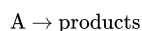*©September 12, 2017 10:35 am*

14.4: The Rate Law: The Effect of Concentration on Reaction Rate

Key Concept Video   The Rate Law for a Chemical Reaction

As we saw in Section 14.2, the rate of a reaction often depends on the concentration of one or more of the reactants. For simplicity, let's consider a reaction in which a single reactant, A, decomposes into products:

$$A \rightarrow products$$

As long as the rate of the reverse reaction (in which the products return to reactants) is negligibly slow, we can express the relationship between the rate of the reaction and the concentration of the reactant—called the **rate law**—as follows:

[14.6]

$$rate = k[A]^n$$

where *k* is a constant of proportionality called the **rate constant** and *n* is the **reaction order**. The value of *n* (usually an integer) determines how the rate depends on the concentration of the reactant:

- If $n = 0$, the reaction is *zero order* and the rate is independent of the concentration of A.
- If $n = 1$, the reaction is *first order* and the rate is directly proportional to the concentration of A.
- If $n = 2$, the reaction is *second order* and the rate is proportional to the square of the concentration of A.

Although other orders are possible, including noninteger (or fractional) orders, we limit our current discussion to three orders.

> By definition, $[A]^0 = 1$, so the rate is equal to *k* regardless of [A].

Reaction Orders

Figure 14.5 shows three plots illustrating how the *concentration of A changes with time* for the three common reaction orders with identical numerical values for the rate constant (*k*) and identical initial concentrations. Figure 14.6 has three plots showing the *rate of the reaction* (the slope of the lines in Figure 14.5) *as a function of the reactant concentration* for each reaction order.

Figure 14.5   Reactant Molar Concentration as a Function of Time for Different Reaction Orders

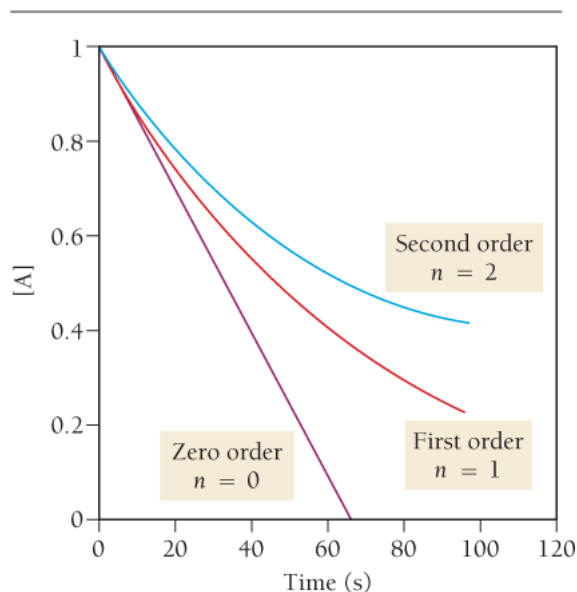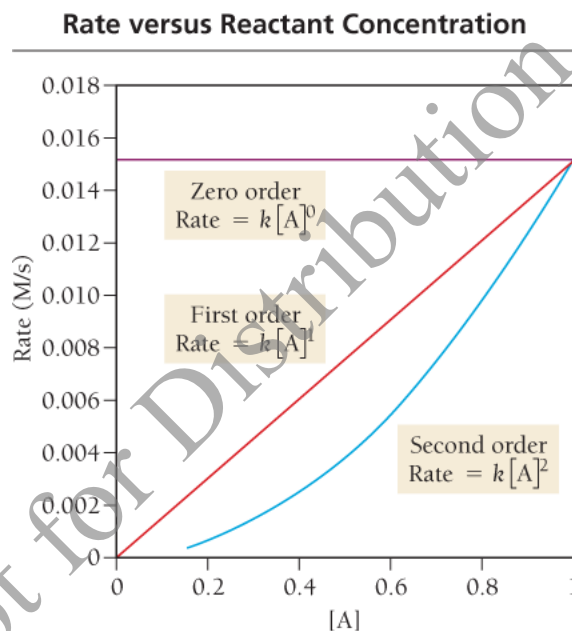## Reactant Concentration versus Time

Figure 14.6 Reaction Rate as a Function of Reactant Molar Concentration for Different Reaction Orders

