Chapter 2
The Hydrosphere and Water Chemistry

1. Alkalinity is determined by titration with standard acid. The alkalinity is often expressed as mg/L of $CaCO_3$. If V_p mL of acid of normality N are required to titrate V_s mL of sample to the phenolphthalein endpoint, what is the formula for the phenolphthalein alkalinity as mg/L of $CaCO_3$?

   Answer: $(V_p \times N)/V_S$

2. Exactly 100 pounds of cane sugar (dextrose), $C_{12}H_{22}O_{11}$, were accidentally discharged into a small stream saturated with oxygen from the air at 25°C. How many liters of this water could be contaminated to the extent of removing all the dissolved oxygen by biodegradation?

   Answer: The calculation is the following, where Dx is dextrose

$$4.54 \times 10^4 \text{ g Dx} \times \frac{1 \text{ mol Dx}}{342 \text{ g Dx}} \times \frac{12 \text{ mol } O_2}{1 \text{ mol Dx}} \times \frac{3.20 \times 10^4 \text{ mg } O_2}{1 \text{ mol } O_2} \times \frac{1 \text{ L}}{8.32 \text{ mg } O_2} = 6.13 \times 10^6 \text{ L}$$

3. Water with an alkalinity of 2.00×10^{-3} equivalents/liter has a pH of 7.00. Calculate $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and $[OH^-]$.

   Answer: At pH = 7.00, the alkalinity is due to the $[HCO_3^-]$ and hence $[HCO_3^-] = 2.00 \times 10^{-3}$ eq/l. The $[OH^-] = 1.00 \times 10^{-7}$ eq/l and the $[CO_2]$ can be calculated by substituting the values of $[HCO_3^-]$ and $[H^+]$ in the k_{a1} expression and then solving for $[CO_2]$. The $[CO_3^{2-}]$ can be calculated by substituting the values of $[HCO_3^-]$ and $[H^+]$ in the k_{a1} expression:

$$K_{a1} = 4.45\times10^{-7} = \frac{[1.00\times10^{-7}]\times[2.00\times10^{-3}]}{[CO_2]}$$
$$[CO_2] = 4.49\times10^{-4}$$

$$K_{a2} = 4.69\times10^{-11} = \frac{[1.00\times10^{-7}]\times[CO_3^{2-}]}{2.00\times10^{-3}}$$
$$[CO_3^{2-}] = 9.38\times10^{-7}$$

4. Through the photosynthetic activity of algae, the pH of the water in Problem 3 was changed to 10.00. Calculate all the preceding concentrations and the weight of biomass, $\{CH_2O\}$, produced. Assume no input of atmospheric CO_2.

   Answer: Since the pH has changed to 10.00, $[H^+] = 1 \times 10^{-10}$ and $[OH^-] = 1.00 \times 10^{-4}$ The alkalinity is calculated by the formula:

   $[alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] = 2.00 \times 10^{-3}$. The values of $[CO_3^{2-}]$ and $[HCO_3^-]$ are related by the formula

$$[CO_3^{2-}] = \frac{K_{a2}\times[HCO_3^-]}{[H^+]} = 0.469[HCO_3^-]$$

   Substitute this expression for $[CO_3^{2-}]$ into the alkalinity formula in which $[OH^-] = 1.00 \times 10^{-4}$ to solve for $[HCO_3^-] = 9.8 \times 10^{-4}$. The value of $[CO_3^{2-}]$ can be calculated by the K_{a2} formula giving $[CO_3^{2-}] = 4.60 \times 10^{-4}$.

   The amount of biomass produced can be calculated by finding out the difference between the amounts of total dissolved inorganic carbon at the 2 pH values as follows $[C] = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$

   At pH= 7.00, $[C] = 2.45 \times 10^{-3}$ and at pH = 10.00 $[C] = 1.44 \times 10^{-3}$. $[C]_{pH7} \times 1L - [C]_{pH10} \text{ x } 1L = 1.01 \times 10^{-3}$. Since the molar mass of biomass $\{CH_2O\}$ = 30 g/mol, this number can be converted to the amount of biomass produced by the following calculation:

$$1.01\times10^{-3}\frac{\text{mol}}{\text{L}}\times30\frac{\text{g}}{\text{mol}} = 3.03\times10^{-2}\frac{\text{g}}{\text{L}} = 30.3\frac{\text{mg}}{\text{L}}$$

5. Calcium chloride is quite soluble, whereas the solubility product of calcium fluoride, CaF_2, is only 3.9×10^{-11}. A waste stream of 1.00×10^{-3} M HCl is injected into a formation of limestone, $CaCO_3$, where it comes into equilibrium. Give the chemical reaction that occurs and calculate the hardness and alkalinity of the water at equilibrium. Do the same for a waste stream of 1.00 $\times 10^{-3}$ M HF.

