

18

Ionic Equilibria I: Acids and Bases



OUTLINE

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| 18-2 | The Autoionization of Water | 18-9 | Salts of Weak Bases and Strong Acids |
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OBJECTIVES

After you have studied this chapter, you should be able to

- *Recognize strong electrolytes and calculate concentrations of their ions*
- *Understand the autoionization of water*
- *Understand the pH and pOH scales and how they are used*
- *Use ionization constants for weak monoprotic acids and bases*
- *Discuss the concepts of solvolysis and hydrolysis*
- *Describe how polyprotic acids ionize in steps and how to calculate concentrations of all species in solutions of polyprotic acids*
- *Apply acid–base equilibrium concepts to salts of strong bases and weak acids*
- *Apply acid–base equilibrium concepts to salts of weak bases and strong acids*
- *Apply acid–base equilibrium concepts to salts of weak bases and weak acids*
- *Apply acid–base equilibrium concepts to salts of small, highly charged cations*



Many foods contain weak acids. Citrus fruits contain citric acid and ascorbic acid (vitamin C).

Aqueous solutions are very important. Nearly three fourths of the earth's surface is covered with water. Enormous numbers of chemical reactions occur in the oceans and smaller bodies of water. Body fluids of plants and animals are mostly water. Life processes (chemical reactions) of all plants and animals occur in aqueous solutions or in contact with water. Before we were born, all of us developed in sacs filled with aqueous solutions, which protected and nurtured us until we had developed to the point that we could live in the atmosphere.


 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 14.1, Solutions and Their Behavior.

TABLE 18-1 *Common Strong Acids and Strong Bases*

Strong Acids	
HCl	HNO ₃
HBr	HClO ₄
HI	HClO ₃
	H ₂ SO ₄
Strong Bases	
LiOH	
NaOH	
KOH	Ca(OH) ₂
RbOH	Sr(OH) ₂
CsOH	Ba(OH) ₂

Recall that we use a single arrow (\rightarrow) to indicate that a reaction goes to completion, or nearly to completion, in the indicated direction.

Recall that we use a double arrow (\rightleftharpoons) to indicate that the reaction can go in either direction to reach equilibrium.

18-1 A REVIEW OF STRONG ELECTROLYTES

In previous discussions we have seen that water-soluble compounds may be classified as either electrolytes or nonelectrolytes. **Electrolytes** are compounds that ionize (or dissociate into their constituent ions) to produce aqueous solutions that conduct an electric current. **Nonelectrolytes** exist as molecules in aqueous solution, and such solutions do not conduct an electric current.

Strong electrolytes are ionized or dissociated completely, or very nearly completely, in dilute aqueous solutions. Strong electrolytes include strong acids, strong bases, and most soluble salts. You should review the discussions of these substances in Sections 4-2 and 10-8. The common strong acids and strong bases are listed again in Table 18-1. See Section 4-2, part 5, for the solubility guidelines for ionic compounds.

Concentrations of ions in aqueous solutions of strong electrolytes can be calculated directly from the molarity of the strong electrolyte, as the following example illustrates.

EXAMPLE 18-1 Calculation of Concentrations of Ions

Calculate the molar concentrations of Ba²⁺ and OH⁻ ions in 0.030 M barium hydroxide.

Plan

Write the equation for the dissociation of Ba(OH)₂, and construct the reaction summary. Ba(OH)₂ is a strong base that is completely dissociated.

Solution

From the equation for the dissociation of barium hydroxide, we see that *one* mole of Ba(OH)₂ produces *one* mole of Ba²⁺ ions and *two* moles of OH⁻ ions.

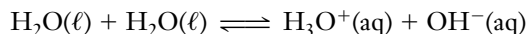
(strong base)	Ba(OH) ₂ (s)	\longrightarrow	Ba ²⁺ (aq)	+	2OH ⁻ (aq)
initial	0.030 M				
change due to rxn	-0.030 M		+0.030 M		+2(0.030 M)
final	0 M		0.030 M		0.060 M

$$[\text{Ba}^{2+}] = 0.030 \text{ M} \quad \text{and} \quad [\text{OH}^-] = 0.060 \text{ M}$$

You should now work Exercises 4 and 6.

18-2 THE AUTOIONIZATION OF WATER

Careful experiments on its electrical conductivity have shown that pure water ionizes to a very slight extent.



Because the H₂O is pure, its activity is 1, so we do not include its concentration in the equilibrium constant expression. This equilibrium constant is known as the **ion product for water** and is usually represented as K_w .

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

The formation of an H_3O^+ ion by the ionization of water is always accompanied by the formation of an OH^- ion. Thus, in *pure* water the concentration of H_3O^+ is *always* equal to the concentration of OH^- . Careful measurements show that, in pure water at 25°C ,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol/L}$$


Substituting these concentrations into the K_w expression gives

$$\begin{aligned} K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) \\ &= 1.0 \times 10^{-14} \quad (\text{at } 25^\circ\text{C}) \end{aligned}$$

Although the expression $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ was obtained for pure water, *it is also valid for dilute aqueous solutions at 25°C* . This is one of the most useful relationships chemists have discovered. It gives a simple relationship between H_3O^+ and OH^- concentrations in *all* dilute aqueous solutions.

The *value* of K_w is different at different temperatures (Table 18-2), but the *relationship* $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$ is still valid.

In this text, we shall assume a temperature of 25°C for all calculations involving aqueous solutions unless we specify another temperature.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 17.3, The Acid-Base Properties of Water.

Solutions in which the concentration of solute is less than about 1 mol/L are usually called dilute solutions.

TABLE 18-2 K_w at Some Temperatures

Temperature ($^\circ\text{C}$)	K_w
0	1.1×10^{-15}
10	2.9×10^{-15}
25	1.0×10^{-14}
37*	2.4×10^{-14}
45	4.0×10^{-14}
60	9.6×10^{-14}

*Normal human body temperature.

EXAMPLE 18-2 Calculation of Ion Concentrations

Calculate the concentrations of H_3O^+ and OH^- ions in a 0.050 M HNO_3 solution.

Plan

Write the equation for the ionization of HNO_3 , a strong acid, and construct the reaction summary, which gives the concentrations of H_3O^+ (and NO_3^-) ions directly. Then use the relationship $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ to find the concentration of OH^- ions.

Solution

The reaction summary for the ionization of HNO_3 , a strong acid, is

(strong acid)	HNO_3	+	H_2O	\longrightarrow	H_3O^+	+	NO_3^-
initial	0.050 M				$\approx 0 \text{ M}$		0 M
change due to rxn	-0.050 M				$+0.050 \text{ M}$		$+0.050 \text{ M}$
at equil	0 M				0.050 M		0.050 M

$$[\text{H}_3\text{O}^+] = [\text{NO}_3^-] = 0.050 \text{ M}$$

The $[\text{OH}^-]$ is determined from the equation for the autoionization of water and its K_w .

	$2\text{H}_2\text{O}$	\rightleftharpoons	$\text{H}_3\text{O}^+(\text{aq})$	+	OH^-
initial			0.050 M		
change due to rxn	$-2x \text{ M}$		$+x \text{ M}$		$+x \text{ M}$
at equil			$(0.050 + x) \text{ M}$		$x \text{ M}$

$$\begin{aligned} K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] \\ 1.0 \times 10^{-14} &= (0.050 + x)(x) \end{aligned}$$

Because the product $(0.050 + x)(x)$ is a very small number, we know that x must be very small. Thus, it will not matter whether we add x to 0.050; we can assume that $(0.050 + x) \approx 0.050$. We substitute this approximation into the equation and solve.

$$1.0 \times 10^{-14} = (0.050)(x) \quad \text{or} \quad x = \frac{1.0 \times 10^{-14}}{0.050} = 2.0 \times 10^{-13} \text{ M} = [\text{OH}^-]$$

We see that the assumption that x is much smaller than 0.050 was a good one.

You should now work Exercise 14.

Recall that

$[\text{OH}^-]_{\text{from H}_2\text{O}} = [\text{H}_3\text{O}^+]_{\text{from H}_2\text{O}}$ in *all* aqueous solutions. So we know that $[\text{H}_3\text{O}^+]_{\text{from H}_2\text{O}}$ must also be $2.0 \times 10^{-13} \text{ M}$.

In solving Example 18-2 we assumed that *all* of the H_3O^+ (0.050 M) came from the ionization of HNO_3 and neglected the H_3O^+ formed by the ionization of H_2O . The ionization of H_2O produces only $2.0 \times 10^{-13} \text{ M}$ H_3O^+ and $2.0 \times 10^{-13} \text{ M}$ OH^- in *this* solution. Thus, we were justified in assuming that the $[\text{H}_3\text{O}^+]$ is derived solely from the strong acid. A more concise way to carry out the calculation to find the $[\text{OH}^-]$ concentration is to write directly

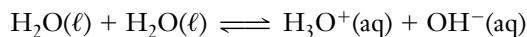
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad \text{or} \quad [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]}$$

Then we substitute to obtain

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{0.050} = 2.0 \times 10^{-13} \text{ M}$$

From now on, we shall use this more direct approach for such calculations.

When nitric acid is added to water, large numbers of H_3O^+ ions are produced. The large increase in $[\text{H}_3\text{O}^+]$ shifts the water equilibrium far to the left (LeChatelier's Principle), and the $[\text{OH}^-]$ decreases.



In acidic solutions the H_3O^+ concentration is always greater than the OH^- concentration. We should not conclude that acidic solutions contain no OH^- ions. Rather, the $[\text{OH}^-]$ is always less than $1.0 \times 10^{-7} \text{ M}$ in such solutions. The reverse is true for basic solutions, in which the $[\text{OH}^-]$ is always greater than $1.0 \times 10^{-7} \text{ M}$. By definition, "neutral" aqueous solutions at 25°C are solutions in which $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$.

Solution	General Condition	At 25°C	
		$[\text{H}_3\text{O}^+] > 1.0 \times 10^{-7}$	$[\text{OH}^-] < 1.0 \times 10^{-7}$
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	$[\text{H}_3\text{O}^+] > 1.0 \times 10^{-7}$	$[\text{OH}^-] < 1.0 \times 10^{-7}$
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$	$[\text{OH}^-] = 1.0 \times 10^{-7}$
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	$[\text{H}_3\text{O}^+] < 1.0 \times 10^{-7}$	$[\text{OH}^-] > 1.0 \times 10^{-7}$

18-3 THE pH AND pOH SCALES

The pH and pOH scales provide a convenient way to express the acidity and basicity of dilute aqueous solutions. The **pH** and **pOH** of a solution are defined as

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] & \text{or} & \quad [\text{H}_3\text{O}^+] = 10^{-\text{pH}} \\ \text{pOH} &= -\log [\text{OH}^-] & \text{or} & \quad [\text{OH}^-] = 10^{-\text{pOH}} \end{aligned}$$

Note that we use pH rather than pH_3O . At the time the pH concept was developed, H_3O^+ was represented as H^+ . Various “p” terms are used. In general a lowercase “p” before a symbol means “negative logarithm of the symbol.” Thus, pH is the negative logarithm of the H_3O^+ concentration, **pOH** is the negative logarithm of the OH^- concentration, and **pK** refers to the negative logarithm of an equilibrium constant. It is convenient to describe the autoionization of water in terms of **pK_w**.

$$\text{p}K_w = -\log K_w$$

When dealing with pH, we always use the base-10 (common) logarithm, *not* the base-*e* (natural) logarithm. This is because pH is *defined* using base-10 logarithms.

EXAMPLE 18-3 Calculation of pH

Calculate the pH of a solution in which the H_3O^+ concentration is 0.050 mol/L.

Plan

We are given the value for $[\text{H}_3\text{O}^+]$; so we take the negative logarithm of this value.

Solution

$$[\text{H}_3\text{O}^+] = 0.050 \text{ M} = 5.0 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [5.0 \times 10^{-2}] = 1.30$$

This answer contains only *two* significant figures. The “1” in 1.30 is *not* a significant figure; it comes from the power of ten.

You should now work Exercise 22.

In a pH value, only the digits after the decimal point are significant figures.

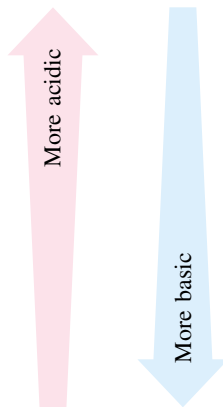
EXAMPLE 18-4 Calculation of H_3O^+ Concentration from pH

The pH of a solution is 3.301. What is the concentration of H_3O^+ in this solution?

Plan

By definition, $\text{pH} = -\log [\text{H}_3\text{O}^+]$. We are given the pH, so we solve for $[\text{H}_3\text{O}^+]$.

pH Range for a Few Common Substances	
Substance	pH Range
Gastric contents (human)	1.6–3.0
Soft drinks	2.0–4.0
Lemons	2.2–2.4
Vinegar	2.4–3.4
Tomatoes	4.0–4.4
Beer	4.0–5.0
Urine (human)	4.8–8.4
Milk (cow's)	6.3–6.6
Saliva (human)	6.5–7.5
Blood plasma (human)	7.3–7.5
Egg white	7.6–8.0
Milk of magnesia	10.5
Household ammonia	11–12



The pH of some common substances is shown by a universal indicator. Refer to Figure 18-2 to interpret the indicator colors.

Solution

From the definition of pH, we write

$$-\log [\text{H}_3\text{O}^+] = 3.301$$

Multiplying through by -1 gives

$$\log [\text{H}_3\text{O}^+] = -3.301$$

Taking the inverse logarithm (antilog) of both sides of the equation gives

$$[\text{H}_3\text{O}^+] = 10^{-3.301} \quad \text{so} \quad [\text{H}_3\text{O}^+] = 5.00 \times 10^{-4} \text{ M}$$

You should now work Exercise 26.

A convenient relationship between pH and pOH in *all dilute solutions at 25°C* can be easily derived. We start with the K_w expression.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Taking the logarithm of both sides of this equation gives

$$\log [\text{H}_3\text{O}^+] + \log [\text{OH}^-] = \log (1.0 \times 10^{-14})$$

Multiplying both sides of this equation by -1 gives

$$(-\log [\text{H}_3\text{O}^+]) + (-\log [\text{OH}^-]) = -\log (1.0 \times 10^{-14})$$

or

$$\text{pH} + \text{pOH} = 14.00$$

We can now relate $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ as well as pH and pOH.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad \text{and} \quad \text{pH} + \text{pOH} = 14.00 \quad (\text{at } 25^\circ\text{C})$$

From this relationship, we see that pH and pOH can *both* be positive only if *both* are less than 14. If either pH or pOH is greater than 14, the other is obviously negative.

Please study carefully the following summary. It will be helpful.

Solution	General Condition	At 25°C
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$ $\text{pH} < \text{pOH}$	$[\text{H}_3\text{O}^+] > 1.0 \times 10^{-7} \text{ M} > [\text{OH}^-]$ $\text{pH} < 7.00 < \text{pOH}$
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$ $\text{pH} = \text{pOH}$	$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M} = [\text{OH}^-]$ $\text{pH} = 7.00 = \text{pOH}$
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$ $\text{pH} > \text{pOH}$	$[\text{H}_3\text{O}^+] < 1.0 \times 10^{-7} \text{ M} < [\text{OH}^-]$ $\text{pH} > 7.00 > \text{pOH}$

To develop familiarity with the pH and pOH scales, consider a series of solutions in which $[\text{H}_3\text{O}^+]$ varies from 10 M to $1.0 \times 10^{-15} \text{ M}$. Obviously, $[\text{OH}^-]$ will vary from $1.0 \times 10^{-15} \text{ M}$ to 10 M in these solutions. Table 18-3 summarizes these scales.

At any temperature, $\text{pH} + \text{pOH} = \text{p}K_w$.

Remember these relationships!


 See the Saunders Interactive General Chemistry CD-ROM, Screen 17.4, The pH Scale.

