

Chapter Preview

- 8.1 Explaining the Properties of Acids and Bases
- 8.2 The Equilibrium of Weak Acids and Bases
- 8.3 Bases and Buffers
- 8.4 Acid-Base Titration Curves

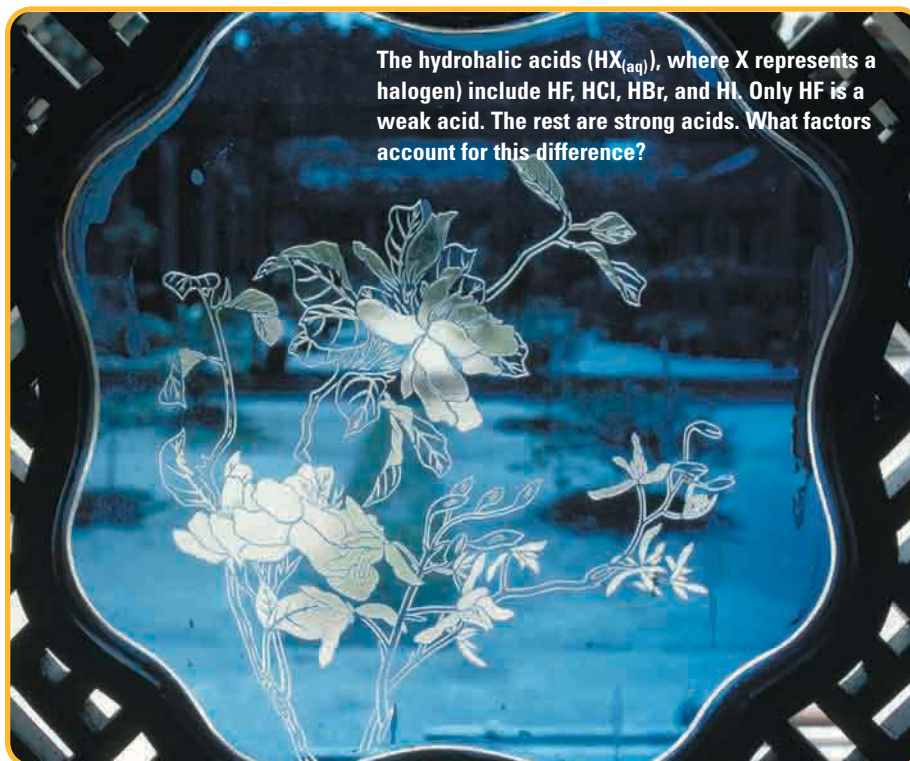
Prerequisite Concepts and Skills

Before you begin this chapter, review the following concepts and skills:

- writing net ionic equations (Concepts and Skills Review)
- calculating molar concentrations (Concepts and Skills Review)
- solving equilibrium problems (Chapter 7, sections 7.3 and 7.4)
- explaining the mathematical properties of logarithms (previous studies)
- performing acid-base titrations (previous studies)

For many people, the word “acid” evokes the image of a fuming, highly corrosive, dangerous liquid. This image is fairly accurate for concentrated hydrochloric acid, a strong acid. Most acids, however, are not as corrosive as hydrochloric acid, although they may still be very hazardous. For example, hydrofluoric acid can cause deep, slow-healing tissue burns if it is handled carelessly. It is used by artists and artisans who etch glass. It reacts with the silica in glass to form a compound that dissolves, leaving the glass with a brilliant surface. Hydrofluoric acid is highly corrosive. Even a 1% solution is considered to be hazardous. Yet chemists classify hydrofluoric acid as a weak acid.

You learned about acids and bases in your previous chemistry course. In this chapter, you will extend your knowledge to learn how the structure of a compound determines whether it is an acid or a base. You will use the equilibrium constant of the reaction of an acid or base with water to determine whether the acid or base is strong or weak. You will apply your understanding of dissociation and pH to investigate buffer solutions: solutions that resist changes in pH. Finally, you will examine acid-base titrations that involve combinations of strong and weak acids and bases.



Explaining the Properties of Acids and Bases

8.1

Table 8.1 outlines properties of acids and bases that you have examined in previous courses. In this section, you will review two theories that help to explain these and other properties. As well, you will use your understanding of molecular structure to help you understand why acids and bases differ in strength.

Table 8.1 Examples and Common Properties of Acids and Bases

| Example | Acids | Bases |
|---|---|---|
| solid | acetyl salicylic acid | sodium hydroxide |
| liquid | acetic acid | aniline |
| gas | hydrogen chloride | ammonia |
| Property | Acids | Bases |
| taste CAUTION Never taste chemicals in a lab. | Acids taste sour. | Bases taste bitter. |
| texture of solution CAUTION Never deliberately touch chemicals. Strong, concentrated acids and bases will burn your skin. | Acids do not have a characteristic texture. | Bases feel slippery. |
| reaction with phenolphthalein | Acidic phenolphthalein is colourless. | Basic phenolphthalein is pink. |
| reaction with litmus paper | Acids turn blue litmus red. | Bases turn red litmus blue. |
| reaction with metals | Acids react with metals above hydrogen in the activity series to displace $H_{2(g)}$. | Bases react with certain metals (such as Al) to form $H_{2(g)}$. |
| reaction with carbonates | Carbon dioxide is formed. | No reaction occurs. |
| reaction with ammonium chloride | No reaction occurs. | Ammonia, NH_3 , a gas with a characteristic odour, is produced. |
| neutralization reaction | Acids neutralize basic solutions. | Bases neutralize acidic solutions. |
| reaction with fatty acids | No reaction occurs. | Bases react to form soap (a saponification reaction). |
| aqueous property of oxides | Non-metal oxides form acidic solutions: for example, $CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)}$ | Metal oxides form basic solutions: for example, $CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)}$ |
| amount of dissociation in aqueous solution (strength) | Strong acids dissociate completely. Weak acids dissociate only partially. | Strong bases dissociate completely. Weak bases dissociate only partially. |

Section Preview/ Specific Expectations

In this section, you will

- **compare** strong acids and bases, and weak acids and bases, in terms of equilibrium
- **identify** conjugate acid-base pairs
- **solve** problems that involve strong acids and strong bases
- **communicate** your understanding of the following terms: *hydronium ion ($H_3O^+_{(aq)}$)*, *conjugate acid-base pair*, *monoprotic acids*, *polyprotic acids*

The following ExpressLab highlights concepts that you will examine in this section, as well as later in the chapter.

ExpressLab



Comparing Acid-Base Reactions

You will perform three acid-base reactions. Before you begin, read the Procedure and make a prediction about the relative rates of these reactions.

