



Chapter 13

Chemical Kinetics

13.1 The Rate of a Reaction

13.2 The Rate Law

13.3 The Relation Between Reactant Concentration and Time

13.4 Activation Energy and Temperature Dependence of Rate Constants

13.5 Reaction Mechanisms

13.6 Catalysis

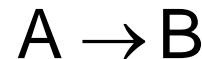
The rates of chemical reactions vary greatly. The conversion of graphite to diamond in Earth's crust may take millions of years to complete. Explosive reactions such as those of dynamite and TNT, on the other hand, are over in a fraction of a second.

Chemical Kinetics (1 of 2)

-Kinetics – how fast does a reaction proceed?

Chemical kinetics is *the area of chemistry concerned with the speeds, or rates, at which a chemical reaction occurs*

Reaction rate is the change in the concentration of a reactant or a product with time (**M/s**).



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

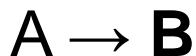
$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[A]$ = change in concentration of A over time period Δt

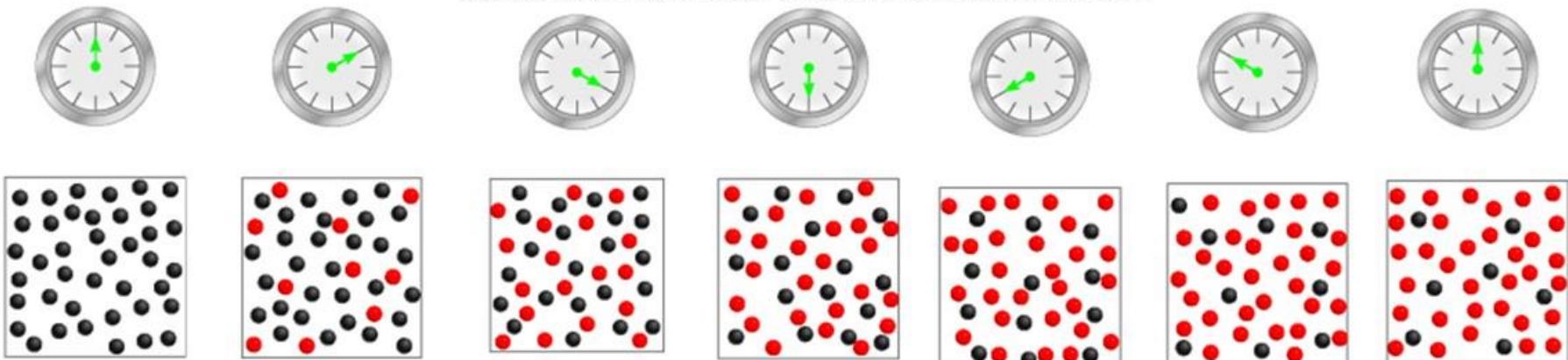
$\Delta[B]$ = change in concentration of B over time period Δt

Because [A] decreases with time, $\Delta [A]$ is negative.

Chemical Kinetics (2 of 2)

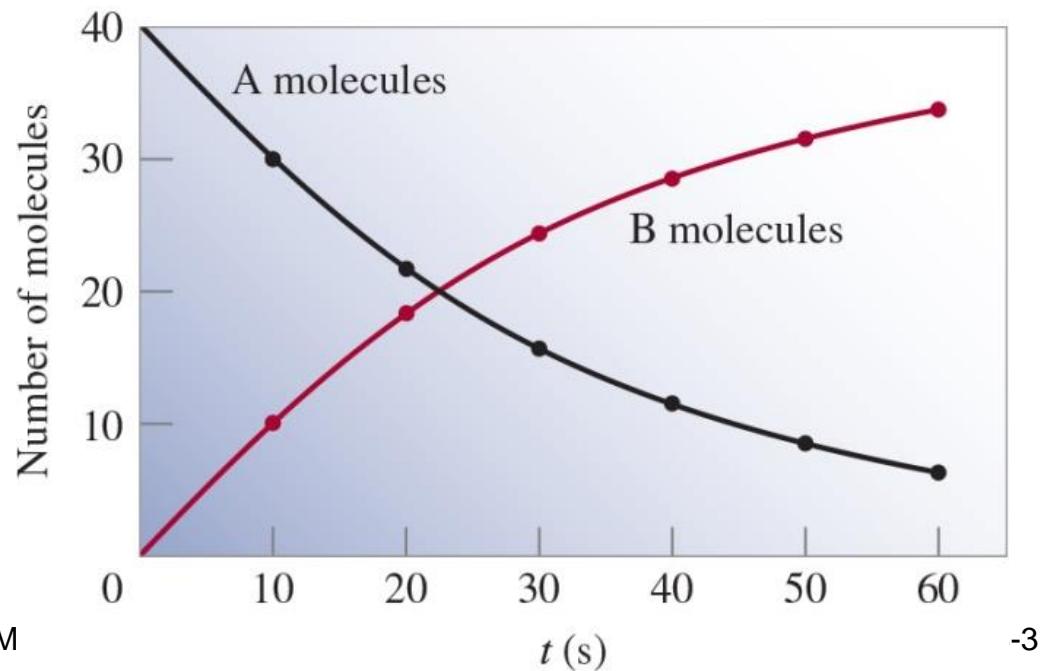


Copyright © McGraw-Hill Education. Permission required for reproduction or display.



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

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$



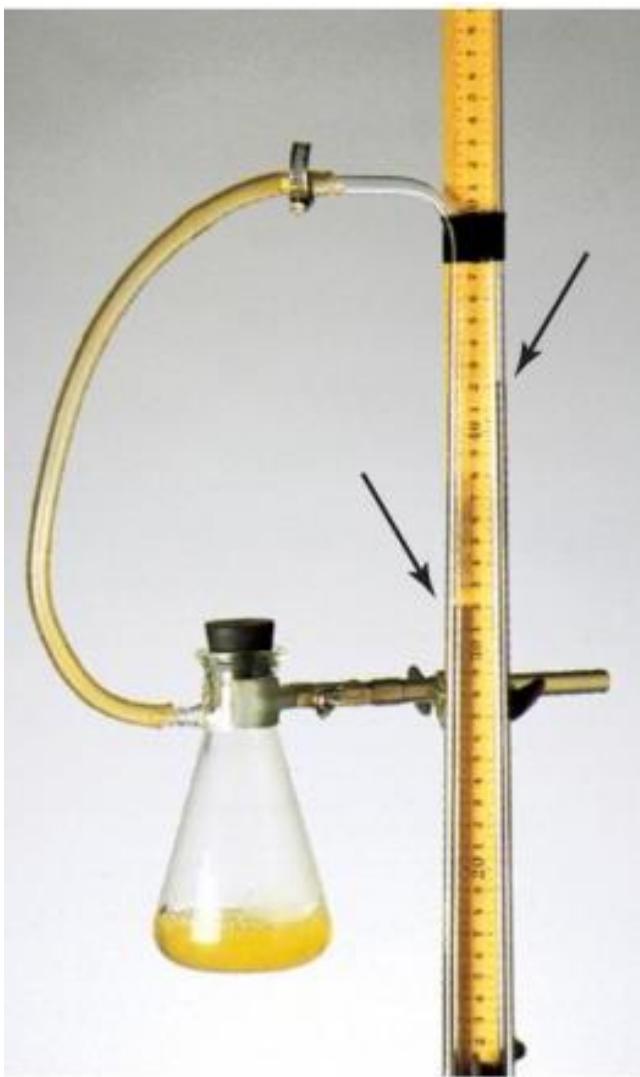
Determination of the rate of a reaction

Experimentally

Our next step is to see how the rate of a reaction is obtained experimentally. By definition, we know that to determine the rate of a reaction we have to monitor the concentration of the reactant (or product) as a function of time. For reactions in solution, the concentration of a species can often be measured by **spectroscopic** means.

If ions are involved, the change in concentration can also be detected by an **electrical conductance measurement**. Reactions involving gases are most conveniently followed by **pressure measurements**. We will consider two specific reactions for which different methods are used to measure the reaction rates.

Monitoring Kinetics



Molarite
Derisim ↑

$$PV = nRT$$
$$P = \frac{n}{V} RT = [\text{O}_2]RT$$

$$[\text{O}_2] = \frac{1}{RT} P$$

$$\text{rate} = \frac{\Delta [\text{O}_2]}{\Delta t} = \frac{1}{RT} \frac{\Delta P}{\Delta t}$$

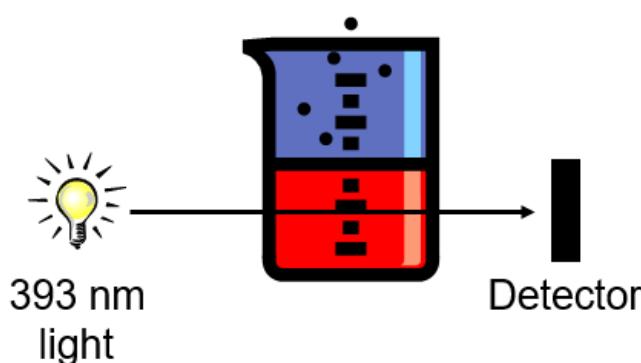
ezberle gerek yok formülden qıkorabilsin.
Amacınız derisim oranının
zamana göre değişimini incelemek