TABLE 18-3 Relationships Among $[\text{H}_3\text{O}^+]$, pH, pOH, and $[\text{OH}^-]$

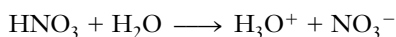
$[\text{H}_3\text{O}^+]$	pH		pOH	$[\text{OH}^-]$
10^{-15}	15		-1	10^1
10^{-14}	14		0	1
10^{-13}	13		1	10^{-1}
10^{-12}	12		2	10^{-2}
10^{-11}	11		3	10^{-3}
10^{-10}	10		4	10^{-4}
10^{-9}	9		5	10^{-5}
10^{-8}	8		6	10^{-6}
10^{-7}	7		7	10^{-7}
10^{-6}	6		8	10^{-8}
10^{-5}	5		9	10^{-9}
10^{-4}	4		10	10^{-10}
10^{-3}	3		11	10^{-11}
10^{-2}	2		12	10^{-12}
10^{-1}	1		13	10^{-13}
1	0	14	10^{-14}	
10^1	-1	15	10^{-15}	

EXAMPLE 18-5 Calculations Involving pH and pOH

Calculate $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH for a 0.015 M HNO_3 solution.

Plan

We write the equation for the ionization of the strong acid HNO_3 , which gives us $[\text{H}_3\text{O}^+]$. Then we calculate pH. We use the relationships $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and $\text{pH} + \text{pOH} = 14.00$ to find pOH and $[\text{OH}^-]$.

Solution

Because nitric acid is a strong acid (it ionizes completely), we know that

$$[\text{H}_3\text{O}^+] = 0.015 \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.015) = -(-1.82) = 1.82$$

We also know that $\text{pH} + \text{pOH} = 14.00$. Therefore,

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 1.82 = 12.18$$

Because $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, $[\text{OH}^-]$ is easily calculated.

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.015} = 6.7 \times 10^{-13} \text{ M}$$

You should now work Exercise 27.

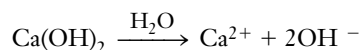
All ions are hydrated in aqueous solution. We often omit the designations (l), (g), (s), (aq), and so on.

EXAMPLE 18-6 *Calculations Involving pH and pOH*

Calculate $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH for a 0.015 M $\text{Ca}(\text{OH})_2$ solution.

Plan

We write the equation for the ionization of the strong base $\text{Ca}(\text{OH})_2$, which gives us $[\text{OH}^-]$. Then we calculate pOH. We use the relationships $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and $\text{pH} + \text{pOH} = 14.00$ to find pH and $[\text{H}_3\text{O}^+]$.

Solution

Because calcium hydroxide is a strong base (it dissociates completely), we know that

$$[\text{OH}^-] = 2 \times 0.015 \text{ M} = 0.030 \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (0.030) = -(-1.52) = 1.52$$

We also know that $\text{pH} + \text{pOH} = 14.00$. Therefore,

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.52 = 12.48$$

Because $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, $[\text{H}_3\text{O}^+]$ is easily calculated.

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.030} = 3.3 \times 10^{-13} \text{ M}$$

You should now work Exercises 28 and 29.

A pH meter is much more accurate than an indicator for obtaining pH values.

The pH of a solution can be determined using a pH meter (Figure 18-1) or by the indicator method. Acid–base **indicators** are intensely colored complex organic compounds that have different colors in solutions of different pH (Section 19-4). Many are weak acids or weak bases that are useful over rather narrow ranges of pH values. *Universal indicators* are mixtures of several indicators; they show several color changes over a wide range of pH values.

Figure 18-1 A pH meter gives the pH of the solution directly. When the electrode is dipped into a solution, the meter displays the pH. The pH meter is based on the glass electrode. This sensing device generates a voltage that is proportional to the pH of the solution in which the electrode is placed. The instrument has an electrical circuit to amplify the voltage from the electrode and a meter that relates the voltage to the pH of the solution. Before being used, a pH meter must be calibrated with a series of solutions of known pH.





Figure 18-2 Solutions containing a universal indicator. A universal indicator shows a wide range of colors as pH varies. The pH values are given by the black numbers. These solutions range from quite acidic (*upper left*) to quite basic (*lower right*).

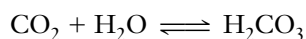
In the indicator method we prepare a series of solutions of known pH (standard solutions). We add a universal indicator to each; solutions with different pH have different colors (Figure 18-2). We then add the same universal indicator to the unknown solution and compare its color to those of the standard solutions. Solutions with the same pH have the same color.

Universal indicator papers can also be used to determine pH. A drop of solution is placed on a piece of paper or a piece of the paper is dipped into a solution. The color of the paper is then compared with a color chart on the container to establish the pH of the solution.

18-4 IONIZATION CONSTANTS FOR WEAK MONOPROTIC ACIDS AND BASES

We have discussed strong acids and strong bases. There are relatively few of these. Weak acids are much more numerous than strong acids. For this reason you were asked to learn the list of common strong acids (see Table 18-1). You may assume that nearly all other acids you encounter in this text will be weak acids. Table 18-4 contains names, formulas, ionization constants, and pK_a values for a few common weak acids; Appendix F contains a longer list of K_a values. *Weak* acids ionize only slightly in dilute aqueous solution. Our classification of acids as strong or weak is based on the *extent to which they ionize in dilute aqueous solution*.

Several weak acids are familiar to us. Vinegar is a 5% solution of acetic acid, CH_3COOH . Carbonated beverages are saturated solutions of carbon dioxide in water, which produces carbonic acid.



Citrus fruits contain citric acid, $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$. Some ointments and powders used for medicinal purposes contain boric acid, H_3BO_3 . These everyday uses of weak acids suggest that there is a significant difference between strong and weak acids. The difference is that *strong acids ionize completely in dilute aqueous solution, whereas weak acids ionize only slightly*.

How can you tell that carbonated beverages are *saturated* CO_2 solutions?

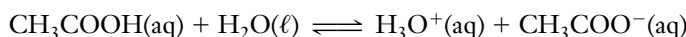
Would you think of using sulfuric or nitric acid for any of these purposes?

TABLE 18-4 Ionization Constants and pK_a Values for Some Weak Monoprotic Acids

Acid	Ionization Reaction	K_a at 25°C	pK_a
hydrofluoric acid	$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$	7.2×10^{-4}	3.14
nitrous acid	$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$	4.5×10^{-4}	3.35
acetic acid	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	1.8×10^{-5}	4.74
hypochlorous acid	$\text{HOCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OCl}^-$	3.5×10^{-8}	7.45
hydrocyanic acid	$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$	4.0×10^{-10}	9.40

Recall that pK_a means $-\log K_a$.

Let us consider the reaction that occurs when a weak acid, such as acetic acid, is dissolved in water. The equation for the ionization of acetic acid is



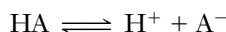
The equilibrium constant for this reaction could be represented as

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$$

The thermodynamic approach is that the activity of the (nearly) pure H_2O is essentially 1. The activity of each dissolved species is numerically equal to its molar concentration.

We should recall that the thermodynamic definition of K is in terms of activities. In dilute solutions, the activity of the (nearly) pure H_2O is essentially 1. The activity of each dissolved species is numerically equal to its molar concentration. Thus the **ionization constant** of a weak acid, K_a , does not include a term for the concentration of water.

We often use HA as a general representation for a monoprotic acid and A^- for its conjugate base. The equation for the ionization of a weak acid can be written as



For example, for acetic acid, we can write either

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

or

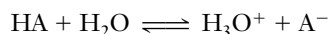
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

This expression tells us that in dilute aqueous solutions of acetic acid, the concentration of H_3O^+ multiplied by the concentration of CH_3COO^- and then divided by the concentration of *nonionized* acetic acid is equal to 1.8×10^{-5} .

Ionization constants for weak acids (and bases) must be calculated from *experimentally determined data*. Measurements of pH, conductivity, or depression of freezing point provide data from which these constants can be calculated.

EXAMPLE 18-7 Calculation of K_a and pK_a from Equilibrium Concentrations

Nicotinic acid is a weak monoprotic organic acid that we can represent as HA .



A dilute solution of nicotinic acid was found to contain the following concentrations at equilibrium at 25°C. What is the value of K_a ? $[HA] = 0.049 M$; $[H_3O^+] = [A^-] = 8.4 \times 10^{-4} M$.

Plan

We are given *equilibrium* concentrations, and so we substitute these into the expression for K_a .

Solution

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_a = \frac{(8.4 \times 10^{-4})(8.4 \times 10^{-4})}{(0.049)} = 1.4 \times 10^{-5}$$

The equilibrium constant expression is

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = 1.4 \times 10^{-5} \quad pK_a = 4.85$$

You should now work Exercise 32.

EXAMPLE 18-8 Calculation of K_a from Percent Ionization

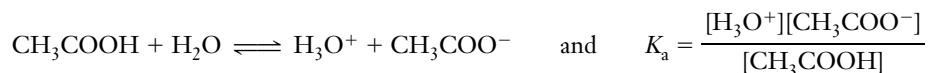
In 0.0100 M solution, acetic acid is 4.2% ionized. Calculate its ionization constant.

Plan

We write the equation for the ionization of acetic acid and its equilibrium constant expression. Next we use the percent ionization to complete the reaction summary and then substitute into the K_a expression.

Solution

The equations for the ionization of CH_3COOH and its ionization constant are



Because 4.2% of the CH_3COOH ionizes,

$$M_{CH_3COOH} \text{ that ionizes} = 0.042 \times 0.0100 M = 4.2 \times 10^{-4} M$$

Each mole of CH_3COOH that ionizes forms one mole of H_3O^+ and one mole of CH_3COO^- . We represent this in the reaction summary.

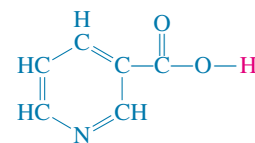
	CH_3COOH	+	H_2O	\rightleftharpoons	H_3O^+	+	CH_3COO^-
initial	0.0100 M				$\approx 0 M$		0 M
change	$-4.2 \times 10^{-4} M$				$+4.2 \times 10^{-4} M$		$+4.2 \times 10^{-4} M$
at equil	$9.58 \times 10^{-3} M$				$4.2 \times 10^{-4} M$		$4.2 \times 10^{-4} M$

Substitution of these values into the K_a expression gives the value for K_a .


$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(4.2 \times 10^{-4})(4.2 \times 10^{-4})}{9.58 \times 10^{-3}} = 1.8 \times 10^{-5}$$

You should now work Exercise 38.

The structure of nicotinic acid is



Nicotinic acid, also called niacin, is a necessary vitamin in our diets. It is not physiologically related to nicotine.

 See the Saunders Interactive General Chemistry CD-ROM, Screen 17.7, Determining K_a and K_b Values.



Some common household weak acids. A strip of paper impregnated with a universal indicator is convenient for estimating the pH of a solution.

EXAMPLE 18-9 Calculation of K_a from pH

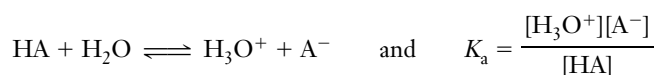
The pH of a 0.115 M solution of chloroacetic acid, ClCH_2COOH , is measured to be 1.92. Calculate K_a for this weak monoprotic acid.

Plan

For simplicity, we represent ClCH_2COOH as HA. We write the ionization equation and the expression for K_a . Next we calculate $[\text{H}_3\text{O}^+]$ for the given pH and complete the reaction summary. Finally, we substitute into the K_a expression.

Solution

The ionization of this weak monoprotic acid and its ionization constant expression may be represented as



We calculate $[\text{H}_3\text{O}^+]$ from the definition of pH.

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 10^{-\text{pH}} = 10^{-1.92} = 0.012 \text{ M} \end{aligned}$$

We use the usual reaction summary as follows. At this point, we know the *original* [HA] and the *equilibrium* $[\text{H}_3\text{O}^+]$. From this information, we fill out the “change” line and then deduce the other equilibrium values.

	HA	+	H ₂ O	⇌	H ₃ O ⁺	+	A ⁻
initial	0.115 M				≈ 0 M		0 M
change due to rxn	-0.012 M				+0.012 M		0.012 M
at equil	0.103 M				0.012 M		0.012 M

Now that all concentrations are known, K_a can be calculated.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.012)(0.012)}{0.103} = 1.4 \times 10^{-3}$$

You should now work Exercise 40.

**Problem-Solving Tip: Filling in Reaction Summaries**

In Examples 18-8 and 18-9 the value of an equilibrium concentration was used to determine the change in concentration. You should become proficient at using a variety of data to determine values that are related via a chemical equation. Let's review what we did in Example 18-9. Only the equilibrium expression, initial concentrations, and the equilibrium concentration of H_3O^+ were known when we started the reaction summary. The following steps show how we filled in the remaining values in the order indicated by the numbered red arrows.

1. $[\text{H}_3\text{O}^+]_{\text{equil}} = 0.012 \text{ M}$, so we record this value
2. $[\text{H}_3\text{O}^+]_{\text{initial}} \approx 0$, so change in $[\text{H}_3\text{O}^+]$ due to rxn must be $+0.012 \text{ M}$
3. Formation of $0.012 \text{ M H}_3\text{O}^+$ consumes 0.012 M HA , so the change in $[\text{HA}] = -0.012 \text{ M}$

4. $[\text{HA}]_{\text{equil}} = [\text{HA}]_{\text{orig}} + [\text{HA}]_{\text{chg}} = 0.115 \text{ M} + (-0.012 \text{ M}) = 0.103 \text{ M}$
5. Formation of $0.012 \text{ M H}_3\text{O}^+$ also gives 0.012 M A^-
6. $[\text{A}^-]_{\text{equil}} = [\text{A}^-]_{\text{orig}} + [\text{A}^-]_{\text{chg}} = 0 \text{ M} + 0.012 \text{ M} = 0.012 \text{ M}$

At equilibrium, $[\text{H}_3\text{O}^+] = 0.012 \text{ M}$ so

	HA	+	H_2O	\rightleftharpoons	H_3O^+	+	A^-	①
initial	0.115 M				$\approx 0 \text{ M}$		0 M	
change due to rxn	-0.012 M				+0.012 M		-0.012 M	
at equil	0.103 M				0.012 M		0.012 M	

Because ionization constants are equilibrium constants for ionization reactions, their values indicate the extents to which weak electrolytes ionize. At the same concentrations, acids with larger ionization constants ionize to greater extents (and are stronger acids) than acids with smaller ionization constants. From Table 18-4, we see that the order of decreasing acid strength for these five weak acids is



Conversely, in Brønsted–Lowry terminology (Section 10-4), the order of increasing base strength of the anions of these acids is



If we know the value of the ionization constant for a weak acid, we can calculate the concentrations of the species present in solutions of known initial concentrations.

EXAMPLE 18-10 Calculation of Concentrations from K_a

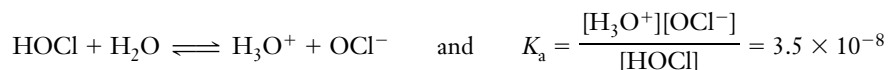
Calculate the concentrations of the various species in 0.10 M hypochlorous acid, HOCl. For HOCl, $K_a = 3.5 \times 10^{-8}$.

Plan

We write the equation for the ionization of the weak acid and its K_a expression. Then we represent the *equilibrium* concentrations algebraically and substitute into the K_a expression.

Solution

The equation for the ionization of HOCl and its K_a expression are



We would like to know the concentrations of H_3O^+ , OCl^- , and nonionized HOCl in solution. An algebraic representation of concentrations is required, because there is no other obvious way to obtain the concentrations.

Let $x = \text{mol/L}$ of HOCl that ionizes. Then, write the “change” line and complete the reaction summary.

	HOCl	+	H_2O	\rightleftharpoons	H_3O^+	+	OCl^-
initial	0.10 M				$\approx 0 \text{ M}$		0 M
change due to rxn	-x M				+x M		+x M
at equil	$(0.10 - x) \text{ M}$				x M		x M

Recall that in Brønsted–Lowry terminology, an acid forms its conjugate base by losing H^+ .

We have written the formula for hypochlorous acid as HOCl rather than HClO to emphasize that its structure is $\text{H}-\text{O}-\text{Cl}$.

We neglect the $1.0 \times 10^{-7} \text{ mol/L}$ of H_3O^+ produced by the ionization of pure water. Recall (see Section 18-2) that the addition of an acid to water suppresses the ionization of H_2O , so $[\text{H}_3\text{O}^+]$ from H_2O is even less than $1.0 \times 10^{-7} \text{ M}$.

