

American Chemical Society



USNCO Coaching Session Tutorial Notes: Kinetics

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Sample Questions



- Local Exam 2016, #27
- Local Exam 2017, #30
- National Exam 20168, #27

Lecture Note – Fundamental Kinetics

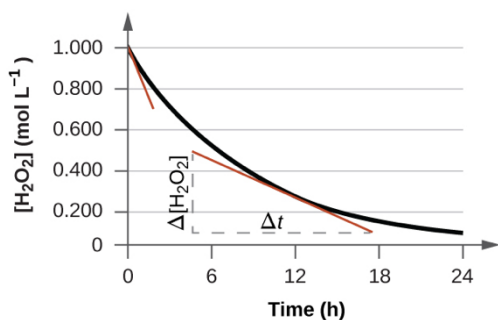
Dec 28th, 2020

[Pre-Reading]: (Zumdahls9e) Chp12.1-12.4; (Atkins7e) Topic7A-7B

[Learning Objectives]

1. Reaction Rates

1.1 Instantaneous rates and relate rate of reactions



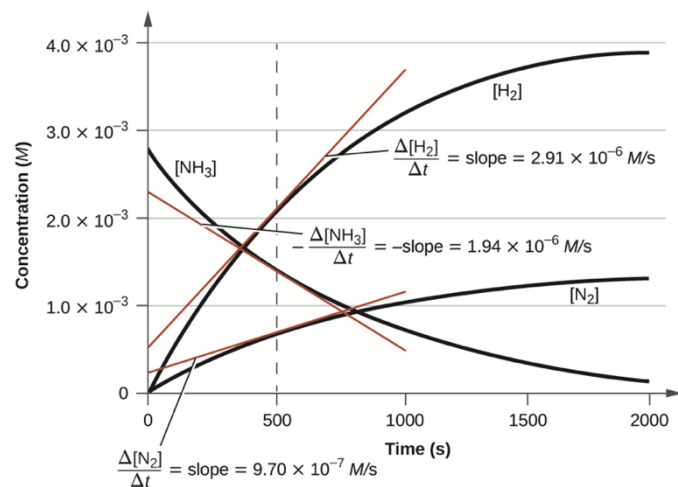
How to define reaction rate?

What is average rate and instantaneous rate, respectively?

What is the unit of reaction rate?

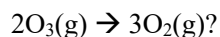
What is initial rate?

*How to *measure* initial rate?



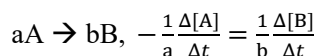
What is the reaction? Write down the balanced chemical equation.

Are the rates of a reaction expressed in terms of the change of $-\text{[reactant(s)]}$ or [product(s)] at $t = 500$. s the same?



If the rate at which O_2 appears, $\Delta[\text{O}_2]/\Delta t$, is $6.0 \times 10^{-5} \text{ M/s}$ at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[\text{O}_3]/\Delta t$?

Relative reaction rates (unique average rates)



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Summary

The _____ rate of a reaction is the change in concentration of a species divided by the time over which the change takes place; the unique average rate is the average rate divided by the **stoichiometric coefficient** of the species monitored. Spectroscopic techniques are widely used to study reaction rates, particularly for fast reactions. The _____ reaction rate is the **slope** of a *tangent* drawn to the graph of concentration as a function of time; for most reactions, the instantaneous rate decreases as the reaction proceeds.

1.2 Factors affecting reaction rate

Factors	How does it affect the reaction rate?
Concentration	higher concentration (reactant) → _____ rates (more particles per volume → more collision → higher rate)
Pressure* (gas involved)	higher pressure (gas reactant) → _____ rates
Temperature	higher temperature → _____ rates
Surface area (phase)	larger surface area (reactant) → _____ rates
Catalyst	with catalyst → _____ rates

2. Rate Laws and Half-life

2.1 Rate constant and reaction order

For a reaction $aA + bB \rightarrow cC + dD$, rate = $k[A]^m[B]^n$

What is the rate law? What is called the order of a reactant and overall order of a reaction, respectively?

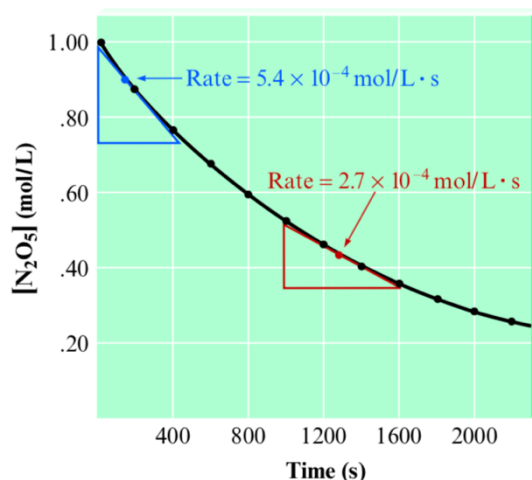
What is the meaning and unit of the rate constant k , respectively?

2.2 Determining the form of the rate law

What is the rate law for the following reaction according to the plot of concentration of N_2O_5 as a function of the time (rate at $[N_2O_5] = 0.90$ M vs rate at $[N_2O_5] = 0.45$ M)?

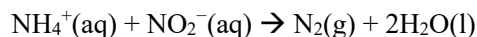


What is the limitation of this method?



Methods of initial rates

Initial rates from three experimental trials for the reaction



Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol/L · s)
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

[Integrative Example] If you pursue a career in inorganic or physical chemistry, you may one day be studying the rate of the reaction of bromate ion with bromide ion. Suppose you conduct four experiments to discover how the initial rate of consumption of BrO_3^- ions varies as the concentrations of the reactants are changed in the reaction,



- (a) Use the experimental data in the following table to determine the order of the reaction with respect to each reactant and the overall order.
- (b) Write the rate law for the reaction and determine the value of k . [Answer = $12 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}$]

Experiment	Initial concentration, [J]/(mol·L ⁻¹)			Initial rate/ ((mmol BrO ₃ ⁻)·L ⁻¹ ·s ⁻¹)
	BrO ₃ ⁻	Br ⁻	H ₃ O ⁺	
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

Summary

The order of a reaction is the power to which the concentration of the species is raised in the rate law; the overall order is the sum of the individual orders. The order of a reaction can *only* be determined by **experiments**, and is *not* related to the **coefficient** of the species in the balanced chemical equation unless it is an **elementary** reaction. Method of initial rates is most commonly used to experimentally measure the rate law.

*The decomposition of ozone to oxygen in the gas phase ($2\text{O}_3 \rightarrow 3\text{O}_2$) has the rate law ($rate = k[\text{O}_3]^2/[\text{O}_2]$).

2.3 The integrated rate law and half-life

For reaction $aA \rightarrow bB$, rate = $k[A]^m$, how does $[A]$ change with time? - **integration**

If the curve of $[A]$ changing with t was measured, how to figure out the order of reactant A?

