{1}{[R]_0}$

For second order rate, plotting $1/[R]_t$ versus t yields a straight line with the slope $= k$ (the *rate constant*)

Exercise-3:

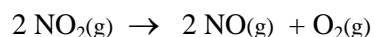
- The following data shows the concentrations of dinitrogen pentoxide as a function of time for the following decomposition reaction:



Time (s)	$[\text{N}_2\text{O}_5]$, M	$\ln[\text{N}_2\text{O}_5]$	$[\text{N}_2\text{O}_5]^{-1}$, M^{-1}
0	0.0165	-4.10	60.6
600	0.0124	-4.39	80.6
1200	0.0093	-4.68	110
1800	0.0071	-4.95	140
2400	0.0053	-5.24	190
3000	0.0039	-5.54	260

Plot graphs of $\ln[\text{N}_2\text{O}_5]$ versus t and $1/[\text{N}_2\text{O}_5]$ versus t . Determine whether the decomposition of N_2O_5 follows a first-order or second-order rate law with respect to $[\text{N}_2\text{O}_5]$.

- The following experimental data are obtained for the decomposition of nitrogen dioxide:



Time, s	$[\text{NO}_2]$, M	$\ln[\text{NO}_2]$	$[\text{NO}_2]^{-1}$, M^{-1}
0	10.0×10^{-3}	-4.605	1.00×10^2
60	6.83×10^{-3}	-4.986	1.46×10^2
120	5.18×10^{-3}	-5.263	1.93×10^2
180	4.18×10^{-3}	-5.477	2.39×10^2
240	3.50×10^{-3}	-5.655	2.86×10^2
300	3.01×10^{-3}	-5.806	3.32×10^2

Plot a graph of $\ln[\text{NO}_2]$ versus t and $1/[\text{NO}_2]$ versus t . Determine the decomposition of NO_2 follows a first order or second order rate law with respect to $[\text{NO}_2]$.



Half-Life of Reactions

The *half-life* ($t_{1/2}$) of a reaction is the time it takes for the reactant concentration to decrease to one-half its initial value.

For *zero-order* reaction, $t_{1/2} = [R]_0/2k$

For *first-order* reaction, $t_{1/2} = 0.693/k$

For *second-order* reactions, $t_{1/2} = 1/(k[R]_0)$

Exercise-4:

1. At high temperature, the decomposition of sulfuryl chloride vapor (SO_2Cl_2) follows a first order kinetics:



- (a) If the rate constant for the decomposition is $2.20 \times 10^{-5} \text{ s}^{-1}$ at 320°C , what is the half-life for the decomposition of SO_2Cl_2 at this temperature? (b) How long (in hrs) does it takes for 75.0% of SO_2Cl_2 to decompose?
2. A jawbone from the archaeological site at Folsom, new Mexico, showed a carbon-14 activity of 4.5 disintegration per minute per gram (dpm/g) carbon at the time it was discovered. If the C-14 activity in a living material is 15.0 dpm/g carbon and its half-life is 5730 years, estimate the age of the jawbone at the time it was discovered. (Radioisotopes decay in first order rate.
 3. The decomposition of nitrogen dioxide follows a second order rate law in NO_2 :

$$2 \text{NO}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$$

The rate constant, $k = 0.775 \text{ M}^{-1}.\text{s}^{-1}$ at 320°C . What is the half-life for the decomposition of NO_2 when the initial concentration of NO_2 is 0.0100 M? How long does it takes for 75.0% of the given NO_2 to decompose? If the initial concentration is $[\text{NO}_2]_0 = 0.0100 \text{ M}$, what concentration of NO_2 remains after 5.00 hrs?

Determining Integrated Rate Law for Reactions with More Than One Reactant

For reactions that involve more than one reactant, the integrated rate law is determined for one reactant at a time. This is done by having the concentration of the limiting reactant (which rate order to be determined) considerably lower than that of the other reactant. Under this condition, the time dependent change in concentration is significant only for the limiting reactant, while the other reactant is assumed approximately constant.