Substituting these algebraic representations into the K_a expression gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{(x)(x)}{(0.10 - x)} = 3.5 \times 10^{-8}$$

This is a quadratic equation, but it is not necessary to solve it by the quadratic formula. The small value of the equilibrium constant, K_a , tells us that not very much of the original acid ionizes. Thus we can assume that $x \ll 0.10$. If x is small enough compared with 0.10, it will not matter (much) whether we subtract it, and we can assume that $(0.10 - x)$ is very nearly equal to 0.10. The equation then becomes

$$\frac{x^2}{0.10} \approx 3.5 \times 10^{-8} \quad x^2 \approx 3.5 \times 10^{-9} \quad \text{so} \quad x \approx 5.9 \times 10^{-5}$$

In our algebraic representation we let

$$[\text{H}_3\text{O}^+] = x \text{ M} = 5.9 \times 10^{-5} \text{ M} \quad [\text{OCl}^-] = x \text{ M} = 5.9 \times 10^{-5} \text{ M}$$

$$[\text{HOCl}] = (0.10 - x) \text{ M} = (0.10 - 0.000059) \text{ M} = 0.10 \text{ M}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-5}} = 1.7 \times 10^{-10} \text{ M}$$

You should now work Exercise 42.



Problem-Solving Tip: Simplifying Quadratic Equations

We often encounter quadratic or higher-order equations in equilibrium calculations. With modern programmable calculators, solving such problems by iterative methods is often feasible. But frequently a problem can be made much simpler by using some mathematical common sense.

When the linear variable (x) in a *quadratic* equation is added to or subtracted from a much larger number, it can often be disregarded if it is sufficiently small. A reasonable rule of thumb for determining whether the variable can be disregarded in equilibrium calculations is this: If the exponent of 10 in the K value is -3 or less (-4 , -5 , -6 , etc.), then the variable may be small enough to disregard when it is added to or subtracted from a number greater than 0.05. Solve the problem neglecting x ; then compare the value of x with the number it would have been added to (or subtracted from). If x is more than 5% of that number, the assumption was *not* justified, and you should solve the equation using the quadratic formula.

Let's examine the assumption as it applies to Example 18-10. Our quadratic equation is

$$\frac{(x)(x)}{(0.10 - x)} = 3.5 \times 10^{-8}$$

Because 3.5×10^{-8} is a very small K_a value, we know that the acid ionizes only slightly. Thus, x must be very small compared with 0.10, so we can write $(0.10 - x) \approx 0.10$.

The equation then becomes $\frac{x^2}{0.10} \approx 3.5 \times 10^{-8}$. To solve this, we rearrange and take the

square roots of both sides. To check, we see that the result, $x = 5.9 \times 10^{-5}$, is only 0.059% of 0.10. This error is much less than 5%, so our assumption is justified. You may also wish to use the quadratic formula to verify that the answer obtained this way is correct to within roundoff error.

The preceding argument is purely algebraic. We could use our chemical intuition to reach the same conclusion. A small K_a value (10^{-3} or less) tells us that the extent of ionization is very small; therefore, nearly all of the weak acid exists as nonionized molecules. The amount that ionizes is insignificant compared with the concentration of nonionized weak acid.

From our calculations we can draw some conclusions. In a solution containing *only a weak monoprotic acid*, the concentration of H_3O^+ is equal to the concentration of the anion of the acid. Unless the solution is *very dilute*, such as less than 0.050 M, the concentration of nonionized acid is approximately equal to the molarity of the solution. When the value of K_a for the weak acid is greater than $\approx 10^{-3}$, then the extent of ionization will be large enough to make a significant difference between the concentration of nonionized acid and the molarity of the solution. In such cases we *cannot* make the simplifying assumption.



The pH of a soft drink is measured with a modern pH meter. Many soft drinks are quite acidic due to the dissolved CO_2 and other ingredients.

EXAMPLE 18-11 Percent Ionization

Calculate the percent ionization of a 0.10 M solution of acetic acid.

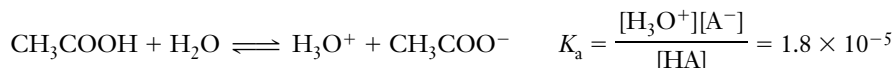
Plan

Write the ionization equation and the expression for K_a . Next, follow the procedure used in Example 18-10 to find the concentration of acid that ionized. Then, substitute the concentration of acid that ionized into the expression for percent ionization. Percentage is defined as (part/whole) $\times 100\%$, so the percent ionization is

$$\% \text{ ionization} = \frac{[\text{CH}_3\text{COOH}]_{\text{ionized}}}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \times 100\%$$

Solution

The equations for the ionization of CH_3COOH and its K_a are



We proceed as we did in Example 18-10. Let $x = [\text{CH}_3\text{COOH}]_{\text{ionized}}$.

	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$
initial	0.10 M ≈ 0 M 0 M
change due to rxn	-x M +x M +x M
at equil	(0.10 - x) M x M x M

Substituting into the ionization constant expression gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

If we make the simplifying assumption that $(0.10 - x) \approx 0.10$, we have

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5} \quad x^2 = 1.8 \times 10^{-6} \quad x = 1.3 \times 10^{-3}$$

We could write the original $[\text{H}_3\text{O}^+]$ as 1.0×10^{-7} M. In very *dilute* solutions of weak acids, we might have to take this into account. In this acid solution, $(1.0 \times 10^{-7} + x) \approx x$.

This gives $[\text{CH}_3\text{COOH}]_{\text{ionized}} = x = 1.3 \times 10^{-3} \text{ M}$. Now we can calculate the percent ionization for 0.10 M CH_3COOH solution.

$$\% \text{ ionization} = \frac{[\text{CH}_3\text{COOH}]_{\text{ionized}}}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \times 100\% = \frac{1.3 \times 10^{-3} \text{ M}}{0.10 \text{ M}} \times 100\% = 1.3\%$$

Note that we need not solve explicitly for the equilibrium concentrations $[\text{H}_3\text{O}^+]$ and $[\text{CH}_3\text{COO}^-]$ to answer the question. From the setup, we see that these are both $1.3 \times 10^{-3} \text{ M}$.

Our assumption that $(0.10 - x) \approx 0.10$ is reasonable because $(0.10 - x) = (0.10 - 0.0013)$. This is only about 1% different than 0.10. When K_a for a weak acid is significantly greater than 10^{-3} , however, this assumption would introduce considerable error.

You should now work Exercise 48.

In dilute solutions, acetic acid exists primarily as nonionized molecules, as do all weak acids; there are relatively few hydronium and acetate ions. In 0.10 M solution, CH_3COOH is 1.3% ionized; for each 1000 molecules of CH_3COOH originally placed in the solution, there are 13 H_3O^+ ions, 13 CH_3COO^- ions, and 987 nonionized CH_3COOH molecules. For weaker acids of the same concentration, the number of molecules of nonionized acid would be even larger.

By now we should have gained some “feel” for the strength of an acid by looking at its K_a value. Consider 0.10 M solutions of HCl (a strong acid), CH_3COOH (see Example 18-11), and HOCl (see Example 18-10). If we calculate the percent ionization for 0.10 M HOCl (as we did for 0.10 M CH_3COOH in Example 18-11), we find that it is 0.059% ionized. In 0.10 M solution, HCl is very nearly completely ionized. The data in Table 18-5 show that the $[\text{H}_3\text{O}^+]$ in 0.10 M HCl is approximately 77 times greater than that in 0.10 M CH_3COOH and approximately 1700 times greater than that in 0.10 M HOCl .

Many scientists prefer to use $\text{p}K_a$ values rather than K_a values for weak acids. Recall that in general, “p” terms refer to negative logarithms. The $\text{p}K_a$ value for a weak acid is just the negative logarithm of its K_a value.

EXAMPLE 18-12 $\text{p}K_a$ Values

The K_a values for acetic acid and hydrofluoric acid are 1.8×10^{-5} and 7.2×10^{-4} , respectively. What are their $\text{p}K_a$ values?

Plan

$\text{p}K_a$ is defined as the negative logarithm of K_a (i.e., $\text{p}K_a = -\log K_a$) so we take the negative logarithm of each K_a .

Solution

For CH_3COOH ,

$$\text{p}K_a = -\log K_a = -\log (1.8 \times 10^{-5}) = -(-4.74) = 4.74$$

For HF ,

$$\text{p}K_a = -\log K_a = -\log (7.2 \times 10^{-4}) = -(-3.14) = 3.14$$

You should now work Exercise 50.

TABLE 18-5 Comparison of Extents of Ionization of Some Acids

Acid Solution	Ionization Constant	$[\text{H}_3\text{O}^+]$	pH	Percent Ionization
0.10 M HCl	very large	0.10 M	1.00	≈ 100
0.10 M CH_3COOH	1.8×10^{-5}	0.0013 M	2.89	1.3
0.10 M HOCl	3.5×10^{-8}	0.000059 M	4.23	0.059

From Example 18-12, we see that the stronger acid (HF in this case) has the larger K_a value and the smaller $\text{p}K_a$ value. Conversely, the weaker acid (CH_3COOH in this case) has the smaller K_a value and the larger $\text{p}K_a$ value. The generalization is

The larger the value of K_a , the smaller is the value of $\text{p}K_a$, and the stronger is the acid.

EXAMPLE 18-13 Acid Strengths and K_a Values

Given the following list of weak acids and their K_a values, arrange the acids in order of (a) increasing acid strength and (b) increasing $\text{p}K_a$ values.

Acid	K_a
HOCl	3.5×10^{-8}
HCN	4.0×10^{-10}
HNO_2	4.5×10^{-4}

Plan

- (a) We see that HNO_2 is the strongest acid in this group because it has the largest K_a value. HCN is the weakest because it has the smallest K_a value.
 (b) We do not need to calculate $\text{p}K_a$ values to answer the question. We recall that the weakest acid has the largest $\text{p}K_a$ value and the strongest acid has the smallest $\text{p}K_a$ value, so the order of increasing $\text{p}K_a$ values is just the reverse of the order in part (a).

Solution

- (a) Increasing acid strength: $\text{HCN} < \text{HOCl} < \text{HNO}_2$
 (b) Increasing $\text{p}K_a$ values: $\text{HNO}_2 < \text{HOCl} < \text{HCN}$

You should now work Exercise 111.

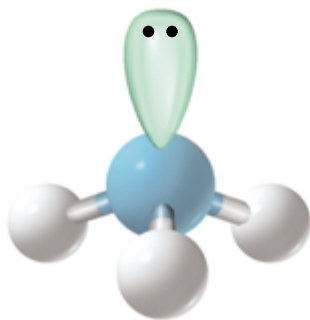
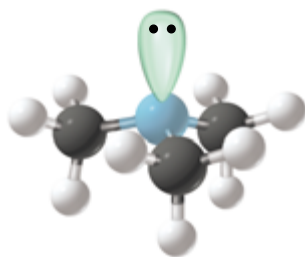
You may know that hydrofluoric acid dissolves glass. But HF is *not* a strong acid. The reaction of glass with hydrofluoric acid occurs because silicates react with HF to produce silicon tetrafluoride, SiF_4 , a very volatile compound. This reaction tells us nothing about the acid strength of hydrofluoric acid.



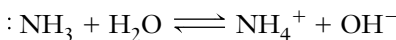
An inert solid has been suspended in the liquid to improve the quality of this photograph of a pH meter.

A similar statement is true for weak bases; that is, a stronger base has the greater K_b value and the smaller $\text{p}K_b$ value.

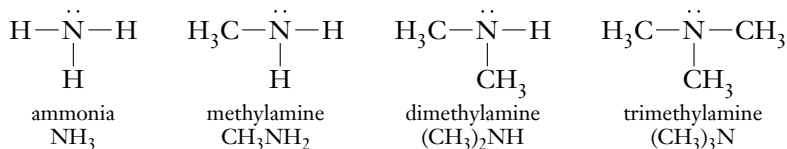
Do not confuse the strength of an acid with its reactivity. Acid strength refers to the extent of ionization of the acid, and not the reactions that it undergoes.

Ammonia, NH₃Trimethylamine, (CH₃)₃N

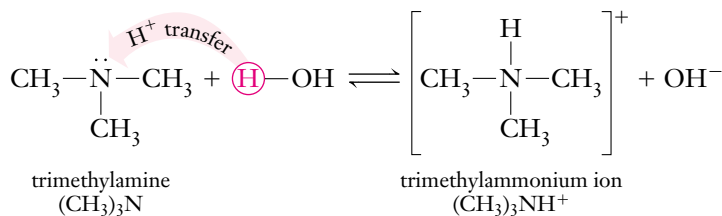
Thus far we have focused our attention on acids. Very few common weak bases are soluble in water. Aqueous ammonia is the most frequently encountered example. From our earlier discussion of bonding in covalent compounds (Section 8-8), we recall that there is one unshared pair of electrons on the nitrogen atom in NH₃. When ammonia dissolves in water, it accepts H⁺ from a water molecule in a reversible reaction (Section 10-4). We say that NH₃ ionizes slightly when it undergoes this reaction. Aqueous solutions of NH₃ are basic because OH⁻ ions are produced.



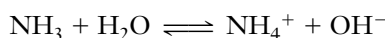
Amines are derivatives of NH₃ in which one or more H atoms have been replaced by organic groups, as the following structures indicate.



Thousands of amines are known, and many are very important in biochemical processes. Low-molecular-weight amines are soluble weak bases. The ionization of trimethylamine, for example, forms trimethylammonium ions and OH⁻ ions.



Now let us consider the behavior of ammonia in aqueous solutions. The reaction of ammonia with water and its ionization constant expression are



and

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

The subscript “b” indicates that the substance ionizes as a base. We do not include [H₂O] in the K_b expression for the same reasons described for K_a.

The fact that K_b for aqueous NH₃ has the same value as K_a for CH₃COOH is pure coincidence. It does tell us that in aqueous solutions of the same concentration, CH₃COOH and NH₃ are ionized to the same extent. Table 18-6 lists K_b and pK_b values for a few common weak bases. Appendix G includes a longer list of K_b values.

We use K_b's for weak bases in the same way we used K_a's for weak acids and pK_b values for weak bases in the same way we used pK_a values for weak acids.

EXAMPLE 18-14 pH of a Weak Base Solution

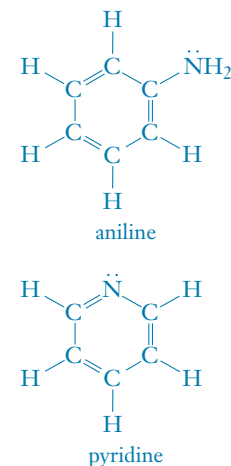
Calculate the [OH⁻], pH, and percent ionization for a 0.20 M aqueous NH₃ solution.

Plan

Write the equation for the ionization of aqueous NH₃ and represent the equilibrium concentrations algebraically. Then, substitute into the K_b expression and solve for [OH⁻] and [NH₃]_{ionized}.

TABLE 18-6 Ionization Constants and pK_b Values for Some Weak Bases

Base	Ionization Reaction	K_b at 25°C	pK_b
ammonia	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.8×10^{-5}	4.74
methylamine	$(\text{CH}_3)\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)\text{NH}_3^+ + \text{OH}^-$	5.0×10^{-4}	3.30
dimethylamine	$(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$	7.4×10^{-4}	3.13
trimethylamine	$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$	7.4×10^{-5}	4.13
pyridine	$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{OH}^-$	1.5×10^{-9}	8.82
aniline	$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	4.2×10^{-10}	9.38

**Solution**

The equation for the ionization of aqueous ammonia and the algebraic representations of equilibrium concentrations follow. Let $x = [\text{NH}_3]_{\text{ionized}}$.

	NH_3	+	H_2O	\rightleftharpoons	NH_4^+	+	OH^-
initial	0.20 M				0 M		≈ 0 M
change due to rxn	$-x$ M				$+x$ M		$+x$ M
at equil	$(0.20 - x)$ M				x M		x M

Substitution into the ionization constant expression gives

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.20 - x)}$$

Again, we can simplify this equation. The small value of K_b tells us that the base is only slightly ionized, so we can assume that $x \ll 0.20$, or $(0.20 - x) \approx 0.20$, and we have

$$\frac{x^2}{0.20} = 1.8 \times 10^{-5} \quad x^2 = 3.6 \times 10^{-6} \quad x = 1.9 \times 10^{-3} \text{ M}$$

Then $[\text{OH}^-] = x = 1.9 \times 10^{-3} \text{ M}$, $\text{pOH} = 2.72$, and $\text{pH} = 11.28$.