Integrated rate laws for Zero-, First-, and Second-Order Reactions (A is the only reactant) - Summary

	Zero-Order	First-Order	Second-Order ^a
Rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
Units of rate constant			
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$1/[A] = kt + (1/[A]_0)$
Plot that gives a straight line			
Relationship of the slope of line to k			
Half-life			

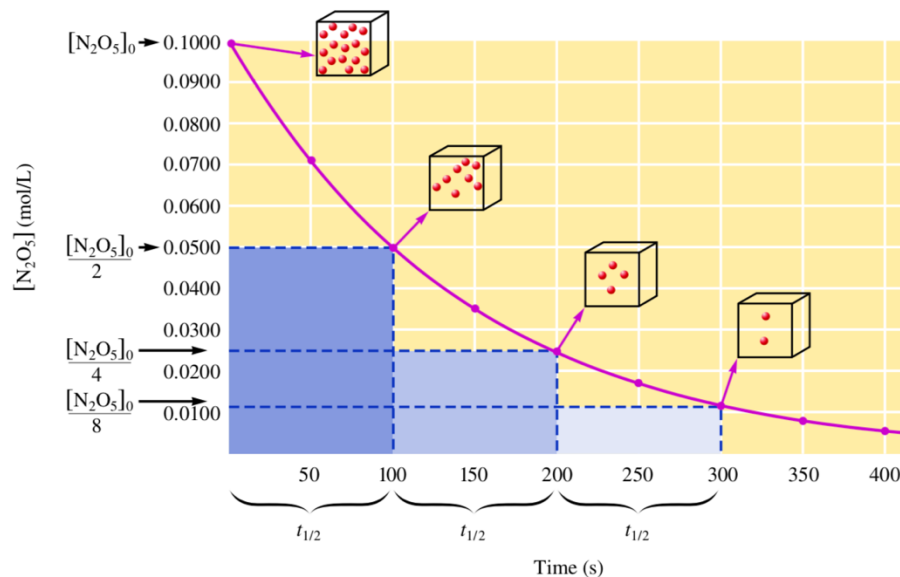
Half-life of first-order reaction

The time required for a reactant to reach *half* its original concentration is called the half-life of a reactant and is designated by the symbol $t_{1/2}$.

For a first order reaction,

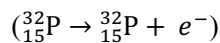
$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

Derive the $t_{1/2}$ according to the above integrated rate law for first-order reaction.



^a Not applied for second order reaction with a rate law of rate = $k[A][B]$

What is the half-life for the decay of phosphorus-32 (**all nuclear decays are first-ordered!**)?



The rate constant for the decay is $4.85 \times 10^{-2} \text{ day}^{-1}$. [Answer = 14.3 days]

[Integrative Example] Many organic compounds can isomerize (turn into another compound with the same molecular formula) when heated. Suppose you are an organic chemist studying cyclopropane. You find that when cyclopropane (C_3H_6 , 1) is heated to $500.^\circ\text{C}$ (773 K), it converts into an isomer, propene (2). You collect the following data, which show the concentration of cyclopropane at a series of times after the start of the reaction. Confirm that the reaction is first order in C_3H_6 and calculate the rate constant. [Answer = 0.040 min^{-1}]

Time, t/min	0	5	10.	15
$[\text{C}_3\text{H}_6]_t/(\text{mol}\cdot\text{L}^{-1})$	1.50×10^{-3}	1.24×10^{-3}	1.00×10^{-3}	0.83×10^{-3}

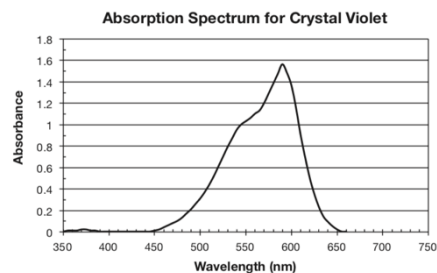
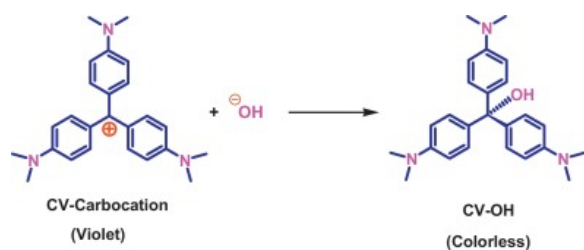
Integrated rate laws for reactions with more than one reactant



$$\text{rate} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

How to investigate the rate law by experiments? $[\text{Br}^-]$ and $[\text{H}^+]$ is also changing with time when investigating the order of BrO_3^- .

[Laboratory – Kinetics of crystal violet fading]



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Background

In strongly basic solutions the purple CV^+ cation slowly combines with hydroxide ions to form a neutral product, CVOH , which is colorless (see Figure 2). The rate of this reaction (Equation 1) is slower than typical acid–base proton transfer reactions and depends on the initial concentration of both crystal violet and hydroxide ions.



Exactly how much the rate changes as the reactant concentration is varied depends on the rate law for the reaction. In the case of the reaction of CV^+ with OH^- ion, the rate law has the general form

$$\text{Rate} = k [\text{CV}^+]^n [\text{OH}^-]^m \quad \text{Equation 2}$$

The exponents n and m are defined as the order of reaction for each reactant and k is the rate constant for the reaction at a particular temperature. The values of the exponents n and m must be determined by experiment. If the reaction is carried out under certain conditions then Equation 2 will reduce to the form

$$\text{Rate} = k' [\text{CV}^+]^n \quad \text{Equation 3}$$

where

$$k' = k [\text{OH}^-]^m \quad \text{Equation 4}$$

The constant k' is a new “pseudo” rate constant incorporating both the “true” rate constant k and the $[\text{OH}^-]^m$ term. Equation 3 is referred to as a pseudo-rate law because it is a simplification of the actual rate law, Equation 2.

The pseudo-rate law is valid when the concentration of OH^- ions is much greater than the concentration of CV^+ ions. Under these conditions the $[\text{OH}^-]^m$ term in Equation 2 will not change much over the course of the reaction and may be treated as a constant in the rate equation.

