25. Calculate the pH of rainwater that is in equilibrium with air that has an SO₂ concentration of 2 ppm.

$$P_{SO_2} = (1 \text{ atm})(2 \times 10^{-6}) = 2 \times 10^{-6} \text{ atm}$$

$$[H_2SO_3] = K_{a1} P_{SO_2} = (1.0 \text{ M/atm})(2 \times 10^{-6} \text{ atm}) = 2 \times 10^{-6} \text{ M}$$

Reaction: $$H_2SO_3 \leftrightarrow H^+ + HSO_3^-$$

$$K_{a1} = 0.017$$

Note: although we can not really use an ICE (initial change equilibrium) table because SO₂ will not be depleted from the gas phase and H₂SO₃ will be constant, we can expect that $$[H^+] = [HSO_3^-]$$ (assuming no other sources of H⁺)

$$K_{a1} = 0.017 = [H^+] [HSO_3^-]/[H_2SO_3] = [H^+]^2/2 \times 10^{-6}$$

$$[H^+] = [(0.017)(2 \times 10^{-6})]^{0.5} = 1.84 \times 10^{-4} \text{ M}$$

$$pH = 3.73$$

3. What percentage of the earth’s water is seawater? About 97%. List the four most concentrated metal ions present in seawater. Sodium, magnesium, calcium, and potassium. What is the approximate concentration (in ppm) of dissolved solids in seawater? 35,000 ppm.

5. How much dissolved solids can each of the following contain?
   a. Brackish water – between 1000 and 35,000 ppm
   b. Freshwater – less than 1000 ppm
   c. Drinking water – less than 500 ppm

6. What is the dominant cation in each of the following:
   a. Seawater – Na⁺
   b. Hard water – There are actually two dominant ions: Mg²⁺ and Ca²⁺.

8. In which of the following steps of the hydrologic cycle is water purified?
   a. Condensation – Not purified
   b. Precipitation – Not purified
   c. Evaporation - Purified
   d. Transpiration - Purified

10. At what temperature does water reach its maximum density? 4°C. What are the implications of this property for life in a pond? The surface layer can be colder than deeper layers, allowing ice to form on the surface without causing freezing throughout the whole pond.
24. Suppose that the concentration of the greenhouse gas CO$_2$ continues to increase in our atmosphere until it reaches 500 ppm. What effect would this increase have on the pH of rainwater? How much would the pH increase or decrease?

The increase in CO$_2$ could decrease the pH of rainwater (if other sources of acidity like SO$_2$ and acidic aerosol particles are minimal).

With the CO$_2$ mixing ratio = 380 ppm, $[\text{CO}_2(\text{aq})] = K_{HPCO_2} = (0.0338 \text{ M/atm})(3.8 \times 10^{-4} \text{ atm}) = 1.28 \times 10^{-5} \text{ M}$

Reaction: $\text{CO}_2(\text{g}) + H_2O \leftrightarrow H^+ + HCO_3^- \quad K_{a1} = 4.45 \times 10^{-7}$

Note: although we can not really use an ICE (initial change equilibrium) table because CO$_2$ will not be depleted from the gas phase and CO$_2$ will be constant, we can expect that $[H^+] = [\text{HCO}_3^-]$ (assuming no other sources of H$^+$)

$K_{a1} = 4.45 \times 10^{-7} = [H^+][\text{HCO}_3^-]/[\text{CO}_2] = [H^+]^2/1.28 \times 10^{-5}$

$[H^+] = (4.45 \times 10^{-7})(1.28 \times 10^{-5})^{0.5} = 2.39 \times 10^{-6} \text{ M}$

$pH = 5.62$

With CO$_2$ mixing ratio = 500 ppm, $[\text{CO}_2(\text{aq})] = 1.69 \times 10^{-5} \text{ M}$, and $pH = 5.56$ (so a decrease of 0.06 units).

25. What is the predominant carbonate species in natural waters with a pH of 
   a. Greater than 11
   These problems can be solved by looking at the $pK_{a1}$ and $pK_{a2}$ for CO$_2(\text{aq})$, which are 6.35 and 10.33, respectively. Since pH > 11 is also > $pK_{a2}$, the dominant species will be CO$_3^{2-}$.
   b. Less than 5
   $pH < pK_{a1}$, so CO$_2(\text{aq})$ is dominant species
   c. Equal to 6.35
   At pH = $pK_{a1}$, CO$_2(\text{aq})$ and HCO$_3^-$ are present at equal concentrations.
   d. Equal to 10.33
   At pH = $pK_{a2}$, CO$_3^{2-}$ and HCO$_3^-$ are present at equal concentrations.

26. Air is 21% oxygen. Calculate the molar concentration of dissolved oxygen in lake water than is saturated with air. What is this concentration in ppm? The Henry's law constant for oxygen is $1.28 \times 10^{-3} \text{ M/atm}$.

$[\text{O}_2(\text{aq})] = (0.21 \text{ atm})(1.28 \times 10^{-3} \text{ M/atm}) = 2.69 \times 10^{-4} \text{ M}$. Assuming sea-level lake.

ppm O$_2$(aq) (by mass) = ($2.69 \times 10^{-4} \text{ mol/L})(32.00 \text{ g/mol})(1000 \text{ mg/g})(1 \text{ ppm/mg/L}) = 8.60 \text{ ppm}$.

This is somewhat different than the answer in the textbook because I have assumed that % oxygen is for the actual atmosphere (rather than for dry air) or that the air in equilibrium with the lake is totally dry rather than saturated with water. The actual answer is probably half way between the two values (e.g. 8.45 ppm) because a typical relative humidity will be around 50%.

35. What is the main cause of acid mine damage? Give an equation to show how this acid is formed.

Acid mine damage is mainly caused by release of sulfuric acid which is formed from sulfides such as pyrite (FeS$_2$) that oxidize to sulfuric acid.

$2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+$
44. San Diego, California, draws its water supply from the Colorado River, which is several hundred miles away. The water flows in open aqueductes from the river to the city. Would you expect this to have any affect on the quality of the water? 

Yes. As water evaporates, the dissolved solids (and concentrations of any low volatility trace species) will increase.