

18 Chemistry of the Environment

Visualizing Concepts

18.1 *Analyze.* Given that one mole of an ideal gas at 1 atm and 298 K occupies 22.4 L, is the volume of one mole of ideal gas in the middle of the stratosphere greater than, equal to, or less than 22.4 L?

Plan. Consider the relationship between pressure, temperature, and volume of an ideal gas. Use Figure 18.1 to estimate the pressure and temperature in the middle of the stratosphere, and compare the two sets of temperature and pressure.

Solve. According to the ideal gas law, $PV = nRT$, so $V = nRT/P$. Since n and R are constant for this exercise, V is proportional to T/P .

(a) The stratosphere ranges from 10 to 50 km, so the middle is at approximately 30 km. At this altitude, $T \approx 230$ K, $P \approx 40$ torr (from Figure 18.1). Since we are comparing T/P ratios, either atm or torr can be used as pressure units; we will use torr.

$$\text{At sea level: } T/P = 298 \text{ K}/760 \text{ torr} = 0.39$$

$$\text{At 30 km: } T/P = 230 \text{ K}/40 \text{ torr} = 5.75$$

The proportionality constant (T/P) is much greater at 30 km than sea level, so the volume of 1 mol of an ideal gas is greater at this altitude. The decrease in temperature at 30 km is more than offset by the substantial decrease in pressure.

(b) Volume is proportional to T/P , not simply T . The relative volumes of one mole of an ideal gas at 50 km and 85 km depend on the temperature and pressure at the two altitudes. From Figure 18.1,

$$50 \text{ km: } T \approx 270 \text{ K}, P \approx 20 \text{ torr}, T/P = 270 \text{ K}/20 \text{ torr} = 13.5$$

$$85 \text{ km: } T \approx 190 \text{ K}, P < 0.01 \text{ torr}, T/P = 190 \text{ K}/0.01 \text{ torr} = 19,000$$

Again, the slightly lower temperature at 85 km is more than offset by a much lower pressure. One mole of an ideal gas will occupy a much larger volume at 85 km than 50 km.

18.2 Molecules in the upper atmosphere tend to have multiple bonds because they have sufficiently high bond dissociation enthalpies (Table 8.4) to survive the incoming high energy radiation from the sun. According to Table 8.4, for the same two bonded atoms, multiple bonds have higher bond dissociation enthalpies than single bonds. Molecules with single bonds are likely to undergo photodissociation in the presence of the high energy, short wavelength solar radiation present in the upper atmosphere.

18.3 Ozone concentration varies with altitude because conditions favorable to ozone formation (and unfavorable to decomposition) vary with altitude. Formation and persistence of O_3 require the presence of O atoms, O_2 molecules, and energy carriers (M^* , usually N_2 or O_2). Above 60 km, there are too few O_2 molecules for significant O_3 formation. Below 30 km, there are too few O atoms. Between 30 km and 60 km, O_3 concentration varies depending on the concentrations of O, O_2 and M^* .

18.4 *Analyze.* Given granite, marble, bronze, and other solid materials, what observations and measurements indicate whether the material is appropriate for an outdoor sculpture? If the material changes (erodes) over time, what chemical processes are responsible?

Plan. An appropriate material resists chemical and physical changes when exposed to environmental conditions. An inappropriate material undergoes chemical reactions with substances in the troposphere, degrading the structural strength of the material and the sculpture. *Solve.*

(a) The appearance and mass of the material upon environmental exposure are both indicators of chemical and physical changes. If the appearance and mass of the material are unchanged after a period of time, the material is well-suited for the sculpture because it is inert to chemical and physical changes. Changes in the color or texture of the material's surface indicate that a chemical reaction has occurred, because a different substance with different properties has formed. A decrease in mass indicates that some of the material has been lost, either by chemical reaction or physical change. An increase in mass indicates corrosion. If the mass of the material is unchanged, it is probably inert to chemical and physical environmental changes and suitable for sculpture.

(b) The two main chemical processes that lead to erosion are reaction with acid rain and corrosion or air oxidation, which is encouraged by acid conditions (see Section 20.8).

Acid rain is primarily H_2SO_3 and/or H_2SO_4 , which reacts directly with carbonate minerals such as marble and limestone. Acidic conditions created by acid rain encourage corrosion of metals such as iron, steel, and bronze. Corrosion produces metal oxides which may or may not cling to the surface of the material. If the oxides are washed away, the material will lose mass after corrosion. Physical erosion due to the effects of wind and rain on soft materials such as sandstone also causes mass to decrease.

18.5 $CO_2(g)$ dissolves in seawater to form $H_2CO_3(aq)$. The basic pH of the ocean encourages ionization of $H_2CO_3(aq)$ to form $HCO_3^-(aq)$ and $CO_3^{2-}(aq)$. Under the correct conditions, carbon is removed from the ocean as $CaCO_3(s)$ (sea shells, coral, chalk cliffs). As carbon is removed, more $CO_2(g)$ dissolves to maintain the balance of complex and interacting acid-base and precipitation equilibria.

18.6 *Analyze/Plan.* Explain how an ion-exchange column "softens" water. See the Closer Look box on "Water Softening" in Section 18.6.

Solve. The plastic beads in an ion-exchange column contain covalently bound anionic groups such as R-COO^- and R-SO_3^- . These groups have Na^+ cations associated with them for charge balance. When "hard" water containing Ca^{2+} and other divalent cations passes over the beads, the $2+$ cations are attracted to the anionic groups and Na^+ is displaced. The higher charge on the divalent cations leads to greater electrostatic attractions, which promote the cation exchange. The "soft" water that comes out of the column contains two Na^+ ions in place of each divalent cation, mostly Ca^{2+} and Mg^{2+} , that remains in the column associated with the plastic beads.

- 18.7 The guiding principle of green chemistry is that "an ounce of prevention is worth a pound of cure." Processes should be designed to minimize or eliminate solvents and waste, generate nontoxic waste, be energy efficient, employ renewable starting materials, and take advantage of catalysts that enable the use of safe and common reagents.
- 18.8 Some of the missing CO_2 is absorbed by "land plants" (vegetation other than trees) and incorporated into the soil. Soil is the largest land-based carbon reservoir. The amount of carbon-storing capacity of soil is affected by erosion, soil fertility, and other complex factors. For more details, search the internet for "carbon budget."

Earth's Atmosphere

- 18.9 (a) The temperature profile of the atmosphere (Figure 18.1) is the basis of its division into regions. The center of each peak or trough in the temperature profile corresponds to a new region.
- (b) Troposphere, 0–12 km; stratosphere, 12–50 km; mesosphere, 50–85 km; thermosphere, 85–110 km.
- 18.10 (a) Boundaries between regions of the atmosphere are at maxima and minima (peaks and valleys) in the atmospheric temperature profile. For example, in the troposphere, temperature decreases with altitude, while in the stratosphere, it increases with altitude. The temperature minimum is the tropopause boundary.
- (b) Atmospheric pressure in the troposphere ranges from 1.0 atm to 0.4 atm, while pressure in the stratosphere ranges from 0.4 atm to 0.001 atm. Gas density (g/L) is directly proportional to pressure. The much lower density of the stratosphere means it has the smaller mass, despite having a larger volume than the troposphere.
- 18.11 *Analyze/Plan.* Given O_3 concentration in ppm, calculate partial pressure. Use the definition of ppm to get mol fraction O_3 . For gases mole fraction = pressure fraction;

$$P_{\text{O}_3} = \chi_{\text{O}_3} \cdot P_{\text{atm}}$$
- $$0.441 \text{ ppm O}_3 = \frac{0.441 \text{ mol O}_3}{1 \times 10^6 \text{ mol air}} = 4.41 \times 10^{-7} = \chi_{\text{O}_3}$$
- Solve.* $P_{\text{O}_3} = \chi_{\text{O}_3} \cdot P_{\text{atm}} = 4.41 \times 10^{-7} (0.67 \text{ atm}) = 2.955 \times 10^{-7} = 3.0 \times 10^{-7} \text{ atm}$
- 18.12 $P_{\text{Ar}} = \chi_{\text{Ar}} \cdot P_{\text{atm}}; P_{\text{Ar}} = 0.00934 (98.6 \text{ kPa}) = 0.921 \text{ kPa}; 0.921 \text{ kPa} \times \frac{760 \text{ torr}}{101.325 \text{ kPa}} = 6.91 \text{ torr}$

$$P_{\text{CO}_2} = \chi_{\text{CO}_2} \cdot P_{\text{atm}}; P_{\text{CO}_2} = 0.000375 (98.6 \text{ kPa}) = 0.0370 \text{ kPa}; 0.0350 \text{ kPa} \times \frac{760 \text{ torr}}{101.325 \text{ kPa}} = 0.277 \text{ torr}$$

- 18.13 *Analyze/Plan.* Given CO concentration in ppm, calculate number of CO molecules in 1.0 L air at given conditions. ppm CO \rightarrow χ_{CO} \rightarrow atm CO \rightarrow mol CO \rightarrow molecules CO. Use the ideal gas law to change atm CO to mol CO, then Avogadro's number to get molecules. *Solve.*

$$3.4 \text{ ppm CO} = \frac{3.4 \text{ mol CO}}{1 \times 10^6 \text{ mol air}} = 3.4 \times 10^{-6} = \chi_{\text{CO}}$$

$$P_{\text{CO}} = \chi_{\text{CO}} \cdot P_{\text{atm}} = 3.4 \times 10^{-6} \times 755 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 3.378 \times 10^{-6} = 3.4 \times 10^{-6} \text{ atm}$$

$$n_{\text{CO}} = \frac{P_{\text{CO}} V}{RT} = \frac{3.378 \times 10^{-6} \text{ atm} \times 1.0 \text{ L}}{295 \text{ K}} \times \frac{\text{K} \cdot \text{mol}}{0.08206 \text{ L} \cdot \text{atm}} = 1.395 \times 10^{-7} = 1.4 \times 10^{-7} \text{ mol CO}$$

$$1.395 \times 10^{-7} \text{ mol CO} \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} = 8.402 \times 10^{16} = 8.4 \times 10^{16} \text{ molecules CO}$$

- 18.14 (a) ppm Ne = mol Ne / 1×10^6 mol air; $\chi_{\text{Ne}} = 1.818 \times 10^{-5}$ mol Ne / mol air

$$\frac{1.818 \times 10^{-5} \text{ mol Ne}}{1 \text{ mol air}} = \frac{x \text{ mol Ne}}{1 \times 10^6 \text{ mol air}}; x = 18.18 \text{ ppm Ne}$$

- (b) $P_{\text{Ne}} = \chi_{\text{Ne}} \cdot P_{\text{atm}} = 1.818 \times 10^{-5} \times 743 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.7773 \times 10^{-5}$
 $= 1.78 \times 10^{-5} \text{ atm}$

$$T = 300^\circ\text{C} + 273 = 573 \text{ K}$$

$$\frac{n_{\text{Ne}}}{V} = \frac{P_{\text{Ne}}}{RT} = \frac{1.7773 \times 10^{-5} \text{ atm}}{573 \text{ K}} \times \frac{\text{K} \cdot \text{mol}}{0.08206 \text{ L} \cdot \text{atm}} = 3.7799 \times 10^{-7} = 3.78 \times 10^{-7} \text{ mol/L}$$

$$\frac{3.7799 \times 10^{-7} \text{ mol Ne}}{\text{L}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}} = 2.2763 \times 10^{17}$$

$$= 2.28 \times 10^{17} \text{ Ne atoms/L}$$

The Upper Atmosphere; Ozone

- 18.15 *Analyze/Plan.* Given bond dissociation energy in kJ/mol, calculate the wavelength of a single photon that will rupture a C-Br bond. kJ/mol \rightarrow J/molecule. $\lambda = hc/E$. ($\lambda = hc/E$ describes the energy/wavelength relationship of a single photon.) *Solve.*

$$\frac{210 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} = 3.487 \times 10^{-19} = 3.49 \times 10^{-19} \text{ J/molecule}$$

$\lambda = c/\nu$ We also have that $E = h\nu$, so $\nu = E/h$. Thus,

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{sec})(3.00 \times 10^8 \text{ m/sec})}{3.487 \times 10^{-19} \text{ J}} = 5.70 \times 10^{-7} \text{ m} = 570 \text{ nm}$$

$$18.16 \quad \frac{339 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} = 5.6294 \times 10^{-19} = 5.63 \times 10^{-19} \text{ J/molecule}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{sec})(3.00 \times 10^8 \text{ m/sec})}{5.6294 \times 10^{-19} \text{ J}} = 3.53 \times 10^{-7} \text{ m} = 353 \text{ nm}$$

$$\frac{293 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} = 4.8655 \times 10^{-19} = 4.87 \times 10^{-19} \text{ J/molecule}$$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{sec})(3.00 \times 10^8 \text{ m/sec})}{4.8655 \times 10^{-19} \text{ J}} = 4.09 \times 10^{-7} \text{ m} = 409 \text{ nm}$$

Photons of wavelengths longer than 409 nm cannot cause rupture of the C–Cl bond in either CF_3Cl or CCl_4 . Photons with wavelengths between 409 and 353 nm can cause C–Cl bond rupture in CCl_4 , but not in CF_3Cl .