Recall that the absorbance for a specific concentration of a solution with a fixed path length varies directly with the absorptivity coefficient of the solution. This relationship is known as Beer's law.

$$A = abc \quad \text{Equation 5}$$

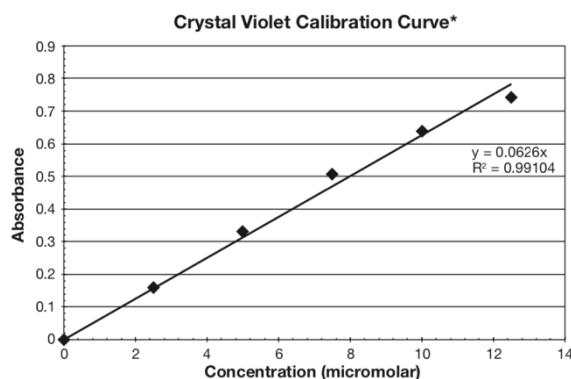
where A is absorbance, a is the molar absorptivity coefficient, b is the path length in cm, corresponding to the distance light travels through the solution, and c is the concentration of the solution. Beer's law provides the basis of using spectroscopy in quantitative analysis. Using this relationship, concentration and absorbance may be calculated if one variable is known while keeping a and b constant. This relationship is also extremely valuable in kinetics experiments, making it possible to follow the rate of disappearance of a colored substance by measuring its absorbance as a function of time.

Sample Data, Results, and Analysis

Calibration Curve for Crystal Violet

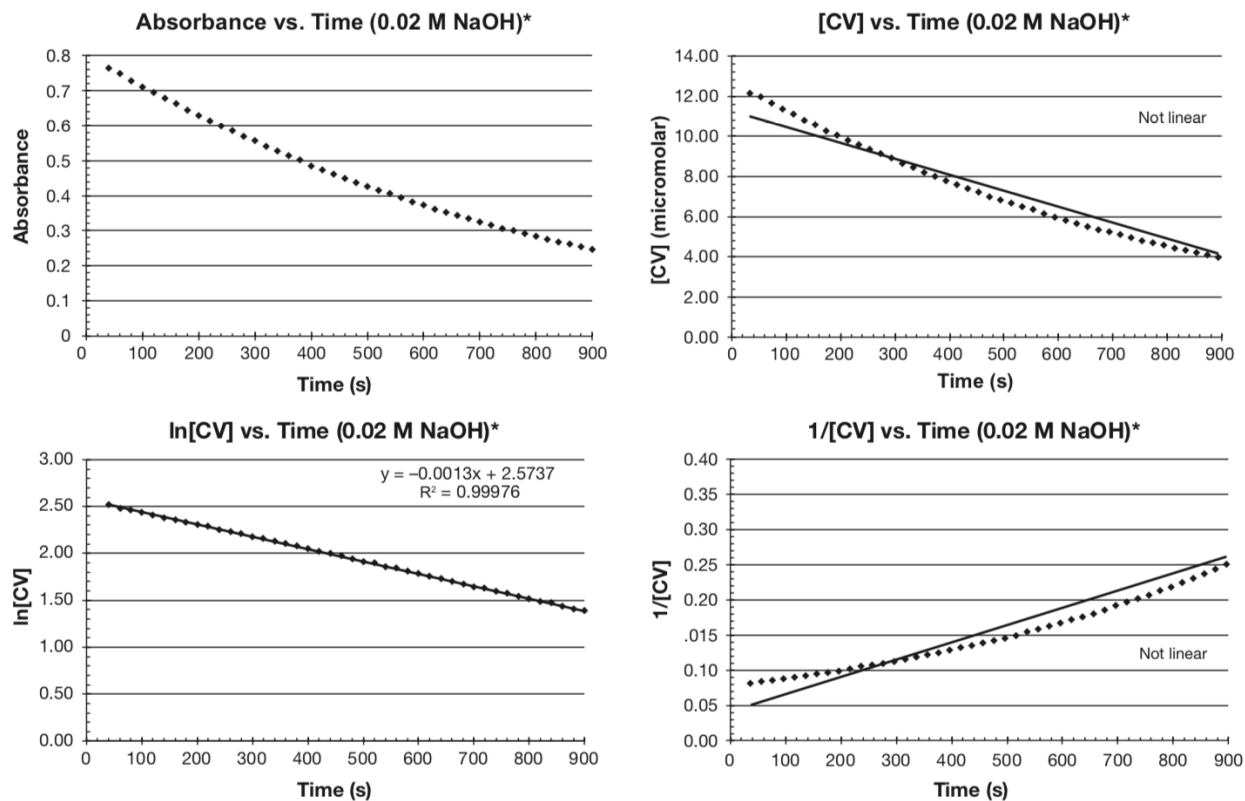
Concentration (μM)	Absorbance*
12.5	0.742
10	0.639
7.5	0.508
5	0.332
2.5	0.159

* Measurement wavelength was 565 nm.



* Measurement wavelength was 565 nm.

What is a calibration curve? What is its application? How to choose the wavelength for calibration curve measurement?



*This is the initial concentration of the sodium hydroxide.

What is the reaction order of CV^+ ? How to further measure the order of OH^- ?

Sketch the curve for $\ln[CV]$ vs. *Time* with a **0.04 M** NaOH and compare the slopes of the lines at different $[OH^-]$. How is the ratio of slopes related to the order of OH^- ?

Summary

In a first-order reaction, the concentration of reactant decays *exponentially* with time. To verify that a reaction is first order, plot the natural logarithm of its concentration against time and expect a straight line; the slope of the straight line is $-k$.

Spectroscopic techniques are widely used to study reaction rate law, and a pseudo-order kinetic analysis is commonly used for reactions with multiple reactants.

[AP-level video: <https://youtu.be/rgzQTTLz4ok> College-level video: <https://youtu.be/tcv5Xk9ZXpg>]

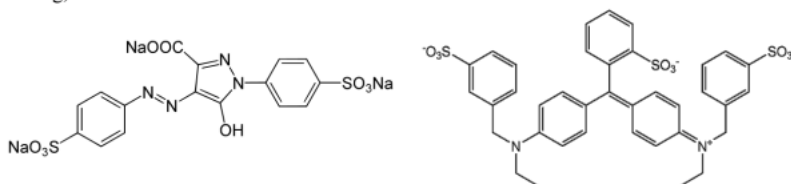
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***Extended Experiment** – what should you do without accessing the spectrophotometer?

○ **Experiment 1** – from MIT Science Olympiad 2016 - Chemistry Lab Q1

INTRODUCTION

Dyes have been an integral part of human life ever since early civilization. These colored substances come in incredibly varied forms, but often contain extensive conjugated organic systems. The structures of FD&C Yellow 5 (left) and Blue 1 (right), the components of green food coloring, are shown below.



This task is split into two parts. In Part I, you will *determine the rate order of green dye in its reaction with commercial bleach under pseudo-order conditions using the initial rate method*. Using the quantities suggested in the procedure, you can assume that $[\text{NaOCl}] \gg [\text{Dye}]$. The initial rate of a reaction can be estimated by the average rate at which the dye becomes colorless. In Part 2, you will *determine the concentration of an unknown sample of dye (G2) relative to G1 using the information obtained from Part 1*.

MATERIALS

Cross check all materials before beginning your experiment. Replacements and refills will *not be permitted* after the laboratory task has been started.