Safety Precautions



The solutions that are used in this lab are irritants and should be handled with care. Wash any spills on your skin or clothing with plenty of water. Inform your teacher immediately.

Materials

powdered calcium carbonate, $\text{CaCO}_{3(s)}$
3 squeeze bottles, each containing one of the following solutions: 2.0 mol/L $\text{HCl}_{(aq)}$;
2.0 mol/L $\text{CH}_3\text{COOH}_{(aq)}$; mixture of
2.0 mol/L $\text{CH}_3\text{COOH}_{(aq)}$ and 2.0 mol/L $\text{NaCH}_3\text{COO}_{(aq)}$
scoopula
3 test tubes
test tube rack
labels or grease pencil

Procedure

1. Label each test tube to identify the solution it will contain. Then fill each test tube with the corresponding solution, to a depth of about 2 cm.
2. Add a small amount of $\text{CaCO}_{3(s)}$ (enough to cover the tip of a scoopula) to each test tube. Try to add the same amount of $\text{CaCO}_{3(s)}$ to all three test tubes.
3. Record your observations. Rank the rates of the three reactions from fastest to slowest.

Analysis

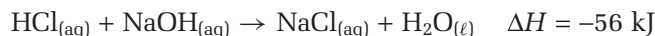
1. (a) What rate-related change did you observe in each test tube?
(b) If you wanted to collect quantitative data for each reaction, how could you modify the experiment?
2. In all three test tubes, the following reaction occurred.
$$\text{CaCO}_{3(s)} + 2\text{H}_3\text{O}^+_{(aq)} \rightarrow \text{CO}_{2(g)} + \text{Ca}^{2+}_{(aq)} + 3\text{H}_2\text{O}_{(l)}$$
The only difference between the test tubes was the concentration of $\text{H}^+_{(aq)}$ in the acidic solutions that reacted with $\text{CaCO}_{3(s)}$. Explain your ranking of the rates of reaction in terms of $[\text{H}_3\text{O}^+]$.
3. The concentrations of $\text{HCl}_{(aq)}$ and $\text{CH}_3\text{COOH}_{(aq)}$ were identical. The following dissociation reactions occurred.
$$\text{HCl}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}$$
$$\text{CH}_3\text{COOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$$
Explain your ranking of the $[\text{H}_3\text{O}^+]$ in these solutions in terms of the extent of the equilibrium dissociation.
4. The third solution was a mixture of 2.0 mol/L $\text{CH}_3\text{COOH}_{(aq)}$ and 2.0 mol/L $\text{NaCH}_3\text{COO}_{(aq)}$. How did the addition of sodium acetate affect the equilibrium of the dissociation reaction of acetic acid?
5. Explain your ranking of the rate of the reaction between calcium carbonate and the solution that was a mixture of acetic acid and sodium acetate.

The Arrhenius Theory of Acids and Bases

According to the Arrhenius theory (1887), acids and bases are defined in terms of their structure and the ions produced when they dissolve in water.

- An acid is a substance that dissociates in water to form $\text{H}^+_{(aq)}$. Two examples of Arrhenius acids are hydrochloric acid, HCl , and sulfuric acid, H_2SO_4 .
- A base is a substance that dissociates in water to form $\text{OH}^-_{(aq)}$. Two examples of Arrhenius bases are sodium hydroxide, NaOH , and potassium hydroxide, KOH .

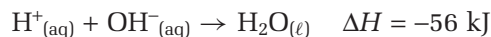
The Arrhenius theory explains acid-base reactions as a combination of $\text{H}^+_{(\text{aq})}$ and $\text{OH}^-_{(\text{aq})}$. It provides insight into the heat of neutralization for the reaction between a strong acid and a strong base. (Strong acids and bases dissociate completely into ions in solution.) For example, consider the following reaction.



The total ionic equation for this reaction is

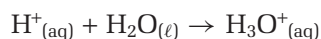


Subtracting spectator ions from both sides, the net ionic equation is



Different combinations of strong Arrhenius acids and bases react with the same exothermic result. Measurements always show the release of 56 kJ of energy per mole of water formed. This makes sense, because the net ionic equation is the same regardless of the specific neutralization reaction that occurs.

The Arrhenius theory has limitations, however. For example, $\text{H}^+_{(\text{aq})}$, a bare proton, does not exist in water. The positive charge on a proton is attracted to the region of negative charge on the lone pair of electrons on a water molecule's oxygen atom. The combination is a hydrated proton called a **hydronium ion**, $\text{H}_3\text{O}^+_{(\text{aq})}$.



The hydronium ion, itself, forms hydrogen bonds with other water molecules. (See Figure 8.1.) Thus, a better formula for the ion that is present in acidic solutions is $[\text{H}(\text{H}_2\text{O})_n]^+$, where n is usually 4 or 5. For convenience, however, chemists usually use a single hydronium ion when writing equations.

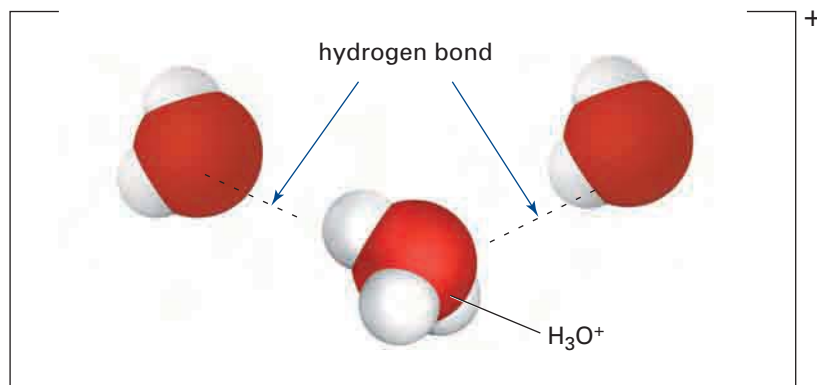
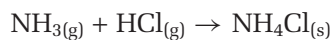


Figure 8.1 In aqueous solution, the hydronium ion, H_3O^+ , forms hydrogen bonds with other water molecules.

The Arrhenius theory also has limitations for explaining certain reactions. For example, aqueous solutions of ammonia are basic. They react with acids in neutralization reactions, even though ammonia does not contain the hydroxide ion. Many aqueous solutions of salts with no hydroxide ions are basic, too. Some reactions take place without any liquid solvent. For example, ammonium chloride can be formed by the reaction between ammonia and hydrogen chloride, which are both gases:



The Brønsted-Lowry Theory

The limitations of the Arrhenius theory of acids and bases are overcome by a more general theory, called the Brønsted-Lowry theory. This theory was proposed independently, in 1923, by Johannes Brønsted, a Danish chemist, and Thomas Lowry, an English chemist. It recognizes an acid-base reaction as a chemical equilibrium, having both a forward reaction and a reverse reaction that involve the transfer of a proton. The Brønsted-Lowry theory defines acids and bases as follows:

- An acid is a substance from which a proton can be removed. (Some chemists describe Brønsted-Lowry acids as “proton-donors.”)
- A base is a substance that can accept a proton. (Some chemists describe Brønsted-Lowry bases as “proton-acceptors.”)

