

TOPIC

14

CHEMICAL KINETICS

The content in this topic is the basis for mastering all the Learning Objectives in Big Idea 4: 4.1–4.9 as found in the Curriculum Framework.

Chemical kinetics provides answers to the question, how and why do chemical reactions occur? Kinetics provides both qualitative and quantitative models to examine how molecular collisions between reactants lead to formation of products.

When you finish reviewing this topic, be sure you are able to:

- Know what rate of reaction is and common ways to express the rate of reaction
- Design an experiment or interpret experimental data that measure rate
- Understand the factors that affect the rate of reaction
- Use the collision model to explain how concentration, pressure, temperature, and the phase of the reactants affect reaction rates
- Know how the frequency and success of molecular collisions and their orientations affect reaction rate
- Examine concentration versus reaction rate data using the method of initial rates to determine the rate law and the order of a reaction
- Know what a rate constant is and how it characterizes a reaction
- Connect the half-life of a first-order reaction to its rate constant
- Infer reaction order from plots of concentration versus time
- Understand how temperature affects a rate constant
- Interpret Maxwell–Boltzmann plots that describe distributions of particle energies
- Use energy profiles to make qualitative predictions about the relative rates of reactions
- Evaluate reaction mechanisms and determine which are consistent with rate data
- Interpret data that infer the presence of reaction intermediates
- Explain how catalysts work, including acid–base catalysts, surface catalysts, and enzymes

Reaction Rates

Section 14.1

Reaction rate is a measure of the speed of a chemical reaction. Rate of reaction is expressed as the change in the amount of reactants or products per unit time. Most often the unit for reaction rate is molarity per second (M/s).

Concentrations of reactants and products and the rate of reaction change with time.

Figure 14.1 illustrates how the concentration of reactant A changes with time in the hypothetical reaction $A \rightarrow B$. Chemical reactions usually start fast and begin to slow down with time. Consequently, the concentration of A usually decreases in a nonlinear fashion.

The **instantaneous rate** of a reaction is the slope of the tangent line at any point $(t, [A])$. The rate is:

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

Rates are always expressed as positive quantities. Because the slope in the graph in Figure 14.1a is negative, a negative sign is used to express rate as a positive quantity. A typical reaction rate starts fast and becomes slower as time goes on. The initial rate at $t = 0$ is always the largest rate.

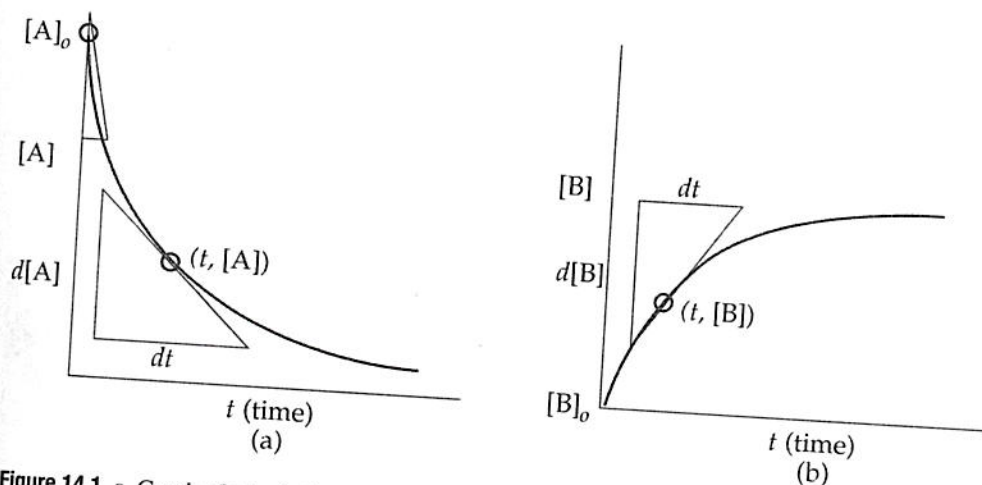


Figure 14.1 a. Graph of a typical reaction $A \rightarrow B$ showing how $[A]$ decreases with time. b. Graph of a typical reaction $A \rightarrow B$ showing how $[B]$ increases with time.