- Green dye samples G1 and G2
- 250 mL beaker with 50 mL 4% commercial bleach
- 250 mL beaker with 4 glass test tubes
- 2 plastic graduated pipettes
- Stopwatch with 0.01 sec accuracy
- Access to waste beaker

PROCEDURE – PART 1

1. Measure out 5.0 mL each of bleach into two test tubes – mark one as the standard, and one as the test solution
2. Add 2 drops of G1 into the test bleach solution; give the solution a quick swirl to ensure the solution is evenly mixed
3. Record the time it takes for the test solution to match the color of the standard solution
 - As more dye is oxidized by the bleach, the color of the bleach will become slightly darker; therefore you should be primarily concerned with matching the saturation of the test and standard.
4. Repeat step 3 with different concentrations of dye in accordance with the data table provided. You may reuse the bleach sample for multiple trials.
5. You may wish to conduct additional trials until you obtain satisfactory results; **points will be awarded for “Accepted value”, and not individual trials**

○ **Experiment 2** – from USNCO2016P3-Q1

You have been provided with three solutions. Solution A contains iron(III) ions, Solution B contains iodide ions, and Solution C contains thiosulfate ions (and some starch indicator).

Devise and carry out an experimental procedure to determine the kinetic order of the reaction that occurs upon mixing them with respect to $[\text{Fe}^{3+}]$ from Solution A and with respect to $[\text{I}^-]$ from Solution B.

NOTE: In carrying out your approved experimental plan, mix Solutions B and C before adding Solution A, and record the time required for the resulting mixture to turn a distinct, permanent color.

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DATA/CALCULATIONS – PART 1

Volume of bleach (mL)	5.0	5.0	5.0	5.0
Volume of dye (drops)	2	4	6	8
Time to completion (sec)	Trial 1			
	Trial 2			
	Trial 3			
	Trial 4			
	Trial 5			
	a. Accepted value			
b. Average rate of reaction (drops/sec)				

c. Calculations:

d. Green dye rate order: _____

DATA/CALCULATIONS

Volume of bleach (mL)	5.0	5.0	5.0	5.0
Volume of dye (drops)	2	4	6	8
Time to completion (sec)	Trial 1			
	Trial 2			
	Trial 3			
	Trial 4			
	Trial 5			
	a. Accepted value	8 pts – values filled in 2 pts – values increase from left to right total of 10 pts example values: 9.39 sec, 11.61 sec, 15.52 sec, 16.92 sec		
b. Average rate of reaction (drops/sec)	value = (drops used in trial)/(answer to a.) total of 4 pts			

c. Calculations:

Compare two pairs of volumes
Should apply the formula $(\text{rate}_1)/(\text{rate}_2) = ([\text{dye}_1]/[\text{dye}_2])^m$ twice
total of 5 pts

d. Green dye rate order: _____

Points were awarded only if answer was within range 0.1-0.9 (with the most points awarded to answer 0.5) and the answer followed from correctly applying the formulas above
total of 10 pts

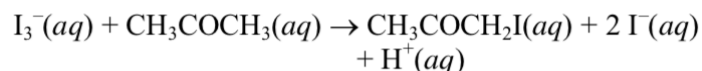
[USNCO Example – N2018-P1-Q28]

An irreversible reaction $A + B \rightarrow \text{products}$ is studied under conditions where the initial concentrations of A and B are equal. Under these circumstances, a graph of $\ln([A])$ as a function of time is linear. What is the order in A?

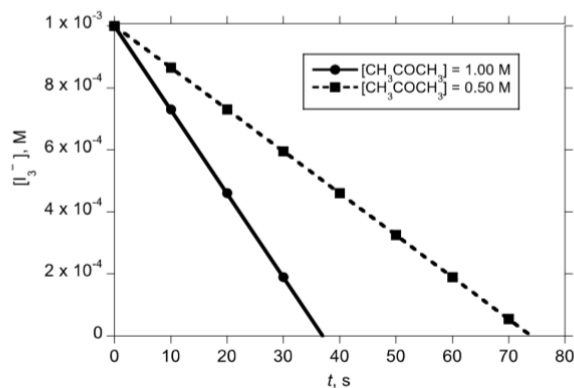
- (A) Zeroth order
- (B) First order
- (C) Second order
- (D) The order in A cannot be determined based on the information given.

[USNCO Example – N2016-P1-Q27]

Triiodide reacts with acetone in acidic aqueous solution:



The reaction is carried out twice, both times with $[\text{I}_3^-]_0 = 1.0 \times 10^{-3} \text{ M}$ and $[\text{H}^+]_0 = 1.00 \text{ M}$, but with two different concentrations of acetone, and the concentration of triiodide is found to vary with time as shown:



What are the orders of triiodide and acetone in the reaction?

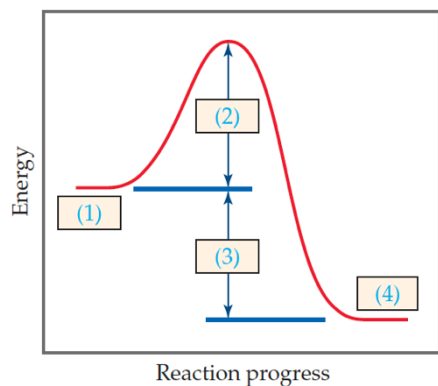
- (A) First-order in I_3^- , first-order in CH_3COCH_3
- (B) Zeroth-order in I_3^- , first-order in CH_3COCH_3
- (C) First-order in I_3^- ; the order in CH_3COCH_3 cannot be determined from the available data
- (D) First-order in CH_3COCH_3 ; the order in I_3^- cannot be determined from the available data

3. Collision Model/Transition State Model and Reaction Profile

3.1 Collision model

Collision model is based on the following postulates:

1. _____ (collisions make reaction occur)
2. _____ (orientation)
3. _____ (energy barrier)

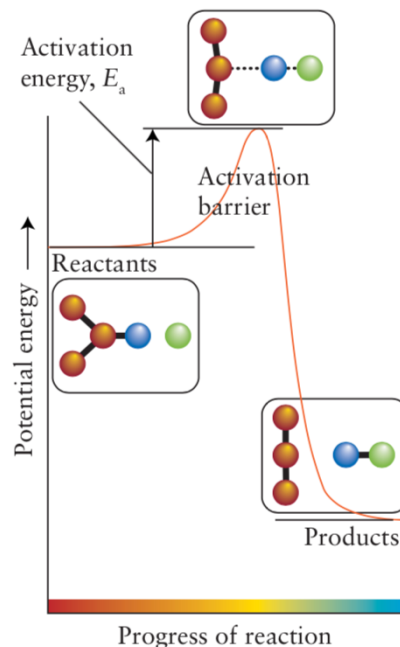
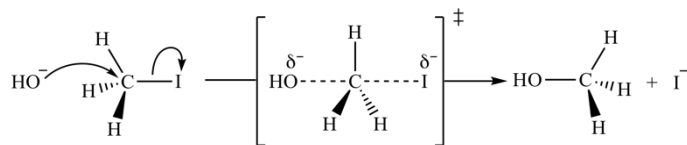
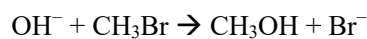


The following diagram shows a reaction profile. Label the components indicated by the boxes. with catalyst added.

