



Chemical Kinetics

Chemistry, Zumdahl & Zumdahl – Chapter 12

Houssam El-Rassy, PhD

Assistant Professor

Department of Chemistry, Room 520

Ext. 4051 , E-mail: Houssam.Rassy@aub.edu.lb

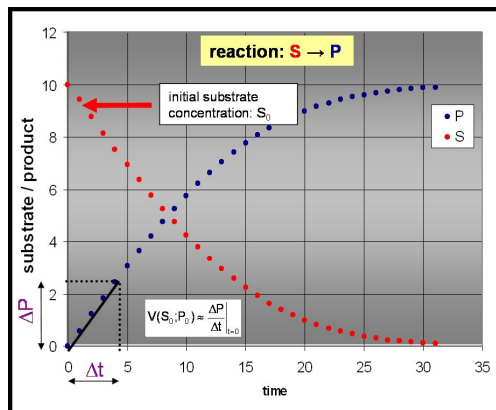
July 1, 2011

American University of Beirut



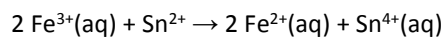
Rate ? Speed ?





Rate of change of concentration with time:

$$\text{Rate} = \frac{\text{concentration of S at time } t_2 - \text{concentration of S at time } t_1}{t_2 - t_1}$$

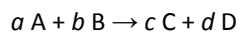


$$t = 38.5 \text{ s} \quad [\text{Fe}^{2+}] = 0.0010 \text{ M}$$

$$\Delta t = 38.5 \text{ s} \quad \Delta[\text{Fe}^{2+}] = (0.0010 - 0) \text{ M}$$

$$\text{Rate of formation of Fe}^{2+} = \frac{\Delta[\text{Fe}^{2+}]}{\Delta t} = \frac{0.0010 \text{ M}}{38.5 \text{ s}} = 2.6 \times 10^{-5} \text{ M s}^{-1}$$

$$\frac{\Delta[\text{Sn}^{4+}]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{Fe}^{2+}]}{\Delta t} = - \frac{1}{2} \frac{\Delta[\text{Fe}^{3+}]}{\Delta t}$$

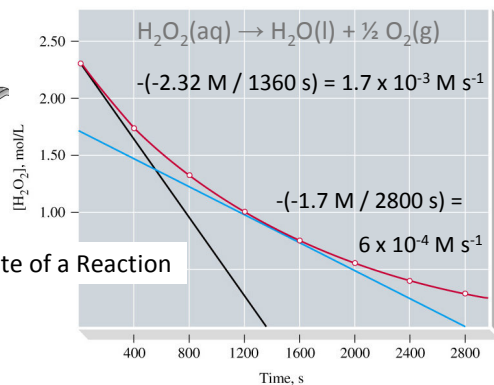
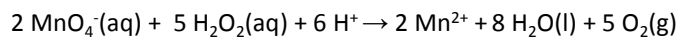
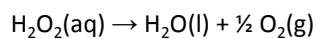
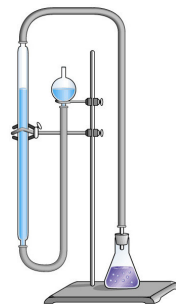


Rate of reaction = rate of disappearance of reactants

$$= - \frac{1}{a} \frac{\Delta[A]}{\Delta t} = - \frac{1}{b} \frac{\Delta[B]}{\Delta t}$$

= rate of appearance of products

$$= \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$



$$\text{Rate} = \frac{-\Delta[\text{H}_2\text{O}_2]}{\Delta t}$$

Instantaneous Rate of a Reaction

What is the concentration at 100s?

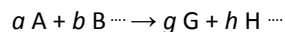
$$[\text{H}_2\text{O}_2]_i = 2.32 \text{ M} \quad \text{Rate} = 1.7 \times 10^{-3} \text{ M s}^{-1} = \frac{-\Delta[\text{H}_2\text{O}_2]}{\Delta t}$$

$$-\Delta[\text{H}_2\text{O}_2] = -([\text{H}_2\text{O}_2]_f - [\text{H}_2\text{O}_2]_i) = 1.7 \times 10^{-3} \text{ M s}^{-1} \times \Delta t$$

$$[\text{H}_2\text{O}_2]_{100 \text{ s}} - 2.32 \text{ M} = -1.7 \times 10^{-3} \text{ M s}^{-1} \times 100 \text{ s}$$

$$[\text{H}_2\text{O}_2]_{100 \text{ s}} = 2.32 \text{ M} - 0.17 \text{ M}$$

$$= 2.15 \text{ M}$$



$$\text{Rate of reaction} = k [\text{A}]^m [\text{B}]^n \cdots$$

$$\text{Rate constant} = k$$

$$\text{Overall order of reaction} = m + n + \cdots$$

Establishing the Order of a reaction by the Method of Initial Rates.