Monitoring Kinetics

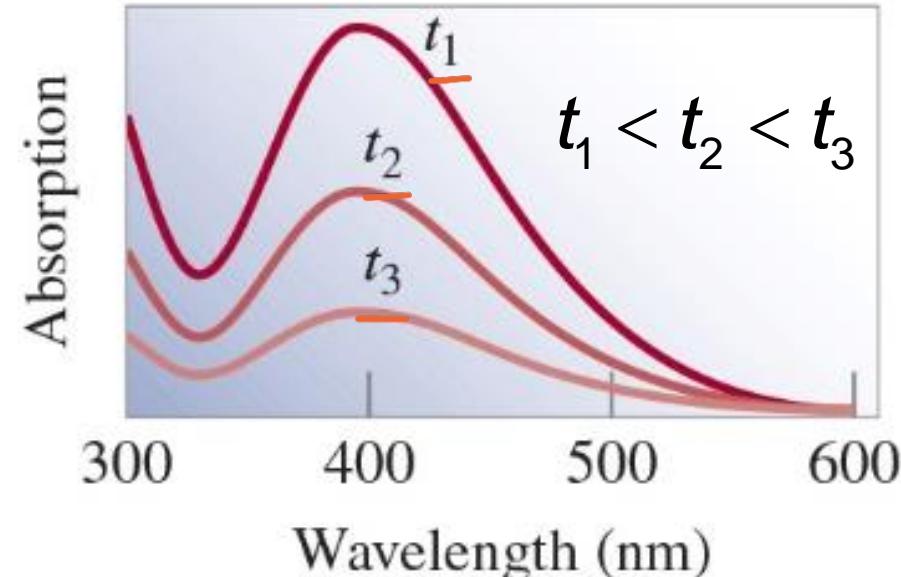
red-brown



$t=0$ $t=10$ $t=20$ $t=30$



$$\Delta [\text{Br}_2] \propto \Delta \text{ Absorption}$$



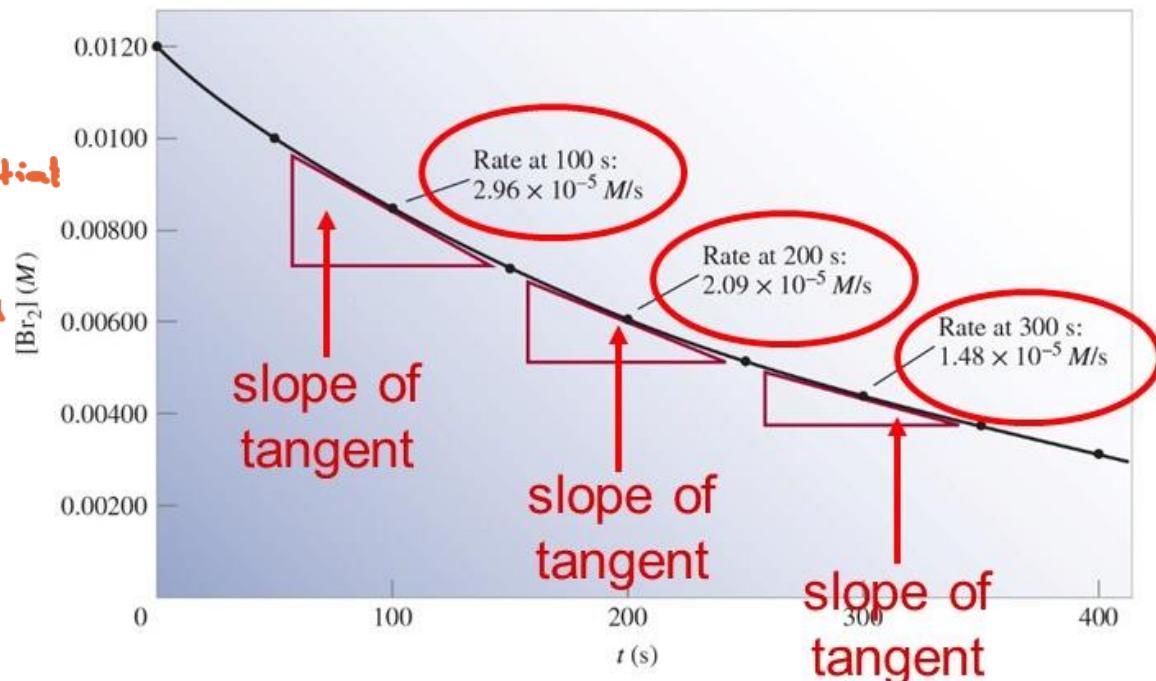
Herkət deqizimini gözlemləyərək
(Dolga boyaları və frekansları, öznəndən)
Reaksiyon hızını belirlemə.

Kinetic Rates (1 of 2)



mecla

Time (s)	[Br ₂] (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296



average rate =

$$\text{average rate} = -\frac{\Delta[\text{Br}_2]}{\Delta t} = -\frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$



Kinetic Rates (1 of 2)



Time (s)	[Br ₂] (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296

$$\text{average rate} = -\frac{\Delta[\text{Br}_2]}{\Delta t} = -\frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

At 50 s:

$$\text{average rate} = -\frac{(0.0101 - 0.0120)M}{50 \text{ s}} = 3.80 \times 10^{-5}$$

At 1000 s:

$$\text{average rate} = -\frac{(0.00846 - 0.0120)M}{100 \text{ s}} = 3.54 \times 10^{-5}$$

Rates of Reaction

Table 13.1

Rates of the Reaction Between Molecular Bromine
and Formic Acid at 25°C

Time (s)	[Br ₂] (M)	Rate (M/s)	$k = \frac{\text{rate}}{[\text{Br}_2]} (\text{s}^{-1})$
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}
300.0	0.00420	1.48×10^{-5}	3.52×10^{-3}
350.0	0.00353	1.23×10^{-5}	3.48×10^{-3}
400.0	0.00296	1.04×10^{-5}	3.51×10^{-3}

$$\text{rate} \propto [\text{Br}_2]$$

$$\text{rate} = k[\text{Br}_2]$$

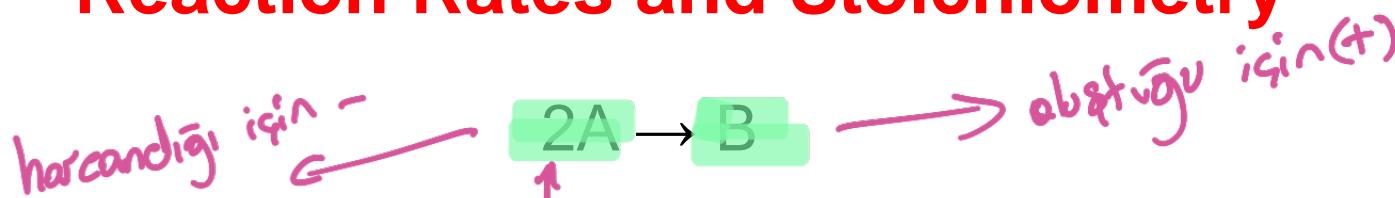
$$k = \frac{\text{rate}}{[\text{Br}_2]} = \text{rate constant}$$

$$= 3.50 \times 10^{-3} \text{ s}^{-1}$$

where the term k is known as
proportionality constant

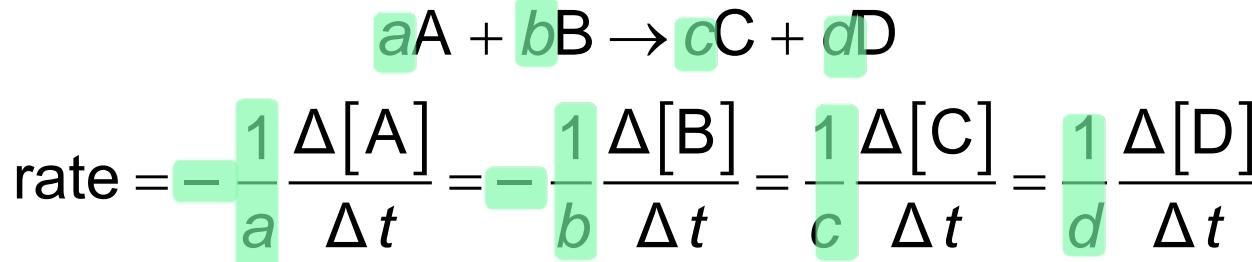
** Yukarıda gördüğümüz
reaksiyondaki herhangi bir maddenin
hızını bilerek diğerine yönelik
bulabiliyoruz.*

Reaction Rates and Stoichiometry



Two moles of A disappear for each mole of B that is formed.

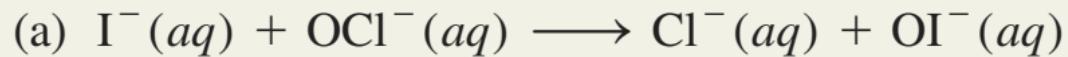
$$\text{rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$



Two moles of A disappear for each mole of B that forms; that is, the rate at which B forms is one-half the rate at which A disappears.

Example 13.1

Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:



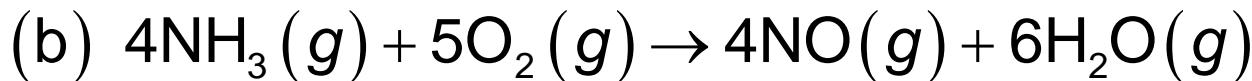
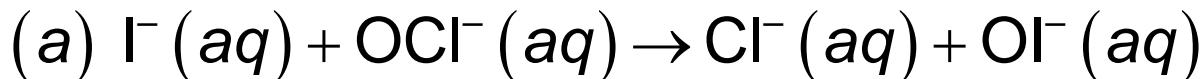
Example 13.1 (2 of 2)

Strategy

To express the rate of the reaction in terms of the change in concentration of a reactant or product with time, we need to use the proper sign (minus or plus) and the reciprocal of the stoichiometric coefficient.

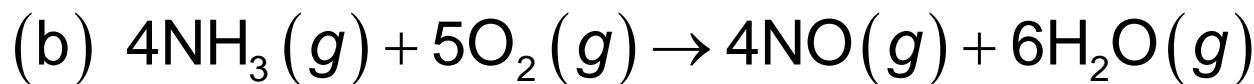
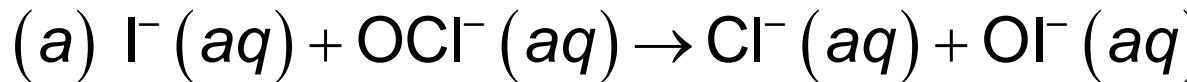
Solution

- a) Because each of the stoichiometric coefficients equals 1,



$$\text{rate} = -\frac{\Delta[\text{I}^-]}{\Delta t} = -\frac{\Delta[\text{OCl}^-]}{\Delta t} = \frac{\Delta[\text{Cl}^-]}{\Delta t} = \frac{\Delta[\text{OI}^-]}{\Delta t}$$

Example 13.1 (2 of 2)

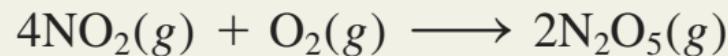


b) Here the coefficients are 4, 5, 4, and 6, so

$$\text{rate} = -\frac{1}{4} \frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{1}{5} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Example 13.2

Consider the reaction



Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.024 M/s . (a) At what rate is N_2O_5 being formed? (b) At what rate is NO_2 reacting?

