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Chapter 5

Chemical Kinetics

5.1 Reaction Rates and Rate Laws

OBJECTIVES

After studying this topic, you should be able to:

- Explain the following terms: rate law; specific rate constant; integrated rate law; zero-, first-, and second-order reaction; exponential decay; and half-life.
- From given experimental data, determine the reaction order for the reactants in a reaction.
- Write a complete rate law for a reaction.
- From a rate law, deduce the value of the specific rate constant, and its units.
- Using the data provided, find the reaction rates, half-lives, and final concentrations of species in zero-, first-, and second-order reactions.

INTRODUCTION

Chemical kinetics is the study of how fast chemical reactions proceed (ie., reaction rates) and the factors that affect those rates. In this topic, basic concepts of chemical kinetics are examined.

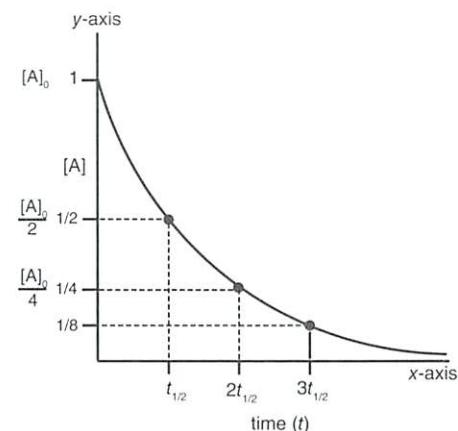
It was obvious — to me at any rate — what the answer was to why an enzyme is able to speed up a chemical reaction as much as 10 million times. It had to do this by lowering the energy of activation — the energy of forming the activated complex. It could do this by forming strong bonds with the activated complex, but only weak bonds with the reactants or products.

Linus Carl Pauling (1901–1994)

Topics Covered:

5.1 Reaction Rates and Rate Laws

5.2 Reaction Mechanisms and the Arrhenius Equation

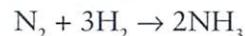


REACTION RATES

The speed at which a reaction takes place is governed by several factors, including:

- What the reactants are, and their concentrations. For example:
 $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{HF}(\text{g})$ is an explosively fast reaction.
 $4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s})$ can take months (rusting of iron).
 $\text{C}(\text{diamond}) \rightarrow \text{C}(\text{graphite})$ is an undetectably slow reaction.
- The temperature: reactions tend to proceed faster at higher temperatures.
- Whether or not a catalyst is present.

The rate of a chemical reaction is a positive quantity usually defined by comparing the change in the product or reactant concentration over time. For example, in the production of ammonia from nitrogen:

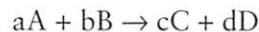


one could measure the rate at which N_2 and H_2 are consumed or the rate at which NH_3 is produced. Due to the stoichiometry of the reaction, the rate of N_2 consumption will be $\frac{1}{3}$ the rate of H_2 consumption and $\frac{1}{2}$ the rate of NH_3 production. Thus, the reaction rate in this case can be defined as:

$$\text{Rate} = -\left(\frac{\Delta[\text{N}_2]}{\Delta t}\right) = -\frac{1}{3}\left(\frac{\Delta[\text{H}_2]}{\Delta t}\right) = +\frac{1}{2}\left(\frac{\Delta[\text{NH}_3]}{\Delta t}\right)$$

The negative signs in front of the N_2 and H_2 terms take into account that $[\text{N}_2]$ and $[\text{H}_2]$ decrease as the reaction takes place.

In summary, for any reaction:



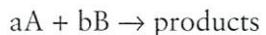
the relationship between the rates for the various reactants and products can be expressed as:

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



Concentration Effects and Rate Laws

The effect of concentration on a reaction is described using *rate laws*, which are mathematical expressions that link the rate of a reaction with reactant concentration. In the reaction:



The rate of the reaction (rate law) is given by the equation below:

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

where:

- k is the *specific rate constant* for the reaction at a given temperature.
- $[A]$ and $[B]$ are concentrations of components A and B in M (mol L^{-1}).
- x and y are the orders for each reactant and can only be found experimentally.

The “order” of a reaction defines how the rate of a reaction is affected by the concentration of the species involved in the reaction.

The exponent values are usually whole numbers (but not always). They determine the order of the reactant as follows:

- If $x = 0$, the reaction is zero order with respect to A. This means that the reaction rate is independent of $[A]$.
- If $x = 1$, the reaction is first order with respect to A.
- If $x = 2$, the reaction is second order with respect to A, and so on.
- If $y = 0$, the reaction is zero order with respect to B, and so on.
- The overall order of the reaction is $x + y$.

Remember, the exponents are experimentally measured and DO NOT correlate with the coefficients in the reaction equation. (This will be explained in more detail in the next topic.) Exponent values higher than 2 are seldom seen, but occasionally an order of $\frac{1}{2}$ or $-\frac{1}{2}$ is seen.

Determining the overall order of a reaction from the rate law is illustrated in the following example:

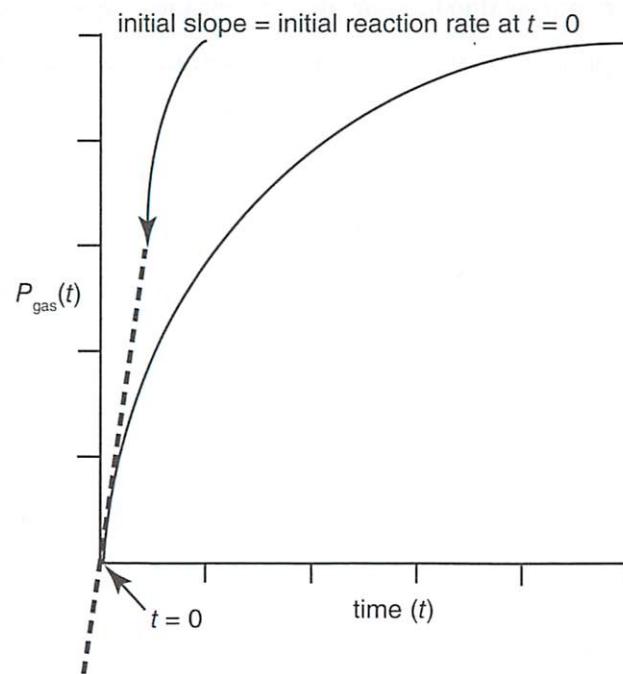


the rate law is: $\text{Rate} = k [\text{H}_2]^1 [\text{NO}]^2$

The reaction is first order with respect to $[\text{H}_2]$ and second order with respect to $[\text{NO}]$. The overall order of this reaction is three (the sum of all the individual orders). Note that the products of a reaction do not normally appear in the rate law because the forward rate is the rate measured most often. If the reverse rate is measured, then the concentrations of products will appear.

Experimental Determination of the Exponents

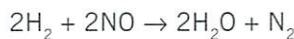
How are the exponents in the rate law determined? First, by measuring initial reaction rates for different concentrations (pressures) of the reactants. For example, for a reaction where a gas is produced, the initial reaction rate can be determined as the slope of the plot of the gas pressure as a function of time, $P_{\text{gas}}(t)$, at $t = 0$.



The experimental reaction rates measured in this manner for various initial concentrations (pressures) of the reactants are then processed as shown in the following examples.

Example 5.1.1. Rate Law Determination #1 (In-Class Exercise)

For the following reaction, use the experimental data provided to determine the exponents and specific rate constant, k .



$$\text{Rate} = k [\text{H}_2]^x [\text{NO}]^y$$

RUN	[H ₂] (mol L ⁻¹)	[NO] (mol L ⁻¹)	RATE (mol L ⁻¹ s ⁻¹)
i	0.1	0.2	5
ii	0.2	0.2	10
iii	0.1	0.4	20

Example 5.1.2. Rate Law Determination #2 (In-Class Exercise)

For the reaction A → products, the data below was collected. Determine the rate law and specific rate constant, k .