For example, the reaction: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ has $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$

The reaction can be carried out using $[\text{NO}]_0 = 1.0 \times 10^{-4} \text{ mol/L}$ and $[\text{O}_2] = 0.10 \text{ mol/L}$. As the reaction progress, $[\text{NO}]$ decreases significantly, but the decrease in $[\text{O}_2]$ is negligible. Under this condition, the integrated rate law equation can be derived in term of $[\text{NO}]$. Then condition can be reversed and the integrated rate law equation is derived in term of $[\text{O}_2]$.

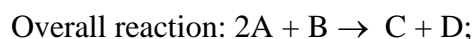
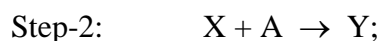
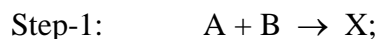
For this reaction, a straight line with positive slope is obtained for the plot of $1/[\text{NO}]$ versus time and for $\ln[\text{O}_2]$ versus time, which yield a rate law: $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$.



6. Reaction Mechanism

A **reaction mechanism** is the detailed picture of how a reaction occurs at molecular level. It consists of a *set of proposed elementary steps* involving molecular species – reactants as well as reaction *intermediates*. A reaction mechanism explains how a given reaction might occur at molecular level and from which a rate law can be derived, which must agree with the one determined experimentally. If the mechanism consists of more than one *elementary step*, the sum of these *steps* must be equal to the overall balanced equation for the reaction.

For example, the reaction: $2A + B \rightarrow C + D$ may involve the following *elementary steps*:



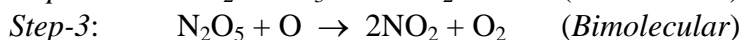
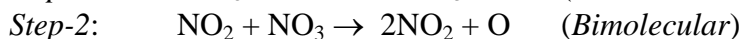
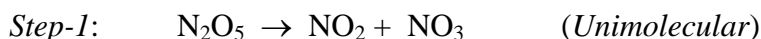
Elementary Steps and Molecularity

Elementary steps or *elementary reactions* are *simple* steps that together make up the *reaction mechanism* for a given reaction. Each *elementary reaction* describes *individual molecular event*, such as two particles combining or a particle (simple or complex) decomposing. An *elementary reaction* is characterized by its **molecularity**, which is the number of particles/molecules involved in the formation of *transition-state complex*. Thus, an elementary reaction may be characterized as *unimolecular*, *bimolecular*, or *termolecular*. Unimolecular and bimolecular reactions are considered the most common elementary processes.

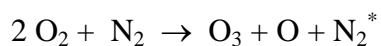
Rate Law for Elementary Reaction Steps:

Elementary Reactions	Molecularity	Rate Law
$A \rightarrow \text{product}$	Unimolecular	$\text{Rate} = k[A]$
$2A \rightarrow \text{product}$	Bimolecular	$\text{Rate} = k[A]^2$
$A + B \rightarrow \text{product}$	Bimolecular	$\text{Rate} = k[A][B]$
$2A + B \rightarrow \text{product}$	Termolecular	$\text{Rate} = k[A]^2[B]$

For example, in the reaction: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, the proposed mechanism is:



Termolecular event is considered very rare; the chances that three particles colliding at the same time, with proper orientation and sufficient energy, are considered extremely small. A possible *termolecular* event is thought to occur during the formation of ozone from oxygen in the outer atmosphere:





Deriving Rate Law from the Rate-Determining Step

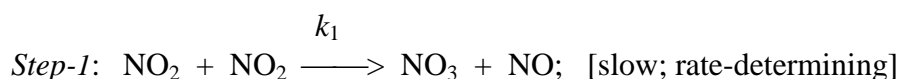
When a proposed mechanism consists of more than one elementary steps, the one with the slowest rate will determine the overall rate of reaction. It is called ***the rate-determining step***, which *step* represents the *rate law for the overall reaction*.

