Assignment 3

Chapter 3 Review Questions (Pg 141, 4th edition / Pg 131, 5th edition)

1. Problem 3
   See pages 76-83 for definition, reactants, and other information (97-103 in 4th ed.)

2. Problem 14
   H₂S, CH₃SH, (CH₃)₂S and CH₃SSCH₃

3. Problem 7
   Convert 1000 kg of NiS (Molar Mass 90.75 g) to moles (1000×10³ g/90.75 g mol⁻¹=11×10³ moles)
   11×10³ mole NiS → 11×10³ mol SO₂ → 11×10³ mole H₂SO₄
   Convert moles of NiS into Volume of SO₂ (V=nRT/P or 1 mole =22.3 L) V=245.3×10³ L
   From #moles of H₂SO₄ determine weight of H₂SO₄ (Molar Mass of H₂SO₄= 98g)

Supplementary Problems

4. See page 78 in the book (98 in 4th ed.)
5. Human activity, especially in industrial nations, generates and releases gases like SO₂, CO₂, and NO₂ into the atmosphere.
   a. Which gases pose serious problems from an "acid rain" perspective? Why?
      SO₂, CO₂, and NO₂ are eventual sources for H₂SO₃, H₂SO₄, H₂CO₃, and HNO₃ acids.
      H₂CO₃ is very weak and H₂SO₃ is weak. However both H₂SO₄ and HNO₃ are strong acids. In light of this, both SO₂ and NO₂ pose serious problems compared to CO₂.
   b. Although industrial emission of SO₂ and NO₂ has decreased drastically in Europe in recent decades the pH of rain is still relatively low. Suggest two reasons for this observation.
      First, increased NO₂ emissions from vehicles have offset any reductions from industry. Secondly, in the same period the emission of alkaline particles (e.g. fly ash) has been reduced. These particles normally neutralize a fraction of the SO₂ released.
6. Explain how a three-way catalytic converter works and why this helps in reducing air pollution. Include chemical equations as a part of your explanation.
   A three-way catalytic converter “cleans” NOₓ using unburned hydrocarbons, CO and H₂ as reductants. See the following unbalanced equation:
   2 NO + reducing agent → N₂ + O₂ (or H₂O)
7. During a photochemical smog episode in the coastal city of Seattle, the steady-state concentration of oxygen radicals at ground level was measured to be 0.080 ppmv at 25°C. Convert this value to:
   a. partial pressure in atm
\[
ppmv(O) = \frac{p(O)}{p(total)} \times 10^6 \Rightarrow p(O) = \frac{ppm(O) \times p(total)}{10^6} = 8.0 \times 10^{-8}
\]

b. the molarity scale

\[
\frac{n}{V} = \frac{P}{RT} \Rightarrow 3.3 \times 10^{-9} \text{mol L}^{-1}
\]

c. the molecules cm\(^{-3}\) scale

\[
2.0 \times 10^{12} \text{molecules cm}^{-3}
\]

8. In one study, the concentration of OH in air at the time was found to be 8.7\(\times10^6\) molecules per cubic centimeter. Calculate its molar concentration and its concentration in parts per trillion, assuming that the total air pressure is 1.0 atm and the temperature is 15°C.

**Problem 2-1**

Original concentration is:

\[
\frac{8.7 \times 10^6 \text{molecules OH}}{1 \text{ cm}^3 \text{of air}}
\]

For a molar concentration, i.e., moles of OH per liter of air, we must convert molecules of OH to moles, and 1 cm\(^3\) air to liters.

\[
8.7 \times 10^6 \text{molecules OH} \times \frac{1 \text{ mole OH}}{6.02 \times 10^{23} \text{molecules OH}} = 1.4 \times 10^{-17} \text{ moles OH}
\]

Thus, the molar concentration is:

\[
1.4 \times 10^{-17} \text{ moles OH} / 10^{-3} \text{ L air}
\]

\[
= 1.4 \times 10^{-14} \text{ moles/L}
\]

To obtain the concentration in ppt, we must deduce the number of trillions of molecules in 1 cm\(^3\) of air, because the numerator of the original concentrations is already in numbers of molecules.

For the 1 cm\(^3\) of air sample,

\[
n = \frac{PV}{RT} = 1.0 \text{ atm} \times 10^{-3} \text{ L} / 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 288 \text{ K}
\]

\[
= 4.2 \times 10^{-5} \text{ moles air}
\]

\[
4.2 \times 10^{-5} \text{ moles air} \times \frac{6.02 \times 10^{23} \text{molecules air}}{1 \text{ mole air}}
\]

\[
= 2.5 \times 10^{14} \text{ molecules of air}
\]

\[
= 2.5 \times 10^7 \times (10^{12} \text{molecules of air}) = 2.5 \times 10^7 \text{ trillion molecules}
\]

Concentration is \[
8.7 \times 10^6 \text{molecules OH} / 2.5 \times 10^7 \text{ trillion molecules of air}, \text{ or } 0.35 \text{ ppt.}
\]
9. Reduce nitrogen in the form of the compound urea, \( \text{CO(NH}_2\text{)}_2 \) is injected directly into the combustion flame to combine there, rather than later in the presence of a catalyst, with NO to produce \( \text{N}_2 \). Deduce the balanced equation that converts urea and nitric oxide and oxygen into \( \text{N}_2 \), \( \text{CO}_2 \) and water. Why is this an important process?

\[
2\text{CO(NH}_2\text{)}_2 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 2\text{CO}_2 + 4\text{H}_2\text{O}
\]

NO will gradually form NOx and can react with oxygen to form ozone. Both NOx and ozone are ground level pollutants.

10. The sulfur species that undergoes oxidation in water droplets is the bisulfate ion, \( \text{HSO}_3^- \), 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 if:

(a) \( \text{O}_3 \) reacts with bisulfate ion

(b) if hydrogen peroxide in the protonated form \( \text{H}_3\text{O}_2^+ \) formed in the equilibrium

\[
\text{H}_2\text{O}_2 + \text{H}^+ \rightleftharpoons \text{H}_3\text{O}_2^+
\]

is the species that interacts with bisulfate.

10. (a) If the pH falls, the concentration of \( \text{H}^+ \) increases, which by LeChatelier’s Principle drives the equilibrium to the left, decreasing the concentration of \( \text{HSO}_3^- \) in the reaction

\[
\text{H}_2\text{SO}_3 \rightleftharpoons \text{H}^+ + \text{HSO}_3^-
\]

Since the concentration of \( \text{HSO}_3^- \) decreases, its rate of oxidation by ozone will decrease.

(b) As in part (a), decreasing the pH decreases the concentration of \( \text{HSO}_3^- \).

However, increasing [\( \text{H}^+ \)] drives the equilibrium in the reaction below to the right, producing more of the ion that oxidizes \( \text{HSO}_3^- \).

\[
\text{H}_2\text{O}_2 + \text{H}^+ \rightleftharpoons \text{H}_3\text{O}_2^+
\]

The two opposing effects on the rate cancel, so pH should have little effect in the rate of oxidation by hydrogen peroxide.