

CHAPTER 17

CHEMISTRY IN THE ATMOSPHERE

- 17.5 For ideal gases, mole fraction is the same as volume fraction. From Table 17.1 of the text, CO₂ is 0.033% of the composition of dry air, by volume. The value 0.033% means 0.033 volumes (or moles, in this case) out of 100 or

$$X_{\text{CO}_2} = \frac{0.033}{100} = 3.3 \times 10^{-4}$$

To change to parts per million (ppm), we multiply the mole fraction by one million.

$$(3.3 \times 10^{-4})(1 \times 10^6) = 330 \text{ ppm}$$

- 17.6 Using the information in Table 17.1 and Problem 17.5, 0.033 percent of the volume (and therefore the pressure) of dry air is due to CO₂. The partial pressure of CO₂ is:

$$P_{\text{CO}_2} = X_{\text{CO}_2} P_T = (3.3 \times 10^{-4})(754 \text{ mmHg}) \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 3.3 \times 10^{-4} \text{ atm}$$

- 17.7 In the stratosphere, the air temperature rises with altitude. This warming effect is the result of exothermic reactions triggered by UV radiation from the sun. For further discussion, see Sections 17.2 and 17.3 of the text.

- 17.8 From Problem 5.102, the total mass of air is 5.25×10^{18} kg. Table 17.1 lists the composition of air by volume. Under the same conditions of P and T , $V \propto n$ (Avogadro's law).

$$\text{Total moles of gases} = (5.25 \times 10^{21} \text{ g}) \times \frac{1 \text{ mol}}{29.0 \text{ g}} = 1.81 \times 10^{20} \text{ mol}$$

Mass of N₂ (78.03%):

$$(0.7803)(1.81 \times 10^{20} \text{ mol}) \times \frac{28.02 \text{ g}}{1 \text{ mol}} = 3.96 \times 10^{21} \text{ g} = 3.96 \times 10^{18} \text{ kg}$$

Mass of O₂ (20.99%):

$$(0.2099)(1.81 \times 10^{20} \text{ mol}) \times \frac{32.00 \text{ g}}{1 \text{ mol}} = 1.22 \times 10^{21} \text{ g} = 1.22 \times 10^{18} \text{ kg}$$

Mass of CO₂ (0.033%):

$$(3.3 \times 10^{-4})(1.81 \times 10^{20} \text{ mol}) \times \frac{44.01 \text{ g}}{1 \text{ mol}} = 2.63 \times 10^{18} \text{ g} = 2.63 \times 10^{15} \text{ kg}$$

- 17.11 The energy of one photon is:

$$\frac{460 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ photons}} = 7.64 \times 10^{-19} \text{ J/photon}$$

The wavelength can now be calculated.

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{7.64 \times 10^{-19} \text{ J}} = 2.60 \times 10^{-7} \text{ m} = \mathbf{260 \text{ nm}}$$

- 17.12 Strategy:** We are given the wavelength of the emitted photon and asked to calculate its energy. Equation (7.2) of the text relates the energy and frequency of an electromagnetic wave.

$$E = h\nu$$

First, we calculate the frequency from the wavelength, then we can calculate the energy difference between the two levels.

Solution: Calculate the frequency from the wavelength.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{558 \times 10^{-9} \text{ m}} = 5.38 \times 10^{14} /s$$

Now, we can calculate the energy difference from the frequency.

$$\begin{aligned} \Delta E &= h\nu = (6.63 \times 10^{-34} \text{ J}\cdot\text{s})(5.38 \times 10^{14} /s) \\ \Delta E &= \mathbf{3.57 \times 10^{-19} \text{ J}} \end{aligned}$$

- 17.21** The formula for the volume is $4\pi r^2 h$, where $r = 6.371 \times 10^6 \text{ m}$ and $h = 3.0 \times 10^{-3} \text{ m}$ (or 3.0 mm).

$$V = 4\pi(6.371 \times 10^6 \text{ m})^2(3.0 \times 10^{-3} \text{ m}) = 1.5 \times 10^{12} \text{ m}^3 \times \frac{1000 \text{ L}}{1 \text{ m}^3} = 1.5 \times 10^{15} \text{ L}$$

Recall that at STP, one mole of gas occupies 22.41 L.