$[\text{NH}_3]_{\text{ionized}} = x$, so the percent ionization may be calculated.

$$\% \text{ ionization} = \frac{[\text{NH}_3]_{\text{ionized}}}{[\text{NH}_3]_{\text{initial}}} \times 100\% = \frac{1.9 \times 10^{-3}}{0.20} \times 100\% = 0.95\% \text{ ionized}$$

You should now work Exercises 54 and 110.

EXAMPLE 18-15 Household Ammonia

The pH of a household ammonia solution is 11.50. What is its molarity?

Plan

We are given the pH of an aqueous NH_3 solution. Use $\text{pH} + \text{pOH} = 14.00$ to find pOH, which we can convert to $[\text{OH}^-]$. Then, complete the ionization reaction summary, and substitute the representations of equilibrium concentrations into the K_b expression.

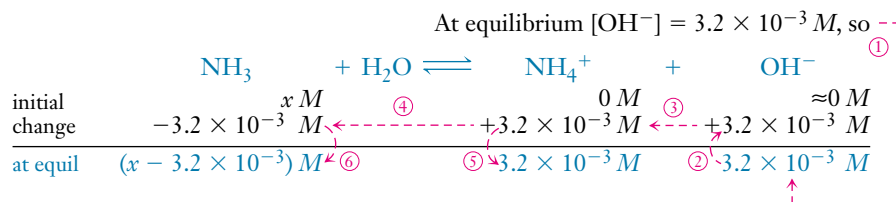
Solution

At equilibrium $\text{pH} = 11.50$; we know that $\text{pOH} = 2.50$, so $[\text{OH}^-] = 10^{-2.50} = 3.2 \times 10^{-3} \text{ M}$. This $[\text{OH}^-]$ results from the reaction, so we can write the change line. Then, letting x represent the initial concentration of NH_3 , we can complete the reaction summary.

The value of x is only about 1% of the original concentration, so the assumption is justified.



Measurement of the pH of a solution of household ammonia.



Substituting these values into the K_b expression for aqueous NH_3 gives

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(3.2 \times 10^{-3})(3.2 \times 10^{-3})}{(x - 3.2 \times 10^{-3})} = 1.8 \times 10^{-5}$$

This suggests that $(x - 3.2 \times 10^{-3}) \approx x$. So we can approximate.

$$\frac{(3.2 \times 10^{-3})(3.2 \times 10^{-3})}{x} = 1.8 \times 10^{-5} \quad \text{and} \quad x = 0.57 \text{ M NH}_3$$

The solution is 0.57 M NH_3 . Our assumption that $(x - 3.2 \times 10^{-3}) \approx x$ is justified.

You should now work Exercises 54, 56, and 58.



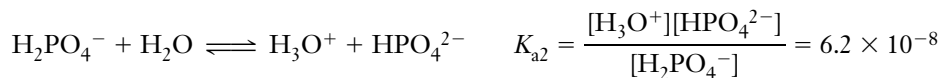
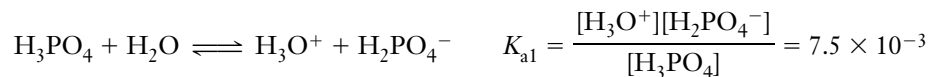
Problem-Solving Tip: It Is Not Always x that Can Be Neglected

Students sometimes wonder about the approximation in Example 18-15, thinking that only x can be neglected. We can consider neglecting one term in an expression only when the expression involves *addition* or *subtraction*. The judgment we must make is whether *either* of the terms is sufficiently smaller than the other that ignoring it would not significantly affect the result. In Example 18-15, x represents the *initial* concentration of NH_3 ; 3.2×10^{-3} represents the concentration that ionizes, which cannot be greater than the original x . We know that NH_3 is a *weak* base ($K_b = 1.8 \times 10^{-5}$), so only a small amount of the original ionizes. We can safely assume that $3.2 \times 10^{-3} \ll x$, so $(x - 3.2 \times 10^{-3}) \approx x$, the approximation that we used in solving the example.

Remember that we can *never* neglect a term in multiplication or division.

18-5 POLYPROTIC ACIDS

Thus far we have considered only *monoprotic* weak acids. Acids that can furnish *two* or more hydronium ions per molecule are called **polyprotic acids**. The ionizations of polyprotic acids occur stepwise, that is, one proton at a time. An ionization constant expression can be written for each step, as the following example illustrates. Consider phosphoric acid as a typical polyprotic acid. It contains three acidic hydrogen atoms and ionizes in three steps.



Each K_a expression includes $[\text{H}_3\text{O}^+]$, so each K_a expression must be satisfied by the *total* concentration of H_3O^+ in the solution.

We see that K_{a1} is much greater than K_{a2} and that K_{a2} is much greater than K_{a3} . This is generally true for polyprotic *inorganic* acids (Appendix F). Successive ionization constants often decrease by a factor of approximately 10^4 to 10^6 , although some differences are outside this range. Large decreases in the values of successive ionization constants mean that each step in the ionization of a polyprotic acid occurs to a much lesser extent than the previous step. Thus, the $[\text{H}_3\text{O}^+]$ produced in the first step is very large compared with the $[\text{H}_3\text{O}^+]$ produced in the second and third steps. As we shall see, except in extremely dilute solutions of H_3PO_4 , the concentration of H_3O^+ may be assumed to be that furnished by the first step in the ionization alone.

EXAMPLE 18-16 Solutions of Weak Polyprotic Acid

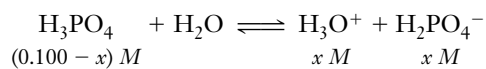
Calculate the concentrations of all species present in 0.100 M H_3PO_4 .

Plan

Because H_3PO_4 contains three acidic hydrogens per formula unit, we show its ionization in three steps. For each step, write the appropriate ionization equation, with its K_a expression and value. Then, represent the equilibrium concentrations from the *first* ionization step, and substitute into the K_{a1} expression. Repeat the procedure for the second and third steps *in order*.

Solution

First we calculate the concentrations of all species that are formed in the first ionization step. Let $x = \text{mol/L}$ of H_3PO_4 that ionize; then $x = [\text{H}_3\text{O}^+]_{1\text{st}} = [\text{H}_2\text{PO}_4^-]$.



Substitution into the expression for K_{a1} gives

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3} = \frac{(x)(x)}{(0.100 - x)}$$

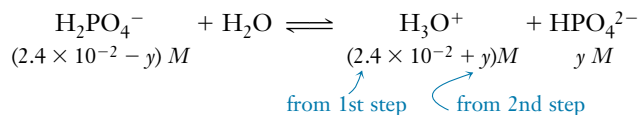
This equation must be solved by the quadratic formula because K_{a1} is too large to neglect x relative to 0.100 M. Solving gives the *positive* root $x = 2.4 \times 10^{-2}$. Thus, from the first step in the ionization of H_3PO_4 ,

$x = -3.1 \times 10^{-2}$ is the extraneous root of the quadratic equation.

$$x M = [\text{H}_3\text{O}^+]_{1\text{st}} = [\text{H}_2\text{PO}_4^-] = 2.4 \times 10^{-2} M$$

$$(0.100 - x) M = [\text{H}_3\text{PO}_4] = 7.6 \times 10^{-2} M$$

For the second step, we use the $[\text{H}_3\text{O}^+]$ and $[\text{H}_2\text{PO}_4^-]$ from the first step. Let $y = \text{mol/L}$ of $\text{H}_2\text{PO}_4^{2-}$ that ionize; then $y = [\text{H}_3\text{O}^+]_{2\text{nd}} = [\text{HPO}_4^{2-}]$.



Substitution into the expression for K_{a2} gives

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.2 \times 10^{-8} = \frac{(2.4 \times 10^{-2} + y)(y)}{(2.4 \times 10^{-2} - y)}$$

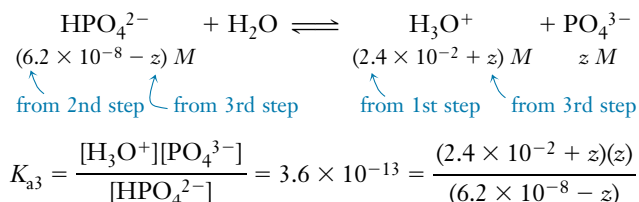
Examination of this equation suggests that $y \ll 2.4 \times 10^{-2}$, so

$$\frac{(2.4 \times 10^{-2})(y)}{(2.4 \times 10^{-2})} = 6.2 \times 10^{-8} \quad y = 6.2 \times 10^{-8} M = [\text{HPO}_4^{2-}] = [\text{H}_3\text{O}^+]_{2\text{nd}}$$

The pH of solutions of most polyprotic acids is governed by the first ionization step.

We see that $[\text{HPO}_4^{2-}] = K_{a2}$ and $[\text{H}_3\text{O}^+]_{2\text{nd}} \ll [\text{H}_3\text{O}^+]_{1\text{st}}$. In general, in solutions of reasonable concentration of weak polyprotic acids for which $K_{a1} \gg K_{a2}$ and that contain no other electrolytes, the concentration of the anion produced in the second ionization step is always equal to K_{a2} .

For the third step, we use $[\text{H}_3\text{O}^+]$ from the first step and $[\text{HPO}_4^{2-}]$ from the second step. Let $z = \text{mol/L}$ of HPO_4^{2-} that ionize; then $z = [\text{H}_3\text{O}^+]_{3\text{rd}} = [\text{PO}_4^{3-}]$.



$[\text{H}_3\text{O}^+]_{2\text{nd}} = y = 6.2 \times 10^{-8}$ was disregarded in the second step and is also disregarded here.

We make the usual simplifying assumption, and find that

$$z M = 9.3 \times 10^{-19} M = [\text{PO}_4^{3-}] = [\text{H}_3\text{O}^+]_{3\text{rd}}$$

The $[\text{H}_3\text{O}^+]$ found in the three steps can be summarized:

$$\begin{array}{l} [\text{H}_3\text{O}^+]_{\text{from 1st step}} = 2.4 \times 10^{-2} M = 0.024 M \\ [\text{H}_3\text{O}^+]_{\text{from 2nd step}} = 6.2 \times 10^{-8} M = 0.000000062 M \\ [\text{H}_3\text{O}^+]_{\text{from 3rd step}} = 9.3 \times 10^{-19} M = 0.00000000000000000093 M \\ \hline [\text{H}_3\text{O}^+]_{\text{total}} = 2.4 \times 10^{-2} M = 0.024 M \end{array}$$

We see that the H_3O^+ furnished by the second and third steps of ionization is negligible compared with that from the first step.

You should now work Exercise 60.

We have calculated the concentrations of the species formed by the ionization of 0.100 M H_3PO_4 . These concentrations are compared in Table 18-7. The concentration of $[\text{OH}^-]$ in 0.100 M H_3PO_4 is included. It was calculated from the known $[\text{H}_3\text{O}^+]$ using the ion product for water, $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$.

Nonionized H_3PO_4 is present in greater concentration than any other species in 0.100 M H_3PO_4 solution. The only other species present in significant concentrations are H_3O^+ and H_2PO_4^- . Similar statements can be made for other weak polyprotic acids for which the last K is very small.

TABLE 18-7 Concentrations of the Species in 0.10 M H_3PO_4 (Example 18-16)

Species	Concentration (mol/L)
H_3PO_4	$7.6 \times 10^{-2} = 0.076$
H_3O^+	$2.4 \times 10^{-2} = 0.024$
H_2PO_4^-	$2.4 \times 10^{-2} = 0.024$
HPO_4^{2-}	$6.2 \times 10^{-8} = 0.000000062$
OH^-	$4.2 \times 10^{-13} = 0.00000000000042$
PO_4^{3-}	$9.3 \times 10^{-19} = 0.00000000000000000093$

Phosphoric acid is a typical *weak* polyprotic acid. Let us now describe solutions of sulfuric acid, a *very strong* polyprotic acid.

EXAMPLE 18-17 Solutions of Strong Polyprotic Acid

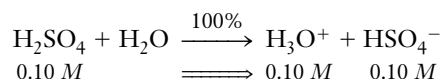
Calculate concentrations of all species present in 0.10 M H_2SO_4 . $K_{a2} = 1.2 \times 10^{-2}$.

Plan

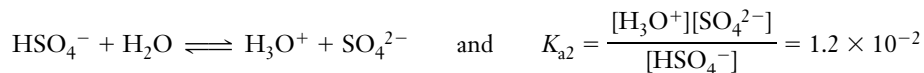
Because the first ionization step of H_2SO_4 is complete, we read the concentrations for the first step from the balanced equation. The second ionization step is *not* complete, and so we write the ionization equation, the K_{a2} expression, and the algebraic representations of equilibrium concentrations. Then we substitute into K_{a2} for H_2SO_4 .

Solution

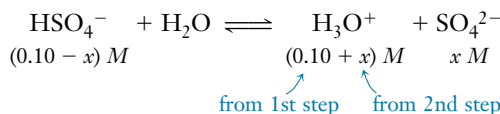
As we pointed out, the first ionization step of H_2SO_4 is complete.



The second ionization step is not complete, however.



Let $x = [\text{HSO}_4^-]$ that ionizes. $[\text{H}_3\text{O}^+]$ is the sum of the concentrations produced in the first and second steps. So we represent the equilibrium concentrations as



Substitution into the ionization constant expression for K_{a2} gives

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 1.2 \times 10^{-2} = \frac{(0.10 + x)(x)}{0.10 - x}$$

Clearly, x cannot be disregarded because K_{a2} is too large. This equation must be solved by the quadratic formula, which gives $x = 0.010$ and $x = -0.12$ (extraneous). So $[\text{H}_3\text{O}^+]_{2\text{nd}} = [\text{SO}_4^{2-}] = 0.010 \text{ M}$. The concentrations of species in 0.10 M H_2SO_4 are

$$\begin{array}{l} [\text{H}_2\text{SO}_4] \approx 0 \text{ M} \quad [\text{HSO}_4^-] = (0.10 - x) \text{ M} = 0.09 \text{ M} \quad [\text{SO}_4^{2-}] = 0.010 \text{ M} \\ [\text{H}_3\text{O}^+] = (0.10 + x) \text{ M} = 0.11 \text{ M} \\ [\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.11} = 9.1 \times 10^{-14} \text{ M} \end{array}$$

In 0.10 M H_2SO_4 solution, the extent of the second ionization step is 10%.

You should now work Exercise 62.

In Table 18-8 we compare 0.10 M solutions of these two polyprotic acids. Their acidities are very different.

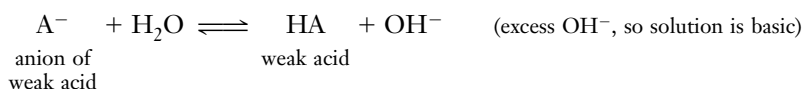


TABLE 18-8 Comparison of 0.10 M Solutions of Two Polyprotic Acids (Examples 18-16, 18-17)

	0.10 M H ₃ PO ₄	0.10 M H ₂ SO ₄
K_{a1}	7.5×10^{-3}	very large
K_{a2}	6.2×10^{-8}	1.2×10^{-2}
K_{a3}	3.6×10^{-13}	—
[H ₃ O ⁺]	$2.4 \times 10^{-2} M$	0.11 M
pH	1.62	0.96
[nonionized molecules]	$7.6 \times 10^{-2} M$	$\approx 0 M$

18-6 SOLVOLYSIS

Solvolysis is the reaction of a substance with the solvent in which it is dissolved. The solvolysis reactions that we will consider in this chapter occur in aqueous solutions so they are called *hydrolysis* reactions. **Hydrolysis** is the reaction of a substance with water. Some hydrolysis reactions involve reaction with H₃O⁺ or OH⁻ ions. One common kind of hydrolysis involves reaction of the anion of a *weak acid* with water to form *nonionized acid* molecules and OH⁻ ions. This upsets the H₃O⁺/OH⁻ balance in water and produces basic solutions. This reaction is usually represented as



Recall that in

$$\text{neutral solutions} \quad [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} M$$

$$\text{basic solutions} \quad [\text{H}_3\text{O}^+] < [\text{OH}^-] \text{ or } [\text{OH}^-] > 1.0 \times 10^{-7} M$$

$$\text{acidic solutions} \quad [\text{H}_3\text{O}^+] > [\text{OH}^-] \text{ or } [\text{H}_3\text{O}^+] > 1.0 \times 10^{-7} M$$

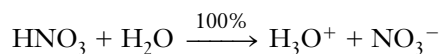
We often omit (aq) from molecules and ions in aqueous solutions to save space and time.

