# 19

# Irreversible aqueous chemistry

Irreversible aqueous chemistry, or irreversible chemistry in liquid water, is an important step in the production of acid rain, acid fog, and acid haze. For example, it is responsible for converting sulfur dioxide gas to aqueous sulfuric acid in aerosol particles, cloud drops, and precipitation. Irreversible aqueous reactions are tightly coupled with reversible (equilibrium) reactions, such as those discussed in Chapter 17. Since many aqueous reactants originate as gases, aqueous chemistry is tightly linked to nonequilibrium gas-to-particle conversion as well. Since aqueous reactions are described by first-order, ordinary differential equations, they are solved with methods similar to those used to solve gas-phase reactions. In this chapter, the significance of aqueous chemistry, identification of important aqueous reactions, and a method of solving aqueous chemistry together with gas-to-particle conversion are discussed.

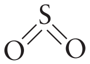
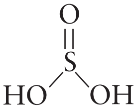
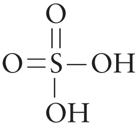
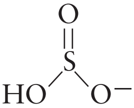
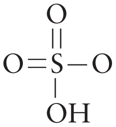
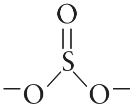
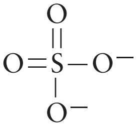
## 19.1 SIGNIFICANCE OF AQUEOUS CHEMICAL REACTIONS

Aqueous chemistry is irreversible chemistry that takes place in liquid water. It occurs following dissolution of gases into liquid aerosol particles, cloud drops, and precipitation as follows: First, soluble gases diffuse to and dissolve in liquid water on a particle surface. Some of the dissolved molecules dissociate reversibly into ions. The chemicals then diffuse through the water. Irreversible chemical reactions take place during diffusion. Some of the dissolved molecules and reaction products may diffuse back to the particle surface and evaporate, whereas others may stay within the particle.

Gas dissolution and irreversible chemistry affect particle composition at a rate proportional to the quantity of liquid water present. As such, aqueous chemistry proceeds faster in cloud drops, which generally have liquid-water contents $>10^5$ μg m$^{-3}$, than in aerosol particles, which have liquid-water contents $<500$ μg m$^{-3}$.

When a gas dissolves in a dilute liquid-water drop and does not react chemically, the quantities of the gas remaining and dissolved in water are governed by Henry's law, which states that, over a dilute solution, the pressure exerted by a gas is proportional to the molality of the dissolved gas in solution (Section 17.4). When Henry's law holds, the quantity of gas over a drop surface is the saturation vapor pressure of the gas, and the gas is in equilibrium with its dissolved phase at the surface. As such, in the absence of aqueous chemistry, only a finite amount of a gas dissolves in a liquid drop.

**Table 19.1** Names, formulae, and lewis structures of S(IV) and S(VI) species

| **S(IV) family** | | **S(VI) family** | |
|---|---|---|---|
| **Chemical name and formula** | **Chemical structure** | **Chemical name and formula** | **Chemical structure** |
| Sulfur dioxide (g,aq)<br>$SO_2$(g,aq) |  | | |
| Sulfurous acid (aq)<br>$H_2SO_3$(aq) |  | Sulfuric acid (aq)<br>$H_2SO_4$(aq) |  |
| Bisulfite ion $HSO_3^-$ |  | Bisulfate ion $HSO_4^-$ |  |
| Sulfite ion $SO_3^{2-}$ |  | Sulfate ion $SO_4^{2-}$ |  |

When irreversible chemistry occurs, the dissolved gas chemically reacts to produce a product, instantaneously decreasing the molality of the dissolved gas. As such, more gas must dissolve into the drop to maintain saturation over the drop surface (i.e., to maintain the Henry's law relation). Once additional gas dissolves, it reacts away irreversibly as well. The continuous dissolution and irreversible reaction that occur in a drop can deplete the gas phase of dissolving species, sometimes within minutes. Below, aqueous chemistry processes of importance are discussed.

## 19.2 MECHANISMS OF CONVERTING S(IV) TO S(VI)

The most important processes affected by irreversible chemistry are those that convert sulfur dioxide gas to dissolved sulfuric acid and its dissociation products, bisulfate and sulfate. These processes are important because sulfuric acid is the most abundant acid in the air and the main culprit in acid deposition. Much of its atmospheric production is due to irreversible chemistry within clouds, precipitation, and aerosol particles.

Sulfur dioxide is a member of the **S(IV) family**. Dissolved sulfuric acid and its products are members of the **S(VI) family** (Table 19.1). In these families, the IV and the VI represent the oxidation states (+4 and +6, respectively) of the members of the respective families. Thus, S(VI) members are more oxidized than are S(IV) members. Because sulfur dioxide is in the S(IV) family and sulfuric acid, the main source of acidity in rainwater, is in the S(VI) family, the oxidation of sulfur dioxide gas to aqueous sulfuric acid represents a conversion from the S(IV) family to the S(VI) family. This conversion occurs through two pathways, described next.

### 19.2.1 Gas-phase oxidation of S(IV)

The first conversion mechanism of S(IV) to S(VI) involves three steps. The initial step is gas-phase oxidation of sulfur dioxide to sulfuric acid by

$$\underset{\substack{\text{Sulfur}\\ \text{dioxide gas}}}{\mathrm{SO_2(g)}} \xrightarrow{+\mathrm{\dot{O}H(g),\,M}} \underset{\text{Bisulfite}}{\mathrm{HS\dot{O}_3(g)}} \xrightarrow[\mathrm{H\dot{O}_2(g)}]{+\mathrm{O_2(g)}} \underset{\substack{\text{Sulfur}\\ \text{trioxide}}}{\mathrm{SO_3(g)}} \xrightarrow{+\mathrm{H_2O(g)}} \underset{\substack{\text{Sulfuric}\\ \text{acid gas}}}{\mathrm{H_2SO_4(g)}} \tag{19.1}$$

The second step is condensation of sulfuric acid gas onto aerosol particles and simultaneous hydration (Section 17.8) of liquid water to the sulfuric acid to produce a sulfuric acid–water solution. Because sulfuric acid has a low saturation vapor pressure, nearly all of it produced by (19.1) condenses, and this process is relatively irreversible. The third step is dissociation of aqueous sulfuric acid. The second and third steps are represented by

$$\underset{\substack{\text{Sulfuric}\\ \text{acid gas}}}{\mathrm{H_2SO_4(g)}} \longrightarrow \underset{\substack{\text{Aqueous}\\ \text{sulfuric acid}}}{\mathrm{H_2SO_4(aq)}} \rightleftharpoons \mathrm{H^+} + \underset{\text{Bisulfate ion}}{\mathrm{HSO_4^-}} \rightleftharpoons \mathrm{2H^+} + \underset{\text{Sulfate ion}}{\mathrm{SO_4^{2-}}} \tag{19.2}$$

At typical pHs of aerosol particles and cloud drops, nearly all aqueous sulfuric acid dissociates to the sulfate ion. The dissociation releases two protons, decreasing pH and increasing acidity of the solution.