Zero-Order Reaction

In a zero-order reaction, the rate of the reaction is independent of the concentration of the reactant:
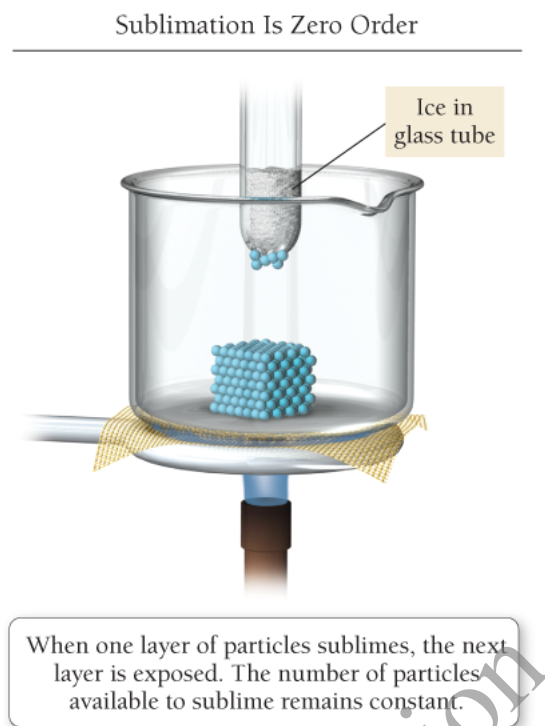
[14.7]

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

Consequently, for a zero-order reaction, the concentration of the reactant decreases linearly with time, as shown in Figure 14.5. The slope of the line is constant, indicating a constant rate. The rate is constant because the reaction does not slow down as the concentration of A decreases. The graph in Figure 14.6 shows that the rate of a zero-order reaction is the same at any concentration of A. Zero-order reactions occur under conditions where the amount of reactant actually *available for reaction* is unaffected by changes in the *overall quantity of reactant*. For example, sublimation is normally zero order because only molecules at the surface can sublime, and their concentration does not change as the amount of

subliming substance decreases (Figure 14.7).

Figure 14.7   Sublimation

Sublimation Is Zero Order

Ice in glass tube

When one layer of particles sublimes, the next layer is exposed. The number of particles available to sublime remains constant.

First-Order Reaction

In a first-order reaction, the rate of the reaction is directly proportional to the concentration of the reactant:

[14.8]

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

For a first-order reaction, the rate slows down as the reaction proceeds because the concentration of the reactant decreases. You can see this in Figure 14.5 —the slope of the curve (the rate) becomes less steep (slower) with time. Figure 14.6 shows the rate as a function of the concentration of A. Notice the linear relationship—the rate is directly proportional to the concentration.

Second-Order Reaction

In a second-order reaction, the rate of the reaction is proportional to the square of the concentration of the reactant:

[14.9]

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

Consequently, for a second-order reaction, the rate is even more sensitive to the reactant concentration. You can see this in Figure 14.5 —the slope of the curve (the rate) flattens out more quickly than it does for a first-order reaction. Figure 14.6 shows the rate as a function of the concentration of A. Notice the quadratic relationship—the rate is proportional to the square of the concentration.

Determining the Order of a Reaction

The order of a reaction can be determined only by experiment. A common way to determine reaction order is the *method of initial rates*. In this method, the initial rate—the rate for a short period of time at the beginning of the reaction—is measured by running the reaction several times with different initial reactant concentrations to determine the effect of the concentration on the rate.

For example, let's return to our simple reaction in which a single reactant, A, decomposes into products:

$$A \rightarrow \text{products}$$
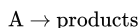
In an experiment, the initial rate is measured at several different initial concentrations with the following results:

[A] (M)	Initial Rate (M/s)
0.10	0.015
0.20	0.030
0.40	0.060

In this data set, when the concentration of A doubles, the rate doubles—the initial rate is directly proportional to the initial concentration. The reaction is therefore first order in A, and the rate law takes the first-order form:

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

We can determine the value of the rate constant, k, by solving the rate law for k and substituting the concentration and the initial rate from any one of the three measurements (here we use the first measurement):

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

$$k = \frac{\text{rate}}{[A]} = \frac{0.015 \text{ M/s}}{0.10 \text{ M}} = 0.15 \text{ s}^{-1}$$

Notice that the rate constant for a first-order reaction has units of s^{-1}.