*Answer***:** The reaction with HCl is:
$CaCO_3 + HCl \rightarrow Ca^{2+} + Cl^- + HCO_3^-$, the hardness = $[Ca^{2+}] = 1.00 \times 10^{-3}$ and the alkalinity = $[HCO_3^-] = 1.00 \times 10^{-3}$
In the presence of the HF the reaction becomes:
$2CaCO_3 + 2HF \rightarrow CaF_2 + 2HCO_3^- + Ca^{2+}$
Based upon the stoichiometry of this reaction $[HCO_3^-] = 1.00 \times 10^{-3}$ = alkalinity and $[Ca^{2+}]$ = 5.00×10^{-4} = hardness. A slightly higher value of $[Ca^{2+}]$ and hardness results from the dissociation of CaF_2.

6. For a solution having 1.00×10^{-3} equivalents/liter total alkalinity (contributions from HCO_3^-, CO_3^{2-}, and OH^-) at $[H^+] = 4.69 \times 10^{-11}$, what is the percentage contribution to alkalinity from CO_3^{2-}? 2.62+2.62+2.62+2.13

*Answer***:** Alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$
Since $[H^+] = 4.69 \times 10^{-11}$, $[OH^-] = 2.13 \times 10^{-4}$. Since $[H^+] = 4.69 \times 10^{-11}$, from the expression for K_{a1}, $[HCO_3^-] = [CO_3^{2-}]$. Thus
Alkalinity = $1.00 \times 10^{-3} = [HCO_3^-] + 2[HCO_3^-] + 2.13 \times 10^{-4}$
$[HCO_3^-] = 2.62 \times 10^{-4}$ and $[CO_3^{2-}] = 2.62 \times 10^{-4}$
The % contribution of the $CO_3^{2-} = (5.24 \times 10^{-4}/1.00 \times 10^{-3}) \times 100\% = 52.4\%$

7. A wastewater disposal well for carrying various wastes at different times is drilled into a formation of limestone ($CaCO_3$), and the wastewater has time to come to complete equilibrium with the calcium carbonate before leaving the formation through an underground aquifer. Of the following components in the wastewater, the one that would not cause an increase in alkalinity due either to the component itself or to its reaction with limestone, is (a) NaOH, (b) CO_2, (c) HF, (d) HCl, (e) all of the preceding would cause an increase in alkalinity.

*Answer***:** (e) All of the preceding would cause an increase in alkalinity

8. Calculate the ratio $[PbT^-]/[HT^{2-}]$ for NTA in equilibrium with $PbCO_3$ in a medium having $[HCO_3^-] = 3.00 \times 10^{-3}$ M.

Answer: The reaction is $PbCO_3(s) + HT^{2-} \leftrightarrow PbT^- + HCO_3^-$ and, designating the equilibrium constant of this reaction as K, the following applies:

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06 \times 10^{-2}}{3.00 \times 10^{-3}} = 13.5$$

9. If the medium in Problem 8 contained excess calcium such that the concentration of uncomplexed calcium, $[Ca^{2+}]$, were 5.00×10^{-3} M, what would be the ratio $[PbT^-]/[CaT^-]$ at pH 7?