RUN	[A] (mol L ⁻¹)	RATE (mol L ⁻¹ s ⁻¹)
i	1.78×10^{-2}	6.00×10^{-5}
ii	2.85×10^{-2}	7.59×10^{-5}

FIRST-ORDER REACTIONS

Suppose $A \rightarrow \text{products}$ is a first-order reaction. The rate law would be:

$$\text{Rate} = k[A] = -\left(\frac{\Delta[A]}{\Delta t}\right)$$

As the reaction proceeds, $[A]$ decreases. Thus the rate can be integrated with respect to time to obtain the *integrated rate law* for a first-order reaction:

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

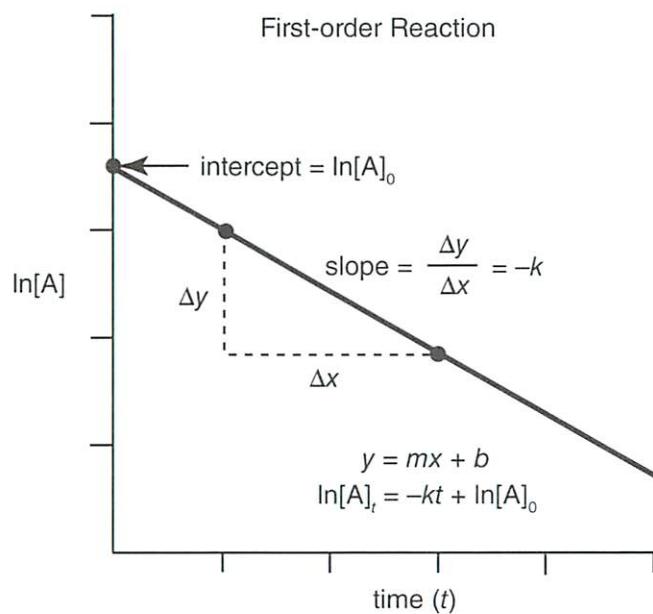
In the equation on the previous page:

- $[A]_t$ = concentration of A after time t has elapsed.
- $[A]_0$ = initial concentration.

The integrated rate law equation can be rearranged into an equation for a straight line (i.e., $y = mx + b$) as follows:

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

Thus, if a reaction is first order, a plot of $\ln[A]_t$ as a function of time should yield a straight line with a slope equal to $-k$ and a y -intercept equal to $\ln[A]_0$ (see graph that follows). This is a useful “test” to see if a reaction is first order or not.

**Example 5.1.3. Integrated First-order Rate Law (In-Class Exercise)**

For the decomposition reaction $B \rightarrow$ products, a plot of $\ln[B]$ versus time yielded a straight line with slope -0.35 min^{-1} .

- If $[B]_0 = 0.160 \text{ M}$, find $[B]$ at $t = 4.00 \text{ minutes}$.
- Find the time required for $[B]$ to drop to 0.100 M .
- Find the time required for half of B to decompose.

Exponential Decay and Half-Life

Solution (c) of the “First-order Rate Law” In-Class Exercise example illustrates the concept of *half-life* ($t_{1/2}$), which is the amount of time it takes to use up half of the reactant. The half-life for a first-order reaction is related to the rate constant as follows:

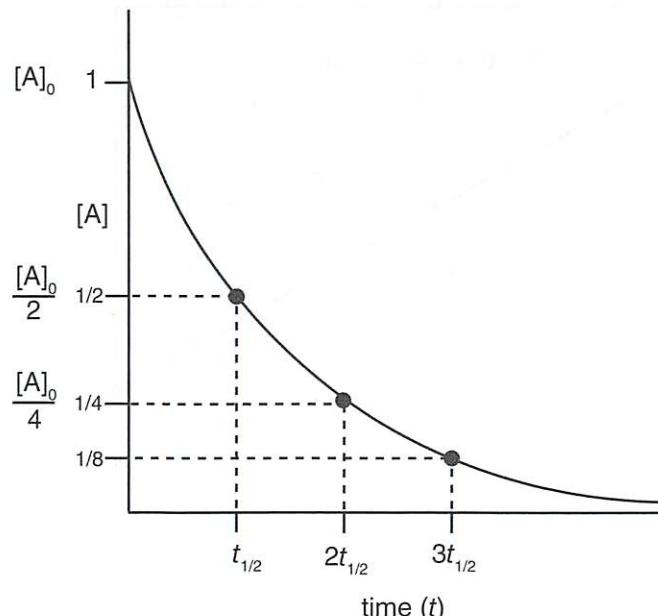
$$\ln \frac{[A]_t}{[A]_0} = -kt$$

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

Therefore,

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

The half-life of a first-order reaction follows an *exponential decay* and is illustrated in the graph that follows. Note that the exponential decay plot is not a straight line. To get a straight line, $\ln[A]$ versus time must be plotted as was previously shown.



For a first-order reaction, the half-life is a constant length of time; it only depends on the rate constant, k , and not the concentration or initial amount of the reactant. As shown by the graph, after one half-life ($t_{\frac{1}{2}}$), half of the original reactant remains. After two half-lives ($2t_{\frac{1}{2}}$), a quarter remains. After three half-lives ($3t_{\frac{1}{2}}$), an eighth remains, etc. Therefore, the fraction of reactant remaining after n half-lives can be expressed as:

$$\text{Fraction remaining} = \frac{[A]_t}{[A]_0} = (0.5)^n$$

In order to use this expression effectively, the number of half-lives elapsed at any given time in a reaction must be known. Note that the symbol n used here does not refer to the number of moles. Also note that n need not be a whole number.

$$\text{Number of elapsed half-lives } (n) = \frac{\text{time elapsed}}{\text{length of half-life}}$$

Example 5.1.4. First-order Half-Life #1 (In-Class Exercise)

Radioactive decay proceeds according to first-order kinetics. The radioactive isotope ^{210}Po has a half-life of 138.4 days. What fraction of ^{210}Po remains after 1 year (365 days)?

Example 5.1.5. First-order Half-Life #2 (In-Class Exercise)

The first-order decomposition of N_2O_5 into NO_2 and O_2 has a half-life of 120 seconds. If the initial concentration of N_2O_5 is 0.850 M , what is its concentration after five minutes?

ZERO-ORDER REACTIONS

Suppose the process $A \rightarrow \text{products}$ is zero order. That is, the rate of the reaction does not depend on $[A]$, only on k .

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^0 = k$$

From the equation above, the integrated zero-order rate law can be obtained:

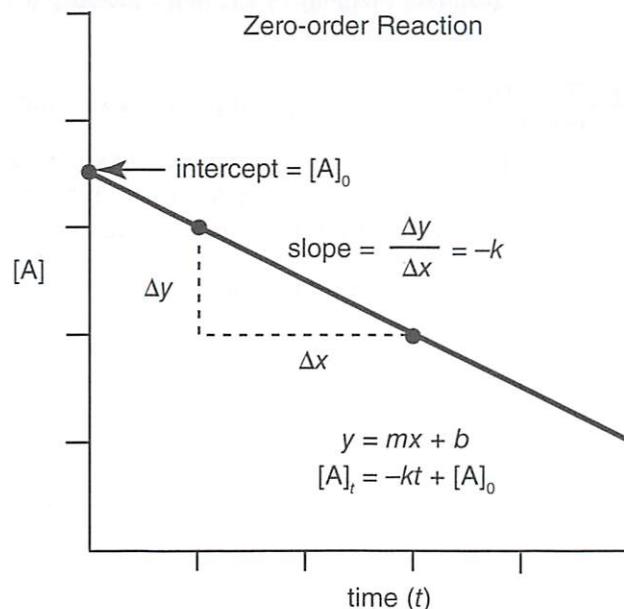
$$[A]_t - [A]_0 = -kt$$

This equation can be rearranged into the form of a straight line equation (note that there are no logarithmic relationships):

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

$$(y = mx + b)$$

Thus a plot of $[A]$ as a function of time yields a straight line with a slope of $-k$ and a y -intercept of $[A]_0$ (see graph that follows).



SECOND-ORDER REACTIONS

Suppose the process $A \rightarrow \text{products}$ is second order. The rate depends on k and the square of $[A]$.

