

## 14.4: Hydrolysis of Salt Solutions

### Learning Objectives

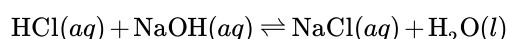
- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the process that causes solutions of certain metal ions to be acidic

As we have seen in the section on chemical reactions, when an acid and base are mixed, they undergo a neutralization reaction. The word “neutralization” seems to imply that a stoichiometrically equivalent solution of an acid and a base would be neutral. This is sometimes true, but the salts that are formed in these reactions may have acidic or basic properties of their own, as we shall now see.

### 14.4.1: Acid-Base Neutralization

A solution is neutral when it contains equal concentrations of hydronium and hydroxide ions. When we mix solutions of an acid and a base, an acid-base neutralization reaction occurs. However, even if we mix stoichiometrically equivalent quantities, we may find that the resulting solution is not neutral. It could contain either an excess of hydronium ions or an excess of hydroxide ions because the nature of the salt formed determines whether the solution is acidic, neutral, or basic. The following four situations illustrate how solutions with various pH values can arise following a neutralization reaction using stoichiometrically equivalent quantities:

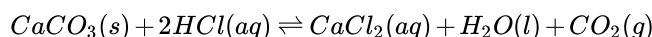
1. A strong acid and a strong base, such as  $\text{HCl}(aq)$  and  $\text{NaOH}(aq)$  will react to form a neutral solution since the conjugate partners produced are of negligible strength:



2. A strong acid and a weak base yield a weakly acidic solution, not because of the strong acid involved, but because of the conjugate acid of the weak base.
3. A weak acid and a strong base yield a weakly basic solution. A solution of a weak acid reacts with a solution of a strong base to form the conjugate base of the weak acid and the conjugate acid of the strong base. The conjugate acid of the strong base is a weaker acid than water and has no effect on the acidity of the resulting solution. However, the conjugate base of the weak acid is a weak base and ionizes slightly in water. This increases the amount of hydroxide ion in the solution produced in the reaction and renders it slightly basic.
4. A weak acid plus a weak base can yield either an acidic, basic, or neutral solution. This is the most complex of the four types of reactions. When the conjugate acid and the conjugate base are of unequal strengths, the solution can be either acidic or basic, depending on the relative strengths of the two conjugates. Occasionally the weak acid and the weak base will have the *same* strength, so their respective conjugate base and acid will have the same strength, and the solution will be neutral. To predict whether a particular combination will be acidic, basic or neutral, tabulated  $K$  values of the conjugates must be compared.

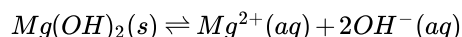
### 14.4.2: Stomach Antacids

Our stomachs contain a solution of roughly  $0.03\text{ M}$   $\text{HCl}$ , which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate,  $\text{CaCO}_3$ . The reaction,



not only neutralizes stomach acid, it also produces  $\text{CO}_2(g)$ , which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ . It works according to the reaction:



The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that :



This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide,  $Al(OH)_3$ , as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

### 14.4.3: Culinary Aspects of Chemistry

Cooking is essentially synthetic chemistry that happens to be safe to eat. There are a number of examples of acid-base chemistry in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking.  $NaHCO_3$  is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter “rises.” Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 14.4.1). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a “sour” taste that we seem to enjoy.