3.2 Transition state model

In transition state theory, a reaction takes place only if two molecules acquire enough energy, perhaps from the surrounding solvent, to form an *activated complex* and cross through a **transition state** at the top of an energy barrier.

Draw the 3-D structure of the transition state of the following reaction



[**Extended Question**] Suppose we have two reactions, $A \rightarrow B$ and $B \rightarrow C$. You can isolate B, and it is stable. Is B the transition state for the reaction $A \rightarrow C$? What is the difference between transition state and intermediate? Draw the energy profile of this two-step reaction.

Lecture Note – Advanced Kinetics

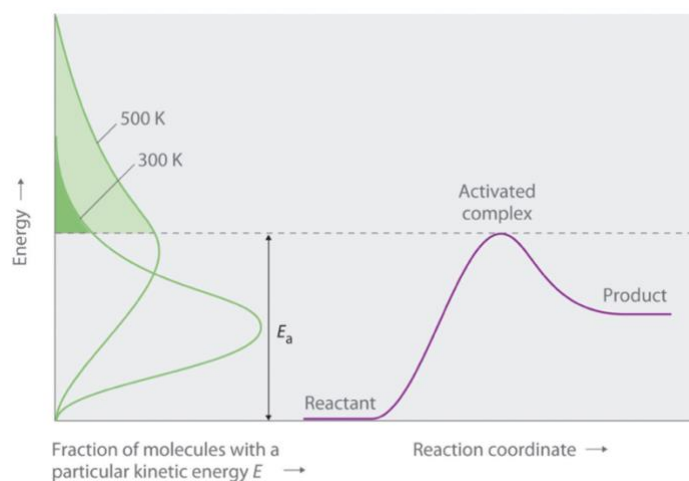
Dec 28th, 2020

[Pre-Reading]: (Zumdahls9e) Chp12.5-12.7; (Atkins7e) Topic7C-7E

[Learning Objectives]

1. Arrhenius Equation - Temperature and Rate

1.1 Arrhenius equation



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

↑ Please explain what is the meaning of each item in the above equation and justify the relationship between temperature and rate in terms of the above figure.

Convert the above equation into the following style and explain what are the variables to be measured for determining the activation energy of a certain reaction.

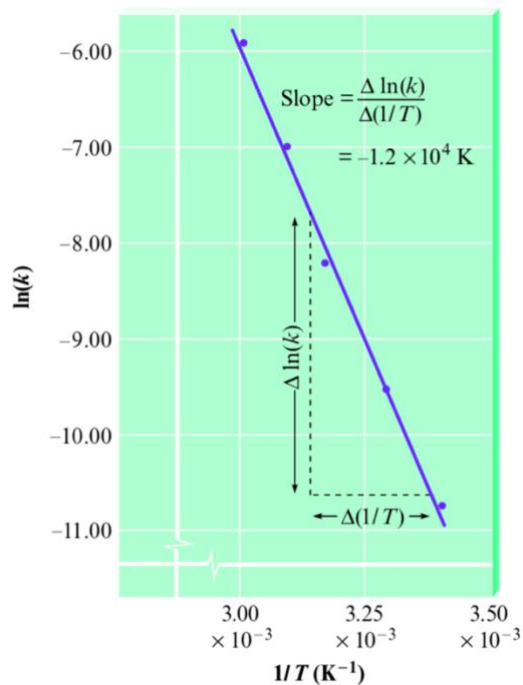
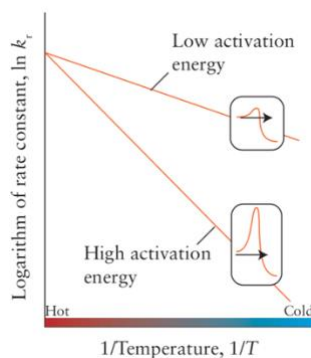
$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

What E_a results in a doubling of the reaction rate with a 10. °C increase in temperature from 20. °C to 30. °C?
(Answer = about 51 kJ/mol)

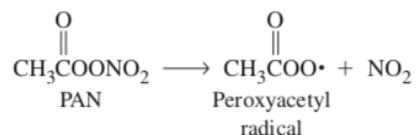
1.2 Determining activation energy

What is the relationship of the slope of the fitting line for $\ln k$ vs $1/T$ with E_a ?

An Arrhenius plot of $\ln k$ against $1/T$ is used to determine the Arrhenius parameters of a reaction; a high activation energy signifies a _____ sensitivity of the rate constant to changes in temperature [*why?].



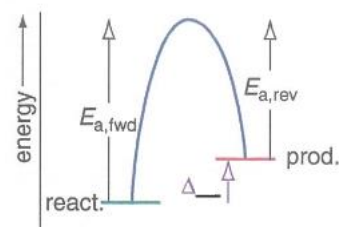
[Integrative Example] Peroxyacetyl nitrate (PAN) is an air pollutant produced in photochemical smog by the reaction of hydrocarbons, oxides of nitrogen, and sunlight. PAN is unstable and dissociates into peroxyacetyl radicals and $\text{NO}_2(\text{g})$. Its presence in polluted air is like a reservoir for NO_2 storage.



The first-order decomposition of PAN has a half-life of 35 hours at 0°C and 30.0 min at 25°C . At what temperature will a sample of air containing 5.0×10^{14} PAN molecules per liter decompose at the rate of 1.0×10^{12} PAN molecules per liter per minute? [Answer = $2.8 \times 10^2 \text{ K}$]

*Extension

How does the forward reaction rate and backward reaction rate change with temperature according to the figure in the right?



2. Catalysis

A catalyst is a substance that speeds up a reaction without being consumed itself.