18.17 (a) *Photodissociation* is cleavage of the $\text{O}=\text{O}$ bond such that two neutral O atoms are produced: $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$

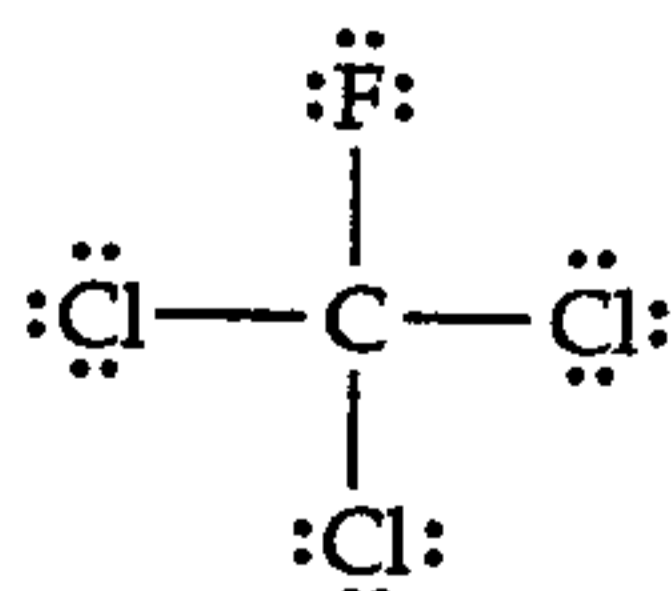
Photoionization is absorption of a photon with sufficient energy to eject an electron from an O_2 molecule: $\text{O}_2(\text{g}) + h\nu \rightarrow \text{O}_2^+ + e^-$

(b) Photoionization of O_2 requires 1205 kJ/mol. Photodissociation requires only 495 kJ/mol. At lower elevations, solar radiation with wavelengths corresponding to 1205 kJ/mol or shorter has already been absorbed, while the longer wavelength radiation has passed through relatively well. Below 90 km, the increased concentration of O_2 and the availability of longer wavelength radiation cause the photodissociation process to dominate.

18.18 Photodissociation of N_2 is relatively unimportant compared to photodissociation of O_2 for two reasons. The bond dissociation energy of N_2 , 941 kJ/mol, is much higher than that of O_2 , 495 kJ/mol. Photons with a wavelength short enough to photodissociate N_2 are not as abundant as the ultraviolet photons that lead to photodissociation of O_2 . Also, N_2 does not absorb these photons as readily as O_2 so even if a short-wavelength photon is available, it may not be absorbed by an N_2 molecule.

18.19 A *hydrofluorocarbon* is a compound that contains hydrogen, fluorine, and carbon; it contains hydrogen in place of chlorine. HFCs are potentially less harmful than CFCs because photodissociation does not produce Cl atoms, which catalyze the destruction of ozone.

18.20 $32 e^-$, $16 e^-$ pr



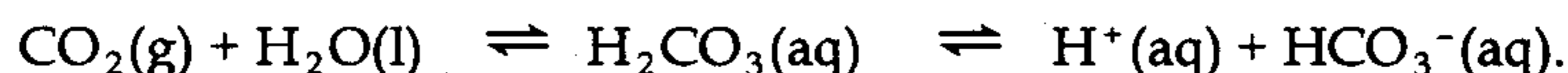
CFC-11, CFCl_3 , contains C–Cl bonds that can be cleaved by UV light in the stratosphere to produce Cl atoms. It is chlorine in atomic form that catalyzes the

destruction of stratospheric ozone. CFC-11 is chemically inert and resists decomposition in the troposphere, so that it eventually reaches the stratosphere in molecular form.

- 18.21 (a) In order to catalyze ozone depletion, the halogen must be present as single halogen atoms. These halogen atoms are produced in the stratosphere by photodissociation of a carbon-halogen bond. According to Table 8.4, the C-F average bond dissociation energy is 485 kJ/mol, while that of C-Cl is 328 kJ/mol. The C-F bond requires more energy for dissociation and is not readily cleaved by the available wavelengths of UV light.
- (b) Chlorine is present as chlorine atoms and chlorine oxide molecules, Cl and ClO.
- 18.22 Yes. Assuming CBr₃ reaches the stratosphere intact, it contains C-Br bonds that are even more susceptible to cleavage by UV light than C-Cl bonds. According to Table 8.4, the average C-Br bond dissociation energy is 273 kJ/mol, compared to 328 kJ/mol for C-Cl bonds. Once in atomic form, Br atoms catalyze the destruction of ozone by a mechanism similar to that of Cl atoms.

Chemistry of the Troposphere

- 18.23 (a) Methane, CH₄, arises from decomposition of organic matter by certain microorganisms; it also escapes from underground gas deposits.
- (b) SO₂ is released in volcanic gases, and also is produced by bacterial action on decomposing vegetable and animal matter.
- (c) Nitric oxide, NO, results from oxidation of decomposing organic matter, and is formed in lightning flashes.
- (d) CO is a possible product of some vegetable matter decay.
- 18.24 Rainwater is naturally acidic due to the presence of CO₂(g) in the atmosphere. All oxides of nonmetals produce acidic solutions when dissolved in water. Even in the absence of polluting gases such as SO₂, SO₃, NO, and NO₂, CO₂ causes rainwater to be acidic. The important equilibria are:



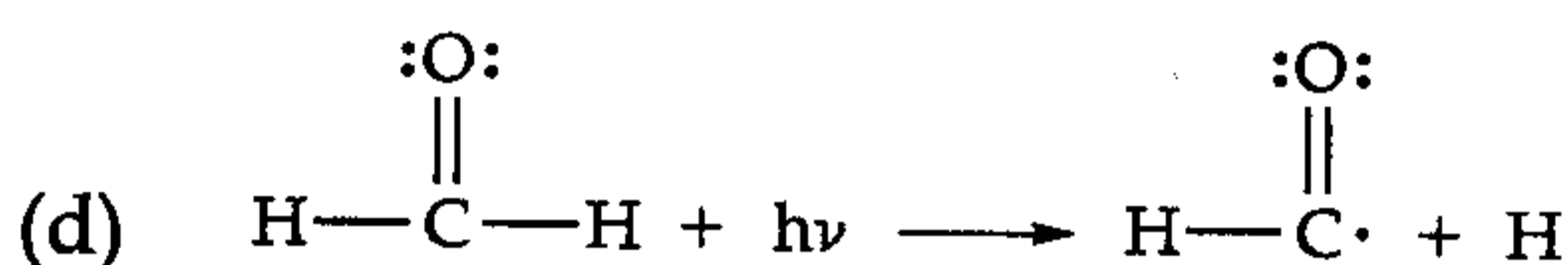
- 18.25 (a) Acid rain is primarily H₂SO₄(aq).
- $$\text{H}_2\text{SO}_4(\text{aq}) + \text{CaCO}_3(\text{s}) \rightarrow \text{CaSO}_4(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$$
- (b) The CaSO₄(s) would be much less reactive with acidic solution, since it would require a strongly acidic solution to shift the relevant equilibrium to the right.
- $$\text{CaSO}_4(\text{s}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{HSO}_4^-(\text{aq})$$
- Note, however, that CaSO₄(s) is brittle and easily dislodged; it provides none of the structural strength of limestone.
- 18.26 (a) $\text{Fe}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
- (b) No. Silver is a "noble" metal. It is relatively resistant to oxidation, and much more resistant than iron. In Table 4.5, The Activity Series of Metals in Aqueous Solution, Ag is much, much lower than Fe and it is below hydrogen, while Fe is above hydrogen. This means that Fe is susceptible to oxidation by acid, while Ag is not.

18.27 *Analyze/Plan.* Given wavelength of a photon, place it in the electromagnetic spectrum, calculate its energy in kJ/mol, and compare it to an average bond dissociation energy. Use Figure 6.4; $E(\text{J}/\text{photon}) = hc/\lambda$. $\text{J}/\text{photon} \rightarrow \text{kJ}/\text{mol}$. *Solve.*

(a) Ultraviolet (Figure 6.4)

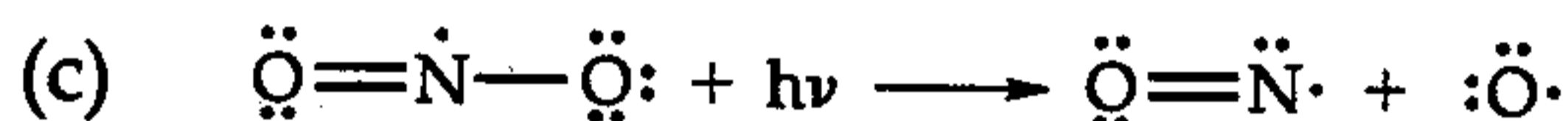
$$\begin{aligned} \text{(b)} \quad E_{\text{photon}} &= hc/\lambda = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s} \times 3.00 \times 10^8 \text{ m/s}}{335 \times 10^{-9} \text{ m}} = 5.934 \times 10^{-19} \\ &= 5.93 \times 10^{-19} \text{ J/photon} \\ \frac{5.934 \times 10^{-19} \text{ J}}{1 \text{ photon}} &\times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 357 \text{ kJ/mol} \end{aligned}$$

(c) The average C–H bond energy from Table 8.4 is 413 kJ/mol. The energy calculated in part (b), 357 kJ/mol, is the energy required to break 1 mol of C–H bonds in formaldehyde, CH_2O . The C–H bond energy in CH_2O must be less than the “average” C–H bond energy.



18.28 (a) Visible (Figure 6.4)

$$\begin{aligned} \text{(b)} \quad E_{\text{photon}} &= hc/\lambda = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s} \times 3.00 \times 10^8 \text{ m/s}}{420 \times 10^{-9} \text{ m}} = 4.733 \times 10^{-19} \\ &= 4.73 \times 10^{-19} \text{ J/photon} \\ \frac{4.733 \times 10^{-19} \text{ J}}{1 \text{ photon}} &\times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 285 \text{ kJ/mol} \end{aligned}$$



18.29 Most of the energy entering the atmosphere from the sun is in the form of visible radiation, while most of the energy leaving the earth is in the form of infrared radiation. CO_2 is transparent to the incoming visible radiation, but absorbs the outgoing infrared radiation.

18.30 (a) A *greenhouse gas* absorbs energy in the 10,000–30,000 nm or infrared region. It absorbs wavelengths of radiation emitted by earth and returns it as heat. A non-greenhouse gas is transparent to radiation in this wavelength range.