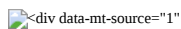
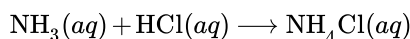


Figure 14.4.1: A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

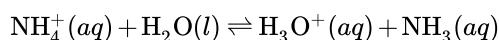
Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

### 14.4.4: Salts of Weak Bases and Strong Acids

When we neutralize a weak base with a strong acid, the product is a salt containing the conjugate acid of the weak base. This conjugate acid is a weak acid. For example, ammonium chloride,  $NH_4Cl$ , is a salt formed by the reaction of the weak base ammonia with the strong acid  $HCl$ :



A solution of this salt contains ammonium ions and chloride ions. The chloride ion has no effect on the acidity of the solution since  $HCl$  is a strong acid. Chloride is a very weak base and will not accept a proton to a measurable extent. However, the ammonium ion, the conjugate acid of ammonia, reacts with water and increases the hydronium ion concentration:



The equilibrium equation for this reaction is simply the ionization constant,  $K_a$ , for the acid  $NH_4^+$ :

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

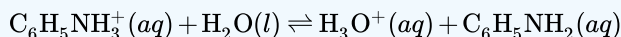
We will not find a value of  $K_a$  for the ammonium ion in Table E1. However, it is not difficult to determine  $K_a$  for  $NH_4^+$  from the value of the ionization constant of water,  $K_w$ , and  $K_b$ , the ionization constant of its conjugate base,  $NH_3$ , using the following relationship:

$$K_w = K_a \times K_b$$

This relation holds for any base and its conjugate acid or for any acid and its conjugate base.

### ✓ Example 14.4.1: pH of a Solution of a Salt of a Weak Base and a Strong Acid

Aniline is an amine that is used to manufacture dyes. It is isolated as aniline hydrochloride,  $[\text{C}_6\text{H}_5\text{NH}_3^+]\text{Cl}$ , a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 M solution of aniline hydrochloride?



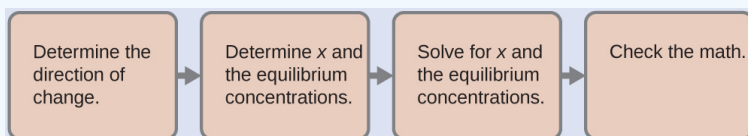
#### Solution

The new step in this example is to determine  $K_a$  for the  $\text{C}_6\text{H}_5\text{NH}_3^+$  ion. The  $\text{C}_6\text{H}_5\text{NH}_3^+$  ion is the conjugate acid of a weak base. The value of  $K_a$  for this acid is not listed in Table E1, but we can determine it from the value of  $K_b$  for aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ , which is given as  $4.6 \times 10^{-10}$ :

$$K_a(\text{for } \text{C}_6\text{H}_5\text{NH}_3^+) \times K_b(\text{for } \text{C}_6\text{H}_5\text{NH}_2) = K_w = 1.0 \times 10^{-14}$$

$$K_a(\text{for } \text{C}_6\text{H}_5\text{NH}_3^+) = \frac{K_w}{K_b(\text{for } \text{C}_6\text{H}_5\text{NH}_2)} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Now we have the ionization constant and the initial concentration of the weak acid, the information necessary to determine the equilibrium concentration of  $\text{H}_3\text{O}^+$ , and the pH:



Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “Determine the direction of change.” The second is labeled “Determine x and the equilibrium concentrations.” The third is labeled “Solve for x and the equilibrium concentrations.” The fourth is labeled “Check the math.”

With these steps we find  $[\text{H}_3\text{O}^+] = 2.3 \times 10^{-3} \text{ M}$  and  $\text{pH} = 2.64$

### ? Exercise 14.4.1

- Do the calculations and show that the hydronium ion concentration for a 0.233-M solution of  $\text{C}_6\text{H}_5\text{NH}_3^+$  is  $2.3 \times 10^{-3}$  and the pH is 2.64.
- What is the hydronium ion concentration in a 0.100-M solution of ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , a salt composed of the ions  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Use the data in Table E1 to determine  $K_b$  for the ammonium ion. Which is the stronger acid  $\text{C}_6\text{H}_5\text{NH}_3^+$  or  $\text{NH}_4^+$ ?