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

From the equation above, the integrated second-order rate law can be obtained:

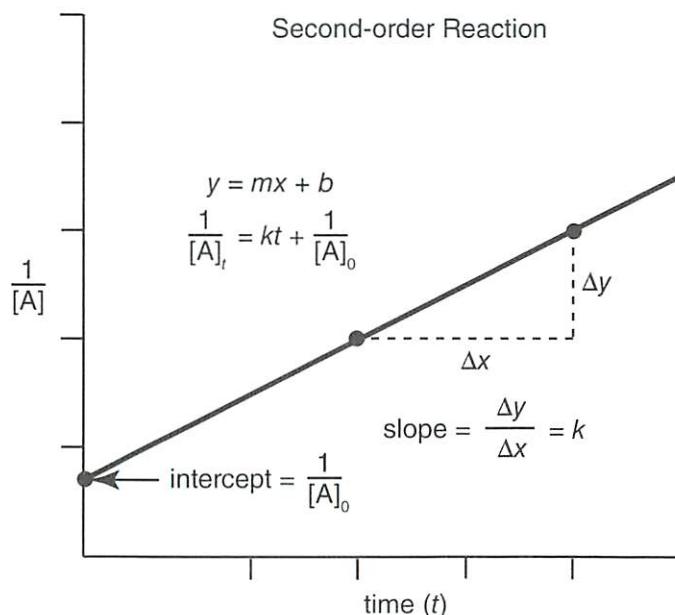
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

Like the integrated first-order and zero-order rate laws, the second-order rate law equation can be rearranged into the form of the equation for a straight line:

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

$(y = mx + b)$

Remember, to determine if a reaction is zero, first or second order, plot $[A]$, $\ln[A]$, or $1/[A]$, respectively, as a function of time. A straight line in one of the plots indicates the reaction order.



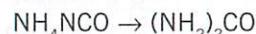
While the half-life of a second-order reaction can be determined, it has little practical value. This is because the half-life of a second-order reaction depends on the concentration of the reactant. As the concentration changes, the length of the half-life also changes.

Example 5.1.6. Rate of a Second-Order Reaction (In-Class Exercise)

For the reaction $\text{AB} \rightarrow \text{products}$, a plot of $[\text{AB}]^{-1}$ versus time (in seconds) results in a straight line with a slope of $0.165 \text{ mol}^{-1} \text{ L s}^{-1}$. What is the rate (in $\text{mol L}^{-1} \text{ s}^{-1}$) of this reaction when $[\text{AB}] = 0.750 \text{ M}$?

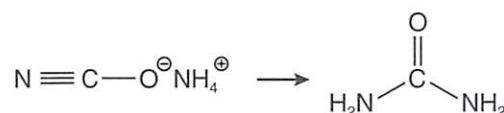
Example 5.1.7. Second-Order Reaction Parameters (In-Class Exercise)

In water, ammonium cyanate (NH_4NCO) rearranges to produce urea, $(\text{NH}_2)_2\text{CO}$, a common fertilizer. (The discovery of this reaction in the early 19th century is considered to be the birth of organic chemistry.)



The rearrangement is a second-order reaction. If it takes 11.6 hours for the NH_4NCO concentration to go from 0.250 M to 0.0841 M :

- What is k for the reaction?
- At what rate is a 0.839 M solution of NH_4NCO changed to urea?



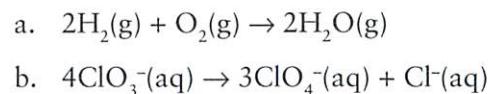
Summary

The chart below provides a summary of rate laws, integrated rate laws, half-lives, and units of k for zero-, first- and second-order reactions.

ORDER	RATE LAW	INTEGRATED RATE LAW	STRAIGHT LINE PLOT	SLOPE OF PLOT	UNITS OF k	HALF-LIFE
0	Rate = k	$[A]_t = -kt + [A]_0$	$[A]$ versus time (t)	negative	$\text{mol L}^{-1} \text{s}^{-1}$	$\frac{[A]_0}{2k}$
1	Rate = $k[A]$	$\ln[A]_t = -kt + \ln[A]_0$	$\ln[A]$ versus time (t)	negative	s^{-1}	$\frac{\ln 2}{k}$
2	Rate = $k[A]^2$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ versus time (t)	positive	$\text{L mol}^{-1} \text{s}^{-1}$	$\frac{1}{k[A]_0}$

Section 5.1 Review Problems

1. For each of the following reactions, express the rate in terms of each reactant and product concentration, ensuring that, whichever is used, “rate” has the same value in mol L⁻¹ s⁻¹.



2. The following data were collected for the reaction A + B → products:

RUN	INITIAL [A] (mol L ⁻¹)	INITIAL [B] (mol L ⁻¹)	INITIAL RATE (mol L ⁻¹ s ⁻¹)
i	0.10	0.20	2.0×10^{-3}
ii	0.10	0.10	5.0×10^{-4}
iii	0.30	0.10	1.5×10^{-3}

- a. Evaluate the order of reaction in A and B and write the complete rate law.
 b. Evaluate the specific rate constant, including its units.
 c. What would the rate of reaction be when [A] = [B] = 0.20 M?
 d. If [A] = 0.30 M, what value of [B] would give a rate of 6.0×10^{-3} mol L⁻¹ s⁻¹?
3. The reaction A + B → products gave the following initial rate data as the concentrations were varied:

RUN	[A] (mol L ⁻¹)	[B] (mol L ⁻¹)	INITIAL RATE (mol L ⁻¹ s ⁻¹)
i	0.75	0.25	1.46×10^{-3}
ii	2.25	0.25	1.32×10^{-2}
iii	0.75	1.00	1.46×10^{-3}

- a. What is the order of the reaction in [A], in [B], and the overall order?
 b. What is the value of the specific rate constant *k*, with units?



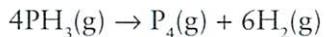
4. It sometimes happens that concentration of a product of a reaction can influence the rate. The following data were found in a study of the decomposition of carbonyl chloride (also known as phosgene, a chemical weapon):



EXPERIMENT	1	2	3	4
Initial $[\text{COCl}_2] \text{ M}$	0.16	0.16	0.040	0.16
Initial $[\text{CO}] \text{ M}$	0.10	0.10	0.10	0.50
Initial $[\text{Cl}_2] \text{ M}$	0.16	0.040	0.16	0.040
Initial Rate M s^{-1}	1.9×10^{-2}	9.6×10^{-3}	4.8×10^{-3}	9.6×10^{-3}

From these data, work out the complete rate law and the value of the rate constant.

5. For the decomposition of phosphine:



the rate equation is rate = $k [\text{PH}_3]$. Under the conditions of the experiment, the half-life for the decomposition was found to be 37.9 seconds.

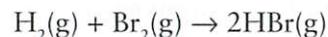
- How much time must elapse until $\frac{3}{4}$ of the sample has decomposed?
 - What is the specific rate constant for this reaction?
 - What fraction of the phosphine would remain after 5.0 minutes?
6. In a first-order process, it was found that $\frac{1}{7}$ of a sample had been consumed in 20 minutes. What is the half-life of this reaction, in minutes?
7. Workers with radioactive isotopes use the generalization that the activity from any radioisotope will be negligible after 10 half-lives have elapsed. What fraction of the original sample of the isotope remains after this period?

8. Although hypochlorous acid, HOCl, has been known since the early 1800s, the fluorine analogue HOF was not synthesized until 1971. It is very unstable, decomposing according to:



with a first-order half-life of 30 minutes at 25 °C. If an experiment is started with a pressure of 100 kPa of HOF in a flask, what will be the total pressure and the partial pressure of HOF after (a) 30 min., (b) 45 min.?

9. It was found experimentally that the rate of the reaction

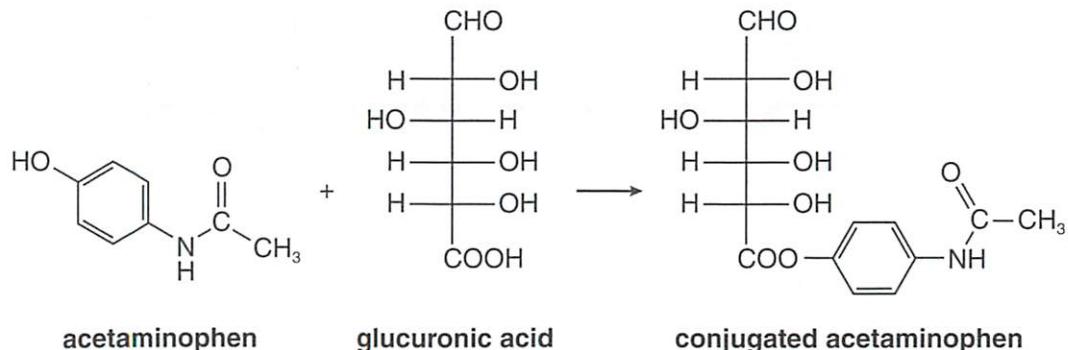


could be expressed by the equation:

$$\log(\text{rate}) = \log[\text{H}_2] + 5.697$$

when $[\text{Br}_2] = 0.10 \text{ mol L}^{-1}$. Another experiment showed that the reaction was first-order in Br_2 . Determine the complete rate law and the value of the specific rate constant.