Note that the word “proton” refers to the nucleus of a hydrogen atom — an H^+ ion that has been removed from the acid molecule. It does not refer to a proton removed from the nucleus of another atom, such as oxygen or sulfur, that may be present in the acid molecule. As mentioned previously, H^+ ions share electrons with any species (ion or molecule) that has a lone pair of electrons. In aqueous solution, the proton bonds with a water molecule to form the hydronium ion. Unlike the Arrhenius theory, however, the Brønsted-Lowry theory is not restricted to aqueous solutions. For example, the lone pair of electrons on an ammonia molecule can bond with H^+ , and liquid ammonia can act as a base.

| Definition Term | Arrhenius Theory | Brønsted-Lowry Theory |
|-----------------|--|---|
| acid | a substance that contains hydrogen and dissociates in water to form $H^+_{(aq)}$ | a substance from which a proton can be removed |
| base | a substance that contains the hydroxide group and dissociates in water to form $OH^-_{(aq)}$ | a substance that can accept a proton from an acid |

Conjugate Acid-Base Pairs

The dissociation of acetic acid in water is represented in Figure 8.2. This dissociation is an equilibrium reaction because it proceeds in both directions. Acetic acid is weak, so only a few ions dissociate. The position of equilibrium lies to the left, and the reverse reaction is favoured. In the reverse reaction, the hydronium ion gives up a proton to the acetate ion. Thus, these ions are an acid and a base, respectively, as shown in Figure 8.3. The acid on the left (CH_3COOH) and the base on the right (CH_3COO^-) differ by one proton. They are called a **conjugate acid-base pair**. Similarly, H_2O and H_3O^+ are a conjugate acid-base pair.

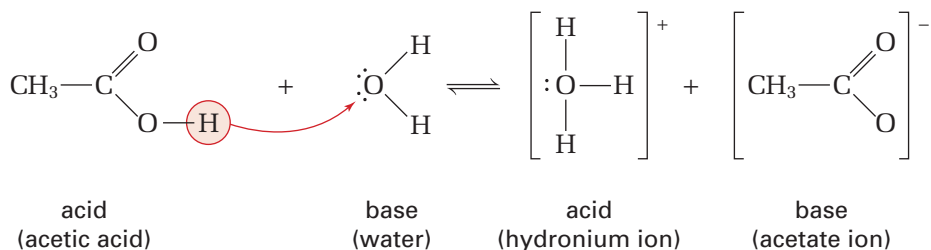


Figure 8.2 The dissociation of acetic acid, a weak acid, in water

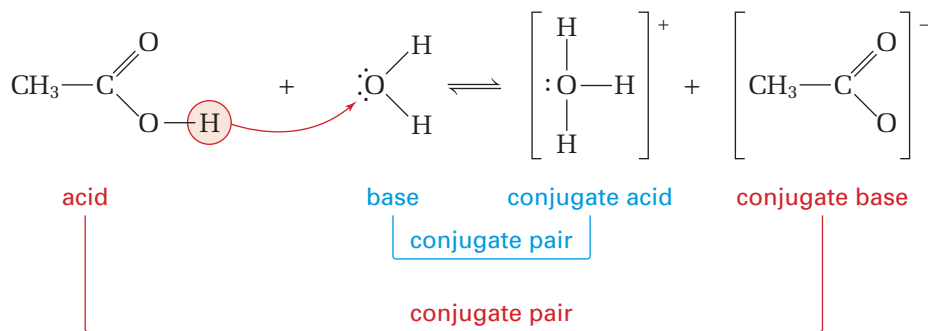


Figure 8.3 Conjugate acid-base pairs in the dissociation of acetic acid in water

Unlike the Arrhenius theory, the Brønsted-Lowry theory of acids and bases can explain the basic properties of ammonia when it dissolves in water. See Figure 8.4.

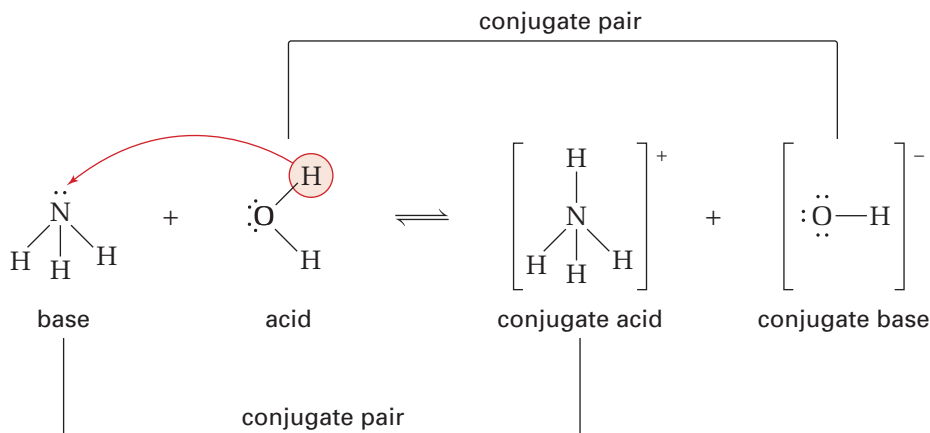


Figure 8.4 The dissociation of ammonia, a weak base, in water

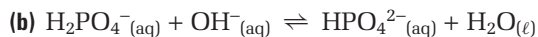
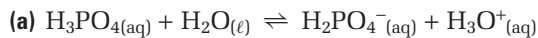
Aqueous ammonia is a weak base, so relatively few hydroxide ions form. The position of equilibrium lies to the left. In the forward reaction, the water molecule gives up a proton and acts as an acid. A substance that can act as a proton donor (an acid) in one reaction and a proton acceptor (a base) in another reaction is said to be *amphoteric*. (Water acts as an acid in the presence of a stronger base, and as a base in the presence of a stronger acid.)

Sample Problem

Identifying Conjugate Acid-Base Pairs

Problem

Identify the conjugate acid-base pair in each reaction.