Use the data provided establish the order of the reaction with respect to HgCl_2 and $\text{C}_2\text{O}_4^{2-}$ and also the overall order of the reaction.

TABLE 15.3 Kinetic Data for the Reaction:
 $2 \text{ HgCl}_2 + \text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{ Cl}^- + 2 \text{ CO}_2 + \text{Hg}_2\text{Cl}_2$

Experiment	$[\text{HgCl}_2], \text{ M}$	$[\text{C}_2\text{O}_4^{2-}], \text{ M}$	Initial rate, M min^{-1}
1	$[\text{HgCl}_2]_1 = 0.105$	$[\text{C}_2\text{O}_4^{2-}]_1 = 0.15$	1.8×10^{-5}
2	$[\text{HgCl}_2]_2 = 0.105$	$[\text{C}_2\text{O}_4^{2-}]_2 = 0.30$	7.1×10^{-5}
3	$[\text{HgCl}_2]_3 = 0.052$	$[\text{C}_2\text{O}_4^{2-}]_3 = 0.30$	3.5×10^{-5}

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$$R_3 = k \times [\text{HgCl}_2]_3^m \times [\text{C}_2\text{O}_4^{2-}]_3^n$$

$$R_2 = k \times [\text{HgCl}_2]_2^m \times [\text{C}_2\text{O}_4^{2-}]_2^n = k \times (2[\text{HgCl}_2]_3)^m \times [\text{C}_2\text{O}_4^{2-}]_3^n$$

$$\frac{R_2}{R_3} = \frac{k \times (2[\text{HgCl}_2]_3)^m \times [\text{C}_2\text{O}_4^{2-}]_3^n}{k \times [\text{HgCl}_2]_3^m \times [\text{C}_2\text{O}_4^{2-}]_3^n}$$

$$\frac{R_2}{R_3} = \frac{k \times 2^m \times [\text{HgCl}_2]_3^m \times [\text{C}_2\text{O}_4^{2-}]_3^n}{k \times [\text{HgCl}_2]_3^m \times [\text{C}_2\text{O}_4^{2-}]_3^n} = \frac{2^m R_3}{R_3} = 2.0$$

$$2^m = 2.0 \text{ therefore } m = 1.0$$

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$$R_2 = k \times [\text{HgCl}_2]_2^1 \times [\text{C}_2\text{O}_4^{2-}]_2^n = k \times (0.105) \times (0.30)^n$$

$$R_1 = k \times [\text{HgCl}_2]_1^1 \times [\text{C}_2\text{O}_4^{2-}]_1^n = k \times (0.105) \times (0.15)^n$$

$$\frac{R_2}{R_1} = \frac{k \times (0.105) \times (0.30)^n}{k \times (0.105) \times (0.15)^n}$$

$$\frac{R_2}{R_1} = \frac{(0.30)^n}{(0.15)^n} = 2^n = \frac{7.1 \times 10^{-5}}{1.8 \times 10^{-5}} = 3.94$$

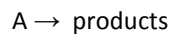
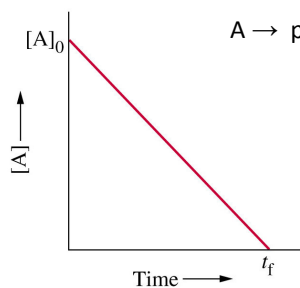
$$2^n = 3.94 \text{ therefore } n = 2.0$$

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$$R_2 = k [\text{HgCl}_2]_2^1 [\text{C}_2\text{O}_4^{2-}]_2^2$$

First order + Second order = Third Order



$$R_{\text{rxn}} = k [\text{A}]^0 = k \quad [k] = \text{mol L}^{-1} \text{s}^{-1}$$

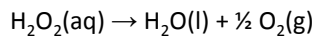
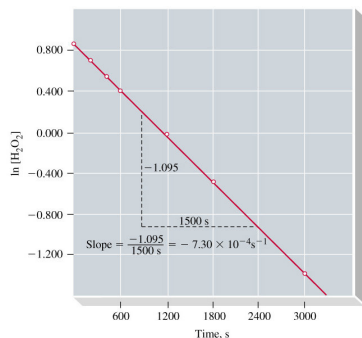
$$\frac{-\Delta[\text{A}]}{\Delta t} = k \quad \xrightarrow[\text{infinitesimal}]{\text{Move to the}} \frac{-d[\text{A}]}{dt} = k$$