10. Drugs are typically metabolized via first-order kinetics. In healthy adults, the metabolic half-life ($t_{1/2}$) of acetaminophen is two hours. The liver reacts acetaminophen with glucuronic acid (a derivative of glucose) so that it becomes more H_2O -soluble and can be excreted in the urine as conjugated acetaminophen (see reactions below).



If 1000 mg of acetaminophen (two extra-strength tablets) are consumed, how many mg of acetaminophen will have been metabolized after 3.25 hours? How many mg of conjugated acetaminophen would be found in the urine?

5.2 Reaction Mechanisms and the Arrhenius Equation

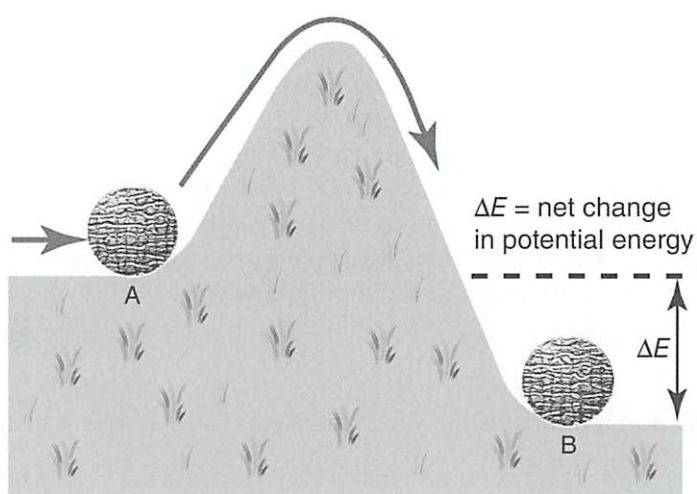
OBJECTIVES

After studying this topic, you should be able to:

- Explain the following terms:
 - a. activation energy and activation barrier
 - b. catalyst and rate enhancement factor
 - c. reaction mechanism and rate determining step
 - d. molecularity
 - e. nucleophilic substitution
- Using data provided, calculate the activation energy and rate of a reaction.
- Using data provided, calculate the change of rate of a reaction after the introduction of a catalyst and/or modification of temperature, and the subsequent impact on E_a .
- Determine the rate law of various reactions given their reaction mechanisms.

INTRODUCTION

Suppose one of several rocks, rumbling along the terrain after an earthquake, reaches the base of a hill (see position A in the figure that follows) and has enough momentum to clear the hill and roll down to position B. At position B, the rock will have less potential energy than it had at position A due to its net reduction in height (altitude). Even though the traverse from A to B reduces the rock's energy and thus would be favourable in a thermodynamic sense, the height of the hill more than anything else determines whether the rock gets to position B. This hill "barrier" would have to be overcome by any of the other post-earthquake rocks trying to roll from position A to B.

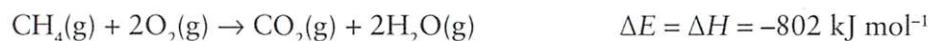


The hill-climbing exercise helps illustrate two separate concepts:

- Thermodynamics: $A \rightarrow B$, which results in a net energy difference (ΔE).
- Kinetics: the speed of $A \rightarrow B$ conversion, which depends on the size of the barrier (hill).

THERMODYNAMICS AND KINETICS

The rock and hill example was used to help emphasize that thermodynamics and kinetics are distinct. The former is a science concerned with the difference in energy between the reactants and the products in a reaction. The latter refers to the study of the rate at which the reaction occurs. For example, in thermodynamic terms the combustion reaction of methane (CH_4) and oxygen (O_2) is highly exothermic. Since the number of gaseous molecules on each side of the reaction are equal, no PV work is done and therefore $\Delta E = \Delta H$.



Kinetically, however, the reaction has a rate near zero at room temperature. The *reaction coordinate* diagram shown in Figure 5.2.1 illustrates the energy changes that occur on the route from reactants to products. (A reaction coordinate is an abstract one-dimensional coordinate that represents progress along a reaction pathway.)

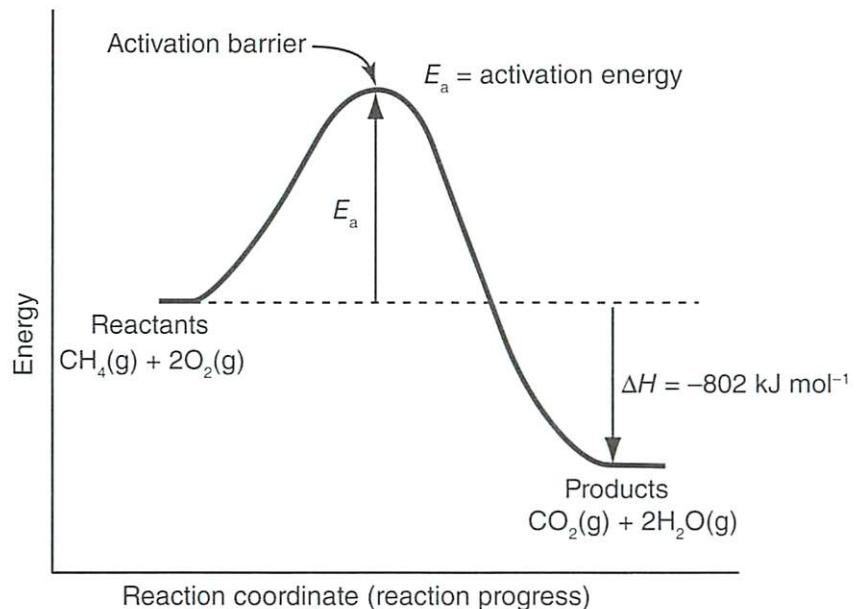


Figure 5.2.1 Reaction coordinate diagram for methane combustion.

COLLISION THEORY

Collision theory is used to explain the various factors that influence reaction rates. In the previous topic, the effect of concentration on reaction rates was examined. What other factors affect whether a collision results in products?

Activation Energy

In order for a chemical reaction to occur, the reactants (in this case CH_4 and O_2) must first overcome an *activation barrier*. (Overcoming the hilltop shown on the second page is analogous to overcoming the activation barrier in the reaction

coordinate diagram.) The energy required to overcome this barrier is called the *activation energy* (E_a). If the reaction proceeds, it releases a net energy of 802 kJ mol⁻¹. However, the reaction does not occur, and no energy is released, unless the reactants have sufficient combined energy to pass over the barrier. The energy needed to overcome the activation barrier comes from heat, which is measured by temperature. The heat–temperature relationship can be described as follows:

1. Heat has a direct impact on the kinetic energy of molecules.
2. Temperature is a measure of the average kinetic energy of a collection of molecules.
3. At any given temperature, there is a distribution of kinetic energies for molecules as shown in Figure 5.2.2.

