

# CHEM103

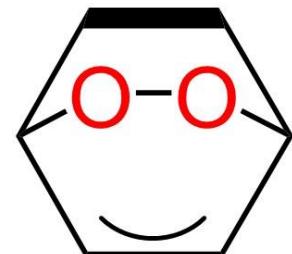
# General Chemistry

## Chapter 14: Chemical Kinetics



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SUSTech



# **Homeworks 11 & 13**

**Homework 11**

**Due date: 23rd Nov. (Wed)**

**Homework 13**

**Due date: 28th Nov. (Mon)**

Chemical  
Kinetics

# **Review on Chapter 13**

Dissolution: Entropy/Randomness, Intermolecular Interactions

Saturated/Supersaturated/Unsaturated Solution ;  
Crystallization, Solubility, Miscible/Immiscible, Henry's Law

Mass Percentage (ppm & ppb), Mole Fraction, Molarity,  
Molality

Colligative Properties: Raoult's Law, Van't Hoff Factor,  
Osmosis (Osmotic Pressure)

Colloid, Tyndall Effect, Hydrophilic, Hydrophobic

# Outline of Chapter 14

Rate (average/instantaneous/initial rate), rate law, rate constant, reaction order, half-life

Collision model, activation energy (barrier), transition state (activated complex), reaction coordinate diagrams, Arrhenius equation

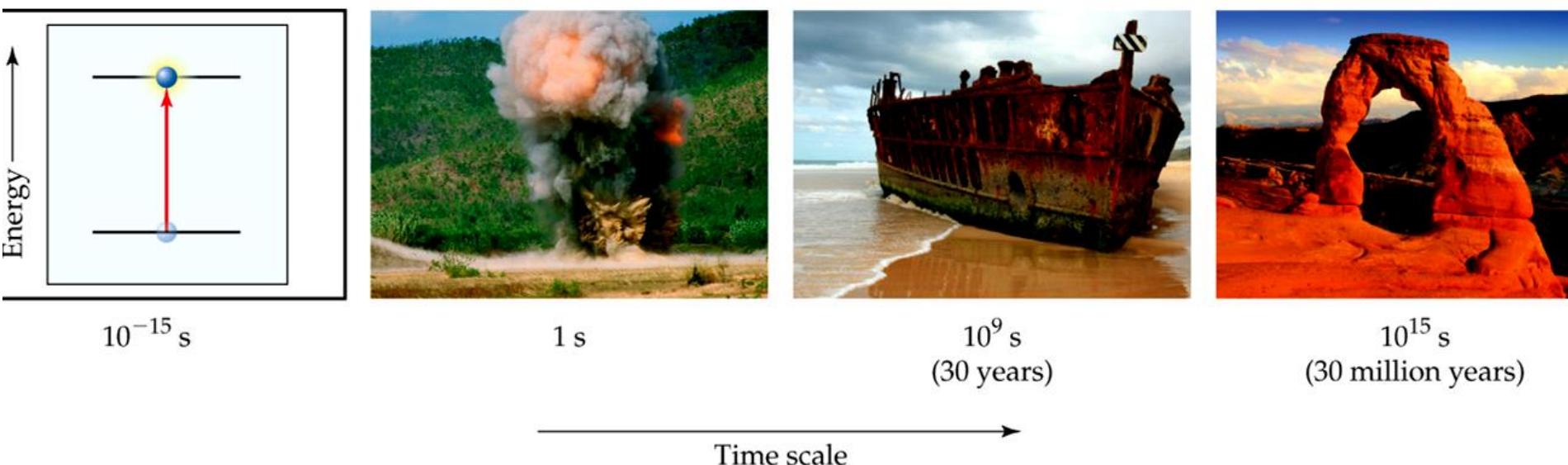
Reaction mechanism: elementary process, intermediate, molecularity (unimolecular, bimolecular, termolecular), rate-determining step

Catalyst: homogeneous/heterogeneous catalysts, enzymes

Chemical  
Kinetics

# Two Goals for Chemical Kinetics

- We study the **rate** (or speed) at which a **chemical process** occurs: *how quickly* a reaction works?
- Kinetics also sheds light on the **reaction mechanism**, a **molecular-level** view of the **path from reactants to products**: *how* the reaction *occurs*?



# Belousov-Zhabotinsky Oscillating Reaction



The Belousov-Zhabotinsky reaction is one of the most famous reactions in the chemical world. The swirls of colors correspond to products forming at different places and times in the unstirred petri dish. However, the mechanism of this oscillating reaction is not well understood.



Chemical

Kinetics

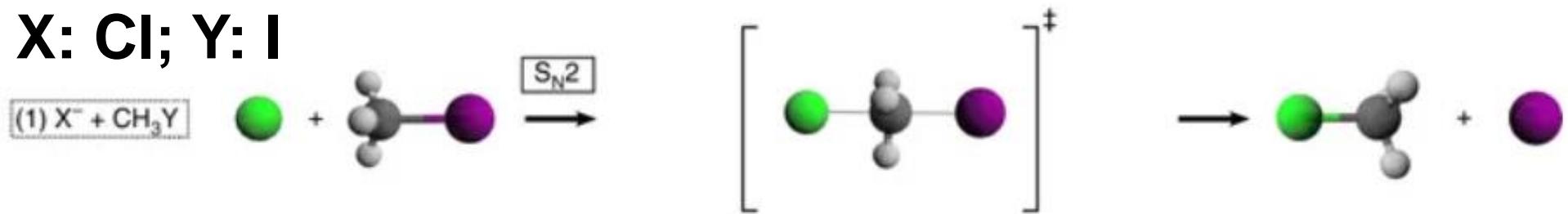
<http://www.rose-hulman.edu/mathjournal/archives/2002/vol3-n1/paper1/v3n1-1pd.pdf>

# Factors that Affect Reaction Rates

- 1) Physical **state** of the reactants
- 2) Reactant **concentrations**
- 3) Reaction **temperature**
- 4) Presence of a **catalyst**

# Physical State of the Reactants

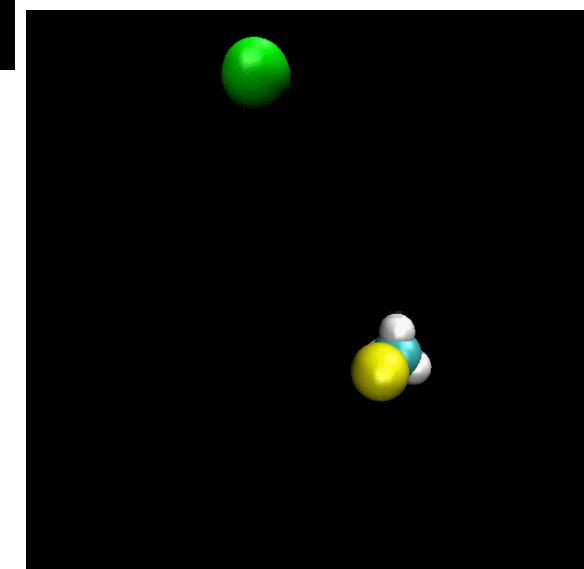
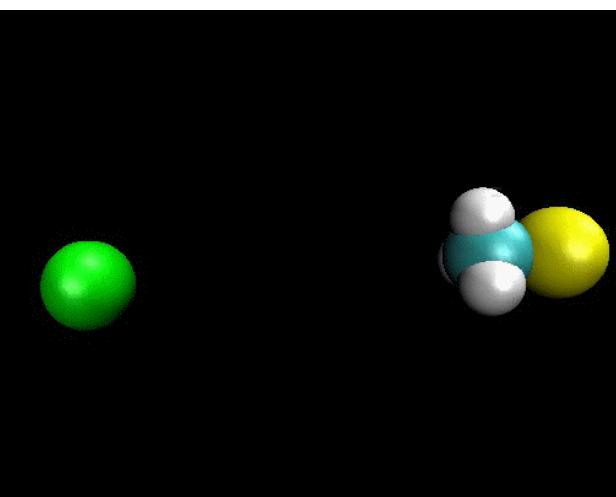
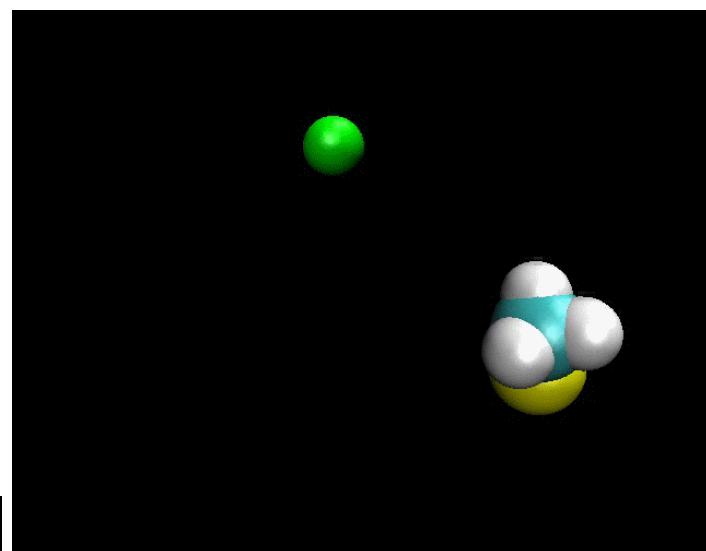
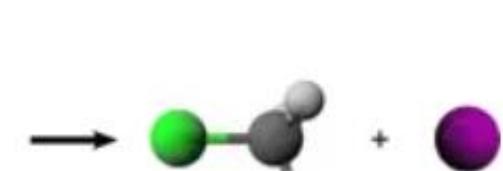
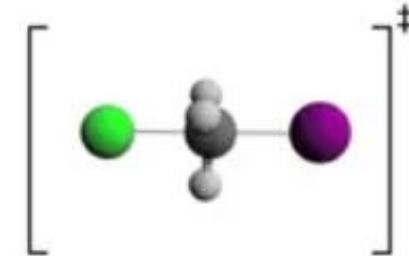
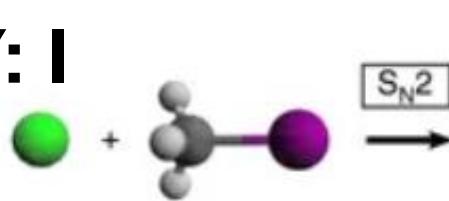
X: Cl; Y: I



- To undergo reaction, molecules generally must come in contact with each other. The **more readily** the **reactants collide**, the **more rapidly** they **react**.
- The **more homogeneous** the mixture of reactants, the **faster** the molecules can react. So, **homogeneous reactions** are often faster. **Heterogeneous reactions** that involve solids are faster if the surface area is increased (e.g. a fine powder reacts faster than a pellet or tablet).

X: Cl; Y: I

(1) X<sup>-</sup> + CH<sub>3</sub>Y

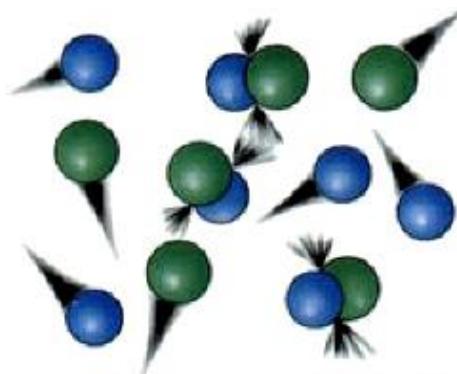


## Imaging Nucleophilic Substitution Dynamics

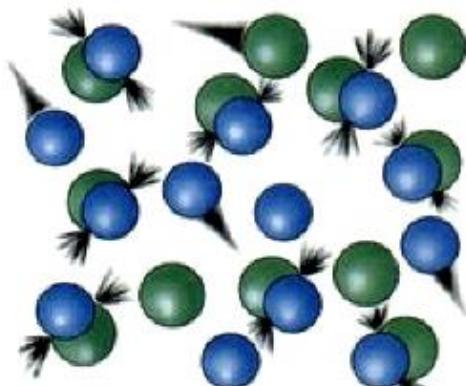
J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J. X. Zhang, W. L. Hase, M. Weidemüller and R. Wester  
*Science 2008, 319, 183*

# Reactant Concentrations

- **Increasing reactant concentration** generally **increases** reaction **rate**.
- Since there are more molecules, **more collisions** occur.



Low concentration = Few collisions



High concentration = More collisions



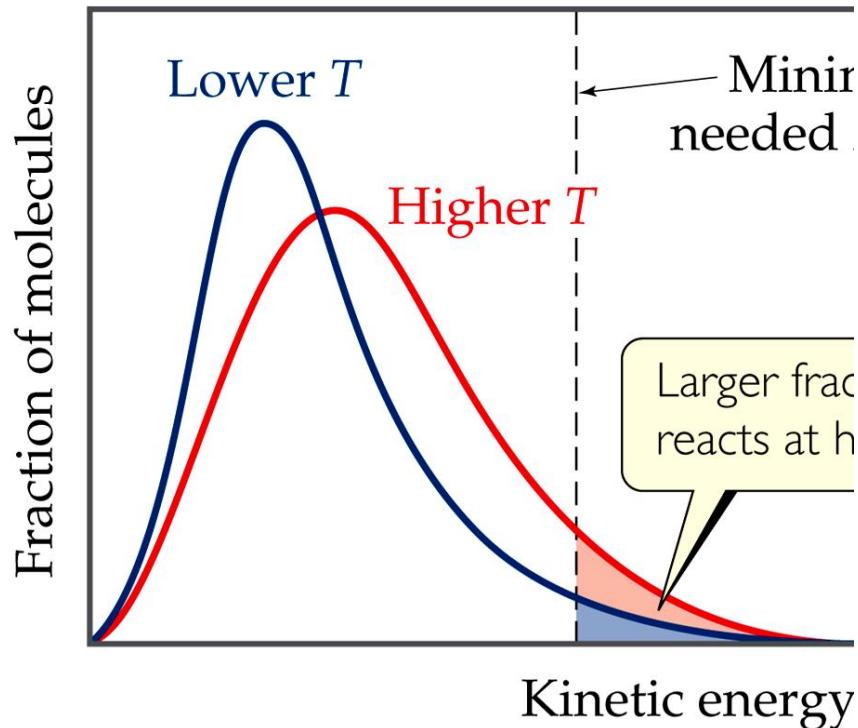
Steel wool heated in air  
(about 20% O<sub>2</sub>) glows red-hot  
but oxidizes to Fe<sub>2</sub>O<sub>3</sub> slowly



Red-hot steel wool in 100% O<sub>2</sub> burns vigorously, forming Fe<sub>2</sub>O<sub>3</sub> quickly

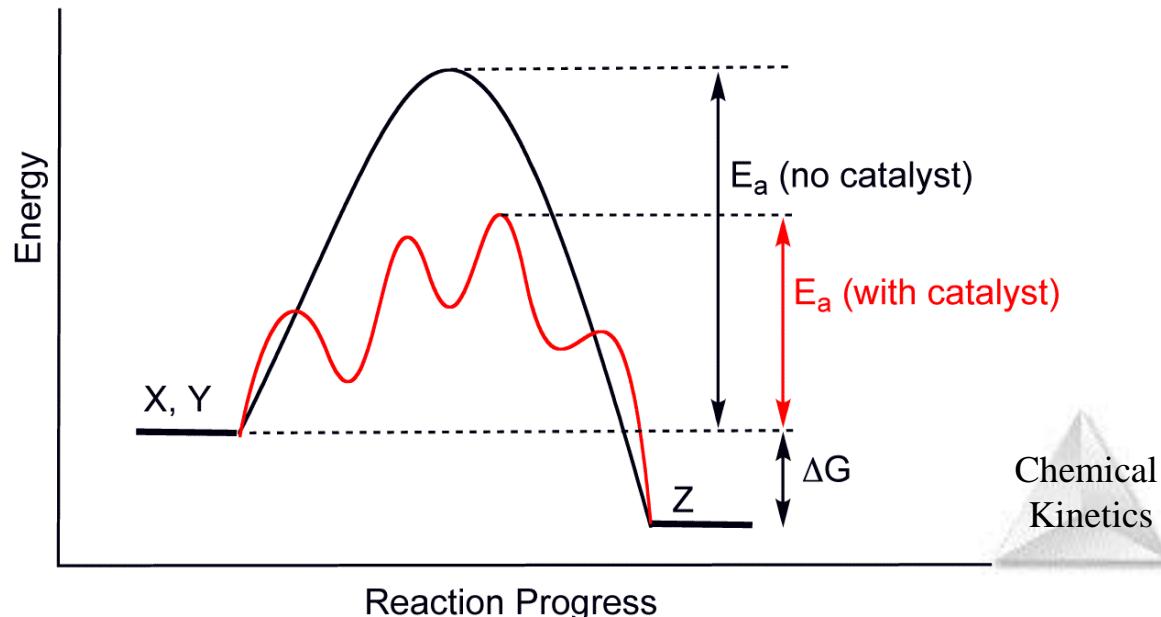
# Temperature

- Reaction rate generally **increases with increased temperature.**
- Average kinetic energy (K.E.) of molecules is related to **temperature:**  $\frac{3}{2} \frac{R}{N_A} T$
- At higher temperatures, molecules **move more quickly** (higher K.E.), **increasing** numbers of **collisions.**

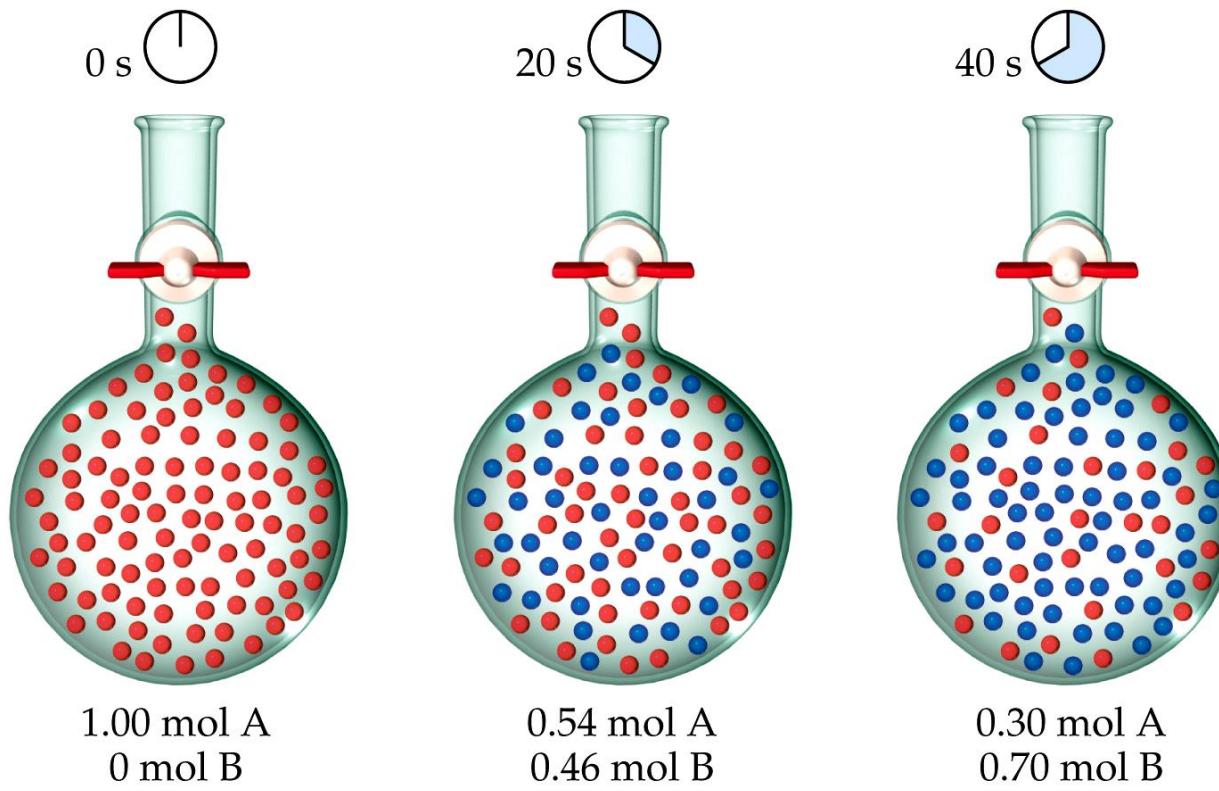


# Presence of a Catalyst

- Catalysts **speed up** reaction without being in the overall balanced equation. **Catalysts are not consumed** during the course of the reaction.
- Catalysts **affect the kinds of collisions, changing the mechanism** (individual reactions that are part of the pathway from reactants to products) and its **activation energy**.



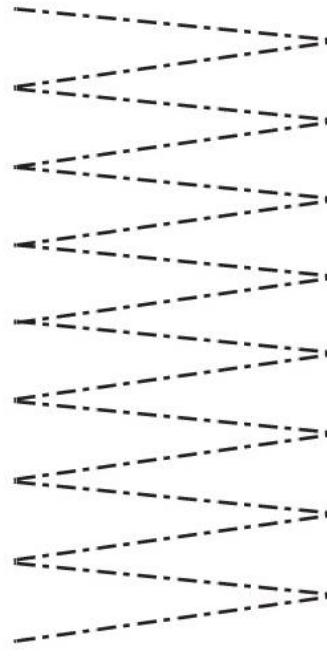
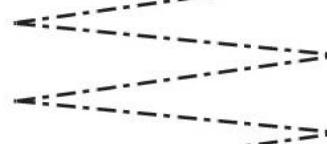
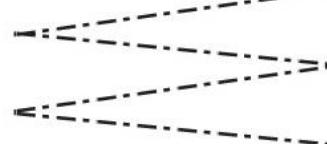
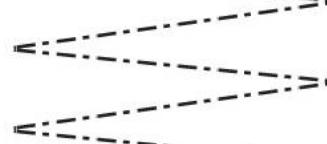
# Reaction Rates



- **Rates of reactions ( $r$ )** can be determined by monitoring the **change in concentration ([ ])** of either **reactants or products** as a function of **time (t)**:  
 $\Delta[ ]/\Delta t$ .
- Types of rate measured: **average rate**, **instantaneous rate** & **initial rate**.



Table 14.1 Rate Data for Reaction of  $\text{C}_4\text{H}_9\text{Cl}$  with Water

Time, t (s)	[ $\text{C}_4\text{H}_9\text{Cl}$ ] (M)	Average Rate (M/s)
0.0	0.1000	
50.0	0.0905	
100.0	0.0820	
150.0	0.0741	
200.0	0.0671	
300.0	0.0549	
400.0	0.0448	
500.0	0.0368	
800.0	0.0200	
10,000	0	

- In this case,  $[\text{C}_4\text{H}_9\text{Cl}]$  was followed/measured.