Example 13.2 (2 of 4)

Strategy

To calculate the rate of formation of N_2O_5 and disappearance of NO_2 , we need to express the rate of the reaction in terms of the stoichiometric coefficients as in Example 13.1:

$$\text{rate} = - \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = - \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

We are given

$$\frac{\Delta[\text{O}_2]}{\Delta t} = -0.024 \text{ M/s}$$

where the minus sign shows that the concentration of O_2 is decreasing with time.

Example 13.2 (3 of 4)

Solution

- a) From the preceding rate expression we have

$$-\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

Therefore

$$\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = -2(-0.024 \text{ M/s}) = 0.048 \text{ M/s}$$

Example 13.2 (4 of 4)

b) Here we have

$$-\frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t}$$

so

$$\frac{\Delta[\text{NO}_2]}{\Delta t} = 4(-0.024 \text{ M/s}) = -0.096 \text{ M/s}$$

Review of Concepts

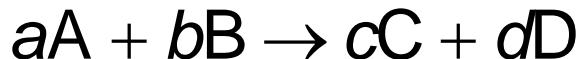
Write a balanced equation for a gas-phase reaction whose rate is given by

$$\text{rate} = -\frac{1}{2} \frac{\Delta[\text{NOCl}]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{\Delta[\text{Cl}_2]}{\Delta t}$$

The Rate Law (1 of 2)

So far, we have learned that the rate of a reaction is proportional to the concentration of reactants and that the proportionality constant k is called the rate constant.

The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers. For the general Reaction :



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

Reaction is **xth order** in A

Reaction is **yth order** in B

Reaction is **(x + y)th order overall**

where x and y are numbers that must be determined experimentally. Note that, in general, x and y are *not* equal to the stoichiometric coefficients a and b . When we know the values of x , y , and k , we can use Equation (13.1) to calculate the rate of the reaction, given the concentrations of A and B.

Topkine Jartcesi = $x+y$
order on

The Rate Law (2 of 2)



Table 13.2 Rate Data for the Reaction Between F_2 and ClO_2

$[F_2] (M)$	$[ClO_2] (M)$	Initial Rate (M/s)
1. 0.10	0.010 <i>slow</i>	1.2×10^{-3}
2. 0.10	0.040	4.8×10^{-3}
3. 0.20	0.010 <i>slow</i>	2.4×10^{-3}

$$\text{rate} = k [F_2]^x [ClO_2]^y$$

Double $[F_2]$ with $[ClO_2]$ constant Rate Doubles

$$x = 1$$

Quadruple $[ClO_2]$ with $[F_2]$ constant Rate quadruples

$$y = 1$$

$$\text{rate} = k[F_2][ClO_2]$$

$$\frac{1.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \frac{k[0.1]^x[0.01]^y}{k[0.2]^x[0.01]^y}$$

Because both $[F_2]$ and $[ClO_2]$ are raised to the first power, the reaction is first order in F_2 , first order in ClO_2 , and $(1 + 1)$ or second order overall.

Reaction order enables us to understand how the reaction depends on reactant concentrations. Suppose, for example, that for the general reaction $aA + bB \rightarrow cC + dD$, we have $x : 1$ and $y : 2$. The rate law for the reaction is

$$\text{rate} = k[A][B]^2$$

This reaction is first order in A, second order in B, and third order overall ($1 + 2 = 3$).

Let us assume that initially $[A] = 1.0 \text{ M}$ and $[B] = 1.0 \text{ M}$. The rate law tells us that if we double the concentration of A from 1.0 M to 2.0 M at constant $[B]$, we also **double the reaction rate**:

For $[A] = 1.0\text{ M}$ $\text{rate}_1 = k(1.0\text{ M})(1.0\text{ M})^2 = k (1.0\text{ M}^3)$

$$\text{For } [A] = 2.0 \text{ M} \quad \text{rate}_2 = k(2.0 \text{ M})(1.0 \text{ M})^2 = k (2.0 \text{ M}^3)$$

On the other hand, if we double the concentration of B from **1.0 M** to **2.0 M** at constant **$[A] = 1\text{ M}$** , the rate will **increase by a factor of 4** because of **the power 2 in the exponent:**

For $[B] = 1.0 \text{ M}$ $\text{rate}_1 = k \cancel{(1.0 \text{ M})} (1.0 \text{ M})^2 = k (1.0 \text{ M}^3)$

$$\text{For } [\text{B}] = 2.0 \text{ M} \quad \text{rate}_2 = k(1.0 \text{ M})(2.0 \text{ M})^2 = k (4.0 \text{ M}^3)$$

If, for a certain reaction, $x = 0$ and $y = 1$, then the rate law is

$$\text{Rate} = k[A]^0[B] = [B]$$

This reaction is zero order in A, first order in B, and first order overall. The exponent zero tells us that the rate of this reaction is independent of the concentration of A. Note that reaction order can also be a fraction.

Rate Laws

The following points summarize our discussion of the rate law:

1. Rate laws are always determined experimentally. From the concentrations of reactants and the initial reaction rates we can determine the reaction order and then the rate constant of the reaction.
2. Reaction order is always defined in terms of reactant (not product) concentrations.
Aksiyon dereceleri mühabeti girenler kismi szerinden yapılır.
3. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation.

Deneysel yapılırlar. \rightarrow denge durumlarına
ve hız oranlarına
göre Tepkime Dereceleri bulunur.

Bulunan verileri Tepkime
dışı hâlinde yerine
yazdığımızda k' yi
bulabiliyoruz.

Example 13.3

The reaction of nitric oxide with hydrogen at 1280°C is



From the following data collected at this temperature, determine (a) the rate law, (b) the rate constant, and (c) the rate of the reaction when $[\text{NO}] = 12.0 \times 10^{-3} M$ and $[\text{H}_2] = 6.0 \times 10^{-3} M$.

Experiment	[NO] (M)	[H₂] (M)	Initial Rate (M/s)
1	<u>5.0 × 10⁻³</u>	<u>2.0 × 10⁻³</u>	<u>1.3 × 10⁻⁵</u>
2	<u>10.0 × 10⁻³</u>	<u>2.0 × 10⁻³</u>	<u>5.0 × 10⁻⁵</u>
3	<u>10.0 × 10⁻³</u>	<u>4.0 × 10⁻³</u>	<u>10.0 × 10⁻⁵</u>

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

k?:

Experiment	[NO] (M)	[H₂] (M)	Initial Rate (M/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

Example 13.3 (2 of 6)

Strategy

We are given a set of concentration and reaction rate data and asked to determine the rate law and the rate constant.

We assume that the rate law takes the form

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

How do we use the data to determine x and y ?

Once the orders of the reactants are known, we can calculate k from any set of rate and concentrations.

Finally, the rate law enables us to calculate the rate at any concentrations of NO and H₂.

Example 13.3 (3 of 6)

Solution

(a) Experiments 1 and 2 show that when we double the concentration of NO at constant concentration of H₂, the rate quadruples. Taking the ratio of the rates from these two experiments

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{5.0 \times 10^{-5} \text{ M/s}}{1.3 \times 10^{-5} \text{ M/s}} \approx 4 = \frac{k(10.0 \times 10^{-3} \text{ M})^x}{k(5.0 \times 10^{-3} \text{ M})^x} \frac{(2.0 \times 10^{-3} \text{ M})^y}{(2.0 \times 10^{-3} \text{ M})^y}$$

Therefore,

$$\frac{(10.0 \times 10^{-3} \text{ M})^x}{(5.0 \times 10^{-3} \text{ M})^x} = 2^x = 4$$

or x = 2, that is, the reaction is second order in NO.

Example 13.3 (4 of 6)

Experiments 2 and 3 indicate that doubling $[H_2]$ at constant $[NO]$ doubles the rate. Here we write the ratio as

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{10.0 \times 10^{-5} \text{ M/s}}{5.0 \times 10^{-5} \text{ M/s}} = 2 = \frac{k(10.0 \times 10^{-3} \text{ M})^x (4.0 \times 10^{-3} \text{ M})^y}{k(10.0 \times 10^{-3} \text{ M})^x (2.0 \times 10^{-3} \text{ M})^y}$$

Therefore,

$$\frac{(4.0 \times 10^{-3} \text{ M})^y}{(2.0 \times 10^{-3} \text{ M})^y} = 2^y = 2$$

or $y = 1$, that is, the reaction is first order in H_2 . Hence the rate law is given by

$$\text{rate} = k[NO]^2 [H_2]$$

which shows that it is a $(2 + 1)$ or third-order reaction overall.

Example 13.3 (5 of 6)

- b) The rate of constant k can be calculated using the data from any one of the experiments. Rearranging the rate law, we get

$$k = \frac{\text{rate}}{[\text{NO}]^2 [\text{H}_2]}$$

The data from experiment 2 give us

$$\begin{aligned} k &= \frac{5.0 \times 10^{-5} \text{ M/s}}{(10.0 \times 10^{-3} \text{ M})^2 (2.0 \times 10^{-3} \text{ M})} \\ &= 2.5 \times 10^2 \text{ /M}^2 \cdot \text{s} \end{aligned}$$

Example 13.3 (6 of 6)

- c) Using the known rate constant and concentrations of NO and H₂, we write

$$\begin{aligned}\text{rate} &= (2.5 \times 10^2 / M^2 \cdot s) (12.0 \times 10^{-3} M)^2 (6.0 \times 10^{-3} M) \\ &= 2.2 \times 10^{-4} M/s\end{aligned}$$

Comment

Note that the reaction is first order in H₂, whereas the stoichiometric coefficient for H₂ in the balanced equation is 2. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation.