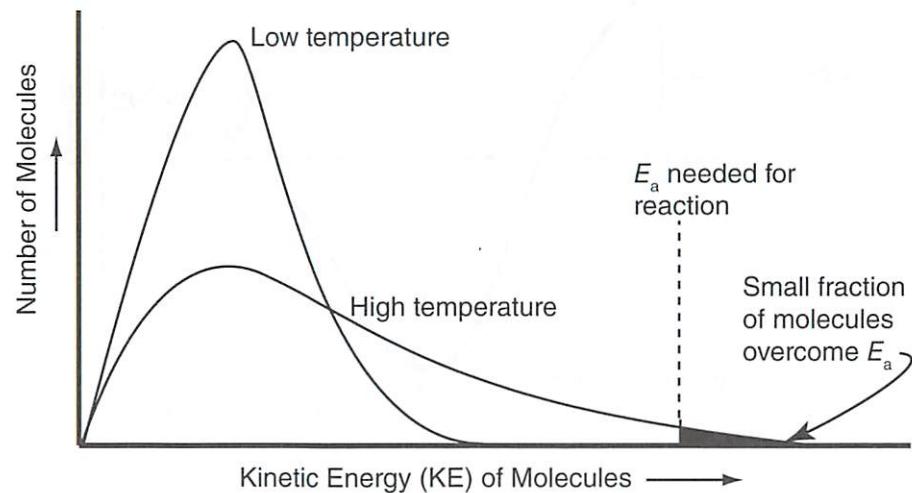
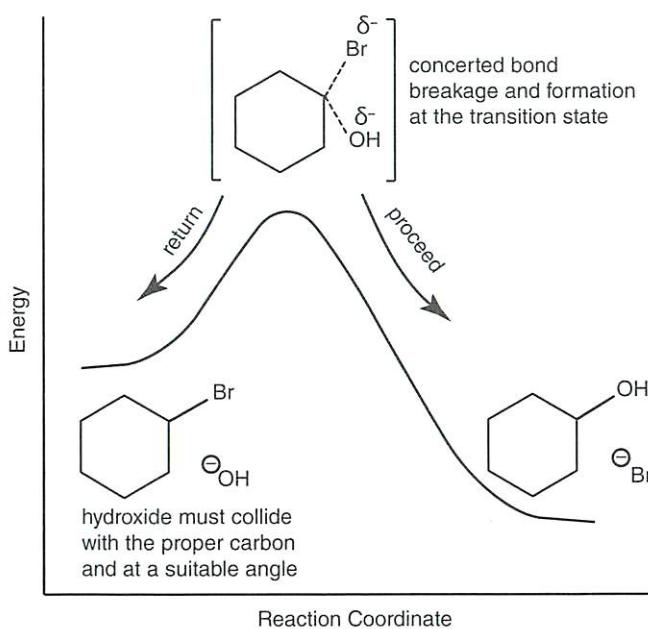


Figure 5.2.2 Boltzmann distribution of molecular kinetic energies.

With respect to the reaction of CH₄ with O₂, at low temperature, none of the reactants have enough energy to overcome the activation barrier. When the temperature is increased by supplying heat, some of the reactant molecules gain enough energy to overcome E_a . The energy can be supplied by heating the entire mixture, by lighting the mixture with a match, or by introducing a spark. (Anyone who has ever taken a fire safety course should know the combustion triangle: fuel,

oxygen, and HEAT.) Once combustion has started, the heat released from the exothermic reaction is enough to propagate the reaction and allow it to continue until the limiting reagent is consumed.

Activation energy is just one aspect of collision theory. For a chemical reaction to occur, reactants must collide with sufficient energy to overcome the activation barrier, they must collide in a proper orientation, and even then the collision may not be successful because, at the moment of transition, the affected species can proceed to products or return to the reactants. An example is the conversion of bromocyclohexane to cyclohexanol (see reaction coordinate diagram below).



The rate of a reaction is affected by these factors:

- Reactant concentration (higher concentration = more collisions).
- Some probability factor based on the probabilities of colliding in a particular geometry (steric factor) and continuing to the products at the transition state.
- E_a and temperature (higher temperature means more reactants have sufficient energy to overcome E_a).

In equation form:

$$\text{Rate} = \frac{\text{number of collisions}}{\text{steric factor}} \times \frac{\text{probability factor}}{\text{enough energy to overcome } E_a} \times \frac{\text{fraction of collisions with enough energy to overcome } E_a}{}$$

The Arrhenius Equation

In 1889, Swedish scientist Svante Arrhenius developed an equation that describes how temperature, E_a , and the probability factor affect the rate constant, k :

$$k = A e^{-E_a/RT} \quad (5.2.1)$$

In the Arrhenius equation:

A = Arrhenius probability factor for a specific reaction

E_a = activation energy for a specific reaction

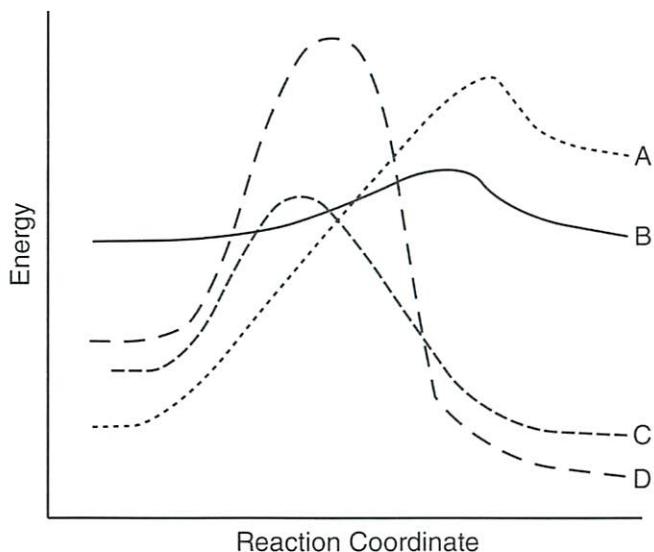
R = gas constant $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

T = temperature (Kelvin)

The Arrhenius equation shows that when the value of E_a increases (the “hill” becomes higher), the value of k decreases.

Example 5.2.1. Thermodynamics Versus Kinetics (In-Class Exercise)

Four different reactions are shown in the reaction coordinate diagram below. Rank them in order of (a) increasing rate constant and (b) increasing thermodynamic favourability. Assume the same temperature and Arrhenius probability factor for all four.

**Effect of Temperature on Rate**

For a given reaction, E_a is a constant and can be determined without knowing the probability factor by performing two experiments at different temperatures while maintaining the same reactant concentrations.

$$\text{Rate}_1 = k_1 [A] [B] \text{ at Temperature 1}$$

$$\text{Rate}_2 = k_2 [A] [B] \text{ at Temperature 2}$$

If [A] and [B] are the same in both experiments:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k_2[A][B]}{k_1[A][B]} = \frac{k_2}{k_1} = \frac{Ae^{-E_a/RT_2}}{Ae^{-E_a/RT_1}} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}} \quad (5.2.2)$$

Taking natural logs:

$$\begin{aligned} \ln \frac{\text{Rate}_2}{\text{Rate}_1} &= \ln \frac{k_2}{k_1} = \ln \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}} = \ln(e^{-E_a/RT_2}) - \ln(e^{-E_a/RT_1}) \\ &= -\frac{E_a}{RT_2} - \left(-\frac{E_a}{RT_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \end{aligned}$$

Thus,

$$\ln \frac{\text{Rate}_2}{\text{Rate}_1} = \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5.2.3)$$

Thus, using two rates or two rate constants obtained at different temperatures allows one to determine the activation energy for a reaction. Note that activation energies are often large. They are typically expressed in units of kJ mol^{-1} while R , the gas constant, has units of $\text{J mol}^{-1} \text{K}^{-1}$. Care must be taken to ensure that all units in the equations are compatible.

Example 5.2.2. Activation Energy and Rate (In-Class Exercise)

When the temperature was increased from 20 to 30 °C, the rate of a reaction increased from 1.5 to 2.4 mol L⁻¹ s⁻¹. Determine (a) the activation energy for this reaction and (b) the rate expected at 100 °C.

Example 5.2.3. Effect of Temperature on Reaction Rate (In-Class Exercise)

A reaction has an E_a of 41.6 kJ mol⁻¹ at 298 K. At what temperature will the reaction be thirty times faster?