Examples of conjugate acid–base pairs.

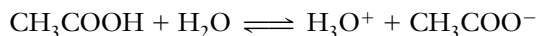
Acid		Conjugate Base
strong (HCl)	→	very weak (Cl ⁻)
weak (HCN)	→	stronger, but still weak (CN ⁻)
Base		Conjugate Acid
strong (OH ⁻)	→	very weak (H ₂ O)
weak (NH ₃)	→	stronger, but still weak (NH ₄ ⁺)

In Brønsted–Lowry terminology anions of strong acids are extremely weak bases, whereas anions of weak acids are stronger bases (Section 10-4). To refresh your memory, consider the following examples.

Nitric acid, a common strong acid, is essentially completely ionized in dilute aqueous solution. *Dilute* aqueous solutions of HNO₃ contain equal concentrations of H₃O⁺ and NO₃⁻ ions. In dilute aqueous solution nitrate ions show almost no tendency to react with H₃O⁺ ions to form nonionized HNO₃; thus, NO₃⁻ is a very weak base.




On the other hand, acetic acid (a weak acid) is only slightly ionized in dilute aqueous solution. Acetate ions have a strong tendency to react with H₃O⁺ to form CH₃COOH molecules. Acetic acid ionizes only slightly.



Hence, the CH_3COO^- ion is a stronger base than the NO_3^- ion, but it is still weak.

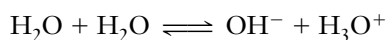
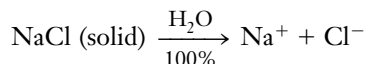
In dilute solutions, strong acids and strong bases are completely ionized or dissociated. In the following sections we consider dilute aqueous solutions of salts. Based on our classification of acids and bases, we can identify four different kinds of salts.

1. Salts of strong bases and strong acids
2. Salts of strong bases and weak acids
3. Salts of weak bases and strong acids
4. Salts of weak bases and weak acids

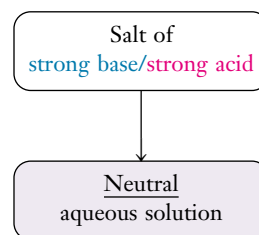
 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 17.10, Acid-Base Properties of Salts.

18-7 SALTS OF STRONG BASES AND STRONG ACIDS

We could also describe these as salts that contain the cation of a strong base and the anion of a strong acid. Salts derived from strong bases and strong acids give *neutral* solutions because neither the cation nor the anion reacts appreciably with H_2O . Consider an aqueous solution of NaCl , which is the salt of the strong base NaOH and the strong acid HCl . Sodium chloride is ionic even in the solid state. It dissociates into hydrated ions in H_2O . H_2O ionizes slightly to produce equal concentrations of H_3O^+ and OH^- ions.

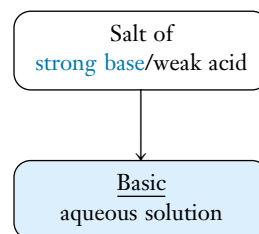
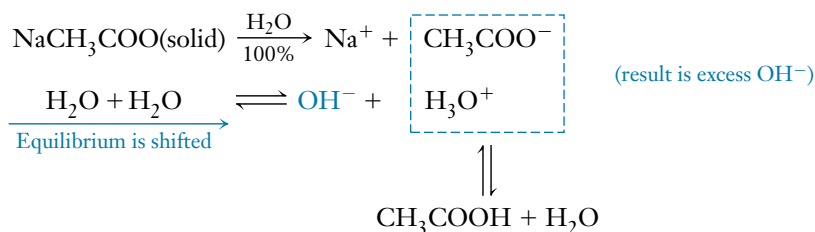


We see that aqueous solutions of NaCl contain four ions, Na^+ , Cl^- , H_3O^+ and OH^- . The cation of the salt, Na^+ , is such a weak acid that it does not react appreciably with water. The anion of the salt, Cl^- , is such a weak base that it does not react appreciably with water. Solutions of salts of strong bases and strong acids are therefore *neutral* because neither ion of such a salt reacts to upset the $\text{H}_3\text{O}^+/\text{OH}^-$ balance in water.



18-8 SALTS OF STRONG BASES AND WEAK ACIDS

When salts derived from strong bases and weak acids are dissolved in water, the resulting solutions are always basic. This is because anions of weak acids react with water to form hydroxide ions. Consider a solution of sodium acetate, NaCH_3COO , which is the salt of the strong base NaOH and the weak acid CH_3COOH . It is soluble and dissociates completely in water.



Acetate ion is the conjugate base of a *weak* acid, CH_3COOH . Thus, it combines to some extent with H_3O^+ to form CH_3COOH . As H_3O^+ is removed from the solution, causing

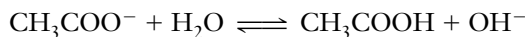
This is like the reaction of a molecular weak base



(excess OH^- is produced; the solution becomes basic)

Just as we can write a K_b expression to describe the extent of ionization of NH_3 , we can do the same for the acetate ion.

more H_2O to ionize, an excess of OH^- builds up. So the solution becomes basic. The net result of the preceding equations can be written as a single equation. This equation describes the **hydrolysis of acetate ions**.



The equilibrium constant for this reaction is called a (base) hydrolysis constant, or K_b for CH_3COO^- .

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad (K_b \text{ for } \text{CH}_3\text{COO}^-)$$

We can evaluate this equilibrium constant from other known expressions. We multiply the preceding expression by $[\text{H}_3\text{O}^+]/[\text{H}_3\text{O}^+]$ to give

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{[\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]} \times \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{1}$$

We recognize that

$$K_b = \frac{1}{K_a(\text{CH}_3\text{COOH})} \times \frac{K_w}{1} = \frac{K_w}{K_a(\text{CH}_3\text{COOH})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

which gives

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = 5.6 \times 10^{-10}$$

We have calculated K_b , the hydrolysis constant for the acetate ion, CH_3COO^- .

We can do the same kind of calculations for the anion of any weak monoprotic acid and find that $K_b = K_w/K_a$, where K_a refers to the ionization constant for the weak monoprotic acid from which the anion is derived.

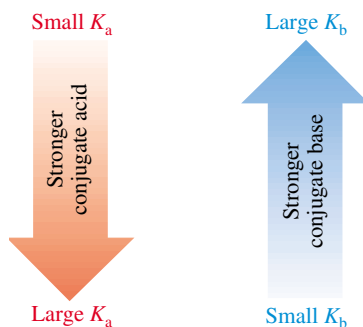
This equation can be rearranged to

$$K_w = K_a K_b \quad (\text{valid for any conjugate acid-base pair in aqueous solution})$$

If either K_a or K_b is known, the other can be calculated.

Base hydrolysis constants, K_b 's, for anions of weak acids can be determined experimentally. The values obtained from experiments agree with the calculated values. Please note that this K_b refers to a reaction in which the anion of a weak acid acts as a base.

For conjugate acid-base pairs



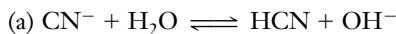
EXAMPLE 18-18 K_b for the Anion of a Weak Acid

(a) Write the equation for the reaction of the base CN^- with water. (b) The value of the ionization constant for hydrocyanic acid, HCN , is 4.0×10^{-10} . What is the value of K_b for the cyanide ion, CN^- ?

Plan

(a) The base CN^- accepts H^+ from H_2O to form the weak acid HCN and OH^- ions. (b) We know that $K_a K_b = K_w$. So we solve for K_b and substitute into the equation.

Solution



(b) We are given $K_a = 4.0 \times 10^{-10}$ for HCN , and we know that $K_w = 1.0 \times 10^{-14}$.

$$K_{b(\text{CN}^-)} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5}$$

You should now work Exercises 78 and 80.

EXAMPLE 18-19 Calculations Based on Hydrolysis

Calculate $[\text{OH}^-]$, pH, and the percent hydrolysis for 0.10 M solutions of (a) sodium acetate, NaCH_3COO , and (b) sodium cyanide, NaCN . Both NaCH_3COO and NaCN are soluble ionic salts that are completely dissociated in H_2O . From the text, K_b for $\text{CH}_3\text{COO}^- = 5.6 \times 10^{-10}$; from Example 18-18, K_b for $\text{CN}^- = 2.5 \times 10^{-5}$.

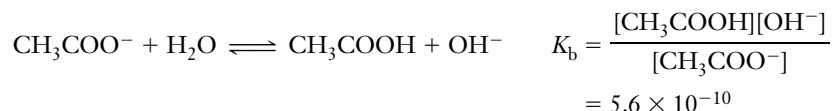
If we did not know K_b , we could use $K_{a(\text{HCN})}$ to find $K_{b(\text{CN}^-)}$.

Plan

We recognize that both NaCH_3COO and NaCN are salts of strong bases and weak acids. The anions in such salts hydrolyze to give basic solutions. As we have done before, we first write the appropriate chemical equation and equilibrium constant expression. Then we complete the reaction summary, substitute the algebraic representations of equilibrium concentrations into the equilibrium constant expression, and solve for the unknown concentration(s).

Solution

(a) The overall equation for the reaction of CH_3COO^- with H_2O and its equilibrium constant expression are



Let $x = \text{mol/L}$ of CH_3COO^- that hydrolyzes. Then $x = [\text{CH}_3\text{COOH}] = [\text{OH}^-]$.

	$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{COOH} + \text{OH}^-$		
initial	0.10 M	0 M	≈ 0 M
change due to rxn	$-x$ M	$+x$ M	$+x$ M
at equil	$(0.10 - x)$ M	x M	x M

Because the value of K_b (5.6×10^{-10}) is quite small, we know that the reaction does not go very far. We can assume $x \ll 0.10$, so $(0.10 - x) \approx 0.10$; this lets us simplify the equation to

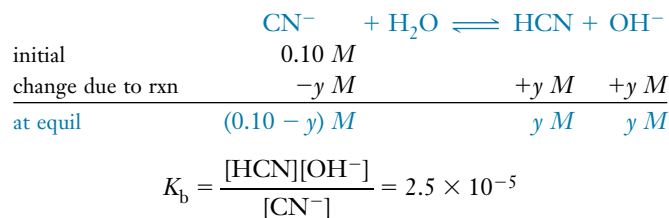
$$5.6 \times 10^{-10} = \frac{(x)(x)}{0.10} \quad \text{so} \quad x = 7.5 \times 10^{-6}$$

$$x = 7.5 \times 10^{-6} \text{ M} = [\text{OH}^-] \quad \text{pOH} = 5.12 \quad \text{and} \quad \text{pH} = 8.88$$

The 0.10 M NaCH_3COO solution is distinctly basic.

$$\begin{aligned} \% \text{ hydrolysis} &= \frac{[\text{CH}_3\text{COO}^-]_{\text{hydrolyzed}}}{[\text{CH}_3\text{COO}^-]_{\text{initial}}} \times 100\% = \frac{7.5 \times 10^{-6} \text{ M}}{0.10 \text{ M}} \times 100\% \\ &= 0.0075\% \text{ hydrolysis} \end{aligned}$$

(b) Perform the same kind of calculation for 0.10 M NaCN . Let $y = \text{mol/L}$ of CN^- that hydrolyzes. Then $y = [\text{HCN}] = [\text{OH}^-]$.



Substitution into this expression gives

$$\frac{(y)(y)}{(0.10 - y)} = 2.5 \times 10^{-5} \quad \text{so} \quad y = 1.6 \times 10^{-3} \text{ M}$$

$$y = [\text{OH}^-] = 1.6 \times 10^{-3} \text{ M} \quad \text{pOH} = 2.80 \quad \text{and} \quad \text{pH} = 11.20$$

The 0.10 M NaCN solution is even more basic than the 0.10 M NaCH₃COO solution in part (a).

$$\begin{aligned}
 \% \text{ hydrolysis} &= \frac{[\text{CN}^-]_{\text{hydrolyzed}}}{[\text{CN}^-]_{\text{initial}}} \times 100\% = \frac{1.6 \times 10^{-3} \text{ M}}{0.10 \text{ M}} \times 100\% \\
 &= 1.6\% \text{ hydrolysis}
 \end{aligned}$$

You should now work Exercises 83 and 84.



The pH of 0.10 M NaCH₃COO is 8.88. The pH of 0.10 M NaCN is 11.20. An inert solid has been suspended in the liquids to improve the quality of photographs of pH meters.

The 0.10 M solution of NaCN is much more basic than the 0.10 M solution of NaCH₃COO because CN⁻ is a much stronger base than CH₃COO⁻. This is expected because HCN is a much weaker acid than CH₃COOH so that the K_b for CN⁻ is much larger than the K_b for CH₃COO⁻.

The percent hydrolysis for 0.10 M CN⁻ (1.6%) is about 210 times greater than the percent hydrolysis for 0.10 M CH₃COO⁻ (0.0075%). In Table 18-9 we compare 0.10 M solutions of CH₃COO⁻, CN⁻, and NH₃ (the familiar molecular weak base). We see that CH₃COO⁻ is a much weaker base than NH₃, whereas CN⁻ is a slightly stronger base than NH₃.

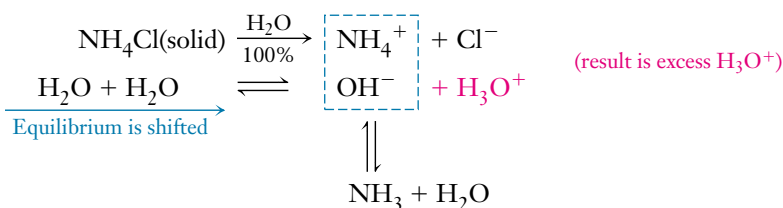
TABLE 18-9 Data for 0.10 M Solutions of NaCH₃COO, NaCN, and NH₃

	0.10 M NaCH ₃ COO	0.10 M NaCN	0.10 M aq NH ₃
K _a for parent acid	1.8 × 10 ⁻⁵	4.0 × 10 ⁻¹⁰	
K _b for anion	5.6 × 10 ⁻¹⁰	2.5 × 10 ⁻⁵	K _b for NH ₃ = 1.8 × 10 ⁻⁵
[OH ⁻]	7.5 × 10 ⁻⁶ M	1.6 × 10 ⁻³ M	1.3 × 10 ⁻³ M
% hydrolysis	0.0075%	1.6%	1.3% ionized
pH	8.88	11.20	11.11

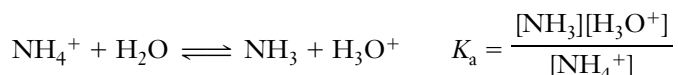
18-9 SALTS OF WEAK BASES AND STRONG ACIDS

The second common kind of hydrolysis reaction involves the reaction of the cation of a weak base with water to form nonionized molecules of the weak base and H₃O⁺ ions. This upsets the H₃O⁺/OH⁻ balance in water, giving an excess of H₃O⁺, and making such solutions *acidic*. Consider a solution of ammonium chloride, NH₄Cl, the salt of aqueous NH₃ and HCl.

Ammonium chloride is an ionic salt that is soluble in water.



Ammonium ions from NH_4Cl react to some extent with OH^- to form nonionized NH_3 and H_2O molecules. This reaction removes OH^- from the system, so it causes more H_2O to ionize to produce an excess of H_3O^+ . The net result of the preceding equations can be written as a single equation with its equilibrium constant expression.