Figure 14.1b illustrates how $[B]$ changes with time. As time increases, the concentration of B increases. The slope of the tangent line at any point $(t, [B])$ represents the instantaneous rate of the reaction. The rate is:

$$\text{Rate} = +\Delta[B]/\Delta t$$

Notice that the slope of the line is positive, so a positive sign in the expression denotes a positive rate.



Common misconception: Molarity per second is often expressed as $\text{mol L}^{-1} \cdot \text{s}^{-1}$.

$$M/s = \text{mol}/L \cdot s = \text{mol L}^{-1} \cdot \text{s}^{-1}$$

Reaction rate can also be expressed in pressure units per time (atm/s or torr/s) or sometimes in absorbance units per time. (For more on how absorbance can be used to monitor the changing concentration of a reactant or product, see A Closer Look: Using Spectroscopic Methods to Measure Reaction Rates in Section 14.2 of *Chemistry: The Central Science*.)

Section 14.2

Factors that Affect Reaction Rates

The **collision model** is a model that explains reaction rates and is based on the idea that molecules must collide to react. The collision model is based on kinetic-molecular theory and accounts for the factors that affect the rate of a reaction.

On a molecular level, reaction rates depend on the frequency of collisions between molecules, the energy with which the molecules collide, and whether the colliding molecules have the proper orientation to provide a successful reaction. Not all collisions are successful. Rate of reaction increases with greater frequency of collisions (and, therefore, greater probability of successful collisions), and/or greater energy with which the collisions occur. Figure 14.2 illustrates an effective collision that results in a reaction and an unsuccessful collision that regenerates reactants.

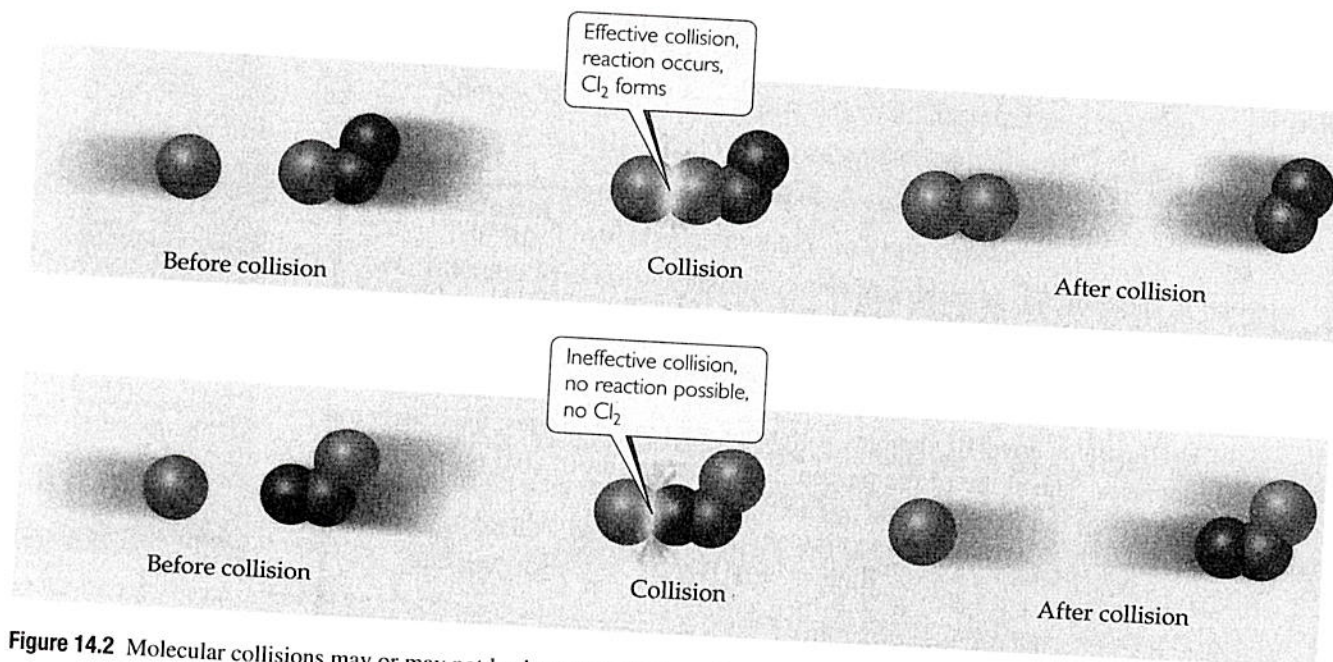


Figure 14.2 Molecular collisions may or may not lead to a chemical reaction between Cl and NOCl: $\text{Cl} + \text{NOCl} \rightarrow \text{Cl}_2 + \text{NO}$.

