

## 14.3: Defining and Measuring the Rate of a Chemical Reaction

The rate of a chemical reaction is a measure of how fast the reaction occurs, as shown in [Figure 14.1](#). If a chemical reaction has a fast rate, a large fraction of molecules reacts to form products in a given period of time. If a chemical reaction has a slow rate, a relatively small fraction of molecules reacts to form products in a given period of time.

**Figure 14.1 The Rate of a Chemical Reaction**



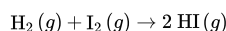
### Defining Reaction Rate

When we measure how fast something occurs, or more specifically the *rate* at which it occurs, we usually express the measurement as a change in some quantity per unit of time. For example, we measure the speed of a car—the rate at which it travels—in *miles per hour*, and we might measure how fast people lose weight in *pounds per week*. We report these rates in units that represent the change in what we are measuring (distance or weight) divided by the change in time:

$$\text{speed} = \frac{\text{change in distance}}{\text{change in time}} = \frac{\Delta x}{\Delta t} \quad \text{weight loss} = \frac{\text{change in weight}}{\text{change in time}} = \frac{\Delta \text{weight}}{\Delta t}$$

Similarly, the rate of a chemical reaction is measured as a change in the amounts of reactants or products (usually in concentration units) divided by the change in time. For example, consider the gas-phase reaction

between  $\text{H}_2(g)$  and  $\text{I}_2(g)$ :



We can define the rate of this reaction in the time interval  $t_1$  to  $t_2$  as follows:

[14.1]

$$\text{rate} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{[\text{H}_2]_{t_2} - [\text{H}_2]_{t_1}}{t_2 - t_1}$$

Recall that  $[\text{A}]$  means the concentration of A in M (mol/L).

In this expression,  $[\text{H}_2]_{t_2}$  is the hydrogen concentration at time  $t_2$  and  $[\text{H}_2]_{t_1}$  is the hydrogen concentration at time  $t_1$ . We define the reaction rate as *the negative* of the change in concentration of a reactant divided by the change in time. The negative sign is usually part of the definition when we define the reaction rate in terms of a reactant because reactant concentrations decrease as a reaction proceeds; therefore, *the change in the concentration of a reactant is negative*. The negative sign thus makes the overall *rate* positive. (By convention, reaction rates are reported as positive quantities.)

We can also define the reaction rate in terms of the other reactant as follows:

[14.2]

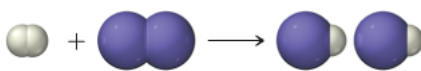
$$\text{rate} = -\frac{\Delta[\text{I}_2]}{\Delta t}$$

Because 1 mol of  $\text{H}_2$  reacts with 1 mol of  $\text{I}_2$ , the rates are defined in the same way. We can also define the rate with respect to the *product* of the reaction as follows:

[14.3]

$$\text{rate} = +\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

Because product concentrations *increase* as the reaction proceeds, the change in concentration of a product is positive. Therefore, when we define the rate with respect to a product, we do not include a negative sign in the definition—the rate is naturally positive. The factor of  $\frac{1}{2}$  in this definition is related to the stoichiometry of the reaction. In order to have a single rate for the entire reaction, the definition of the rate with respect to each reactant and product must reflect the stoichiometric coefficients of the reaction. For this particular reaction, 2 mol of HI are produced from 1 mol of  $\text{H}_2$  and 1 mol of  $\text{I}_2$ .



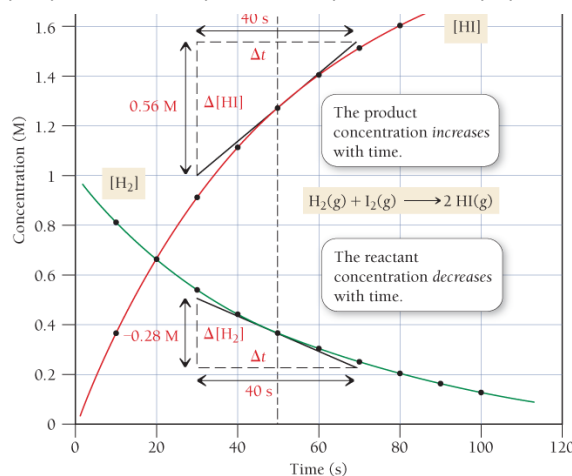
The concentration of HI increases at twice the rate that the concentration of  $\text{H}_2$  or  $\text{I}_2$  decreases. In other words, if 100  $\text{I}_2$  molecules react per second, then 200 HI molecules form per second. In order for the overall rate to have the same value when defined with respect to any of the reactants or products, the change in HI concentration must be multiplied by a factor of one-half.