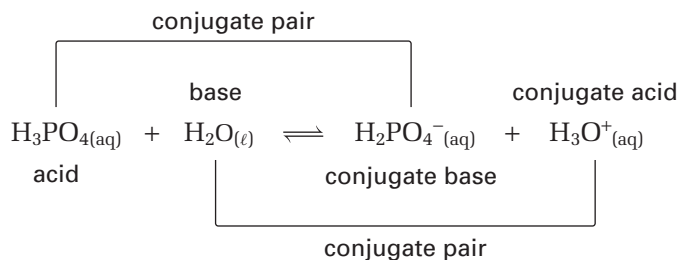


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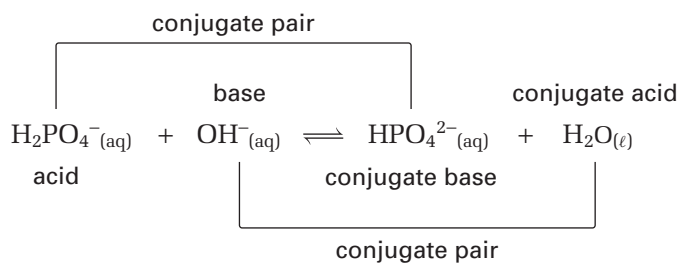
Solution

On the left side of the equation, the acid is the molecule or ion that donates a proton. The base is the molecule or ion that accepts the proton. On the right side of the equation, you can identify the conjugate acid and base by the difference of a single proton from the base and acid on the left side.

(a) The conjugate acid-base pairs are $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$ and $\text{H}_2\text{O}/\text{H}_3\text{O}^+$.



(b) The conjugate acid-base pairs are $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{OH}^-/\text{H}_2\text{O}$.

**Check Your Solution**

In each case, the acid has one more proton than its conjugate base.

Practice Problems

- Name and write the formula of the conjugate base of each molecule or ion.
 - HCl
 - HCO_3^-
 - H_2SO_4
 - N_2H_5^+
- Name and write the formula of the conjugate acid of each molecule or ion.
 - NO_3^-
 - OH^-
 - H_2O
 - HCO_3^-
- Identify the conjugate acid-base pairs in each reaction.
 - $\text{HS}^{-}_{(\text{aq})} + \text{H}_2\text{O}_{(\ell)} \rightleftharpoons \text{H}_2\text{S}_{(\text{aq})} + \text{OH}^{-}_{(\text{aq})}$
 - $\text{O}^{2-}_{(\text{aq})} + \text{H}_2\text{O}_{(\ell)} \rightarrow 2\text{OH}^{-}_{(\text{aq})}$
- Identify the conjugate acid-base pairs in each reaction.
 - $\text{H}_2\text{S}_{(\text{aq})} + \text{NH}_3_{(\text{aq})} \rightleftharpoons \text{NH}_4^{+}_{(\text{aq})} + \text{HS}^{-}_{(\text{aq})}$
 - $\text{H}_2\text{SO}_4_{(\text{aq})} + \text{H}_2\text{O}_{(\ell)} \rightarrow \text{H}_3\text{O}^{+}_{(\text{aq})} + \text{HSO}_4^{-}_{(\text{aq})}$

Molecular Structure and the Strength of Acids and Bases

When a strong acid or base dissolves in water, almost every acid or base molecule dissociates. While there are many acids and bases, most are weak. Thus, the number of strong acids and strong bases is fairly small.

Strong Acids

- binary acids that have the general formula $HX_{(aq)}$, where $X = Cl, Br,$ and I (but not F): for example, hydrochloric acid, HCl , and hydrobromic acid, HBr (HCl and HBr are *hydrohalic acids*: acids that have hydrogen bonded to atoms of the halogen elements.)
- oxoacids (acids containing oxygen atoms) in which the number of oxygen atoms exceeds, by two or more, the number of protons that can be dissociated: for example, nitric acid, HNO_3 , sulfuric acid, H_2SO_4 , perchloric acid, $HClO_4$, and chloric acid, $HClO_3$

The binary acids of non-metals exhibit periodic trends in their acid strength, as shown in Figure 8.5. Two factors are responsible for this trend: the electronegativity of the atom that is bonded to hydrogen, and the strength of the bond.

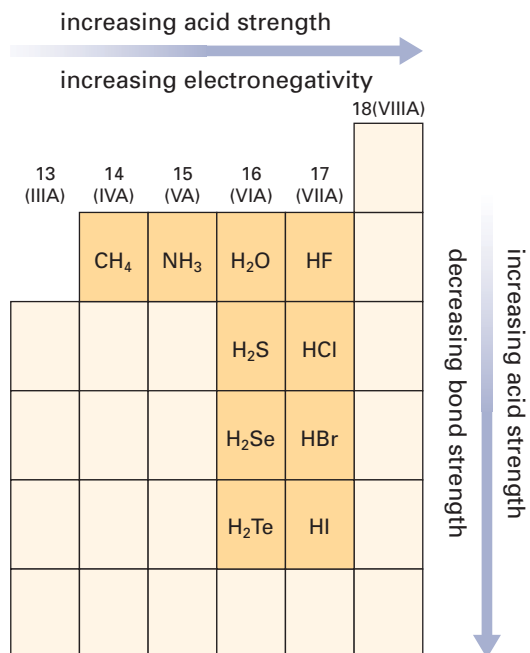


Figure 8.5 The binary acids show periodic trends, which are related to electronegativity and bond strength.

Across a period, electronegativity is the most important factor. The acid strength of hydrides increases as their electronegativity increases. This happens because an electronegative atom draws electrons away from the hydrogen atom, making it relatively positive. The negative pole of a water molecule then strongly attracts the hydrogen atom and pulls it away.

Down a group, bond strength is the most important factor. Acid strength increases as bond strength decreases. A weaker bond means that the hydrogen atom is more easily pulled away from the atom to which it is attached. For example, hydrofluoric acid is a stronger acid than water, but HF is the weakest of the hydrohalic acids because the $H-F$ bond is relatively strong.

**CHEM****FACT**

You might wonder how $\text{HCl}_{(\text{aq})}$, $\text{HBr}_{(\text{aq})}$, and $\text{HI}_{(\text{aq})}$ can be described as increasing in strength, since each acid dissociates completely in water. This trend becomes apparent if you add equal concentrations of the acids to a solvent that is less basic than water, such as pure acetic acid. You will find that the acids dissociate to different extents.

Oxoacids increase in strength with increasing numbers of oxygen atoms, as shown in Figure 8.6. The hydrogen atoms that dissociate in water are always attached to oxygen atoms. Oxygen is more electronegative than hydrogen, so oxygen atoms draw electrons away from hydrogen atoms. The more oxygen atoms there are in a molecule, the greater is the polarity of the bond between each hydrogen atom and the oxygen atom it is attached to, and the more easily the water molecule can tear the hydrogen atom away.

