Topic 5.1

Reaction Rates

Learning Objectives

- Define the kinetics of a chemical reaction and the way that they relate to stoichiometry.
- Describe the factors that affect the rate of a chemical reaction.
- Determine the rate of a chemical reaction given experimental data.

Topic Questions

- How does reaction stoichiometry affect the relative rates of change of reactant and product concentration?
- What factors affect the rate of a chemical reaction?
- How can the rate of a chemical reaction be determined given experimental data?

5.1.01 Reaction Kinetics

[TRA-3.A.1 TRA-3.A.2]

The **kinetics** of a chemical reaction describe how quickly reactants are converted into products. This is quantified by the **reaction rate**, which is the amount of reactant converted to products per unit of time. An **average rate** measures the change in molar concentration Δ[X] over a time interval Δ*t*.

$$\text{Average rate} = \frac{\text{Change in concentration of X}}{\text{Change in time}} = \frac{[\text{X}]_{\text{final}} - [\text{X}]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} = \frac{\Delta[\text{X}]}{\Delta t}$$

For the general reaction

$$w\text{A} + x\text{B} \rightarrow y\text{C} + z\text{D}$$

the rate of the reaction can be shown in terms of the change in concentration of any of the chemical species. As a result, four rate expressions can be written:

$$\text{Rate of consumption of A} = -\frac{\Delta[\text{A}]}{\Delta t}$$

$$\text{Rate of consumption of B} = -\frac{\Delta[\text{B}]}{\Delta t}$$

$$\text{Rate of formation of C} = \frac{\Delta[\text{C}]}{\Delta t}$$

$$\text{Rate of formation of D} = \frac{\Delta[\text{D}]}{\Delta t}$$

The rate expressions of the reactants A and B include a *negative* sign because the reactant concentrations *decrease* as they are consumed during the reaction. However, the rate expressions of the products C and D are *positive* because the product concentrations *increase* during the reaction.

The stoichiometry of a reaction can be used to determine how many reactant molecules are consumed for each product molecule formed. Each rate is related to another by the stoichiometric coefficients of the balanced reaction:

$$\text{Reaction rate} = -\frac{1}{w}\cdot\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{x}\cdot\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{y}\cdot\frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{z}\cdot\frac{\Delta[\text{D}]}{\Delta t}$$

If the consumption of one reactant molecule produces multiple product molecules, the product will appear at a faster rate than the reactant disappears. On the other hand, if multiple reactant molecules are required to form one product molecule, then product formation will occur at a slower rate than reactant consumption.

Kinetic data can be presented in different forms, such as in a table or as a graph of

- the reactant or product concentration versus time
- the rate of consumption or formation versus time

For example, the initial concentration of $SO_2Cl_2(g)$ in a reaction flask is 0.08 M, which decomposes according to the reaction:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Figure 5.1 shows how the concentration of $SO_2(g)$ changes over time as the decomposition of $SO_2Cl_2(g)$ occurs.