**Table 14.1 Rate Data for Reaction of C<sub>4</sub>H<sub>9</sub>Cl with Water**

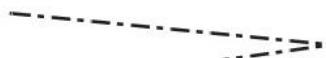
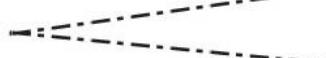
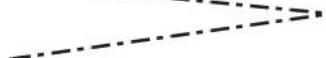
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400.0	0.0448	
500.0	0.0368	
800.0	0.0200	
10,000	0	

- The **average rate** of the reaction over each interval is the change in concentration divided by the change in time:

$$\text{Average rate} = -\frac{\Delta [\text{C}_4\text{H}_9\text{Cl}]}{\Delta t}$$

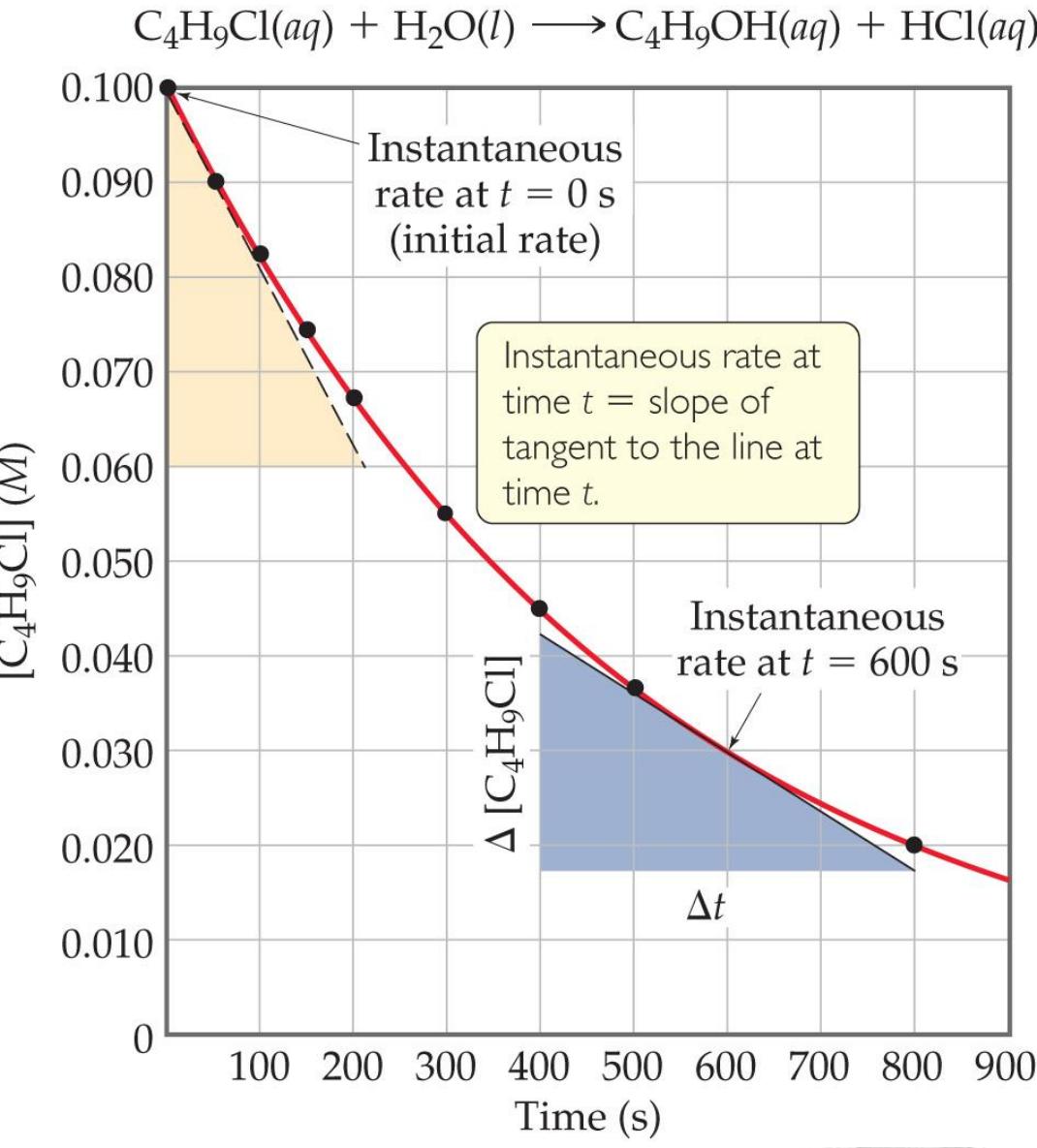
Chemical  
Kinetics

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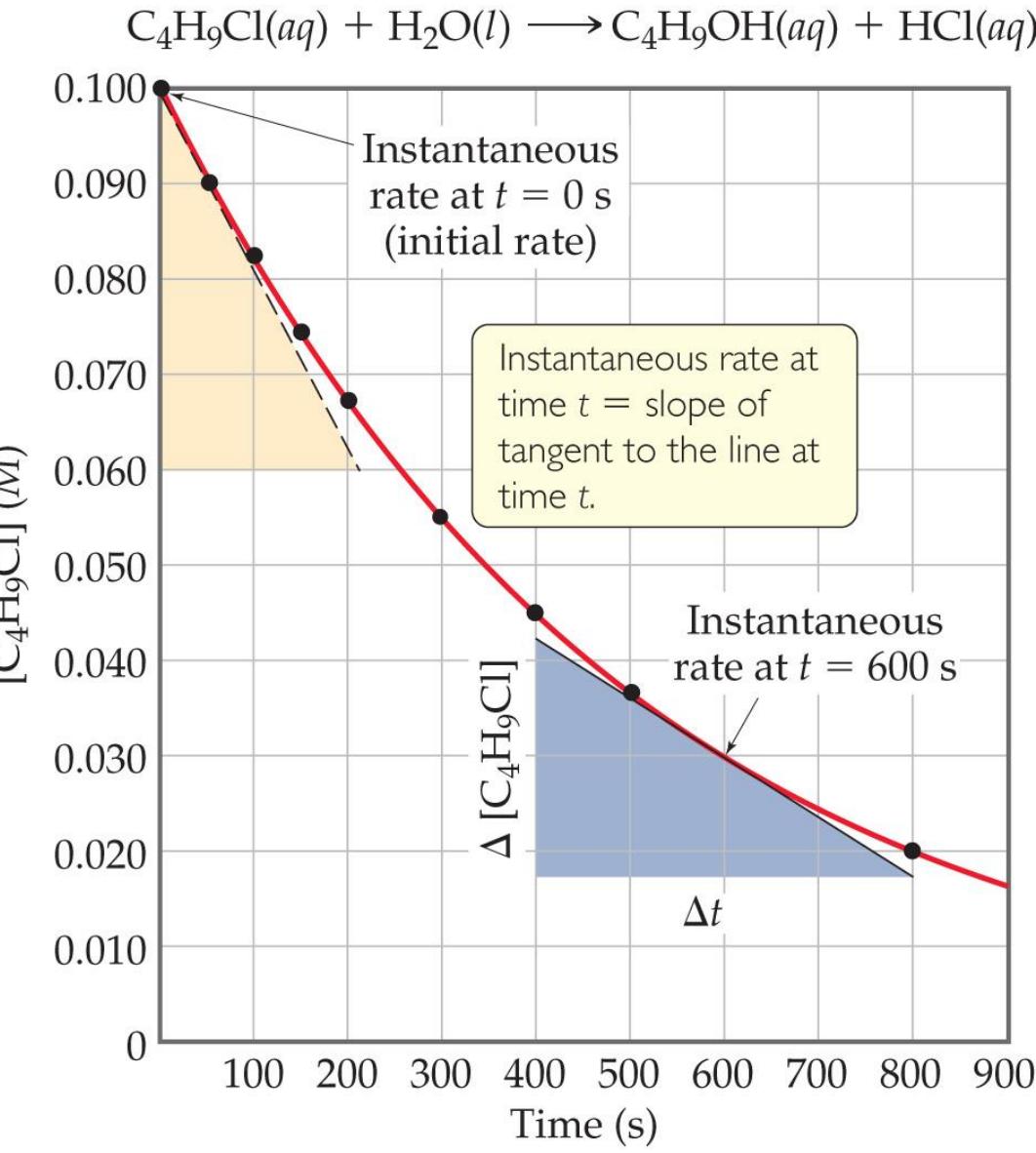
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300.0	0.0549	
400.0	0.0448	
500.0	0.0368	
800.0	0.0200	
10,000	0	

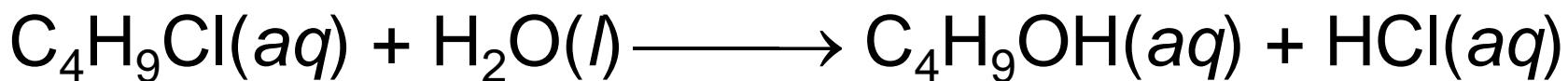
- The **average rate decreases as the reaction proceeds**. This is because as the reaction goes forward, there are **fewer collisions between reactant molecules**.

- A plot of  $[C_4H_9Cl]$  versus time for this reaction yields a curve like this.
- The **slope of the curve at any point** is **instantaneous rate** at that time.
- All reactions slow down over time.



- The **instantaneous rate at time zero** is called the **initial rate**.
- The **best indicator** of the rate of a reaction is the instantaneous rate near the **beginning** of the reaction.



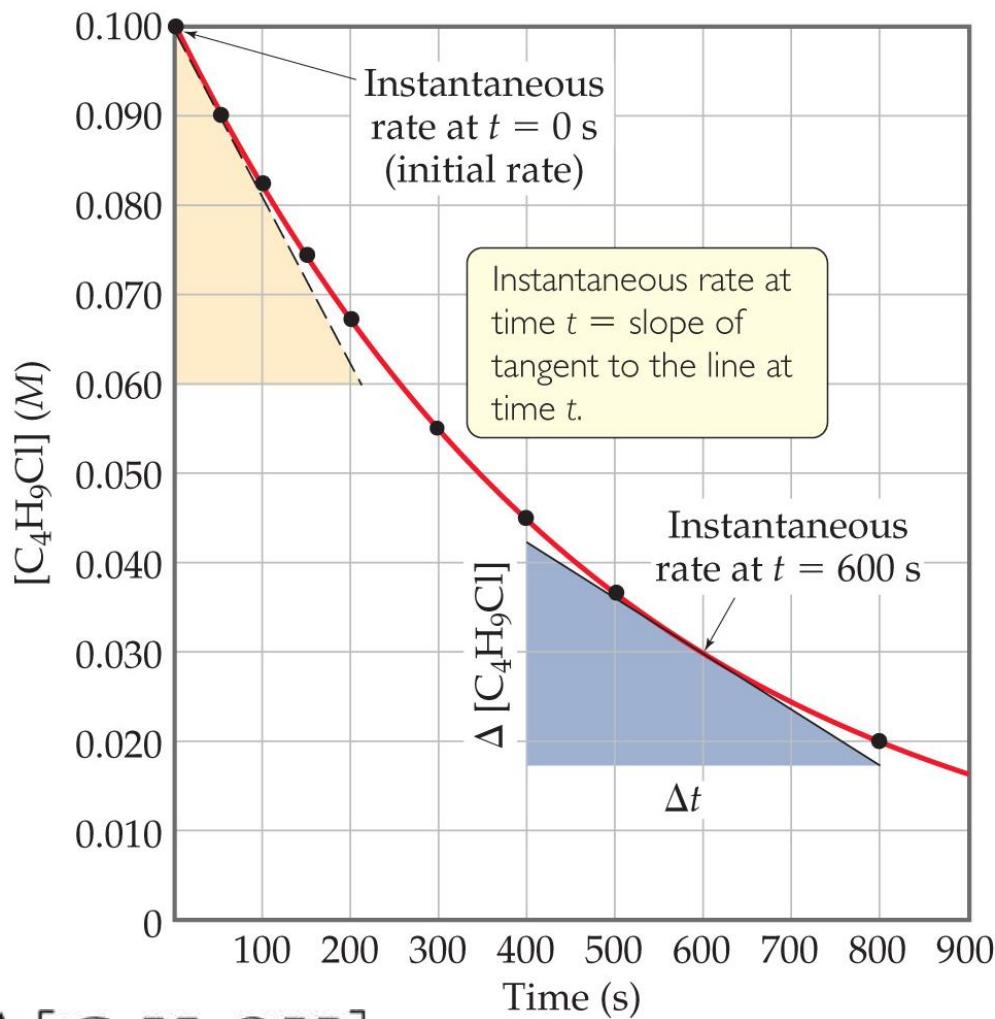


- Rate is dependent on stoichiometry.

- In this reaction, the ratio of  $\text{C}_4\text{H}_9\text{Cl}$  to  $\text{C}_4\text{H}_9\text{OH}$  is 1:1.

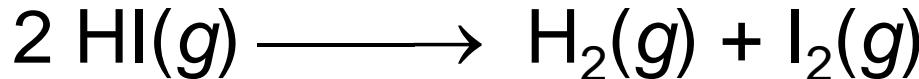
- Thus, the rate of disappearance of  $\text{C}_4\text{H}_9\text{Cl}$  is the same as the rate of appearance of  $\text{C}_4\text{H}_9\text{OH}$ : different sign.

$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t} = \frac{\Delta[\text{C}_4\text{H}_9\text{OH}]}{\Delta t}$$



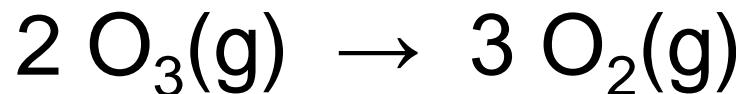
# Reaction Rates and Stoichiometry

- What if the ratio is *not* 1:1?



- In such a case,

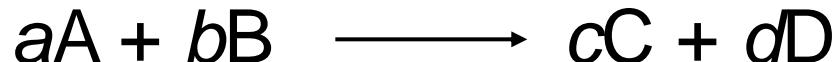
$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$



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

# Reaction Rates and Stoichiometry

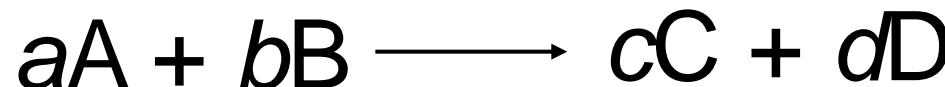
- To generalize, then, for the reaction



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

- sign should be added for any **reactant**.
- 1/coefficient** (a, b, c or d) should be added for all species, if the coefficient is not equal to 1.

# Determining Concentration Effect on Rate



- How do we determine what **effect the concentration of each reactant** has on the **rate** of the reaction?
- We **keep every concentration constant except for one reactant** and see what happens to the rate. Then, we change a different reactant to see how each reactant has affected the rate.

# Concentration and Rate

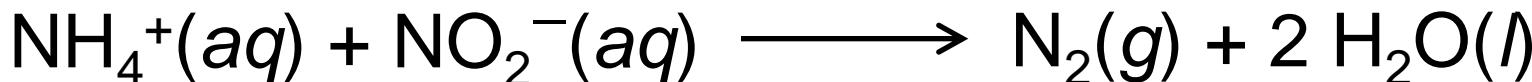


Table 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

Experiment Number	Initial $\text{NH}_4^+$ Concentration (M)	Initial $\text{NO}_2^-$ Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	$5.4 \times 10^{-7}$
2	0.0200	0.200	$10.8 \times 10^{-7}$
3	0.0400	0.200	$21.5 \times 10^{-7}$
4	0.200	0.0202	$10.8 \times 10^{-7}$
5	0.200	0.0404	$21.6 \times 10^{-7}$
6	0.200	0.0808	$43.3 \times 10^{-7}$

- If we compare Experiments 1 and 2, we see that when  $[\text{NH}_4^+]$  doubles, the initial rate doubles.



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- Likewise, when we compare Experiments 5 and 6, we see that when  $[\text{NO}_2^-]$  doubles, the initial rate doubles.



$$\text{Rate} \propto [\text{NH}_4^+]$$

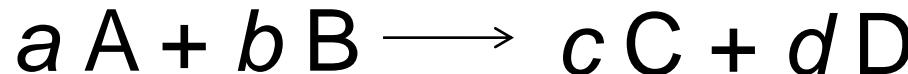
$$\text{Rate} \propto [\text{NO}_2^-]$$

$$\text{Rate} \propto [\text{NH}_4^+]^*[\text{NO}_2^-]$$

$$\text{Rate} = k^*[\text{NH}_4^+]^*[\text{NO}_2^-]$$

- This equation is called the **rate law**, &  $k$  is the **rate constant** (temperature-dependent quantity).

**For the general reaction**



$$\text{Rate} = k^*[\text{A}]^m * [\text{B}]^n$$

- The exponents ( **$m$  or  $n$** ) tell the **order** of the reaction (can be different from  $a$  or  $b$ ) with respect to each reactant.
- The **order** with respect to each reactant is 1 in the above example. The **reaction is second order**.

Table 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

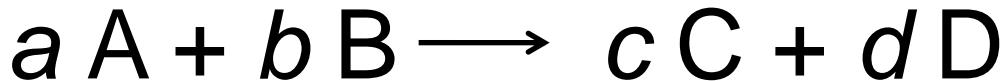
Experiment Number	Initial NH <sub>4</sub> <sup>+</sup> Concentration (M)	Initial NO <sub>2</sub> <sup>-</sup> Concentration (M)	Observed Initial Rate (M/s)
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5	0.200	0.0404	21.6 × 10 <sup>-7</sup>
6	0.200	0.0808	43.3 × 10 <sup>-7</sup>

- A **rate law** shows the relationship between **rate** and **concentration for all reactants**:

$$\text{Rate} = k^*[\text{NH}_4^+]^*[\text{NO}_2^-]$$

Chemical  
Kinetics

# First Order Reactions



- Some **rates** depend *only* on **one reactant** (e.g. A) **to the first power**. The rate law becomes:

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

or

$$\text{rate} = -\Delta[A]/\Delta t \quad (a=1)$$

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

- These are ***first order*** reactions.

# Integrated Rate Laws

$$\text{Rate} = -\frac{\Delta [\text{A}]}{\Delta t} = k[\text{A}]$$

- After rearrangement:

$$\Delta[\text{A}]/[\text{A}] = -k^* \Delta t$$

- Using calculus to integrate the rate law for a first-order process gives us

$$\ln([\text{A}]/[\text{A}]_0) = -k^* t$$

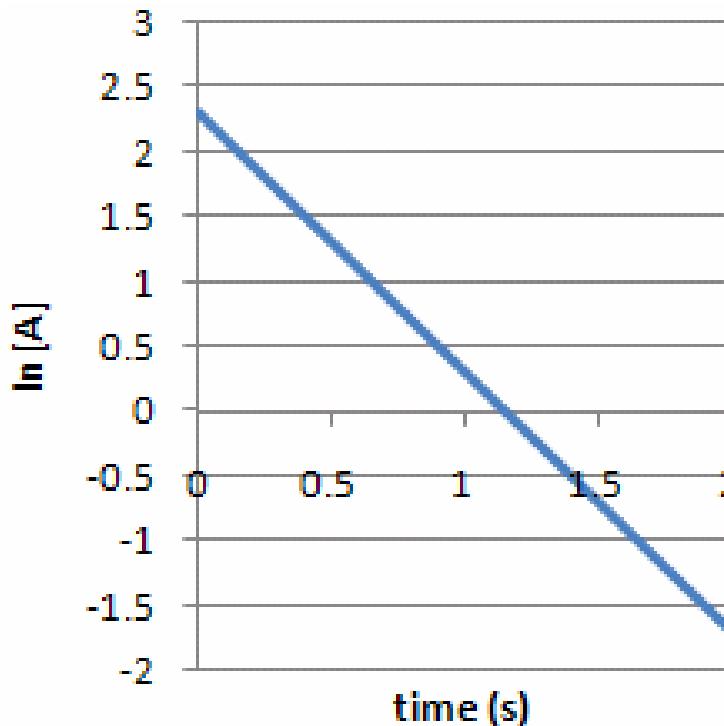
$[\text{A}]_0$  is the **initial** concentration of A at time zero, &  $[\text{A}]$  is the concentration of A at time ( $t$ ) during the course of the reaction.

$$\ln([A]/[A]_0) = -k^*t$$

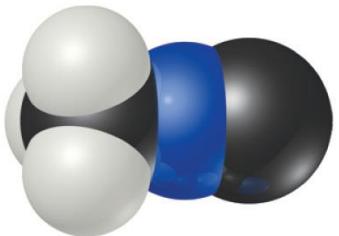
- After rearrangement:

$$\ln[A] = -k^*t + \ln[A]_0$$

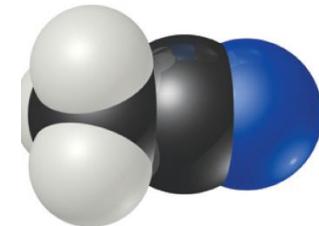
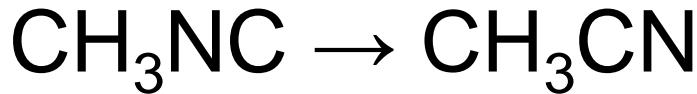
- This follows the equation of a line:  $y = m x + b$
- So, a plot of  **$\ln[A]$  vs.  $t$**  is **linear**. Its **slope** is equal  **$-k$  (Unit:  $s^{-1}$ )**.



# An Example: Conversion of Methyl Isonitrile to Acetonitrile

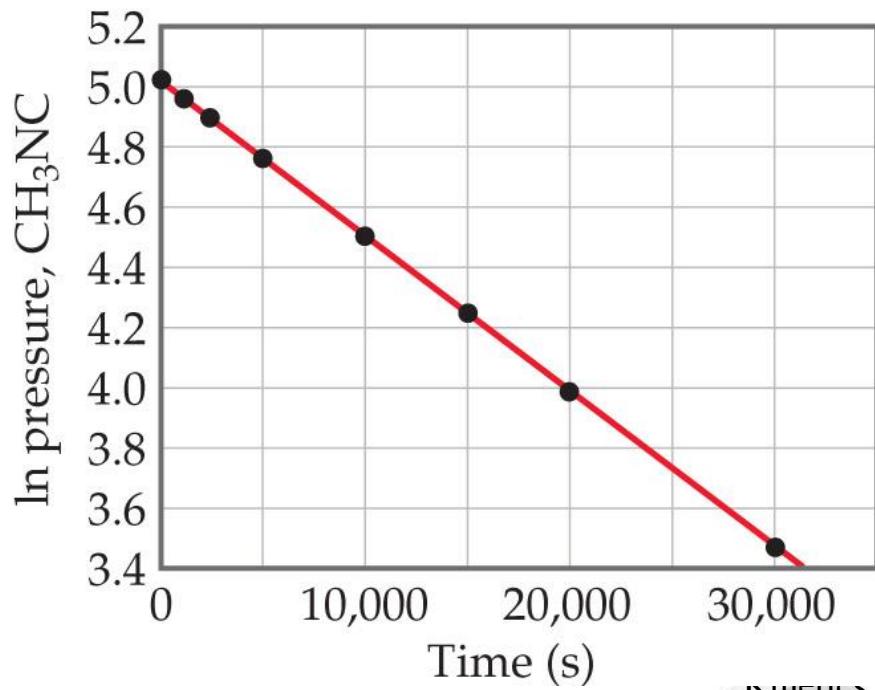
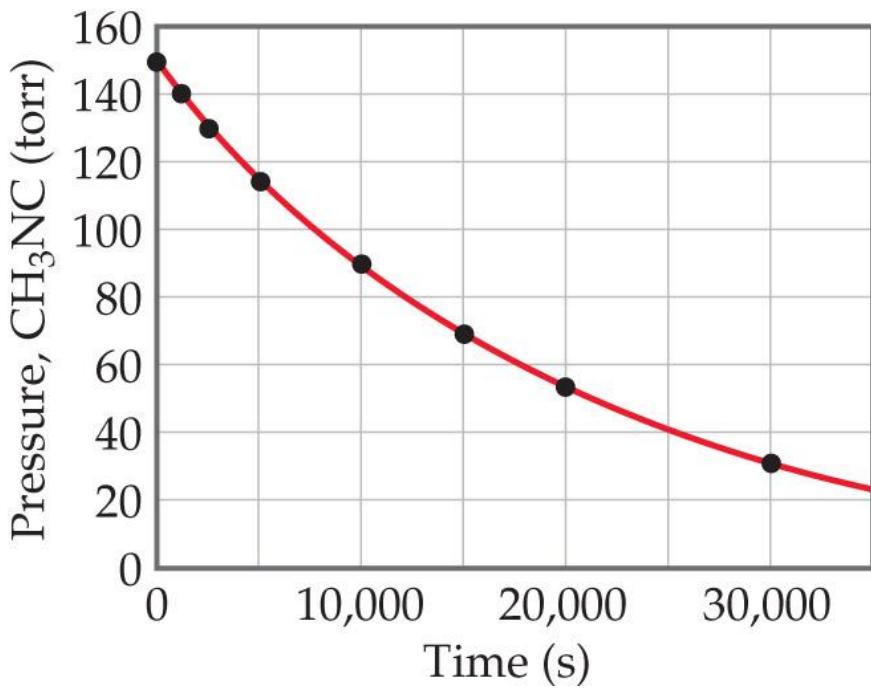


Methyl isonitrile



Acetonitrile

$$\text{Rate} = k[\text{CH}_3\text{NC}]$$



$$k: 5.1 \times 10^{-5} \text{ s}^{-1}$$

# Half-life

- The amount of **time** it takes for **one-half** of a **reactant** to be **used up** in a chemical reaction.