The expression $K_w = K_a K_b$ is valid for *any* conjugate acid–base pair in aqueous solution. We use it for the $\text{NH}_4^+/\text{NH}_3$ pair.

$$K_a(\text{NH}_4^+) = \frac{K_w}{K_b(\text{NH}_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

The fact that K_a for the ammonium ion, NH_4^+ , is the same as K_b for the acetate ion should not be surprising. Recall that the ionization constants for CH_3COOH and aqueous NH_3 are equal (by coincidence). Thus, we expect CH_3COO^- to hydrolyze to the same extent as NH_4^+ does.

EXAMPLE 18-20 pH of a Soluble Salt

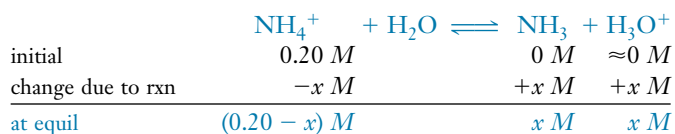
Calculate the pH of a 0.20 M solution of ammonium nitrate, NH_4NO_3 . K_a for $\text{NH}_4^+ = 5.6 \times 10^{-10}$.

Plan

We recognize that NH_4NO_3 is the salt of a weak base, NH_3 , and a strong acid, HNO_3 , and that the cations of such salts hydrolyze to give acidic solutions. We proceed as we did in Example 18-19.

Solution

The cation of the weak base reacts with H_2O . Let $x = \text{mol/L}$ of NH_4^+ that hydrolyzes. Then $x = [\text{NH}_3] = [\text{H}_3\text{O}^+]$.

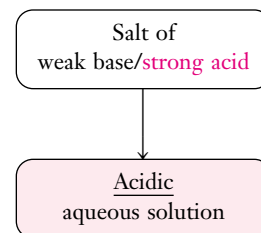


Substituting into the K_a expression gives

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(x)(x)}{(0.20 - x)} = 5.6 \times 10^{-10}$$

Making the usual simplifying assumption gives $x = 1.1 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$ and $\text{pH} = 4.96$. The 0.20 M NH_4NO_3 solution is distinctly acidic.

You should now work Exercise 90.



Similar equations can be written for cations derived from other weak bases such as CH_3NH_3^+ and $(\text{CH}_3)_2\text{NH}_2^+$.

If you wish to derive $K_a = K_w/K_b$ for this case, multiply the K_b expression by $[\text{OH}^-]/[\text{OH}^-]$ and simplify.

Ammonium nitrate is widely used as a fertilizer because of its high nitrogen content. It contributes to soil acidity.



The pH of 0.20 M NH_4NO_3 solution is 4.96.



Taming Acids with Harmless Salts

From yellowing paper in old books and newsprint to heartburn and environmental spills, many Americans encounter unwanted or excessive amounts of acid. Neutralizing unwanted acids with hydroxide bases might appear to be a good way to combat these acids. But even more effective chemicals exist that can neutralize acids without the risks posed by hydroxide bases. These acid-neutralizing chemicals are salts of weak acids and strong bases. Such salts can neutralize acids because hydrolysis makes their aqueous solutions basic. More importantly, there is a significant advantage in using relatively harmless salts such as sodium hydrogen carbonate (baking soda) rather than stronger bases such as sodium hydroxide (lye). For example, if we used too much sodium hydroxide to neutralize sulfuric acid spilled from a car battery, any excess lye left behind would pose an environmental and human health threat about equal to that of the spilled sulfuric acid. (Lye is the major ingredient in such commercial products as oven cleaners and Drano.) We would not be concerned, however, if a little baking soda were left on the ground after the sulfuric acid from the car battery had been neutralized.

The same principle applies to acid indigestion. Rather than swallow lye (ugh!) or some other strong base to neutralize excess stomach acid, most people take antacids. Antacids typically contain salts such as calcium carbonate, sodium hydrogen carbonate (sodium bicarbonate), and magnesium carbonate, all of which are salts of weak acids. These

salts hydrolyze to form hydroxide ions that reduce the degree of acidity in the stomach. Physicians also prescribe these and similar salts to treat peptic ulcers. The repeated use of antacids should always be under the supervision of a physician.

Salts of weak acids and strong bases can be used effectively against a major acid spill in much the same way they are used against sulfuric acid from a car battery or excess stomach acid. In a recent major acid spill, a tank car filled with nitric acid was punctured by the coupling of another rail car, spilling 22,000 gallons of concentrated nitric acid onto the ground. Many thousand residents living near the spill were evacuated. There were no fatalities or serious injuries, and there was no major environmental damage; resident fire fighters neutralized the concentrated nitric acid by using airport snow blowers to spread *relatively* harmless sodium carbonate (washing soda) over the contaminated area.

Salts of weak acids and strong bases are also being used to combat the destructive aging process of paper. Think how serious this problem is for the Library of Congress, which loses 70,000 books each year to the decomposition of aging paper. Many of the twenty million books in the Library of Congress have a life expectancy of only 25 to 40 years. Paper ages because of the hydrolysis of aluminum sulfate. Aluminum sulfate has been used in the paper manufacturing process since the 1850s because it is an inexpensive sizing compound (it keeps ink from spreading out on paper). Aluminum sulfate is the salt of an insoluble weak base and a strong acid; it hydrolyzes in the water in paper (typically 4–7% H₂O) to give an acidic environment. The acid eats away at cellulose fibers, which causes the paper to turn yellow and eventually disintegrate. To combat this aging, the Library of Congress individually treats its collections with solutions of salts of weak acids and strong bases at great cost. Meanwhile, the paper industry is fighting this aging process by increasing its output of alkaline paper. Some alkaline paper contains calcium carbonate, the same salt found in several brands of antacids. Calcium carbonate increases the pH of paper to between 7.5 and 8.5. Special manufacturing techniques produce calcium carbonate that is very fine and that has uniform particle size. Alkaline papers are expected to last about 300 years, in contrast to the average 25- to 40-year life expectancy of standard acidic paper.

Salts that hydrolyze to produce basic solutions can settle upset stomachs, prevent yellowing pages, and neutralize major and minor acid spills. A knowledge of hydrolysis is very useful and has many applications.



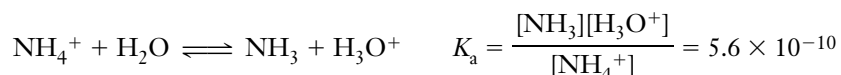
Ronald DeLorenzo
Middle Georgia College

18-10 SALTS OF WEAK BASES AND WEAK ACIDS

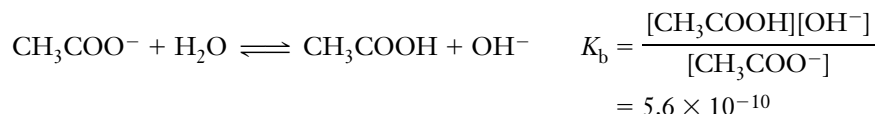
Salts of weak bases and weak acids are the fourth class of salts. Most are soluble. Salts of weak bases and weak acids contain cations that would give acidic solutions and anions that would give basic solutions. Will solutions of such salts be neutral, basic, or acidic? They may be any one of the three depending on the relative strengths of the weak molecular acid and weak molecular base from which each salt is derived. Thus, salts of this class may be divided into three types that depend on the relative strengths of their parent weak bases and weak acids.

Salts of Weak Bases and Weak Acids for Which $K_b = K_a$

The common example of a salt of this type is ammonium acetate, $\text{NH}_4\text{CH}_3\text{COO}$, the salt of aqueous NH_3 and CH_3COOH . The ionization constants for both aqueous NH_3 and CH_3COOH are 1.8×10^{-5} . We know that ammonium ions react with water to produce H_3O^+ .



We also recall that acetate ions react with water to produce OH^- .

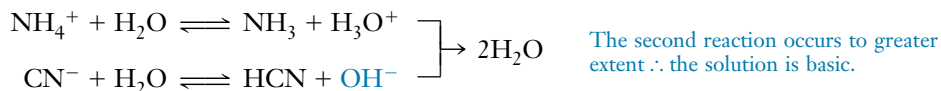


Because these K values are equal, the NH_4^+ produces just as many H_3O^+ ions as the CH_3COO^- produces OH^- ions. Thus, we predict that ammonium acetate solutions are neutral, and they are. There are very few salts that have cations and anions with equal K values.

Salts of Weak Bases and Weak Acids for Which $K_b > K_a$

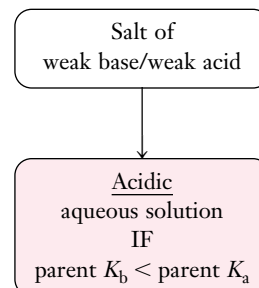
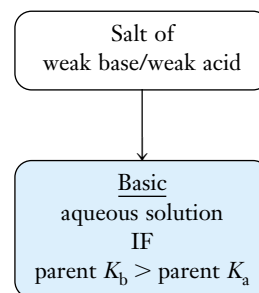
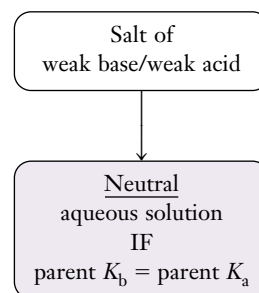
Salts of weak bases and weak acids for which K_b is greater than K_a are always basic because the anion of the weaker acid hydrolyzes to a greater extent than the cation of the stronger base.

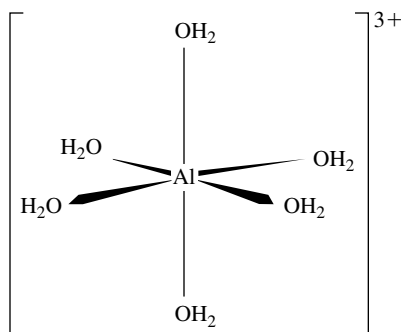
Consider NH_4CN , ammonium cyanide. K_a for HCN (4.0×10^{-10}) is much smaller than K_b for NH_3 (1.8×10^{-5}), so K_b for CN^- (2.5×10^{-5}) is much larger than K_a for NH_4^+ (5.6×10^{-10}). This tells us that the CN^- ions hydrolyze to a much greater extent than do NH_4^+ ions, and so ammonium cyanide solutions are distinctly basic. Stated differently, CN^- is much stronger as a base than NH_4^+ is as an acid.



Salts of Weak Bases and Weak Acids for Which $K_b < K_a$

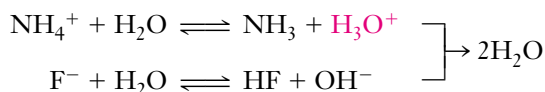
Salts of weak bases and weak acids for which K_b is less than K_a are acidic because the cation of the weaker base hydrolyzes to a greater extent than the anion of the stronger



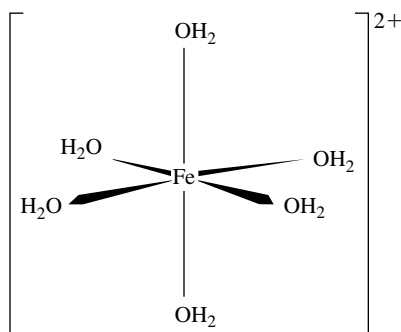


acid. Consider ammonium fluoride, NH_4F , the salt of aqueous ammonia and hydrofluoric acid.

K_b for aqueous NH_3 is 1.8×10^{-5} and K_a for HF is 7.2×10^{-4} . So the K_a value for NH_4^+ (5.6×10^{-10}) is slightly larger than the K_b value for F^- (1.4×10^{-11}). This tells us that NH_4^+ ions hydrolyze to a slightly greater extent than F^- ions. In other words, NH_4^+ is slightly stronger as an acid than F^- is as a base. Ammonium fluoride solutions are slightly acidic.



The first reaction occurs to greater extent \therefore the solution is acidic.



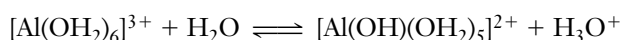
(a)

18-11 SALTS THAT CONTAIN SMALL, HIGHLY CHARGED CATIONS

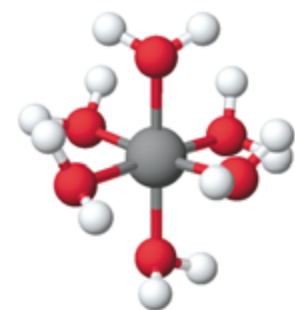
Solutions of certain common salts of strong acids are acidic. For this reason, many homeowners apply iron(II) sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, or aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, to the soil around “acid-loving” plants such as azaleas, camelias, and hollies. You have probably tasted the sour, “acid” taste of alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, a substance that is frequently added to pickles.

Each of these salts contains a small, highly charged cation and the anion of a strong acid. Solutions of such salts are acidic because these cations hydrolyze to produce excess hydronium ions. Consider aluminum chloride, AlCl_3 , as a typical example. When solid anhydrous AlCl_3 is added to water, the water becomes very warm as the Al^{3+} ions become hydrated in solution. In many cases, the interaction between positively charged ions and the negative ends of polar water molecules is so strong that salts crystallized from aqueous solution contain definite numbers of water molecules. Salts containing Al^{3+} , Fe^{2+} , Fe^{3+} , and Cr^{3+} ions usually crystallize from aqueous solutions with six water molecules bonded to each metal ion. These salts contain the hydrated cations $[\text{Al}(\text{OH}_2)_6]^{3+}$, $[\text{Fe}(\text{OH}_2)_6]^{2+}$, $[\text{Fe}(\text{OH}_2)_6]^{3+}$, and $[\text{Cr}(\text{OH}_2)_6]^{3+}$, respectively, in the solid state. Such species also exist in aqueous solutions. Each of these species is octahedral, meaning that the metal ion (M^{n+}) is located at the center of a regular octahedron, and the O atoms in six H_2O molecules are located at the corners (Figure 18-3). In the metal–oxygen bonds of the hydrated cation, electron density is decreased around the O end of each H_2O molecule by the positively charged metal ion. This weakens the H–O bonds in coordinated H_2O molecules relative to the H–O bonds in noncoordinated H_2O molecules. Consequently, the coordinated H_2O molecules can donate H^+ to solvent H_2O molecules to form H_3O^+ ions. This produces acidic solutions (Figure 18-4).

The equation for the hydrolysis of hydrated Al^{3+} is written as follows.



$$K_a = \frac{[[\text{Al}(\text{OH})(\text{OH}_2)_5]^{2+}][\text{H}_3\text{O}^+]}{[[\text{Al}(\text{OH}_2)_6]^{3+}]} = 1.2 \times 10^{-5}$$



(b)

Figure 18-3 (a) Lewis structures of hydrated aluminum ions, $[\text{Al}(\text{OH}_2)_6]^{3+}$, and hydrated iron(II) ions, $[\text{Fe}(\text{OH}_2)_6]^{2+}$. (b) Ball-and-stick models of these ions.

Removing an H^+ converts a coordinated water molecule to a coordinated hydroxide ion and decreases the positive charge on the hydrated species.

Hydrolysis of hydrated small, highly charged cations may occur beyond the first step. In many cases these reactions are quite complex. They may involve two or more cations reacting with each other to form large polymeric species. For most common hydrated cations, consideration of the first hydrolysis constant is adequate for our calculations.

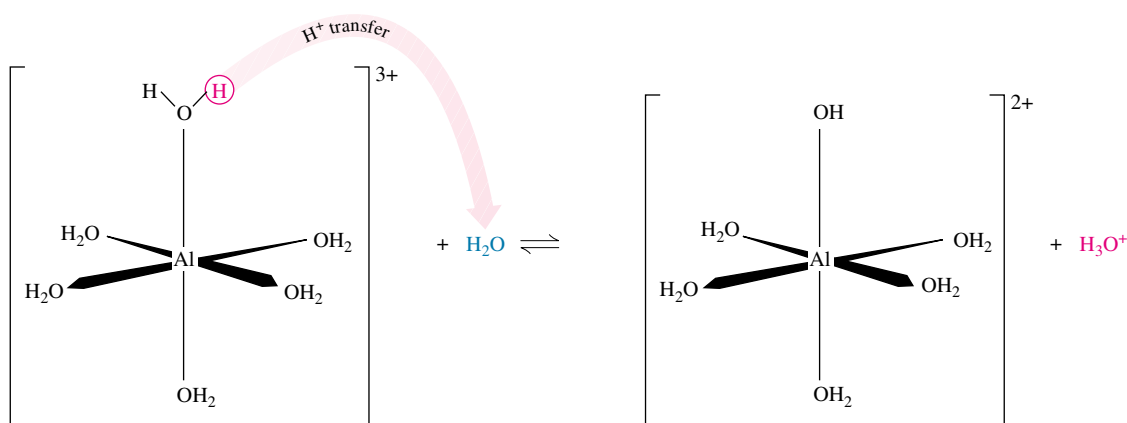


Figure 18-4 Hydrolysis of hydrated aluminum ions to produce H_3O^+ —that is, the removal of a proton from a coordinated H_2O molecule by a noncoordinated one.