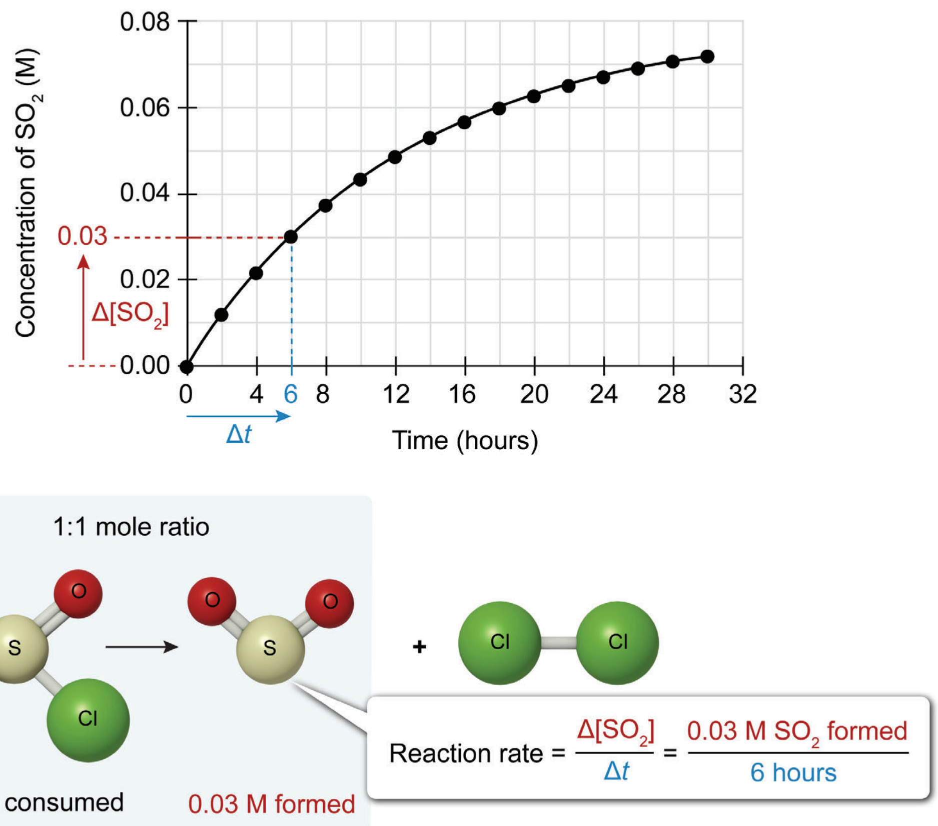

Figure 5.1 Rate of formation of $SO_2(g)$ from the decomposition of $SO_2Cl_2(g)$.

The rate of $SO_2Cl_2(g)$ consumption and $Cl_2(g)$ formation can be calculated using the rate of formation of $SO_2(g)$, which is determined using the slope of the graph in Figure 5.1, and the mole ratios from the balanced reaction. The reaction rates of $SO_2Cl_2(g)$, $SO_2(g)$, and $Cl_2(g)$ can be written as:

$$\text{Reaction rate} = -\frac{1}{1}\cdot\frac{\Delta[\mathrm{SO_2Cl_2}]}{\Delta t} = \frac{1}{1}\cdot\frac{\Delta[\mathrm{SO_2}]}{\Delta t} = \frac{1}{1}\cdot\frac{\Delta[\mathrm{Cl_2}]}{\Delta t}$$

The graph shows that 6 hours after the reaction begins, the molar concentration of $SO_2(g)$ is 0.03 M. Plugging these values into the reaction rate expression for $SO_2(g)$ gives:

$$\text{Rate of formation of } \mathrm{SO_2} = \frac{1}{1}\cdot\frac{[\mathrm{SO_2}]_{6\,\mathrm{hr}} - [\mathrm{SO_2}]_{0\,\mathrm{hr}}}{\Delta t} = \frac{0.03\ \mathrm{M} - 0\ \mathrm{M}}{6\ \mathrm{hr} - 0\ \mathrm{hr}} = 0.005\ \frac{\mathrm{M}}{\mathrm{hr}} \implies 0.005\ \mathrm{M\ hr^{-1}}$$

According to the balanced chemical equation, for every one mole of $SO_2(g)$ that is formed, one mole of $SO_2Cl_2(g)$ is consumed. Because the mole ratio is 1:1, 0.03 M of $SO_2Cl_2(g)$ are consumed. This means that 0.05 M of $SO_2Cl_2(g)$ are left over in the reaction flask at 6 hours:

$$[\mathrm{SO_2Cl_2}]_{\mathrm{leftover}} = [\mathrm{SO_2Cl_2}]_{\mathrm{initial}} - [\mathrm{SO_2Cl_2}]_{\mathrm{consumed}} = 0.08\ \mathrm{M} - 0.03\ \mathrm{M} = 0.05\ \mathrm{M}$$

Plugging these values into the reaction rate expression for $SO_2Cl_2(g)$ gives:

$$\text{Rate of consumption of } \mathrm{SO_2Cl_2} = -\frac{1}{1}\cdot\frac{[\mathrm{SO_2Cl_2}]_{6\ \mathrm{hr}} - [\mathrm{SO_2Cl_2}]_{0\ \mathrm{hr}}}{\Delta t} = -\left(\frac{0.05\ \mathrm{M} - 0.08\ \mathrm{M}}{6\ \mathrm{hr} - 0\ \mathrm{hr}}\right) = 0.005\ \mathrm{M\ hr^{-1}}$$

In addition, the rate of consumption of $SO_2Cl_2(g)$ can be calculated by simply applying the 1:1 mole ratio:

$$\text{Rate of consumption of } \mathrm{SO_2Cl_2} = \left(0.005\ \frac{\frac{\cancel{\mathrm{mol\ SO_2}}}{\mathrm{L}}}{\mathrm{hr}}\right)\times\left(\frac{1\ \mathrm{mol\ SO_2Cl_2}}{1\ \cancel{\mathrm{mol\ SO_2}}}\right) = 0.005\ \frac{\frac{\mathrm{mol\ SO_2Cl_2}}{\mathrm{L}}}{\mathrm{hr}} \Longrightarrow 0.005\ \mathrm{M\ hr^{-1}}$$

Therefore, the relative rates for each chemical species in a reaction can be determined by the stoichiometry of the reaction.