Condensation accounts for much of the increase of S(VI) in particles when the relative humidity is below 100 percent. Below 70-percent relative humidity, nearly all S(VI) production in particles is due to condensation. Because the rate of change of mass of a particle due to condensation is proportional to the radius of the particle, as shown in (16.13), condensation is a **radius-limited** process. Whereas gas-phase oxidation followed by condensation is the dominant mechanism by which S(IV) produces S(VI) in aerosol particles, particularly at low relative humidity, a second mechanism produces S(VI) from S(IV) more rapidly in cloud drops and raindrops.

### 19.2.2 Aqueous-phase oxidation of S(IV)

The second conversion process of S(IV) to S(VI) involves several steps as well. The initial step is reversible dissolution of sulfur dioxide gas into liquid drops by

$$\underset{\substack{\text{Sulfur}\\ \text{dioxide gas}}}{\mathrm{SO_2(g)}} \rightleftharpoons \underset{\substack{\text{Dissolved}\\ \text{sulfur dioxide}}}{\mathrm{SO_2(aq)}} \tag{19.3}$$

Sulfur dioxide is less soluble in water than is hydrochloric acid or nitric acid but more soluble than are many other gases. Because the dissolution rate of sulfur dioxide or any other gas depends on the volume of liquid water present, dissolution is a **volume-limited** process.

The second step is reversible reaction of aqueous sulfur dioxide to sulfurous acid, followed by dissociation of sulfurous acid:

$$\underset{\substack{\text{Dissolved}\\ \text{sulfur}\\ \text{dioxide}}}{SO_2(aq)} + \underset{\substack{\text{Liquid}\\ \text{water}}}{H_2O(aq)} \rightleftharpoons \underset{\substack{\text{Sulfurous}\\ \text{acid}}}{H_2SO_3(aq)} \rightleftharpoons \underset{\substack{\text{Hydrogen}\\ \text{ion}}}{H^+} + \underset{\substack{\text{Bisulfite}\\ \text{ion}}}{HSO_3^-} \rightleftharpoons \underset{\substack{\text{Hydrogen}\\ \text{ion}}}{2H^+} + \underset{\substack{\text{Sulfite}\\ \text{ion}}}{SO_3^{2-}} \tag{19.4}$$

At pH of 2–7, the major dissociation product of sulfurous acid is the bisulfite ion ($HSO_3^-$). All sulfur species in (19.4) are in the S(IV) family, so the bisulfite ion is the major species present in the S(IV) family upon sulfur dioxide dissolution and dissociation.

The third step is irreversible aqueous oxidation of S(IV) to S(VI). Over a range of liquid-water contents (50 μg $m^{-3}$ to 2 g $m^{-3}$), hydrogen peroxide and ozone are the major aqueous-phase oxidants of S(IV) at $pH \le 6$ and $pH > 6$, respectively. Since oxidation of $SO_2$ by $O_3$ reduces pH, $H_2O_2$ often becomes the most important oxidant of $SO_2$ even when the initial $pH > 6$ (e.g., Liang and Jacobson 1999).

When the $pH \le 6$, hydrogen peroxide oxidizes S(IV) by

$$\underset{\substack{\text{Bisulfite}\\ \text{ion}}}{HSO_3^-} + \underset{\substack{\text{Hydrogen}\\ \text{peroxide(aq)}}}{H_2O_2(aq)} + H^+ \longrightarrow \underset{\substack{\text{Sulfate}\\ \text{ion}}}{SO_4^{2-}} + H_2O(aq) + 2H^+ \tag{19.5}$$

This reaction is written in terms of the bisulfite ion and the sulfate ion because, at pH of 2–6, these are the two most prevalent components of the S(IV) and S(VI) families, respectively. This reaction consumes S(IV) within tens of minutes if the $H_2O_2(aq)$ concentration exceeds that of S(IV). If the S(IV) concentration exceeds that of $H_2O_2(aq)$, then $H_2O_2(aq)$ is depleted within minutes (Jacob 1986). The rate coefficient of (19.5) multiplied by $[H^+]$ is 9 times greater at $pH = 0$ than at $pH = 4$ (Appendix Table B.8), suggesting that the coefficient increases with decreasing pH. A cloud drop typically has a pH of 2.5 to 5.6. An aerosol particle often has a pH of −1 to +2. The lower pH in aerosol particles speeds reaction rates in such particles relative to those in cloud drops. But, because aerosol particles contain less $H_2O_2(aq)$ and liquid water than do cloud drops, aerosol particles are still less efficient at converting S(IV) than are cloud drops.

Hydrogen peroxide is also photolyzed within an aqueous solution by

$$H_2O_2(aq) + h\nu \longrightarrow 2\dot{O}H(aq) \tag{19.6}$$

and is lost by reaction with the aqueous hydroxyl radical,

$$\mathrm{H_2O_2(aq)} + \dot{\mathrm{O}}\mathrm{H(aq)} \longrightarrow \mathrm{H_2O(aq)} + \mathrm{H}\dot{\mathrm{O}}\mathrm{_2(aq)} \tag{19.7}$$

Sources of hydrogen peroxide in liquid water are its dissolution by

$$\mathrm{H_2O_2(g)} \rightleftharpoons \mathrm{H_2O_2(aq)} \tag{19.8}$$

and aqueous production from the hydroperoxy radical,

$$\underset{\substack{\text{Hydroperoxy}\\ \text{radical}}}{\mathrm{H}\dot{\mathrm{O}}\mathrm{_2(aq)}} + \underset{\substack{\text{Peroxy}\\ \text{ion}}}{\mathrm{O_2^-}} + \mathrm{H_2O(aq)} \longrightarrow \underset{\substack{\text{Hydrogen}\\ \text{peroxide}}}{\mathrm{H_2O_2(aq)}} + \mathrm{O_2(aq)} + \underset{\substack{\text{Hydroxide}\\ \text{ion}}}{\mathrm{OH^-}} \tag{19.9}$$