EXAMPLE 18-21 Percent Hydrolysis

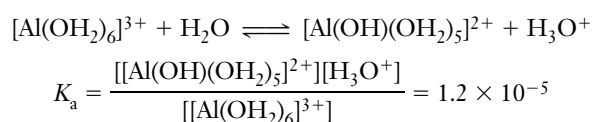
Calculate the pH and percent hydrolysis in 0.10 M AlCl_3 solution. $K_a = 1.2 \times 10^{-5}$ for $[\text{Al}(\text{OH}_2)_6]^{3+}$ (often abbreviated Al^{3+}).

Plan

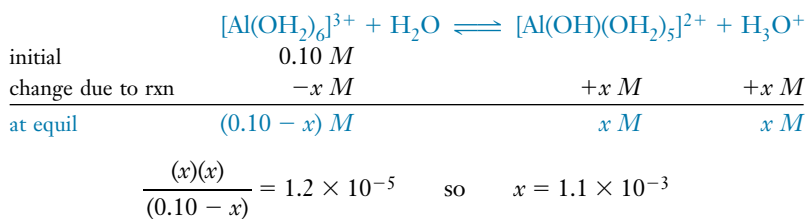
We recognize that AlCl_3 produces a hydrated, small, highly charged cation that hydrolyzes to give an acidic solution. We represent the equilibrium concentrations and proceed as we did in earlier examples.

Solution

The equation for the reaction and its hydrolysis constant can be represented as



Let $x = \text{mol/L}$ of $[\text{Al}(\text{OH}_2)_6]^{3+}$ that hydrolyzes. Then $x = [\text{Al}(\text{OH})(\text{OH}_2)_5]^{2+} = [\text{H}_3\text{O}^+]$.



$[\text{H}_3\text{O}^+] = 1.1 \times 10^{-3} M$, $\text{pH} = 2.96$, and the solution is quite acidic.

$$\% \text{ hydrolysis} = \frac{[\text{Al}^{3+}]_{\text{hydrolyzed}}}{[\text{Al}^{3+}]_{\text{initial}}} \times 100\% = \frac{1.1 \times 10^{-3} M}{0.10 M} \times 100\% = 1.1\% \text{ hydrolyzed}$$

As a reference point, CH_3COOH is 1.3% ionized in 0.10 M solution (see Example 18-11). In 0.10 M solution AlCl_3 is 1.1% hydrolyzed. The acidities of the two solutions are very similar.

You should now work Exercise 96.



The blue color and the acidity of a 0.10 M CuSO_4 solution are both due to the hydrated Cu^{2+} ion.

$[\text{Al}(\text{OH}_2)_6]^{3+}$ is often abbreviated as Al^{3+} . Recall that x represents the concentration of Al^{3+} that hydrolyzes.

The pH of 0.10 M AlCl_3 is 2.96. The pH of 0.10 M CH_3COOH is 2.89.



Pepto-Bismol contains $\text{BiO}(\text{HOC}_4\text{H}_6\text{COO})$, bismuth subsalicylate, a *hydrolyzed* bismuth salt. Such salts “coat” polar surfaces such as glass and the lining of the stomach.

TABLE 18-10 *Ionic Radii and Hydrolysis Constants for Some Cations*

Cation	Ionic Radius (Å)	Hydrated Cation	K_a
Li^+	0.90	$[\text{Li}(\text{OH}_2)_4]^+$	1×10^{-14}
Be^{2+}	0.59	$[\text{Be}(\text{OH}_2)_4]^{2+}$	1.0×10^{-5}
Na^+	1.16	$[\text{Na}(\text{OH}_2)_6]^+$ (?)	10^{-14}
Mg^{2+}	0.85	$[\text{Mg}(\text{OH}_2)_6]^{2+}$	3.0×10^{-12}
Al^{3+}	0.68	$[\text{Al}(\text{OH}_2)_6]^{3+}$	1.2×10^{-5}
Fe^{2+}	0.76	$[\text{Fe}(\text{OH}_2)_6]^{2+}$	3.0×10^{-10}
Fe^{3+}	0.64	$[\text{Fe}(\text{OH}_2)_6]^{3+}$	4.0×10^{-3}
Co^{2+}	0.74	$[\text{Co}(\text{OH}_2)_6]^{2+}$	5.0×10^{-10}
Co^{3+}	0.63	$[\text{Co}(\text{OH}_2)_6]^{3+}$	1.7×10^{-2}
Cu^{2+}	0.96	$[\text{Cu}(\text{OH}_2)_6]^{2+}$	1.0×10^{-8}
Zn^{2+}	0.74	$[\text{Zn}(\text{OH}_2)_6]^{2+}$	2.5×10^{-10}
Hg^{2+}	1.10	$[\text{Hg}(\text{OH}_2)_6]^{2+}$	8.3×10^{-7}
Bi^{3+}	0.74	$[\text{Bi}(\text{OH}_2)_6]^{3+}$	1.0×10^{-2}

Smaller, more highly charged cations are stronger acids than larger, less highly charged cations (Table 18-10). This is because the smaller, more highly charged cations interact with coordinated water molecules more strongly.

For isoelectronic cations in the same period in the periodic table, the smaller, more highly charged cation is the stronger acid. (Compare K_a values for hydrated Li^+ and Be^{2+} and for hydrated Na^+ , Mg^{2+} , and Al^{3+} .) For cations with the same charge from the same group in the periodic table, the smaller cation hydrolyzes to a greater extent. (Compare K_a values for hydrated Be^{2+} and Mg^{2+} .) If we compare cations of the same element in different oxidation states, the smaller, more highly charged cation is the stronger acid. (Compare K_a values for hydrated Fe^{2+} and Fe^{3+} and for hydrated Co^{2+} and Co^{3+} .)

Key Terms

Amines Derivatives of ammonia in which one or more hydrogen atoms has been replaced by organic groups.

Hydrolysis The reaction of a substance with water.

Hydrolysis constant An equilibrium constant for a hydrolysis reaction.

Indicator An organic compound that exhibits different colors in solutions of different acidities.

Ion product for water An equilibrium constant for the ionization of water,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

Ionization constant An equilibrium constant for the ionization of a weak electrolyte.

Monoprotic acid An acid that can form only one hydronium ion per molecule; may be strong or weak.

pH The negative logarithm of the concentration (mol/L) of the H_3O^+ (or H^+) ion; the commonly used scale ranges from 0 to 14.

$\text{p}K_a$ The negative logarithm of K_a , the ionization constant for a weak acid.

$\text{p}K_b$ The negative logarithm of K_b , the ionization constant for a weak base.

$\text{p}K_w$ The negative logarithm of the ion product for water.

pOH The negative logarithm of the concentration (mol/L) of the OH^- ion; the commonly used scale ranges from 14 to 0.

Polyprotic acid An acid that can form two or more hydronium ions per molecule.

Solvolysis The reaction of a substance with the solvent in which it is dissolved.

Exercises

NOTE All exercises in this chapter assume a temperature of 25°C unless they specify otherwise. All logarithms are common (base 10).

Review of Strong Electrolytes

- List names and formulas for (a) the common strong acids; (b) six weak bases; (c) the common strong bases; (d) ten soluble ionic salts.
- (a) How are a strong acid and a weak acid similar? How are they different? (b) How are a strong base and a weak base similar? How are they different?
- Which of the following are strong electrolytes: Group IA hydroxide, Group IIIA hydroxide, $\text{Zn}(\text{OH})_2$, $\text{Be}(\text{OH})_2$, H_3AsO_3 , HBr , H_3PO_4 , salt of a Group IA metal?
- Calculate the molarity of each of the following solutions. (a) 17.52 g of NaCl in 125 mL of solution; (b) 50.5 g of H_2SO_4 in 575 mL of solution; (c) 0.135 g of phenol, $\text{C}_6\text{H}_5\text{OH}$, in 1.5 L of solution.
- Square brackets, [], are often used in some mathematical statements in chemistry. What is the meaning associated with square brackets?
- Calculate the concentrations of the constituent ions in solutions of the following compounds in the indicated concentrations. (a) 0.25 M HBr ; (b) 0.055 M KOH ; (c) 0.0155 M CaCl_2 .
- Calculate the concentrations of the constituent ions in solutions of the following compounds in the indicated concentrations. (a) 0.050 M $\text{Sr}(\text{OH})_2$; (b) 0.050 M HClO_3 ; (c) 0.0040 M K_2SO_4 .
- Calculate the concentrations of the constituent ions in the following solutions. (a) 2.55 g of KOH in 1.50 L of solution; (b) 0.720 g of $\text{Ba}(\text{OH})_2$ in 250. mL of solution; (c) 1.64 g of $\text{Ca}(\text{NO}_3)_2$ in 100. mL of solution.
- Calculate the concentrations of the constituent ions in the following solutions. (a) 1.77 g of $\text{Al}_2(\text{SO}_4)_3$ in 400. mL of solution; (b) 75.8 g of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in 8.00 L of solution; (c) 18.4 g of HBr in 675 mL of solution.

The Autoionization of Water

- (a) Write a chemical equation showing the ionization of water. (b) Write the equilibrium constant expression for this equation. (c) What is the special symbol used for this equilibrium constant? (d) What is the relationship between $[\text{H}^+]$ and $[\text{OH}^-]$ in pure water? (e) How can this relationship be used to define the terms “acidic” and “basic”?
- Use K_w to explain the relationship between the hydronium ion concentration and the hydroxide ion concentration in aqueous solutions.

- (a) Why is the concentration of OH^- produced by the ionization of water neglected in calculating the concentration of OH^- in a 0.10 M solution of NaOH ? (b) Demonstrate that it (OH^- from H_2O) may be neglected.
- Calculate the concentrations of OH^- in the solutions described in Exercises 6(a), 7(b), and 9(c), and compare them with the OH^- concentration in pure water.
- Calculate the concentrations of H_3O^+ in the solutions described in Exercises 6(b), 7(a), and 8(b), and compare them with the H_3O^+ concentration in pure water.
- Calculate $[\text{OH}^-]$ that is in equilibrium with (a) $[\text{H}_3\text{O}^+] = 2.9 \times 10^{-4}$ mol/L (b) $[\text{H}_3\text{O}^+] = 8.5 \times 10^{-9}$ mol/L
- Calculate $[\text{H}_3\text{O}^+]$ that is in equilibrium with $[\text{OH}^-] = 5.62 \times 10^{-6}$ mol/L

The pH and pOH Scales

- Write mathematical definitions for pH and pOH. What is the relationship between pH and pOH? How can pH be used to define the terms “acidic” and “basic”?
- What are the logarithms of the following numbers? (a) 0.000052; (b) 15.2; (c) 5.8×10^{-12} ; (d) 4.9×10^{-7} .
- A sample of milk is found to have a pH of 6.50. What are the concentrations of H_3O^+ and OH^- ions in this sample?
- The normal pH of human blood ranges from 7.35 to 7.45. Calculate the concentrations of H_3O^+ and OH^- ions in human blood that has a pH of 7.45.
- Calculate the pH of a 1.25×10^{-4} M solution of HClO_4 , a strong acid, at 25°C.
- Calculate the pH of the following solutions. (a) 6.00×10^{-1} M HCl ; (b) 0.030 M HNO_3 ; (c) $0.75 \text{ g} \cdot \text{L}^{-1}$ HClO_4 .
- Calculate the pH of the following solutions. (a) 7.5×10^{-2} M HBr ; (b) 0.0062 M HI ; (c) 2.84 g HNO_3 in 250. mL solution.
- Calculate the pH of a 1.8×10^{-4} M solution of NaOH .
- Calculate the pH of a 1.5×10^{-11} M solution of HCl .
- A solution of HNO_3 has a pH of 3.32. What is the molarity of the solution?
- Complete the following table. Is there an obvious relationship between pH and pOH? What is it?

Solution	$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$	pH	pOH
0.15 M HI	_____	_____	_____	_____
0.060 M RbOH	_____	_____	_____	_____
0.020 M $\text{Ba}(\text{OH})_2$	_____	_____	_____	_____
0.00030 M HClO_4	_____	_____	_____	_____

28. Calculate the following values for each solution.

Solution	$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$	pH	pOH
(a) 0.055 M NaOH	_____	_____	_____	_____
(b) 0.055 M HCl	_____	_____	_____	_____
(c) 0.055 M $\text{Ca}(\text{OH})_2$	_____	_____	_____	_____

29. Complete the following table by appropriate calculations.

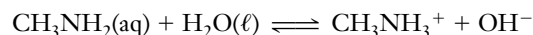
	$[\text{H}_3\text{O}^+]$	pH	$[\text{OH}^-]$	pOH
(a)	_____	3.84	_____	_____
(b)	_____	12.61	_____	_____
(c)	_____	_____	_____	2.90
(d)	_____	_____	_____	9.47

30. Predict which acid of each pair is the stronger acid. Briefly explain how you arrived at your answer. (a) H_3PO_4 or H_3AsO_4 ; (b) HClO_3 or HIO_3 ; (c) HCl or HI. (*Hint*: Review Chapter 10.)
31. Predict which acid of each pair is the stronger acid. Briefly explain how you arrived at your answer. (a) H_2O or H_2S ; (b) H_2SO_3 or H_2SO_2 ; (c) H_2CO_3 or HCO_3^- . (*Hint*: Review Chapter 10.)
32. Write a chemical equation that represents the ionization of a weak acid, HA. Write the equilibrium constant expression for this reaction. What is the special symbol used for this equilibrium constant?
33. What is the relationship between the strength of an acid and the numerical value of K_a ? What is the relationship between the acid strength and the value of $\text{p}K_a$?
34. (a) What is the pH of pure water at body temperature, 37°C ? Refer to Table 18-2. (b) Is this acidic, basic, or neutral? Why?
35. Fill in the blanks in this table for the given solutions.

Sol'n	Temp. ($^\circ\text{C}$)	Concentration (mol/L)		pH
		$[\text{H}_3\text{O}^+]$	$[\text{OH}^-]$	
(a)	25	1.0×10^{-6}	_____	_____
(b)	0	_____	_____	4.75
(c)	60	_____	_____	7.00
(d)	25	_____	4.5×10^{-9}	_____

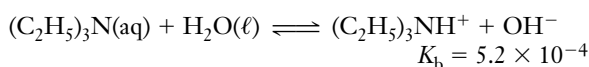
36. Write a chemical equation that represents the equilibrium between water and a weak base, B. Write the equilibrium constant expression for this reaction. What is the special symbol used for this equilibrium constant?
37. What is the relationship between base strength and the value of K_b ? What is the relationship between base strength and the value of $\text{p}K_b$?