And integrate from 0 to time t

$$\int_{[\text{A}]_0}^{[\text{A}]_t} d[\text{A}] = \int_0^t k dt$$

$$-[\text{A}]_t + [\text{A}]_0 = kt$$

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

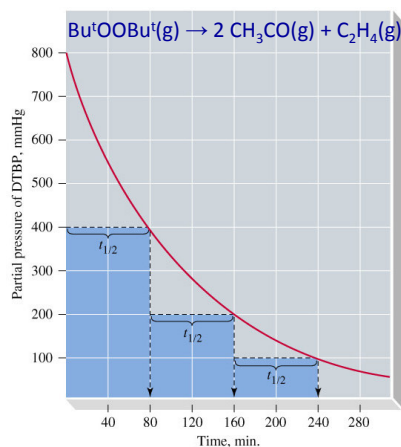


$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -k [\text{H}_2\text{O}_2] \quad [k] = \text{s}^{-1}$$

$$\int_{[\text{A}]_0}^{[\text{A}]_t} \frac{d[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2]} = - \int_0^t k dt$$

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

$t_{1/2}$ is the time taken for one-half of a reactant to be consumed.



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

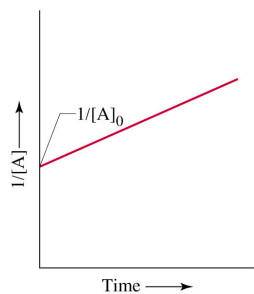
$$\ln \frac{\frac{1}{2}[\text{A}]_0}{[\text{A}]_0} = -kt_{1/2}$$

$$-\ln 2 = -kt_{1/2}$$

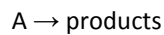
$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

TABLE 15.4 Some Typical First-Order Processes

Process	Half-Life, $t_{1/2}$	Rate Constant k , s^{-1}
Radioactive decay of $^{238}_{92}\text{U}$	4.51×10^9 years	4.87×10^{-18}
Radioactive decay of $^{14}_6\text{C}$	5.73×10^3 years	3.83×10^{-12}
Radioactive decay of $^{32}_{15}\text{P}$	14.3 days	5.61×10^{-7}
$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightarrow{15^\circ\text{C}} \text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) + \text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$ sucrose glucose fructose	8.4 h	2.3×10^{-5}
$(\text{CH}_2)_2\text{O}(\text{g}) \xrightarrow{415^\circ\text{C}} \text{CH}_4(\text{g}) + \text{CO}(\text{g})$ ethylene oxide	56.3 min	2.05×10^{-4}
$2 \text{N}_2\text{O}_5 \xrightarrow[45^\circ\text{C}]{\text{in CCl}_4} 2 \text{N}_2\text{O}_4 + \text{O}_2(\text{g})$	18.6 min	6.21×10^{-4}
$\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) \longrightarrow \text{H}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$	8.9×10^{-7} s	7.8×10^5



Rate law where sum of exponents $m + n + \dots = 2$.

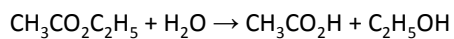


$$\frac{d[\text{A}]}{dt} = -k[\text{A}]^2 \quad [k] = \text{M}^{-1}\text{s}^{-1} = \text{L mol}^{-1}\text{s}^{-1}$$

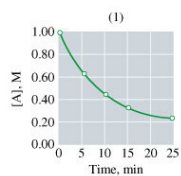
$$\int_{[\text{A}]_0}^{[\text{A}]_t} \frac{d[\text{A}]}{[\text{A}]^2} = - \int_0^t k \, dt$$

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

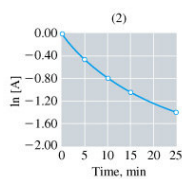
- Simplify the kinetics of complex reactions
- Rate laws become easier to work with.



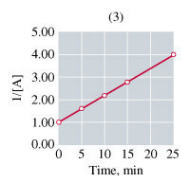
- If the concentration of water does not change appreciably during the reaction.
 - Rate law appears to be first order.
- Typically hold one or more reactants constant by using high concentrations and low concentrations of the reactants under study.



Plot [A] vs t.



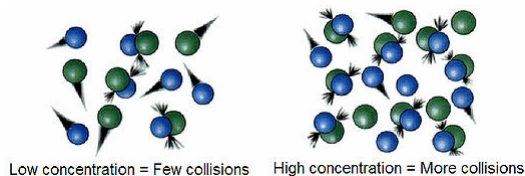
Plot ln[A] vs t.



