Name _____**Chem 163 Section**: _____ **Team Number:** _____

ALE 13. Hydrolysis of Salts + Lewis Acids & Bases

(Reference: 18.6 – 18.7 Silb*erberg 5th edition*)

When a salt is dissolved in water will the solution be acidic, basic or neutral?

The Model: Hydrolysis of a Basic Salt—blame it on the anion!

Recall from Chem 161: Salts are ionic compounds and like all ionic compounds, salts are strong electrolytes—i.e. they dissociate 100% in solution to produce free aqueous ions. Consider the dissolving of sodium acetate in water. Because all sodium salts are soluble, if we take sodium acetate crystals and dissolve them in water, the sodium ions and acetate ions dissociate in solution:

$$\mathbf{NaC_2H_3O_2}(s) \xrightarrow{H_2O} \mathbf{Na^+}(aq) + \mathbf{C_2H_3O_2^-}(aq) \qquad \textbf{(1)}$$

When a salt is dissolved in water, the ions making up *some* salts hydrolyze. **Hydrolysis** is simply the reaction of a substance, in this case an ion or ions, with water. If we were to measure the acidity of the aqueous solution of sodium acetate, we would notice that its pH would be greater than 7. Even though acetate doesn't have a hydroxide ion to donate, it still acts as a base in water since acetate ions react with water to produce hydroxide ions, thereby undergoing **basic hydrolysis**:

$$\mathbf{C_2H_3O_2^-}(aq) + \mathbf{HOH}\ (aq) \rightleftharpoons \mathbf{HC_2H_3O_2}(aq) + \mathbf{OH^-} \qquad \textbf{(2)}$$

Key Questions

1. a. What is the name and formula of the conjugate acid of the acetate ion?

   Name _____ Formula _____

   b. Is this a weak acid or strong acid? (Circle your answer.)

   c. Is the acetate ion a stronger base or a weaker base than water? (Circle your answer.) How does this help explain why sodium acetate is a basic salt?

2 a. While acetate salts (such as sodium acetate) tend to be basic salts, nitrate salts (e.g. sodium nitrate, $NaNO_3$) are neutral salts—i.e. they form neutral solutions. Why doesn't the nitrate undergo basic hydrolysis to generate hydroxide ions? *Hint*: What does Question 1c cite as the reason why the acetate ion does basic hydrolysis?

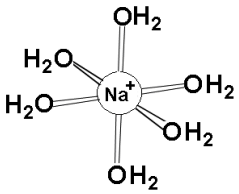
b. What other anions would you *not* expect to hydrolyze in water to generate hydroxide? (The more complete the list, the better. *Hint*: Do you remember your list of strong acids?)

c. Make a list of several weak acids. (The more complete the list, the better.)

d. What anions that you would expect to hydrolyze in water to form to form a basic solution. *Hint*: refer to your list in part c, above.

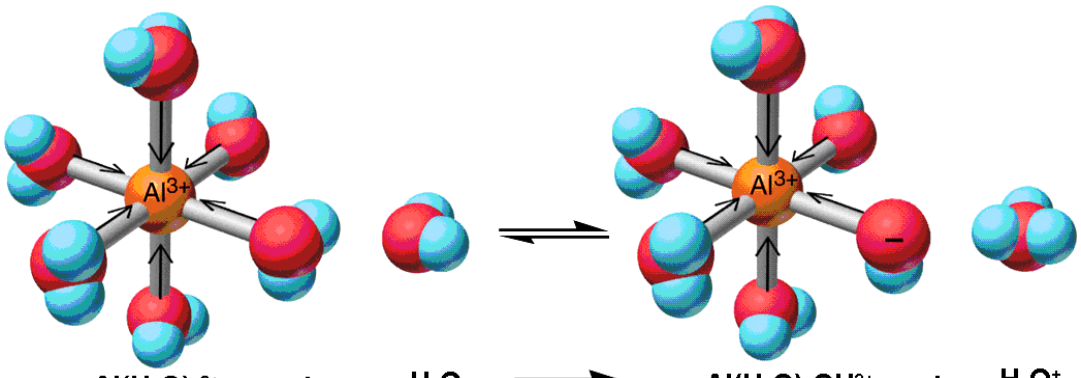
The Model: Hydrolysis of an Acidic Salt—it's the Cation's fault!