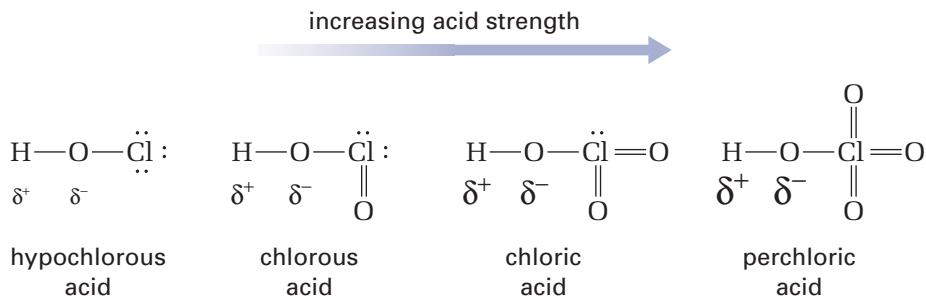
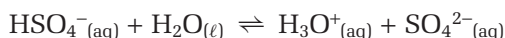
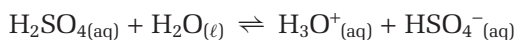


Figure 8.6 The relative strength of oxoacids increases with the number of oxygen atoms.

Acids such as HCl , CH_3COOH , and HF are **monoprotic acids**. They have only a single hydrogen atom that dissociates in water. Some acids have more than one hydrogen atom that dissociates. These acids are called **polyprotic acids**. For example, sulfuric acid has two hydrogen atoms that can dissociate.



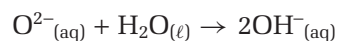
Sulfuric acid is a far stronger acid than the hydrogen sulfate ion, because much more energy is required to remove a proton from a negatively charged ion. *The strength of a polyprotic acid decreases as the number of hydrogen atoms that have dissociated increases.*

Strong bases are confined to the oxides and hydroxides from Groups 1 (IA) and 2 (IIA).

Strong Bases

- all oxides and hydroxides of the alkali metals: for example, sodium hydroxide, NaOH , and potassium hydroxide, KOH
- alkaline earth (Group 2 (IIA)) metal oxides and hydroxides below beryllium: for example, calcium hydroxide, $\text{Ca}(\text{OH})_2$, and barium hydroxide, $\text{Ba}(\text{OH})_2$

The strong basic oxides have metal atoms with low electronegativity. Thus, the bond to oxygen is ionic and is relatively easily broken by the attraction of polar water molecules. The oxide ion always reacts with water molecules to produce hydroxide ions.



Magnesium oxide and magnesium hydroxide are not very soluble. They are strong bases, however, because the small amount that does dissolve dissociates almost completely into ions. Beryllium oxide is a weak base. (It is the exception in Group 2 (IIA).) It is a relatively small atom, so the bond to oxygen is strong and not easily broken by water molecules.

Calculations That Involve Strong Acids and Bases

When a strong acid dissociates completely into ions in water, the concentration of $\text{H}_3\text{O}^+_{(\text{aq})}$ is equal to the concentration of the strong acid. Similarly, when a strong base dissociates completely in water, the concentration of $\text{OH}^-_{(\text{aq})}$ is equal to the concentration of the strong base.

Sample Problem

Calculating Ion Concentrations in Acidic and Basic Solutions

Problem

During an experiment, a student pours 25.0 mL of 1.40 mol/L nitric acid into a beaker that contains 15.0 mL of 2.00 mol/L sodium hydroxide solution. Is the resulting solution acidic or basic? What is the concentration of the ion that causes the solution to be acidic or basic?

What Is Required?

You must determine the ion in excess and its concentration.

What Is Given?

You have the following data:

Volume of nitric acid = 25.0 mL

$[\text{HNO}_3] = 1.40 \text{ mol/L}$

Volume of sodium hydroxide = 15.0 mL

$[\text{NaOH}] = 2.00 \text{ mol/L}$

Plan Your Strategy

Step 1 Write the chemical equation for the reaction.

Step 2 Calculate the amount of each reactant using the following equation.

$$\text{Amount (in mol)} = \text{Concentration (in mol/L)} \times \text{Volume (in L)}$$

Step 3 Determine the limiting reactant.

Step 4 The reactant in excess is a strong acid or base. Thus, the excess amount results in the same amount of H_3O^+ or OH^- .

Step 5 Calculate the concentration of the excess ion by using the amount in excess and the total volume of the solution.

Act on Your Strategy

Step 1 $\text{HNO}_{3(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow \text{NaNO}_{3(\text{aq})} + \text{H}_2\text{O}_{(\ell)}$

Step 2 Amount of $\text{HNO}_3 = 1.40 \text{ mol/L} \times 0.0250 \text{ L}$
 $= 0.0350 \text{ mol}$

Amount of $\text{NaOH} = 2.00 \text{ mol/L} \times 0.0150 \text{ L}$
 $= 0.0300 \text{ mol}$

Step 3 The reactants combine in a 1:1 ratio. The amount of NaOH is less, so this reactant must be the limiting reactant.

Step 4 Amount of excess $\text{HNO}_{3(\text{aq})} = 0.0350 \text{ mol} - 0.0300 \text{ mol}$
 $= 0.0050 \text{ mol}$

Therefore, the amount of $\text{H}_3\text{O}^+_{(\text{aq})}$ is $5.0 \times 10^{-3} \text{ mol}$.

Step 5 Total volume of solution = 25.0 mL + 15.0 mL = 40.0 mL

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{5.0 \times 10^{-3} \text{ mol}}{0.0400 \text{ L}} \\ &= 0.12 \text{ mol/L} \end{aligned}$$

Continued ...

The solution is acidic, and $[\text{H}_3\text{O}^+]$ is 0.12 mol/L.

Check Your Solution

The chemical equation has a 1:1 ratio between reactants. The amount of acid is greater than the amount of base. Therefore, the resulting solution should be acidic, which it is.

