






## 14.5: The Integrated Rate Law: The Dependence of Concentration on Time

### Key Concept Video The Integrated Rate Law

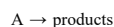
The rate laws we have examined so far show the relationship between *the rate of a reaction and the concentration of a reactant*. But we often want to know the relationship between *the concentration of a reactant and time*. For example, the presence of chlorofluorocarbons (CFCs) in the atmosphere threatens the ozone layer. One of the reasons that CFCs pose such a significant threat is that the reactions that consume them are so slow (see [Table 14.1](#)). Legislation has significantly reduced CFC emissions, but even if we were to completely stop adding CFCs to the atmosphere, their concentration would decrease only very slowly. Nonetheless, we would like to know how their concentration changes with time. How much will be left in 20 years? In 50 years?

Table 14.1 Atmospheric Lifetimes of Several CFCs

CFC Name	Structure	Atmospheric Lifetime*
CFC-11 ( $\text{CCl}_3\text{F}$ ) trichlorofluoromethane		45 years
CFC-12 ( $\text{CCl}_2\text{F}_2$ ) dichlorodifluoromethane		100 years
CFC-113 ( $\text{C}_2\text{F}_3\text{Cl}_3$ ) 1,1,2-trichloro-1,2,2-trifluoroethane		85 years
CFC-114 ( $\text{C}_2\text{F}_4\text{Cl}_2$ ) 1,2-dichlorotetrafluoroethane		300 years
CFC-115 ( $\text{C}_2\text{F}_5\text{Cl}$ ) monochloropentafluoroethane		1700 years

## Integrated Rate Laws

The **integrated rate law** for a chemical reaction is a relationship between the concentrations of the reactants and time. For simplicity, we return to a single reactant decomposing into products:



The integrated rate law for this reaction depends on the order of the reaction; let's examine each of the common reaction orders individually.

### First-Order Integrated Rate Law

If our simple reaction is first order, the rate is directly proportional to the concentration of A:

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

Because  $\text{rate} = -\Delta[A]/\Delta t$ , we can write:

[14.11]

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

In this form, the rate law is also known as the *differential rate law*.

Although we do not show the steps here, we can use calculus (see end-of-chapter [Exercise 114](#)) to integrate the differential rate law and obtain the first-order *integrated rate law*:

[14.12]

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

or

[14.13]

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

where  $[A]_t$  is the concentration of A at any time  $t$ ,  $k$  is the rate constant, and  $[A]_0$  is the initial concentration of A. These two forms of the equation are equivalent.

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

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

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

$$\text{Remember that } \ln A - \ln B = \ln \left( \frac{A}{B} \right).$$

Notice that the integrated rate law shown in [Equation 14.12](#) has the form of an equation for a straight line:

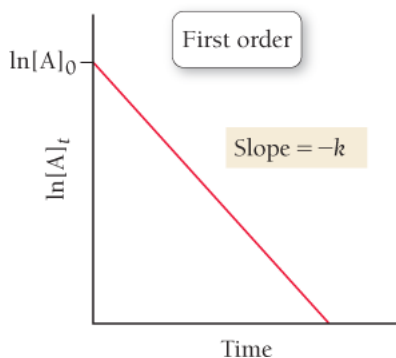
$$\ln[A]_t = -kt + \ln[A]_0$$

$$y = mx + b$$

For a first-order reaction, a plot of the natural log of the reactant concentration as a function of time yields a straight line with a slope of  $-k$  and a  $y$ -intercept of  $\ln[A]_0$ , as shown in [Figure 14.8](#). (Note that the slope is negative but that the rate constant is always positive.)

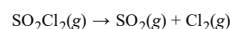
**Figure 14.8 First-Order Integrated Rate Law**

For a first-order reaction, a plot of the natural log of the reactant concentration as a function of time yields a straight line. The slope of the line is equal to  $-k$ , and the  $y$ -intercept is  $\ln[A]_0$ .