$$\text{moles O}_3 = (1.5 \times 10^{15} \text{ L}) \times \frac{1 \text{ mol}}{22.41 \text{ L}} = 6.7 \times 10^{13} \text{ mol O}_3$$

$$\text{molecules O}_3 = (6.7 \times 10^{13} \text{ mol O}_3) \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} = \mathbf{4.0 \times 10^{37} \text{ molecules}}$$

$$\text{mass O}_3 \text{ (kg)} = (6.7 \times 10^{13} \text{ mol O}_3) \times \frac{48.00 \text{ g O}_3}{1 \text{ mol O}_3} \times \frac{1 \text{ kg}}{1000 \text{ g}} = \mathbf{3.2 \times 10^{12} \text{ kg O}_3}$$

- 17.22** The quantity of ozone lost is:

$$(0.06)(3.2 \times 10^{12} \text{ kg}) = 1.9 \times 10^{11} \text{ kg of O}_3$$

Assuming no further deterioration, the kilograms of O₃ that would have to be manufactured on a daily basis are:

$$\frac{1.9 \times 10^{11} \text{ kg O}_3}{100 \text{ yr}} \times \frac{1 \text{ yr}}{365 \text{ days}} = \mathbf{5.2 \times 10^6 \text{ kg/day}}$$

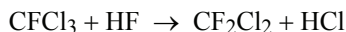
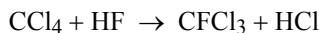
The standard enthalpy of formation (from Appendix 3 of the text) for ozone:



The *total* energy required is:

$$(1.9 \times 10^{14} \text{ g of O}_3) \times \frac{1 \text{ mol O}_3}{48.00 \text{ g O}_3} \times \frac{142.2 \text{ kJ}}{1 \text{ mol O}_3} = 5.6 \times 10^{14} \text{ kJ}$$

17.23 The formula for Freon-11 is CFCl_3 and for Freon-12 is CF_2Cl_2 . The equations are:



A catalyst is necessary for both reactions.

17.24 The energy of the photons of UV radiation in the troposphere is insufficient (that is, the wavelength is too long and the frequency is too small) to break the bonds in CFCs.

17.25 $\lambda = 250 \text{ nm}$

$$\nu = \frac{3.00 \times 10^8 \text{ m/s}}{250 \times 10^{-9} \text{ m}} = 1.20 \times 10^{15} /\text{s}$$

$$E = h\nu = (6.63 \times 10^{-34} \text{ J}\cdot\text{s})(1.20 \times 10^{15} /\text{s}) = 7.96 \times 10^{-19} \text{ J}$$

Converting to units of kJ/mol:

$$\frac{7.96 \times 10^{-19} \text{ J}}{1 \text{ photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 479 \text{ kJ/mol}$$

Solar radiation preferentially breaks the C–Cl bond. There is not enough energy to break the C–F bond.

17.26 First, we need to calculate the energy needed to break one bond.

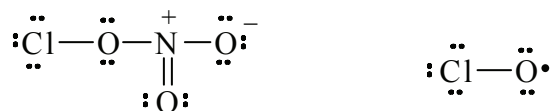
$$\frac{276 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} = 4.58 \times 10^{-19} \text{ J/molecule}$$

The longest wavelength required to break this bond is:

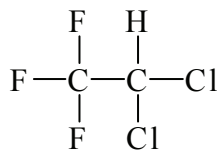
$$\lambda = \frac{hc}{E} = \frac{(3.00 \times 10^8 \text{ m/s})(6.63 \times 10^{-34} \text{ J}\cdot\text{s})}{4.58 \times 10^{-19} \text{ J}} = 4.34 \times 10^{-7} \text{ m} = 434 \text{ nm}$$

434 nm is in the visible region of the electromagnetic spectrum; therefore, CF_3Br will be decomposed in **both** the troposphere and stratosphere.

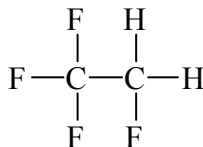
17.27 The Lewis structures for chlorine nitrate and chlorine monoxide are:



17.28 The Lewis structure of HCFC-123 is:



The Lewis structure for CF₃CFH₂ is:



Lone pairs on the outer atoms have been omitted.