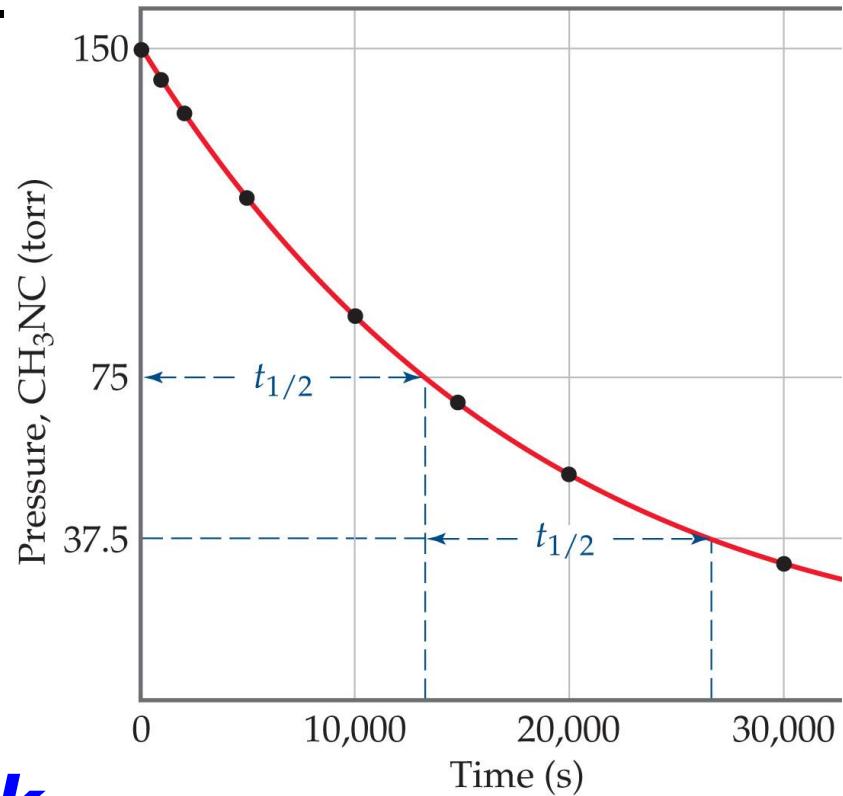
$$\ln[A] = -k^*t + \ln[A]_0$$

$$\ln([A]_0/2) = -k^*t_{1/2} + \ln[A]_0$$

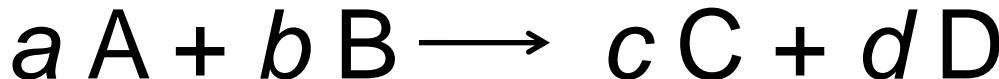
$$\ln[A]_0 - \ln([A]_0/2) = k^*t_{1/2}$$

$$\ln([A]_0/[A]_0/2) = k^*t_{1/2}$$

$$\ln(2) = k^*t_{1/2} \rightarrow t_{1/2} = 0.693/k$$



# Second Order Reactions



- Some rates depend only on **a reactant to the second power or two reactants to the first power.**

The rate law becomes:

$$\text{Rate} = k^*[A]^2$$

or

$$\text{Rate} = k^*[A][B]$$

- These are **second order** reactions.

- For rate =  $k^*[A]^2$
- rate =  $-\Delta[A]/\Delta t$
- So,

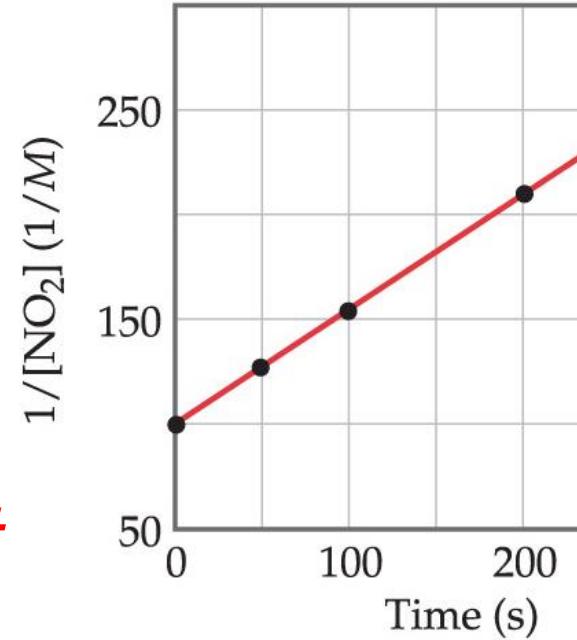
$$k^*[A]^2 = -\Delta[A]/\Delta t$$

- Rearranging:

$$\Delta[A]/[A]^2 = -k^*\Delta t$$

- Using calculus:

$$1/[A] = 1/[A]_0 + k^*t$$



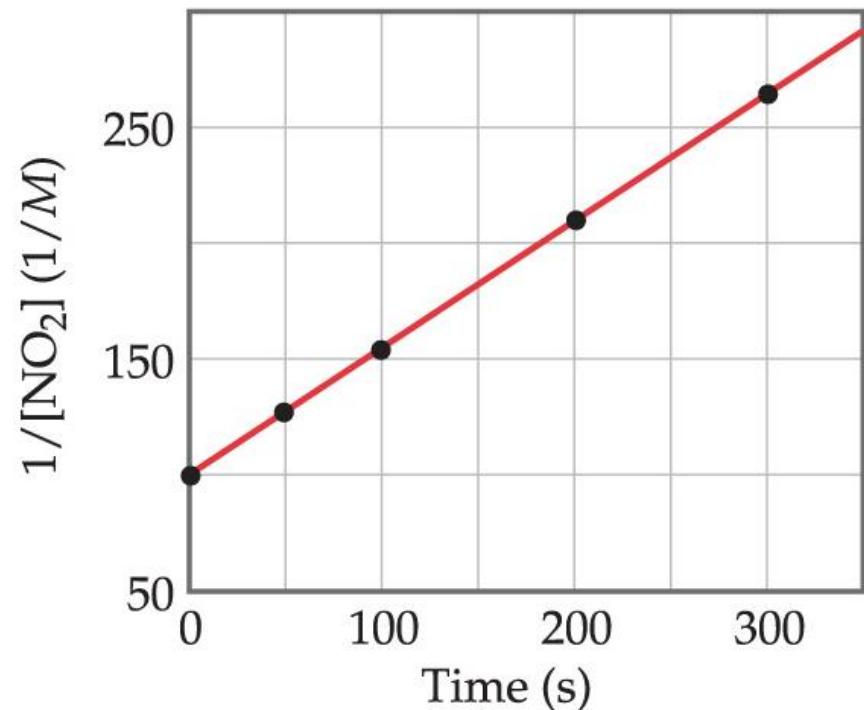
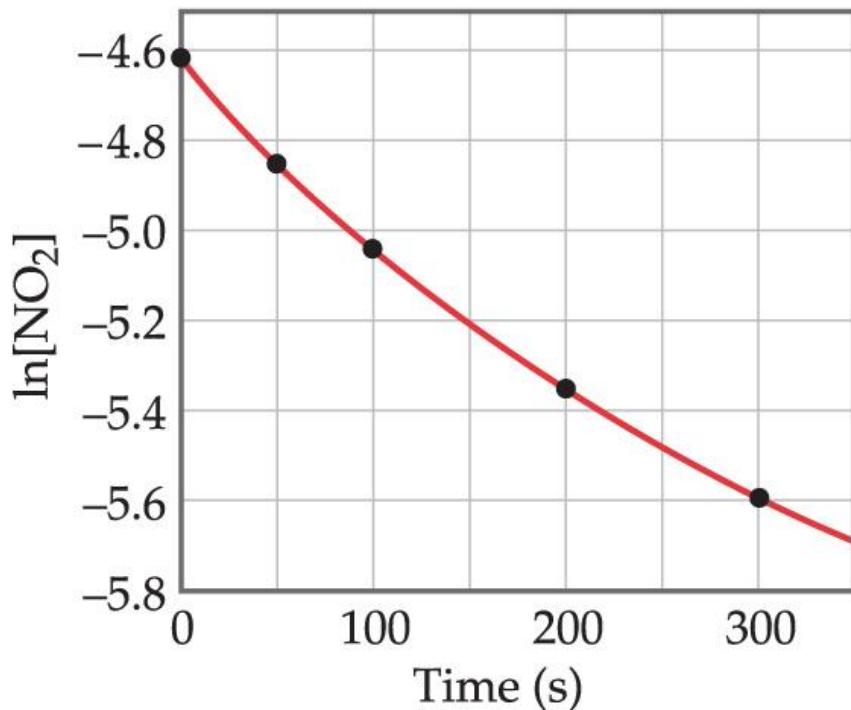
- The **linear** relationships for **first order (below)** and **second order (above)** reactions are different linear forms!

$$\ln[A] = -k^*t + \ln[A]_0$$

# An Example of a Second Order Reaction: Decomposition of $\text{NO}_2$



- A plot must be second order because it is linear for  $1/[\text{NO}_2]$ , *not* linear for  $\ln [\text{NO}_2]$ .



# Half-Life

$$1/[A] = 1/[A]_0 + k^*t$$

$$1/([A]_0/2) = 1/[A]_0 + k^*t_{1/2}$$

$$2/[A]_0 - 1/[A]_0 = k^*t_{1/2}$$

$$t_{1/2} = 1/(k^*[A]_0)$$

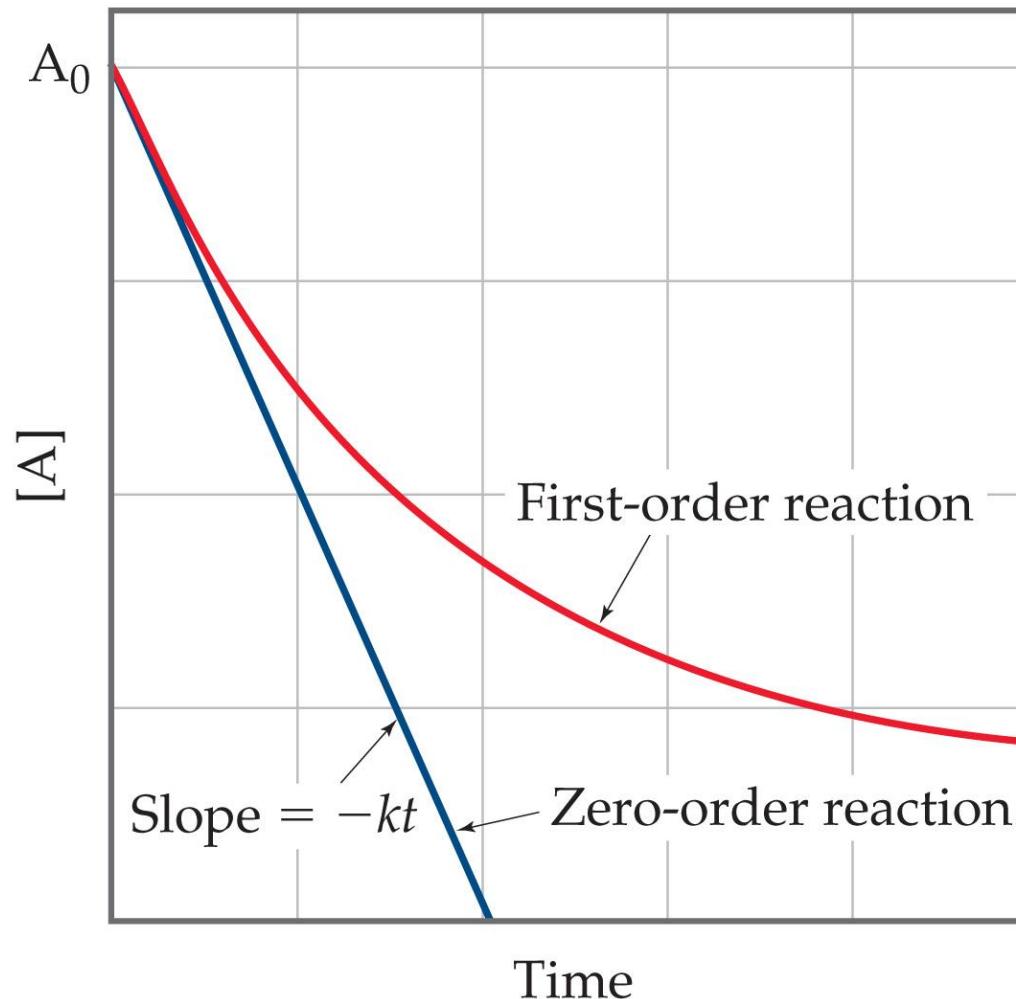
- So, half-life is a **concentration dependent** quantity for second order reactions!

# Zero Order Reactions

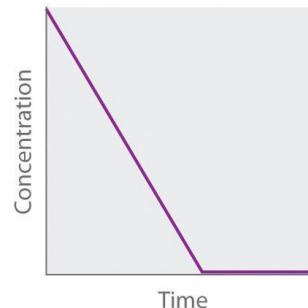
- Occasionally, rate is **independent** of the concentration of the reactant(s).

$$\text{Rate} = k$$
$$[A] = [A]_0 - k^*t$$

- These are **zero order** reactions.
- These reactions are linear in concentration.
- $t_{1/2} = [A]_0/(2k)$

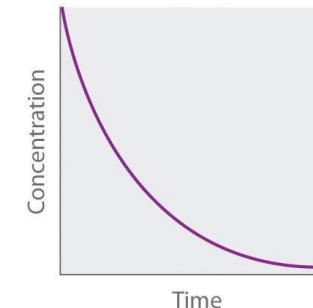


$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$$

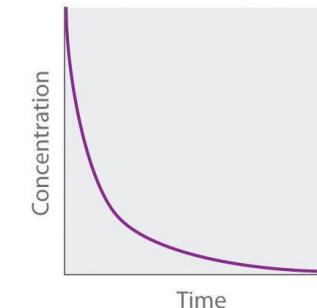
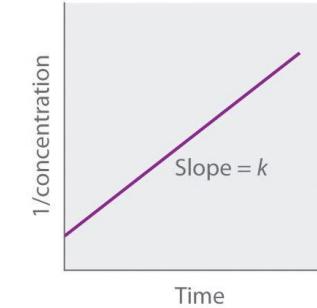
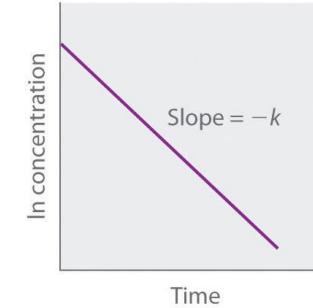
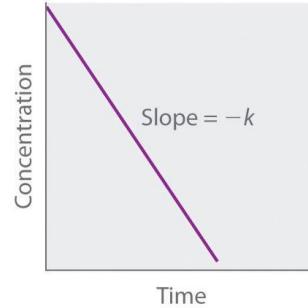
Concentration  
vs. time**Zero Order**Integrated  
rate law

$$[A] = [A]_0 - kt$$

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

**First Order**

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

**Second Order**Straight-line plot  
to determine rate  
constantRelative rate  
vs. concentration

[A], M	Rate, M/s
1	1
2	1
3	1

[A], M	Rate, M/s
1	1
2	2
3	3

[A], M	Rate, M/s
1	1
2	4
3	9

<https://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0m/s18-04-using-graphs-to-determine-rate.html>

## Half-life

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

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

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

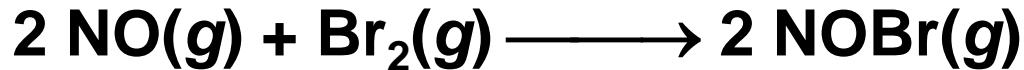
Units of k,  
rate constant

M/s

1/s

M<sup>-1</sup>·s<sup>-1</sup>

# Some examples of experimentally determined rate law



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



$$\text{Rate} = k[\text{N}_2\text{O}]$$



$$\text{Rate} = k[\text{H}_2][\text{Br}_2]^{1/2}$$



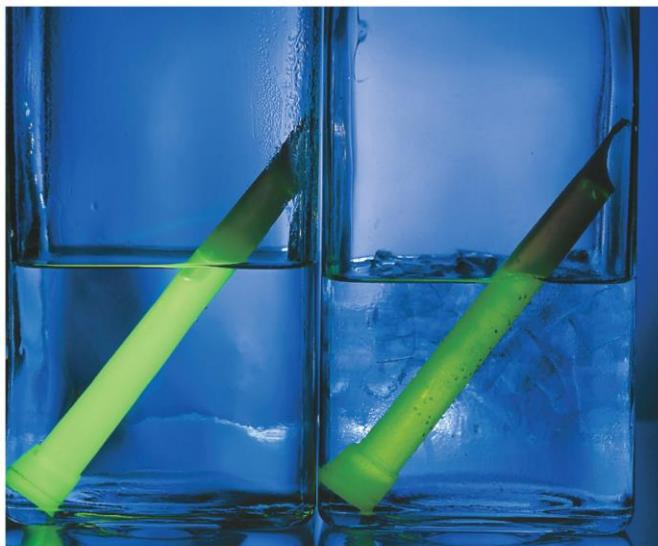
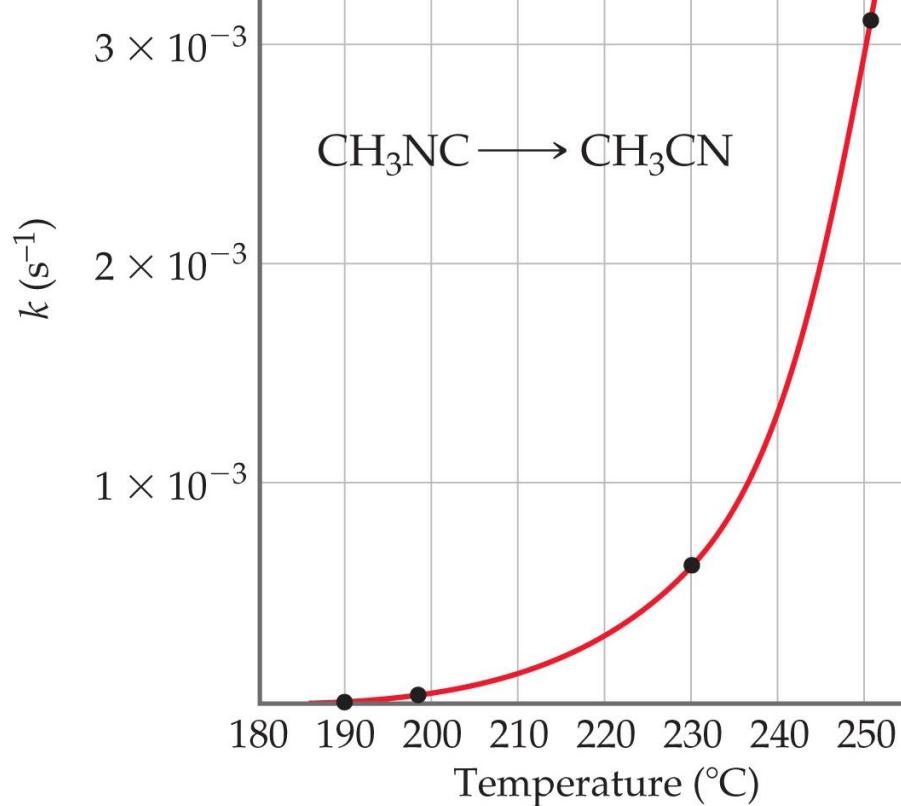
- Rate law are always **determined experimentally**.
- Reaction order is always defined in terms of **reactant** (not product) **concentrations**.
- The **reactant order** is **not necessarily** related to the **stoichiometric coefficient** of the reactant in the balanced chemical equation.

# Factors That Affect Reaction Rate

1. Temperature
2. Frequency of collisions
3. Orientation of molecules
4. Energy needed for the reaction to take place  
**(activation energy or barrier)**

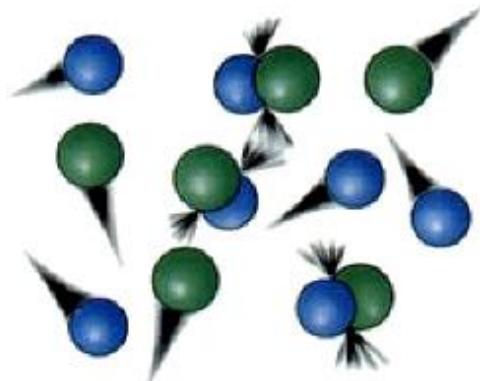
# Temperature

- Generally, as temperature increases, rate ( $r$ ) increases.
- The rate constant ( $k$ ) is temperature dependent: it increases as temperature increases.
- Rate constant ( $k$ ) doubles approximately with every 10 °C rise.

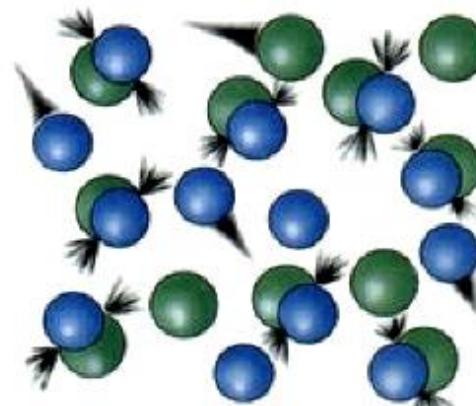


# Frequency of Collisions

- The **collision model** is based on the kinetic molecular theory.
- Molecules must collide to react.
- If there are **more collisions, more reactions** can occur.
- So, if there are **more molecules**, the reaction rate is **faster**.
- Also, if the **temperature** is **higher**, molecules move faster, causing **more collisions** and a **higher rate** of reaction.



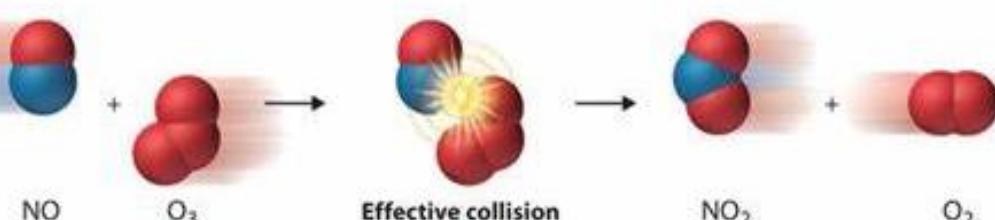
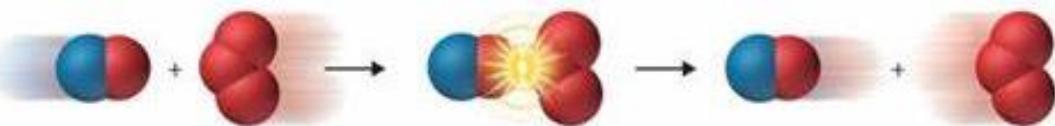
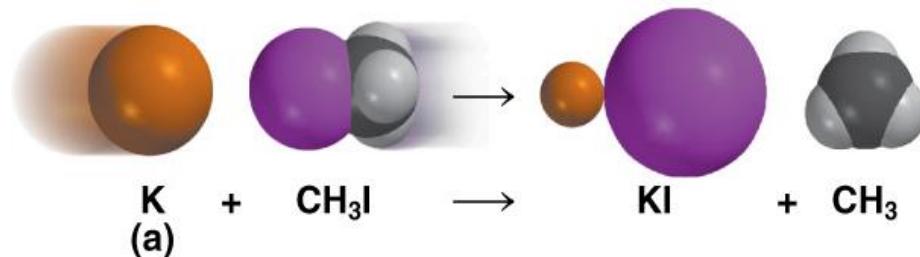
Low concentration = Few collisions



High concentration = More collisions

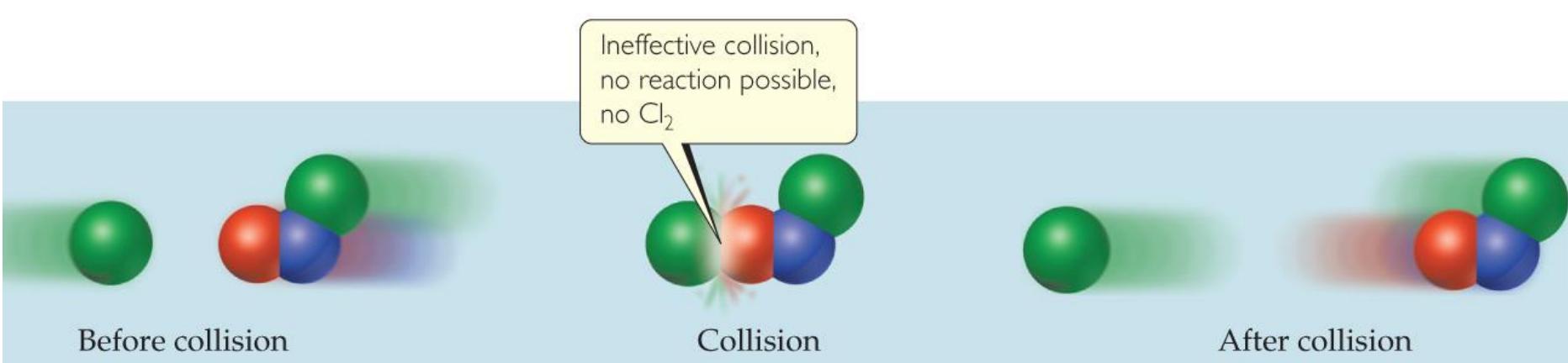
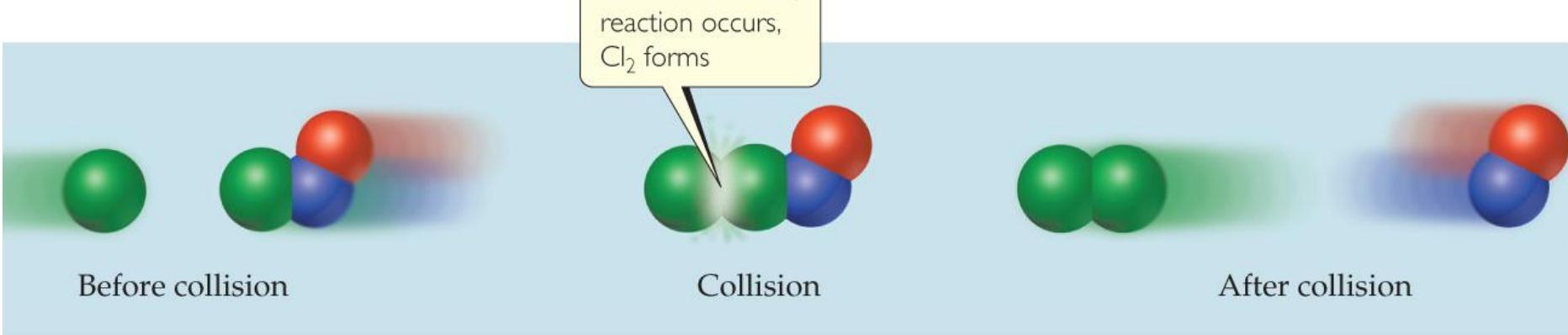
# The Collision Model: Orientation Factor

- In a chemical reaction, **bonds** are **broken** and **new bonds** are **formed**.
- Molecules** can only react if they **collide** with each other in a **suitable orientation & with enough energy**.