Practice Exercise The reaction of peroxydisulfate ion ($\text{S}_2\text{O}_8^{2-}$) with iodide ion (I^-) is



From the following data collected at a certain temperature, determine the rate law and calculate the rate constant.

Experiment	$[\text{S}_2\text{O}_8^{2-}] (M)$	$[\text{I}^-] (M)$	Initial Rate (M/s)
1	0.080	0.034	2.2×10^{-4}
2	0.080	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

$$\text{rate} = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]; k = 8.1 \times 10^{-2}/M \cdot \text{s.}$$

The Relation Between Reactant Concentration and Time

Rate law expressions enable us to calculate the rate of a reaction from the rate constant and reactant concentrations. The rate laws can also be used to determine the concentrations of reactants at any time during the course of a reaction. We will illustrate this application by first considering two of the most common rate laws those applying to reactions that are first order overall and those applying to reactions that are second order overall.

First-Order Reactions

Reaction Half-life

Second-Order Reactions

Pseudo-First-Order Reactions

Zero-Order Reactions

First-Order Reactions

A **first-order reaction** is a reaction whose rate depends on the reactant concentration raised to the first power. In a first-order reaction of the type



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

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

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

$[A]$ is the concentration of A at any time t

$[A]_0$ is the concentration of A at time $t = 0$

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

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

Sadece bu denklemi bilmen yeterli.

$$\frac{[A]}{[A]_0} = e^{-kt}$$

$$[A] = e^{-kt} \cdot [A]_0$$

3)

$$k = \frac{\text{rate}}{[A]} = \frac{M/s}{M} = 1/\text{s or s}^{-1}$$

m^0

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad 2)$$

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

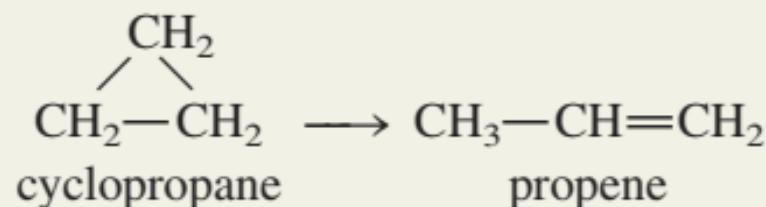
$$[A] = [A]_0 e^{-kt}$$

Example 13.4

nicequestion ✎

The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of $6.7 \times 10^{-4} \text{ s}^{-1}$ at 500°C .

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



(a) If the initial concentration of cyclopropane was 0.25 M , what is the concentration after 8.8 min? (b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from 0.25 M to 0.15 M ? (c) How long (in minutes) will it take to convert 74 percent of the starting material?

a- ***0.18M***

b- ***13min***

c- ***33 min***

Example 13.4 (2 of 4)

for a)

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

Strategy

The relationship between the concentrations of a reactant at different times in a first-order reaction is given by Equation (13.3) or (13.4).

In (a) we are given $[A]_0 = 0.25M$ and asked for $[A]_t$, after 8.8 min.

In (b) we are asked to calculate the time it takes for cyclopropane to decrease in concentration from $0.25M$ to $0.15M$.

for b) $\ln[A] = \ln[A]_0 - kt$

No concentration values are given for (c). However, if initially we have 100 percent of the compound and 74 percent has reacted, then what is left must be $(100\% - 74\%)$, or 26%. Thus, the ratio of the percentages will be equal to the ratio of the actual concentrations; that is, $[A]_t/[A]_0 = 26\%/100\%$, or $0.26/1.00$.

for c) let's say we have 100 percent of the compound in the begining ----

Example 13.4 (3 of 4)

Solution

(a) In applying Equation (13.4), we note that because k is given in units of s^{-1} , we must first convert 8.8 min to seconds:

$$8.8\text{min} \times \frac{60\text{s}}{1\text{min}} = 528\text{s}$$

We write

$$\begin{aligned}\ln[A]_t &= -kt + \ln[A]_0 \\ &= -(6.7 \times 10^{-4}\text{s}^{-1})(528\text{s}) + \ln(0.25) \\ &= -1.74\end{aligned}$$

Hence,

$$[A]_t = e^{-1.74} = 0.18M$$

Note that in the $\ln [A]_0$ terms, $[A]_0$

is expressed as a dimensionless quantity (0.25) because we cannot take the logarithm of units.

Example 13.4 (4 of 4)

b) Using Equation (13.3),

$$\ln \frac{0.15\text{ M}}{0.25\text{ M}} = - (6.7 \times 10^{-4} \text{ s}^{-1}) t$$

$$t = 7.6 \times 10^2 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}}$$
$$= 13 \text{ min}$$

c) From Equation (13.3),

$$\ln \frac{0.26}{1.00} = - (6.7 \times 10^{-4} \text{ s}^{-1}) t$$

$$t = 2.0 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 33 \text{ min}$$

Practice Exercise

The reaction $2A \rightarrow B$ is first order in A with a rate constant of $2.8 \times 10^{-2} \text{ s}^{-1}$ at 80°C . How long (in seconds) will it take for A to decrease from 0.88 M to 0.14 M ?

Answer

66 s.

$$\ln[A] = \ln[A_0] - kt$$

$$\ln[0.14] = \ln[0.88] - t(2.8 \times 10^{-2})$$

$$\ln\left[\frac{0.14}{0.88}\right] = t \cdot 2.8 \times 10^{-2}$$

$$66s = t$$

First-Order Reactions (2 of 3)

The **half-life**, $t_{1/2}$,

\Rightarrow Yarı ömrü bilmenden de anlaşılabilecek, üzerinde giren denklemdeki yarıya düşmesi için geçen süre

is the time required for the concentration of a reactant to decrease to half of its initial concentration.

$$t_{1/2} = t \text{ when } [A] = [A]_0 / 2$$

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

$$\ln\left[\frac{A}{2}\right] = \ln[A]_0 - kt$$

$$kt = \ln\left[\frac{A_0}{\frac{A}{2}}\right]$$

$$kt = \ln 2$$

$$t = \frac{\ln 2}{k}$$

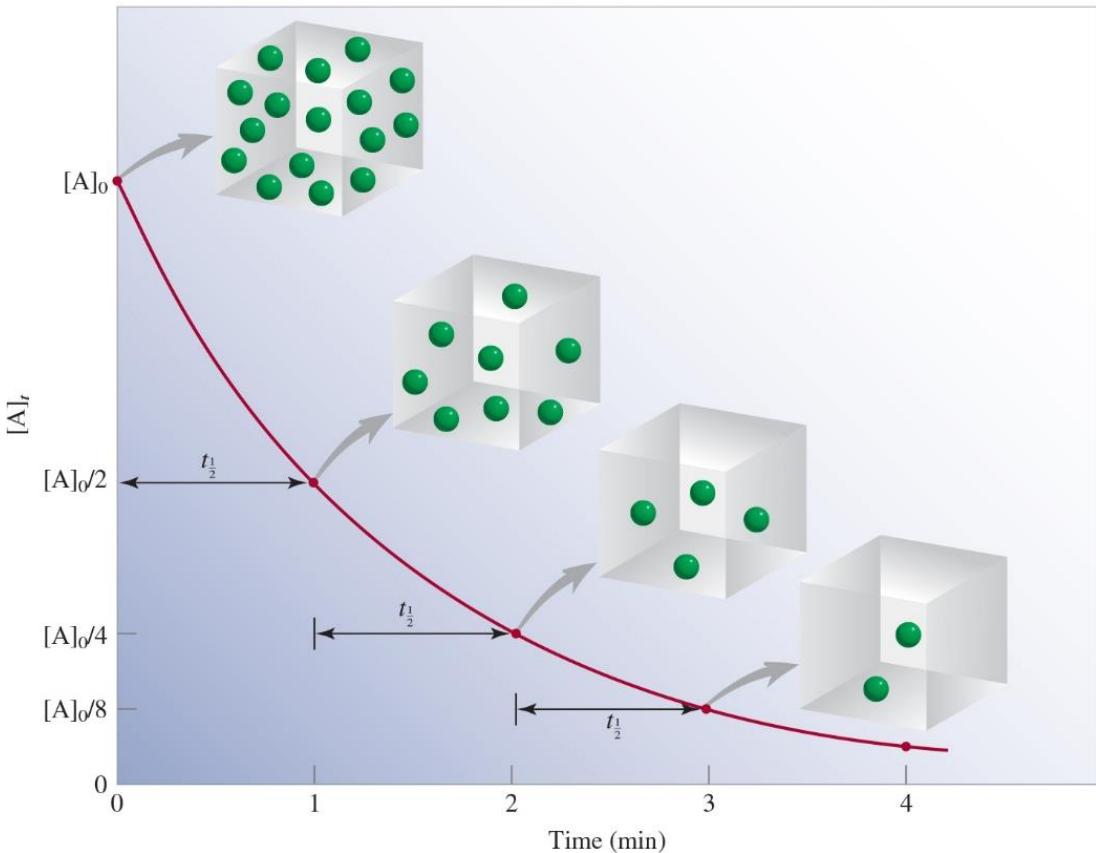
1. Jöle formülini bilmen yetarlı.
Sadece denklemde $[A] = [A]_0 / 2$
esitliğini yerine yazıyzorsun.

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

$$t_{1/2} = \frac{\ln \frac{[A]_0}{[A]/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Equation tells us that the half-life of a first-order reaction is independent of the initial concentration of the reactant.