17.39 The equation is: $2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2$

$$(4.0 \times 10^4 \text{ ton ZnS}) \times \frac{1 \text{ ton} \cdot \text{mol ZnS}}{97.46 \text{ ton ZnS}} \times \frac{1 \text{ ton} \cdot \text{mol SO}_2}{1 \text{ ton} \cdot \text{mol ZnS}} \times \frac{64.07 \text{ ton SO}_2}{1 \text{ ton} \cdot \text{mol SO}_2} = 2.6 \times 10^4 \text{ tons SO}_2$$

17.40 **Strategy:** Looking at the balanced equation, how do we compare the amounts of CaO and CO₂? We can compare them based on the mole ratio from the balanced equation.

Solution: Because the balanced equation is given in the problem, the mole ratio between CaO and CO₂ is known: 1 mole CaO \simeq 1 mole CO₂. If we convert grams of CaO to moles of CaO, we can use this mole ratio to convert to moles of CO₂. Once moles of CO₂ are known, we can convert to grams CO₂.

$$\begin{aligned}
 \text{mass CO}_2 &= (1.7 \times 10^{13} \text{ g CaO}) \times \frac{1 \text{ mol CaO}}{56.08 \text{ g CaO}} \times \frac{1 \text{ mol CO}_2}{1 \text{ mol CaO}} \times \frac{44.01 \text{ g}}{1 \text{ mol CO}_2} \\
 &= 1.3 \times 10^{13} \text{ g CO}_2 = 1.3 \times 10^{10} \text{ kg CO}_2
 \end{aligned}$$

17.41 Total amount of heat absorbed is:

$$(1.8 \times 10^{20} \text{ mol}) \times \frac{29.1 \text{ J}}{\text{K} \cdot \text{mol}} \times 3 \text{ K} = 1.6 \times 10^{22} \text{ J} = 1.6 \times 10^{19} \text{ kJ}$$

The heat of fusion of ice in units of J/kg is:

$$\frac{6.01 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 3.3 \times 10^5 \text{ J/kg}$$

The amount of ice melted by the temperature rise:

$$(1.6 \times 10^{22} \text{ J}) \times \frac{1 \text{ kg}}{3.3 \times 10^5 \text{ J}} = 4.8 \times 10^{16} \text{ kg}$$

17.42 Ethane and propane are greenhouse gases. They would contribute to global warming.

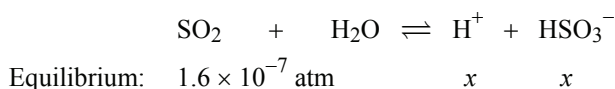
$$17.49 \quad (3.1 \times 10^{10} \text{ g}) \times \frac{2.4}{100} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} \times \frac{1 \text{ mol SO}_2}{1 \text{ mol S}} = 2.3 \times 10^7 \text{ mol SO}_2$$

$$V = \frac{nRT}{P} = \frac{(2.3 \times 10^7 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(273 \text{ K})}{1 \text{ atm}} = 5.2 \times 10^8 \text{ L}$$

17.50 Recall that ppm means the number of parts of substance per 1,000,000 parts. We can calculate the partial pressure of SO₂ in the troposphere.

$$P_{\text{SO}_2} = \frac{0.16 \text{ molecules of SO}_2}{10^6 \text{ parts of air}} \times 1 \text{ atm} = 1.6 \times 10^{-7} \text{ atm}$$

Next, we need to set up the equilibrium constant expression to calculate the concentration of H⁺ in the rainwater. From the concentration of H⁺, we can calculate the pH.



$$K = \frac{[\text{H}^+][\text{HSO}_3^-]}{P_{\text{SO}_2}} = 1.3 \times 10^{-2}$$

$$1.3 \times 10^{-2} = \frac{x^2}{1.6 \times 10^{-7}}$$

$$x^2 = 2.1 \times 10^{-9}$$

$$x = 4.6 \times 10^{-5} \text{ M} = [\text{H}^+]$$

$$\text{pH} = -\log(4.6 \times 10^{-5}) = 4.34$$

17.57 (a) Since this is an elementary reaction, the rate law is:

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

(b) Since [O₂] is very large compared to [NO], then the reaction is a pseudo second-order reaction and the rate law can be simplified to:

$$\text{Rate} = k'[\text{NO}]^2$$

$$\text{where } k' = k[\text{O}_2]$$

(c) Since for a second-order reaction

$$t_{\frac{1}{2}} = \frac{1}{k[\text{A}]_0}$$

then,

$$\frac{\left(t_{\frac{1}{2}}\right)_1}{\left(t_{\frac{1}{2}}\right)_2} = \frac{[(\text{A}_0)_2]}{[(\text{A}_0)_1]}$$

$$\frac{6.4 \times 10^3 \text{ min}}{\left(t_{\frac{1}{2}}\right)_2} = \frac{10 \text{ ppm}}{2 \text{ ppm}}$$

Solving, the new half life is:

$$\left(t_{\frac{1}{2}}\right)_2 = 1.3 \times 10^3 \text{ min}$$

You could also solve for k using the half-life and concentration (2 ppm). Then substitute k and the new concentration (10 ppm) into the half-life equation to solve for the new half-life. Try it.