5.1.02 Reaction Conditions and Rate

[TRA-3.A.3]

The rate of a chemical reaction depends on the frequency of collisions between particles. Infrequent collisions lead to slower reaction rates, whereas frequent collisions lead to faster reaction rates. The frequency of particle collision and the reaction rate are affected by various conditions, including reactant concentration, temperature, surface area, and catalysts.

Concentration and Temperature

At higher concentrations, more molecules exist within a given volume, making it more likely that they will have a productive collision, which is a collision that results in a reaction. At higher temperatures, molecules move faster and with more energy. This increases both the probability of molecular collisions and the average energy of those collisions. Therefore, the rate of a reaction increases as temperature, concentration, or both increase. The effects of concentration and temperature on collision frequency and reaction rate are shown in Figure 5.2.

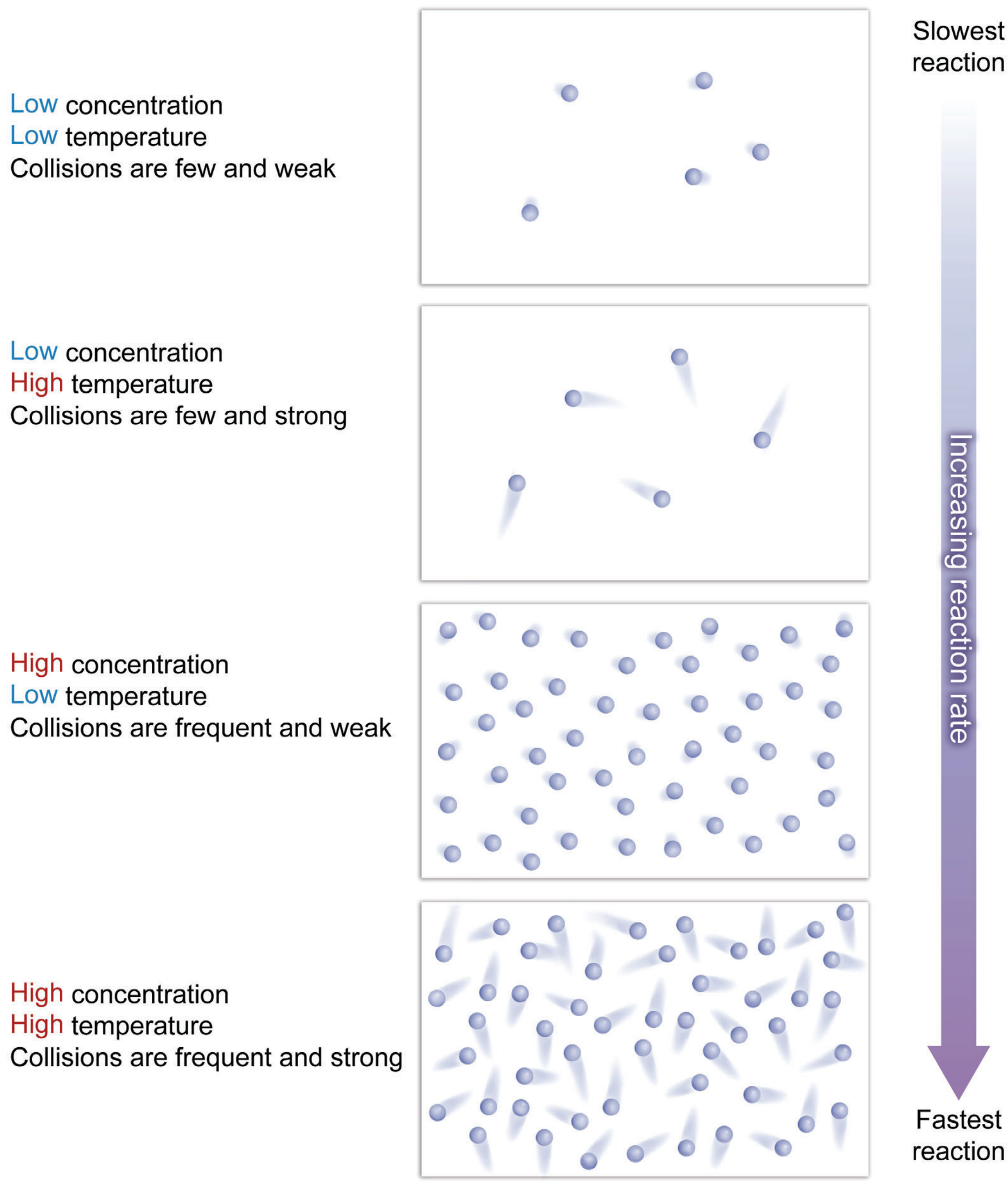

Figure 5.2 Effect of concentration and temperature on the rate of a reaction.

