Expressing and Measuring Reaction Rates

As you learned in the Unit 3 opener, nitroglycerin is an explosive that was used to clear the way for railroads across North America. It decomposes instantly. The reactions that cause fruit to ripen, then rot, take place over a period of days. The reactions that lead to human ageing take place over a lifetime.

How quickly a chemical reaction occurs is a crucial factor in how the reaction affects its surroundings. Therefore, knowing the rate of a chemical reaction is integral to understanding the reaction.

Expressing Reaction Rates

The change in the amount of reactants or products over time is called the reaction rate. How do chemists express reaction rates? Consider how the rates of other processes are expressed. For example, the Olympic sprinter in Figure 6.1 can run 100 m in about 10 s, resulting in an average running rate of 100 m/10 s or about 10 m/s.

The running rate of a sprinter is calculated by dividing the distance travelled by the interval of time the sprinter takes to travel this distance. In other words, running rate (speed) is expressed as a change in distance divided by a change in time. In general, a change in a quantity with respect to time can be expressed as follows.

\[
\text{Rate} = \frac{\text{Change in quantity}}{\text{Change in time}} = \frac{\text{Quantity}_{\text{final}} - \text{Quantity}_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} = \frac{\Delta \text{Quantity}}{\Delta t}
\]

Chemists express reaction rates in several ways. For example, a reaction rate can be expressed as a change in the amount of reactant consumed or product made per unit of time, as shown below. (The letter A represents a compound.)

\[
\text{Rate of reaction} = \frac{\text{Amount of } A_{\text{final}} - \text{Amount of } A_{\text{initial}} (\text{in mol})}{t_{\text{final}} - t_{\text{initial}} (\text{in s})} = \frac{\Delta \text{Amount of } A}{\Delta t} (\text{in mol/s})
\]

When a reaction occurs between gaseous species or in solution, chemists usually express the reaction rate as a change in the concentration of the reactant or product per unit time. Recall, from your previous chemistry course, that the concentration of a compound (in mol/L) is symbolized by placing square brackets, [ ], around the chemical formula. The equation below is the equation you will work with most often in this section.

\[
\text{Rate of reaction} = \frac{\text{Concentration of } A_{\text{final}} - \text{Concentration of } A_{\text{initial}} (\text{in mol/L})}{t_{\text{final}} - t_{\text{initial}} (\text{in s})} = \frac{\Delta [A]}{\Delta t} (\text{in mol/(L \cdot s)})
\]
 Reaction rates are always positive, by convention. A rate that is expressed as the change in concentration of a product is the rate at which the concentration of the product is increasing. The rate that is expressed in terms of the change in concentration of a reactant is the rate at which the concentration of the reactant is decreasing.

Average and Instantaneous Rates of Reactions

If reactions always proceeded at a constant rate, it would be straightforward to find reaction rates. You would just need the initial and final concentrations and the time interval. Reaction rates, however, are not usually constant. They change with time. How does this affect the way that chemists determine reaction rates?

Consider the following reaction.

\[ \text{A}_g \rightarrow \text{C}_g + \text{D}_g \]

Now examine the graph in Figure 6.2. The blue line on the graph shows the concentration of product C as the reaction progresses, based on the data in Table 6.1.

### Table 6.1 Concentration of C During a Reaction at Constant Temperature

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[C] (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>5.0</td>
<td>3.12 \times 10^{-3}</td>
</tr>
<tr>
<td>10.0</td>
<td>4.41 \times 10^{-3}</td>
</tr>
<tr>
<td>15.0</td>
<td>5.40 \times 10^{-3}</td>
</tr>
<tr>
<td>20.0</td>
<td>6.24 \times 10^{-3}</td>
</tr>
</tbody>
</table>

The **average rate** of a reaction is the average change in the concentration of a reactant or product per unit time over a given time interval. For example, using the data in Table 6.1, you can determine the average rate of the reaction from \( t = 0.0 \text{ s} \) to \( t = 5.0 \text{ s} \).

\[
\text{Average rate} = \frac{\Delta [C]}{\Delta t} = \frac{(3.12 \times 10^{-3} \text{ mol/L}) - 0.00 \text{ mol/L}}{5.0 \text{ s} - 0.0 \text{ s}} = 6.2 \times 10^{-4} \text{ mol/(L \cdot s)}
\]

You can see this calculation in Figure 6.2. On a concentration-time graph, the average rate of a reaction is represented by the slope of a line that is drawn between two points on the curve. This line is called a **secant**.