Practice Problems

- Calculate the concentration of hydronium ions in each solution.
 - 4.5 mol/L $\text{HCl}_{(\text{aq})}$
 - 30.0 mL of 4.50 mol/L $\text{HBr}_{(\text{aq})}$ diluted to 100.0 mL
 - 18.6 mL of 2.60 mol/L $\text{HClO}_{4(\text{aq})}$ added to 24.8 mL of 1.92 mol/L $\text{NaOH}_{(\text{aq})}$
 - 17.9 mL of 0.175 mol/L $\text{HNO}_{3(\text{aq})}$ added to 35.4 mL of 0.0160 mol/L $\text{Ca}(\text{OH})_{2(\text{aq})}$
- Calculate the concentration of hydroxide ions in each solution.
 - 3.1 mol/L $\text{KOH}_{(\text{aq})}$
 - 21.0 mL of 3.1 mol/L KOH diluted to 75.0 mL
 - 23.2 mL of 1.58 mol/L $\text{HCl}_{(\text{aq})}$ added to 18.9 mL of 3.50 mol/L $\text{NaOH}_{(\text{aq})}$
 - 16.5 mL of 1.50 mol/L $\text{H}_2\text{SO}_{4(\text{aq})}$ added to 12.7 mL of 5.50 mol/L $\text{NaOH}_{(\text{aq})}$
- Determine whether reacting each pair of solutions results in an acidic solution or a basic solution. Then calculate the concentration of the ion that causes the solution to be acidic or basic. (Assume that the volumes in part (a) are additive. Assume that the volumes in part (b) stay the same.)
 - 31.9 mL of 2.75 mol/L $\text{HCl}_{(\text{aq})}$ added to 125 mL of 0.0500 mol/L $\text{Mg}(\text{OH})_{2(\text{aq})}$
 - 4.87 g of $\text{NaOH}_{(\text{s})}$ added to 80.0 mL of 3.50 mol/L $\text{HBr}_{(\text{aq})}$
- 2.75 g of $\text{MgO}_{(\text{s})}$ is added to 70.0 mL of 2.40 mol/L $\text{HNO}_{3(\text{aq})}$. Is the solution that results from the reaction acidic or basic? What is the concentration of the ion that is responsible for the character of the solution?

Section Summary

Strong acids and bases (and strong electrolytes) dissociate completely in water. Therefore, you can use the concentrations of these compounds to determine the concentrations of the ions they form in aqueous solutions. You cannot, however, use the concentrations of weak acids, bases, and electrolytes in the same way. Their solutions contain some particles that have not dissociated into ions. Nevertheless, important changes in $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ take place because dissolved ions affect the dissociation of water.

In the next section, you will focus on the equilibrium of water. You will discover how the pH scale is related to the concentrations of the ions that form when water dissociates. As well, you will learn how to calculate the pH values of solutions of weak acids and bases.

Section Review

- 1** **K/U** Phosphoric acid, $\text{H}_3\text{PO}_{4(\text{aq})}$ is triprotic. It has three hydrogen ions that may be dissociated.
 - (a)** Write an equation to show the dissociation of each proton.
 - (b)** Show that H_2PO_4^- can act as either an acid or a base.
 - (c)** Which is the stronger acid, $\text{H}_3\text{PO}_{4(\text{aq})}$ or H_2PO_4^- ? Explain your answer.
- 2** **K/U** Para-aminobenzoic acid (PABA) is a weak monoprotic acid that is used in some sunscreen lotions. Its formula is $\text{C}_6\text{H}_4\text{NH}_2\text{COOH}$. What is the formula of the conjugate base of PABA?
- 3** **K/U** Boric acid, $\text{B}(\text{OH})_{3(\text{aq})}$, is used as a mild antiseptic in eye-wash solutions. The following reaction takes place in aqueous solution.
$$\text{B}(\text{OH})_{3(\text{aq})} + 2\text{H}_2\text{O}(\ell) \rightleftharpoons \text{B}(\text{OH})_{4}^-_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$$
 - (a)** Identify the conjugate acid-base pairs.
 - (b)** Is boric acid strong or weak? How do you know?
- 4** **K/U** Classify each compound as a strong acid, weak acid, strong base, or weak base.
 - (a)** butyric acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (responsible for the odour of rancid butter)
 - (b)** hydroiodic acid, $\text{HI}_{(\text{aq})}$ (added to some cough syrups)
 - (c)** potassium hydroxide, KOH (used in the manufacture of soft soaps)
 - (d)** red iron oxide, Fe_2O_3 (used as a colouring pigment in paints)
- 5** **C** Distinguish between a concentrated solution of a weak base, and a dilute solution of a strong base. Give an example of each.

8.2

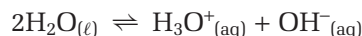
The Equilibrium of Weak Acids and Bases

Section Preview/
Specific Expectations

In this section, you will

- **define and perform** calculations that involve the ion product constant for water, K_w , and the acid dissociation constant, K_a
- **compare** strong acids and bases in terms of equilibrium
- **compare** weak acids and bases in terms of equilibrium
- **communicate** your understanding of the following terms: *ion product constant for water (K_w), pH, pOH, acid dissociation constant (K_a), percent dissociation*

The dissociation of an acidic or basic compound in aqueous solution produces ions that interact with water. The pH of the aqueous solution is determined by the position of equilibrium in reactions between the ions that are present in solution and the water molecules. Pure water contains a few ions, produced by the dissociation of water molecules:



At 25°C, only about two water molecules in one billion dissociate. This is why pure water is such a poor conductor of electricity. In neutral water, at 25°C, the concentration of hydronium ions is the same as the concentration of hydroxide ions: 1.0×10^{-7} mol/L. These concentrations must be the same because the dissociation of water produces equal numbers of hydronium and hydroxide ions. Because this is an equilibrium reaction, and because the position of equilibrium of all reactions changes with temperature, $[\text{H}_3\text{O}^+]$ is not 1.0×10^{-7} mol/L at other temperatures. The same is true of $[\text{OH}^-]$.

The Ion Product Constant for Water

The equilibrium constant, K_c , for the dissociation of water is given by the following expression.

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

So few ions form that the concentration of water is essentially constant. The product $K_c[\text{H}_2\text{O}]^2$ is equal to the product of the concentrations of hydronium ions and hydroxide ions. The equilibrium value of the concentration ion product $[\text{H}_3\text{O}^+][\text{OH}^-]$ at 25°C is called the **ion product constant for water**. It is given the symbol K_w .

$$\begin{aligned} K_c[\text{H}_2\text{O}]^2 &= [\text{H}_3\text{O}^+][\text{OH}^-] \\ &= 1.0 \times 10^{-7} \text{ mol/L} \times 1.0 \times 10^{-7} \text{ mol/L} \\ &= 1.0 \times 10^{-14} \\ &= K_w \end{aligned}$$

The units are commonly dropped, as in other equilibrium expressions you have encountered.