First-Order Reactions (3 of 3)



First-order reaction



of
half-lives

$$[A] = [A]_0 / n$$

1	2
2	4
3	8
4	16

Example 13.6

The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of $5.36 \times 10^{-4} \text{ s}^{-1}$ at 700°C :



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

Calculate the half-life of the reaction in minutes.

$$\ln[A] = \ln[A_0] - kt$$

$$kt = \ln\left[\frac{A_0}{A}\right]$$

$$kt_{\frac{1}{2}} = \ln\left[\frac{2A}{A}\right]$$

$$t_{\frac{1}{2}} = \frac{\ln 2 \cdot \frac{1}{k}}{1293.1 \text{ s}} = 1293.1 \text{ s} \times \frac{1 \text{ dk}}{60 \text{ s}} = \cancel{21.5 \text{ d}}$$

Example 13.6 (2 of 2)

Strategy

To calculate the half-life of a first-order reaction, we use Equation (13.6). A conversion is needed to express the half-life in minutes.

Solution

For a first-order reaction, we only need the rate constant to calculate the half-life of the reaction. From Equation (13.6)

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{0.693}{k} \\ &= \frac{0.693}{5.36 \times 10^{-4} \text{s}^{-1}} \\ &= 1.29 \times 10^3 \text{s} \\ &\times \frac{1 \text{min}}{60 \text{s}} \\ &= 21.5 \text{min} \end{aligned}$$

Reactions

Adi saatde der.teri toplam 2 olur. $\rightarrow [A][B]$

$[A]^2$

A **second-order reaction** is a reaction whose rate depends on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power.

$A \rightarrow \text{product}$

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

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

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

$[A]$ is the concentration of A at any time t

$[A]_0$ is the concentration of A at time $t = 0$

$$\frac{1}{[A_0]} = \frac{1}{[A]} + kt$$

The **half-life**,

$$k = \frac{\text{rate}}{[A]^2} = \frac{M/s}{M^2} = 1/M.s^{M^{-1}}$$

Adın gibi bil!

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

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

yönde yazdığın vakit

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

elde edersin.

Pseudo-First-Order Reactions

Second-Order Reactions

Another type of second-order reaction is :



If the above reaction is carried out under the conditions where one of the reactants is in large excess over the other, then the concentration of the excess reactant will not change appreciably over the course of the reaction. For example, if $[B] \gg [A]$, then $[B]$ will be essentially constant and we have:

Eğer girenlerdeki reaktantlardan birisinin dərşini
diyərincə görə çox çox fazla isə o zaman fazla
olan reaktant sabit kabul edilir. Digəri sərviində işləm yaphılır.

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

Previously, we saw that the reaction between bromine and formic acid can be treated as a first-order reaction because formic acid is present in excess (see p. 564). Another well-studied example is the hydrolysis (meaning reaction with water) of ethyl acetate to yield acetic acid and ethanol:



Örnəğin

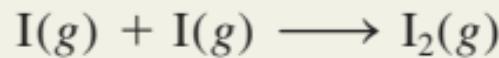
Because the concentration of water, the solvent, is about 55.5 M^{\dagger} compared to 1 M or less for ethyl acetate, $[\text{H}_2\text{O}]$ can be treated as a constant so the rate is given by

$$\text{rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}] = k_{\text{obs}}[\text{CH}_3\text{COOC}_2\text{H}_5]$$

where $k_{\text{obs}} = k[\text{H}_2\text{O}]$.

Example 13.7

Iodine atoms combine to form molecular iodine in the gas phase



$\kappa \kappa$

This reaction follows second-order kinetics and has the high rate constant $7.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 23°C. (a) If the initial concentration of I was 0.086 M , calculate the concentration after 2.0 min. (b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 M and if it is 0.42 M .

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

$\frac{?}{\sqrt{\frac{A_0}{A}}}$

$\checkmark \checkmark$

$\checkmark \checkmark$

$[\text{A}]_t = 1.2 \times 10^{-12} \text{ M}$

b-
$$t_{1/2} = \frac{1}{k[\text{A}]_0} = 2.4 \times 10^{-10} \text{ s}$$

$$= 3.4 \times 10^{-10} \text{ s}$$

Example 13.7 (2 of 4)

Strategy

- The relationship between the concentrations of a reactant at different times is given by the integrated rate law. Because this is a second-order reaction, we use Equation (13.7).
- We are asked to calculate the half-life. The half-life for a second-order reaction is given by Equation (13.8).

Solution

- To calculate the concentration of a species at a later time of a second-order reaction, we need the initial concentration and the rate constant. Applying Equation (13.7)

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

$$\frac{1}{[A]_t} = (7.0 \times 10^9 / M \cdot s) \left(2.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \right) + \frac{1}{0.086 M}$$

Example 13.7 (3 of 4)

where $[A]_t$ is the concentration at $t = 2.0$ min. Solving the equation, we get

$$[A]_t = 1.2 \times 10^{-12} M$$

This is such a low concentration that it is virtually undetectable. The very large rate constant for the reaction means that nearly all the I atoms combine after only 2.0 min of reaction time.

- b) We need Equation (13.8) for this part.

For $[I]_0 = 0.60 M$.

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{1}{k[A]_0} \\ &= \frac{1}{(7.0 \times 10^9 / M.s)(0.60 M)} \\ &= 2.4 \times 10^{-10} s \end{aligned}$$

Example 13.7 (4 of 4)

For $[I]_0 = 0.42 M$

$$t_{\frac{1}{2}} = \frac{1}{(7.0 \times 10^9 / M.s)(0.42M)}$$
$$= 3.4 \times 10^{-10} s$$

Check

These results confirm that the half-life of a second-order reaction, unlike that of a first-order reaction, is not a constant but depends on the initial concentration of the reactant(s).

Does it make sense that a larger initial concentration should have a shorter half-life?

Practice Exercise

The reaction $2A \rightarrow B$ is second order with a rate constant of $51/M \cdot \text{min}$ at 24°C . (a) Starting with $[A]_0 = 0.0092 M$, how long will it take for $[A]_t = 3.7 \times 10^{-3} M$? (b) Calculate the half-life of the reaction.

Answer

- (a) 3.2 min.
- (b) 2.1 min.

Zero-Order Reactions

First- and second-order reactions are the most common reaction types. Reactions whose order is zero are rare. For a zero-order reaction



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

$$\text{rate} = k[A]^0 = k$$

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

$[A]$ is the concentration of A at any time t

$[A]_0$ is the concentration of A at time $t = 0$

The **half-life**, $t_{1/2}$,

$$k = \frac{\text{rate}}{[A]^0} = \boxed{M/s}$$

Just know this one!

$$\begin{aligned} \frac{A_0}{2} &= A_0 e^{-kt} \\ \frac{1}{2} &= e^{-kt} \\ \ln \frac{1}{2} &= -kt \\ t &= \frac{\ln \frac{1}{2}}{-k} \end{aligned}$$

$$t_{1/2} = t \text{ when } [A] = [A]_0 / 2$$

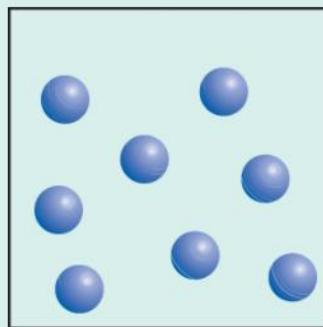
$$t_{1/2} = \frac{[A]_0}{2k}$$

Order	Rate Law	Concentration-Time Equation	Half-Life
0	Rate = k	$[A]_t = -kt + [A]_0$	$\frac{[A]_0}{2k}$
1	Rate = $k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\frac{0.693}{k}$
2†	Rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$

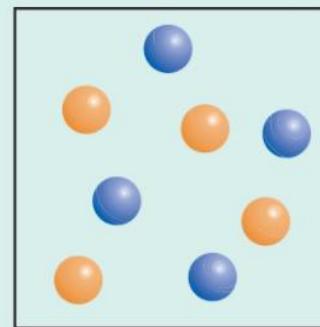
† $A \rightarrow \text{product}$.

- 13.3.1 Consider the first-order reaction $A \rightarrow B$ in which A molecules (blue spheres) are converted to B molecules (orange spheres). (a) What are the half-life and rate constant for the reaction? (b) How many molecules of A and B are present at $t = 20$ s and $t = 30$ s?

Answer



$t = 0$ s



$t = 10$ s

Answer

$$t_{\frac{1}{2}} = 10 \text{ s}, k = 0.069 \text{ s}^{-1}.$$

(b) At $t = 20$ s; two A and six B molecules. At $t = 30$ s; one A and seven B molecules.

- 13.3.3** Consider the first-order reaction $A \rightarrow \text{products}$. The initial concentration of A is 1.56 M and after 48.0 min, the concentration of A is 0.869 M . What is the half-life of the reaction?

$$t_{\frac{1}{2}} = 56.9 \text{ min.}$$

- 13.3.4** What is the initial concentration of a reactant in a first-order reaction ($A \rightarrow \text{products}$) if after 2.0 min, the concentration of reactant is 0.075 M ? The half-life for the reaction is 45 s.

$$0.48\text{ M.}$$

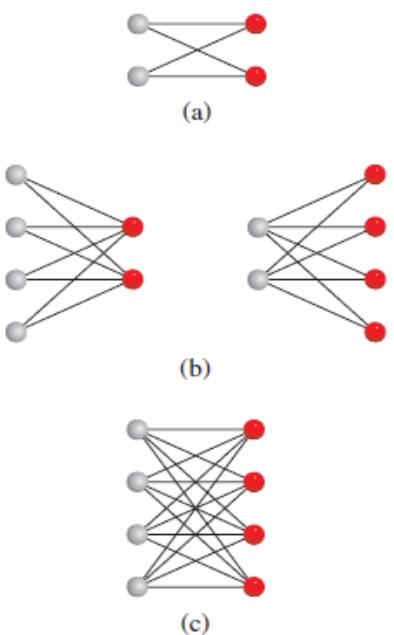
Activation Energy and Temperature Dependence of Rate Constants



With more frequent collisions, reaction rates increase with increasing temperature.