#### Answer a

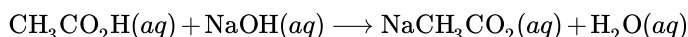
$$K_a(\text{for } \text{NH}_4^+) = 5.6 \times 10^{-10}, [\text{H}_3\text{O}^+] = 7.5 \times 10^{-6} \text{ M}$$

#### Answer b

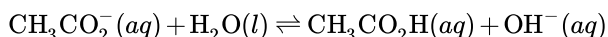
$\text{C}_6\text{H}_5\text{NH}_3^+$  is the stronger acid (a) (b) .

### 14.4.5: Salts of Weak Acids and Strong Bases

When we neutralize a weak acid with a strong base, we get a salt that contains the conjugate base of the weak acid. This conjugate base is usually a weak base. For example, sodium acetate,  $\text{NaCH}_3\text{CO}_2$ , is a salt formed by the reaction of the weak acid acetic acid with the strong base sodium hydroxide:



A solution of this salt contains sodium ions and acetate ions. The sodium ion has no effect on the acidity of the solution. However, the acetate ion, the conjugate base of acetic acid, reacts with water and increases the concentration of hydroxide ion:



The equilibrium equation for this reaction is the ionization constant,  $K_b$ , for the base  $\text{CH}_3\text{CO}_2^-$ . The value of  $K_b$  can be calculated from the value of the ionization constant of water,  $K_w$ , and  $K_a$ , the ionization constant of the conjugate acid of the anion using the equation:

$$K_w = K_a \times K_b$$

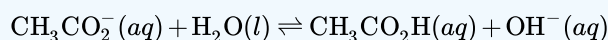
For the acetate ion and its conjugate acid we have:

$$K_b(\text{for } \text{CH}_3\text{CO}_2^-) = \frac{K_w}{K_a(\text{for } \text{CH}_3\text{CO}_2\text{H})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Some handbooks do not report values of  $K_b$ . They only report ionization constants for acids. If we want to determine a  $K_b$  value using one of these handbooks, we must look up the value of  $K_a$  for the conjugate acid and convert it to a  $K_b$  value.

#### ✓ Example 14.4.2: Equilibrium of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with  $[\text{CH}_3\text{CO}_2^-] = 0.050 \text{ M}$  and  $[\text{OH}^-] = 2.5 \times 10^{-6} \text{ M}$  at equilibrium. The reaction is:



##### Solution

We are given two of three equilibrium concentrations and asked to find the missing concentration. If we can find the equilibrium constant for the reaction, the process is straightforward.

The acetate ion behaves as a base in this reaction; hydroxide ions are a product. We determine  $K_b$  as follows:

$$K_b(\text{for } \text{CH}_3\text{CO}_2^-) = \frac{K_w}{K_a(\text{for } \text{CH}_3\text{CO}_2\text{H})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Now find the missing concentration:

$$\begin{aligned} K_b &= \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]} = 5.6 \times 10^{-10} \\ &= \frac{[\text{CH}_3\text{CO}_2\text{H}](2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10} \end{aligned}$$

Solving this equation we get  $[\text{CH}_3\text{CO}_2\text{H}] = 1.1 \times 10^{-5} \text{ M}$ .

#### ? Exercise 14.4.2

What is the pH of a 0.083-M solution of  $\text{CN}^-$ ? Use  $4.9 \times 10^{-10}$  as  $K_a$  for HCN. Hint: We will probably need to convert pOH to pH or find  $[\text{H}_3\text{O}^+]$  using  $[\text{OH}^-]$  in the final stages of this problem.

##### Answer

11.16

#### 14.4.6: Equilibrium in a Solution of a Salt of a Weak Acid and a Weak Base

In a solution of a salt formed by the reaction of a weak acid and a weak base, to predict the pH, we must know both the  $K_a$  of the weak acid and the  $K_b$  of the weak base. If  $K_a > K_b$ , the solution is acidic, and if  $K_b > K_a$ , the solution is basic.