17.58 Strategy: This problem gives the volume, temperature, and pressure of PAN. Is the gas undergoing a change in any of its properties? What equation should we use to solve for moles of PAN? Once we have determined moles of PAN, we can convert to molarity and use the first-order rate law to solve for rate.

Solution: Because no changes in gas properties occur, we can use the ideal gas equation to calculate the moles of PAN. 0.55 ppm by volume means:

$$\frac{V_{\text{PAN}}}{V_{\text{T}}} = \frac{0.55 \text{ L}}{1 \times 10^6 \text{ L}}$$

Rearranging Equation (5.8) of the text, at STP, the number of moles of PAN in 1.0 L of air is:

$$n = \frac{PV}{RT} = \frac{(1 \text{ atm}) \left(\frac{0.55 \text{ L}}{1 \times 10^6 \text{ L}} \times 1.0 \text{ L} \right)}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(273 \text{ K})} = 2.5 \times 10^{-8} \text{ mol}$$

Since the decomposition follows first-order kinetics, we can write:

$$\text{rate} = k[\text{PAN}]$$

$$\text{rate} = (4.9 \times 10^{-4} /s) \left(\frac{2.5 \times 10^{-8} \text{ mol}}{1.0 \text{ L}} \right) = 1.2 \times 10^{-11} \text{ M/s}$$

17.59 The volume a gas occupies is directly proportional to the number of moles of gas. Therefore, 0.42 ppm by volume can also be expressed as a mole fraction.

$$X_{\text{O}_3} = \frac{n_{\text{O}_3}}{n_{\text{total}}} = \frac{0.42}{1 \times 10^6} = 4.2 \times 10^{-7}$$

The partial pressure of ozone can be calculated from the mole fraction and the total pressure.

$$P_{\text{O}_3} = X_{\text{O}_3} P_{\text{T}} = (4.2 \times 10^{-7})(748 \text{ mmHg}) = (3.14 \times 10^{-4} \text{ mmHg}) \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 4.1 \times 10^{-7} \text{ atm}$$

Substitute into the ideal gas equation to calculate moles of ozone.

$$n_{\text{O}_3} = \frac{P_{\text{O}_3} V}{RT} = \frac{(4.1 \times 10^{-7} \text{ atm})(1 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K})(293 \text{ K})} = 1.7 \times 10^{-8} \text{ mol}$$

Number of O₃ molecules:

$$(1.7 \times 10^{-8} \text{ mol O}_3) \times \frac{6.022 \times 10^{23} \text{ O}_3 \text{ molecules}}{1 \text{ mol O}_3} = \mathbf{1.0 \times 10^{16} \text{ O}_3 \text{ molecules}}$$

17.60 The Gobi desert lacks the primary pollutants (nitric oxide, carbon monoxide, hydrocarbons) to have photochemical smog. The primary pollutants are present both in New York City and in Boston. However, the sunlight that is required for the conversion of the primary pollutants to the secondary pollutants associated with smog is more likely in a July afternoon than one in January. Therefore, answer **(b)** is correct.

17.65 The room volume is:

$$17.6 \text{ m} \times 8.80 \text{ m} \times 2.64 \text{ m} = 4.09 \times 10^2 \text{ m}^3$$

Since $1 \text{ m}^3 = 1 \times 10^3 \text{ L}$, then the volume of the container is $4.09 \times 10^5 \text{ L}$. The quantity, $8.00 \times 10^2 \text{ ppm}$ is:

$$\frac{8.00 \times 10^2}{1 \times 10^6} = 8.00 \times 10^{-4} = \text{mole fraction of CO}$$

The pressure of the CO(atm) is:

$$P_{\text{CO}} = X_{\text{CO}} P_{\text{T}} = (8.00 \times 10^{-4})(756 \text{ mmHg}) \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 7.96 \times 10^{-4} \text{ atm}$$

The moles of CO is:

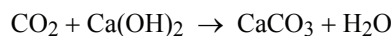
$$n = \frac{PV}{RT} = \frac{(7.96 \times 10^{-4} \text{ atm})(4.09 \times 10^5 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(293 \text{ K})} = 13.5 \text{ mol}$$

The mass of CO in the room is:

$$\text{mass} = 13.5 \text{ mol} \times \frac{28.01 \text{ g CO}}{1 \text{ mol CO}} = \mathbf{378 \text{ g CO}}$$

17.66 Strategy: After writing a balanced equation, how do we compare the amounts of CaCO₃ and CO₂? We can compare them based on the mole ratio from the balanced equation. Once we have moles of CO₂, we can then calculate moles of air using the ideal gas equation. From the moles of CO₂ and the moles of air, we can calculate the percentage of CO₂ in the air.

Solution: First, we need to write a balanced equation.



The mole ratio between CaCO₃ and CO₂ is: 1 mole CaCO₃ \cong 1 mole CO₂. If we convert grams of CaCO₃ to moles of CaCO₃, we can use this mole ratio to convert to moles of CO₂. Once moles of CO₂ are known, we can convert to grams CO₂.

Moles of CO₂ reacted:

$$0.026 \text{ g CaCO}_3 \times \frac{1 \text{ mol CaCO}_3}{100.1 \text{ g CaCO}_3} \times \frac{1 \text{ mol CO}_2}{1 \text{ mol CaCO}_3} = 2.6 \times 10^{-4} \text{ mol CO}_2$$

The total number of moles of air can be calculated using the ideal gas equation.

$$n = \frac{PV}{RT} = \frac{\left(747 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)(5.0 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K})(291 \text{ K})} = 0.21 \text{ mol air}$$

The percentage by volume of CO₂ in air is:

$$\frac{V_{\text{CO}_2}}{V_{\text{air}}} \times 100\% = \frac{n_{\text{CO}_2}}{n_{\text{air}}} \times 100\% = \frac{2.6 \times 10^{-4} \text{ mol}}{0.21 \text{ mol}} \times 100\% = \mathbf{0.12\%}$$

17.67 The chapter sections where these gases are discussed are:

O₃: Section 17.7 SO₂: Section 17.6 NO₂: Sections 17.5, 17.7
 Rn: Section 17.8 PAN: Section 17.7 CO: Sections 17.5, 17.7, 17.8

17.68 An increase in temperature has shifted the system to the right; the equilibrium constant has increased with an increase in temperature. If we think of heat as a reactant (endothermic)



based on Le Châtelier's principle, adding heat would indeed shift the system to the right. Therefore, the reaction is **endothermic**.

17.69 (a) From the balanced equation:

$$K_c = \frac{[\text{O}_2][\text{HbCO}]}{[\text{CO}][\text{HbO}_2]}$$

(b) Using the information provided:

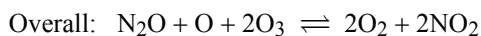
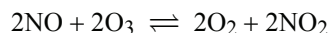
$$212 = \frac{[\text{O}_2][\text{HbCO}]}{[\text{CO}][\text{HbO}_2]} = \frac{[8.6 \times 10^{-3}][\text{HbCO}]}{[1.9 \times 10^{-6}][\text{HbO}_2]}$$

Solving, the ratio of HbCO to HbO₂ is:

$$\frac{[\text{HbCO}]}{[\text{HbO}_2]} = \frac{(212)(1.9 \times 10^{-6})}{(8.6 \times 10^{-3})} = \mathbf{0.047}$$

17.70 The concentration of O₂ could be monitored. Formation of CO₂ must deplete O₂.

17.71 (a) N₂O + O ⇌ 2NO

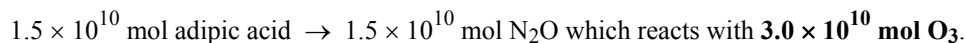


(b) Compounds with a permanent dipole moment such as N₂O are more effective greenhouse gases than nonpolar species such as CO₂ (Section 17.5 of the text).