Consider the graph shown in [Figure 14.2](#), which represents the changes in concentration for  $\text{H}_2$  (one of the reactants) and HI (the product) versus time. Let's examine several features of this graph individually.

**Figure 14.2 Reactant and Product Concentrations as a Function of Time**

The graph shows the concentration of one of the reactants ( $\text{H}_2$ ) and the product (HI) as a function of time. The other reactant ( $\text{I}_2$ ) is omitted for clarity.





## Change in Reactant and Product Concentrations

The reactant concentration, as expected, *decreases* with time because reactants are consumed in a reaction. The product concentration *increases* with time because products are formed in a reaction. The increase in HI concentration occurs at exactly twice the rate of the decrease in  $\text{H}_2$  concentration because of the stoichiometry of the reaction: 2 mol of HI form for every 1 mol of  $\text{H}_2$  consumed.

## The Average Rate of the Reaction

We can calculate the average rate of the reaction for any time interval using Equation 14.1 for  $\text{H}_2$ . The table lists the  $\text{H}_2$  concentration ( $[\text{H}_2]$ ) at various times, the change in  $\text{H}_2$  concentration for each interval ( $\Delta[\text{H}_2]$ ), the change in time for each interval ( $\Delta t$ ), and the rate for each interval ( $-\Delta[\text{H}_2]/\Delta t$ ). The rate is the average rate within the given time interval. For example, the average rate of the reaction in the time interval between 10 and 20 seconds is 0.0149 M/s, while the average rate in the time interval between 20 and 30 seconds is 0.0121 M/s. Notice that the average rate *decreases* as the reaction progresses. In other words, the reaction slows down as it proceeds, because for most reactions, the rate depends on the concentrations of the reactants. As the reactants transform to products, their concentrations decrease, and the reaction slows down.

Time (s)	$[\text{H}_2]$ (M)	$\Delta[\text{H}_2]$ (M)	$\Delta t$ (s)	Rate = $-\Delta[\text{H}_2]/\Delta t$ (M/s)
0.000	1.000	-0.181	10.000	0.0181
10.000	0.819	-0.149	10.000	0.0149
20.000	0.670	-0.121	10.000	0.0121
30.000	0.549	-0.100	10.000	0.0100
40.000	0.449	-0.081	10.000	0.0081
50.000	0.368	-0.067	10.000	0.0067
60.000	0.301	-0.054	10.000	0.0054
70.000	0.247	-0.045	10.000	0.0045
80.000	0.202	-0.037	10.000	0.0037
90.000	0.165	-0.030	10.000	0.0030
100.000	0.135			

## The Instantaneous Rate of the Reaction

The instantaneous rate of the reaction is the rate at any one point in time. We can determine the instantaneous rate by calculating the slope of the tangent to the curve at the point of interest. In Figure 14.2, we have drawn the tangent lines for both  $[\text{H}_2]$  and  $[\text{HI}]$  at 50 seconds and have labeled the changes in  $\text{H}_2$  concentration ( $\Delta[\text{H}_2]$ ) and the changes in time ( $\Delta t$ ) corresponding to the tangent line. As you can see from the graph,  $\Delta[\text{H}_2] = -0.28 \text{ M}$  and  $\Delta t = 40 \text{ s}$ . We calculate the instantaneous rate at 50 seconds by substituting these values into the expression for rate.

Using  $[\text{H}_2]$ :

$$\text{instantaneous rate (at 50 s)} = -\frac{\Delta [\text{H}_2]}{\Delta t} = -\frac{-0.28 \text{ M}}{40 \text{ s}} = 0.0070 \text{ M/s}$$

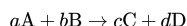
For  $[\text{HI}]$ ,  $\Delta[\text{HI}] = +0.56 \text{ M}$  and  $\Delta t = 40 \text{ s}$ :

$$\text{instantaneous rate (at 50 s)} = +\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = +\frac{1}{2} \frac{0.56 \text{ M}}{40 \text{ s}} = 0.0070 \text{ M/s}$$

As we would expect, the rate is the same whether we use one of the reactants or the product for the calculation. Notice that the instantaneous rate at 50 seconds (0.0070 M/s) is between the average rates calculated for the 10-second intervals just before and just after 50 seconds.