38. A 0.0830 M solution of a monoprotic acid is known to be 1.07% ionized. What is the pH of the solution? Calculate the value of K_a for this acid.
39. A 0.055 M aqueous solution of a weak, monoprotic acid is 0.85% ionized. Calculate the value of the ionization constant, K_a , for this acid.
40. The pH of a 0.025 M solution of butanoic acid, $\text{C}_3\text{H}_7\text{COOH}$, is 3.21. What is the value of the ionization constant, K_a , for butanoic acid?
41. The pH of a 0.35 M solution of uric acid is 2.17. What is the value of K_a for uric acid, a monoprotic acid?
42. Calculate the concentrations of all the species present in a 0.35 M benzoic acid solution. (See Appendix F.)
43. Find the concentrations of the various species present in a 0.25 M solution of HOBr. What is the pH of the solution? (See Appendix F.)
44. Hydrofluoric acid can be used to etch glass. Calculate the pH of a 0.33 M HF solution.
45. The ionization constant, K_a , for propanoic acid, $\text{C}_2\text{H}_5\text{COOH}$, is 1.3×10^{-5} . What is the percent ionization in a 0.65 M solution of propanoic acid? Propanoic acid is a monoprotic acid.
46. Calculate the pH and pOH of a household ammonia solution that contains 2.5 moles of NH_3 per liter of solution.
47. Calculate the percent ionization in a 0.50 M NH_3 solution.
48. What is the percent ionization in a 0.0500 M solution of formic acid, HCOOH?
49. What is the percent ionization in (a) a 0.100 M CH_3COOH solution and (b) a 0.0100 M CH_3COOH solution?
50. The K_a values for two weak acids are 8.3×10^{-5} and 3.5×10^{-10} , respectively. What are their $\text{p}K_a$ values?
51. What is the concentration of OI^- in equilibrium with $[\text{H}_3\text{O}^+] = 0.035 \text{ mol/L}$ and $[\text{HOI}] = 0.427 \text{ mol/L}$?
52. Pyridine is 0.053% ionized in 0.00500 M solution. What is the $\text{p}K_b$ of this monobasic compound?
53. A 0.068 M solution of benzamide has a pOH of 2.91. What is the value of $\text{p}K_b$ for this monobasic compound?
54. In a 0.0100 M aqueous solution of methylamine, CH_3NH_2 , the equilibrium concentrations of the species are $[\text{CH}_3\text{NH}_2] = 0.0080 \text{ mol/L}$ and $[\text{CH}_3\text{NH}_3^+] = [\text{OH}^-] = 2.0 \times 10^{-3} \text{ mol/L}$. Calculate K_b for this weak base.

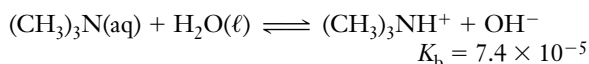


55. What is the concentration of NH_3 in equilibrium with $[\text{NH}_4^+] = 0.010 \text{ mol/L}$ and $[\text{OH}^-] = 1.2 \times 10^{-5} \text{ mol/L}$?
56. Calculate $[\text{OH}^-]$, percent ionization, and pH for (a) 0.10 M aqueous ammonia, and (b) 0.15 M methylamine solution.
57. Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, pOH, and percent ionization for 0.21 M aqueous ammonia solution.

58. Because K_b is larger for triethylamine



than for trimethylamine



an aqueous solution of triethylamine should have a larger concentration of OH^- ion than an aqueous solution of trimethylamine of the same concentration. Confirm this statement by calculating the $[\text{OH}^-]$ for 0.012 M solutions of both weak bases.

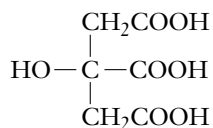
59. The equilibrium constant of the following reaction is 1.35×10^{-15} .



D is deuterium, ^2H . Calculate the pD of pure deuterium oxide (heavy water). What is the relationship between $[\text{D}_3\text{O}^+]$ and $[\text{OD}^-]$ in pure D_2O ? Is pure D_2O acidic, basic, or neutral?

Polyprotic Acids

60. Calculate the concentrations of the various species in a 0.100 M H_3AsO_4 solution. Compare the concentrations with those of the analogous species in 0.100 M H_3PO_4 solution (Example 18-16 and Table 18-7).
61. Citric acid, the acid in lemons and other citrus fruits, has the structure



which we may abbreviate as $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$ or H_3A . It is a triprotic acid. Write the chemical equations for the three stages in the ionization of citric acid with the appropriate K_a expressions.



62. Calculate the concentrations of H_3O^+ , OH^- , HSeO_4^- , and SeO_4^{2-} in 0.12 M H_2SeO_4 , selenic acid, solution.
63. Some kidney stones are crystalline deposits of calcium oxalate, a salt of oxalic acid, $(\text{COOH})_2$. Calculate the concentrations of H_3O^+ , OH^- , COOCOOH^- , and $(\text{COO}^-)_2$ in 0.12 M $(\text{COOH})_2$. Compare the concentrations with those obtained in Exercise 62. How can you explain the difference between the concentrations of HSeO_4^- and COOCOOH^- ? between SeO_4^{2-} and $(\text{COO}^-)_2$?
64. Rust stains can be removed from painted surfaces with a solution of oxalic acid, $(\text{COOH})_2$. Calculate the pH of a 0.050 M oxalic acid solution.
65. Calculate the pH and pOH of a carbonated soft drink that is 0.0032 M carbonic acid solution. Assume that there are no other acidic or basic components.



Hydrolysis

66. Define and illustrate the following terms clearly and concisely: (a) solvolysis; (b) hydrolysis.
67. Predict which base of each pair is the stronger base. Briefly explain how you arrived at your answer. (a) NO_2^- or NO_3^- ; (b) BrO_3^- or IO_3^- ; (c) HSO_3^- or HSO_4^- . (*Hint:* You may wish to review Chapter 10.)
68. Predict which base of each pair is the stronger base. Briefly explain how you arrived at your answer. (a) PH_3 or NH_3 ; (b) Br^- or F^- ; (c) ClO_3^- or ClO_2^- . (*Hint:* You may wish to review Chapter 10.)
69. Some anions, when dissolved, undergo no significant reaction with water molecules. What is the relative base strength of such an anion compared with water? What effect will dissolution of such anions have on the pH of the solution?
70. Some cations in aqueous solution undergo no significant reactions with water molecules. What is the relative acid strength of such a cation compared with water? What effect will dissolution of such cations have on the pH of the solution?
71. How can salts be classified conveniently into four classes? For each class, write the name and formula of a salt that fits into that category. Use examples other than those used in illustrations in this chapter.

Salts of Strong Bases and Strong Acids

72. What determines whether the aqueous solution of a salt is acidic, basic, or neutral?
73. Why do salts of strong bases and strong acids give neutral aqueous solutions? Use KNO_3 to illustrate. Write names and formulas for three other salts of strong bases and strong acids.
74. Which of the following salts is the salt of a strong base and a strong acid? (a) Na_3PO_4 ; (b) K_2CO_3 ; (c) LiNO_3 ; (d) BaSO_4 ; (e) NaClO_3 .
75. Which of the following salts is the salt of a strong base and a strong acid? (a) $\text{Ba}_3(\text{PO}_4)_2$; (b) KNO_3 ; (c) NaCl ; (d) CaCO_3 ; (e) LiClO_4 .

Salts of Strong Bases and Weak Acids

76. Why do salts of strong bases and weak acids give basic aqueous solutions? Use sodium hypochlorite, NaOCl , to illustrate. (Clorox, Purex, and other “chlorine bleaches” are 5% NaOCl .)



77. Some anions react with water to upset the $\text{H}_3\text{O}^+/\text{OH}^-$ balance. What is the relative base strength of such an anion compared with water? What effect will dissolution of such anions have on the pH of the solution?
78. Calculate the equilibrium constant for the reaction of azide ions, N_3^- , with water.
79. Write names and formulas for three salts of strong bases and weak acids other than those that appear in Section 18-8.
80. Calculate hydrolysis constants for the following anions of weak acids: (a) NO_2^- ; (b) OCl^- ; (c) HCOO^- . What is the relationship between K_a , the ionization constant for a weak acid, and K_b , the hydrolysis constant for the anion of the weak acid? (See Appendix F.)
81. Calculate the equilibrium constant for the reaction of hypobromite ions (OBr^-) with water.
82. Calculate the pH of 1.50 M solutions of the following salts: (a) NaCH_3COO ; (b) KOBBr ; (c) LiCN .
83. Calculate the pH of 0.12 M solutions of the following salts: (a) NaNO_2 ; (b) NaOCl ; (c) NaHCOO .
84. (a) What is the pH of a 0.12 M solution of KOI ? (b) What is the pH of a 0.12 M solution of KF ?

Salts of Weak Bases and Strong Acids

85. Why do salts of weak bases and strong acids give acidic aqueous solutions? Illustrate with NH_4NO_3 , a common fertilizer.
86. Write names and formulas for four salts of weak bases and strong acids.
87. Use values found in Table 18-6 and in Appendix G to calculate hydrolysis constants for the following cations of weak bases: (a) NH_4^+ ; (b) CH_3NH_3^+ , methylammonium ion; (c) $\text{C}_6\text{H}_5\text{NH}_3^+$, anilinium ion.
88. Use the values found in Table 18-6 and Appendix G to calculate hydrolysis constants for the following cations of weak bases: (a) $(\text{CH}_3)_2\text{NH}_2^+$, dimethylammonium ion; (b) $\text{C}_5\text{H}_5\text{NH}^+$, pyridinium ion; (c) $(\text{CH}_3)_3\text{NH}^+$, trimethylammonium ion.
89. Can you make a general statement relating parent base strength and extent of hydrolysis of the cations of Exercise 87 by using hydrolysis constants calculated in that exercise?
90. Calculate the pH of 0.12 M solutions of (a) NH_4NO_3 ; (b) $(\text{CH}_3)\text{NH}_3\text{NO}_3$; (c) $\text{C}_6\text{H}_5\text{NH}_3\text{NO}_3$.

Salts of Weak Bases and Weak Acids

91. Why are some aqueous solutions of salts of weak acids and weak bases neutral, whereas others are acidic and still others are basic?
92. Write the names and formulas for three salts of a weak acid and a weak base that give (a) neutral, (b) acidic, and (c) basic aqueous solutions.
93. If both the cation and anion of a salt react with water when dissolved, what determines whether the solution will be acidic, basic, or neutral? Classify aqueous solutions of the following salts as acidic, basic, or neutral. (a) $\text{NH}_4\text{F}(\text{aq})$ and (b) $\text{CH}_3\text{NH}_3\text{OI}(\text{aq})$.

Salts That Contain Small, Highly Charged Cations

94. Choose the hydrated cations that react with water to give acidic solutions. (a) $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$; (b) $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$; (c) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$; (d) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. Write chemical equations for the reactions.
95. Why do some salts that contain cations related to insoluble bases (metal hydroxides) and anions related to strong acids give acidic aqueous solutions? Use $\text{Fe}(\text{NO}_3)_3$ to illustrate.
96. Calculate pH and percent hydrolysis for the following (Table 18-10). (a) 0.15 M $\text{Al}(\text{NO}_3)_3$, aluminum nitrate; (b) 0.075 M $\text{Co}(\text{ClO}_4)_2$; cobalt (II) perchlorate; (c) 0.15 M MgCl_2 , magnesium chloride.
- *97. Given pH values for solutions of the following concentrations, calculate hydrolysis constants for the hydrated cations: (a) 0.00050 M CeCl_3 , cerium(III) chloride, pH = 5.99; (b) 0.10 M $\text{Cu}(\text{NO}_3)_2$, copper(II) nitrate, pH = 4.50; (c) 0.10 M $\text{Sc}(\text{ClO}_4)_3$, scandium perchlorate, pH = 3.44.

Mixed Exercises

98. A solution of nitrous acid, HNO_2 , is 0.20 *M*. (a) Calculate the pH. (b) What is the concentration of the nitrite ion, NO_2^- ?
99. Calculate the pH of the following solutions. (a) 0.0050 *M* $\text{Ca}(\text{OH})_2$; (b) 0.20 *M* chloroacetic acid, ClCH_2COOH , $K_a = 1.4 \times 10^{-3}$; (c) 0.040 *M* pyridine, $\text{C}_5\text{H}_5\text{N}$.
100. Classify aqueous solutions of the following salts as acidic, basic, or essentially neutral. Justify your choice. (a) $(\text{NH}_4)\text{HSO}_4$; (b) $(\text{NH}_4)_2\text{SO}_4$; (c) KCl ; (d) LiBrO ; (e) AlCl_3 .
101. Repeat Exercise 100 for (a) NaClO_4 ; (b) NH_4Cl ; (c) KCl ; (d) NH_4CN . (See Appendix F.)
102. In aqueous solution some cations react with water to upset the $\text{H}_3\text{O}^+/\text{OH}^-$ balance. What is the relative acid strength of such a cation compared with water? What effect will dissolution of these cations have on the pH of the solution?
103. Some plants require acidic soils for healthy growth. Which of the following could be added to the soil around such plants to increase the acidity of the soil? Write equations to justify your answers. (a) FeSO_4 ; (b) Na_2SO_4 ; (c) $\text{Al}_2(\text{SO}_4)_3$; (d) $\text{Fe}_2(\text{SO}_4)_3$; (e) BaSO_4 . Arrange the salts that give acidic solutions in order of increasing acidity. (Assume equal molarities of the salt solutions.)
104. Some of the following salts are used in detergents and other cleaning materials because they produce basic solutions. Which of the following could *not* be used for this purpose? Write equations to justify your answers. (a) Na_2CO_3 ; (b) Na_2SO_4 ; (c) $(\text{NH}_4)_2\text{SO}_4$; (d) Na_3PO_4 .
105. Calculate the pH of each of the following solutions. (a) 0.038 g of barium hydroxide in 250. mL of solution; (b) 0.050 g of hydrogen iodide in 750. mL of solution; (c) 0.00055 g of HCl in 1.00 L of solution.
106. For each of the following pairs, tell which solution would have the lower pH. Tell how you arrive at each answer. (a) 0.010 *M* NH_4Br , ammonium bromide, and 0.010 *M* NH_4NO_3 , ammonium nitrate; (b) 0.010 *M* ammonium perchlorate, NH_4ClO_4 , and 0.010 *M* ammonium fluoride, NH_4Cl ; (c) 0.010 *M* NH_4Cl and 0.050 *M* NH_4Cl . (*Hint*: Think before you calculate.)

CONCEPTUAL EXERCISES

107. How could we demonstrate that 0.010 *M* solutions of HCl and HNO_3 contain essentially no molecules of nonionized acid?
108. How could we demonstrate that 0.010 *M* solutions of HF and HNO_2 contain relatively few ions?
109. Carbonic acid, H_2CO_3 , is diprotic and therefore has two ionization constants, $K_{a1} = 4.2 \times 10^{-7}$ and $K_{a2} = 4.8 \times 10^{-11}$. The pH of a carbonic acid solution can be calcu-

lated without using K_{a2} . Explain using a 0.100 *M* solution of carbonic acid.

110. Answer the following questions for 0.15 *M* solutions of the weak bases listed in Table 18-6. (a) In which solution is (i) the pH highest; (ii) the pH lowest; (iii) the pOH highest; (iv) the pOH lowest? (b) Which solution contains (i) the highest concentration of the cation of the weak base; (ii) the lowest concentration of the cation of the weak base?
111. Answer the following questions for 0.15 *M* solutions of the weak acids listed in Table 18-4. Which solution contains (a) the highest concentration of H_3O^+ ; (b) the highest concentration of OH^- ; (c) the lowest concentration of H_3O^+ ; (d) the lowest concentration of OH^- ; (e) the highest concentration of nonionized acid molecules; (f) the lowest concentration of nonionized acid molecules?

BUILDING YOUR KNOWLEDGE

112. Ascorbic acid, $\text{C}_5\text{H}_7\text{O}_4\text{COOH}$, also known as vitamin C, is an essential vitamin for all mammals. Among mammals, only humans, monkeys, and guinea pigs cannot synthesize it in their bodies. K_a for ascorbic acid is 7.9×10^{-5} . Calculate $[\text{H}_3\text{O}^+]$ and pH in a 0.110 *M* solution of ascorbic acid.



113. Arrange the following common kitchen samples from most acidic to most basic.
- | | |
|----------------------|---------------------------|
| carrot juice, pH 5.1 | blackberry juice, pH 3.4 |
| soap, pH 11.0 | red wine, pH 3.7 |
| egg white, pH 7.8 | milk of magnesia, pH 10.5 |
| sauerkraut, pH 3.5 | lime juice, pH 2.0 |
- *114. The buildup of lactic acid in muscles causes pain during extreme physical exertion. The K_a for lactic acid, $\text{C}_2\text{H}_5\text{O}_2\text{COOH}$, is 8.4×10^{-4} . Calculate the pH of a 0.110 *M* solution of lactic acid. Can you make a simplifying assumption in this case?
115. A 0.0100 molal solution of acetic acid freezes at -0.01938°C . Use this information to calculate the ionization constant for acetic acid. A 0.0100 molal solution is sufficiently dilute that it may be assumed to be 0.0100 molar without introducing a significant error.