When ionic compounds dissolve in water they dissociate 100% into ions. These ions become solvated by water molecules forming "**spheres of hydration**" around each ion—recall from Chem 162 that the water molecules form **ion-dipole bonds** with the ions. If the ion is a metal, the polar water molecules use the lone pairs on the oxygen of the water to coordinate to the positive metal ion. The ions are then enclosed by a 'cage' of water molecules usually in an **octahedral** arrangement as depicted by the hydrated sodium ion in the diagram to the right.



$Na(H_2O)_6^+$

Like sodium ions, aqueous aluminum ions are surrounded by six water molecules in an octahedral arrangement. This is called the **aluminum hexahydrate ion**. The **high charge density** of the aluminum ion **polarizes the water molecules**.



$Al(H_2O)_6^{3+}$ + H_2O ⇌ $Al(H_2O)_5OH^{2+}$ + H_3O^+

Key Questions

3. The arrows in the model that point from the water molecules towards the aluminum ion, Al^{3+}, represent the aluminum ion withdrawing electrons from the oxygen—hydrogen bonds of the attached water molecules. What effect does this electron withdrawal have on the polarity and strength of the oxygen—hydrogen bonds within each water molecule attached to Al^{3+}? How does this account for the acidity of aqueous solutions of aluminum salts?

4. a. Compare the K_a values for the following hydrated ions: Be^{2+}, Cr^{3+}, Fe^{3+} and Ni^{2+}. Which is the most acidic in solution? _____ Which is the least acidic? _____ Which ion polarizes the bonds in the hydrated water molecules the most? _____ The least?_____

   b. Based on their K_a values alone, which ion would you expect to have a smaller ionic radius, Fe^{3+} or Cr^{3+}? Be^{2+} or Ni^{2+}. Circle your choices and *explain your reasoning*.

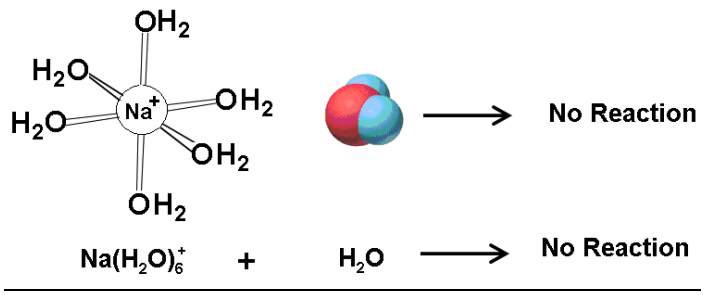
K_a Values of Hydrated Metal ions at 25°C

Free Ion	Hydrated Ion	K_a
Fe^{3+}	$Fe(H_2O)_6^{3+}(aq)$	6×10^{-3}
Sn^{2+}	$Sn(H_2O)_6^{2+}(aq)$	4×10^{-4}
Cr^{3+}	$Cr(H_2O)_6^{3+}(aq)$	1×10^{-4}
Al^{3+}	$Al(H_2O)_6^{3+}(aq)$	1×10^{-5}
Be^{2+}	$Be(H_2O)_4^{2+}(aq)$	4×10^{-6}
Cu^{2+}	$Cu(H_2O)_6^{2+}(aq)$	3×10^{-8}
Pb^{2+}	$Pb(H_2O)_6^{2+}(aq)$	3×10^{-8}
Zn^{2+}	$Zn(H_2O)_6^{2+}(aq)$	1×10^{-9}
Co^{2+}	$Co(H_2O)_6^{2+}(aq)$	2×10^{-10}
Ni^{2+}	$Ni(H_2O)_6^{2+}(aq)$	1×10^{-10}

   c. Based on their *position in the periodic table*, which ion would you expect to have a smaller ionic radius, Fe^{3+} or Cr^{3+}? Be^{2+} or Ni^{2+}. Circle your choices and *explain your reasoning*. Do your choices to this question and the previous question agree? _____

   d. Based on their K_a values alone, which ion would you expect to have the largest charge density, Be^{2+}, Cr^{3+}, Fe^{3+} or Ni^{2+}. *Circle your choice*.