Determining Activation Energy Graphically

Using natural logarithms and then rearranging the Arrhenius equation results in an equation in the format of a straight line ($y = mx + b$) as follows:

$$k = Ae^{-E_a/RT}$$

Using natural logarithms:

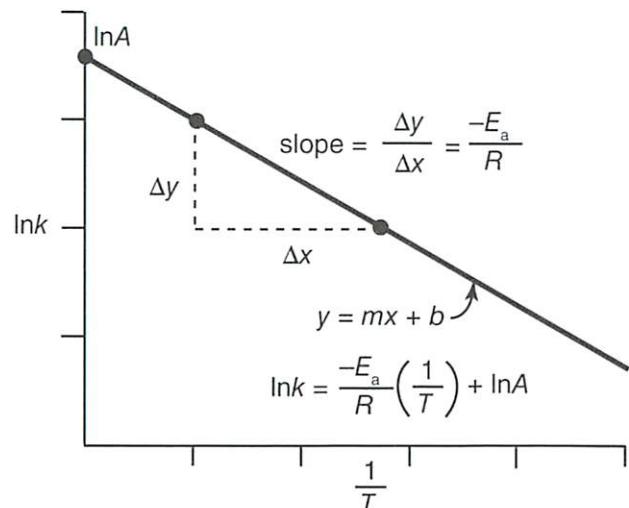
$$\ln k = \ln A - \frac{E_a}{RT}$$

or:

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$y = mx + b$$

Therefore, E_a can be determined experimentally by measuring a reaction rate at different temperatures, then plotting the graph of $\ln k$ (calculated from the rate) versus $1/T$. The straight line has a slope of $-E_a/R$ and a y -intercept of $\ln A$ as shown in the graph that follows.



Effect of a Catalyst on Activation Energy

A catalyst is a species that increases the rate of a reaction but is not consumed in the reaction. It provides an alternate pathway with a lower E_a that, in turn, increases k (see Figure 5.2.3).

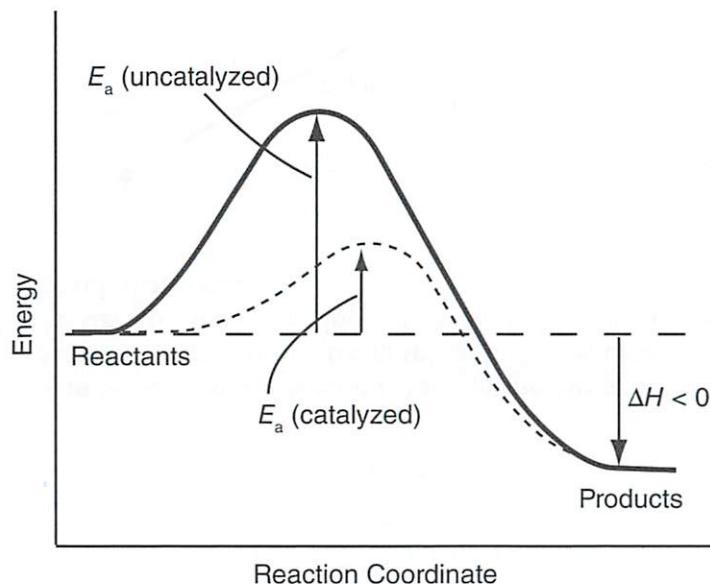
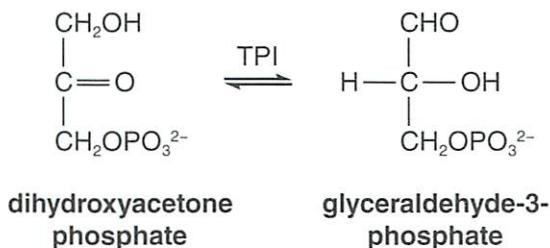


Figure 5.2.3 Effect of a catalyst on activation energy (E_a).

A catalyst has no effect on the net enthalpy change (ΔH) of a reaction. It does not affect the equilibrium constant, but it does allow a system to attain equilibrium faster.

Enzymes, for example, are biological catalysts. One important enzyme is triose phosphate isomerase (TPI), which plays a crucial role in metabolizing glucose (glycolysis). It is thus an essential “energy” enzyme in humans, animals, and other organisms. During glycolysis, TPI interconverts two sugars, dihydroxyacetone phosphate and glyceraldehyde-3-phosphate, as shown in the reaction that follows.



The effect on the rate constant with and without the TPI enzyme (the catalyst) in the reaction is shown below:

- Rate constant (catalyzed): $k_{\text{cat}} = 4.4 \times 10^3 \text{ s}^{-1}$
- Rate constant (uncatalyzed): $k_{\text{uncat}} = 4.3 \times 10^{-6} \text{ s}^{-1}$

A term commonly used in the study of catalysts is the *rate enhancement factor*, which is simply the ratio of k values for the catalyzed and uncatalyzed reaction.

$$\text{In this case, the rate enhancement factor is: } \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{4.4 \times 10^3 \text{ s}^{-1}}{4.3 \times 10^{-6} \text{ s}^{-1}} = 1.0 \times 10^9$$

Note that a deficiency of triose phosphate isomerase in humans is associated with a serious neurological disorder aptly called triose phosphate isomerase deficiency.

To determine the magnitude of the E_a reduction (ΔE_a) resulting from the introduction of a catalyst, keep all variables the same except for the absence or presence of the catalyst (i.e., both uncatalyzed and catalyzed reactions are taking place at the same temperature and with the same reactant concentration).

$$\frac{\text{Rate}_{\text{cat}}}{\text{Rate}_{\text{uncat}}} = \frac{k_{\text{cat}} [\text{reactants}]}{k_{\text{uncat}} [\text{reactants}]} = \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{Ae^{-E_{a(\text{cat})}/RT}}{Ae^{-E_{a(\text{uncat})}/RT}} = \frac{e^{-E_{a(\text{cat})}/RT}}{e^{-E_{a(\text{uncat})}/RT}}$$

After taking the logarithm,

$$\ln \frac{\text{Rate}_{\text{cat}}}{\text{Rate}_{\text{uncat}}} = \ln \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \ln \frac{e^{-E_{a(\text{cat})}/RT}}{e^{-E_{a(\text{uncat})}/RT}} = \ln e^{-E_{a(\text{cat})}/RT} - \ln e^{-E_{a(\text{uncat})}/RT} = \frac{E_{a(\text{uncat})} - E_{a(\text{cat})}}{RT} = \frac{\Delta E_a}{RT}$$

Thus,

$$\ln \frac{\text{Rate}_{\text{cat}}}{\text{Rate}_{\text{uncat}}} = \ln \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{\Delta E_a}{RT}$$

where $\Delta E_a = E_{a(\text{uncat})} - E_{a(\text{cat})}$ is the activation barrier reduction brought about by the catalyst.

Example 5.2.4. Reduction of E_a by an Enzyme (In-Class Exercise)

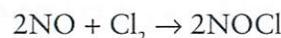
If the triose phosphate isomerase reaction mentioned earlier takes place at 298 K, by how much does the enzyme reduce the E_a ?

Example 5.2.5. Rate Enhancement Factor of an Enzyme (In-Class Exercise)

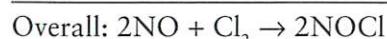
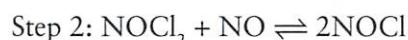
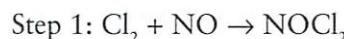
A catalyst lowers E_a for a reaction from 100 to 70 kJ mol⁻¹ at 300 K. By what factor does the rate of the catalyzed reaction increase?

REACTION MECHANISMS

What actually happens at the molecular level when a reaction occurs? Which atoms collide to produce the reaction? Consider the reaction of NO with Cl₂:



Although the balanced reaction shows three molecules on the reactant side, it is unlikely that all three molecules collide in the proper orientation and react together. Rather, chemical reactions often occur in multiple steps. A *reaction mechanism* describes the sequence of steps that occur. Each step in a reaction mechanism is called an *elementary step*. Experimentally, it has been determined that NO and Cl₂ actually react in a two-step mechanism:



Note that NOCl₂ was formed in Step 1 and consumed in Step 2, so it is called a *reaction intermediate*.

Each of the two elementary steps listed above has an E_a and a rate constant. Elementary steps cannot be broken down further, as they are the simplest molecular events that occur. How was this particular mechanism determined? As with other reactions, chemists proposed possible mechanisms, derived their corresponding rate laws, and then noted which one matched the data obtained experimentally.

Molecularity

To understand the use of kinetic data for determining a mechanism, the concept of *molecularity* is needed. Molecularity refers to how many species react together in an elementary step. If a process involves only one reactant species, it is termed a *unimolecular process* and must exhibit first-order kinetics.