### Example 14.3 The First-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

Consider the equation for the decomposition of  $\text{SO}_2\text{Cl}_2$ :



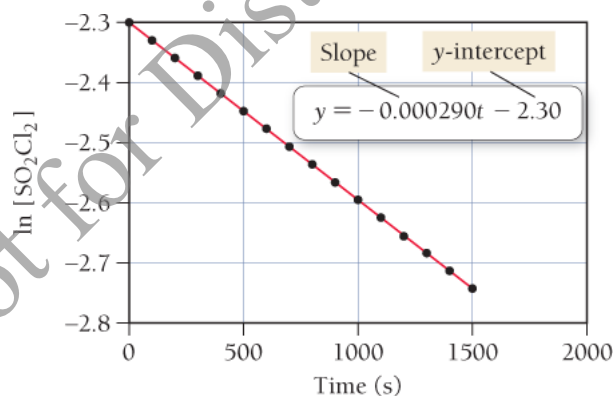
The concentration of  $\text{SO}_2\text{Cl}_2$  is monitored at a fixed temperature as a function of time during the decomposition reaction, and the following data are tabulated:

Time (s)	$[\text{SO}_2\text{Cl}_2]$ (M)	Time (s)	$[\text{SO}_2\text{Cl}_2]$ (M)
0	0.100	800	0.0793
100	0.0971	900	0.0770
200	0.0944	1000	0.0748
300	0.0917	1100	0.0727
400	0.0890	1200	0.0706
500	0.0865	1300	0.0686
600	0.0840	1400	0.0666
700	0.0816	1500	0.0647

Show that the reaction is first order, and determine the rate constant for the reaction.

#### SOLUTION

In order to show that the reaction is first order, prepare a graph of  $\ln[\text{SO}_2\text{Cl}_2]$  versus time as shown.



The plot is linear, confirming that the reaction is indeed first order. To obtain the rate constant, fit the data to a line. The slope of the line will be equal to  $-k$ . Since the slope of the best-fitting line (which is most easily determined on a graphing calculator or with spreadsheet software such as Microsoft Excel) is  $-2.90 \times 10^{-4} \text{ s}^{-1}$ , the rate constant is therefore  $+2.90 \times 10^{-4} \text{ s}^{-1}$ .

**FOR PRACTICE 14.3** Use the graph and the best-fitting line in Example 14.3 to predict the concentration of  $\text{SO}_2\text{Cl}_2$  at 1900 s.

### Example 14.4 The First-Order Integrated Rate Law: Determining the Concentration of a Reactant at a Given Time

In **Example 14.3**, you determined that the decomposition of  $\text{SO}_2\text{Cl}_2$  (under the given reaction conditions) is first order and has a rate constant of  $+2.91 \times 10^{-4} \text{ s}^{-1}$ . If the reaction is carried out at the same temperature and the initial concentration of  $\text{SO}_2\text{Cl}_2$  is 0.0225 M, what is the concentration of  $\text{SO}_2\text{Cl}_2$  after 865 s?

**SORT** You are given the rate constant of a first-order reaction and the initial concentration of the reactant and asked to find the concentration at 865 seconds.

**GIVEN:**

$$k = +2.90 \times 10^{-4} \text{ s}^{-1}$$

$$[\text{SO}_2\text{Cl}_2]_0 = 0.0225 \text{ M}$$

**FIND:**  $[\text{SO}_2\text{Cl}_2]$  at  $t = 865 \text{ s}$

**STRATEGIZE** Refer to the first-order integrated rate law to determine the information you are asked to find.

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

**SOLVE** Substitute the rate constant, the initial concentration, and the time into the integrated rate law.

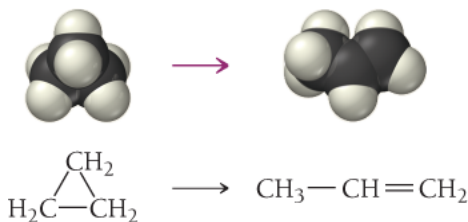
Solve the integrated rate law for the concentration of  $[\text{SO}_2\text{Cl}_2]_t$ .