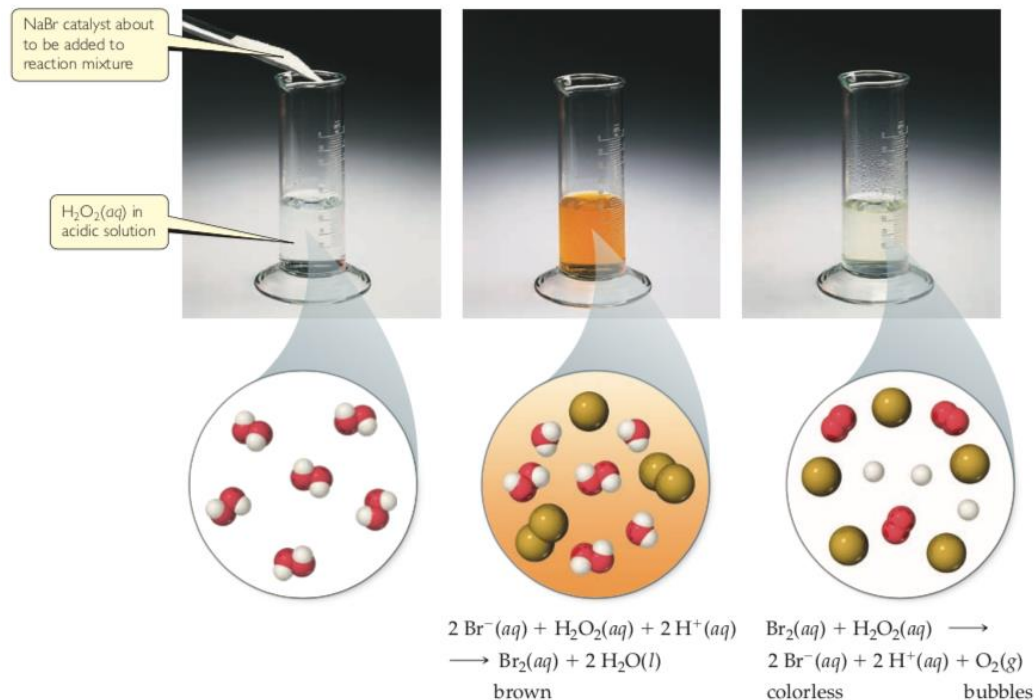
List a few reactions with catalysts involved.

Homogeneous catalyst and heterogeneous catalyst

A _____ catalyst is one that is present in the same phase as the reacting molecules.

A _____ catalyst exists in a different phase, usually as a solid.

Why does the solution in the middle cylinder have a brownish color?



What is the overall reaction shown in the figure? What is the function of Br^- in the reaction? Is it homogenous or heterogenous?

What is the energy curve of the above reaction with and without the catalyst added, respectively?

*How does the forward rate and backward rate change when catalyst is added based on energy curves?

3. Reaction Mechanism

3.1 Elementary reaction

Most chemical reactions occur by a *series of steps* called the reaction mechanism.

What is an elementary reaction?

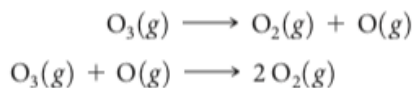


Write down the equation of the reaction above.

Is the above elementary reaction unimolecular, bimolecular, or trimolecular? Write down the rate law of the above elementary reaction.

[Introductory Example]

It has been proposed that the conversion of ozone into O_2 proceeds by a two-step mechanism:

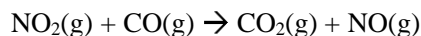


- Describe the molecularity of each elementary reaction in this mechanism.
- Write the equation for the overall reaction.
- Identify the intermediate(s).

3.2 The rate laws of elementary reactions

The rate law of an *elementary* unimolecular reaction is first-order; that of a bimolecular *elementary* reaction is second-order.

3.3 Deriving rate laws using the rate-determining step (RDS)



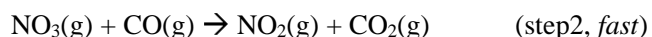
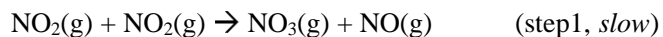
For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate} = k[NO_2][CO]$$

The reaction is first order with respect to NO_2 and first-order with respect to CO . This is consistent with a *single-step bimolecular* mechanism and it is possible that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order: $\text{rate} = k[NO_2]^2$.

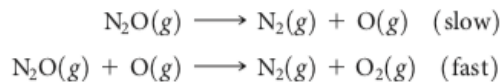
This is consistent with a mechanism that involves the following two elementary reactions:



What is the intermediate in the reaction? Which is the rate-determining step, what does it mean? What will be the rate law of the overall reaction?

[Introductory Example]

The decomposition of nitrous oxide, N_2O , is believed to occur by a two-step mechanism:



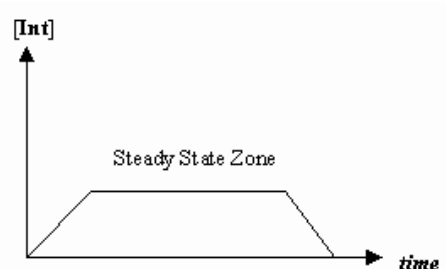
(a) Write the equation for the overall reaction. (b) Write the rate law for the overall reaction.

3.4 Deriving rate laws using the steady-state approximation (SSA)

When a reaction mechanism has several steps of comparable rates, the rate-determining step is often not obvious. However, there is an *intermediate* in some of the steps. An intermediate is a species that is neither one of the reactants, nor one of the products. The **steady-state approximation** is a method used to derive a rate law. The method is based on the **assumption that one intermediate in the reaction mechanism is consumed as quickly as it is generated. Its concentration remains the same in a duration of the reaction.**

When a reaction involves one or more intermediates, the concentration of one of the intermediates remains constant at some stage of the reaction. Thus, the system has reached a *steady-state*, hence the name of the technique is called steady state approximation.

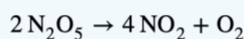
The concentration of one of the intermediate, $[\text{Int}]$ varies with time as shown on the right. At the start and end of the reaction, $[\text{Int}]$ does vary with time.



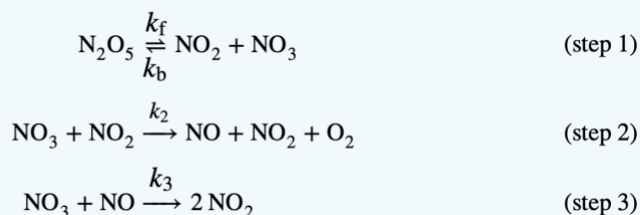
The steady-state approximation implies that you select an intermediate in the reaction mechanism and calculate its *concentration* by assuming that it is consumed as quickly as it is generated.

In the following, an example is given to show how the steady-state approximation method works.

Use the steady-state approximation to derive the rate law for this reaction



assuming it follows the following three-step mechanism:



Detailed work: <http://shorturl.at/pLO58>

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[Key]

$$\frac{d[\text{O}_2]}{dt} = \frac{k_f k_2 [\text{N}_2\text{O}_5]}{k_b + 2k_2} = k[\text{N}_2\text{O}_5]$$

Carry out the above manipulation yourself on a piece of paper. Simply reading the above will not lead to solid learning yet.

