Salt Hydrolysis Problems

1) Write the Brønsted-Lowry reaction between the base CN^- and the weak acid H_2O.

$CN^- + H_2O \rightleftharpoons HCN + OH^-$

2) Write the Brønsted-Lowry reaction between the acid NH_4^+ and the weak base H_2O.

$NH_3^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

3) Write the equilibrium expression for reaction 1 using a K_b.

$$K_b = \frac{[HCN]\,[OH^-]}{[CN^-]}$$

4) Write the equilibrium expression for reaction 2 using a K_a.

$$K_a = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]}$$

In theory, you are able to work with these equilibria in a fashion similar to what you did in the previous exercise. However, if you attempt to look up the K_b and K_a which you need, you are not likely to find them. This is because the K_a for HCN and the K_b for NH_3 are listed and you can derive the respective K_b and K_a from them. This is because the product **$K_aK_b = K_w = 1.0 \times 10^{-14}$**. Notice that this is true for the conjugate acid-base pair. For example:

$K_b\,(CN^-) = K_w/K_a(HCN)$

$K_b\,(CN^-) = 1.0 \times 10^{-14}/\ 4.2 \times 10^{-10}$

$K_b\,(CN^-) = 2.4 \times 10^{-5}$

Also:

$K_a\,(NH_4^+) = K_w/K_a(NH_3)$

$K_a\,(NH_4^+) = 1.0 \times 10^{-14}/\ 1.8 \times 10^{-5}$

$K_a\,(NH_4^+) = 5.6 \times 10^{-10}$

If you need to use these expressions, the problem is referred to as a salt hydrolysis.

5) Calculate the pH of a solution which is 0.010 M in NaOCN. The K_a of HOCN is 3.5×10^{-4}.

$$K_b = \frac{K_w}{K_a} = \frac{[HOCN][OH^-]}{[OCN^-]}$$

$$\frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.9 \times 10^{-11} = \frac{X^2}{0.010}$$

$X = 5.3 \times 10^{-7}$ pOH = 6.27

Ans: pH = **7.73**

6) Calculate the pH of a solution which is 0.10 M in NH_4Cl. The K_b for NH_3 is 1.8×10^{-5}.

$$K_a = \frac{K_w}{K_b} = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{X^2}{0.10}$$

$X = 7.5 \times 10^{-6}$ pH = 5.13

Ans: pH = **5.13**

7) Calculate the pH of a solution which is 0.10 M in HOCN and 0.30 M in NaOCN. The K_a of HOCN is 3.5×10^{-4}. (Careful)

Why? This is a buffer.

$$K_a = \frac{[OCN^-][H_3O^+]}{[HOCN]}$$

$$3.5 \times 10^{-4} = \frac{(0.30)\,X}{0.10}$$

$X = 1.17 \times 10^{-4}$ pH = 3.93

Ans: pH = **3.93**

8) If 100.0 mL of a solution is originally 0.10 M CH_3COOH and one adds exactly enough solid NaOH to neutralize this solution, what would be the resultant pH of the solution? The K_a for CH_3COOH is 1.8×10^{-5}. (What are you really starting with?)

Titration - yields pure salt

$$K_b = \frac{K_w}{K_a} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{X^2}{0.10}$$

$X = 7.5 \times 10^{-6}$ pOH = 5.13

Ans: pH = **8.87**

9) If 100.0 mL of a solution is originally 0.1000 M CH_3COOH and one adds 100.0 mL of 0.1000 M NaOH to this solution, what is the final concentration of the $NaCH_3COO$?

Again Arrhenius: $CH_3COOOH + NaOH \rightarrow NaCH_3COO + H_2O$

but note the dilution in resultant salt: $[CH_3COO^-] = 0.05000$ M

Ans: **0.05000** M

10) What is the pH for the resultant solution described in problem 9.

$$K_b = \frac{K_w}{K_a} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{X^2}{0.05000}$$

$X^2 = 2.78 \times 10^{-11}$

$X = 5.27 \times 10^{-6}$

pOH = 5.28

Ans: pH = **8.72**

11) What is the pH of a solution formed by mixing 200.0 mL of 0.20 M NH_3 with 50.0 mL of water? K_b for $NH_3 = 1.8 \times 10^{-5}$.

Note the dilution to 0.16 M NH_3

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-10} = \frac{X^2}{0.16}$$

$X = 1.7 \times 10^{-3}$ pOH = 2.77

Ans: pH = **11.23**

12) What is the pH of a solution formed by mixing 200.0 mL of 0.2000 M NH_3 with 50.00 mL of 0.8000 M NH_4Cl?

$[NH_3] = 0.16$ and $[NH_4^+] = 0.16$ a buffer.

pOH = 4.74

Ans: pH = **9.26**

13) What is the pH of a solution formed by mixing 200.0 mL of 0.2000 M NH_3 with 50.00 mL of 0.8000 M HCl?

Note to 4 sig. figs. this is neutralized ∴ is an Arrhenius salt and $[NH_4^+] = 0.16$ M

hydrolysis problem similar to 6

Ans: pH = **5.13**

14) What is the pH of a solution formed by mixing 200.0 mL of 0.2000 M NH_3 with 50.00 mL of 0.8000 M HCl and 50.00 mL of 0.8000 M NH_4Cl?