Plot 1/[A] vs t.

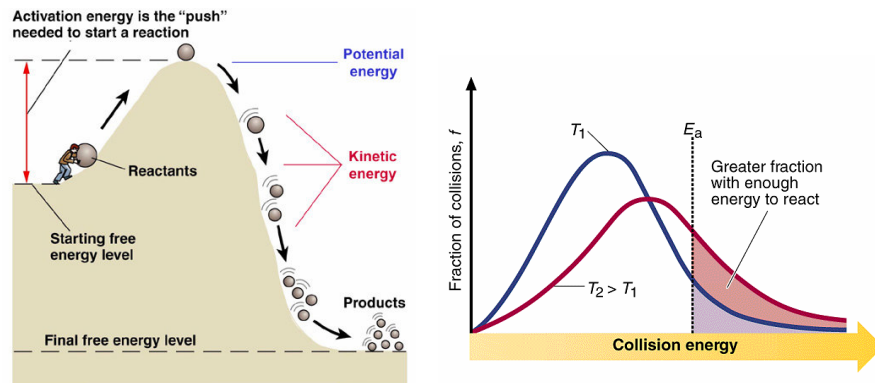
Collision Theory

- Kinetic-Molecular theory can be used to calculate the **collision frequency**.
 - In gases 10^{30} collisions per second.
 - If each collision produced a reaction, the rate would be about 10^6 M s^{-1} .
 - Actual rates are on the order of 10^4 M s^{-1} .
 - Still a very rapid rate.
 - Only a fraction of collisions yield a reaction.



For a reaction to occur there must be a redistribution of energy sufficient to break certain bonds in the reacting molecule(s).

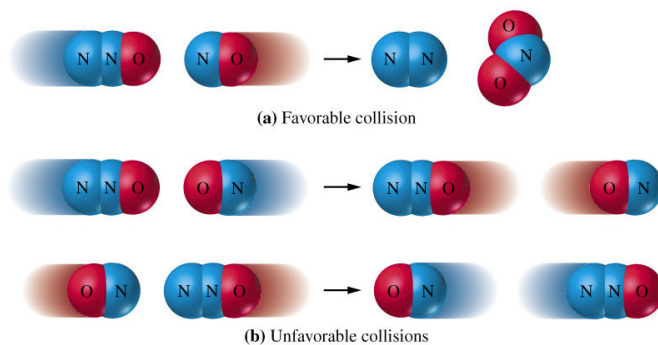
Activation Energy is the minimum energy above the average kinetic energy that molecules must bring to their collisions for a chemical reaction to occur.



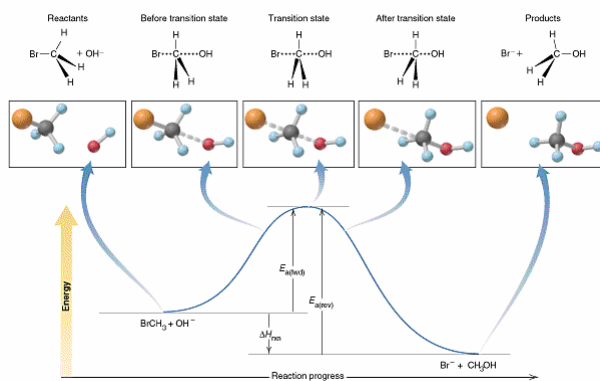
If activation barrier is high, only a few molecules have sufficient kinetic energy and the reaction is slower.

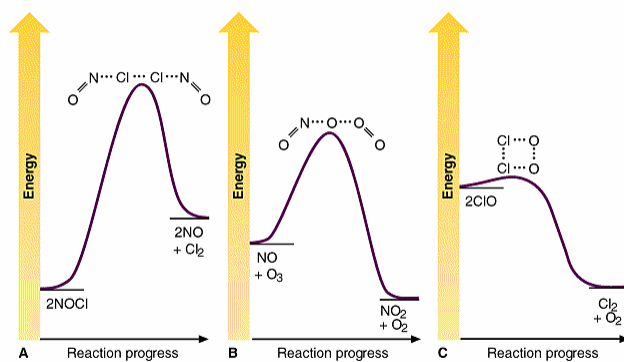
As temperature increases, reaction rate increases.

Orientation of molecules may be important.



The **activated complex** is a hypothetical species lying between reactants and products at a point on the **reaction profile** called the transition state.



