CHEM 20204

Solutions 8

1. The pE equation given in the text for this equilibrium is

\[ \text{pE} = 14.15 - \frac{5}{4} \text{pH} - \frac{1}{8} \log \left( \frac{[NH_4^+]}{[NO_3^-]} \right) \]

(a) Substituting \( \text{pE} = 11 \) and \( \text{pH} = 6 \), then

\[ 11 = 14.15 - \frac{5}{4} \times 6 - \frac{1}{8} \log \left( \frac{[NH_4^+]}{[NO_3^-]} \right) \]

so \( \log \left( \frac{[NH_4^+]}{[NO_3^-]} \right) = -8 \times 4.35 = -34.8 \) and

\( \frac{[NH_4^+]}{[NO_3^-]} = 1.66 \times 10^{-35} \)

(b) Substituting \( \text{pE} = -3 \) and \( \text{pH} = 6 \), then

\[ -3 = 14.15 - \frac{5}{4} \times 6 - \frac{1}{8} \log \left( \frac{[NH_4^+]}{[NO_3^-]} \right) \]

so \( \log \left( \frac{[NH_4^+]}{[NO_3^-]} \right) = -8 \times -3.655 = 29.2 \) and

\( \frac{[NH_4^+]}{[NO_3^-]} = 1.66 \times 10^{77} \)

2. From the text, for the concentration of ions

\[ \text{pE} = 13.2 + \log \left( \frac{[Fe^{3+}]}{[Fe^{2+}]} \right) \]

When the ion concentration ratio is 100:1, then

\[ \text{pE} = 13.2 + \log (100) = 15.2 \]

3. When \( \text{CaSO}_4 \) dissolves in water, the process is \( \text{CaSO}_4 \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} \)

hence

\[ K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] \]

If no reaction of sulfate with water occurs, then \( [\text{Ca}^{2+}] = [\text{SO}_4^{2-}] \) so \( [\text{SO}_4^{2-}]^2 = 3.0 \times 10^{-5} \), because this is the value of \( K_{sp} \).

Consequently, \( [\text{SO}_4^{2-}] = 5.5 \times 10^{-3} \)

Thus the solubility of \( \text{Ca}_2\text{SO}_4 \) is \( 5.5 \times 10^{-3} \) moles/L if no reaction with water occurs; because the molar mass of \( \text{CaSO}_4 \) is 136.14, the solubility corresponds to 0.75 grams per liter

4. Since the hardness index is based upon molar concentration, we convert
the masses of the ions first into molar amounts

\[
0.0040 \, \text{g Ca} \times \frac{1 \, \text{mole Ca}}{40.1 \, \text{g Ca}} = 0.00010 \, \text{moles Ca}
\]

\[
0.0012 \, \text{g Mg} \times \frac{1 \, \text{mole Mg}}{24.3 \, \text{g Mg}} = 0.000049 \, \text{moles Mg}
\]

Thus since the volume is 0.5 L, the ion concentrations are

\[
[\text{Ca}^{2+}] = \frac{0.001}{0.5} = 0.002 \, \text{M}, \quad \text{and} \quad [\text{Mg}^{2+}] = \frac{0.000049}{0.5} = 0.00010 \, \text{M}.
\]

So Hardness = 0.00020 + 0.00010 = 0.00030 M = [CaCO₃ equivalent]

Thus Hardness = 0.00030 moles/L * 100.1 g/mole = 0.030 g CaCO₃/L = 30 mg CaCO₃/L

5. The relevant equilibrium here is

\[
\text{Al(OH)}_3(s) \leftrightarrow \text{Al}^{3+} + 3\text{OH}^-
\]

For which

\[
[\text{Al}^{3+}] \times [\text{OH}^-] = K_{sp} = 1.0 \times 10^{-33}
\]

For \( [\text{Al}^{3+}] = 0.020 \), then

\[
[\text{OH}^-]^3 = \frac{1.0 \times 10^{-33}}{0.020}
\]

So \( [\text{OH}^-] = 3.7 \times 10^{-11} \)

i.e., \( \text{pOH} = 10.4 \), so \( \text{pH} = 3.6 \)