A *bimolecular process* involves two species, either identical or different, and is second order. For example:



When reactions occur in two or more elementary steps, the steps can be of different molecularity. For example, in the decomposition of O₃:

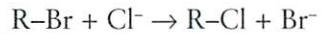


There are two important consequences here:

1. In an elementary step, and ONLY in an elementary step, the coefficients of the reactants become the exponents in the rate law for that step.
2. The overall rate of a reaction is determined by the rate of the slowest or *rate-determining step* (RDS).

Determining Reaction Mechanisms

Consider a reaction of alkyl halides known as a *nucleophilic substitution*. The electron-bearing nucleophile¹ (Cl⁻) replaces the bromide on the *electrophilic* (electron-deficient) carbon atom:

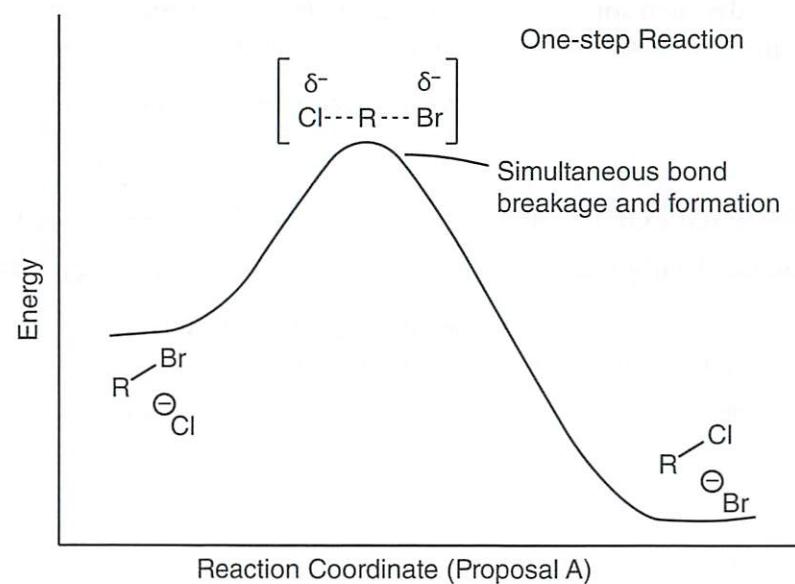


¹ A nucleophile (literally “nucleus lover”) is a reactant that seeks the centers of positive charge in a molecule and forms a chemical bond with its partner (the electrophile or “electron lover”) by donating both bonding electrons. By donating electrons, nucleophiles are, by definition, Lewis bases.

To determine the mechanism, a chemist normally proposes the possible mechanisms. The experimental data are then compared to overall rate laws of the possible mechanisms.

Proposal A

Suppose the reaction occurs in one step. Therefore, the overall reaction equation is the only elementary step. Breakage of the R–Br bond is concomitant with R–Cl bond formation (see diagram that follows).



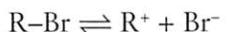
Since the elementary step is the overall reaction (i.e., the only step):

- The reaction is bimolecular.
- The rate law for the reaction is overall second order, as two reactants are involved in the RDS.
- Rate = $k [\text{R}-\text{Br}] [\text{Cl}^-]$.

Proposal B

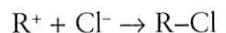
In this case, the reaction occurs in two steps:

- Step 1 involves a slow cleavage of the alkyl halide ($\text{R}-\text{Br}$) to generate a carbocation intermediate in a reversible reaction. Rate = $k[\text{R}-\text{Br}]$



- Step 2 is a fast reaction between the carbocation (R^+) and Cl^- .

$$\text{Rate} = k_2[\text{R}^+] [\text{Cl}^-]$$

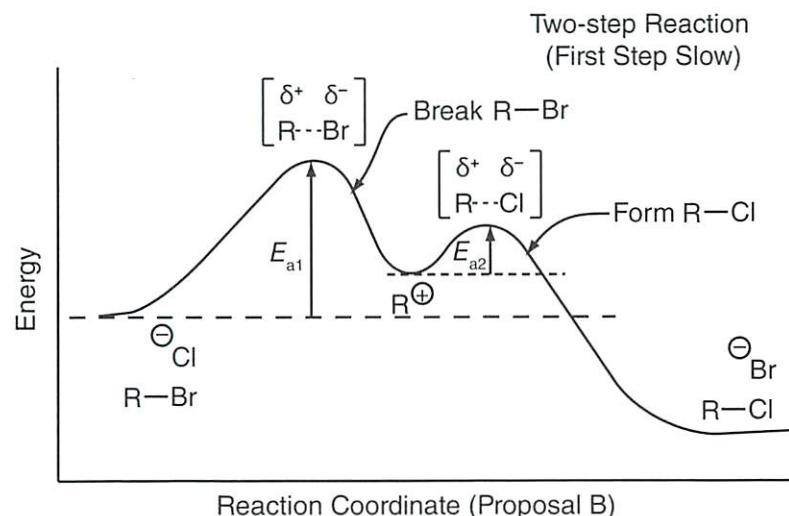


What would the rate law be for the overall reaction in Proposal B?



Based on the RDS (Step 1): Rate = $k[\text{R}-\text{Br}]$

Since there are two steps, the reaction coordinate diagram that follows shows an intermediate and two transition states.



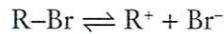
The difference between an intermediate and a transition state is:

- An intermediate is a real species that can be found in the reaction mixture as the reaction progresses. Here, the intermediate is a carbocation, R^+ .
- A transition state, also known as an activated complex, is a postulated high-energy structure that is very short-lived. It cannot be found in the reaction mixture.

Proposal C

Suppose Proposal C is like Proposal B except the slow/fast assignments have been swapped. Again, the reaction occurs in two steps:

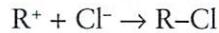
- Step 1 involves a fast cleavage of the alkyl halide to generate a carbocation intermediate in an equilibrium reaction.



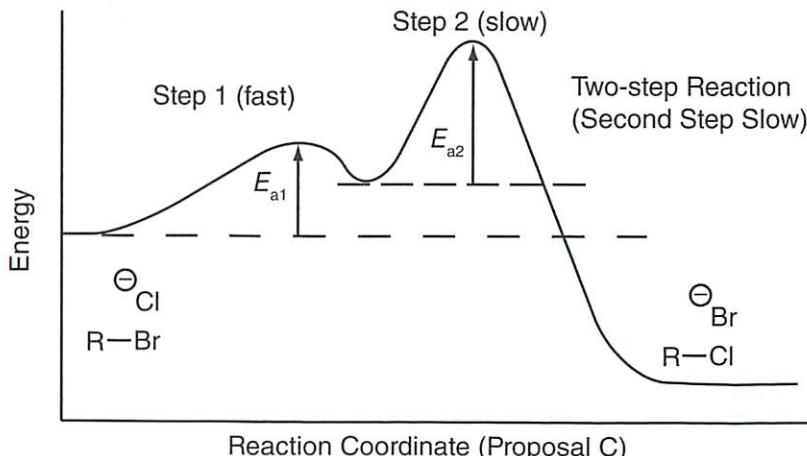
In an equilibrium reaction, the forward and reverse rates are equal.

$$\text{Therefore: rate} = k_{1F}[R-Br] = k_{1R}[R^+] [Br^-]$$

- Step 2 is a slow reaction between the carbocation and the nucleophile.



$$\text{Therefore: rate} = k_2[R^+] [Cl^-]$$



The overall rate law for the Proposal C reaction mechanism is based on the slow step (Step 2), so is it: rate = $k_2[R^+][Cl^-]$? Well, yes. But since intermediates (i.e., R^+) cannot appear in the overall rate law, the rate expression from Step 1 must be rearranged and a substitute for R^+ must be used in the Step 2 (RDS) rate expression.

Remember, the overall reaction is:



- From Step 1: $k_{1F}[R-Br] = k_{1R}[R^+][Br^-]$

Therefore:

- From Step 2: rate = $k_2[R^+][Cl^-]$

Therefore, substituting for $[R^+]$ results in the overall rate law:

$$\text{Rate} = k_2 \left(\frac{k_{1F}[R-Br]}{k_{1R}[Br^-]} \right) [Cl^-] = k'[R-Br][Cl^-][Br^-]^{-1}$$

(k' is used to represent the ratio of constants.)