(c) The moles of adipic acid are:

$$(2.2 \times 10^9 \text{ kg adipic acid}) \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol adipic acid}}{146.1 \text{ g adipic acid}} = 1.5 \times 10^{10} \text{ mol adipic acid}$$

The number of moles of adipic acid is given as being equivalent to the moles of N_2O produced, and from the overall balanced equation, one mole of N_2O will react with two moles of O_3 . Thus,



17.72 In Problem 17.6, we determined the partial pressure of CO_2 in dry air to be 3.3×10^{-4} atm. Using Henry's law, we can calculate the concentration of CO_2 in water.

$$c = kP$$

$$[\text{CO}_2] = (0.032 \text{ mol/L}\cdot\text{atm})(3.3 \times 10^{-4} \text{ atm}) = 1.06 \times 10^{-5} \text{ mol/L}$$

We assume that all of the dissolved CO_2 is converted to H_2CO_3 , thus giving us 1.06×10^{-5} mol/L of H_2CO_3 . H_2CO_3 is a weak acid. Setup the equilibrium of this acid in water and solve for $[\text{H}^+]$.

The equilibrium expression is:

	H_2CO_3	\rightleftharpoons	H^+	$+$	HCO_3^-
Initial (M):	1.06×10^{-5}		0		0
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$(1.06 \times 10^{-5}) - x$		x		x

$$K \text{ (from Table 15.5)} = 4.2 \times 10^{-7} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{(1.06 \times 10^{-5}) - x}$$

Solving the quadratic equation:

$$x = 1.9 \times 10^{-6} \text{ M} = [\text{H}^+]$$

$$\mathbf{pH = -\log(1.9 \times 10^{-6}) = 5.72}$$

17.73 First we calculate the number of ^{222}Rn atoms.

$$\text{Volume of basement} = (14 \text{ m} \times 10 \text{ m} \times 3.0 \text{ m}) = 4.2 \times 10^2 \text{ m}^3 = 4.2 \times 10^5 \text{ L}$$

$$n_{\text{air}} = \frac{PV}{RT} = \frac{(1.0 \text{ atm})(4.2 \times 10^5 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(273 \text{ K})} = 1.9 \times 10^4 \text{ mol air}$$

$$n_{\text{Rn}} = \frac{P_{\text{Rn}}}{P_{\text{air}}} \times (1.9 \times 10^4) = \frac{1.2 \times 10^{-6} \text{ mmHg}}{760 \text{ mmHg}} \times (1.9 \times 10^4 \text{ mol}) = 3.0 \times 10^{-5} \text{ mol Rn}$$

Number of ^{222}Rn atoms at the beginning:

$$(3.0 \times 10^{-5} \text{ mol Rn}) \times \frac{6.022 \times 10^{23} \text{ Rn atoms}}{1 \text{ mol Rn}} = \mathbf{1.8 \times 10^{19} \text{ Rn atoms}}$$

$$k = \frac{0.693}{3.8 \text{ d}} = 0.182 \text{ d}^{-1}$$

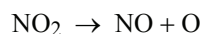
From Equation (13.3) of the text:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{x}{1.8 \times 10^{19}} = -(0.182 \text{ d}^{-1})(31 \text{ d})$$

$$x = 6.4 \times 10^{16} \text{ Rn atoms}$$

17.74 Strategy: From ΔH_f° values given in Appendix 3 of the text, we can calculate ΔH° for the reaction



Then, we can calculate ΔE° from ΔH° . The ΔE° calculated will have units of kJ/mol. If we can convert this energy to units of J/molecule, we can calculate the wavelength required to decompose NO_2 .

Solution: We use the ΔH_f° values in Appendix 3 and Equation (6.18) of the text.

$$\Delta H_{\text{rxn}}^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

Consider reaction (1):

$$\Delta H^\circ = \Delta H_f^\circ(\text{NO}) + \Delta H_f^\circ(\text{O}) - \Delta H_f^\circ(\text{NO}_2)$$

$$\Delta H^\circ = (1)(90.4 \text{ kJ/mol}) + (1)(249.4 \text{ kJ/mol}) - (1)(33.85 \text{ kJ/mol})$$

$$\Delta H^\circ = 306.0 \text{ kJ/mol}$$

From Equation (6.10) of the text, $\Delta E^\circ = \Delta H^\circ - RT\Delta n$

$$\Delta E^\circ = (306.0 \times 10^3 \text{ J/mol}) - (8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})(1)$$

$$\Delta E^\circ = 304 \times 10^3 \text{ J/mol}$$

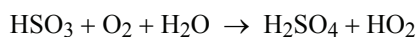
This is the energy needed to dissociate 1 mole of NO_2 . We need the energy required to dissociate *one molecule* of NO_2 .