(b) $\text{Ar}(\text{g})$ is monatomic, while $\text{CH}_4(\text{g})$ contains 4 C–H bonds. Infrared radiation has insufficient energy to cause electron transitions or bond cleavage; but it has an appropriate amount of energy to cause molecular deformations, bond stretching, and angle bending. Monatomic gases such as Ar cannot “use” infrared radiation and are transparent to it.

The World Ocean

18.31 *Analyze/Plan.* Given salinity and density, calculate molarity. A salinity of 5.6 denotes that there are 5.6 g of dry salt per kg of water. *Solve.*

$$\frac{5.6 \text{ g NaCl}}{1 \text{ kg soln}} \times \frac{1.03 \text{ kg soln}}{1 \text{ L soln}} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \times \frac{1 \text{ mol Na}^+}{1 \text{ mol NaCl}} = 0.0987 = 0.099 \text{ M Na}^+$$

- 18.32 If the phosphorous is present as phosphate, there is a 1:1 ratio between the molarity of phosphorus and molarity of phosphate. Thus, we can calculate the molarity based on the given mass of P.

$$\frac{0.07 \text{ g P}}{1 \times 10^6 \text{ g H}_2\text{O}} \times \frac{1 \text{ mol P}}{31 \text{ g P}} \times \frac{1 \text{ mol PO}_4^{3-}}{1 \text{ mol P}} \times \frac{1 \times 10^3 \text{ g H}_2\text{O}}{1 \text{ L H}_2\text{O}} = 2.26 \times 10^{-6} = 2 \times 10^{-6} \text{ M PO}_4^{3-}$$

- 18.33 *Analyze/Plan.* g Mg(OH)₂ → mol Mg(OH)₂ → mol ratio → mol CaO → g CaO. *Solve.*

$$1000 \text{ lb Mg(OH)}_2 \times \frac{453.6 \text{ g}}{\text{lb}} \times \frac{1 \text{ mol Mg(OH)}_2}{58.33 \text{ g Mg(OH)}_2} \times \frac{1 \text{ mol CaO}}{1 \text{ mol Mg(OH)}_2} \times \frac{56.08 \text{ g CaO}}{1 \text{ mol CaO}} = 4.361 \times 10^5 \text{ g CaO}$$

- 18.34 0.05 ppb Au = 0.05 g Au / 1 × 10⁹ g seawater

$$\$1,000,000 \times \frac{1 \text{ oz Au}}{\$400} \times \frac{1 \text{ lb}}{16 \text{ oz}} \times \frac{453.6 \text{ g}}{1 \text{ lb}} = 7.0875 \times 10^4 \text{ g} = 7.09 \times 10^4 \text{ g Au needed}$$

$$7.0875 \times 10^4 \text{ g Au} \times \frac{1 \times 10^9 \text{ g seawater}}{0.05 \text{ g Au}} \times \frac{1 \text{ mL seawater}}{1.03 \text{ g seawater}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 1.3762 \times 10^{12} = 1 \times 10^{12} \text{ L seawater}$$

1 × 10¹² L seawater are needed if the process is 100% efficient; since it is only 50% efficient, twice as much seawater is needed.

$$1.3762 \times 10^{12} \times 2 = 2.7524 \times 10^{12} = 3 \times 10^{12} \text{ L seawater}$$

Note that the 1 sig fig in 0.05 ppb Au limits the precision of the calculation.

- 18.35 *Analyze/Plan.* Given temperature and the concentration difference between the two solutions, ($\Delta M = 0.22 - 0.01 = 0.21 \text{ M}$), calculate the minimum pressure for reverse osmosis. Use the relationship $\pi = MRT$ from Section 13.5. This is the pressure required to halt osmosis from the more dilute (0.01 M) to the more concentrated (0.22 M) solution. Slightly more pressure will initiate reverse osmosis. *Solve.*

$$\pi = \Delta MRT = \frac{0.21 \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K} = 5.135 = 5.1 \text{ atm}$$

The minimum pressure required to initiate reverse osmosis is greater than 5.1 atm.

- 18.36 Calculate the total ion concentration of sea water by summing the molarities given in Table 18.6. Then use $\pi = \Delta MRT$ to calculate pressure.

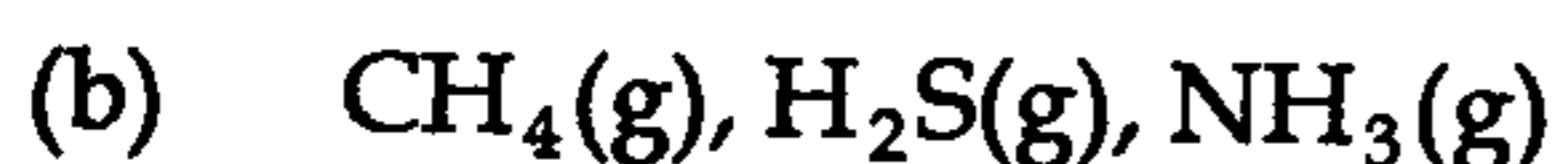
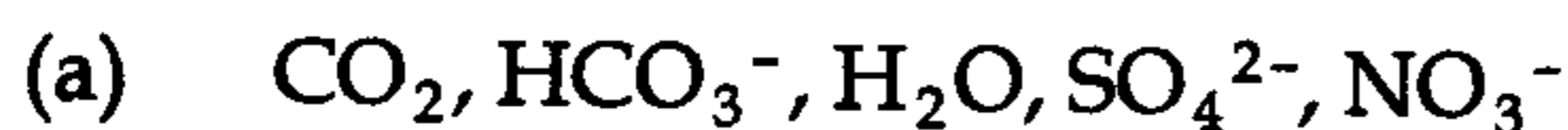
$$M_{\text{total}} = 0.55 + 0.47 + 0.028 + 0.054 + 0.010 + 0.010 + 2.3 \times 10^{-3} + 8.3 \times 10^{-4} + 4.3 \times 10^{-4} + 9.1 \times 10^{-5} + 7.0 \times 10^{-5} = 1.1257 = 1.13 \text{ M}$$

$$\pi = \frac{(1.1257 - 0.02) \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 305 \text{ K} = 27.674 = 27.7 \text{ atm}$$

Check. The largest numbers in the molarity sum have 2 decimal places, so M_{total} has 2 decimal places and 3 sig figs. ΔM also has 2 decimal places and 3 sig figs so the calculated pressure has 3 sig figs. Units are correct.

Fresh Water

18.37 *Analyze/Plan.* Under aerobic conditions, excess oxygen is present and decomposition leads to oxidized products, the element in its maximum oxidation state combined with oxygen. Under anaerobic conditions, little or no oxygen is present so decomposition leads to reduced products, the element in its minimum oxidation state combined with hydrogen. *Solve.*



18.38 (a) Decomposition of organic matter by aerobic bacteria depletes dissolved O_2 . A low dissolved oxygen concentration indicates the presence of organic pollutants.

(b) According to Section 13.3, the solubility of $\text{O}_2(\text{g})$ (or any gas) in water decreases with increasing temperature.

18.39 *Analyze/Plan.* Given the balanced equation, calculate the amount of one reactant required to react exactly with a certain amount of the other reactants. Solve the stoichiometry problem. $\text{g C}_{18}\text{H}_{29}\text{SO}_3^- \rightarrow \text{mol} \rightarrow \text{mol ratio} \rightarrow \text{mol O}_2 \rightarrow \text{g O}_2$. *Solve.*

$$1.0 \text{ g C}_{18}\text{H}_{29}\text{SO}_3^- \times \frac{1 \text{ mol C}_{18}\text{H}_{29}\text{SO}_3^-}{325 \text{ g C}_{18}\text{H}_{29}\text{SO}_3^-} \times \frac{51 \text{ mol O}_2}{2 \text{ mol C}_{18}\text{H}_{29}\text{SO}_3^-} \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} = 2.5 \text{ g O}_2$$

Notice that the mass of O_2 required is 2.5 times greater than the mass of biodegradable material.

$$18.40 \quad 120,000 \text{ persons} \times \frac{59 \text{ g O}_2}{1 \text{ person}} \times \frac{1 \times 10^6 \text{ g H}_2\text{O}}{9 \text{ g O}_2} \times \frac{1 \text{ L H}_2\text{O}}{1 \times 10^3 \text{ g H}_2\text{O}} = 7.9 \times 10^8 = 8 \times 10^8 \text{ L H}_2\text{O}$$

18.41 *Analyze/Plan.* Slaked lime is $\text{Ca}(\text{OH})_2(\text{s})$. The reaction is metathesis. *Solve.*



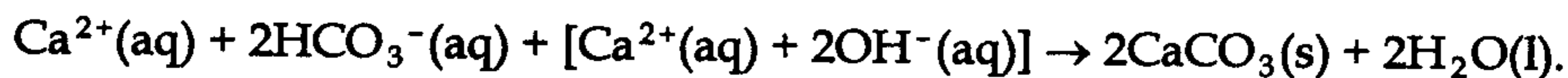
The excess $\text{Ca}^{2+}(\text{aq})$ is removed as CaCO_3 by naturally occurring bicarbonate or added Na_2CO_3 .



(b) Divalent cations (ions with 2+ charges) contribute to water hardness. These ions react with soap to form scum on surfaces or leave undesirable deposits on surfaces, particularly inside pipes, upon heating.

18.43 *Analyze/Plan.* Given $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$ calculate mole $\text{Ca}(\text{OH})_2$ and Na_2CO_3 needed to remove the Ca^{2+} and HCO_3^- . Consider the chemical equations and reaction stoichiometry in the stepwise process. *Solve.*

$\text{Ca}(\text{OH})_2$ is added to remove Ca^{2+} as $\text{CaCO}_3(\text{s})$, and Na_2CO_3 removes the remaining Ca^{2+} .

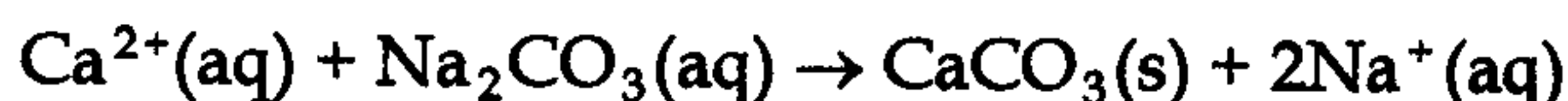


One mole $\text{Ca}(\text{OH})_2$ is needed for each 2 moles of $\text{HCO}_3^-(\text{aq})$ present.

$$\frac{7.0 \times 10^{-4} \text{ mol HCO}_3^-}{\text{L}} \times \frac{1 \text{ mol Ca}(\text{OH})_2}{2 \text{ mol HCO}_3^-} \times 1.200 \times 10^3 \text{ L H}_2\text{O} = 0.42 \text{ mol Ca}(\text{OH})_2$$

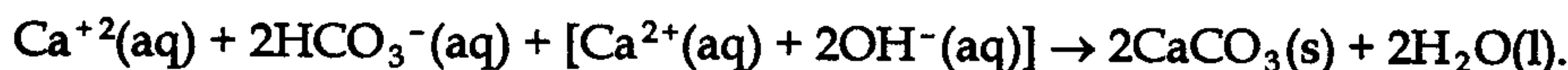
$$1.200 \times 10^3 \text{ L H}_2\text{O} \times \frac{5.0 \times 10^{-4} \text{ mol Ca}^{2+}}{\text{L}} = 0.60 \text{ mol Ca}^{2+}(\text{aq}) \text{ total}$$

0.42 mol $\text{Ca}(\text{OH})_2$ removes 0.42 mol of the 0.60 mol $\text{Ca}^{2+}(\text{aq})$ in the sample. This leaves 0.18 mol $\text{Ca}^{2+}(\text{aq})$ to be removed by Na_2CO_3 .