Answer: The reaction is $PbCO_3(s)$ + CaT^- + HT^2 ↔ Ca^{2+} + HCO_3^- + PbT^- for which the equilibrium constant may be designated K", which has a value of 5.24, and the following applies when $[HCO_3^-] = 3.00 \times 10^{-3}$ M and $[Ca^{2+}] = 5.00 \times 10^{-3}$ M and the ratio is 0.0349:

$$\mathbf{\frac{[PbT^-]}{[CaT^-]} = \frac{[H^+]\,K''}{[Ca^{2+}][HCO_3^-]} = 0.0349}$$

10. A wastewater stream containing 1.00×10^{-3} M disodium NTA, Na_2HT, as the only solute is injected into a limestone ($CaCO_3$) formation through a waste disposal well. After going through this aquifer for some distance and reaching equilibrium, the water is sampled through a sampling well. What is the reaction between NTA species and $CaCO_3$? What is the equilibrium constant for the reaction? What are the equilibrium concentrations of CaT^-, HCO_3^-, and HT^{2-}? (The appropriate constants may be looked up in this chapter.)

    Answer: The reaction is $CaCO_3(s) + HT^{2-} \leftrightarrow CaT^- + HCO_3^-$ from which the following may be calculated:

$$K = \frac{[CaT^-]\,[HCO_3^-]}{[HT^{2-}]} = \frac{K_{sp}\times K'}{K_{a2}} = \frac{4.47\times10^{-9}\times7.75\times10^{-3}}{4.69\times10^{-11}} = 0.739$$

$$[CaT^-] = [HCO_3^-] = 1.00\times10^{-3} \text{ and } [HT^{2-}] = 1.35\times10^{-6}$$

11. If the wastewater stream in Problem 10 were 0.100 M in NTA and contained other solutes that exerted a buffering action such that the final pH were 9.00, what would be the equilibrium value of HT^{2-} concentration in moles/liter?

    Answer: At equilibrium $[CaT^-] = [HCO_3^-]$ and $[HT^{2-}] = 0.100 - [CaT^-]$

$$K = 0.739 = \frac{[CaT^-][CaT^-]}{0.100 - [CaT^-]} \text{ so } = [CaT^-] = 0.0892 \text{ and } [HT^{2-}] = 0.0108$$

12. Exactly 1.00×10^{-3} mole of $CaCl_2$, 0.100 mole of NaOH, and 0.100 mole of Na_3T were mixed and diluted to 1.00 liter. What was the concentration of Ca^{2+} in the resulting mixture?

    Answer: Under these conditions all the Ca is bound to the NTA and excess NTA is present as T^{3-} so that:

$$[CaT^-] = 1.00 \times 10^{-3} \qquad [T^{3-}] = 0.100 - [CaT^-] = 0.099$$

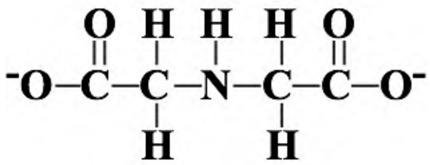
$$K_f = \frac{[CaT^-]}{[Ca^{2+}][T^{3-}]} = 1.48 \times 10^8$$

$$[Ca^{2+}] = 6.83 \times 10^{-11}$$

13. How does chelation influence corrosion?

    Answer: Chelation tends to increase corrosion by shifting redox potentials toward oxidation and by dissolving protective metal oxide coatings.

14. The following ligand has more than one site for binding to a metal ion. How many such sites does it have?



Answer: There are three binding sites, one to each of the two carboxylate groups and one to the N atom

15. If a solution containing initially 25 mg/L trisodium NTA is allowed to come to equilibrium with solid $PbCO_3$ at pH 8.50 in a medium that contains 1.76×10^{-3} M HCO_3^- at equilibrium, what is the value of the ratio of the concentration of NTA bound with lead to the concentration of unbound NTA, $[PbT^-]/[HT^{2-}]$?

Answer: The reaction is $PbCO_3(s) + HT^{2-} \leftrightarrow PbT^- + HCO_3^-$ for which K = 0.046 and from which the following may be calculated:

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06 \times 10^{-2}}{1.76 \times 10^{-3}} = 23.1$$

16. After a low concentration of NTA has equilibrated with $PbCO_3$ at pH 7.00 in a medium having $[HCO_3^-] = 7.50 \times 10^{-4}$ M, what is the ratio of $[PbT^-]/[HT^{2-}]$?

Answer: 54.1

17. What detrimental effect may dissolved chelating agents have upon conventional biological waste treatment?

Answer: The presence of chelating agents in the sewage may prevent heavy metals from being removed by the sewage sludge (biosolids)

18. Why is chelating agent usually added to artificial algal growth media?

Answer: To keep micronutrient iron in solution

19. What common complex compound of magnesium is essential to certain life processes?

Answer: Chlorophyll, which conducts photosynthesis

20. What is always the ultimate product of polyphosphate hydrolysis?

Answer: Orthophosphate, usually as $H_2PO_4^-$ or HPO_4^{2-}

21. A solution containing initially 1.00×10^{-5} M CaT^- is brought to equilibrium with solid $PbCO_3$. At equilibrium, pH = 7.00, $[Ca^{2+}] = 1.50 \times 10^{-3}$ M, and $[HCO_3^-] = 1.10 \times 10^{-3}$ M. At equilibrium, what is the fraction of total NTA in solution as PbT^-?

Answer: The reaction is $PbCO_3(s) + CaT^- + H^+ \leftrightarrow Ca^{2+} + HCO_3^- + PbT^-$ for which the equilibrium constant may be designated K", which has a value of 5.24, and the following applies at pH 7.00 when $[HCO_3^-] = 1.10 \times 10^{-3}$ M and $[Ca^{2+}] = 1.50 \times 10^{-3}$ M.:

$$\text{Fraction of NTA as } PbT^- = \frac{[PbT^-]}{[CaT^-] + [PbT^-]} = \frac{[PbT^-]/[CaT^-]}{[CaT^-]/[CaT^-] + [PbT^-]/[CaT^-]} = 0.318$$

$$= \frac{0.318}{1.000 + 0.318} = 0.241$$

22. What is the fraction of NTA present as HT^{2-} after HT^{2-} has been brought to equilibrium with

solid $PbCO_3$ at pH 7.00 in a medium in which $[HCO_3^-] = 1.25 \times 10^{-3}$ M.

Answer: The reaction is $PbCO_3(s) + HT^{2-} \longleftrightarrow PbT^- + HCO_3^-$ for which K = 0.046 and from which the following may be calculated:

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06 \times 10^{-2}}{1.25 \times 10^{-3}} = 32.5$$

$$\text{Fraction of NTA as } HT^{2-} = \frac{[HT^{2-}]}{[PbT^-] + [HT^{2-}]} = \frac{[HT^{2-}]/[HT^{2-}]}{[PbT^-]/[HT^{2-}] + [HT^{2--}]/[HT^{2-}]}$$

$$= \frac{1.00}{32.5 + 1.00} = 0.030$$

23. Describe ways in which measures taken to alleviate water supply and flooding problems might actually aggravate such problems.

Answer: Diversion of water to municipal and irrigation uses has resulted in depletion of water sources and degradation of water quality, such as by adding salinity. Construction of dikes along rivers to alleviate flooding has resulted in catastrophic flooding when these structures fail during extreme flooding events.

24. The study of water is known as ________________, ________________, ______________ is the branch of the science dealing with the characteristics of fresh water, and the science that deals with about 97% of all Earth's water is called _________________.

Answer: Hydrology, limnology, and oceanography, respectively.

25. Consider the hydrologic cycle in Figure 2.1. List or discuss the kinds or classes of environmental chemistry that might apply to each major part of this cycle.

Answer: Oceanography applies to water in the ocean, by far the largest amount in the cycle; atmospheric chemistry interacts with water in the atmosphere, such as in formation of condensation nuclei around which cloud droplets form; limnology applies to fresh water in streams and lakes; chemistry of the geosphere interacts with aquatic chemistry in groundwater; water in soil is very much involved with soil chemistry.

26. Consider the unique and important properties of water. What molecular or bonding characteristics of the water molecules are largely responsible for these properties. List or describe one of each of the following unique properties of water related to (a) thermal characteristics, (b) transmission of light, (c) surface tension, (d) solvent properties.

Answer: (a) The high heat capacity and high heats of vaporization and fusion of water are due largely to its hydrogen bonding tendencies; (b) the transmission of light is the result of the lack of chromophores that absorb visible light in the water molecule; (c) the high surface tension is largely due to the strong bonding of water molecules with each other; and (d) the solvent properties of water, such as the high solubility of ionic solutes in it, are due largely to the polar nature of the water molecule and its hydrogen bonding capability.

27. Discuss how thermal stratification of a body of water may affect its chemistry.

Answer: (a) The high heat capacity and high heats of vaporization and fusion of water are due largely to its hydrogen bonding tendencies; (b) the transmission of light is the result of the lack of chromophores that absorb visible light in the water molecule; (c) the high surface tension is largely due to the strong bonding of water molecules with each other; and (d) the solvent properties of water, such as the high solubility of ionic solutes in it, are due largely to the polar nature of the water molecule and its hydrogen bonding capability.

28. Relate aquatic life to aquatic chemistry. In so doing, consider the following: autotrophic organisms, producers, heterotrophic organisms, decomposers, eutrophication, dissolved oxygen, biochemical oxygen demand.

Answer: As several examples, photosynthetic autotrophic organisms are producers that generate biomass that provides the base of the aquatic food web; producers require adequate nutrients to generate biomass, but if the nutrients are excessive, eutrophication may result; too much biomass in water can result in excessive biochemical oxygen demand in water with depletion of dissolved oxygen.

29. Assuming levels of atmospheric CO_2 are 400 ppm CO_2, what is the pH of rainwater due to the presence of carbon dioxide? Some estimates are for atmospheric carbon dioxide levels to double in the future. What would be the pH of rainwater if this happens?

Answer: As noted in Section 3.7, the value of [CO_2(*aq*)] in water at 25°C in equilibrium with air that is 400 ppm CO_2 is 1.309×10^{-5} M. In pure rainwater, the carbon dioxide dissociates partially in water to produce equal concentrations of H^+ and HCO_3^- and from the K_{a1} expression for CO_2, [H^+] = 2.41×10^{-6} and pH = 5.61. Doubling atmospheric CO_2 levels would double the concentration of CO_2 in rainwater to 2.618×10^{-5} M and, as shown in Section 2.7, this gives [H^+] = 3.41×10^{-6} and pH = 5.47.

30. Assume a sewage treatment plant processing 1 million liters of wastewater per day containing 200 mg/L of degradable biomass, {CH_2O}. Calculate the volume of dry air at 25°C that must be pumped into the wastewater per day to provide the oxygen required to degrade the biomass (Reaction 2.6.1).

Answer: The reaction is {CH_2O} + $O_2 \rightarrow CO_2 + H_2O$. The amount of biomass present in the 1 million liters of water is 2.00×10^8 mg = 2.00×10^5 g. The moles of O_2 required to react with this biomass are

$$2.00 \times 10^5 \text{ g } \{CH_2O\} \times \frac{1 \text{ mol } \{CH_2O\}}{30 \text{ g } \{CH_2O\}} \times \frac{1 \text{ mol } O_2}{1 \text{ mol } \{CH_2O\}} = 6.67 \times 10^3 \text{ mol } O_2$$

Since only 20.95% of dry air is O_2, the moles of air needed to supply this O_2 = 3.18×10^4 mole. The volume of this amount of air at 25°C and 1 atm pressure can be calculated by the ideal gas law, PV = nRT, where R = 0.0821 L atm mol^{-1} giving 7.78×10^5 L of air. Only a fraction of the oxygen in the air is actually transferred into the sewage, so significantly more air would need to be pumped to supply the oxygen required.

31. Anoxic bacteria growing in a lake sediment produced equal molar amounts of carbon dioxide and carbon monoxide according to the biochemical reaction 2{CH_2O} → CO_2 + CH_4, so that the water in the lake was saturated with both CO_2 gas and CH_4 gas. In units of mol × L^{-1} × atm^{-1} the Henry's law constant for CO_2 is 3.38×10^{-2} and that of CH_4 has a value of 1.34×10^{-3}. At the depth at which the gas was being evolved, the total pressure was 1.10 atm and the temperature was 25°C, so the vapor pressure of water was 0.0313 atm. Calculate the concentrations of dissolved CO_2 and dissolved CH_4.

Answer: Since equimolar amounts of CO_2 and CH_4 are evolved, the mole fraction of each gas = 0.500. The partial pressure of each gas = 0.500 × 1.10 = 0.550 atm. The corrected pressure of each gas = 0.550 - 0.0313 = 0.519. Using Henry's law, [CO_2] = 0.519 atm × 3.38×10^{-2} mol

$\times$ L^{-1} $\times$ atm^{-1} = 1.75 $\times$ 10^{-2} M and [CH_4] = 6.95 $\times$ 10^{-4} M.