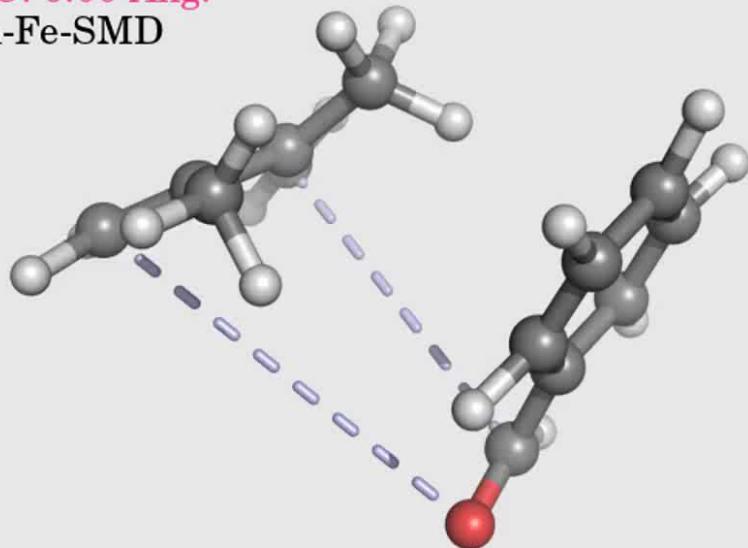


# Orientation of Molecules

- Molecules can often collide without forming products.
- Aligning molecules properly can lead to chemical reactions.
- Bonds must be broken & made and atoms need to be in proper positions.

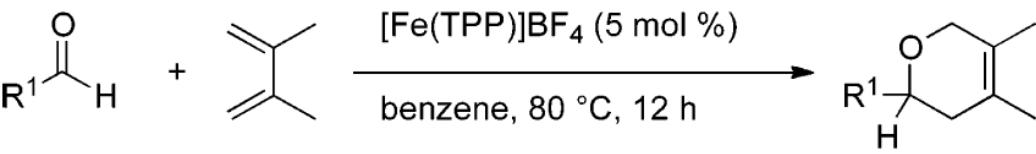


**-150 fs**  
C-C: 5.06 Ang.  
C-O: 6.00 Ang.  
Non-Fe-SMD



# Reaction Dynamics (Quantum Mechanics + Newtonian Eqs)

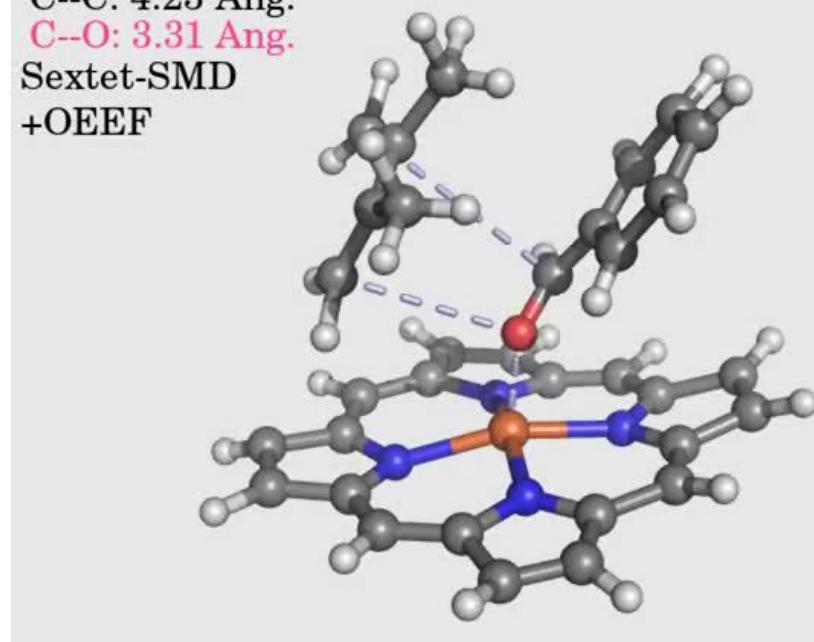
**(extra info.)**



Yang, Zhang, Zhong, Lan, Li, Li,  
Chung, *Nat. Commun.* **2020**, 1850.

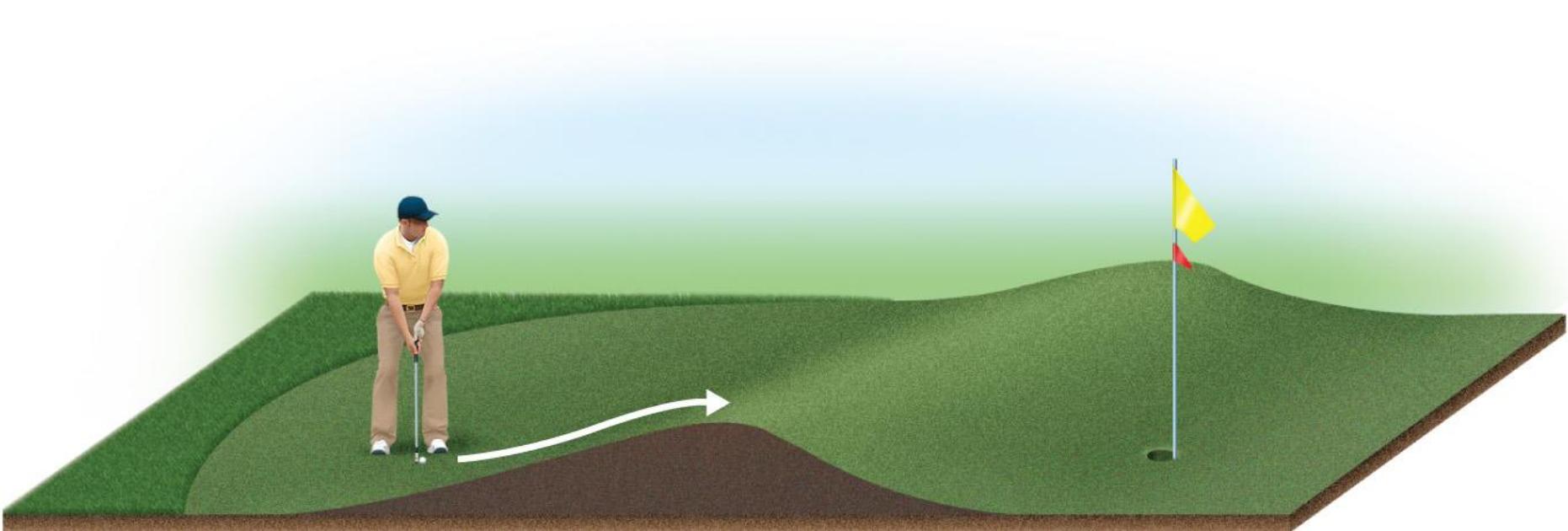
© 2015 Pearson Education

**-174 fs**  
C-C: 4.23 Ang.  
C-O: 3.31 Ang.  
Sextet-SMD  
+OEEF



# Activation Energy

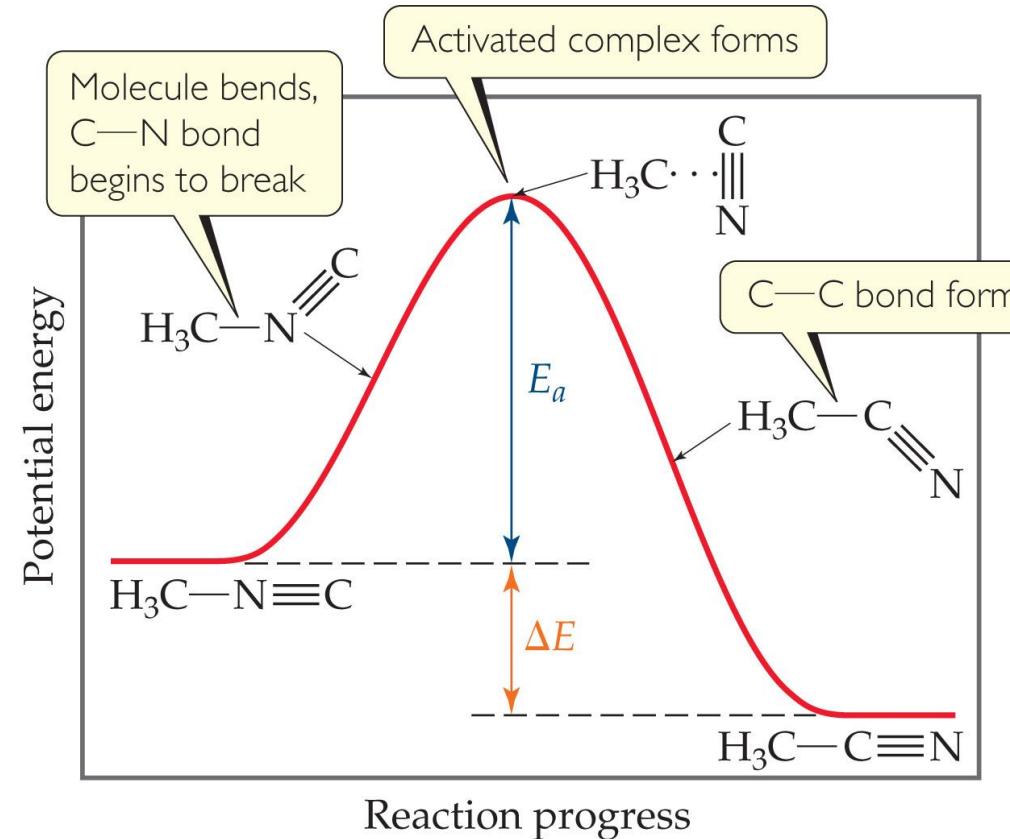
- The **minimum energy** needed for a reaction to take place is called **activation energy** ( $E_a$ ).
- An **energy barrier** must be overcome for a reaction to take place (**collision & bond broken**), much like the ball must be hit to overcome the barrier in the figure below.



# Reaction Coordinate Diagrams

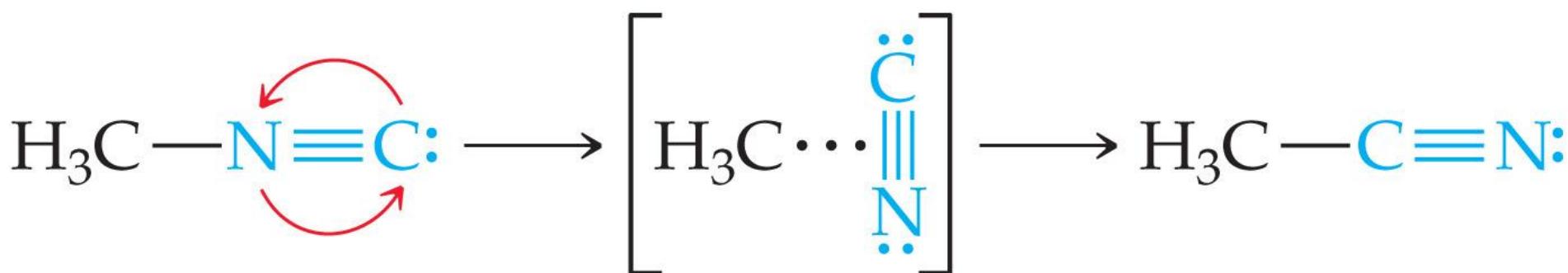
- Plots are made to show the **change in the potential energy** possessed by the particles **as the reaction proceeds.**

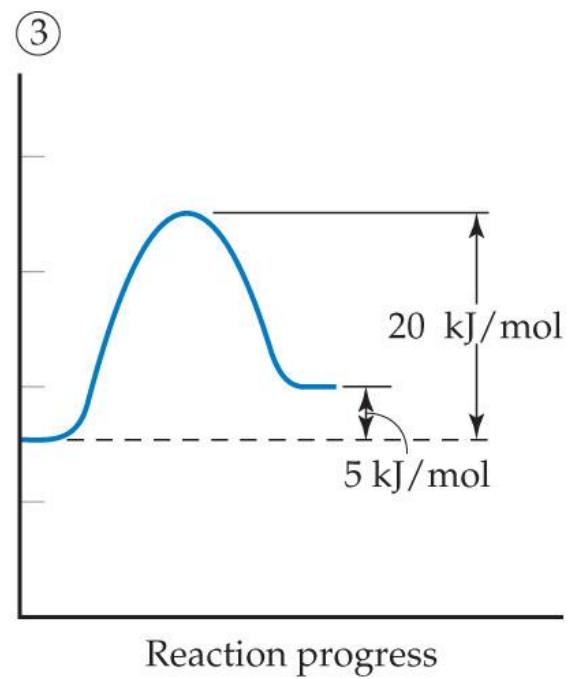
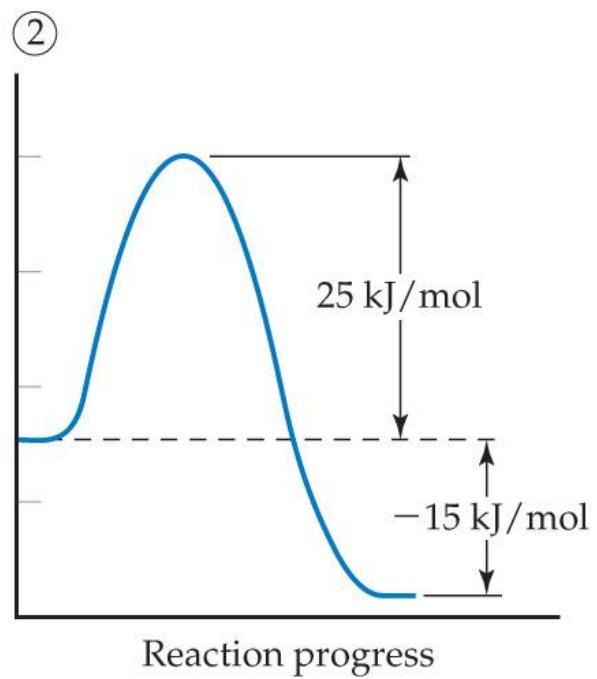
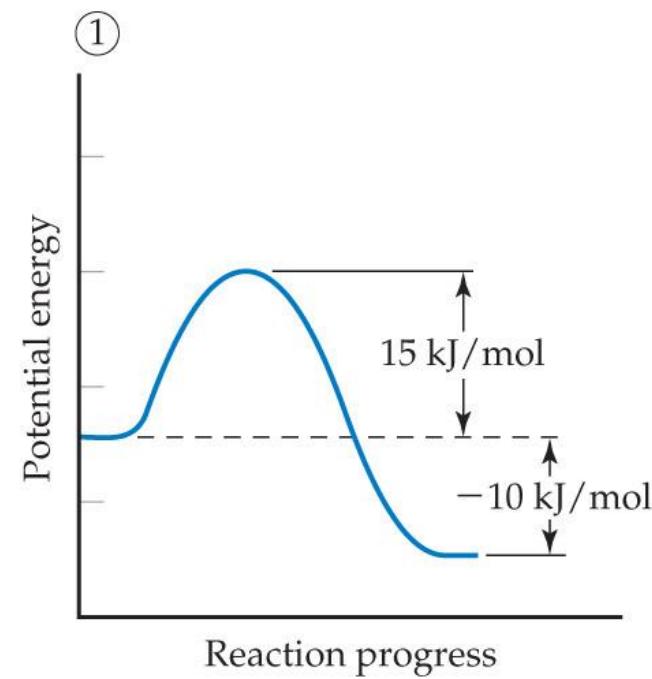
- At the **highest energy state ( $E_a$ )**, the **transition state/activated complex** is formed.
- Reactions can be endothermic or exothermic after this ( $\Delta E$ ).



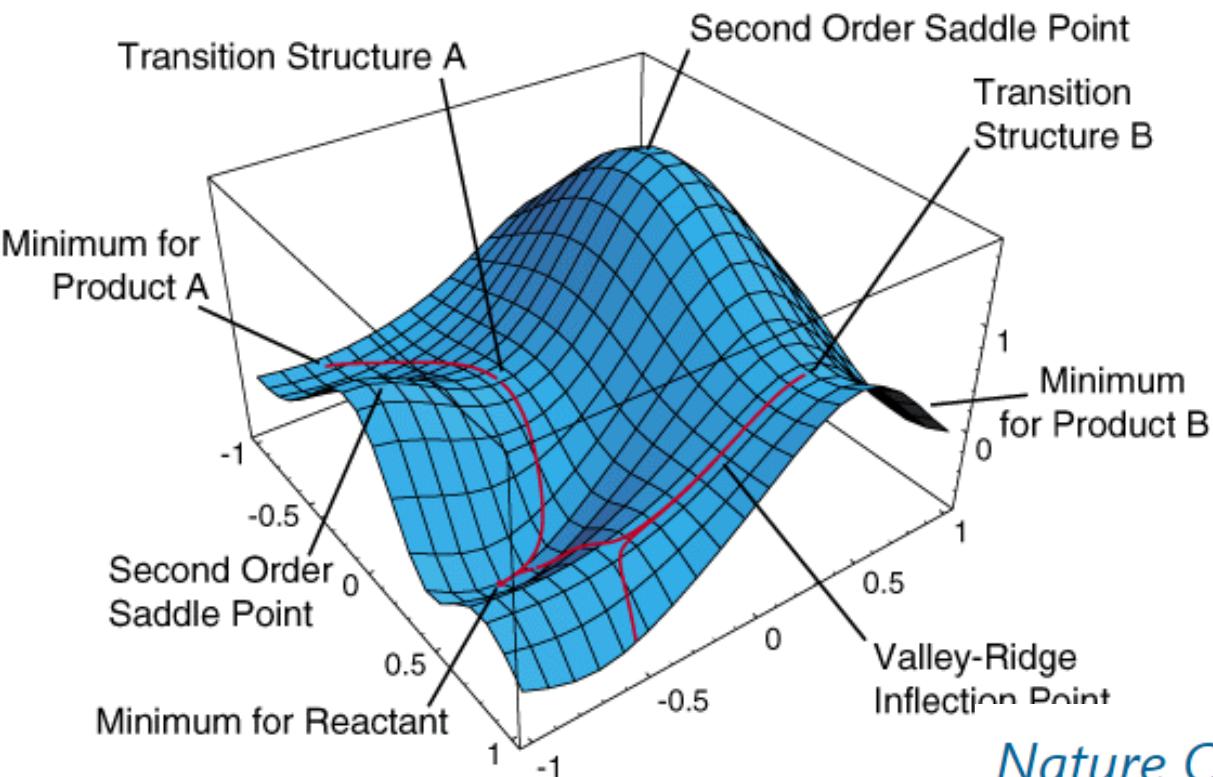
# Transition State (Activated Complex)

- Reactants gain energy as the reaction proceeds until the particles reach the maximum energy state.
- The organization of the atoms at this highest energy state is called the **transition state (or activated complex)**: **ultra-short lifetime** of species.
- The energy needed to form this state is called the *activation energy ( $E_a$ ) or barrier*.



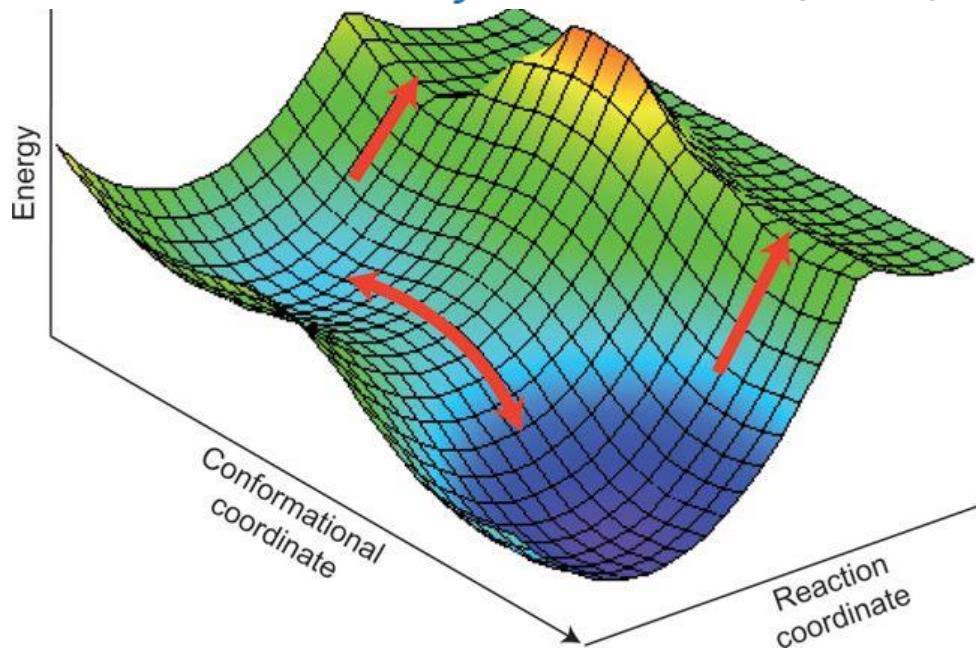


(extra info.)



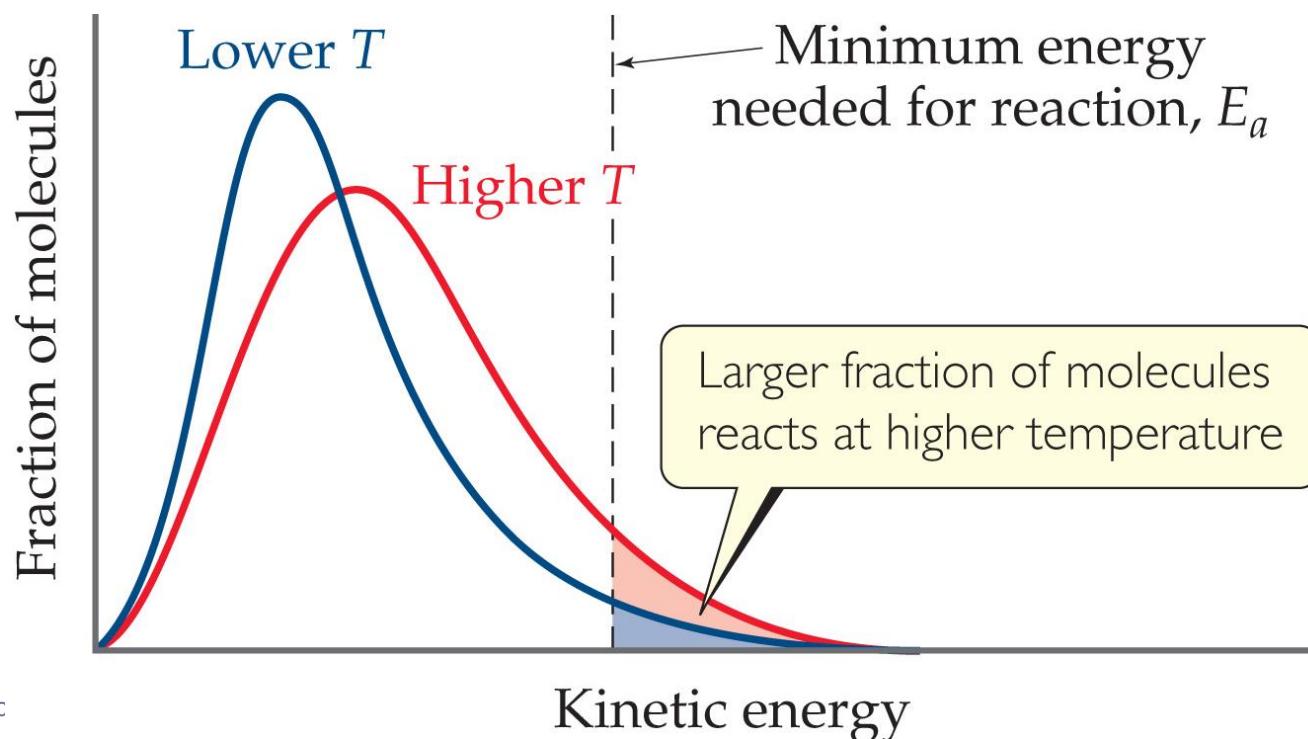
- Generally, non-linear molecules have  $3N-6$  vibrational degree of freedom (vib. DoF; N: no. of atoms). Herein, the plots are added with one more vib. DoF.