The aqueous hydroperoxy radical dissolves from the gas phase. At a pH above 5, much of it dissociates. Dissolution and dissociation are represented by

$$\mathrm{H}\dot{\mathrm{O}}\mathrm{_2(g)} \rightleftharpoons \mathrm{H}\dot{\mathrm{O}}\mathrm{_2(aq)} \rightleftharpoons \mathrm{H^+} + \mathrm{O_2^-} \tag{19.10}$$

When the pH > 6, which occurs only in cloud drops that contain basic substances, such as ammonium or sodium, the most important reaction converting S(IV) to S(VI) is

$$\boxed{\underset{\substack{\text{Sulfite}\\ \text{ion}}}{\mathrm{SO_3^{2-}}} + \underset{\substack{\text{Dissolved}\\ \text{ozone}}}{\mathrm{O_3(aq)}} \longrightarrow \underset{\substack{\text{Sulfate}\\ \text{ion}}}{\mathrm{SO_4^{2-}}} + \underset{\substack{\text{Dissolved}\\ \text{oxygen}}}{\mathrm{O_2(aq)}} \qquad (19.11)}$$

This reaction is written in terms of the sulfite ion and the sulfate ion because the $\mathrm{HSO_3^-}$–$\mathrm{O_3}$ reaction is relatively slow, and at pH levels greater than 6, most S(VI) exists as $\mathrm{SO_4^{2-}}$. This reaction not only oxidizes S(IV), but also helps to deplete gas-phase ozone in a cloud (e.g., Liang and Jacob 1997; Walcek *et al.* 1997; Zhang *et al.* 1998). As the reaction proceeds, more ozone gas must dissolve to maintain saturation over a drop surface.

When the liquid-water content exceeds 0.2 g m$^{-3}$ and the pH ≈ 5, or when $\mathrm{H_2O_2}$ is depleted, OH can also oxidize S(IV) by

$$\boxed{\underset{\substack{\text{Bisulfite}\\ \text{ion}}}{\mathrm{HSO_3^-}} + \dot{\mathrm{O}}\mathrm{H(aq)} + \mathrm{O_2(aq)} \longrightarrow \underset{\substack{\text{Peroxysulfate}\\ \text{ion}}}{\mathrm{S}\dot{\mathrm{O}}\mathrm{_5^-}} + \mathrm{H_2O(aq)} \qquad (19.12)}$$

The hydroxyl radical is not very soluble in water, so its production from aqueous chemistry generally exceeds its production from gas dissolution. The peroxysulfate ion catalyzes oxidation of S(IV) by

$$\boxed{\underset{\substack{\text{Bisulfite}\\\text{ion}}}{HSO_3^-} + \underset{\substack{\text{Dissolved}\\\text{oxygen}}}{O_2(aq)} \xrightarrow{\dot{S}O_5^-} \underset{\substack{\text{Peroxymonosulfate}\\\text{ion}}}{HSO_5^-} \qquad (19.13)}$$

The peroxymonosulfate ion produced from this reaction also oxidizes S(IV) by

$$\boxed{\underset{\substack{\text{Bisulfite}\\\text{ion}}}{HSO_3^-} + HSO_5^- + H^+ \longrightarrow \underset{\substack{\text{Sulfate}\\\text{ion}}}{2SO_4^{2-}} + 3H^+ \qquad (19.14)}$$

Dissolved oxygen oxidizes S(IV) when a **transition metal**, such as Fe(III) or Mn(II), catalyzes the reaction (Jacob *et al.* 1989a). About 85–90 percent of soluble iron appears as Fe(II) in the form of $Fe^{2+}$, and about 10–15 percent appears as Fe(III), although these values are location-dependent. At pH $< 12$, most Fe(III) is present as $Fe^{3+}$ and catalyzes S(IV) oxidation by

$$\boxed{\underset{\text{Sulfite ion}}{SO_3^{2-}} + H_2O(aq) + O_2(aq) \xrightarrow{Fe(III)} \underset{\text{Sulfate ion}}{SO_4^{2-}} + H_2O_2(aq) \qquad (19.15)}$$

Fe(II) does not catalyze S(IV) oxidation. Mn(II) is usually in the form of $Mn^{2+}$ and catalyzes S(IV) by

$$\underset{\text{Bisulfite ion}}{HSO_3^-} + H_2O(aq) + O_2(aq) \xrightarrow{Mn(II)} \underset{\text{Sulfate ion}}{SO_4^{2-}} + H_2O_2(aq) + H^+ \qquad (19.16)$$

Mn(III) does not catalyze S(IV) oxidation significantly.

Slightly soluble carbonyl compounds, such as formaldehyde and acetaldehyde, also affect S(IV) oxidation in clouds and rain (e.g., Munger *et al.* 1989). These species originate from the gas phase, where they are produced by combustion and photochemistry. Dissolved formaldehyde reacts reversibly in solution to form **methylene glycol** by

$$\underset{\text{Formaldehyde}}{HCHO(aq)} + H_2O(aq) \rightleftharpoons \underset{\text{Methylene glycol}}{H_2C(OH)_2(aq)} \qquad (19.17)$$

Methylene glycol is lost during the reaction,

$$\underset{\text{Methylene glycol}}{H_2C(OH)_2(aq)} + \dot{O}H(aq) + O_2(aq) \longrightarrow \underset{\text{Formic acid}}{HCOOH(aq)} + H\dot{O}_2(aq) + H_2O(aq) \qquad (19.18)$$

At high pH, formaldehyde oxidizes the sulfite ion to form **hydroxymethanesulfonate** (HMSA) by

$$\boxed{\underset{\substack{\text{Sulfite}\\ \text{ion}}}{SO_3^{2-}} + \underset{\substack{\text{Formal}\\ \text{-dehyde}}}{HCHO(aq)} + H_2O(aq) \longrightarrow \underset{\text{HMSA}}{HOCH_2SO_3^-} + OH^- \qquad (19.19)}$$

which is subsequently lost during the reaction

$$\underset{\text{HMSA}}{HOCH_2SO_3^-} + \dot{O}H(aq) + O_2(aq) \longrightarrow HCHO(aq) + \underset{\substack{\text{Peroxysulfate}\\ \text{ion}}}{S\dot{O}_5^-} + H_2O(aq) \qquad (19.20)$$

Other slightly soluble organic gases include the methylperoxy radical ($CH_3O_2$), methyl hydroperoxide ($CH_3OOH$), formic acid ($HCOOH$), acetic acid ($CH_3COOH$), and peroxyacetic acid ($CH_3C(O)OOH$). Relevant aqueous reactions for these species appear in Appendix Table B.8, and equilibrium reactions appear in Appendix Table B.7.