**SOLUTION**

$$\begin{aligned} \ln[\text{SO}_2\text{Cl}_2]_t &= -kt + \ln[\text{SO}_2\text{Cl}_2]_0 \\ \ln[\text{SO}_2\text{Cl}_2]_t &= -(2.90 \times 10^{-4} \text{ s}^{-1})(865 \text{ s}) + \ln[0.0225] \\ \ln[\text{SO}_2\text{Cl}_2]_t &= -0.251 - 3.79 \\ [\text{SO}_2\text{Cl}_2]_t &= e^{-4.04} \\ &= 0.0175 \text{ M} \end{aligned}$$

**CHECK** The concentration is smaller than the original concentration as expected. If the concentration were larger than the initial concentration, this would indicate a mistake in the signs of one of the quantities on the right-hand side of the equation.

**FOR PRACTICE 14.4** Cyclopropane rearranges to form propene in the gas phase.



The reaction is first order in cyclopropane and has a measured rate constant of  $3.36 \times 10^{-5} \text{ s}^{-1}$  at 720 K. If the initial cyclopropane concentration is 0.0445 M, what is the cyclopropane concentration after 235.0 minutes?

## Second-Order Integrated Rate Law

If our simple reaction ( $A \rightarrow \text{products}$ ) is second order, the rate is proportional to the square of the concentration of A:

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

Because  $\text{rate} = -\Delta[A]/\Delta t$ , we can write:

[14.14]

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

Again, although we do not show the steps here, this differential rate law can be integrated to obtain the *second-order integrated rate law*:

[14.15]

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

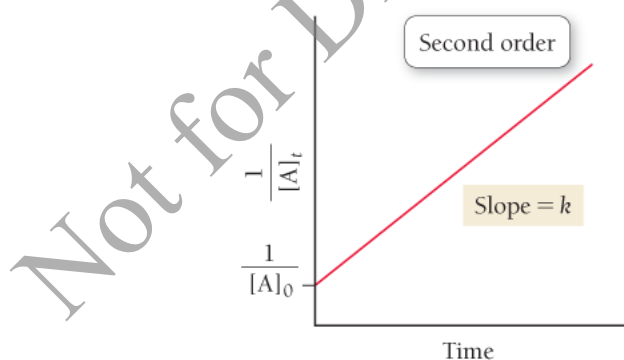
The second-order integrated rate law is also in the form of an equation for a straight line:

$$\begin{aligned} \frac{1}{[A]_t} &= kt + \frac{1}{[A]_0} \\ y &= mx + b \end{aligned}$$

However, you must plot the inverse of the concentration of the reactant as a function of time. The plot yields a straight line with a slope of  $k$  and an intercept of  $1/[A]_0$  as shown in [Figure 14.9](#).

**Figure 14.9 Second-Order Integrated Rate Law**

For a second-order reaction, a plot of the inverse of the reactant concentration as a function of time yields a straight line. The slope of the line is equal to  $k$ , and the  $y$ -intercept is  $1/[A]_0$ .

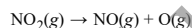


Time (s)	[NO <sub>2</sub> ] (M)
0	0.01000
50	0.00887
100	0.00797
150	0.00723
200	0.00662
250	0.00611
300	0.00567

350	0.00528
400	0.00495
450	0.00466
500	0.00440
550	0.00416
600	0.00395
650	0.00376
700	0.00359
750	0.00343
800	0.00329
850	0.00316
900	0.00303
950	0.00292
1000	0.00282

### Example 14.5 The Second-Order Integrated Rate Law: Using Graphical Analysis of Reaction Data

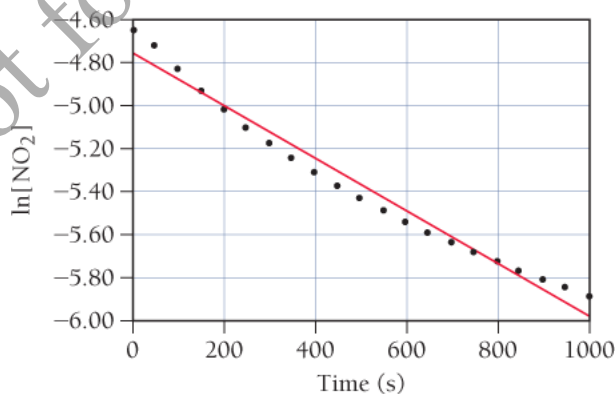
Consider the equation for the decomposition of  $\text{NO}_2$ :