The average rate of a reaction gives an overall idea of how quickly the reaction is progressing. It does not, however, tell you how fast the reaction is progressing at a specific time. For example, suppose that someone asked you how fast the reaction in Figure 6.2 was progressing over 20.0 s. You would probably calculate the average rate from \( t = 0.0 \text{ s} \) to \( t = 20.0 \text{ s} \). You would come up with the answer \( 3.12 \times 10^{-3} \text{ mol/(L \cdot s)} \). (Try this calculation yourself.) What would you do, however, if you were asked how fast the reaction was progressing at exactly \( t = 10.0 \text{ s} \)?

The **instantaneous rate** of a reaction is the rate of the reaction at a particular time. To find the instantaneous rate of a reaction using a concentration-time graph, draw a tangent line to the curve and find the slope of the tangent. A **tangent** line is like a secant line, but it touches the curve at only one point. It does not intersect the curve.
The slope of the tangent is the instantaneous rate of the reaction. Figure 6.2 shows the tangent line at \( t = 10.0 \) s. As shown on the graph, the slope of the tangent (therefore the instantaneous rate) at \( t = 10.0 \) s is \( 2.3 \times 10^{-4} \text{ mol/(L \cdot s)} \).

Notice that near the beginning of the reaction, when the concentration of the reactants is relatively high, the slope of the tangent is greater (steeper). This indicates a faster reaction rate. As the reaction proceeds, the reactants are used up and the slope of the tangent decreases.

In your previous courses in science or physics, you probably learned the difference between instantaneous velocity and average velocity. How did you use a displacement-time graph to determine instantaneous velocity and average velocity? Write a memo that explains instantaneous rate and average rate to a physicist, by comparing reaction rate with velocity.

In the following ThoughtLab, you will use experimental data to draw a graph that shows the change in concentration of the product of a reaction. Then you will use the graph to help you determine the instantaneous rate and average rate of the reaction.
A chemist carried out a reaction to trace the rate of decomposition of dinitrogen pentoxide.

\[ 2\text{N}_2\text{O}_5 (g) \rightarrow 4\text{NO}_2 (g) + \text{O}_2 (g) \]

The chemist collected the following data at a constant temperature.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>([\text{O}_2]) (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>6.00 \times 10^2</td>
<td>2.1 \times 10^{-3}</td>
</tr>
<tr>
<td>1.20 \times 10^3</td>
<td>3.6 \times 10^{-3}</td>
</tr>
<tr>
<td>1.80 \times 10^3</td>
<td>4.8 \times 10^{-3}</td>
</tr>
<tr>
<td>2.40 \times 10^3</td>
<td>5.6 \times 10^{-3}</td>
</tr>
<tr>
<td>3.00 \times 10^3</td>
<td>6.4 \times 10^{-3}</td>
</tr>
<tr>
<td>3.60 \times 10^3</td>
<td>6.7 \times 10^{-3}</td>
</tr>
<tr>
<td>4.20 \times 10^3</td>
<td>7.1 \times 10^{-3}</td>
</tr>
<tr>
<td>4.80 \times 10^3</td>
<td>7.5 \times 10^{-3}</td>
</tr>
<tr>
<td>5.40 \times 10^3</td>
<td>7.7 \times 10^{-3}</td>
</tr>
<tr>
<td>6.00 \times 10^3</td>
<td>7.8 \times 10^{-3}</td>
</tr>
</tbody>
</table>

**Procedure**

1. Using graph paper or spreadsheet software, plot and label a graph that shows the rate of formation of oxygen gas. The concentration of \( \text{O}_2 \) (in mol/L) is the dependent variable and time (in s) is the independent variable.

2. Draw a secant to the curve in the interval from \( t = 0 \) s to \( t = 4800 \) s.

3. Draw a tangent to the curve at \( t = 1200 \) s and at \( t = 4800 \) s.

4. Determine the slope of the secant. What is the average rate of the reaction over the given time interval? Include proper units, and pay attention to significant digits.

5. Determine the slope of each tangent. What is the instantaneous reaction rate at \( t = 1200 \) s and at \( t = 4800 \) s? Include proper units, and pay attention to significant digits.