Other soluble inorganic gases include nitric acid, ammonia, and hydrochloric acid. Under most conditions, the dissolved products of nitric acid and ammonia, $HNO_3(aq)$, $NO_3^-$, $NH_3(aq)$, and $NH_4^+$ are unaffected significantly by irreversible reactions (Pandis and Seinfeld 1989). The chemistry of these species is governed by reversible reactions, discussed in Chapter 18. The chloride ion ($Cl^-$), the dissociation product of HCl(aq), reacts irreversibly in solution. It maintains equilibrium with several aqueous chlorine species through

$$\underset{\substack{\text{Dichloride}\\ \text{ion}}}{Cl_2^-} \rightleftharpoons \underset{\substack{\text{Chlorine}\\ \text{atom}}}{\dot{Cl}(aq)} + \underset{\substack{\text{Chloride}\\ \text{ion}}}{Cl^-} \qquad (19.21)$$

$$\underset{\substack{\text{Chlorine}\\ \text{hydroxide radical}}}{ClOH^-} \rightleftharpoons \underset{\substack{\text{Chloride}\\ \text{ion}}}{Cl^-} + \dot{O}H(aq) \qquad (19.22)$$

(Jayson *et al.* 1973). The chlorine atom reacts irreversibly with hydrogen peroxide by

$$H_2O_2(aq) + \dot{Cl}(aq) \longrightarrow Cl^- + \dot{H}O_2(aq) + H^+ \qquad (19.23)$$

and the dichloride ion oxidizes S(IV) by

$$\boxed{\underset{\substack{\text{Bisulfite}\\ \text{ion}}}{HSO_3^-} + \underset{\substack{\text{Dichloride}\\ \text{ion}}}{Cl_2^-} + O_2(aq) \longrightarrow \underset{\substack{\text{Peroxysulfate}\\ \text{ion}}}{S\dot{O}_5^-} + 2Cl^- + H^+ \qquad (19.24)}$$

but this reaction is less important than other reactions that oxidize S(IV).

In sum, the second conversion process of S(IV) to S(VI) involves dissolution of sulfur dioxide gas to sulfurous acid, reversible dissociation of sulfurous acid to the bisulfite ion and the sulfite ion, and irreversible oxidation of these ions to the sulfate ion. Oxidants of bisulfite and/or sulfite in solution include hydrogen peroxide, ozone, the hydroxyl radical, the peroxymonosulfate ion, formaldehyde, the dichloride ion, and molecular oxygen catalyzed by iron, manganese, and the peroxysulfate ion (e.g., Hoffmann and Calvert 1985; Jacob *et al.* 1989a; Pandis and Seinfeld 1989).

The conversion rate of S(IV) to S(VI) depends on liquid-water content, oxidant concentration, and pH. Aerosol liquid-water contents are generally less than 500 μg $m^{-3}$. Fog liquid-water contents are generally less than 0.2 g $m^{-3}$. Cloud liquid-water contents, which range from 0.2–2 g $m^{-3}$, exceed those of fogs. Thus, a cloud has 500–10 000 times more liquid water than does an aerosol plume.

The Henry's law constants of $H_2O_2$, $HO_2$, OH, and $O_3$ are moderate to low, as shown in Appendix Table B.7. Because of its high liquid-water content, a cloud can absorb all four gases. Because of its low liquid-water content, an aerosol plume absorbs proportionately less of all four gases and absorbs only $H_2O_2$ in significant quantities. Thus, S(IV) conversion in an aerosol plume is often limited by the concentration of $H_2O_2$. In a cloud, the greater abundance of liquid water, $H_2O_2$, $HO_2$, OH, and $O_3$ in solution permits S(IV) to convert to S(VI) faster than in an aerosol plume. Although S(IV) oxidation is slow in aerosol particles, it can be enhanced at low temperatures (268 K) if the relative humidity is high.

The faster that S(IV) oxidation occurs, the faster that sulfur dioxide is depleted from the gas phase, and the faster that S(VI) forms. In cloud drops, dissolution and aqueous reaction can convert 60 percent of gas-phase sulfur dioxide to the sulfate ion within 20 minutes (e.g., Jacobson 1997a; Liang and Jacobson 1999). Figure 19.1 illustrates this point. The figure compares modeled in-cloud concentrations of liquid water, the bisulfate ion, and the sulfate ion over time when sulfur dioxide dissolution and aqueous reaction were and were not included in the calculation. Within 20 min, cloud drops dissolved and converted more than 30 μg $m^{-3}$ (58 percent) out of an initial 52 μg $m^{-3}$ of $SO_2$(g). Aerosol particles, on the other hand, require hours to days to convert the same quantity of sulfur dioxide.

Conversion of S(IV) to S(VI) in aerosol particles, cloud drops, and precipitation drops contributes to **acid deposition**. Acid deposition occurs to some extent in and downwind of all countries worldwide. It is particularly prevalent in provinces of eastern Canada, the northeastern United States (particularly the Adirondack Mountain region), southern Scandinavia, middle and eastern Europe, India, Korea, Russia, China, Japan, Thailand, and South Africa. The natural pH of cloud water and rainwater is 5.6 (Fig. 17.1). Aqueous oxidation of S(IV) to S(VI) generally reduces the pH in fog and rain to 2–5.6, creating acid deposition.