[Extension]

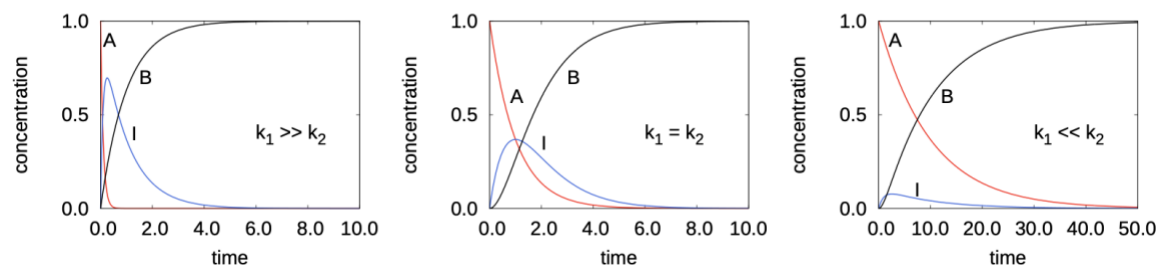
Consider the following reaction



Let us say that the reaction occurs in two steps



The concentrations of the reactant, intermediate and the product for the cases i) $k_1 \gg k_2$, ii) $k_1 = k_2$, and iii) $k_1 \ll k_2$ are shown below



According to the information above, SSA can be applied under what kind of circumstances? Why does it make sense?

Further read: <http://www.theo.chemie.tu-muenchen.de/cfp/steady.state.approximation.pdf>

3.5 Deriving Rate Laws Using the Pre-equilibrium Approximation (PEA)

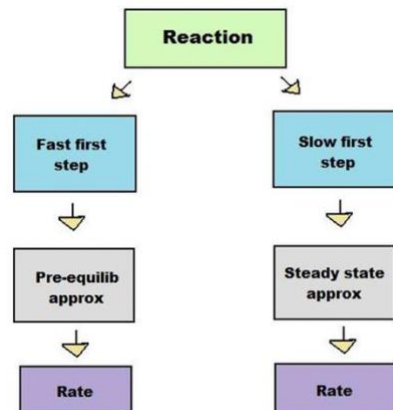
The *pre-equilibrium approximation* assumes that the reactants and intermediates of a multi-step reaction exist in *dynamic equilibrium*.

Pre-equilibrium

According to the steady state approximation, reactions involving many steps can be analyzed using approximations. Like the steady state method, the pre-equilibrium approximation method derives an expression for the rate of product formation with *approximated* concentrations. Unlike the steady state method, the pre-equilibrium approximation does so by assuming that the *reactants and intermediate are in equilibrium*. Although both methods are used to solve for a rate of reaction, they are used under different conditions.

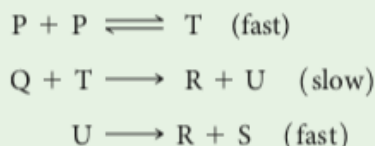
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The steady state method can only be used if the first step of a reaction is much *slower* than the second step, *whereas the pre-equilibrium approximation requires *the first step to be faster and reversible (fast equilibrium, why?)*. These opposing conditions prevent the two methods from being interchangeable (shown in the figure).



[Extended Example]

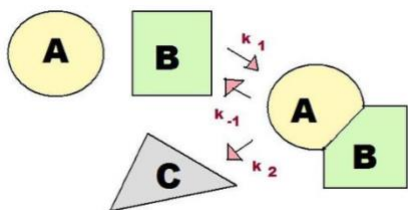
Consider the following hypothetical reaction:
 $2\text{P} + \text{Q} \longrightarrow 2\text{R} + \text{S}$. The following mechanism is proposed for this reaction:



Substances T and U are unstable intermediates. What rate law is predicted by this mechanism?

- (a) Rate = $k[\text{P}]^2$ (b) Rate = $k[\text{P}][\text{Q}]$ (c) Rate = $k[\text{P}]^2[\text{Q}]$
 (d) Rate = $k[\text{P}][\text{Q}]^2$ (e) Rate = $k[\text{U}]$

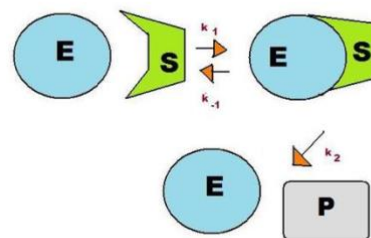
Summary



Both the steady state approximation and pre-equilibrium approximation apply to intermediate-forming *consecutive* reactions, in which the product of the first step of the reaction serves as the reactant for the second step (*intermediate*).

*Extension

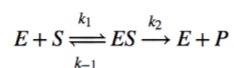
A consecutive reaction found in living systems is the *enzyme-substrate* reaction. In this type of reaction, an enzyme binds to a substrate to produce an enzyme-substrate intermediate, which then forms the final product. The two reactants, **E** (enzyme) and **S** (substrate), form the intermediate **ES**. This enzyme-substrate intermediate forms the product **P**, usually an essential biomolecule. The enzyme then exits the reaction unchanged and able to catalyze future reactions.



As before, there are three reaction rates in this reaction: k_1 , k_{-1} , and k_2 . The pre-equilibrium approximation uses the rate constants to solve for the rate of the reaction, indicating how quickly the reaction is likely to produce the biomolecule.

I. Assume Reactants and Intermediate are in Equilibrium

1. The general reaction used to derive a rate law is as following:



2. Breaking up the overall reaction into elementary steps gives:



$$\text{Rate of formation of } ES = k_1[E][S]$$



$$\text{Rate of decay of } ES = k_{-1}[ES]$$



$$\text{Rate of formation of } P = k_2[ES]$$

3. In the steady state reaction, the intermediate concentration [ES] is assumed to remain at a small constant value. The pre-equilibrium approximation takes a different approach. Because the reversible reaction $E + S \rightarrow ES$ is much faster than the product formation of $ES \rightarrow E + P$, E, S, and ES are considered to be in equilibrium throughout the reaction. This concept greatly simplifies the mathematics leading to the rate law.

II. Solve for the Rate of Product Formation

4. Using the idea that the reactants and intermediate are in equilibrium, the rate of formation of E + P can be written as:

$$\frac{d[P]}{dt} = k_2[ES] = k_2K[E][S] \quad (1.4)$$

where

$$K = \frac{[ES]}{[E][S]} = \frac{k_1}{k_{-1}} \quad (1.5)$$

(K is the equilibrium constant)

5. The rate of product formation is simplified through the **composite rate constant**, k:

$$k = k_2K = \frac{k_1 k_2}{k_{-1}} \quad (1.6)$$

6. The rate of product formation can now be shortened to:

$$\frac{d[P]}{dt} = k[E][S] \quad (1.7)$$

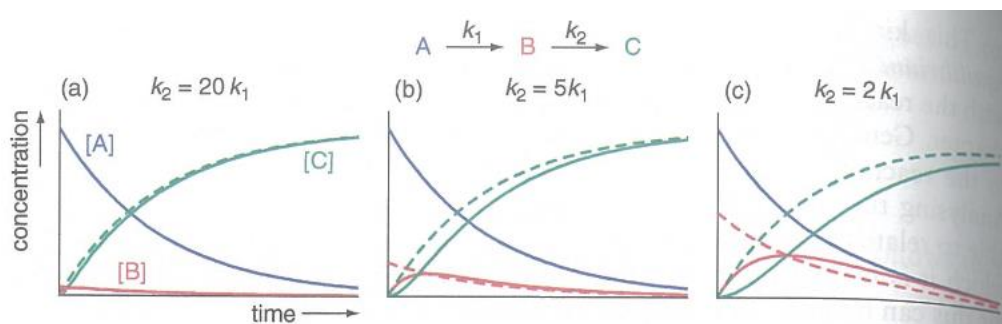
This equation can be solved for unknown variables in consecutive reactions involving intermediates.