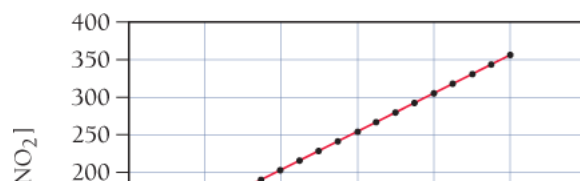
The concentration of  $\text{NO}_2$  is monitored at a fixed temperature as a function of time during the decomposition reaction, and the data are tabulated in the table above. Show by graphical analysis that the reaction is not first order and that it is second order. Determine the rate constant for the reaction.

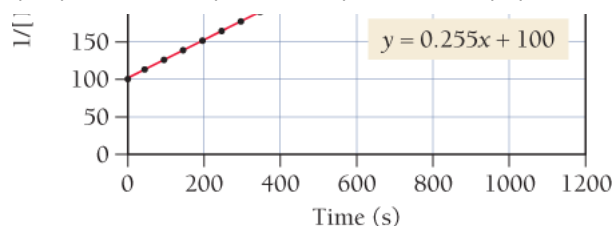
#### SOLUTION

To show that the reaction is not first order, prepare a graph of  $\ln[\text{NO}_2]$  versus time as shown:



The plot is *not* linear (the straight line does not fit the data points), confirming that the reaction is not first order. In order to show that the reaction is second order, prepare a graph of  $1/[\text{NO}_2]$  versus time as shown:





This graph is linear (the data points fit well to a straight line), confirming that the reaction is indeed second order. To obtain the rate constant, determine the slope of the best-fitting line. The slope is  $0.255 \text{ M}^{-1} \cdot \text{s}^{-1}$ ; therefore, the rate constant is  $0.255 \text{ M}^{-1} \cdot \text{s}^{-1}$ .

**FOR PRACTICE 14.5** Use the graph and the best-fitting line in [Example 14.5](#) to predict the concentration of  $\text{NO}_2$  at 2000 s.

## Zero-Order Integrated Rate Law

If our simple reaction is zero order, the rate is proportional to a constant:

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

Since  $\text{rate} = -\Delta[\text{A}]/\Delta t$ , we can write:

[14.16]

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

We can integrate this differential rate law to obtain the *zero-order integrated rate law*:

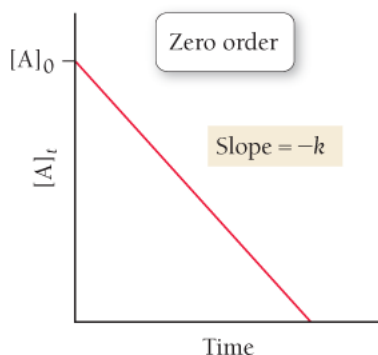
[14.17]

$$[\text{A}]_t = -kt + [\text{A}]_0$$

The zero-order integrated rate law in [Equation 14.17](#) is also in the form of an equation for a straight line. A plot of the concentration of the reactant as a function of time yields a straight line with a slope of  $-k$  and an intercept of  $[\text{A}]_0$ , as shown in [Figure 14.10](#).

**Figure 14.10 Zero-Order Integrated Rate Law**

For a zero-order reaction, a plot of the reactant concentration as a function of time yields a straight line. The slope of the line is equal to  $-k$ , and the  $y$ -intercept is  $[\text{A}]_0$ .