**Analysis**

1. Why are the units for the average rate and the instantaneous rate the same?

2. For a given set of data, two students determined different average reaction rates. If neither student made an error in the calculations, account for the difference in their reaction rates.

3. Propose a reason for the difference in the instantaneous rates at 1200 s and 4800 s.

4. When chemists compare the rates of reactions carried out under different conditions, they often compare the rates near the beginning of the reactions. What advantage(s) do you see in this practice? Hint: Think of slow reactions.

**Reaction Rates in Terms of Products and Reactants**

In the ThoughtLab, you analyzed the rate of the following reaction in terms of the production of oxygen.

\[ 2\text{N}_2\text{O}_5 (g) \rightarrow 4\text{NO}_2 (g) + \text{O}_2 (g) \]

There are two other ways to represent the rate of this reaction:

- in terms of the rate of the disappearance of dinitrogen pentoxide
- in terms of the production of nitrogen dioxide

For every 1 mol of \( \text{O}_2 \) that is produced, 4 mol of \( \text{NO}_2 \) are also produced. This means that the rate of production of \( \text{NO}_2 \) is four times greater than the rate of production of \( \text{O}_2 \). Therefore, the rate of production of \( \text{O}_2 \) is one quarter the rate of production of \( \text{NO}_2 \). You can express the relationship between \( \text{O}_2 \) production and \( \text{NO}_2 \) production as follows:

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

When 1 mol of \( \text{O}_2 \) is produced, 2 mol of \( \text{N}_2\text{O}_5 \) are consumed. Therefore, the rate of production of \( \text{O}_2 \) is half the rate of disappearance of \( \text{N}_2\text{O}_5 \). You can represent this relationship as follows:

\[ \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \]
Notice that the expression involving N₂O₅ (the reactant) has a negative sign. A change in concentration is calculated using the expression below.

\[ \text{Change in concentration} = \text{Concentration}_{\text{final}} - \text{Concentration}_{\text{initial}} \]

Since the concentration of a reactant always decreases as a reaction progresses, the change in concentration is always negative. By convention, however, a rate is always expressed as a positive number. Therefore, expressions that involve reactants must be multiplied by \(-1\) to become positive.

Examine the Sample Problem below to see how to express reaction rates in terms of products and reactants. Then try the Practice Problems that follow.

**Sample Problem**

**Expressing Reaction Rates**

**Problem**

Dinitrogen pentoxide, N₂O₅, decomposes to form nitrogen dioxide and oxygen.

\[ 2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g) \]

NO₂ is produced at a rate of \(5.0 \times 10^{-6}\) mol/(L \(\cdot\) s). What is the corresponding rate of disappearance of N₂O₅ and rate of formation of O₂?

**What Is Required?**

Since N₂O₅ is a reactant, you need to calculate its rate of disappearance. O₂ is a product, so you need to find its rate of formation.

**What Is Given?**

You know the rate of formation of NO₂ and the balanced chemical equation.

**Plan Your Strategy**

First check that the chemical equation is balanced. Then use the molar coefficients in the balanced equation to determine the relative rates of disappearance and formation.

Since 4 mol of NO₂ are produced for every 2 mol of N₂O₅ that decompose, the rate of disappearance of N₂O₅ is \(\frac{2}{4}\), or \(\frac{1}{2}\), the rate of formation of NO₂. Similarly, 1 mol of O₂ is formed for every 4 mol of NO₂. Therefore, the rate of production of O₂ is \(\frac{1}{4}\) the rate of NO₂ production.

**Act on Your Strategy**

Rate of disappearance of N₂O₅ = \(\frac{1}{2}\) \(\times\) \(5.0 \times 10^{-6}\) mol/(L \(\cdot\) s)

\[ = 2.5 \times 10^{-6}\text{ mol/(L }\cdot\text{s)} \]

Rate of production of O₂ = \(\frac{1}{4}\) \(\times\) \(5.0 \times 10^{-6}\) mol/(L \(\cdot\) s)

\[ = 1.2 \times 10^{-6}\text{ mol/(L }\cdot\text{s)} \]

**Check Your Solution**

From the coefficients in the balanced chemical equation, you can see that the rate of decomposition of N₂O₅ is \(\frac{2}{4}\), or \(\frac{1}{2}\), the rate of formation of NO₂. The rate of production of O₂ is \(\frac{1}{4}\) the rate of decomposition of N₂O₅.
1. Cyclopropane, C₃H₆, is used in the synthesis of organic compounds and as a fast-acting anesthetic. It undergoes rearrangement to form propene. If cyclopropane disappears at a rate of 0.25 mol/s, at what rate is propene being produced?