****Further Extension**

Apply SSA to the above reaction to derive the rate law, compare it with the rate law derived based on PEA.

What are the preconditions to convert one rate law into another? [Reference?](#)

This [link \(https://shorturl.at/sxSX2\)](https://shorturl.at/sxSX2) allows students to explore the effect of various kinetic regimes, by displaying the solutions of rate equations, solved by numerical means, and comparing them with the results of various approximations.



The dash lines give the behavior predicted using the steady-state approximation.

Summary

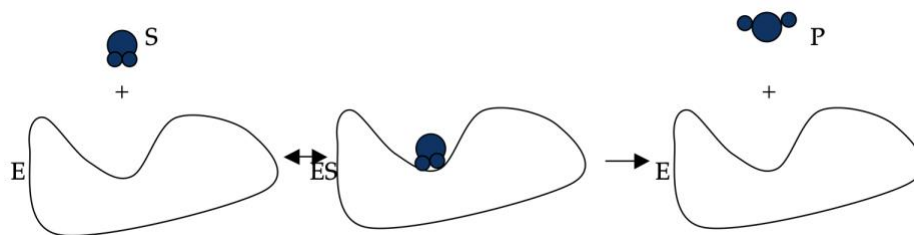
A rate law is often derived from a proposed mechanism by imposing the *steady-state approximation* or assuming that there is a *pre-equilibrium*. To be plausible, a proposed mechanism must be consistent with the experimental rate law and the chemical equation for the overall reaction.

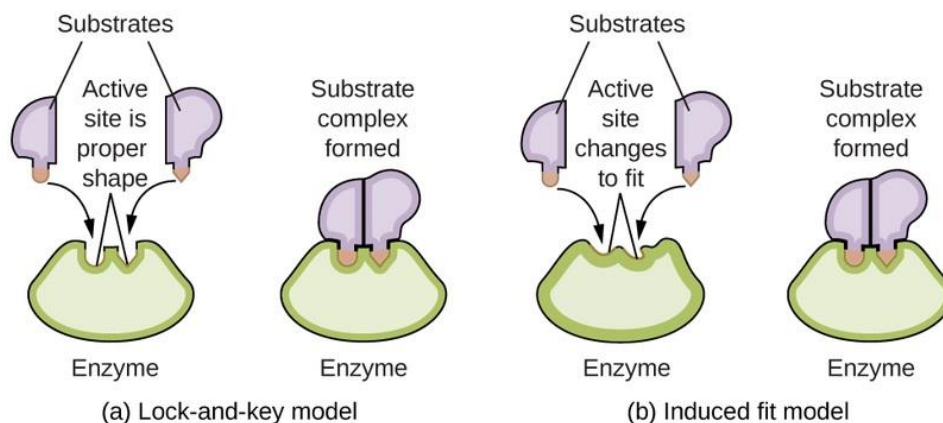
The equilibrium constant for an elementary reaction is equal to the *ratio* of the forward and reverse rate constants of the reaction or, for multistep reactions, the *ratio* of the product of the forward rate constants to the product of the reverse rate constants.

3.6 Enzyme

Reactant molecules are called _____; Substrates bind to an _____ on the enzyme.

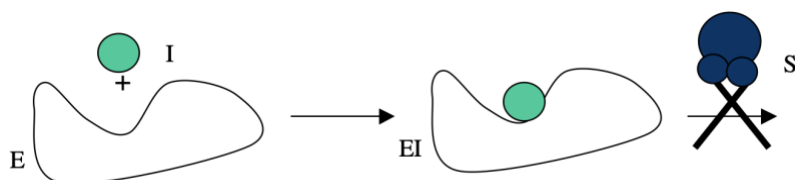
enzyme (E) + substrate (S) \rightleftharpoons enzyme-substrate complex (ES) \rightarrow enzyme (E) + product (P)



Key-lock model vs induced-fit mechanism**Enzyme inhibition**

An inhibitor is the opposite of a catalyst. It _____ the rate of a reaction, typically by increasing the activation energy.

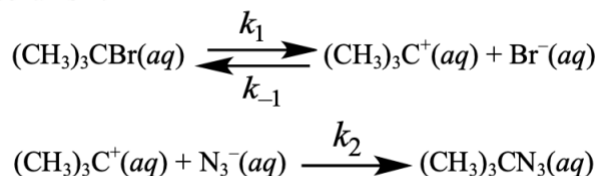
If an inhibitor is bound in the *active site* of an enzyme forming an **enzyme-inhibitor complex (EI)**, then substrate can't bind.



Given that enzymes catalyze reactions by lowering the energy of the "transition state," compounds that resemble the _____ can bind tightly to the enzyme, and thereby block substrate binding.

[USNCO Example – L2017-Q30]

The reaction of *tert*-butyl bromide with azide ion in aqueous solution is proposed to proceed by the following mechanism:



Assuming that $(\text{CH}_3)_3\text{C}^+(aq)$ achieves a steady-state concentration, but making no further assumptions about the relative magnitudes of the three rate constants, what is the rate law for this reaction?

- (A) Rate = $k_1[(\text{CH}_3)_3\text{CBr}]$
 (B) Rate = $k_2[(\text{CH}_3)_3\text{CBr}][\text{N}_3^-]$
 (C) Rate = $\frac{k_1 k_2 [(\text{CH}_3)_3\text{CBr}][\text{N}_3^-]}{k_{-1}[\text{Br}^-]}$
 (D) Rate = $\frac{k_1 k_2 [(\text{CH}_3)_3\text{CBr}][\text{N}_3^-]}{k_{-1}[\text{Br}^-] + k_2[\text{N}_3^-]}$

***Extension**

What is the overall reaction in the question above?

Is the assumption of $(\text{CH}_3)_3\text{C}^+(aq)$ archiving steady-state reasonable here in terms of the bond broken and formed in each step?

**If PEA is used to derive the rate law, how does it look like? Under what circumstances, the two rate laws are exchangeable?

More advanced discussion could be found here:

Leslie C. Bateman, Edward D. Hughes and Christopher K. Ingold *J. Chem. Soc.*, **1940**, 1017-1029