Consider the reaction: $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{NO}_{(g)} + \text{CO}_{2(g)}$

If the reaction follows a *one elementary step* mechanism, the rate law would be: $\text{Rate} = k[\text{NO}_2][\text{CO}]$

However, the experimentally determined rate law is $\text{Rate} = k[\text{NO}_2]^2$

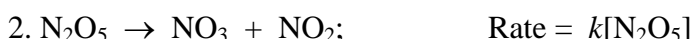
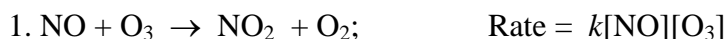
It is proposed that the reaction must involve at least *two elementary steps*:



The rate law for the rate-determining step: $\text{Rate} = k_1[\text{NO}_2]^2$, which is identical in form to the rate law obtained experimentally, in which $k_1 = k$. The second step, which occurs very fast, does not influence the overall rate.

In fact, if the exponents in the rate law differ from the coefficients in the chemical equation, the mechanism for the reaction normally involves more than one elementary step. Most reactions are believed to involve more than one elementary step.

Note that, unlike the overall rate law which must be determined experimentally, the rate law for an *elementary reaction* can be deduced from its *molecularity*, since each elementary reaction is a single step event. The exponents in the expression of rate law are the same as the equation coefficients. For example, the rate laws for the following elementary reactions are written as indicated:



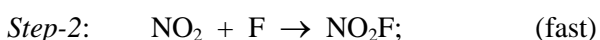
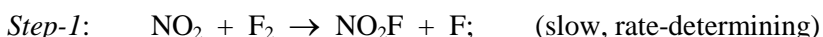
In addition, certain species such as NO_3 may be formed in an *elementary step*, but immediately consumed in subsequent elementary step; they do not appear in the overall equation. These species are called ***reaction intermediates***.

Rate Law Derived from Mechanism with Slow First Elementary Step

Consider the reaction: $2\text{NO}_{2(g)} + \text{F}_{2(g)} \rightarrow 2\text{NO}_2\text{F}_{(g)}$

The experimental rate law is $\text{Rate} = k[\text{NO}_2][\text{F}_2]$

The proposed mechanism for this reaction consists of the following elementary steps:



Rate law for the rate-determining step: $\text{Rate} = k_1[\text{NO}_2][\text{F}_2] = k[\text{NO}_2][\text{F}_2]; \rightarrow (k = k_1)$

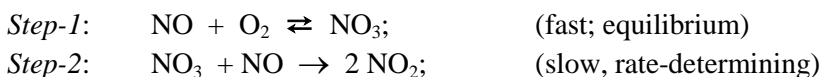


Rate Law Derived from Mechanism with Slow Second Elementary Step:

Consider the reaction: $2 \text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{NO}_2\text{(g)}$;

The rate law is: $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$

The proposed mechanism composed of the following elementary reactions:



Overall Rxn: $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$;

Rate law for the *slow, rate-determining step*: $\text{Rate} = k_2[\text{NO}_3][\text{NO}]$

NO_3 is a *reaction intermediate* formed in a fast reversible reaction (step-1) and its concentration quickly reaches a steady state such that, $[\text{NO}_3] = K_{eq}[\text{NO}][\text{O}_2]$, where K_{eq} is the equilibrium constant for reversible step-1. Substituting for $[\text{NO}_3]$ in the rate law expression, we obtain,

$$\text{Rate} = k_2 K_{eq} [\text{NO}]^2 [\text{O}_2] = k [\text{NO}_2]^2 [\text{O}_2]; \quad (\text{where } k = k_2 K_{eq})$$

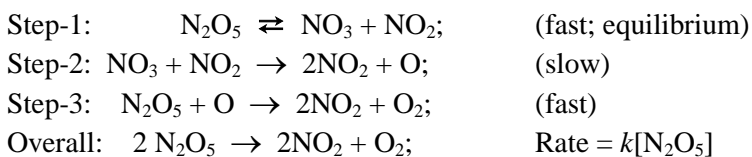
Correlating Reaction Mechanism with Rate Law

For any reaction, the proposed *mechanism* must obey three fundamental criteria:

1. *The elementary steps must add up to give the overall equation.*
2. *The elementary steps must be physically reasonable.* That is, the proposed step can occur with reasonable probability; they are either *unimolecular* or *bimolecular*. A *termolecular* elementary step is considered unlikely.
3. *The mechanism must correlate with the rate law.* That is, the rate law derived from *rate-determining step* must agree with the actual rate law obtained experimentally.