#questioning is the key to knowledge

The Collision Theory of Chemical Kinetics



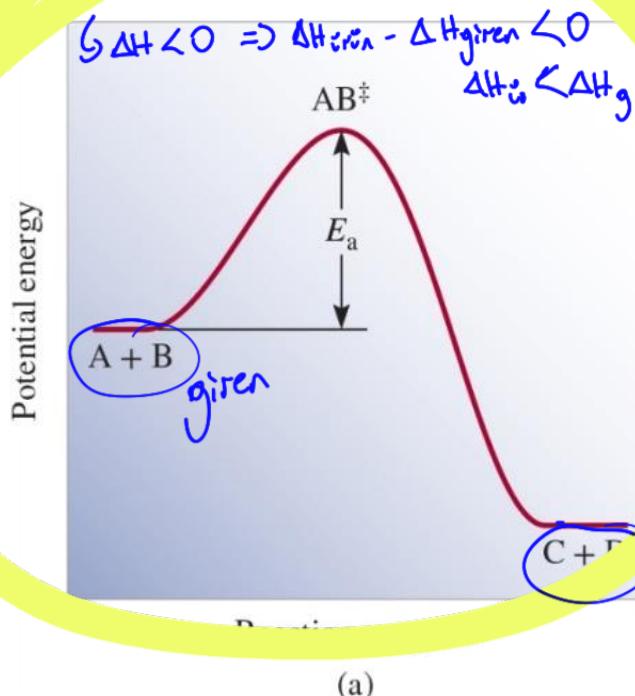
Any molecule in motion possesses kinetic energy; the faster it moves, the greater the kinetic energy. But a fast-moving molecule will not break up into fragments on its own. To react, it must collide with another molecule. When molecules collide, part of their kinetic energy is converted to vibrational energy. If the initial kinetic energies are large, then the colliding molecules will vibrate so strongly as to break some of the chemical bonds. This bond fracture is the first step toward product formation. If the initial kinetic energies are small, the molecules will merely bounce off each other intact. Energetically speaking, there is some minimum collision energy below which no reaction occurs. Lacking this energy, the molecules remain intact, and no change results from the collision.

Exothermic and Endothermic Reactions

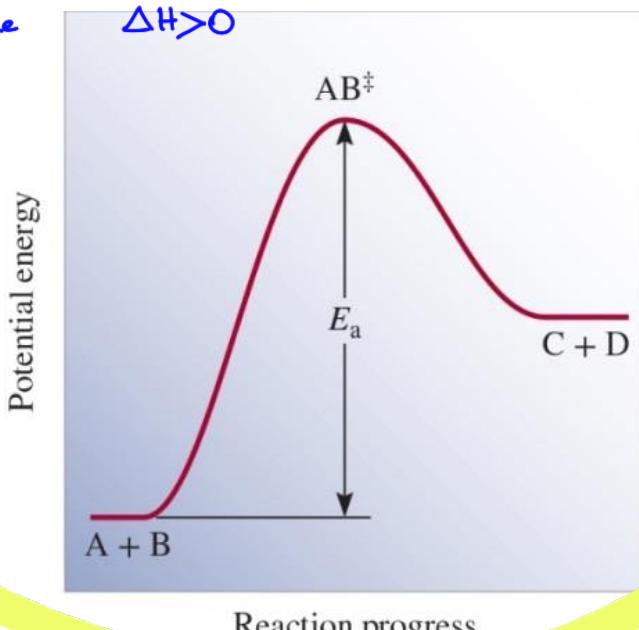
...
...
...
...
...
...
...
...
molecules as a result of the collision before they form the product.



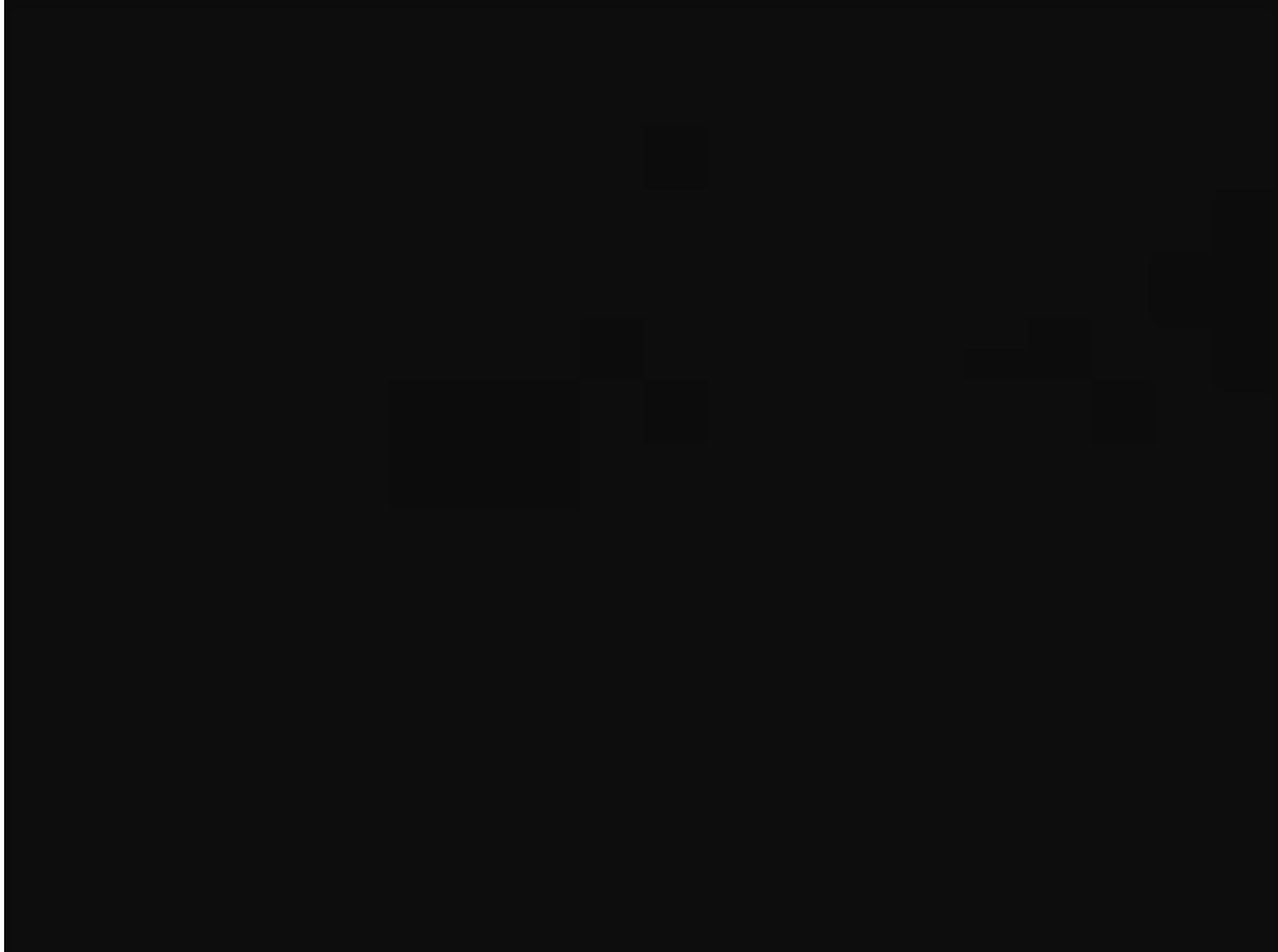
Exothermic Reaction



Endothermic Reaction



(a)

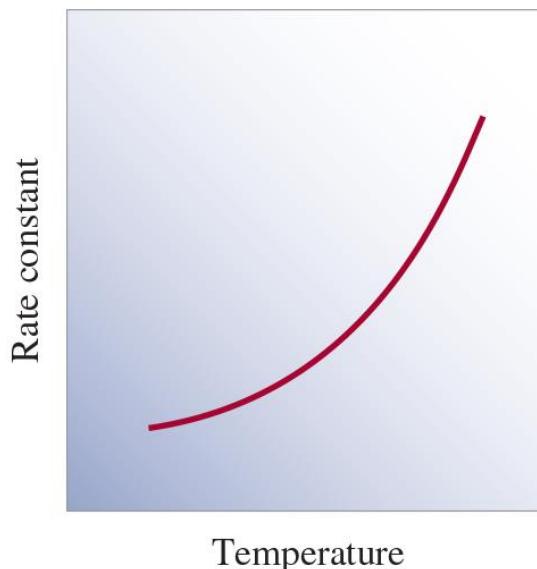


Temperature Dependence of the Rate Constant

The dependence of the rate constant of a reaction on temperature can be expressed by the following equation, known as the *Arrhenius equation*:

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

(Arrhenius equation)



E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K.mol)

T is the absolute temperature

A is the frequency factor

Alternate form:

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$

Alternate Form of the Arrhenius Equation

At two temperatures, T_1 and T_2

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

or

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

Example 13.8

The rate constants for the decomposition of acetaldehyde



were measured at five different temperatures. The data are shown in the table. Plot $\ln k$ versus $1/T$, and determine the activation energy (in kJ/mol) for the reaction. Note that the reaction is “ $\frac{3}{2}$ ” order in CH_3CHO , so k has the units of $1/M^{\frac{1}{2}} \cdot \text{s}$.

k ($1/M^{\frac{1}{2}} \cdot \text{s}$)	T (K)
0.011	700
0.035	730
0.105	760
0.343	790
0.789	810

Example 13.8 (2 of 4)

Strategy

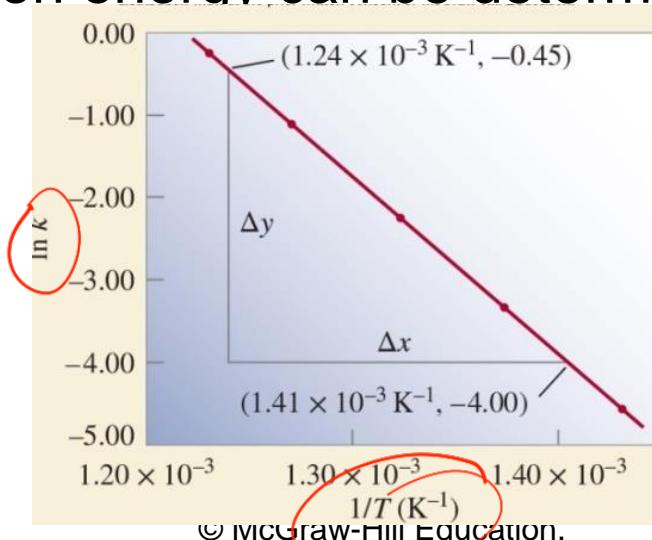
Consider the Arrhenius equation written as a linear equation

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

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

A plot of $\ln k$ versus $1/T$ (y versus x) will produce a straight line with a slope equal to $-E_a/R$.