## The Half-Life of a Reaction

The **half-life** ( $t_{1/2}$ ) of a reaction is the time required for the concentration of a reactant to fall to one-half of its initial value. For example, if a reaction has a half-life of 100 seconds, and if the initial concentration of the reactant is 1.0 M, the concentration will fall to 0.50 M in 100 s. The half-life expression—which defines the dependence of half-life on the rate constant and the initial concentration—is different for different reaction orders.

## First-Order Reaction Half-Life

From the definition of half-life, and from the integrated rate law, we can derive an expression for the half-life.

For a first-order reaction, the integrated rate law is:

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

At a time equal to the half-life ( $t = t_{1/2}$ ), the concentration is exactly half of the initial concentration:

$\left([A]_t = \frac{1}{2}[A]_0\right)$ . Therefore, when  $t = t_{1/2}$  we can write the following expression:

[14.18]

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

Solving for  $t_{1/2}$ , and substituting  $-0.693$  for  $\ln \frac{1}{2}$ , we arrive at the expression for the half-life of a first-order reaction:

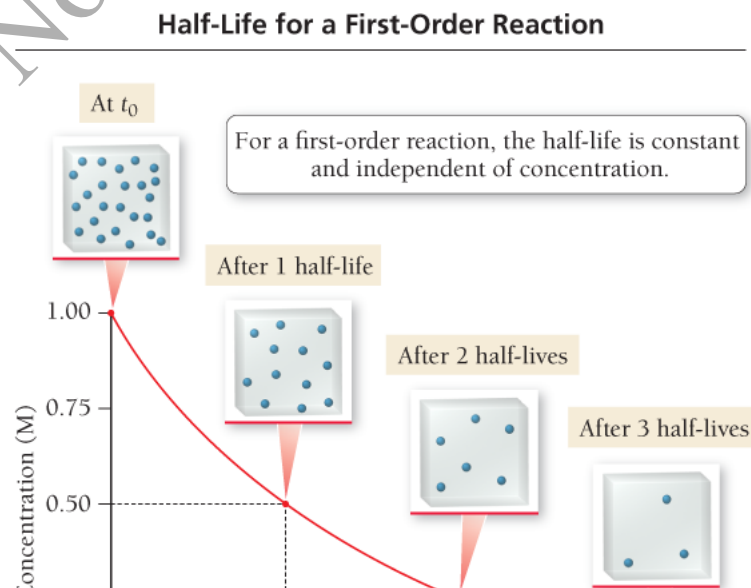
[14.19]

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

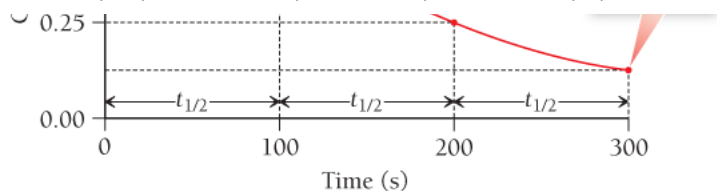
Notice that, for a first-order reaction,  $t_{1/2}$  is independent of the initial concentration. For example, if  $t_{1/2}$  is 100 s, and if the initial concentration is 1.0 M, the concentration falls to 0.50 M in 100 s, to 0.25 M in another 100 s, to 0.125 M in another 100 s, and so on (Figure 14.11). Even though the concentration is changing as the reaction proceeds, the half-life (how long it takes for the concentration to halve) is constant. A constant half-life is unique to first-order reactions, making the concept of half-life particularly useful for first-order reactions.

**Figure 14.11 Half-Life: Concentration versus Time for a First-Order Reaction**

For this reaction, the concentration decreases by one-half every 100 seconds ( $t_{1/2} = 100$  s). The blue spheres represent reactant molecules (the products are omitted for clarity).







### Example 14.6 Determining Half-Life for a First-Order Reaction

Molecular iodine dissociates at 625 K with a first-order rate constant of  $0.271 \text{ s}^{-1}$ . What is the half-life of this reaction?

