information as background, rate laws are related to plausible reaction mechanisms, which are a central focus of this chapter.

14-1 The Rate of a Chemical Reaction

Rate, or speed, refers to something that happens in a unit of time. A car traveling at 60 mph, for example, covers a distance of 60 miles in one hour. For chemical reactions, the rate of reaction describes how fast the concentration of a reactant or product changes with time.

To illustrate, let's consider the reaction that begins immediately after the ions Fe^{3+} and Sn^{2+} are simultaneously introduced into water.

$$2\,Fe^{3+}(aq) + Sn^{2+}(aq) \longrightarrow 2\,Fe^{2+}(aq) + Sn^{4+}(aq) \qquad \textbf{(14.1)}$$

Suppose that 38.5 s after the reaction starts, $[Fe^{2+}]$ is found to be 0.0010 M. During the period of time, $\Delta t = 38.5\,s$, the *change* in concentration of Fe^{2+}, which we can designate as $\Delta[Fe^{2+}]$, is $\Delta[Fe^{2+}] = 0.0010\,M - 0 = 0.0010\,M$. The *average* rate at which Fe^{2+} is formed in this interval is the change in concentration of Fe^{2+} divided by the change in time.

◀ Recall that the symbol [ ] means "concentration." Also, Δ means "the change in," that is, the final value minus the initial value.

$$\text{rate of formation of } Fe^{2+} = \frac{\Delta[Fe^{2+}]}{\Delta t} = \frac{0.0010\,M}{38.5\,s} = 2.6 \times 10^{-5}\,M\,s^{-1}$$

How has the concentration of Sn^{4+} changed during the 38.5 s we were monitoring the Fe^{2+}? Can you see that in 38.5 s, $\Delta[Sn^{4+}]$ will be $0.00050\,M - 0 = 0.00050\,M$? Because only *one* Sn^{4+} ion is produced for every *two* Fe^{2+} ions, the buildup of $[Sn^{4+}]$ will be only one-half that of $[Fe^{2+}]$. Consequently the rate of formation of Sn^{4+} is

$$\text{rate of formation of } Sn^{4+} = \frac{0.00050\,M}{38.5\,s} = 1.3 \times 10^{-5}\,M\,s^{-1}$$

We can also follow the course of the reaction by monitoring the concentrations of the starting reactants. Thus, the amount of Fe^{3+} consumed is the same as the amount of Fe^{2+} produced. The *change* in concentration of Fe^{3+} is $\Delta[Fe^{3+}] = -0.0010\,M$. Thus,

$$\frac{\Delta[Fe^{3+}]}{\Delta t} = \frac{-0.0010\,M}{38.5\,s} = -2.6 \times 10^{-5}\,M\,s^{-1}$$

The quantity above is the average rate of change of change of $[Fe^{3+}]$ in this interval. It is a negative quantity because $[Fe^{3+}]$ decreases with time. The average rate of disappearance of Fe^{3+} is defined as follows.

$$\text{rate of disappearance of } Fe^{3+} = -\frac{\Delta[Fe^{3+}]}{\Delta t} = 2.6 \times 10^{-5}\,M\,s^{-1}$$

Why is a negative sign incorporated into the definition of rate in this case? It is because the term "rate of disappearance" implies that $[Fe^{3+}]$ decreases with time. When told the rate of disappearance of Fe^{3+} is $2.6 \times 10^{-5}\,M\,s^{-1}$, we know the rate of change of *concentration* must be $-2.6 \times 10^{-5}\,M\,s^{-1}$.

In the same way that we related the rate of formation of Sn^{4+} to that of Fe^{2+}, we can relate the rate of disappearance of Sn^{2+} to that of Fe^{3+}. That is, the rate of disappearance of Sn^{2+} is half that of Fe^{3+}, giving

$$\text{rate of disappearance of } Sn^{2+} = -1.3 \times 10^{-5}\,M\,s^{-1}$$

When we refer to the rate of reaction (14.1), which of the four quantities described here should we use? To avoid confusion in this matter, the International Union of Pure and Applied Chemistry (IUPAC) recommends that we use a *general* rate of reaction, which, for the hypothetical reaction represented by the balanced equation,

$$aA + bB \longrightarrow gG + hH$$

is

$$\text{rate of reaction} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{g}\frac{\Delta[G]}{\Delta t} = \frac{1}{h}\frac{\Delta[H]}{\Delta t} \quad (14.2)$$

In this expression, we take the negative value of $\Delta[X]/\Delta t$, when X refers to a reactant to ensure that the **rate of reaction** is a positive quantity. To obtain a single, positive quantity it is necessary to divide all rates by the appropriate stoichiometric coefficients. If we apply this expression to reaction (14.1), we obtain

$$\text{rate of reaction} = -\frac{1}{2}\frac{\Delta[Fe^{3+}]}{\Delta t} = -\frac{\Delta[Sn^{2+}]}{\Delta t}$$

$$= \frac{1}{2}\frac{\Delta[Fe^{2+}]}{\Delta t} = \frac{\Delta[Sn^{4+}]}{\Delta t} = 1.3 \times 10^{-5}\,\text{M s}^{-1}$$

EXAMPLE 14-1

Expressing the Rate of a Reaction. Suppose that at some point in the reaction

$$A + 3\,B \longrightarrow 2\,C + 2\,D$$

$[B] = 0.9986$ M, and that 13.20 min later $[B] = 0.9746$ M. What is the average rate of reaction during this time period, expressed in M s^{-1}?

Solution

The rate of disappearance of B is the *change* in molarity, $\Delta[B]$, divided by the time interval, Δt, over which this change occurs $\Delta[B] = 0.9746\text{ M} - 0.9986\text{ M} = -0.0240\text{ M}$; $\Delta t = 13.20$ min, and

$$\text{rate of reaction} = -\frac{1}{3}\frac{\Delta[B]}{\Delta t} = -\frac{1}{3} \times \frac{-0.0240\text{ M}}{13.20\text{ min}} = 6.06 \times 10^{-4}\text{ M min}^{-1}$$

To express the rate of reaction in moles per liter per second, we must convert from min^{-1} to s^{-1}. We can do this with the conversion factor 1 min/60 s.

$$\text{rate of reaction} = 6.06 \times 10^{-4}\text{ M min}^{-1} \times \frac{1\text{ min}}{60\text{ s}} = 1.01 \times 10^{-5}\text{ M s}^{-1}$$

Alternatively, we could have converted 13.20 min to 792 s and used $\Delta t = 792$ s in evaluating the rate of reaction.

Practice Example A: At some point in the reaction $2\,A + B \longrightarrow C + D$, $[A] = 0.3629$ M. At a time 8.25 min later $[A] = 0.3187$ M. What is the average rate of reaction during this time interval, expressed in M s^{-1}?

Practice Example B: In the reaction $2\,A \longrightarrow 3\,B$, [A] drops from 0.5684 M to 0.5522 M in 2.50 min. What is the average rate of formation of B during this time interval, expressed in M s^{-1}?

CONCEPT ASSESSMENT

In the reaction of gaseous nitrogen and hydrogen to form gaseous ammonia, what are the relative rates of disappearance of the two reactants? How is the rate of formation of the product related to the rates of disappearance of the reactants?

Two of the more recent articles in the *Journal of Chemical Education* describing demonstrations and experiments involving the kinetics of hydrogen peroxide decomposition are Vetter, T. A., Colombo, D. P., Jr. *J. Chem. Educ.* 2003: *80*, 788 and Abramovitch, D. A. et al. *J. Chem.*