The concentration of H_3O^+ in the solution of a strong acid is equal to the concentration of the dissolved acid, unless the solution is very dilute. Consider $[\text{H}_3\text{O}^+]$ in a solution of 0.1 mol/L hydrochloric acid. All the molecules of HCl dissociate in water, forming a hydronium ion concentration that equals 0.1 mol/L. The increased $[\text{H}_3\text{O}^+]$ pushes the dissociation reaction between water molecules to the left, in accordance with Le Châtelier's principle. Consequently, the concentration of hydronium ions that results from the dissociation of water is even less than 1×10^{-7} mol/L. This $[\text{H}_3\text{O}^+]$ is negligible compared with the 0.1 mol/L concentration of the hydrochloric acid. Unless the solution is very dilute (about 1×10^{-7} mol/L), the dissociation of water molecules can be ignored when determining $[\text{H}_3\text{O}^+]$ of a strong acid.

Similarly, the concentration of hydroxide ions can be determined from the concentration of the dissolved base. If the solution is a strong base, you can ignore the dissociation of water molecules when determining $[\text{OH}^-]$, unless the solution is very dilute. When either $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ is known, you can use the ion product constant for water, K_w , to determine the concentration of the other ion. Although the value of K_w for water is 1.0×10^{-14} at 25°C only, you can use this value unless another value is given for a different temperature.

$[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in Aqueous Solutions at 25°C

In an acidic solution, $[\text{H}_3\text{O}^+]$ is greater than 1.0×10^{-7} mol/L and $[\text{OH}^-]$ is less than 1.0×10^{-7} mol/L.

In a neutral solution, both $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are equal to 1.0×10^{-7} mol/L.

In a basic solution, $[\text{H}_3\text{O}^+]$ is less than 1.0×10^{-7} mol/L and $[\text{OH}^-]$ is greater than 1.0×10^{-7} mol/L.

Sample Problem

Determining $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$

Problem

Find $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in each solution.

- (a) 2.5 mol/L nitric acid
 (b) 0.16 mol/L barium hydroxide

Solution

You know that nitric acid is a strong acid and barium hydroxide is a strong base. Since both dissociate completely in aqueous solutions, you can use their molar concentrations to determine $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$. You can find the concentration of the other ion using K_w :

$$K_w = 1.0 \times 10^{-14}$$

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

- (a) $[\text{HNO}_3] = 2.5$ mol/L, so $[\text{H}_3\text{O}^+] = 2.5$ mol/L

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14} \text{ mol/L}}{2.5}$$

$$= 4.0 \times 10^{-15} \text{ mol/L}$$

- (b) $\text{Ba}(\text{OH})_2 \xrightarrow{\text{H}_2\text{O}} \text{Ba}^{2+}_{(\text{aq})} + 2\text{OH}^-_{(\text{aq})}$

Each mole of $\text{Ba}(\text{OH})_2$ in solution forms two moles of OH^- ions.

$$\therefore [\text{OH}^-] = 2 \times 0.16 = 0.32 \text{ mol/L}$$

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14} \text{ mol/L}}{0.32}$$

$$= 3.1 \times 10^{-14} \text{ mol/L}$$

Check Your Solution

For a solution of a strong acid, as in part (a), $[\text{H}_3\text{O}^+]$ should be greater than 1.0×10^{-7} and $[\text{OH}^-]$ should be less than 1.0×10^{-7} . For a solution of strong base, $[\text{OH}^-]$ should be greater than, and $[\text{H}_3\text{O}^+]$ should be less than, 1.0×10^{-7} .

CONCEPT CHECK

Sulfuric acid is the only common strong diprotic acid. Explain why the concentration of hydronium ions in a solution of 1.0 mol/L $\text{H}_2\text{SO}_{4(\text{aq})}$ is 1.0 mol/L, not 2.0 mol/L.

Practice Problems

- Determine $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in each solution.
 - 0.45 mol/L hydrochloric acid
 - 1.1 mol/L sodium hydroxide
- Determine $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in each solution.
 - 0.95 mol/L hydrobromic acid
 - 0.012 mol/L calcium hydroxide
- $[\text{OH}^-]$ is 5.6×10^{-14} mol/L in a solution of hydrochloric acid. What is the molar concentration of the $\text{HCl}_{(\text{aq})}$?
- $[\text{H}_3\text{O}^+]$ is 1.7×10^{-14} in a solution of calcium hydroxide. What is the molar concentration of the $\text{Ca}(\text{OH})_{2(\text{aq})}$?

pH and pOH

You can describe the acidity of an aqueous solution quantitatively by stating the concentration of the hydronium ions that are present. $[\text{H}_3\text{O}^+]$ is often, however, a very small number. The pH scale was devised by a Danish biochemist named Søren Sørensen as a convenient way to represent acidity (and, by extension, basicity). The scale is logarithmic, based on 10. Think of the letter *p* as a mathematical operation representing $-\log$. The **pH** of a solution is the exponential power of hydrogen (or hydronium) ions, in moles per litre. It can therefore be expressed as follows:

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

The *practical* range of the pH scale, shown in Figure 8.7, is from 0 to 14. A solution of a strong acid that is more concentrated than 1.0 mol/L would give a negative pH. Since you can determine $[\text{H}_3\text{O}^+]$ of such solutions directly from the concentration of the acid, the pH scale offers no advantage. Similarly, the pH of a strong base that is more concentrated than 1.0 mol/L is greater than 14. Note that pH is a dimensionless quantity. In other words, it has no units.

You can calculate the **pOH** (the power of hydroxide ions) of a solution from the $[\text{OH}^-]$.

$$\text{pOH} = -\log[\text{OH}^-]$$

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

$$\therefore \text{pH} + \text{pOH} = 14$$

Web LINK

www.mcgrawhill.ca/links/chemistry12

Many people, for both personal and professional reasons, rely on pH meters to provide quick, reliable pH measurements. Use the Internet to find out how a pH meter works, and what jobs or tasks it is used for. To start your research, go to the web site above and click on **Web Links**. Prepare a brief report, a web page, or a brochure to present your findings.

Sample Problem

Calculating pH and pOH

Problem

A liquid shampoo has a hydroxide ion concentration of 6.8×10^{-5} mol/L at 25°C .

- Is the shampoo acidic, basic, or neutral?
- Calculate the hydronium ion concentration.
- What is the pH and the pOH of the shampoo?

Math LINK

Prove the relationship $\text{pH} + \text{pOH} = 14$ as follows. Record the ion product equation and its value at 25°C . Take the logarithm of both sides. Then reverse the sign of each term. What is your result?

Solution

(a) Compare $[\text{OH}^-]$ in the shampoo with $[\text{OH}^-]$ in neutral water at 25°C.

$[\text{OH}^-] = 6.8 \times 10^{-5} \text{ mol/L}$, which is greater than $1 \times 10^{-7} \text{ mol/L}$.

Therefore, the shampoo is basic.