#### SOLUTION

Because the reaction is first order, the half-life is given by Equation 14.19. Substitute the value of  $k$  into the expression and calculate  $t_{1/2}$ .

$$\begin{aligned} t_{1/2} &= \frac{0.693}{k} \\ &= \frac{0.693}{0.271/\text{s}} = 2.56 \text{ s} \end{aligned}$$

**FOR PRACTICE 14.6** A first-order reaction has a half-life of 26.4 seconds. How long does it take for the concentration of the reactant in the reaction to fall to one-eighth of its initial value?

## Second-Order Reaction Half-Life

For a second-order reaction, the integrated rate law is:

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

At a time equal to the half-life ( $t = t_{1/2}$ ), the concentration is exactly one-half of the initial concentration

( $[A]_t = \frac{1}{2}[A]_0$ ). We can therefore write the following expression at  $t = t_{1/2}$ :

[14.20]

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

And solve for  $t_{1/2}$ :

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

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

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

[14.21]

Notice that, for a second-order reaction, the half-life depends on the initial concentration. So if the initial concentration of a reactant in a second-order reaction is 1.0 M, and the half-life is 100 s, the concentration falls to 0.50 M in 100 s. However, the time it takes for the concentration to fall to 0.25 M is now *longer than 100 s* because the initial concentration has decreased. Thus, the half-life continues to get longer as the concentration decreases.

## Zero-Order Reaction Half-Life

For a zero-order reaction, the integrated rate law is:

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

Making the substitutions  $(t = t_{1/2}; [A]_t = \frac{1}{2}[A]_0)$ , we can write the expression at  $t = t_{1/2}$ :

[14.22]

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

We then solve for  $t_{1/2}$ :

[14.23]

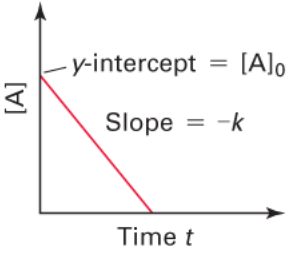
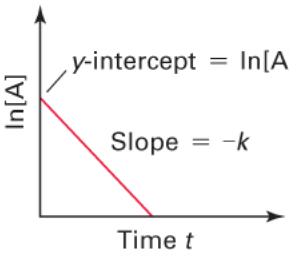
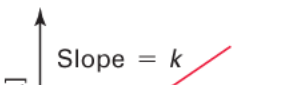
$$t_{1/2} = \frac{[A]_0}{2k}$$

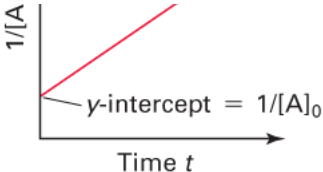
Notice that, for a zero-order reaction, the half-life also depends on the initial concentration; however, unlike in the second-order case, the two are directly proportional—the half-life gets *shorter* as the concentration decreases.

Summarizing Basic Kinetic Relationships (see **Table 14.2**):

- The reaction order and rate law must be determined experimentally.
- The rate law relates the *rate* of the reaction to the *concentration* of the reactant(s).
- The integrated rate law (which is mathematically derived from the rate law) relates the *concentration* of the reactant(s) to *time*.
- The half-life is the time it takes for the concentration of a reactant to fall to one-half of its initial value.
- The half-life of a first-order reaction is independent of the initial concentration.
- The half-lives of zero-order and second-order reactions depend on the initial concentration.

**Table 14.2 Rate Law Summary Table**

Order	Rate Law	Units of $k$	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate = $k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$		$t_{1/2} = \frac{[A]_0}{2k}$
1	Rate = $k[A]^1$	$s^{-1}$	$\ln[A]_t = -kt + \ln[A]_0$ $\ln \frac{[A]_t}{[A]_0} = -kt$		$t_{1/2} = \frac{\ln 2}{k}$
2	Rate = $k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ $\ln \frac{[A]_0}{[A]_t} = kt$		$t_{1/2} = \frac{1}{k[A]_0}$

2	$\text{Rate} = k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$		$t_{1/2} = \frac{1}{k[A]_0}$
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**Conceptual Connection 14.5 Rate Law and Integrated Rate Law**

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