0.18 mol of Na_2CO_3 is needed to remove the remaining $\text{Ca}^{2+}(\text{aq})$.

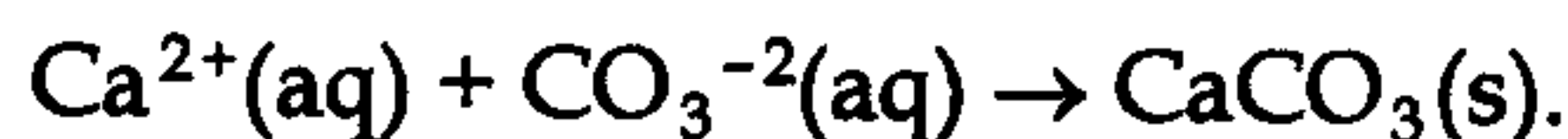
18.44 $\text{Ca}(\text{OH})_2$ is added to remove Ca^{2+} as $\text{CaCO}_3(\text{s})$, and Na_2CO_3 removes the remaining Ca^{2+} .



One mole $\text{Ca}(\text{OH})_2$ is needed for each 2 moles of $\text{HCO}_3^-(\text{aq})$ present.

$$5.0 \times 10^7 \text{ L H}_2\text{O} \times \frac{1.7 \times 10^{-3} \text{ mol HCO}_3^-}{1 \text{ L H}_2\text{O}} \times \frac{1 \text{ mol Ca}(\text{OH})_2}{2 \text{ mol HCO}_3^-} \times \frac{74 \text{ g Ca}(\text{OH})_2}{1 \text{ mol Ca}(\text{OH})_2} = 3.1 \times 10^6 \text{ g Ca}(\text{OH})_2$$

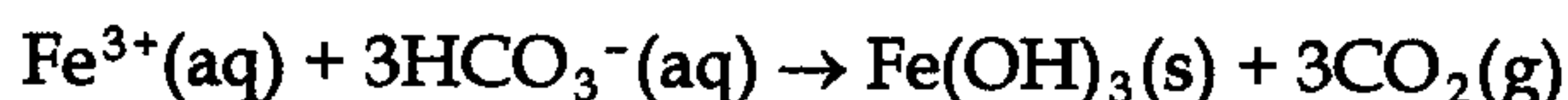
Half of the native HCO_3^- precipitates the added Ca^{2+} so this operation reduces the Ca^{2+} concentration from $5.7 \times 10^{-3} \text{ M}$ to $(5.7 \times 10^{-3} - 8.5 \times 10^{-4}) \text{ M} = 4.85 \times 10^{-3} = 4.9 \times 10^{-3} \text{ M}$. Next we must add sufficient Na_2CO_3 to further reduce $[\text{Ca}^{2+}]$ to $1.1 \times 10^{-3} \text{ M}$ (20% of the original $[\text{Ca}^{2+}]$). We thus need to reduce $[\text{Ca}^{2+}]$ by $(4.85 \times 10^{-3} - 1.1 \times 10^{-3}) \text{ M} = 3.75 \times 10^{-3} = 3.8 \times 10^{-3} \text{ M}$



$$5.0 \times 10^7 \text{ L H}_2\text{O} \times \frac{3.75 \times 10^{-3} \text{ mol Ca}^{2+}}{1 \text{ L H}_2\text{O}} \times \frac{1 \text{ mol Na}_2\text{CO}_3}{1 \text{ mol Ca}^{2+}} \times \frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} = 2.0 \times 10^7 \text{ g Na}_2\text{CO}_3$$



SO_4^{2-} is a spectator, so the net ionic equation is



In this reaction, Fe^{3+} acts as a Lewis acid, and HCO_3^- acts as a Lewis base.

18.46 $\text{Al}_2(\text{SO}_4)_3$ is a typical coagulant in municipal water purification. It reacts with OH^- in a slightly basic solution to form a gelatinous precipitate that occludes very small particles and bacteria. The precipitate settles slowly and is removed by sand filtration.

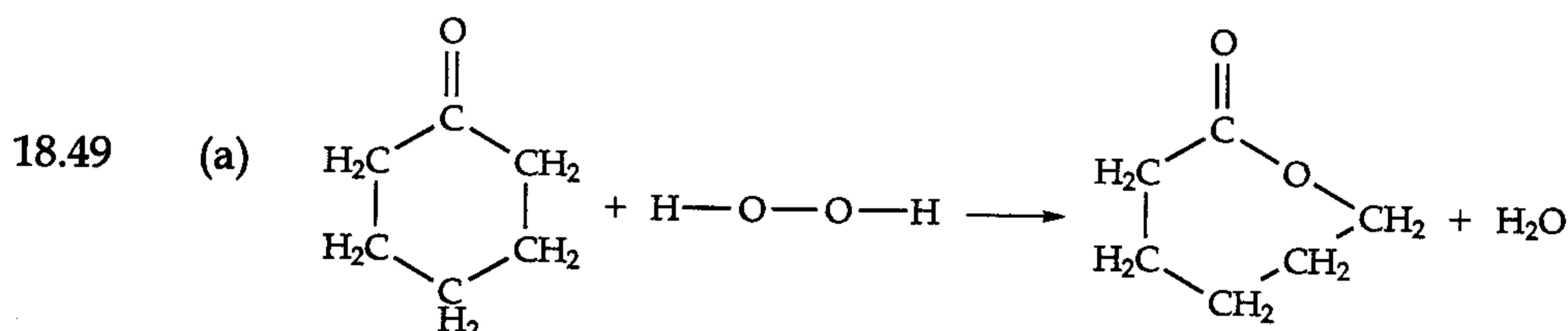
Properties of $\text{Al}_2(\text{SO}_4)_3$ and other useful coagulants are:

- They react with low concentrations of $\text{OH}^-(\text{aq})$. That is, K_{sp} of the hydroxide precipitate is very small. The capacity to form a hydroxide precipitates means that no extra salts must be added to form the precipitate. Also, the $[\text{OH}^-]$ can be easily adjusted by $\text{Ca}(\text{OH})_2$ and other reagents that are part of the purification process.
- The hydroxide precipitate is composed of very small, evenly dispersed particles that do not settle quickly. This is required to remove very small bacteria and viruses from all parts of the liquid, not just the sites of solid formation.

Green Chemistry

18.47 The fewer steps in a process, the less waste (solvents as well as unusable by-products) is generated. It is probably true that a process with fewer steps requires less energy at the site of the process, and it is certainly true that the less waste the process generates, the less energy is required to clean or dispose of the waste.

18.48 Catalysts increase the rate of a reaction by lowering activation energy, E_a . For an uncatalyzed reaction that requires extreme temperatures and pressures to generate product at a viable rate, finding a suitable catalyst reduces the required temperature and/or pressure, which reduces the amount of energy used to run the process. A catalyst can also increase rate of production, which would reduce the net time and thus energy required to generate a certain amount of product.



- (b)
- It is better to prevent waste than to treat it. The alternative process eliminates production of 3-chlorobenzoic acid by-product, chlorine-containing waste that must be treated.
 - Produce as little, nontoxic waste as possible. The by-product of the alternative process is nontoxic water. The low molar mass of water means that a small amount of "waste" is generated.
 - Chemical processes should be efficient. The alternative process is catalyzed, which could mean that the process will be more energy efficient than the Baeyer-Villiger reaction (see Solution 18.48).
 - Raw materials should be renewable. The catalyst can be recovered from the reaction mixture and reused. We don't have information about solvents or other auxiliary substances.

- 18.50
- In either solvent, the reaction is catalyzed, which usually leads to decreased processing temperatures and times, and greater energy efficiency.
 - $scCO_2$ is the preferred solvent. It achieves maximum conversion much faster than CH_2Cl_2 solvent. $scCO_2$ reduces processing time, temperature, and energy requirements. It also results in fewer unwanted by-products to be separated and processed. While use of $scCO_2$ increases the amount of a greenhouse gas released to the environment, it eliminates use of CH_2Cl_2 , which is implicated in stratospheric ozone depletion. Use of $scCO_2$ rather than CH_2Cl_2 is a good green trade-off.

Additional Exercises

- 18.51 (a) *Acid rain* is rain with a larger $[H^+]$ and thus a lower pH than expected. The additional H^+ is produced by the dissolution of sulfur and nitrogen oxides such as $SO_3(g)$ and $NO_2(g)$ in rain droplets to form sulfuric and nitric acid, $H_2SO_4(aq)$ and $HNO_3(aq)$.

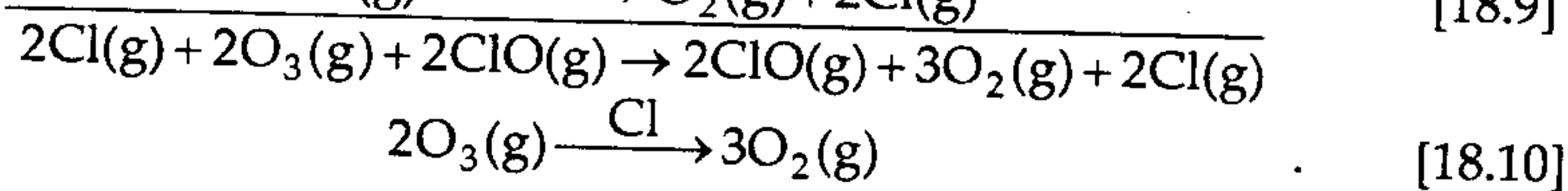
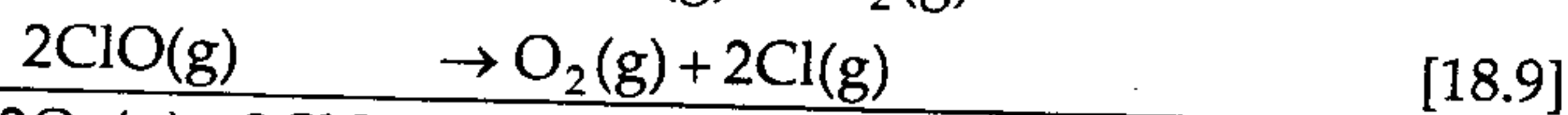
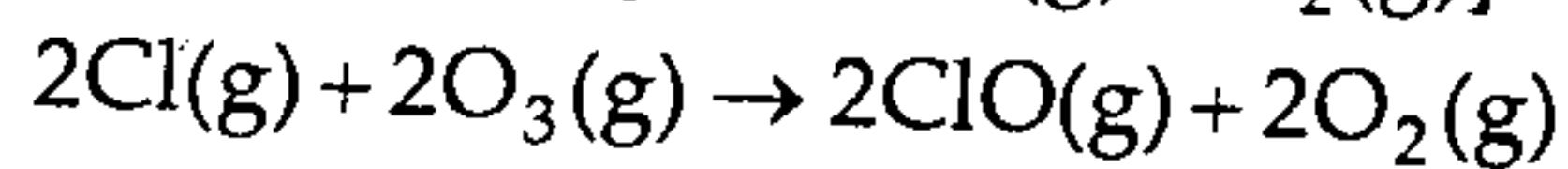
- (b) A *greenhouse gas* absorbs infrared or "heat" radiation emitted from the earth's surface and serves to maintain a relatively constant temperature on the surface. A significant increase in the amount of atmospheric CO_2 (from burning fossil fuels and other sources) could cause a corresponding increase in the average surface temperature and drastically change the global climate.
- (c) *Photochemical smog* is an unpleasant collection of atmospheric pollutants initiated by photochemical dissociation of NO_2 to form NO and O atoms. The major components are $\text{NO}(\text{g})$, $\text{NO}_2(\text{g})$, $\text{CO}(\text{g})$, and unburned hydrocarbons, all produced by automobile engines, and $\text{O}_3(\text{g})$, ozone.
- (d) *Ozone depletion* is the reduction of O_3 concentration in the stratosphere, most notably over Antarctica. It is caused by reactions between O_3 and Cl atoms originating from chlorofluorocarbons (CFC's), $\text{CF}_x\text{Cl}_{4-x}$. Depletion of the ozone layer allows damaging ultraviolet radiation disruptive to the plant and animal life in our ecosystem to reach earth.