## 19.3 DIFFUSION WITHIN A DROP

When a gas dissolves in a liquid drop, it immediately begins to diffuse through the drop and reacts chemically at the same time. The characteristic **time scale** (s) **for**

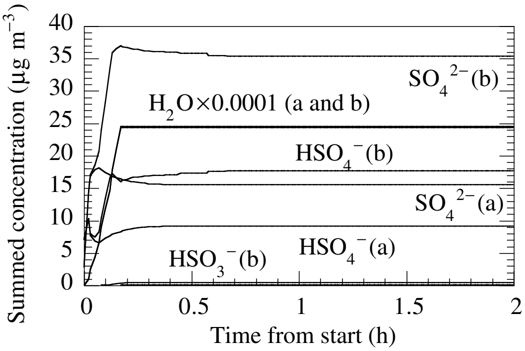


**Figure 19.1** Time-series comparison of dissolved ion and water concentrations, summed over all cloud drop sizes, when cloud drops grew and sulfur dioxide (a) did not and (b) did dissolve in and react within the drops. $H_2SO_4$ condensed in both cases, but $SO_2$ dissolved and reacted in the second case only. Initial conditions were $SO_2$(g), 52 μg m$^{-3}$; $H_2O_2$(g), 10 μg m$^{-3}$; $HNO_3$(g), 30 μg m$^{-3}$; $NH_3$(g), 10 μg m$^{-3}$; HCl(g), 0 μg m$^{-3}$; $H_2SO_4$(g), 15 μg m$^{-3}$; $H_2SO_4$(aq), 10 μg m$^{-3}$; NaCl(aq), 15 μg m$^{-3}$; and $T = 298$ K. The cloud was formed by increasing the relative humidity to 100.01 percent at the start, solving the growth equations with a 1-s time step, and replenishing the relative humidity to 100.01 percent every time step for the first 10 min of simulation. After 10 min, the relative humidity was allowed to relax to its calculated value. From Jacobson (1997a).

**diffusion** of solute $q$ through a liquid drop is

$$\tau_{\mathrm{ad},q} = \frac{r_i^2}{\pi^2 D_{\mathrm{aq},q}} \tag{19.25}$$

(Crank 1975) where $D_{\mathrm{aq},q}$ is the diffusion coefficient of the solute in water at 25 °C (cm$^2$ s$^{-1}$) and $r_i$ is the radius of the drop (cm). A typical diffusion coefficient is $D_{\mathrm{aq},q} = 2 \times 10^{-5}$ cm$^2$ s$^{-1}$ (e.g., Wilke and Chang 1955; Himmelblau 1964; Jacob 1986; Schwartz 1986).

**Example 19.1**

From (19.25), the characteristic time for diffusion within a 30-μm-diameter cloud drop is about 0.011 s. The characteristic time for diffusion within a 10-μm-diameter drop is about 0.0013 s. Thus, for many purposes, diffusion can be assumed instantaneous.

Although the time scale for diffusion is small, chemical reactions often occur on an even smaller time scale. Jacob (1986) found that $O_3(aq)$, $NO_3(aq)$, $OH(aq)$, $Cl(aq)$, $SO_4^-$, $CO_3^-$, and $Cl_2^-$ had chemical lifetimes shorter than diffusion transport times. Such species react near the surface of a drop before they can diffuse to the center. When diffusion and chemical reaction are considered, the time rate of change of concentration of species $q$ in size bin $i$ as a function of radius $r$ is

$$\left(\frac{\mathrm{d}c_{q,i,r}}{\mathrm{d}t}\right)_{\mathrm{ad,aq}} = D_{\mathrm{aq},q}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_{q,i,r}}{\partial r}\right) + P_{\mathrm{c},q,i,r} - L_{\mathrm{c},q,i,r} \tag{19.26}$$

where $P_{\mathrm{c},q,i,r}$ and $L_{\mathrm{c},q,i,r}$ are the net aqueous chemical production and loss rates (mol $\mathrm{cm}^{-3}$ $\mathrm{s}^{-1}$), respectively, of $q$ in size bin $i$ at a distance $r$ from the center of the drop, and the subscript ad, aq indicates that aqueous diffusion is coupled with aqueous chemistry. At the drop center, $\partial c_{q,i,r}/\partial r = 0$.

## 19.4 SOLVING GROWTH AND AQUEOUS CHEMICAL ODES

Aqueous chemical reactions are similar to gas-phase reactions in that both are described by first-order ODEs that can be solved with the methods discussed in Chapter 12. Aqueous chemistry ODEs are more difficult to solve than gas chemistry ODEs for two reasons. First, the e-folding lifetimes of aqueous species against chemical loss are usually shorter than are those of gases. Thus, aqueous reactions are stiffer than gas reactions. Second, when dissolved gases are destroyed by aqueous reactions, the dissolved gases are rapidly replenished by additional dissolution to maintain saturation over the particle surface. When $H_2O_2(aq)$ reacts in solution, for example, $H_2O_2(g)$ dissolves to replace lost $H_2O_2(aq)$ to satisfy (19.8). Thus, in a model that resolves aerosol particles and hydrometeor particles among multiple size bins, aqueous ODEs must be solved within each size bin, and growth ODEs must be solved between the gas phase and all bins simultaneously. Gas chemistry is effectively solved in one size bin.

To make matters more complex, many dissolving gases dissociate reversibly in solution. Thus, dissolution, equilibrium, and aqueous reaction processes must be solved nearly simultaneously. The rate of change of particle concentration due to these processes is

$$\left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{\mathrm{ge,eq,aq}} = \left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{\mathrm{ge}} + \left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{\mathrm{eq}} + \left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{\mathrm{aq}} \tag{19.27}$$

where $c_{q,i,t}$ is the mole concentration of species $q$ in bin $i$ at time $t$, and subscripts ge, eq, and aq identify growth/evaporation, equilibrium, and aqueous chemistry, respectively. The aqueous chemistry term in (19.27) is the same as that in (19.26), except that diffusion is assumed to be instantaneous and particles are assumed to be well mixed in (19.27). The gas-aqueous mole conservation equation corresponding to (19.27) is

$$\frac{\mathrm{d}C_{q,t}}{\mathrm{d}t} = -\sum_{i=1}^{N_B}\left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{\mathrm{ge}} \tag{19.28}$$

where $C_{q,t}$ is the gas mole concentration of species $q$, and $N_B$ is the number of size bins. Together, (19.27) and (19.28) make up a large set of stiff ODEs.