Surface Area

For solids, the size of the surface area available for other reactant molecules to collide with affects the reaction rate, as illustrated in Figure 5.3. A solid with a smaller surface area (eg, a single, large piece) has less frequent collisions with other reactants and reacts more slowly compared to a solid with a larger surface area (eg, a solid cut into several small pieces or ground into a powder). A larger surface area allows the solid to have *more* productive collisions, resulting in a *faster* reaction rate.

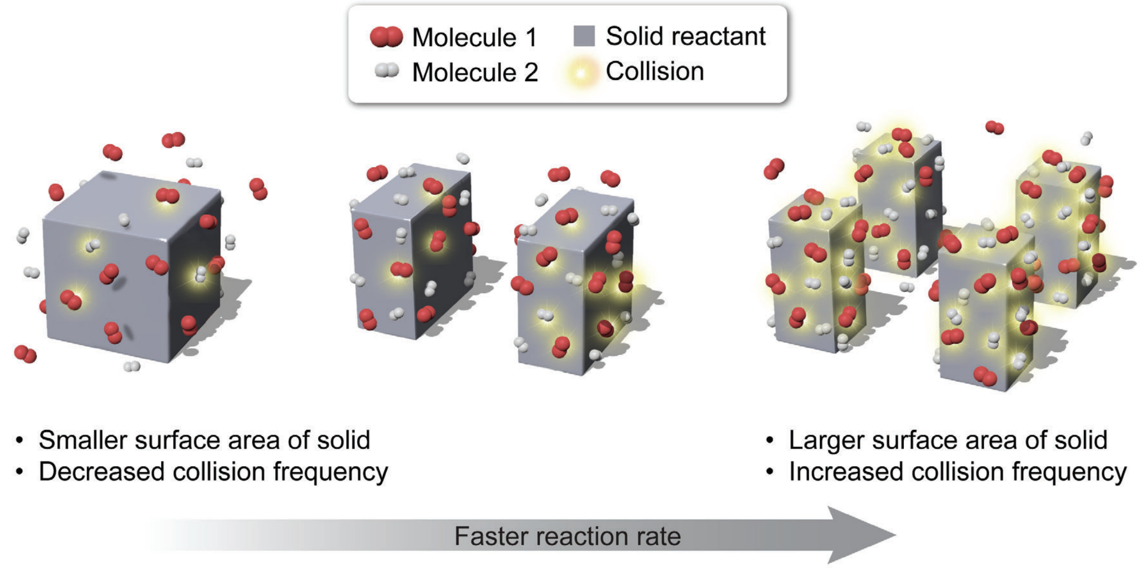

Figure 5.3 Effect of surface area on reaction rate.

Catalyst

Adding a catalyst to a reaction *increases* the rate of the reaction by decreasing the energy needed for the reaction to occur, as shown by the energy diagram in Figure 5.4. Note that catalysts do not affect the *overall* change in energy ΔE of the reaction (ie, the reactant and product energies remain the same). Catalysts are discussed in more detail in Topic 5.11.