$$18.52 \quad \text{MM}_{\text{avg}} \text{ at the surface} = 83.8(0.17) + 16.0(0.38) + 32.0(0.45) = 34.73 = 35 \text{ g/mol.}$$

Next, calculate the percentage composition at 200 km. The fractions can be "normalized" by saying that the 0.45 fraction of O_2 is converted into **two** 0.45 fractions of O atoms, then dividing by the total fractions, $0.17 + 0.38 + 0.45 + 0.45 = 1.45$:

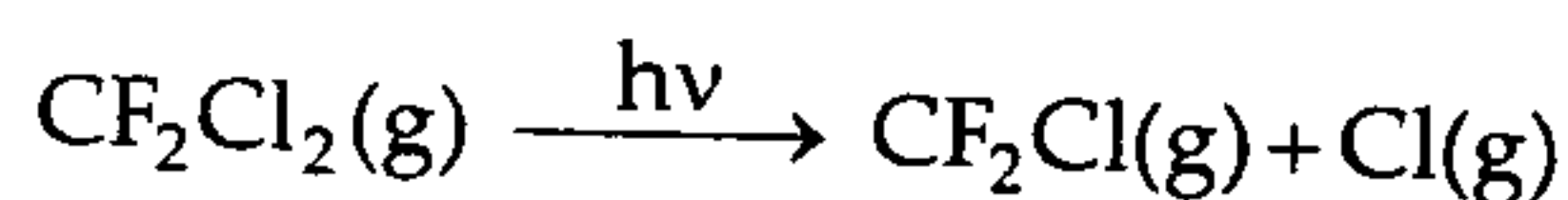
$$\text{MM}_{\text{avg}} = \frac{83.8(0.17) + 16.0(0.38) + 16.0(0.90)}{1.45} = 23.95 = 24 \text{ g/mol}$$

- 18.53 Stratospheric ozone is formed and destroyed in a cycle of chemical reactions. The decomposition of O_3 to O_2 and O produces oxygen atoms, an essential ingredient for the production of ozone. While single O_3 molecules exist for only a few seconds, new O_3 molecules are constantly reformed. This cyclic process ensures a finite concentration of O_3 in the stratosphere available to absorb ultraviolet radiation. (This explanation assumes that the cycle is not disrupted by outside agents such as CFCs.)

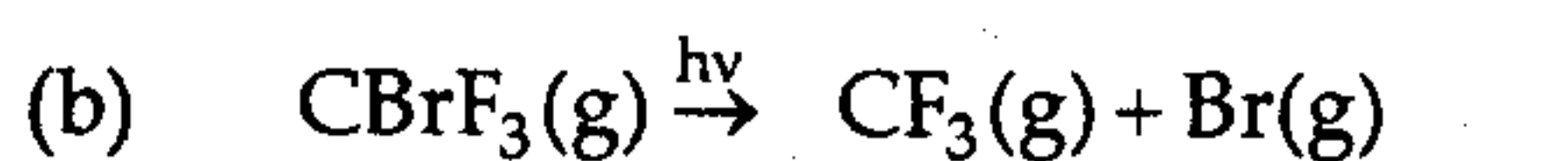


Note that $\text{Cl}(\text{g})$ fits the definition of a catalyst in this reaction.

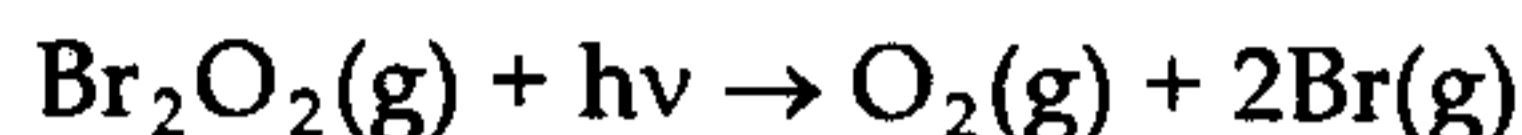
- 18.55 (a) The production of Cl atoms in the stratosphere is the result of the photodissociation of a $\text{C}-\text{H}$ bond in the chlorofluorocarbon molecule.



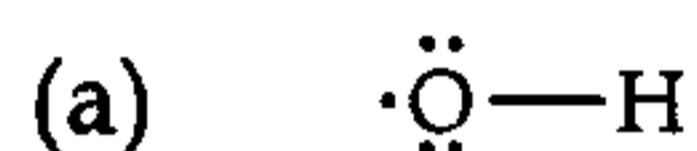
According to Table 8.4, the bond dissociation energy of a $\text{C}-\text{Br}$ bond is 276 kJ/mol, while the value for a $\text{C}-\text{H}$ bond is 328 kJ/mol. Photodissociation of CBrF_3 to form Br atoms requires less energy than the production of Cl atoms and should occur readily in the stratosphere.



Also, under certain conditions



18.56



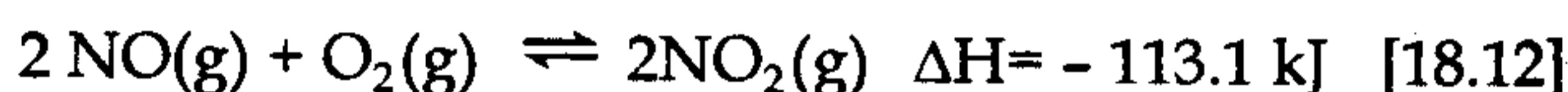
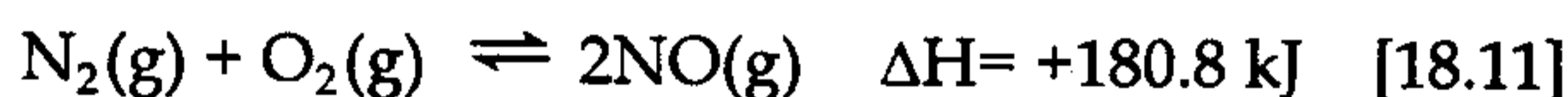
(b) HNO_3 is a major component in acid rain.

(c) While it removes CO, the reaction produces NO_2 . The photodissociation of NO_2 to form O atoms is the first step in the formation of tropospheric ozone and photochemical smog.

(d) Again, NO_2 is the initiator of photochemical smog. Also, methoxyl radical, OCH_3 , is a reactive species capable of initiating other undesirable reactions.

18.57

From section 18.4:

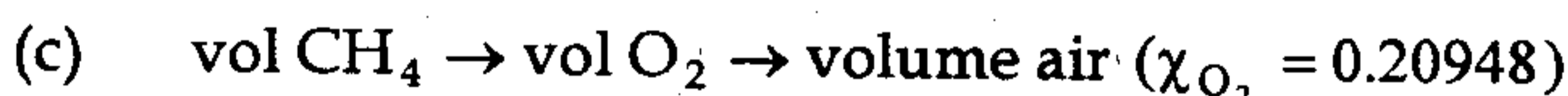
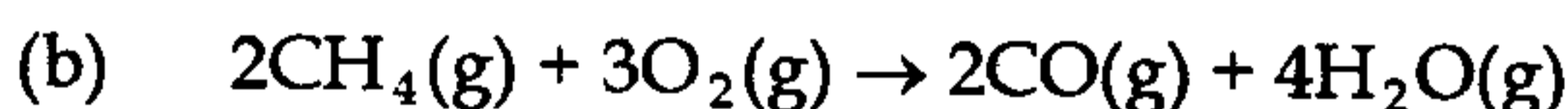
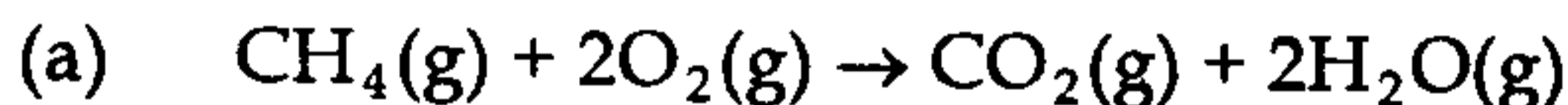


In an endothermic reaction, heat is a reactant. As the temperature of the reaction increases, the addition of heat favors formation of products and the value of K increases. The reverse is true for exothermic reactions; as temperature increases, the value of K decreases. Thus, K for reaction [18.11], which is endothermic, increases with increasing temperature and K for reaction [18.12], which is exothermic, decreases with increasing temperature.

18.58

Oxygen is present in the atmosphere to the extent of 209,000 parts per million. If CO binds 210 times more effectively than O_2 , then the effective concentration of CO is $210 \times 125 \text{ ppm} = 26,250 = 26,300 \text{ ppm}$. The fraction of carboxyhemoglobin in the blood leaving the lungs is thus $\frac{26,250}{26,250 + 209,000} = 0.112$. Thus, 11.2 percent of the blood is in the form of carboxyhemoglobin, 88.8 percent as the O_2 -bound oxyhemoglobin.

18.59



Equal volumes of gases at the same temperature and pressure contain equal numbers of moles (Avogadro's law). If 2 moles of O_2 are required for 1 mole of CH_4 , 2.0 L of pure O_2 are needed to burn 1.0 L of CH_4 .

$$\text{vol O}_2 = \chi_{\text{O}_2} \times \text{vol}_{\text{air}} = \frac{\text{vol O}_2}{\chi_{\text{O}_2}} = \frac{2.0 \text{ L}}{0.20948} = 9.5 \text{ L air}$$

18.60

(a) According to Section 13.3, the solubility of gases in water decreases with increasing temperature. Thus, the solubility of $\text{CO}_2(\text{g})$ in the ocean would decrease if the temperature of the ocean increased.

- (b) If the solubility of $\text{CO}_2(\text{g})$ in the ocean decreased because of global warming, more $\text{CO}_2(\text{g})$ would be released into the atmosphere, perpetuating a cycle of increasing temperature and concomitant release of $\text{CO}_2(\text{g})$ from the ocean.

18.61 Most of the 390 watts/ m^2 radiated from Earth's surface is in the infrared region of the spectrum. Tropospheric gases, particularly $\text{H}_2\text{O}(\text{g})$ and $\text{CO}_2(\text{g})$, absorb much of this radiation and prevent it from escaping into space (Figure 18.11). The energy absorbed by these so-called "greenhouse gases" warms the atmosphere close to Earth's surface and makes the planet livable.

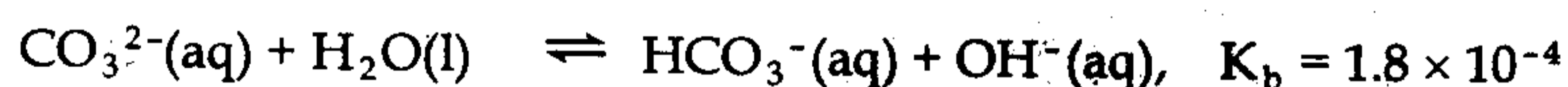
18.62 Given 169 watts/ m^2 at 10% efficiency, find the land area needed to produce 55 watts/ m^2 .
 169 watts/ m^2 (0.10) = 16.9 watts/ m^2 solar energy possible with current technology.

$$\frac{55 \text{ watts}}{\text{m}^2} \times \frac{1 \text{ m}^2}{16.9 \text{ watts}} = 3.254 = 3.3$$

Solar energy must be harvested from 3.3 times the land area of New York City to supply its energy needs. According to *Wikipedia*, http://en.wikipedia.org/wiki/New_York_City, the land area of New York City is 831 km^2 , which is $831 \times 10^6 \text{ m}^2$ or 2.05×10^5 acres. The area needed for solar energy harvesting would then be $2.70 \times 10^3 \text{ km}^2$, $2.70 \times 10^9 \text{ m}^2$ or 6.68×10^5 acres.