5. a. Consider the figure to the right. Would you expect the pH of an aqueous solution containing sodium ions to be *acidic*, *basic* or *neutral*? Circle your choice and *explain your reasoning*.



b. Explain why hydrated sodium ions do *not* undergo acid hydrolysis (as shown in the figure to the above).

The Model: Hydrolysis of a Generic Salt

Consider the solvation and possible hydrolysis of the generic salt MA, where M^+ is a cation and A^- is an anion. (The charges do not have to be +1 and -1, respectively, but let's consider these charges for simplicity's sake.) When MA is dissolved in water, the following hydrolysis reactions *may* occur:

$$\mathbf{M(H_2O)_6^+}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{M(H_2O)_5OH}\,(aq) + \mathbf{H_3O^+}(aq) \qquad (3)$$

$$\mathbf{A^-}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{HA}(aq) + \mathbf{OH^-}(aq) \qquad (4)$$

Key Questions

6 a. When is the reaction in eqn **3** likely to occur? (Circle your choice.)
   i. When M is a small cation with large charge
   ii. When M is a large cation with a large charge
   iii. When M is a small cation with a small charge
   iv. When M is a large cation with a small charge

b. When is the reaction in eqn **4** likely to occur?
   i. When HA is a weak acid (i.e. when A^- is the conjugate base of a weak acid)
   ii. When HA is a strong acid. (i.e. when A^- is the conjugate base of a strong acid)

c. Suppose MA is the product of the reaction between a strong acid (HA) and a strong base (MOH). Which of *one* the following is correct? (Circle your choice.)
   i. The reaction in eqn **3** is more likely to occur than the reaction in eqn **5**, so the solution of the salt is acidic.
   ii. The reaction in eqn **4** is more likely to occur than the reaction in eqn **3**, so the solution of the salt is acidic.
   iii. Neither the reaction in eqn **3** nor the reaction in eqn **4** is likely to occur. The salt does not hydrolyze in water, and the solution of the salt is neutral.
   iv. The reaction in eqn **3** is more likely to occur than the reaction in eqn **4**, so the solution of the salt is basic.
   v. The reaction in eqn **4** is more likely to occur than the reaction in eqn **3**, so the solution of the salt is basic.

7. Suppose MA is the salt formed from the reaction between a weak acid (HA with ionization constant K_a) and a weak base (MOH with ionization constant K_b): **HA(*aq*) + MOH(*aq*) ⇌ MA(*aq*) + H_2O(*l*)**
Identify if each statement below is true or false.

   a. True or False: If $K_a < K_b$, then the reaction in eqn **4** is more likely to occur than the reaction in eqn **3**. Therefore, more OH^- is produced than H^+, and the solution of the salt is basic.

   b. True or False: If $K_a \approx K_b$, then both of the reactions written in eqns **3** and **4** are equally likely to occur. The salt effectively does not hydrolyze in water because as much H^+ is produced as OH^-. Therefore the solution of the salt is essentially neutral.

   c. True or False: If $K_a > K_b$, then the reaction in eqn **3** is more likely to occur than the reaction in eqn **4**. Therefore, more H^+ is produced than OH^-, and the solution of the salt is acidic.

Exercises

For each of the following salts, predict whether or not an aqueous solution of the salt will be acidic, basic, or neutral. For those that do hydrolyze in water, write the hydrolysis reaction that explains why the solution is acidic or basic. Use the following constants as needed and remember that $(K_a)(K_b) = K_w$:
Acid Dissociation Constants, K_a: HCN = 6.2 x 10^{-10}; HNO_2 = 7.1 x 10^{-4}; $Cu(H_2O)_6^{2+}$ = 3 x 10^{-8}; HF = 6.8 x 10^{-4}; $HC_2H_3O_2$ = 1.75 x 10^{-5}; $Zn(H_2O)_6^{2+}$ = 1 x 10^{-9}; HSO_4^{1-} = 1.0 x 10^{-2}
Base Dissociation Constants, K_b: NH_3 = 1.76 x 10^{-5};

8. $NaCl_{(aq)}$

9. $NaCN_{(aq)}$

10. $NaF_{(aq)}$

11. $NH_4Cl_{(aq)}$ (*Hint*: consider the K_a of NH_4^+)

12. $NH_4C_2H_3O_{2(aq)}$ (*Hint*: consider the K_a of NH_4^+ & the K_b of $C_2H_3O_2^-$)

13. $Zn(CH_3COO)_2$

14. $CuCl_{2(aq)}$ (*Hint*: consider the K_a of Cu^{2+})

15. $KNO_{2\ (aq)}$

16. Rank the following salts in order of *decreasing* pH of their 0.1 *M* solutions: $FeCl_2$, $FeCl_3$, $MgCl_2$, $KClO_2$.
Ionic radii: Mg^{2+} = 72 pm; Fe^{2+} = 61 pm. *Briefly explain your reasoning*.

Molecular Properties and Acid Strength: Read Section 18.6 in your textbook and then answer the following questions

17. How does each of the following affect the acidity of its binary hydride?
    a. The electronegativity of the nonmetal

    b. The atomic size of the nonmetal

18. Does it make sense that a strong acid has a weak bond to its acidic proton, whereas a weak acid has a strong bond to its acidic proton? *Explain*.

19. Choose (circle) the *weaker* acid in each of the following pairs. *Briefly explain your reasoning*.
    a. HI or HBr

    b. H_3AsO_4 or H_2SeO_4

    c. HNO_3 or HNO_2

Electron-Pair Donation and the Lewis Acid-Base Definition: Read Section 18.9 in your textbook and then answer the following questions

20. What feature must a molecule or ion have for it to act as a Lewis base? A Lewis acid? Explain the roles of these features.

21. Which are Lewis acids and which are Lewis bases? *Explain your reasoning*.

a. Na^+

b. NH_3

c. CN^-

d. BF_3

22. Identify the Lewis acid and Lewis base in each equation.

a. $Fe^{3+} + 2\ H_2O \rightleftharpoons FeOH^{2+} + H_3O^+$

b. $H_2O + H^- \rightleftharpoons OH^- + H_2$

c. $4\ CO + Ni^{2+} \rightleftharpoons Ni(CO)_4$

Comprehensive Questions

23. Bodily processes in humans maintain the pH of blood with a narrow range. In fact, a condition called acidosis occurs if the blood pH goes below 7.35, and another called alkalosis occurs if the pH goes above 7.45. Given that the pK_w of blood is 13.63 at 37°C (body temperature), calculate the normal range of $[H_3O^+]$ and $[OH^-]$ in blood. *Show your work using units and correct sig. figs*.

24. Sodium phosphate has industrial uses ranging from clarifying crude sugar to manufacturing paper. It is sold as TSP in hardware stores and used in solution to remove boiler scale and to wash painted brick and concrete. What is the pH of a solution containing 33 g of Na_3PO_4 per liter? What is the $[OH^-]$ of the solution? *Show your work using units and correct sig. figs*. *Hints*: (i.) Write the equation for the reaction between sodium phosphate and water. (ii.) You'll need the K_a of the hydrogen phosphate ion, HPO_4^{2-}, to calculate the K_b of the phosphate ion, PO_4^{3-}. (iii.) Set up an I.C.E. table to calculate $[OH^-]$. (iv.) Use the hydroxide ion concentration to determine the hydronium ion concentration and then the pH.