*Nature Chemistry* 4, 169–176(2012)



# Maxwell–Boltzmann Distributions of the Energy of Molecules

- Temperature determines average kinetic energy of the molecules, but each individual molecule has its own kinetic energy: a wide distribution of kinetic energies.
- At higher temperature, more molecules possess the kinetic energy needed for the reaction to occur.

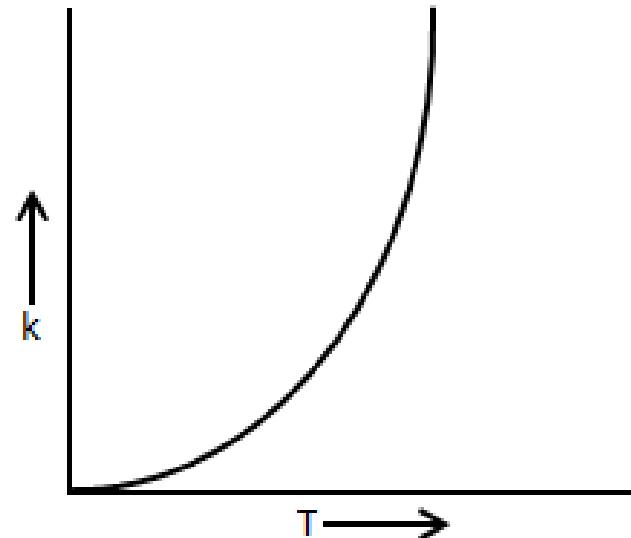


# Arrhenius Equation

- Svante Arrhenius developed a mathematical relationship between  $k$  and  $E_a$ :

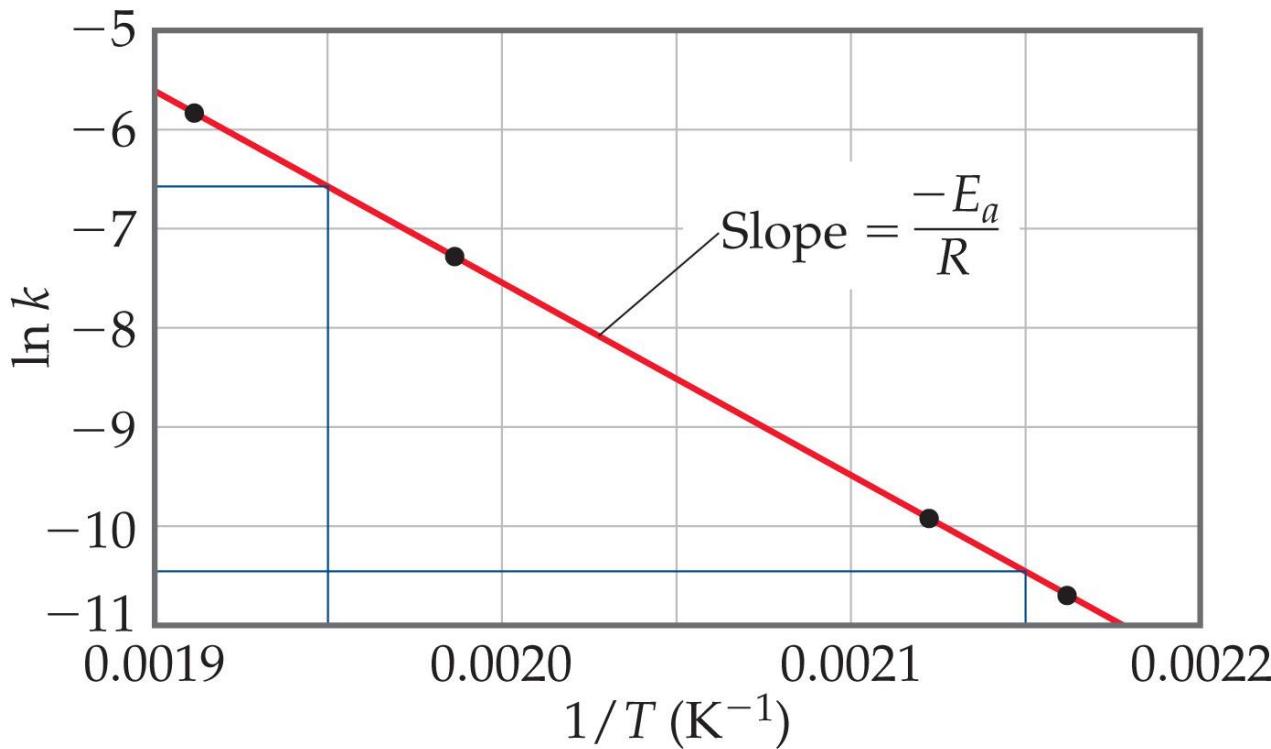
$$k = A e^{-E_a/RT}$$

where  $A$  is the **frequency factor**, a number that represents the **likelihood that collisions** would occur with the proper orientation for reaction (**NOT  $[A]$ !**).



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

- Activation energy can be determined graphically by reorganizing the equation:  $\ln(k) = -E_a/RT + \ln(A)$



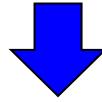
- Thus, if  $k$  is determined experimentally at several temperatures,  $E_a$  can be calculated.

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

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

Subtracting  $\ln k_2$  from  $\ln k_1$  gives

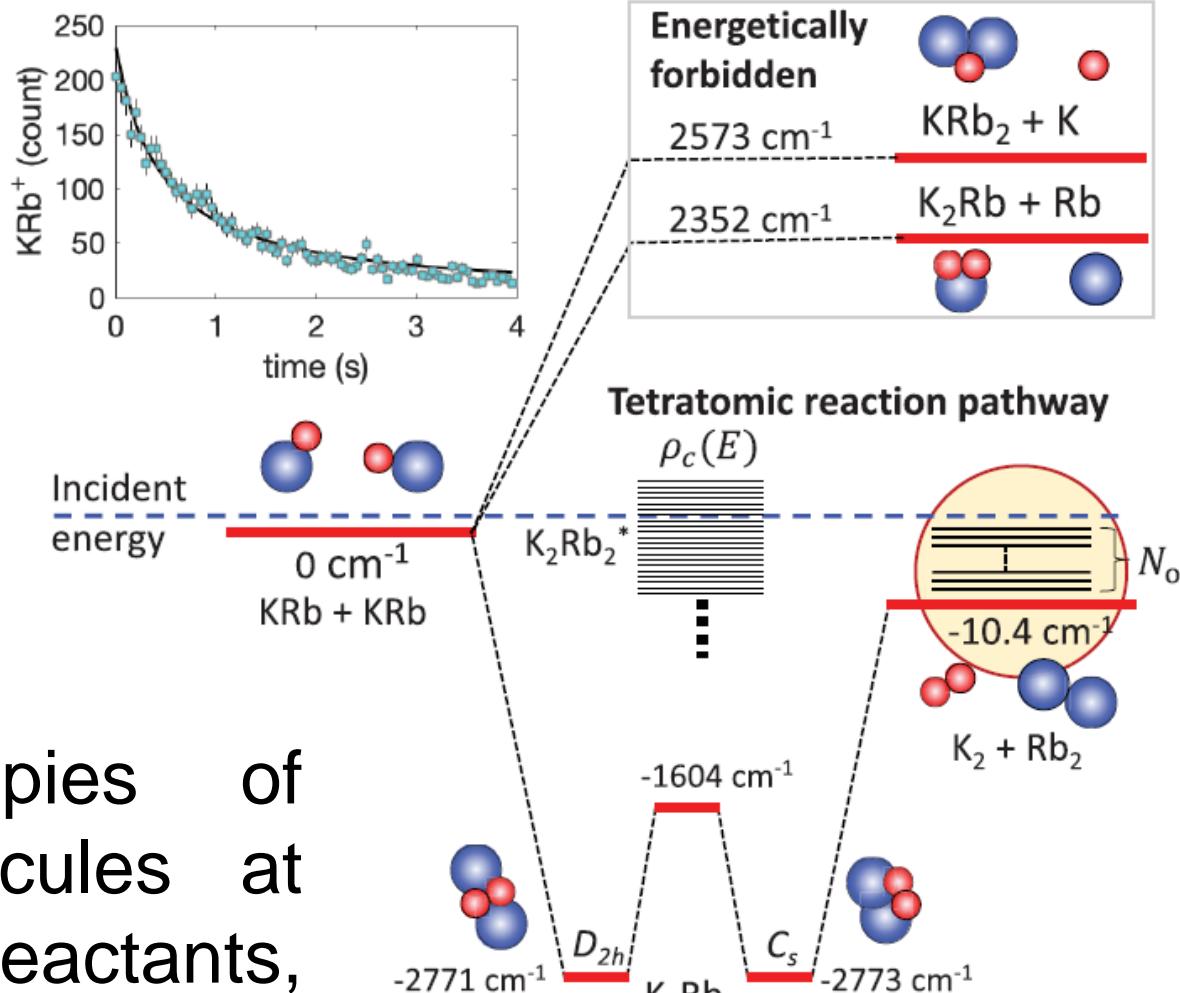
$$\ln k_1 - \ln k_2 = \left( -\frac{E_a}{RT_1} + \ln A \right) - \left( -\frac{E_a}{RT_2} + \ln A \right)$$



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

- We can calculate a rate constant  $k_1$  at  $T_1$ , when we know the activation energy and the rate constant  $k_2$  at other temperature  $T_2$ .

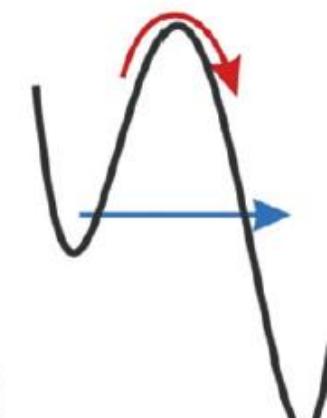
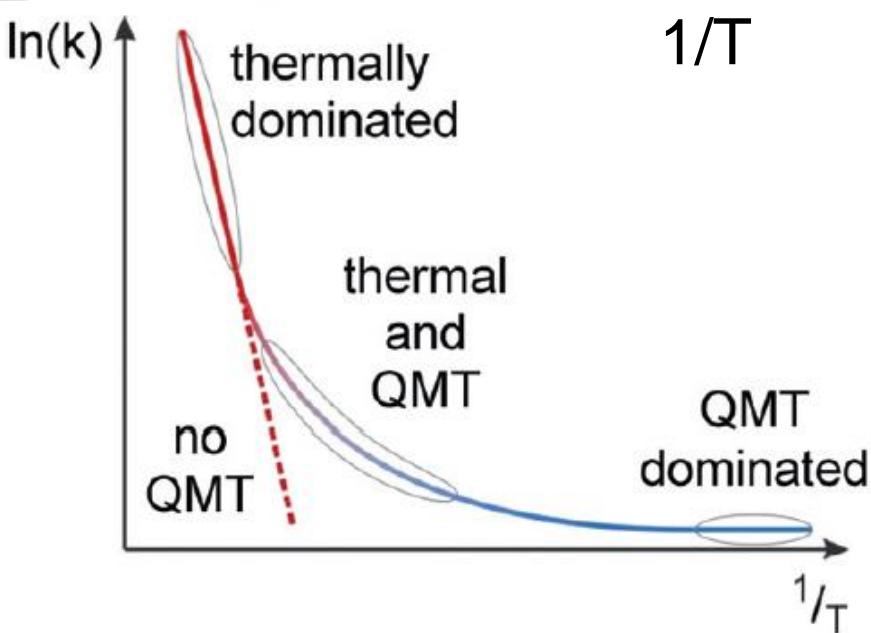
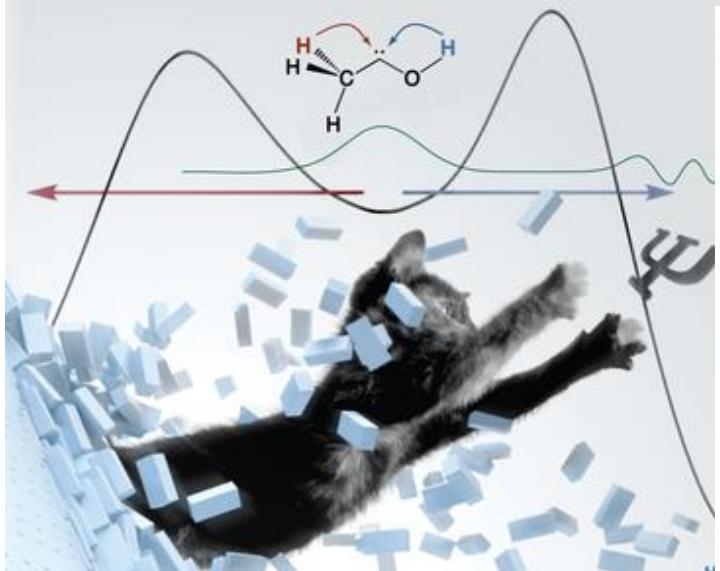
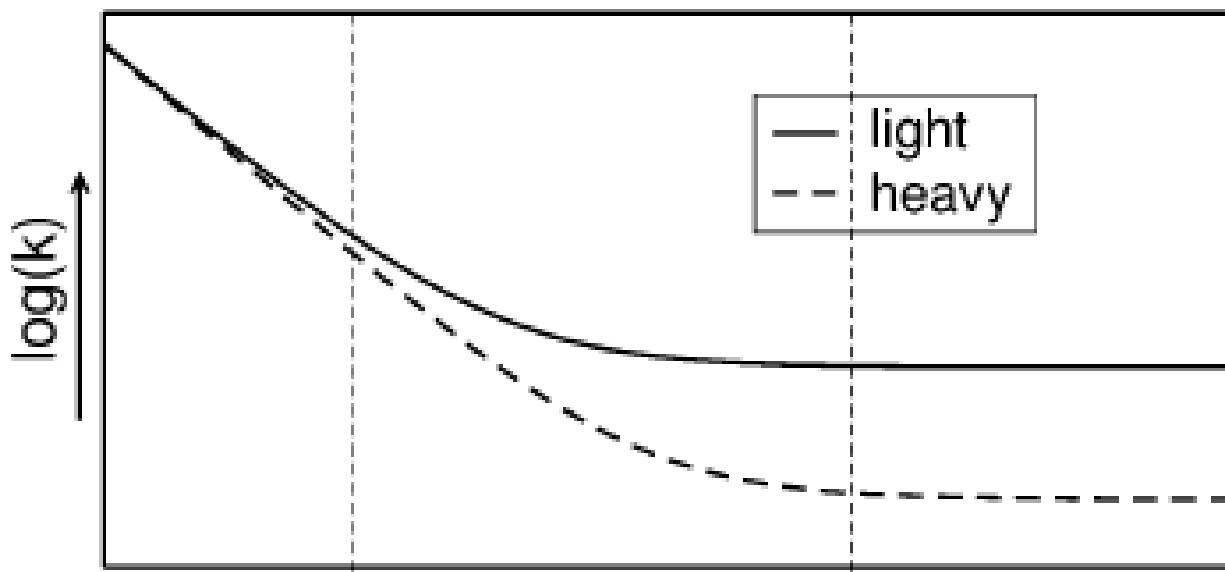
# (extra info.) Ultra-cold reaction



- Using spectroscopies of trapped KRb molecules at **500 nano K**, reactants, intermediates & products were directly observed.
- The **coldest** chemical reaction.

# (extra info.) Quantum-Mechanical Tunneling

classical      intermediate      deep tunneling

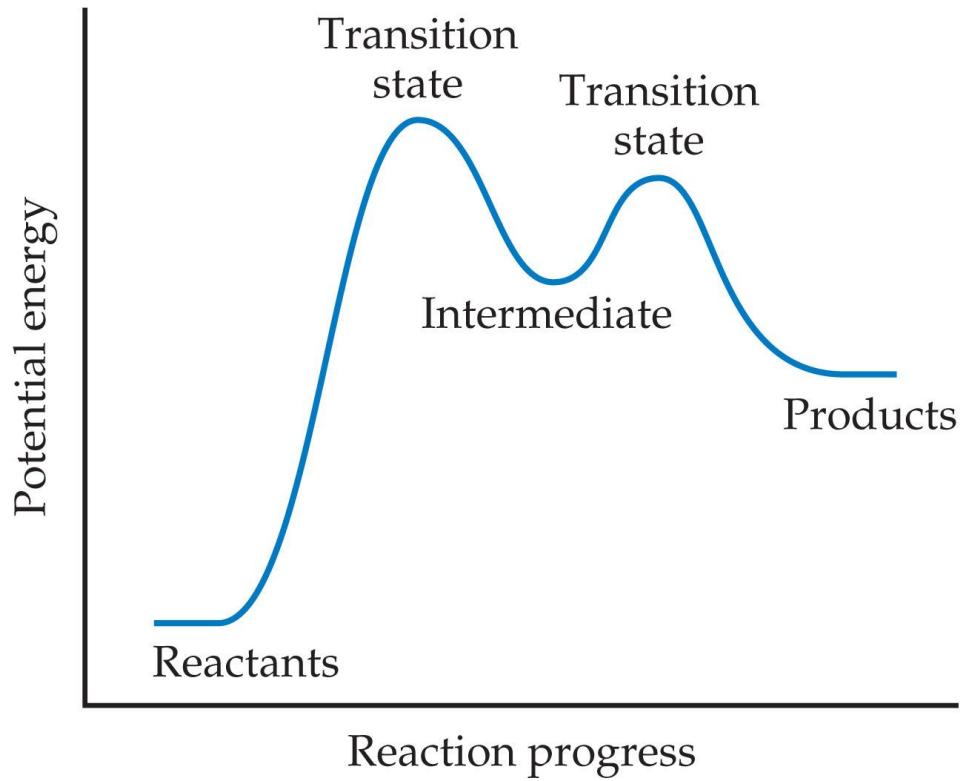


# Law vs. Theory

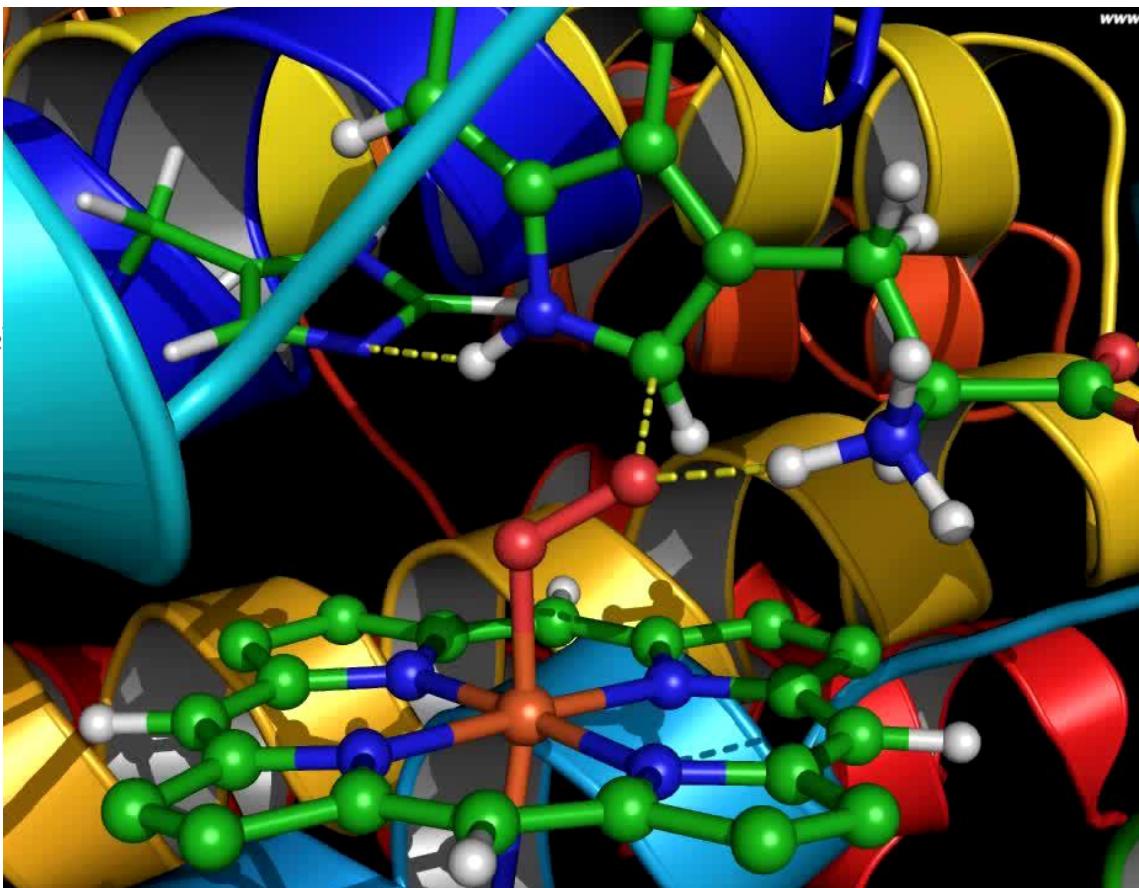
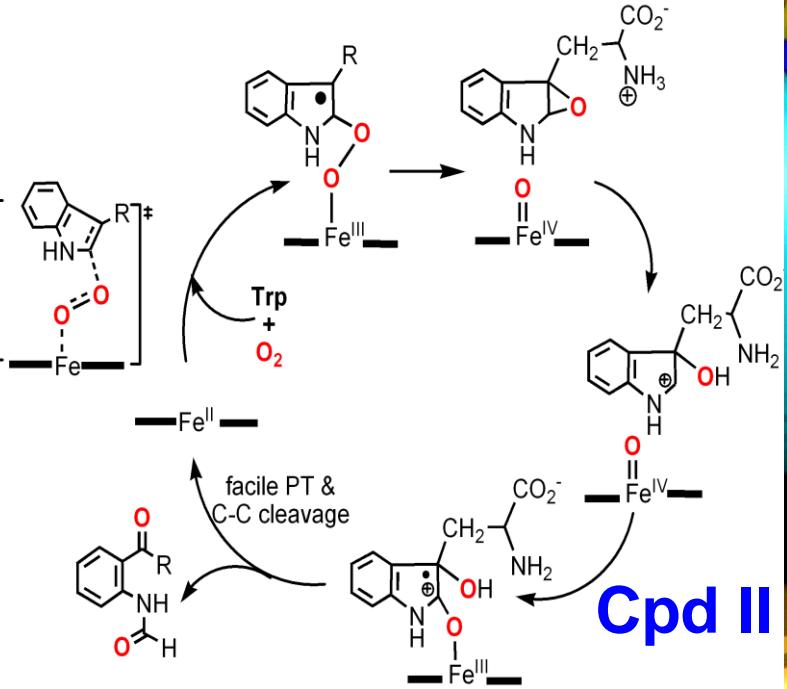
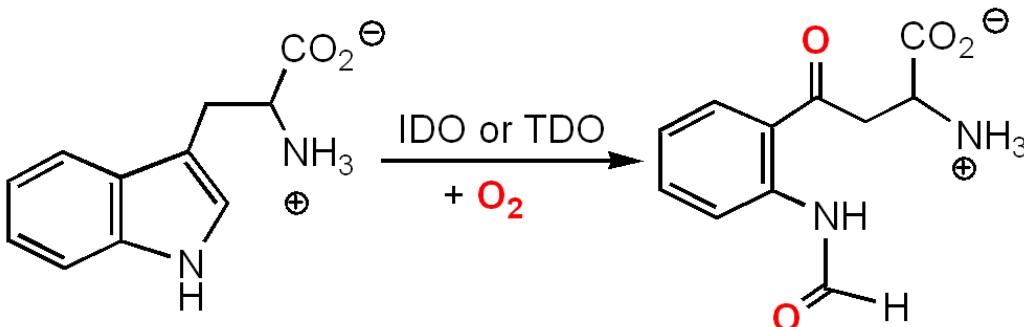
- Kinetics gives *what* happens. We call the description the *rate law*.
- *Why* do we observe that rate law? We explain with a *theory* called a **mechanism**.
- A mechanism can be consisted of a series of stepwise reactions that show **sequence of events (or actual process)** how reactants become products.