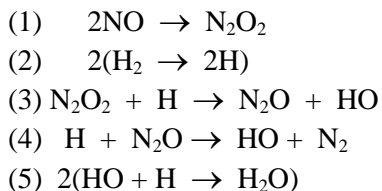
For example, the reaction: $2 \text{N}_2\text{O}_5\text{(g)} \rightarrow 4 \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$ has $\text{Rate} = k[\text{N}_2\text{O}_5]$.

The proposed mechanism involves the following elementary steps:



Exercise-5:

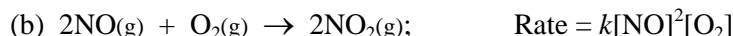
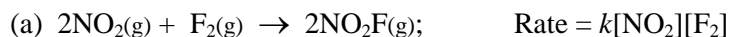
1. The following mechanism is proposed for a reaction:



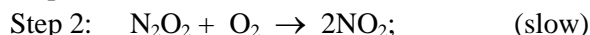
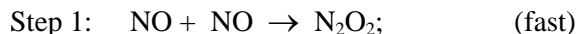
- (a) Write a balanced equation for the overall reaction
- (b) Determine the *molecularity* of each step.
- (c) Write the rate law for each step.



2. Propose a reasonable mechanism for each of the following reactions:



3. Given the following elementary steps:



Write the net equation and derive the rate law for the overall reaction.

7. A Model for Chemical Kinetics

The rate law of a reaction relates the dependence of reaction rates on the concentrations of reactants. As we know, the rate of reaction also depends on other factors, such as temperature. This dependency can be explained by the *collisional theory* of reaction and the formation of **activated complex**, or **transition state**.

Consider the following reaction: $2\text{BrNO}(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$

For the reaction to occur:

- Reactant molecules must collide;
 - Molecular collisions must occur with proper orientations;
 - Collisions must be energetic and lead to the formation of an activated complex;
 - The rate of formation of activated complex is the rate determining step;
 - The activated complex eventually leads to the formation of products;
1. The rate of formation of *activated complex* is proportional to the *frequency of effective molecular collisions*, which is dependent on reactant concentrations.
 2. The *activated complex* or *transition state* is separated from the reactants by an *energy barrier*, called the **activation energy** (E_a). The formation of *transition state complex* depends on the fraction of molecules with sufficient *kinetic energy* that can overcome this *energy barrier*. This fraction is temperature dependent. At low temperature, the *fraction* of molecules with sufficient energy to overcome the *activation energy barrier* and subsequently forms the *transition state complex* will be low. This *fraction* increases with temperature, which also increase the overall reaction rate.
 3. High *activation energy* for a reaction also means a lower fraction of molecules with sufficient energy to form the *transition state complex*. Thus, higher E_a leads to a slower rate of reaction.

The dependence of rate on temperature and *activation energy* (E_a) is shown the Arrhenius equation for the rate constant, k :

$$k = A e^{-E_a/RT}, \quad \text{where } A \text{ is called the Arrhenius frequency factor.}$$

Taking the natural log, yields the equation: $\ln(k) = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A)$.

A plot of $\ln(k)$ versus $1/T$ yields a straight line with slope $= -E_a/R$; ($R = 8.314 \text{ J/mol.K}$).