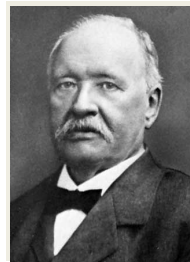


Arrhenius demonstrated that many rate constants vary with temperature according to the equation:

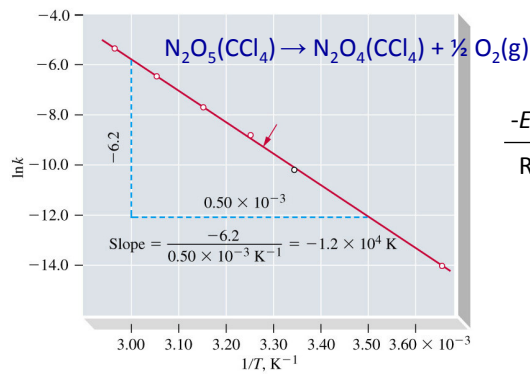
$$k = Ae^{-\frac{E_a}{RT}} \quad \text{or} \quad \ln k = -\frac{E_a}{RT} + \ln A$$

Where:

- k = Chemical Reaction Rate
- A = Pre-exponential Factor
- E_a = Activation Energy
- R = Gas Constant
- T = Temperature in Kelvin



Svante Arrhenius
(1859-1927)
Nobel Prize 1903



$$\frac{-E_a}{R} = -1.2 \times 10^4 \text{ K}$$

$$E_a = 1.0 \times 10^2 \text{ kJ mol}^{-1}$$

$$\ln k_2 - \ln k_1 = \frac{-E_a}{R} \frac{1}{T_2} + \ln A + \frac{E_a}{R} \frac{1}{T_1} - \ln A$$

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

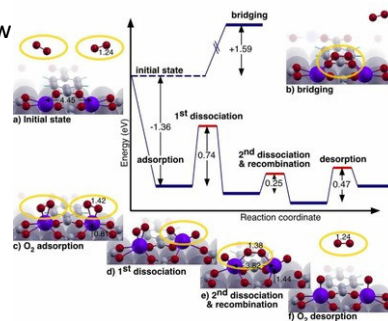
A step-by-step description of a chemical reaction.

Each step is called an *elementary process*.

- Any molecular event that significantly alters a molecule's energy or geometry or produces a new molecule.

Reaction mechanism must be consistent with:

- Stoichiometry for the overall reaction.
- The experimentally determined rate law



Unimolecular or bimolecular.

Exponents for concentration terms are the same as the stoichiometric factors for the elementary process.

Elementary processes are reversible.

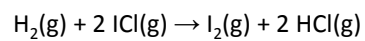
Intermediates are produced in one elementary process and consumed in another.

One elementary step is usually slower than all the others and is known as the rate determining step.

The rate-determining step is a chemistry term for the slowest step in a chemical reaction.

The rate of reaction depends on the rate of the slowest step.





$$\frac{d[\text{P}]}{dt} = k[\text{H}_2][\text{ICl}]$$

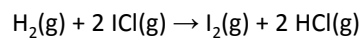
Postulate a mechanism:



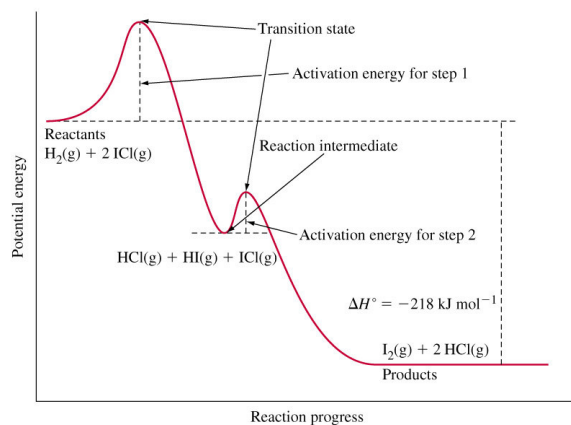
$$\frac{d[\text{HI}]}{dt} = k[\text{H}_2][\text{ICl}]$$



~~$$\frac{d[\text{I}_2]}{dt} = k[\text{HI}][\text{ICl}]$$~~

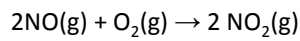


$$\frac{d[\text{P}]}{dt} = k[\text{H}_2][\text{ICl}]$$





Fast Reversible Step Followed by a Slow Step

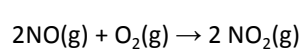
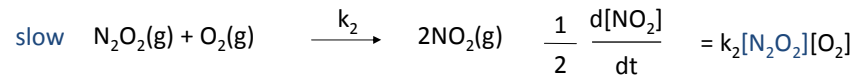


$$\frac{d[\text{P}]}{dt} = k_{\text{obs}}[\text{NO}]^2[\text{O}_2]$$

Postulate a mechanism:



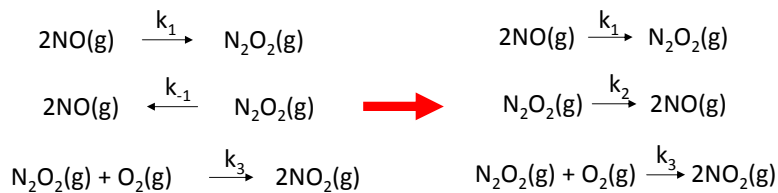
$$K = \frac{k_1}{k_{-1}} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}$$



$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_2 \frac{k_1}{k_{-1}} [\text{NO}]^2[\text{O}_2]$$



The Steady State Approximation



$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_3[\text{N}_2\text{O}_2][\text{O}_2]$$

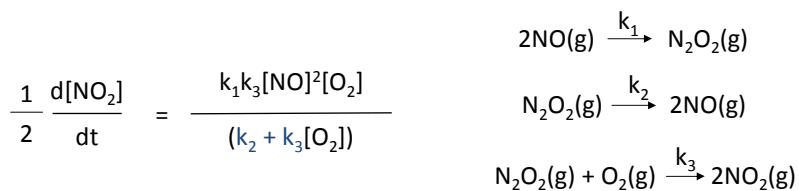
$$\frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2] - k_3[\text{N}_2\text{O}_2][\text{O}_2] = 0$$

$$\frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{NO}]^2 - k_2[\text{N}_2\text{O}_2] - k_3[\text{N}_2\text{O}_2][\text{O}_2] = 0$$

$$k_1[\text{NO}]^2 = [\text{N}_2\text{O}_2](k_2 + k_3[\text{O}_2])$$

$$[\text{N}_2\text{O}_2] = \frac{k_1[\text{NO}]^2}{(k_2 + k_3[\text{O}_2])}$$

$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_3[\text{N}_2\text{O}_2][\text{O}_2] = \frac{k_1 k_3 [\text{NO}]^2 [\text{O}_2]}{(k_2 + k_3[\text{O}_2])}$$



Let $k_2 \ll k_3$

$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{k_1 k_3 [\text{NO}]^2 [\text{O}_2]}{(k_3 [\text{O}_2])} = k_1 [\text{NO}]^2$$

Or

Let $k_2 \gg k_3$

$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{k_1 k_3 [\text{NO}]^2 [\text{O}_2]}{(k_2)} = \frac{k_1 k_3}{k_2} [\text{NO}]^2 [\text{O}_2]$$

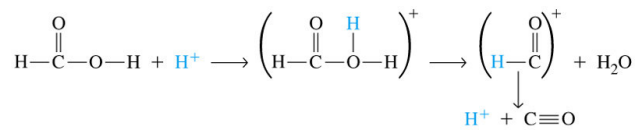
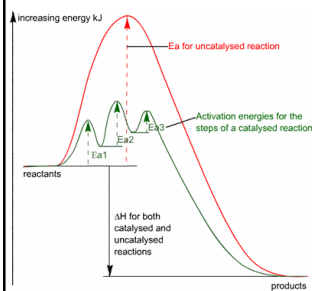
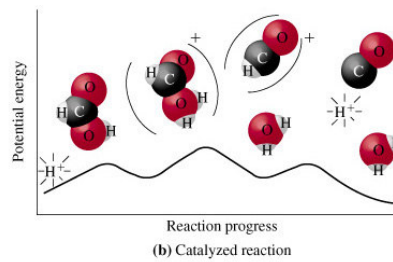
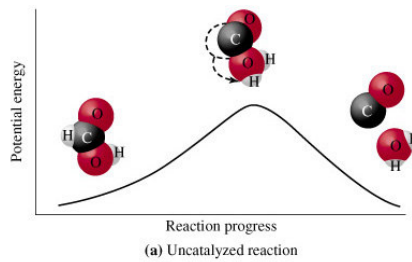
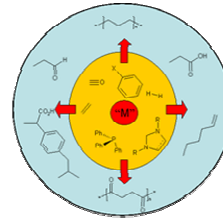
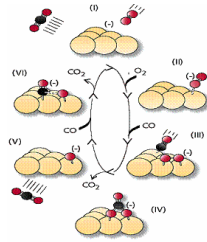
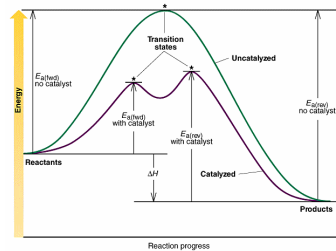
Alternative reaction pathway of lower energy.