$$\frac{304 \times 10^3 \text{ J}}{1 \text{ mol NO}_2} \times \frac{1 \text{ mol NO}_2}{6.022 \times 10^{23} \text{ molecules NO}_2} = 5.05 \times 10^{-19} \text{ J/molecule}$$

The longest wavelength that can dissociate NO_2 is:

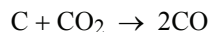
$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{5.05 \times 10^{-19} \text{ J}} = 3.94 \times 10^{-7} \text{ m} = 394 \text{ nm}$$

- 17.75** (a) Its small concentration is the result of its high reactivity.
 (b) OH has a great tendency to abstract an H atom from another compound because of the large energy of the O–H bond (see Table 9.4 of the text).
 (c) $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$

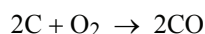


17.76 This reaction has a high activation energy.

17.77 The blackened bucket has a large deposit of elemental carbon. When heated over the burner, it forms poisonous carbon monoxide.

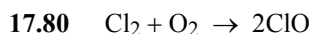


A smaller amount of CO is also formed as follows:



17.78 The size of tree rings can be related to CO_2 content, where the number of rings indicates the age of the tree. The amount of CO_2 in ice can be directly measured from portions of polar ice in different layers obtained by drilling. The “age” of CO_2 can be determined by radiocarbon dating and other methods.

17.79 The use of the aerosol can liberate CFC’s that destroy the ozone layer.



$$\Delta H^\circ = \Sigma BE(\text{reactants}) - \Sigma BE(\text{products})$$

$$\Delta H^\circ = (1)(242.7 \text{ kJ/mol}) + (1)(498.7 \text{ kJ/mol}) - (2)(206 \text{ kJ/mol})$$

$$\Delta H^\circ = 329 \text{ kJ/mol}$$

$$\Delta H^\circ = 2\Delta H_f^\circ(\text{ClO}) - 2\Delta H_f^\circ(\text{Cl}_2) - 2\Delta H_f^\circ(\text{O}_2)$$

$$329 \text{ kJ/mol} = 2\Delta H_f^\circ(\text{ClO}) - 0 - 0$$

$$\Delta H_f^\circ(\text{ClO}) = \frac{329 \text{ kJ/mol}}{2} = \mathbf{165 \text{ kJ/mol}}$$

17.81 There is one C–Br bond per CH_3Br molecule. The energy needed to break one C–Br bond is:

$$E = \frac{293 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} = 4.865 \times 10^{-19} \text{ J}$$

Using Equation (7.3) of the text, we can now calculate the wavelength associated with this energy.

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{4.865 \times 10^{-19} \text{ J}} = 4.09 \times 10^{-7} \text{ m} = 409 \text{ nm}$$

This wavelength is in the visible region of the spectrum and is available in the troposphere. Thus, photolysis of the C–Br bond will occur.

- 17.82** In one second, the energy absorbed by CO₂ is 6.7 J. If we can calculate the energy of one photon of light with a wavelength of 14993 nm, we can then calculate the number of photons absorbed per second.

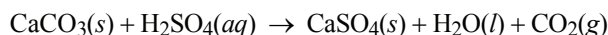
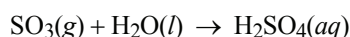
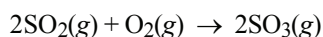
The energy of one photon with a wavelength of 14993 nm is:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{14993 \times 10^{-9} \text{ m}} = 1.3266 \times 10^{-20} \text{ J}$$

The number of photons absorbed by CO₂ per second is:

$$6.7 \text{ J} \times \frac{1 \text{ photon}}{1.3266 \times 10^{-20} \text{ J}} = \mathbf{5.1 \times 10^{20} \text{ photons}}$$

- 17.83 (a)** The reactions representing the formation of acid rain (H₂SO₄(aq)) and the damage that acid rain causes to marble (CaCO₃) statues are:



First, we convert the mass of SO₂ to moles of SO₂. Next, we convert to moles of H₂SO₄ that are produced (20% of SO₂ is converted to H₂SO₄). Then, we convert to the moles of CaCO₃ damaged per statue (5% of 1000 lb statue is damaged). And finally, we can calculate the number of marble statues that are damaged.

