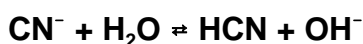
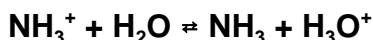


Salt Hydrolysis Problems

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



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



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

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

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

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

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 $K_a K_b = K_w = 1.0 \times 10^{-14}$. Notice that this is true for the conjugate acid-base pair. For example:

$$K_b(\text{CN}^-) = K_w / K_a(\text{HCN})$$

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

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

Also:

$$K_a(\text{NH}_4^+) = K_w / K_b(\text{NH}_3)$$

$$K_a(\text{NH}_4^+) = 1.0 \times 10^{-14} / 1.8 \times 10^{-5}$$

$$K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}$$

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} .

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

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

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

$$\text{Ans: pH} = \underline{\mathbf{7.73}}$$

- 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} .

$$K_a = \frac{K_w}{K_b} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

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

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

$$\text{Ans: pH} = \underline{\mathbf{5.13}}$$

- 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.

$$K_a = \frac{[\text{OCN}^-][\text{H}_3\text{O}^+]}{[\text{HOCN}]}$$

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

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

$$\text{Ans: pH} = \underline{\mathbf{3.93}}$$

- 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

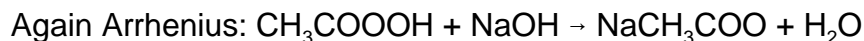
$$K_b = \frac{K_w}{K_a} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

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

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

$$\text{Ans: pH} = \underline{\underline{8.87}}$$

- 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 ?



but note the dilution in resultant salt: $[\text{CH}_3\text{COO}^-] = 0.05000 \text{ M}$

$$\text{Ans: } \underline{\underline{0.05000}} \text{ M}$$

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

$$K_b = \frac{K_w}{K_a} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

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

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

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

$$\text{pOH} = 5.28$$

$$\text{Ans: pH} = \underline{\underline{8.72}}$$

- 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 $\text{NH}_3 = 1.8 \times 10^{-5}$.

Note the dilution to 0.16 M NH_3

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{X^2}{0.16}$$

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

$$\text{Ans: pH} = \underline{\mathbf{11.23}}$$

- 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 ?

$[\text{NH}_3] = 0.16$ and $[\text{NH}_4^+] = 0.16$ a buffer.

$$\text{pOH} = 4.74$$

$$\text{Ans: pH} = \underline{\mathbf{9.26}}$$

- 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 \therefore is an Arrhenius salt and $[\text{NH}_4^+] = 0.16$ M

hydrolysis problem similar to 6

$$\text{Ans: pH} = \underline{\mathbf{5.13}}$$

- 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 $[\text{NH}_4^+]_s = 0.133 + 0.133$

$$[\text{NH}_4^+] = 0.266$$
 M

hydrolysis problem similar to 6

$$\text{Ans: pH} = \underline{\mathbf{4.91}}$$

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} .

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2$$

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

Ans: 3.0×10^{-7}

2. To a 0.1 M solution of $\text{Ca}(\text{NO}_3)_2$ 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?

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

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

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^{2+} 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.)

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

$$4.8 \times 10^{-9} = (0.10)[\text{CO}_3^{2-}] \quad [\text{CO}_3^{2-}] = 4.8 \times 10^{-8}$$

$$\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \quad K_a =$$

$$\frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]}$$

$$4.8 \times 10^{-11} = (4.8 \times 10^{-8})[\text{H}_3\text{O}^+]/(0.10) \quad [\text{H}_3\text{O}^+] = 0.00010$$

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 .

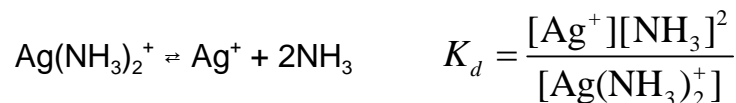
$$\text{CdCl}_4^{2-} \rightleftharpoons \text{Cd}^{2+} + 4\text{Cl}^-$$

$$K_d = \frac{[\text{Cd}^{2+}][\text{Cl}^-]^4}{[\text{CdCl}_4^{2-}]}$$

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

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 $\text{Ag}(\text{NH}_3)_2^+$ is 6.3×10^{-8} .

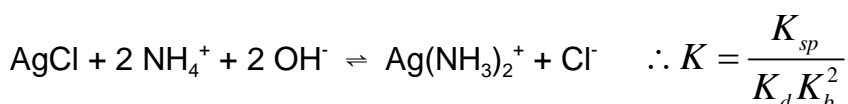
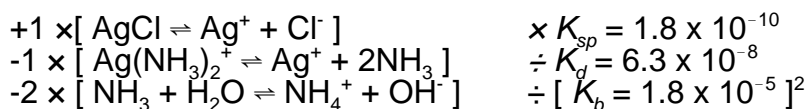


$$[\text{Ag}(\text{NH}_3)_2^+] = 0.010 - x \text{ and } [\text{Ag}^+] = x \quad (\text{Or the other way around})$$

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

$$\text{Ans: } \underline{6.3 \times 10^{-10}}$$

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^- , $\text{Ag}(\text{NH}_3)_2^+$ and NH_4^+ . The K_{sp} for AgCl is 1.8×10^{-10} . The K_d for $\text{Ag}(\text{NH}_3)_2^+$ 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 $[\text{OH}^-]$.)



$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_4^+]^2[\text{OH}^-]^2} \quad \text{But } K = \frac{1.8 \times 10^{-10}}{(6.3 \times 10^{-8})(1.8 \times 10^{-5})^2}$$

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

$$\text{and } \text{pOH} = 3.47 \quad \text{so } \text{pH} = 10.53$$

$$\text{Ans: } \underline{10.53}$$

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 $\text{Zn}(\text{OH})_2$ is 4.5×10^{-17} and the K_d for $\text{Zn}(\text{OH})_4^{2-}$ is 3.5×10^{-16} .

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