Conference Problems: Week of April 7th

1. A 0.100 M Tris buffer is prepared at pH 7.5.

a. Given that $HTris^+$ is a weak acid with a pK_a of 8.1, what is the ratio of Tris to $HTris^+$ in the buffer?

b. What are the absolute concentrations of $HTris^+$ and Tris?

2. Let's say you had 1.00 L of a solution of 0.100 M acetic acid (pK_a = 4.7). How many grams of NaOH would you need to create a buffer of pH 4.1?

3. Consider the following polyprotic acids and their corresponding pK_a values. What are the predominant protonation states of each at pH 1, 5 and 9? It may assist you to draw "pH lines" as demonstrated in lecture.

a. Oxalic acid: H_2Ox (pK_{a1} = 1.2, pK_{a2} = 4.2)

b. Phosphoric acid: H_3PO_4 (pK_{a1} 2.1, pK_{a2} = 7.2, pK_{a3} = 12.7)

3. Given the following K_{sp} values, calculate the concentration of silver when each of the following salts reaches equilibrium.

a. AgI: $K_{sp} = 1.5 \times 10^{-16}\ M^2$

b. Ag_2CrO_4 (salt of Ag^+ and CrO_4^{2-}): $K_{sp} = 9.0 \times 10^{-12}\ M^3$

4. The K_{sp} of $Pb(OH)_2$ is 2.8×10^{-16}.

a. Assuming no buffering, what will the concentration of hydroxide be in a saturated lead(II) hydroxide solution? What pH is that?

b. Calculate the equilibrium concentrations of Pb^{2+} in solutions buffered at pH=6 and pH=10.

6. Lead carbonate ($PbCO_3$) is a weak electrolyte with a K_{sp} of 1.5×10^{-13}.

a. What is the solubility of lead if $PbCO_3$ comes to equilibrium with water (assuming carbonate does not react with hydrogen ions).

b. In reality, carbonate is a moderate base with a pK_b of 4 and its conjugate acid (HCO_3^-) is also a base, with a pK_b of 7.6. In qualitative terms, what will happen to the solubility of lead carbonate, as pH decreases. Explain.

Solutions

1. A 0.100 M Tris buffer is prepared at pH 7.5.

a. Given that $HTris^+$ is a weak acid with a pK_a of 8.1, what is the ratio of Tris to $HTris^+$ in the buffer?

$7.5 = 8.1 + \log_{10}([Tris]/[HTris^+])$; $([Tris]/[HTris^+]) = 10^{7.5-8.1} = 0.25$

b. What are the absolute concentrations of $HTris^+$ and Tris?

$[Tris] + [HTris^+] = 0.100$ M, and $[Tris] = 0.25*[HTris^+]$
$1.25[HTris^+] = 0.100$ M
$[HTris^+] = 0.080$ M, $[Tris] = 0.020$ M

2. Let's say you had 1.00 L of a solution of 0.100 M acetic acid (pK_a). How many grams of NaOH would you need to create a buffer of pH 4.1?

$pH = pK_a + \log_{10}([A^-]/[HA])$
$4.1 = 4.7 + \log_{10}([A^-]/[HA])$
$([A^-]/[HA]) = 10^{-0.6} = 0.25 \rightarrow [A^-] = 0.2[HA]$
$[A^-] + [HA] = 0.10$ M
$1.25[HA] = 0.100$ M, $[HA] = 0.80$ M & $[A^-] = 0.20$ M
so you need to add 0.20 mol of NaOH.

3 a. Oxalic acid: H_2Ox ($pK_{a1} = 1.2$, $pK_{a2} = 4.2$)

pH 1: H_2Ox, pH 5: Ox^{2-}, pH 9: Ox^{2-}

b. Phosphoric acid: H_3PO_4 (pK_{a1} 2.1, $pK_{a2} = 7.2$, $pK_{a3} = 12.7$)

pH 1: H_3PO_4, pH 5: $H_2PO_4^-$, pH 9: HPO_4^{2-}

4. Given the following K_{sp} values, calculate the solubility of each of the following salts in moles per liter. Too lazy to put in reaction tables, but if you do them, this is what you'd get.

a. AgI: $K_{sp} = 1.5 \times 10^{-16}$ M^2

$x^2 = 1.5 \times 10^{-16}$, $[Ag^+] = [\text{"AgI"}] = 1.2 \times 10^{-8}$ M

b. Ag_2CrO_4 (salt of Ag^+ and CrO_4^{2-}): $K_{sp} = 9.0 \times 10^{-12}$ M^3

$[Ag^+]^2[CrO_4^{2-}] = (2x)^2x = 4x^3 = 9.0 \times 10^{-12}$ M^3
$x = 1.3 \times 10^{-4}$ M
$[Ag^+] = 2x = 2.6 \times 10^{-4}$ M

5. The K_{sp} of $Pb(OH)_2$ is 2.8×10^{-16}.

a. Assuming no buffering, what will the pH of a saturated lead(II) hydroxide solution be?

$K_{sp} = [Pb^{2+}][OH^-]^2 = 2.8 \times 10^{-16}$
$(s)(2s)^2 = 4s^3 = 2.8 \times 10^{-16}$
$s = 4.1 \times 10^{-6}$
$[OH^-] = 8.2 \times 10^{-6}$ M, pOH = 5.0 → pH = 9

b. Calculate the equilibrium $[Pb^{2+}]$ in solutions buffered at pH=3 and pH=8.

$K_{sp} = [Pb^{2+}][OH^-]^2$
$[Pb^{2+}] = K_{sp}/[OH]^2$
@ pH = 10, $[OH^-] = 1 \times 10^{-4}$ M, $[Pb^{2+}] = 2.8 \times 10^{-8}$ M
@ pH = 6, $[OH^-] = 1 \times 10^{-8}$ M, $[Pb^{2+}] = 2.8$ M

6. Lead carbonate ($PbCO_3$) is a weak electrolyte with a K_{sp} of 1.5×10^{-13}.

a. What is the solubility of lead if $PbCO_3$ comes to equilibrium with water (assuming carbonate does not react with hydrogen ions).

$[Pb^{2+}][CO_3^{2-}] = x^2 = 1.5 \times 10^{-13}$
$[Pb^{2+}] = x = 3.9 \times 10^{-7}$ M

b. In reality, carbonate is a moderate base with a pK_b of 4 and its conjugate acid (HCO_3^-) is also a base, with a pK_b of 7.6. In qualitative terms, what will happen to the solubility of lead carbonate, as pH decreases. Explain.

As pH goes down, more and more carbonate will become protonated. As a result, there will be a decrease in the concentration of one of the product ions, so the reaction will shift to produce more products, increasing the conc. of lead ions.