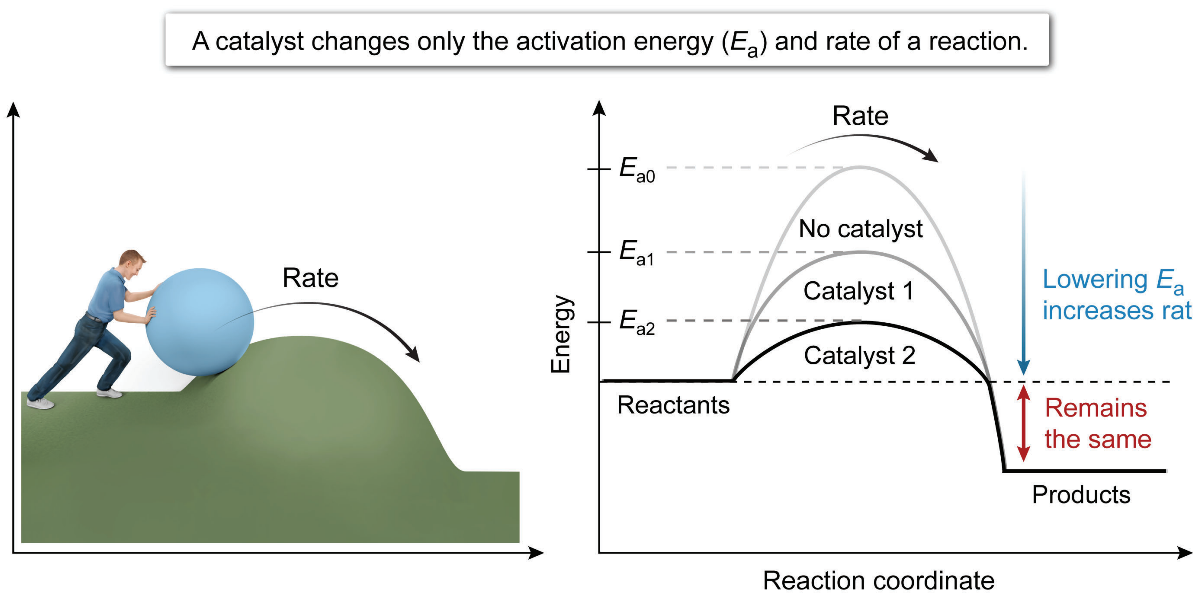

Figure 5.4 Effect of a catalyst on a reaction.

5.1.03 Experimental Determination of Reaction Rate

[TRA-3.B.1]

The rate of a chemical reaction can be determined by monitoring the consumption of reactants or the formation of products over time. Different instruments are used to monitor changes in the amount of a product or reactant present during a reaction by measuring quantities such as pH, absorbance, and pressure in a sealed container. Regardless of the instrument used, the amount of products should increase over time, and the amount of reactants should decrease.

For example, if the reactants or products absorb a specific wavelength of light, the reaction rate can be determined using a UV-vis spectrophotometer, which measures how much light a reaction mixture absorbs. Then the measured absorbance and Beer's law can be used to determine the reaction rate.

Consider the reaction between bromine (Br_2) and formic acid (HCO_2H):

$$Br_2(aq) + HCO_2H(aq) \rightarrow 2\ Br^-(aq) + 2H^+(aq) + CO_2(g)$$

The reaction is monitored by measuring the absorbance of Br_2 at 350 nm in a 10-cm cuvette using a UV-vis spectrophotometer. The absorbance of the sample is measured in 25.0-second increments, as shown in Table 5.1. From the absorbance, the molar concentration of Br_2 at each time was calculated using Beer's law.

Table 5.1 Absorbance of Br_2 during the reaction with HCO_2H.

Time (s)	Absorbance	[Br_2]
0.0	5.28	0.0240
25.0	4.62	0.0210
50.0	4.44	0.0202
75.0	4.09	0.0186

The rate of consumption of Br_2 in the first 75 seconds of the reaction is calculated using the equation:

$$\text{Rate of consumption of Br}_2 = -\frac{1}{1} \cdot \frac{[\text{Br}_2]_{75\text{ s}} - [\text{Br}_2]_{0\text{ s}}}{\Delta t}$$

Plugging in the time and concentration values from Table 5.1 gives the rate of Br_2 consumption:

$$\text{Rate of consumption of Br}_2 = -\frac{0.0186\text{ M} - 0.0240\text{ M}}{75.0\text{ s} - 0.0\text{ s}} = 0.000072\ \frac{\text{M}}{\text{s}} = 7.2 \times 10^{-5}\text{ M s}^{-1}$$

Topic 5.1 Reaction Rates

Check for Understanding Quiz

1. Which of the following terms refers to how quickly reactants are consumed and products are produced during a chemical reaction?

   A. Kinetics

   B. Stoichiometry

   C. Concentration

   D. Reaction order

2. The combustion of methane (CH_4) proceeds according to the equation:

   $$\mathrm{CH_4}(g) + 2\ \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\ \mathrm{H_2O}(g)$$

   Which of the following statements is true about the relative rates at which O_2 is consumed and CO_2 is produced?

   A. O_2 is consumed at the same rate as CO_2 is produced.

   B. O_2 is consumed half as quickly as CO_2 is produced.

   C. O_2 is consumed twice as quickly as CO_2 is produced.

   D. More information about the reaction conditions is necessary to answer the question.

3. Solid iron reacts with nitric acid according to the following equation:

   $$4\ \mathrm{Fe}(s) + 10\ \mathrm{HNO_3}(aq) \rightarrow 4\ \mathrm{Fe(NO_3)_2}(aq) + \mathrm{N_2O}(g) + 5\ \mathrm{H_2O}(l)$$

   Which of the following would decrease the rate of the reaction?

   A. Increasing the temperature

   B. Adding a catalyst

   C. Increasing the concentration of HNO_3(*aq*)

   D. Decreasing the surface area of Fe(*s*)

Note: Answers to this quiz are in the back of the book (appendix).