Note dilutions and addition of $[NH_4^+]$s = 0.133 + 0.133

$[NH_4^+] = 0.266$ M

hydrolysis problem similar to 6

Ans: pH = **4.91**

Solubility and Dissociation Equilibria Problems

1. Calculate the calcium ion concentration for a solution in contact with CaF_2 if the fluoride concentration is 0.010 M and the K_{sp} for CaF_2 is 3.0×10^{-11}.

   $K_{sp} = [Ca^{2+}][F^-]^2$
   $3.0 \times 10^{-11} = [Ca^{2+}](0.010)^2$

   Ans: 3.0×10^{-7} ____________________

2. To a 0.1 M solution of $Ca(NO_3)_2$ is added enough Na_2CO_3 to make the solution 0.10 M in CO_3^{2-} ion. If the K_{sp} for $CaCO_3$ is 4.8×10^{-9} , what is the Ca^{2+} concentration?

   $K_{sp} = [Ca^{2+}][CO_3^{2-}]$

   $4.8 \times 10^{-9} = [Ca^{2+}](0.10)$

   Ans: 4.8×10^{-8} ____________________

3. The K_a for the hydrogen carbonate ion (which is an acid) is 4.8×10^{-11}. Calculate the pH at which the Ca^+ in the above question will redissolve. (Hint: first calculate what the maximum CO_3^{2-} concentration must be for a 0.10 M Ca^{2+} solution.)

   $K_{sp} = [Ca^{2+}][CO_3^{2-}]$

   $4.8 \times 10^{-9} = (0.10)[CO_3^{2-}]$ $[CO_3^{2-}] = 4.8 \times 10^{-8}$

   $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ $K_a =$
$[CO_3^{2-}][H_3O^+]/[HCO_3^-]$

   $4.8 \times 10^{-11} = (4.8 \times 10^{-8})[H_3O^+]/(0.10)$ $[H_3O^+] = 0.00010$

   Ans: 4.00 ____________________

4. The K_d for $CdCl_4^{2-}$ is 1.0×10^{-4}. What is the concentration of Cd^{2+} in a solution of chloride which has 0.010 M of the $CdCl_4^{2-}$ ion present. The Cl^- concentration in this solution was measured and found to be 0.10 M.

   $CdCl_4^{2-} \rightleftharpoons Cd^{2+} + 4Cl^-$

   $K_d = [Cd^{2+}][Cl^-]^4/[CdCl_4^{2-}]$

   $1.0 \times 10^{-4} = [Cd^{2+}](0.10)^4/(0.010)$

   Ans: ____________________

5. A solution is 0.010 M in total silver and 0.010 M in NH_3. What is the Ag^+ ion concentration? The K_d for $Ag(NH_3)_2^+$ is 6.3×10^{-8}.

$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$ $$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

$[Ag(NH_3)_2^+] = 0.010 - x$ and $[Ag^+] = x$ (Or the other way around)

$$6.3\times10^{-8} = \frac{x(0.010)^2}{0.010 - x}$$ $X = 6.3 \times 10^{-10}$

Ans: 6.3×10^{-10}

6. Calculate the minimum pH for which there will be no AgCl precipitate present for a solution that is 0.010 M in each of the following: Cl^-, $Ag(NH_3)_2^+$ and NH_4^+. The K_{sp} for AgCl is 1.8×10^{-10}. The K_d for $Ag(NH_3)_2^+$ is 6.3×10^{-8}. The K_b for NH_3 is 1.8×10^{-5}. (Write all three equilibria first, and then solve algebraically for $[OH^-]$.)

$+1 \times [\, AgCl \rightleftharpoons Ag^+ + Cl^- \,]$ $\times K_{sp} = 1.8 \times 10^{-10}$
$-1 \times [\, Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3 \,]$ $\div K_d = 6.3 \times 10^{-8}$
$-2 \times [\, NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \,]$ $\div [\, K_b = 1.8 \times 10^{-5} \,]^2$

$AgCl + 2\,NH_4^+ + 2\,OH^- \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$ $$\therefore K = \frac{K_{sp}}{K_d K_b^2}$$

$$K = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_4^+]^2[OH^-]^2}$$ But $$K = \frac{1.8\times10^{-10}}{\left(6.3\times10^{-8}\right)\left(1.8\times10^{-5}\right)^2}$$

Thus: $$8.8\times10^{6} = \frac{(0.010)(0.010)}{(0.010)^2[OH^-]^2}$$ $\therefore [OH]^- = 3.6 \times 10^{-4}$

and pOH = 3.47 so pH = 10.53

Ans: 10.53

7. Over what pH range is Zinc in the +2 oxidation state not soluble if the total zinc concentration in solution is 0.10 M? the K_{sp} for $Zn(OH)_2$ is 4.5×10^{-17} and the K_d for $Zn(OH)_4^{2-}$ is 3.5×10^{-16}.

$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^-$ $K_{sp} = [Zn^{2+}][OH^-]^2$ $4.5 \times 10^{-17} = (0.10)[OH^-]^2$ $[OH^-] = 2.1 \times 10^{-8}$ pOH = 7.67 pH = 6.33	$Zn(OH)_2 + 2OH^- \rightleftharpoons Zn(OH)_4^{2-}$ $K = K_{sp} / K_d$ $\therefore K = 4.5 \times 10^{-17} / 3.5 \times 10^{-16}$ $K = \frac{[Zn(OH)_4^{2-}]}{[OH^-]^2}$ $0.129 = 0.10/[OH^-]^2$ $[OH^-] = 0.88$ pOH =0.05 So: pH = 13.95

Ans: 6.33 - 13.95