- 18.63 (a) $\text{NO}(\text{g}) + h\nu \rightarrow \text{N}(\text{g}) + \text{O}(\text{g})$
 (b) $\text{NO}(\text{g}) + h\nu \rightarrow \text{NO}^+(\text{g}) + \text{e}^-$
 (c) $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
 (d) $3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HNO}_3(\text{aq}) + \text{NO}(\text{g})$

18.64 (a) CO_3^{2-} is a relatively strong Brønsted base and produces OH^- in aqueous solution according to the hydrolysis reaction:



If $[\text{OH}^-(\text{aq})]$ is sufficient to exceed K_{sp} for $\text{Mg}(\text{OH})_2$, the solid will precipitate.

$$\begin{aligned} \text{(b)} \quad \frac{125 \text{ mg Mg}^{2+}}{1 \text{ kg soln}} \times \frac{1 \text{ g Mg}^{2+}}{1000 \text{ mg Mg}^{2+}} \times \frac{1.00 \text{ kg soln}}{1.00 \text{ L soln}} \times \frac{1 \text{ mol Mg}^{2+}}{24.305 \text{ g Mg}^{2+}} &= 5.143 \times 10^{-3} \\ &= 5.14 \times 10^{-3} \text{ M Mg}^{2+} \end{aligned}$$

$$\frac{4.0 \text{ g Na}_2\text{CO}_3}{1.0 \text{ L soln}} \times \frac{1 \text{ mol CO}_3^{2-}}{106.0 \text{ g Na}_2\text{CO}_3} = 0.03774 = 0.038 \text{ M CO}_3^{2-}$$

$$\begin{aligned} K_b = 1.8 \times 10^{-4} &= \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} \approx \frac{x^2}{0.03774}; \quad x = [\text{OH}^-] = 2.606 \times 10^{-3} \\ &= 2.6 \times 10^{-3} \text{ M} \end{aligned}$$

(This represents 6.9% hydrolysis, but the result will not be significantly different using the quadratic formula.)

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (5.143 \times 10^{-3})(2.606 \times 10^{-3})^2 = 3.5 \times 10^{-8}$$

K_{sp} for $\text{Mg}(\text{OH})_2 = 1.6 \times 10^{-12}$; $Q > K_{sp}$, so $\text{Mg}(\text{OH})_2$ will precipitate.

- 18.65 Because NO has an odd electron, like Cl(g), it could act as a catalyst for decomposition of ozone in the stratosphere. The increased destruction of ozone by NO would result in less absorption of short wavelength UV radiation now being screened out primarily by the ozone. Radiation in this wavelength range is known to be harmful to humans; it causes skin cancer. There is evidence that many plants don't tolerate it very well either, though more research is needed to test this idea.

In Chapter 22 the oxidation of NO to NO₂ by oxygen is described. On dissolving in water, NO₂ disproportionates into NO₃⁻(aq) and NO(g). Thus, over time the NO in the troposphere will be converted into NO₃⁻, which is in turn incorporated into soils.

- 18.66 *Plan.* Calculate the volume of air above Los Angeles and the volume of pure O₃ that would be present at the 85 ppb level. For gases at the same temperature and pressure, volume fractions equal mole fractions. *Solve.*

$$V_{\text{air}} = 4000 \text{ mi}^2 \times \frac{(1.6093)^2 \text{ km}^2}{\text{mi}^2} \times \frac{(1000)^2 \text{ m}^2}{1 \text{ km}^2} \times 10 \text{ m} \times \frac{1 \text{ L}}{1 \times 10^{-3} \text{ m}^3} = 1.036 \times 10^{14} \\ = 1.0 \times 10^{14} \text{ L air}$$

$$85 \text{ ppb O}_3 = \frac{85 \text{ mol O}_3}{1 \times 10^9 \text{ mol air}} = 8.5 \times 10^{-8} = \chi_{\text{O}_3}$$

$$V(\text{pure O}_3) = 8.5 \times 10^{-8} (1.036 \times 10^{14} \text{ L air}) = 8.805 \times 10^6 = 8.8 \times 10^6 \text{ L O}_3$$

Values for P and T are required to calculate mol O₃ from volume O₃, using the ideal-gas law. Since these are not specified in the exercise, we will make a reasonable assumption for a sunny April day in Los Angeles. The city is near sea level and temperatures are moderate throughout the year, so P = 1 atm and T = 25°C (78°F) are reasonable values.

$$PV = nRT, n = PV/RT$$

$$n = 1.000 \text{ atm} \times \frac{8.805 \times 10^6 \text{ L}}{298 \text{ K}} \times \frac{\text{K} \cdot \text{mol}}{0.08206 \text{ L} \cdot \text{atm}} = 3.601 \times 10^5 = 3.6 \times 10^5 \text{ mol O}_3$$

Check. Using known conditions to make reasonable estimates and assumptions is a valuable skill for problem solving. Knowing when assumptions are required is an important step in the learning process.

Integrative Exercises

18.67 (a) $0.019 \text{ ppm NO}_2 = \frac{0.019 \text{ mol NO}_2}{1 \times 10^6 \text{ mol air}} = 1.9 \times 10^{-8} = \chi_{\text{NO}_2}$

$$P_{\text{NO}_2} = \chi_{\text{NO}_2} \cdot P_{\text{atm}} = 1.9 \times 10^{-8} (755 \text{ torr}) = 1.4345 \times 10^{-5} = 1.4 \times 10^{-5} \text{ torr}$$

(b) $n = \frac{PV}{RT}; \text{ molecules} = n \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} = \frac{PV}{RT} \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}}$

$$V = 15 \text{ ft} \times 14 \text{ ft} \times 8 \text{ ft} \times \frac{12^3 \text{ in}^3}{\text{ft}^3} \times \frac{2.54^3 \text{ cm}^3}{\text{in}^3} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 4.757 \times 10^4 = 5 \times 10^4 \text{ L}$$

$$1.4345 \times 10^{-5} \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times \frac{4.757 \times 10^4 \text{ L}}{293 \text{ K}} \times \frac{\text{K} \cdot \text{mol}}{0.08206 \text{ L} \cdot \text{atm}}$$

$$\times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} = 2.249 \times 10^{19} = 2 \times 10^{19} \text{ molecule}$$

18.68 (a) $8,376,726 \text{ tons coal} \times \frac{83 \text{ ton C}}{100 \text{ ton coal}} \times \frac{44.01 \text{ ton CO}_2}{12.01 \text{ ton C}} = 2.5 \times 10^7 \text{ ton CO}_2$

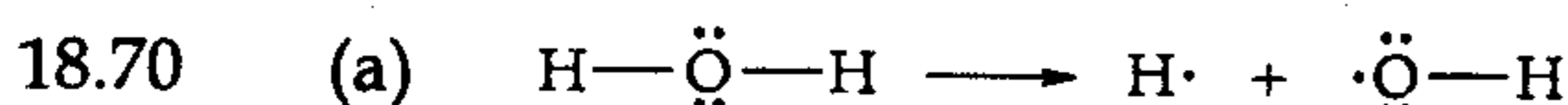
$$8,376,726 \text{ tons coal} \times \frac{2.5 \text{ ton S}}{100 \text{ ton coal}} \times \frac{64.07 \text{ ton SO}_2}{32.07 \text{ ton S}} = 4.2 \times 10^5 \text{ ton SO}_2$$



$$4.18 \times 10^5 \text{ ton SO}_2 \times \frac{55 \text{ ton SO}_2 \text{ removed}}{100 \text{ ton SO}_2 \text{ produced}} \times \frac{120.15 \text{ ton CaSO}_3}{64.07 \text{ ton SO}_2}$$

$$= 4.3 \times 10^5 \text{ ton CaSO}_3$$

18.69 *Coarse sand* is removed by coarse sand filtration. *Finely divided particles* and some *bacteria* are removed by precipitation with aluminum hydroxide. Remaining *harmful bacteria* are removed by ozonation. *Trihalomethanes* are removed by either aeration or activated carbon filtration; use of activated carbon might be preferred because it does not involve release of TCMs into the atmosphere. *Dissolved organic substances* are oxidized (and rendered less harmful, but not removed) by both aeration and ozonation. *Dissolved nitrates* and *phosphates* are not removed by any of these processes, but are rendered less harmful by adequate aeration.



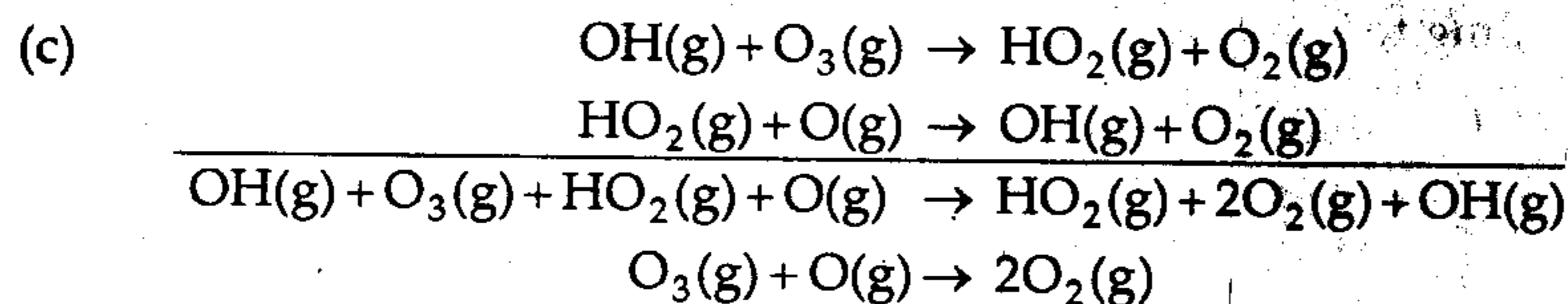
(b) $\Delta H = 2D(\text{O}-\text{H}) - D(\text{O}-\text{H}) = D(\text{O}-\text{H}) = 463 \text{ kJ/mol}$

$$\frac{463 \text{ kJ}}{\text{mol H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{6.022 \times 10^{23} \text{ molecules}} \times \frac{1000 \text{ J}}{\text{kJ}} = 7.688 \times 10^{-19}$$

$$= 7.69 \times 10^{-19} \text{ J/H}_2\text{O molecule}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{sec} \times 2.998 \times 10^8 \text{ m/s}}{7.688 \times 10^{-19} \text{ J}} = 2.58 \times 10^{-7} \text{ m} = 258 \text{ nm}$$

This wavelength is in the UV region of the spectrum, close to the visible.



OH(g) is the catalyst in this overall reaction, another pathway for the destruction of ozone.

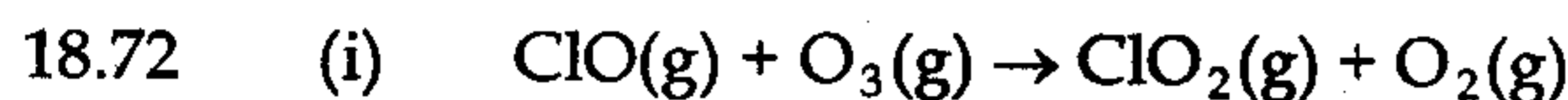
18.71 According to Equation [14.12], $\ln([A]_t / [A]_0) = -kt$. $[A]_t = 0.10 [A]_0$.

$$\ln(0.10 [A]_0 / [A]_0) = \ln(0.10) = -(2 \times 10^{-6} \text{ s}^{-1}) t$$

$$t = -\ln(0.10) / 2 \times 10^{-6} \text{ s}^{-1} = 1.151 \times 10^6 \text{ s}$$

$$1.151 \times 10^6 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ day}}{24 \text{ hr}} = 13.3 \text{ days (1} \times 10 \text{ days)}$$

The value of the rate constant limits the result to 1 sig fig. This implies that there is minimum uncertainty of ± 1 in the tens place of our answer. Realistically, the remediation could take anywhere from 1 to 20 days.



