Review Questions

1. In the "micrograms per cubic meter" concentration scale, to what substances do micrograms and cubic meters refer?

2. What chemical substance initiates the air oxidation of stable molecules? How is it initially formed, and how is it reformed?

3. In general terms, what is meant by *photochemical smog*? What are the initial reactants in the process? Why is sunlight required?

4. What is meant by a *primary pollutant* and by a *secondary pollutant*? Give examples.

5. How does OH react with a stable molecule containing a C═C bond? With an alkane?

6. What is meant by the term *synergism*? Give an example.

7. What is the chemical reaction by which *thermal NO* is produced? From which two sources does most urban NO arise? What is meant by the term NO_X? What is meant by *fuel NO*?

8. Describe the strategies by which reduction of urban ozone levels has been attempted. What difficulties have been encountered in these efforts? Is photochemical smog strictly a localized urban problem?

9. What is meant by geographic regions that are *VOC-limited*? *NO_X-limited*?

10. Describe the operation of the *three-way catalyst* in transforming emissions released by an automobile engine. Does the catalyst operate when the engine is cold? Why is it important for converters that the level of sulfur in gasoline be minimized?

11. Describe the manner in which emissions from diesel-powered vehicles can be controlled, including the use of catalytic converters.

12. Describe the reaction used in the *selective catalytic reduction* of nitrogen oxides. What other techniques are used for NO_X emission control from power plants?

13. What are the main anthropogenic sources of sulfur dioxide? Describe the strategies by which these emissions can be reduced. What is the *Claus reaction*?

14. What species are included in the air pollution index called *total reduced sulfur*?

15. Describe the three strategies used in *clean coal*.

16. What two species, other than O_2, are active oxidizing agents of sulfur dioxide in atmospheric water droplets?

17. State *Henry's law*.

18. Define the term *aerosol*, and differentiate between *coarse* and *fine particulates*. What are the usual origins of these two types of atmospheric particles?

19. What are the usual chemical components of a *sulfate aerosol*?

20. Write a balanced equation illustrating the reactions that occur between one molecule of ammonia and (a) one molecule of nitric acid and (b) one molecule of sulfuric acid.

21. What are the usual concentration units for suspended particulates? What would the designation PM_{40} mean? What do the terms *respirable* and *ultrafine* mean?

Green Chemistry Questions

1. The development of a low-VOC coalescent for paints by ADM won a Presidential Green Chemistry Challenge Award.

(a) Into which of the three focus areas (see page xxviii) for these awards does this award best fit?

(b) List two of the twelve principles of green chemistry that are addressed by this discovery. Justify each of your answers.

2. What are the environmental advantages of the coalescent developed by ADM?

3. Consider the structure (Figure 3-11b) of the coalescent developed by ADM. Using your knowledge of organic chemistry, explain why this molecule undergoes reaction with oxygen so readily. Would you expect linoleic acid to react in a similar manner? Stearic acid?

4. *PERC* replaced gasoline and kerosene in the dry-cleaning process.

(a) Describe any environmental problems or worker hazards that would be associated with these solvents.

(b) Would these same environmental problems or workers hazards be eliminated by the use of PERC?

(c) By the use of carbon dioxide?

5. The development of surfactants for carbon dioxide by Joseph DeSimone won a Presidential Green Chemistry Challenge Award.

(a) Which of the three focus areas (see page xxviii) for these awards does this award best fit into?

(b) List two of the twelve principles of green chemistry (see pages xxiii–xxiv) that are addressed by the green chemistry developed by DeSimone.

6. The ions in ionic liquids (ILs) have weak ionic attractions for one another. This weak interaction is due to one or more factors including

- the presence of bulky nonpolar groups which prevent the close interaction of the charged regions of the ions, and
- delocalized and/or dispersed charges resulting in low charge density.

Inspect the (ILs) in Figure 3-15 and discuss the structural features of these compounds that result in weak interactions between the oppositely charged ions.

7. The discovery of the dissolution of cellulose with ionic liquids and the formation of various cellulose composites by Robin Rogers won a Presidential Green Chemistry Challenge Award.

(a) Which of the three focus areas (see page xxviii) for these awards does this award best fit into?

(b) The use of an abundant, naturally occurring polymer, a microwave heat source, and ionic liquids are three important green chemistry aspects of this study. For each of these aspects list at least two of the twelve principles of green chemistry (see pages xxiii–xxiv) that are addressed in this study.