We can generalize our definition of reaction rate for the generic reaction:

[14.4]



where A and B are reactants, C and D are products, and  $a$ ,  $b$ ,  $c$ , and  $d$  are the stoichiometric coefficients. We define the rate of the reaction as follows:

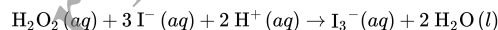
[14.5]

$$\text{rate} = -\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t} = +\frac{1}{c} \frac{\Delta[\text{C}]}{\Delta t} = +\frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t}$$

From the definition, we can see that knowing the rate of change in the concentration of any one reactant or product at a point in time allows us to determine the rate of change in the concentration of any other reactant or product at that point in time (from the balanced equation). *However, predicting the rate at some future time is not possible from just the balanced equation.*

### Example 14.1 Expressing Reaction Rates

Consider this balanced chemical equation:



In the first 10.0 seconds of the reaction, the concentration of  $\text{I}^-$  drops from 1.000 M to 0.868 M.

- Calculate the average rate of this reaction in this time interval.
- Determine the rate of change in the concentration of  $\text{H}^+$  (that is,  $\Delta[\text{H}^+]/\Delta t$ ) during this time interval.

#### SOLUTION

- Use Equation 14.5 to calculate the average rate of the reaction. Since the stoichiometric coefficient is 3, the multiplication factor is 1/3.

$$\begin{aligned} \text{rate} &= -\frac{1}{3} \frac{\Delta[\text{I}^-]}{\Delta t} \\ &= -\frac{1}{3} \frac{[\text{I}^-]_{\text{final}} - [\text{I}^-]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} \\ &= -\frac{1}{3} \frac{(0.868 \text{ M} - 1.000 \text{ M})}{(10.0 \text{ s} - 0.00 \text{ s})} \\ &= 4.40 \times 10^{-3} \text{ M/s} \end{aligned}$$

- Use Equation 14.5 again to determine the relationship between the rate of the reaction and  $\Delta[\text{H}^+]/\Delta t$ . Since the stoichiometric coefficient is 2, the multiplication factor is 1/2.

After solving for  $\Delta [\text{H}^+] / \Delta t$ , substitute the calculated rate from part (a) and calculate  $\Delta [\text{H}^+] / \Delta t$ .

$$\begin{aligned} \text{rate} &= -\frac{1}{2} \frac{\Delta [\text{H}^+]}{\Delta t} \\ \frac{\Delta [\text{H}^+]}{\Delta t} &= -2(\text{rate}) \\ &= -2(4.40 \times 10^{-3} \text{ M/s}) \\ &= -8.80 \times 10^{-3} \text{ M/s} \end{aligned}$$

**FOR PRACTICE 14.1** For the reaction shown in [Example 14.1](#), predict the rate of change in concentration of  $\text{H}_2\text{O}_2$  ( $\Delta [\text{H}_2\text{O}_2] / \Delta t$ ) and  $\text{I}_3^-$  ( $\Delta [\text{I}_3^-] / \Delta t$ ) during this time interval.

### Conceptual Connection 14.2 Reaction Rates

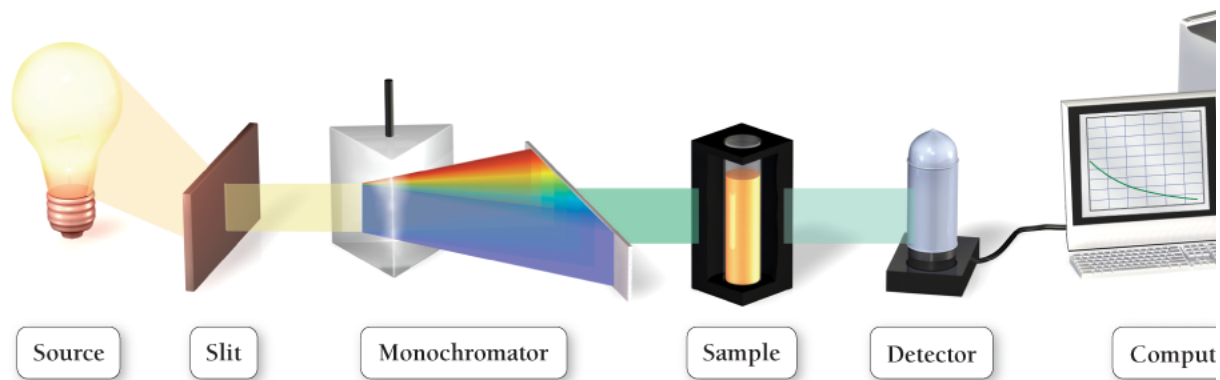
## Measuring Reaction Rates

In order to study the kinetics of a reaction, we must have an experimental way to measure the concentration of at least one of the reactants or products as a function of time. For example, Ludwig Wilhelmy, whose experiment on the rate of the conversion of sucrose to glucose and fructose we discussed briefly in [Section 14.2](#), took advantage of sucrose's ability to rotate polarized light. (Polarized light is light with an electric field oriented along one plane.) When a beam of polarized light is passed through a sucrose solution, the polarization of the light is rotated clockwise. In contrast, the combined products of the reaction (glucose and fructose) rotate polarized light counterclockwise. By measuring the degree of polarization of light passing through a reacting solution—a technique known as polarimetry—Wilhelmy was able to determine the relative concentrations of the reactants and products as a function of time.