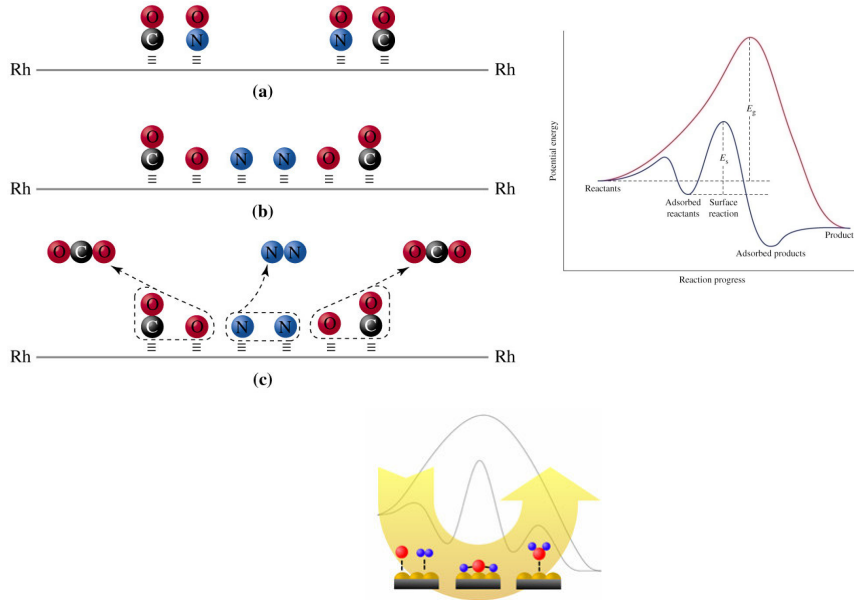
Homogeneous catalysis.

- All species in the reaction are in solution.

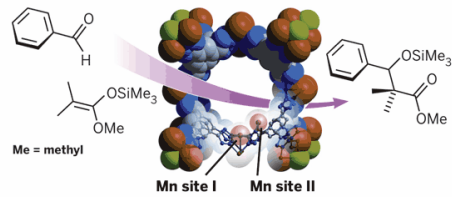
Heterogeneous catalysis.

- The catalyst is in the solid state.
- Reactants from gas or solution phase are adsorbed.
- Active sites on the catalytic surface are important.

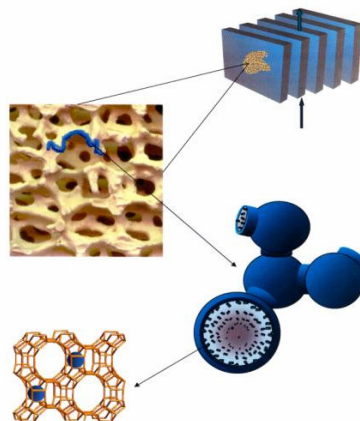
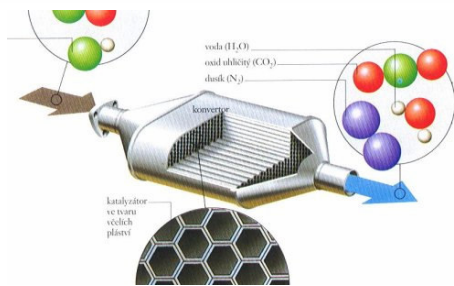