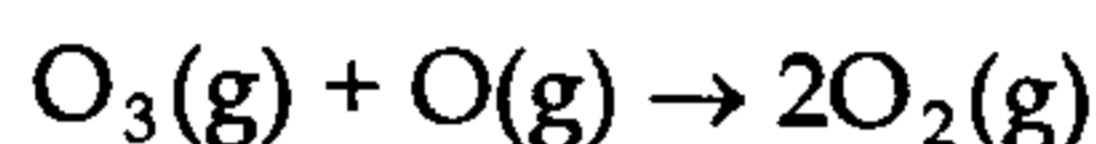
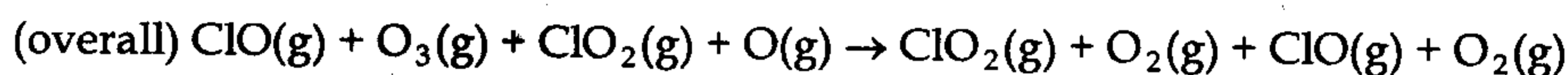
$$\Delta H_i = \Delta H_f^\circ \text{ClO}_2\text{(g)} + \Delta H_f^\circ \text{O}_2\text{(g)} - \Delta H_f^\circ \text{ClO(g)} - \Delta H_f^\circ \text{O}_3\text{(g)}$$

$$\Delta H_i = 102 + 0 - 101 - (142.3) = -141 \text{ kJ}$$



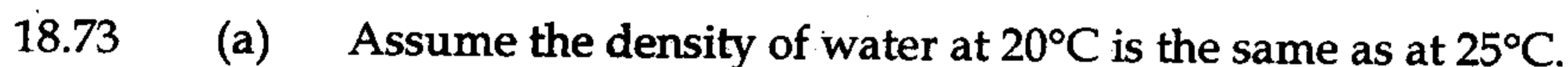
$$\Delta H_{ii} = \Delta H_f^\circ \text{ClO(g)} + \Delta H_f^\circ \text{O}_2\text{(g)} - \Delta H_f^\circ \text{ClO}_2\text{(g)} + \Delta H_f^\circ \text{O(g)}$$

$$\Delta H_{ii} = 101 + 0 - 102 - (247.5) = -249 \text{ kJ}$$



$$\Delta H = \Delta H_i + \Delta H_{ii} = -141 \text{ kJ} + (-249) \text{ kJ} = -390 \text{ kJ}$$

Because the enthalpies of both (i) and (ii) are distinctly exothermic, it is possible that the ClO - ClO₂ pair could be a catalyst for the destruction of ozone.



$$1.00 \text{ gal} \times \frac{4 \text{ qt}}{1 \text{ gal}} \times \frac{1 \text{ L}}{1.057 \text{ qt}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.99707 \text{ g H}_2\text{O}}{1 \text{ mL}} = 3773$$

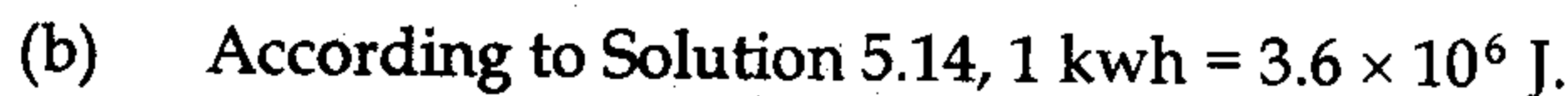
$$= 3.77 \times 10^3 \text{ g H}_2\text{O}$$

The H₂O(l) must be heated from 20°C to 100°C and then vaporized at 100°C.

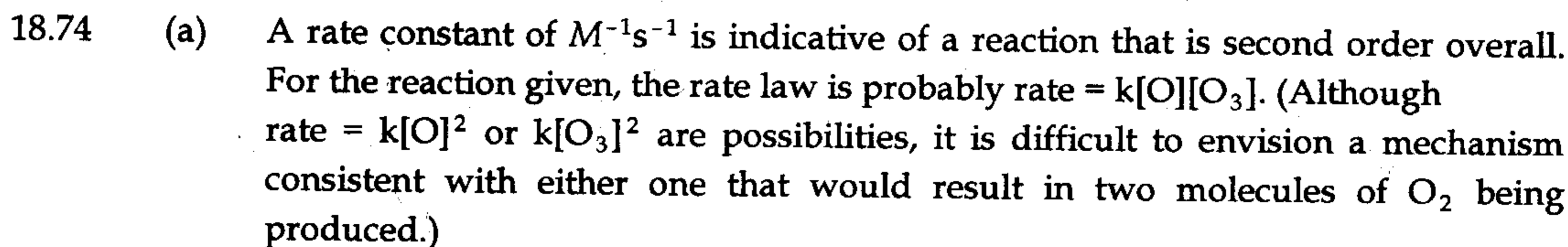
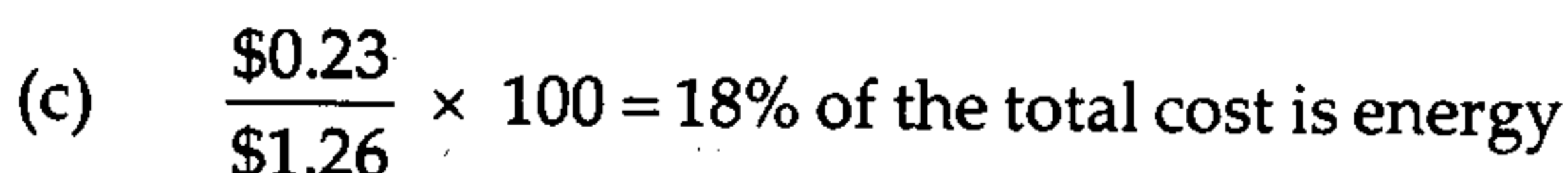
$$3.773 \times 10^3 \text{ g H}_2\text{O} \times \frac{4.184 \text{ J}}{\text{g}^\circ\text{C}} \times 80^\circ\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1263 = 1.3 \times 10^3 \text{ kJ}$$

$$3.773 \times 10^3 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{40.67 \text{ kJ}}{\text{mol H}_2\text{O}} = 8516 = 8.52 \times 10^3 \text{ kJ}$$

$$\text{energy} = 1263 \text{ kJ} + 8516 \text{ kJ} = 9779 = 9.8 \times 10^3 \text{ kJ/gal H}_2\text{O}$$



$$\frac{9779 \text{ kJ}}{\text{gal H}_2\text{O}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1 \text{ kwh}}{3.6 \times 10^6 \text{ J}} \times \frac{\$0.085}{\text{kwh}} = \$0.23/\text{gal}$$



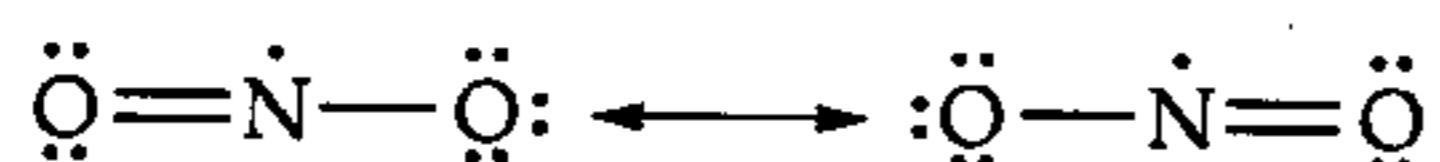
- (b) Yes. Most atmospheric processes are initiated by collision. One could imagine an activated complex of four O atoms collapsing to form two O₂ molecules. Also, the rate constant is large, which is less likely for a multistep process. The reaction is analogous to the destruction of O₃ by Cl atoms (Equation 18.7), which is also second order with a large rate constant.
- (c) According to the Arrhenius equation, $k = Ae^{-E_a/RT}$. Thus, the larger the value of k , the smaller the activation energy, E_a . The value of the rate constant for this reaction is large, so the activation energy is small.

$$(d) \quad \Delta H_f^\circ = 2\Delta H_f^\circ \text{O}_2(g) - \Delta H_f^\circ \text{O}(g) - \Delta H_f^\circ \text{O}_3(g)$$

$$\Delta H_f^\circ = 0 - 247.5 \text{ kJ} - 142.3 \text{ kJ} = -389.8 \text{ kJ}$$

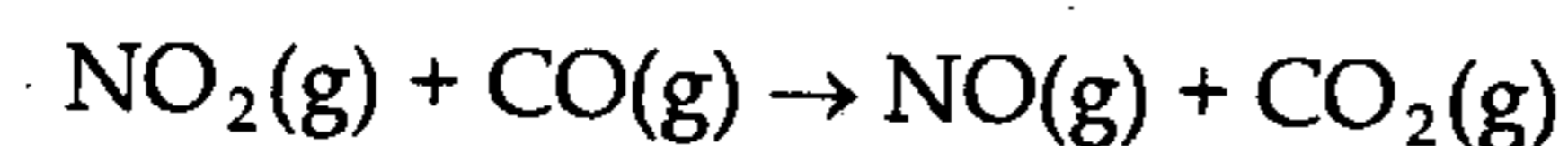
The reaction is exothermic, so energy is released; the reaction would raise the temperature of the stratosphere.

18.75 (a) $17 e^-$, $8.5 e^-$ pairs



Owing to its lower electronegativity, N is more likely to be electron deficient and to accommodate the odd electron.

- (b) The fact that NO₂ is an electron deficient molecule indicates that it will be highly reactive. Dimerization results in formation of a N—N single bond which completes the octet of both N atoms. NO₂ and N₂O₄ exist in equilibrium in a closed system. The reaction is exothermic, Equation [22.65]. In an urban environment, NO₂ is produced from hot automobile combustion. At these temperatures, equilibrium favors the monomer because the reaction is exothermic.



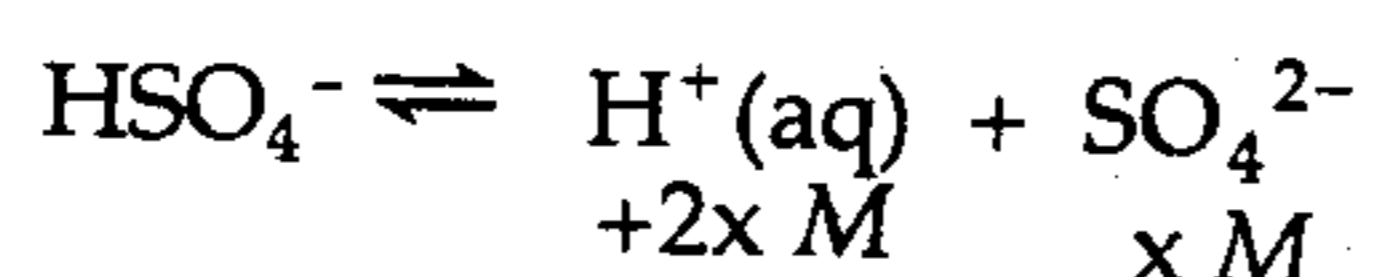
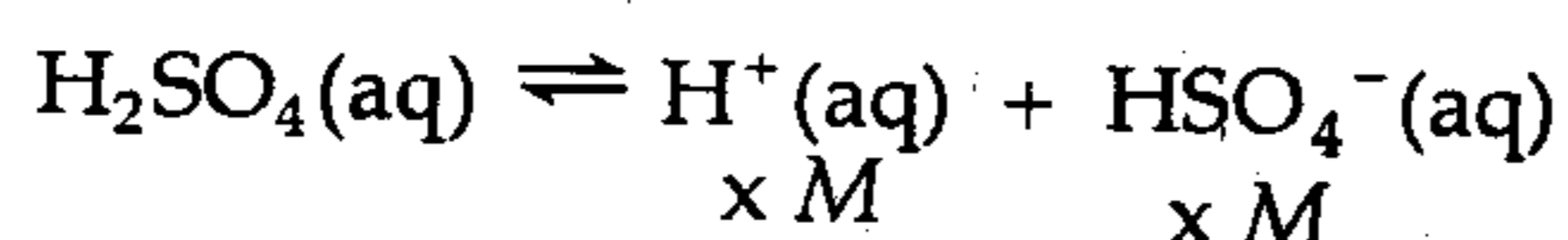
NO₂ is an oxidizing agent and CO is a reducing agent, so we expect products to contain N in a more reduced form, NO or N₂, and C in a more oxidized form, CO₂.