2. Ammonia, NH₃, reacts with oxygen to produce nitric oxide, NO, and water vapour.
   \[ 4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g) \]
   At a specific time in the reaction, ammonia is disappearing at rate of 0.068 mol/(L • s).
   What is the corresponding rate of production of water?

3. Hydrogen bromide reacts with oxygen to produce bromine and water vapour.
   \[ 4\text{HBr}(g) + \text{O}_2(g) \rightarrow 2\text{Br}_2(g) + 2\text{H}_2\text{O}(g) \]
   How does the rate of decomposition of HBr (in mol/(L • s)) compare with the rate of formation of Br₂ (also in mol/(L • s))? Express your answer as an equation.

4. Magnesium metal reacts with hydrochloric acid to produce magnesium chloride and hydrogen gas.
   \[ \text{Mg}(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g) \]
   Over an interval of 1.00 s, the mass of Mg(s) changes by −0.011 g.
   (a) What is the corresponding rate of consumption of HCl(aq) (in mol/s)?
   (b) Calculate the corresponding rate of production of H₂(g) (in L/s) at 20°C and 101 kPa.

Methods for Measuring Reaction Rates

How do chemists collect the data they need to determine a reaction rate? To determine empirically the rate of a chemical reaction, chemists must monitor the concentration or amount of at least one reactant or product. There are a variety of techniques available. The choice of technique depends on the reaction under study and the equipment available.

Monitoring Mass, pH, and Conductivity

Consider the reaction of magnesium with hydrochloric acid.
\[ \text{Mg}(s) + 2\text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g) \]
Hydrogen gas is released in the reaction. You can track the decrease in mass, due to the escaping hydrogen, by carrying out the reaction in an open vessel on an electric balance. The decrease in mass can be plotted against time. Some electronic balances can be connected to a computer, with the appropriate software, to record mass and time data automatically as the reaction proceeds.

Another technique for monitoring the reaction above involves pH. Since HCl is consumed in the reaction, you can record changes in pH with respect to time. Figure 6.3 shows a probe being used to monitor the changing pH of a solution.
A third technique involves electrical conductivity. Dissolved ions in aqueous solution conduct electricity. The electrical conductivity of the solution is proportional to the concentration of ions. Therefore, reactions that occur in aqueous solution, and involve a change in the quantity of dissolved ions, undergo a change in electrical conductivity. In the reaction above, hydrochloric acid is a mix of equal molar amounts of two ions: hydronium, $\text{H}_3\text{O}^+$, and chloride, $\text{Cl}^-$. The $\text{MgCl}_2$ that is produced exists as three separate ions in solution: one $\text{Mg}^{2+}$ ion and two $\text{Cl}^-$ ions. Since there is an increase in the concentration of ions as the reaction proceeds, the conductivity of the solution also increases with time.

**Monitoring Pressure**

When a reaction involves gases, the pressure of the system often changes as the reaction progresses. Chemists can monitor this pressure change. For example, consider the decomposition of dinitrogen pentoxide, shown in the following chemical reaction.

$$2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$$

When 2 mol of $\text{N}_2\text{O}_5$ gas decompose, they form 5 mol of gaseous products. Therefore, the pressure of the system increases as the reaction proceeds, provided that the reaction is carried out in a closed container. Chemists use a pressure sensor to monitor pressure changes.

**Monitoring Colour**

Colour change can also be used to monitor the progress of a reaction. The absorption of light by a chemical compound is directly related to the concentration of the compound. For example, suppose you add several drops of blue food colouring to a litre of water. If you add a few millilitres of bleach to the solution, the intensity of the colour of the food dye diminishes as it reacts. You can then monitor the colour change. (Do not try this experiment without your teacher’s supervision.)

For accurate measurements of the colour intensity of a solution, chemists use a device called a spectrophotometer. (See Figure 6.4.)

**Monitoring Volume**

When a reaction generates gas, chemists can monitor the volume of gas produced. In Investigation 6-A, you will determine average reaction rates by recording the time taken to produce a fixed volume of gas. You will perform several trials of the same reaction to investigate the effects that temperature, concentration of reactants, and surface area of reactants have on the reaction rate. You will also perform one trial using a different reactant.