An exact solution to (19.27) and (19.28) is difficult to obtain. The equilibrium term is not an ordinary differential equation. It is a reversible equation solved with an iterative method, such as the MFI or AEI schemes discussed in Chapter 17. A reversible equation, of the form $\mathrm{D} + \mathrm{E} \rightleftharpoons \mathrm{A} + \mathrm{B}$, can be written as a combination of two ODEs, $\mathrm{D} + \mathrm{E} \rightarrow \mathrm{A} + \mathrm{B}$ and $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{D} + \mathrm{E}$. These equations are very stiff and time-consuming to solve. Instead, the reaction $\mathrm{D} + \mathrm{E} \rightleftharpoons \mathrm{A} + \mathrm{B}$ is usually simulated as a reversible equation that may be operator-split from the other terms in (19.27).

The growth and aqueous-chemistry terms in (19.27) are often solved together in zero- and one-dimensional modeling studies (e.g., Chameides 1984; Schwartz 1984; Jacob 1986; Pandis and Seinfeld 1989; Bott and Carmichael 1993; Sander *et al.* 1995; Zhang *et al.* 1998). In some cases, the equations are solved with an integrator of stiff ODEs. In others, they are solved with a forward Euler method taking a small time step. Here, a method of solving the equations in a three-dimensional model is discussed.

With this method, species involved in dissociation/association reactions among themselves are grouped in **families**. Family species cycle rapidly among each other due to rapid and reversible dissociation/association. Changes in family concentrations are slower than changes in species concentrations. Here, the S(IV), S(VI), $\mathrm{HO}_{2,T}$, $\mathrm{CO}_{2,T}$, $\mathrm{HCHO}_T$, $\mathrm{HCOOH}_T$, and $\mathrm{CH_3COOH}_T$ families are considered. Family mole concentrations (moles per cubic centimeter of air) in size bin $i$ are

$$c_{\mathrm{S(IV)},i} = c_{\mathrm{SO_2(aq)},i} + c_{\mathrm{HSO_3^-},i} + c_{\mathrm{SO_3^{2-}},i} \tag{19.29}$$

$$c_{\mathrm{S(VI)},i} = c_{\mathrm{H_2SO_4(aq)},i} + c_{\mathrm{HSO_4^-},i} + c_{\mathrm{SO_4^{2-}},i} \tag{19.30}$$

$$c_{\mathrm{HO}_{2,T},i} = c_{\mathrm{HO_2(aq)},i} + c_{\mathrm{O_2^-},i} \tag{19.31}$$

$$c_{\mathrm{CO}_{2,T},i} = c_{\mathrm{CO_2(aq)},i} + c_{\mathrm{HCO_3^-},i} + c_{\mathrm{CO_3^{2-}},i} \tag{19.32}$$

$$c_{\mathrm{HCHO}_T,i} = c_{\mathrm{HCHO(aq)},i} + c_{\mathrm{H_2C(OH)_2},i} \tag{19.33}$$

$$c_{\mathrm{HCOOH}_T,i} = c_{\mathrm{HCOOH(aq)},i} + c_{\mathrm{HCOO^-},i} \tag{19.34}$$

$$c_{\mathrm{CH_3COOH}_T,i} = c_{\mathrm{CH_3COOH(aq)},i} + c_{\mathrm{CH_3COO^-},i} \tag{19.35}$$

respectively. Some species, such as $\mathrm{H_2O_2(aq)}$ and $\mathrm{O_3(aq)}$, are each self-contained in their own family since $\mathrm{H_2O_2(aq)}$ dissociates significantly only at a pH higher than observed in cloud drops, and $\mathrm{O_3(aq)}$ does not dissociate in solution. Growth–aqueous-chemical ODEs can be obtained for families by combining (17.99) with chemical production and loss terms. For the S(IV) family, the resulting ODE for a size bin is

$$\frac{\mathrm{d}c_{\mathrm{S(IV)},i}}{\mathrm{d}t} = k_{\mathrm{S(IV)},i}\left(C_{\mathrm{SO_2(g)}} - S'_{\mathrm{S(IV)},i}\frac{c_{\mathrm{SO_2(aq)},i}}{H'_{\mathrm{SO_2(aq)},i}}\right) + P_{\mathrm{c,S(IV)},i} - L_{\mathrm{c,S(IV)},i} \tag{19.36}$$

where $k_{\mathrm{S(IV)},i}$ is the **coefficient for mass transfer** of $\mathrm{SO_2}$ to particles of size $i$ ($\mathrm{s^{-1}}$) from (16.64), $C_{\mathrm{SO_2(g)}}$ is the concentration of $\mathrm{SO_2(g)}$ (mol cm$^{-3}$), $S'_{\mathrm{S(IV)},i}$ is the equilibrium saturation ratio from (16.47), $P_{\mathrm{c,S(IV)},i}$ is the **aqueous chemical production rate** of

S(IV) in size bin $i$ (mol cm$^{-3}$ s$^{-1}$), $L_{c,S(IV),i}$ is the **aqueous chemical loss rate** of S(IV) in bin $i$ (mol cm$^{-3}$ s$^{-1}$), and

$$H'_{SO_2(aq),i} = m_v c_w R^* T H_{SO_2} \tag{19.37}$$

is the **dimensionless Henry's constant** of $SO_2$. Parameters in (19.37) were defined in Section 17.14.1. The concentrations $c_{SO_2(aq),i}$ and $c_{S(IV),i}$ are related by

$$c_{SO_2(aq),i} = c_{S(IV),i} \frac{\mathbf{m}^2_{H^+,i}}{\mathbf{m}^2_{H^+,i} + \mathbf{m}_{H^+,i} K_{1,S(IV)} + K_{1,S(IV)} K_{2,S(IV)}} \tag{19.38}$$

derived from (19.29), (17.97), and

$$K_{1,S(IV)} = \frac{\mathbf{m}_{H^+,i} \mathbf{m}_{HSO_3^-,i} \gamma^2_{i,H^+/HSO_3^-}}{\mathbf{m}_{SO_2(aq),i}} \tag{19.39}$$

$$K_{2,S(IV)} = \frac{\mathbf{m}_{H^+,i} \mathbf{m}_{SO_3^{2-},i} \gamma^2_{i,H^+/SO_3^{2-}}}{\mathbf{m}_{HSO_3^-,i} \gamma^2_{i,H^+/HSO_3^-}} \tag{19.40}$$

which are the **first and second equilibrium dissociation coefficient expressions** for the reversible reactions,

$$SO_2(aq) + H_2O \rightleftharpoons H^+ + HSO_3^- \tag{19.41}$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \tag{19.42}$$

respectively. For simplicity, the activity coefficients in (19.39) and (19.40) may be set to zero when dilute solutions (e.g., cloud drops) are considered.