The following two data sets show how measured initial rates are different for zero-order and for second-order reactions having the same initial rate at $[A] = 0.10$ M

Zero Order ($n = 0$)

[A] (M)	Initial Rate (M/s)
0.10	0.015
0.20	0.015
0.40	0.015

Second Order ($n = 2$)

[A] (M)	Initial Rate (M/s)
0.10	0.015
0.20	0.060
0.40	0.240

| 0.40 | | 0.240 |

For a zero-order reaction, the initial rate is independent of the reactant concentration—the rate is the same at all measured initial concentrations. For a second-order reaction, the initial rate quadruples for a doubling of the reactant concentration—the relationship between concentration and rate is quadratic. If we are unsure about how the initial rate is changing with the initial reactant concentration, or if the numbers are not as obvious as they are in these examples, we can substitute any two initial concentrations and the corresponding initial rates into a ratio of the rate laws to determine the order (n):

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{k[\text{A}]_2^n}{k[\text{A}]_1^n}$$

For example, we can substitute the last two measurements in the data set just given for the second-order reaction as follows:

$$\frac{0.240\ \text{M/s}}{0.060\ \text{M/s}} = \frac{k\left(0.40\ \text{M}\right)^n}{k\left(0.20\ \text{M}\right)^n}$$

$$4.0 = \left(\frac{0.40}{0.20}\right)^n = 2^n$$

$$\log 4.0 = \log\left(2^n\right)$$

$$= n \log 2$$

$$n = \frac{\log 4}{\log 2}$$

$$= 2$$

| Remember that $\dfrac{x^n}{y^n} = \left(\dfrac{x}{y}\right)^n$.

| Remember that $\log x^n = n \log x$

The rate constants for zero- and second-order reactions have different units than for first-order reactions. The rate constant for a zero-order reaction has units of $\text{M} \cdot \text{S}^{-1}$, and the rate constant for a second-order reaction has units of $\text{M}^{-1} \cdot \text{S}^{-1}$.

Conceptual Connection 14.3   Order of Reaction

Reaction Order for Multiple Reactants

So far, we have considered a simple reaction with only one reactant. How is the rate law defined for reactions with more than one reactant? Consider the generic reaction:

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$
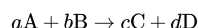
As long as the reverse reaction is negligibly slow, the rate law is proportional to the concentration of [A] raised to the m power multiplied by the concentration of [B] raised to the n power:

[14.10]

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

where m is the reaction order with respect to A and n is the reaction order with respect to B. The **overall order** is the sum of the exponents $(m + n)$. For example, the reaction between hydrogen and iodine has been experimentally determined to be first order with respect to hydrogen, first order with respect to iodine, and thus second order overall:

$$H_2\,(g) + I_2\,(g) \rightarrow 2\,HI\,(g) \quad rate = k[H_2]^1[I_2]^1$$
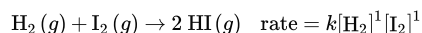
Similarly, the reaction between hydrogen and nitrogen monoxide has been experimentally determined to be first order with respect to hydrogen, second order with respect to nitrogen monoxide, and thus third order overall:

$$2\,H_2\,(g) + 2\,NO\,(g) \rightarrow N_2\,(g) + 2\,H_2O\,(g) \quad rate = k[H_2]^1[NO]^2$$
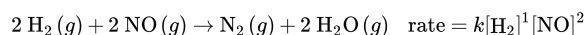
As we have already noted, the rate law for any reaction must always be determined by experiment, often by the method of initial rates described previously. There is no way to simply look at a chemical equation and determine the rate law for the reaction. When the reaction has two or more reactants, the concentration of each reactant is usually varied independently of the others to determine the dependence of the rate on the concentration of that reactant. Example 14.2 ▢ shows how to use the method of initial rates to determine the order of a reaction with multiple reactants.

Example 14.2 Determining the Order and Rate Constant of a Reaction

Consider the reaction between nitrogen dioxide and carbon monoxide:

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$
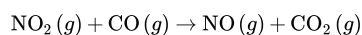
The initial rate of the reaction is measured at several different concentrations of the reactants with the results shown at right.

From the data, determine:

  a. the rate law for the reaction
  b. the rate constant (k) for the reaction

Experiment Number	[NO$_2$] (M)	[CO] (M)	Initial Rate (M/s)
1	0.10	0.10	0.0021
2	0.20	0.10	0.0082
3	0.20	0.20	0.0083
4	0.40	0.10	0.033

SOLUTION

  a. Begin by examining how the rate changes for each change in concentration. Between the first two experiments, the concentration of NO$_2$ doubles, the concentration of CO stays constant, and the rate quadruples, suggesting that the reaction is second order in NO$_2$. Between the second and third experiments, the concentration of NO$_2$ stays constant, the concentration of CO doubles, and the rate remains constant (the small change in the least significant figure is simply experimental error), suggesting that the reaction is zero order in CO.