Use Figure 14.2 and energy considerations to explain why some molecular collisions lead to reaction and others do not. Write your answer in the space provided.

Your Turn 14.1

The major factors that affect reaction rate are the following:

1. **Concentrations of reactants.** Higher concentrations of reactants usually produce a faster reaction. As concentration increases, the frequency of collisions increases, thus increasing reaction rate because more molecules collide with the proper orientation. Figure 14.3 shows a molecular view of two different systems, one with a high concentration of molecules and one with a low concentration. If the molecules are in rapid, random motion, the ones in higher concentration would collide more often giving a faster rate of reaction.

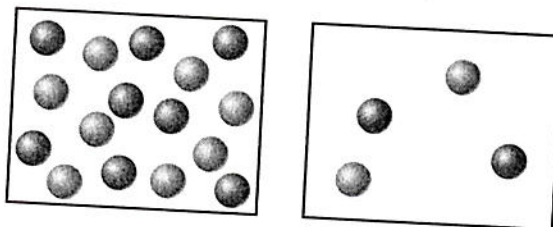


Figure 14.3 A higher concentration of molecules yields more frequent collisions and thus a higher rate of reaction.

2. **Temperature.** Increasing temperature increases reaction rate. Figure 14.4 illustrates the effect of temperature on the Maxwell-Boltzmann distribution of the kinetic energies of a sample of molecules. Higher temperatures provide increased kinetic energies of molecules, so the molecules move more rapidly. At higher temperatures, there is a higher fraction of molecules with the required energy for reaction. Thus, more collisions result in a reaction.

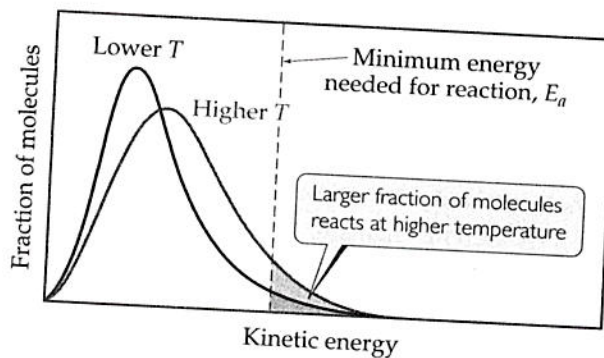


Figure 14.4 The effect of temperature on the distribution of kinetic energies of molecules in a sample.

3. **Physical state of the reactants.** Usually, homogeneous mixtures of either liquids or gases react faster than heterogeneous mixtures. A solid, for example, tends to react more slowly with either a liquid or a gas because molecular collisions are limited to the **surface area** of the solid. Increasing the surface area will increase the frequency of collisions, and thus increase the rate of reaction.
4. **The presence of a catalyst.** A catalyst increases the rate of reaction by affecting the kinds of collisions that lead to a reaction. A catalyst acts by lowering the energy the molecules need to react and/or by changing the pathway of the reaction. A **reaction mechanism**, to be discussed in more detail later, is a step-by-step process or pathway by which reactants become products.

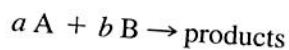
Your Turn 14.2

← Mine explosions from the ignition of powdered coal dust are relatively common, yet lumps of coal burn without exploding. Explain. Write your answer in the space provided.

Section 14.3

Concentration and Rate Laws

A **rate law** is a mathematical relationship that shows how rate of reaction depends on the concentrations of reactants. For any general reaction where:



the rate law takes the form:

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

where k is the rate constant, $[A]$ is the molar concentration of reactant A, $[B]$ is the molar concentration of reactant B, and the exponents m and n are usually small, whole numbers that relate to the number of molecules of A and B that collide in the step-by-step mechanism.

Common misconception: The coefficients that balance the equation, a and b , are not necessarily the same as the exponents, m and n , in the rate law. The exponents n and m must be determined by experiment, not by the balanced equation.