# Reaction Mechanisms

- Reactions may occur all at once or through several discrete steps. The **order of bonds broken/formed** & the **changes of atoms** in relative position are involved.
- Each of these processes is known as an **elementary reaction** or **elementary process**.
- Intermediate** is formed in one elementary reaction & consumed in the next elementary reaction.



# QM:MM for Heme-dependent Tryptophan 2,3-Dioxygenase



# Molecularity

Table 14.3 Elementary Reactions and Their Rate Laws

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 an elementary reaction: how **many molecules** are involved in that step of the mechanism.

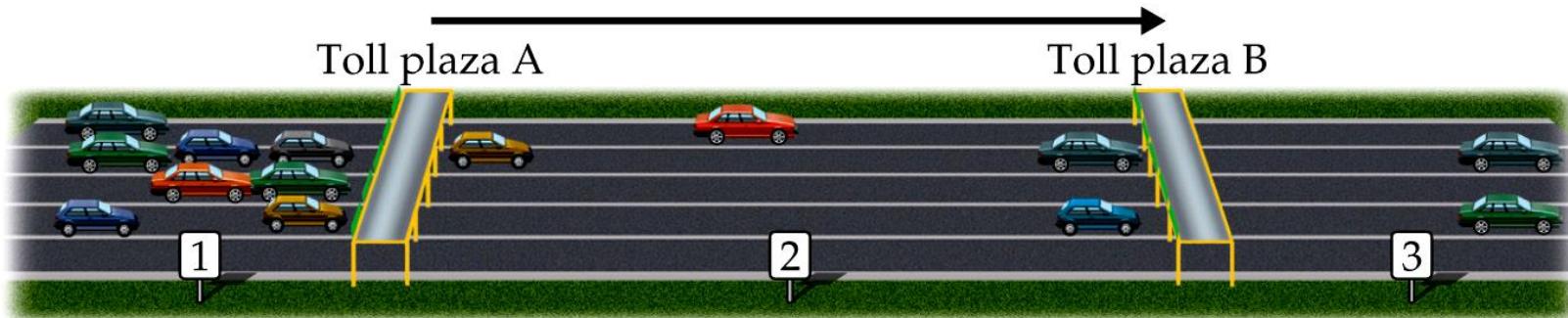
# Termolecular?

- Termolecular steps require three molecules to simultaneously collide with the proper orientation and the proper energy.
- These are **rare**, if they indeed do occur.
- These *must* be **slower** than unimolecular or bimolecular steps.
- Nearly *all* mechanisms use **only unimolecular or bimolecular** reactions.

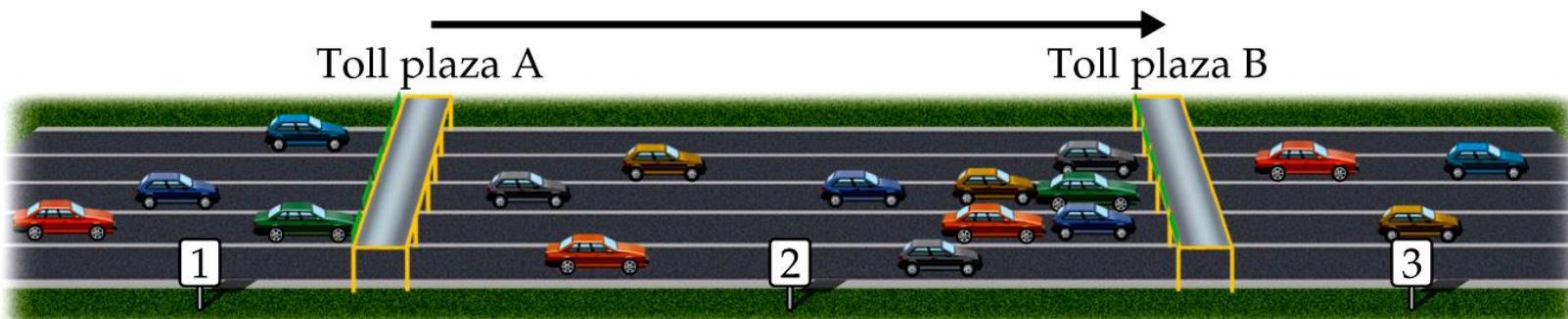
Molecularity	Elementary Step	Rate Law	Example
Unimolecular	$A \rightarrow \text{Products}$	$\text{rate} = k[A]$	$\text{N}_2\text{O}_{4(g)} \rightarrow 2\text{NO}_{2(g)}$
Bimolecular	$A + A \rightarrow \text{Products}$	$\text{rate} = k[A]^2$	$2\text{NOCl} \rightarrow 2\text{NO}_{(g)} + \text{CO}_{2(g)}$
	$A + B \rightarrow \text{Products}$	$\text{rate} = k[A][B]$	$\text{CO}_{(g)} + \text{NO}_{3(g)} \rightarrow \text{NO}_{2(g)} + \text{CO}_{2(g)}$
Termolecular	$A + A + A \rightarrow \text{Products}$	$\text{rate} = k[A]^3$	
	$A + A + B \rightarrow \text{Products}$	$\text{rate} = k[A]^2[B]$	$2\text{NO}_{(g)} + \text{O}_{2(g)}^2 \rightarrow 2\text{NO}_{2(g)}$
<a href="https://qph.fs.quoracdn.net/main-qimg-b2ebc30aa128e5295359bd7fa3ad13fc">https://qph.fs.quoracdn.net/main-qimg-b2ebc30aa128e5295359bd7fa3ad13fc</a>	$A + B + C \rightarrow \text{Products}$	$\text{rate} = k[A][B][C]$	$\text{H} + \text{O}_{2(g)} + \text{M}^{\textcolor{blue}{3}} \rightarrow \text{HO}_{2(g)} + \text{M}$

# Multistep Mechanisms

- In a multistep process, **one** of the **steps** could be **slower** than all others.
- The overall reaction cannot occur faster than this slowest, so-called **rate-determining step**.



(a) Cars slowed at toll plaza A, rate-determining step is passage through A

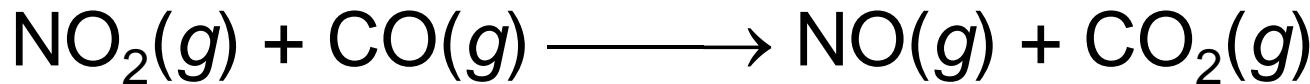


(b) Cars slowed at toll plaza B, rate-determining step is passage through B

# Requirement of a Plausible Mechanism?

- The **rate law** must be able to be devised from the **rate-determining step**.
- The stoichiometry of a reaction must be obtained when all elementary steps are added up. **Each elementary step** must be **balanced**, like any equation.
- All **intermediates** are made and **used up**.
- Any **catalyst** is used and **regenerated**.

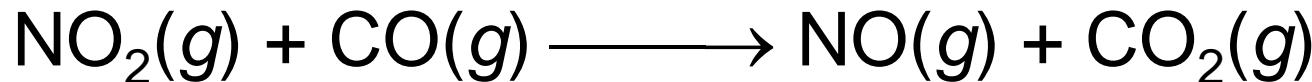
# A Mechanism With a Slow Initial Step



- The rate law for this reaction is found experimentally to be:

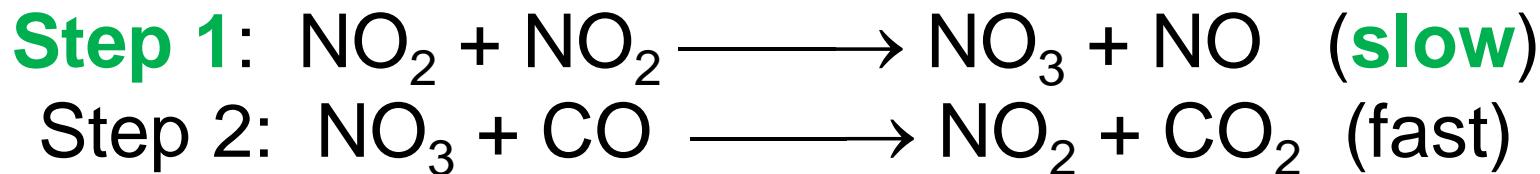
$$\text{Rate} = k[\text{NO}_2]^2$$

- CO is necessary for this reaction to occur, but the rate of the reaction does **not depend** on its concentration.
- This suggests that the reaction occurs in (at least) two steps.



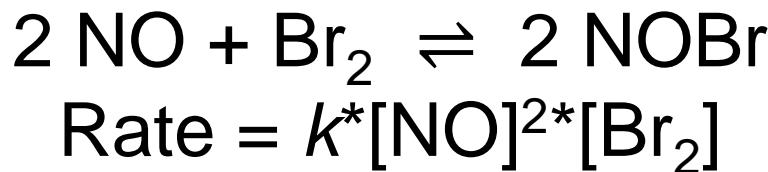
$$\text{Rate} = k[\text{NO}_2]^2$$

- A proposed mechanism for this reaction is



- As the **first** step is the **rate-determining step**, the **coefficients on the reactants side** are the **same** as the **order in the rate law!**
- The **NO<sub>3</sub> intermediate** is formed in the first step, but consumed in the second and faster step.
- As **CO** is **not involved** in the slow, **rate-determining** step, it does **not appear** in the **rate law**.

# A Mechanism With a Fast Initial Step



- As termolecular processes are rare, this rate law suggests a multistep mechanism.
- The rate law indicates that a quickly established equilibrium is followed by a slow step:  
Step 1 (fast):  $\text{NO} + \text{Br}_2 \rightleftharpoons \text{NOBr}_2$   
Step 2 (**slow**):  $\text{NOBr}_2 + \text{NO} \rightarrow 2 \text{NOBr}$
- The rate of the overall reaction depends upon the rate of the slow step. The rate law for that step:

$$\text{Rate} = k_2[\text{NOBr}_2]^*[\text{NO}]$$



- Intermediate  $\text{NOBr}_2$  can react two ways:
  1. React with NO to form NOBr (step 2).
  2. Decompose to reform NO and  $\text{Br}_2$  (step 1).
- The **reactants and products of the first** and faster step are **in equilibrium** with each other.
- For an **equilibrium** (Chapter 15):  $\text{Rate}_f = \text{Rate}_r$

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

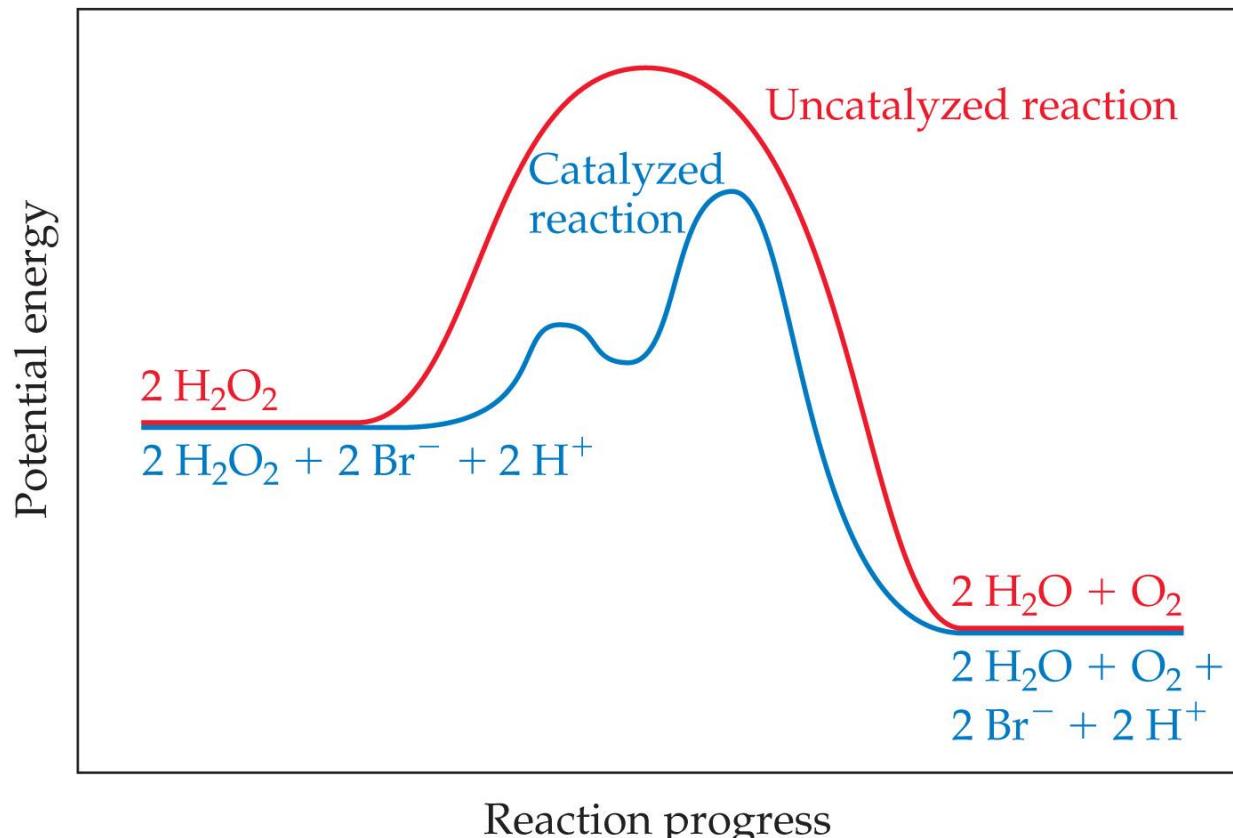
- As  $[\text{NOBr}_2] = (k_1/k_{-1})[\text{NO}]^*[\text{Br}_2]$ , then the rate law becomes:

$$\text{Rate} = k_2(k_1/k_{-1})[\text{NO}]^*[\text{Br}_2]^*[NO]$$

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

# Catalysts

- Catalysts **increase** the **rate** of a reaction by **decreasing** the **activation energy** of the reaction.
- Catalysts can **change** the **mechanism** by which the process occurs.

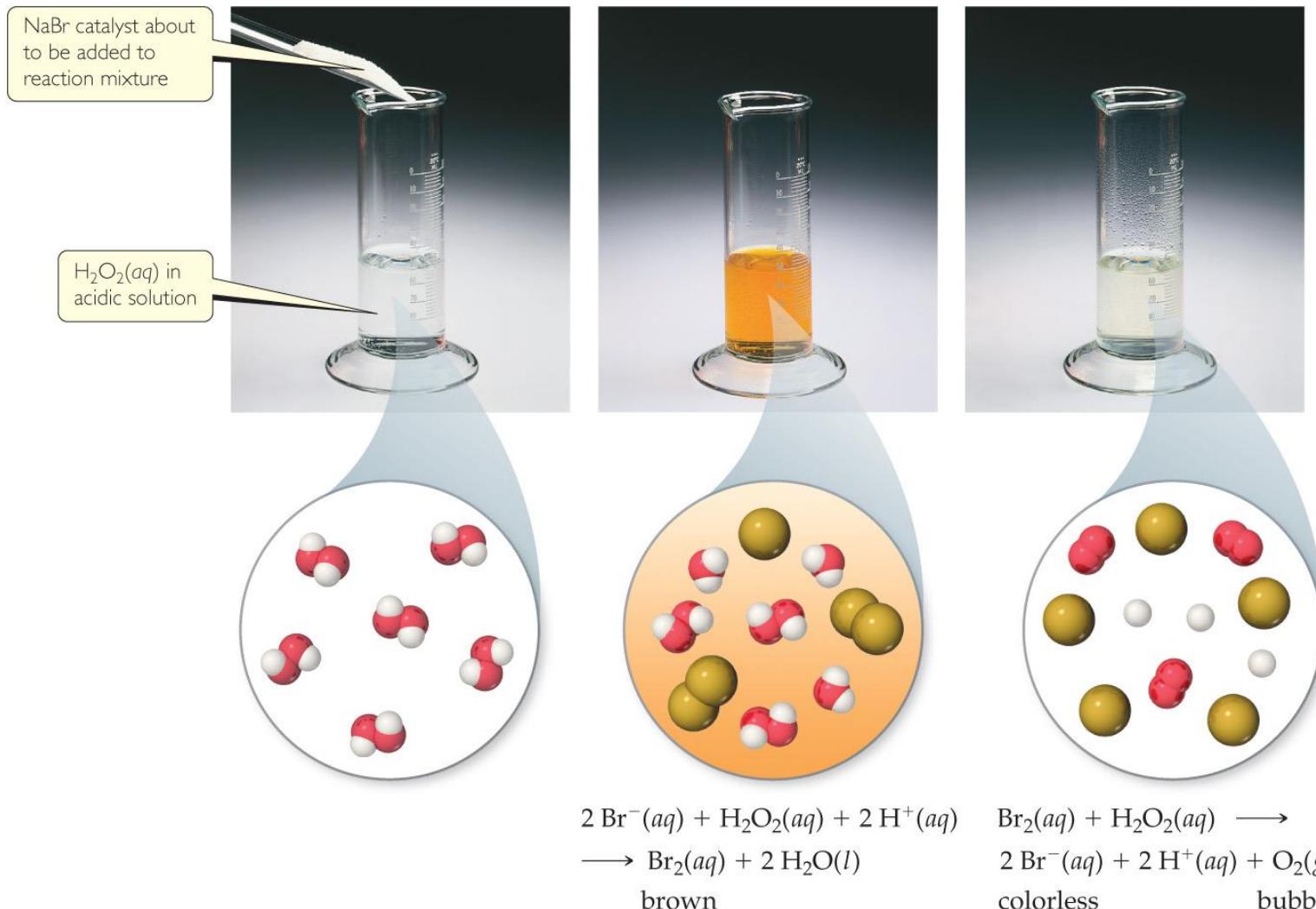


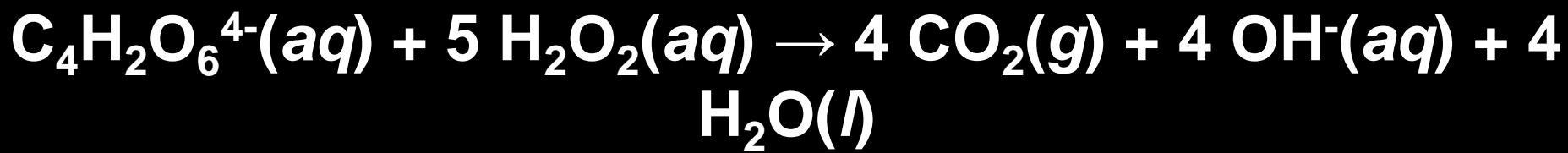
# Types of Catalysts

- 1) Homogeneous catalysts
- 2) Heterogeneous catalysts
- 3) Enzymes (naturally-occurring or engineered)

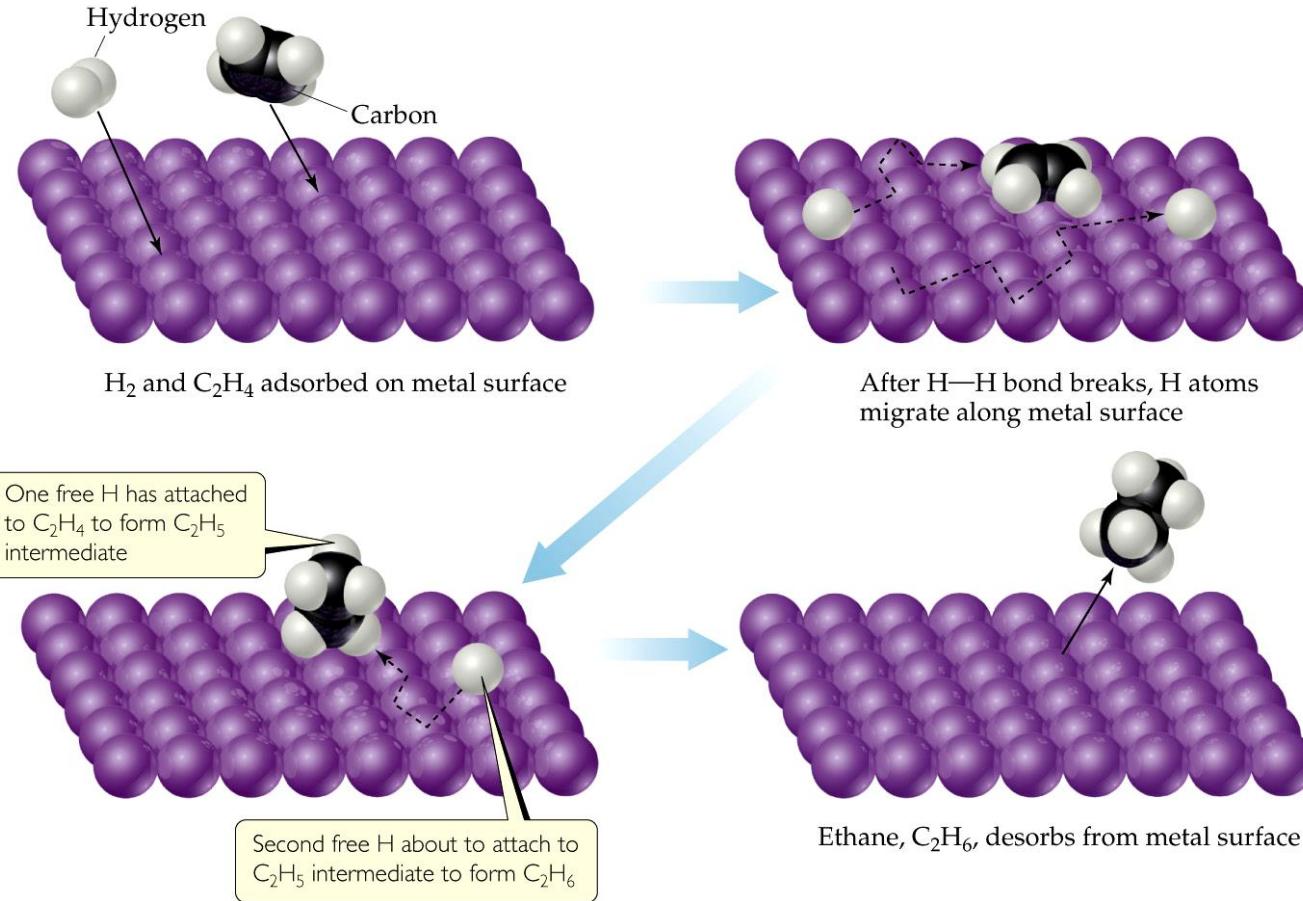
# Homogeneous Catalysts

- The reactants and catalyst are in the **same phase** (in solution or gas phase). Reactants and catalyst can be dissolved in the same solvent, as seen below.



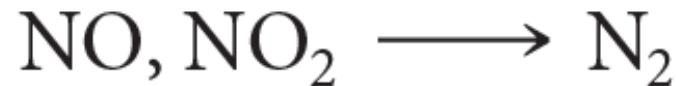
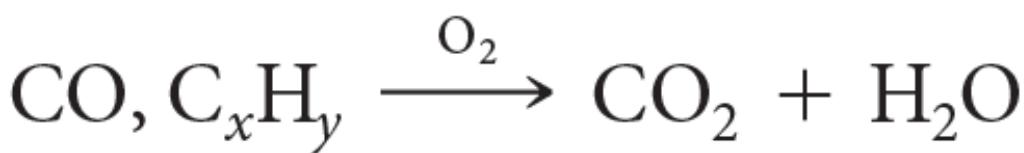
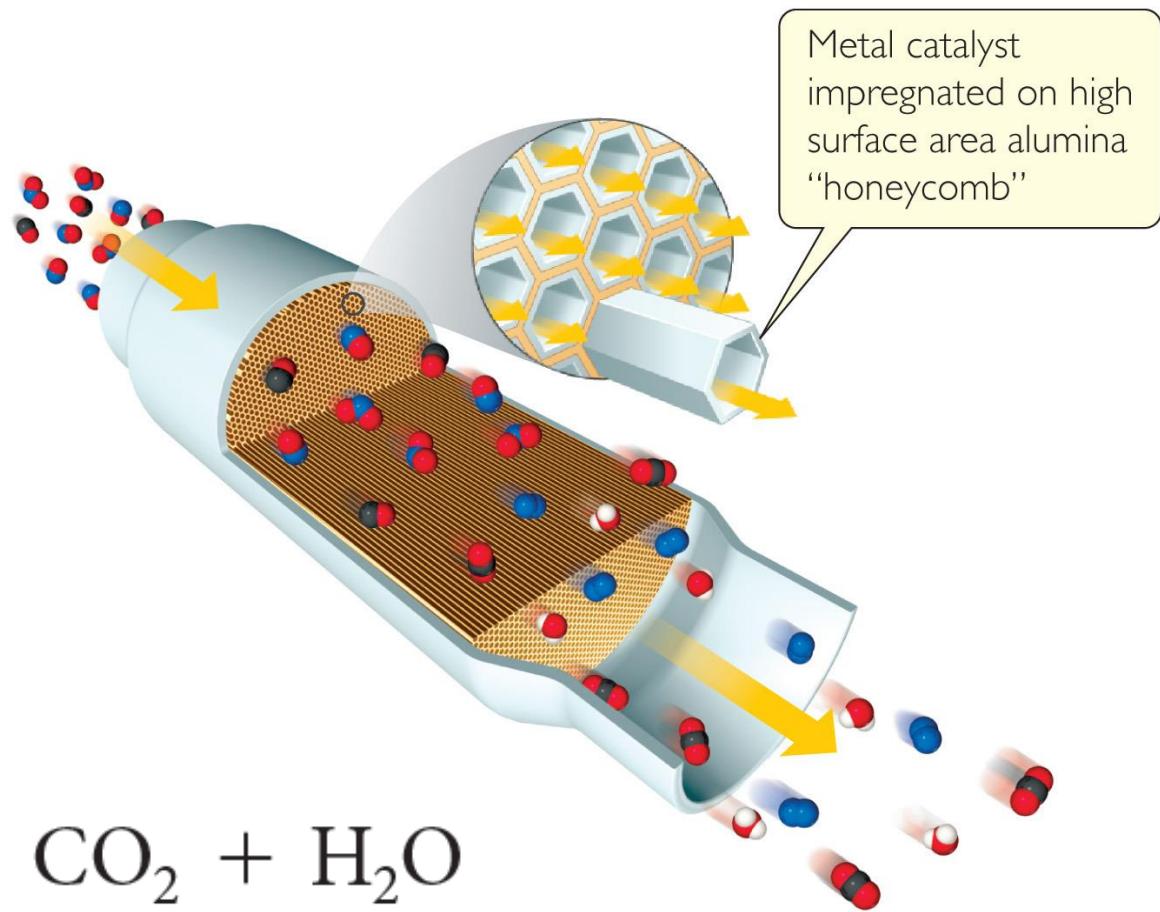


# Heterogeneous Catalysts



- The catalyst is in a **different phase** than the reactants.
- Often, gases are passed over a solid catalyst.
- The adsorption of the reactants is often the rate-determining step.