Thus, the activation energy can be determined from the slope of the plot.



Example 13.8 (3 of 4)

Solution

First we convert the data to the following table

$\ln k$	$1/T(K^{-1})$
-4.51	1.43×10^{-3}
-3.35	1.37×10^{-3}
-2.254	1.32×10^{-3}
-1.070	1.27×10^{-3}
-0.237	1.23×10^{-3}

A plot of these data yields the graph in Figure 13.18. The slope of the line is calculated from two pairs of coordinates:

$$\text{slope} = \frac{-4.00 - (-0.45)}{(1.41 - 1.24) \times 10^{-3} K^{-1}} = -2.09 \times 10^4 K$$

Example 13.8 (4 of 4)

From the linear form of Equation (13.13)

$$\text{slope} = -\frac{E_a}{R} = -2.09 \times 10^4 \text{ K}$$

$$\begin{aligned} E_a &= (8.314 \text{ J/K}\cdot\text{mol})(2.09 \times 10^4 \text{ K}) \\ &= 1.74 \times 10^5 \text{ J/mol} \\ &= 1.74 \times 10^2 \text{ KJ/mol} \end{aligned}$$

Check

It is important to note that although the rate constant itself has the units $1/M^{1/2}\cdot\text{s}$, the quantity $\ln k$ has no units (we cannot take the logarithm of a unit).



Example 13.9

The rate constant of a first-order reaction is $3.46 \times 10^{-2} \text{ s}^{-1}$ at 298 K. What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

$$k_1 = 3.46 \times 10^{-2} \text{ s}^{-1}$$

$$T_1 = 298 \text{ K}$$

$$k_2 = ?$$

$$T_2 = 350 \text{ K}$$

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

or

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

$$\ln \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} = \frac{50.2 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left[\frac{298\text{K} - 350\text{K}}{(298\text{K})(350\text{K})} \right]$$

$$k_2 = 0.702 \text{ s}^{-1}$$

Example 13.9 (2 of 3)

Strategy

A modified form of the Arrhenius equation relates two rate constants at two different temperatures [see Equation (13.14)]. Make sure the units of R and E_a are consistent.

Solution

The data are

$$k_1 = 3.46 \times 10^{-2} \text{ s}^{-1} \quad k_2 = ?$$

$$T_1 = 298 \text{ K} \quad T_2 = 350 \text{ K}$$

Substituting in Equation (13.14),

$$\ln \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} = \frac{50.2 \times 10^3 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}} \left[\frac{298\text{K} - 350\text{K}}{(298\text{K})(350\text{K})} \right]$$

Example 13.9 (3 of 3)

We convert E_a to units of J/mol
to match the units of R . Solving the equation gives

$$\ln \frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} = -3.01$$

$$\frac{3.46 \times 10^{-2} \text{ s}^{-1}}{k_2} = e^{-3.01} = 0.0493$$

$$k_2 = 0.702 \text{ s}^{-1}$$

Check

The rate constant is expected to be greater at a higher temperature. Therefore, the answer is reasonable.

Practice Exercise

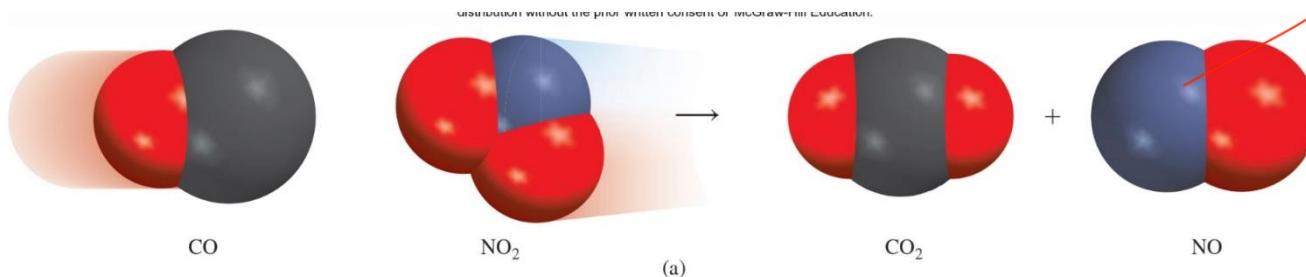
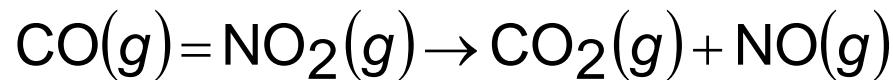
The first-order rate constant for the reaction of methyl chloride (CH_3Cl) with water to produce methanol (CH_3OH) and hydrochloric acid (HCl) is $3.32 \times 10^{-10} \text{ s}^{-1}$ at 25°C . Calculate the rate constant at 40°C if the activation energy is 116 kJ/mol.

$$3.13 \times 10^{-9} \text{ s}^{-1}.$$

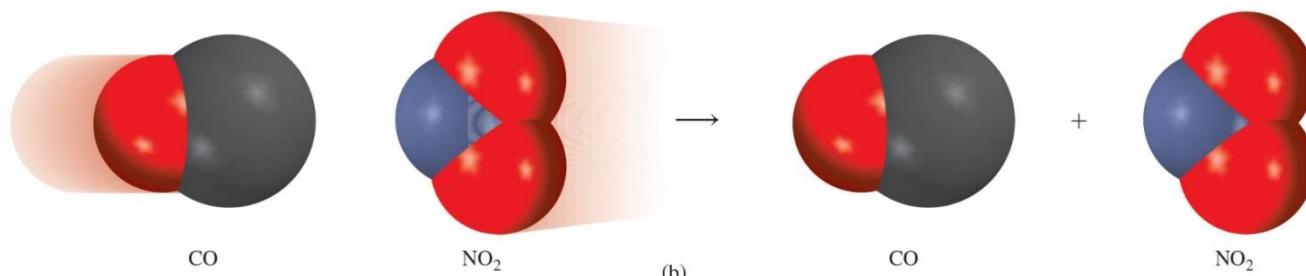
- 13.4.1** What is the activation energy of a particular reaction if the rate constant for the reaction is $2.7 \times 10^{-2} \text{ s}^{-1}$ at 25°C and $6.2 \times 10^{-2} \text{ s}^{-1}$ at 115°C ?

$$8.9 \text{ kJ/mol.}$$

Importance of Molecular Orientation



effective collision

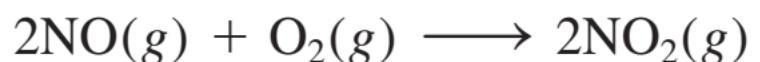


ineffective collision

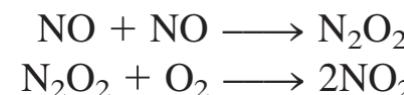
Reaction Mechanisms

Dentkemi veriler
Kimyasal süreçler
Yol haritası

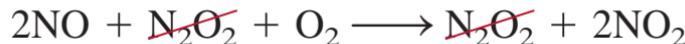
As we mentioned earlier, an overall balanced chemical equation does not tell us much about how a reaction actually takes place. In many cases, it merely represents the sum of several **elementary steps**, or **elementary reactions**, a series of simple reactions that represent the progress of the overall reaction at the molecular level. The term for the sequence of elementary steps that leads to product formation is [REDACTED]. The reaction mechanism is comparable to the route of travel followed during a trip; the overall chemical equation specifies only the origin and destination.



Step 1:
Step 2:



Overall reaction:



The [REDACTED] is the number of molecules reacting in an elementary step. These molecules may be of the same or different types. Each of the elementary steps discussed above is called a [REDACTED], an elementary step that involves two molecules. An example of a [REDACTED], an elementary step in which only one reacting molecule participates, is the conversion of cyclopropane to propene discussed in Example 13.4. Very few [REDACTED] reactions that involve the participation of three molecules in one elementary step, are known, because the simultaneous encounter of three molecules is a far less likely event than a bimolecular collision.

Rate Laws and Elementary Steps

Knowing the elementary steps of a reaction enables us to deduce the rate law. Suppose we have the following elementary reaction:



Because there is only one molecule present, this is a **unimolecular** reaction. It follows that the larger the number of A molecules present, the faster the rate of product formation. Thus, the rate of unimolecular reactions depends on the concentration of A:

$$\text{rate: } k[A]$$

For a bimolecular elementary reaction involving A and B molecules



The rate of bimolecular reactions depends on the concentration of both reactants, which in turn depends on the concentrations of A and B. Thus, we can express the rate as

$$\text{rate: } k[A][B]$$

Similarly, for a bimolecular elementary reaction of the type



the rate becomes **rate: $[A]^2$**

Rate Laws and Elementary Steps

The preceding examples show that the reaction order for each reactant in an elementary reaction is equal to its stoichiometric coefficient in the chemical equation for that step. In general, we cannot tell by merely looking at the overall balanced equation whether the reaction occurs as shown or in a series of steps. This determination is made in the laboratory.



When we study a reaction that has more than one elementary step, the rate law for the overall process is given by the slowest elementary step. This is called the rate-determining step.

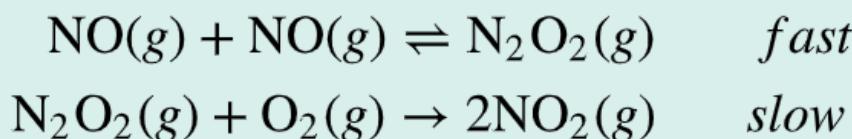
For example, consider the overall reaction $A + B \rightarrow C + D$. If the reaction consists of two elementary steps:

Step 1: $A \rightarrow C$ (slow)

Step 2: $B + C \rightarrow D$ (fast)

then the overall rate of the reaction will be determined by Step 1, which is the rate-determining step.