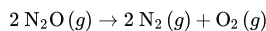
Perhaps the most common way to study the kinetics of a reaction is through spectroscopy (see [Section 3.3](#)). For example, we can follow the reaction of  $\text{H}_2$  and  $\text{I}_2$  to form  $\text{HI}$  spectroscopically because  $\text{I}_2$  is violet and  $\text{H}_2$  and  $\text{HI}$  are colorless. As  $\text{I}_2$  reacts with  $\text{H}_2$  to form  $\text{HI}$ , the violet color of the reaction mixture fades. We can monitor the fading color with a spectrometer, a device that passes light through a sample and measures how strongly the light is absorbed ([Figure 14.3](#)). If the sample contains the reacting mixture, the intensity of the light absorption will decrease as the reaction proceeds, providing a direct measure of the concentration of  $\text{I}_2$  as a function of time. Because light travels so fast and because experimental techniques can produce very short pulses of light, spectroscopy can be used to measure reactions that happen on time scales as short as several femtoseconds.

**Figure 14.3 The Spectrometer**

In a spectrometer, light of a specific wavelength is passed through the sample and the intensity of the transmitted light—which depends on how much light is absorbed by the sample—is measured and recorded.



We can also monitor reactions in which the number of moles of gaseous reactants and products changes as the reaction proceeds by measuring changes in pressure. Consider the reaction in which dinitrogen monoxide reacts to form nitrogen and oxygen gas:

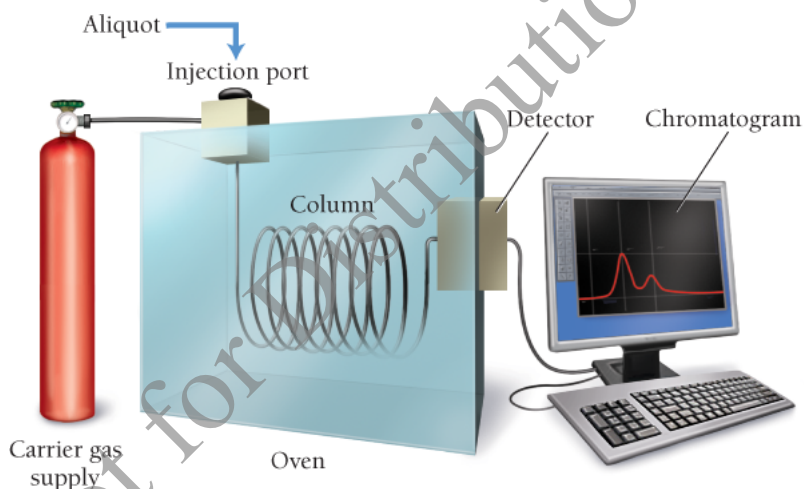


For every 2 moles of  $\text{N}_2\text{O}$  that reacts, the reaction vessel will contain 1 additional mole of gas. As the reaction proceeds and the amount of gas increases, the pressure steadily rises. We can use the rise in pressure to determine the relative concentrations of reactants and products as a function of time.

The three techniques mentioned here—polarimetry, spectroscopy, and pressure measurement—can all be used to monitor a reaction as it occurs in a reaction vessel. Some reactions occur slowly enough that samples, or *aliquots*, can be periodically withdrawn from the reaction vessel and analyzed to determine the progress of the reaction. Instrumental techniques such as gas chromatography (Figure 14.4) or mass spectrometry (see Section 1.9), as well as wet chemical techniques such as titration, can be used to measure the relative amounts of reactants or products in the aliquot. By taking aliquots at regular time intervals, we can determine the relative amounts of reactants and products as a function of time.

**Figure 14.4 The Gas Chromatograph**

In a gas chromatograph (GC), a sample of the reaction mixture, or aliquot, is injected into a specially constructed column. Because of their characteristic physical and chemical properties, different components of the mixture pass through the column at different rates and thus exit at different times. As each component leaves the column, it is identified electronically and a chromatogram is recorded. The area under each peak in the chromatogram is proportional to the amount of one particular component in the sample mixture.



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