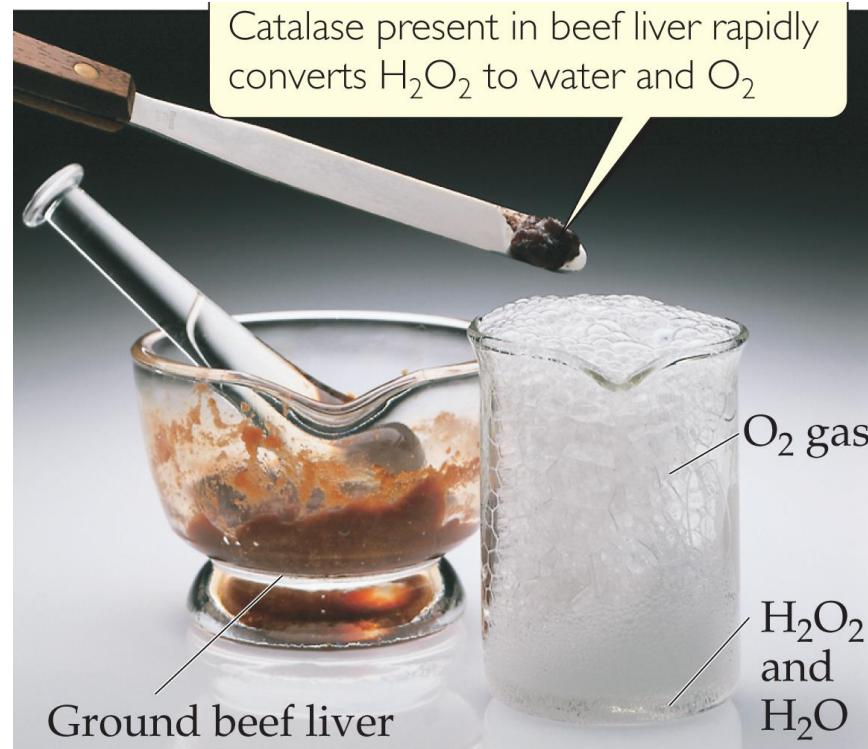
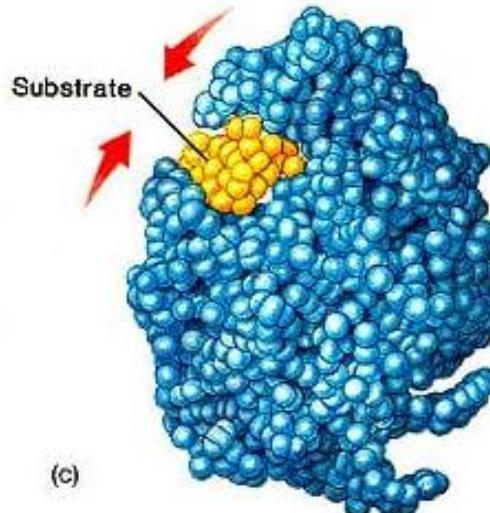
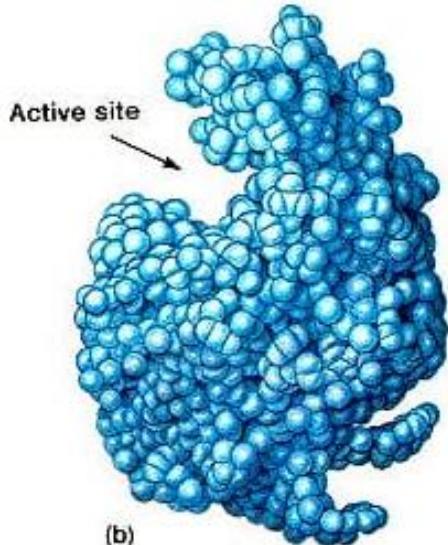
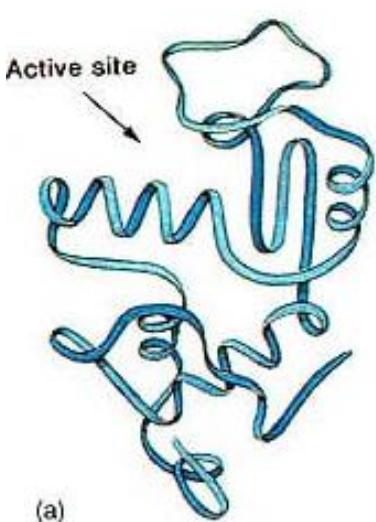
# The catalytic converter in an automobile's exhaust system



Chemical  
Kinetics

# Enzymes

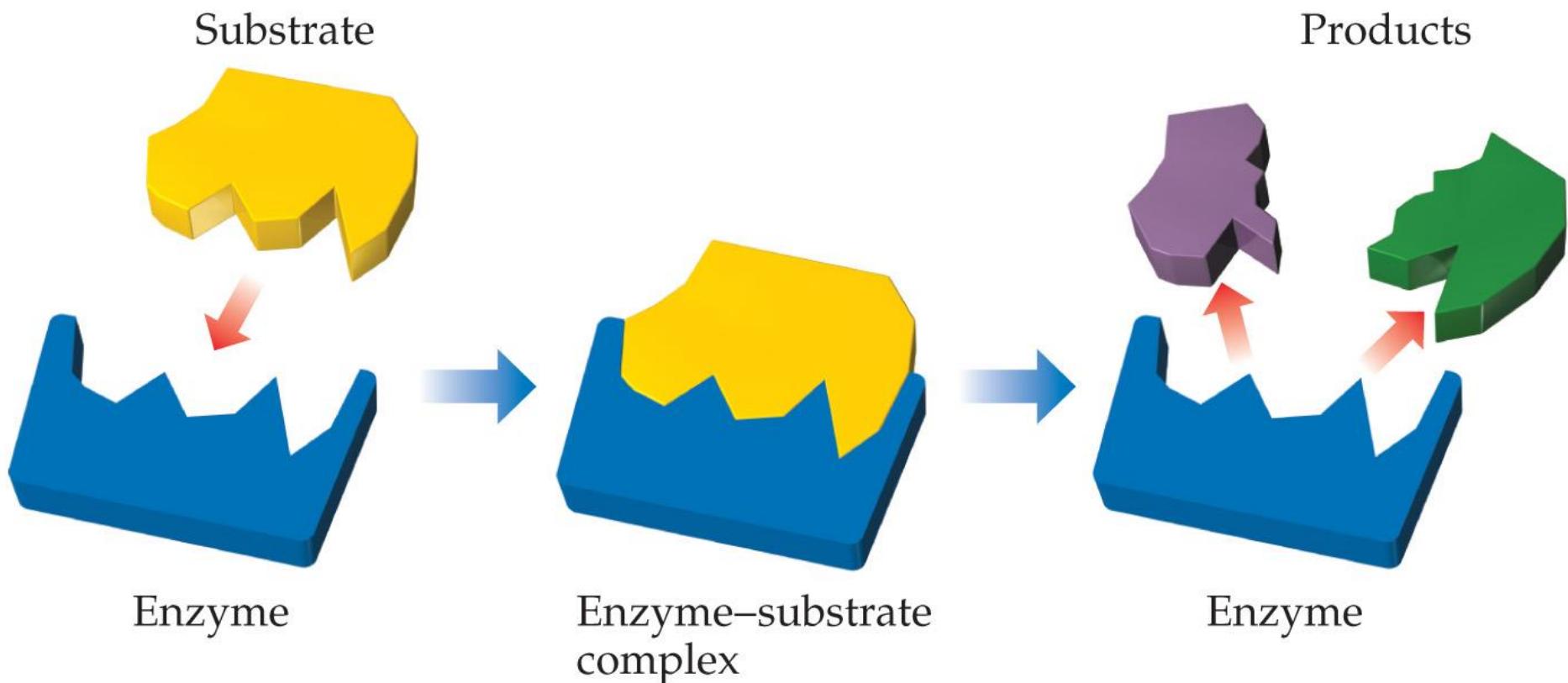
- Enzymes are biological catalysts.
- They have a region where the reactants attach/bind. That region is called the **active site**. The reactants are referred to as **substrates**.



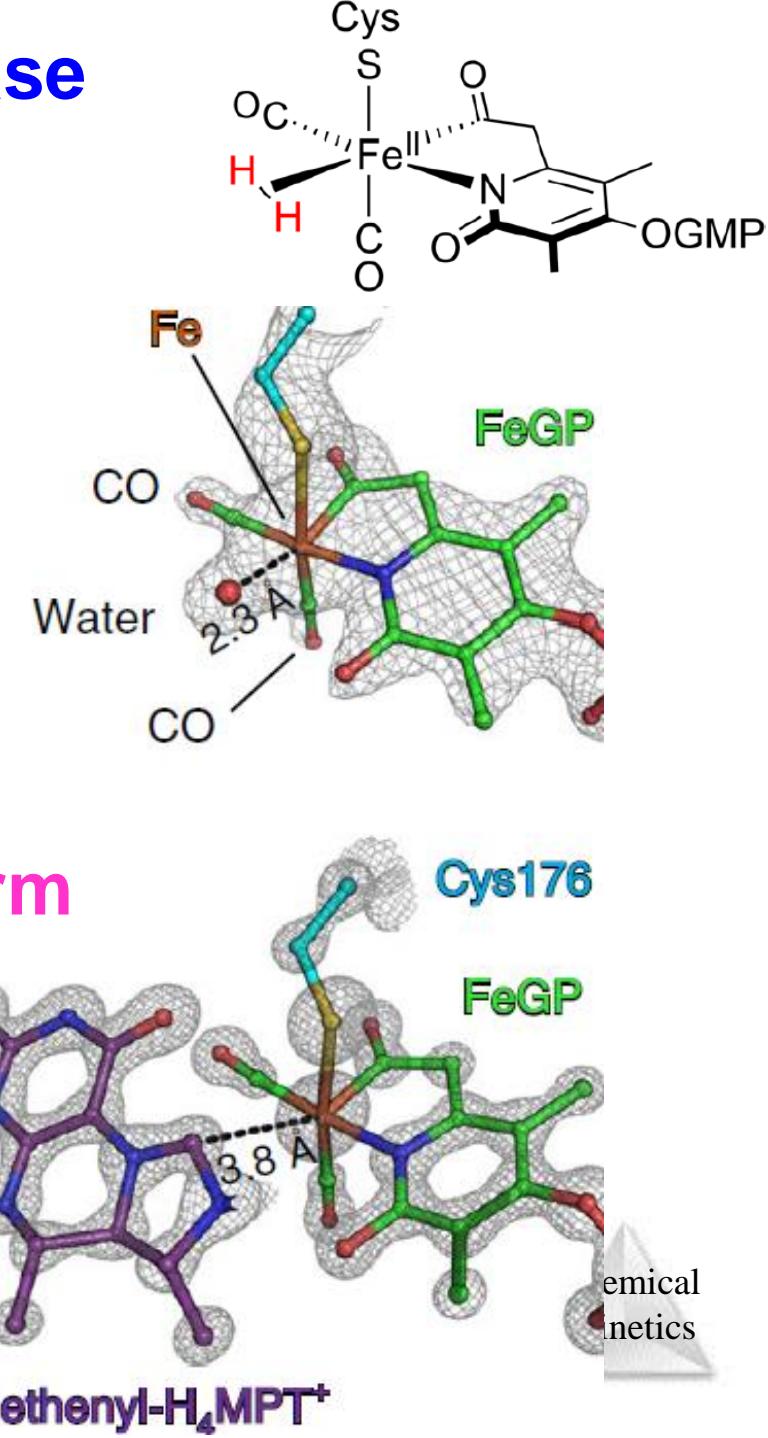
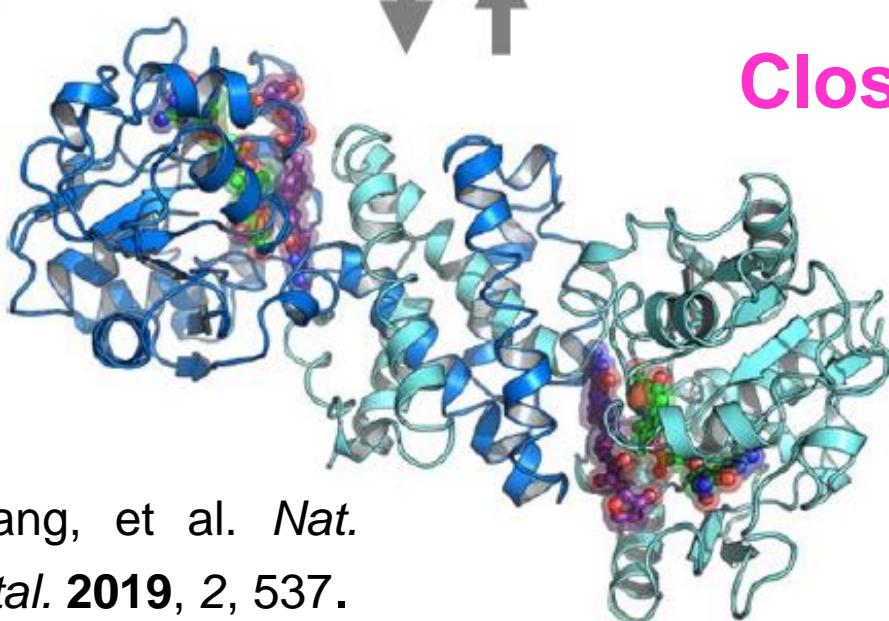
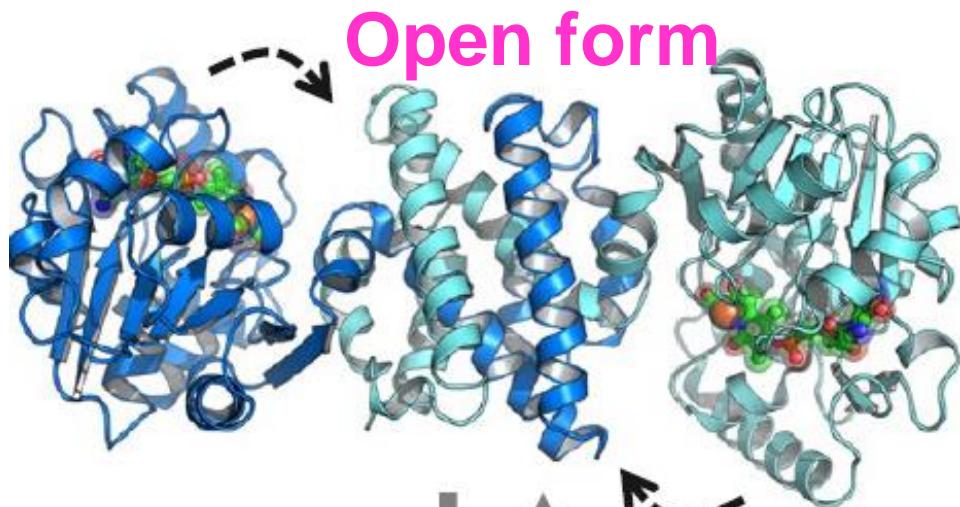
Chemical  
Kinetics

# Lock-and-Key Model

- In the **old and classical enzyme–substrate model**, the substrate fits into the active site of an enzyme, much like a key fits into a lock.
- They are specific.



# (extra info.) [Fe] Hydrogenase



In a reaction involving reactants in the gas state, how does increasing the partial pressures of the gases affect the reaction rate?

- A. The effect of increasing the partial pressures of the reactive components of a gaseous mixture depends on which side of the chemical equation has the most gas molecules.
- B. Increasing the partial pressures of the reactive components of a gaseous mixture has no effect on the rate of reaction if each reactant pressure is increased by the same amount.
- C. Increasing the partial pressures of the reactive components of a gaseous mixture increases the rate of reaction.
- D. Increasing the partial pressures of the reactive components of a gaseous mixture decreases the rate of reaction.

What is the difference between average rate and instantaneous rate? In a given reaction, can these two rates ever have the same numeric value?

- A. An instantaneous rate is measured at a particular point in time of a reaction, whereas average rate is measured over a time period; Yes.
- B. An instantaneous rate is measured at a particular point in time of a reaction, whereas average rate is measured over a time period; No.
- C. An instantaneous rate is measured over a short time period, whereas average rate is measured over a large time period; Yes.
- D. An instantaneous rate is measured over a short time period, whereas average rate is measured over a large time period; No.

The experimentally determined rate law for the reaction  $2 \text{NO}(g) + 2 \text{H}_2(g) \longrightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(g)$  is rate =  $k[\text{NO}]^2[\text{H}_2]$ .

- a. What are the reaction orders in this rate law?
- b. Does doubling the concentration of NO have the same effect on rate as doubling the concentration of  $\text{H}_2$ ?

(a)

- A. 2<sup>nd</sup> order in NO, 1<sup>st</sup> order in  $\text{H}_2$ , 2<sup>nd</sup> order overall
- B. 2<sup>nd</sup> order in NO, 1<sup>st</sup> order in  $\text{H}_2$ , 3<sup>rd</sup> order overall
- C. 1<sup>st</sup> order in NO, 1<sup>st</sup> order in  $\text{H}_2$ , 2<sup>nd</sup> order overall
- D. 1<sup>st</sup> order in NO, 2<sup>nd</sup> order in  $\text{H}_2$ , 3<sup>rd</sup> order overall

(b)

- A. Yes
- B. No

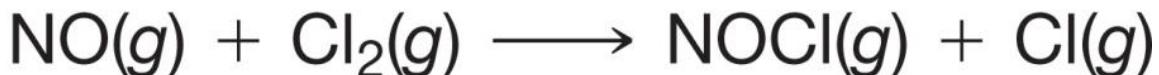
If a solution containing 10.0 g of a substance reacts by first-order kinetics, how many grams remain after 3 half-lives?

- A. 6.00 g
- B. 4.50 g
- C. 1.25 g
- D. 1.11 g

How does the half-life of a second-order reaction change as the reaction proceeds?

- A. The half-life does not change as the reaction proceeds.
- B. The half-life increases as the reaction proceeds.
- C. The half-life decreases as the reaction proceeds.
- D. The half-life increases for some reactions and decreases for others (2<sup>nd</sup> order reactions) as the reaction proceeds.

What is the molecularity of the elementary reaction?



- A. Zero molecularity
- B. Unimolecular
- C. Bimolecular
- D. Trimolecular

If the following reaction occurs in a single elementary reaction, predict its rate law:

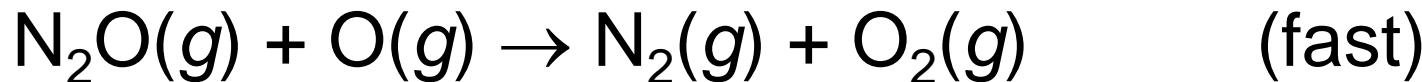


Conversion of ozone into  $O_2$  was proposed to proceed by a two-step mechanism:



- (a) Describe the molecularity of each elementary reaction in this mechanism. (b) Write the equation for the overall reaction. (c) Identify the intermediate(s).

The decomposition of nitrous oxide,  $\text{N}_2\text{O}$ , is believed to occur by a two-step mechanism:



**(a)** Write the equation for the overall reaction. **(b)** Write the rate law for the overall reaction.

In a chemical reaction, why does not every collision between reactant molecules result in formation of a product molecule?

- A. If colliding atoms are of dissimilar sizes, then products are not favored to form.
- B. If collisions do not occur with sufficient energy or proper orientation of colliding molecules, then products may not form.
- C. If reactants are gas molecules, the particles are too far apart to collide over a reasonable time period and thus do not form products.
- D. If reactants are liquid molecules, the particles are moving too slowly to provide sufficient energy to form products.

Suppose we have two reactions,  $A \longrightarrow B$  and  $B \longrightarrow C$ . You can isolate B, and it is stable. Is B the transition state for the reaction  $A \longrightarrow C$ ?

- A. Yes, because B is an intermediate.
- B. Yes, because B can be isolated.
- C. No, because B is not stable.
- D. No, because B can be isolated and transition states are by definition not stable.

The following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures

Temperature (°C)	$k$ (s <sup>-1</sup> )
189.7	$2.52 \times 10^{-5}$
198.9	$5.25 \times 10^{-5}$
230.3	$6.30 \times 10^{-4}$
251.2	$3.16 \times 10^{-3}$

(a) From these data, calculate the activation energy for the reaction. (b) What is the value of the rate constant at 430.0 K?

How does a homogeneous catalyst compare with a heterogeneous one regarding the ease of recovery of the catalyst from the reaction mixture?

- A. A heterogeneous catalyst is easier to remove from a reaction mixture because of phase differences.
- B. A heterogeneous catalyst is easier to remove from a reaction mixture because it is present in the greatest quantity.
- C. A homogeneous catalyst is easier to remove from a reaction mixture because of phase differences.
- D. A homogenous catalyst is easier to remove from a reaction mixture because it is easier to identify in the reaction mixture.

Is it reasonable to say that enzymes stabilize the transition state for a reaction? Explain your answer.

- A. Yes, because an enzyme is a catalyst.
- B. No, because enzymes are different in structure and their properties than typical catalysts in non-biochemical reactions.
- C. Possibly, but the nature of the transition states in the catalyzed and uncatalyzed reaction can be significantly different.
- D. Yes, because it should form a stable intermediate, transition state.

The rate of a reaction can be increased by

- a. increasing reactant concentrations.
- b. increasing the temperature.
- c. adding a suitable catalyst.
- d. All of the above

Over time, the rate of most chemical reactions tends to \_\_\_\_\_.

- a. increase
- b. decrease
- c. remain constant
- d. oscillate

If tripling the concentration of reactant A multiplies the rate by a factor of nine, the reaction is \_\_\_\_\_ order in A.

- a. zeroth
- b. first
- c. second
- d. third

Reaction:  $A + B \rightarrow C + D$

$$\text{Rate} = k[A][B]$$

The overall order of this reaction is

- a. first.
- b. second.
- c. third.
- d. fourth.

Reaction:  $W + X \rightarrow Y + Z$

Rate =  $k[W]$

The order of this reaction with respect to X is

- a. zeroth.
- b. first.
- c. second.
- d. third.

The time required for the concentration of a reactant to be reduced to half of its initial value is called the

- a. midpoint of the reaction.
- b. equivalence point of the reaction.
- c. half-rate of the reaction.
- d. half-life of the reaction.

If  $k$  is the rate constant of a first-order reaction, the half-life of the reaction is:

- a.  $0.693/k$
- b.  $0.693k$
- c.  $k/2$
- d.  $2k$

The value of the rate constant ( $k$ ) for a first-order reaction is  $0.010 \text{ sec}^{-1}$ . What is the half-life of this reaction?