$$(50 \times 10^6 \text{ tons SO}_2) \times \frac{2000 \text{ lb}}{1 \text{ ton}} \times \frac{453.6 \text{ g}}{1 \text{ lb}} \times \frac{1 \text{ mol SO}_2}{64.07 \text{ g SO}_2} = 7.1 \times 10^{11} \text{ mol SO}_2$$

$$(0.20) \times (7.1 \times 10^{11} \text{ mol SO}_2) \times \frac{1 \text{ mol H}_2\text{SO}_4}{1 \text{ mol SO}_2} = 1.4 \times 10^{11} \text{ mol H}_2\text{SO}_4$$

The moles of CaCO₃ damaged per stature are:

$$(0.05) \times (1000 \text{ lb CaCO}_3) \times \frac{453.6 \text{ g}}{1 \text{ lb}} \times \frac{1 \text{ mol CaCO}_3}{100.1 \text{ g CaCO}_3} = 226.6 \text{ mol CaCO}_3/\text{statue}$$

The number of statues damaged by 1.4×10^{11} moles of H₂SO₄ is:

$$(1.4 \times 10^{11} \text{ mol H}_2\text{SO}_4) \times \frac{1 \text{ mol CaCO}_3}{1 \text{ mol H}_2\text{SO}_4} \times \frac{1 \text{ statue}}{226.6 \text{ mol CaCO}_3} = \mathbf{6.2 \times 10^8 \text{ statues}}$$

Of course we don't have 6.2×10^8 marble statues around. This figure just shows that any outdoor objects/statues made of marble are susceptible to attack by acid rain.

- (b)** The other product in the above reaction is CO₂(g), which is a greenhouse gas that contributes to global warming.

17.84 (a) We use Equation (13.14) of the text.

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

$$\ln \frac{2.6 \times 10^{-7} \text{ s}^{-1}}{3.0 \times 10^{-4} \text{ s}^{-1}} = \frac{E_a}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{233 \text{ K} - 298 \text{ K}}{(233 \text{ K})(298 \text{ K})} \right)$$

$$E_a = 6.26 \times 10^4 \text{ J/mol} = \mathbf{62.6 \text{ kJ/mol}}$$

(b) The unit for the rate constant indicates that the reaction is first-order. The half-life is:

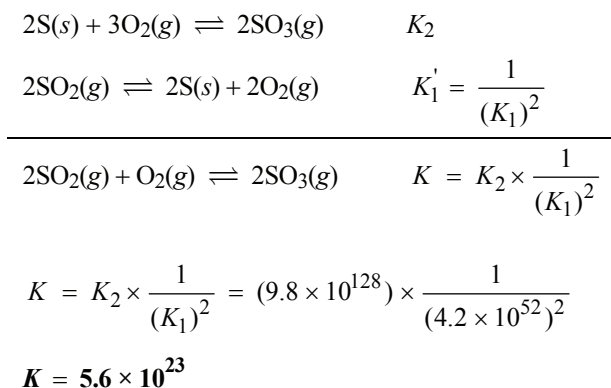
$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{3.0 \times 10^{-4} \text{ s}^{-1}} = \mathbf{2.3 \times 10^3 \text{ s} = 38 \text{ min}}$$

17.85 Actually, this question has two parts: (1) How can we determine the temperature and (2) how do we know the time period.

(1) Hydrogen has two stable isotopes: ^1H (99.985%) and ^2H or deuterium (D) (0.015%). Oxygen has three stable isotopes. The two major ones are: ^{16}O (99.759%) and ^{18}O (0.204%). Therefore, water molecules are made up of these different combinations. H_2O molecules containing heavier isotopes have greater mass and require more energy to evaporate. During cold periods, water that evaporates contains fewer ^{18}O and D than during warm ones. As the moist air is transported toward the North and South Poles and cools, the water that condenses and eventually freezes contains fewer heavy isotopes. The reverse holds for water evaporated during warm periods. By comparing the isotope ratio (using a mass spectrometer) with that of average ocean water (for which the temperature is known), it is possible to estimate the temperature during the period when evaporation-condensation occurred.

(2) The formation of ice cores occurs at a steady rate. Therefore, knowing the rate of formation and the depth from which the ice cores are extracted, we can estimate the time of deposit. Furthermore, from the CO_2 trapped in the ice core, scientists can apply carbon-14 dating (and other radioactive dating techniques) to determine the age of the ice core.

17.86 In order to end up with the desired equation, we keep the second equation as written, but we must reverse the first equation and multiply by two.



Thus, the reaction favors the formation of SO_3 . But, this reaction has a high activation energy and requires a catalyst to promote it.