  Between the third and fourth experiments, the concentration of NO$_2$ again doubles and the concentration of CO halves, yet the rate quadruples again, confirming that the reaction is second order in NO$_2$ and zero order in CO.

  Write the overall rate expression.

[NO$_2$] (M)	[CO] (M)	Initial Rate (M/s)

0.10 M   0.10 M   0.0021

$\downarrow \times 2$ $\downarrow$ constant $\downarrow \times 4$

0.20 M   0.10 M   0.0082 M

$\downarrow$ constant $\downarrow \times 2$ $\downarrow \times 1$

0.20 M   0.20 M   0.0083 M

$\downarrow \times 2$ $\downarrow \times \frac{1}{2}$ $\downarrow \times 4$

0.40 M   0.10 M   0.033 M

$$\text{rate} = k[NO_2]^2[CO]^0 = k[NO_2]^2$$

---

a. ALTERNATIVE APPROACH

If you can't easily see the relationships between the changes in concentrations and the changes in initial rates, you can determine the reaction order for any reactant by substituting any two initial rates and the corresponding initial concentrations into a ratio of the rate laws to determine the order (n).

For NO_2 use the first and second concentrations and rates (because $[NO_2]$ changes here, but $[CO]$ is constant).

Substitute the rates and concentrations into the expression for the ratio of the rate constants.

Take the log of both sides of the equation and solve for n.

For CO, use the second and third concentrations and rates (because $[CO]$ changes here, but $[NO_2]$ is constant).

Substitute the rates and concentrations into the expression for the ratio of the rate constants.

Take the log of both sides of the equation and solve for n.

Write the overall rate expression from the orders of each reactant.

$$\frac{\text{rate } 2}{\text{rate } 1} = \frac{k[A]_2^n}{k[A]_1^n}$$

$$\text{For } NO_2 \quad \frac{\text{rate } 2}{\text{rate } 1} = \frac{k[NO_2]_2^n}{k[NO_2]_1^n}$$

$$\frac{0.082 \text{ M/s}}{0.021 \text{ M/s}} = \frac{k\left(0.20 \text{ M}\right)^n}{k\left(0.10 \text{ M}\right)^n}$$

$$3.9 = \left(\frac{0.20}{0.10}\right)^n = 2^n$$

$$\log 3.9 = \log 2^n$$
$$= n \log 2$$
$$n = \frac{\log 3.9}{\log 2}$$
$$= 1.9\underline{6} = 2$$

$$\text{For CO} \quad \frac{\text{rate } 3}{\text{rate } 2} = \frac{k[CO]_3^n}{k[CO]_2^n}$$

$$\frac{0.083 \text{ M/s}}{0.082 \text{ M/s}} = \frac{k\left(0.20 \text{ M}\right)^n}{k\left(0.10 \text{ M}\right)^n}$$

$$1.01 = \left(\frac{0.20}{0.10}\right)^n = 2^n$$

$$\left(\dfrac{\ }{0.10}\right)$$

$$
\begin{aligned}
\log 1.01 &= \log 2^n \\
&= n \log 2 \\
n &= \dfrac{\log 1.01}{\log 2} \\
&= 0.01 = 0.0
\end{aligned}
$$

$$\text{rate} = k[NO_2]^2[CO]^0 = k[NO_2]^2$$

b. To determine the rate constant the reaction, solve the rate law for k and substitute the concentration and the initial rate from any one of the four measurements. In this case, we use the first measurement.

$$
\begin{aligned}
\text{rate} &= k[NO_2]^2 \\
k &= \dfrac{\text{rate}}{[NO_2]^2} = \dfrac{0.0021 \text{ M/s}}{(0.10 \text{ M})^2} = 0.21 \text{ M}^{-1} \cdot \text{s}^{-1}
\end{aligned}
$$

FOR PRACTICE 14.2　Consider the equation:

$$CHCl_3\,(g) + Cl_2\,(g) \rightarrow CCl_4\,(g) + HCl\,(g)$$
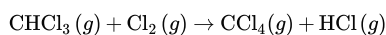
The initial rate of reaction is measured at several different concentrations of the reactants with the following results:

$[CHCl_3]$ (M)	$[Cl_2]$ (M)	Initial Rate (M/s)
0.010	0.010	0.0035
0.020	0.010	0.0069
0.020	0.020	0.0098
0.040	0.040	0.027

From the data, determine:

a. the rate law for the reaction
b. the rate constant (k) for the reaction

Interactive Worked Example 14.2　**Determining the Order and Rate Constant of a Reaction**

Conceptual Connection 14.4　**Rate and Concentration**

Interactive