The *activation energy* (E_a) can also be calculated using two values of the rate constant k according to the expression:

$$\ln(k_2/k_1) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right); \text{ or } \ln(k_1/k_2) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right); \text{ (T must be in Kelvin)}$$

Exercise-6:

1. For the reaction: $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$,
the following rate constants, k , are obtained at different temperatures:

Temp. °C:	45.0	50.0	55.0	60.0
k, s^{-1} :	4.8×10^{-4}	8.8×10^{-4}	1.6×10^{-3}	2.8×10^{-3}

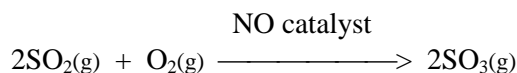
Calculate the activation energy (E_a) for this reaction.

8. Catalysis

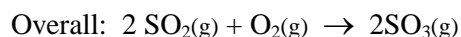
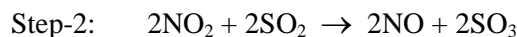
Catalysts are substances that increase the rate of reactions, but do not get used up by the reactions. A catalyst functions by providing an *alternative reaction pathway with lower activation energy*. It increases the reaction rate, but does not affect the reaction enthalpy or the equilibrium position.

Homogeneous Catalysis

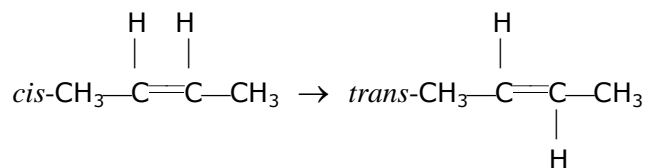
These are catalysts that have the same phase as the reactants. For example, nitric oxide (NO) catalyzes the reaction between SO_2 and O_2 :



The above reaction, though spontaneously and highly exothermic, is very slow because of the very high activation energy. NO molecules provide an alternative pathway that has a lower E_a .

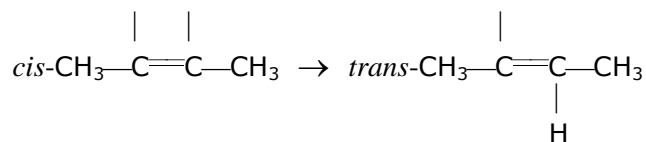


Some catalysts may be involved in the reaction kinetics and the concentration appears in the rate law. For example, iodine which catalyzes the *isomerization* of *cis*-2-butene to *trans*-2-butene is included in the rate law expression. The Uncatalyzed reaction:



$$\text{Rate} = k[\text{cis-2-butene}]$$

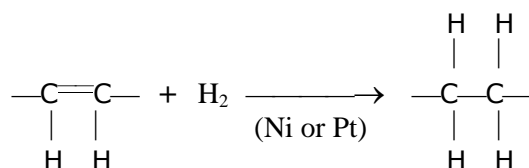




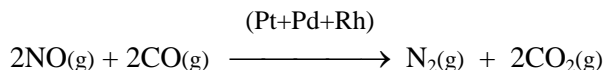
$$\text{Rate} = k[\text{cis-2-butene}][\text{I}_2]^{1/2}$$

Heterogeneous Catalysis

These are catalysts which have a different physical state from the reactants. Most reactions involving gases use inert metals or metal oxides as catalysts. These solid catalysts provide surface areas for molecules to interact effectively. The metal surface also facilitates the breaking and formation of bonds. Ni, Pd and Pt are often used in the hydrogenation of vegetable oil to make margarine and “Crisco oil”, where a hydrogen molecule is added to each carbon-carbon double bond in the unsaturated fatty acid chains:

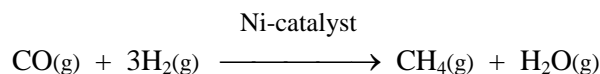


Heterogeneous catalyses are used in automobile catalytic converters, which consist of Pt, Pd and Rh mixture embedded in ceramic honeycombs. The metals catalyze the following reaction:



Catalytic converters reduce the emission of toxic exhaust gases

Some reactions require specific catalysts. For example, Nickel catalyzes the reaction:



Whereas ZnO-Cr₂O₃ mixture catalyzes the formation of methanol from the same reactants:

