Acid-Base Properties of Salt Solutions: Hydrolysis

EXPERIMENT

23

OBJECTIVE

To learn about the concept of hydrolysis and gain familiarity with acid-base indicators.

APPARATUS AND CHEMICALS

500-mL Erlenmeyer flask
Bunsen burner
ring stand and iron ring
wire gauze
dropping bottles of methyl orange, methyl red, bromothymol blue, phenol red, phenolphthalein, and alizarin yellow-R

0.1 *M* solutions of NaCl, $NaC_2H_3O_2$ (sodium acetate), copper nitrate, ammonium chloride, zinc chloride, potassium, aluminum sulfate, and sodium carbonate
test tubes (6)
test-tube rack
10-mL graduated cylinder

DISCUSSION

We expect solutions of substances such as HCl and HNO_2 to be acidic and solutions of NaOH and NH_3 to be basic. However, we may be somewhat surprised at first to discover that aqueous solutions of some salts such as sodium nitrite, $NaNO_2$, and potassium acetate, $KC_2H_3O_2$, are basic while others such as NH_4Cl and $FeCl_3$ are acidic. Recall that salts are the products formed in neutralization reactions of acids and bases. For example, when NaOH and HNO_2 (nitrous acid) react, the salt $NaNO_2$ is formed:

$$NaOH(aq) + HNO_2(aq) \longrightarrow NaNO_2(aq) + H_2O(l)$$

Most salts are strong electrolytes and exist as ions in aqueous solutions. Many ions react with water to produce acidic or basic solutions. The reactions of ions with water are frequently called *hydrolysis reactions*. We will see that anions such as CN^- and $C_2H_3O_2^-$ that are conjugate bases of weak acids react with water to form OH^- ions. Cations such as NH_4^+ and Fe^{3+} come from weak bases and react with water to form H^+ ions.

Hydrolysis of Anions

Let us consider the behavior of anions first. Anions of weak acids react with proton sources. When placed in water these anions react to some extent with water to accept protons and generate OH^- ions and thus cause the solution pH to be greater than 7. Recall that proton acceptors are Brønsted bases. Thus the anions of weak acids are basic in two senses: They are proton acceptors, and their aqueous solutions have pH's above 7. The nitrite ion, for example, reacts with water to increase the concentration of OH^- ions:

$$NO_2^-(aq) + H_2O(l) \rightleftarrows HNO_2(aq) + OH^-(aq)$$

This reaction of the nitrite ion is similar to that of weak bases such as NH_3 with water:

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

Thus both NH_3 and NO_2^- are bases and as such have a basicity or base-dissociation constant, K_b, associated with their corresponding equilibria.

According to the Brønsted theory, the nitrite ion is the conjugate base of nitrous acid. Let's consider the conjugate acid-base pair HNO_2 and NO_2^- and their behavior in water:

$$HNO_2 \rightleftarrows H^+ + NO_2^- \qquad K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

$$NO_2^- + H_2O \rightleftarrows HNO_2 + OH^- \qquad K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

Multiplication of these dissociation constants yields:

$$K_a \times K_b = \left(\frac{[H^+][NO_2^-]}{[HNO_2]}\right)\left(\frac{[HNO_2][OH^-]}{[NO_2^-]}\right) = [H^+][OH^-] = K_w$$

where K_w is the ion-product constant of water.

Thus the product of the acid-dissociation constant for an acid and the base-dissociation constant for its conjugate base is the ion-product constant for water:

$$K_a \times K_b = K_w = 1.0 \times 10^{-14} \qquad [1]$$

Knowing the K_a for a weak acid, we can easily find the K_b for the anion of the acid:

$$K_b = \frac{K_w}{K_a} \qquad [2]$$

By consulting a table of acid-dissociation constants, we can find that K_a for nitrous acid is 4.5×10^{-4}. Using this value, we can readily determine K_b for NO_2^-:

$$K_b = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.2 \times 10^{-11}$$

We further note that the stronger the acid, that is, the larger the K_a, the weaker its conjugate base. Similarly, the weaker the acid (the smaller the K_a), the stronger the conjugate base.

Anions derived from *strong acids,* such as Cl^- from HCl, do not react with water to affect the pH. Nor do Br^-, I^-, NO_3^-, SO_4^{2-}, and ClO_4^- affect the pH, for the same reason. They are spectator ions in the acid-base sense and can be described as neutral ions. Similarly, cations from strong bases, such as Na^+ from NaOH or K^+ from KOH, do not react with water to affect the pH. Hydrolysis of an ion occurs only when it can form a molecule or ion that is a weak electrolyte in the reaction with water. Strong acids and bases do not exist as molecules in dilute water solutions.

Example 23.1

What is the pH of a 0.10 *M* NaClO solution?

K_a for HClO is 3.0×10^{-8}.

SOLUTION: The salt NaClO exists as Na^+ and ClO^-. The Na^+ ions are spectator ions, but ClO^- ions undergo hydrolysis to form the weak acid HClO. Let x equal the equilibrium concentration of HClO (and OH^-):

$$\begin{array}{lcc} ClO^-(aq) + H_2O(l) \rightleftharpoons & HClO(aq) + & OH^-(aq) \\ (0.10 - x)M & xM & xM \end{array}$$

The value of K_b for the reaction is $(1.0 \times 10^{-14})/(3.0 \times 10^{-8}) = 3.3 \times 10^{-7}$. Because K_b is so small, we can neglect x in comparison with 0.10 and thus $0.10 - x \simeq 0.10$.

$$\frac{[HClO][OH^-]}{[ClO^-]} = K_b$$

$$\frac{x^2}{0.10} = 3.3 \times 10^{-7}$$

$$x^2 = 3.3 \times 10^{-8}$$

$$x = 1.8 \times 10^{-4}\,M$$

$$pOH = 3.74$$

$$\text{and } pH = 14 - 3.74 = 10.26$$

Anions with ionizable protons such as HCO_3^-, $H_2PO_4^-$, and HPO_4^{2-} may be either acidic or basic, depending on the relative values of K_a and K_b for the ion. We will not consider such ions in this experiment.

Hydrolysis of Cations

Cations that are derived from weak bases react with water to increase the hydrogen-ion concentration; they form acidic solutions. The ammonium ion is derived from the weak base NH_3 and reacts with water as follows:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

This reaction is completely analogous to the dissociation of any other weak acid, such as acetic acid or nitrous acid. We can represent this acid-dissociation of NH_4^+ more simply:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

Here too the acid-dissociation constant is related to the K_b of NH_3, which is the conjugate base of NH_4^+:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Knowing the value of K_b for NH_3, we can readily calculate the acid dissociation constant from Equation [1]:

$$K_a = \frac{K_w}{K_b} \qquad [3]$$

Cations of the alkali metals (Group 1A) and the larger alkaline earth ions, Ca^{2+}, Sr^{2+}, and Ba^{2+}, do not react with water, because they come from strong bases. Thus these ions have no influence on the pH of aqueous solutions. They are merely spectator ions in acid-base reactions. Consequently, they are described as being neutral in the acid-base sense. The cations of most other metals do hydrolyze to produce acidic solutions. Metal cations are coordinated with water molecules, and it is the hydrated ion that serves as the proton donor. The following equations illustrate this behavior for the iron (III) ion:

$$Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftarrows Fe(OH)(H_2O)_5^{2+}(aq) + H_3O^+(aq) \qquad [4]$$

We frequently omit the coordinated water molecules from such equations. For example, Equation [4] may be written as

$$Fe^{3+}(aq) + H_2O(l) \rightleftarrows Fe(OH)^{2+}(aq) + H^+(aq) \qquad [5]$$

Additional hydrolysis reactions can occur to form $Fe(OH)_2^+$ and even lead to the precipitation of $Fe(OH)_3$. The equilibria for such cations are often complex, and not all species have been identified. However, equations such as [4] and [5] serve to illustrate the acidic character of dipositive and tripositive ions and account for most of the H^+ in these solutions.

Summary of Hydrolysis Behavior

Whether a solution of a salt will be acidic, neutral, or basic can be predicted on the basis of the strengths of the acid and base from which the salt was formed.

1. *Salt of a strong acid and a strong base:* Examples: NaCl, KBr, and $Ba(NO_3)_2$. Neither the cation nor anion hydrolyzes, and the solution has a pH of 7.
2. *Salt of a strong acid and a weak base:* Examples: NH_4Br, $ZnCl_2$, and $Al(NO_3)_3$. The cation hydrolyzes, forming H^+ ions, and the solution has a pH less than 7.
3. *Salt of a weak acid and a strong base:* Examples: $NaNO_2$, $KC_2H_3O_2$, and $Ca(OCl)_2$. The anion hydrolyzes, forming OH^- ions, and the solution has a pH greater than 7.
4. *Salt of a weak acid and a weak base:* Examples: NH_4F, $NH_4C_2H_3O_2$, and $Zn(NO_2)_2$. Both ions hydrolyze. The pH of the solution is determined by the relative extent to which each ion hydrolyzes.

In this experiment, we will test the pH of water and of several aqueous salt solutions to determine whether these solutions are acidic, basic, or neutral. In each case, the salt solution will be 0.1 *M*. Knowing the concentration of the salt solution and the measured pH of each solution allows us to calculate K_a or K_b for the ion that hydrolyzes. Example 23.2 illustrates such calculations.

Example 23.2

Calculate K_b for OBr^- if a 0.10 *M* solution of NaOBr has a pH of 10.85.

SOLUTION: The spectator ion is Na^+. Alkali metal ions do not react with water and have no influence on pH. The ion OBr^- is the anion of a weak acid and thus reacts with water to produce OH^- ions:

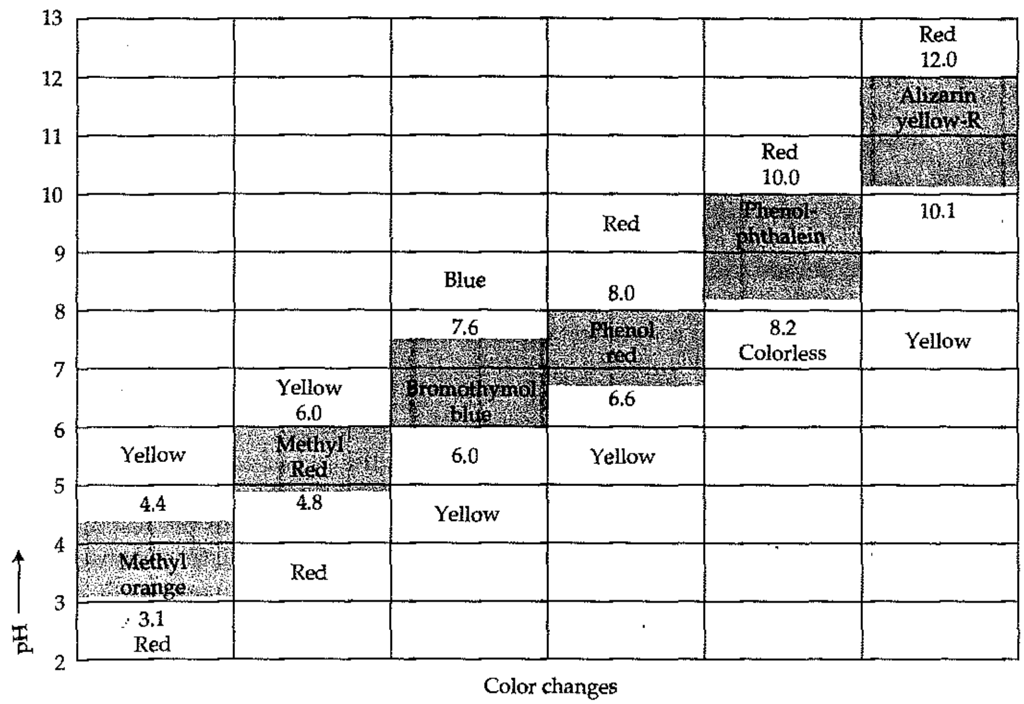
$$OBr^- + H_2O \rightleftarrows HOBr + OH^-$$

and the corresponding expression for the base dissociation constant is:

$$K_b = \frac{[HOBr][OH^-]}{[OBr^-]} \qquad [6]$$

If the pH is 10.85, then

$$pOH = 14.00 - 10.85 = 3.15$$



▲ **FIGURE 23.1** The color behavior of indicators.

and

$$[OH^-] = \text{antilog}\,(-3.15) = 7.1 \times 10^{-4}\,M$$

The concentration of HOBr that is formed along with OH^- must also be $7.1 \times 10^{-4}\,M$. The concentration of OBr^- that has not hydrolyzed is:

$$[OBr^-] = 0.10\,M - 0.00071\,M \simeq 0.10\,M$$

Substituting these values into Equation [6] for K_b yields:

$$K_b = \frac{[7.1 \times 10^{-4}][7.1 \times 10^{-4}]}{[0.10]}$$
$$= 5.0 \times 10^{-6}$$

The behavior of indicators was discussed in Experiment 17. We will use a set of indicators to determine the pH of various salt solutions. The dark areas in Figure 23.1 denote the transition ranges for the indicators you will use.

We will generally find that the solutions that we test will be more acidic than we would predict them to be. A major reason for this increased acidity is the occurrence of CO_2 dissolved in the solutions. CO_2 reacts with water to generate H^+:

$$CO_2(g) + H_2O(l) \rightleftarrows H_2CO_3(aq) \rightleftarrows H^+(aq) + HCO_3^-(aq)$$

The solubility of CO_2 is greatest in basic solutions, intermediate in neutral ones, and least in acidic ones. Even distilled water will therefore be somewhat acidic, unless it is boiled to remove the dissolved CO_2.

PROCEDURE

Boil approximately 450 mL of distilled water for about 10 min to expel dissolved carbon dioxide. Allow the water to cool to room temperature. While the water is boiling and subsequently cooling, add about 5 mL of unboiled distilled water to each of six test tubes. Add 3 drops of a different indicator to each of these six test tubes (one indicator per tube) and record the colors on the report sheet. From these colors and the data given in Figure 23.1 determine the pH of the unboiled water to the nearest pH unit. (Remember that we would expect its pH to be below 7 because of dissolved CO_2). Empty the contents of the test tubes and rinse the test tubes three times with about 3 mL of boiled distilled water. Then pour about 5 mL of the boiled distilled water into each of the six test tubes and add 3 drops of each of the indicators (one indicator per tube) to each tube. Record the colors and determine the pH. Empty the contents of the test tubes and rinse each tube three times with about 3 mL of boiled distilled water.

Repeat the same procedure to determine the pH of each of the following solutions that are 0.1 *M*: NaCl, $NaC_2H_3O_2$, $Cu(NO_3)_2$, NH_4Cl, $ZnCl_2$, $KA1(SO_4)_2$, and Na_2CO_3. Use 5 mL of each of these solutions per test tube. Do not forget to rinse the test tubes with boiled distilled water when you go from one solution to the next.

From the pH values that you determined, calculate the hydrogen- and hydroxide-ion concentrations for each solution. Complete the tables on the report sheets and calculate the K_a or K_b as appropriate.

REVIEW QUESTIONS

Before beginning this experiment in the laboratory, you should be able to answer the following questions:

1. Define Brønsted-Lowry acids and bases.
2. Which of the following ions will react with water in a hydrolysis reaction: Na^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, F^-, SO_3^{2-}, Br^-?
3. For those ions in question 2 that undergo hydrolysis, write net ionic equations for the hydrolysis reaction.
4. The K_a for HCN is 4.9×10^{-10}. What is the value of K_b for CN^-?
5. What are the conjugate base and conjugate acid of $H_2PO_4^-$?
6. From what acid and what base were the following salts made: $CaSO_4$, NH_4Br, and $BaCl_2$?
7. Define the term *salt*.
8. Tell whether 0.1 *M* solutions of the following salts would be acidic, neutral, or basic: $BaCl_2$, $CuSO_4$, $(NH_4)_2SO_4$, $ZnCl_2$, NaCN.
9. If the pH of a solution is 9, what are the hydrogen- and hydroxide-ion concentrations?
10. The pH of a 0.1 *M* MCl (M^+ is an unknown cation) was found to be 4.6. Write a net ionic equation for the hydrolysis of M^+ and its corresponding equilibrium expression K_b. Calculate the value of K_b.

Name ______________________________ Desk ______________

Date ______________ Laboratory Instructor ______________________________

REPORT SHEET | EXPERIMENT

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(See tables on pages 254 to 256)

QUESTIONS

1. Using the K_a's for $HC_2H_3O_2$ and HCO_3^- (from Appendix G), calculate the K_b's for the $C_2H_3O_2^-$ and CO_3^{2-} ions. Compare these values with those calculated from your measured pH's.

2. Using K_b for NH_3 (from Appendix H), calculate K_a for the NH_4^+ ion. Compare this value with that calculated from your measured pH's.

3. How should the pH of a 0.1 *M* solution of $NaC_2H_3O_2$ compare with that of a 0.1 *M* solution of $KC_2H_3O_2$? Explain briefly.

4. What is the greatest source of error in this experiment? How could you minimize this source of error?

	Indicator Color*								
Solution	Methyl orange	Methyl red	Bromo-thymol blue	Phenol red	Phenol-phtha-lein	Alizarin yellow-R	pH	$[H^+]$	$[OH^+]$
H_2O (unboiled)									
H_2O (boiled)									
$NaCl$									
$NaC_2H_3O_2$									
$Cu(NO_3)_2$									
NH_4Cl									
$ZnCl_2$									
$KAl(SO_4)_2$									
Na_2CO_3									

* color key: org = orange; ppl = purple; — = colorless; yell = yellow.

Solution	Ion Expected to Hydrolyze (If Any)	Spectator Ion(s) (If Any)
0.1 *M* $NaCl$	____________________	____________________
0.1 *M* $NaC_2H_3O_2$	____________________	____________________
0.1 *M* Na_2CO_3	____________________	____________________
0.1 *M* NH_4Cl	____________________	____________________
0.1 *M* $ZnCl_2$	____________________	____________________
0.1 *M* $Cu(NO_3)_2$	____________________	____________________
0.1 *M* $KAl(SO_4)_2$	____________________	____________________

CALCULATIONS

Solution	Net-Ionic Equation for Hydrolysis	Expression for Equilibrium Constant (K_a or K_b)	Value of K_a or K_b
$NaC_2H_3O_2$			
Na_2CO_3			
NH_4Cl			
$ZnCl_2$			
$Cu(NO_3)_2$			
$KAl(SO_4)_2$			