7. See section 10.11/13.11 (5th ed, 4th ed)
8.

a. 

\[ \text{Cu}^{2+} + e^- \rightleftharpoons \text{Cu}^+ \quad E_o = 0.16 \text{V} \]

\[ pE_o = \frac{E_o}{0.0591} \]

\[ = \frac{(0.16)}{(0.0591)} \]

\[ = 2.71 \]

\[ pE = pE_o + \log \left( \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]} \right) \]

\[ pE = 2.71 + \log \left( \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]} \right) \]

For \( pE = -4 \)

\[ -4 = 2.71 + \log \left( \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]} \right) \]

\[ -6.71 = \log \left( \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]} \right) \]

\[ \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]} = 195 \times 10^{-7} \]

For \( pE = 14 \) use the same method as above to obtain

\[ \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]} = 195 \times 10^{11} \]

b. Under anaerobic conditions (oxygen-depleted conditions) the \( pE \) values will be low or negative and the medium will be reducing in nature. Under these conditions copper(I) will be favored over copper(II). This is exactly what is observed in the calculation in Part (a).
9.

a. Assume all dissolved CO$_2$ is H$_2$CO$_3$ in water.

365 ppm = $3.65 \times 10^{-4}$ atm

At 25°C

\[ [\text{CO}_2] = [\text{H}_2\text{CO}_3] = K_H \times P(\text{CO}_2) \]

\[ = (3.4 \times 10^{-2} \text{ M atm}^{-1})(3.65 \times 10^{-4} \text{ atm}) \]

\[ = 1.24 \times 10^{-5} \text{ M} \]

\[ K_a = 4.5 \times 10^{-7} - \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} - \frac{[\text{H}^+]^2}{[\text{H}_2\text{CO}_3]} \]

\[ [\text{H}^+] = \left[(4.5 \times 10^{-7})(1.24 \times 10^{-5} \text{ M})\right]^{1/2} \]

\[ = 2.36 \times 10^{-6} \text{ M} \]

pH = 5.6

b. At 5°C

\[ [\text{CO}_2] = [\text{H}_2\text{CO}_3] = K_H \times P(\text{CO}_2) \]

\[ = (6.5 \times 10^{-2} \text{ M atm}^{-1})(0.01 \text{ atm}) \]

\[ = 6.5 \times 10^{-4} \text{ M} \]

\[ K_a = 3.0 \times 10^{-7} - \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} - \frac{[\text{H}^+]^2}{[\text{H}_2\text{CO}_3]} \]

\[ [\text{H}^+] = \left[(3.0 \times 10^{-7})(6.5 \times 10^{-4} \text{ M})\right]^{1/2} \]

\[ = 1.40 \times 10^{-5} \text{ M} \]

pH = 4.9

c. The ground water has more carbonic acid in it than the equilibrium will allow at the surface (less CO$_2$ pressure and warmer temperature). The excess carbonic acid will convert to water and carbon dioxide. The escaping carbon dioxide gives the water its sparkle or fizz.
Problem 9-12

a. \(0.72 \text{ ppb} = 0.72 \text{ µg L}^{-1} = 7.2 \times 10^{-7} \text{ g L}^{-1}\)

\[\text{Molarity} = \frac{(7.2 \times 10^{-7} \text{ g L}^{-1})}{(2698 \text{ g mol}^{-1})}\]

\[= 2.67 \times 10^{-8} \text{ mol L}^{-1}\]

\[[\text{Al}^3][\text{OH}^-]_1 = 10^{-33}\]

\[\left[\text{OH}^-\right] = \frac{(10^{-32})}{(2.67 \times 10^{-8} \text{ M})}\]

\[= 3.35 \times 10^{-9} \text{ M}\]

\[\text{pOH} = 8.47\]

\[\text{pH} = 14 - \text{pOH}\]

\[= 14 - 8.47\]

\[= 5.53\]

b. A gelatinous precipitate of Al(OH)$_3$ can form on the fishes' gills, which would lead to suffocation.

c. No. From Part (a) a pH greater than 5.53 at an aluminum concentration of 0.72 ppb would form Al(OH)$_3$. The fishes' gills are at pH 7.3 which is greater than 6.52.