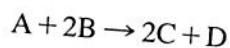
Reaction order is the sum of the exponents m and n in a rate law. For example, consider the rate law:

$$\text{Rate} = k[\text{A}]^1[\text{B}]^2$$

The reaction is said to be “first order in A” and “second order in B.” The **overall order** of the reaction is the sum of m and n . In this example, $1 + 2 = 3$, so the reaction is “third order” overall.

The rate law for any chemical reaction must be determined experimentally, often by observing the effect of changing the initial concentrations of the reactants on the initial rate of the reaction.

Consider the reaction:



The rate law always takes the form:

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

A series of experiments measuring initial rate at various concentrations of reactants might give the data in Table 14.1.

Table 14.1 The effect of changing concentrations on the initial rate of a reaction.

Experiment	[A] (M)	[B] (M)	Rate = $-d[\text{A}]/dt$ (M/s)
1	0.10	0.10	0.04
2	0.10	0.20	0.08
3	0.20	0.20	0.32

Experiments 1 and 2 show that the rate is doubled when [B] is doubled while [A] is constant. This means that the exponent of [B] is 1 ($2^1 = 2$ so $n = 1$).

Experiments 2 and 3 show that the rate is quadrupled when [A] is doubled while [B] is constant. This means that the exponent of [A] is 2 ($2^2 = 4$ so $m = 2$). The data in Table 14.1 show that the rate law is:

$$\text{Rate} = k[\text{A}]^2[\text{B}]^1$$

The reaction is second order in A, first order in B, and third order overall.

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The data in Table 14.1 can be used to calculate the value of the rate constant.

Example:

What is the numerical value of the rate constant for the reaction described in Table 14.1. Specify its units.

Solution:

$$\text{Rate} = k[A]^2[B]^1$$

$$0.04 \text{ M/s} = k[0.1 \text{ M}]^2[0.1 \text{ M}]^1$$

$$k = (0.04 \text{ M/s}) / (0.01 \text{ M}^2 \times 0.1 \text{ M})$$

$$= 40/\text{M}^{-2}\text{s}^{-1}$$

Your Turn 14.3

← What are the units for each rate constant for the following rate laws? Assume each rate is expressed in M/s. a. $\text{Rate} = k[A]$; b. $\text{Rate} = k[A]^2$; c. $\text{Rate} = k[A]^3$. Write your answers in the space provided.

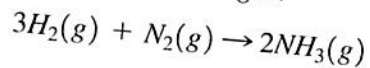
Your Turn 14.4

← Consider the single-step reaction $A + B \rightarrow AB$. a. If the reaction is first order in A and first order in B, what is the rate law? b. If the rate constant for this reaction is large, discuss the relative frequency and success of the collisions. Write your answers in the space provided.

The coefficients that balance a chemical equation are proportional to the rates of appearance or disappearance of reactants and products. Reaction rate relates directly to stoichiometry.

Example:

Consider the reaction between gaseous hydrogen and gaseous nitrogen to produce ammonia gas.



At a particular time during the reaction, $\text{H}_2(\text{g})$ disappears at the rate of 3.0 M/s .

- What is the rate of disappearance of $\text{N}_2(\text{g})$?
- What is the rate of appearance of $\text{NH}_3(\text{g})$?

Solution:

- In the balanced equation, $\text{N}_2(\text{g})$ has a coefficient of 1, whereas $\text{H}_2(\text{g})$ has a coefficient of 3. $\text{N}_2(\text{g})$ disappears at one-third the rate of $\text{H}_2(\text{g})$.
 $1/3(3.0 \text{ M/s}) = 1.0 \text{ M/s}$

- $\text{NH}_3(\text{g})$ appears at two-thirds the rate of $\text{H}_2(\text{g})$.
 $2/3(3.0 \text{ M/s}) = 2.0 \text{ M/s}$

If ammonia appears at 2.6 M/s , how fast does hydrogen disappear? Write your answer in the space provided.

Your Turn 14.5

The following equation applies to the reaction in the example:

$$-\Delta\text{H}_2(\text{g})/\Delta t = -3 \Delta\text{N}_2(\text{g})/\Delta t = +3/2 \Delta\text{NH}_3(\text{g})/\Delta t$$

Notice the use and placement of signs and the coefficients that balance the chemical equation. If they seem counterintuitive, translate the mathematical expression into words: "The rate of disappearance of hydrogen gas is three times the rate of the disappearance of nitrogen gas and three-halves the rate of appearance of ammonia gas."