13.5.2 For the reaction between NO and O₂, the following mechanism has been suggested:



What is the rate law for this reaction?

Katalisator

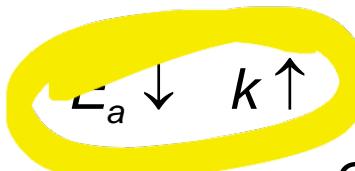
Catalysts (1 of 2)

A **catalyst** is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed.

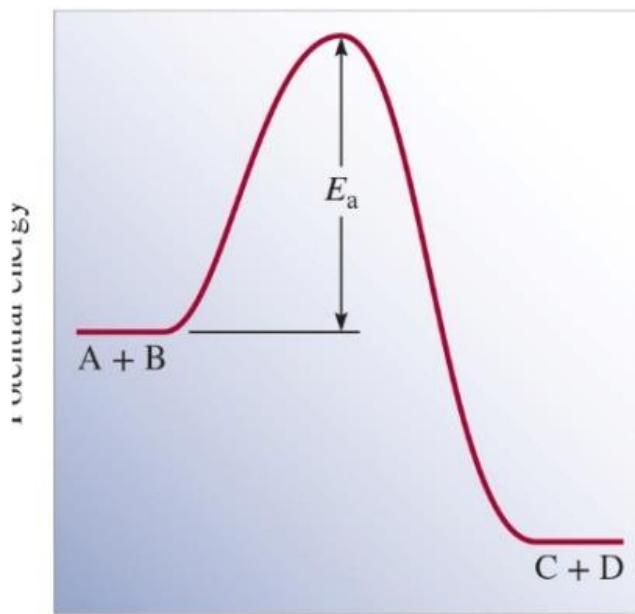
$$k = A \cdot e^{(-E_a/RT)}$$

Uncatalyzed

$$\text{rate}_{\text{catalysed}} > \text{rate}_{\text{uncatalyzed}}$$



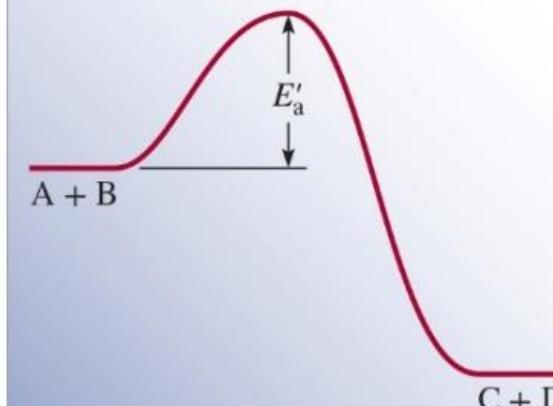
Catalyzed



(a)

$$E'_a < E_a$$

Potential energy



(b)

Catalysts (2 of 2)

In **catalysis**, the reactants and the catalysts are in different phases.

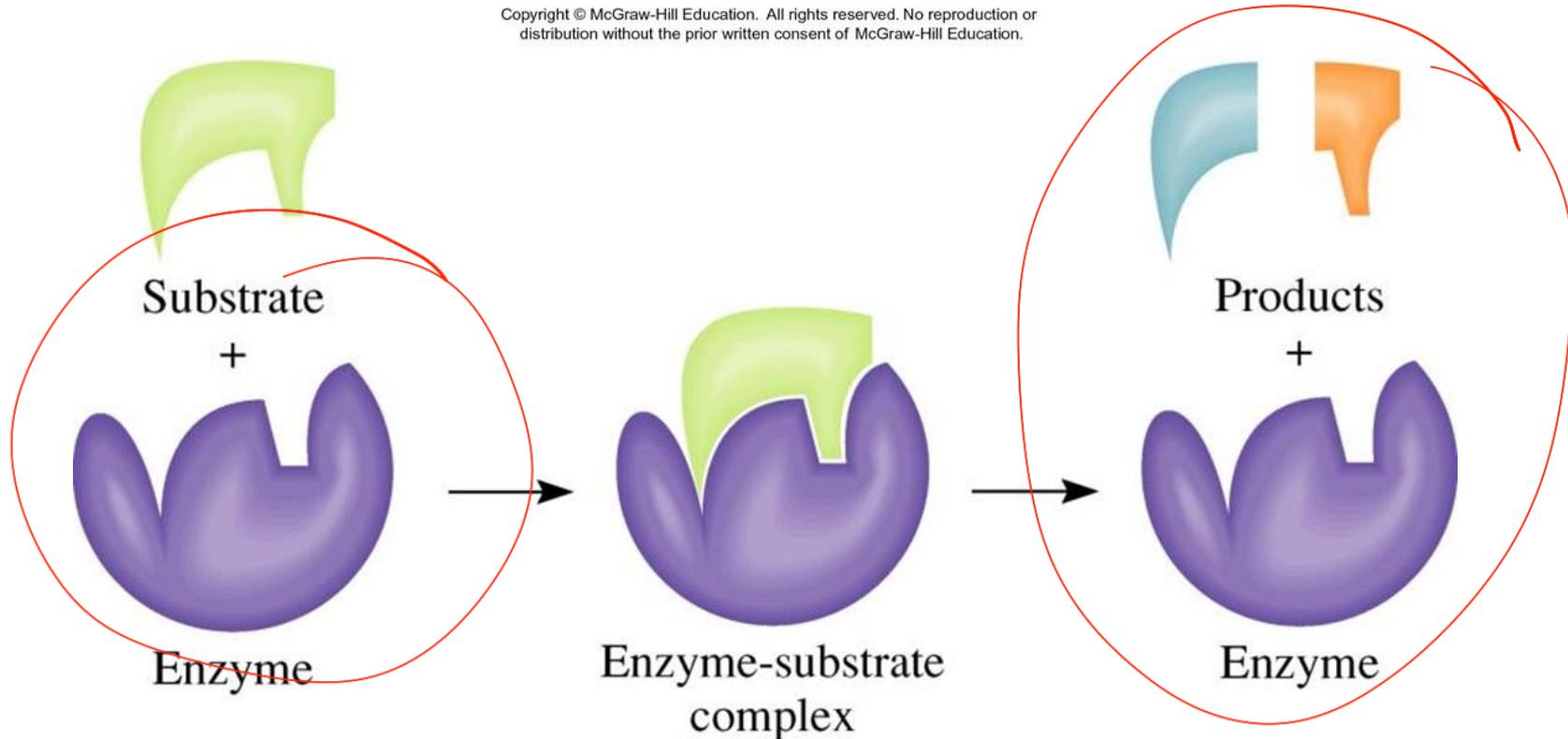
- Haber synthesis of ammonia
- Ostwald process for the production of nitric acid
- Catalytic converters

In **catalysis**, the reactants and the catalysts are in different phases.

- Acid catalysis
- Base catalysis

Enzyme Catalysis

Copyright © McGraw-Hill Education. All rights reserved. No reproduction or distribution without the prior written consent of McGraw-Hill Education.



[Jump to long description](#)

- 13.6.1** Which of the following is false regarding catalysis? (a) E_a is lower for a catalyzed reaction. (b) ΔH_{rxn}° is lower for a catalyzed reaction. (c) A catalyzed reaction has a different mechanism.

(b).

Löppün löppü! !!

Key Equations

$$\text{rate} = k[A]^x[B]^y \quad (13.1) \quad \cancel{x}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (13.3) \quad \ln [A]_t = \ln [A]_0 - kt$$

$$\ln [A]_t = -kt + \ln [A]_0 \quad (13.4)$$

$$t_{\frac{1}{2}} = \frac{0.693}{k} \quad (13.6) \quad \text{esbere gerek yok yukarıyı ezi.}$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad (13.7) \quad \cancel{x}$$

$$k = Ae^{-E_a/RT} \quad (13.11) \quad \cancel{x}$$

$$\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \quad (13.13) \quad \cancel{x}$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right) \quad (13.14) \quad \cancel{x}$$

Rate law expressions. The sum ($x + y$) gives the overall order of the reaction.

Relationship between concentration and time for a first-order reaction.

Equation for the graphical determination of k for a first-order reaction.

Half-life for a first-order reaction.

Relationship between concentration and time for a second-order reaction.

The Arrhenius equation expressing the dependence of the rate constant on activation energy and temperature.

Equation for the graphical determination of activation energy.

Relationships of rate constants at two different temperatures.

Summary of Facts & Concepts

1. The rate of a chemical reaction is the change in the concentration of reactants or products over time.
[REDACTED]
2. The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to appropriate powers.
[REDACTED]
3. Reaction order is the power to which the concentration of a given reactant is raised in the rate law. Overall reaction order is the sum of the powers to which reactant concentrations are raised in the rate law. The rate law and the reaction order cannot be determined from the stoichiometry of the overall equation for a reaction; they must be determined by experiment. For a zero-order reaction, the reaction rate is equal to the rate constant.
4. The half-life of a reaction (the time it takes for the concentration of a reactant to decrease by one-half) can be used to determine the rate constant of a first-order reaction.
5. In terms of collision theory, a reaction occurs when molecules collide with sufficient energy, called the activation energy, to break the bonds and initiate the reaction. The rate constant and the activation energy are related by the Arrhenius equation.
6. The overall balanced equation for a reaction may be the sum of a series of simple reactions, called elementary steps. The complete series of elementary steps for a reaction is the reaction mechanism.
7. If one step in a reaction mechanism is much slower than all other steps, it is the rate-determining step.
8. A catalyst speeds up a reaction usually by lowering the value of E_a . A catalyst can be recovered unchanged at the end of a reaction.
9. In heterogeneous catalysis, which is of great industrial importance, the catalyst is a solid and the reactants are gases or liquids. In homogeneous catalysis, the catalyst and the reactants are in the same phase. Enzymes are catalysts in living systems.