- (d) No. Because it is an odd-electron molecule, NO₂ is very reactive. We expect it to undergo chemical reactions or photodissociate before it can migrate to the stratosphere. The expected half-life of an NO₂ molecule is short.

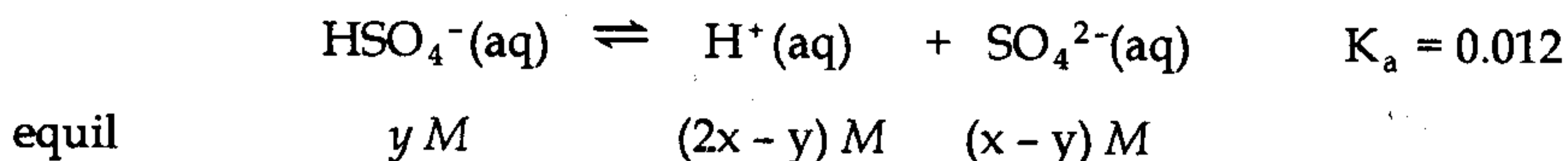
18.76 Calculate [H₂SO₄] required to produce a solution with pH = 3.5. From the volume of rainfall, calculate the amount of H₂SO₄ present.

$$[\text{H}^+] = 10^{-3.5} = 3.16 \times 10^{-4} = 3 \times 10^{-4} \text{ M}$$

Assume initially that both ionization steps are complete.



Since $[\text{HSO}_4^-]$ at equilibrium is small but finite, let $[\text{HSO}_4^-] = y$.



$$K_a = 0.012 = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(2x - y)(x - y)}{y}$$

But we know that $[\text{H}^+]$ at equilibrium = $3.16 \times 10^{-4} M$.

$$2x - y = 3.16 \times 10^{-4}; y = 2x - 3.16 \times 10^{-4}; (x - y) = [x - (2x - 3.16 \times 10^{-4})] = 3.16 \times 10^{-4} - x$$

$$K_a = 0.012 = \frac{(3.16 \times 10^{-4})(3.16 \times 10^{-4} - x)}{2x - 3.16 \times 10^{-4}}$$

$$(0.012)(2x - 3.16 \times 10^{-4}) = 1.00 \times 10^{-7} - 3.16 \times 10^{-4}x;$$

$$0.024x - 3.795 \times 10^{-6} = 1.00 \times 10^{-7} - 3.16 \times 10^{-4}x;$$

$$0.024316x = 3.895 \times 10^{-6}; x = 1.60 \times 10^{-4} = 2 \times 10^{-4} M \text{H}_2\text{SO}_4$$

Check. This result is reasonable, since it is just slightly greater than $[\text{H}^+]/2$. The amount of HSO_4^- at equilibrium, $y = 4.1 \times 10^{-6} M$.

$$\frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(3.16 \times 10^{-4})(1.60 \times 10^{-4} - 4.1 \times 10^{-6})}{4.1 \times 10^{-6}} = 0.012$$

The calculated results are reasonable and self-consistent.

Now proceed to find the volume of rainfall and corresponding mass of H_2SO_4 if $[\text{H}_2\text{SO}_4] = 1.60 \times 10^{-4} = 2 \times 10^{-4} M$.

$$V = 1.0 \text{ in} \times 1500 \text{ mi}^2 \times \frac{5280^2 \text{ ft}^2}{\text{mi}^2} \times \frac{12^2 \text{ in}^2}{\text{ft}^2} \times \frac{2.54^3 \text{ cm}^3}{\text{in}^3} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 9.868 \times 10^{10} \\ = 9.9 \times 10^{10}$$

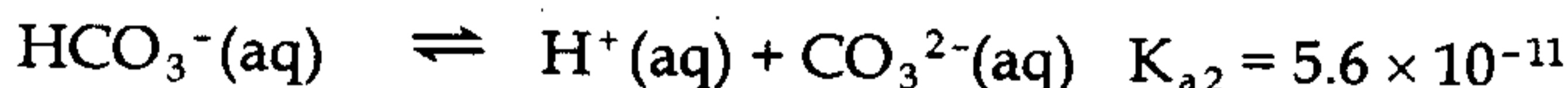
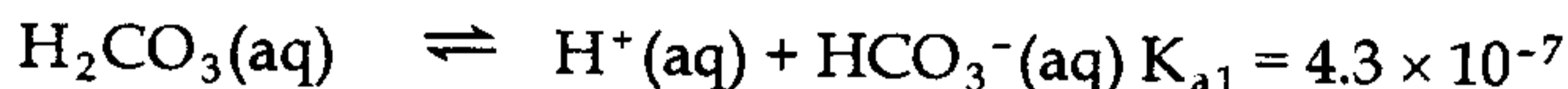
$$\frac{1.60 \times 10^{-4} \text{ mol H}_2\text{SO}_4}{1 \text{ L rainfall}} \times 9.868 \times 10^{10} \text{ L} \times \frac{98.1 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 1.55 \times 10^6 \\ = 2 \times 10^6 \text{ kg H}_2\text{SO}_4$$

- 18.77 (a) According to Table 18.1, the mole fraction of CO_2 in air is 0.000375.

$$P_{\text{CO}_2} = \chi_{\text{CO}_2} \cdot P_{\text{atm}} = 0.000375(1.00 \text{ atm}) = 3.75 \times 10^{-4} \text{ atm}$$

$$C_{\text{CO}_2} = kP_{\text{CO}_2} = 3.1 \times 10^{-2} M/\text{atm} \times 3.75 \times 10^{-4} \text{ atm} = 1.16 \times 10^{-5} = 1.2 \times 10^{-5} M$$

- (b) H_2CO_3 is a weak acid, so the $[\text{H}^+]$ is regulated by the equilibria:



Since the value of K_{a2} is small compared to K_{a1} , we will assume that most of the $\text{H}^+(\text{aq})$ is produced by the first dissociation.

$$K_{a1} = 4.3 \times 10^{-7} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}; [\text{H}^+] = [\text{HCO}_3^-] = x, [\text{H}_2\text{CO}_3] = 1.2 \times 10^{-5} - x$$

Since K_{a1} and $[\text{H}_2\text{CO}_3]$ have similar values, we cannot assume x is small compared to 1.2×10^{-5} .

$$4.3 \times 10^{-7} = \frac{x^2}{(1.2 \times 10^{-5} - x)}; 5.00 \times 10^{-12} - 4.3 \times 10^{-7} x = x^2$$

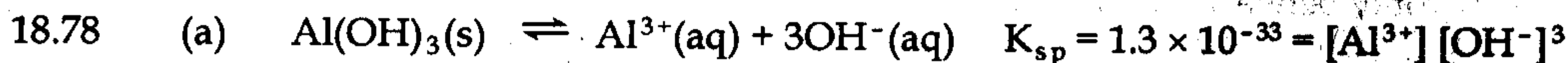
$$0 = x^2 + 4.3 \times 10^{-7} x - 5.00 \times 10^{-12}$$

$$x = \frac{-4.3 \times 10^{-7} \pm \sqrt{(4.3 \times 10^{-7})^2 - 4(1)(-5.00 \times 10^{-12})}}{2(1)}$$

$$x = \frac{-4.3 \times 10^{-7} \pm \sqrt{1.85 \times 10^{-13} + 2.00 \times 10^{-11}}}{2} = \frac{-4.3 \times 10^{-7} \pm 4.49 \times 10^{-6}}{2}$$

The negative result is meaningless; $x = 2.03 \times 10^{-6} = 2.0 \times 10^{-6} \text{ M H}^+$; $\text{pH} = 5.69$

Since this $[\text{H}^+]$ is quite small, the $[\text{H}^+]$ from the autoionization of water might be significant. Calculation shows that for $[\text{H}^+] = 2.0 \times 10^{-6} \text{ M}$ from H_2CO_3 , $[\text{H}^+]$ from $\text{H}_2\text{O} = 5.2 \times 10^{-9} \text{ M}$, which we can ignore.



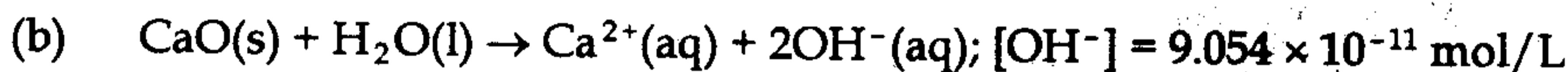
This is a precipitation conditions problem. At what $[\text{OH}^{-}]$ (we can get pH from $[\text{OH}^{-}]$) will $Q = 1.3 \times 10^{-33}$, the requirement for the onset of precipitation?

$Q = 1.3 \times 10^{-33} = [\text{Al}^{3+}][\text{OH}^{-}]^3$. Find the molar concentration of $\text{Al}_2(\text{SO}_4)_3$ and thus $[\text{Al}^{3+}]$.

$$\begin{aligned} \frac{5.0 \text{ lb Al}_2(\text{SO}_4)_3}{2000 \text{ gal H}_2\text{O}} \times \frac{453.6 \text{ g}}{1 \text{ lb}} \times \frac{1 \text{ mol Al}_2(\text{SO}_4)_3}{342.2 \text{ g Al}_2(\text{SO}_4)_3} \times \frac{1 \text{ gal}}{4 \text{ qt}} \times \frac{1 \text{ qt}}{0.946 \text{ L}} \\ = 8.758 \times 10^{-4} \text{ M Al}_2(\text{SO}_4)_3 = 1.752 \times 10^{-3} = 1.8 \times 10^{-3} \text{ M Al}^{3+} \end{aligned}$$

$$Q = 1.3 \times 10^{-33} = (1.752 \times 10^{-3})[\text{OH}^{-}]^3; [\text{OH}^{-}]^3 = 7.42 \times 10^{-31}$$

$$[\text{OH}^{-}] = 9.054 \times 10^{-11} = 9.1 \times 10^{-11} \text{ M}; \text{pOH} = 10.04; \text{pH} = 14 - 10.04 = 3.96$$



$$\begin{aligned} \text{mol OH}^{-} = \frac{9.054 \times 10^{-11} \text{ mol}}{1 \text{ L}} \times 2000 \text{ gal} \times \frac{4 \text{ qt}}{1 \text{ gal}} \times \frac{0.946 \text{ L}}{1 \text{ qt}} = 6.852 \times 10^{-7} \\ = 6.9 \times 10^{-7} \text{ mol OH}^{-} \end{aligned}$$

$$6.852 \times 10^{-7} \text{ mol OH}^{-} \times \frac{1 \text{ mol CaO}}{2 \text{ mol OH}^{-}} \times \frac{56.1 \text{ g CaO}}{1 \text{ mol CaO}} \times \frac{1 \text{ lb}}{453.6 \text{ g}} = 4.2 \times 10^{-8} \text{ lb CaO}$$

This is a very small amount of CaO, about 20 μg .