#### ✓ Example 14.4.3: Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

- KBr
- $\text{NaHCO}_3$

- c.  $\text{NH}_4\text{Cl}$
- d.  $\text{Na}_2\text{HPO}_4$
- e.  $\text{NH}_4\text{F}$

### Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

- a. The  $\text{K}^+$  cation and the  $\text{Br}^-$  anion are both spectators, since they are the cation of a strong base (KOH) and the anion of a strong acid (HBr), respectively. The solution is neutral.
- b. The  $\text{Na}^+$  cation is a spectator, and will not affect the pH of the solution; the  $\text{HCO}_3^-$  anion is amphoteric. The  $K_a$  of  $\text{HCO}_3^-$  is  $4.7 \times 10^{-11}$ , so the  $K_b$  of its conjugate base is  $\frac{1.0 \times 10^{-14}}{4.7 \times 10^{-11}} = 2.1 \times 10^{-4}$ . Since  $K_b \gg K_a$ , the solution is basic.
- c. The  $\text{NH}_4^+$  ion is acidic and the  $\text{Cl}^-$  ion is a spectator. The solution will be acidic.
- d. The  $\text{Na}^+$  ion is a spectator and will not affect the pH of the solution, while the  $\text{HPO}_4^{2-}$  ion is amphoteric. The  $K_a$  of  $\text{HPO}_4^{2-}$  is  $4.2 \times 10^{-13}$  and its  $K_b$  is  $\frac{1.0 \times 10^{-14}}{4.2 \times 10^{-13}} = 2.4 \times 10^{-2}$ . Because  $K_b \gg K_a$ , the solution is basic.
- e. The  $\text{NH}_4^+$  ion is listed as being acidic, and the  $\text{F}^-$  ion is listed as a base, so we must directly compare the  $K_a$  and the  $K_b$  of the two ions.  $K_a$  of  $\text{NH}_4^+$  is  $5.6 \times 10^{-10}$ , which seems very small, yet the  $K_b$  of  $\text{F}^-$  is  $1.4 \times 10^{-11}$ , so the solution is acidic, since  $K_a > K_b$ .

### ? Exercise 14.4.3

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

- a.  $\text{K}_2\text{CO}_3$
- b.  $\text{CaCl}_2$
- c.  $\text{KH}_2\text{PO}_4$
- d.  $(\text{NH}_4)_2\text{CO}_3$
- e.  $\text{AlBr}_3$

#### Answer a

basic

#### Answer b

neutral

#### Answer c

acidic

#### Answer d

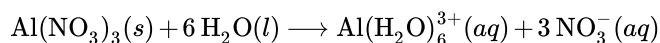
basic

#### Answer e

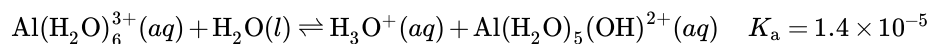
acidic

## 14.4.7: The Ionization of Hydrated Metal Ions

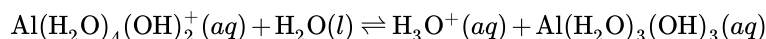
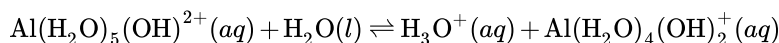
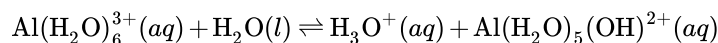
If we measure the pH of the solutions of a variety of metal ions we will find that these ions act as weak acids when in solution. The aluminum ion is an example. When aluminum nitrate dissolves in water, the aluminum ion reacts with water to give a hydrated aluminum ion,  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ , dissolved in bulk water. What this means is that the aluminum ion has the strongest interactions with the six closest water molecules (the so-called first solvation shell), even though it does interact with the other water molecules surrounding this  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  cluster as well:



We frequently see the formula of this ion simply as “ $\text{Al}^{3+}(\text{aq})$ ”, without explicitly noting the six water molecules that are the closest ones to the aluminum ion and just describing the ion as being solvated in water (hydrated). This is similar to the simplification of the formula of the hydronium ion,  $\text{H}_3\text{O}^+$  to  $\text{H}^+$ . However, in this case, the hydrated aluminum ion is a weak acid (Figure 14.4.2) and donates a proton to a water molecule. Thus, the hydration becomes important and we may use formulas that show the extent of hydration:



As with other polyprotic acids, the hydrated aluminum ion ionizes in stages, as shown by:



Note that some of these aluminum species are exhibiting amphiprotic behavior, since they are acting as acids when they appear on the left side of the equilibrium expressions and as bases when they appear on the right side.

