



First-Order Reactions (2 of 3)

The **half-life**, $t_{1/2}$, \Rightarrow Yarı ömrü izinden de anlaşılabilecek, iżere giren dörtlükün yarıya düşmesi için geçen süre

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

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

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

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

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

$$kt = \ln 2$$

1. derece formülün plancı yeter!
Sadece dörtteki $[A] = [A]_0 / 2$
esitligini yazarısın.

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

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

Equation tells us that the half-life of a first-order reaction is **independent** of the initial concentration of the reactant. Thus, it takes the same time for the concentration of the reactant to decrease from 1.0 M to 0.50 M , say, as it does for a decrease in concentration from 0.10 M to 0.050 M . Measuring the half life of a reaction is one way to determine the rate constant of a first-order reaction.

First-Order Reactions (3 of 3)



Second-Order Reactions

Adı 3. derecedir. İleri toplamı 2 olan. $[A]^2$

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.

$A \rightarrow \text{product}$

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

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

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

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

Adını gibi bil!

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

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

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

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

yine yazdığın vakti

The **half-life**,

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

Pseudo-First-Order Reactions

Second-Order Reactions

Another type of second-order reaction is :



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

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.

$$\text{The half-life, } t_{\frac{1}{2}} = \frac{\ln 2}{k[A]_0}$$

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Pseudo-First-Order Reactions

Second-Order Reactions

Another type of second-order reaction is :



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

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 ikinci dereceden bir reaksiyon
birikteki biri çok fazla ise o zaman ikinci
dereceden bir reaksiyon gibi biri çok fazla
olursa反应物 çok fazla ise o zaman ikinci
dereceden bir reaksiyon gibi olur.

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

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:



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

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Example 13.7

Iodine atoms combine to form molecular iodine in the gas phase

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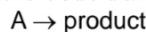
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Zero-Order Reactions

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



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

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

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

Just know this one!

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

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

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

$$\begin{aligned} & \frac{A_0}{2} \xrightarrow{k} t = \frac{A_0}{2k} \\ & 2kt = A_0 \\ & t = \frac{A_0}{2k} \end{aligned}$$

The half-life, $t_{\frac{1}{2}}$,

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

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Table 13.3 Summary of the Kinetics of Zero-Order, First-Order, and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	Rate = k	$[A]_t = -kt + [A]_0$	$[A]_0$

The nail-lite, $\frac{1}{2}$

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

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Table 13.3 Summary of the Kinetics of Zero-Order, First-Order, and Second-Order Reactions

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 = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$

$\dagger A \rightarrow$ product.

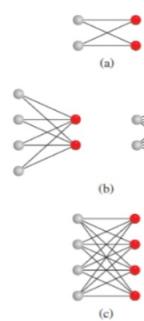
Activation Energy and Temperature Dependence of Rate Constants

With very few exceptions, reaction rates increase with increasing temperature.

How reactions get started ??? #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.

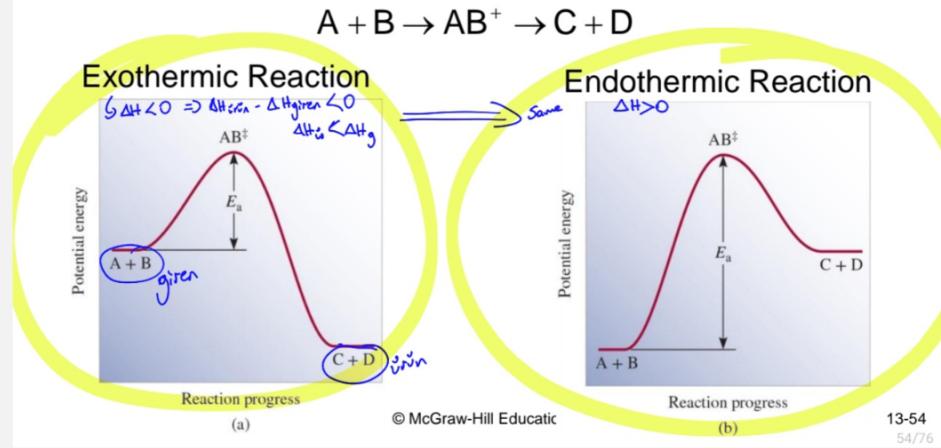
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Exothermic and Endothermic Reactions