The application of stoichiometry to the data in Table 14.1 can be used to calculate various rates.

Example:

From the data for Experiment 1 in Table 14.1, calculate the rate of appearance of C.

Solution:

The initial rate of disappearance of A in Experiment 1 is 0.04 M/s. The balanced equation shows that C has a coefficient twice that of A, so the rate of appearance of C is twice that of A.

$$+\Delta C/\Delta t = -2\Delta A/\Delta t = 2(0.040 \text{ M/s}) = 0.080 \text{ M/s}$$

Section 14.4

The Change of Concentration with Time

A **first-order reaction** (a **unimolecular reaction**) is a reaction whose rate depends on the concentration of a single reactant raised to the first power.

The rate of a first-order reaction is expressed both by the rate law and by the slope of the tangent line at any point $(t, [A])$ on the graph in Figure 14.1a.

$$\text{Rate} = k[A] = -\Delta[A]/\Delta t \quad \text{differential rate law}$$

Using calculus, this equation is transformed into the equation of the curved line in Figure 14.5a. The equation of the line is:

$$\ln[A]_t = -kt + \ln[A]_0 \quad \text{integrated rate law}$$

Notice that the equation takes the form of the simple linear equation, $y = mx + b$, where $y = \ln[A]_t$, $b = \ln[A]_0$, and the slope of the line $= -k$, the rate constant.

For a first-order reaction, a plot of $\ln[A]$ versus time will yield a straight line with a slope of $-k$ as shown in Figure 14.5b. This is a useful graphical method for determining rate constants for first-order reactions.

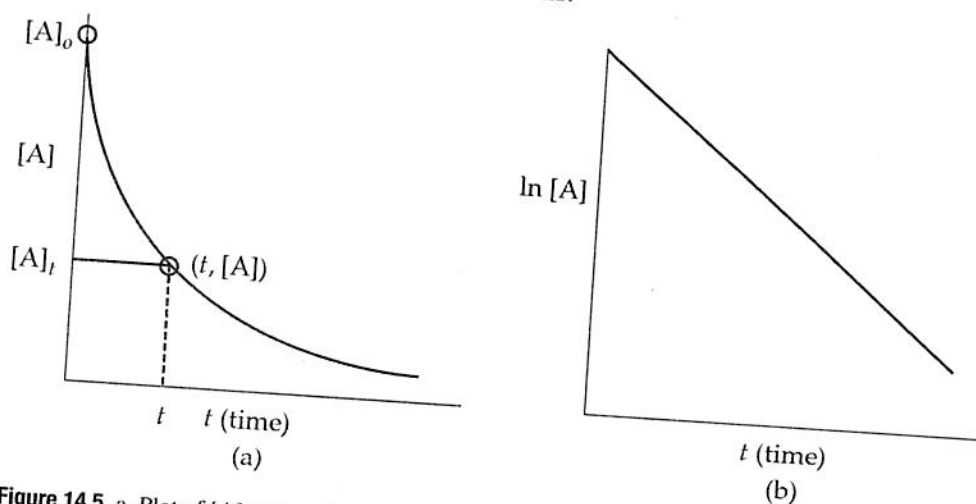


Figure 14.5 a. Plot of $[A]$ versus time for a first-order reaction. b. Plot of $\ln[A]$ versus time for a first-order reaction. The negative slope of the line equals the rate constant.

Often the equation of the line for a first-order reaction is written in the more familiar expression:

$$\ln([A]_0/[A]_t) = +kt$$

A first-order reaction is a **unimolecular process**. That is, it depends only on the concentration of **one reactant**. In a unimolecular process, collisions with other molecules, either reactant molecules or solvent molecules, activate the reactant in a way that it is converted to products. Figure 14.6 illustrates how a single molecule might be activated to produce a reaction. Imagine collisions of solvent molecules with methyl isonitrile in such a way that the C—N bond breaks and a C—C bond forms instead.

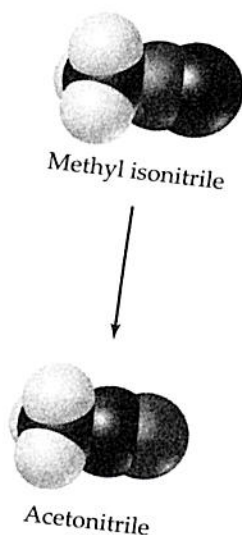


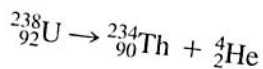
Figure 14.6 The first-order reaction of CH_3NC conversion to CH_3CN .