Additional Problems

1. The rate constant for the oxidation of nitric oxide by ozone is 2×10^{-14} molecule^{-1} cm^3 sec^{-1}, whereas that for the competing reaction in which it is oxidized by oxygen, i.e.,

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

is 2×10^{-38} molecule^{-2} cm^6 sec^{-1}. For typical concentrations encountered in morning smog episodes, namely 40 ppb for ozone and 80 ppb for nitric oxide, deduce the rates of these two reactions and decide which one is the dominant process. [*Hint:* The concentrations of the reactants must be expressed in units appropriate to the rate constant.]

2. In a particular air mass, the concentration of OH was found to be 8.7×10^6 molecules cm^{-3}, and that of carbon monoxide was 20 ppm.

(a) Calculate the rate of the reaction of OH with atmospheric CO at 30°C, given that the rate constant for the process is $5 \times 10^{-13} e^{-300/T}$ molecule^{-1} cm^3 sec^{-1}.

(b) Estimate the half-life of an OH molecule in air, assuming that its lifetime is determined by its reaction with CO. [*Hint:* Re-express the rate law as a pseudo-first-order process with the level of CO fixed at 20 ppm. Consult your introductory chemistry textbook to find the relationship between the half-life of a substance and the rate constant for its first-order decay.]

3. In the overall reaction that produces nitric oxide from N_2 and O_2, the slow step in the mechanism is the reaction between atomic oxygen and molecular nitrogen to produce nitric oxide and atomic nitrogen.

(a) Write out the chemical equation for the slow step and the rate law equation for it.

(b) Given that its rate constant at 800°C is 9.7×10^{10} L mol^{-1} sec^{-1}, and that its activation energy is 315 kJ mol^{-1}, calculate the amount by which the rate constant increases if the temperature is raised to 1100°C.

4. At combustion temperatures, the equilibrium constant for the reaction of N_2 with O_2 is about 10^{-14}. Calculate the concentration of nitric oxide that is in equilibrium with atmospheric levels of nitrogen and oxygen. Repeat the calculation for normal atmospheric temperatures, at which the equilibrium constant is about 10^{-30}. Given that the concentration of NO that exits from the combustion zone in a vehicle is much higher than this latter equilibrium value, what does that imply about equilibrium in the reaction mixture? [*Hint:* Use the stoichiometry of the reaction to reduce the number of unknowns in the expression for *K*.]

5. The concentration of ozone in ground-level air can be determined by allowing the gas to react with an aqueous solution of potassium iodide, KI, in a redox reaction that produces molecular iodine, molecular oxygen, and potassium hydroxide.

(a) Deduce the balanced reaction for the overall process.

(b) Determine the ozone concentration, in ppb, in a 10.0-L sample of outdoor air if it required 17.0 μg of KI to react with it.

6. The percentage of sulfur in coal can be determined by burning a sample of the solid and passing the resulting sulfur dioxide gas into a solution of hydrogen peroxide, which oxidizes it to sulfuric acid, and then titrating the acid. Calculate the mass percent of sulfur in a sample if the gas from an 8.05-g sample required 44.1 mL of 0.114 M NaOH in the titration of the diprotic acid.

7. Calculate the volume, at 20°C and 1.00 atm, of SO_2 produced by the conventional roasting of 1.00 tonnes (1,000 kg) of nickel sulfide ore, NiS. What mass of pure sulfuric acid could be produced from this amount of SO_2?

8. Ironically, SO_2 could be extracted from gas emissions by passing it through a solution of sulfite ion, SO_3^{2-}.

(a) Assuming sulfite ion acts as a base and the sulfur dioxide is present in water initially as sulfurous acid, write an acid–base reaction between the species.

(b) Devise a scheme by which dilute sulfur dioxide in an emission gas could be captured by an aqueous solution of sulfite ion, and later released as a concentrated stream of SO_2.

9. Assuming its concentration in air is 2.0 ppb, calculate the molar solubility of SO_2 in raindrops whose pH is fixed (by the presence of strong acids) to be 4.0, 5.0, and 6.0. The data required for the calculations is present in Section 3.21 of the text.

10. The sulfur species that undergoes oxidation in water droplets is the bisulfite ion, HSO_3^-, so the rate of oxidation is proportional to its concentration multiplied by that of the oxidizing agent. Predict how changes in pH in the droplet will affect the rate of oxidation (a) if O_3 reacts with bisulfite ion, and (b) if hydrogen peroxide in