Substituting (19.38) into (19.36) and adding time subscripts give

$$\boxed{\frac{dc_{S(IV),i,t}}{dt} = k_{S(IV),i,t-h}\left(C_{SO_2(g),t} - S'_{S(IV),i,t-h}\frac{c_{S(IV),i,t}}{H'_{S(IV),i,t-h}}\right) + P_{c,S(IV),i,t} - L_{c,S(IV),i,t} \qquad (19.43)}$$

where

$$H'_{S(IV),i,t-h} = m_v c_{w,i,t-h} R^* T H_{SO_2}\left(1 + \frac{K_{1,S(IV)}}{\mathbf{m}_{H^+,i,t-h}} + \frac{K_{1,S(IV)} K_{2,S(IV)}}{\mathbf{m}^2_{H^+,i,t-h}}\right) \tag{19.44}$$

is the **dimensionless effective Henry's constant** of S(IV).

The chemical production and loss rates of a species $q$ are determined from

$$P_{c,q,i,t} = \sum_{l=1}^{N_{prod,q}} R_{c,n_P(l,q),t} \qquad L_{c,q,i,t} = \sum_{l=1}^{N_{loss,q}} R_{c,n_L(l,q),t} \tag{19.45}$$

where $N_{prod,q}$ ($N_{loss,q}$) is the number of reactions in which species $q$ is produced (lost), $R_{c,n_P(l,q)}$ [$R_{c,n_L(l,q)}$] is the $l$th production (loss) rate of $q$, and $n_P(l,q)$ [$n_L(l,q)$]

gives the reaction number corresponding to the *l*th production (loss) term of species *q*. The terms in (19.44) are similar to those in (12.53) and (12.55), respectively. S(IV) has no important aqueous chemical sources but several sinks.

Appendix Table B.8 lists S(IV) oxidation reactions. Two of the reactions

$$\mathrm{S(IV)} + \mathrm{H_2O_2(aq)} + \mathrm{H^+} \longrightarrow \mathrm{S(VI)} + 2\mathrm{H^+} + \mathrm{H_2O(aq)} \tag{19.46}$$

$$\mathrm{S(IV)} + \mathrm{HO}_{2,T} \longrightarrow \mathrm{S(VI)} + \mathrm{OH(aq)} + 2\mathrm{H^+} \tag{19.47}$$

are considered here to illustrate the calculation of the chemical loss rate of the S(IV) family for use in a chemical solver. Appendix Table B.8 shows that the only important S(IV) reactant in (19.46) is $\mathrm{HSO_3^-}$:

$$\mathrm{HSO_3^-} + \mathrm{H_2O_2(aq)} + \mathrm{H^+} \tag{19.48}$$

In (19.47), $\mathrm{HSO_3^-}$ and $\mathrm{SO_3^{2-}}$ are important S(IV) reactants and $\mathrm{HO_2(aq)}$ and $\mathrm{O_2^-}$ are important $\mathrm{HO}_{2,T}$ reactants. As such, (19.47) is really a combination of the following four reactions:

$$\mathrm{HSO_3^-} + \mathrm{HO_2(aq)} \tag{19.49}$$

$$\mathrm{SO_3^{2-}} + \mathrm{HO_2(aq)} \tag{19.50}$$

$$\mathrm{HSO_3^-} + \mathrm{O_2^-} \tag{19.51}$$

$$\mathrm{SO_3^{2-}} + \mathrm{O_2^-} \tag{19.52}$$

One way to consider the loss of S(IV) in a chemical solver is to treat reactions (19.48)–(19.52) as separate reactions. Doing so requires the simultaneous solution of the equilibrium equations

$$\mathrm{SO_2(aq)} + \mathrm{H_2O(aq)} \rightleftharpoons \mathrm{H^+} + \mathrm{HSO_3^-} \rightleftharpoons 2\mathrm{H^+} + \mathrm{SO_3^{2-}} \tag{19.53}$$

$$\mathrm{HO_2(aq)} \rightleftharpoons \mathrm{H^+} + \mathrm{O_2^-} \tag{19.54}$$

Alternatively, the chemical loss of S(IV) or any other species can be written in terms of the family reactions, (19.46) and (19.47), where the families are defined in (19.29)–(19.35). In this case, the instantaneous equilibrium partitioning that occurs with (19.53) and (19.54) is accounted for in the loss rate coefficient. For example, in the case of S(IV) reacting in (19.46) and (19.47) only, the **chemical loss rate of S(IV)** is

$$\boxed{L_{\mathrm{c,S(IV)},i,t} = k_a c_{\mathrm{S(IV)},i,t} c_{\mathrm{H_2O_2},i,t} c_{\mathrm{H^+},i,t} + k_b c_{\mathrm{S(IV)},i,t} c_{\mathrm{HO}_{2,T},i,t}} \tag{19.55}$$

(mol cm$^{-3}$ s$^{-1}$). In this equation,

$$k_a = k_{a,1}\alpha_{1,\mathrm{S(IV)}} \tag{19.56}$$

is a **third-order rate coefficient** ($\text{cm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$), where $k_{a,1}$ is the rate coefficient for Reaction (19.48), given in Appendix Table B.8 (converted from ($\text{M}^{-2}\ \text{s}^{-1}$) to ($\text{cm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$)), and

$$\alpha_{1,\text{S(IV)}} = \frac{\mathbf{m}_{\text{H}^+,i,t-h} K_{1,\text{S(IV)}}}{\mathbf{m}^2_{\text{H}^+,i,t-h} + \mathbf{m}_{\text{H}^+,i,t-h} K_{1,\text{S(IV)}} + K_{1,\text{S(IV)}} K_{2,\text{S(IV)}}} \tag{19.57}$$

is the **mole fraction of total S(IV) partitioned to $HSO_3^-$**. This fraction depends on pH, so $\mathbf{m}_{\text{H}^+}$ must be solved for simultaneously. The equilibrium coefficients in (19.57) are given in (19.39) and (19.40).