For a first-order reaction, the **exponent of one** in the rate equation,

$$\text{Rate} = k[A]^1,$$

is interpreted to mean that only **one molecule** of A is involved in the reaction.

Radioactive decay is another example of first-order kinetics. For example, the nucleus of a uranium-238 atom spontaneously decomposes into a thorium-234 nucleus and a helium nucleus:



A simple **second-order reaction** (a bimolecular reaction) is one whose rate depends on the concentration of one reactant raised to the second power as in this hypothetical chemical equation: $\text{A} \rightarrow \text{B}$.

The characteristic equations are:

$$\text{Rate} = k[A]^2 = -\Delta A / \Delta t \quad \text{differential rate law}$$

and

$$1/[A]_t = kt + 1/[A]_0 \quad \text{integrated rate law}$$

Note that the integrated rate law is a linear equation of the form:

$$y = mx + b$$

A plot of $1/[A]$ versus time will yield a straight line whose slope is the rate constant k as shown in Figure 14.7b.

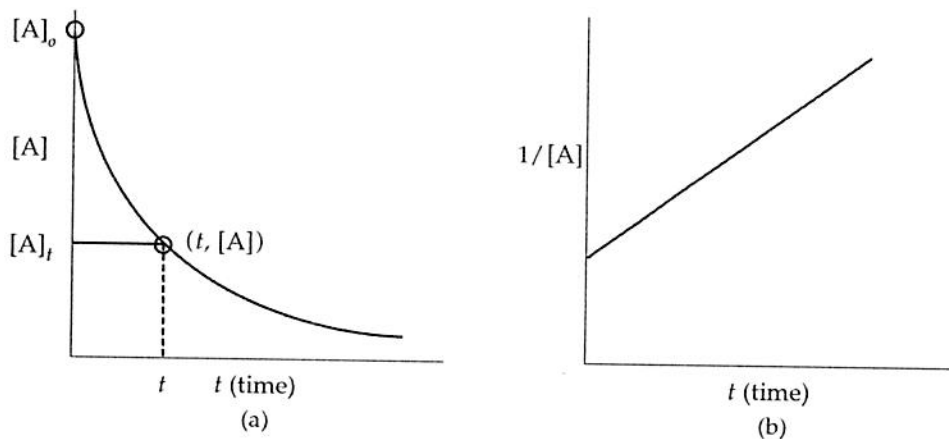


Figure 14.7 a. Plot of $[A]$ versus time for a second-order reaction. b. Plot of $1/[A]$ versus time for a second-order reaction. The slope of the line equals the rate constant.

A second-order reaction is a **bimolecular process**. That is, it depends on the collision of two molecules of reactant to produce a product. In a bimolecular process, collisions between reactant molecules change reactants to products. The **exponent of two** in the rate equation for a second-order reaction,

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

is interpreted to mean that **two molecules** of A collide to produce a reaction.

A **zero-order reaction** is one in which the rate of disappearance of A is independent of the concentration of A: $\text{Rate} = k[A]^0 = k$. A plot of $[A]$ versus time for a zero-order reaction is a straight line as illustrated in Figure 14.8.

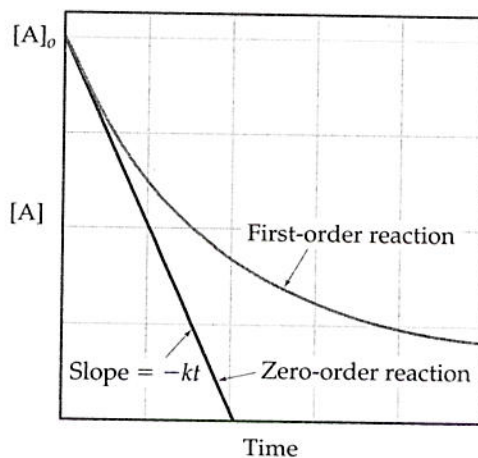


Figure 14.8 Comparison of first-order and zero-order reactions for the disappearance of reactant A with time.