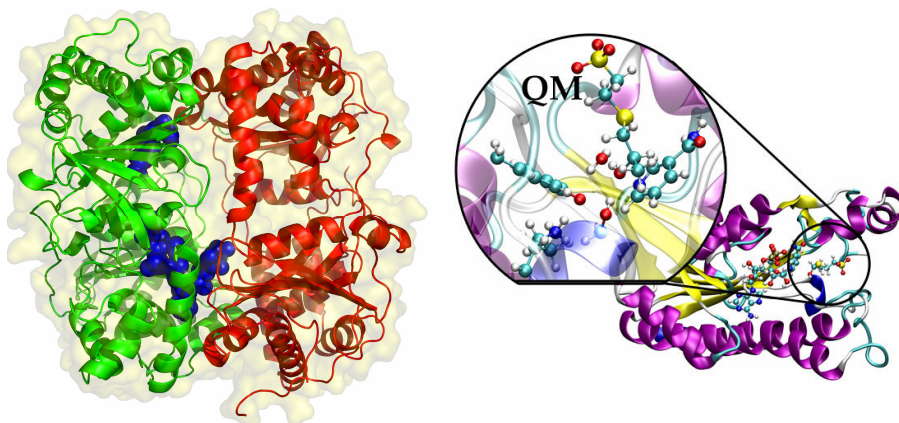
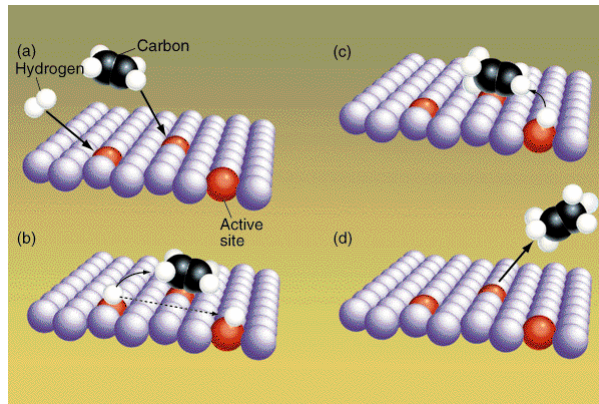


JUST PASSING THROUGH A portion of the Mn-BTT crystal structure illustrates the two types of Mn^{2+} sites—one five coordinate and the other two coordinate—that selectively catalyze reactions such as the Mukaiyama aldol synthesis shown.



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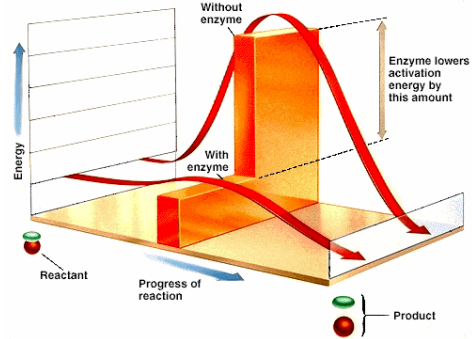
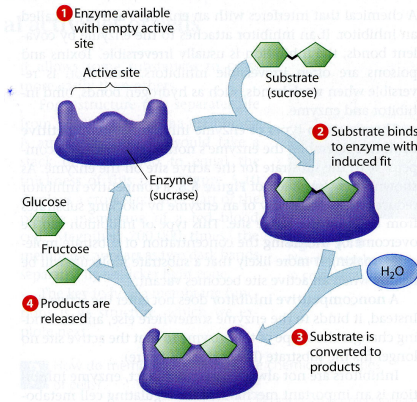
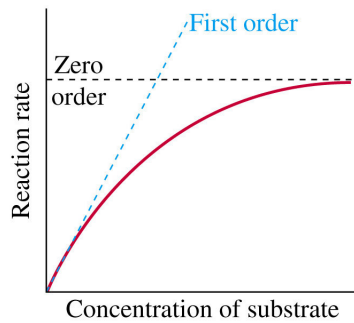
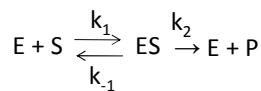


Figure 5.6 The catalytic cycle of an enzyme



$$\frac{d[P]}{dt} = k_2[ES]$$

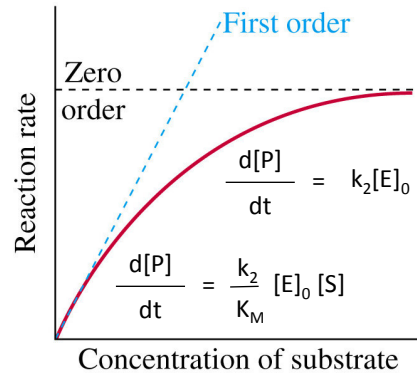
$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0$$

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

$$[E] = [E]_0 - [ES]$$

$$k_1[S]([E]_0 - [ES]) = (k_{-1} + k_2)[ES]$$

$$[ES] = \frac{k_1[E]_0[S]}{(k_{-1} + k_2) + k_1[S]}$$



Leonor Michaelis
(1875-1949)



Maud Menten
(1879-1960)

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [E]_0 [S]}{(k_{-1} + k_2) + k_1 [S]} = \frac{k_2 [E]_0 [S]}{\frac{(k_{-1} + k_2) + [S]}{k_1}}$$

$$\frac{d[P]}{dt} = \frac{k_2 [E]_0 [S]}{K_M + [S]}$$