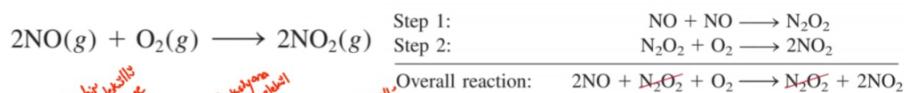
We assume that in order to react, the colliding molecules must have a total kinetic energy equal to or greater than the **activation energy (E_a)**, which is the minimum amount of energy required to initiate a chemical reaction. When molecules collide they form an **activated complex** (also called the **transition state**) a temporary species formed by the reactant molecules as a result of the collision before they form the product.



Reaction Mechanisms



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 **reaction mechanism**. The reaction mechanism is comparable to the route of travel followed during a trip; the overall chemical equation specifies only the origin and destination.



The **molecularity of a reaction** 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 **bimolecular reaction**, an elementary step that involves two molecules. An example of a **unimolecular reaction**, an elementary step in which only one reacting molecule participates, is the conversion of cyclopropane to propene discussed in Example 13.4. Very few **termolecular reactions**, 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.

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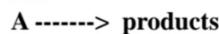
Rate Laws and Elementary Steps

Rate Laws and Elementary Steps

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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 a unimolecular reaction is directly proportional to the concentration of A, or is first order in A:**

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

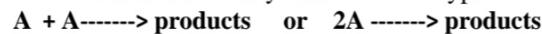
For a bimolecular elementary reaction involving A and B molecules



The rate of product formation depends on how frequently A and B collide, which in turn depends on the concentrations of A and B. Thus, we can express the rate as

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

Similarly, for a bimolecular elementary reaction of the type



the rate becomes **rate: $[\text{A}]^2$**

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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.

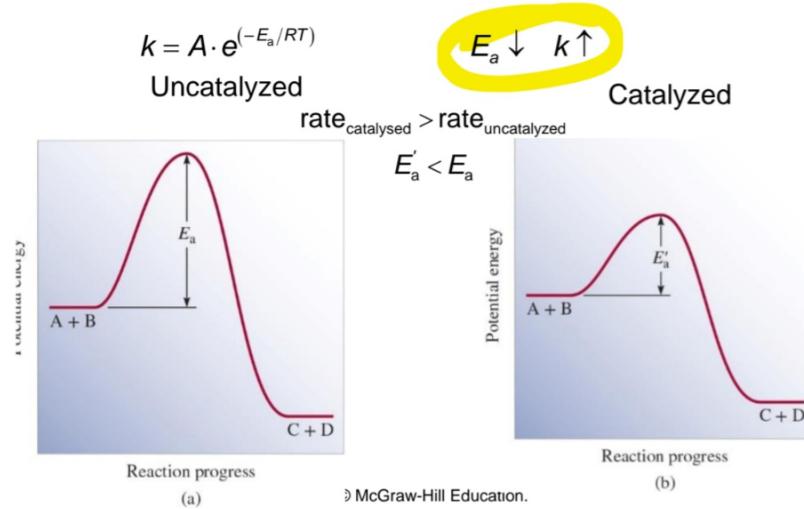
* When we study a reaction that has more than one elementary step, the rate law for the overall process is given by the **rate-determining step, which is the slowest step in the sequence of steps leading to product formation.**

An analogy for the rate-determining step is the flow of traffic along a narrow road. Assuming the cars cannot pass one another on the road, the rate at which the cars travel is governed by the slowest-moving car.

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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.



Catalysts (2 of 2)

In **heterogeneous 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 ***homogeneous catalysis***, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid catalysis
 - Base catalysis



Summary of Facts & Concepts

1. The rate of a chemical reaction is the change in the concentration of reactants or products over time. **The rate is not constant, but varies continuously as concentrations change.**
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. **The rate constant k for a given reaction changes only with temperature.**
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.