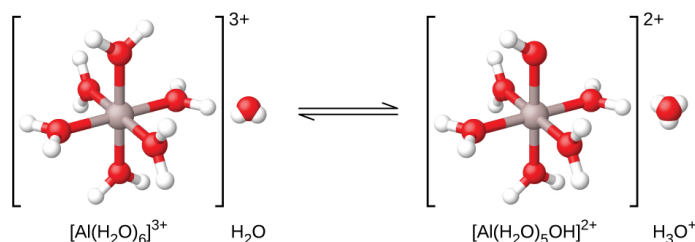
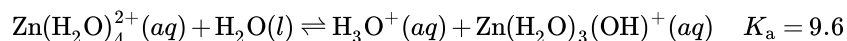
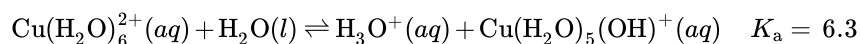
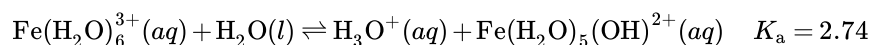


Figure 14.4.2: When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

A reaction is shown using ball and stick models. On the left, inside brackets with a superscript of 3 plus outside to the right is structure labeled “[ A l ( H subscript 2 O ) subscript 6 ] superscript 3 plus.” Inside the brackets is a central grey atom to which 6 red atoms are bonded in an arrangement that distributes them evenly about the central grey atom. Each red atom has two smaller white atoms attached in a forked or bent arrangement. Outside the brackets to the right is a space-filling model that includes a red central sphere with two smaller white spheres attached in a bent arrangement. Beneath this structure is the label “H subscript 2 O.” A double sided arrow follows. Another set of brackets follows to the right of the arrows which have a superscript of two plus outside to the right. The structure inside the brackets is similar to that on the left, except a white atom is removed from the structure. The label below is also changed to “[ A l ( H subscript 2 O ) subscript 5 O H ] superscript 2 plus.” To the right of this structure and outside the brackets is a space filling model with a central red sphere to which 3 smaller white spheres are attached. This structure is labeled “H subscript 3 O superscript plus.”

However, the ionization of a cation carrying more than one charge is usually not extensive beyond the first stage. Additional examples of the first stage in the ionization of hydrated metal ions are:

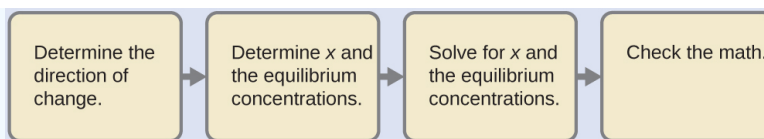


#### ✓ Example 14.4.4: Hydrolysis of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

Calculate the pH of a 0.10-M solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  in solution.

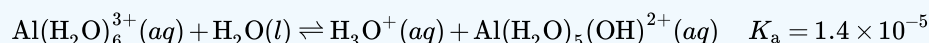
#### Solution

In spite of the unusual appearance of the acid, this is a typical acid ionization problem.