- a. 10 seconds
- b. 69 seconds
- c. 100 seconds
- d. 690 seconds

$A + B \rightarrow$  products, Rate =  $k[A]$ ,  $k = 0.010 \text{ sec}^{-1}$ , Initial  $[A] = 0.100 \text{ M}$ , Final  $[A] = 0.00100 \text{ M}$  How long will this take?

- a. 69 seconds
- b. 138 seconds
- c. 460 seconds
- d. 690 seconds

Rate =  $k[A]^2$ , Initial  $[A] = 0.100 \text{ M}$ ,  $k = 0.0214 \text{ M}^{-1} \text{ sec}^{-1}$ . What is the half-life of this second-order reaction?

- a. 69 seconds
- b. 138 seconds
- c. 467 seconds
- d. 690 seconds

Rate =  $k[A]^2$ , Initial  $[A] = 0.100 \text{ M}$ ,  $k = 0.0214 \text{ M}^{-1} \text{ sec}^{-1}$ . After 1.00 hour, what is the concentration of reactant A?

- a. 0.0500 M
- b. 0.0250 M
- c. 0.0189 M
- d. 0.0115 M

The minimum energy that a collision between molecules must have for a reaction to occur is called the

- a. initial energy.
- b. internal energy.
- c. external energy.
- d. energy of activation.

At 298 K,  $k = 1.36 \times 10^{-7} \text{ sec}^{-1}$ .

At 323 K,  $k = 2.72 \times 10^{-6} \text{ sec}^{-1}$ .

The energy of activation for this reaction is

- a. 100 kJ/mole.
- b. 310 kJ/mole.
- c. 690 kJ/mole.
- d. 1000 kJ/mole.

The rate-determining step is the \_\_\_\_\_ step in a reaction mechanism.

- a. first
- b. last
- c. fastest
- d. slowest

Adding a catalyst increases the rate of a chemical reaction because the presence of the catalyst

- a. increases molecular velocities.
- b. increases molecular collisions.
- c. decreases energy of activation.
- d. All of the above

# Catalysis (Extra Info.)



威廉·奥斯特瓦尔德  
Friedrich Ostwald  
“对催化作用的研究工作和对化学平衡以及化学反应速率的基本原理的研究”



弗里茨·哈伯  
Fritz Haber  
“对从单质合成学高压技术”



卡尔·博施  
Carl Bosch  
“发明与发展化学高压技术”



欧文·兰米尔  
Irving Langmuir  
“对表面化学的研究与发现”



卡尔齐格勒  
Karl Ziegler  
“在高聚物的化学性质和技术领域中的研究发现”



居里奥·纳塔  
Giulio Natta  
“对高聚物的化学性质和技术领域的研究发现”



杰弗里·威尔金森  
Wilkinson·Geoffrey  
“对金属有机化合物化学性质的开创性研究”



恩斯特·奥托·菲舍尔  
Ernst Otto Fischer  
“对手性催化氢化反应的研究”



威廉·诺尔斯  
William Knowles  
“对高聚物的化学性质和技术领域的研究发现”



野依良治  
Ryoji Noyori  
“对手性催化氢化反应的研究”



卡尔·夏普莱斯  
Karl Sharpless  
“对手性催化氢化反应的研究”



理查德·施罗克  
Richard R. Schrock  
“发展了有机合成中的复分解法”



罗伯特·格拉布  
Robert H. Grubbs  
“发展了有机合成中的复分解法”



伊夫·肖万  
Yves Chauvin  
“发展了有机合成中的复分解法”



格哈德·埃特尔  
Gerhard Ertl  
“对固体表面化学进程的研究”



理查德·赫克  
Richard F. Heck  
“对有机合成中钯催化偶联反应的研究”



根岸英一  
Ei-ichi Negishi  
“对有机合成中钯催化偶联反应的研究”



铃木章  
Akira Suzuki



本亚明·利斯特  
Benjamin List  
“在不对称有机催化方面的研究”



戴维·麦克米伦  
David MacMillan  
“在不对称有机催化方面的研究”

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## The Nobel Prize in Chemistry 1909

**Wilhelm Ostwald** “in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction”

## The Nobel Prize in Chemistry 1912

**Paul Sabatier** “for his method of hydrogenating organic compounds in the presence of finely disintegrated metals whereby the progress of organic chemistry has been greatly advanced in recent years”

## The Nobel Prize in Chemistry 1918

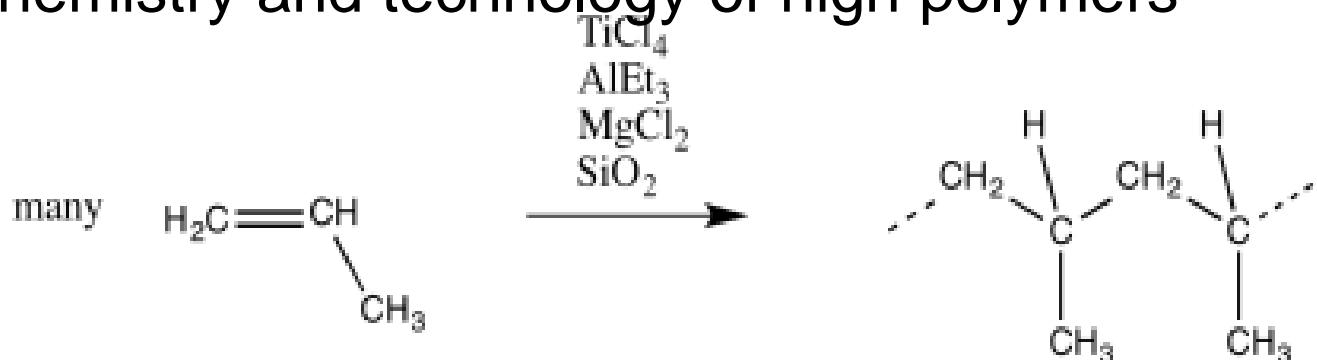
**Fritz Haber** “for the synthesis of ammonia from its elements”

Chemical  
Kinetics

# The Nobel Prize in Chemistry 1963

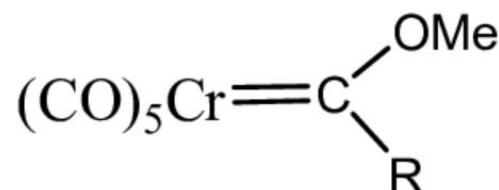
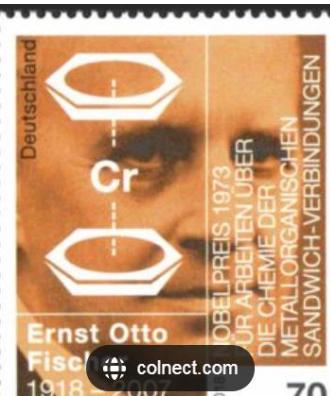
## (Extra Info.)

**Karl Ziegler and Giulio Natta** “for their discoveries in the field of the chemistry and technology of high polymers”

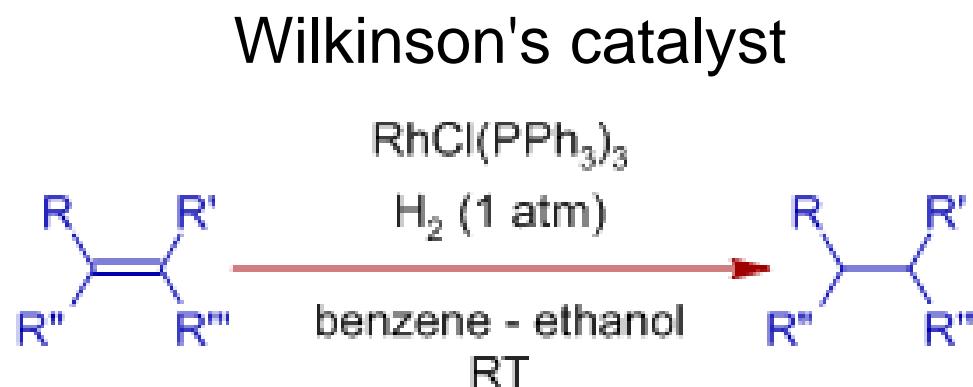


# The Nobel Prize in Chemistry 1973

**Ernst Otto Fischer and Geoffrey Wilkinson** "for their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds"



A Fisher Carbene

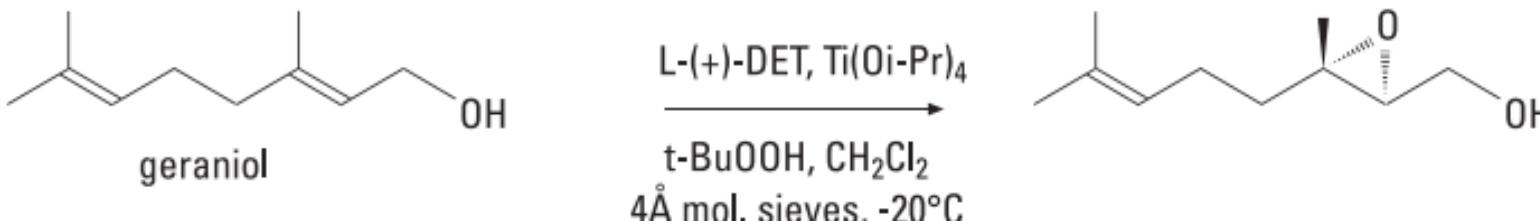
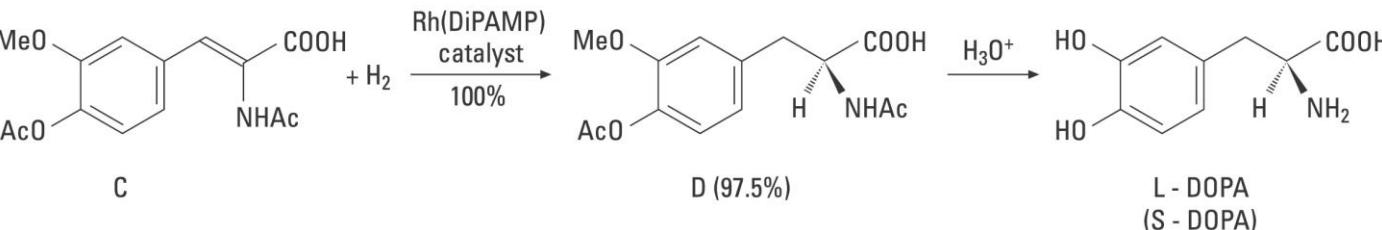
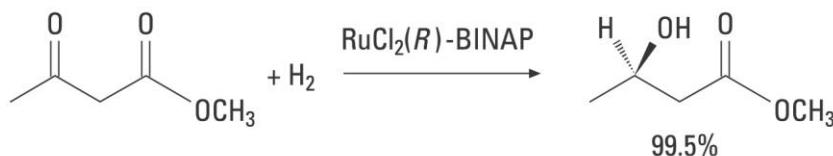
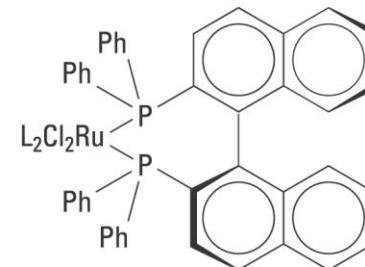
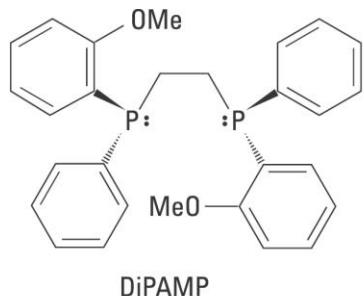


# The Nobel Prize in Chemistry 2001

(Extra Info.)

**William S. Knowles and Ryoji Noyori** "for their work on chirally catalysed hydrogenation reactions"

**K. Barry Sharpless** "for his work on chirally catalysed oxidation reactions"

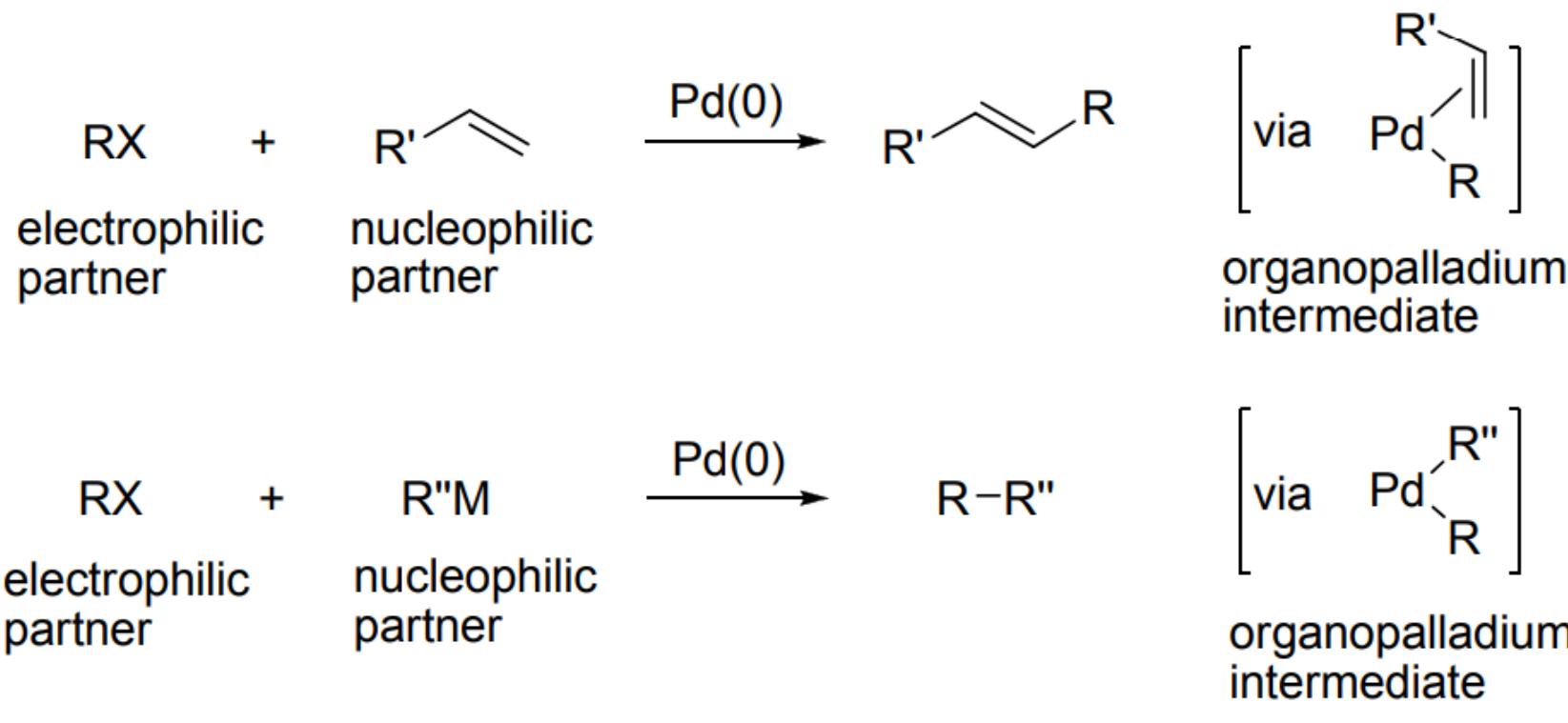


Chemical  
kinetics

# The Nobel Prize in Chemistry 2010

(Extra Info.)

**Richard F. Heck, Ei-ichi Negishi and Akira Suzuki** “for palladium-catalyzed cross couplings in organic synthesis”



$\text{R}', \text{R}$  = Aryl, Vinyl, Alkyl, etc.

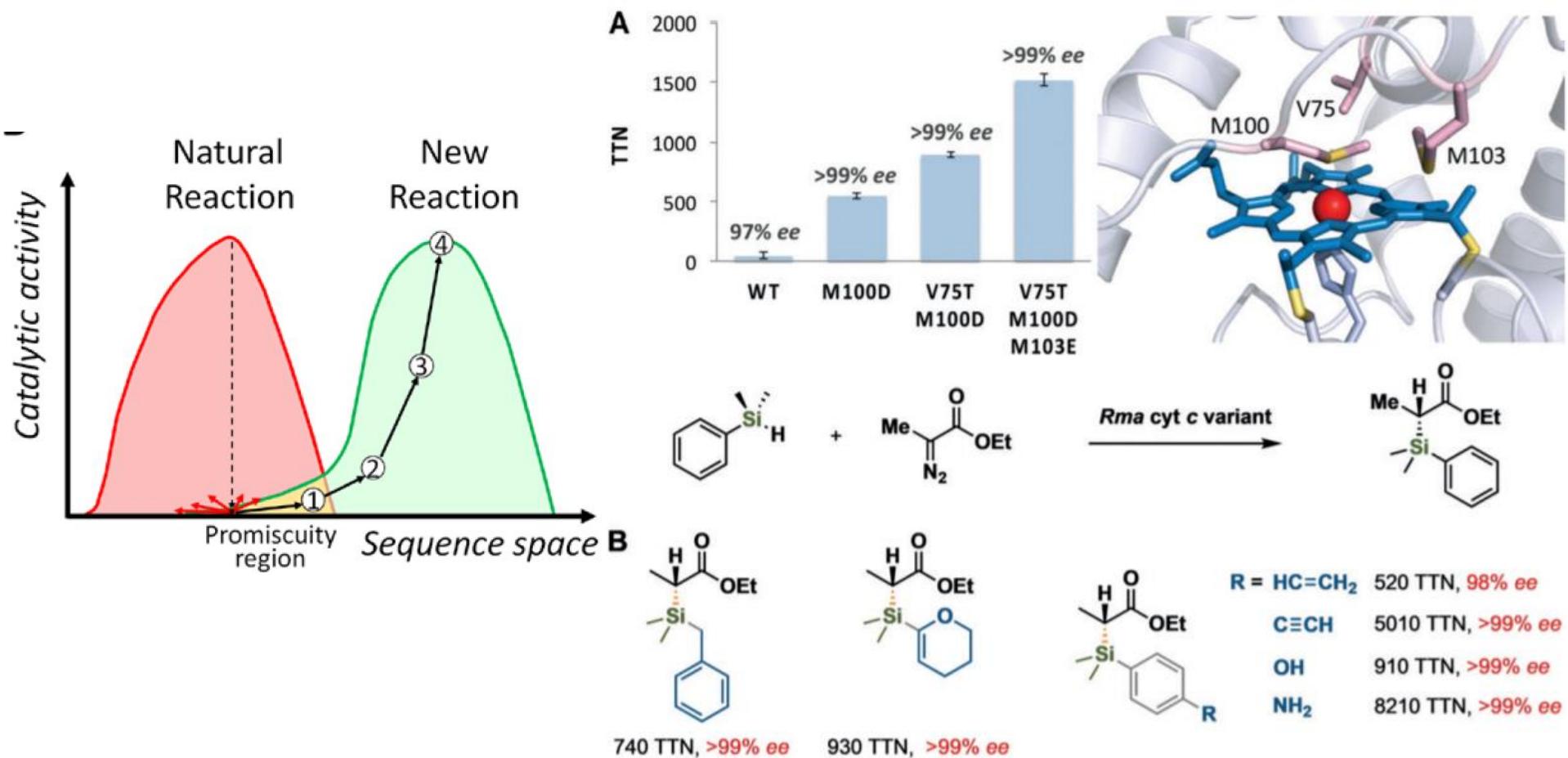
X: leaving group, e.g. Cl, Br, I, OTf, OSO<sub>2</sub>R.

$\text{M} = \text{MgX}$  (**Kumada**),  $\text{BX}_2$  (**Suzuki**),  $\text{SnR}''_3$  (**Stille**),  $\text{ZnX}$  (**Negishi**), etc.

# The Nobel Prize in Chemistry 2018

(Extra Info.)

Frances H. Arnold "for the directed evolution of enzymes"

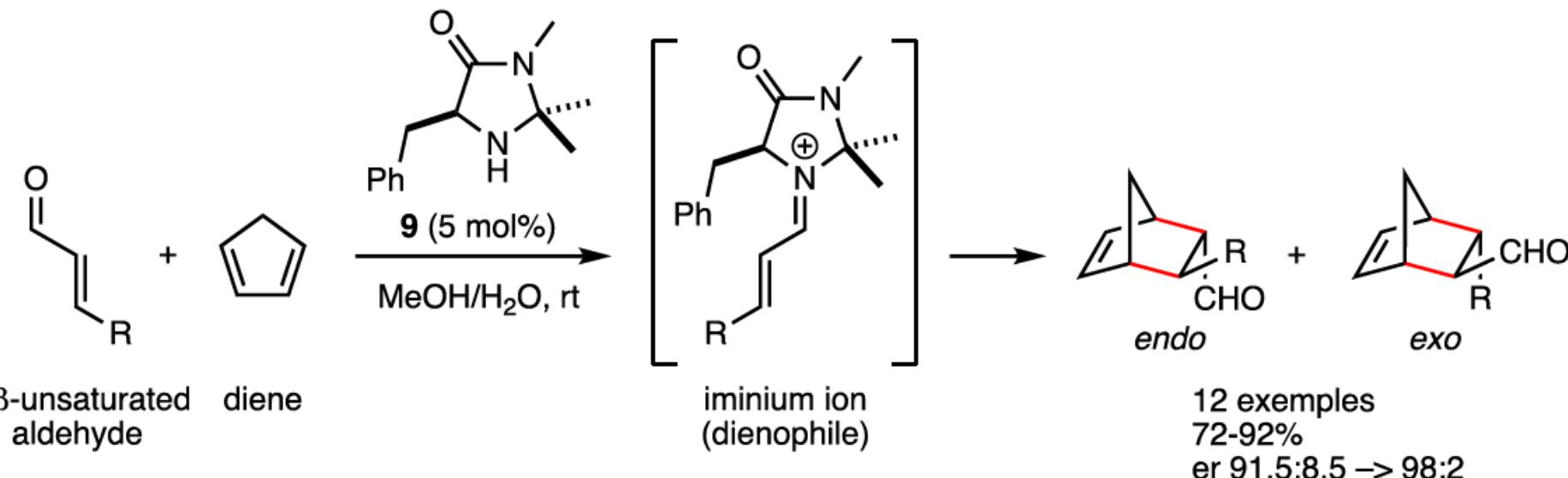
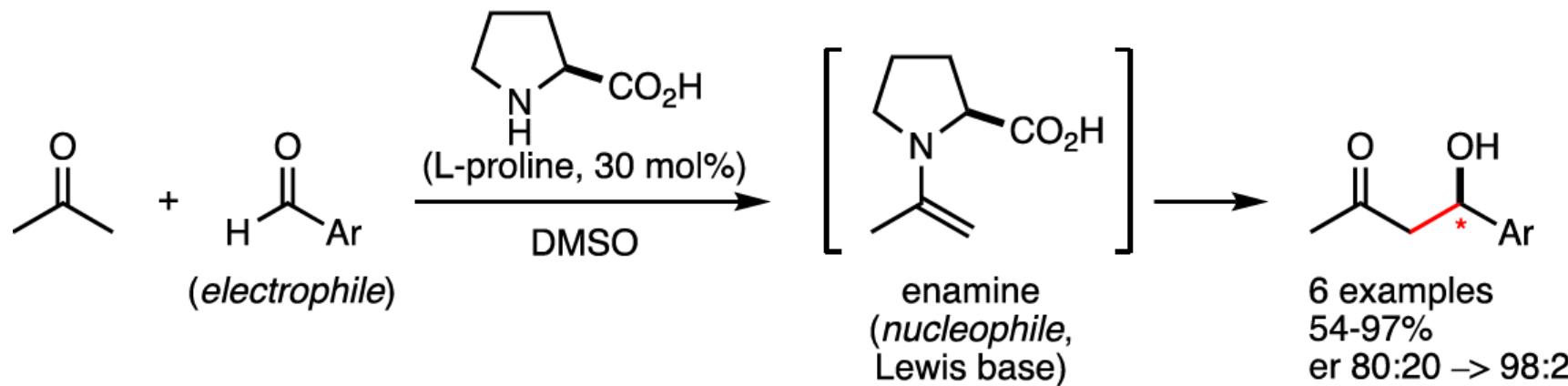


Directed Evolution of  
New or Artificial Enzymes (Biocatalysis)

# The Nobel Prize in Chemistry 2021

(Extra Info.)

**Benjamin List and David MacMillan** “for the development of asymmetric organocatalysis”



# Summary of Chapter 14

Rate (average/instantaneous/initial rate), rate law, rate constant, reaction order, half-life

Collision model, activation energy (barrier), transition state (activated complex), reaction coordinate diagrams, Arrhenius equation

Reaction mechanism: elementary process, intermediate, molecularity (unimolecular, bimolecular, termolecular), rate-determining step

Catalyst: homogeneous/heterogeneous catalysts, enzymes

**Thank You for Your  
Attention!  
Any Questions?**

Chemical  
Kinetics