Note that Proposal C is an example where Br^- (a product) slows the reaction and therefore shows up in the rate law. High $[Br^-]$ reduces $[R^+]$, which in turn slows down Step 2, the RDS. (This is Le Châtelier's principle at work. The equilibrium shifts to the left to minimize the disturbance caused by the high $[Br^-]$.)

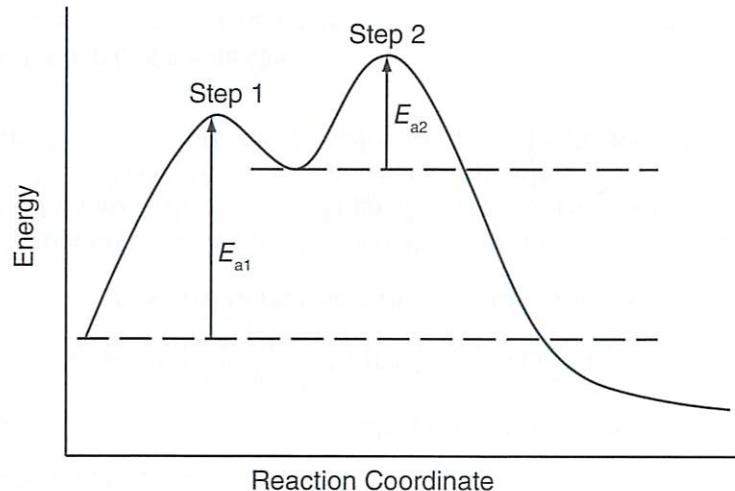
Guidelines for Deriving a Rate Law

The actions required to derive a rate law from a proposed reaction mechanism are summarized below:

- Look for the slow or rate-determining step (RDS).
- Write a rate law in terms of concentrations of reactants in the RDS. A maximum of two species should appear in the rate law at this stage.
- If there are intermediates in the rate law, express their concentrations in terms of stable reactants appearing in the overall reaction equation. This may be done by writing equilibrium constant expressions for steps preceding the RDS.
- Substitute concentrations of stable reactants for concentrations of intermediates in the rate law.
- Fast steps following the RDS in the mechanistic sequence may be ignored.

6. The rate-determining step is not necessarily the one with the largest value of E_a for the step, as measured according to these figures. The rate-determining step is the step whose transition state has the highest overall energy in the reaction coordinate diagram. Completion of the reaction depends on getting to that highest energy point, since it is the overall peak of energy.

Consider the diagram below:



While Step 1 has the larger activation energy, it is more likely that step 2 will be the RDS due to its higher peak energy.

Even so, this analysis does not include a discussion of the pre-exponential term in the rate constant expression:

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

As we have seen, the parameter A contains terms related to geometrical factors, which may also influence the rate of the step.

In general however, the highest point on the reaction coordinate diagram will indicate the RDS.

Example 5.2.6. Mechanism of Substitution for *Tert*-butyl Bromide (In-Class Exercise)

Using *tert*-butyl bromide, which is a tertiary alkyl halide (the carbon bearing the Br is connected to three carbons), the experimental data below were obtained. By which one of the proposed A, B, or C mechanisms does the reaction proceed?



RUN #	$[t\text{-BuBr}]^x$	$[\text{Cl}^-]^y$	$[\text{Br}^-]^z$	RATE (mol L ⁻¹ min ⁻¹)
i	0.1	0.1	0.1	5
ii	0.1	0.2	0.1	5
iii	0.2	0.2	0.1	10
iv	0.2	0.4	0.2	10

Example 5.2.7. Mechanism of Substitution for Ethyl Bromide (In-Class Exercise)

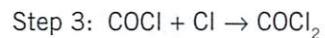
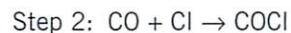
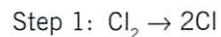
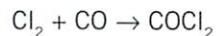
Using ethyl bromide, a primary alkyl halide, the experimental data below was obtained. By which proposed mechanism (A, B, or C) does the reaction proceed?



RUN #	$[\text{EtBr}]^x$	$[\text{Cl}^-]^y$	$[\text{Br}^-]^z$	RATE (mol L ⁻¹ min ⁻¹)
i	0.1	0.1	0.1	5
ii	0.1	0.2	0.1	10
iii	0.2	0.2	0.1	20
iv	0.4	0.4	0.2	80

Example 5.2.8. Proposing Mechanisms for the Reaction of Cl₂ with CO (In-Class Exercise)

The following reaction occurs in three steps:

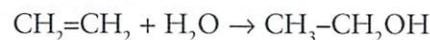


- a. What would be the overall rate law expected if Step 1 is slow and Steps 2 and 3 are fast?
 - b. What if Step 2 is slow, Step 3 is fast, but Step 1 is a fast equilibrium?
 - c. What if Step 3 is slow, but Steps 1 and 2 are fast equilibria?
-

Section 5.2 Review Problems

1. Which of the following statements is/are correct?
 - a. A rate law can be deduced from the balanced equation for an overall reaction.
 - b. If a reaction takes place in a series of steps, each step must proceed at the same rate.
 - c. A catalyst must be in the same phase as the reactants in order to be effective.
 - d. The difference between E_a for the forward reaction and E_a for the reverse reaction is equal to ΔH for the overall reaction.
2. A certain reaction has an activation energy of 45 kJ mol^{-1} . If the rate of reaction is $1.2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ at 25°C , calculate
 - a. The rate at 80°C , other things being kept equal.
 - b. The temperature at which the rate has increased to $7.2 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$.
3. Keeping reactant concentrations constant, it was found that the rate of a certain reaction increased by a factor of 4.0 when the temperature was raised from 100°C to 125°C . What is the activation energy for this reaction?
4. The rate of a certain reaction increases from 2.5×10^{-2} to $6.0 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ when the temperature is raised from 0°C to 15°C .
 - a. What is the activation energy for this reaction?
 - b. What would be the rate of reaction at 40°C with the same reactant concentrations?
5. A reaction has an activation energy of 60 kJ mol^{-1} .
 - a. By what factor would the rate increase if the temperature were to be increased from 100°C to 125°C ?
 - b. At what temperature would the rate be three times the rate at 60°C ?

6. An uncatalyzed reaction proceeds at a rate of $7.5 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ at 25°C . If a catalyst lowers E_a by 25 kJ mol^{-1} , what will be the rate of the catalyzed reaction at this temperature?
7. A reaction has specific rate constant $k = 1.2 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ at 25°C . Introduction of a catalyst increases the rate constant to $1.0 \text{ L mol}^{-1} \text{ s}^{-1}$ at the same temperature. Calculate the change in activation energy, in kJ mol^{-1} , made by the catalyst.
8. The addition of water to ethylene is catalyzed by an acid, such as H_2SO_4 :



The following mechanism is suggested:

- (1) $\text{CH}_2=\text{CH}_2 + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{CH}_2^+ + \text{H}_2\text{O}$
- (2) $\text{CH}_3\text{CH}_2^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH}_2^+$
- (3) $\text{CH}_3\text{CH}_2\text{OH}_2^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_3\text{O}^+$

- a. What species appear in the reaction scheme as intermediates?
- b. What species is acting as a catalyst? Why is the term “catalyst” appropriate?
- c. What other species is present in the solution, but takes no part in the reaction?
- d. What rate law would be expected for the overall reaction:
 - i. If Step (1) is slow and the others are fast equilibria?
 - ii. If Step (3) is slow and the others are fast equilibria?

Note that the catalyst *may* appear in the rate law because it is considered a reactant.

9. For the overall reaction: $\text{CHCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{g}) + \text{HCl}(\text{g})$ the following step-wise mechanism is suggested:

- (1) $\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl}(\text{g})$ (fast equilibrium)
- (2) $\text{CHCl}_3(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{CCl}_3(\text{g}) + \text{HCl}(\text{g})$ (slow)
- (3) $\text{CCl}_3(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{CCl}_4(\text{g})$ (fast)



- a. Which is the rate-determining step (RDS)?
- b. Which species are unstable intermediates in this scheme?
- c. What rate law would be expected for this reaction?