A reaction is shown using ball and stick models. On the left, inside brackets with a superscript of 3 plus outside to the right is structure labeled “[Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>”. Inside the brackets is a central grey atom to which 6 red atoms are bonded in an arrangement that distributes them evenly about the central grey atom. Each red atom has two smaller white atoms attached in a forked or bent arrangement. Outside the brackets to the right is a space-filling model that includes a red central sphere with two smaller white spheres attached in a bent arrangement. Beneath this structure is the label “H<sub>2</sub>O.” A double sided arrow follows. Another set of brackets follows to the right of the arrows which have a superscript of two plus outside to the right. The structure inside the brackets is similar to that on the left, except a white atom is removed from the structure. The label below is also changed to “[Al(H<sub>2</sub>O)<sub>5</sub>(OH)]<sup>2+</sup>”. To the right of this structure and outside the brackets is a space filling model with a central red sphere to which 3 smaller white spheres are attached. This structure is labeled “H<sub>3</sub>O<sup>+</sup>”.

1. *Determine the direction of change.* The equation for the reaction and  $K_a$  are:



The reaction shifts to the right to reach equilibrium.

2. *Determine x and equilibrium concentrations.* Use the table

:

|                           | $\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ |    |   |
|---------------------------|---|----|---|
| Initial concentration (M) | 0.10  | ~0 | 0 |
| Change (M)                | -x  | x  | x |
| Equilibrium constant (M)  | 0.10 - x  | x  | x |

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following in the first column: Initial concentration (M), Change (M), Equilibrium concentration (M). The second column has the header of “[Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> + H<sub>2</sub>O ⇌ H<sub>3</sub>O<sup>+</sup> + [Al(H<sub>2</sub>O)<sub>5</sub>(OH)]<sup>2+</sup>”. Under the second column is a subgroup of four columns and three rows. The first column has the following: 0.10 (which appears in red), negative x, 0.10 minus x. The second column is blank. The third column has the following: approximately 0, x, x. The fourth column has the following: 0, x, x.

*Solve for x and the equilibrium concentrations.* Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

$$\begin{aligned}
 K_a &= \frac{[\text{H}_3\text{O}^+][\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} \\
 &= \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}
 \end{aligned}$$

Solving this equation gives:

$$x = 1.2 \times 10^{-3} \text{ M}$$

From this we find:

$$\begin{aligned}
 [\text{H}_3\text{O}^+] &= 0 + x = 1.2 \times 10^{-3} \text{ M} \\
 \text{pH} &= -\log[\text{H}_3\text{O}^+] = 2.92 (\text{an acidic solution})
 \end{aligned}$$

*Check the work.* The arithmetic checks; when  $1.2 \times 10^{-3} \text{ M}$  is substituted for x, the result =  $K_a$ .

### ? Exercise 14.4.4

What is  $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}]$  in a 0.15-*M* solution of  $\text{Al}(\text{NO}_3)_3$  that contains enough of the strong acid  $\text{HNO}_3$  to bring  $[\text{H}_3\text{O}^+]$  to 0.10 *M*?

#### Answer

$$2.1 \times 10^{-5} \text{ M}$$

The constants for the different stages of ionization are not known for many metal ions, so we cannot calculate the extent of their ionization. However, practically all hydrated metal ions other than those of the alkali metals ionize to give acidic solutions. Ionization increases as the charge of the metal ion increases or as the size of the metal ion decreases.

### Summary

The characteristic properties of aqueous solutions of Brønsted-Lowry acids are due to the presence of hydronium ions; those of aqueous solutions of Brønsted-Lowry bases are due to the presence of hydroxide ions. The neutralization that occurs when aqueous solutions of acids and bases are combined results from the reaction of the hydronium and hydroxide ions to form water. Some salts formed in neutralization reactions may make the product solutions slightly acidic or slightly basic. Solutions that contain salts or hydrated metal ions have a pH that is determined by the extent of the hydrolysis of the ions in the solution. The pH of the solutions may be calculated using familiar equilibrium techniques, or it may be qualitatively determined to be acidic, basic, or neutral depending on the relative  $K_a$  and  $K_b$  of the ions involved.

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