(b) Use the equation $[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]}$ to find the hydronium ion concentration.

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-5}} \\ &= 1.5 \times 10^{-10} \text{ mol/L} \end{aligned}$$

(c) Substitute known values into the equations $\text{pH} = -\log[\text{H}_3\text{O}^+]$ and $\text{pOH} = -\log[\text{OH}^-]$.

$$\text{pH} = -\log(1.5 \times 10^{-10})$$

$$= 9.83$$

$$\text{pOH} = -\log(6.8 \times 10^{-5})$$

$$= 4.17$$

Check Your Solution

$$\text{pH} + \text{pOH} = 14$$

PROBLEM TIP

When you work with logarithms, the number of significant digits in a number must equal the number of digits after the decimal in the number's logarithm. Here 1.5×10^{-10} has two significant digits. Therefore, the calculated pH, 9.83, must have two significant digits after the decimal.

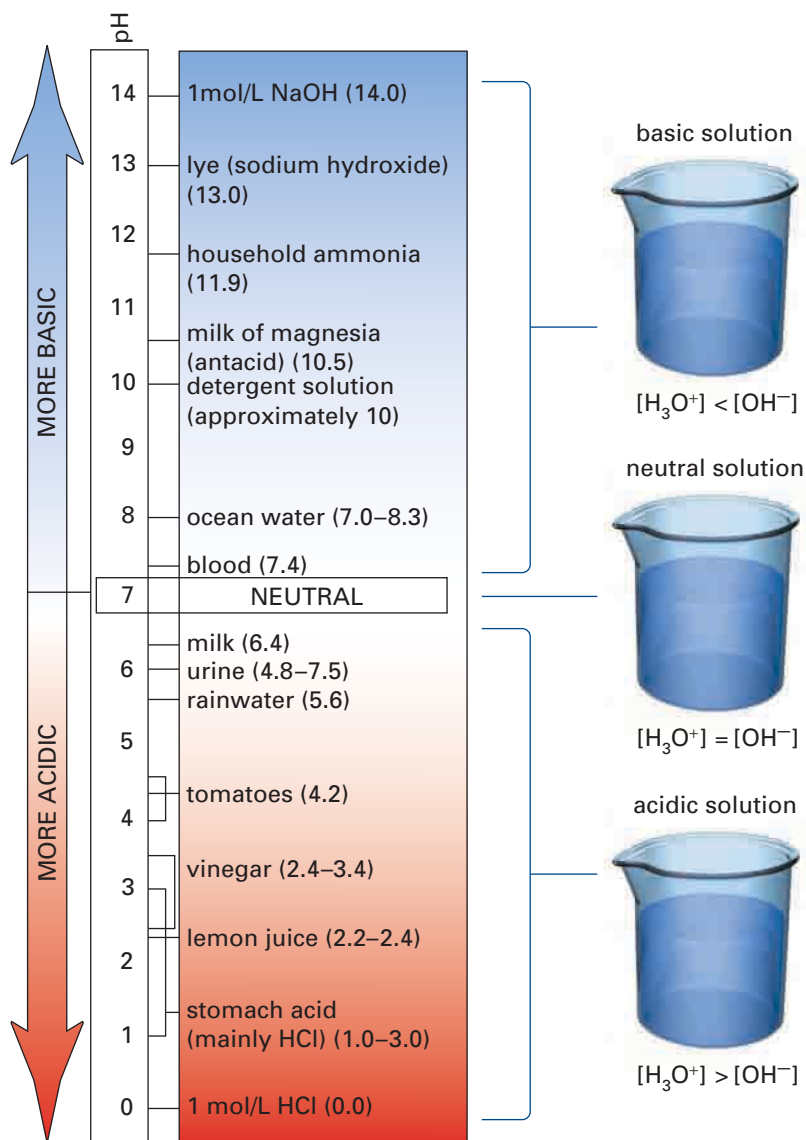


Figure 8.7 The pH scale is logarithmic. Each change by one unit on the scale represents a change of 10 in the hydronium ion concentration of a solution.

Another Way to Find $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$

You can calculate $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ by finding the *antilog* of the pH or pOH.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

If you are using a calculator, you can use it to find the antilog of a number in one of two ways. If the logarithm is entered in the calculator, you can press the two keys $\boxed{\text{INV}}$ and $\boxed{\text{LOG}}$ in sequence. (Some calculators may have a $\boxed{10^x}$ button instead.) Alternatively, since $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$ and $[\text{OH}^-] = 10^{-\text{pOH}}$, you can enter 10, press the $\boxed{y^x}$ button, enter the negative value of pH (or pOH), and then press $\boxed{=}$.

Sample Problem

Finding pOH, $[\text{H}_3\text{O}^+]$, and $[\text{OH}^-]$

Problem

If the pH of urine is outside the normal range of values, this can indicate medical problems. Suppose that the pH of a urine sample was measured to be 5.53 at 25°C. Calculate pOH, $[\text{H}_3\text{O}^+]$, and $[\text{OH}^-]$ for the sample.

Solution

You use the known value, pH = 5.53, to calculate the required values.

$$\begin{aligned}\text{pOH} &= 14.00 - 5.53 \\ &= 8.47\end{aligned}$$

$$\begin{aligned}[\text{H}_3\text{O}^+] &= 10^{-5.53} \\ &= 3.0 \times 10^{-6} \text{ mol/L}\end{aligned}$$

$$\begin{aligned}[\text{OH}^-] &= 10^{-8.47} \\ &= 3.4 \times 10^{-9} \text{ mol/L}\end{aligned}$$

Check Your Solution

In this problem, the ion product constant is a useful check:

$$\begin{aligned}[\text{H}_3\text{O}^+][\text{OH}^-] &= (3.0 \times 10^{-6}) \times (3.4 \times 10^{-9}) \\ &= 1.0 \times 10^{-14}\end{aligned}$$

This value equals the expected value for K_w at 25°C.

Practice Problems

- $[\text{H}_3\text{O}^+]$ of a sample of milk is found to be 3.98×10^{-7} mol/L. Is the milk acidic, neutral, or basic? Calculate the pH and $[\text{OH}^-]$ of the sample.
- A sample of household ammonia has a pH of 11.9. What is the pOH and $[\text{OH}^-]$ of the sample?
- Phenol, $\text{C}_6\text{H}_5\text{OH}$, is used as a disinfectant. An aqueous solution of phenol was found to have a pH of 4.72. Is phenol acidic, neutral, or basic? Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, and pOH of the solution.
- At normal body temperature, 37°C, the value of K_w for water is 2.5×10^{-14} . Calculate $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ at this temperature. Is pure water at 37°C acidic, neutral, or basic?