The second rate coefficient in (19.55) is

$$k_b = \left[k_{b,1}\alpha_{1,\text{S(IV)}} + k_{b,2}\alpha_{2,\text{S(IV)}}\right]\alpha_{0,\text{HO}_{2,T}} + \left[k_{b,3}\alpha_{1,\text{S(IV)}} + k_{b,4}\alpha_{2,\text{S(IV)}}\right]\alpha_{1,\text{HO}_{2,T}} \tag{19.58}$$

($\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$) where $k_{b,1}$, $k_{b,2}$, $k_{b,3}$, and $k_{b,4}$ are the rate coefficients from Appendix Table B.8 for Reactions (19.49)–(19.52), respectively,

$$\alpha_{2,\text{S(IV)}} = \frac{K_{1,\text{S(IV)}} K_{2,\text{S(IV)}}}{\mathbf{m}^2_{\text{H}^+,i,t-h} + \mathbf{m}_{\text{H}^+,i,t-h} K_{1,\text{S(IV)}} + K_{1,\text{S(IV)}} K_{2,\text{S(IV)}}} \tag{19.59}$$

is the **mole fraction of total S(IV) partitioned to $SO_3^{2-}$**, and

$$\alpha_{0,\text{HO}_{2,T}} = \frac{\mathbf{m}_{\text{H}^+,i,t-h}}{\mathbf{m}_{\text{H}^+,i,t-h} + K_{1,\text{HO}_{2,T}}} \tag{19.60}$$

$$\alpha_{1,\text{HO}_{2,T}} = \frac{K_{1,\text{HO}_{2,T}}}{\mathbf{m}_{\text{H}^+,i,t-h} + K_{1,\text{HO}_{2,T}}} \tag{19.61}$$

are the **mole fractions of $HO_{2,T}$ partitioned to $HO_2$(aq) and $O_2^-$**, respectively. In these expressions, $K_{1,\text{HO}_{2,T}}$ is the equilibrium coefficient for Reaction (19.54). The family method described above significantly reduces the number of reactions required for a solution to aqueous chemical equations.

The gas conservation equation corresponding to (19.43) is

$$\boxed{\frac{\mathrm{d}C_{\text{SO}_2(g),t}}{\mathrm{d}t} = -\sum_{i=1}^{N_B} k_{\text{S(IV)},i,t-h}\left[C_{\text{SO}_2(g),t} - S'_{\text{S(IV)},i,t-h}\frac{c_{\text{S(IV)},i,t}}{H'_{\text{S(IV)},i,t-h}}\right]} \tag{19.62}$$

Together, (19.43) and (19.62) make up a set of ODEs whose order depends on the number of dissolving gases, particle size bins, and species taking part in chemical reactions. This set of equations can be solved in a three-dimensional model with a sparse-matrix solver. Table 19.2 shows that such a solver reduced the number of multiplications during one call to a matrix decomposition subroutine by over two million (99.7 percent) for a given set of species, reactions, and size bins.

The last four rows show the number of operations in each of four loops of matrix decomposition and backsubstitution. The percentages are values in the second

**Table 19.2** Reduction in array space and number of matrix operations before and after the use of sparse-matrix techniques for ODEs arising from 10 gases transferring to 16 size bins, and 11 aqueous chemistry reactions occurring among 11 species within each bin

| | Initial | After sparse reductions |
|---|---|---|
| Order of matrix | 186 | 186 |
| No. init. matrix positions filled | 34 596 | 1226 (3.5%) |
| No. final matrix positions filled | 34 596 | 2164 (6.3%) |
| No. operations decomp. 1 | 2 127 685 | 6333 (0.3%) |
| No. operations decomp. 2 | 17 205 | 1005 (5.8%) |
| No. operations backsub. 1 | 17 205 | 1005 (5.8%) |
| No. operations backsub. 2 | 17 205 | 973 (5.6%) |

column relative to those in the first. The solver used was SMVGEAR II (Jacobson 1998a).

## 19.5 SUMMARY

In this chapter, aqueous chemical reactions and their effects on aerosol and hydrometeor composition were discussed. Aqueous reactions are important because they affect the rate of chemical conversion of sulfur dioxide gas, a member of the S(IV) family, to the sulfate ion, a member of the S(VI) family. Production of the sulfate ion in a liquid drop increases the acidity of the drop. Thus, conversion of S(IV) to S(VI) in atmospheric particles enhances acid deposition. The rate of S(IV) conversion to S(VI) depends on liquid-water content, S(IV) oxidant concentrations, and pH. Conversion is faster in cloud drops than in aerosol particles because clouds have higher liquid-water contents than do aerosol particles. Numerical methods of solving aqueous chemistry ODEs are the same as those for solving gas-chemistry ODEs. Aqueous ODEs are more difficult to solve because they are stiffer and more tightly coupled to other processes than are gas-phase ODEs.

## 19.6 PROBLEMS

**19.1** What are the two primary formation mechanisms of S(VI) in particles? How might changes in relative humidity affect the rate of growth of particles due to each mechanism?

**19.2** Why do aerosol particles convert S(IV) species to S(VI) species at a lower rate than do cloud drops?

**19.3** Draw approximate curves of relative concentration versus radius when the time scale for diffusion in a drop is (a) less than, (b) equal to, (c) greater than that for chemical reaction loss of an aqueous species. Assume the relative concentration at the drop center is unity.

**19.4** Why are aqueous-phase reactions generally stiffer than gas-phase reactions?

**19.5** Calculate the e-folding lifetimes of $HSO_3^-$ against loss by reaction with $O_3(aq)$, $H_2O_2(aq)$, and OH(aq), respectively. Assume $\chi_{O_3(g)}$, $\chi_{H_2O_2(g)}$, and $\chi_{OH(g)}$ are 0.1, $8 \times 10^{-4}$, and $4.0 \times 10^{-8}$ ppmv, respectively. Estimate aqueous molalities of these species using Henry's constant from Appendix Table B.7. Assume that $T = 280$ K, $p_d = 950$ hPa, the solution is dilute, and pH = 4.5.

## 19.7 COMPUTER PROGRAMMING PRACTICE

**19.6** Write a computer script to read reactions and rate coefficients. Use the script to calculate rate coefficients for all reactions in Appendix Table B.8 when $T = 298$ K and when 273 K.